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AD No.

THE DEFLAGRATION OF PURE AND ISOMORPHOUSLY DOPED AMMONIUM PERCHLORATE

by

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ABSTRACT. The deflagration behavior of pure and doped ammonium perchlorate (AP) was studied over the pressure range 300 to 6,000 psia, using cinephotomicrography of burning samples and scanning electron microscopy of quenched samples. Materials studied were pure AP in single-crystal and pressed-pellet form, and single crystals with controlled isomorphous substitution of K^+, MnO_4^- and $Cr_2O_7^{2-}$ ions. This study shows that previous speculations regarding the combustion of AP are based on erroneous assumptions, and more realistic views, based on the observations, are proposed. In addition, some serious questions regarding the relevance of low-temperature, low-heating-rate, and low-pressure decomposition data to actual combustion are posed.

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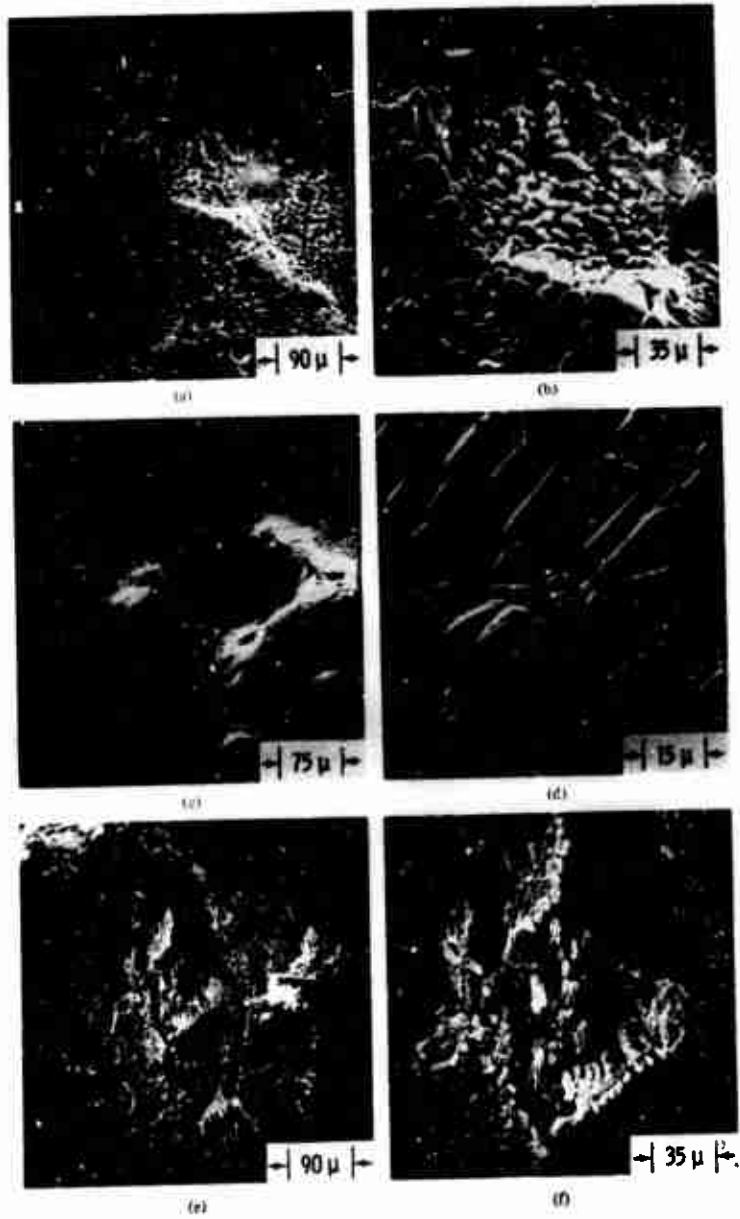CHINA LAKE, CALIFORNIA • SEPTEMBER 1970

FIG. 7. Scanning Electron Microscope Micrographs of Dichromate-Doped AP Crystals Quenched at 2,500 psia. (a) and (b) 0.0023 wt.%; (c) and (d) 0.0083 wt.%; (e) and (f) 0.015 wt.%.

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INTRODUCTION

Because of its extensive use in solid propellants for rockers, the deflagration of ammonium perchlorate (AP) has been the subject of considerable study. Early research was carried out on samples prepared by dry-pressing granular material, and the primary object of study was the dependence of deflagration rate on pressure. In 1965, studies were initiated using samples consisting of high purity single crystals, and observational methods were extended to include high speed cinephotomicrography of deflagration and microscopic studies of quenched samples. In 1966, the quenched-sample studies were advanced by application of the scanning electron microscope (SEM), and more recently studies have included crystals with isomorphously substituted dopants.

As a result of these studies, some rather pronounced changes have evolved in our views of AP deflagration, and an extremely complex range of behavior is observed over the pressure range studied (300 to 6,000 psia). The most conspicuous "new" aspects of the behavior are (a) evidence of a liquid layer on the burning surface; (b) complicated, pressure-dependent surface structure; (c) a visible flame at high pressure; and (d) a region of decrease in deflagration rate with pressure increase in the pressure range 2,000 to 4,000 psi. The present paper describes these aspects of AP deflagration briefly and compares them with results obtained with new, higher purity crystals, with dry-pressed pellets, and with crystals with various concentrations of K^+, $Cr_2O_7^{2-}$, and MnO_4^- ions.

