

Waterproofing Materials for Ammonium Nitrate

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ABSTRACT

This study explores the possibility of overcoming the problem of hygroscopicity of ammonium nitrate by coating the particles with selected waterproofing materials. Gravimetric analysis of the samples of ammonium nitrate coated with eight different waterproofing materials, vis-a-vis, uncoated ammonium nitrate, were conducted at different relative humidity and exposure time. The results indicate that mineral jelly is the promising waterproofing material for ammonium nitrate among the materials tested, viz, calcium stearate, dioctyl phthalate, kaoline, diethyl phthalate, dinitrotoluene, shelac varnish, and beeswax. Attempts were made to confirm the waterproofing ability of mineral jelly to ammonium nitrate using differential thermal analysis and x-ray diffraction patterns as an experimental tool. Suitability of mineral jelly as an additive for the gun propellant was also assessed on the basis of theoretical calculations using THERM program.

Keywords: Hygroscopicity, phase transition, waterproofing ability, mineral jelly, ammonium nitrate, high energy materials, coating materials

1. INTRODUCTION

The search for the new clean burning propellants is necessitated by the demand for smokeless and less-sensitive propellants, which can suit the ecological requirements calling for *HCl*-free burning. The solution of these problems requires the replacement of commonly used ammonium perchlorate by a different oxidiser¹. Though the ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are energetic oxidisers, but these are not available in the required quantities². Hence, ammonium nitrate has received renewed attention as a possible eco-friendly oxidiser for use in solid propellants in the near future³. The innocuous nature of the combustion products of ammonium nitrate, its low cost, and easy availability, makes it an attractive oxidiser to the propulsion community. However, the major drawback of ammonium

nitrate is its dimensional instability due to its polymorphic forms (Table 1). A remarkable change in ammonium nitrate volume during transition from phase IV to phase III at 32 °C is detrimental from practical point of view⁴. Its high hygroscopicity is also an undesirable factor⁵. However, chemically pure and water-free ammonium nitrate requires higher temperature for the transformation of phase IV. At 50 °C, it directly transforms into tetragonal phase II, whereas a trace of water favours the normal transition of phase IV to phase III at 32 °C and causes cacking. Hence, hygroscopicity of ammonium nitrate has been pinpointed as the major cause for cacking. Cacking of ammonium nitrate is highly undesirable as far as the use of ammonium nitrate for solid propellant is concerned as it affects the structural integrity, energetics, and ballistic regularity of the propellant.

Table 1. Phases of ammonium nitrate

Phase	V	IV	III	II	I
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Tetragonal	Cubic
Humid (°C)	< -18	-18/+32	32/84	84/125	125/melt
Dry (°C)	< -18	-18/+50	--	50/125	125/melt

To overcome these drawbacks, various researchers have carried out extensive work to achieve the phase stabilisation of ammonium nitrate, particularly to overcome the problem of transition⁶⁻¹⁰ from phase IV to phase III at 32 °C. The present study also deals with the same problem. However, the approach to resolve the problem is different. In the present study, the attempts are aimed at overcoming the hygroscopicity of ammonium nitrate by coating its particles with waterproofing materials, whereas the already reported work is based on the phase stabilisation of ammonium nitrate by incorporating the metal oxides and nitrates, such as *CuO*, *NiO*, *KNO₃*, etc.

Various viable methods and number of waterproofing materials have been reported in the literature to reduce the hygroscopicity of ammonium nitrate¹¹⁻¹³. It is also reported that fertiliser-grade ammonium nitrate is coated with fert flow to avoid cacking and to improve the free-flow characteristics commercially¹⁴. However, the quantitative data on the waterproofing ability of the coating materials to ammonium nitrate is not reported. In view of this, the results of gravimetric analysis obtained on eight different waterproofing materials aimed at reducing the hygroscopicity, and thus, arresting phase transition of ammonium nitrate at 32 °C so as to establish the utility of ammonium nitrate into gun propellant, are presented in this paper.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Crystalline ammonium nitrate having an average particle size of 120 µm, purity 99 per cent, and specific gravity 1.7 was used. Waterproofing materials used were:

