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Role of Binders in Solid Propellant Combustion

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This paper describes a preliminary investigation into the effects of inert binder properties on composite solid propellant burning rate. Surface pyrolysis data were obtained for many polymers over a wide range of conditions, using a focused radiation source. These data were used to extract kinetics constants from Arrhenius plots, and heat of decomposition from an energy balance. Motion pictures were taken of the pyrolyzing surfaces, and gas samples were extracted for spectrometric analysis. Pyrolysis kinetics varied between the polymers, but were found to be independent of nitrogen pressure, the presence of ammonium perchlorate or catalysts in the sample, and their combinations. All of the polymers exhibited molten, boiling surfaces mingled with char, to varying degrees; the low activation energies measured may be associated with the boiling, or with a weak-link decomposition mechanism. Relevant data were input into the Derr-Beckstead-Price combustion model in order to associate binder properties with known effects on burning rate in simple propellants. Although the effects were predictable, they stemmed from properties other than pyrolysis kinetics. It appears that the role of binder lies in its contributions to controlling gas phase processes, and not in surface pyrolysis properties.

Introduction

COMPARED to the considerable effort that has been devoted to improved understanding of the role of ammonium perchlorate in solid propellant combustion, little attention has been given the binder.[1] The rationale for this difference in emphasis arises from the use of oxidizer to control propellant combustion characteristics, whereas the binder fulfills an essentially different role. However, as sophistication of combustion modeling and combustion tailoring has advanced, the need for additional attention to the role of the binder in the combustion process has become recognized.

Hypotheses concerning the role of binder in solid propellant combustion may encompass a variety of conceivable physical and chemical processes. Physical processes include the binder as inert interstitial spacing between oxidizer particles to impede the combustion front on the local microscopic scale; surface melting that would result in physical interference with oxidizer processes and thereby the ability of the oxidizer to react with binder or otherwise manifest itself; heat transfer and phase changes; diffusion of binder decomposition products in the gas phase; and processes that have a feedback effect upon the physical geometry of the combustion zone. Chemical processes include thermal and/or oxidative degradation of the polymer; and reactions between the products of binder decomposition with those of oxidizer decomposition or combustion in various regions of the gas phase or in stages. The kinetics and energetics of these processes serve to quantify the burning rate of the propellant and the various details that relate to burning rate (e.g., surface temperatures, flame heights, whether the oxidizer particles are recessed into the binder surface or protrude above it). These processes actually contribute to a total picture, and must be considered in that context. The extraction of an individual hypothesis concerning the role of binder, with nothing more, has not yet provided a reconciliation of propellant combustion behavior with the binder as a variable.

Combustion models of the type developed by Hermance[2] and by Derr, Beckstead, and Price[3] have attempted to include most of these processes in a reasonable manner, to the extent justified by experimental knowledge but within the limits of tractability, so that they may be analytically studied individually and coupled. However, many of the essential parameters affected by the binder have been quantified by assumptions based on limited data of questionable relevance. Typical criticisms are that the information used was acquired at heating rates many orders of magnitude below the rates that occur in the combustion zone, or under conditions of otherwise limited applicability to propellant combustion, or for polymers that are of limited or no interest to the propellant industry. Several recent programs have moved to overcome these criticisms[4–9]; however, they are limited in scope with reference to the acquisition of model input parameters. Accordingly, one purpose of this work was to expand

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Table 1 Kinetics of polymer thermal pyrolysis

Polymer	Prefactor, A_f (g/cm^2-sec)	Activation energy, E_f (kcal/molr)	$E_f/\log A_f$
CTPB	12.8	10.5	9.49
HTPB	299	16.9	6.83
Polyurethane	49.4	10.2	6.02
PBAN	270	16.7	6.87
Polysulfide	5.6	8.7	11.6
Telagen-S	7.3	9.0	10.4
Fluorocarbon	2.6	17.0	40.9

existing information by a systematic study of a variety of polymers that would yield some of these parameters and check certain model assumptions. Additionally, the predictive capability of the model would be verified as to binder effects on propellant burning rate, and the model would be examined to evaluate the principal role of binder.

Model Parameters

The combustion model utilized is that of Derr, Beckstead, and Price.[3] A listing of model input parameters is contained in Table 1 of their paper. Those parameters affected by the binder are the flame temperature of the propellant, the binder density, the kinetics of binder pyrolysis, the binder heat of decomposition, the oxidizer/fuel stoichiometric ratio, the kinetics of various flame processes, and certain physical properties of the gases (thermal properties, molecular weight, gaseous diffusivity). Some of these parameters are readily determinable, but many are not.[3]

This work would serve to quantify the kinetics of binder pyrolysis and binder heat of decomposition as measured under heating rates and pressures representative of a combustion environment. Gas samples would be acquired as an initial step toward determination of gas phase parameters, and to observe how the species change between binders. Motion picture observations would provide supplemental modeling or interpretive information. Remaining binder parameters would be routinely measured or calculated.