RESULTS WITH PURE AP CRYSTALS

Early single-crystal studies were reported previously (Ref. 1-6). In order to avoid the possible effect of unintentional impurities being incorporated into the crystals, higher purity crystals were grown from an aqueous solution prepared from double-vacuum-distilled perchloric acid and ammonium hydroxide (Ref. 7). One result of the present studies was a comparison of the behavior of these crystals with that of earlier ones grown in an aqueous solution of commercial high purity AP. No difference was observed. The results are summarized briefly here as a basis for comparison later of the behavior of the pressed and doped AP.

The burning rate of the single crystals is shown in Fig. 1. Above 300 psi, deflagration was self-sustaining and the rate was insensitive to sample size (except when very thin samples were burned at pressures between 2,000 and 4,000 psia) or flow rate of the flushing gas (N_2) in the window bomb. The region of decreasing burning rate between 2,000 and 4,000 psi is associated with a sporadic, uneven regression of the surface, and the rate shown is an average rate over a time long compared to the fluctuations. Above 4,000 psi the surface regression is uniform. Although the region of decreased burning rate was believed by earlier investigators (Ref. 8, 9) to be an artifact of
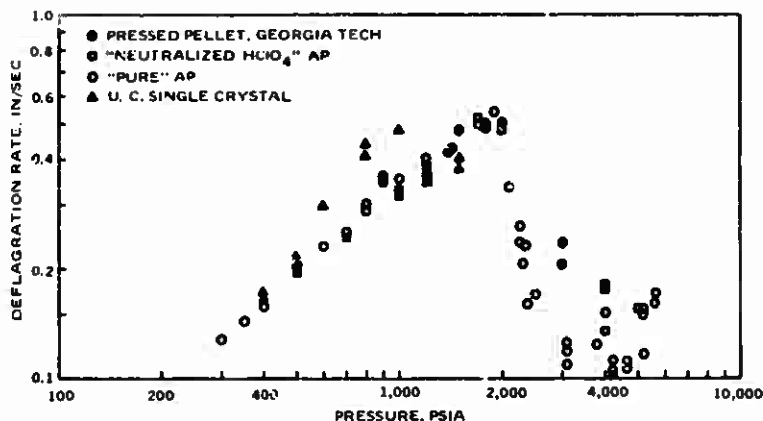
FIG. 1. Deflagration Rate of Ammonium Perchlorate. "Neutralized $HClO_4$" refers to crystals grown from solution prepared from $NH_4OH + HClO_4$; "pure" AP refers to crystals reported in Ref. 1-6, 11; U.C. single crystal refers to the crystals provided by E. E. Petersen. Initial sample temperature $\simeq 21°C$.

their experiment, it has more recently been shown (Ref. 5, 10, 11) that the dip in the curve is a natural attribute of AP deflagration.

High speed photography shows that the deflagration is without "visible" flame at pressures below 1,500 psi. Orange flamelets become increasingly conspicuous with further increase in pressure. Above 4,000 psi, the flame exists over the entire surface; in the interval from 2,000 to 4,000 psi, the location of the flamelets correlates with the sporadic fluctuations in regression rate (Ref. 5). Real-time photography also reveals intricate surface structure, which is visible in even greater detail on quenched samples (Ref. 5, 6, 11), as shown in Fig. 2. The movies taken of AP deflagrating at 300 to 800 psia show that the surface regresses in a flat, uniform manner. At the lower pressures (300, 400 psia) a relatively stable pattern of "discrete sites" on the surface is observed while at higher pressures (600, 800 psia) the individual sites are no longer individually discernible but cover the entire surface. When samples quenched from these pressures are examined, what appears to have been a thin layer of reacting liquid is seen. The only difference between samples is that the 600-psia samples seem

