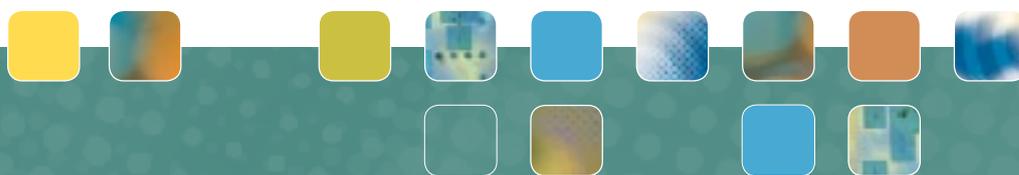




FFI-rapport 2015/02430

# Evaluation of the compatibility between aluminum tank material and ammonium nitrate under fire conditions



Maria Elisabeth Due-Hansen and Tom Cato Johannessen



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## English summary

On 17 December 2013 an explosion occurred at Drevja in Nordland county, Norway. The explosion was the consequence of a prolonged fire in a mobile explosives manufacturing unit (MEMU) loaded with materials for the on-site production of ammonium nitrate based explosives. During the investigations of the accident, concerns have been raised on the compatibility between the aluminum in the cargo tanks and ammonium nitrate (AN) during fire. This was investigated by using methods such as thermal analysis (differential scanning calorimetry (DSC)) combined with fire experiments. The experiments were designed to resemble fire conditions in such a way that high temperatures could be maintained throughout the experiment.

None of the experiments indicated any serious incompatibility between melted aluminum and AN. Instead, a relatively controlled and familiar decomposition of AN into visible water fumes was observed in all experiments. This also correlates with similar reported experiments, which conclude on a relatively poor reactivity between the two materials. This is due to the rapid formation of a protective oxide layer on the metal surface caused by AN, which prevents further reactions at the interface. Thus, when solely considering the compatibility, we suggest that the use of aluminum tanks when transporting AN does not aggravate the already present risk of explosion in AN during fire.

The thermolysis of AN is especially dependent on temperature and pressure, which these experiments also suggest. Thus, these parameters are of particular importance when evaluating the risk of explosion of AN during fire. During the experiments, some distinct changes in the decomposition of AN could at times be observed with apparent flames, accompanied by orange-brown fumes, characteristic for nitrogen dioxide formation. This was observed in particular when melted AN splattered out and landed on the hot steel surfaces, which correlates well with the formation of nitrogen oxides from AN being more prevalent at high temperatures and pressure. Decomposition products such as nitric oxide and nitrogen dioxide are not only known to have sensitizing effects on AN, but can also react further by highly exothermic and possibly explosive reactions if maintained at these extreme conditions. However, the role and importance of the formation of nitrogen oxides in explosions of AN resulting from fire is yet to be more thoroughly investigated.

## Sammendrag

Som en del av oppfølgingen til eksplosjonsulykken i en mobil produksjonsenhet for eksplosiver (MEMU) i Drevja i Nordland 17. desember 2013 har det blitt uttrykt bekymring for kompatibiliteten mellom den type aluminiumlegering som brukes i transporttanker og porøs prillet ammoniumnitrat (ANPP) ved brann.

For å undersøke dette ble det i denne studien tatt i bruk metoder som termisk analyse (differential scanning calorimetry (DSC)) samt ulike brannforsøk med aluminium og ANPP. Brannforsøkene ble utført slik at det var mulig å opprettholde en høy temperatur gjennom hele forsøket, selv etter tilsetning av ANPP. Ingen av forsøkene indikerte noen alvorlig inkompatibilitet mellom smeltet aluminium og ANPP. I stedet ble en relativt kontrollert og velkjent dekomponering av ammoniumnitrat, resulterende i blant annet synlige hvite vanndamper, observert i alle forsøkene. Dette korrelerer også godt med lignende publiserte forsøk, som konkluderer med at den hurtige dannelsen av aluminiumoksid på metallets overflate forhindrer videre reaksjoner mellom aluminium og ammoniumnitrat (AN). På grunnlag av dette antar vi derfor at bruken av aluminium som tankmateriale i transport av AN ikke øker den allerede tilstedeværende risikoen for eksplosjon i AN ved brann hvis man ser på kompatibilitet mellom metallet og AN alene.