Binder Materials

Binder materials included in the investigation are summarized in Table 2.

Companion samples were made containing 10% ammonium perchlorate (AP) of 40-μ particle size. The use of nitrogen pressurant in the experimental apparatus was based on the assumption that a thermal degradation mechanism applies to the polymer in propellant combustion. The inclusion of AP affords the opportunity to explore possible oxidative degradation effects. The concentration of AP was limited in order to avoid sample ignitions under the conditions to be imposed; ignitions in the sense of gas phase reactions would cloud the pyrolysis data.

All samples contained 3% subμ Thermax carbon powder in order to render the samples opaque to the radiation heat source used. Thus the thermal wave for an imposed heat flux would be representative of the conduction-convection modes of heat transfer that are primary in solid propellant combustion. Also, the emissivities of the sample would be uniformly known with sufficient certainty to permit accurate surface temperature measurements with a radiometer, and reflection of the incident radiation would be minimized (representative of the calibrating calorimeter).

Table 2 Binder materials

1) Carboxyl-terminated polybutadiene (Thiokol HC-434, CTPB)
2) Hydroxyl-terminated polybutadiene (ARCO R-45, HTPB)
   a) Baseline
   b) Containing n-butylferrocene (Arapaho, NBF)
   c) Containing polycarboranesiloxane (Olin DEXSIL-202)
3) Hydroxyl-terminated polybutadiene, saturated (GT&R Telagen-S)
4) Polypropylene glycol polyurethane (Union Carbide, PU)
5) Polybutadiene/acrylic acid/acrylonitrile (Am. Synthetic, PBAN)
6) Mercaptan-terminated polysulfide (Thiokol LP-33, PS)
7) Polymerized DEXSIL-202 (Lockheed)
8) C_7 fluoroalkylacrylate fluorocarbon (Du Pont, FC)

Experimental Apparatus

The experimental apparatus consisted of an arc-image furnace to supply radiative heat at known flux levels, a suitable test chamber to contain and pressurize the sample, instrumentation to measure mass loss and surface temperature, a high-speed motion picture camera, a gas sampler, and a spectrometer to analyze the gas sample.

The Lockheed arc-image system incorporates a 20-kw xenon lamp in conjunction with opposing dual-ellipsoidal mirrors to focus the radiation at a uniform level over a finite focal volume. Heat flux attainable is 300 cal/cm^2-sec. Lower heat flux is achieved by reducing lamp power or by interposing attenuators. Exposure time is controlled by means of a fast-response shutter system located at the optical crossover point between the two mirrors. The shutter is controlled by an electronic programmer/timer, and permits exposure times ranging from 1 msec. to 10 sec. Heat flux is calibrated by a calorimeter placed at the focal point of the secondary mirror prior to testing; samples to be tested are subsequently placed at the same point.

The test chamber is of U.S. Naval Weapons Center design, as reported by Hightower.[10] It contains windows to transmit the radiation and to allow observation of the sample during a test. The chamber is mounted on a micrometer stage to permit location of the sample at the exact focal point of the secondary mirror. The dimensions of the sample are chosen to fill the focal volume, and are therefore dependent upon the particular lamp; samples here were $\frac{1}{8}$-in. in diameter, contained within a glass ring. The sample was mounted in a stainless steel plug installed in the base of the chamber. With this design, the chamber may be evacuated, or may be pressurized to 250 psia.

Higher pressure capability was achieved by strengthening the window portions of the chamber, but at a sacrifice in flux capability. At a pressure of 1000 psi, the maximum flux achievable was 50 cal/cm^2-sec. A Lucite-dome test chamber was constructed to combine maximum pressure and heat flux, but it turned out that the spectral transmission characteristics of the Lucite precluded acquisition of surface temperature data with the radiometer.

Mass loss was determined by before-after measurements with an analytical balance. Surface temperature was measured by an Infra-Red Industries Co. Model TD-6 fast-response pyrometer, with wavelength sensitivity compatible with the xenon lamp and quartz window. The pyrometer output was recorded on an oscilloscope permanent record. The pyrometer was calibrated against a blackbody source, which entails a maximum 2% temperature error when applying it to the blackened samples. The $\frac{1}{8}$-in.-diam sample completely filled the recticle of the pyrometer to provide a temperature reading averaged over the entire sample surface. For motion picture observation, the radiometer was replaced by a Hy-Cam 16mm camera.

