Small-scale fire performance assessment of intumescent coatings on

metal tubes containing ammonium nitrate. A stepping-stone towards

their application as a fire safety measure on road transportation tanks?

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ABSTRACT

Ammonium nitrate is used in vast amounts globally, first and foremost as a component of fertilizers and

explosive formulations. This usage necessitates its transportation which, as for most hazardous

materials, involves certain risks. For oxidizing materials such as ammonium nitrate, the ultimate

consequence of road transportation incidents is usually considered to be fire followed by explosion.

Even though the probability in general is low, substantial reduction in its risk is a great gain for public

safety. Thus, identifying novel and improving current safety measures for risk reduction, is an important

aspect in the field of hazardous materials. Herein, a series of experiments are reported, which

demonstrate the fire protection performance of two state-of-the-art intumescent passive fire protection

materials on small-scale metal test tubes containing ammonium nitrate. Albeit being initial experiments

on laboratory-scale, these results provide a promising starting point for further investigations on the

potential of these materials for the fire protection of ammonium nitrate when carried in metal tanks. At

its best, a prominent protection of ammonium nitrate from heat exposure was observed, as the

temperature was kept well below its boiling point for more than 2.5 hours. Successively, it resulted in a

complete recovery of the sample material. This was in large contrast to the observed results for the

unprotected test tubes, which led to complete decomposition of the sample after 11 minutes.

KEYWORDS

Passive fire protection, transportation, ammonium nitrate, hazardous materials, fire safety

1. Introduction

The inorganic salt ammonium nitrate (AN), is manufactured and used in vast amounts globally, primarily as a high-nitrogen ingredient in fertilizers, but also as the main component of most industrial explosives and blasting agents for civil applications. The world's annual amount of AN production is estimated to more than 20 million metric tons (Knoema, 2020).

Land transportation is a common transportation mode of AN, e.g. in the US, road transportation have accounted for approximately 60% of its transport, when both considering quantities and travelled distance (DOT, 2015). For the land transport of hazardous goods, the UN Recommendation on the Transport of Dangerous Goods is a commonly applied regulatory scheme for the safe transportation of hazardous materials (hazmat), and most regional, national and international regulatory schemes refer to this. As pure AN exists in several types of grades and qualities, they are classified and transported under different UN-numbers¹ such as 2067 (Fertilizer grade), 1942 (Porous prilled ammonium nitrate (ANPP) explosives grade), 2426 (Liquids) and 3375 (Ammonium nitrate emulsion (ANE)), all common high concentrated AN-based products.

AN is not a combustible compound in itself, but it does have oxidizing properties, thus posing its greatest risk during fires. In general, it is considered a chemically stable substance under normal handling conditions (Weston, *et al.*, 2000, Zapp, *et al.*, 2000). When AN is heated above its melting point (169.6 °C) at atmospheric pressure, two concurrent reactions predominate: an endothermic dissociation (eq. 1) and an exothermic decomposition (eq. 2) (Zapp, *et al.*, 2000).

$$NH_4NO_3 \rightleftharpoons HNO_3 + NH_3$$
, $\Delta H_r^{\Theta} = + 184 \text{ kJ/mol}$ (1)

$$NH_4NO_3 \rightarrow N_2O + 2H_2O, \Delta H_r^{\Theta} = -36 \text{ kJ/mol}$$
 (2)

The decomposition under such conditions can be observed visually by the formation of copious white fumes. Despite the exothermic contribution from the decomposition, when unconfined, all the available heat from the decomposition will be absorbed by the reversible endothermic dissociation. Thus, the decomposition of AN is limited by its own dissociation and tends to seek towards a self-limiting decomposition temperature, as long as the gaseous products are able to freely escape (Feick, 1954, Feick and Hainer, 1954a, Feick and Hainer, 1954b). At adiabatic conditions, this temperature has been found to be 292 °C at 1 atm and steady-state decomposition usually takes place at temperatures between 250–300 °C (Feick and Hainer, 1954a, Feick and Hainer, 1954b).

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¹ Unique four-digit numbers used world-wide in international commerce and transportation to identify hazardous materials and articles. Identical to NA (North America) numbers issued by the United States Department of Transportation.

