considered here. At the same time, the core to face thickness ratio that has been considered here is much smaller than what would occur in a normal honeycomb sandwich construction.

At present the author is engaged in the theoretical investigation of a semi-infinite sandwich beam subjected to statically equivalent load systems, in order to find the effect of the various parameters in greater detail.

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Catalytic Effects of $KMnO_4$ on the Deflagration of Ammonium Perchlorate: A Preliminary Study

D. M. Watt Jr.*
Cornell University, Ithaca, N. Y.

AND

E. E. Petersen†
University of California, Berkeley, Calif.

Introduction

FOR ammonium perchlorate (AP) catalysts can significantly alter the rate of thermal decomposition, the burning rate, and the deflagration pressure limit, which is the inert gas pressure below which stable, unassisted deflagration is impossible. Various additives give widely differing effects which may be drastically changed by using different concentrations of the same catalyst. (See the review of these data by Pittman.[1]) Since the process of AP deflagration is not completely understood, many questions concerning the mechanism of catalyzed AP deflagration remain unresolved. This research was designed to investigate the importance of the degree of dispersion of the catalyst in the ammonium perchlorate and to investigate the correlation of catalytic effectiveness on AP thermal decomposition and in AP deflagration.

Most studies of catalysts for AP deflagration have used pellets pressed from mechanical mixtures of AP and catalyst, and very little work has been done to see if the catalyst particle size influences the catalytic effectiveness. Although there is growing evidence for a molten zone of AP at the burning surface,[2] it might still be expected that the surface area of the catalyst, rather than the total mass, controlled the reaction rate. Potassium permanganate was chosen for this catalytic study because it has the same crystal structure as ammonium perchlorate and can be isomorphically cocrystallized with ammonium perchlorate. In addition, the $KMnO_4$ was also mechanically mixed with the AP to observe the effects of catalyst dispersion on deflagration.

Considerable attention has been given to the thermal decomposition of AP single crystals doped with potassium permanganate[3] and of AP cocrystallized with potassium permanganate.[4-6] These studies[4,5] indicated that the rate of thermal decomposition increased as the fraction of $KMnO_4$ was increased from 0.5 mole % to 2 mole %. In addition, the activation energy for this process with 2 mole % $KMnO_4$ was found to be about 20 kcal/mole at all temperatures studied[4]; this value is extremely close to the value of 17–20 kcal/-mole determined by Bircumshaw and Newman[7,8] for AP above 240°C in the cubic modification. Below this temperature Bircumshaw and Newman[8] found the activation energy for the thermal decomposition of orthorhombic AP to be 28–29 kcal/mole. In all cases the $KMnO_4$ considerably accelerated the thermal decomposition of AP. At present it is not certain that the AP thermal decomposition is a step in the deflagration process; consequently a second objective of the present preliminary work was to compare the catalytic effects of $KMnO_4$ on AP deflagration with its reported effects on AP thermal decomposition.

Experimental Procedure

Large single crystals were grown with 0.4 mole % $KMnO_4$ isomorphically substituted in the AP lattice by the same method that has been used for growing pure AP single crystals.[9,10] The temperature of a saturated aqueous solution of AP and $KMnO_4$ was lowered very slowly, and small AP crystals were used as the initial seeds. From the resulting crystals perfect sections measuring about 0.4 cm on each side and 1.2 cm in length were cleaved for the deflagration studies. Imperfect crystals were powdered to make pellets with 0.4 mole % $KMnO_4$, and, for comparison, pellets were pressed with a mechanical mixture of 0.4 mole % $KMnO_4$. Pellets of 2 mole % $KMnO_4$ were also prepared from cocrystallized AP-$KMnO_4$ powder. In addition, a layered pellet was made by pressing pure AP powder on top of an AP-0.4 mole % $KMnO_4$ pellet; the pure section was ignited and this, in turn, ignited the AP-$KMnO_4$ section of the pellet.

The combustion chamber was pressurized with nitrogen and the deflagration was photographed with a 16-mm Bolex camera at 64 frames/sec. The samples were ignited by a jet of hot nitrogen impinging normal to the pellet or crystal surface. While the pellet or crystal surface was being heated by the igniter, thermal decomposition caused the surface to recede slowly, but considerably faster than during the ignition of pure AP. Unlike the more usual hot Nichrome wire ignition technique,[2,10,11] the hot nitrogen ignition gas was uniquely adapted to following the gradually receding surface during the ignition transient. A detailed description of the apparatus and procedure has been presented elsewhere.[11]

Discussion of Results

The single crystals of AP with 0.4 mole % $KMnO_4$ isomorphously substituted into the crystal lattice, the pellets pressed from powder with 0.4 and 2 mole % $KMnO_4$ in AP, and the pellets pressed from a mechanical mixture of 0.4 mole % $KMnO_4$ in AP were ignited at either 1000 or 2000 psig and all failed to sustain deflagration. High-speed motion photography indicated that with the hot gas impinging on the surface rapid decomposition would take place and occasional puffs of smoke would be emitted, but all reactions extinguished rapidly with the removal of the ignition gas jet.