to have had a more frothy surface than did the 300-psia samples, indicating that the sites seen in the movies may have been associated with sites of gas evolution in and/or beneath the melt. Above 1,000 psi the surface exhibits an increasingly conspicuous and intricate surface pattern of ridges and valleys, with the pattern relatively stable with time as the surface regresses. The liquid material is increasingly localized to the "valleys" of the surface patterns, and as pressure is further increased, crater-like depressions also become evident in the valleys (1,200 to 2,000 psi). As the region of decreasing burning rate is approached, the surface also exhibits areas of porous material (seen on quenched samples). The porous material consists of an ordered array of needle-like crystallites. As the pressure is increased into the region of negative slope of the burning rate-pressure curve, the "needle areas" are seen to occur only in regions of the surface that have regressed ahead of the average plane of the burning surface. Although the necessity to use the SEM to see the needle areas makes determination of time sequence difficult, it appears that needle areas occur in regions of the burning surface where the regression rate has previously been rapid
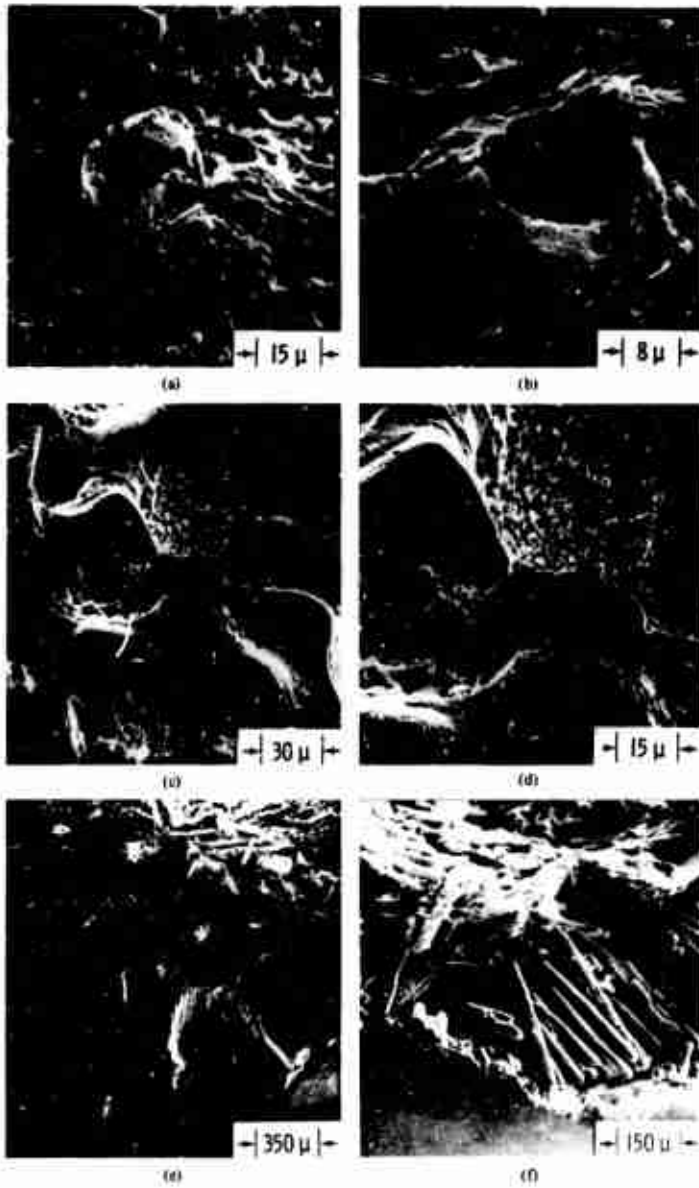
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FIG. 2. Scanning Electron Microscope Micrographs of Samples of Pure AP Quenched at (a) 300 psia; (b) 600 psia; (c) and (d) 1,200 psia; (e) 4,000 psia; (f) 6,200 psia. Micrographs (a) through (d) are of surfaces, while (e) and (f) are profiles of samples.

3

but is then retarded. It also appears that the orange flamele's occur predominantly over regions of the surface where retardation of regression rate has occurred. Above 4,000 psi, the entire surface is covered by a layer of the needle-like crystals (see details in Fig. 2), a steady flame is visible over the surface, and uniform surface regression occurs. The uniformity of the lateral dimensions of the individual needles suggests that they are formed by propagation of the subsurface (at the base of the needles) in sites between the needles (possibly in part by crack propagation along crystal planes), with reaction proceeding laterally at these sites to some limiting dimension of the intervening material in a way analogous to the low-temperature decomposition of AP (Ref. 3, 6).

It should be emphasized that the above description of surface details is inferred from high magnification SEM studies of quenched samples. The relevance of these results to real-time conditions during burning is inferred from the correlation with burning-rate trends, surface details, and flame behavior seen in cinephotomicrography (Ref. 11). Relevance is further assured at pressures below 1,200 psia by comparison of results from samples quenched by two quite different methods: rapid depressurization and thermal quench (compare the photographs of Ref. 1 and 2 to those of Ref. 4-6).

RESULTS WITH SAMPLES OF PRESSED GRANULAR AP

Most early work on AP deflagration was performed using pressed pellets. In order to establish the relation between recent single-crystal studies and earlier studies, tests were made using pressed samples supplied by Strahle and Varney of the Georgia Institute of Technology. These samples were of particular interest because they were pressed at unusually high pressure, and held at pressure for 24 hours. These samples were translucent and smooth when removed from the die, whereas pressed samples used by most other investigators have been chalky in appearance.