This heat-limiting mechanism is, however, highly dependent on the external pressure, heating rate and presence of contaminants. Confinement suppresses the endothermic dissociation while excessive heating and contaminants can introduce a range of alternative exothermic decomposition pathways ultimately altering the thermal stability of AN (Babrauskas and Leggett, 2020, Berthelot, 1883, Brill, et al., 1993, Brower, et al., 1989, Cagnina, et al., 2013, Due-Hansen, 2018, Feick, 1954, Feick and Hainer, 1954a, Feick and Hainer, 1954b, Oxley, et al., 2002, Patil, et al., 1992, Saunders, 1922). Eventually, at the proper conditions, the decomposition of AN can reach reaction rates associated with run-away reactions, ignition and explosive behavior (Izato, et al., 2017, King, 1980, Saunders, 1922, Skarlis, et al., 2014). Here, some degree of confinement seems to be crucial for the successful transition from decomposition to explosion (Babrauskas and Leggett, 2020, Due-Hansen, 2018). Being of a complex nature, elaboration on these chemical pathways are beyond the scope of this paper. The thermal decomposition of AN under fire conditions have recently been addressed in two reviews (Babrauskas and Leggett, 2020, Due-Hansen, 2018).

Even though explosive events during storage and transport of AN are rare, they can be detrimental when they do occur and have thus been the cause of some of the largest industry and transport-related accidents to date (Babrauskas, 2016, Due-Hansen and Dullum, 2017, Mainiero, 2009, Pittman, *et al.*, 2014). Most of these have involved uncontrollable fires and a phenomenon known as deflagration-to-detonation transition (DDT).

1.1 Fire. The main cause of explosion accidents in the road transportation of ammonium nitrate.

The manufactory and use of hazardous materials will typically involve some type of logistics, most commonly road transportation due aspects such as cost and accessibility. Indeed, a 2006 survey showed that the most accidents involving ground transportation of hazardous goods, occur by road (Oggero, *et al.*, 2006). It also showed an upward trend in terms of frequency, mainly due to the annual increase of amounts being transported. Interestingly, the cost of such incidents does not seem to be significantly higher than the cost of a non-hazmat incident. However, an exception is, when such incidents result in fire and/or explosion. The cost increase will then be considerable and include aspects such as injuries and fatalities, clean-up costs, property damage, evacuation, product loss, environmental damage and even traffic incident delay (Erkut, *et al.*, 2007).

As dangerous goods can be harmful to both human health and the environment if unintentionally released, special precautions are required to render them safe enough for transport and storage. The unremitting work for reduction of hazardous material transportation risks now comprise a vast amount of topics in the continuously growing field of safety research, such as risk assessment, risk modeling, operation research (routing) and development and use of novel safety measures for risk reduction (Ditta, et al., 2019, Erkut, et al., 2007, Holeczek, 2019).

Due to the more or less unpredictable behavior of AN during fire incidents, much effort has been put into the investigations of its thermochemical and explosive behavior. However, due to the complex decomposition patterns that take place at high temperatures and in the presence of contaminants, the essential determinants in the transition from decomposition to explosion by AN exposed to high temperature, can be extremely difficult, if not impossible, to predict. The most reliable safety measure to avoid such a transition during transport and storage, is thus to prevent the fire happening in the first place (Babrauskas, 2016), a topic also discussed in our review on an explosion accident in Drevja, Norway, caused by fire in a mobile explosives manufacturing unit (MEMU) carrying ANPP and ANE for the on-site production of explosives (Due-Hansen and Dullum, 2017). The accident in Drevja was a consequence of a fire starting in the engine fuse box of the transportation unit (DSB, 2015). This escalated quickly to comprise the whole vehicle, including the transportation tanks in the manufacturing unit. After almost 2.5 hours, the fire culminated in a large explosion, which was most likely initiated by the rupturing of at least one of the aluminum transportation tanks carrying AN-based materials. This is probably the longest time span of a fire leading to explosion, ever to be reported for a road transportation of AN (DSB, 2015, Due-Hansen and Dullum, 2017).

