EFFECTS OF OXIDIZER PARTICLE SIZE ON COMPOSITE SOLID PROPELLANT BURNING: NORMAL BURNING, PLATEAU BURNING AND INTERMEDIATE PRESSURE EXTINCTION

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EFFECTS OF OXIDIZER PARTICLE SIZE ON COMPOSITE SOLID PROPELLANT BURNING:
NORMAL BURNING, PLATEAU BURNING AND INTERMEDIATE PRESSURE EXTINCTION

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ABSTRACT

A review of existing burning rate data show that highly loaded, medium particle size (20-200μ) AP composite solid propellants burn normally and conform to the granular diffusion flame theory. Underoxidized, small particle size propellants show plateau and extinguishment behavior at normal rocket pressures. Further measurements have been made to confirm these views and to show that plateau and extinguishment behavior is due to intermittent burning.

INTRODUCTION

Burning rate studies in various laboratories in the U. S. and abroad, most notably at O.N.E.R.A. and Princeton, have shown the granular diffusion flame theory to be valid for normal ammonium perchlorate-based composite solid propellants, i.e., those with high oxidizer content and/or wide-range unimodal oxidizer particle size distributions. No exceptions to the theory have been found for any propellant within this practical range of composition. This paper has two main objectives, one, to review the experimental evidence that supports the theory, and two, to analyze an interesting class of deviations (abnormal burning rate curves).

In the thesis research of Bastress at Princeton, anomalous particle size effects in the intermediate pressure range (100-1000 psia) were found when oxidizer content was reduced. Reduction of oxidizer/fuel mixture ratio produced first, pronounced plateau burning behavior, and then, upon further reduction, a region of negative slope in the burning rate-pressure dependence curve; for the finest particles, a pressure limit could be found above which self-sustained burning was not possible. This behavior (plateaus and extinguishment) was ascribed to spotty flame-outs caused by intermittent local depletion of exposed oxidizer crystals at the decomposing propellant surface, a phenomenon thought to result from the large difference between the individual pyrolysis rates of the fuel and oxidizer under weak flame conditions. This contradiction in burning rate behavior between propellants of high oxidizer loading and those of low oxidizer loading suggested interesting implications from both the theoretical and practical points of view. It was important, therefore, to re-examine thoroughly the data and the underlying mechanism.

(1) This paper is based on the results of research conducted under ONR Contract Nonr 1858(32) under the supervision of the Power Branch of the Office of Naval Research.

(2) Ph.D. Candidate, Member of Professional Technical Staff, and Professor of Aerospace Propulsion, respectively.
GRANULAR DIFFUSION FLAME MODEL; RANGE OF APPLICABILITY

Earlier studies have shown the granular diffusion flame model to be valid for normal burning propellants. As shown in Fig. 1, this model considers an AP-based composite solid propellant to burn sequentially in three stages: first, an endothermic step involving pyrolysis of the binder to form fuel vapors and dissociative sublimation of AP to form ammonia and perchloric acid; then, an exothermic pre-mixed reaction between the NH$_3$ and HClO$_4$ (called A/PA reaction zone), and finally, an exothermic gas phase reaction between the oxygen-rich A/PA zone combustion products and the, as yet, not-oxidized fuel vapors (O/F zone). Gasification of both constituents at the burning propellant surface is driven by conductive heat feedback from the A/PA and O/F reaction zones. The pyrolyzed fuel vapors are presumed to emerge from the propellant surface in the form of gaseous fuel pockets and so, the rate of generation of heat in the O/F zone is controlled by the chemical reaction rate and/or diffusional mixing rate, depending on the prevailing pressure.

