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Effect of Catalyst Mixing Procedure on Subatmospheric Combustion Characteristics of Composite Propellants

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Subatmospheric combustion characteristics of ammonium perchlorate (AP)/hydroxyl-terminated-polybutadiene (HTPB) propellants prepared using two different catalyst mixing procedures were studied. In the first one, identified as the wet-mixing process, copper chromite catalyst (CC) was mixed with the binder (HTPB + di-2-ethylhexyl adipate); and to this CC–binder mix, AP and the curing agent [toluene di-isocyanate (TDI)] were then added. In the second, identified as the dry-mixing process, CC was first mixed with AP, and to this dry-mixture, the binder and toluene di-isocyanate were then added. For such propellants of different mixing procedures, with various AP particle sizes, the measurements of burning rates up to 1 bar, low-pressure deflagration limit (LPDL), and the scanning electron microscope (SEM) study of extinguished samples at LPDL were carried out. Results of the study show a higher burning rate for dry-mix propellants, and this higher burning rate is AP particle-size and pressure dependent. LPDL is also AP particle-size dependent, and for catalyzed propellant it is lower than that of an uncatalyzed one. The two procedures of CC mixing do not demonstrate any significant difference in LPDLs. The micrographs of wet-mix and dry-mix propellants look similar; however, the strong effect of low pressure in increasing the surface and subsurface reactions is brought out by the SEM study.

Introduction

BETTER understanding of subatmospheric and low-pressure combustion of solid propellants is necessary for the development of missile base–bleed propellant grains[1–4] and stop–start solid motors, and for the accurate prediction of early stages of solid motor ignition transients. Further, the subatmospheric combustion of composite solid propellants (by its premixed flame-dominated gas-phase reaction zone, less severe temperature gradient at the burning surface, and better spatial and temporal resolutions), offers for mechanistic study a simpler perspective of the complex phenomenon.

Subatmospheric burning rate studies on composite solid propellants were first reported by Silla.[5] Other low-pressure combustion studies on composite propellants conclude the following:

1) Low-pressure deflagration limit (LPDL) generally increases as the fuel/oxidizer ratio moves away from the stoichiometric value.[6,7]

2) The addition of a catalyst decreases the LPDL, whereas that of a depressant augments it.[8]

3) With a thicker and slower thermal wave the gas phase flame processes are at a larger standoff distance, frequently with the dark zone above the burning surface, a few tenths of a millimeter to a few millimeters thick.[9–11]

4) With the gas-phase flame dominated by the premixed flame processes, the value of a pressure exponent in the burning rate equation $r = ap^n$ is higher, say, 0.8 or more.[9]

5) A wide variety of flames exists for propellants with catalysts or depressants.[8]

6) Complicated three-dimensional structures with potholes and burrows, observed at the extinguished propellant surface, point out increased surface and subsurface reactions.[8,11]

7) The burning rate is still oxidizer-particle-size dependent.[9–11]

8) From the burning surface, for certain oxidizer particle-size distributions, partially reacted oxidizer particles are ejected, and at pressures near LPDL, white fumes are emanated.[10–12]

Although the earlier studies on ammonium perchlorate (AP) composite propellants indicated that the catalyst addition, along with the expected burning rate enhancement, could decrease LPDL, a systematic study on the effect of AP particle-size variation on LPDL has not been reported. Further, we have noted that catalyzed AP/hydroxyl-terminated-polybutadiene (HTPB) propellants of the same composition, but of two different mixing procedures in the matter of adding catalyst, can give different burning rates below about 15 bar. This difference is very significant for certain AP particle sizes in the subatmospheric pressure ranges of interest in base–bleed applications. How this difference is affected with AP particle-size variation is not known. Therefore, using unmetallized AP/HTPB propellants with various sizes of AP particles, a systematic study has been carried out on the effect of the copper chromite catalyst (CC) on 1) the difference in burning rates with respect to two different CC mixing procedures and 2) the LPDL, and the results are presented in this paper.