Gas samples were extracted by means of a Loenco Model L-208-6 valve, mounted on the test chamber. Samples were analyzed with a Perkin-Elmer Model 270 mass spectrometer equipped with a Bendix multiphase inlet system. Tare outputs were obtained for the machine background and for nitrogen drawn from the test chamber without a sample.

Experimental Conditions

Extensive testing was performed over the range of 7 to 200 cal/cm^2-sec in nitrogen at a pressure of 1 atm. Data at levels

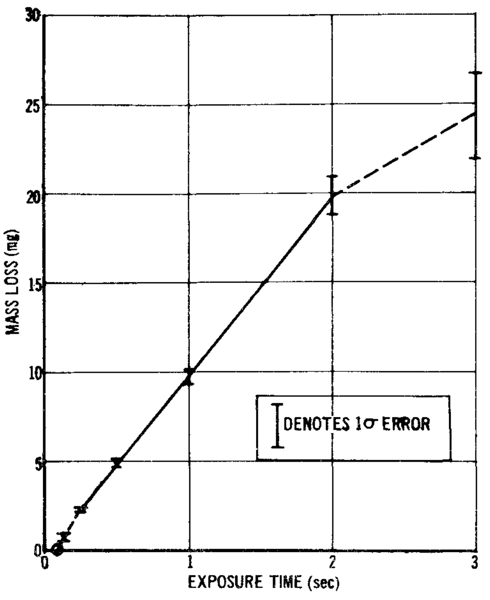

Fig. 1 Mass loss vs exposure time for CTPB at 100 cal/cm^2-sec.

above 200 cal/cm^2-sec were invalidated by phenomena affecting data reliability and reproducibility. Testing also was performed at selected flux levels over this range at pressures of 100 psia and 250 psia, and at a flux level of 50 cal/cm^2-sec at 1000 psi.

Another test variable, for each condition, was exposure time. Variation of exposure time permitted definition of a linear equilibrium region of mass loss vs time or total specific energy delivered, and provided information with which to compute heat of decomposition from an energy balance. An example of a plot of mass loss vs exposure time is shown in Fig. 1. A linear region is observed at exposure times between $\frac{1}{4}$ and 2 sec. At times of less than $\frac{1}{4}$ sec., the test is dominated by the startup transient. At times greater than 2 sec., nonequilibrium phenomena such as buildup of unpurged smoke or surface char, or regression beyond the focal volume, begin to manifest themselves. The extent of the linear region was mapped as a function of heat flux. With increasing flux, it was found that the region shifted to lower exposure times and became narrower in extent. At 220 cal/cm^2-sec, it was concluded that equilibrium could not be achieved and that nonreproducibility was beginning to be excessive.

The full range of tests was performed to acquire data on mass loss and surface temperature, except for the combined condition of 200 cal/cm^2-sec and 1000 psi, for which only mass loss data were acquired because of the Lucite dome chamber.

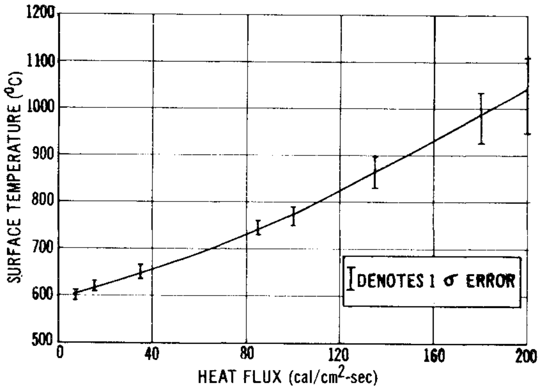

Fig. 2 Variation of surface temperature with heat flux for CTPB binder.

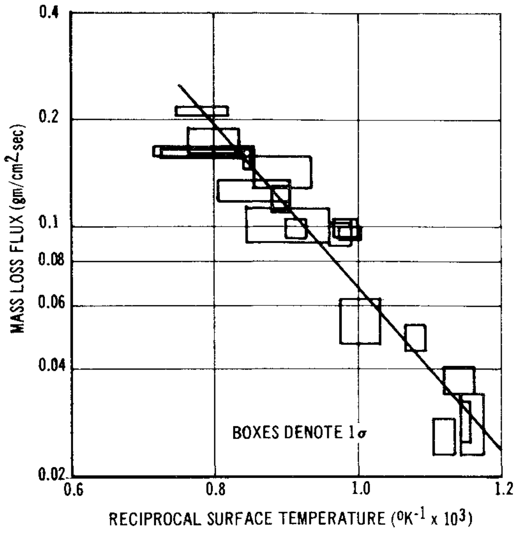

Fig. 3 Arrhenius plot for HC-434 CTPB in 1 atm of N_2.