- (a) Mineral jelly (MJ) (JSS-8030-9)
- (b) Calcium stearate (CS) (AR-grade, bulk density = 2)
- (c) Diethyl phthalate (DEP) (CP-grade)
- (d) Dinitrotoluene (DNT) (CP-grade)
- (e) Shellac varnish (SV) (CP-grade)
- (f) Kaoline (hydrated aluminium silicate, white powder)
- (g) Dioctyl phthalate (DOP) (CP-grade)
- (h) Beeswax (BW)

2.2 Preparation of the Samples

Six different samples of ammonium nitrate coated with mineral jelly, calcium stearate, Kaoline, dioctyl phthalate, diethyl phthalate and dinitrotoluene, respectively were prepared using petroleum ether (60 : 40) as a solvent whereas ethyl alcohol was used for the coating of shellac varnish to ammonium nitrate. Selection of the solvent for the coating has been based on the solubility of the coating (waterproofing) material. Ammonium nitrate was insoluble in the solvents used for the experiments. The samples were air dried initially and thereafter kept inside the desiccator. Complete evaporation of the solvent was confirmed on the basis of constant-weight criteria.

2.3 Gravimetric Analysis of Coating Materials

The waterproofing ability of eight different coating materials to ammonium nitrate was assessed on the basis of gravimetric analysis carried out at

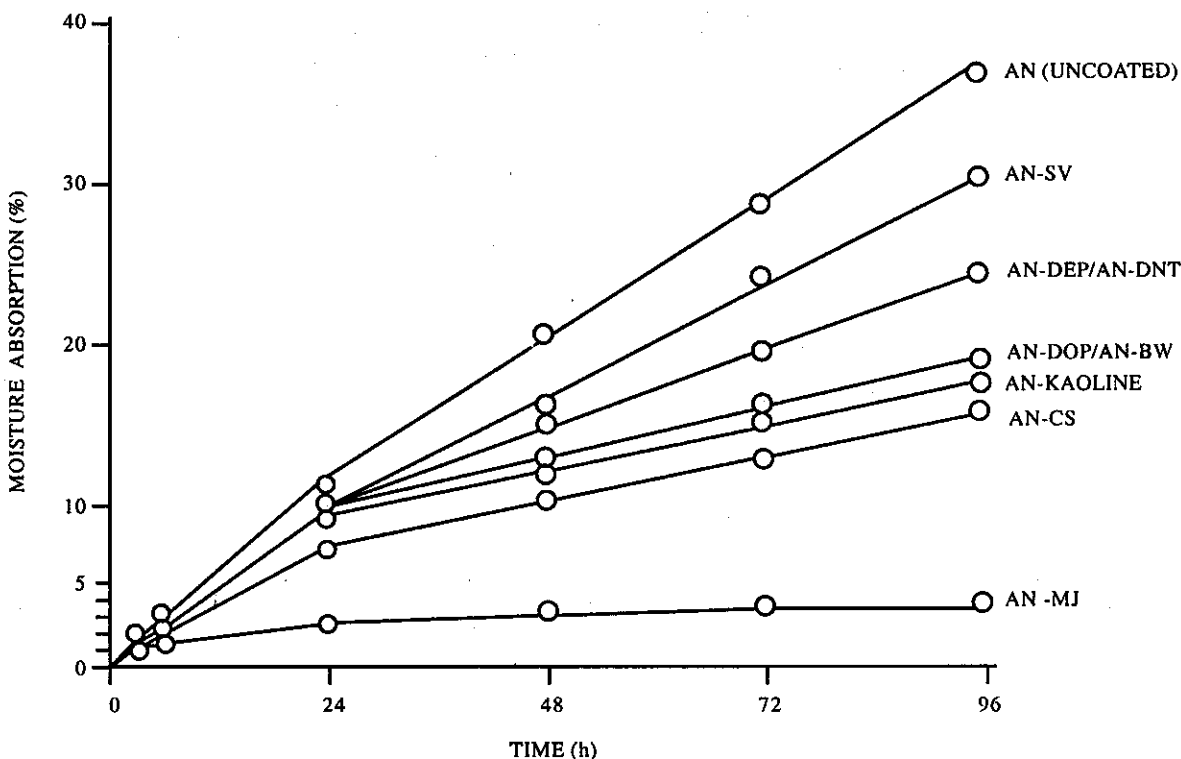


Figure 1. Comparative data of moisture absorption for ammonium nitrate coated with waterproofing materials at 65 % RH [AN: coating materials (10.0:0.1)].

