Ammonium nitrate: a promising rocket propellant oxidizer

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Abstract

Ammonium nitrate (AN) is extensively used in the area of fertilizers and explosives. It is present as the major component in most industrial explosives. Its use as an oxidizer in the area of propellants, however, is not as extensive as in explosive compositions or gas generators. With the growing demand for environmental friendly chlorine free propellants, many attempts have been made of late to investigate oxidizers producing innocuous combustion products. AN, unlike the widely used ammonium perchlorate, produces completely ecofriendly smokeless products. Besides, it is one of the cheapest and easily available compounds. However, its use in large rocket motors is restricted due to some of its adverse characteristics like hygroscopicity, near room temperature phase transformation involving a volume change, and low burning rate (BR) and energetics. The review is an attempt to consolidate the information available on the various issues pertaining to its use as a solid propellant oxidizer. Detailed discussions on the aspects relating to phase modifications, decomposition chemistry, and BR and energetics of AN-based propellants, are presented. To make the review more comprehensive brief descriptions of the history, manufacture, safety, physical and chemical properties and various other applications of the salt are also included. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ammonium nitrate; Solid composite propellants; Clean burning propellants; Phase modification; Explosives; Burning rate

1. Introduction

Ammonium nitrate (AN) is one of the most commercially important ammonium compounds in terms of usage. It finds extensive use in the area of nitrogen fertilizers and

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explosives [1,2]. While it acts as a source of ammonia and nitrate ion vital to the plants in the form of nitrogen fertilizer, in explosives and propellants the nitrate ion is a source of oxygen and finds its application as an oxidizer. AN is the principal component of most industrial explosives. Several compositions of AN such as ANFO (ammonium nitrate-fuel oil), amatol, etc. are well known explosives. However, its use in the field of propellants/pyrotechnics, unlike potassium nitrate which is the principal constituent of the black powder or gun powder and even known to be used in the earliest solid rockets or ammonium perchlorate (AP) which is the main oxidizer of modern solid propellants, is rather limited. Its principal use in propellants is restricted to low burning rate (BR), low performance applications, such as gas generators for turbopumps of liquid propellant rocket engines or emergency starters for jet aircraft [3].

Owing to their operational simplicity, the solid propellants have found extensive usage both in the space and military missions. Solid propellants are essentially comprised of two major ingredients, namely a gas producing solid oxidizer and an organic polymeric fuel which also acts as a binder. Most solid rocket motors currently in use employ AP as the main oxidizer. Of late, with the increasing concern for environmental friendly, chlorine free propellants, there is a growing interest in AN, which produces innocuous products of combustion, as an alternative rocket propellant oxidizer although it is well known that inorganic nitrates are low performance oxidizers as compared to perchlorates. Besides the low energetics, AN is hygroscopic, undergoes a room temperature phase transformation involving a significant volume change and burns very slowly. These adverse properties make it even less attractive as an alternative oxidizer. Nevertheless, it is evident from the extensive literature that many of these problems of AN which restrict its use as an efficient oxidizer have proven to be surmountable. However, much of the information concerning the various properties of the salt, especially those relevant to its use as an oxidizer, remain either classified or scattered due to its application in strategic areas. The present review is an attempt to consolidate the relevant information with emphasis on the properties, such as, phase transformation, decomposition chemistry, BR and energetics, which are related to its use as a solid propellant oxidizer. In our endeavour to focus on the feasibility of using AN as a propellant oxidizer alone, we have not attempted to cover the entire gamut of voluminous information available on the salt. However, since no reviews on AN has appeared in recent years a brief description on the history, manufacture, physical and chemical properties, and applications in other areas is also included to make the review more comprehensive.

2. Manufacture and storage

AN does not occur in nature as such. The salt was first discovered by Glauber [4] in 1659 who prepared it by the action of nitric acid on volatile alkali, ammonium carbonate and called it nitrum flammans because its yellow flame (from traces of sodium) was different from that of potassium nitrate. Many of the procedures reported in the literature in the early times for the preparation of AN are summarized by Mellor [5].

It is now commercially manufactured from synthetic ammonia and nitric acid. The relevant information about the reactors and various processes employed at different stages of production are available in the literature [1,2]. Neutralization of nitric acid with ammonia first produces a concentrated solution which is later evaporated to a melt. The melt is subsequently processed by prilling or granulation to get the final commercial product. This phase happens to be the most crucial as adequate mechanical properties of the final grain is imparted at this stage. In a typical prilling process round granular solids are formed when molten droplets are allowed to fall through a fluid cooling medium. A 96–97% AN solution is sprayed into towers 33 to 60 m high to produce low density ($770 \text{ kg}/\text{m}^3$) prills favoured for use in AN-fuel oil blasting agents. The porous product promotes propagation of detonation and allows for a higher fuel oil loading. On the other hand, a still higher concentrated (99.7 to 99.8%) solution is used to produce high density ($860 \text{ kg}/\text{m}^3$) prills preferred by the fertilizer industry.

The crystal transition point (discussed later) at 32°C and the hygroscopicity adversely affect the storability of granulated AN. Most manufacturers seek to overcome the problem of degradation of the grains arising out of the phase transition in humid atmosphere at storage temperature by adding stabilizing agents to the melt [2]. Some of the internal stabilizers that are added to the melt before spraying include, anhydrous $CaSO_4$, $H_3BO_3 + (NH_4)_2HPO_4 + (NH_4)_2SO_4$, ammonium and potassium polyphosphate and nucleating agents, such as chalk, silica gel, metal oxides or kaolin, $Mg(NO_3)_2$ and $Al_2(SO_4)_3$. Usually AN granules are prevented from caking during storage by a final surface treatment (coating). The grains are treated with effective organic surfactants, such as cationic long chain fatty amines or anionic alkylarylsulfonates. Anticaking effectiveness is enhanced by addition of nonionic organic substances, such as polyethylene waxes or paraffins. The fatty amines are applied as melts or oil solutions. The use of carboxymethyl cellulose and calcium stearate together has been suggested. The former will gel on coming into contact with water and can prevent water from permeating. Calcium sterate is a substance very difficult to wet and hence can further slow down the initial wetting. Some of these valuable suggestions made in this direction are summarized by Urbanski [6].

3. Physical and chemical properties

AN is a colorless, crystalline salt, highly soluble in water. Although it is hygroscopic, it does not form hydrates. It is also soluble in alcohol, acetic acid and nitric acid. AN dissolves in liquid ammonia to form what is known as Divers solution and can be used to strip ammonia from gases. AN has a negative heat of solution in water, and can therefore be used to prepare freezing mixtures. The chemical reactivity of AN has been well documented by Mellor [5]. The boiling point of pure material is around 210°C at 11 mmHg and it distills without decomposition. It decomposes around 230°C at 760 mmHg pressure, and above 325°C it deflagrates. If confined AN may explode between 260 and 300°C [7]. The decomposition chemistry of AN is discussed in detail later. Data on solubility, vapour pressure, boiling point, specific heat of aqueous AN solutions and many other properties especially those relevant to its use as a component of explosive

Table 1
Properties of AN

Property	Value
Molecular formula	NH_4NO_3
Molecular weight	80
Heat of combustion	346 cal/g
Heat of formation	1098 cal/g
Heat of explosion	346 cal/g
Heat of fusion	18.23 cal/g
Density	1.725 g/cm^3
Color	Colorless
Melting point	169.6°C
Specific volume	0.580 cm^3/g
Solubility in water at 20°C	66 g/100 g
Oxygen content	60%
Available oxygen	20%
Estimated flame temperature	1500°C
Detonation velocity	1250–4650 m/s
Coefficient of thermal expansion at 20°C	9.82×10^{-4} %/°C
Specific heat from 0 to 31°C	1.72 J/mol
Vapour pressure at 205°C	7.4 mmHg

mixtures are well documented [1,2,5,8]. Some of these properties are summarized in Table 1.

4. Applications of AN

Major applications of AN are in the field of explosives and fertilizers. Before World War II most AN was consumed as an ingredient in high explosives. Subsequently its use as a nitrogen fertilizer grew significantly, absorbing about 90% of the production in 1975 [1]. As a straight fertilizer it accounts for 24% of world consumption of nitrogen fertilizers and in addition is present in many blend and complex fertilizers like calcium AN, ammonium sulfate nitrate, potassium AN, nitromagnesia, etc. It is also used with urea in liquid fertilizers. As mentioned, AN fertilizer incorporates nitrogen in both of the forms taken up by crops: ammonia and nitrate ion.

