Studies on Coning in End-Burning Rocket Motors

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Coning of the burning propellant surface in end-burning rocket motors arises from an increased burn rate at the side walls of the propellant grain. Causes of this increased burn rate have been investigated, mainly through the use of small scale motor firings. The nature of the propellant inhibitor material is shown to be important, and various possible mechanisms are examined. Mechanisms identified by other workers in previous studies were found to be not involved. Strain in the propellant has been shown to produce coning. Considerable evidence was found that coning also results from migration of curing agent while the propellant is curing during manufacture although the precise mechanism involved has not been established.

Introduction

THE phenomenon of coning in end-burning solid propellant rocket motors has been known for many years; yet, in spite of having hindered development programs of motors, it has received scant attention in the literature. Coning refers to the characteristic feature of end-burning charges when the propellant burns faster at or near the periphery than in the bulk propellant. This feature gives rise to a burning surface with a truncated-cone configuration or, if burning proceeds long enough, to the formation of a fully developed cone as depicted in Fig. 1. When coning occurs, the propellant burning surface area and, hence, the motor pressure and thrust generated increases. Also, the effective motor burn time is shortened. For some motor applications, such deviations from design values can be important and even critical.

The development of a coned surface resulting from a faster burn rate at the interface than in the bulk propellant can be seen from the conventional ray theory construction shown in Fig. 2. The constant cone angle θ is given by

$$\theta = \arccos\ (r_b/r_i) \tag{1}$$

where r_b is the bulk propellant burn rate and r_i the burn rate at the interface. The cone angle is thus a function of the ratio of the two burn rates. Equation (1) is plotted in an inverse form in Fig. 3, showing that a substantial cone angle can result from an enhancement of the burn rate at the interface of only a few percent.

Coning has been observed with both double-base propellants and composite propellants, and studies have been undertaken to determine the causes. This paper is concerned with the results of our investigations with composite propellants.

Results and Discussion

Several possible mechanisms leading to an increased burn rate at the inhibited propellant interface, some of which have been considered previously,[1-3] can be postulated. These include the following.

1) Chemical migration of plasticizers and liquid burn rate catalysts across or towards the interface.
2) Heat transfer longitudinally along and/or axially through the inhibitor wall.
3) Concentration of fine particles of oxidizer or solid burn rate catalyst at the interface.
4) Stresses in the propellant adjacent to the interface.

In the present study, all of these possible mechanisms were investigated. For the most part, experimental testing was carried out using small scale end-burning motors with charge dimensions approximately 50 mm diameter by 130 mm as shown in Fig. 4. Except for two special sets of case-bonded charges, the motors were cartridge-loaded. A number of larger motors, 130 mm diameter by 720 mm, were also fired. The motors were fired at a nominal pressure of 7 MPa and at temperatures usually of 0 and 40°C, and they were interrupted before burn-out to examine the extinguished propellant charge and measure any cone angle. The same propellant formulation was used in nearly all tests and a variety of materials were used to inhibit the sides of the propellant grains. The inhibitor materials which were used are listed in Table 1 together with their measured characteristic cone angles and various physical properties of interest. Each value of cone angle listed was determined from a minimum of three motor tests; some values, particularly with the hydroxyl terminated polybutadiene (HTPB)/Adiprene system, were determined from many more.

Migration of Species at the Interface

It has been shown[1] that where a propellant/inhibitor system contains mobile species, such as plasticizer or a liquid burn rate catalyst, migration can occur across the interface causing a modification to the propellant burn rate at the interface region through a localized change in oxidant/fuel ratio or concentration of burn rate catalyst.

The propellant used in these studies was a simple composite propellant consisting of a DDI-cured HTPB binder and a bimodal blend of 200μm and 20μm ammonium perchlorate oxidizer, with added antioxidant and solid burn rate catalyst. The formulation was as follows: 18.8% R45M HTPB and dimer acid diisocyanate (DDI) curvature, 80.5% ammonium perchlorate, 0.2% Calco 2246 (antioxidant), and 0.5% copper chromite.