Experimental Procedure

The industrial-grade ingredients and their propellant mass fractions adopted for the present study are given in Table 1. AP powders, of purity >98.6%, of five different weight mean diameters [$D(4,3) = \Sigma\, n_i d_i^4 / \Sigma\, n_i d_i^3$] = 30, 68.5, 106, 224, and 310 μm were used. Fine AP powder of 30 μm was prepared

Table 1 Propellant ingredients

Ingredients	Mass fractions[a]
AP–oxidizer	0.7300
HTPB–binder	0.2160
DOA–plasticizer	0.0405
TDI–curing agent	0.0135

[a] CC fraction in catalyzed propellant = 0.02; the balance fraction of 0.98 has the same ingredients' mass fractions as shown.

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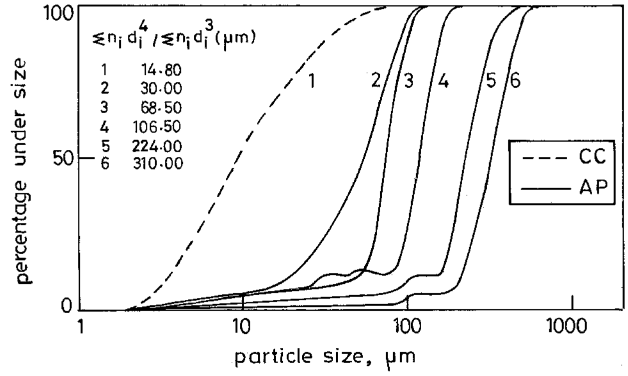

Fig. 1 Particle size distributions of CC and AP powders.

by fluid energy mill grinding of an as-received lot of 310-μm powder; 224-μm powder was the fraction of the 310-μm powder passed through mesh number 60 (250 μm), and the other two AP powders were from two different as-received lots from industry. AP-particle-size distributions measured through a laser diffraction particle size analyzer (Particle Sizer 3600 E, Malvern, England) are shown in Fig. 1. For this measurement the recommended slurry liquids, *n*-butyl acetate and isobutanol, were first tried, but, because of the high-density difference between slurry–liquid and AP, the particles were observed to get quickly settled at the bottom of the sample–cell and get ground by the magnetic stirrer provided there, leading to nonreproducible results with time. After many trials, a mixture of isobutanol and carbon tetrachloride in the volume–ratio of 30:70 was found to be a suitable slurry liquid for AP. Even for this liquid, AP particles were seen to get settled and get ground by the stirrer, but at a much slower rate. Hence, the measurements were taken as fast as possible and the results were reproducible. CC containing 33% Cu and 29% Cr of $D(4,3) = 14.8$ μm was used (Fig. 1).

An extra-coarse, sixth AP powder was prepared by a special process developed in-house and sized by choosing the fraction that passed through mesh number 16 (1000 μm) and was retained in mesh number 30 (500 μm). This extra-coarse AP along with the 30-μm-fine AP were used in the preparation of a bimodal propellant composition of AP (extra-coarse):AP (fine):HTPB:di-2-ethylhexyl adipate (DOA):toluene di-isocyanate (TDI):CC = 0.6174:0.1470:0.1725:0.0323:0.0108:0.0200. Initially, we tried to cast a propellant using only the extra-coarse AP at the same composition indicated in Table 1; but the resulting cured propellant block had an excessive settlement of AP at the bottom and a thick binder layer at the top, and did not therefore qualify for uniform-density check; for qualification in this study, the density variation within a block was specified to be within 2%. Hence, after some trials, the previous bimodal composition containing 0.78 AP fraction in uncatalyzed propellant was found.