In a recent paper$^5$ it was shown that it is valid to consider the exothermic gas-phase A/PA reaction zone collapsed to the propellant surface in the intermediate pressure range ($\sim 100-1500$ psia), because in this pressure range the A/PA reaction is much faster (20 to 200 times) than the O/F reaction. This implies that the A/PA zone is much closer to the propellant surface than is the O/F zone (see Fig. 2) and so thin that its thermal resistance to heat feedback from the hot flame to the cold surface is negligible. Under these circumstances, the pressure dependence of the reaction rate in the A/PA zone contributes little towards the pressure dependence of the overall burning process of a composite solid propellant, which is then determined mainly by the pressure effect on the thermal resistance of the O/F granular diffusion flame. The granular diffusion flame theory with a collapsed A/PA flame is the essence of the original 1960 formulation$^3$ of the theory. (An interesting point of the theory is that the pressure dependence of the propellant burning rate comes almost entirely from the pressure dependence of the kinetics of the O/F zone, even though the heat feedback to the unburned propellant from this source is generally less than that contributed by the AP mono-propellant reaction.) The validity of the theory in the intermediate pressure range for highly oxidized propellants with medium-sized AP particles (20-200µ) is borne out by the many results$^{1, 2, 3, 4, 5, 7, 11}$ which fall on a straight line when plotted as (p/r) vs. (p$^{2/3}$). Typical of such fits are those shown in Figs. 3 and 4. Similar plots and equally good straight lines are shown for other propellants in the cited references. The only data in the literature known to us which does not conform to the predictions of this model are those of Adams, Newman, and Robins$^{12}$ for pressed fuel-AP strands. There is no apparent explanation at this time for their observed burning rate behavior; the curves are highly unusual.

As initially predicted, there is a maximum particle size and a maximum pressure for which the granular diffusion flame theory can be valid because, at large values of either or both of these parameters, the O/F flame zone thickness becomes comparable to or smaller than the scale of roughness of the regressing propellant surface, and then the burning process can no longer be viewed as one-dimensional. A quasi-planar surface is the basis of the GDF theory. Some other theoretical description would be necessary out-
side these limits. In Ref. 4, for example, burning rate data show that the theory breaks down at intermediate pressures for particles larger than about 200μ. A review of available high pressure burning rate data shows that the theory breaks down above some pressure between 2000 and 5000 psia for particle sizes between 20 and 200μ. As shown in Fig. 2, the latter observation is in general agreement with estimates from the theory. It is also shown in Fig. 2 that the thickness (and hence also the reaction times) of the A/PA and O/F reaction zones become comparable at pressures of 1 atm and below. Thus, at these low pressures, the complete three-stage granular diffusion flame theory with the A/PA zone of finite reaction time must be treated. With this extension to the theory, very low pressure burning rate and extinction behavior can be successfully explained. The breakdown of the GDF theory at very high pressures and for propellants with very large particles was anticipated from the theory itself; the extension to low pressures by explicit treatment of the underlying A/PA flame was also a logical sequel to the 1960 theory.

What was not anticipated in the original 1960 theory was the finding that underoxidized, small particle size, AP-based composite propellants do not burn normally at intermediate pressures and that plateaus and extinctions occur. The finding showed up first in the thesis research of Bastress at Princeton in the course of a systematic study aimed at finding a quantitative relation between the b-parameter in the GDF formula and particle size. The burning rate curves seemed so erratic that publication in the journal literature was withheld until confirming tests could be made. This paper reports the confirming tests. A new phenomenon not accounted for by the GDF theory takes over in these special propellants. The results of the new investigation of this type of abnormal burning are reported below.

**EXPERIMENTAL RESULTS: ABNORMAL BURNING**

Burning rate plateaus (Figs. 5 and 6) can be produced by lowering AP content and reducing AP particle size. With further reduction of oxidizer loading, a region of negative slope (mesa burning) in the burning rate versus pressure curve develops; for still lower loading, extinction occurs for pressures above about 800 psia. This behavior was observed for polysulfide-AP, polyester-styrene-AP, and epoxy-AP propellants. (Rumbel[1]) reported an identical effect of reduced AP content in polyvinyl chloride based propellants. In one case, a polystyrene propellant with 72.5% 20μ AP, extinction was found only in the range 300 to 1200 psia. Since other propellants were not tested above 1600 psia, the upper limit of the apparatus, the latter observation might imply that a pressure exists for all such propellants above which steady self-sustained burning is again possible. Fig. 6 shows that similar regions of plateau burning, mesa burning and intermediate pressure extinction can be produced by reducing oxidizer particle size while the oxidizer loading is held at a constant low value.

It was decided to try to reproduce the anomalous burning rate results of Ref. 4 in order to ensure that the observed behavior could not be attributed to defects in experimental technique or in propellant quality. Steps were taken in the new experiments to modify the existing burning rate apparatus and to modify the test procedure in order to obtain more accurate measurements; also, more careful propellant manufacture and quality control methods were instituted. The result was that the data for polysulfide propellants containing 65% ammonium perchlorate with different mean particle sizes in
Ref. 4 were found to be reproducible and this was demonstrated with good accuracy. Similar plateau and extinguishment behavior was found with polybutadiene acrylic acid propellants containing 75% AP of different mean sizes (Fig. 7). Very careful investigation of propellant density excluded void content as a possible cause of the burning rate anomalies. It was concluded, therefore, that the anomalies are an inherent characteristic of small AP particle size propellants, particularly when severely underoxidized.