For these purposes, five samples were tested at each condition and exposure time; results were reported as averages and 1σ standard deviations. Motion pictures were taken at combinations of extreme conditions, and gas samples were acquired only at 100 cal/cm^2-sec. Limited testing also was performed in chlorine and in air environments, to further explore oxidative degradation, but at subatmospheric pressures in an attempt to avoid ignitions.

Experimental Results

Effects of Heat Flux and Pressure

Variations in heat flux provided the variations in mass loss rate and surface temperature necessary to construct an Arrhenius plot. The effect of heat flux upon surface temperature is shown for CTPB in Fig. 2. The Arrhenius plot for CTPB is shown in Fig. 3, illustrating typical 1σ envelopes.

A combined plot showing the results for the various polymers is presented in Fig. 4. Over the range of heat fluxes from 15 to 200 cal/cm^2-sec, fluorocarbon exhibited the highest surface temperatures (1394 to 2550°C) and polyurethane the lowest (471 to 768°C). Kinetics constants are summarized in Table 1.

For samples not containing AP, no effect of nitrogen pressure could be determined within the 1-σ error bands. Bases for comparison were results at a given heat flux, and position of the results on the Arrhenius plot. At the conditions of 200 cal/cm^2-sec and 1000 psi, where surface temperature was not measured, the mass loss measured was within the error of the 1-atm. result.

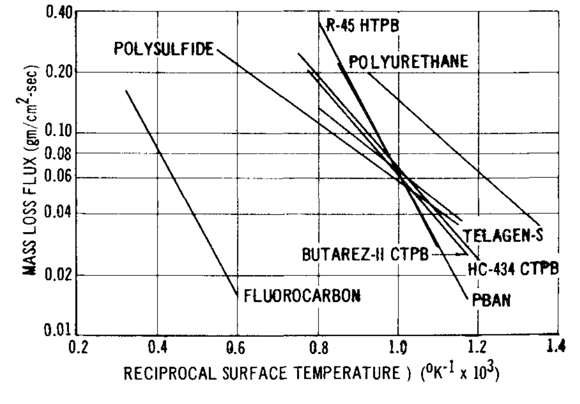

Fig. 4 Arrhenius plots for the various binders in 1 atm of N_2.

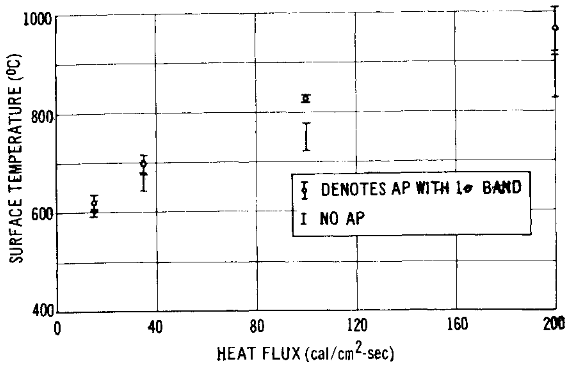

Fig. 5 Effect of ammonium perchlorate on surface temperature for PBAN binder.

Effect of the Presence of AP

In general, surface temperatures for a given heat flux were increased somewhat with samples containing AP. The effect is typified by results for PBAN shown in Fig. 5. However, increasing pressure with samples containing AP produced no additional effect, as was the case for samples not containing AP.

Although surface temperature increased for a given heat flux, the mass loss also increased such that there were no significant displacements from the Arrhenius plots constructed for samples not containing AP.

The most significant effect of AP appeared in the polycarboranesiloxane polymer. Without AP, acquisition of equilibrium data was precluded by the formation of a unique white surface crust, which merely heated with time. With AP, equilibrium data were obtained and it was noted that the crust changed in character to a small amount of loose, white powder. The Arrhenius plot for this polymer containing AP was similar to that for fluorocarbon in that it was located in a relatively high temperature regime, and the ratio $E_f/\log A_f$ was relatively high compared to those of the other polymers. These two polymers have similar commercial applications in the area of thermal resistance, but produce different propellant combustion effects.

Over the range of pressures from 1 atm to 250 psia, no pressure effect was observed for the polycarboranesiloxane containing AP. However, at 1000 psi, the surface temperature markedly increased. The motion pictures revealed microscopic flames distributed across the surface, indicating an ignition rather than a pyrolysis condition. No ignitions were observed in samples not containing catalytic materials.