With the exception of one case to be discussed later, the motor charges were prepared by casting the propellant into a previously manufactured beaker of inhibitor material, then

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Table 1 Measured cone angles and physical properties for inhibitor materials[a]

Inhibitor	Cone angle, deg		Maximum stress, MPa		Maximum strain, %		Initial modulus, MPa		Coefficient of linear expansion, (1/K)×10⁴	Thermal conductivity, W/mK
	0°C	40°C	0°C	40°C	0°C	40°C	0°C	40°C		
HTPB/Adip L315	14	14	1.8	1.0	985	405	2.0	1.3	2.6	0.20
HTPB/Adip L315/ZC[b]	13	13	2.3	1.3	940	390	3.3	2.4	2.3	0.31
HTPB/Adip L315/FCH[c]	12	12	2.0	1.6	67	45	13	11	4.9	0.26
HTPB/Adip L315/ALU[b]	17	18	1.9	1.2	376	200	8.5	4.8	1.9	0.29
Lucite	7	0	~50	~50	~5	~5	~3000	~3000	~0.8	~0.2
HTPB/Adip L315/AS[b]	0	0	1.1	0.8	68	68	7.3	5.0	1.8	0.3
HTPB/Adip L315/KS[b]	(7)[d]	3	1.1	0.8	137	142	4.7	3.2	1.6	0.28
Adip L100/Epi 828/MOCA	0	0	30	7.6	1194	648	29	27	~2.0	0.20
Adip L315/TMP	0	0	40.9	16.5	268	379	422	44		0.22
Adip L315/BD	0	0	72.9	3.5	1123	1163	141	3.7		
Adip L315/PCP0300	0	0	46.2	4.1	745	245	45.1	5.4		0.21
Adip L315/TMP/AS[b]	0	0	18	6.4	4	45	590	107	1.0	0.26
Adip L315/BD/AS[b]	0	0	12		12		507		1.5	0.30
Adip L315/PCP0300/AS[b]	0	0	8.7	2.0	28	22	356	23	1.5	0.29
HTPB/Adip L315/Iso	0	0	17.2	1.0	814	>1340	103	2	2.1	0.19
Hypalon	(0)[d]	(0)[d]	18.1	5.0	224	220	21.7	10.5		

[a]Binder ingredients: Adip = Adiprene; Epi = Epikote; TMP = trimethylolpropane; BD = butanediol; PCP = polycaprolactone; and Iso = Isonol C-100; Fillers: ZC = zirconium carbide; FCH = Fiberfrax C-H (alumina silica); ALU = alumina; AS = ammonium sulphate; and KS = potassium sulphate. [b]50% by weight of filler present. [c]29% by weight of filler present. [d]( ) indicates some uncertainty about the value.

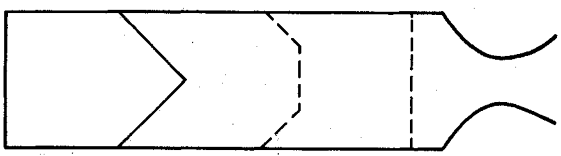

Fig. 1 Coning in an end-burning motor.

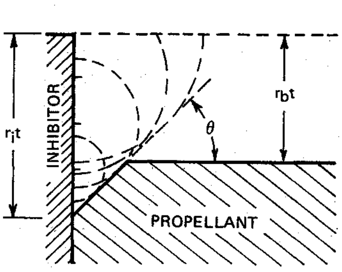

Fig. 2 Formation of coned propellant surface.

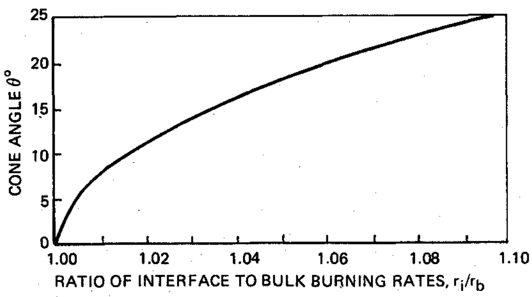

Fig. 3 Variation of cone angle with differential burn rate.

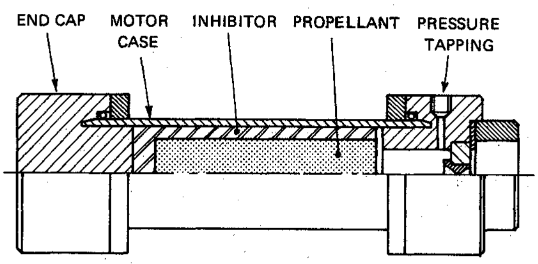

Fig. 4 Small scale end-burning test motor.

curing without vibration at 60°C. The base-line inhibitor used in these studies was similar to the propellant binder, except that Adiprene L-315 was used as the curative. In neither the cured propellant nor inhibitor was there a plasticizer, liquid burn rate catalyst or any other known mobile species. Hence, although coning occurred with this combination, the migration of species within the manufactured charge could not be identified as its direct cause. The other inhibitor materials used, listed in Table 1, similarly contained no known mobile species.