Areas like coal mining, metal mining, nonmetal mining and quarrying find extensive use of AN as an explosive. AN being an oxidizer has found ample application in gas producing compositions and propellants. Details of some of these compositions are given by Ellern [9]. Though in small quantities it is being used in the production of nitrous oxide. Nitrous oxide which is used primarily as an anesthetic and as an aerosol propellant for food products is generated by the controlled heating of AN.

4.1. Use in explosives

AN is the cheapest source of oxygen available in the condensed form for commercial explosives. The original experiments with it as a component of explosive mixtures began in the second half of the nineteenth century. Grindel and Robin were the first, in the

beginning of 19th Century, to use AN in explosives as a replacement of potassium nitrate in black powder [7]. In 1867, Sweedish chemists Ohlosson and Norrbin patented an explosive called *Ammoniakust*. The explosive properties of AN, such as sensitivity to detonation, impact and heat, rate of detonation, etc. were reported first in the beginning of the present century.

AN is used by itself in conjunction with fuels or in admixture with solid fuels and sensitizers, such as nitroglycerine and TNT to give more sensitive explosives [10]. Some of the known military explosives which use AN are amatol, ammonals and minols. Properties of AN, such as density and porosity also need to be tailored depending upon the application. For use in explosives sensitized by high explosive ingredients AN should be of a dense and nonabsorbent character in order to get highest strength per unit volume and this is achieved by attaining the maximum density. Whilst absorbant AN can be employed, it tends to lower density and therefore gives lower bulk strength to the final explosives; it also absorbs a larger amount of nitroglycerine and requires more of this expensive ingredient to give a suitable gelatinous consistency. For use in conjunction with fuel oil an absorbent form of AN which is porous and of low density is required. This absorbs 7–8% of light oil without appearing wet and is usually called, ANFO. The oil used should be of volatile type as the more volatile oils give the greatest sensitivity. The choice of the composition is generally determined by the necessity of oxygen balance, explosive property required like power of detonation, sensitivity and products of detonation. Aluminum is sometimes added to increase the sensitiveness of the explosives. Though the idea of using AN with a fuel as a commercial explosive formulation was proposed as early as 1867, ANFO explosives were finally developed only in 1955. They can be made on-site in a mobile unit and are inexpensive and safe to handle. However, they have low strength and detonation velocity and cannot be used in presence of water [11,12].

Water explosives, developed since 1956, based on solutions of nitrates have been another area where AN is used. They have taken over much of the market at the expense of dynamite and AN powder [11]. Slurries and water gels are made of aqueous solutions of AN and sodium or calcium nitrate and gelled by the addition of guar gum or cross-linking agents and further sensitized by nitro explosives. Combustible materials, such as aluminum, and urea are mixed with these solutions.

More cost effective AN based water-in-oil and oil-in-water emulsion explosives were developed later in 1962 [11]. Water-in-oil emulsion explosives have been made, as typified by the formulation containing 20% water, 12% oil, 2% microspheres, 1% emulsifier and 65% AN. The micro-droplets of the emulsion explosive offer the advantage of intimate contact between fuel and oxidizer and outperform conventional water based slurries. In fact, ANFO and water based commercial explosives have largely displaced the nitroglycerine-based dynamites, thanks to their low cost, safety, versatile performance and application.

5. Safety aspects

The development of AN into a versatile oxidizer in the present form was not without setbacks and hazards. It has long been thought that AN is one of the most difficult

explosive material to detonate. However, this belief was shattered by a series of explosions involving AN [2,6,13]. In upper Silesia, in the summer of 1921, while unloading caked AN from a railway car a severe explosion took place claiming numerous victims. Later in September, one of the largest catastrophe in the history of the chemical industry wherein about 1000 men were killed took place at Oppau following a partial detonation of about 4000 tons of a double salt composed of more or less equal amounts of AN and ammonium sulphate. The year 1947 witnessed two more major disasters in Brest and Texas City where whole ships' cargo of wax coated fertilizer grade ammonium nitrate (FGAN) exploded. Heiner [13] quotes many more accidents involving AN in his paper exploring the hazardous nature of FGAN and chemically pure ammonium nitrate (CPAN). These accidents showed that AN even diluted by another ammonium salt is an explosive capable of detonating under sufficiently powerful explosive stimulus and call for more precautions to be taken in handling and transporting.

Pure AN, highly concentrated hot solution of AN, some mixtures of AN and fertilizer AN, unless stabilized are included among explosives detonated by shock waves [2]. Although heat released is small, many foreign materials like chloride ions and heavy metals can catalyze the decomposition posing serious risks in storing large quantities. AN must be considered a high explosive under the following three conditions: bolstering by a high velocity explosive, confinement at elevated temperatures, and presence of oxidizable material. Although AN does not burn by itself, it is a strong oxidizer capable of supporting combustion. AN when detonated can have about 70% of the disruptive strength of nitroglycerine. The sensitivity of AN and its mixtures to shock is determined by tests in which a sample tamped in a closed steel tube is exposed to a shock. In addition, oil retention, a measure of porosity is a basis for assessing the safeness of AN. In general AN, when used in large amounts need to be handled carefully due to its oxidizing nature and sensitivity to many materials likely to be present as impurities.

6. Decomposition chemistry

The fact that, though AN is stable at room temperature, on storage a little ammonia is evolved leaving the salt slightly acidic is long known [14]. Berthelot [15] in as early as 1883 formulated the equations of decomposition, and gave values for heat of explosion, heat of formation, temperature of explosion, etc. Owing to its application as an explosive component the decomposition chemistry of AN has been quite extensively studied [16–26] [27,28]. As for most energetic materials, the thermolysis of AN depends upon various factors like pressure, temperature, and experimental conditions like sample size, rate of heating, sample purity, monitoring techniques and presence of foreign substances. Obviously, no single mechanism could explain all the aspects of its decomposition characteristics. Some of the possible modes of decomposition pathways reported are given in Table 2 [29].

It is generally accepted that thermal decomposition is initiated by an endothermic proton transfer reaction as shown in reaction 1 (Table 2). When the salt is heated from 200 to 230°C, exothermic decomposition occurs (reaction 6). The reaction is rapid, but

Table 2
Modes of thermal decomposition of AN

Reaction	Heat evolved (cal/g)	Gas volume (ml/g) at NTP	Temperature (°C)
(1) $NH_4NO_3 \rightarrow NH_3(g) + HNO_3(g)$	-521		
(2) $NH_4NO_3 \rightarrow N_2O + 2H_2O$	108	840	320
(3) $NH_4NO_3 \rightarrow 3/4N_2 + 1/2NO_2 + 2H_2O$	316	910	860
(4) $NH_4NO_3 \rightarrow N_2 + 2H_2O + 1/2O_2$	354	980	950
(5) $8NH_4NO_3 \rightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O$	201	945	560
(6) $NH_4NO_3 \rightarrow 1/2N_2 + NO + 2H_2O$	86	980	260

can be controlled and is the basis for commercial preparation of nitrous oxide (reaction 2). Above 230°C, the decomposition follows reaction 3. The reaction pathway is reported to follow reaction 4 during detonation while reaction 5 has been suggested when AN undergoes explosion.
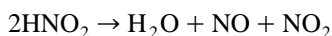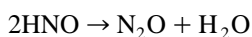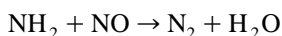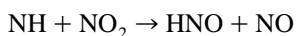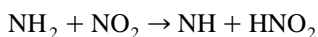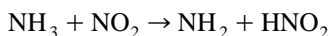
Most mechanisms proposed for AN decomposition assume first the production of ammonia and nitric acid and subsequent oxidation of NH_3 by the decomposition products of HNO_3. Roser et al. [23] assumed the following known equilibrium reaction for HNO_3 that leads to the oxidizing species NO_2^+ and explained the formation of N_2O and water as the main products as in reaction 2 (Table 2).

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

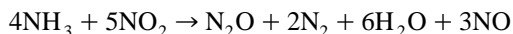$$NH_3 + NO_2^+ \rightarrow products(N_2O, H_2O).$$
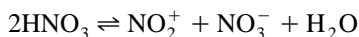
However, no details of the mechanism were given. Recent in situ decomposition under rapid heating and immediate analysis of the products, using rapid scan FT-IR spectroscopy, however, clearly reveals the formation of HNO_3 [27] as an intermediate. Apart from N_2O and H_2O, NO_2 is also formed during the decomposition [27,28]. Furthermore, NO_2 is known to be a product in other modes of decomposition [7]. This calls for the inclusion of NO_2 also in the reaction scheme. Since HNO_3 is formed only at high temperature during the decomposition of AN, the following mode of decomposition of HNO_3 was thought to be more realistic [28].

