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### HIGH PERFORMANCE N204/AMINE ELEMENTS

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DATA DUMP COVERING TASK I. LITERATURE REVIEW

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## CONTENTS

Introduction	]
Review of Theoretical Models	2
Steady Reactive Stream Separation (RSS)	2
Popping	9
Impinging Jet Stability	12
Review of Experimental Data	14
Model Rocket Engine Data	14
Chemical Reaction Studies	28
Development of Improved Models	31
Application of Data to Mechanisms That Can Control Popping	31
Application of Data to Mechanisms That Can Control RSS	43
Nomenclature	46
References	48

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-i-

## ILLUSTRATIONS

1.	Schematic of Unlike Impinging Doublet	3
2.	Comparison of Model Predictions of RSS with Experimental Data (Ref. 4)	5
3.	Separation Ranges from $N_2O_4/N_2H_4$ as Determined in Ref. 10	6
4.	Impingement Detonation Correlation (Ref. 11)	11
5.	Several Topologies for the Flow Field of a Pair of Impinging Jets (Fig. 2 of Ref. 14)	12
6 <b>.</b> ,	Correlation for the Incidence of Popping with Stagnation Pressure Ratio in a Liquid Propellant Rocket Engine (Fig. 9 of Ref. 14)	13
7.	Typical Sequence Showing Cyclic Behavior of NTO/50-50 (Class A Blowapart) Reactive Stream Blowapart with 0.173-inch (60-degree Impingement Angle) Diameter Unlike Stream Orifice Pair Element	17
8.	Typical Sequence Showing Cyclic Behavior of NTO/Hydrazine Reactive Stream Blowapart with O.072-Inch-Diameter (60-Degree Impingement Angle) Unlike Impinging Stream Orifice Pair Element, Edge View of Spray Fan from Injector Face to 4 Inches Downstream	18
9.	Effect of Dynamic Pressure Ratio on Separate/Mix for CPF/Hz Propellants Using an 0.026-inch Diameter Unlike Impinging Stream Orifice Pair Element	20
10.	Single-Element, Unlike-Doublet Performance Characteristics Under Blowapart Conditions (Ref. 17)	21
11.	Effect of Mixing Uniformity on Blowapart (Ref. 13)	21
12.	Effect of Contact Time on Pop Rate (Ref. 19)	23
13.	Effect of Chamber Pressure on c* Performance under RSS Conditions (Ref. 17)	24
14.	Effect of Fuel Temperature on c* Performance . for Differing Unlike Impinging Elements (Ref. 21)	27

15.	Effect of Contact Time on Pop Rate for Several Propellant Combinations	32
16.	Determination of the Induction Time for NTO/N <sub>2</sub> H <sub>4</sub> Propellants at 14.2 psia	34
17.	Orientation of Film with Respect to Injector Fan	35
18.	Section of Stream Photograph Showing Disturbances and Description of Events	37
19.	Theoretical Induction Time as a Function of Ambient Pressure for Ignition Explosions	39
20.	Comparison of the Data of Reference 16 with the Theoretical Prediction of Induction Time	39
21.	Schematic of Popping Limits	42
22.	Schematic of Reactive Stream Separation	44

## TABLE

1. Maximum Heat Release Rates for  $\rm HNO_3/Amine$  and  $\rm N_2O_4/Amine$  Liquid Phase Reactions Under Jet Mixing Conditions

28

#### INTRODUCTION

The hypergolic  $N_2O_4$ /Amine earth-storable propellant combinations are the prime candidates for the Space Shuttle orbital maneuvering engine (OME). When these propellants are employed with injectors which utilize unlike jet impingement to mix and atomize the propellants, performance losses are sometimes encountered from a phenomenon called reactive stream separation or "blowapart". This phenomenon can occur either as a steady turning of the incoming liquid jets away from their normal impingement point (a process which will be denoted as RSS) or as a series of small explosions near the impingement point (usually called popping). In addition to reducing combustion efficiency, popping is also considered to be one of the triggering mechanisms for acoustic mode combustion instability. Because of the high performance and reliability required of Space Shuttle engines, it is imperative that blowapart phenomena be understood and their undesirable effects be minimized.

