Burning Rate Study of PSAN-HTPB Based Solid Rocket Propellants

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Abstract: Composite propellants based on Ammonium Perchlorate (AP) as oxidizer are in major role in solid rocket. However, because of their high toxic exhaust, it is not suggested for global environmental pollution issue. Therefore, researchers want to replace AP based propellants with clean exhaust propellant. Ammonium Nitrate (AN) has the properties which can satisfy the present environmental need in the field of propellant. However, the disadvantage for the application of AN - as solid propellant oxidizer is its dimensional instability in different temperature ranges due to phase transformation which causes change of volume and porosity of the propellant grain. This was be resolved by the use of Phase Stabilized Ammonium Nitrate (PSAN) for propellant processing. Synthesized mixed metal oxides were used to enhance burning rate. These propellant samples were then tested for measuring burn rate in a Crawford High Pressure Strand Burner and thermal degradation studies carried out Simultaneously in Thermal Analyzer (STA). It is observed that the thermal decomposition and burn rate of the propellant is maximum by adding anyone of the mixed metal oxide catalyst among 3 different catalysts. In this research the different samples are formulated to test and get results. It has been observed that only two propellants burnt properly as compared to other propellants taken for the analysis.

Keywords: Burn rate, Catalytic combustion, Preparation of catalyst, Preparation of PSAN, Solid propellants, Thermal decomposition.

I. Introduction

AN has become a noticeable oxidizer in present environmental scenario due to its low cost, smokeless eco-friendly exhaust. It is also a chlorine free oxidizer. AN has not been used yet for high performance and for larger rockets because of its lower burn rate but only for low performance rocket and for gas generator. Another disadvantage of AN is its phase instability with different temperature ranges. So it is necessary to make it phase stabilized before propellant processing, and enhance the burning rate using any catalyst or by other method. Efforts has been made in the present to make phase stabilized ammonium nitrate by incorporating Potassium Nitrate in two different way. And the same phase stabilized PSAN was used for propellant processing to be tested for this research. Catalysts were also prepared for getting for getting different propellant samples for test results. Three different catalysts were synthesized using two metal oxides by mixing in different molar ratio.

Catalytic and non catalytic propellant samples were prepared and the propellant compositions are mentioned in the table. Different propellant samples help to get different comparative result to enhance burn rate. All propellant samples were tested in Crawford Strand burner.

Table I: Composition of Copper Cobalt Mixed Metal Oxides

Catalyst	Copper Nitrate (gm)	Cobalt Nitrate (gm)	Citric Acid (gm)	Molar Ratio (Cu/Co)
CuCo-I	0.6	0.72	3.15	1.0
CuCo-II	0.6	1.44	3.15	0.5
CuCo-III	1.2	0.72	3.15	2.0

metal oxide catalysts. Thermal analysis was also carried out for AN and PSAN. The results from the present investigation are further studied and discussed which leads to get some important conclusion.

II. Experimental

The present experiment includes Preparation of (PSAN), grinding and sieving of AN and PSAN, Preparation of catalysts, Propellant processing with and without catalysts, burn rate measurement and thermal decomposition study of the oxidizer.

A. Preparation of Phase Stabilized Ammonium Nitrate (PSAN)

The growing demand for environmental friendly chlorine free propellants, many attempts have been made to investigate oxidizers producing innocuous combustion products. AN produces eco-friendly smoke free exhaust after combustion where as the widely used AP produces much toxic exhaust. Also AN is one of the cheapest and easily available compounds. But AN has some disadvantages i.e. hygroscopicity, volume change in different temperature ranges and low performance so these must be overcome before using it for propellant processing.

There are various chemicals which are used to stabilize the phase changes of AN and among those chemicals KN was used here to stabilize the AN. The amount of chemicals used to stabilize the AN varies from 0.5% to 15% of the AN. These chemicals can be added by solid mixing, solution mixing or by spray. In this present research PSAN was prepared by solid mixing and solution mixing.