various levels of relative humidity under controlled conditions using appropriate saturated salt solutions [NaNO_2 (65 % RH), K_2SO_4 (75 % RH), SrNO_3 (85 % RH), and H_2O (95 % RH)] and different exposure time intervals. The maximum time interval up to which the present experiments were conducted was 96 h. Criteria for the assessment of waterproofing ability of the coating material was worked out on the basis of percentage gain in weight of the sample as a function of relative humidity and exposure time. The minimum gain in weight percentage indicates the superiority of the coating material in respect of waterproofing ability, whereas the maximum gain in weight indicates the inferiority of the coating material. Moisture absorption profiles were obtained by plotting percentage moisture content against the exposure time. The results obtained by the gravimetric analysis have been presented in the Fig. 1 and a comparative data on moisture content for the samples of ammonium nitrate coated with mineral jelly and uncoated ammonium nitrate obtained at various relative humidity levels is given separately in the Fig. 2. Gravimetric analysis was also carried

out for the samples of ammonium nitrate coated with mineral jelly to the extent of 0.5 per cent, 1.0 per cent, and 1.5 per cent, respectively, to optimise the quantity of the coating material to ammonium nitrate.

2.4 Differential Thermal Analysis of Samples

Thermal behaviour of the samples was studied using NETZCH, a German make differential thermal analyser (DTA). The DTA curves were recorded in an inert atmosphere using a 10 mg sample in alumina crucibles at heating rate of 10 °C/min.

2.5 X-Ray Diffraction Patterns of Samples

The x-ray diffraction patterns of samples were determined using Philips analytical x-ray equipment. Studies were carried out at ambient temperature ($35 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$) with *Fe* target. The *d* values obtained were converted to those for *Cu* and *Cr* targets applying the following relationship:

$$d(\text{Fe})/d(x) = \lambda(\text{Fe})/\lambda(x)$$

2.6 Evaluation of Mineral Jelly as an Additive for Gun Propellant

Two series of the compositions were formulated. The first series comprised three different compositions based on standard triple-base (NQ) propellants containing additional ammonium nitrate to the extent of 5 parts, 6 parts, and 8 parts, respectively designated as ammonium nitrate-based compositions (AN-1, AN-2, and AN-3) and the second series comprised the same three compositions containing additional mineral jelly to the extent of 10 per cent to ammonium

nitrate in the composition designated as ANMJ-based compositions (ANMJ-1, ANMJ-2, and ANMJ-3), respectively (Table 3). The theoretical performance of the compositions was computed using THERM program¹⁴ and is presented in Table 4.

3. RESULTS & DISCUSSION

The data available from the gravimetric experiments clearly indicate that mineral jelly is the best waterproofing material for ammonium nitrate. Calcium stearate and kaoline were found to be the

