Experimental and Theoretical Approach to the Assessment of Stability Criteria for Safe Transport of Ammonium Nitrate Based Emulsions

B. Fabiano[a,*], R. J. A. Kersten[b], A. Barbucci[a], and M. N. Boers[b]

[a]DICCA-Civil, Chemical and Environmental Engineering
Department, Polytechnic School – University of Genoa,
Via Opera Pia 15, 16145 Genoa, Italy

[b]TNO Defence, Security and Safety,
P.O. Box 45, 2280 AA Rijswijk, The Netherlands

The safety issues connected to storage and transportation of ammonium nitrate and ammonium nitrate emulsions are to be considered of primary importance, as demonstrated by the Tolouse explosion and various handling and storage accidents in different countries. This paper is focused on the assessment of the self-heating behaviour of ammonium nitrate emulsions (ANE) and the establishment of stability criteria for transport or storage conditions. The influence of low level contaminants on ANE reactivity is experimentally explored as well. The reaction patterns of ANE were studied by miniautoclave and Dewar experiments. An assessment of the experimental results against the Frank-Kamenetskii model for self-heating showed that small levels of heat production will already lead to self-heating. In principle, a Dewar test can be not sensitive enough to detect this level of heat production in the relevant temperature range. However, extrapolation in the downward direction of the results obtained at higher temperatures appears to provide a way to assess the safety of large-scale transport or storage. The results of such an evaluation are most likely conservative, as self-heating is also suppressed by evaporation of small amounts of water from the emulsion under "open" conditions.

Key words:
Ammonium nitrate, emulsion, explosion hazard, impurities, transport

Introduction

Ammonium nitrate (AN) is a crystalline solid with a melting point of 170 °C, which decomposes above 210 °C. It is extensively used in nitrogen fertilizer as a source of ammonia and NO_3^- ion essential for the vegetal life, while in explosives and propellants nitrate ion constitutes an oxygen source. Since the 1870's, ammonium nitrate has been widely used as a supplemental oxidant in dynamites[1] and then in admixture with solid fuels and sensitizers, such as nytroglycerine to give more sensitive explosives. Ammonium nitrate and derived explosives show non-ideal detonation behaviour, due to the relatively low decomposition rate of AN, which cause a wide reaction zone, in combination with lateral heat losses and rarefaction which extinguish the decomposition reactions.[2] Moreover, ammonium nitrate is a promising rocket propellant oxidizer as it produces, unlike the widely used ammonium perchlorate, completely eco-friendly products. AN-based oil in water and water in oil emulsion explosives have been developed since 1926, owing to their superior characteristics and cost-effectiveness. A typical formulation includes 20 % water, 12 % oil, 2 % microsphere, 1 % emulsifier and 65 % ammonium nitrate.[3] Several major accidents involving ammonium nitrate were recorded in the first half of the XX century, (Oppau, Germany, September 21, 1921; Texas City, USA April 16, 1947; Brest, France, July 28, 1947) and the more recent explosion occurred on 21st September 2001 at Tolouse – AZF plant (30 persons killed, up to 2242 people injured and an estimated cost of 1.5 billion EUR)[4] reveals that still much effort is to be devoted to investigate the hazards connected to energetic material storage and transport, despite the standards and procedures for safe storage and use. This evidence is confirmed by more recent high profile AN accidents during transportation, e.g.: on 24th May 2004, a major accident involved a cylindrical vessel used for AN transportation at Mihăileşti (Romania), when a truck loaded with 20 tons of ammonium nitrate rolled over, caught fire and exploded one hour later, causing 18 fatalities and 10 severely injured persons; on 12th September 2005, at Shengangzhai (China) a truck loaded with 18 t of ammonium nitrate exploded, destroying 17 village houses, killing

*Corresponding author. Tel.:+39–0103532585; E-mail address: brown@unige.it (B. Fabiano).

at least 11 people and injuring 43.[5] Occupational accident analysis over the long trend allows analyzing the factors contributing to accidents in industrial activities[6] and evidenced that, for example in Italy, the transport sector is characterized by higher severity, in terms of fatalities and permanent disabilities.[7] Learning from accidents by using analytical techniques to establish the root cause of incidents, so as to identify and classify technical, organizational and human factors which may have contributed to the incident[8] is one of the important factors which has led to the improvements in process safety. Provided that enough detailed data and a statistical significant number of accidents are available, the analysis can be performed by utilizing suitable statistical techniques, e.g., by Structural Equation Modelling (SEM).[9] An overview of recent high profile incidents with non-sensitised emulsion is given in Table 1. One can notice that these accidents are typical examples of low probability-high severity events, for which a probabilistic approach, including the evaluation of probability or frequency, is rather difficult, also for non completeness of data and parameters relevant to the accident scenario. The ANE types of explosives consist of a solution of ammonium nitrate dispersed in an oil phase. The emulsion is intended to produce a blasting explosive only after further processing prior to its use. Hot wire ignition experiments on ammonium nitrate emulsions were performed to identify minimum burning pressure and to predict the onset temperature.[10] Experimental tests on the detonation of ammonium nitrate and fuel oil mixtures evidenced that the physical properties of AN exert a strong influence on the sensitivity and the propagation behaviour of the detonation, with the highest detonation velocity (3.85 km s^{-1}) connected to the smallest particle diameter (0.85 mm) of ANFO.[11] Although ammonium nitrate emulsion explosives (ANEs) have been applied for quite some time, only recently has much attention been paid to their hazard characteristics at moderate conditions. This has resulted in the introduction of a dedicated classification procedure for this type of material into the relevant regulations for the transport of dangerous substances.[12] In the first instance, safe transport, storage and use of ANE are strongly related to the thermal stability of the emulsion when subjected to an elevated thermal condition. The question of how to estimate quantitatively the risk level of explosive material handling is still an up-to-date research topic, also in view of developing novel theoretical risk criteria.[13] An interesting study on the onset of runaway reactions in AN-based explosives provided experimental information appropriate to confined pumping situations and vented storage vessels, with possible application extended to bulk quantities.[14] Because of its potential reactive behaviour, proper classification of ANE is of the utmost importance for the safe transport (and storage) of this material. However, the classification of this substance is not easy. Emulsion sensitivity to explosion can vary depending on density, ratio of aeration, droplet size in the emulsion, quality of raw material, additives like nitrites and so on. Some experts on classification pointed out that the properties can even vary with time, depending on factor such as pH, chloride content and amount of NOx present. The safety conditions during transport and eventually the limitations at which the transport of this substance can be submitted are directly related to the transportation class. In principle, the following classes might apply:

An explosive of Class 1

"Solid or liquid substance (or a mixture of substances) which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings. Pyrotechnic substances are in-

Table 1 – *High profile accidents incidents involving AN emulsions*

Year	Country	Event
1988	Canada	An explosion while pumping an emulsion matrix (ignited under pressure) caused four fatalities.
1990's	USA	An increasing frequency of accidents/near-misses is recorded during maintenance work to equipment contaminated with ANE explosives or explosive precursors.
1994	Papua (New Guinea)	At 9:45 am a severe explosion in the AN emulsion plant at Porgera Gold Mine resulted in 11 fatalities and large property damage. The fatal explosion involved at most a few t of explosive and was originated by a fire in a tank of emulsion matrix in close proximity to a fuel oil tank.
		At 11:02 am a larger explosion of nearly 80 t of emulsion (Ammonium Nitrate Emulsion, ANE, UN 3375) was caused by fires under storage facilities at the same site. There were no fatalities in the second explosion due to proper and timely site evacuation.
2010	Saudi Arabia	The transport contractor to a Saudi Chemical Company customer was transporting a container loaded with 18 t of AN and fuel oil, when following a collision, the truck rolled over resulting in a fire scenario without explosion.

cluded even when they do not evolve gas." ANEs are manufactured for explosive use.

Desensitised explosive (liquid of Class 3 or solid of Class 4)

Class 3:"Explosive substances that are dissolved or suspended in water or other liquid substances to form a homogeneous liquid mixture to suppress their explosive properties."

Class 4:"Explosive substances that are wetted with water or alcohol or are diluted with other substances to form a homogeneous solid mixture to suppress their explosive properties."

An oxidising substance (solid or liquid) of Class 5 Division 5.1; and /or Class 9

ANEs contain a substantial proportion of ammonium nitrate; their primary hazardous property (if not Class 1) is that of an oxidiser. Oxidising substances are defined as:" Substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute, the combustion of other material." Class 9, miscellaneous substances:" Substances and articles which during transport present a danger not covered by other classes. This class includes substances that are transported or offered for transport at temperatures equal to or exceeding 100°C in a liquid state or at temperatures equal to or exceeding 240 °C in a solid state".

Not dangerous

It is clear that a substance included in class 1 needs a higher safety procedure and, consequently, larger investment, than if included in a lower class. The need for a safe, but not overly conservative classification procedure, thus becomes evident. A well-documented method to determine the thermal stability of ANE with respect to practical applications is test 8(a) of the UN transport classification scheme.[12] This test is used to measure the stability of a candidate for "ANE intermediate for blasting explosives" when subjected to an elevated thermal condition and determines whether or not the emulsion is too dangerous to be transported. The test is normally carried out in Dewar with a volume of 0.5 L, which is filled with ANE for a volume corresponding to 80 % and placed in an oven. The oven is kept at a constant pre-defined temperature. If the loading temperature of the ANE intermediate exceeds the pre-defined oven temperature, the temperature of the oven is increased to the loading temperature. The actual test starts when the temperature of the sample is two degrees below the oven temperature. The test is interrupted if the temperature of the substance exceeds the temperature of the

oven by more than six degrees. If this condition is not met over a period of seven days, the ANE is considered thermally stable and can be further tested as a candidate for ANE intermediate for blasting explosives. Otherwise, the substance is not suitable for transport. In fact, in that case it would not be possible to avoid potential hazardous conditions during the transportation phase, contrarily to an industrial plant, where a dynamical analysis of the exothermic system allows determining necessary safety actions.[15] Whether or not an ANE intermediate is stable under transport conditions depends on the balance between the exothermic reaction patterns of the ANE and the heat loss from a given storage or transport container. Possible inconsistencies in applying the Dewar method were evidenced by Fisher et al.[16] As discussed above, the main disadvantage of the Dewar test is that its heat loss characteristics only correspond to storage sizes up to nearly 2 m³. In order to extrapolate the test result to larger sizes, the test is performed at an elevated temperature. This working hypothesis is tantamount to saying that the increase in temperature increases the heat production, which, in turn, compensates the too high level of heat loss. In analogy with the results from peroxide testing, a temperature increase of 20 °C is proposed for 20 m³ containers. It must be remarked that the above-mentioned test method is based on two important assumptions. Firstly, it is assumed that the decomposition patterns of the ANE intermediate obey a "simple scalable" mechanism over the temperature range of interest. Secondly, it is assumed that the heat loss mechanism from a given package is determined by the heat loss over the wall of the package. The latter assumption seems rather questionable, as, contrarily for example to the low viscous peroxide solutions, ANE are high viscous pastes with relatively low heat conductivity. This study is focused on the reactive properties of ANE, so as to shed light on its thermal behaviour by applying an integrated, two-technique approach based on miniautoclave DTA and Dewar calorimeter. Considering that the Tolouse accident occurred with off-spec materials and impurities recognized as possible contributing factors, an experimental view is also taken on the possible effect of contaminants (namely HNO_3 and $NaCl$) on the susceptibility to self-heating of ammonium nitrate emulsions.