In the Nordic countries, the use of aluminum transportation tanks has been considered a general safety measure in preventing fire to explosion transitions for AN-based materials when exposed to fire (Due-Hansen and Dullum, 2017). These contemplations are based on three large scale tests performed on both aluminum and steel tanks, respectively, carrying ANE for explosives production (Kalström, 2002, Kalström, *et al.*, 2007, Vestre, 1996). They demonstrated that the use of aluminum tanks would prevent confinement by weakening and rupturing at temperatures far below that of steel. Nevertheless, looking back at the accident in Drevja, one might argue that introducing aluminum tanks as a safety measure merely substituted one potential risk with another

The ultimate consequence of incidents involving the transportation of oxidizing materials such as AN, is fire followed by explosion. It is also the most common domino effect in chemical accidents (Darbra, et al., 2010). Good maintenance and operating procedures are crucial measures in avoiding fire in transportation vehicles. This can substantially reduce the risk of a fire, however, never entirely. Accordingly, measures that can reduce the consequence when such fires in fact do take place, can be just as important from a prevention perspective. Especially in such cases as in Drevja, where high concentrated AN products are carried in combination with other hazardous goods, leading to fire scenarios of great complexity. Even though the probability in general is low, a substantial reduction in its risk is a great gain for public safety. Here, the use of materials based on passive fire protection (PFP) could be a rational approach to improve the outcomes of such transport accidents involving fire, and are already widely applied for the purpose of thermal protection of e.g. commercial and industrial high-rise and steel-framed constructions (Puri and Khanna, 2017).

1.2 Intumescent coating as passive fire protection

The purpose of PFP materials, is to prevent the consequences of thermal influence on a protected object, minimize the spread of fire in addition to providing its protective function without the need of additional manual intervention (Landucci, *et al.*, 2009). They are usually produced as either thermal shields or thermal coatings, however, in most applications, coatings are preferred as they do not modify mechanical properties, are easily processed and can protect most materials (Jimenez, *et al.*, 2006).

Examples on such thermal coating are flame retardant polymers i.e. fire resistant resins, thermal barriers such as cementitious coatings, dense concrete, mineral fiber or ceramic wool and intumescent coatings. The latter are an especially efficient form of PFP and are thermally reactive materials comprising of an acid source, a carbon source, binder and a blowing agent. At its best, intumescent coatings can provide several hours of passive fire protection and can be formulated and designed for specific needs (Puri and Khanna, 2017). Furthermore, modern intumescent coatings can provide properties that are essential for a feasible application for transportation tanks such as lightweight protection, retrofitting possibilities, lower cost and ability to withstand road transport conditions such as vibrations.

As heat exposure initiates an endothermal process, the components react and form an efficient insulating and protective porous char, which swells several times to its original thickness. When reaching the appropriate temperature, the binder softens and acid is released from the acid source, promoting dehydration and char formation of the carbon source. Then, as the blowing agent decomposes, gas is released and trapped in the char matrix, ultimately forming an insulating layer with low density and low thermal conductivity. Excellent reviews on the technical details and fire performance of modern intumescent coatings, can be found in the literature (Lucherini and Maluk, 2019, Puri and Khanna, 2017, Weil, 2011).

In Europe, the general requirements and provisions concerning road transport of hazardous goods are governed by a UN treaty known as the European Agreements Concerning the International Carriage of Dangerous Goods by Road, also known as ADR² (ADR, 2019a). Herein, technical requirements and test regimes specifically concerning the construction and safety of road transportation tanks are described (ADR, 2019b), including the mentioned MEMU-vehicles as a subcategory (ADR, 2019c). When reviewing this, there are no standard requirements for the fire protection systems of vessels containing the hazardous compounds, apart from pressure relief systems. From a safety point of view, the main efforts of fire prevention and protection seems thus to currently be focused on the transport unit rather than the hazardous compounds of concern.

² ADR is the abbreviation for the French title of the treaty: Accord européen relatif au transport international des marchandises Dangereuses per Route.

To the best of our knowledge, the potential of more state-of-the-art intumescent coatings for the localized fire protection of AN transportation tanks have not been assessed in available literature. However, their use have received more attention for their fire protection potential of pressurized gas such as liquefied natural/petroleum gas (LNG/LPG) and high-pressure hydrogen (Dao *et al.*, 2014, Droste, 1992, Kandola, *et al.*, 2012, Kim, *et al.*, 2017, Gambone and Wong, 2007, Moradi and Groth, 2019, Paltrinieri, *et al.*, 2009, Scarponi, *et al.*, 2017, Webster, 2010, Zheng, *et al.*, 2013). Yet, few of these focus on bulk scale transport containers and tanks.

