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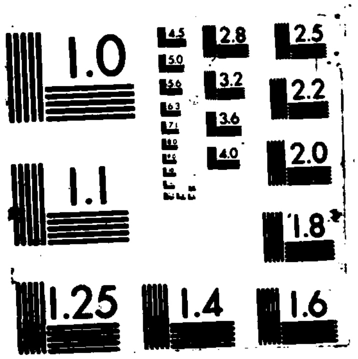
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Interim Report
for the period
March 1986 to
March 1987

The Correlation of HMX Particle Characterization Techniques to Propellant Burn Rate

September 1987

Author:
Kurt G. Chandler

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FOREWORD

This interim report describes a study on the correlation of HMX particle characterization techniques to propellant burn rate performed at the Air Force Astronautics Laboratory (AFAL), Edwards Air Force Base, CA. AFAL Project Manager was Kurt Chandler.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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Present methods of correlating solid propellant burn rate to oxidizer particle parameters solely depend upon the weight median diameters of the particle distribution. With the broad and variable distribution of the oxidizer particles, vastly different particle surface areas may result in variations in propellant burn rates. This study compares the burn rate of solid propellant to weight median diameters, calculated surface areas from size measurements, measured surface areas, and a new surface area distribution dependent solvolysis method. Comparison of the characterization techniques is performed to determine the role of surface area in the burning process, and the best parameter for propellant burn rate correlations.

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INTRODUCTION

Weight-median-diameter measurements are presently the sole characterization parameter used to predict propellant burn rates. Whether or not a propellant burn rate prediction is accurate depends on the ingredients in the formulation. Ingredient particles such as ammonium perchlorate (AP) and ammonium nitrate (AN) show surface area dependent burning characteristics. At present, it is uncertain whether the burning of cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX) are surface area or volume dependent processes. If HMX burning is surface area dependent, then the best correlation would be with surface area measurements or surface area dependent characterization techniques. If HMX burning is volume dependent, then the best correlation would be with volume dependent analyses such as the weight- median-diameter.

The main thrust of this report compares the correlation of burn rates of HMX containing solid propellant to measured surface area, calculated surface area, weight-median-diameters, 10% diameters, 90% diameters, and a new surface area dependent particle solvolysis characterization technique. The particle solvolysis technique is of particular importance to HMX burning, as it is used to determine whether the burning of HMX is a surface area or volume dependent process. The most useful characterization technique for routine burning analysis is to be determined, based upon the type of burning process and the correlation coefficients of the characterization techniques to burn rate.

THEORY

Work by Alley et al. (Ref. 1) and Bosserman et al. (Ref. 2) has shown that weight-median-diameters do not always provide a sufficient burn rate correlation for propellants which use ingredients, such as ammonium perchlorate (AP), that exhibit surface area dependence. Bosserman et al. (Ref. 2) found other characterization parameters which were more closely related to surface area, and provided more accurate burn rate predictability. Derr et al. (Ref. 3) investigated several ingredients, including AP and cyclotetramethylenetetranitramine (HMX), but used only the weight-median-diameter as the characterization parameter.

Novel Approaches: The failure of the common characterization parameter to provide accurate information for propellant formulations using particles displaying surface area dependent burning characteristics, warrants the investigation into novel characterization techniques. In an earlier report of this work, Chandler (Ref. 4) developed a new technique of particle solvolysis that was proven surface area dependent. With the present uncertainty as to whether HMX burning is a surface area dependent or a volume dependent process, the application of this technique presented a potential means to explore the problem. This particle solvolysis technique, as used to characterize HMX, will be more fully explained later in this report. In addition, actual surface area measurements were also performed on these particles. In the past surface area measurements have not been performed on oxidizer and explosive particles because the common method of BET surface area analysis (the nitrogen gas adsorption technique) required high temperatures and a high vacuum to remove adsorbed gases from the surface. These types of particles easily sublimate or decompose, resulting in an inaccurate analysis and system contamination.