A 3.5-l capacity double-sigma blade mixer was used for propellant preparation. AP and CC were well-dried in an oven before mixing. Two different mixing procedures in the matter of adding CC to the propellant were adopted. In the first procedure, identified as the wet-mixing process, CC was mixed with the already mixed binder (HTPB + DOA), and to this CC-binder mix, AP and the curing agent TDI were then added one after the other; this process is generally adopted in propellant mixing. In the second procedure, identified as the dry-mixing process, CC was first mixed with AP for 30 min, and to this dry-mixture, the binder and TDI were then added one after the other. Thus, of the total equal mixing duration of 180 min adopted for each of the mixing procedures, the AP in the dry-mixing process was in the mixer for a longer duration by 30 min. In certain large propellant plants, in situations where finely granulated AP fractions are to be added to propellant mix, and CC is also an ingredient, to have better flow characteristics for fine fractions, CC is dry-mixed with the fine AP. Such a procedure has not resulted in any nonuniform solid distributions in the cured propellant. However, in this plant procedure, the dry-mixed CC–AP mixture is added to the liquid binder, not vice versa as adopted in this study. Nevertheless, in this study, under the qualification procedure to be detailed, no particular process-dependent property-variation-pattern beyond the acceptable limit (density variation within and between wet-mix and dry-mix or burning rate variation for a chosen pressure for a particular mix) was noted.

General details of mixing, casting, and qualifying procedures for propellants and burning rate measurements were explained elsewhere.[11] However, certain specific details are given here. Rectangular propellant blocks of about 2 kg from a mix of 2.5 kg were cast in molds of 190 × 120 × 80 mm size. Each block was qualified by measuring densities of cubes of 15 mm size removed at the top, middle, and bottom of the block along its main diagonal. A volume displacement method using analytical-grade toluene was adopted for density measurement. The maximum density variation in the block for the extra-coarse AP propellant was within the limit of 2%, as mentioned earlier, and for others this was within 1%. To find the burning rate of a propellant, the time to burn a known length of propellant-strand was measured. The meltings of the three fuse wires, introduced in a strand at two consecutive equal distances, were used to create necessary signals in a suitable relay circuitry to operate two timers. For the chosen pressure, every burning rate test was repeated at least once to check the consistency of data. The maximum burning rate variation between the tests was within 3%; but the variation between the two burning rates for the consecutive equal distances was always less than 1%. All HTPB, DOA, and TDI were drawn from the same batches. To check the repeatability of results, two propellant samples for each of the 30-, 68.5-, and 310-μm AP sizes were prepared and found to give burning rate and LPDL values within 3% variations.

In the literature, two different methods are found for the measurement of LPDL. In the first, known as the dynamic method, it is measured by igniting the strand at a higher pressure and carefully lowering the pressure very slowly until the flame extinguishes.[4,6,8,10,11] In the second, known as the go/no-go method, for a fixed strand cross section, the strand is ignited at a constant pressure; if stable burning is attained, the experiment is repeated at the next lower constant pressure until stable burning is not possible.[13] To study the effect of strand cross section on LPDL, Miller and Holmes,[4] adopting the latter method, chose a fixed pressure and decreased the strand diameter. In the present study we followed the dynamic method using strands of a fixed square cross section of 6 × 6 mm. LPDL-extinguished propellant samples of 30- and 250-μm AP, after vacuum deposition of approximately 100 Å of gold, were examined through a scanning electron microscope (SEM) (JSM-5300, Jeol, Japan). To have minimum heat loss effects on the surface feature of LPDL-extinguished propellant, only central regions were examined.

Results and Discussion

Burning Rate Characteristics

The subatmospheric burning rate results of the propellants are given in Fig. 2. All values of burning rates were fitted by the method of least-squares to the fifth-degree polynomial of pressure; the correlation coefficients of fits were found to be greater than 99.7%. While the burning rate enhancement by the addition of catalyst is as expected, a significant difference in burning rates between wet- and dry-mix propellants is observed. This effect is noted to be AP particle-size and pressure dependent. To further elucidate this we define Z as $(r_{cd} - r_0)/(r_{cw} - r_0)$, where r_{cd} and r_{cw} are the measured burning rates of catalyzed dry- and wet-mix propellants, respectively, and r_0 is the measured burning rate of uncatalyzed propellant. The var-