Theoretical approach to self-heating

As well known, self-heating is the occurrence of a rise in temperature in a material in which heat is being generated by some process taking place within the material.[17] Under certain circumstances, the temperature rise may increase both in magni-

tude and rate sufficiently to lead to combustion or explosive effects; that is, there may be "self-ignition", or "spontaneous ignition", or there may be a "thermal explosion". Whether or not self-heating occurs under practical conditions depends on the balance between heat generation and heat loss. In 1928, Semenov[18] proposed a rather simple model to calculate the self-heating potential of a system with a homogeneous temperature. This model turned out to be valuable at small scale and for systems characterized by a high apparent thermal conductivity. Semenov's uniform spatial distribution of temperature and Newtonian heat transfer to the surroundings apply to situations in which the heat conductivity in the reactant is large compared with heat loss to the surroundings. Under different conditions, the reactant heats non-uniformly and a temperature gradient will be formed. The thermal explosion with a temperature gradient within the reactant was described by Frank-Kamenetskii.[19] The model usually applies to solids, pastes and high viscous liquids. The so-called Biot number enables to decide which of the models describes the practical situation. The Biot number (Bi) is defined as:

$$Bi = \frac{h \cdot r}{\lambda} \qquad (1)$$

According to Merzhanov et al.,[20] the Semenov model is applicable for situations with a Biot number below 0.3, whereas the Frank-Kamenetskii model is applicable with a Biot number exceeding 10. An ammonium nitrate emulsion (ANE) is a high viscous substance that can have various compositions with respect to the relative amounts of ammonium nitrate, water, oil and additives. In order to select a theoretical model suitable to describe the critical condition and the behaviour in typical storage or transport sizes the range of physical parameters and the characteristic of the "packages" must be defined. Subsequently, on the basis of these parameters and characteristics, a range of values for the Biot number for a given package can be derived. At last, from an evaluation of the ranges of the Biot number for the various storage or transport situations, a theoretical model can be selected. The char-

acteristics of commercial packages can be calculated on the basis of their so-called heat loss factor (HLF), according to eq. (2):

$$HLF = \frac{hA}{m} \qquad (2)$$

As remarked by Fierz,[21] this factor represents the specific heat loss of a transport package showing Newtonian cooling. It should be noticed that this definition is more related to the Semenov model. In fact, according to this model, the HLF simple provides the heat loss per unit mass of material in the package. The values for typical commercial packages are calculated in Table 2, where the values of A and h were derived from literature.[12] Using the values for the heat transfer area, the overall heat transfer coefficient given in Table 2 and a range for the heat conductivity between 0.1 and 0.3 W m^{-1} K^{-1}, the Biot number for each package can be evaluated. Table 2 shows that the calculated values of Bi for standard packages of different nominal capacity, all exceed a value of at least 3. It can be concluded that the Frank-Kamenetskii model applies to the given common situations. It must be remarked that only for a heat conductivity of 0.2 or 0.3 W m^{-1} K^{-1}, in connection with the small 50 L package, or with the insulated container, the heat transfer over the surface of package starts to play a rather limited role in the heat balance.

Under the assumption of cylindrical configurations and infinite length, according to the well known Frank-Kamenetskii model, the critical condition is as follows:

$$F_k = \frac{(-\Delta H)\rho}{\lambda} \frac{E}{RT_0^2} r^2 k_0 \exp\left(-\frac{E}{RT_0}\right) = 2 \qquad (3)$$

Based on the activation energy of the decomposition reaction of ammonium nitrate (AN) and AN in water, a conservative range for the activation energy is 120 to 160 kJ mol^{-1}. Equation 3 allows obtaining the critical dimensions of a package for a given level of heat production at T_0, once given or estimated the values for λ, ρ and E. From one side, it is worth noting that eqs. (2) and (3), based on the

Table 2 – *Characteristics of typical ANE packaged systems*

Package	h [W m^{-2} K^{-1}]	A [m^2]	HLF [mW kg^{-1} K^{-1}]	Biot number		
				$\lambda = 0.1$ [W m^{-1} K^{-1}]	$\lambda = 0.2$ [W m^{-1} K^{-1}]	$\lambda = 0.3$ [W m^{-1} K^{-1}]
50 L plastic drum	5.8	0.8	94	10	5	3
200 L plastic drum	5.8	1.9	56	16	8	5
5000 L container	4.4	17	17	28	14	9
25000 L container	4.4	51	10	47	24	16
25000 L insulated ISO container	1.0	51	2.3	11	5	4

semi-analytical simplified theory of Frank-Kamenetskii, give only an approximate index value, as long as they are valid for a single stage zero-order reaction, i.e. the reaction rate is independent of the conversion. On the other side, they allow obtaining convenient analytical relations without applying more complex and comprehensive models and can be used, with proper caution, as a rule for the simple estimation of critical parameters.

The heat production per unit mass is defined as:

$$q_{prod} = (-\Delta H) k_0 \exp\left(-\frac{E}{RT_0}\right) \qquad (4)$$

Moreover, by combining equations 3 and 4, the maximum allowable heat production for a given package or storage size can be determined. The maximum allowable heat production per unit mass or critical heat production q_{max} follows as:

$$q_{max} = \frac{F_k R T_0^2 \lambda}{r^2 \rho E} \qquad (5)$$

For values above the maximum allowable heat production, the system reaches its super critical state and self-heating (or eventually a thermal explosion and subsequent destruction of the package) will occur. We can observe that the maximum heat production is inversely proportional to the squared radius of the package or, dealing with a more general configuration, to the squared characteristic length of the container. It must be observed that the approach is based on the assumption of infinite cylinder, to be clearly considered as an ideal approximation of the aspect ratio of a real container. However, the approximations made allow the attainment of conservative results in determining the critical values for the safe transport of ANE.