Termolysen av AN er spesielt avhengig av temperatur og trykk, noe som disse forsøkene også peker på, og er nettopp derfor av avgjørende betydning for eksplosjonsrisikoen i AN ved brann. På visse tidspunkter i forsøkene kunne man se en endring i dekomponeringen av AN, som førte til tydelige flammer og dannelsen av karakteristiske oransjebrune gasser som er typisk for dannelsen av nitrogendioksid. Dette ble især observert da smeltet AN sprøytet ut på varme ståloverflater under forsøkene. Nitrøse dekomponeringsprodukter som nitrogenmonoksid og nitrogendioksid dannes ved høye temperatur og høyt trykk og er kjent for å ha en sensitiverende effekt på AN alene, men kan også, hvis de forblir ved høye nok temperaturer og/eller trykk, reagere videre via meget eksoterme og potensielt eksplosive reaksjoner. Hvilken effekt dannelsen av nitrøse gassene har på AN under brann, gjenstår å bli undersøkt i detalj. Mer metodiske forsøk og analytisk monitorering vil i større grad kunne belyse om disse spiller en avgjørende rolle i eksplosjoner i AN som resultat av brann.

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## List of Abbreviations

ADR	Accord européen relatif au transport international des marchandises Dangereuses per Route (The European Agreement concerning the International Carriage of Dangerous Goods by Road)
AN	Ammonium nitrate
ANE	Ammonium nitrate emulsion
ANPP	Ammonium nitrate, porous prilled
DSB	Direktoratet for Samfunnssikkerhet og Beredskap (Norwegian Directorate for Civil Protection)
DSC	Differential Scanning Calorimetry

# 1 Introduction

## 1.1 Explosion in Drevja; ammonium nitrate and its thermal hazards

On 17 December 2013 an explosion occurred at Drevja, Nordland, Norway. The explosion was the consequence of a prolonged fire in a mobile explosives manufacturing unit (MEMU) loaded with approximately 5000 kg porous ammonium nitrate prills (ANPP), 8000 kg ammonium nitrate based emulsion (ANE), 100 kg 25% NaNO<sub>2</sub>-solution, 100 kg 60% AcOH-solution, and 450 L diesel oil. The accident was later investigated by the Norwegian Directorate for Civil Protection (DSB), however, a direct cause of the explosion could not be deduced [1]. Still, it was concluded that the temperature range must have been close to the melting point of steel, that the aluminum tanks must have been at least partly melted and that the explosion must have originated from a point below and close to the engine block, probably causing a detonation in both the ANPP and ANE tank[1].

All tanks on the production unit of the MEMU-truck were ADR<sup>1</sup> approved aluminum tanks. Aluminum alloys, together with steel, are of the most important materials used in cargo tanks. In addition to being a relatively light metal, thereby reducing fuel costs, aluminum is also considered to have an improved security profile during fire when transporting materials such as ammonium nitrate based emulsions. Three large-scale tests which investigated the consequence of a fire when ANE is transported in ADR approved steel- and aluminum tanks, respectively, lead to a general practical approach concerning tanks used for transport of these types of compound mixtures in the Nordic countries [2-4]. These tests demonstrated that when subjected to fire, aluminum tanks weaken by the heat and pressure and ruptures, allowing the ANE to pour out and burn until extinguished. When subjected to similar fire conditions, steel tanks, on the contrary, resulted in a powerful blow-out as a consequence of a rapid pressure build-up. Due to these results, the general practice approach in the Nordic countries has till now been, that a demonstration of suitability of carrying substances such as ANE in tanks is not necessary when the substance is transported in tanks of aluminum or fiber-reinforced plastic. Seeing that this general practical approach has only been investigated for ANE alone, it has been raised a concern on the compatibility of aluminum tanks and ANPP under fire conditions. This issue will be investigated through the experiments described in this report.