In the new results (see Figs. 6 and 7), when the particle size is medium ($\sim 100\mu$), the burning rate versus pressure curves for the above two propellants (PBAA-and polysulfide-AP) are monotonic, with steadily decreasing slope as pressure is increased. Between 15 and 45$\mu$, plateau burning is evident in the range 300 to 800 psia. With AP particle size less than 10$\mu$, the burning rate curve reaches a maximum at about 350 psia and decreases with further increase of pressure; extinction occurs at about 500 psia for the PBAA propellant and at about 700 psia for the polysulfide propellant. Increasing strand size from 1/8 inch square to 3/8 inch square has the effect of increasing the extinction pressure from 375 to 600 psia in the case of PBAA propellant with 75% AP of 5$\mu$ mean particle size; however, the burning rate curves have the same shape independent of strand size. Reid observed a similar narrowing of the intermediate pressure extinction region with increasing strand size in the case of polystyrene-AP propellant; for strands larger than 5/16 inch square, no extinction region could be found at all. It was observed in our investigations that the propellant samples that were ignited but suffered such extinction had highly irregular burned surfaces. Consistent with this is the finding that irregular pressure oscillations of about 5 psi amplitude persisted in the combustion chamber whenever a strand burning test was made at a pressure in the mesa region; the slope of the burning rate versus pressure curve in this domain is negative. Where the pressure exponent was positive, the pressure was always found to be steady. Barrere's photographs show that whenever plateau burning occurs, the flame is intermittent in the sense that temporary localized extinctions occur on the surface.

To further demonstrate that the phenomenon of intermittent burning is a small particle size phenomenon, a small percentage of medium-sized AP particles (10% 80$\mu$) was added to a predominantly small unimodal particle size distribution (90% 5$\mu$). As seen in Fig. 8 mesa burning is suppressed; the propellant still extinguishes, but the burning rate curve does not show the droop that is characteristic of small unimodal particle size propellants; also, pressure oscillations in the chamber are hardly noticeable. In line with Bastress' hypothesis for the mechanism of intermittent burning, the large AP particles will always be exposed to the gas phase flame and thereby prevent the scale of the localized extinctions from becoming too large; effectively, they act as "flame holders". (Data reported in Ref. 11 with PVC propellants seem to indicate also that small particles accentuate plateaus.)

To demonstrate that a highly loaded, small particle size, PBAA-AP propellant burns normally, a propellant with 80% AP of bimodal distribution (70% 45$\mu$ + 30% 5$\mu$) was made. The results appear in Fig. 9. In the same figure it is seen that lowering oxidizer content causes the behavior characteristic of propellants which burn intermittently, i.e., mesa burning and extinction. As expected, the highly loaded propellant, which burns normally, conforms to the granular diffusion flame correlation: $l/r=a/p+b/p^{1/3}$ (see Fig. 10).
It is of interest that the addition of 40.4% AP of 5\(\mu\) mean particle size to a double base propellant consisting of 19.2% nitrocellulose (NC), 39.2% tri-ethylene glycol dinitrate (TEGDN) and 1.2% stabilizer causes a striking difference in its burning behavior. This composite-modified double-base (CMDB) propellant burns like a normal type of highly oxidized, medium particle size, AP-based propellant with a non-energetic binder; the \((\log r) vs. (\log p)\) curve is monotonic and bends concave downwards. No dark zone is evident in the flame above the burning surface when burning in nitrogen at atmospheric pressure (a phenomenon always exhibited by double base propellants) and the burning rates satisfy the granular diffusion flame correlation: \(1/r = a/p + b/p^{1/3}\) (see Fig. 11). In contrast to this, typical uncatalyzed double base propellants have burning rate curves which bend sharply concave upwards at about 500 psi and, as expected, they do not satisfy the granular diffusion flame correlation. The dark zone in the DB flame is plainly visible for all pressures up to 500 psi. (The contraction of the dark zone above 500 psi to zero thickness is presumably the cause for the rather sharp bend upwards in the burning rate curve). The addition of AP apparently converts the DB gaseous flame from a three-zone gas flame of premixed reactants to essentially a one-zone gas flame dominated by a granular diffusion flame mechanism. It is to be noted that since the binder in a CMDB propellant is itself a monopropellant, there is no reason to suppose that a CMDB propellant will under any circumstances burn intermittently, and no extinctions are ever observed. (Plateaus observed in some DB propellants are always the result of special catalysis and take the form of a super-rate; the AP propellant plateaus described here are always the result of a reduction in burning rate. The two phenomena seem similar but should not be confused.)