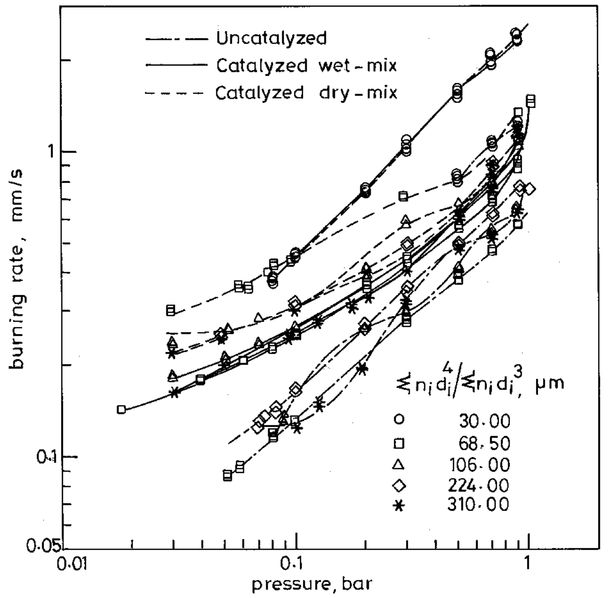

Fig. 2 Subatmospheric burning rate characteristics of CC-catalyzed AP/HTPB propellants.

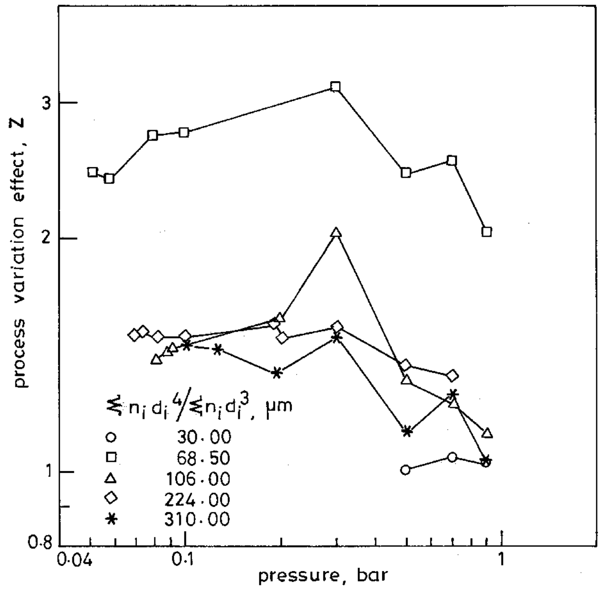

Fig. 3 Effect of processing on CC-catalyzed AP/HTPB propellants.

iations of Z for all of the propellants are shown in Fig. 3. It is not clear why Z is maximum for the propellant of the 68.5-μm AP lot. However, for propellants of 106-, 224- (sieved from 310 μm), and 310-μm AP lots, the Z values are significantly higher than 1.

To ascertain that the process variation effect Z is caused only by the catalyst mixing procedure, two separate investigations were subsequently carried out. The motivation for the first investigation is as follows. As indicated earlier, the AP in the dry-mix process was in the mixer for a longer duration by 30 min; hence, doubt arose that the enhanced burning rate for the propellant under this process could be because of the possible finer granulation of AP during mixing. This doubt was erased by measuring the particle sizes of the AP powder samples, drawn at various times from the mixer that was turning a particular AP powder under dry conditions; the results are given in Table 2. Considering the accuracy in the measurement of particle size, the results show that no significant finer granulation in a dry-mix process could take place by the difference of 30 min. It is also of interest to check whether there is any agglomeration as the catalyst powder is mixed with the binder. For this, in the second investigation, CC particle size was measured under two different conditions. In the former, a CC powder was added in the slurry liquid mixture of benzene, HTPB, and DOA, and the $D(4,3)$ size was found as 10.61 μm. In the latter condition, the same CC powder was added first to the HTPB–DOA mix, and after vigorous blending this mixture was added to benzene, and the $D(4,3)$ size was found 26.58 μm. In both conditions, the CC concentration in the HTPB–DOA mix was as in the propellant and the composition of the slurry liquid mixture of benzene–HTPB–DOA was maintained as constant. This indicates that there is CC particle agglomeration in the wet-mix process. With these two investigations it is clear that the noted burning rate enhancement is the process variation effect caused by the variation in the catalyst mixing procedure.