Micromeritics Inc. introduced an instrument that uses a flowing gas technique combined with the heat of adsorption to remove surface gases. With this technique, these easily sublimated or decomposed particles can now be subjected to surface area measurements for burn rate predictions. The relation to burn rate for both particle solvolysis and surface area measurement techniques were compared to standard diameter measurement techniques using the light blocking technique and the ensemble light scattering technique. These common diameter measurement techniques provide size distribution information and the weight-median-diameter. From these diameter measurements, calculated specific surface areas were determined. These calculations segment the distribution into intervals, sum the total surface areas, and assume smooth spherical particles. Bosserman et al. (Ref. 2) found such calculations to provide a fairly accurate correlation to burn rate. With the ability to measure surface areas, it is now possible to determine the differences in predictability caused by the differences in surface area due to the lack of sphericity and a rough or porous surface as found on real world particles. In addition, the particle distribution analyses report the 10% diameter and 90% diameter. Predictability differences within the distribution may be used to determine if the burning process is affected more by smaller particles with higher surface area per mass or larger particles with greater volume per particle.

Particle Solvolysis Theory: The first application of the particle solvolysis technique involved ammonium perchlorate (AP) and ammonium nitrate (AN) characterization, and used electrochemical methods for detection (Ref. 4). The technique proved to be surface area distribution dependent. It is a heterogeneous process where particles are independently dissolved in a solvent system with detection of the liberated species. For AP or AN the ions or solution conductivity are detected. The technique is based on the fact that smaller particles have a higher surface area per mass than larger particles. The particles lose material from the surface inward, so smaller particles are dissolved or consumed into solution before larger particles. The result of this technique is illustrated in Fig. 1., which is a plot of the dissolved species vs time. The slope of the curve represents the rate at which the particles are dissolved into solution. The high surface area of the smaller particles produces a sharp rise on the plot which is the initial slope. This initial slope was shown in an earlier report (Ref. 4) to be directly related to the total surface area of the particles. Smaller particles have higher surface areas and so produce higher slopes. As particles dissolve, they are consumed into the solvent, thus leaving fewer particles and less surface area to continue the dissolving process. Consequently, the dissolving process slows and the curve slope decreases. The slope continually decreases to zero (where the plot is level) indicating all of the particles are dissolved. The location on the curve, where the slope decreases the most, is the point where the greatest number of particles are consumed into the liquid system. A tangent line drawn at this point is directly related to the surface median diameter.

