

Research Article

## Effect of Addition of Hydrophobic Hydrocarbons on the Hygroscopic Tendency of Ammonium Nitrate Crystals

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Accepted 10 July 2015, Available online 17 July 2015, Vol.5, No.4 (Aug 2015)

### Abstract

The present study is aimed towards the use of selected hydrophobic hydrocarbons to attain a waterproof coating on Ammonium Nitrate crystals. High hygroscopic nature of Ammonium Nitrate makes it impractical for its use as oxidizer in composite solid propellant formulations as absorption of water molecules by Ammonium Nitrate from moisture in the atmosphere negatively affects the structural integrity, energetics and ballistic performance of the Ammonium Nitrate based propellant grains. Hydrocarbons, generally waxes and oils, are hydrophobic in nature and may thus be utilized to repel water molecules resulting in a reduced water absorption by Ammonium Nitrate crystals. In the present study, the effect of addition of Paraffin Wax, Micro-crystalline Wax & Bees Wax along with pure Ammonium Nitrate is observed and compared. Samples were prepared by adding varying and significantly small weight percentages of waxes with Untreated Ammonium Nitrate and were kept under normal laboratory conditions. A weight increment rate study of all the prepared samples were conducted on a daily basis for a period of 20 days. All prepared samples, under same atmospheric conditions, exhibited different water absorption rates which were then compared to reveal the waterproofing capabilities of specific additives.

**Keywords:** Ammonium Nitrate, Hydrophobic Hydrocarbons, Paraffin Wax, Micro-crystalline Wax, Bees Wax, Waterproofing.

### 1. Introduction

Ammonium Nitrate (AN), though being an economical and eco-friendly oxidizer, suffers a very limited use in the formulations of composite solid propellant (CSP) grains due to its high hygroscopic nature. The Nitrate salt of Ammonium with chemical formula  $\text{NH}_4\text{NO}_3$ , with appearance of white crystalline solid, is highly soluble in water (Zapp *et al*, 2000). Ammonium Nitrate tends to absorb water molecules from moisture present in the atmosphere which results in liquefaction and/ or a change in state of the compound. Another major drawback of AN is its dimensional instability due to its five phase state transitions ranging from  $-200\text{ }^\circ\text{C}$  to its boiling point, i.e.  $125\text{ }^\circ\text{C}$ . These phase modifications leads to a decrease in the adherence between the crystallites and result in severe structural changes in the crystal lattice of Ammonium Nitrate (Hendricks *et al*, 1932), (Brown *et al*, 1962). Owing to these inherent shortcomings, structural strength of AN based propellant grains decrease significantly during these thermal cycles and leads to the formation of cracks in the propellant grains.

Such cracks result in an unexpected increase in burning surface area of the propellant (Flack-Muss *et al*, 1972). At any instant, mass flow rate of hot gases generated and flowing from the motor under stable combustion conditions is governed by the following empirical formula (Sutton *et al*, 2001):

$$\dot{m} = \rho_p \cdot A_b \cdot r \quad (1)$$

Where,

$\dot{m}$  = mass flow rate of hot gases generated,  
 $\rho_p$  = density of propellant prior to motor start,  
 $A_b$  = burning area of the propellant grain,  
 $r$  = propellant burn rate.

Formation of cracks in the propellant grains open up new additional burning surfaces causing an unexpected increase in the generation of mass flow of hot gases as is evident from Equation 1. Such increased mass flow may over pressurize the solid rocket motor (SRM) leading to a disastrous failure of the mission. Hence, any inherent property of an ingredient used in the formulation of CSPs which may lead to occurrence of cracks, should be diminished.

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A remarkable change in volume of AN during transition from phase IV to phase III at 32 °C tends to create cracks in the propellant grain from practical point of view (Hahn *et al*, 1977). It is observed that chemically pure and water-free AN requires higher temperatures for the transition of phase IV. At 50 °C, AN directly transforms into tetragonal phase II, whereas a trace of water favors the normal transition of phase IV to phase III at 32 °C that causes cacking. Hence, hygroscopic tendency of AN has been pinpointed as the major cause for cacking (Damse, 2004).