Experimental

Materials

The tested ANE was supplied by Dyno Nobel Europe (Marked, Norge) and tested as received. Both unsensitized emulsion and sensitised emulsion explosive were tested. A polymeric emulsifier and a mineral oil was used as the fuel phase. The average specifications of the sensitised product are as follows: density 1.01 g cm^{-3}; energy 3200 J g^{-1}; detonation velocity 4000 m s^{-1}.

During experimental runs addressed to a preliminary evaluation on ammonium nitrate emulsion stability in the presence of possible low concentration contaminants, samples were prepared by adding to the above mentioned ANE reagent grade nitric acid (Sigma Chemicals, St. Louis, MO, USA) or sodium chloride, respectively at 1 % and 0.14 % w/w.

Miniautoclave DTA

The miniautoclave DTA is a temperature controlled reaction system, consisting of two autoclaves and one reference autoclave that are placed in an oven. Basically, the miniautoclave system is a gram-scale differential thermal analysis system (DTA) that allows the measurement of pressure, as well as temperature, using vessels (autoclaves), which are equipped with a thermocouple and a pressure transducer. The temperature is measured via a thermowell in the test sample. The pressure is measured via a capillary tube with a length of 30 cm. Each autoclave is characterized by a free volume of 6 mL and is capable of operating up to a temperature of 350 °C and a pressure of 400 bar (see Fig. 1). In these experiments, a glass sample tube and thermowell were applied to avoid a direct contact between the sample and the metal of the test vessel. The tests on ammonium nitrate emulsion were performed as "open" and "closed" tests, as recently suggested in other studies.[14] In the open tests, the vent line to the bursting disc is replaced by a 1/8" capillary tube with a length of 20 cm, which, in turn, is connected to a 1/16" capillary tube with a length of 6 cm, reducing the effective vent area. In the closed test, the system was sealed, so as to record any pressure resulting from vaporization or decomposition of the sample. More information on miniautoclave testing, can be found in Whitmore et al.,[22] while its potential use for the screening of
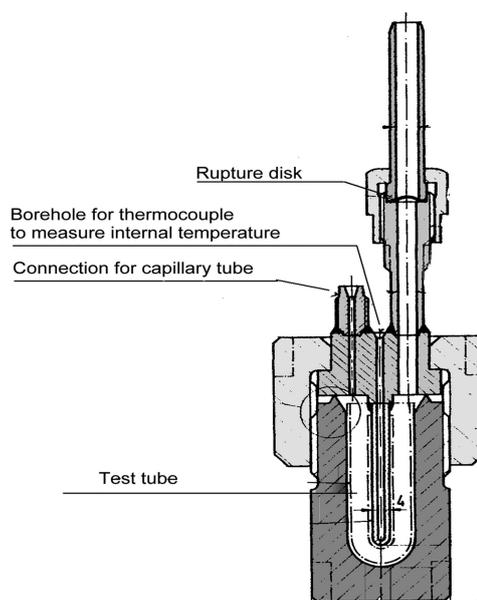
Fig. 1 – *Simplified layout of the autoclave in the miniautoclave DTA apparatus*

chemical reactivity hazards was explored in Mak et al.[23] The experiments were performed with a sample mass equal to 1 and 2 g in the closed and open test, respectively. All the scanning tests (for both pure and additivated ANE) were performed in the temperature range 20–350 °C, with a scanning rate of 2.5 °C min^{-1}. The reference autoclave was filled with 2 g of sand.

Dewar calorimeter

In principle, Dewar experiments can be used to determine the self-heating behaviour of materials under various conditions. Because of the low heat loss from a Dewar, small amounts of produced heat can be accurately determined. The main advantages of Dewar experiments are the use of a relatively simple experimental set-up, a simple experimental procedure and results that can be directly related to practical situations. Apart from the determination of the onset temperature of an exothermic reaction, the Dewar experiments enable the assessment of the thermal properties of the investigated substance. The Dewar apparatus used in the tests consists of a 0.5 litre glass vessel that is normally used in the already mentioned HAST -UN test H[11]. The experiments, detailed elsewhere,[24] were performed both in an insulated and a non-insulated Dewar. The insulated Dewar set-up comprises the standard apparatus as normally used in the HAST test. The non-insulated Dewar was simply made by breaking the vacuum of a standard Dewar. The air then present in between the double glass wall significantly increases the heat loss from the Dewar. For safety reasons, firstly the non-insulated Dewar was used to assess the stability of the ANE as a self-heating is more likely to proceed with a lower temperature excursion in this configuration, as compared with the same process in an insulated Dewar. The heat loss factor, calculated for both types of Dewar, making reference to sand and water, are given in Table 3. The heat loss from the Dewar corresponds to the heat loss of typical packages as commonly adopted during transport or storage, up to a size of approximately 2 m^3 (typically within the range 20–40 mW kg^{-1} K^{-1}, depending upon the type of material tested).