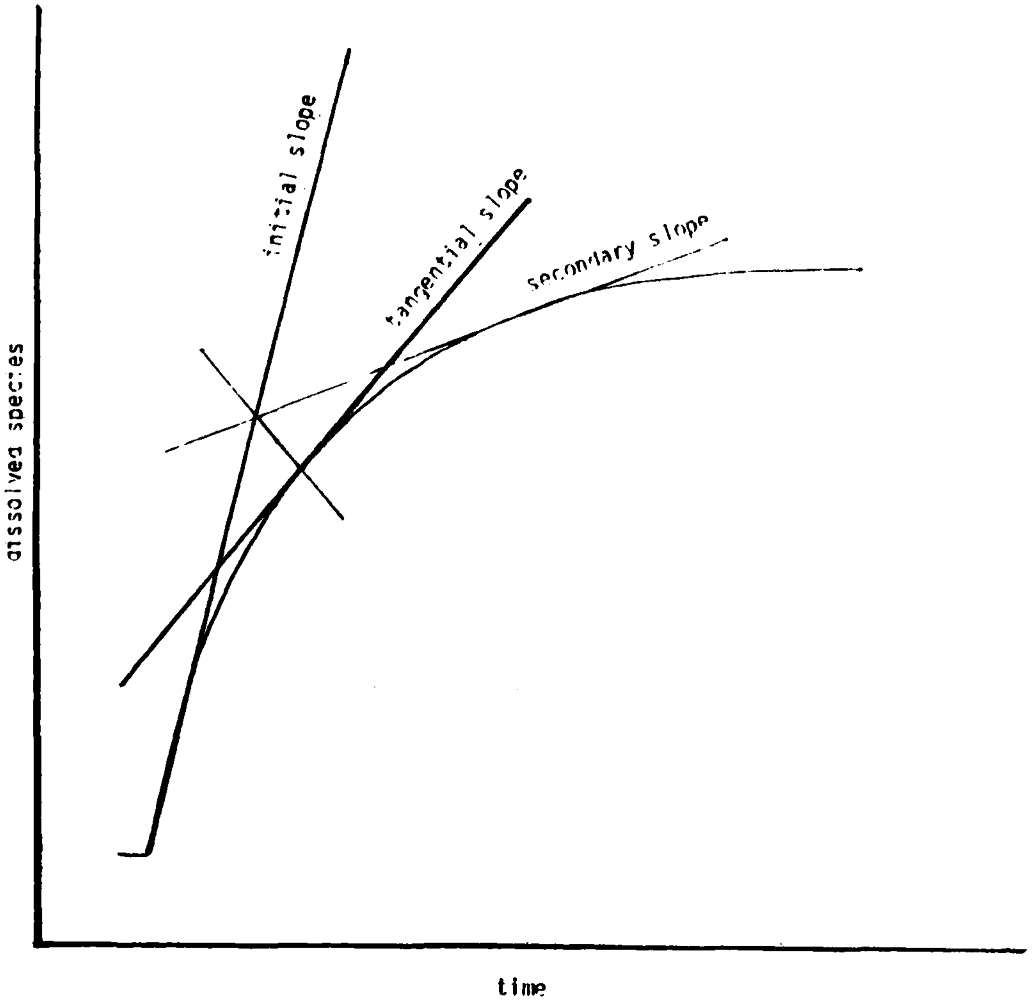

FIGURE 1. Particle Solvolysis Plot

<u>Particle Solvolysis Relation To Burn Rate</u>: The solid-gas system of burning propellant and the solid-liquid system of dissolving particles are both controlled by the interdependence of particle size and consumption rate. Surface area dependent systems have a similar relationship, where smaller particle sizes per mass produce higher consumption rates, and consumption produces smaller particles. It is a dynamic system that possibly may be simulated only by another dynamic system. This relationship should hold true for surface active systems until the system is perturbed by interferences such as rate limiting mechanisms that hinder energy transfer, or reaction limiting mechanisms such as binder melt interference of particle sublimation. A direct relationship between the consumption processes can determine if such interferences are present in a burning system. This new characterization technique has been proven much more surface area dependent than weight-median diameter measurements, so it should provide an improved ability to predict propellant burn rate and transfer formulation technology for propellants with surface area dependent processes (Ref. 4).

<u>Particle Solvolysis For HMX</u>: A similar technique has now been developed for HMX and RDX particles that involves the detection of the liberated molecules by ultraviolet spectrophotometry (Ref. 5). In this application, the available surface area of the combined particles produces a plot of solvated molecules per time. In the detection window, due to minor turbidity, the particles produce only a small noise spike. However, as the particles dissolve, the solvated molecules become able to absorb the UV radiation. A greater total surface area for all of the particles produces a higher slope on the curve, very similar to the electrochemical detection method used for AP and AN. The tangent to the point of greatest slope decrease produces data related to the diameter of particles with the highest

number of similar surface areas. This is the point of the greatest population of particles being consumed, so it is a bulk property indicator.

Why particle solvolysis?: The value of the particle solvolysis analysis is in the ability to determine whether a process is surface area or bulk material dependent. Each characterization technique provides a certain view of the burning process. Finding the morphology character most closely resembling the dependent parameter in the burning process, should be reflected by producing a more linear correlation to burn rate. Where the diameter measurements give an indication of bulk particle character, and the surface area measurement indicates the relation of burn rate to surface area; these analyses are independent; which precludes comparison for determining surface area dependence. The independence of these analyses prevent a direct comparison due to the variation in measuring principle and dependent relative degree of error. Although calculated surface areas can be compared to diameter measurements from the same instrument, the inaccurate assumption of smooth spherical particles creates enough error to invalidate comparison. By displaying surface area distribution, the particle solvolysis technique can differentiate surface area dependence from bulk dependence in one analysis. This makes the comparison of the correlation coefficients independent from relative error. Burning rates of propellants that correlate with the initial slope and with the greatest linearity indicate surface area dependence of the burning process. However, greater linearity in the correlation to the tangent indicates that the high surface area of the smaller particles are not as significant of a contributor to the burning process. If the HMX relationship of higher-burn-rates-with-larger-particles is a surface area mechanism, with heat transfer limitations, then the best correlation to burn rate should be at the initial slope, since the highest surface area smaller particles should react first. If the best correlation is at the tangent to the greatest slope decrease, then, either the smaller particles are interfered with by binder hindrance, or reaction, or the rate limiting mechanism is not a surface process.