### 1.1.1 Ammonium nitrate; properties and thermal hazards

At room temperature, pure ammonium nitrate (AN) is considered to be a stable and non-explosive compound and the risk associated with the use, production, transportation and storage of AN is in general low. However, the thermal decomposition of AN is known to be the cause of accidental explosions as the sensitivity and shock initiation characteristics of AN are a strong function of density which again is dependent on temperature. Confinement is believed to be a crucial parameter for causing an AN explosion by the action of heat alone. In fact, an explosion due to

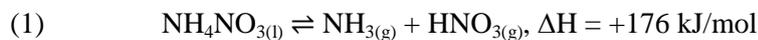
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<sup>1</sup> Accord européen relatif au transport international des marchandises Dangereuses per Route (The European Agreement concerning the International Carriage of Dangerous Goods by Road), a 1957 United Nations treaty.

heating of pure AN in an open system is yet to be reported. The sensitivity, and thus explosive hazard of AN increases considerably when exposed to impurities such as combustible materials, certain metals and acids in amounts as low as 0.2 % [5]. However, tests involving the direct addition of highly reactive contaminants in molten AN, has suggested that impurities cannot be a direct cause of explosion, but is only able to increase the shock sensitivity of AN [6]. Still, contaminants are an important contributing factor to the unpredictability of AN under fire conditions.

Over the last century, AN has been involved in several incidents involving fire of both minor and major consequence, causing some of the greatest industrial accidents in history [7-10]. AN itself does not burn, but being an oxidizing agent, it can promote and sustain fires in combustible materials. The nature of the thermal decomposition of AN depends on several conditions such as temperature, pressure, degree of confinement, rate of heating, purity, and bulk amount. Consequently, the decomposition of AN both pure and containing additives has been comprehensively investigated [11], including *in silico* experiments [12, 13].

If heated and unconfined, AN will decompose in to  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  in a controlled manner with characteristic white water fumes. These are indeed the dominant gas phase products at temperatures between the melting- and boiling point (169.6 °C and 210 °C, respectively). These gaseous compounds are a product of first, the endothermic dissociation of AN into ammonia and nitric acid (Reaction (1)) followed by an irreversible exothermic reaction producing  $\text{N}_2\text{O}$  and water (Reaction (2)).



If the gasses are rapidly cooled and removed from the system, i.e. in an unconfined system, reaction (1) and (2) will remain dominant, and the total decomposition process will be of an endothermic nature. This can provide a temperature limiting mechanism, even with considerable amount of external heating. However, if the formed gases are under confinement or maintained at temperatures above at which they were formed, they may further decompose and even react with one another to form species such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NO}$  and orange-brown fumes of  $\text{NO}_2$  by a range of various pathways, depending on the particular conditions and heating-rate on the system. Several of these reactions are highly exothermic, self-accelerating and of possible explosive nature [14].

One of the initiatives to help improve the safety and handling of AN based explosives has been the development of ANE technologies. Both aqueous and anhydrous ANE is considered to be more stable to thermal decomposition than neat AN. This has been found to be a consequence of the emulsion's ability to inhibit the vaporization of AN, a process that usually is responsible for the initiation of the exothermic decomposition of AN and hydrocarbons. Furthermore, the emulsification has proved to be crucial, as AN and mineral oil mixed rather than emulsified show a reduced thermal stability compared to that of pure AN [15].

### 1.1.2 Molten aluminum explosions

In the aluminum industry, the mixing of molten aluminum with contaminants is associated with accidental explosions and seen as a safety hazard [16]. Water contaminations are first, and foremost, the greatest concern. When molten aluminum comes in contact with water, a steam film can form on the surface of the metal. The steam film can destabilize as the molten aluminum contacts other surfaces in the pit. When this occurs, the water spontaneously vaporizes which can consequently lead to a high pressure steam explosion. While severe explosions of such kind are infrequent [17], the possible consequences are a major concern for the casting industry. Still, their prevalence have been greatly diminished due to the introduction of protective organic coatings on equipment and casting pit surfaces as a general practice in most of the aluminum casting industry [18-20]. Even though other contaminants such as oxides and oxidizing materials are generally believed to have a similar hazard potential, little is conclusive on this matter.

In the case of compatibility between molten aluminum and AN, published material is quite scarce, however, a couple of relevant examples can be found. In a 1997 Light Metals proceeding a series of cast shop accidents where AN is believed to have been involved is reviewed [21]. Even though the theoretical discussions conclude on a high reactivity between the two materials, none of these deductions are supported by nor referring to any empirical results. In fact, these conclusions are quite contradictory to experiments reported in literature.