Ta b l e 3 – *Specific heat loss (HLF) of the Dewar apparatus*

Dewar configuration	HLF $_{Sand}$ [mW kg^{-1} K^{-1}]	HLF $_{Water}$ [mW kg^{-1} K^{-1}]
Insulated	20	38
Not Insulated	234	485

Results and discussion

Fig. 2 depicts as a typical example the experimental results of the DTA closed experiment with ANE: it evidences a sudden increase in pressure upon the start of the decomposition reaction, with the exothermic peak detected at T = 245 °C, in connection with p$_{max}$ = 323 bar, measured prior to the rupture of the bursting disk (design pressure 360 bar at 20 °C). The pressure curve shows an apparent "overshoot" in pressure characterized by a maximum rate of pressure rise equal to 612.0 bar s^{-1}. This effect is caused by a rapid cool down of produced gasses, condensation of volatile components, or recombination of gaseous products upon the peak in reaction. As a result, after the pressure peak, pressure reduces to a nearly constant level with p$_{final}$ = 87.0 bar. Fig. 3 shows the DTA signal as a function of the reference temperature for both the open and closed experiments with ANE samples. The DTA signal equals the measured temperature in the sample autoclave minus the measured temperature in the reference autoclave, at a given time. Comparison of results from closed and open
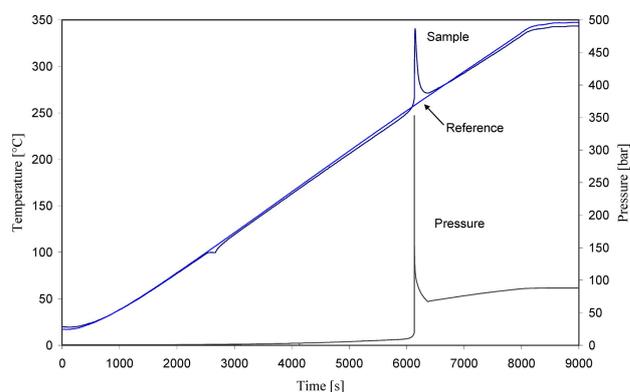
F i g . 2 – *Typical temperature and pressure profiles from miniautoclave DTA closed experiment with ammonium nitrate emulsion (ANE)*
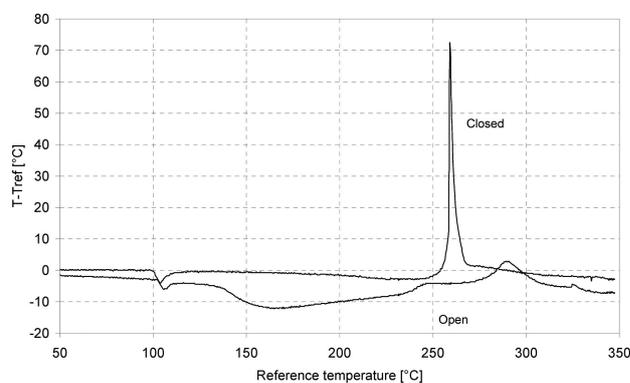
F i g . 3 – *Comparison of DTA output as a function of temperature for ammonium nitrate emulsion (ANE) in open and closed experimental runs*

Table 4 – *Summary of results for DTA runs with ammonium nitrate emulsion under different conditions*

Data	Unit	Open system	Closed system
Mass	[g]	2.00	1.04
Onset decomposition	[°C]	267	246
ΔT_{max}	[°C]	10	84
T_p	[°C]	290	259
P_{max}	[bar]	1	352
$(dPdt)_{max}$	[bar s^{-1}]	0	612
P_{end}	[bar]	1	87

F i g . 4 – *Comparison of AN, ANE and AN94 miniautoclave experimental runs, under closed conditions*

F i g . 5 – *Comparison of AN, ANE and AN94, miniautoclave experimental runs, under open conditions*

runs is to be performed carefully as the system actually modifies in the open tests due to evaporation or relief of gases. Making reference to the same Fig. 3, one can notice not only the sharp reduction in the heat effect of the reaction under open conditions, but also the occurrence of an endothermic process at temperatures above 135 °C. This endothermic process is caused by the evaporation of water from the emulsion. The key parameters obtained from the experimental series with ANE are summarized in Table 4. As discussed in the following, more information on the decomposition patterns of the ANE can be obtained by comparing the above-mentioned data with the results of mini-autoclave experimental runs on pure ammonium nitrate and ammonium nitrate/water mixture. As reported elsewhere,[11] the decomposition of AN involves a number of consecutive and simultaneous reactions and phase equilibria, with initial endothermic decomposition of ammonium nitrate into ammonia and nitric acid. As anticipated, closed systems behave very different from open systems, as in the latter AN vaporization can occur easily and a significant loss of the starting material can occur. AN-based emulsion is characterized by a more complex thermal decomposition than that of the oxidizers, owing to the presence of the oil phase. From experimental runs, we can notice a longer time to the onset of decomposition in the open runs, which could be ascribed to higher heat loss by evaporation during decomposition under this experimental configuration. Fig. 4 shows the comparative experimental results of DTA runs under closed conditions. The ammonium nitrate-water mixture had a water concentration of 6 % w/w (designated as AN94). From the same Fig. 4, one can easily identify in the corresponding profile the phase transitions of pure ammonium nitrate and the corresponding melting peak at 170 °C. The onset of the decomposition reaction in the pure ammonium nitrate and AN94 occur at approximately the same temperature. This onset temperature appears to correspond with the onset temperature of ammonium nitrate emulsion. However, the ANE sample evidences a much faster acceleration of the
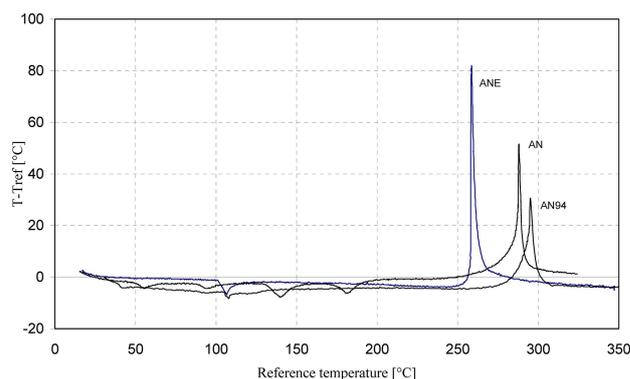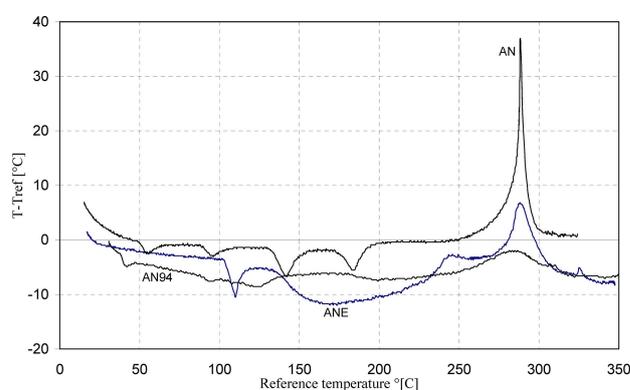
reaction (connected to higher apparent activation energy). This enhancement is also observed from the difference in peak heights. The results of the open tests on ANE, AN and AN94 are depicted in Fig. 5. The pure AN curve does not show any endothermic reaction. The reason for this empirical evidence is that the sample contains no water that might cause evaporative cooling. Any endothermic effects connected to the dissociation of AN into ammoniac and nitric acid, or to the evaporation of water produced in the decomposition of AN into N_2O and water are masked by the exothermic decomposition reaction. A comparison between the results of the ANE and AN94 shows that the endothermic effect caused by the evaporation of water is much more pronounced in the ANE than in the AN94. Again, the decomposition reaction in the ANE appears to accelerate faster than the reaction in the AN94. The shape of the curve of ANE in between 200 and 250 °C most likely results from a reduction in evaporation, as the water content in the sample decreases. The miniautoclave results showed that under completely confined conditions, the exothermic decomposition of the ANE starts at elevated temperatures, well over the handling temperature. However, it must be remarked that some reaction

