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Theoretical Performance of Polyvinyl Chloride Plastisol Propellants: A Comparative Study

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Introduction

AMONG the possible plastisol composite propellant systems polyvinyl chloride (PVC) propellants are used extensively. Despite this, theoretical performance of these propellants are not fully available in open literatures. Rumbel[1] briefly gives the theoretical performance of an unmetallized propellant and a metallized propellant in this class. The aim of the present work is to make available the results of the theoretical performance of ammonium perchlorate (AP) - PVC plastisol propellants for many plasticizers of relatively wide variation in properties and to present a useful comparative study. Although the final composition of a propellant is usually decided on through various other factors like processing, physical properties, and aging requirements rather than through small changes in theoretical performance, the present work can be of help as an initial step towards propellant formulation.

II. Analysis

Rumbel[1] mentions dibutyl sebacate (DBS), dioctyl sebacate (DOS), and di-2-ethylhexyl adipate (DOA) as good plasticizers; dioctyl phthalate (DOP) is also used. Dibutyl phthalate (DBP) is rarely used as a sole plasticizer because of its poor low temperature flexibility characteristics and high volatility. Nevertheless, in addition to these four plasticizers, DBP is also considered for the analysis as a typical high-density low-molecular-weight plasticizer of relatively high oxygen and low hydrogen content. The method of group contribution technique by Handrick[2] was used for the estimation of heats of formation of the plasticizers. Properties of the plasticizers are summarized in Table 1. For the PVC resin, a mean value of 1.25 g/cm^3 is assumed for the density, and -22.6 kcal/mole is taken as the heat of formation per monomer.[3] The analysis is carried out for the propellants, having equal parts by weight of PVC and plasticizer along with aluminum, as the only metallic component. Chamber pressure of 70 atm with optimum expansion to one atmospheric pressure is assumed throughout. The computer program and the other thermochemical data given in Ref. 4 were used for the performance calculations.

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Index categories: Fuels and Propellants, Properties of; Solid and Hybrid Rocket Engines.

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III. Results and Discussions

A. Unmetallized Propellants

For the simple two component system of PVC binder and AP oxidizer, variation of specific impulse and density specific impulse for the cases of equilibrium flow and frozen flow are shown in Fig. 1. The vertical arrows in the figure indicate the stochiometric conditions. In the useful binder content range (around 20%), the high-density plasticizers along with the property of "low fuel rich" proportion give higher values of density specific impulse. But this advantage can be offset by the low-density plasticizers because of their capacity to accommodate higher solid loading with lower binder content without much loss in the mechanical properties of the propellant. However, one disadvantage of the low density plasticizers, should be noted. For any particular type of plasticizers, say the esters of sebacic acid, as the molecular weight increases the density decreases while the viscosity shows an upward trend (Table 1). Therefore considering the limitations imposed on the fluidity of mixed propellant controlled by the plasticizer viscosity, the improved solid loading capacity of the low-density plasticizers may not be fully realized.

B. Aluminized Propellants

Triangular composition diagrams of all five propellant systems were obtained for equilibrium flow, and these show the same pattern of constant specific impulse curves. The values of the overall maximum specific impulse and the corresponding percentage composition for the propellant systems are given in Table 1. The DBS-system is shown in Fig. 2 as a representative composition diagram.

With a close variation in the aluminum loading, maximum specific impulse and the corresponding aluminium loading were determined for different values of the binder content.

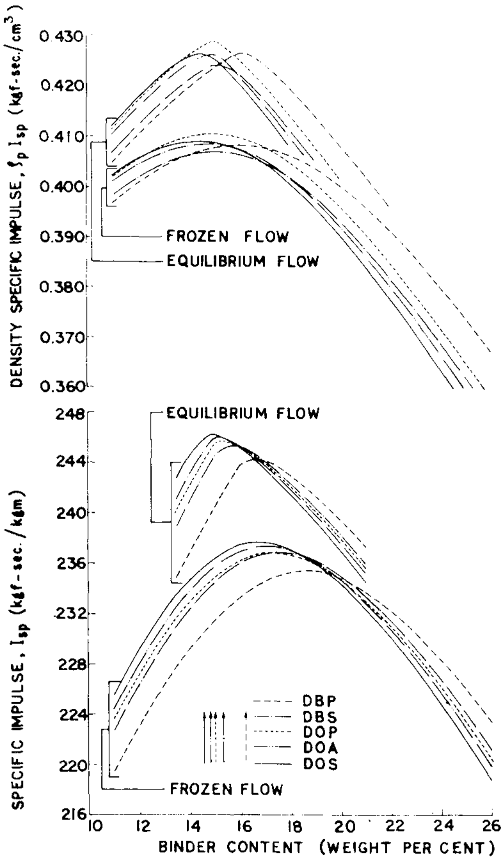

Fig. 1 Specific impulse and density specific impulse for AP-PVC propellants.