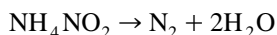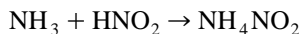$$2HNO_3 \rightleftharpoons 2NO_2 + H_2O + 1/2O_2.$$
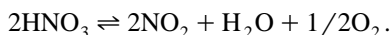
NO_2 formed can subsequently oxidize NH_3 as follows in the temperature range 342–387°C.

$$NH_3 + NO_2 \rightarrow NH_2 + HNO_2$$

$$NH_2 + NO_2 \rightarrow NH + HNO_2$$

$$NH + NO_2 \rightarrow HNO + NO$$

$$NH_2 + NO \rightarrow N_2 + H_2O$$

$$2HNO \rightarrow N_2O + H_2O$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2$$

leading to an overall stoichiometry:

$$4NH_3 + 5NO_2 \rightarrow N_2O + 2N_2 + 6H_2O + 3NO$$
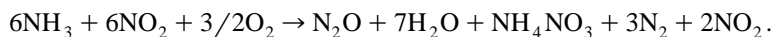
On the other hand, oxygen from the decomposition of nitric acid reacts rather slowly with NH_3. Whereas the reaction between oxygen and NO is instantaneous. It is likely, therefore, that the involvement of oxygen may be limited to the further oxidation of NO formed in the above reaction. The subsequent reactions can be represented by the following equations [28].

$$3NO + 3/2O_2 \rightarrow 3NO_2$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

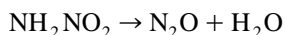$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

$$NH_3 + HNO_2 \rightarrow NH_4NO_2$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$
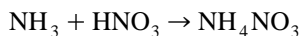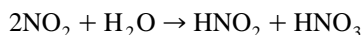
The overall stoichiometry becomes:

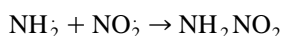$$6NH_3 + 6NO_2 + 3/2O_2 \rightarrow N_2O + 7H_2O + NH_4NO_3 + 3N_2 + 2NO_2.$$
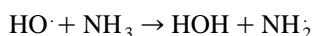
The above reaction scheme indeed accounts for the observed decomposition products of AN namely AN aerosol, NO_2, N_2O, NH_3 and H_2O when heated at high heating rate, $80°C/s$, and examined in situ by rapid scan FT-IR spectroscopy within the first second [28]. The AN decomposition can thus be represented as follows.

$$6NH_4NO_3 \rightarrow N_2O + 10H_2O + NH_4NO_3 + 3N_2 + 2NO_2.$$
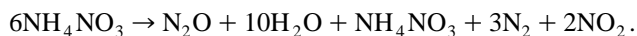
Contrary to the mechanism discussed so far, Davies and Abrahams [30] assumed that the decomposition of AN proceeds through the formation of nitramide intermediate.

$$NH_4NO_3 \rightarrow NH_2NO_2 + H_2O$$

$$NH_2NO_2 \rightarrow N_2O + H_2O$$
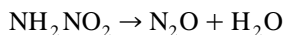
Recently, Brower et al. [26] decomposed AN in a sealed capillary and examined the products using IR spectroscopy. No NO_2 was observed under these conditions. They suggested that at high temperature a homolytic mechanism for the decomposition of HNO_3 is more likely. The observed activation energy changes continuously from 118 kJ/mol at low temperature to 193 kJ/mol at high temperature which is nearly equal to the N–O bond energy in nitric acid. Water and ammonia strongly inhibit the ionic reaction at low temperature, but the effect fades away at high temperature. In this mode, the decomposition proceeds through the formation of nitramide, although the initial step involves a proton transfer. The following mechanism has been proposed:

$$NH_4^+NO_3^- \rightleftharpoons NH_3 + HONO_2$$

$$HONO_2 \rightarrow HO^. + NO_2^.$$

$$HO^. + NH_3 \rightarrow HOH + NH_2$$

$$NH_2^. + NO_2^. \rightarrow NH_2NO_2$$

$$NH_2NO_2 \rightarrow N_2O + H_2O$$
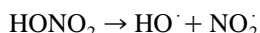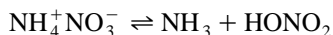
The enthalpy changes and temperatures involved during the various modes of decomposition are given in Table 2. The activation energy reported for the thermal decomposition of AN varies from 30 to 41 kcal/mol [6,31] and is suggested to be of first order. AN being susceptible to considerable evaporation, the validity of these values is also questioned. It is also worthwhile to mention that completely dry AN evaporates away after melting and does not decompose [21].

Many of the decomposition studies reported earlier were carried out at low heating rates. The importance of heating rate was pointed out by Anderson et al. [32,52]. While surface decomposition occurs at high heating rates, slower heating rate experiments results in bulk decomposition. The high heating rate surface decomposition is endothermic and produces NH_3 and HNO_3 while slow heating rate bulk decomposition is exothermic and produces N_2O and H_2O. Fast thermolysis studies of AN are important as they more or less simulate combustion conditions [27,28,34]. The reaction scheme evolved out of these studies can indeed throw more light into the complex processes during propellant ignition and combustion.

Apart from the decomposition chemistry of pure AN, a number of authors have examined the effect of addition of various compounds on the thermolysis [5,16,24,35–52]. The additives studied include ammonium chloride, fluoride, bromide and iodide, sodium chloride, chromium salts such as potassium chromate and dichromate, chromium oxide, chromium nitrate, pure chromium, cobalt salts, carbon, metals such as magnesium and zinc, first row transition metal oxides, nitric acid, organic species, and various other metal cations. The references listed here are rather limited compared to the literature available in this area and only highlight the sensitivity of AN decomposition to various compounds. The studies are significant in relation to the hazards associated with the extensive use of AN in bulk as a fertilizer or oxidizer. Apart from the safety aspects associated with handling and storage, the catalytic decomposition studies are important in the field of AN propellants.

Since AN does not burn easily and needs a catalyst to sustain combustion, some of the above compounds have been incorporated in AN based propellant formulations to catalyze the combustion reaction. Catalysts such as ammonium dichromate, copper chromate and chromium oxide are reported to increase the BR of AN propellants. Ammonium dichromate not only facilitates the decomposition of AN, but decomposes itself into water, nitrogen and chromium oxide, and thus is not solely catalytic in action. Chromium compounds in particular show a greater catalytic action than other cations. It has been suggested that the NO_3^- in the acidic melt is deoxygenated to NO_2^+ by the dichromate ion. NO_2^+ further undergoes a number of reactions with NH_3 or NH_2^-, forming intermediate nitramides or nitrosamines which are then decomposed to nitrogen or nitrous oxide and water. The mechanism of catalysis is, however, debatable [36,38,53–55].

The influence of fuels on the decomposition of AN is also explored with a view to produce easily ignitable metallized fuel-rich compositions. The thermal ignition behaviour of various mixtures of organic fuels, magnesium and AN has been studied by Jain and Oommen [44]. It was observed that the thermal decomposition/ignition of organic fuel-AN mixtures is modified significantly in the presence of magnesium metal. Many compositions comprising of organic fuel-AN have been studied [56]. Some of

these include ammonium oxalate and picrates, 2,4-dinitro-resorcinol, glucose, guanidine nitrate, pitch, bitumen and styrene polymers. By suitable choice of fuels and proper composition it has been possible to make cast compositions that yield product gases at a wide range of temperature, from about 360 to 2000°C [9]. The surface temperature of burning AN and gas phase AN flame have been a subject of many investigations [33]. The surface temperature is reported to be around 300°C. Since BR of AN and AN propellants are of similar order it is assumed that the decomposition of AN in a composite propellant is similar to that of a monopropellant.

7. AN as a propellant oxidizer

7.1. Clean burning propellants

The composite solid propellant essentially consists of an oxidizer powder, loaded up to 85–90%, held together in a matrix of polymeric binder which acts as fuel. Most solid rocket motors currently in use including the space shuttle solid rocket boosters (SRB) use AP as the main solid oxidizer as has been stated in Section 1. One of the primary products of combustion of AP based propellants is HCl which in the presence of water forms hydrochloric acid which produces smoke and is highly toxic. When the space shuttle is launched each of its SRB produces over 100 tons of HCl [33,57]. It is estimated that in the initial 120 s of flight the SRBs burn 502 000 kg of propellant. The resulting residue is 21% HCl and 30.2% Al_2O_3. Al_2O_3 is a chemically inert powder but HCl alters its surface properties so that clean up and corrosion problems are more severe than expected. Similarly, ARIANE 5 with its two solid fuel boosters each holding 237 tons of propellant during the 2 mts. of burning produces 156 tons of Al_2O_3 and 96 tons of HCl all of which fall on the ocean and forest around the launch pad [58]. Impact of HCl pollution has been established on tests conducted on animals and vegetation around the launch pad. Though some of these effects are short lived, cumulative effect of these 'acid shocks' due to frequent launching of rockets will be of serious concern. Yet another anticipated threat by the chlorine compounds emitted by AP-propellants is on the stratospheric ozone layer and global warming. It is likely that hydroxyl radicals could react with HCl to release atomic chlorine, which destroys ozone by reducing it to oxygen. To overcome these environmental problems it became necessary to investigate the use of the so called clean burning propellants which eliminate chlorine as an ingredient. Less than 1.0% by weight HCl in the SRB exhaust has been the common goal for the solid rocket industry.