The injector design problems associated with blowapart have been recognized and studjed for over 15 years. In 1959, Elverum and Staudhammer (Ref. 1) showed with photographic studies of single element injector firings that low values of c\* measured with the  $N_2O_4/N_2H_4$  combination resulted from extremely rapid reaction which separated the fuel and oxidizer streams before mixing was complete. In 1960, Somogyi and Feiler attributed limits in measured heat release rates for rapidly contacted  ${\rm HNO}_3/{\rm N_2H_4}$  and HNO<sub>3</sub>/UDMH to gas evolution which prevented complete liquid mixing. Since that time, numerous investigations have been made in order to identify the thrust chamber operating conditions under which RSS and popping occur and to formulate physical models for these phenomena in terms of controllable design parameters. Over this same period, additional studies have been made of the reaction chemistry of the  $N_2O_4$ /Amine and  $HNO_3$ /Amine systems. Although the considerable information which has been accumulated concerning the physical and chemical processes associated with .RSS and popping has so far resulted in models which give satisfactory correlation of only selected sets of the available experimental data, a survey of this information provides

-1-

the background both for further experimental studies and for formulation of more advanced theoretical models of the complicated blowapart mechanisms.

The following sections of this report present a review of (1) theoretical models of RSS and popping, (2) experimental combustion data under simulated rocket conditions, and (3)  $N_2O_4$ /Amine combustion chemistry data, all gathered in a literature survey prior to the start of Rocketdyne's current investigation of fundamental blowapart mechanisms under contract NAS9-14126.

#### REVIEW OF THEORETICAL MODELS

#### STEADY REACTIVE STREAM SEPARATION (RSS)

Perhaps the first theoretical prediction of the conditions under which impinging hypergolic fuel and oxidizer streams might be expected to separate was made by Beltran (Ref. 3). His approach was to compare the pressure force imposed by the transverse momentum of the impinging propellant jets to the pressure of the product vapors generated by chemical reaction at the interface between the respective fuel and oxidizer sheets formed at the jet impingement point. Using the Clapyron Equation to define the product gas pressure, Beltran derived the following criterion for the case of the equal diameter unlike doublet. Separation occurs when

$$\frac{(\Delta H_{R} - \Delta H_{L}) - \Delta H_{v}}{C_{p}} > \frac{nRT^{2}}{\Delta H_{v}p} \left[ \frac{4wV_{g} (sinr)^{2}}{\pi d_{j}^{2}g_{c}} \right]$$
(1)

However, it appears from the discussion in Ref. 3 that Eq. (1) can only be used when the effective heat of reaction  $(\Delta H_R - \Delta H_L)$ , equal to the difference between the thermodynamic heat of reaction and the heat lost to the unreacted liquid propellants, can be estimated reasonably accurately. Otherwise, Eq. (1) can be used only as a scaling factor to determine the effects of propellant combination, chamber pressure, orifice diameter, injection velocity, impingement angle, and (possibly) injection temperature. However, because ( $\Delta H_R - \Delta H_I$ )

\*All symbols are defined in the nomenclature section.

is a function of the impingement point mixing process, and therefore of orifice diameter, injection velocity, and mixture ratio, the use of Eq. (1) as even a scaling parameter is limited.

Kushida and Houseman (Ref. 4) developed an analytical model for RSS which treats the steady process as occurring by either of two mechanisms, distinguished by whether the chemical reaction(s) responsible for separation occurs primarily at a liquid/liquid interface or in a thin stable interface gas film of thickness  $\delta$ . Mean pressure and temperatures are defined by heat and mass transfer together with the  $\Delta p$  between film and chamber pressures required to expel the gaseous reaction products from the interface film. Consider the unlike doublet geometry shown in Fig. 1. Kushida contends that there is a control volume of mixed propellants which starts at the impingement point and extends downstream for a distance that depends on element geometric and hydraulic factors. This volume is considered to be the "reactor" volume of propellants. If the average residence time of the propellants in the reactor volume is sufficient that the temperature of the propellants is raised to the bubble point due to heat transfer, then separation will result. This is characterized by equating the average fluid particle residence time to a bubble point heat transfer control time

$$\frac{d_j}{v_j} = t_r = t_b = \frac{\sum_{f,ox} c_p (T_b - T_{inj})}{\dot{q}}$$