As a follow-up to the explosion incident in Norway, we were interested in pursuing this idea of using intumescent coatings on road transportation tanks for AN as a possible safety measure to prevent the most disastrous outcome of fire in AN, namely explosion. Thus, for screening purposes, we set out to investigate the fire protection ability of two commercially available intumescent PFP materials and its effect on the thermolysis of AN subjected to a 1200 °C propane flame in small-scale metal tubes.

2. Material and methods

2.1 Experimental method and equipment

2.1.1 Experimental set-up

The experiments comprised the heating of a small container filled with low-density porous prilled AN (0.80 g/cm³, Yara Int.), a product formulated for explosives production. The set-up included a uniquely designed test tube equipped with two individual thermocouples, to monitor the temperatures of the sample. The bottom thermocouple was submerged into the AN during the experiment while the top thermocouple measured the temperature directly above the AN (Figure 1A). A hole was incorporated to ensure proper venting during the experiment, enabling visual observation of the decomposition (Figure 1B). The tubes were constructed in either aluminum (6082-T6) or stainless steel (S235), representing the most common materials used in hazmat transportation tanks. A thickness of 3 mm corresponds to ADR requirements (ADR, 2019a). Before each experiment, the tubes were cleaned with a detergent, rinsed with acetone and dried. All experiments were performed using ~180 g AN, corresponding to 50% of the tube's total volume.

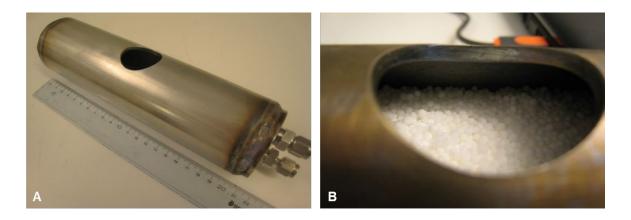


Figure 1 A) Test tube in steel including two inlets for thermocouples. Dimensions: 200 mm (l), 53 mm (ID), 60 mm (OD); B) Test tube filled with AN (~180 g) corresponding to a 50% fill volume.

The tubes were subjected to a localized heat impact from a propane torch with an effect of approximately 800 W on the bare metal tubes. The flame temperature was measured to \sim 1200 °C. Further details on the experiments yielding these measurements, can be found in the supplementary information.

All experiments were video and temperature monitored (Figure 2). As soon as the familiar, white decomposition smoke stopped appearing from the test tube, the heat source was removed, as it indicated complete decomposition of the AN. If this point was not reached after 2 hours, the experiments were stopped.

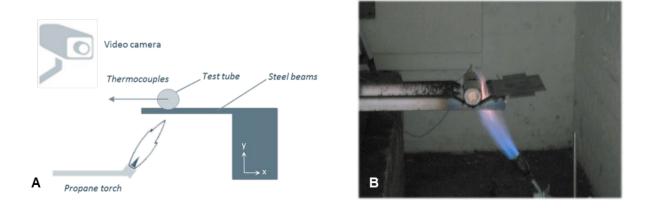


Figure 2 A) Schematic drawing of the experimental set-up; B) Picture showing the set-up during an experiment. The propane torch was positioned at x = 150 mm, y = 200 mm relative to the bottom of the test tube. At the point of flame exposure, the tube was exposed to a maximum temperature of ~ 1200 °C.

2.1.2 Tubes coated with passive fire protection

Two commercially available intumescent PFP products were investigated; the two-component solid amine cured-epoxy mesh free intumescent coating Jotachar 1709 from Jotun and Firestop[™] from Trelleborg Offshore's operation in Norway, a rubber based PFP-technology with intumescent properties.

These products are applied in and originally designed for the offshore industries, both providing their own unique technologies and properties in the field of PFP.

As both materials are based on intumescent technology, they swell into carbonaceous chars upon heat exposure, which function as the insulating material. The steel and aluminum tubes were coated with a 5 mm layer of each material, respectively (Figure 3).