Several compounds have been studied by researchers all over the globe which may tend to act as waterproofing agents for Ammonium Nitrate. Mineral Jelly had been found to reduce the hygroscopicity of AN over a wide range of relative humidity levels (Serizava *et al*, 1998). Calcium Stearate had been extensively studied and had been reported to slow down the initial wetting of AN crystals by acting as a partitioning agent (Philen *et al*, 1969), (Taylor *et al*, 1984).

Kaoline had also been found to provide the required waterproofing effect when added in 0.1 to 5.0 weight percentages (Dimitrijevic *et al*, 1965). It had been reported that Kaoline suppresses the moisture absorption thereby reducing the coalescence of AN crystals (Katayamaz, 1982). Dioctyl phthalate and Diethyl Phthalate are two more compounds that had been found to create a sort of barrier between AN and water droplets resulting in a reduction in hygroscopicity (Erhz *et al*, 1966).

Various oils and greases had been studied for their waterproofing abilities but the addition of larger quantities of such compounds had been proved to negatively affect the ballistic performance of Ammonium Nitrate (Young, 1961).

Hydrophobic hydrocarbons like Beeswax, Paraffin wax & Microcrystalline wax have a tendency to repel water molecules and thus lead to a reduction in the absorption of water molecules by creating a waterproof coat on AN crystals. Beeswax (BW) having chemical formula is  $C_{15}H_{31}COOC_{30}H_{61}$ , is a natural wax produced by honey bees and is formed from a mixture of several compounds. It has low melting point range of 62- 64 °C (Thorpe, 1916). Paraffin wax (PW) is a white soft solid derived from petroleum, coal & oil shale which consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms. It is solid at room temperatures, begins to melt above 37 °C and its boiling point is >370 °C. PW is unaffected by most chemical reagents but burns readily (Freund, *et al*, 1982). Micro-crystalline wax (MW) is produced during petroleum refining process. Its melting point ranges from 60 to 80 °C. It is often used in industries such as tires and rubbers, candles, adhesives, cosmetics & castings (MSDS, 2010).

The present study is focused on observing the effects of coating of aforementioned hydrocarbons on Untreated Ammonium Nitrate (UAN) crystals. Different weight percentages of selected hydrocarbons were added to UAN in varying and significantly small weight

percentages. Prepared samples, kept uncovered under normal laboratory conditions for a period of 20 days, were observed and compared to analyze the capability of the chosen hydrocarbons in providing the desired waterproofing effect.

## 2. Experimental Procedure

### 2.1 Preparations of Test Samples

Ten different samples with a quantity of approximately 10g were prepared for the present study. Nine of the samples were coated with aforementioned waxes in different weight percentages and one sample of UAN was prepared to provide the baseline for rate of water absorption. Required quantity of a wax was taken in a 20ml glass beaker and was allowed to melt using slow heating through a hot plate. Required quantity of AN was then added to the molten wax and the mixture was stirred continuously with a glass rod under constant slow heating. The incessant heating of the mixture just above the melting point of the wax ensured a proper and consistent coating of AN crystals. The mixture was allowed to cool down under room temperature to facilitate solidification of the wax and the mixture was then transferred to properly labeled sample bottles. Table 1 represents the compositions and weight percentages of the ingredients in various prepared test samples.

**Table 1:** Compositions of Prepared Samples

Test Sample	AN (wt. %)	AN (g)	Additive	(wt. %)	Weight (g)
1	100 %	10.0 g	None	--	--
2	99 %	9.9 g	BW	1 %	0.1 g
3	98 %	9.8 g		2 %	0.2 g
4	97 %	9.7 g		3 %	0.3 g
5	99 %	9.9 g	PW	1 %	0.1 g
6	98 %	9.8 g		2 %	0.2 g
7	97 %	9.7 g		3 %	0.3 g
8	99 %	9.9 g	MW	1 %	0.1 g
9	98 %	9.8 g		2 %	0.2 g
10	97 %	9.7 g		3 %	0.3 g

### 2.2 Water Absorption Rate Study

Weight of each empty sample bottle was noted down to calculate the total weight of the sample. Each mixture absorbed moisture at a different rate which was reflected as increment in total weight of each sample showed at different rates. Each sample bottle containing mixture was weighed accurately up to thousandth of a gram using electronic weight balance. The weight increment of each sample was observed daily within the same timeframe and the study was carried out for a period of 20 days.

