

the hot nitrogen gas igniter was quite sufficient for the ignition¹¹ of pure AP. It is extremely difficult to prove that deflagration is not possible without definitive experimental results such as those which delineate the low-pressure deflagration limit¹² for pure AP and hence these results must be considered tentative.

Since similar results have been reported¹³ for AP catalyzed by NH_4MnO_4 , these data emphasize the need for a better understanding of the mechanism of catalyzed AP deflagration, particularly for the case of catalysis with the permanganate ion. Since no deflagration occurred, further work will be necessary to explore the effect of catalyst dispersion on AP deflagration. Although KMnO_4 strongly accelerates the thermal decomposition³⁻⁶ of AP, no KMnO_4 catalyzed AP deflagration could be maintained and, hence, it was impossible to correlate catalytic effectiveness in AP thermal decomposition and deflagration. However, since no concentration of KMnO_4 less than 0.4 mole % was used, it seems possible that a smaller concentration of KMnO_4 would permit deflagration and alter the burning rate. Since AP thermal decomposition appeared to be providing a heat sink which prevented complete ignition, the maximum KMnO_4 concentration for AP deflagration may be a strong function of the igniter heat flux strength. Hence this preliminary research has shown that a more complete study of AP ignition and deflagration catalyzed by KMnO_4 may reveal the significance of thermal decomposition in both AP ignition and deflagration.

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Siloxane Polyurethane Composite Propellant Binders

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FUEL atoms such as aluminium, boron, and silicon have been incorporated into the molecular structure of composite propellant binders in order to modify ballistic properties.¹ Most studies have been concerned with providing more energetic propellants although there have been few accounts where the prime interest is in the effect on burning rate. Schwarz and Lowrey² have reported that incorporation of silicon into polysulfide polymers can lead to a 50% increase in propellant burning rate. Silicon in these polymers was present as the silane (-C-Si-C-) moiety. Whereas metals in elemental form do not usually influence burning rate to a large extent, their oxides often have a pronounced effect as evidenced by their role in ammonium perchlorate deflagration.³ It appeared likely therefore that superior burning rate enhancement might be achieved if silicon were already bonded to oxygen when incorporated into the polymer.

The effect of the siloxane (-O-Si-O-) moiety was investigated in polyurethane binders. Siloxane copolymer glycols were prepared by etherifying 1,3,5,7,9,11-hexaphenyl-5,11-dihydroxytricyclo[7,3,1,1^{3,7}]hexasiloxane (Dow Corning Z-6018⁴) with a twofold excess of polyoxypropylene glycol (PPG) at 200-240°C employing 0.2 wt % stannous octoate as a catalyst. Examination of the products by gel permeation chromatography showed that all the Z-6018 had reacted but about half the PPG remained unreacted. The etherification thus appears to proceed via self-condensation of Z-6018 and terminate by capping of the siloxane block with PPG. The -Si-OH group is known to condense readily with itself but to condense more slowly with -OH attached to carbon. The -OH groups in PPG did not undergo reaction when PPG was subjected to the same conditions as used for etherification. PPG is thus a convenient chain stopper for Z-6018 self-condensation and by use of a twofold excess of PPG, block copolymer glycols that were useful in preparing propellant binders were obtained. When equimolar amounts of PPG and Z-6018 were employed the reaction product was solid and not suitable as a propellant binder.

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

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

Table 1 Summary of etherification reactions

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

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containing 0.75 lb of propellant. Comparison of the burning rate of an ammonium perchlorate propellant based on PPG2025/Z-6018 copolymer glycol polyurethane binder containing 2.07% silicon with that of a conventional polyurethane propellant based on PPG2025 instead of the copolymer glycol, but otherwise identical, showed burning rate to be increased from 0.20 in./sec to 0.575 in./sec at 1000 lb/in.² by the inclusion of silicon. The copolymer glycols derived from higher molecular weight PPG had higher viscosities than the PPG2025/Z-6018 copolymer glycol and were less useful for preparing propellants.

Although any argument can only be speculative in explaining the effectiveness of Z-6018 in increasing (by 188%) the burning rate of polyurethane propellant compared with the much smaller increases observed by Schwarz and Lowrey for silane polysulfide propellants (48% increase for binder containing 2.14% silicon; 52% increase for 8.1% silicon), the bonding of oxygen to silicon before combustion provides the most attractive explanation, paralleling the effect of elemental metals vs metal oxides on burning rate. In the case of the silane moiety, oxidation of silicon may occur too late during combustion to effect maximum enhancement of burning rate.

