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Alternate Propellant Program Phase I Final Report

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PREFACE

This final report describes the work done to develop candidate alternate propellants for the Shuttle Booster Solid Rocket Motor. This work was done by the Solid Propulsion and Environmental Systems Section, Control and Energy Conversion Division, of the Jet Propulsion Laboratory for the NASA Marshall Space Flight Center, Huntsville, Alabama.

DEFINITION OF SYMBOLS

AD	ammonium dichromate
AFRPL	Air Force Rocket Propulsion Laboratory
A_e	exit area
Al	aluminum
Al_2O_3	aluminum oxide
Alros	Alrosperse
AN	ammonium nitrate
AP	ammonium perchlorate
BATES	Ballistic Test and Evaluation System
C*	characteristic exhaust velocity
CU-0202 P	copper chromite catalyst (trade name of Harshaw Chemical Co.)
D_e	exit diameter
DOA	dioctyl adipate
DSC	differential scanning calorimeter
D_t	throat diameter
ESD	electrostatic discharge
ETS	Edwards Test Station
DTBH	2,5 di-tertiary butyl hydroquinone
e_b	elongation at break, %
e_m	elongation at maximum stress
ϵ	expansion ratio
F	thrust
$\bar{F}$	average thrust
F_eF_3	ferric fluoride
Fe_2O_3	iron oxide
FEM	fluid energy mill

HCl	hydrogen chloride
HMX	cyclotetramethylene tetranitramine
HTPB	hydroxy-terminated polybutadiene
IDP	isodecyl pelargonate
IPDI	isophorone diisocyanate
I_{sp}^{o}	specific impulse, sea level optimum, P_c = 690 N/cm^2 (1000 psia)
I_{sp} ms	measured specific impulse
I_t	total impulse
KP	potassium perchlorate
K_N	ratio of propellant burn area to throat area
kP	kilopoise (1 kP = 100 N-s/m^2)
Mg	magnesium
μm	microns
MSFC	Marshall Space Flight Center
n	pressure exponent
NASA	National Aeronautics and Space Administration
NOS	Naval Ordnance Station (Indian Head, Md.)
P_a	ambient pressure
PBAN	polybutadiene acrylic acid acrylonitrile terpolymer
P_e	exit pressure
P_c	chamber pressure
$\bar{P}_c$	average chamber pressure
PPG-1225	polypropylene glycol
Protech 2002	CSD proprietary metal-deactivating antioxidant (trade name)
r	burning rate
R-18	hydroxy-terminated polyester
R-45M	hydroxy-terminated polybutadiene

S_b	tensile strength at break
SL opt	sea level optimum
S_m	maximum tensile strength
SRM	solid rocket motor
t_a	action time
t_b	web burn time
t_{EWAT}	time at end of web action time
TMETN	1,1,1-trimethylolethane trinitrate
RAM-225	silicone oil in solvent (release agent)
UOP-36	N-phenyl-N'-cyclohexyl-P-phenylene diamine
UV	ultraviolet
$\dot{W}$	weight flow rate
W_p	Propellant weight
Zr	Zirconium
ρ	density

ABSTRACT

This report documents the work done by the Caltech-Jet Propulsion Laboratory of NASA for the Marshall Space Flight Center of NASA on a Shuttle Alternate Propellant Program. The work was done as a Phase I follow-on effort to a previous Phase 0 feasibility study. The program was designed to investigate three candidate propellant systems for the Shuttle Booster Solid Rocket Motor (SRM), which would eliminate, or greatly reduce, the amount of HCl produced in the exhaust of the Shuttle SRM. Ammonium nitrate was selected for consideration as the main oxidizer, with ammonium perchlorate and the nitramine, cyclo-tetramethylene-tetranitramine (HMX), as secondary oxidizers. The amount of ammonium perchlorate used was limited to an amount which would produce an exhaust containing no more than 3% HCl.

Development work was carried out on three basic candidate propellant systems: (1) a mixed oxidizer of ammonium nitrate and ammonium perchlorate (2) a mixed oxidizer consisting of ammonium nitrate and HMX, and (3) a mixed oxidizer consisting of ammonium nitrate, ammonium perchlorate, and HMX. All three systems contained 15% aluminum powder and had a total solids loading of 88%. A urethane binder based on a hydroxy-terminated polybutadiene cured with a diisocyanate was selected as the binder system.

The first and third propellant systems outlined above were developed to the point of successful scale-up and loading of 113-kg (250-lb) batch mixes and successful test firing of 4.5-kg (10-lb) test motors and 32-kg (70-lb) BATES motors. The second propellant system, the AN/HMX oxidizer system, received only very limited development due to a cut-back in both the funds and schedule time initially planned for this program. All three propellants had satisfactory processing characteristics, however, at the 88% solids loading.

The first and third propellant systems (the AN/AP and the AN/HMX/AP oxidizer systems) were both also subjected to hazard testing and were demonstrated to conform to Class 2 hazard classification with HMX levels up to 17 wt % in the HMX-containing propellant. The second oxidizer combination system (the AN/HMX) was not characterized as to hazards classification for the reasons mentioned earlier.

The utilization of the low-HCl-producing alternate propellant was planned to be in combination with the current baseline PBAN propellant in a dual propellant design. Therefore, mutual compatibility between the two propellants was essential. In order to lessen the severity of the burning rate requirement for the alternate propellant it was decided to decrease the burning rate specification for the PBAN baseline propellant to 0.81 cm/s (0.32 in./s) at 690 N/cm^2 (1000 psia). A modified baseline PBAN propellant formulation was therefore developed to conform to the lower burning rate specification. It should be pointed out here that this modified baseline propellant system applies only to the dual propellant grain design and does not relate in any way to the specifications of the present system being developed for the current Shuttle SRM. The ballistic properties of the modified baseline PBAN propellant were demonstrated in several 4.5-kg (10-lb) motor firings.

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SECTION I

INTRODUCTION

This report presents results from the JPL study to investigate the feasibility of developing an acceptable alternate propellant system for the Shuttle solid rocket motor (SRM) boosters based on the non-chlorine containing oxidizer ammonium nitrate (AN). The following basic criteria for this Phase 0 feasibility study were established by the NASA-MSFC.

(1) A five-month feasibility study would be undertaken.

(2) Any candidate propellants must conform to a hazards classification of Class 2 as determined by card gap tests.

(3) The propellant exhaust must not contain more than 3% HCl. Zero HCl was to be the goal.

Following the above guidelines the JPL began a Phase Zero five-month feasibility program in September of 1974 (Ref. 1). JPL was directed by MSFC to investigate four basic propellant systems mutually agreed upon by MSFC and JPL. These four basic propellant systems were the following:

(1) AN/20% Al/binder

(2) AN/10% Al/binder

(3) AN/5% AP/20% Al/binder

(4) AN/5% AP/10% Al/binder

Toward the end of the Phase 0 program, the above four basic propellants had been developed to a point of scale-up of each formulation to 113-kg (250-lb) batch mixes, loading and test firing of 2.27-kg (5-lb) test motors followed by 32-kg (70-lb) BATES motor tests. Program results at this point had demonstrated that:

(1) Good processability of an 88% solids loaded ammonium nitrate propellant was possible. (Previous to this work the maximum solids achieved with ammonium nitrate systems was approximately 80%.)

(2) A few percent (5 to 10) of ammonium perchlorate as a co-oxidizer in the ammonium nitrate systems was essential to satisfactory aluminum combustion.

(3) An aluminum content of 20% in the ammonium nitrate system was considerably above optimum for maximum delivered specific impulse.

With these results serving as new guidelines, a fifth formulation was developed and evaluated in BATES motor tests. This propellant formulation was an 88% solids formulation of the following composition: 63% AN/10% AP/15% Al/12% HTPB binder.

The main conclusion drawn from the results of this five-month feasibility study was that with the necessary time and funds, the development of an alternate propellant system for the Shuttle SRM, based largely on ammonium nitrate as the oxidizer, was feasible. The fifth propellant described above was selected as a baseline candidate system and served as the basis for establishing the goals and criteria for a Phase I follow-on effort to this feasibility study.

The concept for the utilization of the alternate propellant was a dual propellant solid rocket motor. The Shuttle Solid Rocket Motor would be manufactured containing the alternate low-HCl propellant first as an outer layer of propellant followed by an inner layer of the current PBAN propellant modified to the new burning rate requirement. During a Shuttle vehicle launch, the baseline PBAN propellant would burn for the first phase of Shuttle Booster operation. At an altitude of approximately 19.81 km (65,000 ft) the PBAN propellant would be expended and the burning transitioned into the low-HCl (less than 3% by weight of the exhaust products) alternate propellant. The feasibility of a satisfactory transition from a propellant with an all-ammonium perchlorate oxidizer to one consisting primarily of ammonium nitrate oxidizer was also demonstrated during the Phase 0 program by successfully manufacturing and test firing a dual propellant BATES motor charge.

SECTION II

SUMMARY

This summary is a general over-view of the Alternate Propellant Program. A more detailed summary of each respective area of effort is included in the main body of this report. The primary objective of the program was to develop a candidate alternate propellant for the Shuttle SRM boosters which would eliminate, or minimize, the HCl in the exhaust from the solid propellant boosters during operations above 19.81-km (65,000-ft) altitude. A set of program constraints was defined to serve as guidelines for the Phase I program effort. Among the constraints was the requirements of a Class 2 hazards classification for any candidate propellant. The detailed constraints have been outlined in the foregoing pages. Along with these program guidelines, specific goals were established that were as follows:

(1) Propellant burning rate = 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia)

(2) Propellant pressure exponent of the burning rate $\leq$ 0.42

(3) Vacuum delivered specific impulse $\geq$ 2402 N-s/kg (245 s) at an expansion ratio of 7.16

(4) Matched burning rates of the alternate propellant and the baseline PBAN propellant system at 400 N/cm^2 (580 psia)

(5) HCl content of the propellant exhaust $\leq$ 3%

Goal (4) also introduced the requirement of modifying the burning rate of the existing Shuttle baseline propellant to meet a burning rate requirement consistent with the foregoing goals for the alternate propellant. The burning rate requirement for the modified Shuttle baseline propellant, PBAN propellant; was established to be 0.81 cm/s (0.32 in./s) at 690 N/cm^2 (1000 psia) chamber pressure.

Three basic propellant systems were defined as candidate systems to be developed within these constraints and guidelines. The three systems were:

(1) An AN/AP/Al/HTPB binder system

(2) An AN/HMX/Al/HTPB binder system

(3) An AN/HMX/AP/Al/HTPB binder system

Based on the results from the Phase 0 program that preceded this Phase I program, it was established that the aluminum content would be held constant at 15 wt % in all formulations. Also the AP content of the No. 1 and No. 3 system was to be 10%. A status summary of each of the three alternate propellant systems and the modified PBAN Shuttle baseline propellant follows.

A. SYSTEM NO. 1: AN/AP/Al/HTPB

This propellant system contains 10% ammonium perchlorate (AP) and 15% aluminum powder. The development has progressed through the static testing of 32-kg (70-lb) propellant charges in the BATES motor, static testing being limited to sea level conditions. A vacuum delivered I_{sp} at an expansion ratio ϵ of 7.0, corrected from the sea level data, of 2281 N-s/kg (232.6 s) has been demonstrated. This measured value of I_{sp} is equivalent to 88.8% of the theoretical value at the test conditions. A burning rate at 690 N/cm^2 (1000 psia) of 0.546 cm/s (0.215 in./s) with a pressure exponent of the burning rate of 0.278 has also been demonstrated with BATES motor firings. As can be seen, the I_{sp} and burning rate goals have not been attained, whereas the pressure exponent goal has been exceeded by a considerable margin. It is doubtful at this point whether the I_{sp} or the burning rate goals can be achieved with this basic system within the present program constraints. One way of achieving the ballistic goals would be to increase the AP content of this propellant. To do so, however, would increase the HCl content of the exhaust above that of the current exhaust constraint of not more than 3 wt % of HCl.

In order to meet the specific impulse and burning rate goals a propellant formulation containing 20 wt % of AP was developed and tested first in 4.5-kg (10-lb) motors followed by two 32-kg (70-lb) BATES motor firings. The specific impulse goal of 2402 N-s/kg (245 s) was attained with this propellant. The burning rate at 690 N/cm^2 (1000 psia) exceeded the 0.89-cm/s (0.35-in./s) goal. A burning rate of 0.97 cm/s (0.38 in./s) was measured. The pressure exponent measure was 0.48, which is higher than the goal. However, it is believed that this pressure exponent can be reduced. The HCl content in the exhaust, at an expansion ratio of 7.16, is calculated to be 6 wt %. This 6% HCl still represents an 80% reduction in the HCl content from that of the baseline PBAN propellant system. The hazards classification of the AN/AP/Al/HTPB system is Class 2.

B. SYSTEM NO. 2: AN/HMX/Al/HTPB

This system contains 15% aluminum also, but no AP. Due to a cutback in projected program funds, however, the decision was made to discontinue the development of this system. This decision was made very early in the development phase of this propellant, and therefore no useful ballistic data is available at this time.

C. SYSTEM NO. 3: AN/HMX/AP/Al/HTPB

Of the three alternate propellant systems initially planned for development, this system is the best candidate, to date, for meeting all the program goals. Theoretical calculations showed that the maximum specific impulse for this propellant system was in the range of 17.0 to 17.5% HMX (Table 3-2). Therefore, this system with three levels of HMX was developed, scaled up to 113-kg (250-lb) mixes, and loaded and test fired in 4.5-kg (10-lb) test motors followed by 32-kg (70-lb)

BATES motor firing. Of the three levels of HMX evaluated in motor firing, the highest I_{sp} was measured with the formulation containing 15 wt % HMX, showing that the experimental optimum HMX level is somewhat less than 17 wt % for this system. The 15% and 17 wt % HMX formulations were demonstrated to be Class 2, whereas the 17.5 wt % HMX propellant was borderline Class 7.

Preliminary results from Crawford Bomb burning rates showed a burning rate of 0.950 cm/s (0.374 in./s) at 690 N/cm^2 (1000 psia) for the 17 wt % HMX formulation. Time did not permit verifying this burning rate in motor tests prior to committing to the scale-up and loading of the 32-kg (70-lb) BATES motors. However, indications were that the 0.89-cm/s (0.35-in./s) burning rate would be achieved in motor tests with 3% ballistic modifier in the formulation -- a cutback from the 4% in the other two HMX formulations. In the interest of time, a reduction in the ballistic modifier (a mixed burning rate catalyst) of 1% was made in the scale-up propellant batch from which the BATES motors were loaded. Unfortunately, this was too large a reduction in modifier and test results from firing the BATES motors showed a burning rate of 0.81 cm/s (0.32 in./s) for the 17 wt % HMX formulation (ANH-33).

The formulations of the five candidate alternate propellants and the modified PBAN baseline propellant are shown in Table 2-1. Table 2-2 lists the theoretical ballistic properties of the six propellants, and also the HCl and Al_2O_3 (particulates) contents. Table 2-3 summarizes the measured performance values as determined by BATES motor firings. The test firings were conducted under sea level conditions with nozzle expansion ratios of 7.16. The measured sea level values were then corrected to vacuum values by the following equation:

$$I_{sp} \text{ vac ms} = I_{sp} \text{ act ms} + \frac{P_e A_e}{\dot{W}}$$

D. SYSTEM NO. 4: MODIFIED PBAN BASELINE

The work statement of this Alternate Propellant Program also called for modifying the current Shuttle baseline propellant to meet a new burning-rate requirement of 0.81 cm/s (0.32 in./s) at 690 N/cm^2 (1000 psia) while not changing the major ballistic properties, such as I_{sp}, of the system. This effort has been completed and the 0.81-cm/s (0.32-in./s) burning rate met and demonstrated in motor firings. The desired modification was accomplished by removing the iron oxide burning-rate catalysts (Fe_2O_3) and adjusting the particle size blend of the oxidizer. The burning-rate equation for this modified baseline is $r = 0.0668\ P_c^{0.228}$.

A detailed discussion of the three candiate alternate propellant systems as well as the total program effort follows.

Table 2-1. Shuttle SRM Alternate Propellant Candidates, Phase I

Ingredients	TP-H1148[a]	AN-25	AN-71	ANH-12	ANH-33	ANH-18
% Solids	86	88	88	88	88	88
% AN	--	59.00	51.00	44.00	43.00	41.50
% AP	69.60	10.00	20.00	10.00	10.00	10.00
% HMX (Class E)	--	--	--	15.00	17.00	17.50
% Al	16.00	15.00	15.00	15.00	15.00	15.00
% Fe_2O_3	0.40[b]	--	--	--	--	--
% AD	--	2.00	--	2.00	1.00	2.00
% CU-0202 P	--	2.00	2.00	2.00	2.00	2.00
% Binder						
HTPB[c]	--	12.00	12.00	12.00	12.00	12.00
PBAN[d]	14.00	--	--	--	--	--

[a]Current Shuttle baseline propellant; also to be adjusted

[b]To be adjusted

[c]Cured with a diisocyanate (IPDI)

[d]Cured with an epoxy (Der-331)

Table 2-2. Theoretical Performance of Shuttle SRM Alternate Propellant Candidates, Phase I

Parameter	TP-H1148	AN-25	AN-71	ANH-12	ANH-33	ANH-18
T_f, K	3471	2695	2845	2748	2765	2756
T_e, K	2327	1563	1678	1570	1575	1571
C*, m/s (ft/s)	1371 (5155)	1481 (4860)	1508 (4949)	1505 (4937)	1513 (4965)	1509 (4950)
I_{sp}^o, N-s/kg (s)	2572.3 (262.3)	2420.3 (246.8)	2462.4 (251.1)	2450.7 (249.9)	2463.4 (251.2)	2455.6 (250.4)
I_{sp}, vac (at ϵ = 7.16), N-s/kg (s)	2713.5 (276.7)	2568.4 (261.9)	2611.5 (266.3)	2600.7 (265.2)	2614.4 (266.6)	2606.6 (265.8)
% HCl in exhaust	20.9	3.03	6.1	3.03	3.03	3.03
% Al_2O_3 in exhaust	30.2	28.3	28.3	28.3	28.3	28.3

Table 2-3. Measured Performance of Shuttle SRM Alternate Propellant Candidates, Phase I

Ballistic Property	Program Goal	Candidate Propellant Test Results[a]				
		AN-25	AN-71	ANH-12	ANH-33	ANH-18
C*, m/s (ft/s)	-	1432 (4700)	1460 (4791)	1450 (4759)	1431 (4694)	1415 (4643)
C* efficiency, %	-	95.3	97.2	96.2	94.5	94.5
I_{sp} vac at ϵ = 7.16, N-s/kg (s)	≥2403 (245)	2284.9 (233.0)	2402.6 (245.0)	2375.2 (242.2)	2318.3 (236.4)	2317.3 (236.3)
I_{sp} efficiency, %	-	88.8	92.3	91.2	88.7	89.01
Burning rate, cm/s at 690 N/cm^2, (in./s at 1000 psia)	≥0.89 (0.35)	0.53 (0.21)	0.97 (0.38)[b]	0.79 (0.31)	0.81 (0.32)	0.74 (0.29)
Pressure exponent n	≤0.42	0.28	0.48	0.31	0.37	0.31
Hazard classification	2	2	2	2	2	7 (marginal)

[a]Test data from 32-kg (70-lb) BATES motor firings at $P_c \simeq 345$ N/cm^2 (500 psia)

[b]Data point based on 4.5-kg (10-lb) motor firings

SECTION III

PHASE I PROGRAM

A. OBJECTIVE

The program objective of the Phase I program, the results of which are documented in this report, was to develop an alternate propellant for the Space Shuttle Solid Rocket Booster motors which would eliminate, or minimize, the HCl in the exhaust from the motors.

B. PROGRAM CONSTRAINTS

The Phase I development effort was conducted within some very specific constraints. These program constraints were:

(1) Minimize the design impact on the present solid booster.

(2) Eliminate, or minimize ($\leq$ 3%), the HCl release from the booster motors during operation above 19.81-km (65,000-ft) altitude.

(3) Any candidate alternate propellant must conform to a Class 2 hazards classification.

(4) The program was to be conducted within government as a contingency.

(5) The payload, schedule, and cost impact of the Phase I effort on the Shuttle project were to be assessed concurrently.

C. CANDIDATE PROPELLANT SYSTEMS

Three basic candidate propellant systems were selected for consideration in this development program. These propellant systems were:

(1) An AN/AP/Al/HTPB binder system

(2) An AN/HMX/Al/HTPB binder system

(3) An AN/HMX/AP/Al/HTPB binder system

In addition to the above three completely new propellant systems, a modification of the current baseline PBAN propellant was to be made. This modification consisted of adjusting the burning rate of the PBAN propellant to a burning rate of 0.81 cm/s (0.32 in./s) at 690 N/cm^2 (1000 psia). [The baseline PBAN propellant burning rate was approximately 1.07 cm/s (0.42 in./s) at 690 N/cm^2 (1000 psia).]

D. PROGRAM CRITERIA

As has been stated, the criteria for the Phase I program effort was established as a result of the Phase 0 feasibility study. The scope of effort and propellant performance goals thus established were as follows:

(1) Initiate the development of three basic candidate alternate propellant systems

(2) Modify the current Shuttle baseline PBAN propellant to meet the new burning-rate requirement of 0.81 cm/s (0.32 in./s)

(3) The propellant performance goals were:

  (a) Burning rate = 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia)

  (b) Pressure exponent $\leq$ 0.42

  (c) Delivered vacuum specific impulse at an expansion ratio of 7.16 $\geq$ 2403 N-s/kg (245 s)

  (d) The burning rates of the candidate alternate propellants and the Shuttle baseline PBAN propellant should be matched at a pressure of 400 N/cm^2 (580 psia)

  (e) HCl in the exhaust $\leq$ 3%

(4) The development program was to include, in addition to the above:

  (a) Processing studies

  (b) Physical property studies

  (c) Propellant aging studies

  (d) Propellant hazards classification testing

  (e) Propellant performance testing

  (f) Investigation of the compatibility between the alternate propellant and the current baseline PBAN propellant, and between the alternate propellant and the Shuttle Solid Rocket Motor (SRM) insulation

E. PROGRAM APPROACH

The following outline details the general approach taken in the investigation of the various aspects of this program.

1. Theoretical Studies

(1) Maximize delivered specific impulse at 88% solids

(a) Aluminum content

(b) HMX content

(c) High-energy plasticizer content (TMETN)

2. Burning Rate Studies: 0.89 cm/s (0.35 in./s) Goal

(1) Particle size blend of oxidizer

(2) Investigate and compare catalyst type and concentration

(a) Fe_2O_3

(b) Ferrocene

(c) Milori blue

(d) CU-0202 P

(e) Inert plasticizer level (DOA)

(f) High-energy plasticizer (TMETN)

(g) HMX

(h) Zirconium powder

(i) Other

Burning rates to be determined via Crawford Bomb strand burning and 5 x 6 motor tests.

3. Physical Property Studies

(1) Binder stoichiometry

(2) Plasticizer level and type

(a) Free plasticizer

(b) Internal plasticizer (chemically bonded)

(3) Degree of crosslinking

(4) Cure time and temperature

Evaluate properties: Tensile strength

Elongation

Modulus

Hardness

Density

4. Processing Studies

   (1) Process variables

      (a) Mixer speeds

      (b) Mix duration

      (c) Ingredient addition sequence

      (d) Other

5. Compatibility Studies

   (1) PBAN propellant to alternate propellant bond

      (a) As cured surfaces

      (b) Machined surfaces

   (2) Alternate propellant to insulation bond

6. Safety Hazard Tests

   (1) Card gap

   (2) Impact

   (3) Auto-ignition

   (4) Blasting cap

   (5) Friction sensitivity

   (6) Spark sensitivity

7. Aging Studies

(1) Propellant aging-physical properties

(a) Ambient temperature

(2) Propellant-propellant bond

(a) Ambient temperature

8. Motor Testing

(1) 5 x 6 motors - pressure only

(2) BATES motors - pressure and thrust

9. Shuttle Baseline Propellant Modification

Adjust burning rate to 0.81 cm/s (0.32 in./s) at 690 N/cm^2 (1000 psia).

F. NOS PARTICIPATION

The Naval Ordnance Station, Indian Head, Maryland was funded by JPL to participate in certain aspects of the Alternate Propellant Program. This funding of the NOS was a relatively low level of funding and designed to support the program through the investigation of certain very specific tasks. The general areas of the NOS participation were:

(1) Investigation of the solubility of the high-energy plasticizer TMETN in (a) R-45 HTPB polymer, and (b) R-45 HTPB polymer/DOA plasticizer.

(2) Determine the limits of TMETN for a Class 2 propellant in an (a) all AN propellant system, (b) AN/AP system, and (c) AN/AP/HMX system.

(3) Investigation of the limits of HMX for a Class 2, inert binder propellent.

(4) Hazards testing of candidate propellant formulations.

(5) Investigation of HMX and AP particle size effects and ballistic modifier effects on candidate propellant ballistics.

G. PROGRAM SCHEDULE

The Phase I effort of the Shuttle Alternate Propellant Program began April 1, 1975 as an 18-month program. The program schedule was later revised and lengthened to a 30-month program. Much later in the program (April 1976), following several revisions to the program schedule, the planned scope of effort was reduced and the schedule cut to conclude the program on June 30, 1976. This reduction in scope and schedule time became necessary due to a cut in the anticipated program funds.

H. DISCUSSION

Theoretical Studies

As has been discussed in the introduction to this report, the Phase 0 feasibility study (Ref. 1) results established the basis for the Phase I effort. Theoretical studies had been conducted during the Phase 0 work analyzing the effects of solids loading, oxidizer ratios, binder composition, etc., on the thermoballistic properties of the propellant types under consideration. Therefore, at the start of the Phase I program effort, the guidelines for formulating the candidate alternate propellants to be developed were fairly well defined. Consequently the theoretical studies reported here involved only formulations with certain constant parameters, such as 88% total solids, 15% aluminum, and a binder based on plasticized HTPB.

Table 3-1 gives summary tabulations of the primary thermoballistic properties of a number of candidate formulations containing AN, AP, and HMX as oxidizers and the binder plasticized with the high-energy plasticizer TMETN. Iron oxide at the 1% level was included as a burning rate modifier. The relevant Shuttle SRM baseline PBAN propellant properties are also shown in the table for reference. As can be seen, the formulation containing 25% HMX, 10% AP, and 25% TMETN plasticizer in the binder (12% HTPB binder) matches within 4.9 N-s/kg (0.5-s) specific impulse to that of the Shuttle baseline propellant. That formulation, however, would be a Class 7 propellant and, therefore, could not be considered as a candidate.

Table 3-2 shows the effects of varying the AP content, the HMX content, and the type and content of the burning rate modifiers. A combination of ammonium dichromate (AD) and copper chromite (CU-0202 P) was selected as the primary burning rate modifiers for this work. Approximately two seconds of impulse difference is calculated for equal amounts of Fe_2O_3 and mixed AD and CU-0202 P (4% Fe_2O_3 versus 2% AD and 2% CU-0202 P). The calculations also show that for the 88% total solids system with 15% aluminum and 10% ammonium perchlorate (AP) the theoretical optimum amount of HMX for maximum impulse is in the range of 17 to 17.5%. The experimental optimum HMX level for maximum delivered I_{sp}, however, appears to be something less than 17 wt %. This is evidenced by the results from 32-kg (70-lb) BATES motor tests of propellants containing 15.0%, 17.0% and 17.5% HMX. The measured ballistics of these formulations are tabulated in Table 2-3 in the summary section of this report. As will be seen in Table 2-3, the highest measured I_{sp} with an HMX formulation was with Formulation Number ANH-12, which contains 15.0% HMX.

These theoretical calculations referred to above were made using a JPL computer program based on the minimization of free energy to calculate both the equilibrium and frozen flow thermoballistic properties of chemical compositions.

Table 3-1. Theoretical Performance of Propellant Systems With TMETN

Formulation[a]								Ballistics			
Wt % of Ingredients (88% Total Solids)								Theoretical Equilibrium Flow Calculations P_c = 690 N/cm^2 (1000 psia)			
					% Burning Rate Modifier						
AN	AP	HMX	Al	% TMETN in Binder	Fe_2O_3	AD	CU-0202 P	T_c, K	C*, m/s (ft/s)	I_{sp} (Sea Level Optimum), N-s/kg (s)	Vac I_{sp}, (ϵ = 7), N-s/kg (s)
Shuttle PBAN Baseline Propellant[b] (Density 1.7714 g/cm^3, 0.0640 lb/in.^{3})								3515	1578 (5176)	2575.2 (262.6)	2713.6 (276.7)
62	10	0	15	0	1			2825	1503 (4931)	2453.6 (250.2)	2596.6 (264.8)
62	10	0	15	10	1			2902	1511 (4956)	2467.4 (251.6)	2609.5 (266.1)
62	10	0	15	20	1			2977	1518 (4980)	2479.1 (252.8)	2621.3 (267.3)
62	10	0	15	25	1			2982	1521 (4991)	2485.0 (253.4)	2627.2 (267.9)
62	0	10	15	20	1			2910	1526 (5005)	2487.0 (253.6)	2632.1 (268.4)
52	0	20	15	20	1			2973	1546 (5072)	2517.4 (256.7)	2664.5 (271.7)
47	0	25	15	20	1			3005	1557 (5108)	2532.1 (258.2)	2690.0 (274.3)
62	0	10	15	25	1			2916	1529 (5016)	2492.9 (254.2)	2638.0 (269.0)
52	0	20	15	25	1			2978	1550 (5084)	2523.3 (257.3)	2670.4 (272.3)
47	0	25	15	25	1			3010	1561 (5120)	2538.0 (258.8)	2686.0 (273.9)
52	10	10	15	10	1			2964	1532 (5028)	2496.8 (254.6)	2641.9 (269.4)
42	10	20	15	10	1			3027	1554 (5100)	2527.2 (257.7)	2675.3 (272.8)
37	10	25	15	10	1			3058	1565 (5136)	2541.9 (259.2)	2690.9 (274.4)
52	10	10	15	20	1			3039	1540 (5052)	2509.5 (255.9)	2651.9 (270.6)

Table 3-1. Theoretical Performance of Propellant Systems With TMETN (Continuation 1)

Formulation[a]								Ballistics			
Wt % of Ingredients (88% Total Solids)								Theoretical Equilibrium Flow Calculations P_c = 690 N/cm² (1000 psia)			
				% TMETN in Binder	% Burning Rate Modifier						
AN	AP	HMX	Al		Fe_2O_3	AD	CU-0202 P	T_c, K	C*, m/s (ft/s)	I_{sp} (Sea Level Optimum), N-s/kg (s)	Vac I_{sp}, (ϵ = 7), N-s/kg (s)
42	10	20	15	20	1			3102	1562 (5124)	2539.9 (259.0)	2687.0 (274.0)
37	10	25	15	20	1			3134	1573 (5160)	2554.6 (260.5)	2703.7 (275.7)
52	10	10	15	25	1			3044	1543 (5063)	2515.4 (256.5)	2659.6 (271.2)
42	10	20	15	25	1			3107	1565 (5135)	2544.8 (259.5)	2692.9 (274.6)
37	10	25	15	25	1			3138	1576 (5171)	2559.5 (261.0)	2708.6 (276.2)

[a]All formulations contain HTPB binder.

[b]The Shuttle baseline propellant has 16% Al, 86% total solids.

Table 3-2. Theoretical Performance of Propellant Systems Without TMETN

Density, g/cm^3 (lb/in.^{3})	AN	AP	HMX	Al	Propellant Formulation No.	Fe_2O_3	AD	CU-0202 P	T_c, K	C*, m/s (ft/s)	I_{sp} (Sea Level Optimum), N-s/kg (s)	Vac I_{sp} (ϵ = 7), N-s/kg (s)
Formulation[a]									Ballistics			
Wt % of Ingredients (88% Total Solids)						% Burning Rate Modifier			Theoretical Equilibrium Flow Calculations P_c = 690 N/cm^2 (1000 psia)			
1.6634 (0.0601)	62	10	-	15		1			2728	1500 (4920)	2446.8 (249.5)	2595.0 (264.7)
1.6717 (0.0604)	61	10	-	15		2			2716	1490 (4887)	2432.0 (248.0)	2580.1 (263.1)
1.6800 (0.0607)	56	15	-	15		2			2778	1497 (4913)	2443.8 (249.2)	2592.9 (264.4)
1.6911 (0.0611)	51	20	-	15		2			2839	1505 (4938)	2456.6 (250.5)	2604.6 (265.6)
1.6994 (0.0614)	46	25	-	15		2			2904	1512 (4962)	2467.4 (251.6)	2616.4 (266.8)
1.7105 (0.0618)	41	30	-	15		2			2969	1519 (4985)	2479.1 (252.8)	2628.2 (268.0)
1.7188 (0.0621)	36	35	-	15		2			3032	1526 (5007)	2489.9 (253.9)	2439.0 (269.1)
1.6939 (0.0612)	59	10	-	15		4			2692	1469 (4820)	2401.6 (244.9)	2547.8 (259.8)
1.6939 (0.0612)	59	10	-	15	(AN-25)	-	2	2	2695	1481 (4860)	2420.3 (246.8)	2568.4 (261.9)
1.6745 (0.0605)	51	20	-	15		-	2	-	2841	1513 (4965)	2469.3 (251.8)	2619.4 (267.41)

Table 3-2. Theoretical Performance of Propellant Systems Without TMETN (Continuation 1)

Formulation[a]									Ballistics			
Wt % of Ingredients (88% Total Solids)									Theoretical Equilibrium Flow Calculations P_c = 690 N/cm^2 (1000 psia)			
						% Burning Rate Modifier						
Density, g/cm^3 (lb/in.^{3})	AN	AP	HMX	Al	Propellant Formulation No.	Fe_2O_3	AD	CU-0202 P	T_c, K	C*, m/s (ft/s)	I_{sp} (Sea Level Optimum), N-s/kg (s)	Vac I_{sp} (ϵ = 7), N-s/kg (s)
1.6911 (0.0611)	51	20	-	15	(AN-71)	-	-	2	2845	1508 (4949)	2462.4 (251.1)	2611.5 (266.3)
1.6828 (0.0608)	51	20	-	15		-	1	1	2841	1511 (4957)	2465.4 (251.4)	2614.5 (266.6)
1.7160 (0.0620)	44	10	15	15		4			2748	1492 (4895)	2432.0 (248.0)	2581.1 (263.2)
1.7216 (0.0622)	42	10	17	15		4			2756	1495 (4906)	2436.0 (248.4)	2585.0 (263.6)
- (-)	41.5	10	17.5	15		4			2581	1500 (4921)	-	2585.0 (263.6)
- (-)	40	10	19.0	15		4			2794	1495 (4906)	-	2578.2 (262.9)
- (-)	39	10	20.0	15		4			2776	1490 (4888)	-	2572.3 (262.3)
1.7049 (0.0616)	44	10	15	15	(ANH-12)	-	2	2	2748	1504 (4937)	2450.7 (249.9)	2603.7 (265.2)
1.7077 (0.0617)	42	10	17	15		-	2	2	2754	1508 (4947)	2454.6 (250.3)	2605.6 (265.7)
1.7049 (0.0616)	43	10	17	15	(ANH-33)	-	1	2	2765	1513 (4965)	2463.4 (251.2)	2614.5 (266.6)

Table 3-2. Theoretical Performance of Propellant Systems Without TMETN (Continuation 2)

Formulation[a]									Ballistics			
Wt % of Ingredients (88% Total Solids)									Theoretical Equilibrium Flow Calculations P_c = 690 N/cm^2 (1000 psia)			
						% Burning Rate Modifier						
Density, g/cm^3 (lb/in.^{3})	AN	AP	HMX	Al	Propellant Formulation No.	Fe_2O_3	AD	CU-0202 P	T_c, K	C*, m/s (ft/s)	I_{sp} (Sea Level Optimum), N-s/kg (s)	Vac I_{sp} (ϵ = 7), N-s/kg (s)
1.6828 (0.0608)	44	10	17	15		-	2	-	2779	1525 (5005)	2478.1 (252.7)	2631.1 (268.3)
1.6994 (0.0614)	44	10	17	15		-	-	2	2784	1518 (4981)	2472.3 (252.1)	2624.3 (267.6)
1.6911 (0.0611)	44	10	17	15		-	1	1	2778	1522 (4994)	2475.2 (252.4)	2627.2 (267.9)
1.7077 (0.0617)	41.5	10	17.5	15	(ANH-18)	-	2	2	2757	1509 (4950)	2455.6 (250.4)	2606.6 (265.8)

[a]All formulations contain HTPB binder.

