REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
December 2014	Briefing Charts	December 2014- December 2014

4. TITLE AND SUBTITLE

Peculiar Traits of Coarse AP

5a. CONTRACT NUMBER In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER N/A

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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AFRL/RQRP
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8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive.
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

AFRL-RQ-ED-VG-2014-283

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES

Briefing Charts presented at JANNAF, Albuquerque, NM, 8-11 Dec 2014. PA#14519.

14. ABSTRACT

Through various environments a factor influencing AP chemical activity is the propensity of coarse AP to produce porosity formation within its crystals. Porosity formation in coarse AP seems similar although at differing rates due to pressure and temperature influences in both isolated crystals and solid propellant combustions. Consolidated coarse AP crystals appear to be chemically unstable so that pure consolidated crystals cannot be made. Natural and accumulated trace impurities are responsible for observed porosity formation. In combustion environments kinetic action rates for coarse AP can be altered by materials on crystal surfaces and within the crystal bodies. Since orthorhombic crystal AP reaction rates are much faster in combustion environments than cubic crystal AP, orthorhombic phase AP is a primary actor during combustions. At very high pressures AP self combustion exhibits differential recession rates depending on whether surface regression is normal or transverse to the principal axis of its orthorhombic crystal structure. This behavior might be described as biaxial burning. Coarse AP oxidizer has observable chemical interactions that have not been observed for fine AP oxidizer during thermal decomposition and combustion environments. Coarse AP oxidizer has widely different chemical kinetic reaction rates between low and high heat fluxes. Widely different reaction rates are also observed between low and high pressure confinements. In solid propellants coarse AP promotes dark zone combustion, low burn rate pressure exponent, ease of burn rate adjustment, burn rate pressure exponent slope break, and slow cookoff violence.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Claude Merrill
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NO *(include area code)*
Unclassified	Unclassified	Unclassified	SAR	31	661-275-5169

Peculiar Traits of Coarse AP

C. E. Merrill

AFRL/RQRP, Edwards Rocket Site, CA

Objectives

Global view of AP large crystal reactivity

AP in decompositions, self-combustion, & propellants

Coarse AP seems an individual chemical

Coarse AP combustions differ from fine and porous AP

Orthorhombic phase is most reactive

It's all about the gremlins in coarse AP

Microscopic active centers origin

Bircumshaw and Newman

Active center traits

Raevskii, Manelis, Boldyrev, Khairetdinov

Orthorhombic AP crystal burning

Thom L. Boggs

AP Combustions and Active Centers

Coarse AP in reduced smoke propellant

Richard M. Miller

Exponent shifts

Slow cookoff

Erosive burning

Dan Meyer

Active centers in coarse AP

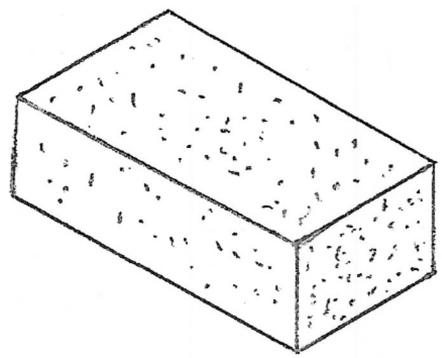
Bircumshaw, Newman

Active centers are sources of AP decomposition gases

AP low temperature decomposition (LTD)