There is a large volume of literature on decomposition of nitramines, yet little has been done to convert the mechanistic data to actual propellant measurements. The particle solvolysis technique is a means of validating decomposition pathways by measuring parameters dependent on the burning process. Schroeder (Ref. 6) suggests that HMX decomposition may be an autocatalytic process. Since HMX decomposition is necessary to initiate burning, this could indicate a burning process of autocatalytic decomposition, with the rate limitation dependent on heat transfer for initiation. This could also be a volume dependent process, as indicated by Shackelford and Coolidge (Ref. 7). By determining the surface area or volume dependency in actual propellants, the solvolysis data can aid in confirming or denying mechanistic theories based on pure HMX.

Comparisons are made between the correlation coefficients to burn rate for each of these techniques with the purpose of increasing understanding about the burning process. The application of these techniques will determine which is the most useful for the routine analysis of burn rate.

EXPERIMENTAL

Propellant slabs were prepared in 60 gram slabs with normal broad distribution monomodal HMX in the following formulation: HMX 73.1%, TMETN 16.87%, R-18 8.5%, IPDI 1.39% and DBTDA 0.01%. Burn rates were determined by using a window bomb at 500, 1000, 1500 and 2000 psig, and quarter inch slabs with a high speed video camera. Particle solvolysis analysis was performed with initial and tangential slopes measured. Particle size analyses were performed using the ATM sonic sifter, Hiac-Royco PA 720 particle sizer instrument (light blocking technique), and the Malvern particle sizer 3600E (ensemble light scattering technique). The 10% and 90% diameters and calculated specific surface area were also provided by the Malvern instrument. Calculations were also made from the Hiac and sieve data for specific surface area. Table 1 shows the particle weight-median-diameters marked on the containers as received; as analyzed by the Hiac-Royco instrument and ATM sonic sifter (200 and 400 micron); as analyzed by the Malvern particle sizer. It also shows the calculated and measured surface areas, and the initial and tangential solvolysis slopes.

Table 1

PARTICLE SIZE DISTRIBUTIONS USED

Wt Med Dia on container as received, μ	4	26	57	200	400
Wt Med Dia As Analyzed By Hiac/Sieve, μ	8.3	19.4	19.7	110	200
Wt Med Dia As Analyzed By Malvern, μ	4.9	14.4	62.2	196	257
90% Diameter from Malvern, μ	12.0	38.7	116	320	422
10% Diameter from Malvern, μ	2.0	4.0	12.9	87.6	90.1
Hiac/Sieve Calculated Specific Surface Area, m^2/gm	0.41	0.20	0.20	0.030	0.020
Malvern Calculated Specific Surface Area, m^2/gm	0.52	0.15	0.067	0.020	0.020
Measured Specific Surface Area, m^2/gm	1.47	0.27	0.16	0.077	0.041
Initial solvolysis slope, mm/mm	7.51	3.34	2.62	0.435	0.352
Tangential solvolysis slope, mm/mm	1.63	1.39	1.10	0.338	0.267

The Apparatus: Hewlett Packard 8450A diode array spectrophotometer; Masterflex peristaltic pump; NSG quartz UV flow cell with 10mm pathlength; Bronwill biosonic IV ultrasonic probe; Tri-R model K43 propeller type stirrer; Hiac Royco PA 720 particle size analyzer; ATM sonic sifter; Malvern particle sizer model 3600E; Micromeritics Flowsorb II 2300; McDowell 75 gram propellant mixer; Kodak Ektapro 1000 high speed video camera and recorder.

Reagents: For the particle solvolysis, 200 ml of solvent consisting of 130 ml ethanol (military specification 3A denatured), and 70 ml of acetonitrile. Carbon tetrachloride was used for the malvern particle size analysis. Distilled water was used for the Hiac-Royco analysis. Each used one drop of twitchel base as a dispersant. The measured surface area analysis used a gas mixture of 70% helium and 30% nitrogen. The propellent formulation used cyclotetramethylenetetranitramine (HMX), hydroxyl terminated poly(diethylene glycol adipate) (R-18), trimethylolethane trinitrate (TMETN), isophorone diisocyanate (IPDI), and dibutyl tin diacetate (DBTDA). All chemicals were reagent grade, unless otherwise noted.