2. Exhaust Products

The exhaust compositions of the five candidate propellants listed in Table 2-1 in the report summary and that of the Shuttle PBAN baseline propellant are shown in Table 3-3. The exhaust species are shown as weight percent of the total exhaust; and the exhaust composition is that at the exit plane of the nozzle with an expansion ratio of 7.16, calculated as the equilibrium composition.

3. Combustion and Burning Rate

Two problems, which were anticipated and confirmed as problems early in the Phase 0 program, were low combustion efficiency and low burning rates of the aluminized ammonium nitrate propellant. These subjects are discussed individually in the sections covering the different propellant systems. However, a few brief general comments will be made here.

It was demonstrated during the Phase 0 program by way of 32-kg (70-lb) BATES motor firings that a few percent of AP was essential in the ammonium nitrate propellants in order to effect satisfactory combustion of aluminum. An 88% solids, 15% Al, ammonium nitrate formulation containing no AP was test fired in several 2.27-kg (5-lb) test motors and 32-kg (70-lb) BATES motors. In each case large amounts of aluminum slag remained in the motors after firing. Molten aluminum could be seen being ejected through the nozzle during the test firings. Greatly improved combustion resulted from incorporating 5% AP in the formulation. The incorporation of 10% AP resulted in virtually zero slag remaining in the motor. Therefore, 10% AP was selected as a standard for this Alternate Propellant Program. The three photographs of BATES motor tests (Figs. 3-1 to 3-3 containing 0%, 5% and 10% AP, respectively, in the formulations) show rather dramatically the effect of AP on the combustion. The glowing streaks in the 0 and 5% AP firings (greatly reduced in the 5% AP test, however) are produced by molten aluminum.

A second technique investigated as a combustion improvement technique was the incorporation of zirconium metal powder into the propellant. The basis for this idea was due to the fact that zirconium powder has a much lower ignition temperature than that of aluminum powder, and has a relatively high heat of combustion. The idea was to take advantage of this lower ignition temperature of zirconium powder to facilitate the ignition and burning of the aluminum by igniting, and burning, and thereby supplying sufficient added heat to the system to more effectively ignite and burn the aluminum. This technique, however, did not demonstrate any real improvement in the measured performance, but rather a decrease, and was therefore not investigated beyond the initial BATES motor test firings.

Table 3-3. Propellant Exhaust Composition

Propellant	PBAN	AN-25	AN-71	ANH-12	ANH-33	ANH-18
% Solids	86	88	88	88	88	88
% AP	69.60	10	20	10	10	10
% HMX	-	-	-	15	17	17.5
T_e, K	2327	1563	1678	1570	1575	1571
Mol Wt of Products	27.56	23.09	23.60	22.85	22.75	22.81
Species[a], wt %						
AlCl	0.0094	-	-	-	-	-
AlClO	0.0086	-	-	-	-	-
$AlCl_2$	0.0098	-	-	-	-	-
$AlCl_3$	0.0053	-	-	-	-	-
$AlHO_2$	0.0012	-	-	-	-	-
Cl	0.2961	-	0.0007	-	-	-
CO	23.2928	18.9953	19.1619	25.6367	26.4700	26.7944
CO_2	3.9486	6.1302	5.8679	4.6105	4.4899	4.2773
Cr_2O_3(L)	-	1.0020	0.2090	1.0020	0.6050	1.0020
Cu	-	0.0038	0.0184	0.0044	0.0044	0.0044
CuC(L)	-	1.4543	1.1840	1.4513	1.4475	1.4513
CuCl	-	0.0891	0.4188	0.0901	0.0940	0.0901
Fe	0.0134	-	-	-	-	-
$FeCl_2$	0.5998	0.0621	0.0621	0.0596	0.0583	0.0583
H	0.0191	0.0001	0.0002	0.0001	0.0001	0.0001
H_2	1.8804	2.9663	2.7301	3.2744	3.2941	3.3221
HCl	20.9284	3.0346	6.0149	3.0357	3.0346	3.0357
HO	0.0321	-	0.0002	-	-	-
H_2O	10.1499	15.4534	15.7204	9.5971	9.1721	8.6539
N_2	8.5862	22.1739	20.3436	22.5998	22.8954	22.6707
NH_3	-	0.0005	0.0003	0.0005	0.0005	0.0005
NO	0.0018	0.5780	-	-	-	-
O	0.0005	-	-	-	-	-
O_2	0.0003	-	-	-	-	-
Al_2O_3(C)	30.2097	28.3418	28.3418	28.3418	28.3418	28.3418

[a]Concentrations less than 1×10^{-5} moles/100 g exhaust are omitted.
L = liquid
C = crystalline

Figure 3-1. BATES Motor Firing of 0% AP in AN/AP/Al/HTPB

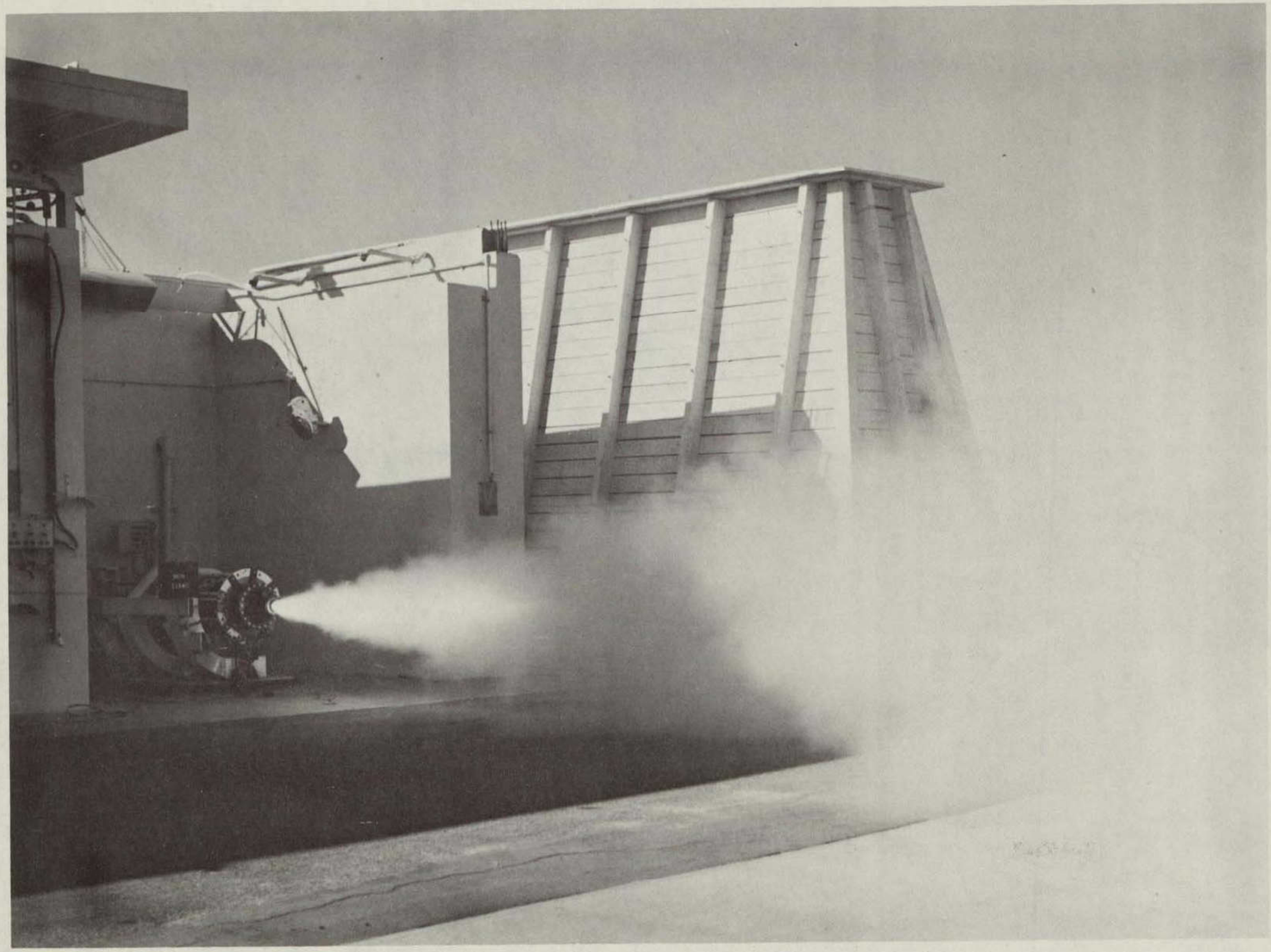

Figure 3-2. BATES Motor Firing of 5% AP in AN/AP/Al/HTPB

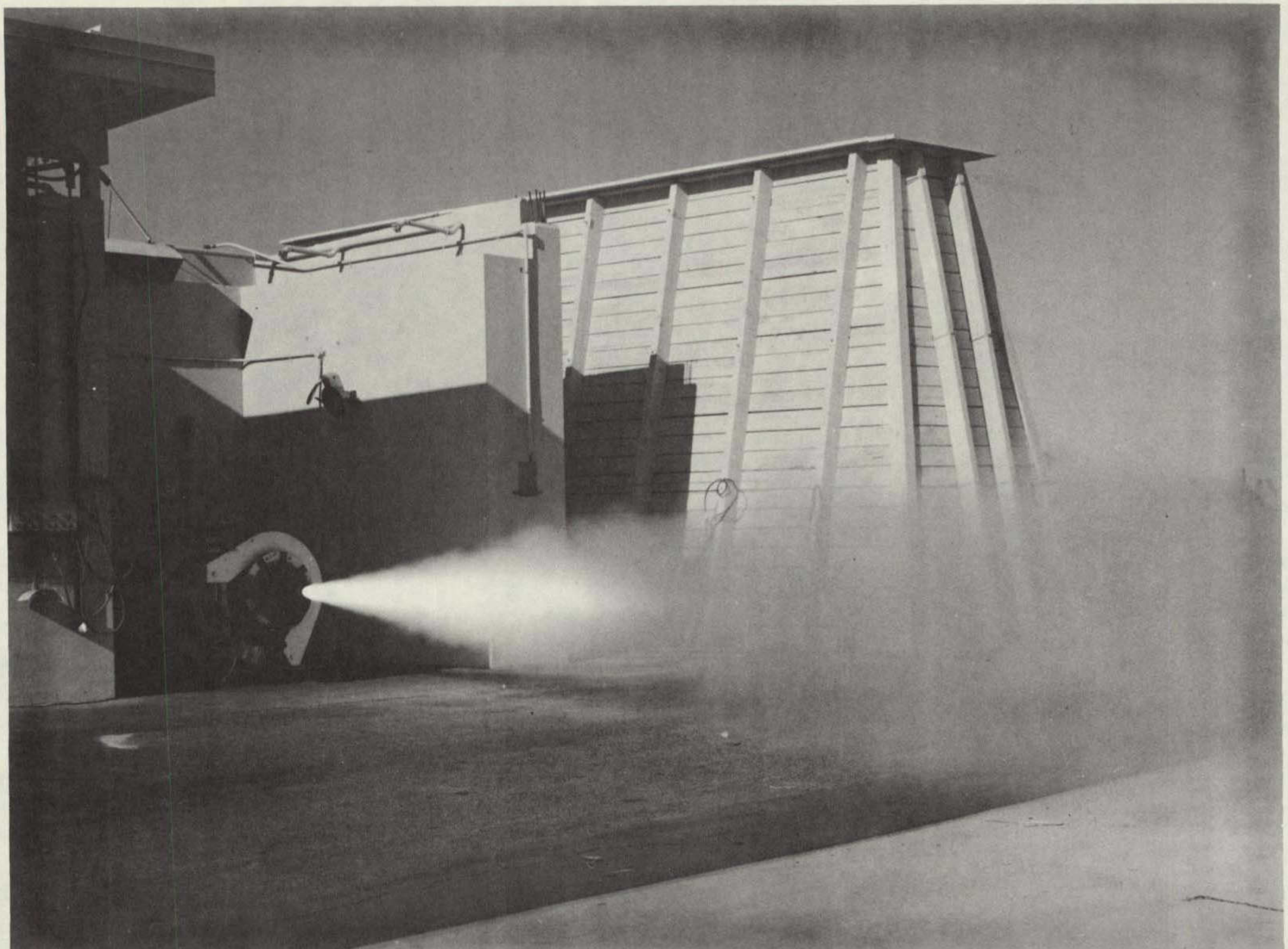

Figure 3-3. BATES Firing of 10% AP in AN/AP/Al/HTPB

A third technique investigated was that of using a chromate-coated aluminum powder in place of the standard aluminum powder. This technique also failed to produce increased combustion efficiency of the aluminum in the propellant.

Specific burning rate subjects are discussed in the discussions of the different propellant systems; however, some general comments will be made here. As can be seen in Table 3-2, the proper selection of a burning rate catalyst must be based on more than burning-rate considerations when a rigorous effort is made to maximize specific impulse. As can be seen, a significant difference is calculated for the theoretical I_{sp} between incorporating the different burning rate modifiers at the same concentration. Also, the modifier used can have a strong effect on the physical properties of the propellant.

4. Physical Properties

This effect of specific ingredients on the physical properties of an ammonium nitrate system arises from the fact that chemical reactions other than the normal curing reactions between the prepolymer and the curing agent enter into the overall curing reactions. In most composite propellant systems the physical properties are determined largely, in addition to binder type and solids loading, by the degree of crosslinking and completeness of reactions with available cure sites. In the ammonium nitrate system, however, it appears that free protons produced in the system react with the double bond in the prepolymer (HTPB) backbone causing crosslinks at these sites. Ammonium dichromate appears to contribute in a greater way to this crosslinking at the double bonds than some of the other burning-rate modifiers investigated. On the other hand, the AD subtracts less from the calculated I_{sp}. The formulating and development of an AN system, therefore, is complicated by these considerations. The physical property problems are greatly complicated. Nonconventional techniques must be found and employed in the physical property considerations in order to develop satisfactory control of adequate physical properties.

5. High-Energy Plasticizer Studies

One of the approaches investigated on the program was use of high-energy plasticizers to achieve higher delivered specific impulse propellants. A review of available nitrate ester plasticizers indicated that TMETN (1,1,1-trimethylolethane trinitrate) was the most promising candidate. This selection was made on the basis of overall considerations of compatibility, performance, cost, and availability. Theoretical performance calculations on some typical propellant formulations with 20 wt % TMETN are shown in Table 3-4.

Propellant development work on this effort was done by NOS (Naval Ordnance Station, Indian Head, Md.). Two basic formulations were investigated, one with no ammonium perchlorate and one with 5 wt % ammonium perchlorate. A polyester (R-18) binder was selected, and initial development work was done at the 82 wt % solids level with 12.00 wt % TMETN. Small

Table 3-4. Theoretical Performance Calculations - 20 Wt % TMETN Formulations

Formulation	1-A	1-B	1-C	1-D
Ammonium nitrate	36.0%	31.0%	41.0%	41.0%
Aluminum	18.0%	18.0%	18.0%	18.0%
R-18	6.0%	6.0%	6.0%	6.0%
HMX	10.0%	10.0%	5.0%	-
TMETN	20.0%	20.0%	20.0%	20.0%
Ammonium perchlorate	10.0%	15.0%	10.0%	15.0%
	100.0%	100.0%	100.0%	100.0%
Density, g/cm^3 (lb/in.^{3})	1.7300 (0.0625)	1.7411 (0.0629)	1.7217 (0.0622)	1.7244 (0.0623)
Flame temperature, K ($^\circ$F)	3434 (5723)	3481 (5806)	3410 (5678)	3430 (5714)
Vacuum specific impulse, N-s/kg (s) ϵ = 7.16; P_c = 483 N/cm^2 (700 psi)	2711.5 (276.5)	2715.5 (276.9)	2698.8 (275.2)	2688.0 (274.1)
Weight percent HCl in exhaust	2.78	4.17	2.78	4.16

mixes were made to check ingredient compatibility and propellant laboratory safety properties. Results of the safety tests are shown in Table 3-5 along with the formulations. These tests indicated that the ingredients were compatible and safety properties were adequate. The two formulations were then scaled up into larger batches and card gap samples were loaded and tested. Both formulations were uncastable so that the card gap samples had to be hand packed. The card gap test results are shown in Table 3-5 and suggest both formulations meet the card gap requirements for Class 2 propellant (< 70 cards). However, these results may be biased to give lower card gap sensitivity because of voids in the samples.

Four additional formulations were then evaluated at the reduced solids level of 74 wt % to improve propellant castability. The polyester (R-18) binder system was used and TMETN level was held constant at 20 wt %. The variations made with these four formulations were variations in the levels of HMX, AP, and AN. All the formulations were castable and card gap samples were prepared and tested on each. The details of the formulations and card gap test results are summarized in Table 3-6. General conclusion from this work was that for this propellant system with 20 wt % TMETN a maximum level of 5 to 10 wt % HMX can be used and meet Class 2 card gap requirements (< 70 cards).

Work with the polyester (R-18) binder system was terminated and shifted to the HTPB (R-45) binder system when the early experimental work indicated that program goals would probably not be achieved with the polyester (R-18). Initial tests by NOS showed the solubility of TMETN (also referred to as MTN) in R-45 at 21°C (70°F) was less than 1 wt %. They then conducted cosolubility studies with other plasticizers. Complete details of these studies are shown in Appendix A. Summary conclusions from this effort are as follows:

(1) R-18 and adiponitrile are not soluble in R-45M.

(2) DOA is more effective as a coplasticizer than TP90B and PPG-1225.

(3) Maximum theoretical performance gains possible by replacement of DOA with TMETN within solubility limits are about 17.6 N-s/kg (1.8-s) impulse and 0.028 g/cm^3 (0.001 lb/in.^{3}) density.

A decision was made to terminate further work with TMETN at this point in the program. Primary reason for the decision was that the small potential performance gains possible with TMETN did not justify the potential risks of compatibility problems with ballistic modifiers, TMETN migration, and aging degradation.

6. Evaluation of Ammonium Nitrates

An evaluation of available ammonium nitrate (AN) types was made to provide a basis for selection of the AN in development of the propellant formulations. Ammonium nitrate is the major oxidizer used in all

Table 3-5. Alternate Propellant Formulations with TMETN (Polyester (R-18) Binder - 82 Wt % Solids)

Formulation No.	NOS SCC-74-69	NOS SCC-74-074
Ingredients, wt %		
R-18 Binder	6.00	6.00
TMETN	12.00	12.00
Aluminum	18.00	18.00
HMX	20.00	10.00
Ammonium perchlorate	-	5.00
Ammonium nitrate	44.00	49.00
	100.00	100.00
Initial card gap tests:		
0 Cards	-	pos
35 Cards	pos	pos
50 Cards	pos	-
70 Cards	neg	neg
Laboratory safety tests:		
Impact, mm (3 consecutive positive values; 5-kg weight)	150, 125, 150, 200	-
Sliding friction, kg (lb) 2.4 m/s (8 ft/s)	≥435 (≥960), ≥435 (≥960), ≥435 (≥960), ≥435 (≥960)	-
Electrostatic discharge, J (5000 V)	≥12.5, ≥12.5, ≥12.5, ≥12.5	-

Table 3-6. Alternate Propellant Formulations With TMETN (Polyester (R-18) Binder - 74 Wt % Solids)

Formulation No.	NOS Mod. I	NOS Mod. II	NOS 1C	NOS 1D
Ingredients, wt %				
R-18 Binder	6.00	6.00	6.00	6.00
TMETN	20.00	20.00	20.00	20.00
Aluminum	18.00	18.00	18.00	18.00
HMX	20.00	20.00	5.00	-
Ammonium perchlorate	-	5.00	10.00	15.00
Ammonium nitrate	36.00	31.00	41.00	41.00
	100.00	100.00	100.00	100.00
No. 8 Blasting Cap Test	neg	neg	-	-
Card Gap Tests:				
35 Cards	-	-	-	pos
40 Cards	-	-	pos	neg (42 cards)
50 Cards	pos	-	pos	neg
60 Cards	-	-	neg	-
65 Cards	pos	-	-	-
70 Cards	-	pos	neg	neg
75 Cards	-	pos	-	-
80 Cards	-	pos	-	-
85 Cards	-	1 pos and 1 neg	-	-
90 Cards	-	2 pos	-	-
100 Cards	pos	1 pos and 1 neg	-	-
112 Cards	pos	-	-	-
120 Cards	pos	neg	-	-
121 Cards	1 pos and 2 neg	-	-	-
123 Cards	neg	-	-	-
125 Cards	neg	-	-	-
150 Cards	neg	-	-	-

three of the basic alternate propellants: AN/AP/Al/HTPB, AN/HMX/Al/HTBP, and AN/HMX/AP/Al/HTPB.

Some of the problems associated with making propellants with AN are:

(1) Low true density of AN (1.725 g/cm^3) which limits solids loading for processable propellants.

(2) Large size and hollowness of unground, as-received prills.

(3) Hygroscopicity of AN and particle agglomeration.

(4) Slow burning rates.

(5) Low specific impulse.

(6) Volumetric changes with crystal phase changes.

The following three types of AN were selected for evaluation:

(1) Gulf Oil special fertilizer grade, uncoated.

(2) U. S. Agri-Chemicals industrial with anti-caking agent.

(3) Monsanto industrial E-2 phase stabilized.

These three were selected because they are generally representative of what is currently available from industry. Table 3-7 compares the as-received properties of the three AN types. Table 3-8 compares some of the processing characteristics of the three AN types.

The Gulf Oil special fertilizer grade, uncoated, has the advantage of having no additives that generally tend to reduce propellant specific impulse. However, this AN has a soft prill that breaks readily and is very hygroscopic. Both the unground and ground materials agglomerate severely even in controlled environments. These difficulties in controlling particle-size distribution with this type AN pose real problems in achieving and reproducing maximum specific impulse and burning rate in processable propellants. Cost of this type AN is higher than the other two types, because it is a specialty product.

The U. S. Agri-Chemicals industrial AN has a 0.43 to 0.77 wt % coating of anticaking agent on the prills. The coating consists of 90% talc and 10% Petro-Ag. It keeps the material free flowing with reasonable protection from moisture. In addition it makes a harder prill which does not break readily. Good control of particle-size distribution is possible with this type of AN. Consequently, processable propellants are achievable with reproducible burning rates and delivered specific impulse.

Table 3-7. Comparison of Ammonium Nitrate Types As-Received Properties

Vendor	Gulf Oil	U.S. Agri-Chemicals, Div. of U.S. Steel Corp.	Monsanto Agricultural Products Co.
Type	Special Fertilizer Grade, Uncoated (No Anticaking Agent)	Industrial (Coated with Anticaking Agent)	Industrial E-2[a]
Appearance	White prills	White, free-flowing spheres (prills)	Pearly white, free-flowing spheres (prills)
Total nitrogen		34.0 wt % min	34.0 wt % min
Approx. assay		97.1 wt % min	97.1 wt % min
Moisture (when manufactured)		0.25 wt % min	0.5 wt % min
Additive	None	0.43 to 0.77 wt % coating agent[b]	0.4 to 0.6 wt % E-2 additive[c]
Screen size (U.S. Sieve Series)		0.0 wt % max retained on No. 6 5.0 wt % max through No. 6, and on a No. 8 94.0 wt % max through No. 8 and on No. 20 1.0 wt % max through No. 20	1.0 wt % max retained on No. 6 10.0 wt % through No. 14
Loose bulk density, g/cm^3 (lb/ft^3)			0.9611 (60)
Prill Density, g/cm^3		1.54	1.61
Approx. cost, ¢/kg (¢/lb)	25.4 (11.5)	15.4 (7.0)[d]	15.7 (7.1)[a]

[a]Phase stabilized.
[b]90% talc and 10% petroleum agent.
[c]MgO according to U.S. Patent 3,030,179.
[d]Bulk costs - carload quantities typically 54,431-kg (60-ton) minimum. Does not include freight or taxes.

Table 3-8. Comparison of Ammonium Nitrate Types Processing Characteristics

	Gulf Oil	U.S. Agri-Chemicals, Div. of U.S. Steel Corp.	Monsanto Agricultural Products Co.
Property	Special Fertilizer Grade, Uncoated (No Anticaking Agent)	Industrial (Coated with Anticaking Agent)	Industrial E-2 (Phase-Stabilized)
Handling characteristics unground	Soft prill, breaks easily. Very hygroscopic and agglomerates severely	Fairly hard prill, does not break readily. Remains free flowing with reasonable protection from moisture	Very hard and dense prill, does not bread readily. Remains free flowing with reasonable protection from moisture
Particle size after tumble drying, unground	104 to 1000 μm ≅480 μm (avg)	840 to 3360 μm ≅2200 μm (avg)	1410 to 3360 μm ≅2000 μm (avg)
Grinding characteristics, particle size after coarse grinding in Raymond hammer mill with 4000-rpm hammer speed, 160-rpm feed speed, 0.32-cm (1/8-in.) screen	-	140 μm (avg)	≅260 μm (avg)

The Monsanto industrial E-2 phase-stabilized AN has 0.4 to 0.6 wt % E-2 additive. This material is MgO, which phase stabilizes the ammonium nitrate according to U. S. Patent 3,030,179 (assigned to Monsanto Company). Figure 3-4 shows the specific volume of Monsanto E-2 AN and of AN that has not been phase stabilized versus temperature. The solid line is for the Monsanto E-2 AN and the dotted line is for the AN that has not been phase stabilized. Note that the volumetric changes associated with Phase III have been eliminated in the phase-stabilized Monsanto E-2 AN. Comparing Monsanto E-2 AN with the other types in Table 3-7 and 3-8, the following conclusions can be made:

(1) Monsanto E-2 AN has a higher prill density than U. S. Agri-Chemicals AN (1.61 g/cm^3 versus 1.54 g/cm^3).

(2) Because Monsanto E-2 is a very hard and dense prill, normal handling and tumble drying does not significantly break prills. Particle-size distribution remains in the range of 1410 to 3360 μm with an average size of about 2000 m.

(3) Coarse grinds of Monsanto E-2 AN have an average particle size of about 280 μm, which is in the size range (200 to 400 μm) for better fit with the other solids.

(4) The Monsanto E-2 AN remains free flowing in both the unground and ground states with reasonable protection from moisture.

(5) Cost of the Monsanto E-2 AN in large bulk quantities is 15.7 {/kg (7.1 {/lb), which is comparable to other AN types which are not phase stabilized.

AN/HMX/AP/Al/HTPB propellant batches have been made with all three of the AN types discussed above. In general results were as follows:

(1) The propellant made with Monsanto E-2 AN had lower end-of-mix viscosities and longer casting lives than the propellant made with the other two types of AN.

(2) Burning rates with the Monsanto E-2 AN were either comparable or slightly faster.

Based on these results Monsanto E-2 AN was selected as the preferred AN type for the following reasons:

(1) It is easily processed with good particle-size control. It remains free flowing in both the unground and ground states with reasonable protection from moisture. The prill does not readily break with normal handling or tumble drying.

(2) It has typically a 5% higher prill density. This lowers propellant volumetric solids loading which improves castability.

(3) This AN can be ground to more optimum size distributions for improved solids packing.

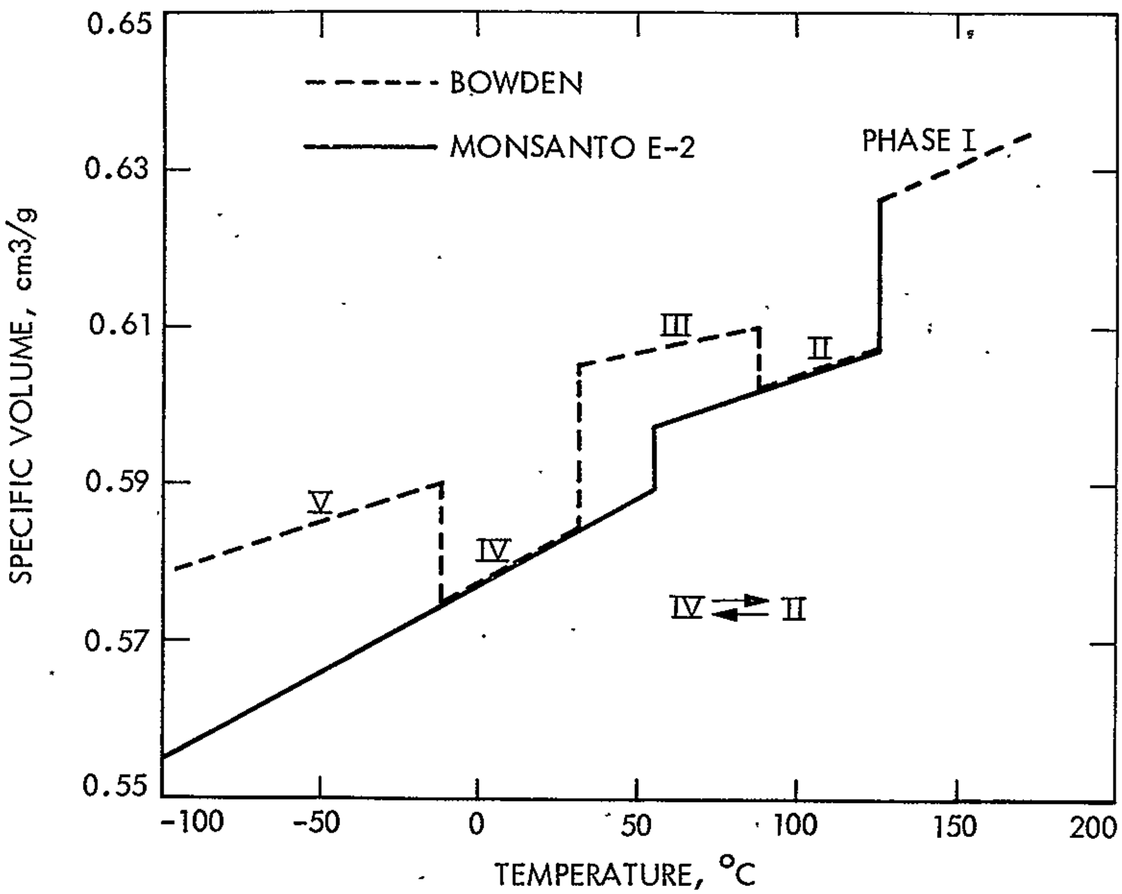

Figure 3-4. Specific Volume of Monsanto E-2 Ammonium Nitrate vs Temperature

(4) It does not have a talc anticaking coating, which appears to accelerate propellant viscosity buildup.

(5) Phase stabilization minimizes volumetric changes with varying temperature due to phase changes.

(6) This AN gives comparable or slightly faster burning rates.

(7) It has a comparable price to other AN types in large bulk quantities.

7. AN/AP/Al/HTPB ($\leq$ 3 Wt % HCl Exhaust)

This section discusses the propellant development work accomplished on the basic AN/AP/Al/HTPB propellant to achieve the defined performance goals within the constraint of $\leq$ 3 wt % HCl in the propellant exhaust. This constraint is met by limiting the AP level in the formulation to $\leq$ 10 wt %.

a. Burning Rate Studies. Initial burning rate studies were made to evaluate different ballistic modifier types and levels with the basic 88 wt % solids AN/AP/Al/HTPB propellant. The selection of the ballistic modifiers was limited to those that were:

(1) Commercially available.

(2) Proved successful for use within rubber base propellants.

(3) Non-migrating.

(4) Reasonably priced.

Ammonium dichromate, $(NH_4)_2Cr_2O_7$, at the 2 wt % level was selected as the primary ballistic modifier for the following reasons:

(1) AN is the major oxidizer.

(2) AD has been used successfully for years with AN propellants.

Other ballistic modifiers were used in conjunction with the AD to enhance burning rate and attempt to achieve the burning rate goal of 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia). Table 3-9 shows the formulations evaluated and the cured strand burning rates obtained.

The propellant formulations were mixed as small (1000 to 1500 g) batches using a 3.8-liter (1-gal) vertical Bramley mixer. The propellant was cast into RAM-225 released molds that formed individual propellant strands and was then cured. After cure the propellant strands were tested in a conventional Crawford Bomb strand burner. A subsequent study, discussed in the section on AN/HMX/AP/Al/HTPB propellant, showed that

Table 3-9. Evaluation of Ballistic Modifier Type and Level, AN/AP/Al/HTPB Propellant

	Formulation, wt %							Crawford Bomb Data[a] r_b, cm/s (in./s)	
Batch No.	Total Solids	AN	AP	Al	AD (7 m)	Other Ballistic Modifier	Oxidizer Blend Coarse/Fine	At 345 N/cm^2 and 21°C (500 psia and 70°F)	At 690 N/cm^2 and 21°C (1000 psia and 70°F)
30	88	60	10	15	2	Fe_2O_3 1%	45/55	0.376 (0.148)	0.538 (0.212)
31		59			2	Fe_2O_3 2%	44.2/55.8	0.300 (0.118)	0.475 (0.187)
55		57			2	Fe_2O_3 4%	42.5/57.5	0.279 (0.110)	0.432 (0.170)
32		60			2	Copper Chromite 1%	45/55	0.462 (0.182)	0.627 (0.247)
33		59			2	Copper Chromite 2%	44.2/55.8	0.564 (0.222)	0.759 (0.299)
49		57			2	Copper Chromite 4%	42.5/57.5	0.472 (0.186)	0.671 (0.264)
34		59			2	Copper Chromite 1% Fe_2O_3 1%	44.2/55.8	0.493 (0.194)	0.737 (0.290) estimated
50		57			2	Copper Chromite 2% Fe_2O_3 2%	42.5/57.5	0.511 (0.201)	0.699 (0.275)
54		57			2	Copper Chromite 2% FeF_3 (unground) 2%	42.5/57.5	0.485 (0.191)	0.648 (0.255)
35		60			2	Milori Blue 1%	45/55	0.399 (0.157)	0.625 (0.246)
56		57			2	Milori Blue 4%	42.5/57.5	0.371 (0.146)	0.528 (0.208)

Table 3-9. Evaluation of Ballistic Modifier Type and Level, AN/AP/Al/HTPB Propellant (Continuation 1)

	Formulation, wt %							Crawford Bomb Data[a] r_b, cm/s (in./s)	
Batch No.	Total Solids	AN	AP	Al	AD (7 m)	Other Ballistic Modifier	Oxidizer Blend Coarse/Fine	At 345 N/cm^2 and 21°C (500 psia and 70°F)	At 690 N/cm^2 and 21°C (1000 psia and 70°F)
36	88	60	10	15	2	Ferrocene 1%	45/55	0.381 (0.150)	0.569 (0.224)
42	↓	60	↓	↓	2	Ferric fluoride (as received) 1%	45/55	0.429 (0.169)	0.594 (0.234)
53	↓	57	↓	↓	2	Ferric fluoride (as received) 4%	42.5/57.5	0.356 (0.140)	0.490 (0.193)
41	↓	60	↓	↓	2	Iron phthalocyanine 1%	45/55	0.358 (0.141)	0.490 (0.193)

[a]Strand burn rates possibly biased by RAM-225 mold release.

the strand burning rates may have been biased to give faster rates by the RAM-225 release agent. However, the burning rate trends and ranking of the ballistic modifiers do not appear to be biased by the RAM-225.