#### Figure 1. Schematic of Unlike Impinging Doublet

-3-

(2)

where

 $t_{r} = residence time$   $d_{j} = jet diameter$   $V_{j} = injection velocity$   $t_{b} = time to reach the bubble point temperature$   $T_{b} = bubble point temperature$   $T_{inj} = injection temperature$   $C_{p} = liquid specific heat, Btu/mole<sup>0</sup>$  $\dot{q} = liquid phase heat generation rate (Btu/mole sec)$ 

The principal difficulty encountered in the use of Eq. (2) is the definition of  $\dot{Q}$ , the liquid phase reactive heating rate. Kushida used the experimental data of Somogyi and Feiler (Ref. 2) for "fully mixed" HNO<sub>3</sub>/N<sub>2</sub>H<sub>4</sub> in his calculations as an estimate of the rate for the N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>H<sub>4</sub> combination. Although Lawver and Tkachenko (Ref. 5) later measured equivalent heat generation rates for the N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>H<sub>4</sub> using a contained flow cup mixing apparatus similar to that used in Ref. 2, Rodriguez (Ref. 6) measured significantly lower values of  $\dot{Q}$ in a free jet mixing apparatus which more closely simulated real rocket engine injector elements. From these data, it appears that the liquid reaction rate is very sensitive to the impingement point mixing; therefore this mixing must be incorporated into the model as a function of injector element configuration and operating conditions. Both the Beltran and Kushida-Houseman models, as represented in Eqs. (1) and (2) consequently suffer from the lack of a systematic method of defining the heat release rate at the impingement point for useful element configurations.

It should also be noted that the liquid separation criteria of Eq. (2) has never been experimentally observed, and in private communications with Dr. Kushida he has suggested that this portion of the model may be unreal. Quite possibly, if sufficient time is available for liquid-phase separation, then cyclic blowapart might occur.

\*The apparatus of Refs. 5 and 2 used normally-impinging fuel and oxidizer jets discharging into a cylindrical cup with a diameter of only .313 inch.

For the gas-phase separation, the Kushida and Houseman model assumes that if sufficient heat is transferred to the approaching jets to generate oxidizer and fuel vapors, then the vapors will react and form a gas barrier between the jets. This gas pocket can, under some conditions, substantially dissipate the momentum of the approaching jets, thereby preventing their mixing. The gas-phase separation criterion for  $NTO/N_2H_4$ , as derived in Ref. 4 is:

Separation occurs when: 
$$\frac{d_j}{V_j} > 35 \left(\frac{100}{P}\right)^{-1.5}$$
, in µsec (3)

Prediction of RSS (gas phase) using the above criterion is shown in Fig. 2.





Experimental data from several sources are included on the figure. These data suggest that the model formulation is too simplified to adequately account for RSS. This contention is suggested first from consideration of the results from Ref. 7 which show that the model would predict that liquid

-5-

phase separation should occur at atmospheric pressure while experimental data reveals that mixing of the propellant streams was accomplished. In addition, data from Ref. 8 reveals that mixing actually occurs in both the liquid- and gas-phase separation zone.

In addition to the above study, Houseman at JPL has studied the RSS phenomena in a combusting rocket engine using a water-cooled probe attached to an online mass spectrometer. His rather perplexing results are shown in Fig. 3. His data show that the jets become mixed as the contact time is increased, which is completely contrary to the above model, or for that matter, other models. At this time there appears to be no rational explanation for these results; however, there is sufficient belief in the validity of the experimental approach used by Houseman that these results should be considered in any eventual model formulation. (As a minimum, the experimental conditions should be duplicated in verification tests using photographic techniques instead of the probe.)