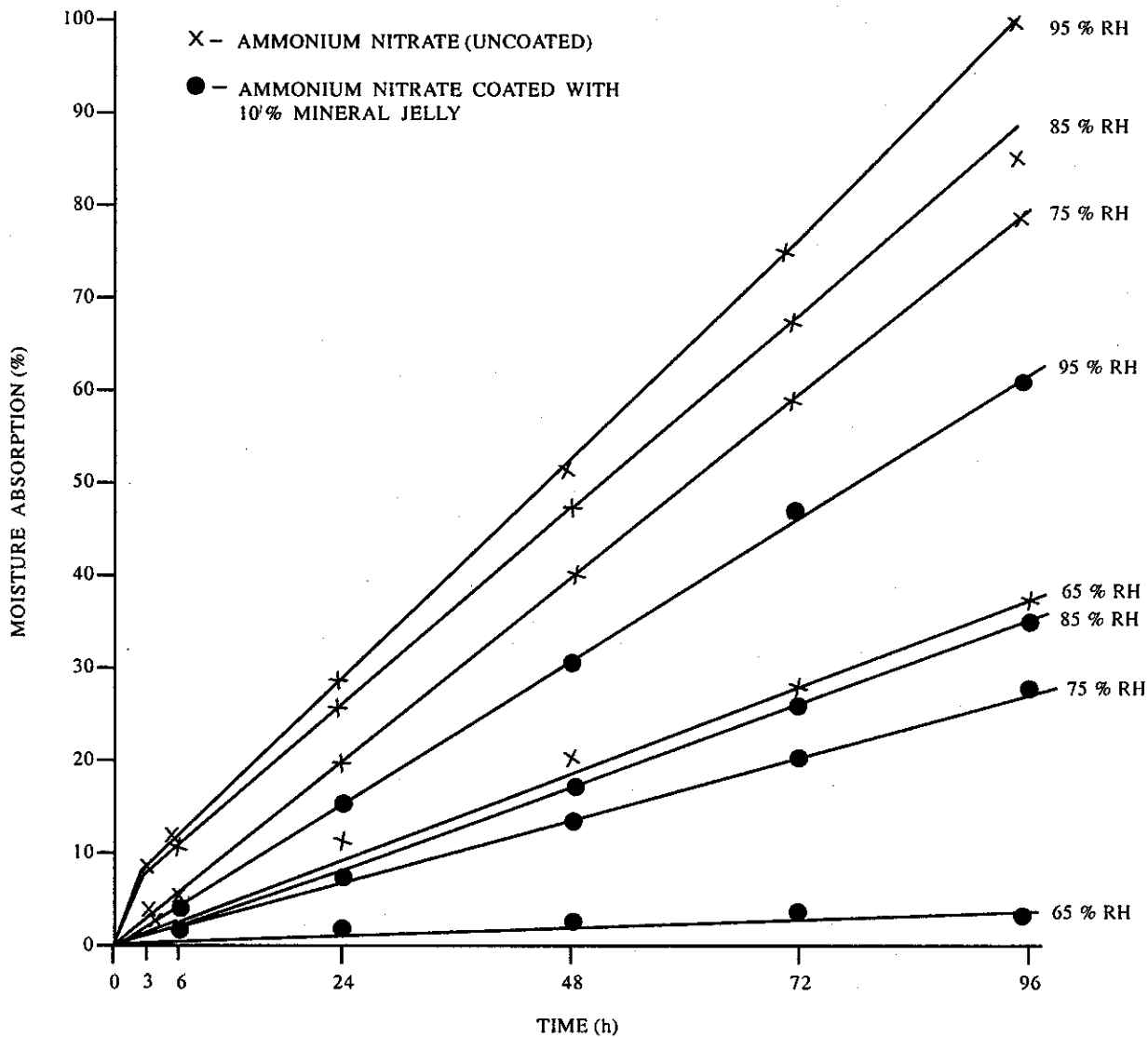


Figure 2. Moisture absorption of ammonium nitrate (uncoated) and ammonium nitrate coated with mineral jelly (AN:MJ 10:0.1) (65 % RH to 95 % RH).

second and the third best, respectively, whereas dioctyl phthalate, beeswax, diethyl phthalate, dinitrotoluene, and shellac varnish followed the order sequentially (Fig. 1). It is seen that mineral jelly is the promising waterproofing material for ammonium nitrate under a wide range of relative humidity (65 % RH to 95 % RH) (Fig. 2) and that coating of ammonium nitrate with mineral jelly (0.5 part) leads to relatively higher moisture content, whereas coating with mineral jelly (1.5 parts) does not show any appreciable difference than that of the coating with mineral jelly (1 part) in respect of moisture content. Hence, the weight ratio for ammonium nitrate and mineral jelly in the sample has been worked out as ammonium nitrate:mineral jelly (10.0:0.1).

Various mechanisms have been proposed for the waterproofing action of the coating materials to ammonium nitrate by different scientists. However, the phenomenon of the formation of hydrophobic film over the granular surface of ammonium nitrate is widely agreed upon. It is postulated by Serizava¹⁵, *et al.* that the mineral jelly, a mixture of straight chain hydrocarbons (paraffinic), acts as a hydrophobic barrier between ammonium nitrate crystals and ingressing moisture. Thus, it reduces the hygroscopicity of ammonium nitrate significantly for a wide range of relative humidity. According to Kust¹⁶, the coatings of hydrophobic materials, such as paraffinic hydrocarbons or polymeric resins increase the water

Table 2. The x-ray diffraction patterns (*d* values) of ammonium nitrate and ammonium nitrate coated with MJ (32-84 °C)