An additional motivation for developing chlorine free propellants is the need for low hazards, low observable (minimum smoke) propellants. Minimum smoke propellants are those which eliminate both primary smoke (e.g. Al_2O_3) and secondary smoke (i.e. water aerosol condensed from the atmosphere) from the exhaust plume [33]. They are important in missile system as detection of military launch location is an area of primary concern. Since HCl serves as a nucleation site for water vapour, chlorine must either be eliminated from the propellant or scavenged from the exhaust products in order to eliminate secondary smoke.
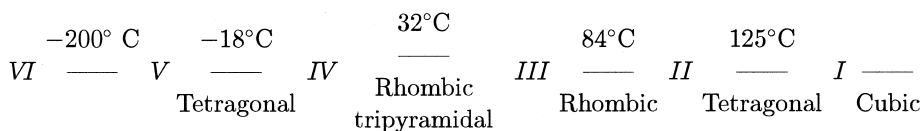
Yet another use of chlorine free propellants is in gas generators. Solid propellant gas generators are used to start and drive turbine for power generation. For such a purpose, the propellants have to burn with a low flame temperature and the combustion gases should not contain corrosive constituents such as chlorine or chlorine compounds. Besides, the amount of solid particles in the combustion gases should be kept as low as possible [59]. AN can be looked upon as the most appropriate oxidizer for propellant compositions that meet the above requirements. While the experiments on AN as a high performance oxidizer for SRB in place of AP is at its infancy, gas generator compositions have established its use as an efficient oxidizer. Both double base and composite (without metal) propellants are used extensively with AN or as a mixture of AN and guanidine nitrate [3] in gas generators. AN composite propellants give desired exhaust properties like: (a) a high nitrogen content (55 wt.%), (b) a low water content (10 wt.%), (c) modest amounts of solid particles (8 to 12% wt), and (d) a relatively nonhazardous exhaust. Further, AN propellant formulations are relatively insensitive to temperature and impact and have good strength properties over a wide range of temperature.

Though AN based systems have several positive features like clean burning and smoke less exhaust they are not free from drawbacks and substitution of AP with AN for high performance systems is not straight forward. The main problems associated with AN in its use as an oxidizer in propellants are: (a) phase transformation around room temperature (32°C) which is accompanied by a significant volume expansion which results in crack formation in the propellant grain, (b) hygroscopicity, (c) low BR, and (d) low energy. Many attempts have been made to overcome these problems and to realize a better phase transition and combustion behaviour for AN based propellants. These topics are discussed in detail in the following sections.

7.2. Phase transitions and modifications

The crystal transformation of AN has been the subject of examination by numerous investigators. Under ordinary pressure AN occurs in no fewer than five stable polymorphic modifications as shown below [60–64].

The transition temperatures of the various phases are,

$$
\underset{}{VI} \; \overset{-200° \; C}{\underline{\quad\quad}} \; \underset{\text{Tetragonal}}{V} \; \overset{-18°C}{\underline{\quad\quad}} \; \underset{\substack{\text{Rhombic}\\\text{tripyramidal}}}{IV} \; \overset{32°C}{\underline{\quad\quad}} \; \underset{\text{Rhombic}}{III} \; \overset{84°C}{\underline{\quad\quad}} \; \underset{\text{Tetragonal}}{II} \; \overset{125°C}{\underline{\quad\quad}} \; \underset{\text{Cubic}}{I} \; \underline{\quad\quad}
$$

The crystallographic data and stability ranges of the various phases of AN are given in Table 3 [65]. Besides the above transitions a metastable transition at 45–50°C has also been reported. Reports of existence of low temperature modifications, phase VII below −170°C and a high pressure transition above 160°C at pressures > 9000 kg/cm^2 are also seen in the literature.

Table 3
Crystallographic data and stability ranges of the AN phases [65]

Phase	V	IV	III	II	I
Crystal system	Orthorh.	Orthorh.	Orthorh.	Tetrag.	Cubic
Space group	$Pccn$	$Pmmm$	$Pnma$	$P4/mbm$	$Pm3m$
Formula per unit cell (Z)	8	2	4	2	1
Lattice parameters	$a = 7.943$	$a = 5.745$	$a = 7.7184$	$a = 5.7193$	$a = 4.366$
	$b = 7.972$	$b = 5.438$	$b = 5.8447$		
	$c = 9.832$	$c = 4.942$	$c = 7.162$	$c = 4.932$	
Measured at (K)	173	295	318	355	423
Stability ranges (K)					
Humid	< 255	255–305	305–357	357–398	> 398
Dry	< 255	255–328	–	328–398	> 398

As mentioned earlier the mechanical strength of the AN prills is dependent on the phase transition behaviour. The technical significance hence attached to the thermal transitions is a prime reason for the extensive literature available on this area. Many of the studies on the phase transformation support the generally accepted idea that the mechanical strength of the prill should be related to the AN(IV)–AN(III) polymorphic transition at 32°C which is accompanied by a sensible volume change (3.8%). The volume changes associated with the other transitions also are given in Table 4 [65]. AN prill is a polymorphic aggregate. The volume change of the elementary cell causes a change in the crystal packing in the polycrystalline aggregate and consequently, the adherence between crystallite decreases. The product mechanical strength, thus decreases after several thermal cycles through the transition temperature and the granular product breaks down into dust or fine particles, and increase the caking tendency. Attempts to break up the caked salt by explosives have resulted in serious accidents as mentioned earlier. Implications of the volume change associated with the transition on the efficient use of AN as a propellant oxidizer is even more serious. Since the composite propellant grain which contain oxidizer (AN) usually about 85% by weight could be subjected to temperatures which causes the IV–III transition during storage or transportation, the volumetric changes associated with the phase change may lead to

Table 4
Volume changes of the phase transitions of AN

Transition	Temperature (K)	Volume change	
		(A^3)	(%)
II/I	404	1.88	2.3
III–II	365	1.37	1.7
IV/II	323	1.61	2.0
II–V	317	0.23	0.3
IV–III	314	2.94	3.7
V–IV	272	2.20	2.8
IV–V	224	2.49	3.2

defects (cracks) in the propellant grain. The cracks in a propellant grain are undesirable as they can lead to catastrophic burning behaviour. It is imperative, therefore, to understand the phase transition fully and modify it suitably to make the salt fit for reliable practical use.

A search in the literature shows wide variations in the reported phase transition temperature. While the fusion temperature and transition temperature at 125°C remain unambiguous in most of the schemes, the transition IV–III is debated widely. The reason for the dissimilarity in the literature on the transition temperature is ascribed to its dependence on various factors [63–73] [74–81]. Some of these include moisture [67], mode of crystallization [73], thermal history of the sample [74], sample weight [75], number of previous transformation and heating mode [77], purity of sample [78], grain size [70,82], experimental technique, etc. Interestingly, a multitude of experimental techniques have been employed to study the phase transformation of AN. These include, X-ray diffraction [60–62], neutron diffraction [83,84], dilatometry [85–89], thermome-chanical analysis [90], DTA, DSC [91,92], calorimetric measurements [93], dielectric constant measurement [94–96], ionic conductivity measurements [97], single crystal microscopic examination [98], birefringence [99], optical studies [63,100], ultraviolet spectroscopy [101], density measurements [102], and grain size measurements [103]. The ultimate picture arising out of these studies is often inconsistent.

The cell parameters and other structural data for various phases of AN are compiled in Table 3 [65]. The structural changes involved during the transitions at different temperatures were studied by Hendrikcs et al. [61]. In sequence from phase I to V, the ammonium and nitrate ions have less freedom of movement. The crystal structure of these modifications revert to the CsCl pattern of arrangement, except phase III which has a completely different, loose packing mode of molecules in a crystal lattice that resemble NiAs [104]. Unlike other transitions, the transition of II and IV into III require drastic changes of the crystal lattice. Brown and McLaren [62] observed that the phase IV–III transformation involve severe structural changes and therefore do not occur in dry solid. Since a higher moisture content is said to promote IV–III transition it has been suggested that the transition proceeds via a dissolution and crystallization occurring at a disordered phase boundary or in a bulk layer of solution. The mechanism, however, is debatable [105,106]. van Driel et al. [107] suggest various orientational relationships between phase III and IV from in situ microscopic and texture gonimetric experiments. They propose the existence of a solid–solid transition mechanism in single crystals which is continuously catalyzed from the surface of the crystals by solvent molecule. A recent EPR study [108] on the X-ray irradiated crystals of AN reveals the differences in the crystal structure of phase III and IV. While the N–H bonds in phase IV are mirror related, phase III does not have mirror symmetry related bonds. It is inferred that mirror symmetry related bonds as in phase IV provide radiation immunity to chemical bonds while those in phase III break producing radicals.