Table 5 – *Evaluation of the maximum allowable heat production [mW kg⁻¹] in different ANE packaged systems, at two loading temperatures*

Temperature [K]	Activation energy [kJ mol⁻¹]	200 L plastic drum λ [W m⁻¹ K⁻¹]		5000 L container λ [W m⁻¹ K⁻¹]		25000 L non-insulated container λ [W m⁻¹ K⁻¹]	
		0.1	0.3	0.1	0.3	0.1	0.3
298	120	17	50	3	8	1	3
298	160	13	38	2	6	1	2
333	120	21	63	3	9	1	3
333	160	16	47	2	7	1	2

might take place below the onset temperature. This will not be detected due to the calorimetric accuracy of the miniautoclave system. In the open system, the evaporation of water appears to determine the thermal behaviour in the temperature range below 200 °C. This empirical finding suggests that any self-heating behaviour will stop when the ANE temperature reaches the melting or evaporation point. Exothermic effects are only to be expected after prolonged external heat input. As a comparison, to further investigate the stability of the ANE under storage/transport conditions, we consider as well experiments performed with standard Dewar apparatus, at oven temperature corresponding to 85, 100 and 125 °C, according to the standard testing procedure previously mentioned. None of the Dewar tests showed the occurrence of self-heating evidencing that the heat produced by the tested ANE, if any, is significantly less than the heat loss to the surroundings.[24] On the basis of the heat loss factor of the Dewar and considering that no temperature excursion was observed in the test period, it follows that the heat production is at least below a calculated conservative value corresponding to 40 mW kg⁻¹. From the experimental results, it appears that under open or non-confined conditions (Dewar and open mini-autoclave test) no detectable heat production takes place. From the closed miniautoclave experiment, considering as well the comparison with pure ammonium nitrate and ammonium nitrate/water mixture, it appears that heat production only takes place at temperatures well above 200 °C. Despite the overall experimental evidence showing no presence of any reactivity in the low temperature range, a careful evaluation of the tests should be made before any solid conclusions can be drawn on the practical situation. In fact, it must be underlined that in a storage system where internal heat may be generated it is essential that the small-scale test used to assess behaviour in bulk reflects as far as possible the parameters relevant to modelling the bulk system. An important matter in this respect is a comparison between the accuracy of the Dewar and the required accuracy to assess the safety of large-scale storage or transport. Such a comparison can be made on the basis of the model for self-heating

derived by Frank-Kamenetskii, according to the critical condition given by equation (3) (for an ideal cylinder). The maximum allowable heat production can be calculated for different values of the activation energy and the heat conductivity, as shown in Tables 5 and 6. Results are calculated making reference to three different standard packages or containers at an ambient temperature of 25 °C or a loading temperature of 60 °C. Furthermore, two limiting values for the activation energy were used. The higher value of 160 kJ mol⁻¹ relates to the activation energy of pure ammonium nitrate. The lower value of 120 kJ mol⁻¹ can be used as a conservative value for the extrapolation of the heat production as a function of temperature. Tables 5 and 6 show that the maximum allowable heat production for the 200 L drum is close to, or above the accuracy of the Dewar test. This test could be considered not accurate enough for the container with nominal capacity 5000 or 25000 L, thus evidencing the need of further investigation. For these containers, independently of the used heat conductivity, the Dewar test is only applicable if the experimental results are extrapolated to a lower temperature range. Such an extrapolation is possible when the heat production of the ANE at a given temperature is assumed equal to the accuracy of the Dewar. Just as an illustrative application, the evaluation of the extrapolated heat production according to equation (4), in connection with an apparent activation energy of 120 kJ mol⁻¹, leads to the conclusion that the tested emulsion would be safe for transport on a 25000 L scale with