## 3. Results & Discussion

A consistent & steady increment in the weight of the UAN sample was observed with an average increment of 0.01057g per day. The overall weight increment for

UAN sample over a period of 20 days was found to be 0.2114g. Figure 1 indicates the increment in UAN sample weight during the course of study. The graph exhibits a comparatively higher slope during the early days of the study which tends to become almost linear by the end.

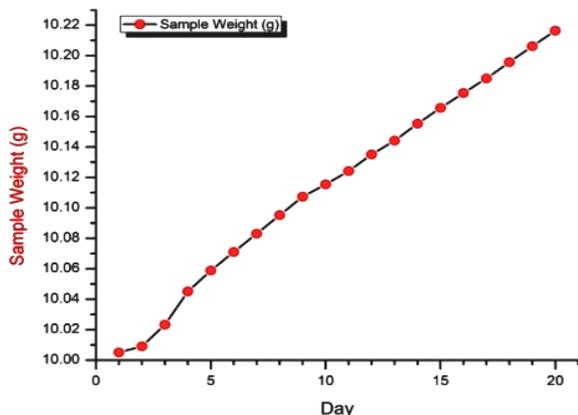


Figure 1: Weight Increment Rate for UAN Sample

The water absorption rate of AN was affected differently by the introduction of different hydrophobic additives and was dependent on both type and quantity of the additive. Table 2 represents a comparative data showing the overall weight increment of test samples for various types and weight percentages of the additives. Minimum quantity of water was absorbed by the mixture containing 3% PW as additive and is evident by the sample’s minimum average and overall increment in weight over the span of study.

Table 2: Overall Weight Increments for Various Samples

Sample	Additive	Additive Weight Percentage	Overall Weight Increment in 20 days (g)
1	BW	1 %	0.2291
2		2 %	0.2039
3		3 %	0.1961
1	PW	1 %	0.1797
2		2 %	0.2492
3		3 %	0.15
1	MW	1 %	0.3347
2		2 %	0.2058
3		3 %	0.1967

Figure 2, 3, and 4 represent the comparative graphs showing increments in sample weight for BW, PW and MW added samples, respectively over the period of 20 days.