In 1980, King and Bauer published a report including a series of experiments compiled into an extensive investigation to determine the detonation conditions of AN [22]. An especially relevant experiment involved the addition of molten aluminum to liquid AN. The metal immediately sank to the bottom of the vessel during which some spattering of the molten metal was observed. However, this ended quickly and ceased when the aluminum solidified. When molten, aluminum is rapidly oxidized by AN, which can function as a protective oxide barrier on the metals surface and inhibit further reactions at the interface.

Similar observations were made in a second study where molten aluminum was dropped into a liquid pool of oxygen has also been reported [23]. No explosive boiling was observed for temperatures up to 1300 °C. The aluminum was totally recovered in the bottom of the test vessel and its surface was completely oxidized.

## 2 Experimental Methods and Results

The following experiments were conducted to investigate the compatibility between aluminum tank material and ANPP under fire conditions. 5083-H111, a common aluminum alloy used for cargo tanks, was used in all experiments (melting point = ~570 °C). The ANPP was a technical quality for explosives production ( $d = 0.8 \text{ g/cm}^3$ ).

## 2.1 Differential scanning calorimetry

Thermo analysis by differential scanning calorimetry (DSC) was performed as an initial indicator of the compatibility between the porous prills and the aluminum alloy, using a TA instruments Q1000 and standard aluminum crucibles. The sample was prepared from crushed ANPP and 5 wt% shavings of the aluminum alloy which was thoroughly mixed in a mortar. The addition of alloy had minor influence on the thermal stability of AN. No changes were observed in the crystallographic transformation nor the melting process of AN (53 and 127 °C and 170 °C, respectively), when compared to the reference sample. Furthermore, the characteristics of the endothermic decomposition of AN, which commences when exceeding its boiling point (210 °C), is only subjected to small and little decisive changes. In the light of these results, the compatibility of AN and the aluminum alloy may, at these conditions, be considered as adequate.

## 2.2 Crude fire experiments

### 2.2.1 General methods and equipment

The fire experiments were performed by using a commercial barbeque and wood charcoal. An air compressor fitted with a steel tube was installed directly into the burning charcoal pile to optimize the burning and elevate the flame temperature (Figure 2.1A). Unfortunately, due to a limited budget, thermocouples were not used to monitor temperatures, which instead had to be qualitatively evaluated. Steel parts from the barbeque were visibly affected by the heat and indicated temperatures close to the melting point of steel (1300-1400 °C). Subsequently, the efficiency of the furnace was tested by heating 20 g of the aluminum alloy in a stainless steel pot (Figure 2.1B). The aluminum pieces melted readily and were fully melted after 3 minutes, indicating a sufficient furnace temperature. All experiments were monitored by live camera recordings.