The deflagration rate of the pressed material was essentially the same as that of the single crystals (Fig. 1), as was the visual appearance of the deflagrating sample (except for lack of transparency of the sample). The evidence of liquid layer, surface pattern, craters, and needles on the pressed pellet samples (Fig. 3) is surprisingly similar to the structures seen on the crystal samples (Fig. 2). Although the granular microstructure is visible in sectioned samples (Fig. 3a), it is hardly detectable in SEM pictures of the quenched surfaces. This is apparently due at least in part to the liquid nature of the surface at low pressures and in part due to an inherent instability of a planar burning surface with spontaneous stabilization on combustion-controlled nonplanar configurations.
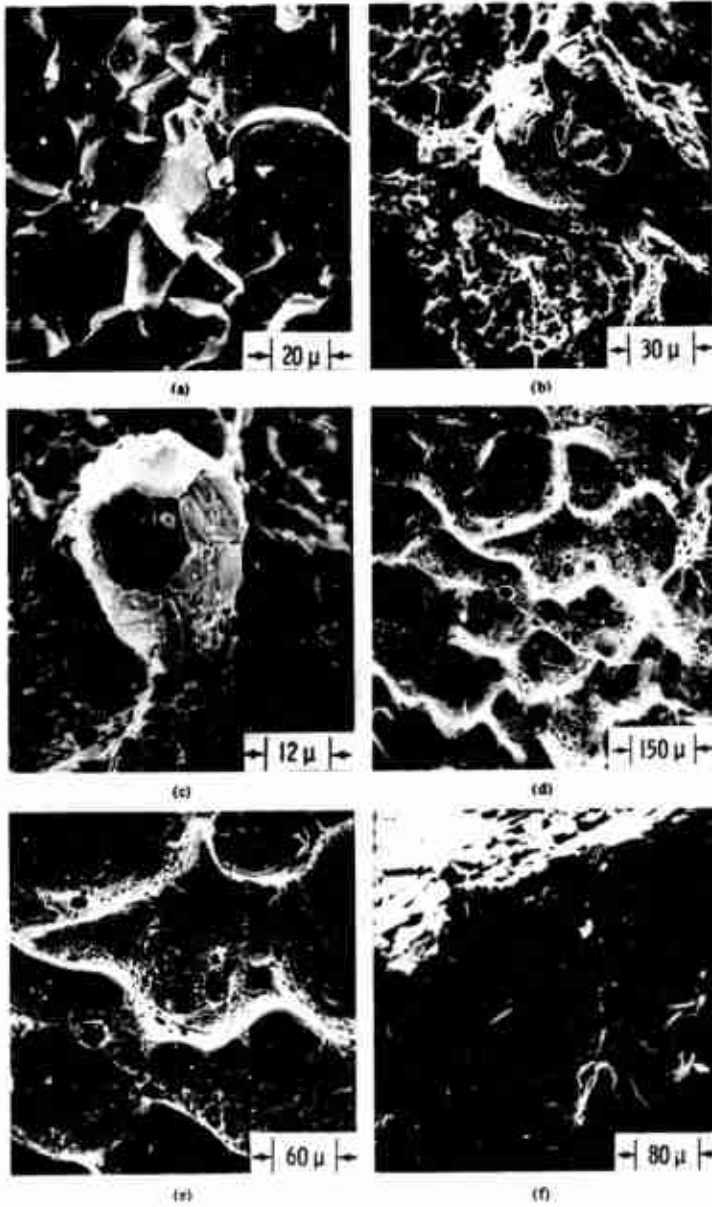
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FIG. 3. Scanning Electron Microscope Micrographs of Samples of Pressed Pellets. (a) Unreacted; (b) and (c) quenched at 400 psia; (d) and (e) quenched at 1,200 psia; (f) quenched at 4,800 psia.

COMPARISON WITH SINGLE CRYSTAL STUDIES BY OTHER INVESTIGATORS

It was noted that burning rates observed by Engleman and Petersen (Ref. 12) were appreciably different from those of our studies (Ref. 1-6, 11, 13), from the limited data of Hackman and Beachell (Ref. 14), and from the sources of pressed pellet data summarized in Ref. 11. In the present work, tests were run on crystals supplied by Petersen. When these crystals were tested in our apparatus, they gave essentially the same results reported by Watt and Petersen (Ref. 10) and Engleman and Petersen (Ref. 12). Since this indicated the crystals were of significantly different composition from those we had used, the two sets of crystals were subjected to spectrographic analysis. The analysis showed the presence of Fe, Pb, Cu, Mg, Al, and Si in Petersen's crystals. The same type of tests showed trace amounts of Mg, Si, and Cu present in the "neutralized $HClO_4$" crystals, the amounts being quantitatively less than in Petersen's crystals.

EFFECT OF ISOMORPHOUS DOPANTS

Doped crystals were grown in aqueous solution in the same manner as the pure AP crystals. Kinds and concentrations of dopants are shown in Table 1. The concentrations were determined by actual analysis of the crystals, as the concentration of the impurity in solution was not always duplicated in the crystal. In fact, the concentration of each deflagration sample was measured because often concentration gradients existed in the large parent crystal from which the sample was cleaved. For a more thorough discussion of the methods of crystal growth, sample preparation, and analysis to detect the gradients, Ref. 7 and 13 should be consulted.

TABLE 1. Crystal Batches and Concentrations.

Crystal batch no.	Dopant ion	Average dopant concentration, wt.%	Dopant concentration range, wt.%
4-12-17-69 . . .	K^+	0.05	0.052-0.056
5-5-1-68	K^+	.13	0.123-0.131
5-12-26-67 . . .	K^+	.33	0.30-0.34
4-12-26-67 . . .	K^+	.54	0.52-0.56
4-9-20-68	K^+	.80	0.75-0.85
4-2-10-69	$Cr_2O_7^{2-}$	.001	. . .
4-4-16-69	$Cr_2O_7^{2-}$	.002	0.0020-0.0025
4-5-14-69	$Cr_2O_7^{2-}$	.007	0.0054-0.0088
4-7-16-69	$Cr_2O_7^{2-}$	.015	0.012-0.019
4-9-26-66	MnO_4^-	0.030	0.028-0.035

K$^+$ DOPANT

The K$^+$ dopant was the one most thoroughly studied. The effect on burning rate is shown in Fig. 4 (data points omitted for clarity; see Ref. 13 for data). The motion pictures showed more evidence of a liquid surface layer than with pure AP, especially at higher concentrations of K$^+$. The dashed lines in the figure indicate regions where the regression was sporadic and uneven, associated with product accumulation. The amount of liquid on the surface increased with pressure in the range below about 1,200 psi, with the accumulation being particularly conspicuous locally on surface sites of low regression rate in the pressure range of irregular regression. The general trend of the curves suggests that mild enhancement of the liquid layer increases exothermic reaction in the surface layer with correspondingly enhanced burning rate, while excessive accumulation of unreactive products (such as KCl) locally inhibits reaction, vaporization and/or heat transfer in the pressure range of irregular and reduced burning rate. The effect of K$^+$ on burning rate was surprisingly independent of concentration above 1,500 psi, and in all cases a visible flame was observed at these pressures. The region of depressed burning rate above 2,000 psi exhibited by pure AP was completely eliminated by K$^+$ at all concentrations tested.