Enhanced Heat Transfer at the Interface

In these experiments, the motor case and propellant charge were always at a constant uniform temperature at the start of firing. If sufficient heat could be conducted during a firing along the inhibitor from the region projecting beyond the burning propellant to a region ahead of it, it would be possible to have an increased burn rate adjacent to the inhibitor. However, this would require the inhibitor to have a thermal diffusivity which is substantially greater than that of the propellant. This is an unlikely event in practice because binders and other polymeric materials used as the major constituents in inhibitors have lower thermal diffusivities than the propellant. Even for inhibitors incorporating salts or insulating materials as fillers, it is unlikely that the inhibitor thermal diffusivities would be more than that of the propellant, mostly because of the lower level of filler compared to that in propellant.

In the case of cartridge-loaded charges, heat conducted through the inhibitor during the firing from the hot gases filling the small gap between the motor case and the charge might be significant in long burn time applications. However, in these experiments with inhibitor thicknesses of 4 to 6 mm and burn times of up to 8 s, the heat reaching the propellant would have been negligible. Furthermore, near the start of firing, penetration of heat would have been even less; yet the constancy of cone angle, i.e., straightness of the cone sides, observed whenever coning occurred implied that

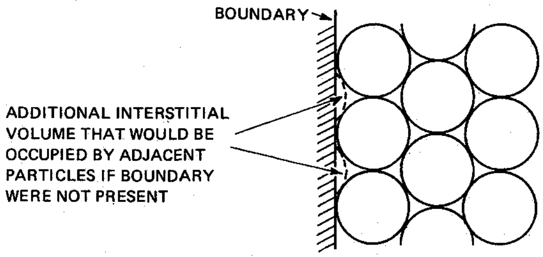

Fig. 5 Close packing of particles against a boundary.

the faster interface burn rate r_i must have been constant throughout the firing according to Eq. (1).

It is also most unlikely that any heat transfer through the inhibitor wall by reflected radiation would be significant. This is confirmed by the observation that of the seven translucent inhibitor materials tested only one, HTPB/Adiprene, showed coning.

Concentration of Fine Particles at the Interface

One of the most common and plausible theories for explaining cone-burning is that an increased concentration of fine oxidant particles exists at the interface relative to the bulk propellant, due to a larger interstitial volume between the coarse oxidant particles against the boundary wall. In a system of close-packed particles of approximately spherical shape, the interstitial volume will be greater in the layer adjacent to a plane boundary than in the bulk of the material as illustrated schematically in Fig. 5. Hence, for a propellant containing a bimodal blend of oxidant particles, it would be expected that the concentration of fine particles in the layer adjacent to the boundary would be higher than in the bulk propellant, especially for a highly loaded propellant. Accordingly, since in general a higher concentration of the fine oxidant fraction increases propellant burn rate, the rate would be expected to be higher at the interface, thus inducing coning.

The same argument applies to the distribution of fine particles of solid burn rate catalyst. Assuming a uniform dispersion in the binder there should be a higher local concentration against the boundary, resulting in a higher local burn rate. The propellant used in these studies contained copper chromite as the burn rate catalyst with a particle size range of about 1 to 7 μm.

Previous workers[1,2] have reported the existence of such a classification effect on the distribution of particles at the inhibitor interface. Messner[2] cites burn rate enhancements at the interface of up to 70% as being attributable to increased levels of fine iron oxide catalyst at the boundary. In Ref. 1 evidence is reported of classification of fine oxidant particles at the propellant boundary, inferred from micro-strand burn rates and confirmed by measurements of particle size distributions at successive locations from the boundary.

In our studies, an attempt was made to obtain direct evidence for the possible existence of a higher concentration at the interface of the fine particles of burn rate catalyst, copper chromite. By inference such evidence would also have indicated a higher concentration of fine oxidant particles. A section from a charge of the base-line system (HTPB/Adiprene inhibitor), which always exhibited coning, was examined by electon probe micro analysis. The results showed that the copper chromite was evenly dispersed in the binder, but no evidence was observed of any greater concentration at the interface.

If the occurrence of coning with a given propellant formulation were due to this classification effect at the interface, then it would be expected that this same propellant would always exhibit coning irrespective of the inhibitor material used. The exception might be if this effect were masked by some additional effect preventing coning. Our results (see Table 1) with a single propellant formulation and a variety of inhibitor materials showed coning in varying degrees with some inhibitors and none at all with others. Thus, these results are inconsistent with a coning mechanism based on classification of particles.