Ammonium nitrate		AN + 1 % MJ	Ammonium nitrate		AN + 1 % MJ
<i>Cu</i> -target			<i>Cr</i> -target		
Theor	Exptl		Theor	Exptl	
3.94	3.92	3.99	3.99	3.94	-
3.23	3.24	-	3.40	3.41	3.45
3.20	3.19	3.28	2.83	2.85	3.89
2.61	2.63	-	2.55	2.56	2.65
2.41	2.45	2.49	2.53	2.50	-
2.26	2.28	-	2.52	2.55	-

Table 3. Chemical formulations of the propellants based on NQ containing additional ammonium nitrate and mineral jelly

Sr.No.	Propellant composition
Series 1	
AN-1	NQ + AN (5 parts)
AN-2	NQ + AN (6 parts)
AN-3	NQ + AN (8 parts)
Series 2	
ANMJ-1	NQ + AN (5 parts) + MJ (0.5 parts)
ANMJ-2	NQ + AN (6 parts) + MJ (0.6 parts)
ANMJ-3	NQ + AN (8 parts) + MJ (0.8 parts)

Chemical composition of NQ propellant = NC (12.95 N%)
20.80 + NG 20.60 + Picrite 55.00 + Carbamite 3.60
+ K_2SO_4 0.30

resistance of ammonium nitrate particles. The second best waterproofing material, calcium stearate, is a substance very difficult to wet with water and so helps waterproofing by slowing down the initial wetting and acts as a sort of barrier to the hygroscopicity of ammonium nitrate as reported by Taylor and Sillitto¹⁷. Dobrovfol' Skii¹⁸ attributed the waterproofing action of calcium stearate to the physico-chemical properties of ammonium nitrate. According to him, the addition of calcium stearate up to 3 per cent to ammonium nitrate decreases the hygroscopicity of ammonium nitrate to a considerable extent. The microstructure becomes significantly compact and dense due to the decrease of voids and fine spaces within the powder. It is also postulated by Philen¹⁹, *et al.* that calcium stearate reacts with ammonium nitrate to form a tightly adhering and moisture-resistant coating of $Ca_2NH_4-(NO_3)_2(OH)_3 \cdot 3H_2O$ and thus reduces the hygroscopicity of ammonium nitrate. It was experimentally shown that the interface of ammonium nitrate and calcium stearate has both physical and chemical stability. According to Korpedak and Edward²⁰, calcium stearate acts as a partitioning agent to ammonium nitrate granules. Kaoline, in a fine powder form, acts as an inert coating material, which adheres to the surface of ammonium nitrate crystals or granules and is

Table 4. Theoretically calculated thermochemical parameters of the propellants based on NQ containing additional ammonium nitrate and mineral jelly

Propellant	Force constant (J/g)	Flame Temp (K)	Cal-Val (cal/g)	Mw (g/mole)	n value (mole/g)	Ratio of sp. heat of gases (γ)
AN-1	1032	2802	898	22.58	0.04429	1.2468
ANMJ-1	1022	2747	878	22.34	0.04477	1.2486
AN-2	1033	2809	904	22.61	0.04423	1.2460
ANMJ-2	1023	2751	884	22.35	0.04474	1.2479
AN-3	1036	2825	915	22.67	0.04410	1.2445
ANMJ-3	1021	2738	885	22.30	0.04484	1.2473

simultaneously capable of absorbing moisture. Therefore, it was realised as the third promising waterproofing material for ammonium nitrate. Dimitrijevic and Sikirica²¹ postulated that 0.1 per cent to 5.0 per cent kaoline is more effective surfactant for reducing hygroscopicity of ammonium nitrate due to its ability to form the uniform dispersion envelope around the ammonium nitrate crystals. Katayama²², *et al.* have investigated that the action of kaoline as a readily dispersible sludge coagulant suppresses the moisture absorption and prevents the coalescence of ammonium nitrate crystals. Kust¹⁶, also postulated that the coating of finely divided kaoline to ammonium nitrate acts as a conditioning agent, leading to the formation of free-flowing particulates.