Operating Procedure: Solvolysis technique: 0.025 grams of HMX was placed in 200 ml of the solvent in a beaker, stirred, and pumped through the UV cell at 100 ml/min. HMX was introduced as a dry powder and scanned at a 230 nm wavelength. Slopes were taken for plots at 120 seconds. For the particle size analysis the HMX was introduced after dispersing in twitchel base in the appropriate solvent with the ultrasonic probe set to the lowest setting for 15 sec. Specific surface area measurements used the single point type analysis with a gas mixture of 70% helium and 30% nitrogen.

RESULTS AND DISCUSSION

Figure 2 shows the plot of burn rate vs pressure for the particle sizes used. With this formulation, larger particles produced higher burn rates for all pressures used. Figure 3 shows the burn rate vs the measured specific surface area. Since the relationship of the initial solvolysis slope is linear to log of the surface area, the particle solvolysis slope, the measured specific surface area, and calculated specific surface area have a similar relationship to burn rate. In general, all measurement techniques shown in Table 1 can be made linear to the burn rate with only log scaling where appropriate. The degree of linearity of these characterization techniques varies as the appropriateness of the measurement matches the burning characteristics of the propellant. One limiting factor involves achieving a uniform propellant. Error is produced by a lack of easy access to all reacting species in the burning process. Since changes in particle size change the mixing characteristics between batches, each batch has its own characteristics dictated by the size of the HMX. Additionally, the burning characteristics of each particle size changes with pressure. Where one size burns well at low pressure, and is erratic at high pressure, another size may act just the opposite. Initially, strand burns were performed, but the burn rates were erratic due to the lack of sufficient acoustical emission and various other problems encountered when burning strands. The window bomb burns were much less erratic for measurement purposes. Problems inherent with burning small pieces of propellant make the correlation coefficients appear lower than may be acceptable in other type analyses. However, the plotted relationships are quite linear to the burn rate, even with the slight scatter.