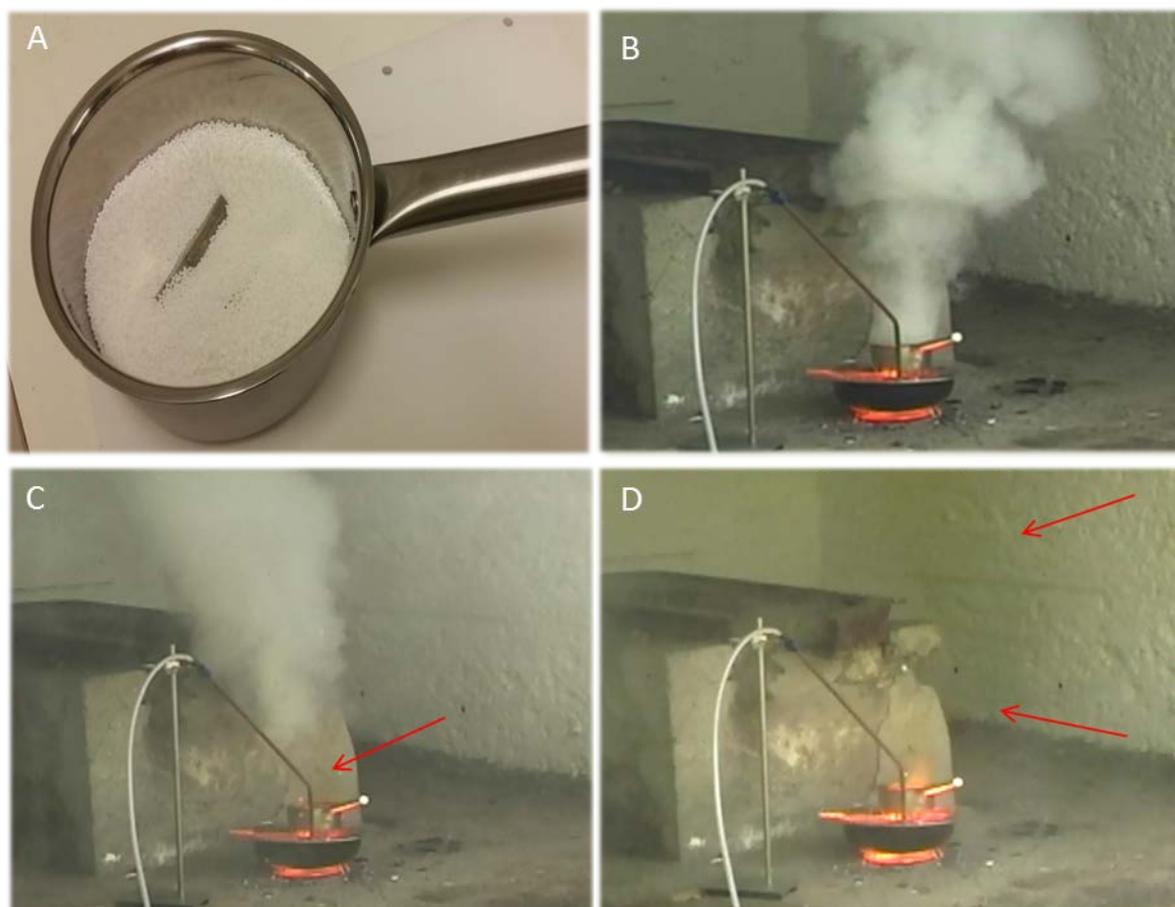


Figure 2.1 A) Furnace set-up using a commercial barbeque, wood charcoal and an air compressor; B) Aluminum melt.

#### 2.2.1.1 Simultaneous heating of aluminum and ANPP

Simultaneous heating of aluminum (20 g) and ANPP (180 g) in a stainless steel pot (Figure 2.2A) was performed, to indicate if any immediate incompatibilities were present. After approximately

3 minutes on the furnace, the AN started decomposing vigorously, but in a controlled manner, indicated by the characteristic white water fumes (Figure 2.2B). There were no visible signs of any explosive or violent reactions during this decomposition; however, fuming white projectiles were at times shooting from the pot. At 4:40 a sudden change of appearance in the experiment was observed. The white fumes were now replaced by orange-brown fumes and shooting flames which continued for over one minute until the flames extinguished (Figure 2.2C and D). Reference experiments using only ANPP (200 g) were also performed; however, these did not show any noticeable difference in behavior to the samples containing aluminum pieces. All experiments were repeated twice.



*Figure 2.2 A) Stainless steel pot containing ANPP and aluminum pieces; B)4:10, AN is decomposing vigorously; C)4:40, orange-brown fumes are starting to appear D)5:20, shooting flames appears from the pot while orange-brown fumes can be observed above the furnace.*

After the decomposition had completed, the steel pot was inspected. Traces of melted aluminum could be seen (Figure 2.3A) and the surface of the aluminum pieces were visibly affected (Figure 2.3B).

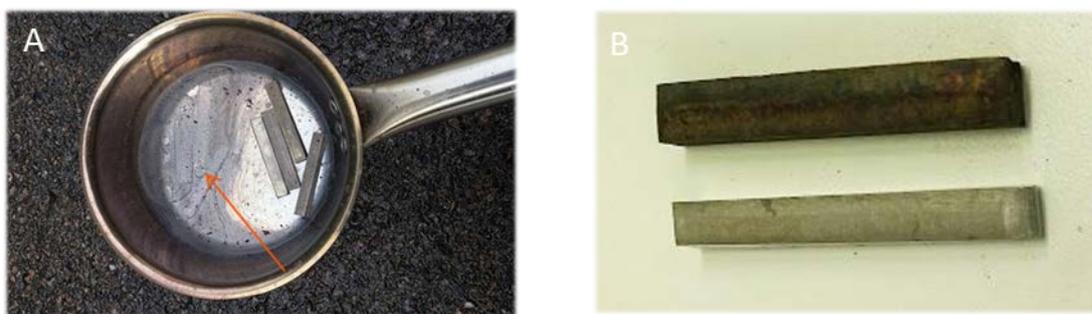


Figure 2.3 A) Traces of melted aluminum as indicated by the red arrow; B) Aluminum piece, before and after the experiment (bottom and top, respectively).