The dioctyl phthalate and diethyl phthalate are non-polar in nature, and thus, create a sort of barrier between ammonium nitrate and water droplets, resulting in hydrophobising effect. The dioctyl phthalate has more non-polar nature than the diethyl phthalate due to long carbon chain, resulting into more hydrophobic action. Therefore, the dioctyl phthalate was found to be better waterproofing agent than the diethyl phthalate. Beeswax, an ester of long chain fatty acids, has shown comparable waterproofing ability as dioctyl phthalate. The waterproofing ability of beeswax to ammonium nitrate is attributed to the formation of water-insoluble soaps which form thin films around ammonium nitrate particles

and decrease their hygroscopicity²³. According to Pagowski and Subos²⁴, mixing of molten wax with granulated ammonium nitrate, intensifies the process of porosity, and thus, decreases the hygroscopicity. The dinitrotoluene and shalac varnish were found to be the non-promising waterproofing materials for ammonium nitrate as compared to other materials.

Samples of ammonium nitrate coated with mineral jelly along with the uncoated ammonium nitrate were tested using DTA to confirm the phase stabilisation of ammonium nitrate. It was found from the DTA results that uncoated ammonium nitrate exhibited four endotherms under ambient conditions (initial temperature 20 °C). The endotherms at 32 °C, 84 °C and 125 °C can be attributed to phase IV to phase III, phase III to phase II, and phase II to phase I transitions, respectively. The endotherm at 169 °C corresponds to the melting point of ammonium nitrate. In the samples where the ammonium nitrate was coated with the mineral jelly, instead of the endotherm obtained at 32 °C in case of uncoated ammonium nitrate, a new endotherm was observed at around 49 °C (Fig. 3). This behaviour is similar to that exhibited by phase-stabilised ammonium nitrate (PSAN) as reported in the literature⁶⁻¹⁰. However, approach in both the cases was different. From the practical point of view, the effect of coating of mineral jelly on moisture susceptibility of ammonium nitrate was evaluated under controlled relative humidity conditions. The moisture absorption profiles obtained

at 65 % RH, 75 % RH, 85 % RH, and 95 % RH (Fig. 2) clearly bring out that coating of mineral jelly reduces the hydrophilic nature of ammonium nitrate, which is an important attribute because water is reported to facilitate the formation of phase III at 32 °C. In view of these findings, mineral jelly is also considered to act as phase stabiliser to ammonium nitrate by virtue of its waterproofing effect.

To obtain supporting evidences, samples of ammonium nitrate-coated with mineral jelly were subjected to x-ray diffraction along with uncoated ammonium nitrate. The d values obtained on Cu target for uncoated ammonium nitrate were 3.92, 3.24, 3.19, 2.63, 2.45, and 2.28, which are close to the values reported in the literature¹⁰. However, samples of ammonium nitrate-coated with 1.0 per