**CONCLUDING DISCUSSION**

Our review of existing propellant burning rate data shows that propellants with high oxidizer content and medium-sized particles (20-200\(\mu\)) burn normally, that is, the burning rate curves are monotonic and show no evidence of plateau burning, negative pressure exponents, etc. The results of those propellants in the intermediate pressure range (100-1500 psia) are correlated quite well by the Summerfield relation \((1/r = a/p + b/p^{1/3})\) for the granular diffusion theory. Support for the validity of the formula is based on burning rate data drawn from diverse sources: Princeton, S.R.I., A.R.C., U/Tokyo, O.N.E.R.A. No exceptions have been found. The validity of the theory can be extended down to about 1 psi, the low pressure limit at which extinction occurs, if the pressure dependence of the ammonia/perchloric acid reaction zone is taken into account in the GDF theory. This is shown in Ref. 5. The burning rate correlation is then more complicated, of course, but it asymptotically agrees with the Summerfield relation at pressures above 1 atm. As indicated above, underoxidized, small particle size (< 20\(\mu\)) propellants burn intermittently and may approach extinction. This anomalous behavior is not explained by the theory since it considers the regressing propellant surface to be planar, and it appears that such intermittency is the result of severe non-planar burning. Thus, the granular diffusion flame theory appears valid for highly loaded, medium-sized particle propellants, (i.e., the usual practical propellants) and no contradiction exists.

One reservation with respect to this conclusion is in order. The GDF theory was derived on the premise of a "dry" burning surface, i.e., that the state of unmixedness in the emerging gas is independent of burning rate or pressure. Propellants based on such fuels as polyurethane and polyisobutylene have been reported to exhibit very fluid, molten surfaces, especially at slow burning rates. This might alter the basic premise of the theory so as to distort the \(r-p\) curve; we have not yet tested such propellants.
It is of interest to delineate the boundaries between normal burning and anomalous burning, as defined above. One can visualize a three-parameter Cartesian space, one axis being particle size, a second being oxidizer equivalence ratio, and a third axis being a differential pyrolysis index. With the three-parameter propellant space in mind, we can identify the transition between normal burning (no plateaus, no extinction limits) and anomalous burning for several ammonium perchlorate propellants. On the basis of data available in the range from about 10-200 microns, AP-polysulfide propellants exhibit anomalous burning for small particle sizes at 65% AP by weight and less, normal burning for all sizes at 70% AP and more. For AP-PVC propellants, the transition AP loading is 67-73%; for an AP-epoxy propellant, the transition loading is 65-68%; for an AP-PBAA propellant the transition range is around 75%; and for an AP-polystyrene polyester propellant, the transition range is 72.5-77.5%. For every AP propellant for which data are known to us, the anomalous plateaus can be produced by reducing the AP loading below the transition value; plateaus can be eliminated by raising the AP loading above the transition value. The oxidizer equivalence ratio \( \frac{(O/F)}{(O/F)_{stochiometric}} \) corresponding to the transition appears to fall between about 0.35 and 0.45.

In conclusion, we have shown additional evidence for the applicability of the GDF theory for normal AP-based rocket propellants and we have defined a class of underoxidized AP propellants (perhaps useful as gas generators) that exhibit an interesting type of anomalous burning behavior.

**IMPLICATIONS FOR FUTURE WORK**

The following remarks represent our assessment of the present position in research on the mechanism of burning of solid propellants. It appears to us that the physical-chemical model underlying the GDF theory is the correct one for normal types of AP composite propellants. It is consistent with all the known facts concerning the physical and chemical structure of the flame, and its predictions are quantitatively in accord with all known and substantiated burning rate measurements. No contradictory evidence is known to us. No other theory has been published that meets the two tests - agreement with all the known facts of physical and chemical structure, and quantitative agreement with burning rate curves of all normal-type AP propellants. Unless contradictory evidence of a reliable nature should turn up, we see no reason to pursue this particular line of research any further.

