

Eliminate λ_j^0 using Eq. (7); thus,

$$\{\phi_j^0\}^T [K_I] \{\phi_j^0\} = \lambda_j^0 \quad (A5)$$

But, since $\{\phi_j^0\}$ is compatible for structure $[K_I]$,

$$\{\phi_j^0\}^T [K_I] \{\phi_j^0\} \geq \{\phi_j^1\} [K_I] \{\phi_j^1\} = \lambda_j^1 \quad (A6)$$

Between Eqs. (A5) and (A6), $\lambda_j^1 \leq \lambda_j^0$.

Acknowledgment

The work reported herein was supported by Jet Propulsion Laboratories, California Institute of Technology. The author expresses his gratitude for useful discussions with Ben Wada and J. Chen at the Jet Propulsion Laboratories, and C. Babcock, California Institute of Technology.

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Effect of Catalyst Concentration on Burning Rate of Composite Solid Propellants

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Introduction

VARIOUS catalysts/additives have been known to affect the combustion of composite solid propellants and the oxidizer ammonium perchlorate (AP), but the exact mechanism of this phenomenon is by no means clear. Among the various types of catalysts/additives, the transition metal oxides such as Fe_2O_3 , MnO_2 , etc., form a special class, since they are known to modify AP decomposition, deflagration, and also the combustion of AP based sandwiches and composite propellants. The effect of these oxides has been the subject matter of study by various investigators. The data on this have been reviewed by Jacobs and Whitehead,¹ Hall and Pearson,² and also appeared in a recent paper by Boggs et al.³

In spite of the availability of much data in open literature on the quantitative effect of the catalysts/additives on the varieties of the propellant systems, no systematic study has been done on the decomposition and burning of the propellants as a function of catalyst concentration. It may be mentioned here that Burnside⁴ has studied the burning of the AP/HTPB propellants at higher pressures as a function of Fe_2O_3 concentration. Although Burnside's studies were on

real systems, the effect of the catalyst on AP/HTPB cannot be singled out because the system did contain aluminum. Metal/metal oxide systems are known to form pyrotechnic mixtures.

The study of the catalyst concentration is important because the propellant composition can take only a limited amount of extra solid material apart from the solid oxidizer, which constitutes a major portion of the propellant composition. Second, the catalyst concentration must be as low as possible, so that it does not affect the propellant energy level. The present paper describes the effect of catalyst concentration on the burning rate of solid propellants containing AP and polystyrene (PS) only.

Experimental

The PS/AP propellants were prepared by the method described earlier.⁵ Once recrystallized commercial grade AP was used in the propellant formulations. The particle size of AP used was between 53 to 106 μ . Analytical grade Fe_2O_3 , Ni_2O_3 , Co_2O_3 , and MnO_2 of the same particle size as AP were used as catalysts. In the propellant composition, an oxidizer to fuel ratio equal to 3 was maintained constant, while the concentration of the additive alone was varied from 0.5% to 2% of the total propellant weight. AP + catalyst mixtures also were prepared, keeping the proportion of the catalyst the same as in the case of the propellant.

Burning rates of the propellants at ambient pressure and temperature (25°C in air) were determined in the following manner. Cylindrical propellant strands after curing were inhibited by coating with a zinc oxide enamel and then dried. Each strand was marked at two positions, and the distance between the two was measured using vernier calipers. The accuracy in the length measurement was 99%. The time taken for the strand to burn from one mark to the other was measured with a stop watch. The accuracy in the time measurement was 99%. The burning rate was determined from the length time data, and the accuracy achieved in the measurement was 95%.

The thermal decomposition studies on AP with and without catalysts were carried out by differential thermal analysis (DTA). A home-made DTA apparatus was used, and the details are given elsewhere.⁶ The temperature was recorded

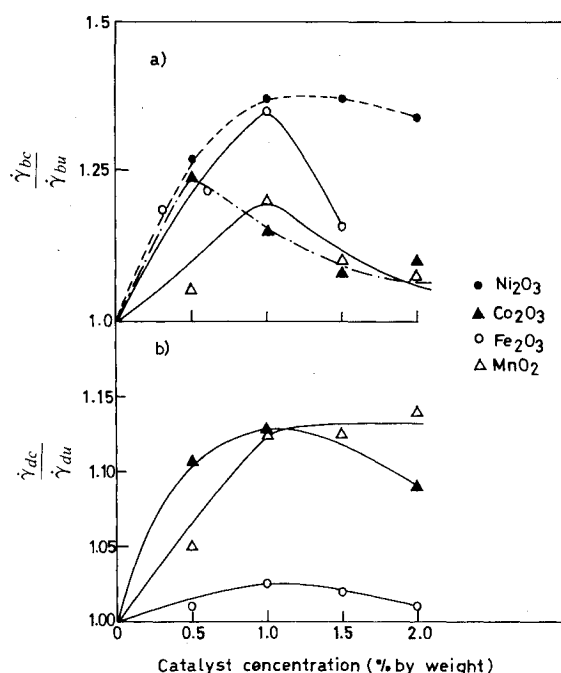


Fig. 1 Dependence of burning rate ratio and thermal decomposition ratio on the catalyst concentration in PS/AP propellant and AP systems, respectively.