Most unstable AP particles ~100 to 200 μ size

Impure AP has shorter induction periods



Coarse AP active center traits

Raevskii, Manelis

Grow to maximum size of ~2μ

Have non-uniform distribution

Active site numbers multiplied by impurities

Density of pores estimated as being up to $10^6/cm^2$

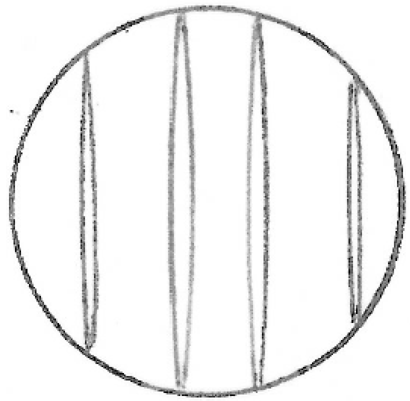
Coarse AP active center traits 2

Raevskii, Manelis

Holes produced were called elipsoids of revolution

Active centers are sub-surface by 3 μ or more

Active center internal pressures are ~20 atmospheres



Coarse AP active center traits 3

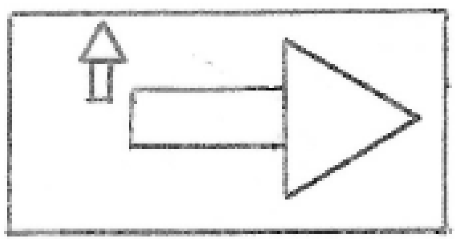
Raevskii, etal

Active sites in coarse AP move in multiple directions

Smaller centers called "germs" coalesce up to maximum size of 2 μ

Movement quicker along major orthorhombic axis, E_a = 31 kcal

Transverse movement, E_a = 33 kcal



Active center chemistry

Khairetdinov and Boldyrev

Active sites contain chlorate ion and AP decomposition products

Chlorate content increases LTD rates; shortens induction periods

Gassing activation for high purity AP, E_a = 70 kcal

Activation for impure AP (~99%), E_a = 50 kcal

Active center chemistry 2

Khairetdinov and Boldyrev

AP crystal impurities greatly multiply active centers

Coarse AP cannot be made completely pure

No AP LTD with 5 micron AP

Active center chemistry 3

Boldyrev

Perchlorate ions are nonrotating in orthorhombic AP

***Chlorate ion movement cannot push aside perchlorate ions**

***Chlorate ions can migrate by oxygen atom swapping with adjacent perchlorate ions**

AP Self Combustion