Scanning electron microscope micrographs of quenched samples were consistent with observations from the motion pictures. Figure 5 presents micrographs of two samples, one of 0.33 wt.% K$^+$ and the other of 0.8 wt.% K$^+$ concentration, which were quenched at 600 psia (in the pressure range of maximum sensitivity of burning rate to K$^+$ concentration). The sample with lesser K$^+$ concentration displays a surface covered by much froth and many bubbles while the higher doped samples show large patches of what must have been relatively inert molten material. Above 1,500 psia all the samples show areas of needles. Probably of even greater significance, evidence for condensed-phase reactions exists for samples quenched at pressures up to 3,000 psia (fumarole-like sites can be found on the surface). Unfortunately, samples were not quenched at pressures greater than 3,000 psia due to difficulties with the apparatus.
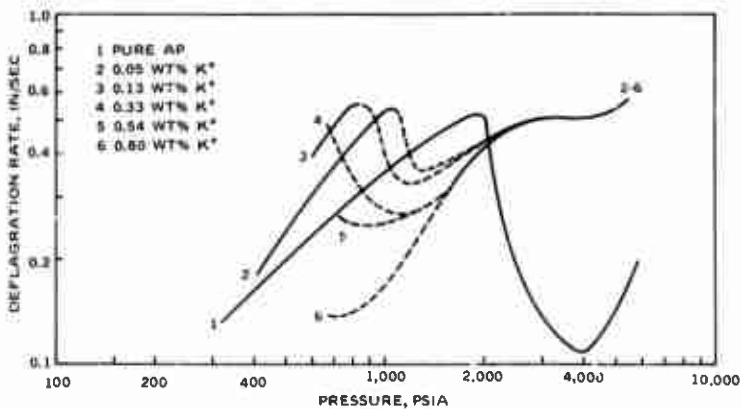

FIG. 4. Deflagration Rates of Potassium-Doped AP. Dashed lines indicate areas of temporal and spatial nonuniformity of surface regression.
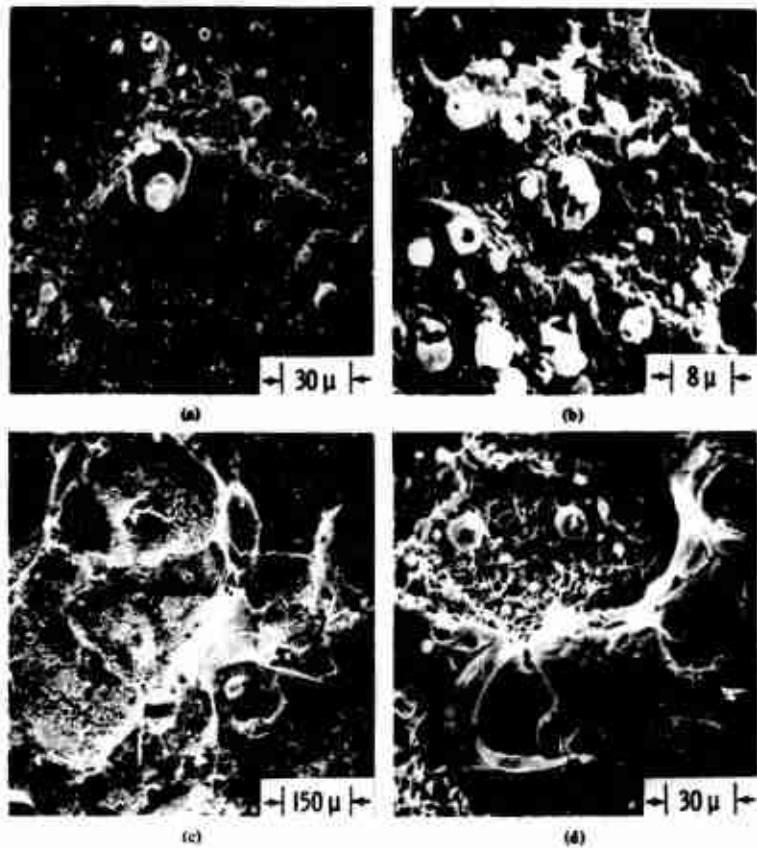
FIG. 5. Scanning Electron Microscope Micrographs of Potassium-Doped Samples Quenched at 600 psia. (a) and (b) 0.33 wt.% K^+; (c) and (d) 0.8 wt.% K^+.