Figure 3-5 shows strand burning rates plotted at 690 N/cm^2 (1000 psia) versus the second ballistic modifier level for the ballistic modifier systems evaluated. General conclusions from the study were as follows:

(1) The ballistic modifier system using 2 wt % ground ammonium dichromate (AD) and 2 wt % copper chromite (CU-0202 P) gave the fastest burn rate.

(2) Increasing the combined level of burning rate modifiers to greater than 4 wt % of the formulation decreased the burn rate.

Although the attritor-ground (1 m) ferric fluoride (FeF_3) gave a faster burning rate than CU-0202 P at the 1 wt % second ballistic modifier level, FeF_3 was not selected because it would have contributed HF in the propellant exhaust. A preliminary selection of the ballistic modifier system was made for subsequent work. The system selected was 2 wt % ground AD and 2 wt % as-received CU-0202 P.

Achievement of the burning rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) had not been accomplished by simple manipulation of the ballistic modifier type and level. Consequently propellant development effort was continued toward this goal along the following approaches:

(1) Finer particle size ballistic modifiers

(2) Finer particle size AN

(3) Greater level of fine AN

(4) Finer particle size AP

(5) Use of potassium perchlorate

Two approaches were evaluated to reduce ballistic modifier particle sizes to sizes smaller than those achievable with a hammer mill. They were dry ball milling and attritor grinding. The dry ball milling approach was unsuccessful with AD and CU-0202 P because they packed into a hard cake. Attritor grinding of AP and FeF_3 to particle sizes smaller than 1 m has been successfully demonstrated within the solid propellant industry. This method uses an attritor mill to grind material suspended in Freon between zircoa beads. Attritor grinds were successfully made with AD and CU-0202 P, and the particle-size reductions accomplished are summarized in Table 3-10.

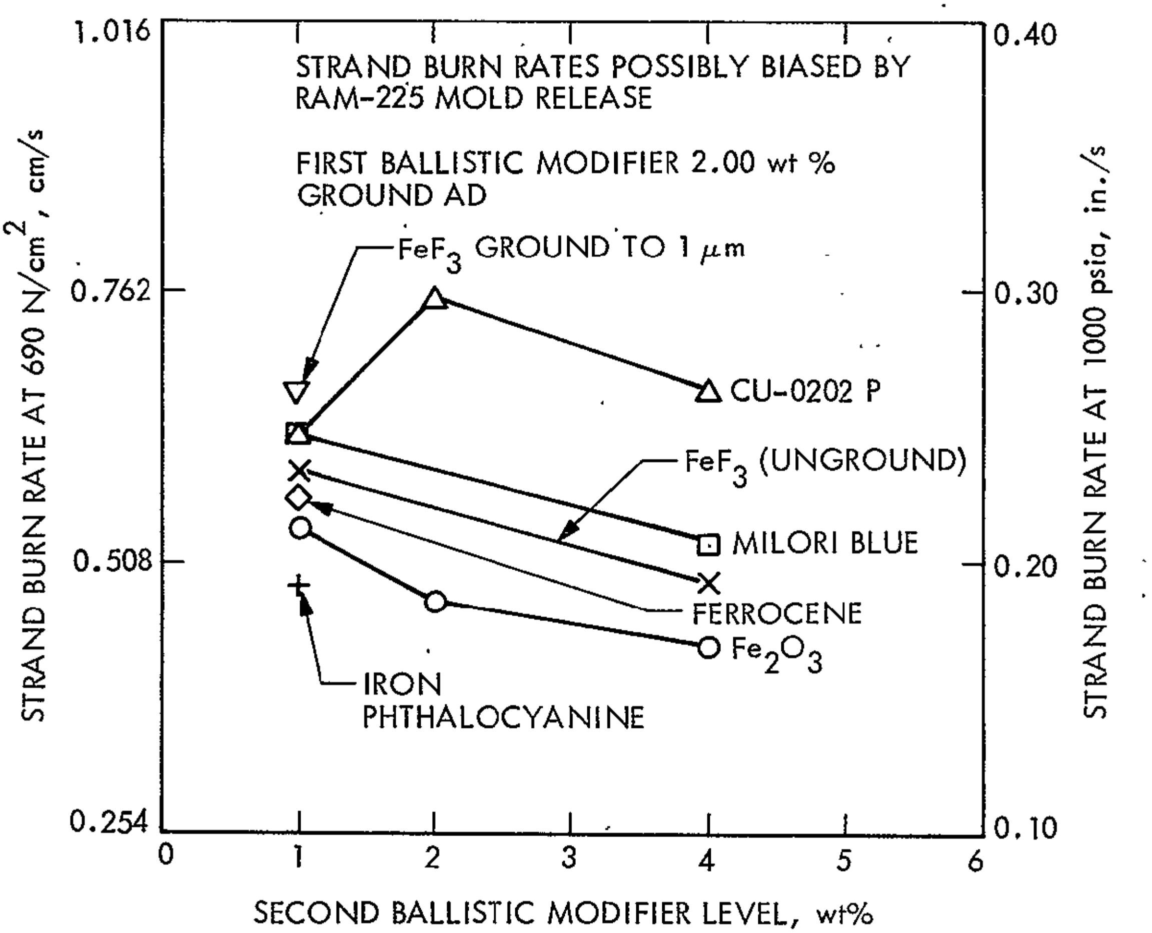

Figure 3-5. Strand Burn Rate vs Second Ballistic Modifier Level, AN/AP/Al/HTPB Propellant

Table 3-10. Particle-Size Reductions of Attritor-Ground AD and CU-0202 P

Material	Screen Analysis, 50 wt % pt, Particle Size, μm	Micromerograph, 50 wt % pt, Particle Size, μm
AD		
As received	≅575	—
Attritor ground (21 h)	—	4.4
CU-0202 P		
As received	—	2.1
Attritor ground (21 h)	—	1.7

Small-scale (1000 to 1500 g) propellant batches were made to evaluate the effects of the smaller ballistic modifier particle sizes on strand burning rates. Results of this study are summarized in Table 3-11. General conclusions from this study are as follows:

(1) In a DOA-plasticized propellant formulation using 1 wt % FeF_3, fine ground AN, and 9-μm AP, reducing the FeF_3 particle size from a coarse as-received to attritor-ground 1 μm material increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.594 to 0.668 cm/s (0.234 to 0.263 in./s) (≅12%).

(2) In an IDP-plasticized propellant formulation using 2 wt % CU-0202 P, coarse ground AN, and 6.3- AP, reducing the AD particle size from 7.2 to 4.4 μm did not significantly change strand burning rate.

(3) In a DOA-plasticized propellant formulation using 2 wt % CU-0202 P, fine ground AN, and 6.3-μm AP, reducing the CU-0202 P particle size from 2.1 to 1.7 μm increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.528 to 0.556 cm/s (0.208 to 0.219 in./s) (≅5%).

(4) In a DOA-plasticized propellant formulation using 2 wt % CU-0202 P, fine ground AN, and 6.3-μm AP, reducing the AD particle size from 7.2 to 4.4 μm increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.528 to 0.556 cm/s (2.208 to 0.218 in./s) (≅5%).

Table 3-11. Evaluation of Ballistic Modifier Particle Size, AN/AP/Al/HTPB Propellant

Batch No.	SB-42	SB-43	SB-103	SB-105	SB-118	SB-122	SB-123
Formulation No.	AN-34	AN-35	AN-65B	AN-65D	AN-25A	AN-25B	AN-25C
Ingredients, wt %							
HTPB binders:							
40% DOA plasticized	12.00	12.00	-	-	12.00	12.00	12.00
40% IDP plasticized	-	-	12.00	12.00	-	-	-
Aluminum, MD 105	15.00	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium dichromate:							
Hammer mill ground, 7.2 μm	2.00	2.00	2.00	-	2.00	2.00	-
Attritor ground, 4.4 μm	-	-	-	2.00	-	-	2.00
Ferric fluoride:							
As received	1.00	-	-	-	-	-	-
Attritor ground, 1 μm	-	1.00	-	-	-	-	-
Copper chromite:							
As received, 2.1 μm	-	-	2.00	2.00	2.00	-	2.00
Attritor ground, 1.7 μm	-	-	-	-	-	2.00	-
Ammonium nitrate:							
Unground Gulf Oil	31.50	31.50	-	-	-	-	-
Unground Monsanto	-	-	30.50	30.50	30.50	30.50	30.50
Fine Ground Gulf Oil	28.50	28.50	-	-	-	-	-
Fine ground Monsanto	-	-	-	-	28.50	28.50	28.50
Coarse ground Monsanto	-	-	28.50	28.50	-	-	-
Ammonium perchlorate:							
Hammer mill ground, 9 μm	10.00	10.00	-	-	-	-	-
FEM ground, 6.3 μm	-	-	10.00	10.00	10.00	10.00	10.00
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 3-11. Evaluation of Ballistic Modifier Particle Size, AN/AP/Al/HTPB Propellant (Continuation 1)

Batch No.	SB-42	SB-43	SB-103	SB-105	SB-118	SB-122	SB-123
Formulation No.	AN-34	AN-35	AN-65B	AN-65D	AN-25A	AN-25B	AN-25C
Strand Burning Rates,[a] at 298 K (77°F), cm/s (in./s)							
At 690 N/cm^2 (100 psia)	0.429 (0.169)	0.465 (0.183)	0.422 (0.166)	0.419 (0.165)	0.424 (0.167)	0.439 (0.173)	0.437 (0.172)
At 345 N/cm^2 (500 psia)	0.594 (0.234)	0.668 (0.263)	0.467 (0.184)	0.475 (0.187)	0.528 (0.208)	0.556 (0.219)	0.554 (0.218)
Strand Pressure Exponent 345 to 690 N/cm^2 (500 to 1000 psia)	0.47	0.53	0.14	0.18	0.30	0.33	0.33

[a]Strand burn rates possibly biased by RAM-225 mold release.

In summary, reduction of the ballistic modifier particle size did not prove to be an effective approach to increasing burning rates for the selected ballistic modifier system.

As discussed earlier, particle-size control of the unground Gulf Oil AN was a problem because of breakage of the prills during drying and handling. A partial approach to this problem was to screen the unground Gulf Oil AN into a selected size range after drying and handling. Small-scale propellant batches (1000 to 1500 g) were made using Gulf Oil AN and strand burn rate tests were performed on these batches to evaluate:

(1) The effect of screened +60 to -32 mesh (250 to 570 μm) AN as coarse fraction on castability and burn rate.

(2) The effect of screened +32 to -16 mesh (570 to 1190 μm) AN as coarse fraction on castability and burn rate.

(3) The effect of varying the fraction of AN as fine ground on castability and burn rate.

The fine ground AN was ground using a hammer mill with the following settings:

9600 rpm hammer speed
80 rpm feed speed
0.033-cm (0.013-in.) screen

Fisher sub-sieve average particle size for this material was typically 20 μm. The fraction of AN as fine ground was limited to less than 55 wt % to keep propellant processable in the small scale batches. (Larger batches typically have better castability.) Table 3-12 and Fig. 3-6 summarize test results. General conclusions from these results were:

(1) All batches had poor relative castability.

(2) Using unscreened unground Gulf Oil AN (broad particle-size distribution with a significant portion of fines) and varying the fraction of AN fine ground from 48.3 to 54.2 wt % increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.505 to 0.577 cm/s (0.199 to 0.227 in./s).

(3) Using screened +60 to -32 mesh AN as coarse fraction reduced strand burning rate at 690 N/cm^2 (1000 psia) from 0.419 to 0.462 cm/s (0.199 to 0.182 in./s).

(4) Using screened +60 to -32 mesh AN as coarse fraction and varying the fraction of AN fine ground from 30.0 to 48.3 wt % increased strand burning rate at 690 N/cm^2 (100 psia) from 0.419 to 0.462 cm/s (0.165 to 0.182 in./s).

(5) Changing the coarse fraction from screened +60 to -32 AN to screened +32 to -16 mesh AN reduced strand burning rate at 690 N/cm^2 (1000 psia) from 0.419 to 0.404 cm/s (0.165 to 0.159 in./s).

Changing the type of ammonium nitrate type from Gulf Oil to Monsanto phase stabilized AN eliminated the problem of prill breakage, but did not improve castability even with IDP plasticizer as shown by Batch SB-101 in Table 3-12. The slower burning rate at 690 N/cm^2 (1000 psia) and lower pressure exponent with Batch SB-101 compared to Batch SB-64 is due to use of IDP as the plasticizer. A small-scale propellant batch, SB-102, was made with a coarse ground Monsanto AN to evaluate the effect of this material on castability and burn rate. The coarse ground was made using a hammer mill with the following setting: 4000 rpm hammer speed, 160 rpm feed speed, and 0.32-cm (1/8-in.) screen.

Screen analysis indicated this coarse ground AN had an average particle size of approximately 280 μm. Propellant castability using this material was excellent, but strand burning rate at 690 N/cm^2 (1000 psia) was reduced from 0.485 to 0.442 cm/s (0.191 to 0.174 in./s), ≅9%. The burning rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) was not achieved by varying AN type, AN particle size, or fraction of AN fine ground.

The effect of replacing hammer mill ground AP by fluid energy mill ground AP on propellant burning rate was evaluated in a series of five small-scale (1000 to 1500 g) batches. Three batches were made using DOA plasticizer and fine ground Gulf AN, and varied AP particle size from 9.0 to 5.5 μm. Two batches were made using IDP plasticizer and coarse ground Monsanto AN, and varied AP particle size from 9.0 to 6.3 μm. Results of this study are shown in Table 3-13 and Fig. 3-7.

Table 3-12. Evaluation of Ammonium Nitrate Particle Size, AN/AP/Al/HTPB Propellant

Batch No.	SB-64	SB-75	SB-48	SB-48A	SB-61	SB-101	SB-102
Formulation No.	AN-25	AN-63	AN-40	AN-40A	AN-53	AN-65	AN-65A
Ingredients, wt %							
HTPB binders:							
40% DOA plasticized	12.00	12.00	12.00	12.00	12.00	-	-
40% IDP plasticized	-	-	-	-	-	12.00	12.00
Ammonium dichromate, hammer mill ground, 6.3 to 7.2 μm	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Copper chromite, as received, 2.1 μm	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Aluminum, MD-105	15.00	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium nitrate:							
Unground Gulf Oil	30.50	27.00	-	-	-	-	-
Screened (+60-32) Gulf Oil	-	-	41.30	-	30.50	-	-
Screened (+32 to -16 mesh) Gulf Oil	-	-	-	41.30	-	-	-
Unground Monsanto	-	-	-	-	-	30.50	30.50
Fine ground Gulf Oil	28.50	32.00	17.70	17.70	28.50	-	-
Fine ground Monsanto	-	-	-	-	-	28.50	-
Coarse ground Monsanto	-	-	-	-	-	-	28.50
Ammonium perchlorate, hammer mill ground, 9 μm	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Fraction of AN fine ground (wt %)	48.3	54.2	30.0	30.0	48.3	48.3	-
Relative Castability	Poor	Poor	Poor	Poor	Poor	Poor	Excellent

Table 3-12. Evaluation of Ammonium Nitrate Particle Size, AN/AP/Al/HTPB Propellant (Continuation 1)

Batch No.	SB-64	SB-75	SB-48	SB-48A	SB-61	SB-101	SB-102
Formulation No.	AN-25	AN-63	AN-40	AN-40A	AN-53	AN-65	AN-65A
Strand Burning Rates,[a] at 298 K (77°F), cm/s (in./s)							
At 345 N/cm^2 (500 psia)	0.366 (0.144)	0.414 (0.163)	0.277 (0.109)	0.284 (0.112)	0.338 (0.133)	0.419 (0.165)	0.351 (0.138)
At 690 N/cm^2 (1000 psia)	0.505 (0.199)	0.577 (0.227)	0.419 (0.165)	0.404 (0.159)	0.462 (0.182)	0.485 (0.191)	0.442 (0.174)
Strand Pressure Exponent 345 to 690 N/cm^2 (500 to 1000 psia)	0.47	0.49	0.60(?)	0.50	0.45	0.22	0.32

[a]Strand burn rates possibly biased by RAM-225 mold release.

These results indicated the following:

(1) Using DOA plasticizer, fine ground Gulf AN, and reducing the AP particle size from 9.0 to 5.5 µm increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.508 to 0.635 cm/s (0.200 to 0.250 in./s).

(2) Using IDP plasticizer, coarse ground Monsanto AN, and reducing the AP particle size from 9.0 to 6.3 µm increased strand burning rate at 690 N/cm^2 (1000 psia) from 0.442 to 0.467 cm/s (0.174 to 0.184 in./s).

(3) Use of the finer (5.5 to 6.3 µm) fluid energy ground AP did not increase pressure exponent.

Maximum burning rate achieved using fluid energy ground AP was 0.635 cm/s at 690 N/cm^2 (0.250 in./s at 1000 psia) compared to the burning rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

Table 3-13. Evaluation of Ammonium Perchlorate Particle Size, AN/AP/Al/HTPB Propellant

Batch No.	SB-62	SB-64	SB-66	SB-102	SB-103
Formulation No.	AN-25	AN-25	AN-56	AN-65A	AN-65B
Ingredients, wt %					
HTPB binders:					
40 wt % DOA plasticized	12.00	12.00	12.00	-	-
40 wt % IDP plasticized	-	-	-	12.00	12.00
Ammonium dichromate, Hammer mill ground, 7 μm	2.00	2.00	2.00	2.00	2.00
Copper chromite, as received, 2.1 μm	2.00	2.00	2.00	2.00	2.00
Aluminum, MD-105	15.00	15.00	15.00	15.00	15.00
Ammonium nitrate:					
Unground Gulf Oil	30.50	30.50	30.50	-	-
Unground Monsanto	-	-	-	30.50	30.50
Fine ground Gulf Oil	28.50	28.50	28.50	-	-
Coarse ground Monsanto	-	-	-	28.50	28.50
Ammonium perchlorate:					
Hammer mill ground, 9 μm	10.00	10.00	-	10.00	-
Fluid energy ground, 5.5 μm	-	-	10.00	-	-
Fluid energy ground, 6.3 μm	-	-	-	-	10.00
Totals	100.00	100.00	100.00	100.00	100.00
Strand Burning Rates,[a] cm/s at 25°C (in./s at 77°F)					
At 345 N/cm² (500 psia)	0.368 (0.145)	0.366 (0.144)	0.457 (0.180)	0.351 (0.138)	0.422 (0.166)
At 690 N/cm² (1000 psia)	0.508 (0.200)	0.505 (0.199)	0.64 (0.25)	0.442 (0.174)	0.467 (0.184)
Strand Pressure Exponent 345 to 690 N/cm² (500 to 1000 psia)	0.49	0.49	0.48	0.32	0.14

[a] Strand burn rates possibly biased by RAM-225 mold release.

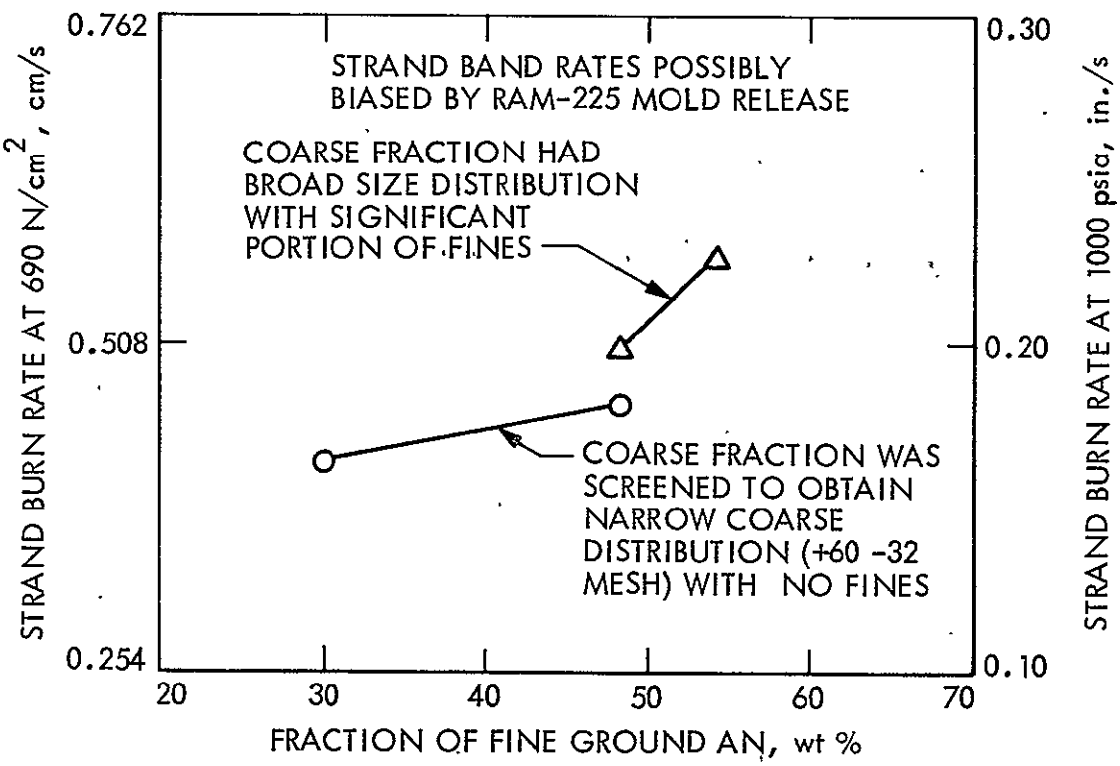

Figure 3-6. Strand Burn Rate vs Fraction AN Fine Grind AN/AP/Al/HTPB Propellant (Gulf AN)

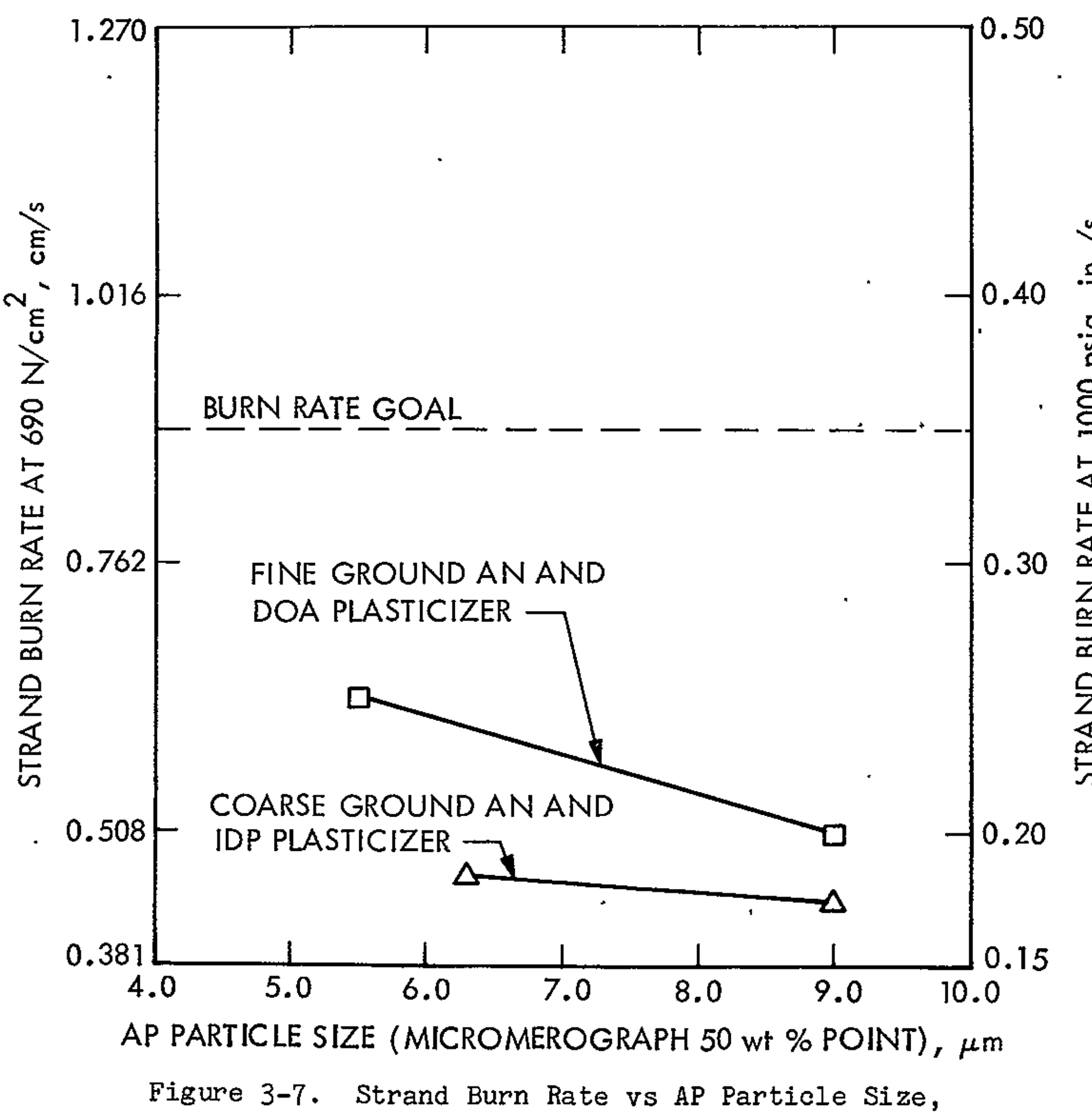

Figure 3-7. Strand Burn Rate vs AP Particle Size, AN/AP/Al/HTPB Propellant

A small-scale propellant batch, SB-65, was made to determine whether the burning rate could be increased significantly by replacing the ground AP by ground potassium perchlorate (KP). Strand burn rate tests were made on this batch and compared to the reference Batch SB-64 as shown in Table 3-14. Strand burning rate at 690 N/cm^2 (1000 psia) was increased from 0.505 to 0.531 cm/s (0.199 to 0.209 in./s), ≅5%, but pressure exponent increased from 0.47 to 0.65. This approach was dropped because of the minimal increase in burning rate at 690 N/cm^2 (1000 psia) and the significant increase in pressure exponent.

b. Combustion Problems. One of the problems in using ammonium nitrate as an oxidizer in solid propellants is the incomplete combustion of aluminum within the motor with subsequent loss of delivered specific impulse. This problem was studied in the Phase 0 effort and partially resolved by modifying the formulations to include 10 wt % AP. Other approaches considered on this program to improve aluminum combustion and performance were:

(1) Use of aluminum and zirconium mixtures. Zirconium has lower ignition temperature than aluminum.

(2) Use of dichromate-coated aluminum powder.

(3) Use of aluminum/magnesium alloys.

(4) Use of plasticizers containing more oxidizer to obtain a more favorable oxidizer/fuel ratio.

Some increases in propellant burning were also considered possible with several of these approaches. Because of limited time and funds, only the first two approaches were evaluated to any extent with the basic AN/AP/Al/HTPB propellant. Results of these studies are covered in the following discussion.

A small-scale propellant batch, SB-104, was made using the dichromate-coated H-5 aluminum to evaluate the effect on strand burning rates. Results of these strand burning rate tests are compared to strand burning rates of reference Batch SB-103 in Table 3-15. The replacement of the uncoated MD-105 aluminum by the dichromate-coated H-5 aluminum reduced strand burning rate at 690 N/cm^2 (1000 psia) from 0.467 to 0.424 cm/s (0.184 to 0.167 in./s), ≅9%. No motors were loaded and tested to evaluate the effects of this dichromate-coated aluminum on delivered specific impulse.

Table 3-14. Evaluation of Potassium Perchlorate, AN/AP/Al/HTPB Propellant

Batch No.	SB-64	SB-65
Formulation No.	AN-25	AN-55
Ingredient, wt %		
HTPB binder, 40 wt % DOA plasticized	12.00	12.00
Aluminum, MD-105	15.00	15.00
Ammonium dichromate, hammer mill ground 7 μm	2.00	2.00
Copper chromite, as received 2.1 μm	2.00	2.00
Ammonium nitrate, unground Gulf Oil	30.50	30.50
Ammonium nitrate, fine grind Gulf Oil	28.50	28.50
Ammonium perchlorate, hammer mill ground 9 μm	10.00	-
Potassium perchlorate, hammer mill ground 30 μm	-	10.00
Total	100.00	100.00
Strand Burning Rates in cm/s at 25°C (in./s at 77°F)		
At 345 N/cm^2 (500 psia)	0.366 (0.144)	0.340 (0.134
At 690 N/cm^2 (1000 psia)	0.505 (0.199)	0.531 (0.209
Strand Pressure Exponent		
345 to 690 N/cm^2 (500 to 1000 psia)	0.49	0.65

Six small-scale propellant batches were made to evaluate the effects of Al/Zr mixtures on propellant castability and strand burning rates. Three batches were made using the ballistic modifier system of 2.00 wt % ground AD and 1.00 wt % Fe_2O_3. The other three batches were made using the ballistic modifier system of 2.00 wt % ground AD and 1.00 wt % CU-0202 P. Zirconium powder level was varied at 0, 2.50, and 5.00 wt % of propellant formulation (0, 1/6, and 1/3 replacement of Al). Results of this study are summarized in Table 3-16 and Fig. 3-8. General conclusions were as follows:

Table 3-15. Evaluation of Dichromate-Coated Aluminum for AN/AP/Al/HTPB Propellant

Batch No.	SB-103	SB-104
Formulation No.	AN-65B	AN-65C
Ingredient, wt %		
HTPB binder, 40 wt % DOA plasticized	12.00	12.00
Aluminum, MD-105 (uncoated)	15.00	-
Aluminum, H-5 (dichromate coated)	-	15.00
Ammonium dichromate, hammer mill ground 7 μm	2.00	2.00
Copper chromite, as received 2.1 μm	2.00	2.00
Ammonium nitrate, unground Monsanto	30.50	30.50
Ammonium nitrate, coarse ground Monsanto	28.50	28.50
Ammonium perchlorate, fluid energy mill ground 6.3 μm	10.00	10.00
Total	100.00	100.00
Strand Burning Rates in cm/s at 25°C (in./s at 77°F)		
At 345 N/cm² (500 psia)	0.422 (0.166)	0.366 (0.144)
At 690 N/cm² (1000 psia)	0.467 (0.184)	0.424 (0.167)
Strand Pressure Exponent		
345 to 690 N/cm² (500 to 1000 psia)	0.14	0.22

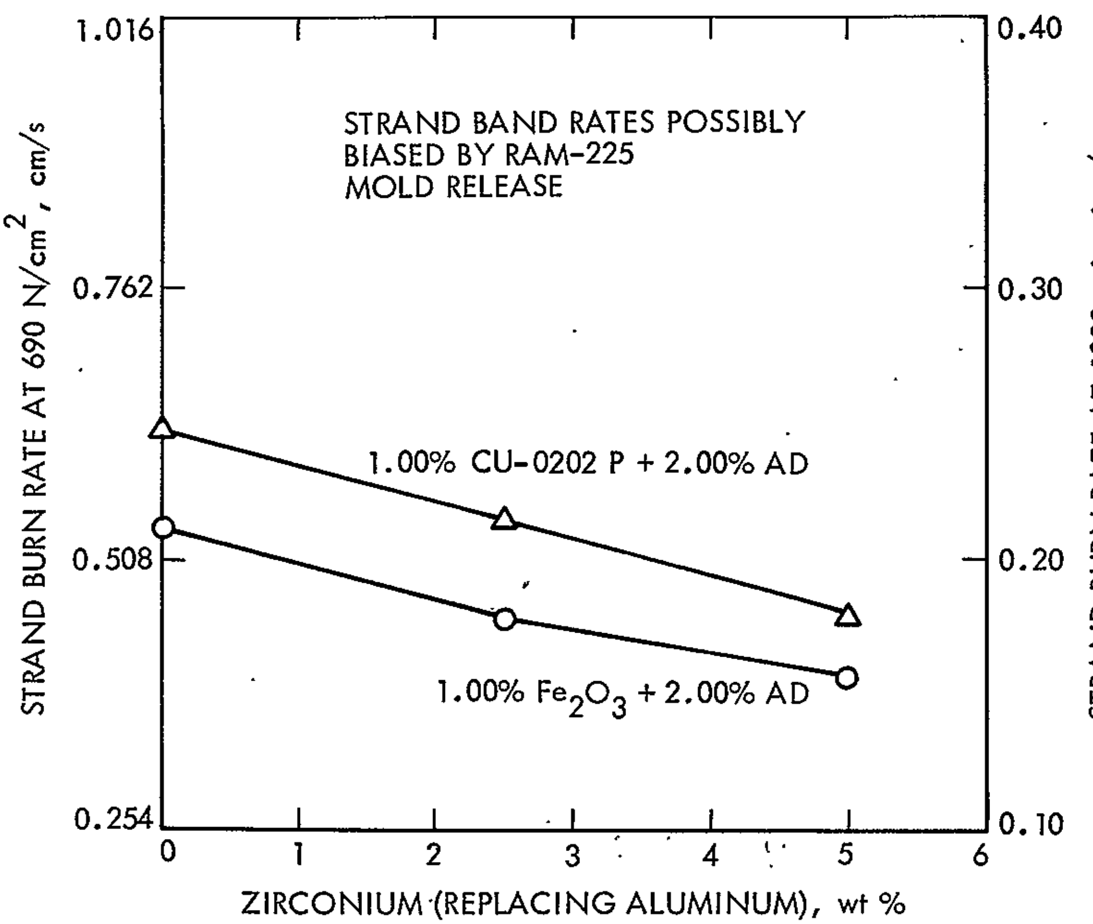

Figure 3-8. Strand Burn Rate vs Weight Percent Zirconium, AN/AP/Al/HTPB Propellants

Table 3-16. Evaluation of Zirconium/Aluminum Mixtures for AN/AP/Zr/Al/HTPB Propellants

Batch No.	SB-30	SB-37	SB-38	SB-32B	SB-39	SB-40
Formulation No.	AN-22[a]	AN-29[b]	AN-30[b]	AN-24[a]	AN-31[b]	AN-32[b]
Ingredients, wt %						
HTPB binder, 40 wt % DOA plasticized	12.00	12.00	12.00	12.00	12.00	12.00
Aluminum, MD-105	15.00	12.50	10.00	15.00	12.50	10.00
Zirconium powder	---	2.50	5.00	---	2.50	5.00
Ammonium dichromate, hammer mill ground 6.3 μm	2.00	2.00	2.00	2.00	2.00	2.00
Fe_2O_3, as received	1.00	1.00	1.00	---	---	---
Copper chromite, as received	---	---	---	1.00	1.00	1.00
Ammonium nitrate, unground Gulf Oil	31.50	31.50	31.50	31.50	31.50	31.50
Ammonium nitrate, fine grind Gulf Oil	28.50	28.50	28.50	28.50	28.50	28.50
Ammonium perchlorate, hammer mill ground 8 μm	10.00	10.00	10.00	10.00	10.00	10.00
Totals	100.00	100.00	100.00	100.00	100.00	100.00
Strand Burning Rates, cm/s at 25°C (in./s at 77°F)[c]						
At 345 N/cm^2 (500 psia)	0.376 (0.148)	0.300 (0.118)	0.272 (0.107)	0.462 (0.182)	0.376 (0.148)	0.307 (0.121)
At 690 N/cm^2 (1000 psia)	0.538 (0.212)	0.452 (0.178)	0.399 (0.157)	0.627 (0.247)	0.546 (0.215)	0.455 (0.179)

Table 3-16. Evaluation of Zirconium/Aluminum Mixtures for AN/AP/Zr/Al/HTPB Propellants (Continuation 1)

Batch No.	SB-30	SB-37	SB-38	SB-32B	SB-39	SB-40
Formulation No.	AN-22[a]	AN-29[b]	AN-30[b]	AN-24[a]	AN-31[b]	AN-32[b]
Strand Pressure Exponent 345 to 390 N/cm^2 (500 to 1000 psia)	0.52	0.58	0.58	0.44	0.54	0.57

[a]Poor relative castability.
[b]Uncastable.
[c]Possibly biased by RAM-225 mold release.