It seems significant that in Ref. 1 it was found that from a number of propellants tested, classification of particles was found to occur in only one formulation and was significant in this formulation only when the propellant was vibrated during cure. If concentration of fine particles at the interface were a persistent cause of coning, then it would be expected that evidence of its presence would be more prevalent. However, there does not appear to be a wealth of direct evidence for classification of fine particles at the propellant/inhibitor interface, and the occurrence of the classification of five particles appears to be not as universal as might be assumed.

High Propellant Stress

These present studies grew out of a development program for an end-burning motor in which some motors were initially manufactured in a case-bonded configuration. With these motors severe coning was immediately evident. The radial strain in the propellant in this configuration was considered to be responsible as it has been shown[4] that at sufficient levels of strain propellant burn rate will increase. To verify this, several motors were manufactured such that part of the grain was stress-relieved by a boot inhibitor while the inhibitor for the remainder of the grain was bonded directly to the motor case. In these motors, cone burning was always evident where the grain was case-bonded; whereas in the stress-relieved region, coning was either absent or less severe.

Case-Bonded Motor Tests

To investigate further the influence of propellant strain in causing cone-burning, a series of experiments was carried out using case-bonded charges to intentionally introduce strain in the propellant. HTPB/Adiprene and Adiprene/Epikote/MOCA (AEM) inhibitor materials were used in these tests. It had previously been found that the use of AEM inhibitor produced no coning with cartridge-loaded charges at temperatures of 0, 20, and 40°C; cartridge-loaded charges with HTPB/Adiprene inhibition gave a 14 deg cone angle at these temperatures.

Thirty-six case-bonded motors with AEM inhibitor/liner were manufactured and nine each fired at temperatures of 0, 20, 40 and 60°C. The measured cone angles resulting from these firings are shown in Fig. 6a where an essentially linear dependence of cone angle on firing temperature is seen. Since the cone angle for the corresponding cartridge-loaded motors was zero, the observed cone angles with these case-bonded motors can be attributed to the strain in the propellant.

During the firing of these motors, two known causes of strain in the propellant adjacent to the interface were present. One was the thermally induced loading due to differential contraction of the various materials at each temperature; the other was the pressure loading which, for a case-bonded end-burning charge, would also result in a tensile stress at the propellant/inhibitor interface. The stress-free temperature for thermally induced loads in conventional HTPB propellants is known to be approximately 8°C above the cure temperature,[5] i.e., 68°C for these motors. At this temperature, the strain in the propellant during firing would then be due only to the pressure loading, and the corresponding cone angle would be the pressure induced component. Because these motors were all fired at the same nominal pressure (7 MPa), the pressure loading and, hence, the amount of coning due to the pressure induced strain would have been essentially constant for each motor. If this contribution is subtracted from the measured cone angles, the degree of coning

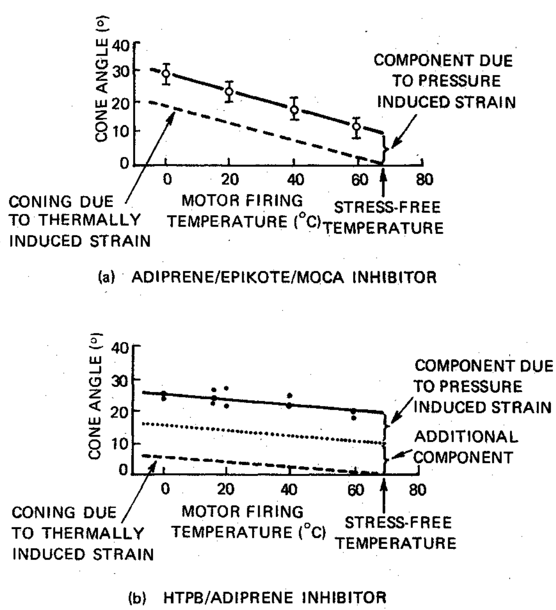

Fig. 6 Measured cone angles for case-bonded motors.

due to the thermally induced strain at each firing temperature is obtained. This is represented by the dashed line in Fig. 6a.