Another feature of the complex phase behaviour is that AN exhibits interesting hysteresis on thermal cycling. The transition behaviour on thermal cycling was found to depend upon the water content and the maximum temperature [109]. Cycling dry AN to $20/150/-50$°C, beyond the transition II/I at 125°C, transition path IV/II/I/II/IV/V is found. With a water content greater than 0.1%, phase III appears at least partially on

heating, but not on cooling: IV/III/II/I/II/IV/V. When a maximum temperature below 125°C is chosen, humid AN shows the transitions IV/III/II/III/IV/V, while with dry AN the transition IV/II/IV/V takes place. It can be seen from the literature cited that when II to III transition occurs anywhere between 48 and 84°C, III to II transition occurs between 84 and 89°C. It is also observed that when IV to III transition take place between 37.5 and 55.5°C, III to IV transition occur between 0 and 35°C.

Studies by Herrmann and Engel [65], Engel and Charbit [69], Engel and Menke [109] and Engel et al. [110] using X-ray diffraction have given much insight into the lattice dynamics and transition behaviour of AN on thermal cycling. The technique has the advantage over normal methods of thermal analysis like DSC and DTA as the latter techniques report thermal effects without identifying the occurring phases. These studies indicate existence of more than one crystalline structure occurring at a time. Heating a sample to 100°C and subsequent cooling, the transition IV/II/V + IV/V/V + IV/II + IV/II have been observed. On cooling from phase II, II changes into V followed by a partial transition into IV at about 47°C. The complete transition into phase V occurs below −40°C. On heating, a part of it changes into phase IV at about 0°C. The phase V in the resulting mixture V/IV changes into II at about 47°C whereas the part of phase IV shows the known transition into phase II at 55°C. They have also observed that the transition sequence of humid AN on thermal cycling depends upon the rate of cooling. The volume changes, involved during the transitions while thermal cycling have been calculated from X-ray diffraction measurements [65]. The expansion behaviour on thermal cycling of AN pellets has been studied recently using TMA by Oommen and Jain [111]. A typical TMA trace of AN pellet subjected to thermal cycling shown in Fig. 1 shows hysteresis in expansion behaviour. Similarly, a typical DSC thermogram of AN shown in Fig. 2, shows the hysteresis on thermal cycling. The corresponding transition temperature and energy of transition calculated are given in Table 5 [111]. The heat of transition values measured by different techniques are available in the literature [31,64].

Evidently, the phase IV–III transition has been the focus of most of the studies on AN phase transition. There have been many attempts in the past to modify the transition; modification implies prevention of IV–III transition during storage. More serious attempts have been reported recently with AN emerging as a promising oxidizer in rocketry. Muller as early as 1899 showed that KNO_3 forms solid solution with AN and thereby lower the transition temperature [112]. The phase modification of AN by K^+ and resulting changes in the transition temperatures have been explained based on the replacement of some of the ammonium ions by potassium ions. The cation:anion radius ratio for AN is 0.76. This value closely approaches the ratio of 0.73 below which salts of the type $R(MX_3)$ are stable in a six-fold coordinated NiAs structure, which is the structure type of AN(III). The radius of potassium ion is 1.33 A° compared with 1.48 A° for the ammonium ion and hence, replacement of NH_4^+ by K^+ favours the AN(III) structure. Consequently, a steady fall in the IV–III transition temperature is observed as the replacement of ammonium ions by potassium ions increases. The replacement of ammonium ions by potassium ions in AN(III) decreases its unit cell size and this hinders the onset of oscillation of the nitrate ion which causes the III–II transition. Thus, as the concentration of potassium ion increases, the nitrate ion oscillation is more hindered and III–II transition temperature rises as observed in DTA studies [111]. The II–I transition
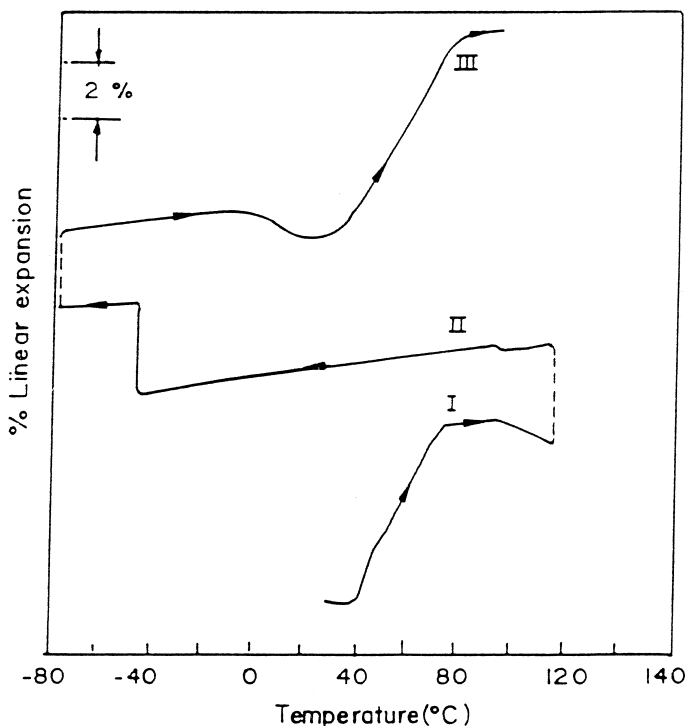
Fig. 1. TMA trace of AN on thermal cycling.

takes place when full spherical rotation of the nitrate ion occurs and its transition temperature is unaffected by the substitution of potassium ions for ammonium ions.

A series of AN–alkali nitrate systems have been subsequently examined. Campbell and Campbell [87] showed that the transition IV—III can be repressed (metastably) by using a solid solution of potassium nitrate in AN in place of pure AN. Thus, a solid solution of potassium nitrate in AN containing say, 5% KNO_3, can be kept indefinitely in form III (instead of the stable form IV) at room temperature. Such solid solutions can be prepared either by fusing the components together or by co-crystallizing from a mixed aqueous solution. It can be said that AN–KNO_3 remain one of the extensively studied systems [112–119]. Besides potassium nitrate, other alkali metal nitrates also have been examined for their influence on phase modification [110,120]. While KNO_3 is reported to stabilize phase III, cesium nitrate is found to stabilize phase II. Rubidium nitrate and sodium nitrate on the other hand do not seem to have any effect at all.

Thermal cycling studies of phase stabilized ammonium nitrate (PSAN) are also significant. Studies carried out by Deimling et al. [120] on AN–KNO_3 systems show strong hysteresis. With 3 and 5 mol% phase III appears stable at room temperature. On heating, the phase transition III/II is shifted towards higher temperature whereas II/I and I/II are not influenced. On cooling, strong hysterisis is observed as in the case of pure AN. The crystal structures involved during these transitions were followed by
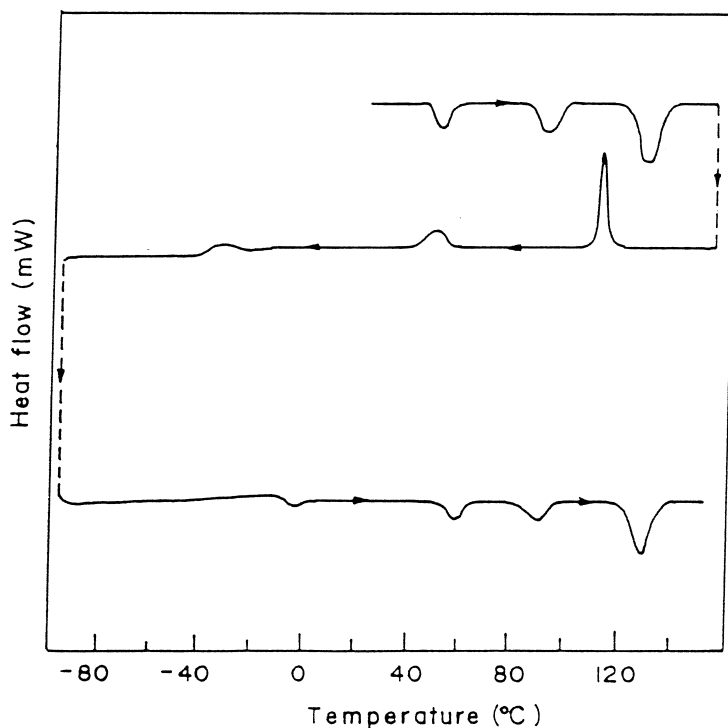
Fig. 2. DSC trace of AN on thermal cycling.