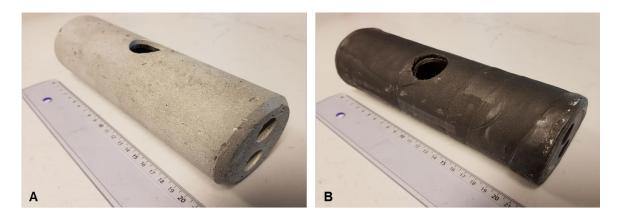


Figure 3 A) Test tube coated with 5 mm (~300 g) 1709 Jotachar; B) Test tube coated with 5 mm (~400 g) Firestop.

Reported time durations of fire incidents in road transport of AN indicate that fire resistances of considerable lengths are necessary to protect the transported goods from thermal impact (Babrauskas, 2016). E.g. the earlier mentioned explosion accident in Drevja took place after 2.5 hours and the cargo was subjected to fire impact for at least 1 hour (DSB, 2015, Due-Hansen and Dullum, 2017).

For AN, it is imperative to keep the temperatures below its boiling point (210 °C) during the time span of a fire, as the decomposition rate then will be close to negligible if proper ventilation is present (Feick and Hainer, 1954a, Feick and Hainer, 1954b). In this case, the thickness, and thus the fire resistance efficacy of the intumescent coating, must reflect this. For the experiments described herein, a thickness of 5 mm was chosen for the investigations, as this afforded an optimum compromise between weight, fire resistance efficacy and comparability between the test materials. It is also the typical recommended dry film thickness minimum for Jotachar (Jotun, 2020).

3. Results and discussion

3.1 Aluminum and steel tubes without fire protection

All experiments were performed as described in section 2.1. Reference experiments on unprotected tubes were carried out for steel and aluminum, respectively (Exp 1.1 and 1.2, Table 1). The temperature-time plot and relevant captions from the video monitoring of the experiments, are shown in Figure 4. The characteristic white fumes from AN decomposition are well depicted in Figure 4E, 4G and 4J.

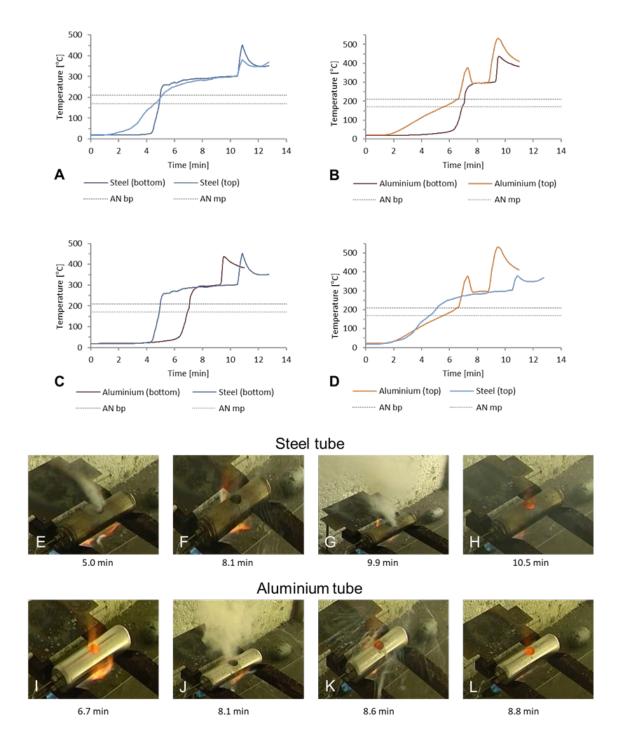


Figure 4 Temperature measurements vs time for A) Experiment 1.1 (steel tube), top and bottom thermocouples; B) Experiment 1.2 (aluminum tube), top and bottom thermocouples; C) Bottom thermocouple for experiment 1.1 (steel) and 1.2 (aluminum), respectively; D) Top thermocouple for experiment 1.1 (steel) and 1.2 (aluminum), respectively; E-H) Selected pictures from experiment 1.1. Heating AN in a steel tube; I-L) Selected pictures from experiment 1.2. Heating AN in an aluminum tube. The grey dashed lines represent the boiling and melting points of AN, respectively.