Figure 3. Separation Ranges from  $N_2O_4/N_2H_4$  as Determined in Ref. 10

-6-

Lawver (Ref. 11) developed a model for steady RSS by defining an ignition delay time,  $\tau_{ign}$ , as the time required for the reaction between mixed liquid propellants downstream of an element impingement point to proceed to a stage where the resultant gas evolution is sufficient to separate the liquid phases. Similarly, a mixing delay time,  $\tau_{mix}$ , is defined as the average time required for the liquid propellants to pass from their point of initial jet impingement to the downstream plane at which a satisfactory liquid phase mixing has been accomplished. The criterion for steady RSS then becomes:

Separation occurs when:

$$\tau_{ign} \leq \tau_{mix}$$
 (4)

If Eq. (4) is to be used for injector design, both  $\tau_{ign}$  and  $\tau_{mix}$  must be defined in terms of such controllable parameters as orifice diameter, injection velocity, chamber pressure, propellant temperature, etc., which have been experimentally shown to influence separation. To define  $\tau_{ign}$ , Lawver assumes that a first order reaction rate formulation can be applied to the liquid phase reaction

$$\dot{r} = \frac{dC}{dt} = ACe^{-E/RT}$$
(5)

Then the ignition delay can be defined as

$$\tau_{\text{ign}} = \frac{\ln (C_{\text{ign}}/C_{\text{o}})}{Ae^{-E/RT}}$$
(6)

Since  $C_{ign}$ , A and E are all unknown, the first order reaction model serves only to define

$$\tau_{ign} = Y e^{B/T}$$
(7)

The mixing time delay of the propellants is defined by Lawver as

$$\tau_{\rm mix} = L_{\rm mix}/V_{\rm j}$$
(8)

-7-

where the mixing length is equal to

$$L_{mix} = X(d_j)$$
(9)

and X is a constant depending only on the impingement angle. (This type of assumption seems questionable because it requires the mixing length to be dependent only on jet size and be insensitive to the relative momenta of the jets or to their overall momentum level. Unpublished Rocketdyne cold flow studies made in conjunction with the program reported in Ref. 12 indicate that the total sheet length-- and therefore most probably the mixing length-- for small like-doublets is inversely related to the jet velocity.)

Combining Eqs. (4) and (7) and then substituting for  $L_{mix}$  from Eq. (9) gives Lawver's criterion for the transition between jet mixing and separation.

$$\frac{Y}{X} e^{E/RT} = \frac{Y}{X} e^{B/T} = \frac{d_j}{V_j}$$
(10)

Taking logarithms of both sides of Eq. (1) gives

$$\ln \left(\frac{Y}{X}\right) + \frac{E}{R} \left(\frac{1}{T}\right) = \ln \left(\frac{d_j}{V_j}\right)$$
(11)

By plotting  $\ln(d_j/V_j)$  versus  $\frac{1}{\text{Tinj}}$  for a series of single unlike doublet tests at one atmosphere and a single nominal mixture ratio of 1.2 and drawing the boundary between the mixing and separated regions, Lawver determined values of kinetic rate constants E and K for the  $N_2O_4/N_2H_4$  propellant combination. With these constants defined, Lawver's model provides a method of estimating the effects of propellant injection temperature and of residence time  $(d_j/V_j)$  on steady RSS phenomena for otherwise-fixed operating conditions. However, the apparent generality of the model may be deceiving. For example, inspection of the above expression seems to suggest that separation should be insensitive to pressure since E is a weak function of pressure. This of course is inconsistent with the model of Kushida and Houseman and the results of Ref. 8 and 10. Similarly, the model gives no clue as to the effects of mixture ratio or orifice diameter ratio. From these considerations, it would

-8-

appear that the RSS model proposed by Lawver is inadequate as a general index for reactive stream impingement. However, with a single change in the starting assumptions, it may be possible to develop a similar ignition delay model which is anticipated to provide a more general description of the steady RSS regime. Such a model will be proposed in a later report.

#### POPPING

Lawver (Ref. 11) extended his ignition delay model for steady RSS to a description of popping by noting (from high speed motion pictures) that pops seemed to originate as random explosions of mixed incompletelyatomized propellants downstream of the impingement point. The main feature of this model is that popping will be initiated if the ignition time is greater than the mixing time but less than the ligament zone residence time. The ligament zone residence time, determined experimentally from water/freon cold flows with jets of equivalent diameter, is (Ref. 7)

$$\tau_{lig} = 200 d_j / V_j^2$$
 (12)

This equation and Eq. (7) and (8) form the basis for limits on popping. Just considering the popping of a single element, the above expression introduces no new aspect of combustion or a mechanism that would trigger a detonation. This criteria simply states that an explosion will be initiated when:

$$\tau_{\rm mix} < \tau_{\rm ign} \leq \tau_{\rm lig} \tag{13}$$

or

$$\frac{Xd_{j}}{V_{j}} < Ye^{E/RT} \leq 200 \frac{d_{j}}{V_{j}^{2}}$$
(14)