X-ray diffraction. It was observed that the IV–III transition reappears on further heating close to room temperature and the transition temperature was found to depend upon the concentration of potassium nitrate. It implies that KNO_3 or the amount of KNO_3 is insufficient to stabilize AN undergoing thermal cycling.

A recent observation of the stabilizing effect of KF is significant mainly because of the relatively small amount of KF compared to the other phase modifiers like potassium nitrate, required for phase modification [121–123]. It is suggested that a 2% by weight of KF can suppress the phase transition of AN completely. This, apparently, is intriguing

Table 5
Heat of phase transitions of AN

Apparent phase change	Peak temperature (°C)	Enthalpy change (ΔH, cal/g)
IV–III	49	3.68
III–II	92	3.94
II–I	129	11.89
I–II	116	10.60
II–IV	43.8	4.87
IV–V	−36.9	1.37
V–IV	−5	0.89

as modification of phase by potassium salts is believed to be just a result of replacement of ammonium ions by potassium ions as explained earlier. In recent studies by Oommen and Jain [111] the effect of anions of various potassium salts on the phase transition of AN has been compared. Co-crystallized salts of AN with KF, KCl, KI, KNO_3, K_2CO_3, K_2SO_4, KSCN and $K_2Cr_2O_7$ were prepared and their thermal behaviour was studied using techniques like DTA, DSC and TMA. No phase transition was observed when AN containing 1–2% by weight of these potassium salts is heated from room temperature onwards in DTA and DSC scans while the linear expansion was still shown in TMA measurements. Thermal cycling studies carried on PSAN pellets show that a very high percentage (9%) of the potassium salts is required in order to completely arrest the phase transformation in a broad temperature range (-80 to $100°C$) implying the need of higher amount of potassium salt for complete phase modification. A typical TMA trace of PSAN(KSCN) shown in Fig. 3 points out the need of higher percentage of potassium salt in inhibiting the thermal expansion on thermal cycling [111]. Though KF has been suggested to have higher efficiency as mentioned earlier, the thermal cycling studies show the need of much higher percentage of KF for thermal expansion inhibition. It is also shown that potassium dichromate when used as an additive modifies the phase as well as the decomposition pattern of AN. This is significant as potassium dichromate can act both as a phase modifier as well as a catalyst for the decomposition of AN thereby allowing loading of more oxidizer into the propellant composition [124]. Effect of other salts like $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $MnSO_4$, $Na_2B_4O_7$, $(NH_4)_2SO_4$, NH_4Cl, etc. is compiled in a review by Rao et al. [64]. Phase stabilized AN is reported to have been made by the addition of metal dinitramide salts having formula MX_n where M is a metal cation, X is a dinitramide anion and $n = 1$, 2 or 3 [125]. It has also been reported that small amount of potassium dinitramide (KDN) introduction into AN can have phase stabilization effect on AN without energy penalty [126]. KDN–AN system also has improved ballistic performance—increased thrust per unit time, reduced variability, and better predictability, compared with AN propellants without KDN.

Besides potassium salts, different metal oxides have been reported to have phase stabilization effect on AN. These include NiO, Al_2O_3, ZnO, CuO, etc. [33]. Nickel oxide is reported to give good stabilizing effect by forming nickeldiamine dinitrate complex [59,110]. CuO in the form of diamine copper complex restricts the phase III to part of the sample and keep the transition above $50°C$ [90,110,127,128]. ZnO when used as a phase modifier, exhibits characteristics similar to diamine complex copper (II) doped material [110,129]. Studies on the effect of $Cu(NO_3)_2$, $Mg(NO_3)_2$, and $Zn(NO_3)_2$ as impurities on the phase transition of AN are also noteworthy [64,130]. It is known that transition metals/metal compounds are capable of increasing BR and ignitability of AN propellants [131,132]. Another welcome side effect of PSAN is the reduced hygroscopicity. So phase stabilizing of AN with metal oxide is also beneficial with respect to BR, ignition and hygroscopicity. However, there appears to be no comprehensive study of these systems in relation to their usage in actual propellant systems featuring the efficacy of individual additives, actual amount required to meet the propellant specifications, effect of long time storage, influence on other properties like combustion, etc. Nevertheless, it is abundantly clear that it is now possible to prepare stabilized AN right from -50 to $80°C$ using small amounts of additives.
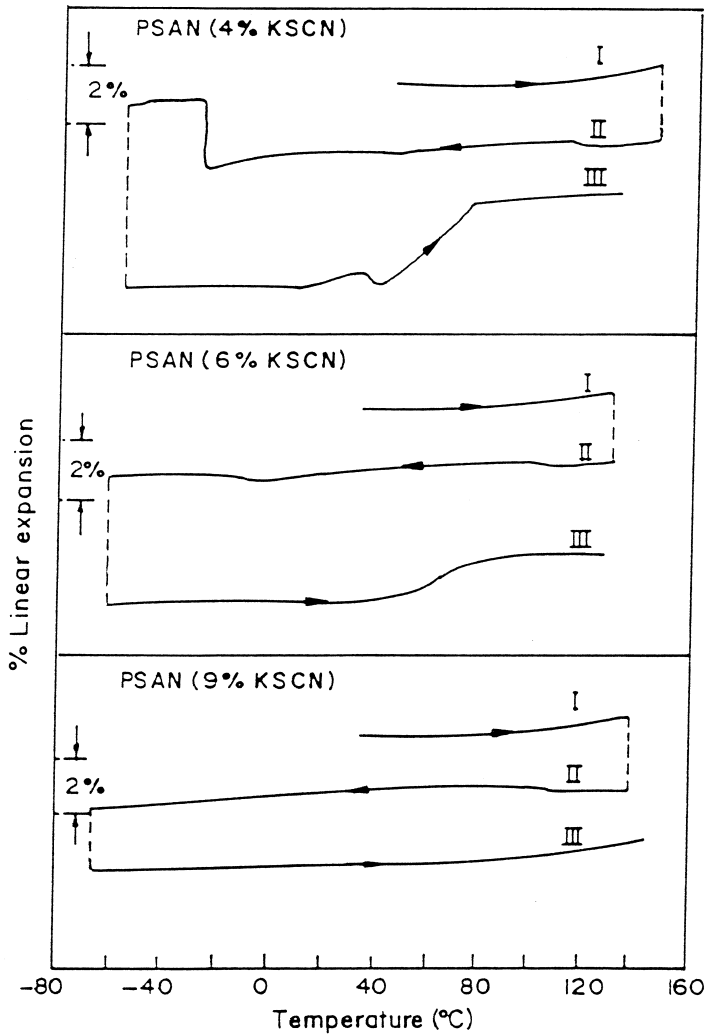
Fig. 3. TMA traces of PSAN(KSCN) on thermal cycling.

7.3. AN based propellants

The need of chlorine free and minimum smoke propellants have already been discussed. Realizing the significance of chlorine free propellants there have been many attempts of late to develop clean burning propellants [126,133–156]. Many of these attempts as can be seen are based on AN as the oxidizer. Before going to AN based systems, however, it is interesting to review a few of the approaches to develop clean burning propellants reported in the literature. One such approach to the production of

low acid propellant is based on HCl neutralization [142,143,156] using sodium nitrate ($NaNO_3$) and magnesium in the propellant compositions. AP remained the oxidizer in both approaches, but the mechanisms for reducing exhaust HCl are different. The $NaNO_3$ scavenging approach relies on sodium from sodium nitrate oxidizer to combine with chlorine from AP, in the combustion process to form NaCl salt instead of generating HCl. On the other hand, magnesium fuel forms MgO in the combustion process which then form the base $Mg(OH)_2$ upon contact with water in the exhaust plume. The reduction of HCl is facilitated by a simple acid/base neutralization in the plume by $Mg(OH)_2$. Yet another method of eliminating chlorine suggested is the use of nitramines (HMX and RDX) instead of AP. Incorporation of 10–20% by weight of HMX into a AP/HTPB propellant composition reduces the HCl smoke by 20–30% by weight at the same time improving the specific impulse [153]. However, nitramines are relatively hazardous materials. It would be desirable to develop propellants based on less hazardous, chlorine free oxidizers. Ammonium dinitramide (ADN) is a compound that is currently discussed as an alternative to AP. ADN is chlorine free and is predicted to have 15% higher performance (lift capacity) than the current propellant formulations available [149–152]. However, at the moment it remains as an experimental material due to its low decomposition temperature and extremely high production cost, although the Russians claim to have and ready to market the ADN based propellants [126]. In the light of the drawbacks of many of these approaches, AN appears to be a promising alternative oxidizer in composite solid propellant, and it does appear so from the current literature on clean burning propellants.