Effects of Catalysts

In the case of *n*-butylferrocene or DEXSIL added to HTPB as plasticizer-catalysts, there were no effects compared to results without them. The absence of pressure effects also was maintained.

The effect of including AP was the same with the catalysts present as without catalysts, except at combinations of high heat flux and pressure where ignitions were observed.

Effects of Oxidizing Gases

Consideration was given to testing in perchloric acid, chlorine dioxide, or chlorine environments as representative of possible processes occurring in AP-oxidized propellants. Chlorine was selected on the basis of availability, safety, and convenience in handling as a gas. Furthermore, it has been argued that chlorine atoms may be the ultimate manifestation of AP as an oxidizer in composite propellants[11]; perchloric acid derived from AP decomposition is merely a source of ClO or ClO_2 upon further decomposition,[12] these species being readily dissociable into chlorine atoms. The ability to achieve chlorine atoms from molecular chlorine becomes a question of temperature, which is determinable from the surface temperature data acquired.

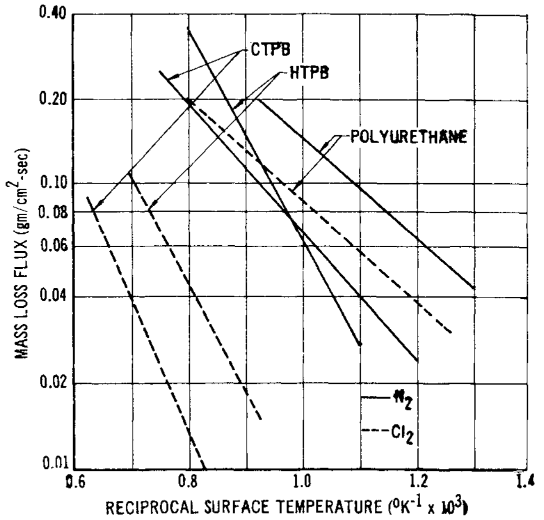

Fig. 6 Effect of Cl_2 on pyrolysis of CTPB, HTPB, and polyurethane.

Testing of CTPB at 1 atm of Cl_2 clearly produced gas phase flames, based upon the fluctuating character of the pyrometer output and motion picture observations. Testing at 3 and 7 psia Cl_2 did not appear to indicate flames; however, for a given heat flux, the surface temperatures were increased approximately 400°C and the mass loss rates decreased. This behavior also appeared with HTPB and polyurethane, but to a lesser extent with polyurethane, as shown in Fig. 6. Samples containing AP produced no additional effects.

Although it appears that chlorine depressed the pyrolysis kinetics for these polymers, the results are considered open to the question of the possible existence of gas phase reactions masking the oxidative degradation sought to be measured.

Additional testing of CTPB was performed in 7 psia air. There was no effect on surface temperature for a given heat flux. However, the mass loss rates changed in such a way as to increase the apparent activation energy. As shown in Fig. 7, it

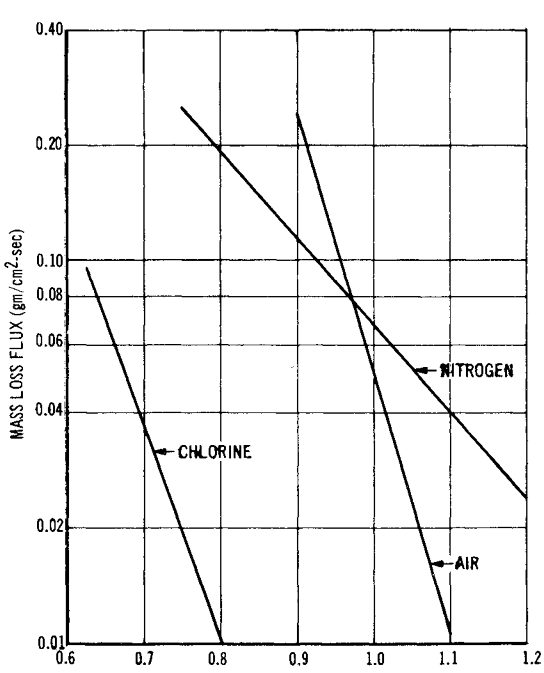

Fig. 7 Effect of environmental gases on pyrolysis of CTPB.