Table 6 – *Comparative results for DTA runs under closed configuration with pure ammonium nitrate emulsion and contaminated ammonium nitrate emulsion (HNO_3 1% w/w or NaCl 0.14 % w/w)*

Data	Unit	ANE closed test	ANE -HNO_3 closed test	ANE NaCl closed test
Mass	[g]	1.04	0.97	1.05
Onset decomposition	[°C]	246	193	229
ΔT_{max}	[°C]	84	41	78
T_p	[°C]	259	316	256
P_{end}	[bar]	87	96	91

an ambient or loading temperature of approximately 85–90 °C (the heat production is below 1 mW kg⁻¹ in this range if no heat production is detected at 125 °C in the Dewar test during the required test period). The approach could also be used the other way around. For a maximum allowable heat production at 60 °C of 1 mW kg⁻¹ K⁻¹ and an activation energy of 120 kJ mol⁻¹, the test should be performed at a temperature of 90 °C.[24] It is worth observing that the temperature difference of 30 °C is higher than the difference of 20 °C mentioned in the introduction. In principle, according to the evaluation discussed above it should be verified that no exothermic reactions occur which are masked by physical processes, such as evaporation or melting. Such a verification can be performed on the basis of the heat-up period of the Dewar in which deviations from the heat-up of a thermally inert material are easily detected. Furthermore, it must be mentioned that the evaporation of small amount of water effectively removes produced heat. Under a situation like this, in the absence of an internal exothermic chemical process that drives the endothermic physical changes, exothermic effects are only to be expected after prolonged external heat input. Clearly, scale-up methods are only approximations, with no assurance of real thermal equivalence of reactive systems of different size; in this regard, an advanced method based on the theory of regular cooling mode[25] can ensure more reliable results of the Dewar test application, with the drawback of complex mathematical simulation.

It is amply known that impurity traces (e.g. peroxides, rust or metal ions from corrosion) may catalyze decomposition reactions. Considering that possible impurities of ammonium nitrate can be contributing factors to the origin of an explosion, as for example in the Tolouse accident, a preliminary experimental evaluation on contaminated ANE was carried out as well. Figs. 6 and 7 depict a compari-

F i g . 7 – *Influence of HNO₃ contamination on ANE decomposition under open condition (ammonium nitrate emulsion acidified with HNO₃ 1 % w/w)*

son between the experimental results of pure ANE and acidified ANE in the closed and open experimental runs respectively. From Fig. 6 it can be noticed that the onset of the exothermic reaction shifts to a lower temperature. Furthermore, three decomposition peaks are experimentally observed instead of one. The two last peaks are in fairly good agreement with those observed in the open run for the sample with the same composition shown in Fig. 7. From the same figure, it can be argued that due to the endothermic effect of water evaporation, the previously mentioned exothermic peak does not appear. Overall, it results that a low level contamination with HNO₃ exerts a more marked effect under closed, rather than under open conditions. The key findings of experimental runs performed utilizing ANE contaminated with NaCl are that at the tested concentration the curves hardly evidence any significant quantitative difference, contrary to the results available in case of ammonium nitrate with the same contaminant.[26] In fact, during the closed tests the curves were practically superimposed while, as shown for example in Fig. 8, the slight differences detected under open conditions

F i g . 6 – *Influence of HNO₃ contamination on ANE decomposition under closed condition (ammonium nitrate emulsion acidified with HNO₃ 1 % w/w)*
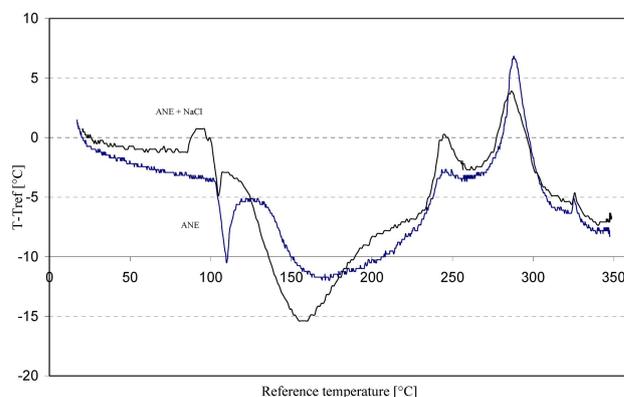
F i g . 8 – *Influence of NaCl contamination on ANE decomposition, under open condition (ammonium nitrate emulsion added with NaCl 0.14 % w/w)*

are not significant from the safety side. A comparative summary of quantitative results obtained under closed conditions runs is shown in Table 6, from which the main conclusion is that the onset of the exothermic decomposition reaction is reduced in the presence of acidification and, to a lower degree, also in the presence of NaCl, if compared with the onset of pure ANE, corresponding to 246 °C.

Conclusions

From an evaluation of theoretical models for self-heating, the characteristics of typical packages and the properties of ammonium nitrate emulsions it can be concluded that the more relevant parameters for assessing the occurrence of self-heating under storage, or transport conditions are heat conductivity of the material and the "package" dimensions, rather than the heat transfer coefficient of the package. The self-heating of ANE under realistic conditions can be described by applying the Frank-Kamenetskii model. From the present work, it is concluded that according to the relevant model for self-heating, low levels of heat production could already lead to self-heating of ANE. In principle, a Dewar test is not accurate enough to detect this level of heat production in the relevant temperature range. However, downward extrapolation of the results obtained at higher temperatures, appears to provide a way to assess the safety of large-scale transport sizes, at least at a preliminary level. The results of such an evaluation are most likely conservative as self-heating is also suppressed by evaporation of small amounts of water from the emulsion (under "open" conditions), or melting of the ammonium nitrate component. Hence, exothermic effects liable to affect transport safety are only to be expected after prolonged external heat input for the considered ANE system. As regards the amply unexplored topic of ANE contamination, globally, contrary to what is reported for ammonium nitrate, it does not appear that the contamination of ammonium nitrate emulsion with HNO_3 or NaCl at the tested levels affects the decomposition in a way determining for the reactivity in the low temperature range, typical of transport conditions.