(1) Partial replacement of the aluminum by zirconium tended to make the propellant less castable on the 3.8-liter (1-gal) batch scale.

(2) The 2.00 wt % AD and 1.00 wt % CU-0202 P ballistic modifier system gave faster burning rates than the 2.00 wt % AD and 1.00 wt % Fe_2O_3 ballistic modifier system.

(3) Partial replacement of the aluminum by zirconium tended to reduce propellant strand burning rate and increase strand pressure exponent.

Based on this study and the study of ballistic modifiers a formulation using 5.00 wt % zirconium was selected for scale-up and evaluation in BATES motor firings. Results of these additional tests are discussed in Section III-H-d and III-H-e.

c. Processing Studies. Limited funds and time did not allow for any systematic study of processing variables to optimize processing conditions. However, processing methods and conditions were optimized based on experience. Some of the specific approaches used for propellant mixing were:

(1) Careful selections of order and manner of ingredient addition to disperse and wet solids.

(2) Elevated temperatures prior to curative addition to wet and disperse solids, and reduced temperatures after curative addition to minimize cure reactions.

(3) Extended vacuum mix times prior to curative addition to wet and disperse fine solids.

(4) Controlled moisture of ingredients and of the process.

The effects of AN particle sizes and fraction of AN fine ground on propellant castability were discussed in conjunction with the burning rate studies.

Antioxidants are commonly used with the R-45 HTPB binder to improve propellant pot life and aging stability. The combination of UOP-36 (N-phenyl-N'-cyclohexyl-p-phenylene diamine) and DTBH (2,5 di-tertiary butyl hydroquinone) appears to give synergistic effects and is very effective in extending pot life. Protech 2002 (UTC proprietary metal-deactivating antioxidant) and others of the Protech series have the additional advantage of being metal scavengers. They tie up the transition metals that catalyze radical oxidations. Four small-scale propellant batches were made initially to evaluate these pot-life extenders. Table 3-17 summarizes results of this initial study. The combination of UOP-36 and DTBH gave some improvement in propellant castability with no significant effect on propellant burning rate. No improvement in propellant castability was observed with use of the Protech 2002. The combination of UOP-36 and DTBH was selected as the pot-life extender system to be used for additional evaluation.

DOA was chosen initially as the plasticizer for use with the basic AN/AP/Al/HTPB propellant. It is one of the most commonly used plasticizers, and its low cost is an advantage. IDP has a lower viscosity and freezing point than DOA, but is more costly than DOA. Six small-scale propellant batches were made and tested to compare the two plasticizers, DOA and IDP, under the following three conditions:

(1) At the 40% plasticizer in binder level without pot-life extenders.

(2) At the 40% plasticizer in binder level with UOP-36 and DTBH pot-life extenders.

(3) At the 50% plasticizer in binder level with UOP-36 and DTBH pot-life extenders.

Results of the study are summarized in Table 3-18. General conclusions from the study were:

(1) The IDP consistently gave better castability than the DOA.

(2) Use of pot-life extenders UOP-36 and DTBH improved castability with both of the plasticizers, DOA and IDP.

(3) No major improvement in castability was observed by increasing the plasticizer in binder level from 40 to 50 wt %.

Table 3-17. Evaluation of Pot-Life Extenders for AN/AP/Zr/Al/HTPB Propellants

Batch No.	SB-63	SB-69	SB-71	SB-72
Formulation No.	AN-54[a]	AN-59[b]	AN-61[a]	AN-62[a]
Ingredient, wt %				
HTPB binder, 40 wt % DOA plasticized	12.00	11.92	11.77	11.85
DTBH (2,5 di-tertiary butyl-hydroquinone)	—	0.04	0.04	—
UOP-36 (N-phenyl-N'-cyclohexyl-phenylene diamine)	—	0.04	0.04	—
Protech 2002 (UTC proprietary antioxidant)	—	—	0.15	0.15
Aluminum, MD-105	10.00	10.00	10.00	10.00
Zirconium powder	5.00	5.00	5.00	5.00
Ammonium dichromate, hammer mill ground, 6.3 μm	2.00	2.00	2.00	2.00
Copper chromite, as received, 2.1 μm	2.00	2.00	2.00	2.00
Ammonium nitrate, unground Gulf Oil	30.50	30.50	30.50	30.50
Ammonium nitrate, fine ground Gulf Oil	28.50	28.50	28.50	28.50
Ammonium perchlorate, hammer mill ground 9 μm	10.00	10.00	10.00	10.00
Total	100.00	100.00	100.00	100.00

Table 3-17. Evaluation of Pot-Life Extenders for AN/AP/Zr/Al/HTPB Propellants (Continuation 1)

Batch No.	SB-63	SB-69	SB-71	SB-72
Formulation No.	AN-54[a]	AN-59[b]	AN-61[a]	AN-62[a]
Strand Burning Rates, cm/s at 25°C (in./s at 77°F)[c]				
At 345 N/cm² (500 psia)	0.323 (0.127)	0.295 (0.116)	0.282 (0.111)	0.269 (0.106)
At 690 N/cm² (1000 psia)	0.475 (0.187)	0.467 (0.184)	0.483 (0.190)	0.460 (0.181)
Strand Pressure Exponent 345 to 690 N/cm² (500 to 1000 psia)	0.57	0.66	0.78	0.78

[a]Uncastable.
[b]Poor castability.
[c]Possibly biased by RAM-225 mold release.

The effect of plasticizer type on propellant burning rate was not conclusively determined from this study. Two out of the three cases indicated that the IDP gave slower strand burning rates at 690 N/cm² (1000 psia). To resolve this question two additional propellant batches, SB-100 and SB-101, were made where the strand burn rate test results could not possibly be biased by the RAM-225 release agent. The batches were formulated to have 40 wt % plasticizer in binder and to use the pot-life extenders UOP-36 and DTBH. Results of tests on these two batches are shown in Table 3-19. These results indicated the change from DOA to IDP plasticizer reduced the strand burning rate at 690 N/cm² (1000 psia) from 0.544 to 0.485 cm/s (0.214 to 0.191 in./s) (≅11%).

Based on results of these processing studies the following propellant selections were made for additional evaluation in scale-up batches and motor tests:

(1) DOA plasticizer.

(2) 40 wt % plasticizer in binder level.

(3) Use of the pot-life extenders UOP-36 and DTBH, each at the 0.04 wt % level.

Table 3-18. Evaluation of Plasticizers and Pot-Life Extenders for AN/AP/Al/HTPB Propellants

Batch No.	SB-67	SB-68	SB-64	SB-70	SB-75	SB-76
Formulation No.	AN-57[a]	AN-58[b]	AN-25[c]	AN-60[a]	AN-63[a]	AN-64[b]
Ingredients, wt %						
HTPB binder	5.92	5.92	7.20	7.20	7.12	7.12
DTBH (2,5 di-tertiary butyl hydroquinone)	0.04	0.04	—	—	0.04	0.04
UOP-36 (N-phenyl-N'-cyclohexyl-P-phenylene diamine)	0.04	0.04	—	—	0.04	0.04
DOA	6.00	—	4.80	—	4.80	—
IDP	—	6.00	—	4.80	—	4.80
Aluminum, MD-105	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium dichromate, hammer mill ground 6.3 μm	2.00	2.00	2.00	2.00	2.00	2.00
Copper chromite, as received 2.1 μm	2.00	2.00	2.00	2.00	2.00	2.00
Ammonium nitrate, screened unground Gulf Oil +60 -32 mesh	27.00	27.00	—	—	—	—
Ammonium nitrate, unground Gulf Oil	—	—	30.50	30.50	27.00	27.00
Ammonium nitrate, fine ground Gulf Oil	32.00	32.00	28.50	28.50	32.00	32.00
Ammonium perchlorate, hammer mill ground 9 μm	—	—	10.00	10.00	10.00	10.00

Table 3-18. Evaluation of Plasticizers and Pot-Life Extenders for AN/AP/Al/HTPB Propellants (Continuation 1)

Batch No.	SB-67	SB-68	SB-64	SB-70	SB-75	SB-76
Formulation No.	AN-57[a]	AN-58[b]	AN-25[c]	AN-60[a]	AN-63[a]	AN-64[b]
Ammonium perchlorate, fluid energy mill ground 5.5 μm	10.00	10.00	—	—	—	—
Total	100.00	100.00	100.00	100.00	100.00	100.00
Strand Burning Rates[d], cm/s at 25°C (in./s at 77°F)						
At 345 N/cm² (500 psia)	0.376 (0.148)	0.371 (0.146)	0.366 (0.144)	0.478 (0.188)	0.414 (0.163)	0.353 (0.139)
At 690 N/cm² (1000 psia)	0.572 (0.225)	0.533 (0.210)	0.505 (0.199)	0.658 (0.259)	0.577 (0.227)	0.500 (0.197)
Strand Pressure Exponent, 345 to 690 N/cm² (500 to 1000 psia)	0.59	0.53	0.47	0.46	0.49	0.48

[a]Good castability.
[b]Excellent castability.
[c]Poor castability.
[d]Possibly biased by RAM-225 mold release.

Table 3-19. Evaluation of Plasticizers for AN/AP/Al/HTPB Propellants

Batch No.	SB-100	SB-101
Formulation No.	AN-25[a]	AN-65[b]
Ingredients, wt %		
HTPB binder	7.12	7.12
DTBH (2,5 di-tertiary butyl hydroquinone)	0.04	0.04
UOP-36 (N-phenyl-N'-cyclohexyl-P-phenylene diamine)	0.04	0.04
DOA	4.80	—
IDP	—	4.80
Aluminum, MD-105	15.00	15.00
Ammonium dichromate, hammer mill ground 7.2 μm	2.00	2.00
Copper chromite, as received 2.1 μm	2.00	2.00
Ammonium nitrate, unground Monsanto	30.50	30.50
Ammonium nitrate, fine ground Monsanto	28.50	28.50
Ammonium perchlorate, hammer mill ground 9 μm	10.00	10.00
Total	100.00	100.00
Strand burning rates, cm/s at 25°C (in./s at 77°F)		
At 345 N/cm^2 (500 psia)	0.406 (0.160)	0.419 (0.165)
At 690 N/cm^2 (1000 psia)	0.544 (0.214)	0.485 (0.191)
Strand Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.41	0.22

[a]Poor castability.
[b]Fair castability.

Results of these additional tests are discussed in sections on scale-up and ballistic evaluation.

d. Scale-up Evaluation of Selected Formulations. Two propellant formulations were selected for evaluation in scale-up batches [94.6 liters, 104 to 113 kg (25 gal, 230 to 250 lb)] and motor tests. Formulation AN-25 was an AN/AP/Al/HTPB propellant with 88 wt % total solids, 15 wt % aluminum, and 4 wt % ballistic modifier. Formulation AN-59 was identical except one-third of the aluminum (5 wt % of the propellant formulation) was replaced by zirconium powder. Details of the formulations are shown in Table 3-20. Both formulations were successfully mixed and loaded into BATES motors and small-scale samples. The BATES motors were successfully tested, and results are discussed in Section e. The following additional tests were made on the small-scale samples from each batch:

(1) Brookfield end-of-mix viscosities and pot life

(2) Strand burning rate

(3) Card gap

(4) Density

(5) JANNAF uniaxial physical properties

Results of these tests are shown in Table 3-20. General conclusions from these tests were as follows:

(1) The end-of-mix viscosities and pot lives on both batches were excellent. There was no degradation of castability with zirconium as suggested by the small-scale batch studies.

(2) Strand burning rates were slightly faster at 690 N/cm^2 (1000 psia) for the formulation with zirconium. The small-scale studies had suggested slower burning rates for formulations containing zirconium.

(3) Both formulations had burning rates which were well below the burning rate goal: 0.478 and 0.513 cm/s at 690 N/cm^2 (0.188 and 0.202 in./s at 1000 psia) versus goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

(4) Card gap tests on both formulations were negative at 0 cards and therefore met requirements for Class 2 propellant.

(5) Density of the propellant containing zirconium was slightly higher than the propellant containing just aluminum as expected.

Table 3-20. Scale-Up Evaluation of Selected Formulations

Propellant Type	AN/AP/Al/HTPB	AN/AP/Al/Zr/HTPB
Batch Number	SB-73	SB-74
Formulation Number	AN-25	AN-59
Batch Size, kg (lb)	113 (250)	104 (230)
Ingredients, wt %		
HTPB binder (40 wt % DOA plasticized)	11.92	11.92
UOP-36	0.04	0.04
DTBH	0.04	0.04
Ammonium dichromate, ground 6.3 μm	2.00	2.00
Copper chromite, as received 2.1 μm	2.00	2.00
Aluminum powder	15.00	10.00
Zirconium powder	—	5.00
Ammonium nitrate		
Gulf Oil unground	30.50	30.50
Gulf Oil fine ground	28.50	28.50
Ammonium perchlorate, hammer mill ground, 8 μm	10.00	10.00
Total	100.00	100.00
Brookfield apparent viscosities, kP at °C (°F)		
Time after curative addition		
0.7 h (end-of-mix)	6.0 at 55 (130)	4.1 at ~57 (~135)
1.3 h	7.3 at 57 (135)	5.0 at ~57 (~135)
3.4 h	9.5 at 55 (130)	
Strand burning rates at 25°C (77°F), cm/s (in./s)		
At 172 N/cm^2 (250 psia)	0.257 (0.101)	0.224 (0.088)
At 345 N/cm^2 (500 psia)	0.373 (0.147)	0.353 (0.139)
At 517 N/cm^2 (750 psia)	0.462 (0.182)	0.437 (0.172)
At 690 N/cm^2 (1000 psia)	0.478 (0.188)	0.513 (0.202)

Table 3-20. Scale-Up Evaluation of Selected Formulations (Continuation 1)

Propellant Type	AN/AP/Al/HTPB	AN/AP/Al/Zr/HTPB
Batch Number	SB-73	SB-74
Formulation Number	AN-25	AN-59
Batch Size, kg (lb)	113 (250)	104 (230)
Card Gap Tests	10 negative at 0 cards	10 negative at 0 cards
Physical Properties:		
Density at 25°C (77°F), g/cm^3 ($lb/in.^3$)	1.6497 (0.0596)	1.6636 (0.0601)
JANNAF Uniaxial properties		
S_m, N/cm^2 (psi)	90 (130)	88 (127)
e_m, %	4.7	4.8
S_b, N/cm^2 (psi)	90 (130)	88 (127)
e_b, %	4.7	4.8

(6) JANNAF uniaxial properties for both batches were comparable. Maximum stress, S_m, was in the range of 88 to 90 N/cm^2 (127 to 130 psi) and strain at maximum stress, e_m, was in the range of 4.7 to 4.8%. The low strain values are adequate for propellant ballistic development, but would probably have to be improved for use in the Shuttle booster motors.

e. Ballistic Evaluation: AN/AP/Al/HTPB System (3% HCl in Exhaust). The five candidate alternate propellants listed and defined in Tables 3-1 and 3-2 were all scaled up to processing of 113-kg (250-lb) batches, loaded into BATES motors, and test fired. The test firings were conducted under sea level conditions using nozzles manufactured and cut to actual expansion ratios of 7.16. Both chamber pressure and thrust were measured. The tests were conducted at ambient temperature conditions, with propellant charges conditioned to 25°C (77°F). The measured sea level I_{sp} was corrected to a vacuum I_{sp} by simply adding the back-pressure correction. The following equations define the pertinent ballistic parameters:

$$\bar{P}_c = \int_{t \text{ at } 0.75 P_c \text{ init}}^{t_{EWAT}} P dt / t_b$$

$$\overline{F} = \int_{t \text{ at } 0.75\ P_c \text{ init}}^{t_{EWAT}} Fdt/t_b$$

$$K_N = \frac{A_b}{A_t} = \frac{gP_c}{c^* r\rho}$$

$$C^* = g\ \overline{A}_t \int_{t_o}^{t_a} Pdt/\underline{W_p} \equiv g\ P_c/K_N\ r\rho$$

$$I_{sp}\ ms = \frac{I_t}{W_p}$$

$$I_t = \int_{t_o}^{t_a} Fdt$$

$$I_{sp}\ vac\ ms = I_{sp}\ ms + \frac{P_a A_e}{\dot{W}}$$

$$\dot{W} = \frac{W_p \text{ expended}}{(t_a + t_b)/2}$$

Figure 3-9 shows the burning rate of the formulation number AN-25, the AN/AP/Al/HTPB propellant system with 10% AP. Table 3-21 is a tabulation of the BATES motor test data from the test firings of batch number SB-74 of formulation AN-25.

f. <u>Ballistic Evaluation: AN/AP/Al/Zr/HTPB</u>. BATES motors were also loaded and tested with the modified AN/AP/Al/HTPB formulation containing 5% Zr powder, a 15-μm powder. The burning rates determined in BATES motors are shown in Fig. 3-10, and the ballistic data from the BATES motors tests are tabulated in Table 3-22.

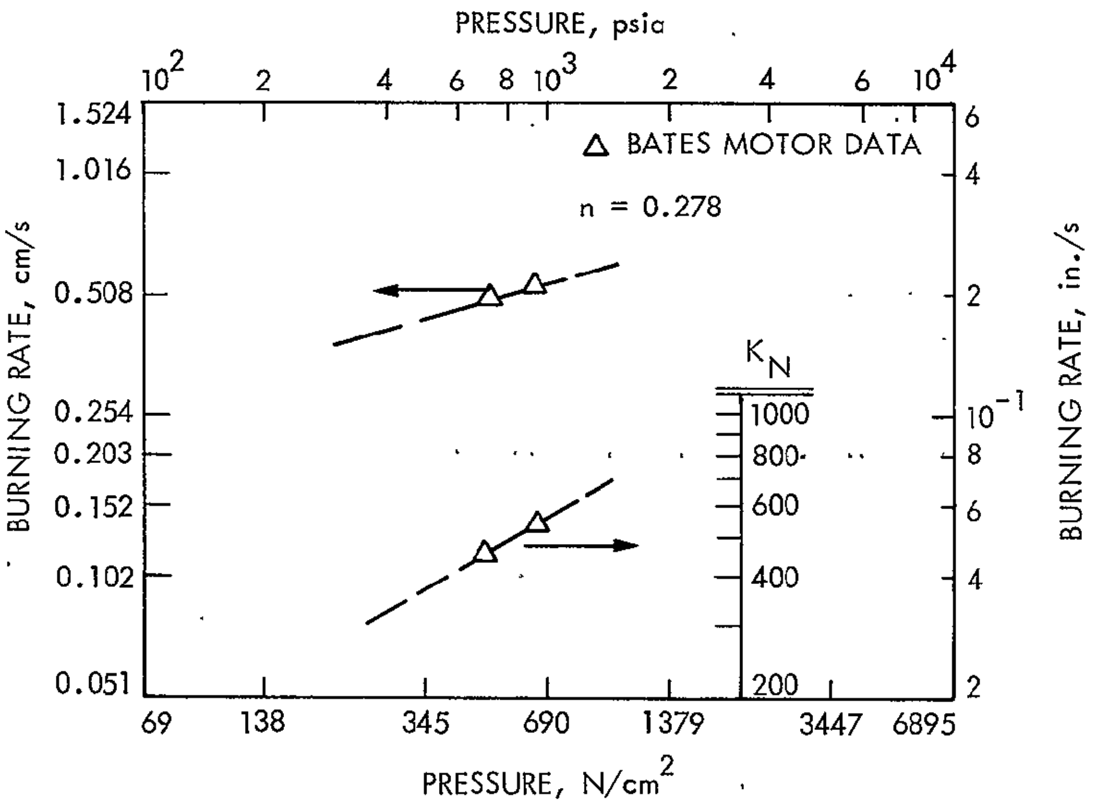

Fig. 3-9. Shuttle Alternate Propellant Burning Rates and K_N for AN/AP/Al/HTPB, Batch No. SB-73

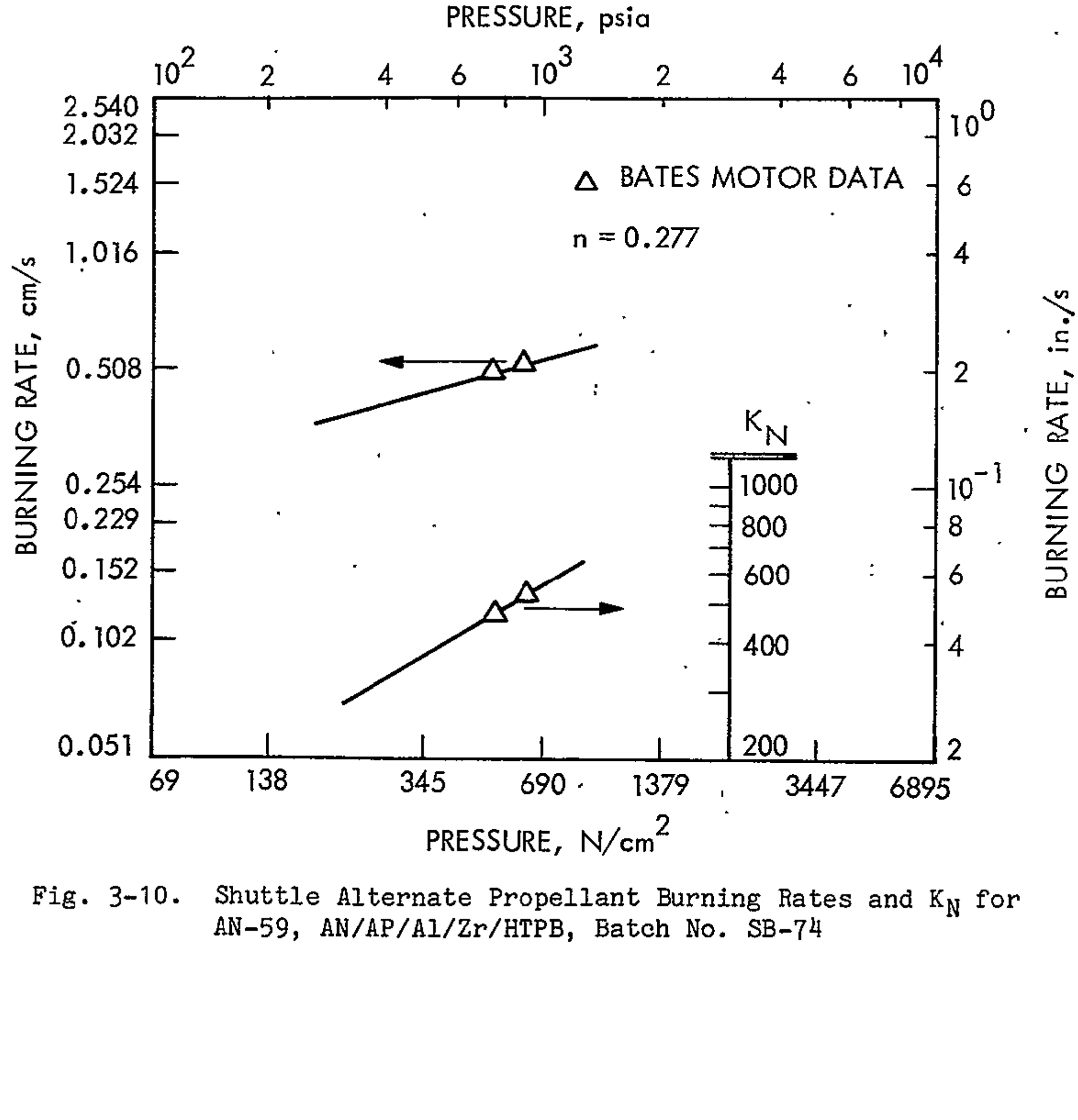

Fig. 3-10. Shuttle Alternate Propellant Burning Rates and K_N for AN-59, AN/AP/Al/Zr/HTPB, Batch No. SB-74

Table 3-21. BATES Motor Tests Data Summary, AN-25 Propellant

% Solids	88	
% Aluminum	15	
% Oxidizer	AP-10, AN-59, HMX 0	
Run No.	E-1453	E-1455
Test data	9-15-75	9-23-75
Batch/charge number	SB-73/2	SB-73/3
Nozzle D_t initial, cm (in.)	3.376 (1.329)	3.109 (1.224)
Nozzle D_t final, cm (in.)	3.393 (1.336)	3.119 (1.228)
W_p loaded, kg (lb)	25.225 (55.611)	25.25 (55.67)
W_p expended, kg (lb)	25.028 (55.177)	25.01 (55.13)
% Wt expended	99.22	99.04
Web thickness, cm (in.)	3.840 (1.512)	3.855 (1.5178)
t_b (burn time), s	8.11	7.42
t_a (action time), s	8.81	7.97
P_c initial, N/cm^2 (psia)	425 (616)	576 (835)
P_c maximum, N/cm^2 (psia)	493 (715)	634 (919)
P_c final, N/cm^2 (psia)	459 (666)	590 (856)
$\int P\,dt\,(t_b)$, $N\text{-}s/cm^2$ (lb-s)	3884.4 (5633.9)	4587.8 (6654.1)

Table 3-21. BATES Motor Tests Data Summary, AN-25 Propellant (Continuation 1)

% Solids 88
% Aluminum 15
% Oxidizer AP-10, AN-59, HMX 0

Run No.	E-1453	E-1455
$\int P\,dt\,(t_a)$, $N\text{-}s/cm^2$ (lb-s)	4019.6 (5830.0)	4723.2 (6850.4)
$\overline{P}_c$, $(\int P\,dt/t_b)$, N/cm^2 (psia)	479.0 (694.7)	618.3 (896.8)
r at P_c, cm/s (in./s)	0.483 (0.190)	0.518 (0.204)
K_N initial	453.32	534.4
K_N average	447.39	528.5
C*, m/s (ft/s)	1432 (4700)	1424 (4673)
C* efficiency, %	95.3	94.8
$\int F\,dt$, (t_b), N-s (lb-s)	50665 (11390)	5174.6 (11.633)
$\overline{F}$, $(\int F\,dt/t_b)$, N (lb)	6191.0 (1391.8)	6973.4 (1567.7)
I_t, $(\int F\,dt)$, (t_a), N-s (lb-s)	52257 (11,748)	53745.8 (12,082.6)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2071.65 (211.25)	2128.44 (217.04)
I_{sp} efficiency, %	88.20	88.82
I_{sp} vac ms, N-s/kg (s)	2265.34 (231.0)	2281.32 (232.63)

Table 3-21. BATES Motor Tests Data Summary, AN-25 Propellant (Continuation 2)

% Solids 88
% Aluminum 15
% Oxidizer AP-10, AN-59, HMX 0

Run No.	E-1453	E-1455
Expansion ratio	6.88	7.00

Table 3-22. BATES Motor Tests Data Summary, AN-59 Propellant

% Solids 88
% Aluminum 10% Al & 5% Zr
% Oxidizer AP-10, AN-59, HMX 0

Run No.	E-1454	E-1456
Test date	9-18-75	9-26-75
Batch/charge number	SB-74/1	SB-74/2
Nozzle D_t initial, cm (in.)	3.287 (1.294)	3.119 (1.228)
Nozzle D_t final, cm (in.)	3.307 (1.302)	3.142 (1.237)
W_p loaded, kg (lb)	25.61 (56.47)	25.61 (56.46)
W_p expended, kg (lb)	25.34 (55.86)	25.28 (55.74)
% Wt expended	98.91	98.72
Web thickness, cm (in.)	3.835 (1.510)	3.8298 (1.5078)

Table 3-22. BATES Motor Tests Data Summary, AN-59 Propellant (Continuation 1)

% Solids 88
% Aluminum 10% Al & 5% Zr
% Oxidizer AP-10, AN-59, HMX 0

Run No.	E-1454	E-1456
t_b (burn time), s	7.69	7.40
t_a (action time), s	8.24	7.84
P_c initial, N/cm^2 (psia)	465 (675)	552 (800)
P_c maximum, N/cm^2 (psia)	541 (785)	620 (899)
P_c final, N/cm^2 (psia)	540 (783)	614 (890)
$\int P\,dt$ (t_b), $N\text{-}s/cm^2$ (lb-s)	4031.1 (5846.7)	4482.0 (6500.
$\int P\,dt$, (t_a), $N\text{-}s/cm^2$ (lb-s)	4180.6 (6063.4)	4600.0 (6671.8)
$\overline{P}_c$, ($\int P\,dt/t_b$), N/cm^2 (psia)	524.2 (760.3)	605.7 (878.5)
r at $\overline{P}_c$, cm/s (in./s)	0.498 (0.196)	0.518 (0.204)
K_N initial	478	531
K_N average	472.6	523
C*, m/s (ft/s)	1394.0 (4573.6)	1431.9 (4697.7)
C* efficiency, %	92.8	95.27

Table 3-22. BATES Motor Tests Data Summary, AN-59 Propellant (Continuation 2)

% Solids 88
% Aluminum 10% Al & 5% Zr
% Oxidizer AP-10, AN-59, HMX 0

Run No.	E-1454	E-1456
$\int F\,dt$, (t_b), N-s (lb-s)	50,189 (11,283)	50,576 (11,370)
$\bar{F}$, ($\int F\,dt/t_b$), N (lb)	6526 (1467)	6835 (1536.5)
I_t, ($\int F\,dt$), (t_a), N-s (lb-s)	52,044 (11,700)	52,044 (11,770)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2031.9 (207.2)	2044.7 (208.5)
I_{sp} efficiency, %	85.98	86.5
I_{sp} vac ms, N-s/kg (s)	2205.5 (224.9)	2201.6 (224.5)
Expansion ratio	6.96	6.94

8. AN/AP/Al/HTPB Propellant (>3 Wt % HCl in Exhaust)

The propellant development work accomplished on the basic AN/AP/Al/HTPB propellant to this point indicated that the burn rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) with the constraint of $\leq$3 wt % HCl in the propellant exhaust was probably not achievable. Development work was continued on this propellant with the HCl constraint removed, but held to a minimum. This section discusses that propellant development effort.

a. Burning Rate Studies. Four small-scale batches (1500 g) were made varying the FEM AP (fluid energy mill-ground ammonium perchlorate) level from 10 to 30 wt %. The ballistic modifier system using 2 wt % ground AD and 2 wt % CU-0202 P was used. End-of-mix viscosities, pot life, and cured strand burning rates were measured on each batch. Objective of this work was to determine what FEM AP level was needed to achieve the burning rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia). The formulations and test results are shown in Table 3-23 and Fig. 3-11. These results lead to the following conclusions:

(1) The strand burning rate of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) is achievable using 18 wt % FEM AP. A motor burning rate of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) may require a slightly higher FEM AP level.

(2) End-of-mix viscosities were in the range of 8.8 to 15.2 kP at 52°C (125°F) for FEM AP levels ranging from 10 to 20 wt %. Casting lives for these batches were $\geq$3.5 h at 52°C (125°F).

(3) Using FEM AP and increasing the AP level from 10 wt % to ≅18 wt % increases HCl in the exhaust from 2.9% to ≅5.0%.

Thermoballistic calculations indicated that reducing the ballistic modifier level to 2 wt % by elimination of the AD increased theoretical I_{sp} by 19.6 N-s/kg (2 s). Elimination of the AD was desirable from other considerations. Studies had shown that it crosslinks the R-45 prepolymer (probably through the double bond) and degrades propellant castability and physical properties. Three small-scale (1500 g) batches were made varying the FEM AP level over the range of 15 to 25 wt % level. Only 2 wt % as received CU-0202 P was used as ballistic modifier. End-of-mix viscosities and cured strand burning rates were measured. Results of this study are shown in Table 3-24 and Fig. 3-11. General conclusions from this work were:

(1) Approximately 20 wt % FEM AP is required to meet the burning rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

(2) End-of-mix viscosities were in the range of 18 to 19 kP at 52°C (125°F).