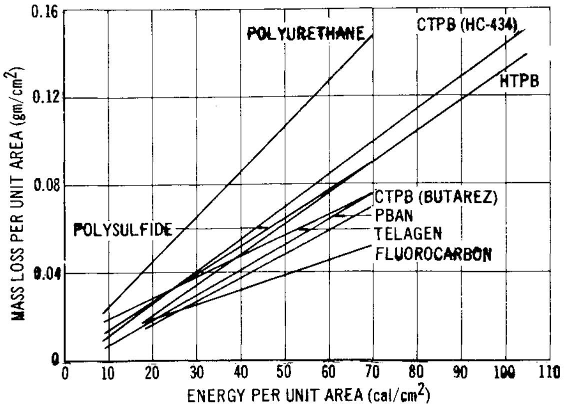

Fig. 8 Mass loss of binders as a function of total energy input for a heat flux of 35 cal/cm^2-sec.

is interesting that the activation energies in air and chlorine are similar to each other.

Motion Picture Observations

Without AP present, and in nitrogen, all binders exhibited molten, boiling surfaces intermingled with char to varying degrees. The amount of char tended to increase with increasing heat flux, appearing as clusters of islands around which were rivulets of boiling binder. Among the polybutadienes, the HTPB exhibited the most char. The nature of the boiling fluid varied from clear and watery for polyurethane (which exhibited the least amount of char), to tar-like for fluorocarbon. Increasing pressure tended to reduce the size of the boiling bubbles. As mentioned earlier, the polycarbonesiloxane exhibited a unique noncarbonaceous surface residue; high-magnification movies showed this residue to be clusters of clear bubbles that would not break. The presence of AP in the binder samples tended to increase the extent of carbonaceous char formation, and with catalytic compounds also present, localized flames appeared on the surface at combinations of high heat flux and pressure.

Black smoke was observed to issue from the surface. At lower heat flux, the smoke was effectively removed by the purge system. At fluxes above 100 cal/cm^2-sec, however, the purge was less effective. This raised questions about the heat flux actually received by the sample and the validity of the temperature readings. The heat flux actually received by the surface does not bear upon the Arrhenius plots as long as mass loss and surface temperature data are being obtained, whatever the flux. Further study of the data, the spectral sensitivity of the pyrometer, and the properties of the smoke led to the conclusion that the smoke was pervious relative to the pyrometer. However, the attenuated flux would bear upon the validity of the energy balance used to determine heat of decomposition; therefore, the energy balance was limited to the flux of 35 cal/cm^2-sec, where the smoke was absent.

At 1000 psi, the character of the smoke changed. It became white and, intermittently, a heavy globule of orange-brown smoke would come forth. With AP present, puffs of white smoke were also observed.

In chlorine at 1 atm, streaks of orange flames were observed; these were rapidly blotted out by an accumulation of relatively large carbon particles on the window. The interior of the chamber was covered with soot after the test, a result not previously encountered. Post-test examination of the binder surfaces revealed a much dryer and more charred surface than resulted in nitrogen. At 7 psia, the gas, originally transparent with a hint of yellow-green, became a light transparent orange, and the boiling binder surface could be observed. The window remained clear and no soot was observed in the chamber after the test.

Gas Sample Analysis

Data were acquired for CTPB, HTPB, polyurethane, and fluorocarbon at 100 cal/cm^2-sec in nitrogen at 1 atm. Mass numbers 82 and 84 consistently showed highest spectral intensities. Other mass numbers common to all four polymers were 14, 47, 48, 49, and 86. Mass numbers significant for all but HTPB were 35 and 36; mass numbers unique to HTPB were 27, 29, 39, 41, 43, 57, 78, 80, and 94. Mass number 52 appeared only for HTPB and fluorocarbon. Mass numbers unique to fluorocarbon were 38 and 44.

A surprising result is the absence of H_2O (18) and CO_2 (44) from polyurethane. It was not possible to separate CO (28) because of the dominance of N_2 (28). H_2 (2) is not reported, because of range sensitivity limitations of the instrument. CH_3 (15) and CH_4 (16) do not appear as major species, but CH_2 (14) commonly appeared. O_2 (16) was not detected from polyurethane, but F_2 (38) may have appeared in fluorocarbon. Major species appear to be heavy hydrocarbons, with the greatest variety evolved from HTPB.

Heat of Decomposition

Heat of decomposition was determined from an energy balance, following the method of Shannon.[5] First, a plot is constructed of specific mass loss vs specific total energy delivered. Such plots for all of the polymers are shown in Fig. 8. The slope is inversely related to the effective heat of decomposition. The effective heat of decomposition, in turn, is equal to the sum of the energy required to achieve the surface temperature and the heat of decomposition. Heat capacity of the material and surface temperature are known from separate measurements. Results are summarized in Table 3. Polyurethane has the lowest value and fluorocarbon the highest.