As mentioned earlier, apart from the awkward phase transition, another main disadvantage of AN propellants is its low energetics/performance and BR which are far inferior to those based on AP. The significance of these parameters is explained as follows. Rocket motors are rated according to their performance in terms of specific impulse (I_{sp}) which is defined as the reaction force or thrust resulting from the expulsion of unit weight of the propellant combustion products per second.

$$I_{sp} = F/\dot{w}$$

where F is the thrust and $\dot{w}$ the propellant weight flow rate. The propellant under a optimized engine specification is normally expected to have a high specific impulse. This is possible only when the propellant has a high calorimetric value and produces gaseous combustion products which are of low molecular weight, since,

$$I_{sp} \propto \sqrt{\Delta H_c/M}$$

where ΔH_c is the enthalpy change and M is the mean molecular weight of the exhaust gases.

Besides specific impulse, characteristic velocity, flame temperature, mean molecular weight of product species are also usually associated with the performance of a propellant formulation. The linear BR is one of the important ballistic properties of the propellant. On ignition, the burning surface of a propellant grain regresses in a direction essentially perpendicular to the surface and burn layer by layer. The linear rate of regression, expressed in mm/s or in./s is called the burning rate (r). BR of a solid

propellant show strong dependence on pressure (P_c) that may be described by the empirical equation (Saint Robert's law),

$$r = aP_c^n$$

where a is a constant and n is known as the pressure exponent.

The propellant should have a burn rate that may be adjusted to deliver the desired mass discharge rate without invoking a complex design or unusually high pressure. The AN propellants burn very slowly compared to AP based systems. The low BR of AN propellants can be attributed to the slower reaction kinetics of the nitrogen oxides (from AN) compared with chlorine oxides (from AP) and the lower enthalpy of combustion of AN with typical hydrocarbon based binders [133]. As a result of these thermochemical and kinetic differences between AN and AP, the gas phase flame in AN propellants is colder and farther from the condensed surface resulting in reduced heat feed back and lower BR. AN does not appear to be a substitute to AP in relation to BR and performance. However, there have been many attempts, despite the odds, to increase the BR and performance of AN based propellants. Admittedly it is not possible to give complete details of the development in this area as many of the important references cited here are either inaccessible in full form or available only as abstracts. Only an overall picture of the development in AN propellants is presented with the state of art formulations available in the literature.

It is seen that AN was used in propellant formulation as early as late 19th century [7]. In 1885, Gans patented a powder made from AN 35–38%, KNO_3 40–45% and charcoal 14–22% which came into use under the name 'Amidpulver'. Another propellant first manufactured in Austria in 1890 and used during WW I by Austrians and Germans was called 'Ammonpulver' which is a combination of AN, charcoal and an aromatic compound. There has been many compositions proposed and developed since then that found application especially as a gas generator composition.

One of the major approaches aimed at increasing the BR is to catalyze the AN combustion. The catalysts which have proven to be the most effective for increasing the AN burning rate are, chromium compounds such as, ammonium dichromate, copper chromate, chromium oxide (Cr_2O_3), etc. Carbon is a particularly effective catalyst when used in conjunction with one of the other catalysts. Metals like aluminum do not burn efficiently with AN as temperatures of the order of 2000°C are necessary near the propellant surface to ignite aluminum. However, addition of catalysts like cryolite [157] or AP into AN based propellants has been found to enhance the oxidation of aluminum [158]. The addition of AP along with AN has other advantages like the concentration and particle size of AP can be used to regulate the BR [159]. This is all the more important as BR of the AN compositions unlike those based on AP cannot be altered by variation in the particle size of AN. However, there are reports where AN particle size also was found to alter the BR, but only slightly [59]. An increase in BR of roughly 30% with a reduction of particle size from 160 μm to 60 μm at a pressure of 400 psi in a 76% solids, unimodal AN/HTPB propellant is reported. This method of using AN/AP mixture has been employed by many investigators [160,161].

Addition of magnesium to AN/AP/Al compositions has been found to enhance the oxidation of Al besides neutralizing the acidic species [158]. When Mg was included in

AN/ polypropylene glycol (PPG) propellant at constant AN/PPG ratio, a remarkable influence on propellant BR was observed. As Mg loading was increased from 0 to 30%, the BR of propellant also increased monotonically from 0.7 to 2.6 mm/s at 400 psi [33], an increase of over 300%. The increase in BR of AN/PPG with increased Mg loading is due to a combination of increased radiative heat feed back, conductive heat feed back and condensed phase heat release. However, it was observed that at high solid loading of Mg the ash formed by the surface combustion of Mg retained the metal near the surface of the propellant as it burned and prevented it from being carried away efficiently by the gas stream. Though the BR is enhanced, substituting Mg for Al has the performance penalties of reduced energy, density and flame temperature. Magnesium aluminum alloy is also reported to be a promising metallic fuel ingredient in AN propellant compositions [162].

The binder in the composite solid propellant which also acts as the fuel plays a significant role in the combustion process despite being present in small amount. This realization has led to a pursuit for more energetic binders for use in rocketry [163,164]. The binder does seem to have a significant role in the AN based propellants as evident from the literature. Among the three binders reported to have been examined in a study [55] along with AN are namely: HTPB, polyester/polyether and silicone binder; the more oxygenated binders were found to produce higher burn rate. The HTPB propellants apart from having low BR are also reported to leave carbon skeleton after combustion [33]. The BR of a propellant containing polyester or polyether binder was higher approximately 40% over that of an HTPB propellant. The silicone binder enhances the BR even more. Propellants based on PSAN and HTPB have been used successfully in thrust chamber igniter of the VULCAIN liquid rocket engine for the ARIANE 5 [165]. HTPB has been used quite widely with AN and the effect of various catalysts like Fe_2O_3 and other BR modifiers [165–167] has been studied. Rheology of polyurethane based AN compositions [168,169] have also been investigated. However, the enhancement in BR achieved in these studies are still not of the magnitude required to make AN an acceptable composite propellant oxidizer. With the emergence of glycidyl azide polymer (GAP) as an energetic binder, many propellant compositions based on GAP and AN have been reported [132,170–176]. The hydroxy terminated azide polymers (characterized by their positive heat of formation) are reported to give higher performance compared to inert hydrocarbon binders like HTPB. The BR of GAP/AN propellants are also found to be high in comparison with HTPB/AN propellant formulations. However, poor ignitability, combustion instability and heavy plasticization for adequate mechanical properties are some of the drawbacks of these systems. A plasticizer was found necessary for both mechanical properties modification and some improvements in burning stability and ignitability. A propellant composition with AN and GAP (70/30 weight ratio) does not sustain combustion at low pressure but burns with a rate of less than 4 mm/s at 70 atm [175,177]. However, energetic plasticizers like BTTN, TMETN, nitrate esters, etc. can be incorporated into the composition to improve the specific impulse and BR considerably. The BR of these compositions with energetic plasticizers and catalysts like chromium compounds incorporated in adequate amounts are quite impressive [176,132]. By using molybdenum/vanadium oxide catalysts called MOVO, BR of the order of 7–8 mm/s at 70 atm with the pressure exponent 0.5–0.55 has been

achieved with GAP and AN with nitrate ester plasticizers [132]. Introduction of BTTN/TMETN plasticizer into AN/GAP formulation in desired amounts can offer a theoretical specific impulse of 235 s [132]. Some of the GAP/AN propellants are found to have excellent insensitive munitions (IM) characteristics [176].

Yet another class of energetic binders used with AN is N–N-bonded epoxy resins. The development of these binders with N–N bonds in their backbone similar to hydrazines, was conceived by Jain and coworkers while working on hypergolic (self-igniting) hybrid systems [178–180]. The resinous compounds with suitable end groups for curing were synthesized from carbohydrazides and thiocarbohydrazides, and were found to have extremely high reactivity towards oxidizers like nitric acid, as in the case of hydrazines or hydrazones. In fact some of the resins ignite instantaneously on coming into contact with HNO_3 [180]. A high combustion reactivity towards solid oxidizers like AP and AN was envisaged and was subsequently proved to be true when these resins were used as binders. A number of such resins were synthesized subsequently [179,181,182]. Solid composite propellant formulations based on these binders and AP were found to have BR almost three times higher than those based on hydrocarbon binders [183,184]. A similar enhanced BR was observed when the binders were processed with AN [124,185]. The combustion reactivity of N–N-bonded resins towards oxidizers like AP and AN was explained based on the reactivity of N–N bonds towards acidic species like nitric acid [183]. It was further shown that the BR of these systems could further be improved by the inclusion of magnesium metal and small percentage of AP (Fig. 4) [185]. These compositions also appear to have better combustion characteristics in the strand burner as they burn without leaving any residue or skeleton unlike hydrocarbon binders and sustain combustion even at low pressures.