Table 2 Variation of AP particle size with mixing time

Time in mixer, min	Weight mean diameters, $D(4,3)$ μm
0	107.80
30	105.00
60	106.17
90	102.66
120	103.49
135	100.25
180	97.20

In the wet-mixing process as the catalyst powder is added to the binder-mix, the powder, with certain agglomeration on mixing as noted earlier, gets dispersed in the binder matrix; the densities of binder-mix and CC are 0.92 and 5.80 g/cm^3, respectively. For our propellant composition the binder-mix is approximately 63 times the volume of CC. When we add AP powder to this binder–CC mix and process the propellant, there are two possible types of locations of CC catalyst in cured matrix: one at the AP/binder interfaces and the other well within the binder-mix. Whereas, in the dry-mixing process as the catalyst powder is added to AP crystals, the crystals are expected to be coated with the catalyst powder. For our propellant composition, AP is approximately 109 times the volume of CC. The extent of coating is affected by the particle sizes of AP and catalyst. If we assume perfectly spherical particles and uniform coating, for our CC–AP fraction of 2/71.54, the coating factor (ratio of the projected areas of catalyst to the mean AP–CC surface area) can be shown to be equal to $0.00234(r_1/r_c)^3/(1 + r_1/r_c)^2$, where r_1 and r_c are the radii of AP and CC spheres, respectively. Also, between two spheres of radii r_a and r_b, the interparticle attraction for agglomeration is proportional to R for van der Walls forces or electrostatic forces if the two spheres are conducting, and to R^2 for electrostatic forces if they are nonconducting; here $R = 2r_a r_b/(r_a + r_b)$.[14,15] In view of the foregoing considerations on coating and interparticle attraction, larger AP crystals are expected to have more CC particles coated over their surfaces. Now on adding HTPB and DOA, the AP particles coated with CC, and the uncoated AP and free CC particles if any, get mixed with the binder. In this process some of the CC particles on AP crystals may get dislodged and go well into the binder-mix. Alternatively, the free CC particles may get located at the AP/binder interfaces. With AP particle-size variation, the net result of the CC particles getting dislodged from and acquiring locations into the AP/binder interfaces is not known. However, it is expected that the extent of catalyst particles occupying the AP/binder interfaces is more in the dry-mix process than in the wet-mix process, particularly for certain large AP particle size range.

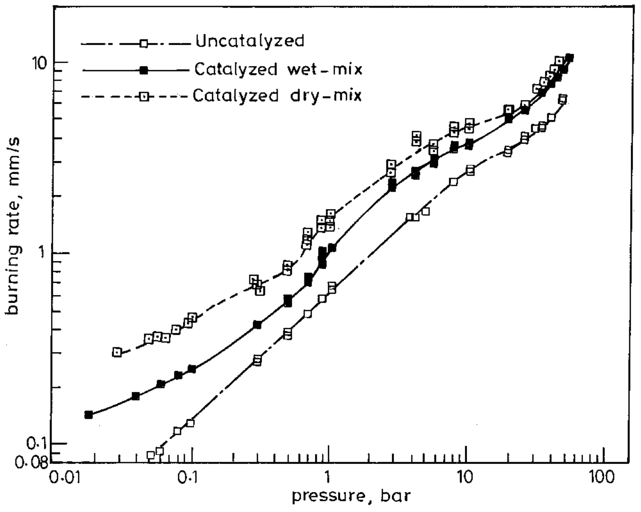

Fig. 4 Burning rate characteristics of AP/HTPB propellants, particle size of AP 68.5 μm.