When comparing experiment 1.1. and 1.2, the results indicate that the initial melting phase of AN is extended in time with approximately 40% when heated in the aluminum tube (Figure 4C). On the other hand, the steady-state decomposition phase between 250–300 °C is prolonged in the steel tube. Thus,

the total duration of the decomposition is shorter in the aluminum tube even though AN is kept at a lower temperature range for a longer time (Table 1). This behavior must be linked to the different heat conductive properties of the two metals and thus the heat distribution to the sample material. As a consequence, gas-phase ignitions of the decomposing AN seems to be more frequent in the aluminum tube when the temperature finally passes the boiling point of AN. This is clearly demonstrated by the two distinct temperature rises above the AN sample in the aluminum tube (Figure 4D), which correlates to the captures seen in Figure 4I and 4L. In addition, spattering and boil overs were more distinct in the aluminum test tube (Figure 4K) than in steel (Figure 4F).

Table 1: Time passed before reaching melting point, boiling point and total decomposition when heating AN in aluminum and steel tubes, respectively.

Exp	Tube material	Mp reached [min]	Bp reached [min]	Duration [min] ^a
1.1	Steel	4.9	5.0	11
1.2	Al	6.9	7.1	10

^aTime at which decomposition fumes are no longer observed

3.2 Aluminum and steel tubes coated with intumescent passive fire protection

Tubes coated with either Firestop (Exp 2.1–2.2, Table 2) or Jotachar 1709 (Exp 3.1–3.2, Table 2) were subjected to the same experimental conditions as described for the reference experiments 1.1 and 1.2 (Table 2). The expansion of both intumescent materials upon heat exposure are shown in Figure 5. Both materials provided evident protection from the heat exposure. The most significant effect was, however, observed for the tubes protected with Jotachar.

3.2.1 Tubes coated with Firestop

The decomposition of AN in the Firestop-protected steel tube (Exp 2.1) was slow and controlled during the experiment. The rubber was visibly expanding under the influence of heat and the effect of the protected tube is evident (Figure 5A–B). The time before reaching the melting point and boiling point of AN, was increased four and five fold, respectively, compared to the unprotected tube (Table 2). The experiment ended after approximately 52 minutes with a gas-phase ignition, resulting in a small spurt of flame and a minor temperature rise (Figure 6A).

The Firestop-protected aluminum tube followed a similar process (Exp 2.2). Somewhat lower, but still significant increases, were also found in this case as the time before reaching the critical temperatures were close to four times higher compared to the reference experiment (Table 2). However, in contrast to the protected steel tubes, no spurt of flame was observed at any point. In addition, a somewhat faster temperature increase between the melting- and boiling point of AN was observed when compared to the

Exp 2.1 (Figure 6A–B). Also, the maximum temperature reached during the experiments was reduced with more than 135 °C.

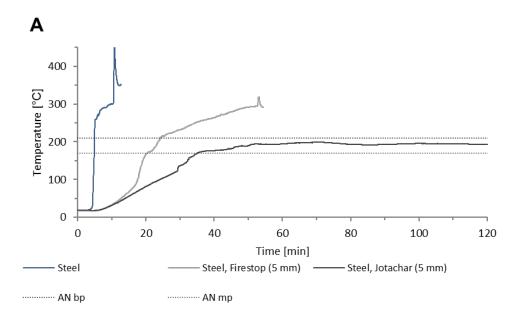
3.2.2 Tubes coated with Jotachar

Little other activity was observed when the Jotachar-protected tubes were exposed to heat, except for the expansion of the intumescent coating (Figure 5C–D). The AN samples reached maximum temperatures between 180–200 °C after approximately 60–70 minutes and remained in this temperature range until the experiment was terminated after 120 and 170 minutes (Figure 6, Table 2), thus never reaching the boiling point of AN. For comparison, the same temperature range was reached 14–15 times faster in the unprotected tubes, underlining the evident effect of the protective material.

Further comparison shows that the time before reaching the melting point of AN was increased seven fold for the protected steel tube (Exp 3.1) and eight fold for the protected aluminum tube (Exp 3.2). Thus, it may seem that the thermal properties of aluminum complement the protective properties of Jotachar. The remaining mass of AN was extracted and weighed after the experiments, indicating a mass reduction of less than 5%, complying with the low decomposition rate of unconfined AN in this temperature range (Feick and Hainer, 1954a, Feick and Hainer, 1954b).