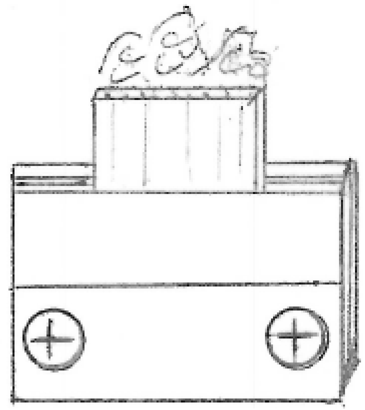
Thom L. Boggs

Cleaved platelets of AP crystals burned from 300 to 6200 psi

Copper vise mount heat absorption provided flame quenching

At low pressures AP recession was uniform with bubbling

AP cubic phase participation was minimal during burning



AP Self Combustion 2

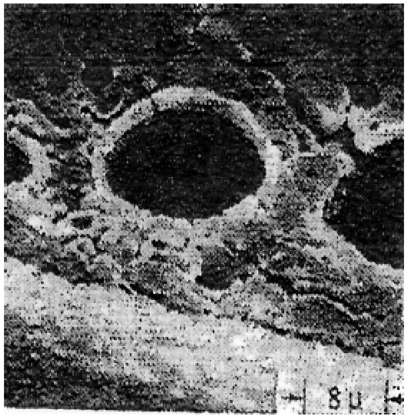
Thom L. Boggs

Identified 4 pressure zones based upon exponent behavior

Up to 800 psi burning showed agitated, frothing material

Up to 2000 psi a few large craters were observed

Froth disappeared as pressures were raised toward 2000 psi



AP Self Combustion 3

Thom L. Boggs

Parallel ridges and valley surfaces seen at 1000 to 1500 psi

Isolated AP vertical needle pockets at 1500 and 1800 psi

Negative exponents, bouncing flamlets between 2000 to 4000 psi

Extremely irregular AP surface regression

Hightower and Price

AP Self Combustion 4

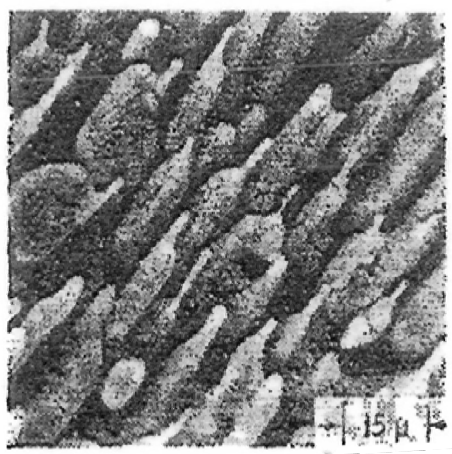
Thom L. Boggs

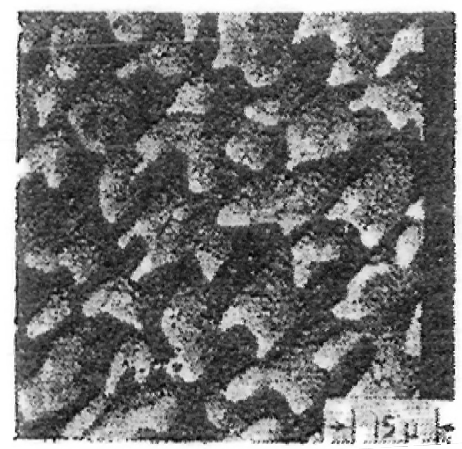
Above 4000 psi AP regressed uniformly

Quenched AP surface had irregular AP needles

***AP needles seemed from partial tubelike, curved surfaces**

Boggs



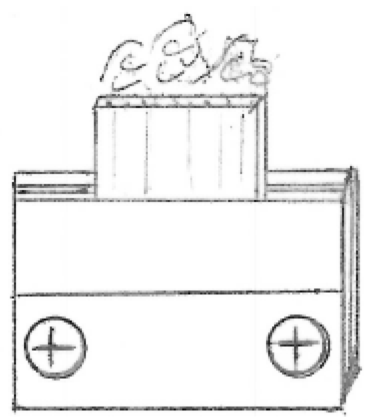


AP Burn Discussion

Was Boggs' bubbling from AP mist supported by vertical gas jetlets from active centers?

Did Boggs burn a few samples at 1000 to 2000 psi with orthorhombic main axis normal to regressing surface?

How can AP needles be formed? Bidirectional recession?