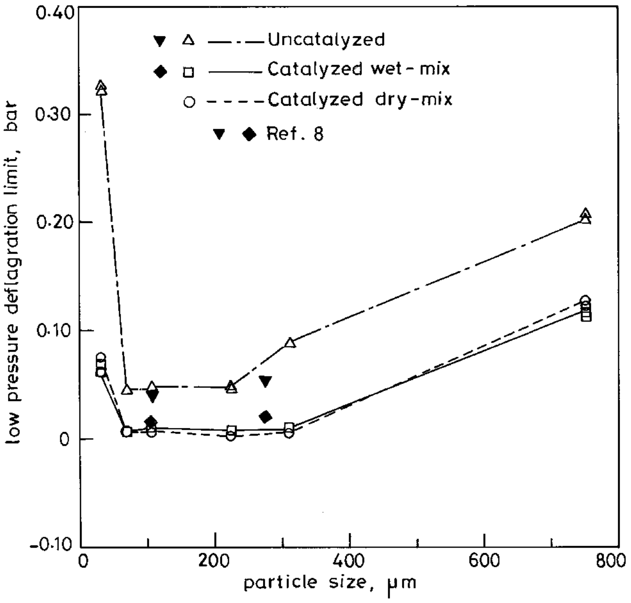

Fig. 5 LPDL characteristics of AP/HTPB propellants.

The burning rate controlling reactions in composite propellants with catalysts, at the macroscopic level, are located in the surface and subsurface and are evidenced by many experimental and theoretical studies.[16] At low pressures, for example, the gas phase combustion thickness is large, and therefore, the heat feedback from the gas phase is expected to be less. But, because of the deeper high-temperature penetration and, hence, the longer residence time allotted for the reactions at and beneath the surface, surface and subsurface reactions take a dominant role in maintaining the necessary surface temperature. And the catalyst effectiveness at low pressures under these conditions is experimentally found to be higher than at elevated pressures.[8,10] About the controlling reactions at the microscopic level, many authors have argued that catalyst acts by catalysis of reactions at the oxidizer/binder interfaces, for example, by catalyzing the condensed phase exothermic decomposition of AP and consequently enhancing AP/binder interfacial heterogeneous reactions.[17] However, in his recent study, Price[18] attributes such a possibility only at low pressures, but at high pressures he considers that the catalyst acts by accelerating the breakdown of heavy binder product molecules to more reactive fragments. Considering this point we conducted burning rate experiments up to 70 bar for a propellant of 68.5-μm AP lot; the results are shown in Fig. 4. Here, it is seen that the burning rate difference between dry- and wet-mix propellants vanishes around 20 bar. Thus, our results that the dry-mix propellants have higher low-pressure burning rates than the wet-mix ones, and that burning rate differences vanish at high pressures support our argument that in the dry-mix process the catalyst particles occupy more AP/binder–interfacial locations and catalyze heterogeneous reactions there, particularly at low pressures.

LPDL and SEM Studies

Measured LPDL values for various propellants are plotted in Fig. 5. LPDL values from Ref. 8 are also indicated in the figure for comparison. Because these values are for the same propellant composition, but from entirely different propellant batches, the repeatability of the LPDL values is quite satisfactory. It is known that the addition of a catalyst decreases the LPDL[8] and this is brought out by the present study. As observed earlier,[10–12] near LPDL extensive ejection of partially reacted AP particles occurred for all propellants except for those of 30-μm AP, more extensive ejection for catalyzed propellants. Importantly, the present study reveals that LPDL in HTPB propellants is very much AP particle-size dependent. A minimum of LPDLs occurs for a certain range of AP particle size, and the LPDL increases when the particle size is decreased or increased from around this size. No significant difference in LPDL is observed between wet- and dry-mix processes.