$Cr_2O_7^{2-}$ DOPANT

Burning rates of crystals containing this dopant are shown in Fig. 6. (Data points are presented instead of curves because the number of tests run with this dopant was not sufficient to unequivocally establish curves as was the case with K^+.) The most conspicuous difference from pure AP is the location of the peak in the burning rate curve in the pressure range 500 to 1,500 psi, and the gradual elimination of the depressed rate region above 2,000 psi as dopant concentration is increased. Making allowances for the relatively

lower concentrations of $Cr_2O_7^{2-}$ used, the effects on burning rate are similar to the K^+ dopant, including rate enhancement (concentration-dependent) in the 600- to 1,000-psi pressure range, rate depression in the 1,000- to 2,000-psi interval, and elimination of the low-rate region above 2,000 psia. As in the case of all crystals tested, the burning surface was seen to regress in a spatially and temporally nonuniform manner in the pressure range where the slope of the burning rate curve is negative. However, the
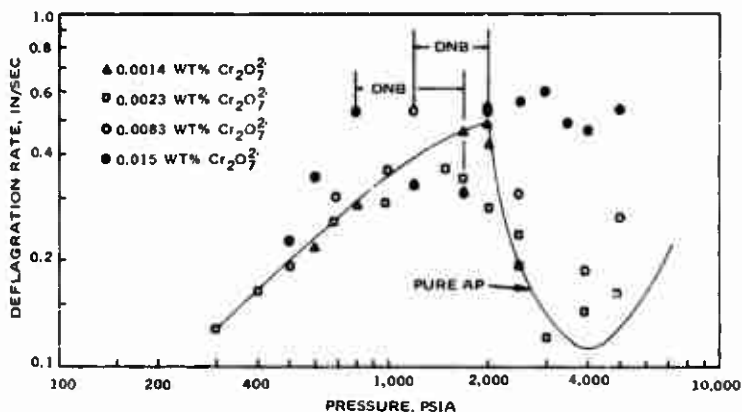
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FIG. 6. Deflagration Rates of Dichromate-Doped AP. DNB refers to did not burn.

two $Cr_2O_7^{2-}$ crystals having the highest doping would not sustain combustion (with the size sample tested—2 by 5 by 12 mm) in that pressure range (intervals denoted by DNB in Fig. 6).

At pressures below 600 psi, the samples doped with $Cr_2O_7^{2-}$ behaved in a manner similar to pure AP with the exception that much more smoke was evident and that oscillations within the smoke were readily visible. In the range 600 to 800 psi, the reaction zone became increasingly thick, with increasing smoke (and continued oscillations) and nonuniformity in regression as dopant concentration was increased. The same trend was exhibited with increasing pressure, culminating in the nonburning domain noted above in the case of the two highest dopant concentrations. Samples that were ignited and did not sustain deflagration exhibited areas of needles at pressures as low as 800 psi.

At higher pressures the crystals with lowest dopant concentration behaved much like pure AP, with irregular regression, localized flames, and needle areas occurring at pressures corresponding to the negative-slope region of the burning rate curve. However, the crystals with highest dopant concentration burned smoothly in the same pressure range, with visible flame over the entire surface. Scanning electron microscope photographs at 2,500 psi (Fig. 7) show localized areas of

needles similar to pure AP in the case of low dopant concentrations, but a relatively smooth surface with only localized patches of needles (which had the unusual structure seen in Fig. 7e, f) occurred with 0.015 wt.% dopant.

MnO_4^- DOPANT

The work on the MnO_4^- material has been limited to date. Rates which have been measured are shown in Fig. 8 (additional data by Hightower have been published in Ref. 15). The material tested in this study (0.030 wt.% MnO_4^-) would not burn at pressures below 1,700 psia, and those tests where ignition occurred, at and above 1,700 psia, displayed long ignition delays (up to 2 seconds after the igniter wire was heated). The response of the material to the ignition stimulus was to rapidly undergo a partial decomposition of the surface adjacent to the wire, followed by a long "cooking," followed later by ignition and sustenance of the burn. Because of the long "heat soak" period and the dependence of AP deflagration rate on initial sample temperature (Ref. 10, 16), the results presented in Fig. 8 cannot be compared *a priori* with the other results presented in this study.