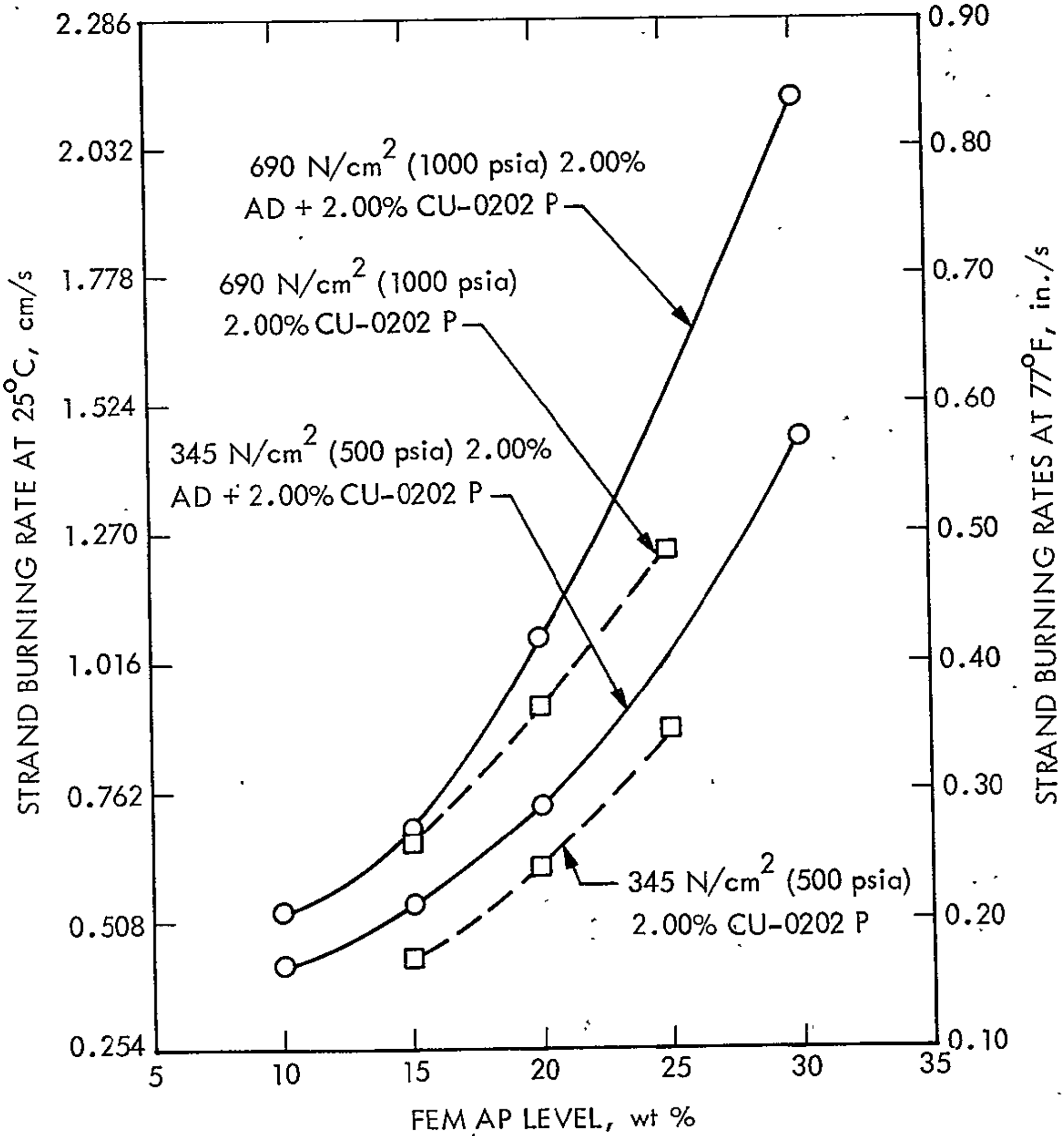

Fig. 3-11. Strand Burning Rates vs FEM AP Level, AN/AP/Al/HTPB Propellants

Table 3-23. AN/AP/Al/HTPB Formulations-AP Level Variations (4 Wt % Ballistic Modifier)

Batch No.	SB-118	SB-119	SB-120	SB-121
Formulation No.	AN-25A	AN-66	AN-67	AN-68
Ingredients, wt %				
HTPB Binder 40% DOA plasticized	12.00	12.00	12.00	12.00
Aluminum MD-105	15.00	15.00	15.00	15.00
Ammonium dichromate hammer mill ground (7.2 μm)	2.00	2.00	2.00	2.00
Copper chromite as received (2.1 μm)	2.00	2.00	2.00	2.00
Ammonium nitrate Monsanto unground	30.50	30.50	30.50	30.50
Ammonium nitrate Monsanto fine grind	28.50	23.50	18.50	8.50
Ammonium perchlorate fluid energy ground (6.3 μm)	10.00	15.00	20.00	30.00

Table 3-23. AN/AP/Al/HTPB Formulations-AP Level Variations (4 Wt % Ballistic Modifier) (Continuation 1)

Batch No.	SB-118	SB-119	SB-120	SB-121
Formulation No.	AN-25A	AN-66	AN-67	AN-68
Brookfield Viscosities at 52°C (125°F), kP/h after CA				
End-of-mix	15.2/0.67	11.2/0.62	8.8/0.38	28/0.6
Pot life	18.4/1.7 25.6/2.7 32/3.7	26.4/1.8 32/2.8 40/3.8	22.4/1.4 27.2/2.4 40.8/3.4	- - -
Strand Burning Rates, cm/s at 25°C (in./s at 77°F)				
At 345 N/cm^2 (500 psia)	0.424 (0.167)	0.536 (0.211)	0.739 (0.291)	1.461 (0.575)
At 690 N/cm^2 (1000 psia)	0.528 (0.208)	0.693 (0.273)	1.067 (0.420)	2.136 (0.841)
Strand Pressure Exponent 345 to 690 N/cm^2 (500 to 1000 psia)	0.30	0.38	0.51	0.52

CA = curative addition.

Table 3-24. Evaluation of AP Level for AN/AP/Al/HTPB Propellant (2 Wt % Ballistic Modifier)

Batch No. Formulation No.	SB-135 AN-69	SB-136 AN-70	SB-137 AN-71
Ingredients, wt %			
HTPB binder, 40 wt % DOA plasticized	12.00	12.00	12.00
Aluminum, MD-105	15.00	15.00	15.00
Copper chromite, as received 2.1 μm	2.00	2.00	2.00
Ammonium nitrate, unground Monsanto	30.50	30.50	30.50
Ammonium nitrate, fine ground Monsanto	25.50	15.50	20.50
Ammonium perchlorate, FEM ground 6.3 μm	15.00	25.00	20.00
	100.00	100.00	100.00
Brookfield End-of-Mix viscosity, kP at 52°C (125°F)	19	18	
Strand Burning Rates, cm/s at 25°C (in./s at 77°F)			
At 345 N/cm^2 (500 psia)	0.437 (0.172)	0.884 (0.348)	0.615 (0.242)
At 690 N/cm^2 (1000 psia)	0.660 (0.260)	0.242 (0.489)	0.930 (0.366)
Strand Pressure Exponent at 345 to 690 N/cm^2 (500 to 1000 psia)	0.58	0.51	0.60

Based on these results formulation AN-71 with 2 wt % as received CU-0202 P and 20 wt % FEM AP was selected for additional evaluation with a scale-up batch and motor tests.

b. Scale-Up Evaluation of Selected Formulation. Formulation AN-71 was selected for evaluation in a scale-up batch [94.6 liter (25 gal), 113 kg (250 lb)] and motor tests. It was an AN/AP/Al/HTPB propellant with 88 wt % total solids, 15 wt % aluminum, 20 wt % FEM AP, and 2 wt % ballistic modifier. Details of the formulation are shown in Table 3-25. Formulation AN-71 was successfully mixed in the 94.6-liter (25-gal) mixer and loaded into BATES motors and small-scale samples. The BATES motors were successfully tested and results are discussed in Section III-H-8-c and d, Ballistic Evaluation. The following additional tests were made on the small-scale samples:

(1) Brookfield end-of-mix viscosities and pot life

(2) Strand burning rates

(3) Card gap

(4) Density

(5) JANNAF uniaxial physical properties

Results of these tests are also summarized in Table 3-25. General conclusions from these tests were:

(1) The propellant end-of-mix viscosity was 28 kP at 53°C (127°F), which is high but acceptable. Pot life was about 2 hours.

(2) The strand burning rate at 690 N/cm^2 (1000 psia) was 0.922 cm/s (0.363 in./s), which met the goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

(3) Strand pressure exponent was 0.61. Motor pressure exponents are typically lower than strand pressure exponents. The generally high pressure exponent is associated with the low ballistic modifier level (2 wt % CU-0202 P) and the fine (FEM) AP.

(4) Card gap tests were negative at 0 cards. Therefore, they met requirements for Class 2 propellant.

(5) The propellant density and JANNAF uniaxial properties obtained were typical of properties obtained with the AN/AP/Al/HTPB propellant. Measured density was 1.6497 g/cm^3 at 25°C (0.0596 lb/in.^{3} at 77°F). S_m was 89 N/cm^2 (129 psi) with an e_m of 3.7 %. The low strain values were adequate for propellant ballistic development, but would probably have to be improved for use in the Shuttle booster motors.

Table 3-25. Scale-Up Evaluation of Selected Formulation

Propellant Type	AN/AP/Al/HTPB
Batch Number	SB-140
Formulation No.	AN-71
Batch Size	113 kg (250 lb)
Formulation, wt %	
HTPB binder (40 wt % DOA plasticized)	11.92
UOP-36	0.04
DTBH	0.04
Copper Chromite, as received 2.1 μm	2.00
Aluminum powder, MD-105	15.00
Ammonium nitrate:	
Monsanto unground	30.50
Monsanto fine ground	20.50
Ammonium perchlorate, fluid energy mill ground 6.3 μm	20.00
Total	100.00
Brookfield Apparent Viscosities, kP at °C (°F)	
Time after curative addition	
0.9 h (end-of-mix)	28 at 53 (127)
1.9 h	52 at 52 (125)
2.9 h	73 at 52 (125)
Strand Burning Rates at 25°C (77°F), cm/s (in./s)	
At 172 N/cm^2 (250 psia)	0.445 (0.175)
At 345 N/cm^2 (500 psia)	0.612 (0.241)
At 517 N/cm^2 (750 psia)	0.785 (0.309)
At 690 N/cm^2 (1000 psia)	0.922 (0.363)
Strand Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.61
Card Gap Tests	Negative at 0 cards
Physical Properties:	
Density at 25°C (77°F), g/cm^3 ($lb/in.^3$)	1.6497 (0.0596)
JANNAF Uniaxial Properties	
S_m, N/cm^2 (psi)	89 (129)
e_m, %	3.7
S_b, N/cm^2 (psi)	89 (129)
e_b, %	3.7

c. Ballistic Evaluation: AN/AP/Al/HTPB (>3% HCl in Exhaust). As has been discussed, the effects on this candidate propellant system resulting from increasing the AP content were studied. A formulation with 20 % AP, and burning rate modifier reduced to 2%, met the burning rate and I_{sp} goal. This formulation is identified as AN-71. The burning rates and measured I_{sp} are shown in Fig. 3-12 and Table 3-26, respectively.

d. Summary. One AN/AP/Al/HTPB propellant formulation was developed that conformed to the program constraints for ≤3 wt % HCl in the exhaust products and for a Class 2 propellant hazards classification. This formulation, AN-25, had a motor burning rate of only 0.53 cm/s at 690 N/cm^2 (0.21 in./s at 1000 psia) and a delivered vacuum I_{sp}, ϵ = 7.16, of only 2285 N-s/kg (233 s). A maximum strand burning rate of only 0.64 cm/s at 690 N/cm^2 (0.25 in./s at 1000 psia) (unbiased by RAM-225 release agent) was achieved within the program constraints with a small-scale batch using fluid energy mill ground (5.5 μm) AP. Since the development work indicated that the burn rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) was probably not achievable with the constraint of ≤3 wt % HCl in the propellant exhaust, development work was continued with this constraint removed but held to a minimum. Formulation AN-71 was developed to meet the program goals on that basis. This formulation used only 2.00 wt % copper chromite as ballistic modifier and 20.00 wt % fluid energy mill ground (6.3 μm) AP. It had a motor burning rate of 0.97 cm/s at 690 N/cm^2 (0.38 in./s at 1000 psia) and a delivered vacuum I_{sp}, ϵ = 7.16, of 2403 N-s/kg (245 s). Table 3-27 summarizes and compares the properties of these two formulations versus the program goals.

The following summarizes the status of the AN/AP/Al/HTPB propellant development:

(1) The basic AN/AP/Al/HTPB propellant is the second most promising candidate of the three basic propellants.

(2) Demonstrated that a few % of AP is essential to good aluminum combustion.

(3) Demonstrated that more than 10% of AP is required to meet the burn rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

(4) Formulation AN-71 with 20 wt % AP met the program goals for burning rate at 690 N/cm^2 (1000 psia) [0.97 cm/s (0.38 in./s) achieved versus goal of 0.89 cm/s (0.35 in./s)] and delivered vacuum I_{sp}, at ϵ = 7.16 [2403 N-s/kg (245 s) achieved versus goal of ≥2403 N-s/kg (245 s)], but did not meet the goal for pressure exponent (0.48 achieved versus goal of ≤0.42). It conformed to the constraint for a Class 2 propellant, but did not conform to the constraint for ≤3 wt % HCl in the propellant exhaust.

Table 3-26. BATES Motor Tests Data Summary, AN-71 Propellent

% Solids: 88
% Aluminum: 15
% Oxidizer: AP 20, AN 51.0, HMX ---

Run No.	E-1484	E-1491
Test Date	6-10-76	6-25-76
Batch/Chg. No.	SB-140/1	SB-140/2
Nozzle D_t init., cm (in.)	4.8636 (1.9148)	4.8636 (1.9148)
Nozzle D_t final, cm (in.)	4.6380 (1.826)	4.6355 (1.825)
W_p loaded, kg (lb)	30.25 (66.70)	30.16 (66.50)
W_p expended, kg (lb)	30.25 (66.68)	30.03 (66.21)
% Wt expended	99.97	99.56
Web thickness, cm (in.)	4.648 (1.830)	4.630 (1.823)
t_b, s	6.98	6.54
t_a, s	7.30	7.05
P_c initial, N/cm^2 (psia)	313 (454)	317 (460)
P_c maximum, N/cm^2 (psia)	380 (551)	421 (610)
P_c final, N/cm^2 (psia)	317 (460)	238 (345)
$\int P\,dt$, (t_b), N-s/cm^2 (lb-s)	2450.6 (3554.35)	2452.5 (3557.10)
$\int P\,dt$, (t_a), N-s/cm^2 (lb-s)	2495.2 (3619)	2494.8 (3618.4)
$\overline{P}_c$, ($\int P\,dt/t_b$), N/cm^2 (psia)	351 (509)	375.0 (543.9)
r at $\overline{P}_c$, cm/s (in./s)	0.665 (0.262)	0.709 (0.279)
K_N initial	210.3	210.3
K_N average	219.87	219.98
C*, m/s (ft/s)	1460.4 (4791.4)	1463.8 (4802.6)
C* efficiency	97.2	97.5

Table 3-26. BATES Motor Tests Data Summary, AN-71 Propellant (Continuation 1)

% Solids: 88
% Aluminum: 15
% Oxidizer: AP 20, AN 51.0, HMX ---

$\int F\,dt$, (tb), N-s (lb-s)	62,487.97 (14,047.86)	62,811.31 (14,120.55)
$\bar{F}$, ($\int F\,dt/t_b$), N (lb)	8,952.49 (2012.6)	9604.15 (2159.1)
I_t, ($\int F\,dt$ for t_a), N-s (lb-s)	63,569.96 (14,291.1)	63,823.82 (14,348.17)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2101.17 (214.26)	2155.88 (215.76)
I_{sp} efficiency, %	92.26	92.56
I_{sp} vac ms (corr.)	2402.14 (244.95)	2410.08 (245.76)
Expansion ratio	7.16	7.26

(5) Formulation AN-25 with 10 wt % AP met the program goal for pressure exponent (0.28 achieved versus goal of $\leq$0.42), but did not meet the goals for burning rate at 690 N/cm^2 (1000 psia) [0.53 cm/s (0.21 in./s) achieved versus goal of 0.89 cm/s (0.35 in./s)] or for delivered vacuum I_{sp}, ϵ = 7.16 [2285 N-s/kg (233 s) achieved versus goal of $\geq$2403 N-s/kg (245 s)]. It conformed to the constraints for a Class 2 propellant and $\geq$3 wt % HCl in the propellant exhaust.

(6) Demonstrated good castability, and a pot life greater than 3.4 hours for formulation AN-25.

(7) Demonstrated acceptable castability for formulation AN-71.

(8) Successfully loaded and test fired 32-kg (70-lb) BATES motors with both formulations.

(9) Measured physical properties and determined a need for additional development effort in this area.

9. AN/HMX/Al/HTPB Propellant

This section discusses the propellant development work accomplished in the basic AN/HMX/Al/HTPB propellant to achieve the defined performance goals within the constraints specified. One of the advantages of this basic propellant is that it contains no AP and consequently generates no HCl in the exhaust. However, typical formulations using

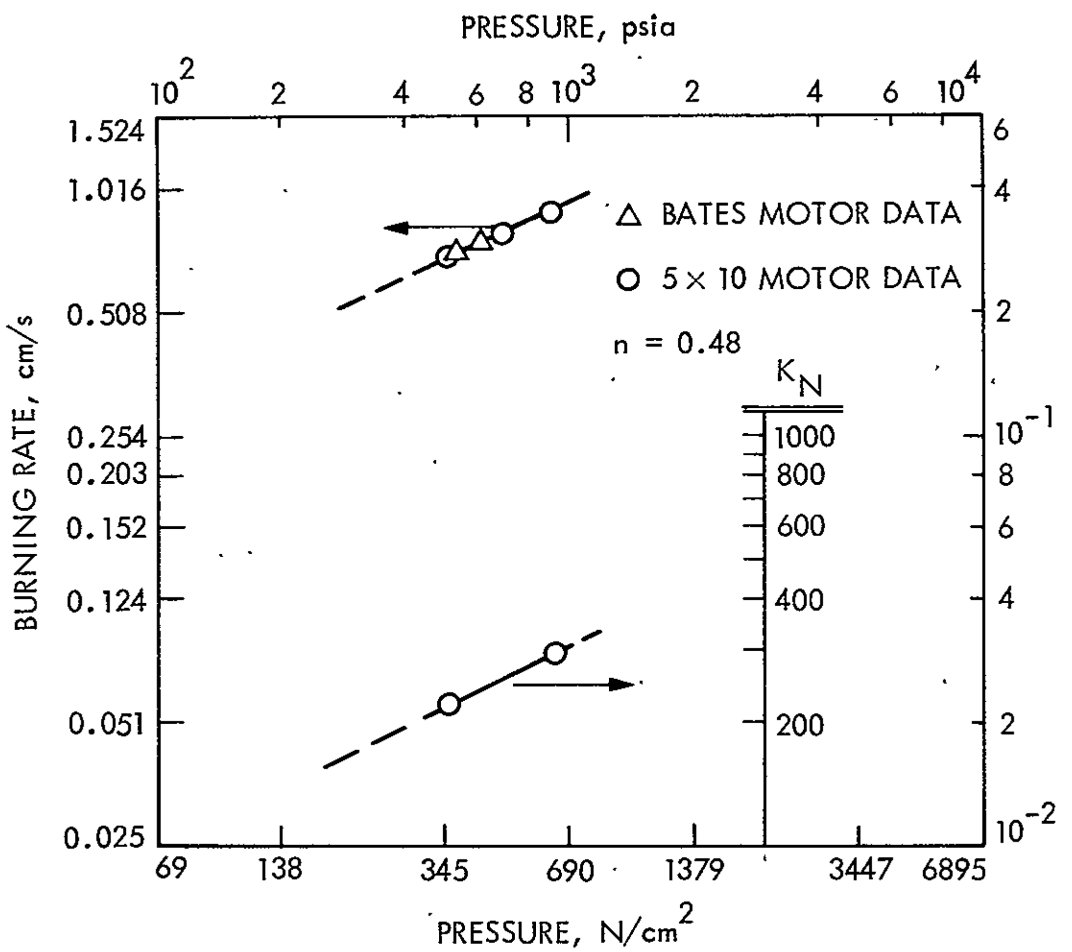

Fig. 3-12. Shuttle Alternate Propellant Burning Rates and K_N for AN/AP/Al/HTPB, Batch No. SB-140

Table 3-27. AN/AP/Al/HTPB Propellant Achieved Properties vs Goals

Alternate Propellant Property	Goal	Achieved Value: SB-73 AN-25 (10 wt % AP)	Achieved Value: SB-140 AN-71 (20 wt % AP)
BATES motor Burning rate at 690 N/cm^2 (1000 psia), cm/s (in./s)	0.89 (0.35)	0.53 (0.21)	0.97 (0.38)[a]
BATES motor pressure exponent	≤0.42	0.28	0.50[a]
Delivered vacuum I_{sp}, ϵ = 7.16, N-s/kg (s)	2403 (≥245)	2285 (233)	2403 (245)
HCl in exhaust	≤3%	3.0%	6.0%
Meets card gap requirement for Class 2	Required	yes (negative at 0 cards)	yes (negative at 0 cards)

[a]4.5-kg (10-lb) motor test data

15 to 20 wt % HMX have theoretical I_{sp} values (vacuum and ϵ = 7) about 19.6 N-s/kg (2 s) less than comparable AN/HNX/AP(10%)/Al/HTPB formulations. Reduction in program funds and scope limited development effort on this basic propellant to only four exploratory mixes.

a. Safety Tests. Two 10-g hand mixes, one uncured and one cured, were made of formulations with 20 wt % Class A HMX to initially check material compatibility and propellant safety properties. Impact tests (DSC-differential scanning calorimeter) were made on both mixes. The formulations and results of the safety tests are shown in Table 3-28. For comparison purposes these same safety tests were made on propellant samples of the current PBAN baseline propellant (TP-H-1123). Table 3-29 compares the safety properties of the candidate AN/HMX/Al/HTPB formulation, AN-52, with the safety properties of PBAN baseline formulation, TP-H-1123. These tests indicated:

Table 3-28. Summary of Propellant Safety Tests - Candidate Alternate AN/HMX/Al/HTPB Propellant (10-g hand mixes)

Batch No.	SB-59	SB-60
Formulation No.	AN-51 (uncured)	AN-52
Formulation (parts by weight)		
R-45, Alrosperse, DOA (40%) } Premix	11.08	11.08
Aluminum	15.00	15.00
Ammonium dichromate, ground 6 μm	2.00	2.00
Copper chromite, as received	2.00	2.00
Ammonium perchlorate, ground 9 μm	-	-
HMX, Type II, Class A (DOA coated)	20.20	20.20
Ammonium nitrate, ground	34.10	34.10
Ammonium nitrate, unground (+60 -32 mesh screened fraction)	15.00	15.00
IPDI	none	0.62
	99.38	100.00
Impact Sensitivity, cm (in.) for 1.8-kg (4-lb) weight		
0% fire	43.18 (17)[a]	45.72 (18)
50% fire	48.26 (19)[a]	50.8 (20)
Electrostatic Sensitivity, J	>12.8	>12.8
Thermal Stability (DSC - 10°C/min heating rate)	No exotherm over temperature range 21 to 149°C (70 to 300°F)	No exotherm over temperature range 21 to 149°C (70 to 300°F)

[a]Mixes very dry. Impact tests may be biased by voids in samples.
DSC = Differential scanning calorimeter

Table 3-29. Comparison of Safety Properties - Candidate Alternate AN/HMX/Al/HTPB Propellant Formulations vs Baseline (PBAN) Formulation (AN-52)

Formulation Batch No.	TP-H-1123 (PBAN Baseline) SB-77	AN-52 SB-60
Ingredients, wt %		
PBAN binder	14.00	-
HTPB binder	-	11.90
Aluminum	16.00	15.00
Ballistic modifiers	0.40	4.00
Ammonium perchlorate	69.60	-
Ammonium nitrate	-	49.10
HMX, Type II, Class A	-	20.00
Impact sensitivity, cm (in.) for 1.8 kg (4-lb) weight		
0% fire	43.18 (18)	45.72 (18)
50% fire	49.53 (19.5)	50.8 (20)
Electrostatic sensitivity, J	>12.8	>12.8
Thermal stability (DSC - 10°C/min heating rate)	No exotherm over temperature range 21 to 149°C (70 to 300°F)	No exotherm over temperature range 21 to 149°C (70 to 300°F)

DSC = Differential scanning calorimeter

C-2

(1) Formulation AN-52 had essentially the same sensitivity to impact and electrostatic discharge as the current PBAN baseline propellant (TP-H-1123).

(2) DSC data suggested that thermal stability of the 20 wt % HMX propellant, and gross material compatibility, over the temperature range 21 to 149°C (70 to 300°F), were adequate.

(3) Formulations with up to 20 wt % HMX could be safely processed in the JPL ETS facilities as per established standard operating procedures.

b. Burning Rate Studies. Two small-scale batches (1000 g) were made varying the level of Class A HMX from 15.00 to 20.00 wt %. Strand burn rate tests were made on cured propellant from both batches. The formulations and results of strand burn rate tests are shown in Table 3-30. Strand burning rates increased from 0.414 to 0.450 cm/s at 690 N/cm^2 (0.163 to 0.177 in./s at 1000 psia) with the 15.00 to 20.00 wt % increase in Class A HMX, while the strand pressure exponent remained constant at 0.42. Although the strand pressure exponent met the performance goal of $\leq$0.42, the burning rates at 690 N/cm^2 (1000 psia) were well below the goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia). These very slow burn rates suggest that the basic AN/HMX/Al/HTPB propellant may not be a viable candidate for achieving program goals.

c. Hazard Classification. Card gap samples were cast, cured, and tested from the two batches shown in Table 3-30. Results of the card gap tests indicated positive tests at 35 and 70 cards on both batches. Therefore, these formulations with 15 and 20 wt % Class A HMX did not meet the card gap requirements for Class 2 propellant hazard classification, one of the major constraints. Propellant development work on the AN/HMX/Al/HTPB propellant was terminated at this point.

d. Summary. The following summarizes the status of the AN/HMX/Al/HTPB propellant development:

(1) Demonstrated that 15.00 and 20.00 wt % Class A HMX resulted in Class 7 propellants.

(2) Achieved a strand burning rate of 0.450 cm/s (0.177 in./s) at 690 N/cm^2 (1000 psia) and a strand pressure exponent of 0.42 with a formulation containing 20.00 wt % Class A HMX.

(3) Demonstrated good castability of the basic AN/HMX/Al/HTPB propellant.

(4) Discontinued development of this basic propellant as a result of reduction in funds.

Table 3-30. AN/HMX/HTPB Formulations (Class A HMX)

Batch No.	SB-82A (HMX)	SB-81 (HMX)
Formulation No.	ANH-1	ANH-1
Ingredients, wt %		
HTPB binder	12.00	12.00
Aluminum	15.00	15.00
Ammonium dichromate, ground	2.00	2.00
Copper chromite	2.00	2.00
HMX Class A	15.00	20.00
Ammonium nitrate	54.00	49.00
Card gap tests:		
0 cards		
35 cards	1 positive	1 positive
70 cards	2 positive	2 positive
Strand burning rates at 25°C (77°F), cm/s (in./s)		
At 345 N/cm^2 (500 psia)	0.310 (0.122)	0.340 (0.134)
At 690 N/cm^2 (1000 psia)	0.414 (0.163)	0.450 (0.177)
Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.42	0.42

10. AN/HMX/AP/Al/HTPB Propellant

This section discusses the propellant development work accomplished on the basic AN/HMX/AP/Al/HTPB propellant to achieve the defined performance goals within the constraints specified. The constraint of ≤ 3 wt % HCl in the propellant exhaust was accomplished by limiting the AP level in the formulation to ≤ 10 wt %. The constraint of a Class 2 propellant hazard classification was primarily accomplished by limiting the HMX Class (particle size) and level to meet the card gap requirements for Class 2 propellant (<70 cards).

a. <u>Safety Tests</u>. Safety tests were performed on samples from 10-g hand mixes containing 20 wt % Class A HMX to check material compatibility and safety properties. The formulations and the test results are shown in Table 3-31. As in the case of the AN/HMX/Al/HTPB propellant, these safety tests results were compared to similar safety test results on the PBAN baseline propellant (TP-H-1123). Table 3-32 shows this comparison. General conclusions were:

(1) Formulation AN-50 had essentially the same sensitivity to impact and electrostatic discharge as TP-H-1123.

(2) Thermal stability and gross material compatibility were adequate over the temperature range 21 to 149°C (70 to 300°F) as determined by the DSC.

(3) Formulations with up to 20 wt % HMX could be safely processed in the JPL-ETS facilities as per established standard operating procedures.

Safety tests were also performed on samples from 10-g hand mixes to check material capability and propellant safety properties when the pot-life extenders UOP-36 and DTBH were incorporated into AN/HMX/AP/Al/HTPB propellants. Selected level for both UOP-36 and DTBH was 0.04 wt %. Impact sensitivity, electrostatic sensitivity, and thermal stability (DSC) tests were made on samples from the mix with the pot-life extenders, SB-127, and on samples from a control mix without the pot-life extenders, SB-126. The formulations and test results were shown in Table 3-33. General conclusions from these tests were:

(1) The mix with the pot-life extenders had essentially the same impact sensitivity and electrostatic sensitivity as the control mix.

(2) Thermal stability and gross material compatibility were adequate over the temperature range 21 to 149°C (70 to 300°F) (DSC).

b. <u>Burning Rate Studies</u>. Six small-scale batches were made varying HMX particle size at two sizes, Class A ($\cong$149 μm) and Class E (15 to 20 μm), and HMX level at three levels: 10, 15 and 20 wt %. Objective of this study was to determine the effects of HMX particle

Table 3-31. Summary of Propellant Safety Tests (10-g hand mixes)

Batch No.	SB-57 (uncured)	SB-58
Formulation No.	AN-49	AN-50
Formulation (parts by weight)		
R-45		
Alrosperse Premix	11.08	11.08
DOA (40%)		
Aluminum	15.00	15.00
Ammonium dichromate, ground 6 μm	2.00	2.00
Copper chromite, as received	2.00	2.00
Ammonium perchlorate, ground 9 μm	10.00	10.00
HMX, Type II, Class A (1% DOA coated)	20.20	20.20
Ammonium nitrate, ground	39.10	39.10
IPDI	none	0.62
	99.38	100.00
Impact Sensitivity, cm (in.) for 1.8-kg (4-lb) weight		
0% Fire	38.1 (15)[a]	53.34 (21)
50% Fire	43.18 (17)[a]	57.15 (22.5)
Electrostatic Sensitivity, J	>12.8	>12.8
Thermal Stability (DSC at 10°C/min heating rate)	No exotherm over temperature range 21 to 149°C (70 to 300°F)	No exotherm over temperature range 21 to 149°C (70 to 300°F)

[a]Mixes very dry. Impact tests may be biased by voids in samples.

Table 3-32. Comparison of Safety Properties - Candidate Alternate AN/HMX/AP/Al/HTPB Propellant Formulation vs Baseline (PBAN) Formulation (AN-50)

Formulation	TP-H-1123 (PBAN baseline)	AN-50
Batch Number	SB-77	SB-58
Ingredients, wt %		
PBAN binder	14.00	---
HTPB binder	---	11.90
Aluminum	16.00	15.00
Ballistic modifiers	0.40	4.00
Ammonium perchlorate	69.60	10.00
Ammonium nitrate	---	39.10
HMX, Type II, Class A	---	20.00
Impact Sensitivity, cm (in.) for 1.8-kg (4-lb) weight		
0% fire	45.72 (18)	53.34 (21)
50% fire	49.53 (19.5)	57.15 (22.5)
Electrostatic Sensitivity, J	>12.8	>12.8
Thermal Stability (DSC at 10°C/min heating rate)	No exotherm over temperature range 21 to 149°C (70 to 300°F)	No exotherm over temperature range 21 to 149°C (70 to 300°F)

size and level on propellant hazard classification (card gap tests), strand burning rates, and relative castability. Tests were performed on samples from each of these batches, and the results are summarized in Tables 3-34 and 3-35 along with the formulations. Results of the card gap tests and relative castability are discussed in the hazards classification and processing sections, respectively. The strand burning rates at 690 N/cm^2 (1000 psia) were plotted versus HMX level in Fig. 3-13 for the two different HMX particle sizes, Class A and Class E. Although the strand burning rates are biased to faster values by the

Table 3-33. UOP-36 and DTBH in AN/HMX/AP/Al/HTPB Propellant Safety Tests

Formulations for 10-g Hand Mixes		
Batch No.	SB-126	SB-127
Formulation No.	ANH-16A (Control)	ANH-30
Ingredients, wt %		
HTPB binder (40% IDP plasticized)	12.00	11.92
Aluminum	15.00	15.00
Ammonium dichromate, attritor ground (4.4 μm)	2.00	2.00
Copper chromite, attritor ground (1.7 μm)	2.00	2.00
HMX, Class E	17.00	17.00
Ammonium nitrate, unground Monsanto	29.00	29.00
Ammonium nitrate, coarse ground Monsanto	13.00	13.00
Ammonium perchlorate, fluid energy mill ground (6.3 μm)	10.0	10.00
UOP-36 (N-phenyl-N'-cyclohexyl-P-phenylene diamine)	—	0.04
DTBH (ditertiary butyl hydroquinone)	—	0.04
	100.00	100.00
Safety Tests (Cured Propellant)		
Impact Sensitivity, cm (in.) for 1.8-kg (4-lb) weight)		
0% Fire	43 (17)	57 (19)
50% Fire	52 (20.5)	51 (20)

Table 3-33. UOP-36 and DTBH in AN/HMX/AP/Al/HTPB Propellant Safety Tests (Continuation 1)

Electrostatic Sensitivity, J	>12.8	>12.8
Thermal Stability (DSC at 10°C/min heating rate)	No exotherm over temperature range 21 to 149°C (70 to 300°F)	No exotherm over temperature range 21 to 149°C (70 to 300°F)

RAM-225 release agent, the relative ranking and trends are believed to be valid. General conclusions from these rankings and trends are as follows:

(1) The fine particle size HMX, Class E (15-20 μm) gave significantly faster burning rates than the coarse Class A (≅149 μm) HMX.

(2) The fine particle size HMX, Class E, gave lower pressure exponent than the coarse Class E HMX.

(3) Strand burning rates at 690 N/cm^2 (1000 psia) increased significantly with HMX level to about 15 wt % and tended to level in the 15 to 20 wt % range.

From burning rate considerations the fine size, Class E, HMX was preferred because it gave faster burning rates at 690 N/cm^2 (1000 psia) and lower pressure exponents. Formulation ANH-5A [Batch SB-85A(HMX)] was selected for additional evaluation in a scale-up batch and motor tests. Results of these additional tests are discussed in Sections III-H-10-f and III-H-10-g on Scale-up and Ballistic Evaluation.

Cured propellant strands to this point in the program had been prepared by casting the uncured propellant into molds which formed individual strands and which had been coated with RAM-225 release agent. Test data from the 4.5-kg (10-lb) motor firings from Batch SB-89 (first scale-up batch) revealed a large discrepancy between strand burn rates and the 4.5-kg (10-lb) motor burn rates. An investigation of this discrepancy revealed that the RAM-225 was the cause. Strands were prepared in the following three ways and tested for comparison:

(1) Strands cured in the RAM-225 release molds and restricted.

(2) Strands cut from a solid block of cured propellant and restricted.

(3) Strands cut from a block of cured propellant, then given light spray coat of RAM-225, dried in 71°C (160°F) oven, then restricted.

Table 3-34. AN/HMX/AP/Al/HTPB Formulations - HMX Level Variation (Class A HMX)

Batch No.	SB-88	SB-83	SB-84
Formulation No.	ANH-8	ANH-3	NH-4
Ingredients, wt %			
HTPB binder (40% DOA plasticizer)	12.00	12.00	12.00
Aluminum	15.00	15.00	15.00
Ammonium dichromate, ground	2.00	2.00	2.00
Copper chromite	2.00	2.00	2.00
HMX, Class A	10.00	15.00	20.00
Ammonium nitrate (Gulf Oil without anticaking agent)	49.00	44.00	39.00
Ammonium perchlorate, ground	10.00	10.00	10.00
Card Gap Tests:			
0 cards	2 negative	—	—
35 cards	1 negative	1 positive	1 positive
70 cards	—	2 positive	2 positive
Strand Burning Rates[a] at 25°C (77°F), cm/s (in./s)			
At 345 N/cm^2 (500 psia)	0.480(0.189)[a]	0.622(0.245)[a]	0.541(0.213)[a]
At 690 N/cm^2 (1000 psia)	0.665(0.262)[a]	0.826(0.325)[a]	0.747(0.294)[a]
Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.48	0.41	0.47

Table 3-34. AN/HMX/AP/Al/HTPB Formulations - HMX Level Variation (Class A HMX) (Continuation 1)

Shore A Hardness (3 s)	81	80	82
Relative Castability	Good	Good	Good

[a]Strands were cast into a mold with RAM-225 release agent. This release agent caused strands to show erroneously fast burn rates.

Results of the tests are summarized in Table 3-36 and Fig. 3-14. Very good agreement was obtained between the burn rate of strands cured in the RAM-225 release mold and strands cut from a cured block of propellant and then sprayed with RAM-225. However, both these sets of burn rates were erroneously fast compared to the 5 x 10 motor burn rates. In contrast the strand burn rates obtained from cut strands which were not treated with RAM-225 were much slower and agreed fairly well with motor data.