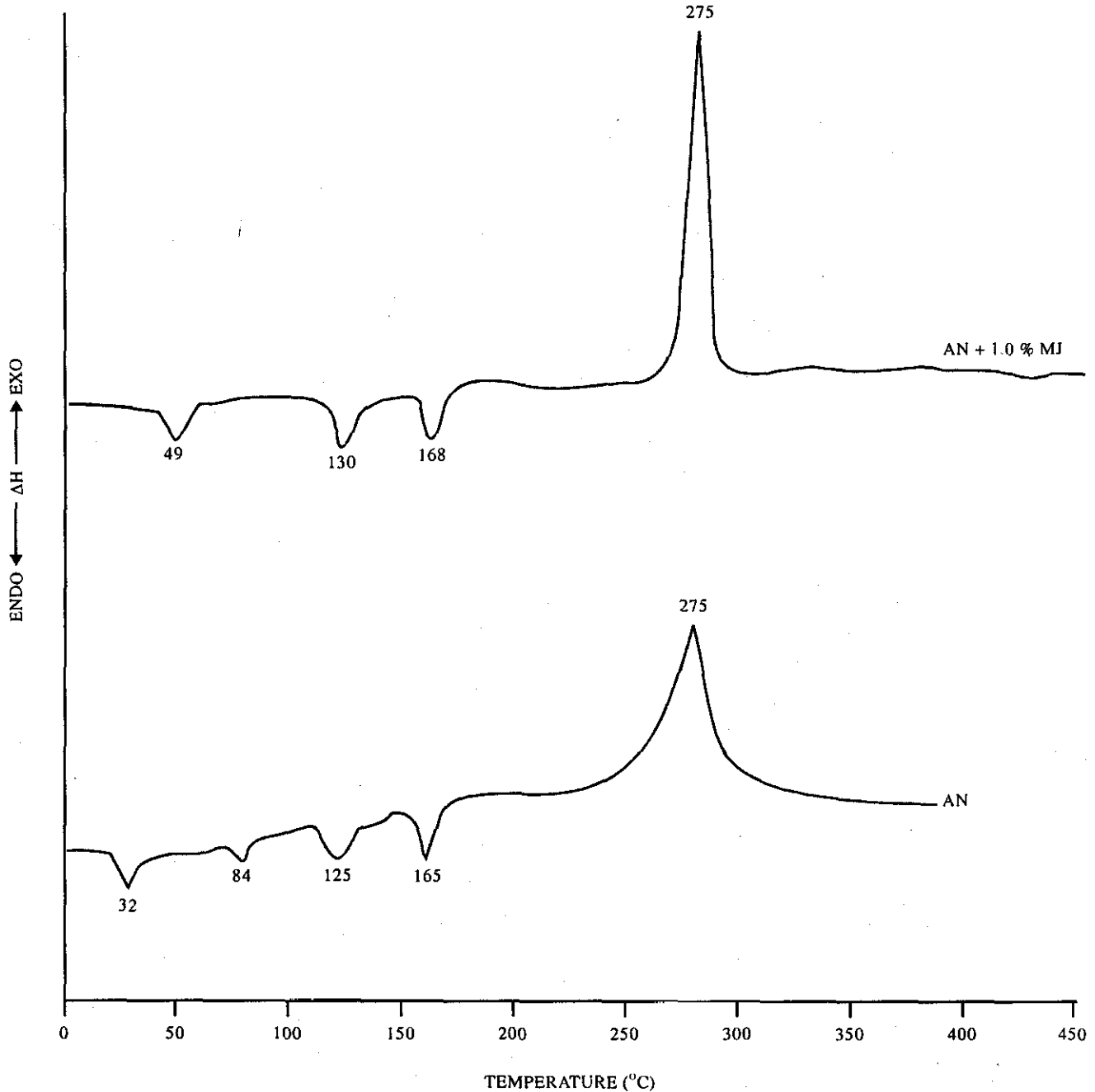


Figure 3. DTA thermograms

cent mineral jelly gave d values of 3.99, 3.28, and 2.49. These results are similar to those obtained for ammonium nitrate incorporating¹⁰ CuO (d values 3.91 and 2.47) and suggest a change in the morphological structure of ammonium nitrate-coated with mineral jelly. Similarly, the d values obtained on Cr target also conclude the same fact (Table 2). This finding is an evidence to the mechanisms for coating to ammonium nitrate as proposed by different scientists¹⁸⁻²⁰. Further evidence was obtained from the relative intensity calculated from the x-ray diffraction patterns for ammonium nitrate-coated with the mineral jelly and the uncoated ammonium nitrate for the corresponding 2θ value.

The chemical compositions of the propellants based on NQ containing additional ammonium nitrate and mineral jelly were formulated to evaluate the ballistic performance of mineral jelly as an additive for gun propellant (Table 3). Theoretically calculated thermochemical parameters of the propellants are given in Table 4. It has been observed from the data that the addition of mineral jelly (0.5-0.8 part) into propellant (ANMJ-based propellant) decreases the flame temperature (by 55 K) with only marginal decrease in the force constant (10 J/g). The marginal decrease in force constant is attributed to the decrease of calorimetric value of the ANMJ-based composition (15 cal/g) because of lower oxygen balance of the mineral jelly. Hence, the mineral jelly plays an additional role of reducing the flame temperature of the propellant, and thus the gun erosion. It has also been reported that mineral jelly, to the extent of 5-6 weight per cent, was used as a stabiliser in the early cordites²⁵.

4. CONCLUSION

The mineral jelly has been found to be the best waterproofing material for ammonium nitrate among the materials tested in this study. The coating of ammonium nitrate with 1 per cent mineral jelly decreases the hygroscopicity of ammonium nitrate nearly by five times at 65 % RH, three times at 75 % RH, and two times at 85 % RH. However, beyond 95 % RH level, the waterproofing effect of mineral jelly decreased drastically. Further, mineral jelly is found to act as a phase stabiliser to ammonium

nitrate and a coolant for the gun propellant. Hence, it is used as an additive for the gun propellants containing ammonium nitrate.

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