Combustion bomb trials

Richard M. Miller

Reduced smoke HTPB propellant, 200/2 microns

Several millisecond time delay before coarse AP ejection

***Coarse AP particle flame retardancy**

Combustion bomb trials 2

AP phase change may enable coarse particle breakage

Fractured coarse AP ejection agrees with dark zone

Time delay before coarse AP ejection may cause low exponent

Porous AP in solid propellant

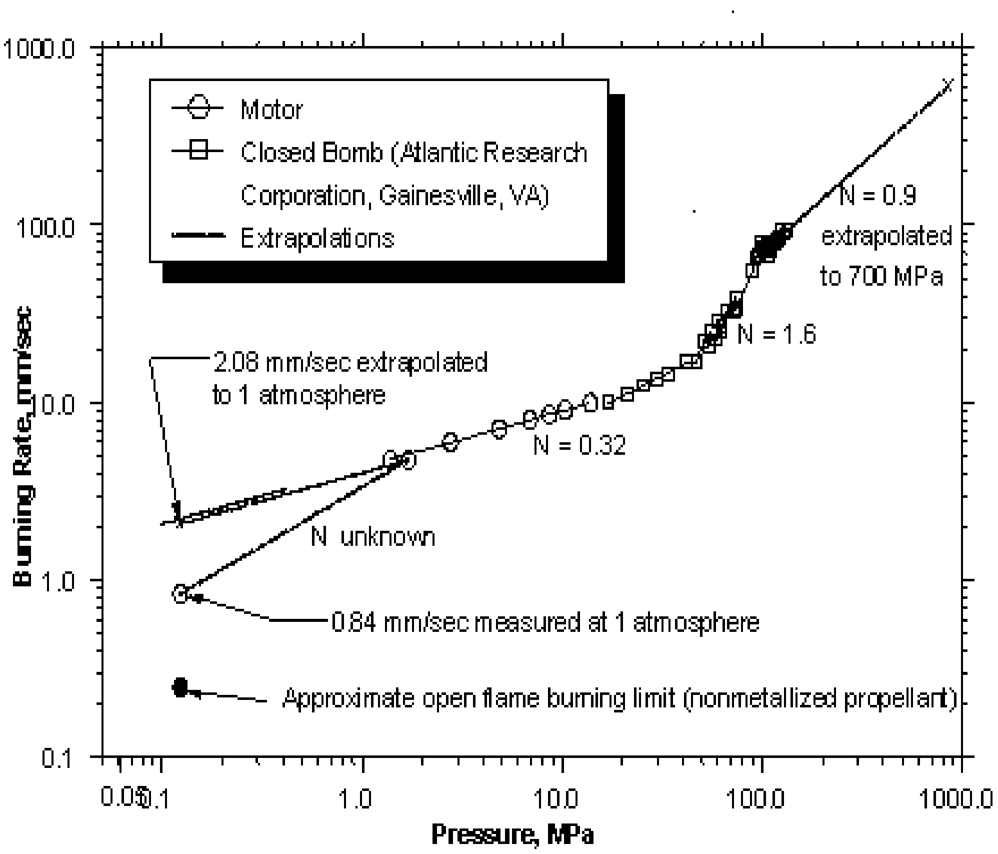
Edwin L. Lista, China Lake

Demonstrated 3.5 ips @ 2000

Burn rate pressure exponents were 0.6

Low densities and erratic burn rates not suitable for systems

Coarse AP propellant exponent slope break



Coarse AP propellant exponent slope break 2

Slope break thresholds inversely related to AP particle size

With 90 micron coarse AP no slope break observed to 60k psi

Pressure exponent threshold shifted marginally as 200 micron AP content reduced to 5%

Ready gains in burn rate by using smaller coarse oxidizer

AP LTD drive combustion slope breaks

Propellant slope break behavior similar to Boggs' data above 4000 psi

Minimization of induction period may transfer fire through coarse AP faster than normal binder regression

Coarse AP LTD gives higher burn w/pressure

Increasing proportion of abruptly triggered coarse AP particles continues to increase burn rate

AP LTD process became saturated at about 12,500 psi

Motor slow cookoffs with coarse AP oxidizer

Slow heating rate provides high temperature duration

AP decomposition gases and porosity provide void volumes

Organic components can provide AP-organic molecular association

Coarse AP active sites influence erosive burning

High purity coarse AP LTD has activation energy = 70 kcal

99% purity coarse AP LTD has activation energy = 50 kcal

Low purity AP should provide faster propellant erosion rates

Dan Meyer has data about AP purity and erosion rates

Summary, coarse AP active centers

Coarse AP never 100% pure

Crystalline AP contains small active centers

Active centers move by directional preference

Center movements may be oxygen atom swapping

Summary, coarse AP active centers 2

When initiated, active centers cause ellipsoid pores

Pore emissions may have levitated AP powder

Activation energies for pore emissions vary

Hi pressure AP needle residues indicate bidirectional burns

Summary, coarse AP active centers 3

Subsurface active centers may cause induction periods

Induction periods seen in coarse AP ejections

Coarse AP ejections may be primary combustion mode

AP ejections support dark zones

Summary, coarse AP active centers 4

Ejection delays may promote low exponents

Exponent slope break due to minimal induction period?

Loss of AP crystal structure suggests slow cookoff violence

Low purity AP should enhance propellant erosive burning