The motion pictures showed that once a sample fully ignited, it regressed in a steady planar
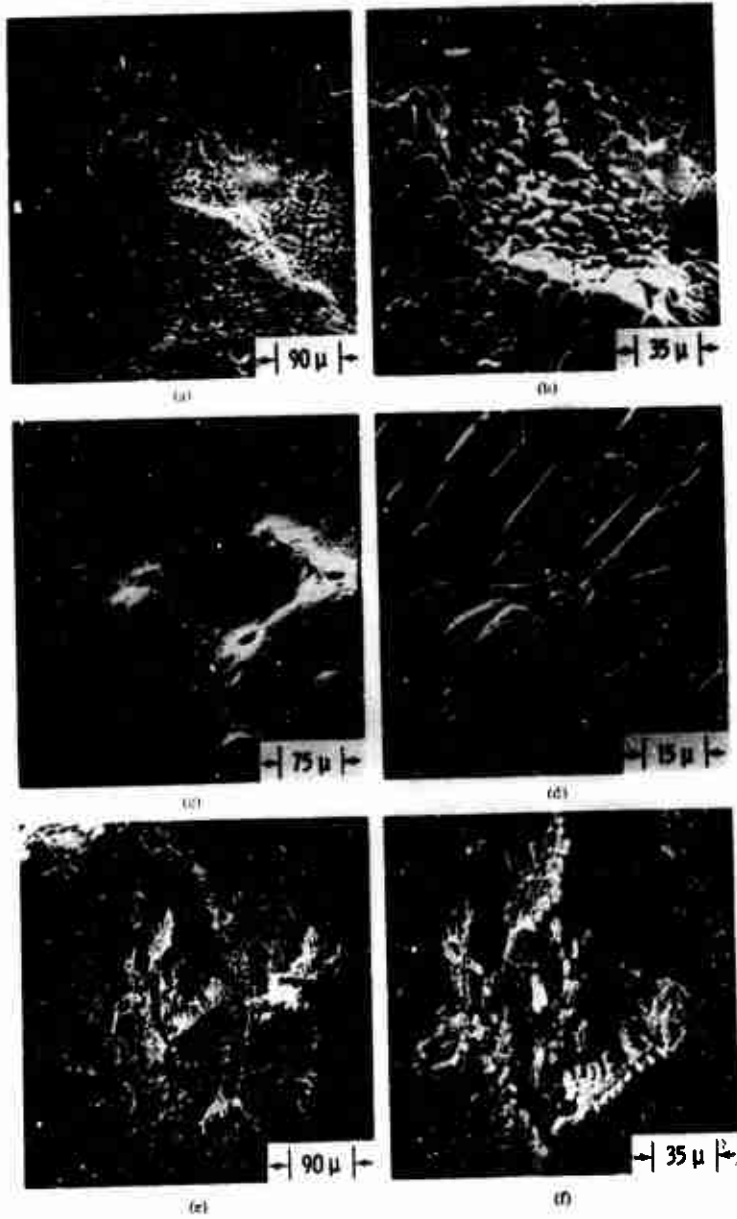
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FIG. 7. Scanning Electron Microscope Micrographs of Dichromate-Doped AP Crystals Quenched at 2,500 psia. (a) and (b) 0.0023 wt.%; (c) and (d) 0.0083 wt.%; (e) and (f) 0.015 wt.%.
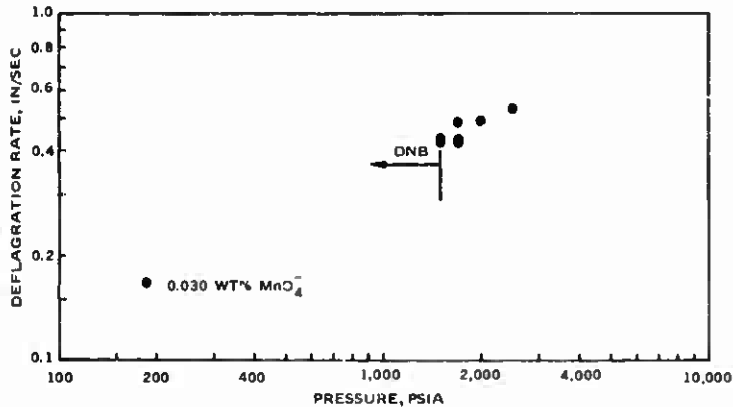
FIG. 8. Deflagration Rates of Permanganate-Doped AP. DNB refers to did not burn.

manner (although these samples were only tested to 2,500 psia). Scanning electron microscope micrographs of the few quenches taken showed a pattern of ridges and valleys on the 1,700-psia samples and a few areas of needles on the 2,500-psia sample.

DISCUSSION OF RESULTS

The primary purpose of this paper is to report new experimental results made possible by the availability of improved quality of test samples and improved observational tools. The results reported earlier (Ref. 1-6, 11, 13) made it clear that the burning-rate behavior was much more complex than indicated by early work, and that the detailed structure of the combustion zone was also more complicated than generally described by or assumed in analytical models. Although the complexity of the combustion zone and its variability with pressure render all explanation speculative at this time, the effect of the dopants suggests plausible mechanistic arguments that may help in planning future work.

It is proposed that liquid layers on pure AP provide the opportunity for exothermic reaction at the surface where heat is more readily available for endothermic steps. When the products of these reactions are gaseous, the liquid layer is a complicated froth, very likely with bubbles of diameter comparable to the layer thickness (because reaction rates are so high). Although the reason is not clear, the reactive liquid layer apparently becomes less important at higher pressure with pure AP. Burning rate drops off, the burning surface becomes nonplanar, with more of the heat apparently released in the gas phase (inferred from the concurrent encounter of visible gas-phase flame and reduced burning rate). The transition to a gas phase-dominated process is complete at about 4,000 psi. Above this pressure, the leading edge of the reaction front is evidently a low-energy process at the bottom of the needle layer, with further heat release presumably occurring at the top of the needle layer and in the gas-phase flame where heat is not easily transferred into the crystal.

The marked similarity of both surface structure and burning rates between

11

polycrystalline-pressed-pellet and single-crystal samples indicates that the shape of the deflagration rate curve and the surface structure are characteristics of AP itself rather than being dependent on method of sample preparation.

The influence of dopants may be either physical or chemical. In the case of K^+, it seems likely that enhancement of the liquid layer would result because of depression of the melting point and because of stable reaction products, notably KCl. While nothing is known about the solubility of products in molten AP, one would expect a high concentration of stable products on the surface, with a correspondingly high surface temperature required in steady state, to maintain evaporation of the stable species. This in turn enhances the opportunity for reaction of the AP in the surface layer, with enhanced burning rate at low pressure. As pressure is increased, evaporation of stable species is increasingly less favored and concentrations at the surface increase. The movies showed just such accumulation of inert product, which locally retards the burning, until the material is removed by violent expulsion.