Apart from the influence of binder and catalyst, BR of AN propellants seem to depend upon the nature of AN used. Compositions having PSAN appear to have much higher BR than those having nonstabilized untreated AN based on N–N bonded resins [124]. The phase stabilizers used in this study were various salts of potassium, such as KF, $K_2Cr_2O_7$ and KNO_3. BR close to 6 mm/s could be achieved using these resins and PSAN without the use of any energetic ingredients in the form of plasticizers (Fig. 4). The pressure exponent calculated for some of these fast burning systems, however, appear to be high. Studies using Ni-PSAN, Cu-PSAN, Zn-PSAN, KNO_3-PSAN, $CsNO_3$-PSAN and GAP are also reported to give higher BR indicating the effect of phase modifier on the combustion [132,159]. For example, Cu complex based PSAN seems to have higher BR compared to Zn and Ni complex based PSAN when processed with GAP. However, there are problems associated with these phase modifiers. They seem to affect adversely other properties like stability [132]. Furthermore, as evident from the earlier discussions on phase modification, higher amounts of the phase modifier in the oxidizer are indeed necessary for adequate phase modification, which could ultimately lead to the performance loss of the propellant.

The pressure exponent and temperature sensitivity of AN propellants are found to be high [159]. The values for pressure exponents without catalysts are reported to be around 0.8 or higher, while with catalysts the values are lower and varies with the system. The pressure exponent of a HTPB based system loaded with ammonium dichromate or copper chromite catalyzed AN is reported to be 0.28–0.35 [59]. A value of 0.59 is
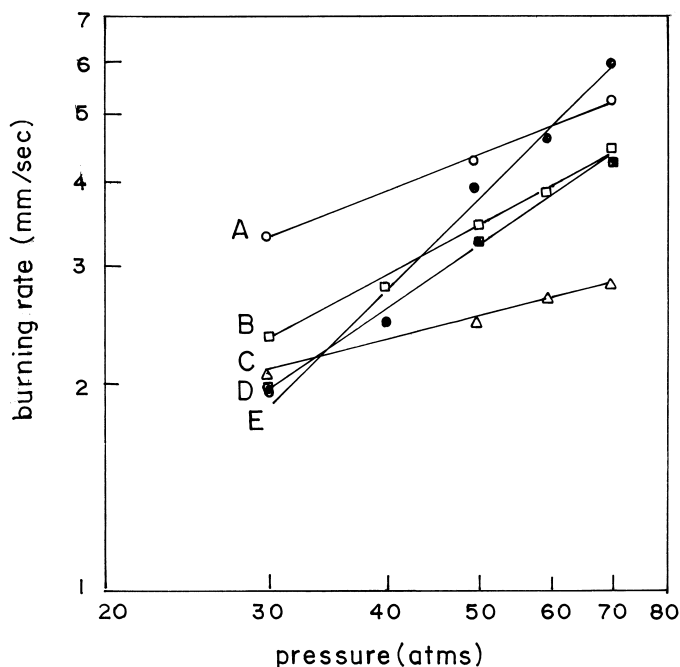
Fig. 4. Burning rate vs. pressure plots of propellants having DEFCH binder with (A) AN–AP (25:75), (B) AN–Mg (95:5), (C) AN, (D) PSAN(KNO$_3$) and (E) PSAN(KF) at 80% solid loading (DEFCH: diepoxide of furfuraldehyde carbonohydrazone).

reported in a PPG/AN system. When Mg was added, it varies from 0.087 to 0.45 depending upon the magnesium concentration [33]. A variation from 0.45 to 0.8 can be seen in AN/GAP propellants depending upon the phase stabilizer or catalyst used [132,176]. The pressure index of systems based on AN and N–N bonded binders also are found to be high, as mentioned earlier, especially when the systems are fast burning. After a careful analysis of some of these results, however, it appears that ammonium dichromate does not increase pressure exponent much like other catalysts.

The lower I_{sp} of AN propellants at stoichiometric ratio, $\phi = 1$ in comparison to AP based systems is obvious from Table 6. However, most often the practical solid loading hardly exceeds 86% solids, because of the processing difficulties. The performance limits of AN can be extended by the addition of energetic ingredients such as nitramines like HMX or RDX, or plasticizers such as TMETN [132,153]. However, the incorporation of such sensitive materials in large amounts to enhance the performance also brings a safety concern. A theoretical performance calculation on propellant compositions based on N–N bonded resins and AN shows that higher specific impulse compared to hydrocarbon based systems can be obtained at lower solid loadings for these systems [124]. Calculation using a typical resin DEFTCH, shows that a maximum I_{sp} of 222 s could be achieved at 85% ($\phi = 1$) AN solid loading as compared to CTPB which gives 205.5 s with the same solid loading due to the lower stoichiometric oxidizer requirement of the binder. Interestingly, the addition of Mg metal or AP, mentioned earlier in

Table 6
Theoretical specific impulse at $\phi = 1$ and at 85% solid loading for AN, AP and ADN based propellant compositions

Propellant	I_{sp} at $\phi = 1$		I_{sp} at 85% oxidizer loading
	% Oxidizer	I_{sp}	
DEFTCH-AN	89.76	228.3	222.0
DEBTCH-AN	91.65	225.1	210.4
CTPB-AN	94.2	223.6	205.5
DEFTCH-AP	83.73	247.4	244.1
DEBTCH-AP	86.4	244.5	243.5
CTPB-AP	90.0	253.0	242.6
DEFTCH-ADN	87.17	260.6	259.4
DEBTCH-ADN	89.29	258.6	251.8
CTPB-ADN	92.7	265.1	248.6

DEFTCH: Diepoxide of furfuraldehydethiocaronohydrazone.
DEBTCH: Diepoxide of benzaldehydethiocarbonohydrazone.
CTPB: Carboxyl terminated polybutadiene.

connection with increasing the BR (Fig. 4) also results in good performance parameters, comparable to CTPB/AP systems, as shown in Fig. 5. It may be worthwhile to mention here that the N–N-bonded binders are promising from the processing point of view as
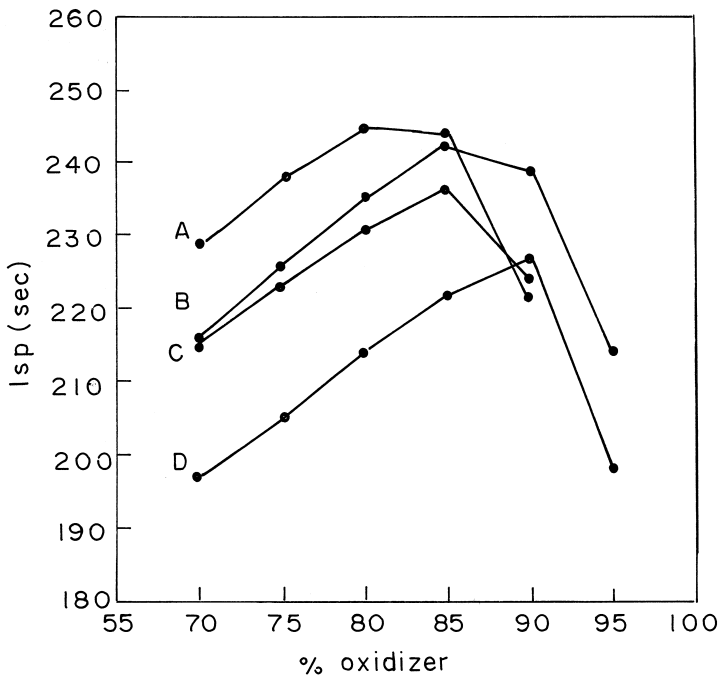

Fig. 5. Variation of specific impulse with percentage of oxidizer for DEFTCH based propellants using (A) AP, (B) AP/AN (25:75), (C) AN–Mg (5%) and (D) AN (DEFTCH: diepoxide of furfuraldehydethiocarbonohydrazone).

they give higher performance at relatively lower solid loadings when processed with other oxidizers also, like AP or ADN (Table 6). Of all the oxidizers, the performance of AN systems is the one greatly affected by the N–N-bonded binders. It is thus clear that the performance of AN systems could be improved significantly by using energetic binders and other ingredients.

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