Cookson and Fenn[6] and Park et al.[13] discuss possible mechanisms for LPDL. Cookson and Fenn[6] argue that for the infinite strand, a simple heat loss mechanism will not be applicable. The propellant surface temperature will decrease with a decrease in pressure. By this temperature decrease, the vaporization rate for AP, because of its higher activation energy for linear pyrolysis, decreases faster than that for the binder. Because of this, one possibility is the extinguishment of the gas-phase flame on attainment of a fuel-rich limit, the other possibility is the fuel surface going too far below the oxidizer surface to receive enough heat to vaporize, and the third possibility is the oxidizer depletion at the burning surface caused by the AP particles ejection because of their fragile superstructure developed by the fast receding binder. Results of Park et al.,[13] for polyurethene (PU) propellants, indicate increased LPDL for fine AP particle size and a sharp decrease in it with an increase in particle size. They attributed the increased LPDL for fine AP particle size to the molten PU coating the AP particles, and thus, preventing their participation in surface reactions; coarse AP particles could, however, project beyond the molten layer and react. We may consider these postulates[6,13] in light of certain experimental observations. At subatmospheric pressures, Fe_2O_3-catalyzed AP/HTPB propellants were observed to smolder without a gas-phase flame.[8] Also, the gas-phase flame, when it exists for the other AP/HTPB propellants at such pressures, has a larger standoff distance, frequently with a dark zone. Further, SEM micrographs of the LPDL extinguished propellants of the present study (Figs. 6 and 7) do not indicate the fuel surface going too far below the oxidizer surface to receive enough heat (the fuel surface is very much near the mean surface); but, the existence of extensive AP-binder interfacial reactions is evidenced by the presence of the wide and deep crevices found between AP and binder. In this study, as well as in other studies,[10–12] near LPDL extensive ejection of partially reacted AP particles was observed for coarse and extra coarse AP propellants, but not for fine AP propellant. However, for the 30-μm-fine AP propellants, the SEM micrographs (Figs. 8 and 9) indicate the existence of a less viscous molten layer (the bulk of it possibly binder) pointing, as proposed by Park et al.,[13] to the molten binder coating the AP particles and thus preventing their participation in sur-

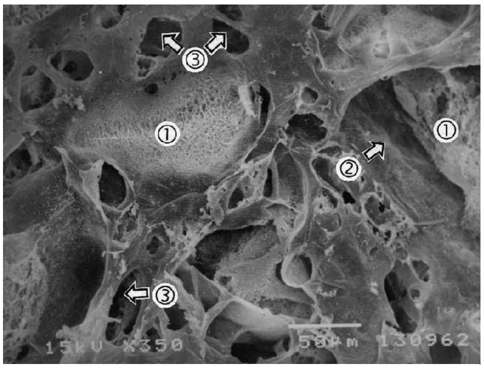

Fig. 6 **Extinguished surface of uncatalyzed AP (250 µm)/HTPB propellant extinguished at LPDL: ①, AP particle; ②, crevices around AP particle; and ③, potholes and burrows.**

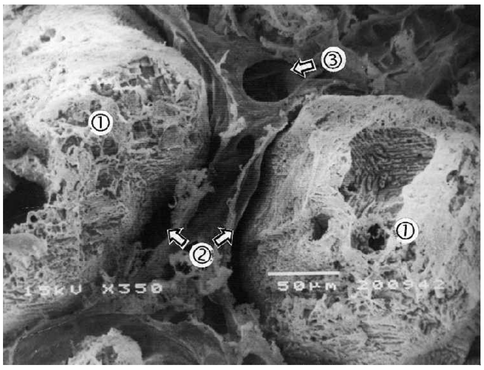

Fig. 7 **Extinguished surface of CC-catalyzed AP (250 µm)/HTPB propellant extinguished at LPDL: ①, AP particle; ②, crevices around AP particle; and ③, potholes and burrows.**

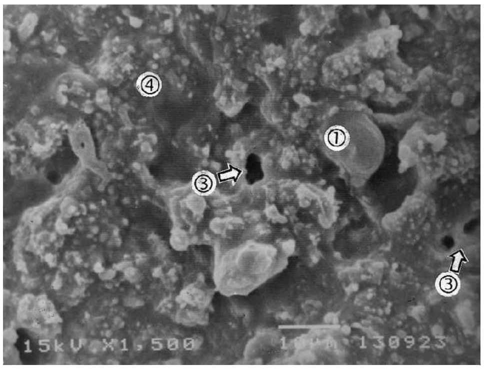

Fig. 8 **SEM micrograph of uncatalyzed AP (30 µm)/HTPB propellant extinguished at LPDL: ①, AP particle; ③, potholes and burrows; and ④, molten binder layer.**