Here again, this equation does not include the effect of pressure on the explosion limits for a single element. Therefore, this limit contradicts all known popping data where pressure was extensively varied (Ref. 8 and 10). In addition, the relationship suggests that the critical popping contact time

$$d_j / V_j = \frac{\gamma}{200} e^{E/RT} V_j$$

is constant (for a fixed temperature) multiplied by the velocity and is, therefore, directly dependent on velocity. This result is also not in agreement with that of Ref. 10.

To complement the popping initiation model defined by Eq. (14), Lawver also introduced a trigger coupling model (Ref. 11) to characterize the strength of a popping disturbance and therefore of the tendency of the initial disturbance to grow into a detonation which can propagate to adjacent elemental spray fans. The trigger coupling model is based on the initial disturbance generating a shock wave which grows into a detonation as it passes through a burning spray. The tendency to detonation is characterized by a detonation parameter  $\mathcal{D}$  defined as

$$\mathscr{D} = \frac{(.4a)^{2/3}}{S} \left(\frac{\varepsilon}{\rho}\right)^{1/3}$$
(16)

with

$$\varepsilon = \frac{4}{3} \pi \Delta H_R J_{\rho_p} r_f^3$$
(17)

and by an impingement parameter I defined as

$$I = \frac{\binom{\tau_{ign}}{separate}}{\binom{\tau_{ign}}{operate}}$$

I = expf 
$$\left[ \ln \left( \frac{d_j}{V_j} \sin \gamma \right) + 46.8 - \frac{21,800}{T} \right]$$
 (18)

While the trigger coupling model has certain attractive features, it is nevertheless suspect. This is due to the experimental results presented in Ref. 13, which have clearly demonstrated that the initiation of the disturbance is just slightly downstream of the impingement point and is itself an explosion (determined from measurement of pressure and velocity) which completely consumes the spray that emanated from that element. This would suggest that for practical injector designs, the "disturbance" will

-10-

(15)

always be of high enough amplitude to couple with adjacent elements regardless of spacing. That is, once the detonation wave consumes the spray of its parent element, it will spread to the adjoining elements simply because the sprays are sufficiently distributed across the combustion chamber some distance downstream of the injector and the sprays contain unreacted mass. The popping coupling model as "verified" by Lawver is presented in Fig. 4.

Note that these data were obtained at essentially constant chamber pressure. In addition, inspection of the data reveal that about an equal number of data points fall within the shaded area as are outside. This would appear to be an inadequate proof of the model.

In summary, although there are features contained in all of the above models that are valid, it is obvious that they all lack essential features which are necessary for an adequate description of reactive stream separation and cyclic blowapart. The essential feature would appear to be the description of the mechanisms controlling these phenomena. Once they are defined, then it would be a rather straightforward process to develop models that can be used to describe and predict blowapart characteristics.



Figure 4. Impingement Detonation Correlation (Ref. 11)

#### IMPINGING JET STABILITY

Whereas the theoretical models of Beltran, Kushida-Houseman and Lawver discussed above were primarily concerned with describing the effects of injection temperature, chamber pressure, and of combinations of orifice diameter and injection velocity, a theory of impingement dynamics proposed by Rupe, Dipprey, et al (Ref. 14), provides at least a partial explanation for the experimentally-observed sensitivity of blowapart to cold flow mixing efficiency. Cold flow mixing efficiency (defined either as  $E_M$  or  $n_{mix}$ ) maximizes when the centerline momentum ratio defined as

$$\frac{\text{Momentum}_{F}}{\text{Momentum}_{ox}} = \frac{\rho_{F} V_{F}^{2} d_{F}}{\rho_{ox} V_{ox}^{2} d_{ox}}$$

is equal to unity. Rupe and Dipprey show this condition is also intrinsically unstable for equal jet diameters in which case the stagnation pressures of the jets are equal. At this condition, substantial changes in effluent mixture ratio and jet direction downstream of the impingement point for infinitesimal changes in stagnation pressure ratio can occur.