A brief investigation was made to determine the composition of RAM-225 and whether it could be used as an improved ballistic modifier in the propellant formulation. Chemical analysis of RAM-225 indicated that it is a high molecular weight silicone oil in the solvents isopropanol and heptane. Two 3.8-liter (1-gal) batches of propellant were made with 0.15 wt % dimethyl silicone (1000 cS). One batch had 4.00 wt % mixed ballistic modifiers (ammonium dichromate and copper chromite) and the other batch had 2.00 wt % mixed ballistic modifier. Both batches made with the 0.15 wt % dimethyl silicone showed signs of viscosity buildup even before curative addition. The batch with the 2.00 wt % mixed ballistic modifier became too viscous to process to completion. Tests results on the successfully completed batch with 0.15 wt % dimethyl silicon [Batch SB-107 (HMX)] are shown in Table 3-37. Test results from Batch SB-108 (HMX) are also included in this table for comparative purposes. General conclusions from these tests are as follows.

(1) No significant changes in strand burning rates were observed due to addition of 0.15 wt % dimethyl silicone.

(2) The dimethyl silicone caused rapid propellant viscosity buildup even before curative addition, and therefore the material appears impractical from propellant processing considerations.

A series of six small-scale (1000 g) batches was made with the specific objectives of increasing propellant burn rate, improving castability, and improving burn rate reproducibility. U.S. Agri-Chemicals (U.S. Steel) ammonium nitrate with anticaking agent was used for all six batches. The following variables were evaluated.

Table 3-35. AN/HMX/AP/Al/HTPB Formulations -- HMX Level Variation (Class E HMX)

Batch No.	SB-87	SB-85A	SB-86
Formulation No.	ANH-7	ANH-5A	ANH-6
Ingredients, wt %			
HTPB Binder (40% DOA plasticizer)	12.00	12.00	12.00
Aluminum	15.00	15.00	15.00
Ammonium dichromate, ground	2.00	2.00	2.00
Copper chromite	2.00	2.00	2.00
HMX, Class E	10.00	15.00	20.00
Ammonium nitrate (Gulf Oil without anticaking agent)	49.00	44.00	39.00
Ammonium perchlorate, ground	10.00	10.00	10.00
Card Gap Tests:			
0 cards	2 neg.	—	—
32 cards	—	1 neg.	—
35 cards	1 neg.	2 neg.	1 pos.
70 cards	—	—	1 pos.
Strand Burning Rates at 25°C (77°F), cm/s (in./s)			
At 345 N/cm^2 (500 psia)	0.767(0.302)[a]	0.930(0.366)[a]	0.912(0.359)[a]
At 690 N/cm^2 (1000 psia)	0.970(0.382)[a]	1.105(0.435)[a]	1.128(0.444)[a]
Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.33	0.24	0.31

Table 3-35. AN/HMX/AP/Al/HTPB Formulations - HMX Level Variation (Class E HMX) (Continuation 1)

Shore A Hardness (3 s)	90	89	88
Relative Castability	Fair	Fair	Marginal

[a]Strands were cast into a mold with RAM-225 release agent. This release agent caused strands to show erroneously fast burn rates.

(1) Ammonium nitrate particle size. Replacement of part or all of the large unground prills by a coarse-ground ammor nitrate.

(2) Plasticizer type. Replacement of DOA (dioctyl adipate) by IDP (isodecyl pelargonate).

Relative castability and strand burn rates were measured on each batch. Results of this study are summarized in Tables 3-38 and 3-39 and Fig. 3-15. General conclusions regarding propellant burn rates from the study were as follows:

(1) Replacement of the very large unground ammonium nitrate prills by coarsely ground ammonium nitrate <u>reduced</u> propellant burning rate.

(2) Replacement of DOA by IDP slightly reduced propellant burning rate ($\cong$2%).

(3) Strand pressure exponents were typically 0.36 or less, well within the goal of $\leq$0.42.

(4) The U.S. Agri-Chemical (U.S. Steel) ammonium nitrate with anticaking agent handled without caking and had less tendency to size reduce during handling and mixing. These factors should improve propellant burn rate reproducibility.

The reduction in burn rate by replacement of unground prills with coarsely ground AN was unexpected and inconsistent with usual solid propellant experience. Usually propellant burn rate increases with increasing fractions of ground oxidizer. The mechanism for this unusual response has not been identified to date. Formulation ANH-12, Batch SB-94 (HMX), had the fastest burn rate, 0.836 cm/s at 690 N/cm^2 (0.329 in./s at 1000 psia), consistent with acceptable castability. Therefore, it was selected for additional evaluation in a scale-up batch and motor tests.

Two small-scale batches (1500 g) were made to evaluate the effect of replacing hammer mill ground AP with the finer fluid energy mill (FEM) ground AP on propellant properties. Micromerograph analysis

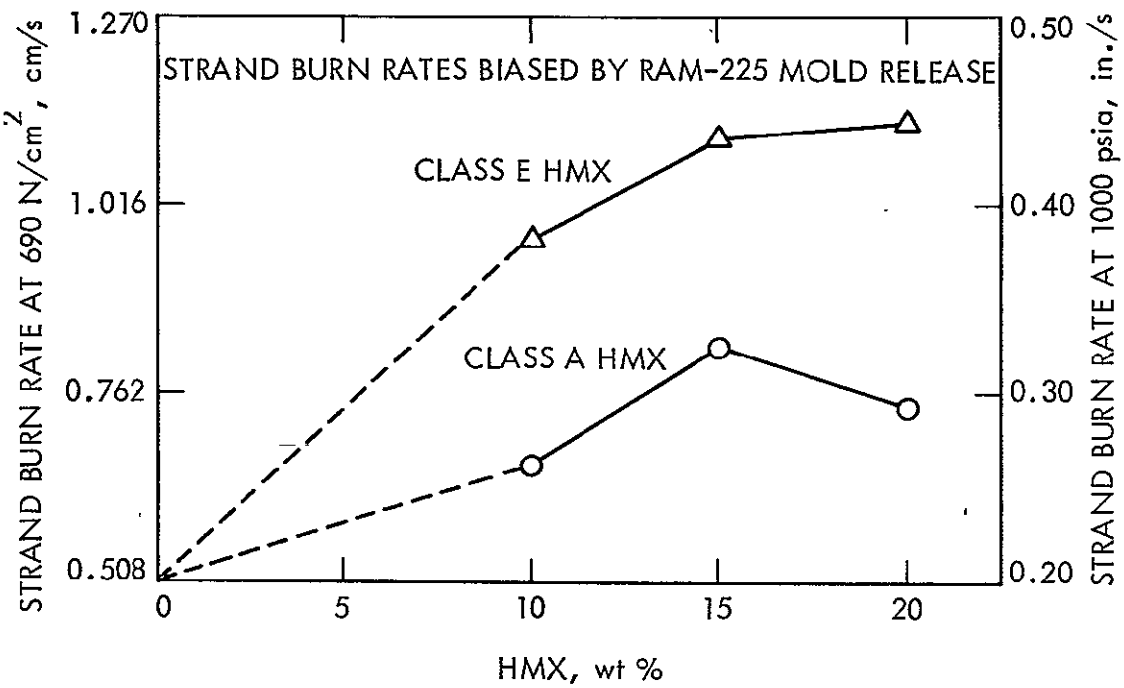

Fig. 3-13. Strand Burn Rate vs Weight Percent HMX for AN/HMX/AP/Al/HTPB Propellant

Table 3-36. Investigation of RAM-225 Release Agent Burning Rates of Propellant Batch No. SB-89 (HMX)

Pressure, N/cm^2 (psia)	Strand Burning Rate, cm/s at 25°C (in./s at 77°F)			
	Strands cured in RAM-225 released mold	Strands cut from cured block of propellant	5 x 10 motor firings	Strands cut from cured block of propellant, sprayed with RAM-225, dried, and tested
690 (1000)	0.991 (0.390)	0.721 (0.284)	0.660 (0.260)	0.983 (0.387)
517 (750)	0.876 (0.345)	—	0.662 (0.245)	—
345 (500)	0.765 (0.301)	0.599 (0.236)	0.549 (0.216)	0.785 (0.309)
172 (250)	0.572 (0.225)	—	0.457 (0.180)	—
Pressure exponent	0.42	0.27	0.28	0.33

indicated that the fluid energy mill AP had a mass median diameter of 6.3 μm compared to 9.0 μm for typical hammer mill ground AP. Batch SB-110 (HMX) was made using 17.00 wt % Class E HMX and 10.00 wt % of the FEM AP. A reference batch, SB-98 (HMX), was made using the hammer mill ground AP. Strand burn rates and relative castability were determined on both of the batches. Results are shown in Table 3-40 and Fig. 3-16.

(1) Replacement of the hammer mill ground (9 μm) AP by the FEM ground (6.3 μm) AP increased strand burn rate to 0.950 cm/s at 690 N/cm^2 (0.374 in./s at 1000 psia). This exceeds the burn rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia).

(2) Strand pressure exponent appeared to be reduced with use of the FEM ground AP.

Two small-scale batches (1500 g) were made to evaluate the effect of finer ballistic modifier particle size on propellant properties. As discussed in the AN/AP/HTPB propellant development section, an attritor mill was used to size reduce the ballistic modifiers, ammonium dichromate and copper chromite. Batch SB-117 (HMX) was made using 2.00 wt %

Table 3-37. AN/HMX/AP/HTPB Formulations - Ballistic Modifier Type and Level Variation

Batch No. Formulation No.	SB-108 (Reference) AN-20	SB-107 ANH-19	SB-109 ANH-21
Ingredients, wt %			
HTPB binder (40% plasticizer)	12.00	11.85	11.85
Aluminum	15.00	15.00	15.00
Ammonium dichromate, ground	2.00	2.00	1.00
Copper Chromite	2.00	2.00	1.00
Dimethyl silicone (1000 cS)	—	0.15	0.15
HMX, Class E	20.00	20.00	20.00
Ammonium nitrate, unground U.S. Steel with anti-caking agent	—	29.00	31.00
Monsanto phase stabilized	29.00	—	—
Ammonium nitrate, coarse ground U.S. Steel with anti-caking agent	—	10.00	10.00
Monsanto phase stabilized	10.00	—	—
Ammonium perchlorate, ground	10.00	10.00	10.00

Table 3-37. AN/HMX/AP/HTPB Formulations - Ballistic Modifier Type and Level Variation (Continuation 1)

Relative Castability	Excellent castability	Uncastable	Mix could not be completed; cured up in mix bowl
Strand burning rates at 25°C (77°F), cm/s (in./s)			
At 345 N/cm^2 (500 psia)	0.665 (0.262)	0.673 (0.265)	—
At 690 N/cm^2 (1000 psia)	0.818 (0.322)	0.808 (0.318)	—
Pressure exponent 345 to 690 N/cm^2 (500 to 1000 psia)	0.30	0.26	—
Card gap tests:			
35 cards	—	—	—
55 cards	—	—	—
69 cards	3 positive	3 positive	—

attritor ground (1.7 μm) copper chromite, 17.00 wt % Class E HMX, and FEM ground (6.3 μm) AP. No ammonium dichromate was used in this batch as a part of the overall effort to achieve the burning rate goal, 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia), with improved performance (I_{sp}), castability, and physical properties. Reference Batch SB-116 (HMX) was made using as received (2.1 μm) copper chromite. Table 3-41 summarizes results of Brookfield end-of-mix viscosity and strand burn rate tests on these two batches. These results led to the following conclusions:

(1) In an IDP plasticized formulation using only 2.00 wt % CU-0202 P as ballistic modifier, coarse ground AN, and 6.3 μm FEM ground AP, reducing the CU-0202 P particle size from 2.1 to 1.7 m increased the strand burn rate at 690 N/cm^2 (1000 psia) from 0.724 to 0.737 cm/s (0.285 to 0.290 in./s), $\cong$2%.

(2) No significant change in strand pressure exponent was observed.

(3) Castability was good for both batches.

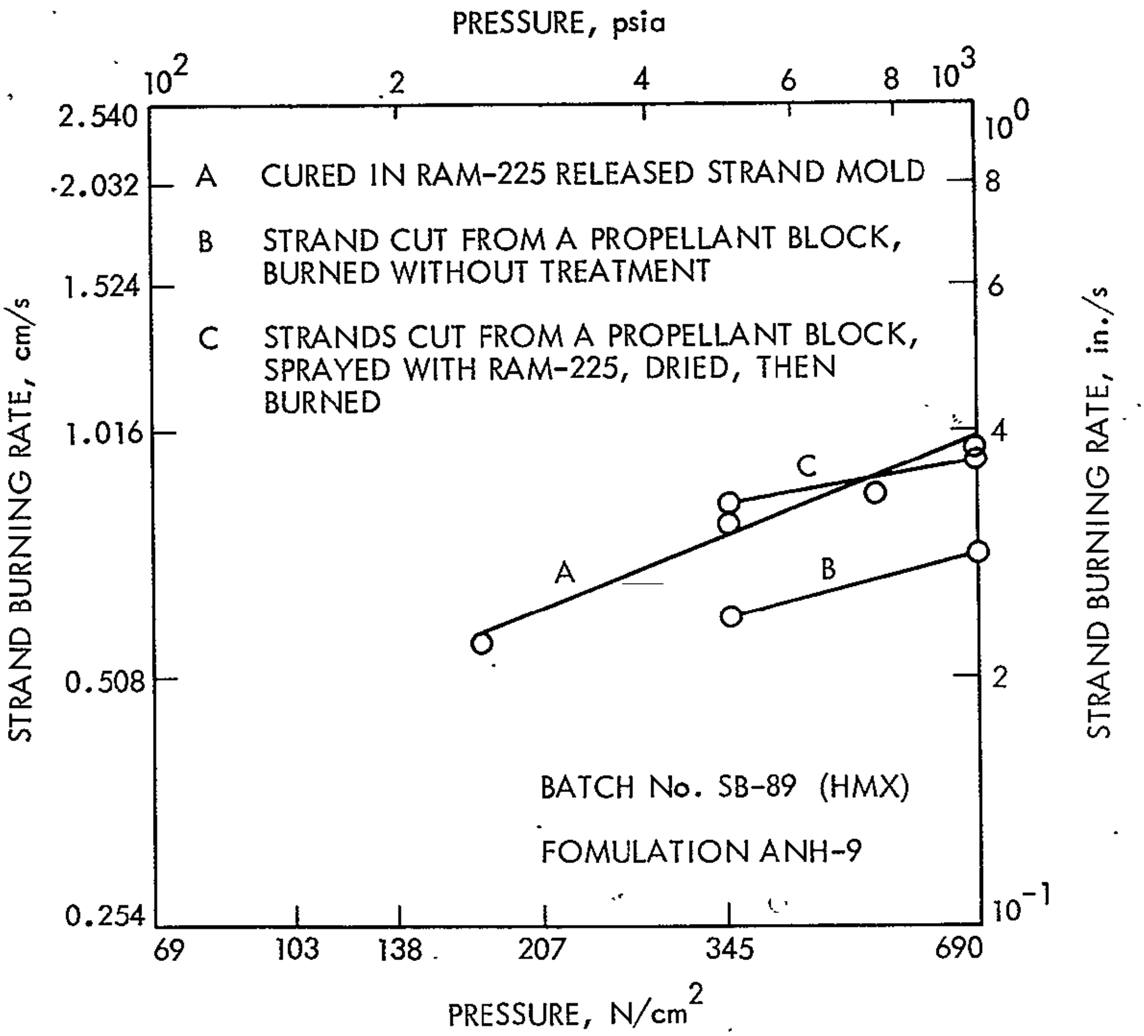

Fig. 3-14. Crawford Bomb Burning Rates, Batch No. SB-89 (HMX), Formulation ANH-9

Table 3-38. AN/HMX/AP/Al/HTPB Formulations - AN Particle Size Variation (Class E HMX - DOA Plasticizer)

Batch No. Formulation No.	SB-90 ANH-9	SB-91 ANH-10	SB-93 ANH-11	SB-95 ANH-13
Ingredients, wt %				
HTPB binder (40% DOA plasticizer)	12.00	12.00	12.00	12.00
Aluminum	15.00	15.00	15.00	15.00
Ammonium dichromate, ground	2.00	2.00	2.00	2.00
Copper chromite	2.00	2.00	2.00	2.00
HMX, Class E	15.00	15.00	15.00	15.00
Ammonium nitrate, unground (U.S. Steel with anti-caking coating)	44.00	29.00	17.60	—
Ammonium nitrate, coarse ground (U.S. Steel with anticaking coating)	—	15.00	26.40	44.00
Ammonium perchlorate, ground	10.00	10.00	10.00	10.00
Relative castability	Uncastable	Uncastable	Marginally castable	Castable
Strand burning rates at 25°C (77°F), cm/s (in./s)[a]				
At 345 N/cm^2 (500 psia)	—	0.678 (0.267)[a]	0.678 (0.234)[a]	0.516 (0.203)[a]
At 690 N/cm^2 (at 1000 psia)	0.953 (0.375)[a]	0.859 (0.338)[a]	0.859 (0.299)[a]	0.665 (0.262)[a]
Pressure exponent 345 to 690 N/cm^2 (500 to 1000 psia)	—	0.34	0.35	0.36

[a]Propellant was cast into bulk propellant sample and strands were cut from bulk sample into final form. Strand burn rates are not biased by RAM-225 release agent.

Table 3-39. AN/HMX/AP/Al/HTPB Formulations - AN Particle Size Variation (Class E HMX - IDP Plasticizer)

Batch No.	SB-94	SB-96
Formulation No.	ANH-12	ANH-14
Ingredients, wt %		
HTPB binder (40% IDP plasticizer)	12.00	12.00
Aluminum	15.00	15.00
Ammonium dichromate, ground	2.00	2.00
Copper chromite	2.00	2.00
HMX, Class E	15.00	15.00
Ammonium nitrate, unground (U.S. Steel with anticaking coating)	29.00	—
Ammonium nitrate, coarse ground (U.S. Steel with anticaking coating)	15.00	44.00
Ammonium perchlorate, ground	10.00	10.00
Relative Castability	Good castability	Excellent castability
Strand burning rates at 25°C (77°F), cm/s (in./s)[a]		
At 345 N/cm^2 (500 psia)	—	0.518 (0.204)[a]
At 690 N/cm^2 (1000 psia)	0.836 (0.329)[a]	0.655 (0.258)[a]
Pressure exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	—	0.35

[a]Propellant was cast into bulk propellant sample and strands were cut from bulk sample into final form. Strand burn rates are <u>not</u> biased by RAM-225 release agent.

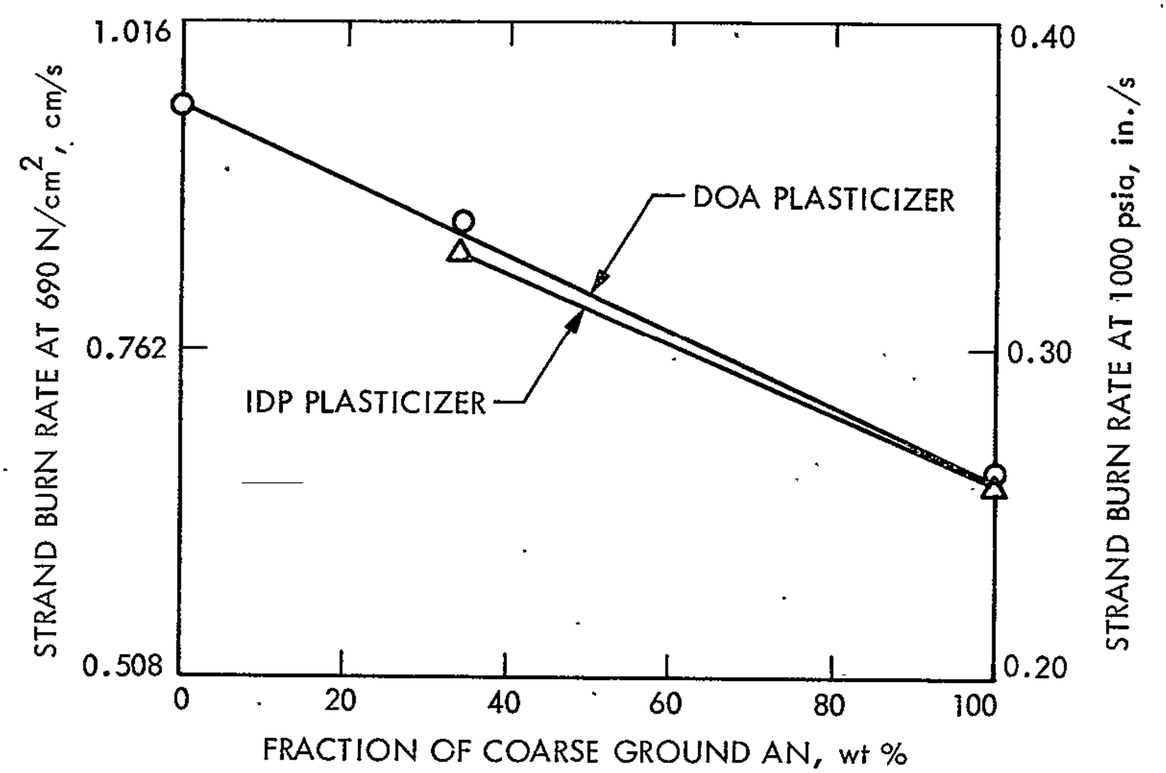

Fig. 3-15. Strand Burn Rates vs Fraction AN Coarse Ground AN/HMX/AP/Al/HTPB Propellant, U.S. Steel AN

Table 3-40. AN/HMX/AP/Al/HTPB Formulations - AP Particle Size Variation (HMX)

Batch No. Formulation No.	SB-98 ANH-16 Reference	SB-110 ANH-16
Ingredients, wt %		
HTPB binder (40% plasticizer)	12.00	12.00
Aluminum	15.00	15.00
Ammonium dichromate, ground	2.00	2.00
Copper chromite	2.00	2.00
HMX, Class E	17.00	17.00
Ammonium nitrate, unground	27.00	27.00
Ammonium nitrate, coarse ground	15.00	15.00
Ammonium perchloriate, hammer mill ground (Micromerograph, 50 wt % point 9 μm)	10.00	—
Ammonium perchlorate, fluid energy mill ground (Micromerograph, 50 wt % point 6.3 μm)	—	10.00
Strand Burning Rates at 25°C (77°F), cm/s (in./s)		
At 345 N/cm² (500 psia)	0.653 (0.257)	0.843 (0.332)
At 690 N/cm² (1000 psia)	0.810 (0.319)	0.950 (0.374)
Strand Pressure Exponent, 345 to 690 N/cm² (500 to 1000 psia)	0.30	0.17
Relative Castability	Good castability	Good castability, slightly more viscous than SB-98 (HMX)

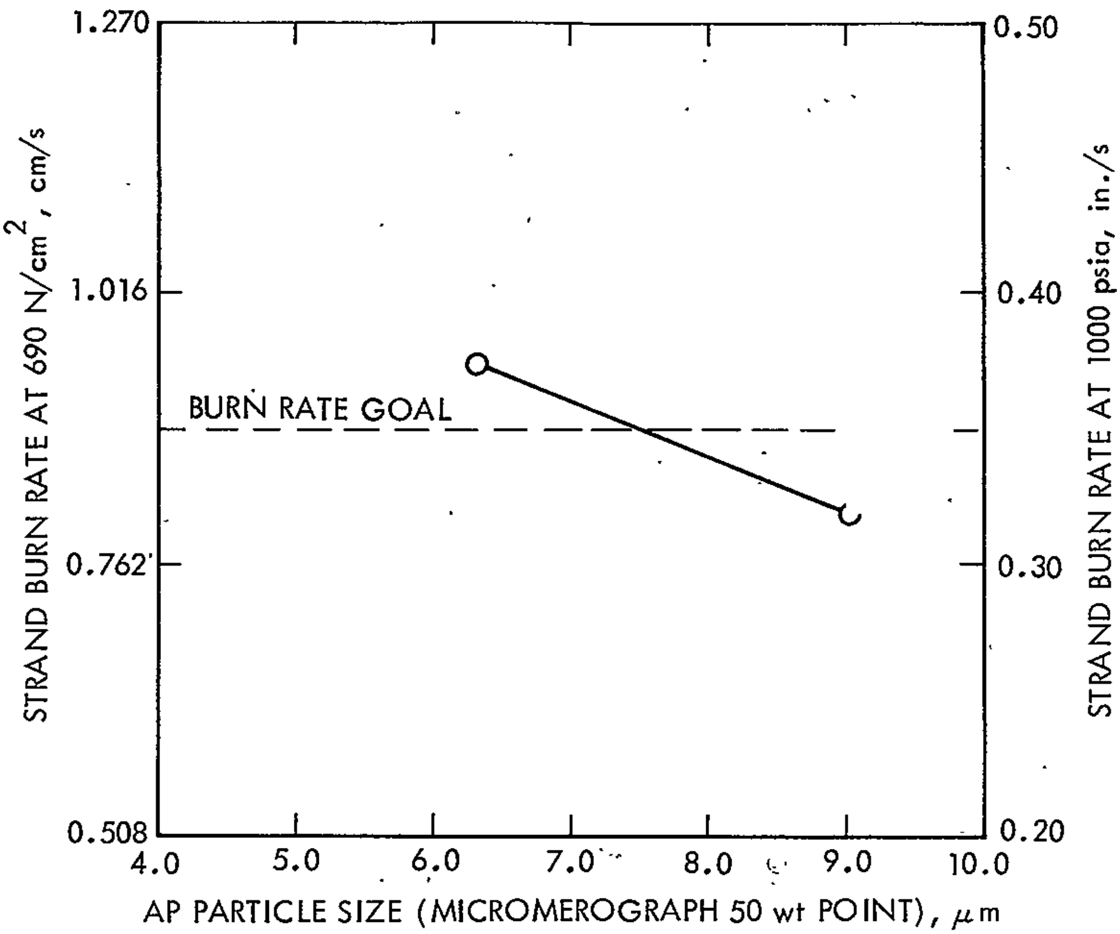

Fig. 3-16. Strand Burn Rates vs AP Particle Size, AN/HMX/AP/Al/HTPB Propellant

Table 3-41. AN/HMX/AP/Al/HTPB Formulations - Ballistic Modifier Particle Size Variation

Batch No.	SB-116 (Reference)	SB-117
Formulation No.	ANH-24A	ANH-24B
Ingredients, wt %		
HTPB binder (40 wt % IDP plasticized)	12.00	12.00
Aluminum	15.00	15.00
Copper chromite		
As received (2.1 μm)	2.00	—
Attritor ground (1.7 μm)	—	2.00
HMX, Class E	17.00	17.00
Ammonium nitrate, unground Monsanto	29.00	29.00
Ammonium nitrate, coarse ground Monsanto	15.00	15.00
Ammonium perchlorate, FEM ground	10.00	10.00
Total	100.00	100.00
Relative castability	Good	Good
Brookfield end-of-mix viscosity, kP at 52°C (125°F)	16.8	13.6
Strand burning rates at 25°C (77°F), cm/s (in./s)		
At 345 N/cm^2 (500 psia)	0.610 (0.240)	0.627 (0.247)
At 690 N/cm^2 (1000 psia)	0.724 (0.285)	0.737 (0.290)
Strand pressure exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.28	0.24

As was observed with the AN/AP/Al/HTPB propellant reduction of the ballistic modifier, particle size did not prove to be an effective approach to increasing burn rates.

Three small-scale (1500 g) batches were made to better optimize the ballistic modifier system for the basic AN/HMX/AP/Al/HTPB propellant. Previous to this point in the program, the mixed ballistic modifier system of 2.00 wt % ground ammonium dichromate (AD), with 2.00 wt % copper chromite (CU-0202 P), was used. It was desirable to reduce the total ballistic modifier level to less than 4.00 wt % and recover some performance (I_{sp} delivered.) Elimination of AD was also desirable because of its tendency to crosslink the R-45 prepolymer with subsequent degradation of propellant castability and physical properties. Batches SB-132 (HMX) and SB-138 (HMX) were made using only as-received CU-0202 P as the ballistic modifier at the 2.00 wt % and 3.00 wt % levels, respectively. The objective of testing these two batches was to determine whether the burning rate goal of 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia) could be achieved by using only CU-0202 P at levels less than 4.00 wt %. Brookfield end-of-mix and strand burning rates were measured on both batches. Results of these tests are shown in Table 3-42 and they indicated the following:

(1) Strand burning rate achieved with 3.00 wt % as-received CU-0202 P was only 0.810 cm/s (0.319 in./s) at 690 N/cm^2 (1000 psia).

(2) Based on extrapolation, the burning rate goal of 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia) does not appear achievable even at 4.00 wt % as-received CU-0202 P.

(3) A mixed ballistic modifier system of AD and CU-0202 P appears necessary to meet the burning rate goal.

The third batch, SB-134 (HMX), was made using the mixed ballistic modifier system of 1.00 wt % hammer mill ground (7.2 m) AD and 2.00 wt % as-received CU-0202 P. Brookfield viscosity and strand burning rates were also measured on this batch and results are also shown in Table 3-42. They indicated the following:

(1) Strand burning rate of 0.879 cm/s at 690 N/cm^2 (0.346 in./s at 1000 psia) was achieved with Batch SB-134 (HMX). This almost meets the goal of 0.89 cm/s (0.35 in./s) at 690 N/cm^2 (1000 psia).

(2) End-of-mix viscosity of 21 kP at 52°C (125°F) indicated the propellant had acceptable castability.

Limited time and budget did not allow for any additional optimization of the ballistic modifier system. Therefore, Formulation ANH-33 [Batch SB-134 (HMX)] was selected for evaluation in a scale-up batch and motor tests. Results of these additional tests are discussed in the sections on Scale-Up and Ballistic Evaluation.

Table 3-42. Optimization of Ballistic Modifier System for AN/HMX/AP/Al/HTPB Propellant

Batch No.	SB-132	SB-138	SB-134
Formulation No.	ANH-34	ANH-32	ANH-33
Ingredients, wt %			
HTPB binder (40 wt % IDP plasticized)	12.00	12.00	12.00
Aluminum, MD-105	15.00	15.00	15.00
Copper chromite, as received 2.1 μm	2.00	3.00	2.00
Ammonium dichromate, Hammer mill ground 7.2 μm	---	---	1.00
Ammonium nitrate, unground Monsanto	29.00	28.00	28.00
Ammonium nitrate, coarse ground Monsanto	15.00	15.00	15.00
HMX, Class E	17.00	17.00	17.00
Ammonium perchlorate, FEM ground 6.3 μm	10.00	10.00	10.00
	100.00	100.00	100.00
Brookfield End-of-mix Viscosity, kP at 52°C (125°F)	33	Could not measure	21
Strand burning rates at 25°C (77°F), cm/s (in./s)			
At 345 N/cm^2 (500 psia)	0.594 (0.234)	0.630 (0.248)	0.615 (0.242)
At 690 N/cm^2 (1000 psia)	0.757 (0.298)	0.810 (0.319)	0.879 (0.346)
Strand Pressure Exponent, 345 to 690 N/cm^2 (500 to 1000 psia)	0.35	0.36	0.51

In summary the following approaches were investigated as methods of achieving faster propellant burning rates and the goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia):

(1) HMX class (particle size).

(2) HMX level.

(3) Dimethyl silicone as ballistic modifier.

(4) Finer AN particle size.

(5) Finer AP particle size.

(6) Finer CU-0202 P particle size.

(7) Ballistic modifier type and level.

Of these only (1), (2), (5), and (7) proved to be effective approaches to faster burning rates.

c. Hazards Classification. The Naval Ordnance Station (NOS) did some of the initial propellant hazard classification testing to define the maximum level of HMX which could be used and remain a Class 2 propellant. The basic AN/HMX/AP/Al/HTPB formulation selected for testing was an 88 wt % total solids HTPB (R-45) formulation with 15.0 wt % aluminum and 10 wt % ammonium perchlorate. Tests were planned on formulations with and without the ballistic modifiers AD and CU-0202 P. Table 3-43 summarizes results of these hazard tests. These results indicated that 20 wt % Class E HMX (15 μm)in non-ballistic modified formulations gave propellants which marginally met card gap requirements for Class 2 propellant (<70 cards). AP particle size appeared to affect card gap test results. No firm conclusions could be made regarding the ballistic modified formulations.

This effort to define the maximum HMX level for a Class 2 ballistic modified propellant was continued by the Jet Propulsion Laboratory (JPL) with AFRPL support. Card gap tests made on the ballistic modified formulations reported in Tables 3-34 and 3-35 are summarized in Table 3-44 for convenience.

General conclusions from this work were as follows:

(1) Maximum level of Class A HMX is greater than 10.00 wt % and less than 15.00 wt % for a ballistic modified formulation to meet Class 2 card gap requirements (<70 cards).

(2) Maximum level of Class E HMX is greater than 15.00 wt % and less than 20.00 wt % for a ballistic modified formulation to meet Class 2 card gap requirements (<70 cards).

Table 3-43. NOS Hazard Test Data

	Propellant Formulations					
Batch No.	64	66	68	69	73	81
Ingredients, wt %						
AN (unground)	43.0	43.0	47.76	42.79	39.0	38.62
AP 45 µm	10.0	—	—	—	—	—
AP 6 µm	—	—	9.95	9.95	—	—
AP 4 µm	—	10.0	—	—	—	—
AP 2 µm	—	—	—	—	10.0	9.9
HMX 15 µm	20.0	20.0	14.93	19.90	20.0	19.8
Al, H-12	15.0	15.0	14.93	14.93	15.0	14.85
HTPB Binder	12.0	12.0	12.43	12.43	12.0	12.87
AD (Ballistic Modifier)	—	—	—	—	2.0	1.98
CU-0202 P (Ballistic Modifier)	—	—	—	—	2.0	1.98
Lab Safety Tests:						
Impact sensitivity, mm	375	375	350	275	—	—
Friction, kg (lb)	≥444 (980)	≥444 (980)	≥444 (980)	≥444 (980)	—	—
ESD, J	≥12.5	≥12.5	≥12.5	≥12.5		
Field Safety Tests:						
Card gap, cards	55 to 60	65 to 70	0	60 to 65	35 to 50	55 to 60
Cap	neg	neg	neg	neg	neg	neg

Table 3-43. NOS Hazard Test Data (Continuation 1)

	Propellant Formulations					
Batch No.	64	66	68	69	73	81
Unconfirmed burning	neg	neg	neg	neg	neg	neg
Critical dia., cm (in.)	>6.4 (2.5)	>6.4 (2.5)	>6.4 (2.5)	>6.4 (2.5)	<8.9 (3.5)	<8.9 (3.5)

[a]X-ray of samples showed evidence of voids.

Table 3-44. JPL Hazard Test Data (Comparing Class A with Class E)

Batch No.	HMX		Card Gap		
	Wt %	Class	Positive	Negative	Cards
SB-88	10	A	—	2	0
			—	1	35
SB-83	15	A	1	—	35
			2	—	70
SB-84	20	A	1	—	35
			2	—	70
SB-87	10	E	—	2	0
			—	1	35
SB-85A	15	E	—	1	32
			—	2	35
SB-86	20	E	1	—	35
			1	—	70

Class E HMX was selected because higher levels could be incorporated and remain a Class 2 propellant, and because it gave the best ballistic properties.

Two additional small-scale (1500 g) batches were made to better define the maximum level of Class E HMX. The Class E HMX was varied to the 19.00 wt % and 17.00 wt % levels for Batches SB-97 (HMX) and SB-98 (HMX), respectively. Card gap sensitivity, strand burning rates, and relative castability were measured in both batches. Table 3-45 shows the test results. These tests indicated the maximum level of Class E HMX is greater than 17.00 wt % and less than 19.00 wt % for a ballistic modified formulation to meet Class 2 card gap requirements (< 70 cards).