Received Dec. 13, 1976; revision received July 20, 1977.

Index categories: Fuels and Propellants, Properties of; Combustion in Heterogeneous Media.

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Table 1 Effect of catalyst concentration on the calorimetric value of AP/PS propellant

Propellant composition, O/F = 3	Heat of combustion per gram of propellant, cal/g	Heat required to raise the temperature of the oxide from ambient to flame, cal/g	Net calorimetric value, cal/g
AP/PS	1100	0	1100
AP/PS + 1% Fe ₂ O ₃	1090	4	1086
AP/PS + 5% Fe ₂ O ₃	1046	20	1026

using a potentiometer, and the differential temperature signal (ΔT) on a galvanometer scale was recorded manually. Samples of 100 mg were used in these studies, and the heating rate employed was 7°C min^{-1} .

Results and Discussion

The ratios $\dot{\gamma}_{bc}/\dot{\gamma}_{bu}$ and $\dot{\gamma}_{dc}/\dot{\gamma}_{du}$ were calculated from the burning rate and DTA data as follows:

$$\frac{\dot{\gamma}_{bc}}{\dot{\gamma}_{bu}} = \frac{\text{burning rate of the catalyzed propellant}}{\text{burning rate of the uncatalyzed propellant}}$$

$$\frac{\dot{\gamma}_{dc}}{\dot{\gamma}_{du}} = \frac{\text{rate of thermal decomposition of catalyzed AP}}{\text{rate of thermal decomposition of uncatalyzed AP}}$$

The rate of thermal decomposition was taken as the inverse of the time taken for the complete decomposition of the AP sample.

The plot of $\dot{\gamma}_{bc}/\dot{\gamma}_{bu}$ vs catalyst concentration is presented in Fig. 1a. A study of this figure shows that the burning rate of the catalyzed propellant increases as the catalyst concentration is increased, and reaches a maximum value around 1% of the catalyst concentration in all the cases, except in the case of cobalt oxide, for which the maximum is seen around 0.5% of the catalyst concentration. After this concentration, either a saturation value is reached, or there is a fall in the burning rate.

The effect of Fe₂O₃ on AP deflagration and propellant combustion has been studied by various investigators. Bakhman⁷ et al. have shown recently that AP containing Fe₂O₃ in a perspex casing shows a maximum around 1% of the catalyst concentration. Investigators^{8,9} also have shown that Fe₂O₃ weakens the dependence of burning rate on the initial temperature. It has been reported that this behavior is observed because the higher percentage of Fe₂O₃ reduces the heat of combustion.⁹

A similar observation has been made by Shidlovskiy et al.¹⁰ on the catalytic activity of various oxides such as MnO₂, Cr₂O₃, Co₂O₃, CoO, etc., on the burning velocity of phenol formaldehyde/KClO₃ condensed mixtures; they found that the strongest catalytic effect was experienced when the catalysts were present in concentrations ranging between 3 and 5%. Shadman-Yazdi and Petersen,¹¹ in their studies, found that KMnO₄, Fe₂O₃, CuO, and copper chromite increased the lower pressure limit when present in small concentrations, and decreased the same when present in higher concentrations. The optimum effect was around 1% of the catalyst concentration.

Friedman,¹² in his studies on AP deflagration, observed that Fe₂O₃ (3%) increased the lower deflagration limit, and the effectiveness of the catalyst was pronounced above 1500 psi. A similar effect of Fe₂O₃ on the lower deflagration limit of AP has been reported by Boggs et al.³

Strahle and co-workers^{13,14} have reported the catalytic effect of iron oxide and copper chromite on the AP/polymer (CTPB, HTPB) sandwich burning rate at higher pressures. The mechanism of action of these oxide catalysts on sandwich burning and AP deflagration may or may not hold true in the case of AP-based composite propellants, and this is a question open to discussion. Pittman¹⁵ has shown Fe₂O₃ (1 and 2%) to

be an effective burning rate catalyst even at higher pressures for AP/CTPB propellants.

Our investigations reveal that better catalytic effect may be obtained by employing lower concentration (~1%) of the catalyst. Our present data are only at ambient pressures, and the validity of the same in actual propellant combustion may be questioned. However, as shown by Pittman,¹⁵ these catalysts also may be effective at actual motor pressures.

The exact mechanism for the effect of catalyst concentration on the propellant combustion is difficult to speculate upon, but some attempts have been made to understand this behavior, and are presented as follows.