In light of the catalytic effect on the $KMnO_4$ on the thermal decomposition of AP it seemed that while the hot ignition gas was striking the crystal or pellet surface the thermal decomposition provided a heat sink that prevented the surface temperature from reaching the ignition temperature. If deflagration is possible, a considerably stronger ignition stimulus may be necessary to overcome this heat sink effect. This consideration led to the experiments with the layered pellets in which the deflagrating AP section was used to ignite the catalyzed section of the pellet, and, again, the catalyzed pellet did not deflagrate. Although this preliminary work did not explore other ignition techniques, it should be noted that

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* Assistant Professor of Chemical Engineering.

† Professor of Chemical Engineering. Member AIAA.

the hot nitrogen gas igniter was quite sufficient for the ignition[11] of pure AP. It is extremely difficult to prove that deflagration is not possible without definitive experimental results such as those which delineate the low-pressure deflagration limit[12] for pure AP and hence these results must be considered tentative.

Since similar results have been reported[13] for AP catalyzed by NH_4MnO_4, these data emphasize the need for a better understanding of the mechanism of catalyzed AP deflagration, particularly for the case of catalysis with the permanganate ion. Since no deflagration occurred, further work will be necessary to explore the effect of catalyst dispersion on AP deflagration. Although $KMnO_4$ strongly accelerates the thermal decomposition[3–6] of AP, no $KMnO_4$ catalyzed AP deflagration could be maintained and, hence, it was impossible to correlate catalytic effectiveness in AP thermal decomposition and deflagration. However, since no concentration of $KMnO_4$ less than 0.4 mole % was used, it seems possible that a smaller concentration of $KMnO_4$ would permit deflagration and alter the burning rate. Since AP thermal decomposition appeared to be providing a heat sink which prevented complete ignition, the maximum $KMnO_4$ concentration for AP deflagration may be a strong function of the igniter heat flux strength. Hence this preliminary research has shown that a more complete study of AP ignition and deflagration catalyzed by $KMnO_4$ may reveal the significance of thermal decomposition in both AP ignition and deflagration.

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Siloxane Polyurethane Composite Propellant Binders

J. M. Hammond,[*] S. Hryhorciw,[†]
and J. E. Stutchbury[‡]
Weapons Research Establishment, Salisbury,
South Australia

Fuel atoms such as aluminium, boron, and silicon have been incorporated into the molecular structure of composite propellant binders in order to modify ballistic properties.[1] Most studies have been concerned with providing more energetic propellants although there have been few accounts where the prime interest is in the effect on burning rate. Schwarz and Lowrey[2] have reported that incorporation of silicon into polysulfide polymers can lead to a 50% increase in propellant burning rate. Silicon in these polymers was present as the silane (-C-Si-C-) moiety. Whereas metals in elemental form do not usually influence burning rate to a large extent, their oxides often have a pronounced effect as evidenced by their role in ammonium perchlorate deflagration.[3] It appeared likely therefore that superior burning rate enhancement might be achieved if silicon were already bonded to oxygen when incorporated into the polymer.

The effect of the siloxane (-O-Si-O-) moiety was investigated in polyurethane binders. Siloxane copolymer glycols were prepared by etherifying 1,3,5,7,9,11-hexaphenyl-5,11-dihydroxytricyclo[7,3,1,1,^{3,7}]hexasiloxane (Dow Corning Z-6018[4]) with a twofold excess of polyoxypropylene glycol (PPG) at 200–240°C employing 0.2 wt % stannous octoate as a catalyst. Examination of the products by gel permeation chromatography showed that all the Z-6018 had reacted but about half the PPG remained unreacted. The etherification thus appears to proceed via self-condensation of Z-6018 and terminate by capping of the siloxane block with PPG. The -Si-OH group is known to condense readily with itself but to condense more slowly with -OH attached to carbon. The -OH groups in PPG did not undergo reaction when PPG was subjected to the same conditions as used for etherification. PPG is thus a convenient chain stopper for Z-6018 self-condensation and by use of a twofold excess of PPG, block copolymer glycols that were useful in preparing propellant binders were obtained. When equimolar amounts of PPG and Z-6018 were employed the reaction product was solid and not suitable as a propellant binder.

The etherification reactions are summarized in Table 1. Number average molecular weights ($\bar{M}_n$) of the PPG/Z-6018 copolymer glycols were calculated from the amount of unreacted PPG, and from $\bar{M}_n$ values determined for PPG and the unseparated reaction products.

Ammonium perchlorate-based propellants were prepared from the siloxane copolymer glycols by using toluene-2,4-diisocyanate for chain extension and a polyoxypropylene triol for crosslinking. The propellants were cast into test motors

Table 1 Summary of etherification reactions

	Reaction product properties			
Siloxane comonomer	Unreacted PPG, %	Hydroxyl number, mg KOH/g	Bulk viscosity at 20°C, centipoise	Copolymer glycol $\bar{M}_n$
PPG2025	56	38.2	2,300	7,500
PPG3025	44	27.0	3,000	7,090
PPG4025	53	19.0	6,000	17,000

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[*] Research Scientist.

[†] Experimental Officer.

[‡] Senior Research Scientist.