The chemical involved in this process were ordered from Central Drug House New Delhi. Digital weighing machine was used to weigh accurately. 500ml AN was added to 251ml of water and the mix was stirred till all the AN dissolved. Mixing was done at $85^{o}C$ it is because to change the density to make easily soluble and to get uniform mixing. A clear and colorless aqueous solution was obtained. The complete process of mixing and drying take around 20 hours. Here the dying process was done at $75^{o}C$. A dry solid crystalline was obtained. The same process and the weight percentage of AN and KN was repeated whenever the PSAN was required. Two different methods were used to make PSAN and in both the process approximately 8-10% KN was added.

The PSAN collected from the phase stabilization process was then made usable for propellant processing by grinding. It was sieved by using different mess sieves in a sieve shaker. Here two different particle size of PSAN was collected for propellant sample making. PSAN retained on 60mess and 100 mess was used for processing the propellant. The approximate particle sizes of PSAN were 250 microns and 150 microns.

B. Preparation of Cu-Co Mixed Catalyst

The catalysts used in the present investigation were prepared in 1, 0.5 and 2 molar ratios. Chemicals with particular name used in the catalyst making were, copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$). China dish and distilled water was used at the first stage of catalyst making to get mixed metal aqueous solution. The second stage was to get viscous gels that was obtained by keeping the aqueous solutions at 115°C for around 4-5 hours.

The gels were then dried at170°C in a muffle furnace for 2 hours. The resulting mass was the bubbly dark powders. Then again they were at 650°C. The final product was dark powders. The same synthesis process has been carried out to get the required amount of catalysts. In a single synthesis around 0.4 to 0.5 grams of one sample catalysts was collected. The products were stored separately in desiccators to keep away from environmental effect. Table I shows the catalysts prepared in the present work. And plate above show the 2^{nd} stage of catalytic synthesis.

C. Processing of Solid Propellants

The two different particle sizes of PSAN i.e. course to fine ratio was 75:25. All other chemicals that are HTPB, DOA and IPDI were used in proper weight ratio. Before the process started, the HTPB and DOA were dehumidified. The mixing was done at $65^{o}C$. HTPB was heated in a container using wax bath. The IPDI was added in the mix and stirred for again 10 minutes. Finally the PSAN were added in slots that are also first course then fine while mixing. Mixing was again continued for around 25-30 minutes or until it was mixed uniformly. The propellant slurry was obtained. It was then casted in properly foiled and greased mold which helps easy removal after it is cured.

The casted mold was then kept in vibrator to settle the slurry properly also to remove air bubbles from the slurry for around half an hour. The mold was then again kept in vacuum oven for curing the propellant slurry and for gaining mechanical strength for 5-7 day at 65°C. The curing can also be done at room temperature but that is time taking so for fast and easy process vacuum Oven was used. The mold was then taken out from the oven and the propellant was removed from mold. The propellant samples were then covered properly to avoid moisture and environmental effects kept in desiccators.

Table II: Composition of Solid Propellants

S. No	PSAN	HTPB	DOA	IPDI	Cu/Co-I	Cu/Co-II	Cu/Co-III
1	75	18.92	4.6	1.46	-	-	-
2	75	18.92	4.6	1.46	2	-	-
3	75	18.92	4.6	1.46	-	2	-
4	75	18.92	4.6	1.46	-	-	2
5	75	18.92	4.6	1.46	-	-	-
6	80	15.14	3.68	1.168	-	-	-