#### 2.2.1.2 Addition of ANPP to melted aluminum

The earlier described set-up was also used in the two following experiments where ANPP was directly added to melted aluminum (Figure 2.4A). A bigger pan was used to make the addition of the larger amount of prills even more precise (Figure 2.4D).

In the first experiment 80 g ANPP was added to 50 g melted aluminum. Approximately 10 seconds after the addition of ANPP, an apparent exothermic reaction accompanied by flames commences and what appears to be ANPP is shooting from pot. However, the flames abated after 5 seconds and no further reactions were observed (Figure 2.4B-C). As the amount of ANPP was too small to show any visible formation of fumes, the experiment was scaled up to 220 g ANPP and 150 g aluminum. A similar scenario was observed, however, the vigorous reaction now happened instantly accompanied by visible orange-brown fumes, most likely being nitrogen dioxide (Figure 2.4E). After 4-5 seconds the vigorous reaction is clearly succumbed by the endothermic decomposition of AN into water and nitrous oxide, as the white water fumes become more dominant.



*Figure 2.4 A) Experimental set-up with steel pot; B) Addition of ANPP to melted aluminum; C) Shooting flames appear after 10 seconds; D) Experimental set-up with steel pan; E) Flames light up immediately after addition of ANPP. Orange-brown fumes can be seen, as indicated by the red arrows; F) The vigorous flames are replaced by the decomposition of AN yielding water fumes.*

As earlier, the pot was inspected after the experiment clearly showing melted aluminum pieces and yet again a visibly affected aluminum surface (Figure 2.5).



*Figure 2.5 Resulting pot after the first direct addition experiment revealing deformed aluminum pieces.*

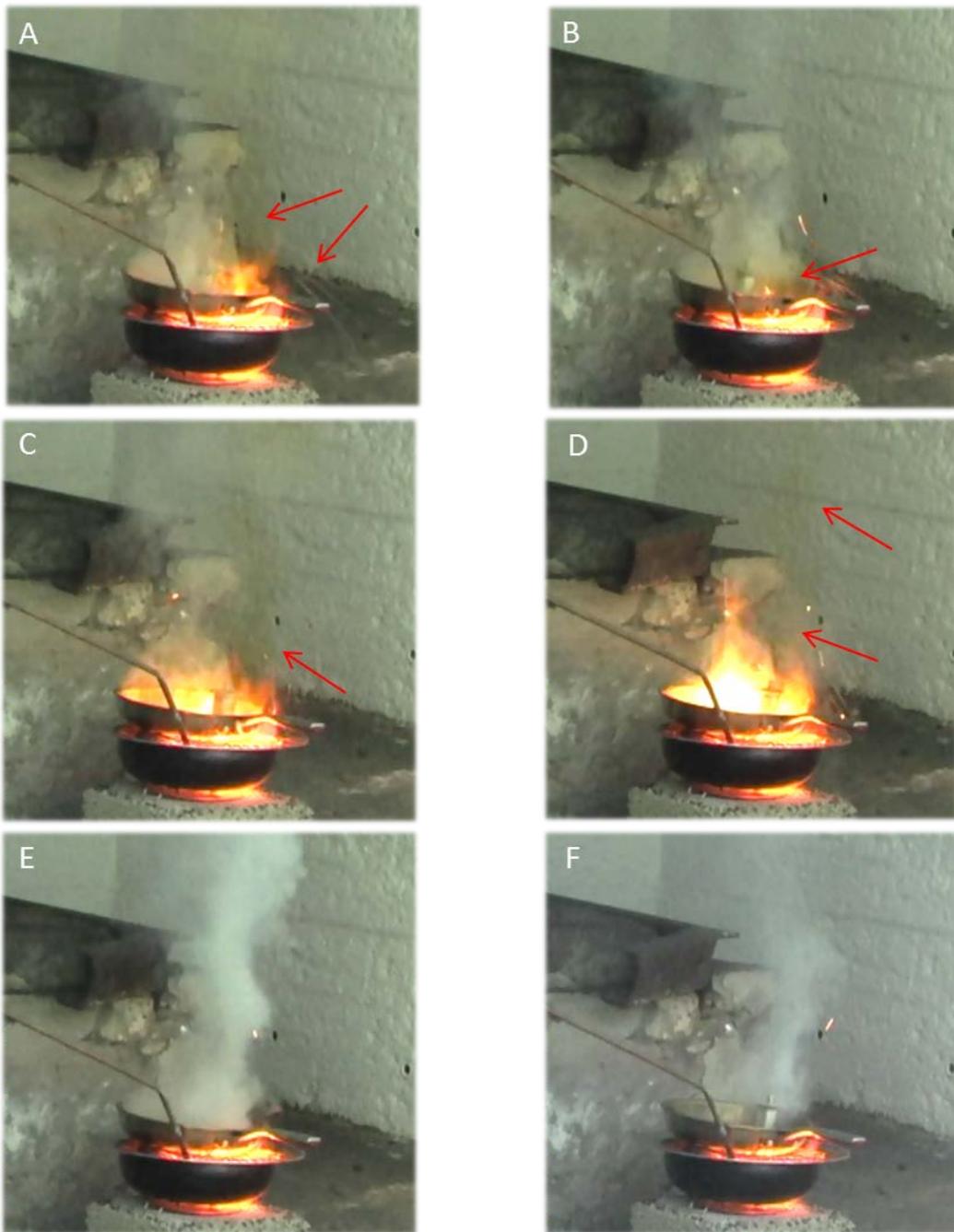
#### 2.2.1.3 Small scale vented pipe test