A similar series of case-bonded charges using HTPB/Adiprene inhibitor were fired at temperatures of 0, 20, 40 and 60°C, after which their cone angles were measured. The results, which were less numerous and less consistent than the first series, are shown in Fig. 6b. In these motors, although the mechanical properties of the inhibitor were different, the pressure loading on the propellant was nevertheless substantially the same as in the previous set of motors. Hence, the constant amount of coning due to pressure induced strain was essentially the same as for the previous motors. If this amount, obtained from Fig. 6a, is subtracted from the least squares fit to the data on Fig. 6b, the dotted line is obtained. This line does not give a zero cone angle at the thermally strain-free temperature of approximately 68°C, but instead indicates a cone angle component of about 10 deg which must arise from another unidentified factor. The cone angle determined from numerous firings of cartridge-loaded charges with the HTPB/Adiprene inhibitor was an essentially constant 14 deg at firing temperatures ranging from 0 to 40°C. It seems reasonable to identify this 14 deg value with the 10 deg residual component from Fig. 6b, i.e., it is assumed that this component of the cone angle from the case-bonded motors arises from the same source as the cone angle obtained with the cartridge-loaded motors. If the value of this component is subtracted from the dotted line in Fig. 6b, the dashed line is obtained which then represents the coning due to the thermally induced component of strain in those motors.

It is seen that the dashed line of Fig. 6b has a lower slope than the dashed line of Fig. 6a indicating a weaker temperature dependence of the thermally induced strain for the HTPB/Adiprene inhibited charges. This is consistent with the measured values of modulus for the two inhibitor materials (see Table 1) since more of the thermally induced stress would be absorbed by the HTPB/Adiprene inhibitor at corresponding temperatures resulting in relatively less strain in the adjacent propellant layer.

The above analysis indicates that there is a component of the cone angle with the HTPB/Adiprene charges which is not accounted for by pressure induced or thermally induced strains. It has also been suggested that this component and, therefore, its origin is common to both the case-bonded and the cartridge-loaded motors.

Possible effects other than propellant strain which could have contributed to the cone-burning have been discussed in previous sections and each has been discounted for the motors tested in this investigation. Because of the clearly demonstrated effect of strain as a cause of coning, it is reasonable to enquire if there are sources of propellant strain other than the two discussed above which might arise in both case-bonded and cartridge-loaded charges. At the propellant surface, there exists a steep temperature gradient into the propellant, falling typically from about 600°C at the surface to the initial bulk temperature of the propellant over a distance of some 100 to 200 μm.[6] Similar temperature gradients exist in the projecting inhibitor walls. The expansion of the material in this thermal zone at the burning face of the propellant, which is of the same order of thickness as the coarse oxidant particles, would be expected to give rise to stresses, some of which could be tensile, in this layer. Moreover, these stresses would be expected to be higher at the corner region where the burning propellant surface meets the inhibitor wall. Such stresses arising from the physical processes of burning would exist in both case-bonded and cartridge-loaded charges. Finite element analysis has been unable to provide useful information on details of this conjectured stress field due to unavailability of material data at the temperatures existing in this thin zone and to the grossly heterogeneous nature of the material at these dimensions.

The existence of these stresses, which for the same propellant should be effectively constant and independent of the inhibitor material, need not necessarily be sufficient alone to cause a differential burn rate at the interface. Indeed, the results with different inhibitors, as given in Table 1, show that with many materials, coning does not occur although these stresses would always be present. An additional factor to the stress created by the burning action would also then have to be involved for those propellant/inhibitor systems where coning is observed.

Migration of Curing Agent

In a recent paper on migration of species in rocket motors, Davis et al.[7] have reported that in HTPB propellants cured with DDI or IPDI (isophorone diisocyanate) a soft layer is formed in the propellant immediately adjacent to the inhibitor interface, due to migration of the curative out of the propellant during cure. The propellant used in these present studies was cured with DDI; therefore, it could be assumed that such a soft layer existed in these motors when an absorbent inhibitor was present, although no attempt was made to verify this by measurement. However, confirmatory evidence of this effect was obtained from two motors, inhibited with HTPB/Adiprene, which were identical to previous motors, except that the manufacturing steps were reversed. Instead of casting the propellant into an already cured inhibitor beaker, the propellant grain was first prepared as a bare block of cured propellant and then inhibited. Since the curative was already tied up chemically in the cured propellant, there was no opportunity for it to migrate into the inhibitor. These motors when fired at 0 and 40°C showed no coning, in contrast to the large number of otherwise similar motors which were prepared by casting the propellant against the cured inhibitor.

Consistent with the migration of curative, a further observation was that during the course of these studies when it became necessary to use a new batch of HTBP prepolymer the measured cone angles were found to be somewhat more than obtained previously. It was also observed that with this new batch of HTPB the pot-life of the propellant was about 10 h compared to 3 h for previous mixes. This would have allowed correspondingly more migration of DDI to occur, resulting ultimately in more severe coning.