All quantities are in weight percentage

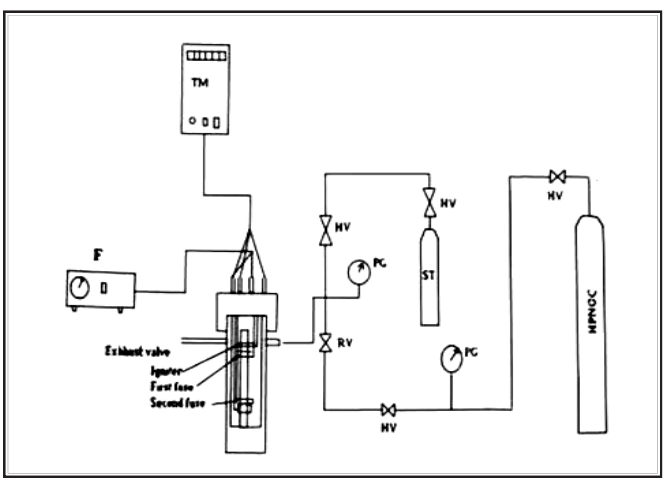
Crawford Burner is self made apparatus by a research institute which allows propellant strand to burn at different pressure ranges and the timer connected to it gives the burn rate of the propellant strand. The propellant is burned in a pressurized firing vessel. Here propellant strand is coated to keep uniform cross section burning to get accurate burn time. Here in Crawford Burner setup wires are connected to the timer via an electric relay. Wires are also connected at the both ends of the strand so that when one wire cuts then timer starts and when the seconds cut then timer stops. The burn time is recorded and the burn rate is determined with the help of burn time and burn length. The figure below shows the schematic of Crawford Burner. The rate measured here is not 100% accurate but for reference purpose to enhance the burn rate of particular propellant. The burn rate measured here may be 5-15% lesser than the actual burn rate measured in the rocket because it is hard to simulate the actual burning environment in the combustion as in the rocket, As the high temperature condition in strand burning and the complete solid grain burning is different and the temperature matters the burn rate of the propellant.

Details of the Crawford Strand Burner
Model & Make: Indigenously made by BIT, Mesra, India

Micro Pulverizer is a high speed hammers and screen mill, which accomplishes size reduction by mechanically impacting process material. The method of size reduction is characterized by relative high energy and short residence time, minimizing heat build-up during the milling process. Micro pulverizer consists of a rotor assembly fitted with hammers and operates generally at high speeds. A cover fitted with a liner, a retaining screen at the point of mill discharge and a feed screw mechanism whereby the ungrounded material is uniformly fed to the grinding chamber.

The grinding action in the micro pulverizer is the impact between rapid moving hammers and particles themselves.

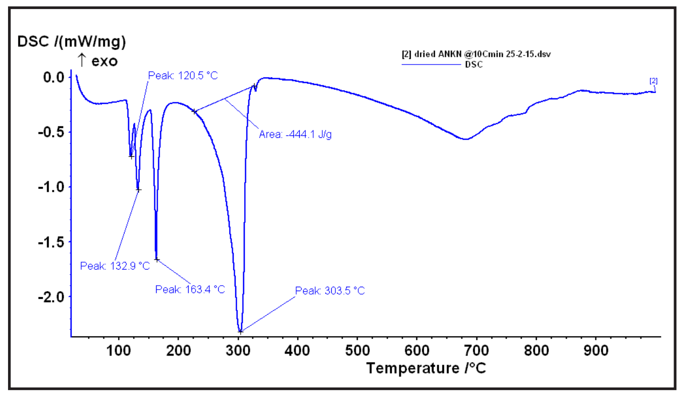
The energy of the moving hammers dissipates itself into the particles by virtue of their inertia thus causing size reduction.