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Breakup of a Liquid Jet in a High-Pressure Environment

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Nomenclature

- α = liquid to gas density ratio
- b_i = mixing layer thickness
- C_d = concentration of discharge fluid $\dot{m}_d/(\dot{m}_d + \dot{m}_e)$
- f = velocity distribution function
- g = concentration distribution function
- L_b = jet breakup length
- \dot{m}_d = mass flow rate of discharge fluid
- \dot{m}_e = mass flow rate of entrained fluid
- r = radial coordinate
- r_0 = orifice radius
- r_1 = location of inner boundary of mixing layer
- r_2 = location of outer boundary of mixing layer
- U = mean axial velocity
- U_0 = axial discharge velocity
- $\bar{U} = U/U_0$
- ΔU_c = critical velocity difference for secondary atomization
- $\Delta \bar{U}_c = \Delta U_c/U_0$
- x_i = length of initial region
- $\bar{x}_i = x_i/r_0$
- $\eta = (r_2 - r)/b_i$
- $\eta_0 = (r_2 - r_0)/b_i$

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LIQUID issuing from an orifice into gaseous surroundings will always atomize, i.e., disintegrate into liquid droplets. An important parameter when describing the atomization process is the jet breakup or atomization length L_b . This is defined as the distance downstream from the orifice exit to the point where atomization is complete. Except for a few idealized cases,^{1,2} it has not been possible to determine this distance analytically for any given liquid. This is simply because the atomization process is so very complex. However, the results of a recent study³ indicate that under certain realistic circumstances it should be possible to ascertain the value of this parameter.

The study in question was concerned with the behaviour of propellant sprays in high-pressure combustors. Here it was observed that, in a large number of cases, the dynamic and geometric characteristics of the spray closely resembled those of the so-called turbulent submerged jet.

Shown in Fig. 1 is the customary representation of the inner and outer boundaries of the initial region of such a jet. The situation depicted here usually arises when a fluid exits from a circular orifice into a large quiescent medium of the same phase (i.e., liquid into liquid, gas into gas). In such cases there are three identifiable regions. The core, bounded by the surface $\eta = 1$, consists entirely of discharge fluid moving at velocity U_0 . The region beyond the outer boundary $\eta = 0$, is totally environmental fluid and has zero axial velocity. The mixing layer bounded by $\eta = 0$ and $\eta = 1$ is comprised of discharge and environmental fluid with continuous distributions of velocity and mass concentration.

In a great many cases, the velocity and concentration profiles can be represented by equations of the form $U/U_0 = f(\eta)$ and $C_d = g(\eta)$. That is, the profiles are self preserving.

These are several functional forms available for $f(\eta)$ and $g(\eta)$. Two simple forms which closely approximate reality are given by^{4,5}

$$f(\eta) = 2\eta^{3/2} + \eta^3 \quad (1)$$

and

$$g(\eta) = \eta \quad (2)$$

In the case of a liquid discharged into a high-pressure gas, the core region consists entirely of liquid and the ambient region is solely dense gas. The mixing region consists of atomized liquid droplets moving with the entrained gas; assuming of course that conditions are such that the atomization process is sufficient to produce a finely dispersed spray. When this is in fact the case, the length of the core region x_i represents quite well the breakup length. However before equating L_b to x_i , it is well to consider exactly what conditions must be met to insure the validity of this identity.

These are two mechanisms of atomization. Primary atomization is that form of breakup caused by deformation of the liquid stream at the liquid gas interface due to internal turbulence. Secondary atomization on the other hand, occurs

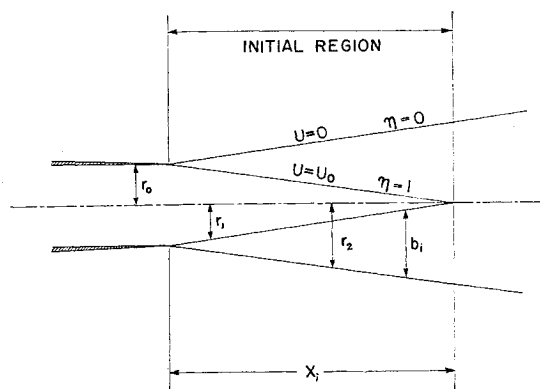


Fig. 1 Initial region of turbulent submerged jet.