The UN manual of tests and criteria describes a series of test methods and procedures to be used for the classification of hazardous goods, and thus which recommendations to follow during transport of such materials[24]. In December 2002, the enclosure of the Series 8 tests was approved. Tests 8(a), 8(b) and 8(c) were introduced to establish if an ANE candidate could be classified as a UN 3375 substance. Test 8(d), which describes the two tests known as vented pipe test and a modified vented pipe test, was included in this series as a method to evaluate the suitability for the transport in tanks, but was not intended for classification purposes. Test 8(d) has later been subjected to scrutiny due to a lack of reproducibility. However, for our purpose, the vented pipe test was seen as a suitable method to observe the behavior of ANPP when partly confined in aluminum at elevated temperatures. Thus, the specifications found in the UN manual were used to construct a small scaled VPT in a 1:10 scale using the earlier mentioned aluminum alloy (Figure 2.6).



*Figure 2.6 Down-scaled vented pipe test-tube with appropriate measurements in mm.*

The test tube was filled with ANPP, but the venting pipe was left empty. The tube was then placed in a vertical position on a stainless steel pan which was subsequently heated on the furnace using the earlier described method. After being heated for approximately 3 minutes a small amount of white fumes could be observed from the venting pipe followed by spattering due to AN being pushed out of the venting pipe from the increase in internal pressure. When landing on the stainless steel pan, the spattering quickly led to a development of white fumes. This was immediately followed by orange-brown fumes and a violent reaction with large shooting flames (Figure 2.7A). During the following 30 seconds the fumes alternated between white and orange-brown and vigorous flames also accompanied the formation of orange-brown fumes (Figure 2.7B-D). After 40 seconds, the white fumes became dominant and the decomposition continued in a controlled manner. The tube was inspected and found intact after the experiment.



*Figure 2.7 A-B) A combination of white and orange-brown fumes can be seen. The orange-brown fumes are accompanied by flames and spattering; C-D) As the amount of white fumes are reduced the flames burn more vigorously, and the amount of orange-brown fumes increases. The tube has shifted position from the left to the right; E) The white fumes are becoming dominant and the decomposition continues in a controlled manner; F) White fumes are now dominant, and only originating from the pipe.*

### 3 Discussion

To the best of our knowledge, there has never been reported any explosions in aluminum known to be directly caused by a reaction between the molten metal and AN alone. Seeing that thermal explosions with water are the best known and most commonly reported cause of explosions in aluminum melts, raises questions on the intuitive thought that melted aluminum and AN contaminations must be of low compatibility.

In fact, earlier published studies on molten aluminum and oxidizing materials points toward a surprisingly good compatibility [22, 23]. Our DSC experiments further supported this observation, as they presented small and little decisive changes in thermal stability between pure ANPP and ANPP with 5 wt% aluminum when using a heating rate of +10 °C/min terminating at 400 °C. The formation of a protective oxide layer on the metal surface in addition to a rapid cooling of the molten metal is believed to be essential to the relatively mild reactions seen between molten aluminum and liquid AN and O<sub>2</sub>, respectively.