The 94.6-liter (25-gal) scale-up batches were made varying Class E HMX level to 15.00, 17.00, and 17.50 wt %. Card gap verification tests were made on these batches as shown later in Table 3-49, and test results are summarized in Table 3-46.

Results of all the tests indicated the maximum level of Class E HMX is greater than 17.00 wt % and less than 17.50 wt % for a ballistic modified formulation to meet Class 2 card gap requirements (< 70 cards).

d. Processing Studies. The relative castability of propellant was observed on the small-scale (1000 to 1500 g) development batches and used in the selection of formulations for evaluation in the 94.6-liter (25-gal) scale-up batches. Brookfield end-of-mix and pot life tests were measured on all of the 94.6-liter (25-gal) scale-up batches.

The coarse Class A HMX (≅149 μm) has a better particle size than the fine Class E HMX (15 - 20 μm) for solids packing. Consequently, the Class A HMX yielded propellants with better castability than the Class E HMX (Table 3-35). However, Class E HMX was selected for all the scale-up batches, because higher HMX levels could be used and ballistic properties were better (faster burn rates and lower pressure exponents). The level of HMX was generally limited by Class 2 card gap constraints before castability became unacceptable.

The lower viscosity plasticizer IDP yielded propellants with significantly better castability than the plasticizer DOA with only a slight loss in propellant burning rate at 690 N/cm^2 (1000 psia) (Tables 3-38 and 3-39). Therefore, IDP was the selected plasticizer.

Replacement of the very coarse unground AN prills by coarsely ground AN improved castability but reduced propellant burning rate. Consequently, the fraction of AN coarse ground was limited to 34% to maximize burn rate consistent with good castability (Tables 3-38 and 3-39.

Replacement of the hammer mill ground (9.0 μm) AP by the fluid energy mill ground (6.3 μm) AP made the propellant more viscous, but castability remained good (Table 3-40). This change significantly increased propellant burning rate and made the goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) achievable (Fig. 3-16.) Therefore, the fluid energy mill ground AP (6.3 μm) was selected for use when it became available.

Table 3-45. AN/HMX/AP/Al/HTPB Formulation - HMX Level (Class E HMX)

Batch No.	SB-97 ANH-15	SB-98 ANH-16
Ingredients, wt %		
HTPB binder (40% plasticizer)	12.00	12.00
Aluminum	15.00	15.00
Ammonium dichromate, ground	2.00	2.00
Copper chromite	2.00	2.00
HMX, Class E	19.00	17.00
Ammonium nitrate, unground (U.S. Steel with anticaking coating)	25.00	27.00
Ammonium nitrate, coarse ground (U.S. Steel with anticaking coating)	15.00	15.00
Ammonium perchlorate, ground	10.00	10.00
Relative Castability	Good castability	Good castability
Strand Burning Rates at 25°C (77°F), cm/s (in./s)		
At 345 N/cm^2 (500 psia)	0.678 (0.267)	0.653 (0.257)
At 690 N/cm^2 (1000 psia)	0.826 (0.325)	0.810 (0.319)
Pressure Exponent at 345 to 690 N/cm^2 (500 to 1000 psia)	0.28	0.30
Card Gap Tests:		
35 Cards	---	1 positive
55 Cards	---	1 positive
69 Cards	4 positive	2 negative

Table 3-46. JPL Hazard Test Data (Class E)

Batch No.	HMX		Card Gap		
	Wt %	Class	Positive	Negative	Cards
SB-89 (HMX)	15	E	4	6	0
			---	10	35
SB-92 (HMX)	15	E	3	2	0
			1	---	5
			1	---	10
			1	---	15
			1	---	20
			1	---	27
			---	3	30
			---	5	35
SB-106 (HMX)	17.5	E	2	---	69
			6	2	70
			1	---	35
SB-141 (HMX)	17	E	1	---	60
			1	---	61
			2	---	62
			1	3	63
			---	1	65
			---	10	69

Replacement of the as-received CU-0202 P (2.1 μm) by attritor ground CU-0202 P (1.7 μm) did not significantly affect propellant castability. Since this change increased burning rate by only 2%, the as-received (2.1 μm) CU-0202 P was selected. Increasing the Cu-0202 P level from 2.00 to 3.00 wt % significantly increased propellant viscosity, making it less castable (Table 3-42).

Use of the pot-life extenders UOP-36 and DTBH were shown to significantly improve castability and pot life with the AN/AP/Al/HTPB propellant. After checking to determine these materials were compatible and safety properties were adequate, these pot-life extenders were incorporated into the AN/HMX/AP/Al/HTPB propellant.

e. Combustion Problems. The problem of incomplete combustion of aluminum within the motor with subsequent loss of delivered specific impulse was addressed for the basic AN/HMX/AP/Al/HTBP propellant early in the program. Two approaches evaluated to improve metal combustion and delivered specific impulse were:

(1) Use of aluminum/magnesium (Al/Mg) alloys

(2) Replacement of aluminum by magnesium

This work (by NOS) was done concurrently with the development of the basic AN/HMX/AP/Al/HTPB propellant using conventional aluminum. For convenience and clarity all of the NOS propellant development work done with the R-45 HTPB binder is reported and discussed in this section.

Table 4-47 summarizes results of motor tests on AN/HMX/AP/Al/HTPB propellants with no ballistic modifiers. Propellant formulation variations made were:

(1) Total solids loading (87 to 88 wt %)

(2) AP particle size (20 and 200 μm)

(3) HMX (Class E) level (20 and 30 wt %)

(4) Metal level (15 to 20 wt %)

(5) Metal type (Al and Al/Mg alloy)

The motors tested were either 4.536-kg (10-lb) charge (TPC) motors or 18.14-kg (40-lb) charge (FPC) motors at sea level conditions. Corrections to vacuum conditions with $\epsilon = 6.85$ were made as shown in Table 4-47. General conclusions from this work were as follows:

(1) Motor burning rates at 483 N/cm^2 (700 psia) were all in the range of 0.356 to 0.457 cm/s (0.14 to 0.18 in./s). Ballistic modifiers are required to meet burning rate goal of 0.89 N/cm^2 (0.35 in./s) with a pressure exponent of $\cong$0.42.

Table 3-47. NOS Space Shuttle Alternate Propellant Development, Measured Ballistic Evaluation

Propellant Data						Specific Impulse, N-s/kg (s)		
Motor Type[b]	Percent of AP	AP Particle Size, m	Percent of HMX	Percent of Metal	Type of Metal	Delivered	Vacuum[d] $\epsilon = 6.85$	Burning rate at 483 N/cm^2 (700 psi), cm/s (in./s)
TPC	10	200	20	20	Aluminum	1947.6 (198.6)	-	0.356 (0.14)
TPC[a]		200	20	19	Al/Mg (90/10)	1976.0 (201.5)	2163.3 (220.6)	0.381 (0.15)
TPC		200	20	15	Aluminum	2111.4 (215.3)	2227.1 (227.1)	0.381 (0.15)
TPC		200	20	15	Al/Mg (90/10)	2035.9 (207.6)	2090.8 (231.2)	0.356 (0.14)
TPC		200	30	15	Aluminum	2039.8 (208.0)	2246.7 (229.1)	0.356 (0.14)
TPC		200	30	15	Aluminum	2090.8 (213.2)	2313.4 (235.8)	0.356 (0.14)
TPC		20	20	15	Aluminum	2104.5 (214.6)	2322.2 (236.8)	0.457 (0.18)
TPC		20	20	15	Aluminum	2090.8 (213.2)	2324.2 (237.0)	0.457 (0.18)
FPC		200	20	15	Aluminum	1919.2 (195.7)	2189.8 (223.3)	0.445 (0.175)

[a] 87.00 wt % total solids loaded propellant; the remainder are 88 wt %.
[b] TPC are 4.536-kg (10-lb) charge motor grains.
[c] FPC are 18.14-kg (40-lb) charge motor grains.
[d] All motor tests were made at sea level. Correction to vacuum conditions was made as follows:

$$\text{Vac } I_{sp} \text{ ms} = \frac{\int F dt \text{ ms} + P_a A_e t_a}{\text{[illegible]}}$$

Correction to desired expansion ratio (ϵ req.) was done by multiplying vac I_{sp} ms by $\frac{C_F \, \epsilon_{req}}{C_F \, \epsilon_{act}}$

(2) The maximum vac I_{sp} ms, $\epsilon = 6.85$, obtained for this series of tests were 2324.2 N-s/kg (237.0 s). This was obtained using 15 wt % conventional Al, 20 wt % Class E HMX, and 10 wt % 20 μm AP. The performance goal was vac I_{sp} ms, $\epsilon = 7.1 \geq 2403$ N-s/kg (245 s).

(3) Reducing the AP particle size from 200 to 20 μm significantly improved vac I_{sp} ms [117.7 N-s/kg (≅12 s)] and increased burning rate.

(4) Increasing the Class E HMX level from 20 to 30 wt % significantly increased vac I_{sp} ms, 68.6 N-s/kg (≅7 s). However, propellant with 30 wt % Class E HMX did not meet the card gap requirements for Class 2 propellant.

(5) Increasing the metal level from 15 wt % to 19 or 20 wt % significantly reduced vac I_{sp} ms.

(6) Replacement of the conventional aluminum by the Al/Mg alloy (90/10) appeared to give a small performance gain, 39.2 N-s/kg (≅4 s). However, the data was too limited to draw firm conclusions.

Propellant development effort was continued in an effort to achieve the performance goals. The ballistic modifiers, AD and CU-0202 P, were selected based on work done by JPL. In addition, finer AP particle sizes were selected based on the ability of this approach to achieve both improved performance and faster burning rates. A Class E HMX level of 20 wt % was selected as the maximum to meet card gap requirements for Class 2 propellants based on card gap tests available at that time. Table 3-48 summarizes motor test and theoretical performance results on the three ballistic modified propellant formulations evaluated. Formulation 2A used 2 wt % mixed ballistic modifier system, 10 wt % 5.5 μm AP, and 15 wt % conventional aluminum. Formulation 2B used 1 wt % AD as ballistic modifier, 10 wt % 10 μm AP, and 15 wt % Al/Mg alloy (90/10). Formulation 2C used 2 wt % mixed ballistic modifier system, no AP, and 15 wt % magnesium. The motor test results shown are all from 4.5-kg (10-lb) charge (TPC) motors. Since several formulation variables were varied between the three formulations, it is not possible to isolate just the effect of metal type on propellant performance. However, the following general conclusions can be made from this work:

(1) Formulation 2A, which used conventional aluminum, was the most promising candidate. The vac I_{sp} ms, $\epsilon = 6.84$, of 2414.4 N-s/kg (246.2 s) met the goal of vac I_{sp} ms, $\epsilon = 7.1$, ≅2403 N-s/kg (245 s). Burning rate achieved was 0.76 cm/s at 483 N/cm^2 (0.30 in./s at 700 psia) compared to the goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia) with a pressure exponent ≅0.4.

(2) Formulation 2B, which used the Al/Mg alloy (90/10), had a theoretical I_{sp} (1000/14.7) nearly the same as formulation 2A, but Vac I_{sp} ms, $\epsilon = 6.84$ was only 2325.2 N-s/kg (237.1 s). In addition, the burning rate was only 0.53

Table 3-48. NOS Space Shuttle Alternate Propellant Development - Ballistic Evaluation, Theoretical vs Measured

Propellant No.	2A	2B	2C
Ingredients, wt %			
AN	41.0	42.0	51.0
AP	10.0 (5.5 μm)	10.0 (10 μm)	---
HMX (15 μm)	20.0	20.0	20.0
Al	15.0	---	---
Al/Mg alloy (90/10)	---	15.0	---
Mg	---	---	15.0
AD	1.0	1.0	1.0
CU-0202 P	1.0	---	1.0
R-45M	8.0	10.0	8.0
DOA	4.0	2.0	4.0
Theoretical Density, g/cm^3 ($lb/in.^3$)	1.7051 (0.0616)	1.6829 (0.0608)	1.6027 (0.0579)
Theoretical I_{sp} (1000/14.7),[a] N/cm^2 (s)	2497.8 (254.7)	2495.8 (254.5)	2399.7 (244.7)
Measured I_{sp}, N-s/kg (s) at ϵ = 5.5	2281.0 (232.6)	2131.0 (217.3)	2011.3 (205.1)
Measured Vac I_{sp}, N-s/kg (s) corr to ϵ = 6.84	2414.4 (246.2)	2325.2 (237.1)	2267.3 (231.2)
Burn rate at 483 N/cm^3 (700 psia), cm/s (in./s)	0.76 (0.30)	0.53 (0.21)	0.41 (0.16)

[a]Standard Conditions: Chamber pressure of 690 N/cm^2 (1000 psia) and expanded to 1 atm (14.7 psia).

cm/s at 483 N/cm^2 (0.21 in./s at 700 psia) for this formulation. This data suggests that there was no performance advantage in using the Al/Mg alloy compared to conventional aluminum.

(3) Formulation 2C, which used magnesium as the metal, had theoretical density and theoretical I_{sp} (1000/14.7) values significantly lower than formulation 2A. The measured I_{sp} and burning rates confirmed that this was the least attractive of the three formulations.

This work was ended at this stage of the program. Good I_{sp} efficiencies were being achieved with conventional aluminum using 10 wt % fine particle size AP and the selected ballistic modifiers, AD and CU-0202 P.

f. Scale-Up Evaluation of Selected Formulations. Four formulations were selected for scale-up evaluation and motor tests throughout the AN/HMX/AP/Al/HTPB propellant development effort. Table 3-49 shows these four formulations. Major changes in the formulations which were made as a result of the development effort on the small scale were:

(1) Change from DOA to lower viscosity plasticizer IDP to improve castability.

(2) Use of the pot-life extenders UOP-36 and DTBH to improve castability and pot life.

(3) Reductions of the total ballistic modifier level from 4.00 wt % to 3.00 wt % to improve performance.

(4) Selection of 17 wt % Class E HMX to achieve maximum performance and burning rate within the constraint of a Class 2 propellant.

(5) Changes in the AN type to the higher density, harder prill Monsanto AN to improve castability and burn rate control.

(6) Change from hammer mill ground 8-9 μm AP to the finer fluid energy mill ground 6.3 μm AP to achieve faster burning rates.

All four formulations were successfully mixed and loaded into 5 x 10 motors, BATES motors and small-scale samples. The motors were successfully tested and results are summarized and discussed in Subsection g, Ballistic Evaluation. The following additional tests were made on the small-scale samples:

(1) Brookfield end-of-mix viscosities and pot life.

(2) Strand burning rates.

(3) Card gap.

(4) Density.

(5) JANNAF uniaxial physical properties.

Table 3-49. Scale-Up Evaluation of Selected Formulations, AN/HMX/AP/Al/HTPB Propellant Type

Batch No.	SB-89	SB-92	SB-106	SB-141
Formulation No.	ANH-9	ANH-12	ANH-18	ANH-33
Batch size, kg (lb)	61 (135)	104 (230)	104 (230)	113 (250)
Ingredients, wt %				
R-45 polymer	6.470	6.582	6.528	6.397
DOA plasticizer	4.613	---	---	---
IDP plasticizer	---	4.647	4.609	4.615
DOA plasticizer (HMX coating)	0.187	0.153	0.191	0.185
Alrosperse 11 P	0.113	0.113	0.113	0.113
UOP-36	---	---	---	0.040
DTBH	---	---	---	0.040
IPDI	0.617	0.559	0.559	0.610
Ammonium dichromate (ground 7 μm)	2.00	2.00	2.00	1.00
Copper chromite (as received 2.1 μm)	2.00	2.00	2.00	2.00
Aluminum powder, MD-105	15.00	15.00	15.00	15.00

Table 3-49. Scale-Up Evaluation of Selected Formulations, AN/HMX/AP/Al/HTPB Propellant Type (Continuation 1)

Batch No.	SB-89	SB-92	SB-106	SB-141
Formulation No.	ANH-9	ANH-12	ANH-18	ANH-33
Batch size, kg (lb)	61 (135)	104 (230)	104 (230)	113 (250)
HMX, Class E	15.00	15.00	17.50	17.00
Ammonium nitrate, unground				
Gulf Oil	44.00	---	---	---
U. S. Steel	---	29.00	---	---
Monsanto	---	---	29.00	28.00
Ammonium nitrate, coarse ground				
U. S. Steel	---	15.00	---	---
Monsanto	---	---	12.50	15.00
Ammonium perchlorate				
hammer mill ground, 8-9 μm	10.00	10.00	10.00	---
fluid energy mill ground, 6.3 μm	---	---	---	10.00
Totals	100.00	100.00	100.00	100.00
Brookfield apparent viscosities at 52°C (125°F) (Viscosity, kP/time after curative addition)				
End-of-mix	22/0.8	16/0.9	10/0.8	7/0.8
	20/1.8	28/1.9	14/1.8	13/1.8
	21/2.8	29/2.9	22/2.8	15/2.7
		41/3.9	24/3.8	21/3.7
		41/4.9	---	---

Table 3-49. Scale-Up Evaluation of Selected Formulations, AN/HMX/AP/Al/HTPB Propellant Type (Continuation 2)

Batch No.	SB-89	SB-92	SB-106	SB-141
Formulation No.	ANH-9	ANH-12	ANH-18	AHN-33
Batch size, kg (lb)	61 (135)	104 (230)	104 (230)	113 (250)
Strand Burning Rates at 25°C (77°F), cm/s (in./s)				
At 172 N/cm² (250 psia)	---	0.503 (0.198)	0.566 (0.223)	0.544 (0.214)
At 345 N/cm² (500 psia)	0.599 (0.236)	0.617 (0.243)	0.683 (0.269)	0.622 (0.245)
At 517 N/cm² (750 psia)	---	0.691 (0.272)	0.767 (0.302)	0.719 (0.283)
At 690 N/cm² (1000 psia)	0.721 (0.284)	0.775 (0.305)	0.818 (0.322)	0.805 (0.317)
Strand Pressure Exponent, 345 to 690 N/cm² (500 to 1000 psia)	0.27	0.31	0.27	0.37
Card Gap Tests:				
0 cards	6 negative 4 positive	2 negative 3 positive	--- ---	--- ---
20 cards	---	1 positive	---	---
27 cards	---	1 positive	---	---
30 cards	---	3 negative	---	---
35 cards	10 negative	5 negative	---	---
60 cards	---	---	---	1 positive
61 cards	---	---	---	1 positive
62 cards	---	---	---	2 positive
63 cards	---	---	---	3 negative 1 positive
65 cards	---	---	---	1 negative

Table 3-49. Scale-Up Evaluation of Selected Formulations, AN/HMX/AP/Al/HTPB Propellant Type (Continuation 3)

Batch No.	SB-89	SB-92	SB-106	SB-141
Formulation No.	ANH-9	ANH-12	ANH-18	AHN-33
Batch size, kg (lb)	61 (135)	104 (230)	104 (230)	113 (250)
Card Gap Tests (Contd):				
69 cards	---	---	---	10 negative
70 cards	---	---	2 negative 6 positive	---
Physical Properties:				
Density at 25°C (77°F), g/cm^3 ($lb/in.^3$)	1.6746 (0.0605)	1.6359 (0.0591)	1.6691 (0.0603)	1.6663 (0.0602)
JANNAF Uniaxial Properties				
S_m, N/cm^2 (psi)	---	49 (71)	---	64
e_m, %	---	1.9	---	6.8
S_b, N/cm^2 (psi)	---	49 (71)	---	44 (64)
e_b, %	---	1.9	---	6.8

Results of these tests are shown in Table 3-49. General conclusions from these tests were:

(1) End-of-mix viscosities and pot life improved as changes were made to IDP plasticizer, use of pot-life extenders UOP-36 and DTBH, and Monsanto AN. End-of-mix viscosity for batch SB-141 (HMX) was 7 kP at 52°C (125°F) and pot life was greater than 3.7 h.

(2) Faster burning rates were achieved as the HMX level was increased, as the Gulf Oil AN was replaced by U.S. Steel AN and then by Monsanto AN, and as the hammer mill ground AP was replaced by the finer fluid energy mill ground AP.

(3) Maximum strand burning rate achieved at 690 N/cm^2 (1000 psia) was 0.81 cm/s (0.32 in./s) with batch SB-106 (HMX).

(4) Strand pressure exponents on all four formulations were in the range of 0.27 to 0.37. Motor pressure exponents were lower than strand pressure exponents. These low-pressure exponents are advantageous and meet the goal of ≤ 0.42.

(5) Card gap tests verified that the maximum level of Class E HMX which meets the card gap requirements for a Class 2 propellant is greater than 17.00 wt % and less than 17.50 wt %.

(6) Measured densities were in the range of 1.6359 to 1.6746 g/cm^3 (0.0591 to 0.0605 $lb/in.^3$) for the four formulations.

(7) The JANNAF uniaxial properties were poor with maximum stress values in the range of 44 to 49 N/cm^2 (64 to 71 psi) and strain at maximum stress values in the range of 1.9 to 6.8%.

g. Ballistic Evaluation: AN/HMX/AP/Al/HTPB Systems. The candidate alternate propellant containing HMX was evaluated in BATES motor firings at three levels of HMX: 15.0%, 17.0%, and 17.5%. The 15.0% HMX formulation yielded the highest measured I_{sp}. Theoretical calculations had shown 17.0 to 17.5% to be optimum for maximum I_{sp}. Data from the BATES motor tests suggests that the actual optimum HMX level is somewhere between 15 and 16%. This level of HMX in the propellant has been demonstrated to be within the Class 2 requirement. The ballistic test data for the three HMX systems follows.

(1) Formulation ANH-12 (15.0% HMX). Figure 3-17 shows the burning rate, K_N, and pressure exponent for this propellant. The BATES motor test data is summarized in Table 3-50.

(2) Formulation ANH-33 (17.0% HMX). The ballistic evaluation test results from this formulation are shown in Fig. 3-18 and Table 3-51.

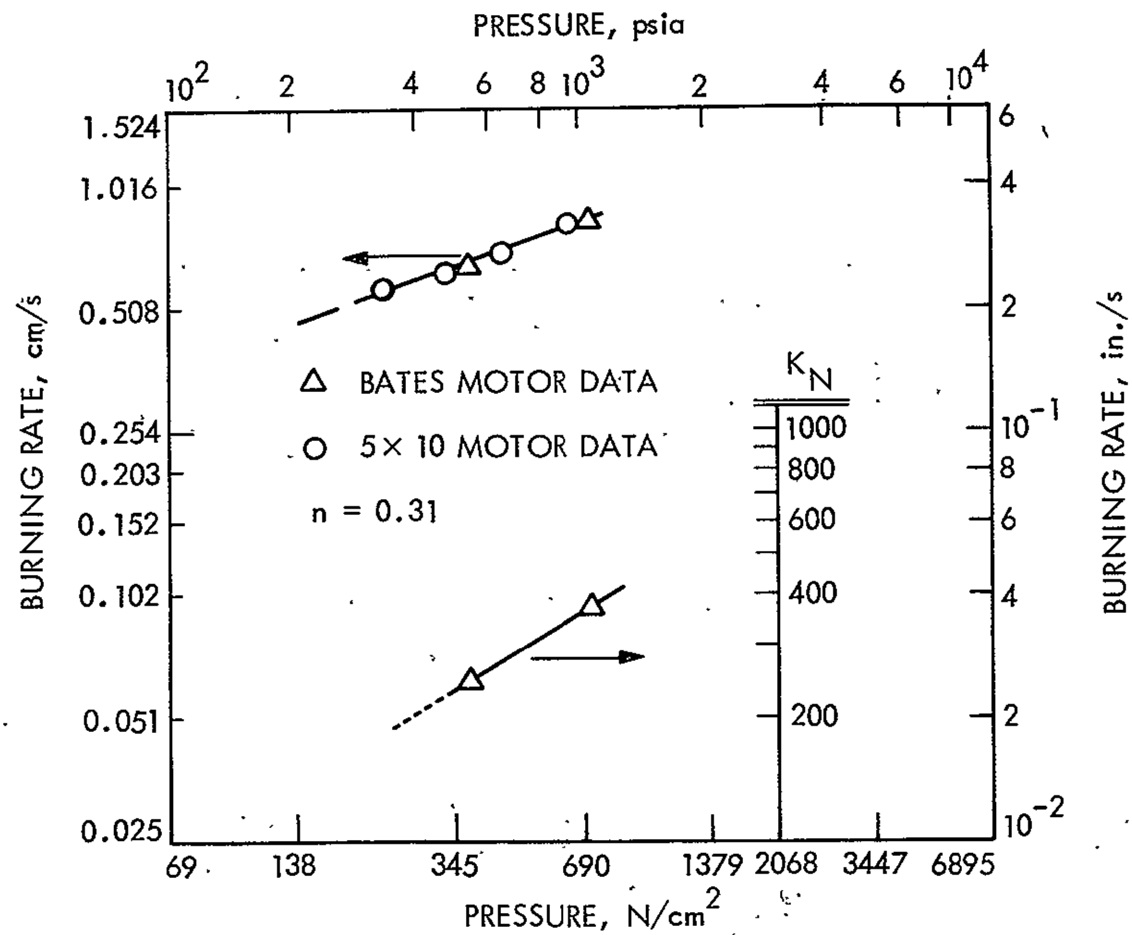

Figure 3-17. Shuttle Alternate Propellant Burning Rates and K_N for ANH-12, AN/HMX/AP/Al/HTPB (15% HMX), Batch No. SB-92

Table 3-50. BATES Motor Tests Data Summary, ANH-12 Propellant

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 44, HMX 15 (Class E)

Run No.	E-1466	E-1467
Test Date	Nov. 14, 1975	Nov. 26, 1975
Batch/Change No.	SB-92/1	SB-92/2
Nozzle D_t initial, cm (in.)	4.699 (1.850)	3.764 (1.482)
Nozzle D_t final, cm (in.)	4.374 (1.722)	3.571 (1.406)
W_p loaded, kg (lb)	29.81 (65.72)	29.79 (65.67)
W_p expended, kg (lb)	29.395 (64.806)	29.40 (64.82)
% wt expended	98.6	98.7
Web thickness, cm (in.)	4.5789 (1.8207)	4.610 (1.815)
t_b (burn time), s	7.35	5.86
t_a (action time), s	7.64	6.24
P_c initial, N/cm^2 (psia)	310 (450)	531 (770)
P_c max, N/cm^2 (psia)	386 (560)	731 (1060)
P_c final, N/cm^2 (psia)	376 (545)	702 (1018)
$\int P\,dt$, (t_b), $N\text{-}s/cm^2$ (lb-s)	2624.5 (3806.6)	4105.6 (5954.7)
$\int P\,dt$, (t_a), $N\text{-}s/cm^2$ (lb-s)	2677.9 (3884.0)	4228.5 (6132.9)

Table 3-50. BATES Motor Tests Data Summary, ANH-12 Propellant (Continuation 1)

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 44, HMX 15 (Class E)

Run No.	E-1466	E-1467
Test Date	Nov. 14, 1975	Nov. 26, 1975
Batch/Change No.	SB-92/1	SB-92/2
$\overline{P}_c$, ($\int P\,dt/t_b$), N/cm^2 (psia)	351.1 (517.9)	700.6 (1016.2)
r at P_c, cm/s (in./s)	0.630 (0.248)	0.787 (0.310)
K_N initial	225.3	351.1
K_N average	241.1	368.9
C*, m/s (ft/s)	1450.7 (4759.4)	1498.3 (4915.6)
C* efficiency, %	96.2	100.6 ?
$\int F\,dt$ (t_b), N-s (lb-s)	61,936.79 (13,923.95)	63,493.09 (14,273.82)
$\overline{F}$ ($\int F\,dt/t_b$), N (lb)	8,426.75 (1894.41)	10,834.97 (2435.8)
I_t ($\int F\,dt$ for t_a), N-s (lb-s)	61,980.03 (13,933.67)	65,597.90 (14,747.0)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2,079.21 (212.02)	2,202.18 (224.56)
I_{sp} efficiency, %	92.49	91.6
I_{sp} vac ms (corr), N-s/kg (s)	2,375.46 (242.23)	2,355.26 (240.17)
Expansion Ratio	7.0	7.0

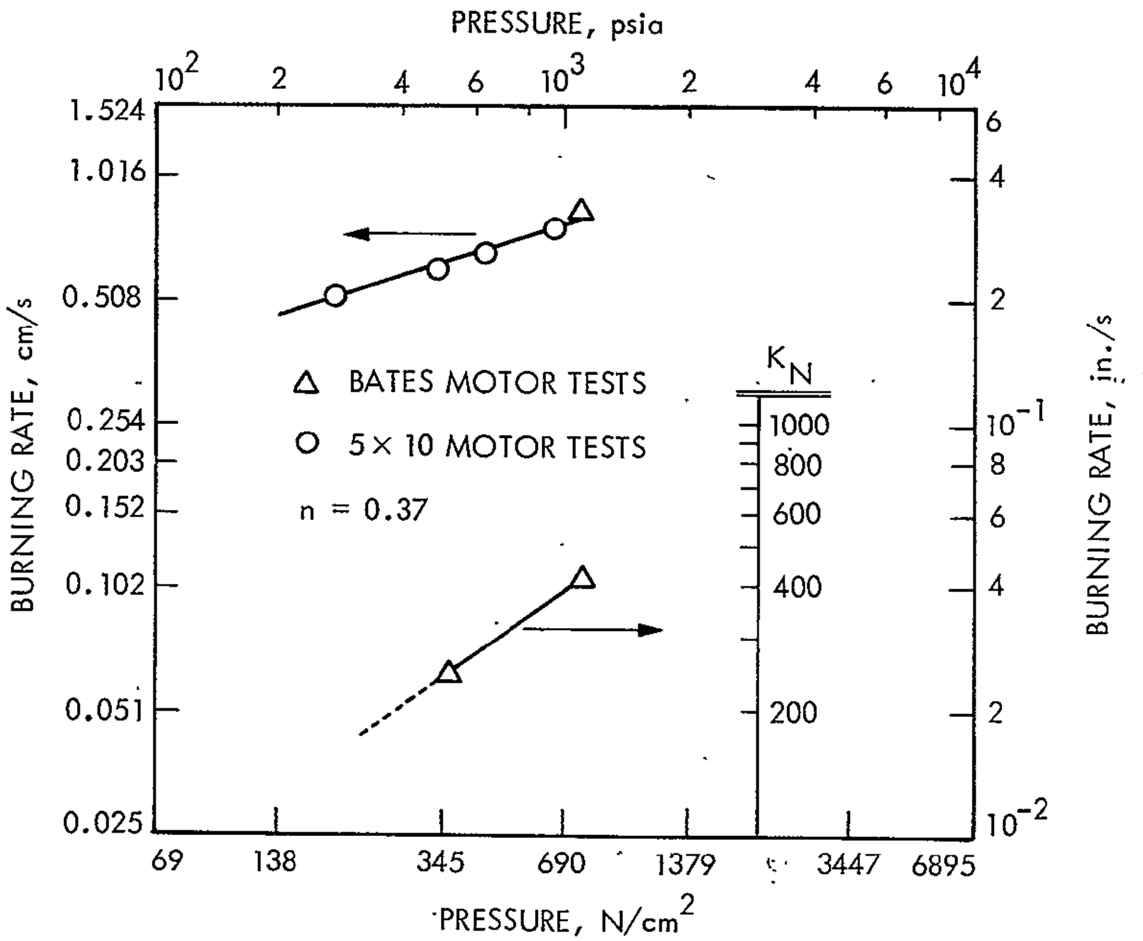

Figure 3-18. Shuttle Alternate Propellant Burning Rates and K_N for ANH-33, AH/HMX/AP/Al/HTPB (17% HMX), Batch No. SB-141

Table 3-51. BATES Motor Tests Data Summary, ANH 33 Propellant

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 43, HMX 17.0

Run No.	E-1489	E-1490
Test Date	6/23/76	6/24/76
Batch/Change No.	SB-141/2	SB-141/1
Nozzle D_t initial, cm (in.)	4.572 (1.800)	3.5268 (1.3885)
Nozzle D_t final, cm (in.)	4.531 (1.784)	3.444 (1.356)
W_p loaded, kg (lb)	30.17 (66.51)	30.13 (66.43)
W_p expended, kg (lb)	29.38 (64.77)	29.33 (64.66)
% wt expended	97.38	97.33
Web thickness, cm (in.)	4.633 (1.824)	4.643 (1.828)
t_b (burn time), s	7.47	5.70
t_a (action time), s	7.94	6.38
P_c initial, N/cm^2 (psia)	345 (500)	683 (990)
P_c maximum, N/cm^2 (psia)	362 (525)	752 (1090)
P_c final, N/cm^2 (psia)	324 (470)	649 (942)
$\int P\,dt$, (t_b), N-s/cm^2 (lb-s)	2596.1 (3765.4)	4166.5 (6043)
$\int P\,dt$, (t_a), N-s/cm^2 (lb-s)	2655.4 (3851.4)	4280.2 (6208)
$\bar{P}_c$ (P dt/t_b), N/cm^2 (psia)	347 (504)	731 (1060)

Table 3-51. BATES Motor Tests Data Summary, ANH 33 Propellant (Continuation 1)

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 43, HMX 17.0

Run No.	E-1489	E-1490
Test Date	6/23/76	6/24/76
Batch/Change No.	SB-141/2	SB-141/1
r at $\overline{P}_c$, cm/s (in./s)	0.620 (0.244)	0.815 (0.321)
K_N initial	233.0	398.9
K_N average	239.5	407.7
C*, m/s (ft/s)	1430.7 (4694.0)	135.40 (4442.1)
C* efficiency, %	94.5	89.5
F dt (t_b), N/s (lb-s)	59796.80 (13442.86)	62583.48 (14069.33)
$\overline{F}$ (∫F dt/t_b), N (lb)	8007 (1800)	10978 (2468)
I_t (∫F dt for t_a), N-s (lb-s)	60958 (13704)	6444.1 (14487)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2020.56 (206.04)	2138.8 (218.1)
I_{sp} efficiency, %	88.7	87.2
I_{sp} vac ms (corr), N-s/kg (s)	2318.3 (236.4)	2281.0 (232.6)
Expansion ratio (ϵ)	7.16	7.16
D_e, cm (in.)	12.233 (4.816)	9.426 (3.711)
A_e, cm^2 ($in.^2$)	117.522 (18.216)	69.781 (10.816)

(3) Formulation ANH-18 (17.5% HMX). The ballistic evaluation test results from this formulation are shown in Fig. 3-19 and Table 3-52.

h. Summary. Two AN/HMX/AP/Al/HTPB propellant formulations were developed that conformed to the program constraints for ≤ 3 wt % HCl in the exhaust products and for a Class 2 propellant hazards classification. These two formulations are ANH-12 (15 wt % Class E HMX) and ANH-33 (17 wt % Class E HMX). Table 3-53 summarizes and compares the properties of these two formulations versus the program goals. Both formulations met the goals for pressure exponent and hazard classification but not the goal for burning rate or delivered vacuum I_{sp}.

The following summarizes the status of the AN/HMX/AP/Al/HTPB propellant development:

(1) The basic AN/HMX/AP/Al/HTPB propellant is the most promising candidate of the three basic propellants.

(2) Demonstrated the propellant is Class 2 with levels of Class E HMX up to 17 wt %.

(3) Demonstrated good castability, and pot life greater than 3.7 h for formulations with 15.00 to 17.50 wt % Class E HMX.