Table 3 Polymer heats of decomposition

Polymer	Heat of decomposition (cal/g)
CTPB	381
HTPB	433
Polyurethane	260
PBAN	564
Polysulfide	530
Telagen-S	760
Fluorocarbon	1004

Analysis

Combustion Model Inputs

Binder-related constants for input into the combustion model are summarized in Table 4. Nomenclature is the same as used by Derr, Beckstead, and Price.[3]

Table 4 Binder input constants for the combustion model

	CTPB	HTPB	PU	PBAN	PS	T-S	FC
A_f (g/cm^2-sec)	12.8	299	49.4	270	5.6	7.3	2.6
E_f (kcal/mole)	10.5	16.9	10.2	16.7	8.7	9.0	17.0
Q_{fuel} (cal/g)	381	433	260	564	530	760	1004
W (g-mole)	18.5	18.7	20.8	18.9	26.2	18.7	28.5
Stoichiometric ratio	9.5	9.3	6.2	9.0	4.9	9.3	1.5
T_f, 70% AP (°K)	1437	1451	1787	1430	2545	1446	2265
ρ_f	0.92	0.92	1.01	0.93	1.27	0.91	1.60

A striking difference from the parameters assumed by Derr, Beckstead, and Price is in the kinetics prefactors. On the common basis of an activation energy of 15 kcal/mole, which they assumed, and for a given propellant surface temperature, binder pyrolysis rates would now be from one to three orders of magnitude less than previous. Another difference arises as to heat of decomposition; values in Table 4 are an order of magnitude higher than previously assumed.

Parameters relating to the AP and to the flame kinetics were left unchanged and constant between the various binders. The "primary flame" kinetics were based upon data from ClO_2-CH_4 flame studies. It now appears that heavy hydrocarbons are more representative than methane.

Combustion Model Results

Results of applying the model to polysulfide, polyurethane, and the polybutadiene binders formulated on a common basis are compared with data in Fig. 9. It is observed that the relative positions of the burning rate curves are correctly predicted, but the exact positions of the curves are somewhat low. Since the polysulfide data were predicted exactly in the previous work,[3] the drop in the theoretical burning rate curve can be attributed to the new pyrolysis and heat of decomposition values. It is noteworthy that such extreme changes in these parameters have relatively little effect upon burning rate. The polysulfide propellant is correctly predicted to have the highest burning rate, then polyurethane, and then a close grouping of the polybutadienes. These relative positions correlate well with flame temperature. Parametric study with the model reveals that flame temperature is an influential parameter; heat of decomposition has a secondary effect, and pyrolysis prefactor has a minor effect. In practical propellants containing aluminum and a high total solids concentrations, these flame temperature differences will be mitigated.

The new binder constants did have one significant impact upon the model results, which introduces a question bearing upon model validity. One characteristic of the computations discussed previously[3] is that the AP is correctly predicted to protrude above the binder surface at low pressure, and become recessed into the binder at high pressure. With the new constants, the AP is predicted to be fully recessed to the limits of statistical probability at all pressures. The local regression rate of the binder is now so low relative to the AP that the model cannot predict a correct statistical surface structure consistent with burning rate and the uniform surface temperature assumption. The plausible implication is that the uniform surface temperature assumption is incorrect; the binder in fact has a higher surface temperature than the AP. However, further study revealed that the sole benefit of a two-temperature model would be to restore the correct prediction of the surface structure; the impact upon the burning rate prediction would be minor. Consequently, it is concluded that pyrolysis kinetics affect the surface structure or binder surface temperature, but these in turn do not significantly affect burning rate.

The experimental data revealed that catalysts incorporated into the polymer produce no effect on pyrolysis kinetics. The polymerized catalyst exhibited relatively slow pyrolysis kinetics. In any event, the model revealed that pyrolysis kinetics have little effect upon burning rate. Therefore, it would be concluded that catalysts do not manifest themselves by direct influence upon binder pyrolysis. Parametric study with the model reveals that AP kinetics and primary flame kinetics are parameters that significantly influence burning rate.

If pyrolysis kinetics are not important, then it would appear that whether the mechanism of pyrolysis is thermal or oxidative would not be important as far as the kinetics effect upon burning rate is concerned. Use of the chlorine data, even if they are valid, would have no significant effect.