Furthermore, our fire experiments did not result, even with temperatures well above the melting point of aluminum, in any explosive reactions. The general impression was that the endothermic decomposition yielding visible water fumes was dominant throughout most of the process, keeping the decomposition at a steady pace. Still, more vigorous reactions yielding flames accompanied by orange-brown fumes could at times be observed. The flames are most likely a product of the combustion of gaseous ammonia, formed during the decomposition of AN, while the orange-brown fumes are characteristic for the formation of nitrogen dioxide. The formation of nitric oxide and nitrogen dioxide is also known to have sensitizing effects on AN and may also, if heated further, react exothermically and explosively [25]. Thus, it may be proposed that explosions in fires involving AN does not necessarily have to start inside the molten mass itself, but can be a consequence of these particular gases of decomposition forming a detonable mixture able to initiate the detonation of any remaining molten AN. This, however, remains to be further investigated.

If the nitrogen dioxide fumes originated from local hot-spots in the melt or the heating pan surface or even local areas of confinement in the sample, is extremely difficult to deduce from these experiments. Still, the observed changes in reaction behavior correlate to the thermolysis of AN being highly dependent on conditions such as temperature and pressure. A more thorough temperature monitoring of these experiments could probably help elucidate this. Furthermore, it is important to investigate the effect of immediate elevated temperatures on the thermolysis of AN.

Regarding the concerns of a chemical incompatibility between ANPP and aluminum as tank material, all results from the fire tests suggests that these are most probably unjustified. In fact, it could even be claimed that aluminum is an advantageous material as it can function as a heat scavenger during a fire and also distribute the heat more evenly. This might in turn prevent the formation of local hot-spots, and thus promote a more controlled heating and decomposition of the whole mass of AN.

It is well-known that the behavior of AN during fire is dependent on bulk size [22, 26-28]. This has been suggested to be related to the creation of local areas of heating in the bulk itself, which can lead to local confinement and ultimately run-away reactions. However, the latter has not yet been experimentally confirmed. Thus, it is important to bear in mind that results from these types of experiments involving AN at high temperatures are also highly dependent on sample size.

Even though it has been suggested that confinement and thermal run-away are more directly responsible of explosions in AN during fire compared to that of contaminants[6], an increase of sensitivity of AN materials will of course also consequently contribute to a greater risk of explosion. Due to this complexity, it is important to elucidate the behavior of other compounds commonly co-transported with AN to be able to provide a more comprehensive risk-assessment for transport of such hazardous material on the same vehicle. This is an important point as one of the main hazard preventing features when using aluminum tanks compared to steel, is the ability to release the hazardous compound from the tank itself. This can prevent confinement, but will consequently expose the material to possible contaminations. In addition, as ANE is generally considered to have a safer hazard profile during fire than ANPP, it is also important to further investigate and evaluate the risk of explosion due to fire when transporting these two components on the same vehicle.

## 4 Conclusion

A series of fire experiments have been conducted investigating the compatibility between melted aluminum alloy 5083-H111, commonly used in cargo tanks, and ANPP. None of the experiments resulted in any apparent explosive behavior and the melted aluminum did not indicate any immediate sensitizing effect on the added AN. In fact, a steady endothermic decomposition of AN yielding water fumes seemed to be dominant throughout most of the process. However, flames accompanied by characteristic orange-brown nitrogen dioxide fumes were briefly observed during the experiments when liquid AN hit hot steel surfaces. Nitrogen oxides are known to have sensitizing effects on AN and may also, if heated further, react exothermically with explosive effects. As the thermolysis of AN is highly dependent on temperature, this indicates that local areas of elevated temperatures in the system can promote this possibly explosive inductive pathway. We suggest further and more methodical investigations including a more thorough technical monitoring to elucidate the role of nitrogen oxide formation on the explosive potential of AN during fire. In addition, to be able to provide a more comprehensive risk-assessment concerning fires in MEMU vehicles and the transportation of ANPP in bulk, we also suggest that similar experiments are performed with other commonly co-transported materials to elucidate if their presence could increase the risk of explosion compared to that of fire alone.

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