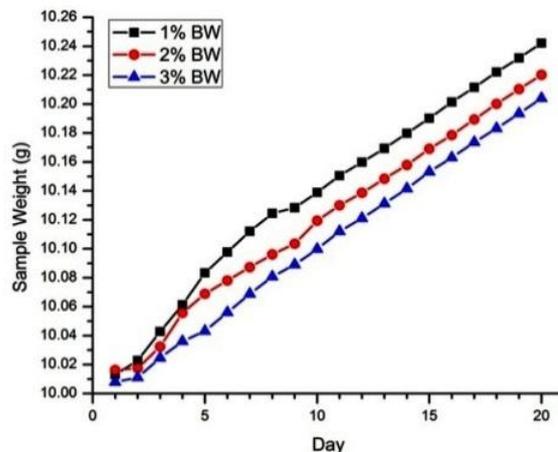


Figure 2: Weight Increment Rates for Bees Wax Added Samples

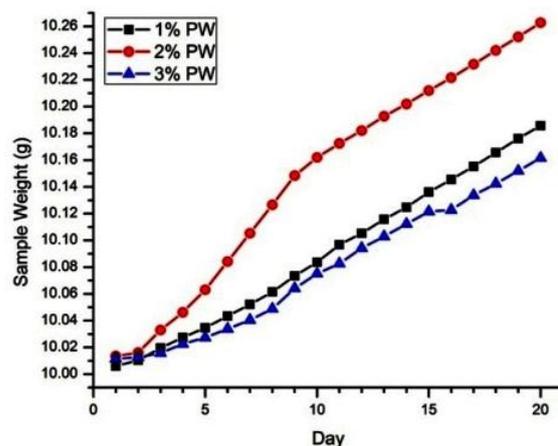


Figure 3: Weight Increment Rates for Paraffin Wax Added Samples

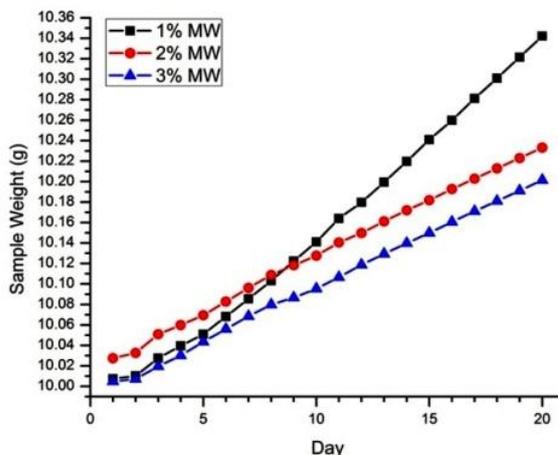


Figure 4: Weight Increment Rates for Micro-crystalline Wax Added Samples

It was observed from Figure 2 that water absorption rates for all three samples of BW tend to become linear by the end of the study duration. Increasing the weight percentage of BW in the mixture tends to increase the waterproofing effect as 3% BW shows minimum overall increment in weight of the mixture. Figure 3

depicts an unexpected high slope and weight increment in the mixture with 2% Paraffin wax. The slope for 1% and 3% PW samples were found to be comparatively less indicating reduced rates of absorption of water molecules by AN crystals. The water absorption rate for 1% MW was found to be highest as is illustrated in Figure 4, whereas, an increase in the weight percentage of the additives resulted in a reduction in water absorption by the mixtures. Figure 5 shows comparison graphs for overall weight increment for various mixtures.

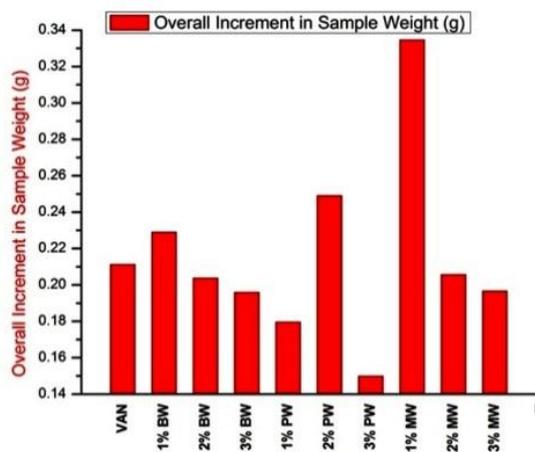


Figure 5: Overall Weight Increments of all Samples

## Conclusion

Almost all of the compositions proved to be effective in providing the desired waterproofing effect for the AN crystals but at different weight percentages. It was apparent through the study that increasing weight percentages of the additives result in a reduced rate of water absorption by the mixtures when compared to VAN sample. Among all of the prepared samples, mixture containing 3% PW was found to be the most effective additive. It is evident from figure 5 and 6 that the addition of 3% PW resulted in a decrease of approximately 29% in overall increment in weight as compared to UAN sample. It can safely be concluded from the present study that AN shows highest retentive nature from water, i.e. its hygroscopic tendency is reduced to its most, when Paraffin wax is utilized in optimum weight percentages as the waterproofing additive. A significant reduction in hygroscopic nature of AN crystals can reduce the occurrence of phase transitions in the range of normal room temperatures and can minimize the chances of caking of AN-based propellant grains. Minimizing such inherent drawbacks associated with the use of AN as oxidizer can further promote its enhanced usage in the formulation of environment-friendly composite solid propellants in near future.

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