The use of photography and sample quenching has made it "painfully" clear that the behavior of the combustion zone cannot be described or explained in terms of one-dimensional models. The presence of nonuniform layers of liquid, the presence of areas or a layer of needles, the presence of localized flamelets above the surface, and the occurrence of nonuniform regression of the surface are evidently dominant aspects of the behavior under various conditions, and the consistent relation among these features and the mean surface regression rate surely reflects cause and effect. It is still too early to construct detailed mechanistic arguments for three-dimensional behavior, but the observations regarding the effect of needles illustrates how the results from the different observational techniques must be combined to approach mechanistic understanding. The results show that the development of a needle-covered surface with increasing pressure is associated with reduced burning rates (in the range 2,000 to 4,000 psi

with pure AP). Such observation could be rationalized in one-dimensional theory if one considers that the needles hold the flame away from the otherwise solid surface and that transpiration cooling occurs in the needle layer. In this case any area of needles could be considered as having a retarding effect on the combustion; therefore, those areas of the surface that have needles (e.g., Fig. 2e, f) should lag behind the rest of the combustion front (those areas not having needles). However, the SEM pictures show that the needles occur in *depressed* regions of the sample surface (leading edge of the deflagration front, suggesting that areas of needles are conducive to locally high burning rate). This apparent anomaly is explained when motion pictures are available, for they show that under these conditions the deflagration front proceeds in a spacewise nonuniform, locally intermittent way, with the "leading edge" proceeding at first rapidly (apparently until the needle formation is developed) and then proceeding perhaps only 10% as fast thereafter while being overtaken by surrounding areas. Thus most of the leading regions of the irregular regression front at the moment of quench are actually needle-covered regions of retarded rate, consistent with the low average regression rate under those test conditions. The point to be made here is that it would be quite impossible to rationalize the results obtained unless (a) a three-dimensional, locally nonuniform behavior of the deflagration wave is accepted, and (b) results from all three types of observations (burning rate, combustion-zone photography, quenched-sample study) are considered together.

One may be tempted to explain the effects of dopants in terms of chemical kinetics or molecular-scale surface processes. Indeed, there is a venerable body of precedents for obtaining "kinetic" data (see, for example, Ref. 17) from more controllable "low" temperature experiments such as differential thermal analyses and using the results in one-dimensional deflagration wave models. From the present results it seems clear that such an approach is fated for failure. Not only are physical and geometrical considerations

essential to valid models and to observed effects of dopants, but many of the kinetic effects of dopants seen in differential thermal analysis, etc., do not show up in the deflagration rate. As one example, it has been reported that K^+ doping has little effect on surface nucleation or decomposition (Ref. 18).[1] This is in sharp contrast to the effect on deflagration described above. Further, it has been reported (Ref. 19) that doping with MnO_4^- causes a drastic increase in nucleation rate yet the effect on deflagration is to render the samples very difficult to ignite. Further, there is nothing in the low-temperature decomposition results to indicate that melts will occur, or indicate what their effect would be on deflagration. Thus, while chemical kinetics is undoubtedly important in deflagration, it will most likely find its place in a framework that acknowledges the physical and geometrical intricacies of the combustion zone. At the present time it is not entirely clear that the "kinetics" obtained from the low temperature experiments are free of geometrical contributions (topochemistry). In deflagration it is clear that geometrical and physical considerations play a major role.

CONCLUSIONS

1. The shape of the deflagration rate curve reported in Ref. 6 and 11 is a characteristic of AP, not of sample preparation nor of apparatus used. Samples made by dry-pressing granular AP gave the same rates as did very pure single crystals.

2. The surface structures inferred from high speed motion pictures and scanning electron microscopy were similar for both the single crystals and for the pressed pellets and consisted of a frothy melt at pressures from 300 to 800 psia, a pattern of ridges and valleys from 1,000 to 2,000 psia, and areas of needles for pressures greater than 2,000 psia.

3. The deflagration rate is extremely sensitive to foreign ions included within otherwise pure AP.

    a. Potassium inclusion causes changes in the deflagration primarily associated with condensed phase processes such as melt enhancement and inert product accumulation. The effects are concentration-dependent at pressures below 2,000 and relatively concentration-independent from 2,500 to 6,000 psia.

    b. The inclusion of dichromate ion into the crystal is responsible for increasing the deflagration rate as a function of dopant concentration and pressure.

    c. The inclusion of permanganate ion into the crystal increased the lower deflagration limit pressure and also resulted in long (up to 2-second) ignition delays for those crystals that would burn.

4. The deflagration of AP (and doped AP) cannot be described only in terms of kinetic parameters obtained from low-temperature, low-heating-rate studies; rather, consideration of such physical processes as melt formation must also be given if the description is to be adequate.

5. The behavior of either doped or pure AP deflagrating at certain ranges of pressure (e.g., pure AP at 2,000 to 4,000 psia, K^+ doped crystals between 600 and 1,500 psia) cannot be described or explained in terms of one-dimensional models, but must include temporal and spatial dimensions.

[1] Personal communication between the author and K. J. Kraeutle, NWC, China Lake, Calif. 1969.

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13 ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Dichromate Doped Ammonium Perchlorate						
Permanganate Doped Ammonium Perchlorate						
Cinephotomicrography						
Scanning Electron Microscopy						

ABSTRACT CARD

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