Table 1 Properties of plasticizers and their propellant systems

Propellant systems	Plasticizer properties: Formula	Density[a] at 25°C gm/cc	Viscosity[a] centipoise	Heat of formation at 298.16 K kcal/mole	Propellant characteristics[b]: Overall maximum specific impulse kgf sec/kgm	Composition AP: Al: binder
DBP	$C_{16}H_{22}O_4$	1.046	20.50[c]	−211.240	258.7	64.4:22.6:13.0
DOP	$C_{24}H_{38}O_4$	0.982	78.00[c]	−266.514	259.8	65.0:22.5:12.5
DBS	$C_{18}H_{34}O_4$	0.934	9.12	−285.088	260.0	64.5:23.0:12.5
DOS	$C_{26}H_{50}O_4$	0.911	21.40	−344.000	260.6	64.7:22.8:12.5
DOA	$C_{22}H_{42}O_4$	0.927	13.50	−312.860	260.4	64.5:23.0:12.5

[a] Average values taken from the manufacturers' information bulletins.
[b] For equilibrium flow, chamber pressure = 70 atm; optimum expansion to 1 atm.
[c] At 20°C; remaining viscosity values at 25°C.

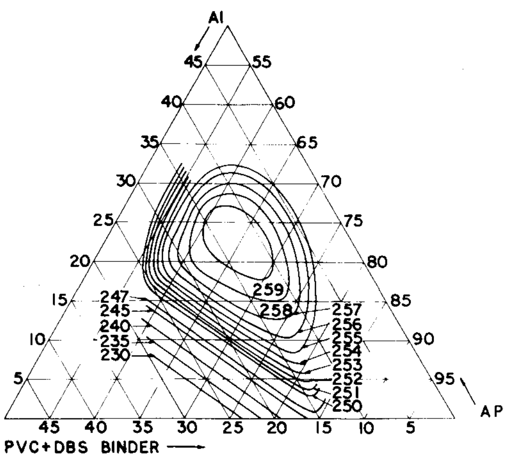

Fig. 2 Theoretical specific impulse for AP + Al + (PVC + DBS) propellants.

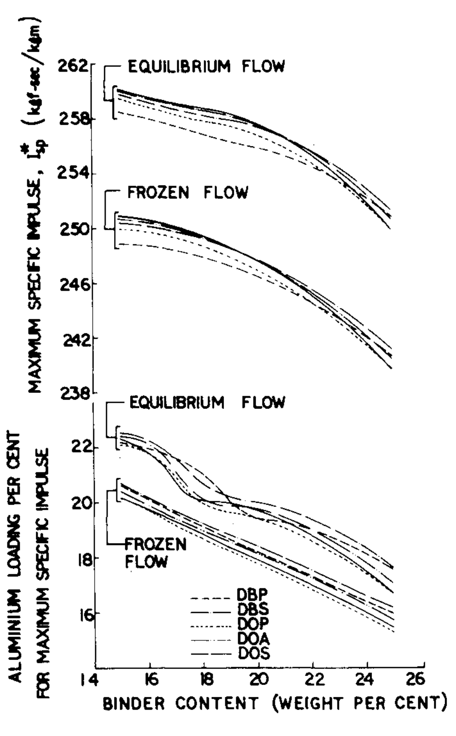

Fig. 3 Maximum specific impulse and the corresponding aluminium loading.

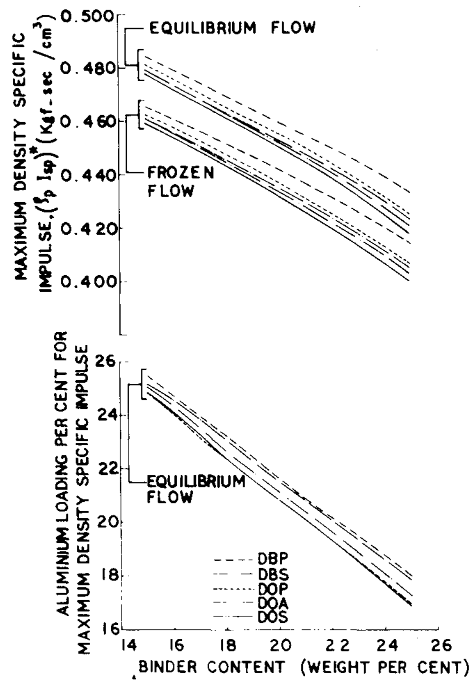

Fig. 4 Maximum density specific impulse and the corresponding aluminium loading.

The results are shown in Fig. 3. Having fixed all the constituents except plasticizer, high specific impulse can be attributed either 1) to the low molecular weight of product gas, which can be obtained by having plasticizers of high hydrogen content, or 2) to the high combustion chamber temperature, achieved by having plasticizers of low negative, if not positive, heats of formation. The maximum temperature is also influenced by the proportion of oxygen in the plasticizer in the case of the metallized propellant, which is oxygen starving. From the maximum specific impulse curves for the normally adopted binder contents (Fig. 3), it is clear that the hydrogen content in the plasticizers has pronounced effect in fixing the maximum specific impulse of the propellants. This is in spite of the fact that the plasticizers of high hydrogen content tend to have more negative heats of formation.