List of symbols

A   – surface area of the package, m^2

E   – activation energy, $J\ mol^{-1}$

$\dfrac{dp}{dt}_{max}$ – maximum rate of pressure rise, $bar\ s^{-1}$

F_k – Frank-Kamenetskii number

h   – heat transfer coefficient, $W\ m^{-2}\ K^{-1}$

k_0 – pre-exponential factor, s^{-1}

m   – mass of packaged material, kg

P_{max} – maximum pressure, bar

q_{max} – critical heat production according to eq. (5), $W\ kg^{-1}$

q_{prod} – heat production according to eq. (4), $W\ kg^{-1}$

R   – ideal gas constant, $J\ mol^{-1}\ K^{-1}$

r   – radius of a cylinder, sphere or half thickness of slab, m

T_0 – critical ambient temperature, K

Tp   – peak temperature during DTA runs, °C

V   – package volume, m^3

ΔH   – heat of reaction, $J\ kg^{-1}$

ΔT_{max} – maximum temperature difference between sample and reference during DTA runs, °C

λ – thermal conductivity, $W\ m^{-1}\ K^{-1}$

ρ – density, $kg\ m^{-3}$

Abbreviations

AN   – ammonium nitrate

AN94 – ammonium nitrate 94 % water 6 % [w/w]

ANE   – ammonium nitrate emulsion

ANFO – ammonium nitrate and fuel oil

Bi   – Biot number (eq. 1)

DTA   – differential thermal analysis

HLF   – heat loss factor

SEM   – structural equation modelling

References

1. *Meyers, S., Shanley, E.,* J. Hazard. Mater. **23** (1990) 183.
2. *Cook, M.A.*, The Science of High Explosives, Van Nostrand Rheinhold, New York USA, 1958.
3. Ullman's Encyclopedia of Industrial Chemistry 5th ed., vol 10, pp.49–53, Wiley & Sons, New York, USA, 1992.
4. *Dechy, N., Bourdeaux, T., Ayrault, N., Kordek, M.-A., Le Coze, J.C.,* J. Hazard. Mater. **111** (2004) 131.
5. *Nygaard, E.C.,* Safety of ammonium nitrate. In: ISEE Proceedings 2006, vol II, pp. 1–11, International Society of Explosives Engineers, Cleveland, 2006.
6. *Fabiano, B., Parentini, I., Ferraiolo, A., Pastorino, R.,* Saf. Sci. **21** (1995) 65.
7. *Fabiano, B., Currò, F., Pastorino, R*., Occup. Environ. Med. **58** (2001) 330.
8. *Fabiano, B., Currò, F*., Process Saf. Environ. **90** (2012) 357.
9. *Šrekl, J., Golob, J.,* Chem. Bio. Eng. Q. **23** (2009) 309.
10. *Turcotte, R, Goldthorp, S., Badeen, C.M., Chan, S.K*., Propellants Explos. Pyrotech. **33** (2008) 472.

11. *Miyake, A., Takahara, K., Ogawa, T., Ogata, Y., Wada Y., Arai, H*., J. Loss Prev. Process Ind. **14** (2001) 533.

12. United Nations. Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 4th rev. ed.: United Nations, New York and Geneva, 2003.

13. *Dubovik, A.V., Akinin, N.I., Annikov, V.E., Apolenis, A.V.*, Theor. Found. Chem. Eng. **43** (2009) 218.

14. *Turcotte, R., Lightfoot P.D., Fouchard R., Jones, D.E.G.,* J. Hazard. Mater. **A101** (2003) 1.

15. *Varga, T., Abonyi, J.,* Chem. Bio. Eng. Q. **24** (2010) 283.

16. *Fisher, H.G., Goetz, D.D.,* J. Loss Prev. Process **6** (1993) 183.

17. *Bowes, P.C.,* Self heating: Evaluating and Controlling the Hazards, Elsevier Science Publisher Amsterdam, The Netherlands, 1984.

18. *Semenov, N.N.,* Zur Theorie des Verbrennungsprozesses Z. fur Physik **48** (1928) 571.

19. *Frank-Kamenetzkii, D. A.,* Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York USA, 1969.

20. *Merzhanov, A.G., Abramov, V.G.,* Propellants Explos. Pyrotech **6** (1981) 130.

21. *Fierz, H.,* J. Hazard. Mater. **A96** (2003) 121.

22. *Whitmore, M.W., Baker, G.P.,* J. Loss Prev. Process **14** (2001) 223.

23. *Mak, W.A., Kersten, R.J.A., Boers, M.N., Creemers, A.F.L.,* J. Loss Prev. Process **17** (2004) 347.

24. *Kersten, R.J.A., Fabiano, B., Boers, M.N.,* Loss Prevention 2004. H.J. Pasman, J. Škarka and F. Babinec (Ed.), Vol. B, pp 2377–2383, PCHE Publ., Praha, 2004.

25. *Kossoy, A.A., Sheinman, I.Ya.,* J. Hazard. Mater.**142** (2007) 626.

26. *Zhang, W.P.* Chinese J. Explos. Propellants **27** (2004) 33.