Fig. 5, taken from Ref. 14, is a schematic representation of three possible cases for the impingement of two jets. At equal stagnation pressures (the middle case), there is a common stagnation point for both streams together with a back flow which contains fluid from each incoming stream. When (as shown in the two outer cases) the stagnation pressures of the stream are not equal, only the lower pressure stream is stagnated, and only fluid from this stream appears in the back flow which is directed toward the high pressure stream. Because the change in stagnation and back flow with pressure ratio is very abrupt, the



Figure 5. Several Topologies for the Flow Field of a Pair of Impinging Jets (Fig. 2 of Ref. 14) impingement zone and spray fan mixture ratio is correspondingly sensitive to small changes in the incoming streams. Although the physical arguments of Ref. 14 are documented with simplified theoretical calculations, the accompanying experimental evidence is inconclusive because it was obtained with equal jet diameters such that an equal dynamic pressure condition corresponded to equal jet momenta. The latter condition was shown to represent optimized mixing in the study of Ref. 17. The importance of the physical processes at this common (for equal diameter jets) equilibrium point are shown in Fig. 6 which was also taken from Ref. 14. Popping is seen to maximize at equilibrium. No mechanism is proposed by Rupe and Dipping. If dynamic pressure ratio governs, it is possible that the presence of small amounts of both hypergolic propellants in a stagnation condition, i.e., for residence times much longer than the average time defined by  $d_i/V_i$ , could lead to a heating of these propellants to the point where an Arrhenius type of temperature effect would produce either separation or detonation. If centerline jet momenta (i.e., mixing) governs, then popping intensity is simply related to mixing intensity.



Figure 6. Correlation for the Incidence of Popping with Stagnation Pressure Ratio in a Liquid Propellant Rocket Engine (Fig. 9 of Ref. 14)

-13-

#### REVIEW OF EXPERIMENTAL DATA

A variety of experimental techniques have been employed to investigate reactive stream separation under rocket engine conditions. These methods include:

- Photography of the spray field for single element injectors either under open air combustion conditions or in small transparent combustors at elevated pressures.
- Performance evaluation of both single- and multi-element injectors under hot fire conditions and comparison to the results of equivalent cold flow mixing and atomization experiments.
- Localized gas sampling across the combustion gas flow field downstream of single element injectors.
- Measurement of pressure oscillations near subscale (particularly single element) injectors.

In addition, other investigations have been made of the liquid phase (or liquid interface) chemical reactions which occur when two hypergolic propellants are brought together. The purpose of these latter experiments has been to establish the heat generation rates, initial reaction products, and other fundamental kinetic data which, together with fundamental fluid dynamic data, are necessary to formulate reasonable theoretical models.

#### MODEL ROCKET ENGINE DATA

The results of experiments under simulated rocket engine conditions have demonstrated that the following parameters can influence blowapart for injectors using unlike-impinging elements:

- 1) Propellant combination
- 2) Relative jet momenta
- 3) Contact time
- 4) Pressure
- 5) Orifice size
- 6) Propellant temperature

-14-

While a considerable amount of data exists, only selected representative studies are discussed.

#### Propellant Combination

To assess the potential effect of propellant combinations of  $N_2O_4$  with amine fuels, the reactivity of  $N_2 \rho_4 / N_2 H_4$ ,  $N_2 \rho_4 / MMH$  and  $N_2 \rho_4 / UDMH$  were studied by Rodriguez and Axworthy (Ref. 6). In these experiments, the heat release rates were measured using impinging unlike-doublet jets where the reaction was quenched immediately downstream of impingement. The results were somewhat surprising in that they suggested that the propellant combinations, in order of decreasing chemical reactivity, were (1)  $N_2O_4/UDMH$ , (2)  $N_2O_4/MMH$ , and (3)  $N_2O_4/N_2H_4$ . The authors state that machine-gun-like sounds were heard emanating from the impingement region of the  $N_2O_4/N_2H_4$  propellants and visible light was observed near the reaction zone for the  $N_2O_4/MMH$  propellants. Neither sound nor light were observed for the  $N_2O_4/UDMH$  propellants. This suggested that the order of the actual propellant reaction rates could have been altered due to popping (which has been related to sound and light emanating from the region of jet impingement in other, more definitive tests, Ref. 13). If this were the case, then the order of reactivity would be (1)  $N_2O_4/N_2H_4$ , (2)  $N_2O_4$ /MMH, and (3)  $N_2O_4$ /UDMH. To illustrate the difficulty of designing definitive experiments, this possible interpretation can be carried one step further. If all three propellants produce reactive nitrate intermediates, then the measurements could be interpreted as: the lower the reactivity, the greater the amount of propellant that will be mixed before ignition is initiated and the greater will be the heat released to a quenching fluid. Consequently,  $N_2O_4/N_2H_4$  would result in the smallest quantity of mixed propellants while  $N_20_4/UDMH$  would have the largest quantity. Tests conducted at the Bureau of Mines (Ref. 15) have shown that the order of explosion sensitivity for these propellants are (1)  $N_2O_4/N_2H_4$ , (2)  $N_2O_4/MMH$ , and (3)  $N_2O_4/UDMH$ . This order is consistent with the audible sound and visible light observations discussed above.