Further evidence supporting the role of curative migration as a contributory factor in causing coning comes from examination of the results from the HTPB/Adiprene-based inhibitors shown in Table 1. The HTPB/Adiprene material could be expected to absorb mobile species comparatively readily, and cone angles are correspondingly high. When the

HTPB/Adiprene inhibitor incorporates a fairly high level of inorganic or refractory filler, there is less material available to absorb the curative, and cone angles are much less or absent. Similarly, comparison of the results for ammonium sulphate or potassium sulphate filler with, for example, zirconium carbide filler shows essentially no coning for the former but substantial coning with the latter. Even though the filler level was constant at 50% by weight for each, volumetrically there was considerably less zirconium carbide present and, correspondingly, more polymer to absorb the DDI because of the large difference in densities.

With other inhibitor materials, it has been observed that low or zero cone angles generally seemed to be associated with high inhibitor modulus values. This is reflected in the results shown in Table 1. The high modulus values are a result of a high degree of cross-linking in the polymer resulting in a closely-knitted and more rigid molecular network which would resist infiltration by the free curative molecules and, thus, prevent their migration.

Tests were also conducted with strands taken from charges inhibited with HTPB/Adiprene and AEM. Propellant strands 5 mm square in section were cut from the bulk of each charge and from the inhibited sides. The inhibitor was retained on the latter. The strands were burnt for several seconds at the test pressure of 7 MPa, and then they were quenched and the extinguished surface was examined. All strands taken from the centers of both sets of charges and those from the edge with AEM inhibitor attached had a flat surface showing uniform regression during burning. Those strands with the HTPB/Adiprene inhibitor attached all exhibited a surface which slanted towards the inhibitor interface, thus indicating faster burning at the interface. These tests showed that the coning effect resulted from a property of the particular inhibitor/propellant interface and not as a consequence of the motor internal environment.

Additionally, results from preliminary tests measuring the uptake of DDI by several of the inhibitor materials listed in Table 1 indicate a degree of absorption in line with the corresponding measured values of cone angle.

All the above evidence is consistent with DDI migration being associated with coning. However, the precise reason for the consequent faster burn rate at the interface has not been established. A plausible explanation is that the migration of the DDI leaves a thin layer in the propellant with a higher oxidant/fuel ratio which would be expected to burn faster. However, this explanation appears inadequate.

As mentioned above, it has been observed that, in general, those inhibitors that were more rigid, i.e., those with high modulus values, were effective in preventing cone burning. It was also observed that the wall thickness of the inhibitor beaker was a factor in the occurrence or degree of coning, apparently because a thicker wall made the system more rigid. Tests with ammonium sulphate filled HTPB/Adiprene inhibitor showed that with inhibitor wall thicknesses of less than 2 mm some variable amounts of coning often occurred; whereas with greater thicknesses, no coning was ever observed. The apparent importance of the mechanical properties of the inhibitor suggests that it may be the softness of the layer identified by Davis et al.[7] resulting from the migration of curing agent that is of significance rather than the change in oxidant/fuel ratio. It is then conceivable that interaction of the restraining forces exerted by a rigid inhibitor, with stresses existing in the soft layer and arising from the burning processes as described earlier, could be effective in preventing a faster burn rate which might otherwise occur in that layer due essentially to a strain mechanism.

Conclusion

Test firings of small scale motors have shown that the propellant inhibitor material has an important influence on whether coning will occur with an end-burning solid propellant motor. Several likely properties of these materials were measured in an effort to identify critical ones. Of these, only initial modulus appeared important.

The more obvious and common theories for explaining the origins of cone burning were examined and found to be inadequate for the motors used in these studies.

It was shown that strain in the propellant, arising from known sources, was a primary cause for coning. Considerable indirect evidence supported the conclusion that migration of the curing agent into adjacent inhibitor material during propellant cure can also result in coning. The mechanism involved may simply be one of localized increase in oxidant/fuel ratio resulting in faster burn rate at the interface. However, another previously identified effect of curative migration is the formation of a soft layer in the propellant adjacent to the interface, and there is evidence to suggest that this may be of more importance for coning. In this case, the primary mechanism would be one involving mechanical strain which could arise on the micro scale from the combustion processes at the burning surface and be of consequence in the soft layer region adjacent to the propellant/inhibitor interface. Further experiments would confirm the role of curative migration as a cause of cone burning and distinguish the essential mechanism involved.

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