The inflexions in the aluminium loading curves for the maximum specific impulse of equilibrium flow are due to the energy of phase transition that is made available to the nozzle flow above certain binder content. For a fixed binder content, the attainment of maximum specific impulse, at a relatively higher aluminium loading, is a good feature of the plasticizer because this means lower oxidizer loading. The density of aluminium being greater than that of AP, the replacement relatively increases the fluidity of the propellant while processing, and gives better mechanical properties and higher density to the cured propellant. Thus having the binder content fixed,for a propellant system to have its maximum specific impulse at a higher aluminium loading, the plasticizer should not only have higher oxygen content (to have its maximum temperature at a higher aluminium loading) but also relatively higher hydrogen proportion (to have a relatively lower molecular weight product gas such that the aluminium loading value of the maximum specific impulse will be relatively closer to that of the maximum temperature). This is the reason for the DBS system to have its maximum specific impulse at the highest aluminium loading values. In general plasticizers of higher oxygen and relatively higher hydrogen content are of higher densities. Therefore, as mentioned earlier, these plasticizers, in spite of their usually low viscosity values, have a poor solid loading capacity in the two-component systems. However, this difficulty is reduced to a certain extent in the three-component systems because of the high aluminium loadings for the maximum specific impulse.

Figure 4 shows the variation of maximum density specific impulse for equilibrium and frozen flows. Since the aluminium loading values are essentially same for both equilibrium and frozen flows, the variation of aluminium loading for equilibrium flow only is shown. From the plot of maximum density specific impulse, it is clear that density plays a pronounced role in keeping the maximum density specific impulse high.

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Compilation and Correlation of Stagnation Convective Heating Rates on Spherical Bodies

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Nomenclature

C, m = constants in Eq. (1)
P_{T_S} = stagnation-point total pressure, atm
$\dot{q}_w$ = stagnation-point heat flux, Btu/ft^2/sec
R_N = nose radius, ft
U_O = freestream velocity fps
Z = altitude, ft
σ = standard deviation

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Introduction

SAFETY considerations involved with the space application of radioisotope thermoelectric power supplies dictate a requirement to design and evaluate the fuel capsule for a wide range of re-entry conditions that could be encountered during an abortive launch. A fundamental aspect of such re-entry analyses is the evaluation of the stagnation point coldwall convective heating rate over a wide range of velocity ($U_0 \approx 0$ to 44,000 fps). For the suborbital, hypersonic regime ($U_0 = 7000$ to 26,000 fps) the Detra, Kemp and Riddell[1] correlation is available. It is a simple, semi-empirical expression based on experimental shock tube data. No such data correlation has been completed for the superorbital velocity regime although a number of theoretical formulations are available, i.e., Hoshizaki,[2] Fay and Kemp,[3] and Pallone and Von Tassell.[4]

In the present study, published experimental stagnation-heating-rate data have been compiled. The data include both the suborbital and superorbital velocity regimes. A least-squares analysis of the data indicates that the Detra, Kemp and Riddell[1] correlation provides a valid representation of the superorbital data as well as the suborbital velocity data for which it was originally derived. Statistical analyses of the data have been prepared in order to provide estimates of the variability in stagnation point heating rate data.

Results

Convective stagnation-point heating rate measurements have been compiled from ten sources[2,5-13] which cover a simulated freestream velocity (U_0) range of 7600 to 57,900 fps and a simulated altitude, Z, range of 20,000 to 170,000 ft. Approximately 500 data points have been collected for hemispherical nose shapes ranging in nose radius, R_N, from 0.125 in. to 2.50 in. The overwhelming majority of the data (97%) were measured in shock-tube facilities (one test series[9] utilized a ballistic range and provided 15 data points). To accomplish the correlation, the factor $\dot{q}_w (R_N/P_{T_S})^{1/2}$ has been utilized as the heating rate parameter. Since portions of the data was not reported in this form, it was necessary to evaluate this parameter from the published results. Details of the transformation for each of the tests are given in Ref. 14.

The heating rate data were curve-fit by a standard least-squares technique, assuming a functional relationship of the form

$$\dot{q}_w (R_N/P_{T_S})^{1/2} = C(U_0/26{,}000)^m \qquad (1)$$

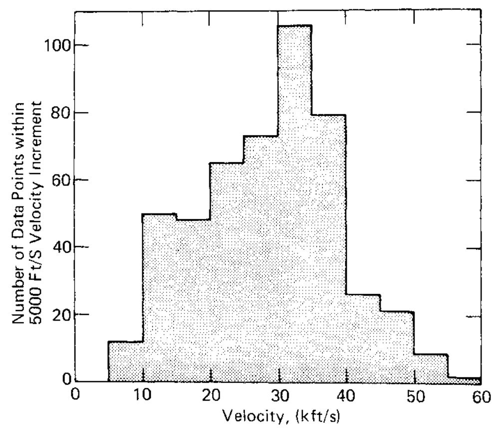

Fig. 1 Distribution of experimental data with velocity.