(4) Successfully loaded and test fired 4.5-kg (10-lb) motors and 32-kg (70-lb) BATES motors with formulations containing 15.00 to 17.50 wt % Class E HMX.

(5) Demonstrated a delivered vacuum I_{sp} ($\epsilon = 7.16$) of 2375.2 N-s/kg (242.2 s) with formulation ANH-12.

(6) Demonstrated a BATES motor burning rate of 0.81 cm/s at 690 N/cm^2 (0.32 in./s at 1000 psia) and a pressure exponent of 0.37 with formulation ANH-33.

(7) Measured physical properties and determined a need for additional development effort in this area.

(8) The maximum HMX content for maximum delivered I_{sp} is between 15.0 and 17.0%.

11. Baseline PBAN Propellant Modification

The current baseline propellant system in the Shuttle SRM is an 86% solids, 16% aluminum PBAN propellant developed by the Thiokol Corporation. This baseline propellant has a burning rate of approximately 1.07 cm/s (0.42 in./s) at 690 N/cm^2 (1000 psia) pressure. In order to simplify the task of matching the burning rates of the alternate propellant and the PBAN baseline propellant at 400 N/cm^2 (580 psia)

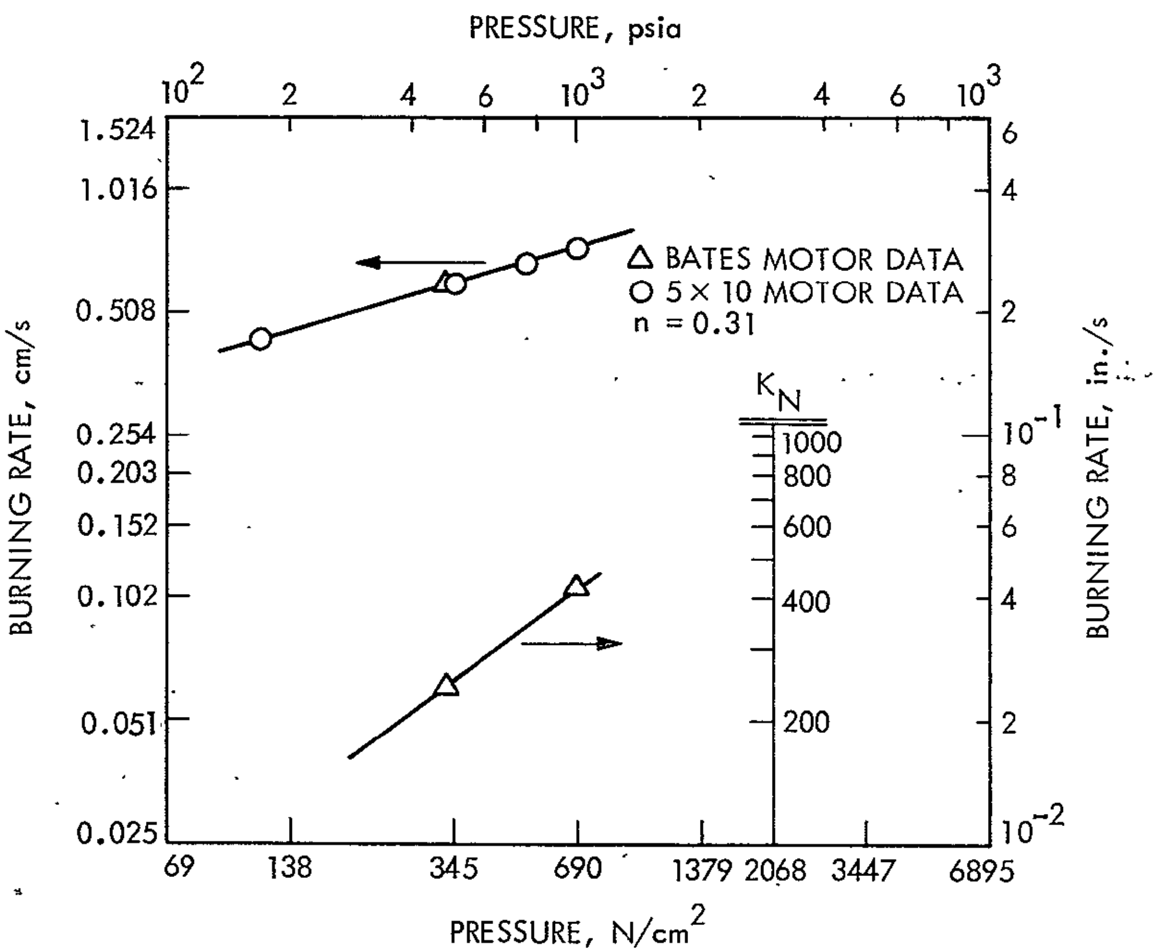

Figure 3-19. Shuttle Alternate Propellant Burning Rates and K_N for ANH-18, AN/HMX/AP/Al/HTPB (17.5% HMX), Batch No. SB-106

Table 3-52. BATES Motor Tests Data Summary, ANH 18 Propellant

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 41.5, HMX 17.5 Class E

Run No.	E-1472	E-1473
Test Data	12-11-75	12-12-75
Batch/Change No.	SB-106/1	SB-106/2
Nozzle D_t initial, cm (in.)	4.592 (1.808)	3.543 (1.395)
Nozzle D_t final, cm (in.)	4.463 (1.757)	3.388 (1.334)
W_p loaded, kg (lb)	30.22 (66.62)	30.23 (66.64)
W_p expended, kg (lb)	29.56 (65.16)	29.57 (65.19)
Wt % expended	97.81	97.82
Web thickness, cm (in.)	4.615 (1.817)	4.615 (1.817)
t_b (burn time), s	7.88	6.28
t_a (action time), s	8.18	6.65
P_c initial, N/cm^2 (psia)	248 (360)	483 (700)
P_c maximum, N/cm^2 (psia)	352 (510)	717 (1040)
P_c final, N/cm^2 (psia)	296 (430)	622 (902)
$\int P\,dt$, (t_b), N-s/cm^2 (lb-s)	2621.46 (3802.12)	4299.1 (6235.3)
$\int P\,dt$, (t_a), N-s/cm^2 (lb-s)	2658.74 (3856.19)	4407.4 (6392.4)

Table 3-52. BATES Motor Tests Data Summary, ANH 18 Propellant (Continuation 1)

% Solids: 88

% Aluminum: 15

% Oxidizer: AP 10, AN 41.5, HMX 17.5 Class E

Run No.	E-1472	E-1473
Test Data	12-11-75	12-12-75
Batch/Change No.	SB-106/1	SB-106/2
$\overline{P}_c$, ($\int P\,dt/t_b$), N/cm^2 (psia)	147.1 (482.5)	302.6 (992.9)
r at $\overline{P}_c$, cm/s (in./s)	0.587 (0.231)	0.734 (0.289)
K_N initial	235.3	395.3
K_N average	242.1	413.1
C*, m/s (ft/s)	1415.9 (4642.5)	1374.1 (4508.3)
C* efficiency, %	94.5	91.6
$\int F\,dt$ (t_b), N-s (lb-s)	59,905.5 (13,467.3)	63,205.60 (14,209.19)
$\overline{F}$, ($\int F\,dt/t_b$), N (lb)	7602 (1709)	10064.5 (2262.6)
I_t ($\int F\,dt$ for t_a), N-s (lb-s)	60882.3 (13,686.9)	64988.85 (14,610.08)
I_{sp} ms (I_t/W_p), N-s/kg (s)	2014.78 (205.45)	2150.01 (219.24)
I_{sp} efficiency, %	89.01	88.68
I_{sp} vac ms (corr), N-s/kg (s)	2317.61 (236.33)	2292.40 (233.76)
Expansion ratio	7.1	7.2

Table 3-53. AN/HMX/AP/Al/HTPB Propellant Achieved Properties vs Goal

Alternate Propellant Property	Goal	Achieved Value: SB-92 (HMX) ANH-12 (15% HMX)	Achieved Value: SB-141 (HMX) ANH-33 (17% HMX)
Burning Rate at 690 N/cm^2 (1000 psia), BATES Motor, cm/s (in./s)	0.89 (0.35)	0.785 (0.309)	0.813 (0.32)
Pressure Exponent, BATES motor	$\leq$0.42	0.32	0.37
Delivered Vacuum I_{sp}, N-s/kg (s) (ϵ = 7.1)	2403 ($\geq$245)	2373.2 (242.2)	2318.3 (236.4)
HCl in Exhaust	$\leq$3%		3
Meets Card Gap Requirement for Class 2	Class 2 required	yes (negative at 30 cards)	yes (negative at 30 cards)

pressure, it was decided to modify the baseline propellant system to meet a burning rate of 0.81 cm/s at 690 N/cm^2 (0.32 in./s at 1000 psia). This modified baseline applies to the dual propellant concept with the alternate propellant only. It does not apply to the current Shuttle design requirements. The 0.81 cm/s (0.32 in./s) burning rate has been achieved and demonstrated in 4.5-kg (10-lb) motor firings. The modified PBAN formulation is referred to in this report as the PBAN Mod-1 propellant.

In modifying the basic PBAN formulation to meet the new burning rate requirement, a study was made of the effect on the burning rate of adjusting the Fe_2O_3 burning rate catalyst concentration and the particle size blend of the AP oxidizer. The desired burning rate was achieved with a formulation containing a biomodal blend of oxidizer and 0% Fe_2O_3. Table 3-54 gives the final formulation, the density, and some burning characteristics of the PBAN Mod-1 propellant.

Table 3-54. PBAN Mod-1 Formulation, Bimodal 70/30 Oxidizer Blend

Ingredients	Wt %
Ammonium perchlorate	
200 μm	49.00
10 μm	21.00
Aluminum (Alcoa 1230)	16.00
PBAN polymer	12.04
DER-331	1.96
	100.00

Density, 25°C (77°F) = 1.7743 g/cm³ (0.0641 lb/in.³)
Burn Rate at 690 N/cm² (1000 psia) = 0.81 cm/s (0.32 in./s)
Pressure exponent n = 0.228 at
345 N/cm² (500 psia) < P_c < 690 N/cm² (1000 psia)

The burning rate of the PBAN Mod-1 propellant was verified by test firing several 5 x 10 motors using 4.5 kg (~10 lb) of propellant over a range of pressures. Figure 3-20 shows the burning rates and corresponding K_n values. The burning rate equation for this modified PBAN propellant, based on the 4.5-kg (10-lb) motor firings, is

$$r = 0.0668\ P_c^{0.228}$$

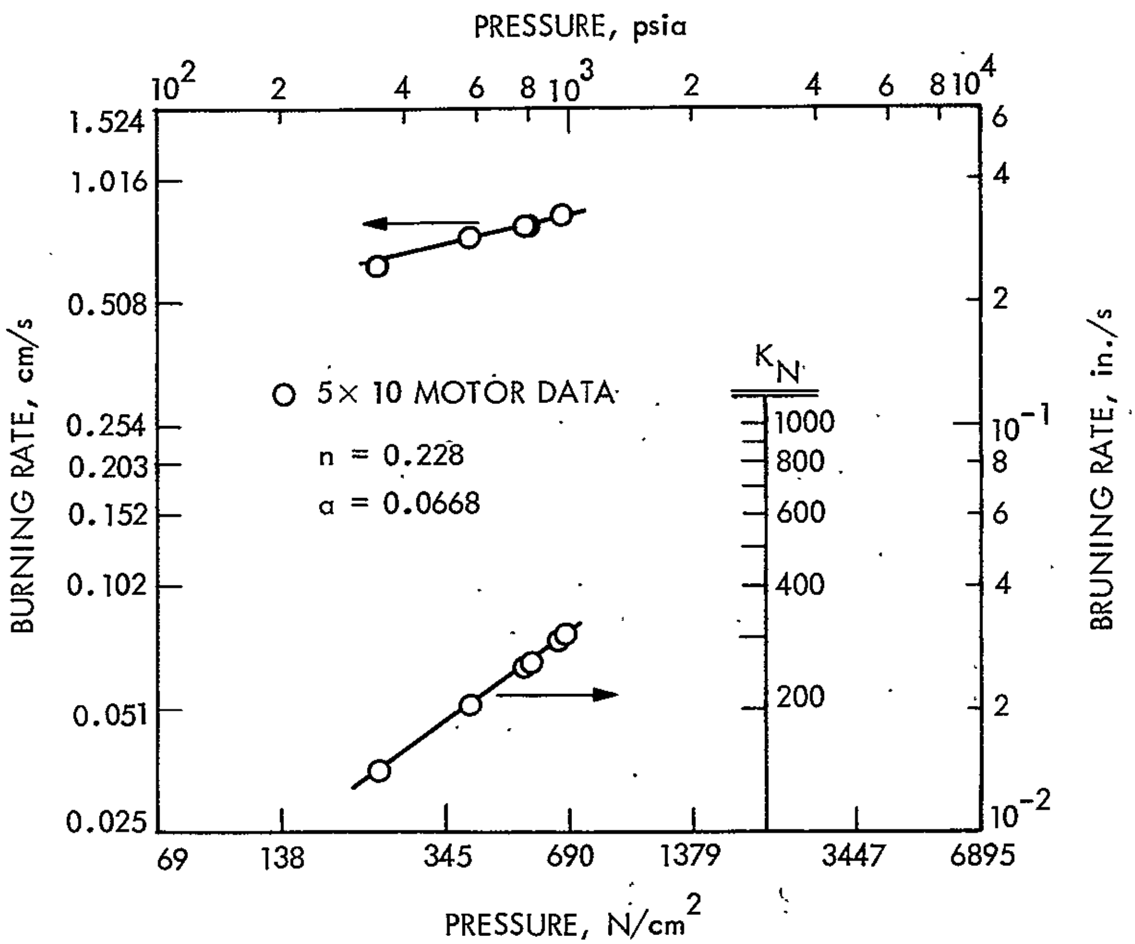

Figure 3-20. Shuttle Alternate Propellant Burning Rates and K_N for PBAN Mod 1 (Modified Baseline Propellant), Batch No. SB-78

SECTION IV

UNWORKED AREAS

The program as originally planned included a significant effort in the development of the candidate alternate propellant physical properties and checks to verify adequacy of candidate alternate propellant in the bipropellant grain. The reduction of funds and scope of the program left many of these tasks "unworked." If the alternate propellant concept for Space Shuttle Solid Rocket Booster Motor is pursued on another program, then the following unworked areas should be worked:

(1) Candidate alternate propellant physical property improvement

(2) Physical property characterization of unaged alternate propellant

(3) Aging of alternate propellant

(4) Bipropellant interface bond: unaged and aged

(5) Alternate propellant insulation interface bond: unaged and aged

(6) Performance tests at altitude on candidate alternate propellant

(7) Motor tests with bipropellant grain

(8) Characterization of alternate propellant safety properties

The generally poor physical properties (primarily low strain) measured with both the AN/AP/Al/HTPB and the AN/HMX/AP/Al/HTPB propellants are believed due primarily to the following causes:

(1) Poor bond of the HTPB binder to the oxidizer particles, AN and HMX

(2) Crosslinking of the R-45 HTPB polymer through the double bonds caused by the acidity of AN.

The approach planned to solve the poor bonding properties to the oxidizer particles was development of bonding agents for both the AN and the HMX. Aerojet Solid Propulsion Company has demonstrated significantly improved physical properties in HMX/AP/Al/HTPB propellants using polyureas as bonding agents. Epoxides and polyureas were considered as candidate bonding agents for the AN. Development of an acid scavenger was considered as one of the approaches to the second cause of the poor physicals.

SECTION V

CONCLUSIONS

The results of this alternate propellant development effort led to the following general conclusions:

(1) It is technically feasible to minimize (≤3 wt %) release of HCl above 19.81 km (65,000 ft).

(2) The basic AN/HMX/AP/Al/HTPB propellant is the most promising candidate of the three basic alternate propellants. Formulation ANH-12 is the best formulation developed to date.

(3) Propellant with ≤17 wt % Class E HMX meets card gap requirements for Class 2 propellant.

(4) The basic AN/AP/Al/HTPB propellant is the second most promising candidate of the three basic alternate propellants.

(5) More than 10.00 wt % AP (>3% HCl in propellant exhaust) is required in the AN/AP/Al/HTPB propellant to meet the burn rate goal of 0.89 cm/s at 690 N/cm^2 (0.35 in./s at 1000 psia). Formulation AN-71 with 20.00 wt % AP is the best formulation of this type developed to date.

(6) The basic AN/HMX/Al/HTPB propellant (0% HCl) is the least promising candidate and probably not viable for achieving program goals.

(7) A few % of AP is essential to achieve good aluminum combustion.

(8) Good castability and acceptable pot life were achieved with all three basic alternate propellants.

(9) Additional development effort is needed to improve the physical properties of any of the candidate propellants.

(10) The small potential performance gains possible with TMETN did not justify the potential risks of compatibility problems with ballistic modifiers, TMETN migration, and aging degradation.

(11) The Monsanto phase stabilized E-2 AN is the preferred AN type, because it has the best physical and handling properties at comparable cost compared to other AN types.

(12) The maximum HMX content for maximum delivered I_{sp} is between 15 and 17%.

(13) With additional effort to optimize the formulation with regard to HMX level, burning rate modifier level, and oxidizer particle size, the program goals can be met with an AN/HMX/AP/Al/HTPB propellant system.

APPENDIX A

MEMORANDUM

SOLUBILITY OF MTN IN HYDROCARBON BINDER

2051B/C:CEJ:pbh (4352)
2051:120:75
3900
15 May 1975

MEMORANDUM

From: 2051B/C
To: 563
Via: 205

Subj: Solubility of MTN in hydrocarbon binder (TMETN)

1. A study was conducted to determine if MTN could be used in the R45 binder system for the NASA II propellant. Dioctyl adipate (DOA) would be used for a co-solvent.

2. Figure 1 is a portion of a phase diagram for the MTN-DOA-R45 system. Areas to the right of the curve are two phase. Areas to the left of the curve are single phase. The effect of temperature is also shown.

3. For Figure 2, TP90B was used instead of DOA. TP90B is not as effective a co-solvent as DOA.

4. Because PPG-1225 (a polypropylene glycol) is soluble both in R45 and MTN, it also was investigated. PPG-1225 has an advantage over DOA in that it is a reactive polymer and could contribute to the mechanical strength as well as providing co-solubility. In Figure 3, a 50/50 mixture of R45 and PPG-1225 was used for the starting material. The solubility of MTN was determined. Because PPG-1225 was not a very good co-solvent, DOA was added to enhance the solubility. Areas to the right of the curve are two phase, and areas to the left of the curve are single phase.

5. For Figure 4, a starting material of 73.3% R-45 and 26.7% PPG-1225 was used. DOA was used to enhance the solubility of MTN in the system.

6. It was determined that adiponitrile was not soluble in R45 and therefore could not be used to replace DOA.

7. It was determined that R-18 (a polyglycol adipate) was not soluble in R45 and therefore could not be used to replace PPG-1225.

8. A sample from Figure 1 was cured with IPDI. This will be used to evaluate the long term effect of the nitrate ester on the binder system.

Enclosure (1)

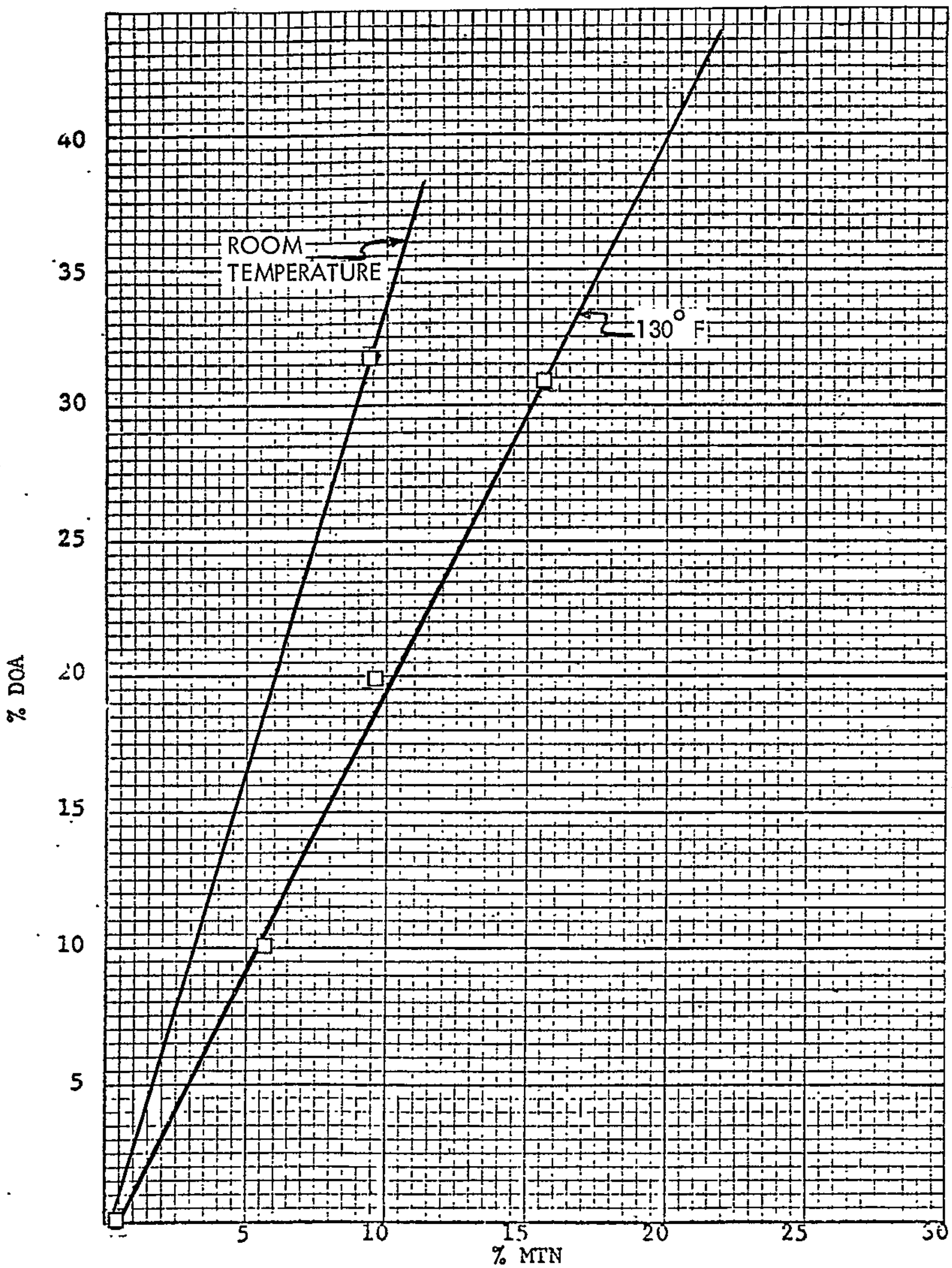

Figure 1. Solubility of DOA and MTN in R-45

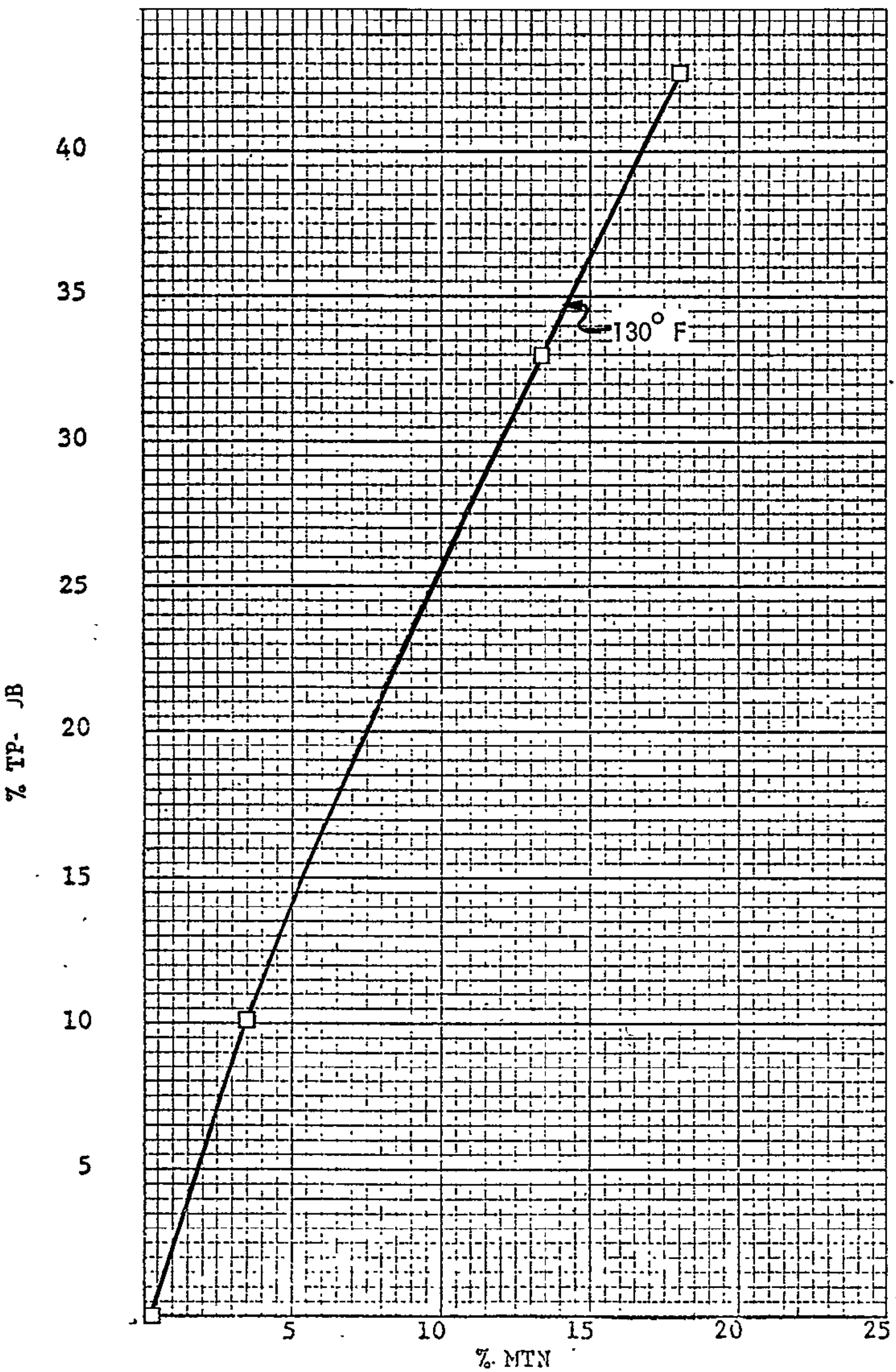

Figure 2. Solubility of TP-90B and MTN in R-45

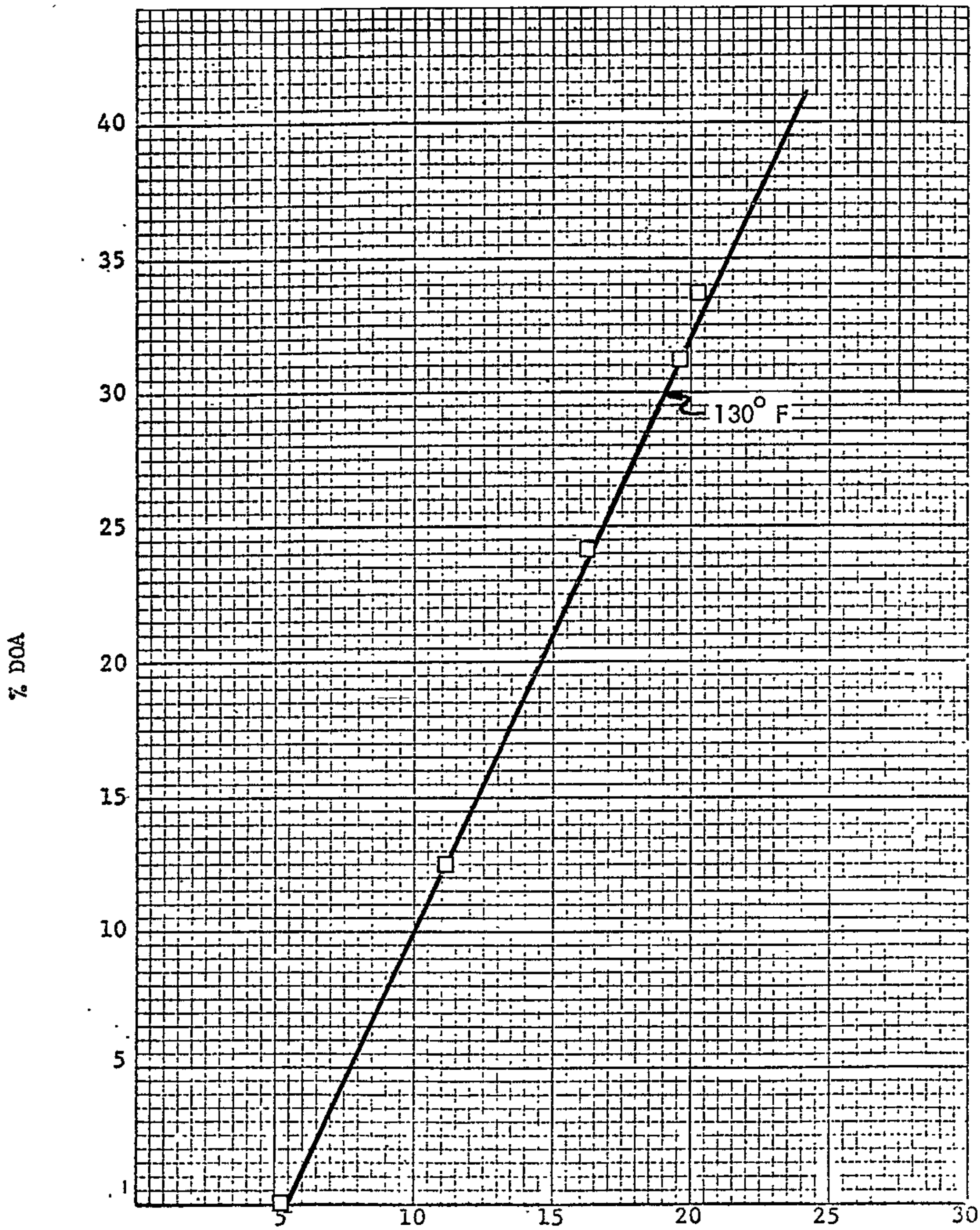

Figure 3. Solubility of DOA and MTN in 50% R-45/50% PPG-1225

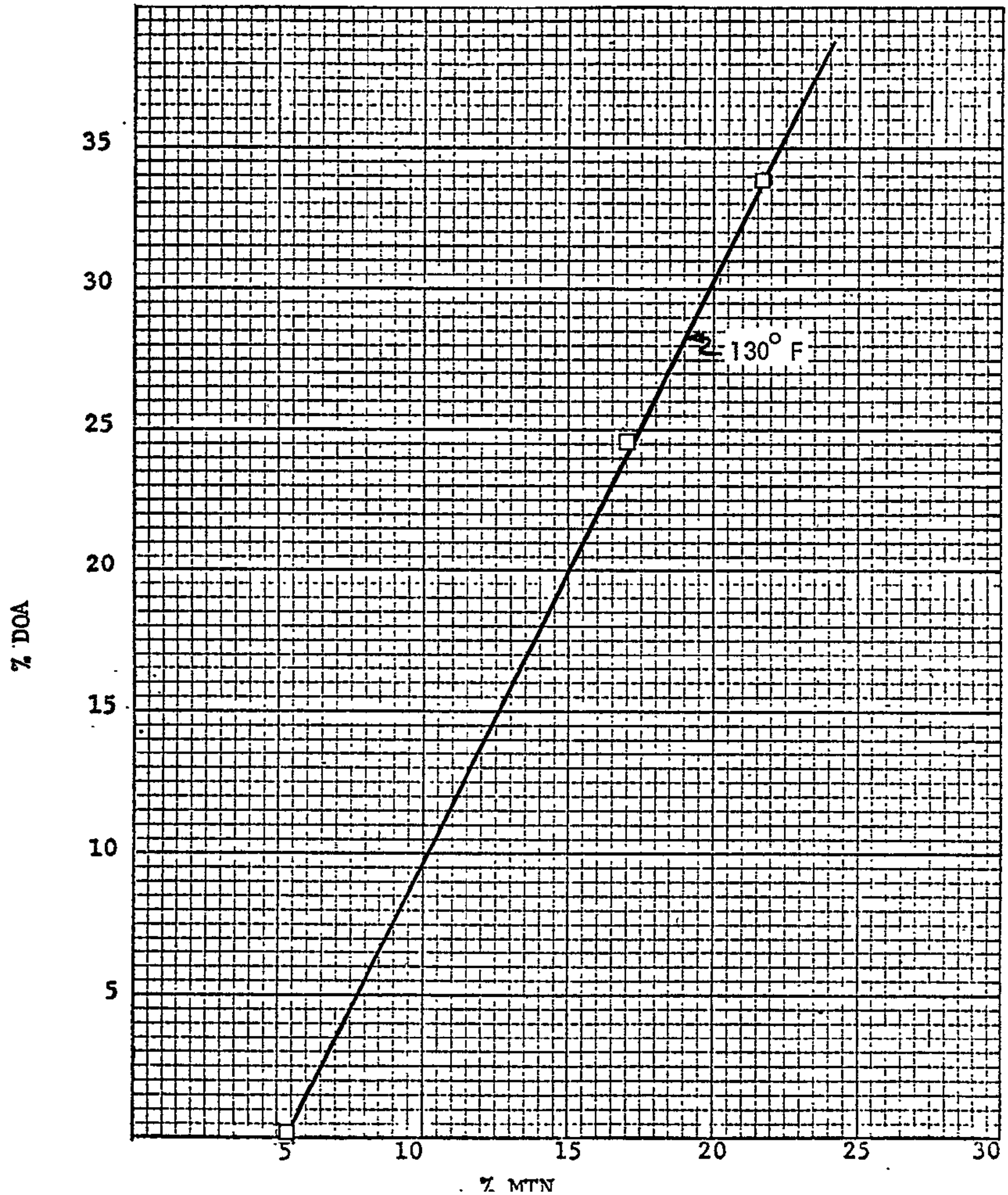

Figure 4. Solubility of DOA and MTN in 73.3% R-45/26.7% PPG-1225

2051B/C:CEJ:pbh (4352)
2051:120:75
3900
15 May 1975

9. If an 88% (or 84%) solids loaded, 6% polymeric binder system will give acceptable physical properties, then the following formulations should be investigated:

R-45	PPG1225	DOA	MTN	Al	AP	HMX	AN
6.0	-	4.0	2.0	15	10	20	43
4.4	1.6	3.6	2.4	15	10	20	43
6.0	-	4.0	2.0	15	10	10	53
4.4	1.6	3.6	2.4	15	10	10	53
6.0	-	6.6	3.4	15	10	20	39
4.4	1.6	6.2	3.8	15	10	20	39

To properly evaluate these, they should be compared to:

R-45	DOA	AL	AP	HMX	AN
6.0	6.0	15	10	20	53
10.0	2.0	15	10	20	53

A quick look at some of the theoretical results to date indicate that these substitutions of MTN for inert polymer may result in a gain of about 1.8 pounds sec/lb. in impulse and a gain of 0.001 pounds/cu. in. in density.

C. E. JOHNSON

Copy to:
205
2051B/C
2051C1
TD1

PUBLICATION 79-29