Figure 5 A-B) Effect of heat exposure on the PFP materials, exemplified by Exp 2.1 (steel tube with Firestop); C-D) Effect of heat exposure on the PFP materials, exemplified by Exp 3.1 (steel tube with Jotachar);



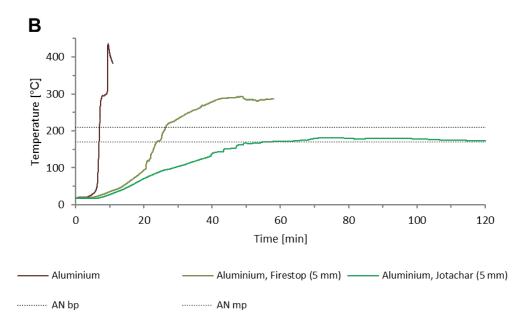


Figure 6 A) Temperature-time measurements heating of AN in a steel tube without intumescent coating (Exp 1.1), with 5 mm Firestop (Exp 2.1) and 5 mm Jotachar (Exp 3.1), respectively. The grey, dashed lines represent the boiling and melting point of AN; B) Temperature-time measurements for heating of AN in an aluminum tube without intumescent coating (Exp 1.2), with 5 mm Firestop (Exp 2.2) and with 5 mm Jotachar (Exp 3.2), respectively.

Table 2: Time passed before reaching melting point, boiling point and total decomposition when heating AN in unprotected and protected aluminum and steel tubes, respectively

Exp	Material (coating)	Mp reached [min]	Bp reached [min]	Duration [min] ^a	Max. temp. [°C]
1.1	Steel	4.9	5.0	11	452
2.1	Steel (Firestop)	20.2	24.2	53	317
3.1	Steel (Jotachar)	35.1	n.a.	120 ^b	200
1.2	Al	6.9	7.1	10	436
2.2	Al (Firestop)	23.8	26.4	58	292
3.2	Al (Jotachar)	54.8	n.a.	170 ^b	181

^aTime at which decomposition fumes are no longer observed ^bExperiment terminated due to stabilized temperature

3.3 Protective shield with Firestop

An alternative approach with Firestop was also explored. By protecting a 200 x 200 mm aluminum plate (5 mm) with 2.5 mm Firestop, the effect of this as a protective shield for an uncoated tube filled with AN was investigated (Figure 7). The thickness of the aluminum plate corresponds to the thickness of an aluminum plate heat shield, that was used below the production unit of the MEMU-vehicle in the Drevja incident (DSB, 2015). Reference experiments using an aluminum plate (5 mm) without Firestop was also performed (Exp 4.1–4.2).





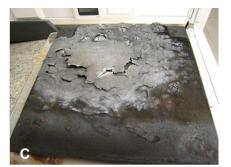
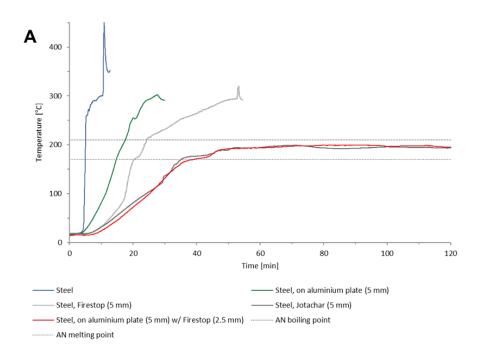


Figure 7 A) 200 x 200 mm aluminum plate (5 mm) vulcanized with 2.5 mm Firestop; B) Experimental set-up; C) Protected plate after heat exposure for more than 120 min.

All experiments were performed on both steel and aluminum tubes (Exp 4.1–4.4). The temperature-time plot for all experiments are shown in Figure 8 and summarized in Table 3.

Experiments 4.1 and 4.3 showed that an uncoated aluminum plate provides some protection on its own, as the time span for reaching the melting and boiling point of AN was between two to three times greater

compared to the unprotected tubes. However, vulcanized with only 2.5 mm of Firestop (Exp 4.2 and 4.4), this approach performed just as well as metal tubes coated with 5 mm Jotachar as the time span increased six and eight fold for the aluminum and steel tube, respectively.