*The differential pyrolysis index may be defined as:

\[
\Delta T_s = \frac{(T_{S_f} - T_{S_o})_r}{(T_F - T_{S_o})_r}
\]

where

- \( T_{S_f} \) = fuel surface temperature
- \( T_{S_o} \) = oxidizer surface temperature

at regression rates \( r = \) propellant burning rate

and \( T_F = \) adiabatic flame temperature

Paraphrasing Bastress' hypothesis, the surface becomes strongly non-planar and intermittent burning will ensue when \( \Delta T_s > \Delta T_s^* > 0 \). The critical value \( \Delta T_s^* \) probably increases with increasing oxidizer content and/or particle size; that is, highly loaded AP propellants with larger particles resist anomalous burning.
A comprehensive report is being written at present that expands on the evidence in detail and that analyzes each of the various published papers that have been offered as rival theories. The conclusions are those stated above. The report will be issued in about two months.

It would be useful now to press forward with studies designed to capitalize on the knowledge thus gained. For example, in the search for burning rate catalysts, (or burning rate suppressants), it would be very useful to identify the site of the action of each catalyst. A particular catalyst might act so as to enhance the pyrolysis rate of one or the other constituent, or it might induce sub-surface interfacial reactions where normal AP propellants exhibit none, or it might hasten the A/PA flame and thus promote more efficient low pressure combustion, and so on. In the light of what is now known of the structure and propagation mechanism, such questions begin to take on much more precise meaning than ever before.

Additional lines of research in composite propellant burning become feasible now. The effect of aluminum powder addition on flame structure of AP composite propellants deserves exploration. Substitution of potassium perchlorate, ammonium nitrate, hydrazinium perchlorate, or other granular oxidizing salts for AP may make an important change in structure and in propagation mechanism. Fuel binder characteristics, in particular, fuel pyrolysis kinetics, are very important in the theory for determining burning rate behavior; this can guide the search for more advantageous binders. The effect of ambient temperature, particularly up to temperatures above 100°C, is a significant question for some applications. The high pressure domain, from 200 atm to 2000 atm and higher, is known to bring in a new flame structure and a new propagation mechanism. Erosive burning should be studied in the light of the granular diffusion flame structure. The effect of centrifugal force (spinning rockets) has been studied on the basis of the GDF structure, but more remains to be done. Finally, as a broad observation, it may be noted that nitrocellulose-base homogeneous propellants are completely different from composite propellants (the reactants are homogeneously premixed and not heterogeneous), and so a whole new field opens up if one should wish to produce a quantitative theory for NC-homogeneous propellants equivalent to the GDF theory for AP-composites.

A word about non-steady burning rates. A number of theoretical papers have appeared in the past ten years or so, each purporting to offer a flame model and a theory for the dynamic behavior under oscillatory pressure conditions (i.e., acoustic admittance theories) or under rapid depressurization (i.e., extinguishment theories). It is astonishing that most of these papers make no attempt to demonstrate that the model used for a non-steady theory must be quantitatively consistent with known steady-state burning rate behavior, when the rate of change of pressure in the analysis is set equal to zero. It is astonishing that formulas for flame speed originally derived for pre-mixed flames are used without apology to describe the dynamic behavior of AP propellant flames. It is the belief of the senior author of this paper that all such theories are wrong. It is time that theorists concerned with non-steady burning made an attempt to base their theories on facts revealed by our research and by others as well concerning AP-composite propellant flames. For a more detailed explanation of these criticisms of previous non-steady theories, and for a presentation of a new theoretical approach that recognizes the structure of the flame zone, see Ref. 15.
ACKNOWLEDGEMENTS

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REFERENCES


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20% POLYBUTADIENE ACRYLIC ACID
80% BIMODAL AMMONIUM PERCHLORATE
AP DISTRIBUTION: 70% 45 µ + 30% 5 µ

EQUIVALENCE RATIO $\phi_m = 0.45$

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**FIGURE 10** 80% AP + 20% PBAA DATA
FLOTTED AS $(p/r)$ VS $(p^{2/3})$

**FIGURE 11** DB AND CMDB PROPELLANT
DATA FLOTTED AS $(p/r)$ VS $(p^{2/3})$