Problems were encountered in applying the input constants for fluorocarbon. The model predicted negative flame heights, and unusual burning rate characteristics associated with negative flame heights. The problem was traced to the diffusion equations, specifically caused by the uniquely low stoichiometric ratio for fluorocarbon. The diffusional mixing length appears as a function of geometric terms derived from AP particle size, AP concentration, AP/binder density ratio, and a term (η) that additionally includes a dependence upon the stoichiometric ratio.[3] The problem is analogous to that discussed for surface structure: with a certain combination of parameters, a diffusional mixing length cannot be correctly predicted consistent with the assumed diffusional geometry (coaxial bunsen burner in this case, with fuel and oxidizer initially segregated); if eta is negative, the diffusional mixing distance will be negative.[‡] The implication is that the substantial oxidizer content of the fluorocarbon polymer gives rise to an essentially premixed flame. Interpreting the physical significance as such, a computer program statement was input, forcing the model to use a finite positive mixing distance in cases where a negative eta would be calculated. The result was the prediction of a uniform high-pressure exponent, and an independence of burning rate on AP particle size, two known characteristics of fluorocarbon propellants.

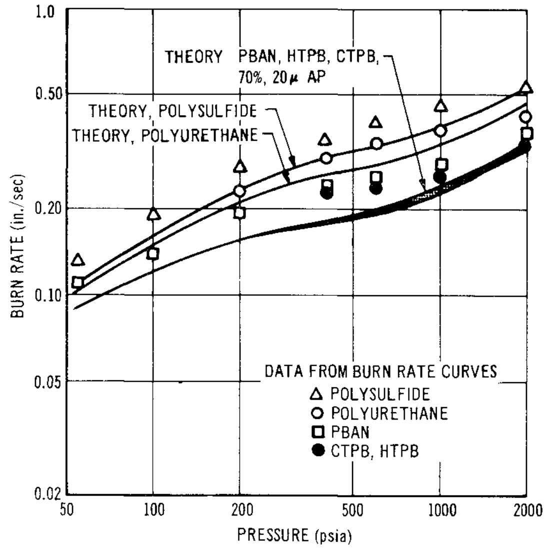

Fig. 9 Combustion model predictions with new binder constants.

Although the applicability of the model to inert polymers containing appreciable oxidizer in their structure is now questionable, it never was stipulated that the model would apply to the extreme case of double-base or reactive binders. But if new flame (as well as diffusional considerations) is to be introduced in composite propellant modeling, it would appear that the time is ripe for such a model advancement.

Conclusions

Polymers of interest to solid rocket propulsion exhibit a molten, boiling surface intermingled with carbonaceous char over a wide range of heating rates and pressures. The addition of AP, or the imposition of a chlorine environment, increases the extent of char formation. Combinations of thermal and oxidative degradation may be operative in propellants.

The kinetics of polymer pyrolysis are independent of heat flux, pressure, the presence of AP, and the presence of catalysts over the range of ingredients and conditions tested. The kinetics do appear, however, to be significantly affected by an oxidizing gas environment, subject to the possibility of gas phase reactions occurring in the experiments.

The different binders exhibit a range of kinetics constants, but activation energies do not exceed 17 kcal/mole. Kinetics constants cannot be consistently correlated with polymer structure. Therefore, a weak-link degradation mechanism, or the physical process of boiling observed, and not molecular bond rupture, appears to describe polymer degradation under the conditions imposed.

Major gaseous pyrolysis products are relatively constant between several differing binders tested. Mass numbers 82 and

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[‡] A third similar situation would be encountered at very high AP concentration; the binder interstitial spacing would be computed negative. A propellant manufacturer would refer to this as an unmixable propellant.

84, probably heavy hydrocarbon fragments, consistently dominated.

The experimental data and the combustion model could not account for burning rate trends or catalytic effects in terms of pyrolysis kinetics. The only evidence of catalytic activity appeared in the form of localized sample ignitions with AP present under certain conditions. The inference is that catalysts affect AP processes, or gas phase reaction processes involving AP and binder decomposition products, and not the binder per se.

The combustion model predicts binder effects on burning rate as observed in specialized research-type propellants. However, because flame temperature varies appreciably with binder type in those propellants, the predicted results are considered not representative of practical solid propellants.

The combustion model suggests that major alternations in pyrolysis kinetics will significantly affect the binder surface temperature for a given propellant burning rate, but predicts that the propellant burning rate itself will not be significantly changed. Major changes in the heat of polymer decomposition are predicted to have a larger but still comparatively small effect.

Parameters computed to be most influential on burning rate are flame temperature and parameters associated with AP processes or AP-binder flame processes. To the extent that polymers can be tailored to affect those processes, the binder can play a significant role in combustion tailoring. Because the AP-binder flame is particularly influential, future study of the role of binder in solid propellant combustion should be directed toward the gas phase.

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