In small concentrations, the role of the catalysts used is to increase the burning rate without significantly affecting the calorimetric value of the propellant system. However, when the catalyst concentration becomes large, it cuts into the weight of the actual propellant, thereby reducing the calorimetric value. The calorimetric value is further reduced because the catalyst takes away some heat to raise its temperature in the flame. A calculation to show the decrease in calorimetric value is given in Table 1. The data have been taken from the earlier work by Rastogi, Kishore, and Singh.^{5,16} The table shows that 1% Fe₂O₃ changes the calorimetric value only by 1%, whereas the lowering of the calorimetric value due to the presence of 5% catalyst is approximately 7%. The reproducibility in the measurement of calorimetric value is about 1%, Fe₂O₃ does not alter the calorimetric value to a significant extent; however, beyond 1% catalyst concentration the change becomes significant. These two factors will result in a decrease in the flame temperature, and this may affect the burning rate.

In the case of AP decomposition also, it is seen that, beyond a certain concentration of the catalyst, the effectiveness reaches a saturation; further increase in the catalyst concentration does not contribute significantly toward changing the thermal decomposition characteristics of AP. Figure 1b gives a plot of $\dot{\gamma}_{dc}/\dot{\gamma}_{du}$ vs catalyst concentration, which shows a break at 1% concentration of the catalyst, where the maximum effect is observed. Boggs et al.³ have cited the work of Flanigan in their recent paper, which states, that at pressures above ambient, the three phases of AP decomposition merge into a single step; this step is sensitized in the presence of Fe₂O₃, and this sensitization is further dependent on Fe₂O₃ concentration.

Although it is difficult to envisage the actual behavior in propellant combustion, the previously mentioned similarity in the decomposition and combustion behavior in the presence of catalysts suggests that the mechanism of action of the catalyst is the same, at least to a certain extent, in both the processes. Solymosi and Revesz¹⁷ have shown that Fe₂O₃ has very little catalytic effect below 240°C, but shows pronounced catalytic activity above 240°C. This behavior has been explained on the basis of the enhancement of the electron transfer process.

The effect of catalyst concentrations on the combustion of propellants may be explained if the thermal decomposition is assumed to be an integral part of combustion. Investigations in our laboratory have shown that the propellant decomposition is related to propellant burning rate.¹⁸ It also has been shown that the intermediates obtained after quenching the burning surface of the propellant essentially are the same

as those formed when the propellant is decomposed.¹⁹

Recently, it has been observed by Glazkova²⁰ that the deflagration rate of AP is inhibited when AP is mixed with compounds that inhibit AP decomposition. This effect becomes insignificant beyond 3000 psi, but in the pressure range of interest in rocket motors the data show two- to threefold change. Boggs et al.²¹ have observed that, within certain dopant concentration ranges and pressure below 2000 psi, the deflagration rate of AP increases as a function of the dopant concentration. The above-mentioned features indicate the thermal decomposition of the propellant and that of AP to be related to the burning rate of the propellant and AP, respectively.

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Structure of a Radially Directed Underexpanded Jet

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THE performance characteristics of conventional aerodynamic resonator cavities are influenced greatly by the structure of the underexpanded choked jets that are used to excite them.¹ For pressure ratios less than 4.5 in air, no Mach disk is present, and the exciting jet has a repetitive, cellular structure.² Resonance is achieved only when the cavity mouth is located where the pitot pressure increases in the downstream direction, that is, in the downstream half of each jet cell. A 3-in.-diam cylindrical resonator,³ excited by a circumferentially located and radially directed underexpanded choked jet, has reached its peak performance at a pressure ratio of 3.76. The aim of the present work is a supplement of Ref. 3 for examining more closely those properties of such a jet which affect the performance of this type of resonator.

Calculations are performed according to the method of characteristics for axisymmetric, irrotational flow. In terms of the flow angle θ , Mach angle α , and Prandtl-Meyer angle ω , the slopes of the characteristics and the compatibility relations are

$$\frac{dr}{dx} = \tan(\theta \pm \alpha) \quad (1)$$

$$d\omega \mp d\theta - \frac{\sin \alpha \sin \theta}{\cos(\theta \pm \alpha)} \frac{dx}{r} = 0 \quad (2)$$

From these relations, the jet structure was calculated. The theoretical results are compared to experimental measurements obtained from schlieren photography and a cone-probe traverse in the jet along the centerline in the radial direction.

A cross-sectional view of the nozzle configuration³ is shown in Fig. 1. A toroidal plenum chamber with a rectangular cross section and outer diameter of 7.5 in. is fitted with five equally spaced compressed air inlets. A narrow slit of width $W=0.125$ in. with a $1/4$ -in. rounded entrance in the inner wall serves as a nozzle for the jet which discharges to the atmosphere and is directed radially toward the center of the toroid, for which the radius $R=1.5$ in.

Figure 2 shows a typical schlieren photograph of the jet structure for a jet pressure ratio of 3.04 and with the optical

Received Feb. 9, 1977; revision received July 7, 1977.

Index categories: Jets; Wakes, and Viscid-Inviscid Flow Interactions; Nozzle and Channel Flow.

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