face reactions. Our experimental results, therefore, indicate that for coarse particles, the LPDL is caused by the oxidizer depletion at the burning surface because of the AP particles ejections arising out of extensive AP-binder interfacial reactions; and for fine particles it is caused by the molten binder coating the AP particles. Comparing the LPDLs of catalyzed and uncatalyzed propellants, at the LPDL pressure of uncatalyzed propellant the corresponding catalyzed propellant is still able to burn at an increased rate because of the enhanced macroscopic surface and subsurface reactions, and these enhanced reactions are responsible for delaying the inevitable LPDL to a lower value.

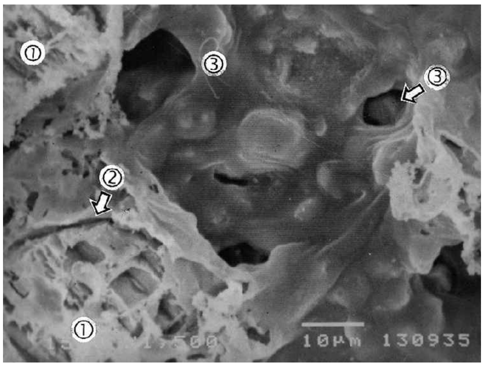

Fig. 9 **SEM micrograph of CC-catalyzed AP (30 µm)/HTPB propellant extinguished at LPDL: ①, AP particle; ②, crevices around AP particle; ③, potholes and burrows; and ④, molten binder layer.**

Examination of the SEM micrographs of the LPDL-extinguished propellants reveals no observable difference in surface features between wet- and dry-mix propellants. The complicated three-dimensional surface structure with crevices around AP particles, and potholes and burrows in the binder, can be caused by the addition of a catalyst, AP particle-size distribution, and/or an oxidizer–fuel ratio. Uncatalyzed 30-µm-fine AP propellant (Fig. 8) appears to have had a less viscous molten layer than the catalyzed one (Fig. 9); the surface of the catalyzed one, because of the presence of more potholes and burrows on it, has had enhanced surface and subsurface activity. As these two 30-µm fine AP propellants extinguished at two significantly different pressures (Fig. 5), questions arise whether the enhanced surface and subsurface activity in the catalyzed propellant are caused by the addition of catalyst or by the reduced LPDL. Hence, we compare the surface features of the catalyzed 30-µm-fine AP propellant (Fig. 9) with those of the uncatalyzed 250-µm AP propellant (Fig. 6), as these two propellants extinguished at nearly the same pressures (Fig. 5). Similar potholes and burrows activity is also seen in this uncatalyzed propellant. The appearance of much more extensive potholes and burrows in the binder of the catalyzed 250-µm AP propellant (Fig. 7), which extinguished at a still lower pressure, confirms the strong low-pressure effect on surface and subsurface reactions.

Conclusions

1) Copper chromite catalyzed AP/HTPB propellants of the same composition, but of two different catalyst mixing procedures (wet-mix and dry-mix), can give different burning rates at low pressures (≤ 15 bars, higher burning rates for dry mix). This AP particle-size-dependent process–variation–effect can be effectively used in the burning rate tailoring of such propellants used in low-pressure applications, say, base–bleed.

2) The extent of catalyst particles occupying the AP/binder interfacial locations is more probable in the dry-mix process than in the wet-mix one, particularly for certain large AP particle-size ranges.

3) The experimental results of the present study indicate that such catalyst particles occupying more AP/binder interfacial locations can effectively catalyze heterogeneous reactions there at low pressures and cause a higher burning rate.

4) For coarse AP propellant, the LPDL is possibly caused by the oxidizer depletion at the burning surface because of the AP particle ejections arising out of extensive AP/binder interfacial reactions, and for the fine AP propellant, it is caused by the molten binder coating the AP particles.

Acknowledgments

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