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A method to determine total moisture content of Propellant Oxidizer-- Ammonium perchlorate (coarse and fine grade)

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ABSTRACT

Ammonium perchlorate(AP) is a major ingredient of solid propellant, plays a vital role (oxidizer) in its formulation and presence of moisture can have disastrous in the final product, so it's important to find out the moisture level of the identified batch to be used for the process. Most of the cases the results are 0.02-0.03% which is surface moisture in both AP coarse and fine using Methanol, specially dried grade alone as solvent. An attempt was made to find out the total moisture content using Methanol-N, N-dimethyl formamide (DMF) solvent combination and Methoxy ethanol as solvent medium in KF titration. In this account, we have carried out analysis for the total moisture of few batches of AP and the results are reported here.

Keywords: ammonium perchlorate, DMF, moisture content

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INTRODUCTION

Ammonium perchlorate is the workhorse oxidizer used in propellant [1] processing all over the world in the last 3-4 decades as it satisfies most of the requirements of a good oxidizer. Its greatest advantage is the immense experience and vast information gathered for propellant formulation over the last several decades. After manufacture, it undergone several in process and then classified to different particle size fractions, blended, packed in drums for further use. Invention of chemical rockets is one of the landmarks in the history of space science for human exploration. Modern composite [2,3] solid propellant consists of mainly Ammonium perchlorate (AP) as the inorganic oxidizer, aluminum powder (Al) as the metallic fuel and hydroxyterminated polybutadiene(HTPB) as the polymeric fuel binder.

A typical HTPB propellant formulation is as follows:

HTPB: 10.0 %, Plasticizer: 3.0%, Aluminum: 18.0%, AP: 67.7% Ballistic modifier: 0.3%, Chain extender/Cross linker: 0.1%, Antioxidant: 0.1%, Curing agent: 0.80%.

Propellants are structural components of a rocket motor and hence they should have good physical and mechanical properties to withstand the stresses and strains imposed on it during the various stages of its development, handling, storage, transportation, ignition, firing and flight. The processability, ballistic, mechanical and interfacial properties of composite propellants are affected by not only on particle size, shape, concentration but also on moisture (humid) level of AP Crystals. If moisture content in AP crystals exceed certain limit (0.1%) which causes problem in processability and affects mechanical property strongly11, 12, shown in Fig. 1

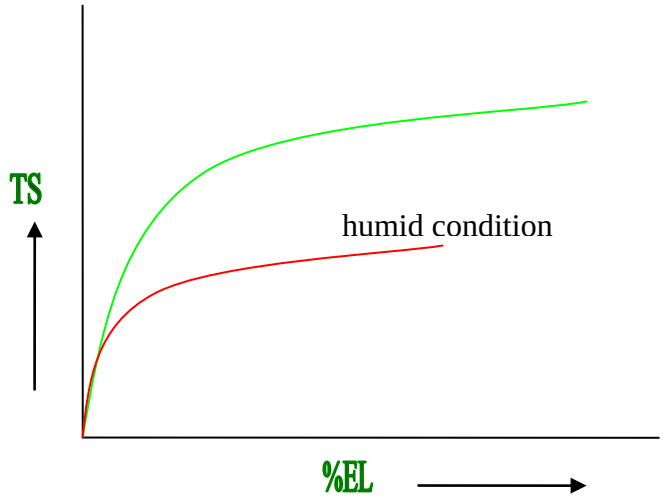

Fig. 1 Effect of moisture on mechanical properties of propellant

Ammonium perchlorate has a tendency to form cake by absorbing moisture and this is overcome by drying the material in rotary vacuum dryer.

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Hence, the most crucial parameter to be tested is moisture level check up before its use in process so that the materials do not exceed the permissible limit, thereby not causing any complexity in processing. As moisture level is very stringent to be use for propellant processing, hence it will be more appropriate to look into total moisture instead of surface moisture.

MATERIALS AND METHODS

Experimental

Few batches of Ammonium perchlorate both coarse (source: Ammonumperchlorate experimental Plant, ALUVA) and fine (Source: Solid Propellant Plant, SDSC) were taken for study.

Reagents

Methanol specially dried, Qualigens; 526 Karl Fischer Reagent (Pyridine free), singlesolution, Qualigens; N,N-dimethyl formamide, GR,Merck; Methoxyethanol, synthesis grade, Merck; Distilled water(pH~7,conductivity <10µs.)

Apparatus

Karl Fischer Titrator (Automatic), Make: LABINDIA; Suitable glass jar (five port beaker) with magnetic bar; Analytical balance (Mettler Toledo, XS204, 0.1mg).

Fig. 2 Karl Fischer Titrator and balance

Principle and Procedure

The Karl Fischer titration[5] is a widely used titrimetric method for water determination in various substances. The determination of water is important to check the product quality and to ensure even physical and chemical properties of the product. The original Karl Fischer reagent is a mixture of sulfur dioxide, iodine, imidazole and 2-methoxyetanol.