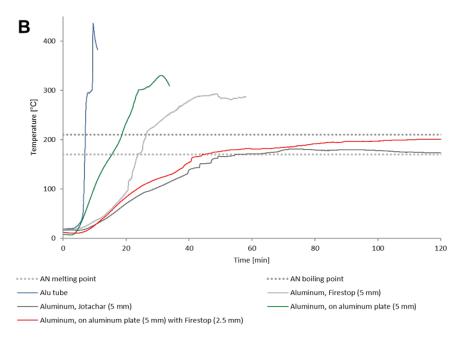


Figure 8 A) Temperature-time measurements for heating of AN in steel tubes: unprotected tube (blue), indirectly protected placed on a Firestop-protected aluminum plate (green), indirectly protected placed on a Firestop-protected aluminum plate (red), directly protected coated with Firestop (grey) and directly protected coated with Jotachar (dark grey). The grey, dashed lines represent the boiling and melting point of AN; B) Temperature-time measurements for heating of AN in aluminum tubes: unprotected tube (blue), indirectly protected placed on an aluminum plate (green), indirectly

protected placed on a Firestop-protected aluminum plate (red), directly protected coated with Firestop (grey) and directly protected coated with Jotachar (dark grey). The grey, dashed lines represent the boiling and melting point of AN.

Table 3: Time passed before reaching melting point, boiling point and total decomposition when heating AN in unprotected aluminum and steel tubes, respectively, on a protective aluminum shield (5 mm) with and without 2.5 mm Firestop.

Exp	Material (plate) ^a	Mp reached [min]	Bp reached [min]	Duration [min] ^b	Max. temp. [°C]
1.1	Steel (none)	4.9	5.0	11	452
4.1	Steel (Al)	11.3	17.5	28	306
4.2	Steel (Al-FS)	38.0	n.a.	120°	199
1.2	Al (none)	6.9	7.1	10	436
4.3	Al (Al)	15.4	18.7	30	322
4.4	Al (Al-FS)	44.1	n.a.	120°	200

^aAl = 5 mm aluminum plate, Al-FS = 5 mm aluminum plate with 2.5 mm Firestop ^bTime at which decomposition fumes are no longer observed ^cExperiment terminated due to stabilized temperature

3.4 Limitations and considerations

The results from the described laboratory-scale experiments underlines the ability of the tested state-of-the-art intumescent PFP to protect and even prevent AN from thermolysis when subjected to excessive heating. When considering the significant effect even at recommended minimum coating thicknesses, these are promising results for further work on improving the fire safety of road transportation tanks carrying AN.

Clearly, it must be appreciated that these small-scale experiments are for screening purposes only, as they could never simulate a real-scale fire performance. They are initial experiments designed to demonstrate the potential of these specific intumescent coatings to protect AN from excessive heating when contained in a metal container. It must rather be seen as a first step for identifying methods whereby AN can be kept contained during a fire event, thus avoiding compatibility issues, while at the same time protecting it from over heating.

To further assess if an effective thermal protection scheme has been identified for this specific use, advanced analysis and dedicated studies of the fireproofing performances are required. Such efforts should also include large-scale fire resistance tests based on international standardized tests e.g. ISO 834, where critical factors such as complex geometries are considered.

4. Conclusion

By performing a series of small-scale experiments on two state-of-the-art intumescent PFP materials,

we have demonstrated an evident thermal protection of AN from thermolysis when exposed to a 1200

°C flame in metal tubes. At its best, temperatures below 180 °C, slightly above the melting point of AN,

could be maintained for more than 2.5 hours. In comparison, the unprotected tubes reached temperatures

well above 400 °C where the sample material was completely decomposed in less than 11 minutes.

Furthermore, these significant effects were observed already at the recommended minimum coating

thicknesses, encouraging further assessments on these materials potential as a fire safety measure for

AN transported in metal road tankers.

As fire experiments on a laboratory-scale could never mimic real fire scenarios, the results are only to

be interpreted as a screening effort and a demonstration of the potential of these materials, to protect AN

enclosed in a metal container from thermolysis. Further studies, including large-scale fire tests for their

intended use, are thus needed to validate if an effective thermal protection scheme has been identified.

Regardless, in the field of fire science, proof-of-concept studies as these can be a stepping-stone to new

achievements in the continuous efforts to control fire and explosion risks for bulk road transport of AN

in tanks. With the opportunities and varieties found in modern intumescent coatings, improved safety

and greater risk reduction are conceivable future objectives.

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