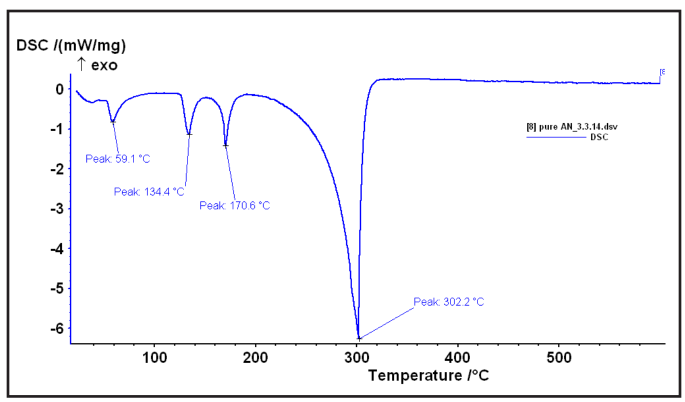


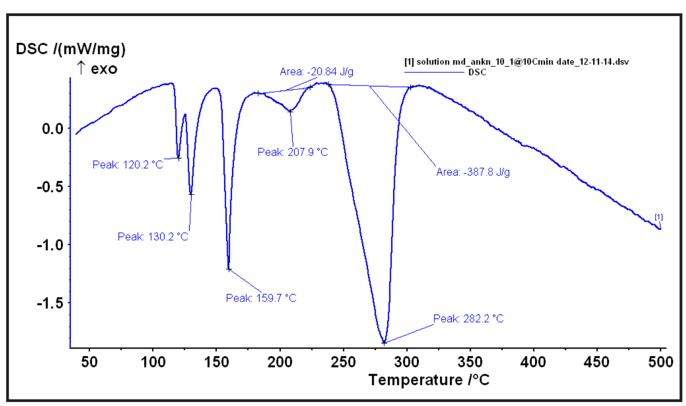
Sieve Shakers agitate a stacked series of test sieves to separate materials by size over progressively finer mesh sizes. The proper sieve shaker saves considerable time and effort, and yields superior accuracy, consistency, and repeatability compared to manual sieve shaking methods for particle sizing. It makes easy to collect various sizes in microns for bi-modals, Tri- modals or more. The different particle sizes can be collected in series. This is not only used in these size ranges but can be possible for larger particle sizes to based on requirement and application.

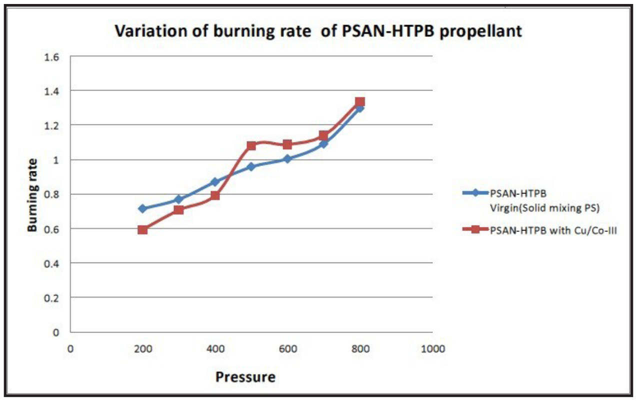
III. Results and Discussion

PSAN-HTPB based solid propellant can get the substitute for AP-HTPB based propellant as per the requirement of present scenario. As the Phase stabilization of AN makes the AN as suitable oxidizer and the another disadvantage of AN is low performance which is overcome by mixed metal oxide catalyst. Present investigation finds that the mixed metal oxide catalysts of higher molar ratios enhances the burn rate by letting the faster decomposition of the PSAN-HTPB based solid propellant. If again the higher molar ratio of Cu-Co catalyst synthesized then again we can get more faster decomposition of PSAN-HTPB based solid propellant.









In this present investigation the Cu-Co catalysts were synthesized in different molar ratio. And the different propellant samples catalyzed and non catalyzed also with propellant with different time periods, were tested for burn rate. The propellants used in the present study consisted of 80% PSAN and 75% PSAN. The other propellant ingredients were fuel binder, plasticizer, curing agent and catalyst in a proper weight ratio.