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The sample containing water (moisture) reacts with KFR in a two-stage process whereby one molecule of iodine disappears for each molecule of water present. The mechanism of the reaction may be represented by the following equations:

$$I_2 + SO_2 + H_2O + 3C_5H_5N \longrightarrow 2C_5H_5NH^+I^- + C_5H_5N^+SO_2O^-$$

$$C_5H_5N^+SO_2O^- + CH_3OH \longrightarrow C_5H_5NHOSO_2OCH_3$$

60ml solvent(4:1 ratio of N,N dimethylformamide+methanol / Methoxyethanol) was taken in glass jar of aqua meter and then neutralized by addition of KFR; wait for 30minutes till system gets stabilized(no addition of reagent mV25-30); KFR was then standardized with addition of 10mg water, wt and titre value was recorded. The method was repeated till concurrent results are obtained.

$$\text{Strength of KFR} = \frac{W}{TVs} \text{ mg/ml}$$

Specimen samples were tested in the same way after loading appropriate method and results were recorded.

RESULTS AND DISCUSSION

Sample	Batch No/GB No	Moisture (%)	Average data	Solvent used
AP Coarse	110384/2	0.061;0.063	0.06	DMF+Methanol
	110381/1	0.054; 0.052	0.06	
	110356/1	0.059; 0.056	0.06	
	110356/3	0.058; 0.057	0.06	
	110382/1	0.055; 0.056	0.06	
	110383/2	0.060; 0.055	0.06	
	110384/4	0.059; 0.061	0.06	
AP Fine	528	0.015; 0.017	0.02	
	529	0.016; 0.016	0.02	
	530	0.016; 0.016	0.02	
AP Coarse	110384/2	0.087; 0.088	0.09	Methoxyethanol
	110381/1	0.082; 0.079	0.08	
	110356/1	0.076; 0.083	0.08	
	110356/3	0.077; 0.078	0.08	
	110382/1	0.086; 0.092	0.09	
	110383/2	0.088; 0.085	0.09	
	110384/4	0.080; 0.081	0.08	
AP Fine	528	0.031;0.029	0.03	
	529	0.028; 0.030	0.03	
	530	0.029; 0.028	0.03	

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Some observations

It took 7-9 minutes for standardization of KFR in 60 ml solvent (4:1 ratio of DMF+Methanol); Strength > 5.5mg/ml.

1g sample took < 3 minutes for titration

As AP added into titration port, e m f reached to 400-450 mV and then decreases to 30 mV at the vicinity of end point.

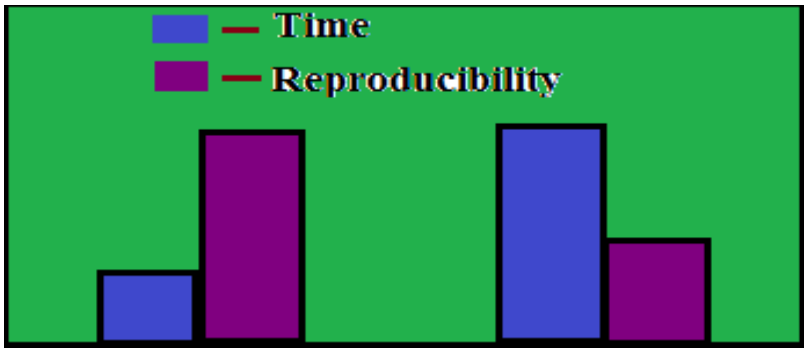
15 g sample i.e. seven different batch of AP can be tested in the same titration port

The data obtained with binary solvent used in the study and as well as with methoxyethanol are repeatable but former solvent combination gave the reproducible data as when compared with true value.

The used methanol esterifies the sulfur dioxide, present in the KFR and imidazole base neutralize the acid (HI) produced in the reaction.

Moisture content of AP fine is low as because mostly water is removed in the process of grinding and cannot be removed completely by drying.

Table of contents Graphic



Binary solvent (DMF + Methanol) **Single solvent (Methoxy ethanol/ Methanol)**

Karl Fisher Titration: Moisture determination of propellant oxidizer - Ammonium percholorate

Conclusion

The binary solvent (4:1 ratio of DMF+Methanol) is a very good combination in KF titration for determining total moisture of Ammonium perchlorate.

This method will save time; frequent change of titration port can be avoided whereas in case of only dried methanol max. 4g AP for 60 ml solvent can be titrated and then again have to replace the five port vessel for further analysis. This is the limitation for determination of total moisture with dried methanol only. DMF does not react with KFR components, only helps to dissolve AP quickly (<60sec, stirring speed 4), It generates repeatable& reproducible data.

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Acronyms: AP-- Ammonium perchlorate; KFR--Karl Fisher Reagent; DMF--Dimethyl formamide; HTPB -- Hydroxylterminated polybutadiene

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