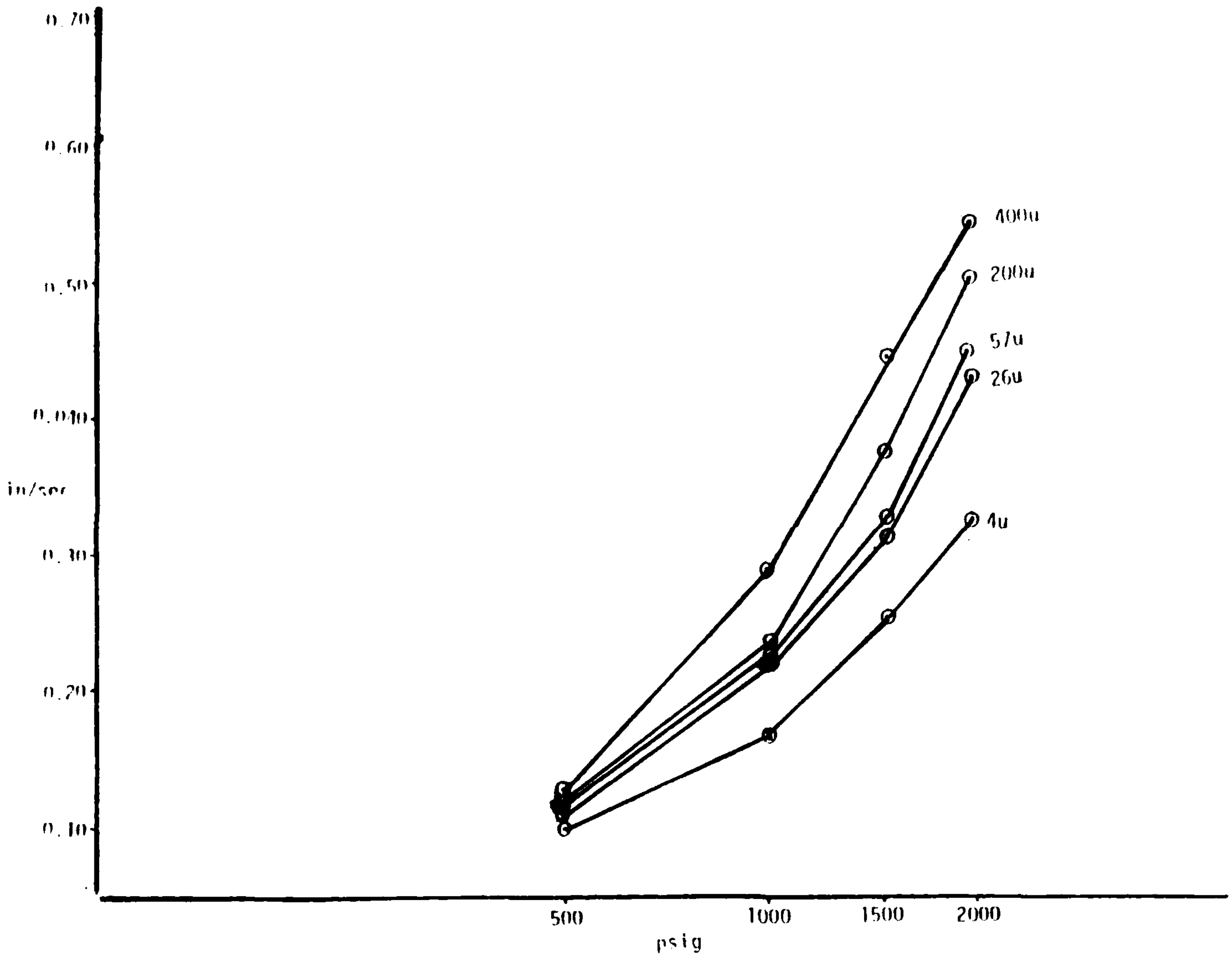

FIGURE 2. HMX Burn Rate vs Pressure

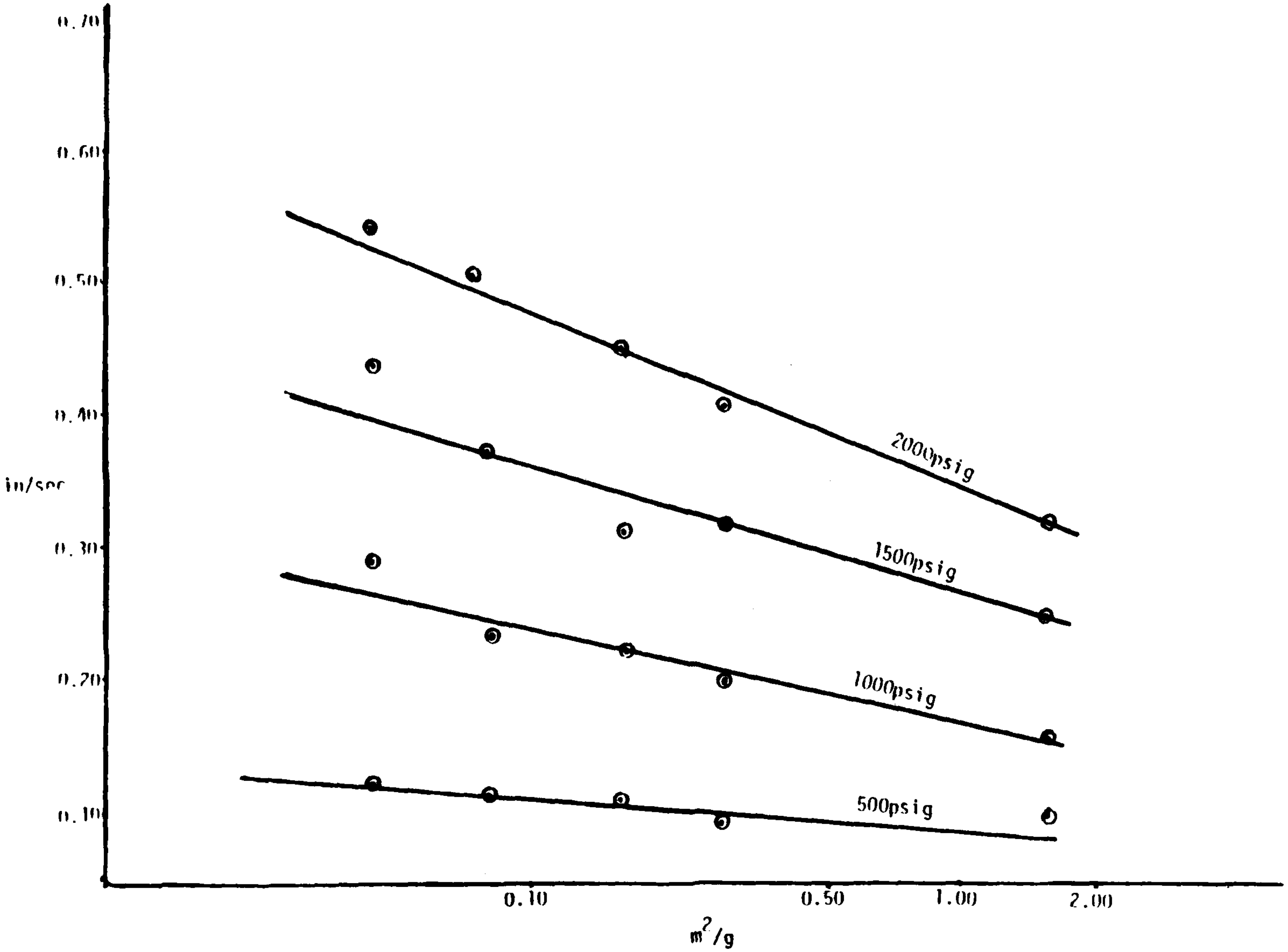

FIGURE 3. HMX Burn Rate vs Measured Specific Surface Area

Table 2 shows the correlation coefficients for the various characterization techniques to the burn rates, and the mean of the correlation coefficients for the four pressures. Comparison of the means indicate that the highest correlation is that of the weight-median-diameter marked on the containers, as received from the vendor. Since the size dependent particle burning stability varies with pressure, this make comparisons of the means the only method to determine the best characterization parameter.

Table 2

BURN RATE TO CHARACTERIZATION TECHNIQUE CORRELATIONS

CHARACTERIZATION	500 PSI	1000 PSI	1500 PSI	2000 PSI	MEAN
Wt Med Dia as Rec	0.9036	0.9666	0.9521	0.9993	0.9554
Wt Med Dia Hiac	0.8889	0.9258	0.9736	0.9437	0.9330
Wt Med Dia Malv	0.9485	0.9270	0.9501	0.9819	0.9519
90% Dia Malv	0.9332	0.9382	0.9134	0.9902	0.9438
10% Dia Malv	0.9459	0.8932	0.9022	0.9553	0.9241
Hiac Calc SSA	0.8847	0.9014	0.9572	0.9300	0.9183
Malv Calc SSA	0.9055	0.9203	0.9089	0.9854	0.9300
Measured SSA	0.8711	0.9701	0.9447	0.9961	0.9455
Initial Slope	0.6875	0.9180	0.9030	0.9772	0.8714
Tangential Slope	0.8867	0.8978	0.9245	0.9488	0.9144

Comparing the correlation coefficients for the initial and tangential solvolysis slopes to burn rate, indicates that the smaller particles in the distribution and their higher surface area are not major contributors in the burning process. Since the tangential slope correlation is superior to the initial slope correlation, this indicates a bulk process mechanism or larger particle controlling mechanism for the burning propellant. It still appears to be a surface active mechanism due to the superior correlation of the measured specific surface area versus calculated specific surface area. The measured specific surface area, may be typically over twice the amount of calculated specific surface area, which indicates a much greater area for surface reactions. Neglecting these reaction sites lowers the correlation. This indicates that the surface irregularities of the particles play an active part in the burning process, but the rate controlling mechanism is not surface area dependent. Comparing the 10% diameter to the weight-median-diameter, and the 90% diameter, it is seen that the larger particles contribute more to the rate limiting mechanism than the smaller particles. But since the 90% diameter correlation is less than the weight-median-diameter correlation, it does not appear to be a mechanism that limits small particle participation by melt interference.

CONCLUSIONS AND RECOMMENDATIONS

Comparisons of the correlation coefficients and their significance, indicate that the burning of HMX propellants is a surface active process, but not a surface area dependent process. It appears to be a volume or bulk particle dependent process, with a possible heat transfer rate limitation, due to the need for HMX decomposition to initiate burning. As a bulk process mechanism, surface area and surface area dependent analyses, on the average, provide no better correlation than weight-median-diameter measurements, and may be worse in individual circumstances. For routine analyses, weight-median-diameter measurements provide as accurate a correlation to burn rate as is presently available, and is recommended for such measurements.

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