A. DSC of Oxidizer

In Differential Scanning Calorimetry, the instantaneous temperature of a sample is compared with that treated AN. Different graphs shows the peaks for heat absorption of Oxidizer at different condition like dried AN, Pure AN, fresh PSAN and stored PSAN at different temperature. It is noticed that melting temperature of treated AN has shifted. It has been observed that, there are shifting in onset temperature of the peaks in the stored PSAN clears that it may be due to moisture. It is also noticed that among two types of phase stabilization process the solid mixing was quite effective as the PSAN obtain by solid mixing has higher rate of decomposition.

B. Burn Rate Studies

Attempt has been made to study the burn rate in strand burner. The same was done at different pressure ranging from 200psi to 800 psi. The propellant samples were burnt at strand burner to get the time taken to complete the strand and by that time the rate of burning was calculated. As the nitrogen gas has inert atmospheric condition so nitrogen gas was used to pressurize the fire vessel, Which was able to sustain at different pressure ranges and temperature.

Table IV presents the burning rate of all PSAN-HTPB (catalyzed and un-catalyzed) at different pressures ranging from 200-800 psi. Present research clears that the lower molar ratio of Cu-Co catalyst either do not effect or degrade the decomposition of the PSAN-HTPB based solid propellant. The result of burning of different propellant samples at different pressure are shown in the table. From the basic concept increasing the pressure increasing the burn here also it satisfies, Also it was noticed that the catalyzed propellant has higher burn rate then the virgin propellant.

Table III: Phase Change of Ammonium Nitrate at Different Temperature

Systems	Temperature (^oC)	States	Volume changes (%)
-	>169.6	Liquid	-
I	125.2 to 169.6	Cubic	+2.1
II	84.2 to 125.2	Tetragonal	-1.3
III	32.3 to 84.2	α - rhombic	+3.6
IV	-16.8 to 32.3	β - rhombic	-2.9
V	-16.8	Tetragonal	-

Table IV: Burn Rate of Propellant Samples

Si.No	Pressure (psi)	PSAN-HTPB Virgin (Solid mixing)	PSAN-HTPB Virgin	PSAN-HTPB80/20 Virgin	PSAN-HTPB With M/R-0.5 Catalyst	PSAN-HTPB With M/R-1Catalyst	PSAN-HTPB With M/R-2Catalyst
1	200	0.714	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	0.593
2	300	0.768	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	0.707
3	400	0.869	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	0.791
4	500	0.957	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	1.077
5	600	1.003	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	1.086
6	700	1.090	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	1.138
7	800	1.297	Didn't sustain	Didn't sustain	Didn't sustain	Didn't sustain	1.335

IV. Conclusions

Present investigation helps us to come up with some conclusion in the decomposition properties of PSAN, AN and catalyzed and non catalyzed PSAN-HTPB based solid propellants.

1. From the phase stabilization of AN, potassium nitrate is the effective chemical for making PSAN for making AN as suitable oxidizer for propellant processing.
2. From phase stabilization of AN point of view the purpose it was done was achieved that there was negligible change in the dimension of PSAN-HTPB based propellant.
3. It was noticed that addition catalyst with higher molar ratio alone boosts up the burning rate of the propellant. Also the burning rate increases with increase in pressure. The same rise in burning rate occurred in virgin propellant with solid mixed PSAN.
4. The propellant with 2% catalysts with 2 molar ratio was more effective with pressure variation upto 800psi but above 400psi as shown in graph, where as with other catalysts propellant didn't burn.
5. Phase stabilization effect of AN, Propellant processing, synthesizing of mixed metal oxide catalysts and their study by burning rate and thermal analysis have been done to explain the results obtained in the present work is quite effective to enhance the burning rate of PSAN-HTPB based solid propellant.
6. Attempt was made to make the AN based solid propellant a worth as AP based propellant, somehow the drawback of AN based propellant was resolved but the rate of burning was not up to the level to replace AP but if burning rate is enhanced then we can get an eco friendly solid propellant.
7. From the above research among two types of phase stabilization process, solid mixing was effective in point of particle decomposition.

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