Nurick and Cordill (Ref. 13) have studied the popping and RSS characteristics of  $N_2O_4/N_2H_4$ ,  $N_2O_4/A-50$ , RFNA/UDMH and  $ClF_5/N_2H_4$  at equivalent flow conditions. The results showed that cyclic blowapart occurred for  $N_2O_4/N_2H_4$ ,  $N_2O_4/A-50$  and RFNA/UDMH while RSS occurred with  $ClF_5/N_2H_4$ . Typical photographic sequences depicting the flow characteristics for several of the propellant combinations

studied are presented in Fig. 7, 8, and 9. For the propellants that experienced popping, the magnitude of the disturbances differed considerably and were ranked in descending order of detonation level as class A, B, and C, where:

Class A (strong blowapart) results in complete destruction of the spray fan and the impinging jets.

Class B (weak blowapart) results in only a partial destruction of the spray fan.

Class C (puffs) are small local explosions with little fan disturbance.

Based on this somewhat arbitrary definition, the various propellant combinations were ranked as (1)  $N_2O_4/N_2H_4$  (only class A detonations),  $N_2O_4/A-50$ mostly B and C), and (3) RFNA/UDMH (primarily class C disturbances). Lastly, Houseman (Ref. 16) conducted some popping experiments with  $N_2O_4/MMH$  as well as with  $N_2O_4/N_2H_4$ . He found that the popping characteristics of  $N_2O_4/MMH$  are very similar to  $N_2O_4/N_2H_4$ , suggesting that the final order would be (1)  $N_2O_4/N_2H_4$ , (2)  $N_2O_4/MMH$ , (3)  $N_2O_4/A-50$ , and (4) RFNA/UDMH.

#### Relative Jet Momenta

Experimental cold-flow and hot-fire studies (Ref. 17) have shown that as the relative jet momenta (and consequently their dynamic pressure ratio) are varied, c\* performance changes in the manner shown in Fig. 10.

The data in Fig. 10 indicate that an improvement in cold flow mixing uniformity increases the tendency for blowapart as evidenced by lowered c\* performance. In fact, the minimum performance occurs where the non-reactive mixing efficiency maximizes. These results suggest that the degree of blowapart is dependent on the quality of mixing. Similar results are shown for a multi-element, unlike-doublet injector (Ref. 13) in Fig. 11.



Figure 7. Typical Sequence Showing Cyclic Behavior of NTO/50-50 (Class A Blowapart) Reactive Stream Blowapart with 0.173-inch (60-degree Impingement Angle) Diameter Unlike Stream Orifice Pair Element



Figure 8. Typical Sequence Showing Cyclic Behavior of NTO/Hydrazine Reactive Stream Blowapart with 0.072-Inch-Diameter (60-Degree Impingement Angle) Unlike Impinging Stream Orifice Pair Element, Edge View of Spray Fan from Injector Face to 4 Inches Downstream



(d) TIME = 0.73 MILLISECOND (SPRAY IS CONSUMED)

(e) TIME = 2.0 MILLISECONDS (RE-FORMATION OF SPRAY FAN)

(f) TIME = 3.4 MILLISECONDS

Figure 8. (Concluded)



Figure 9. Effect of Dynamic Pressure Ratio on Separate/Mix for CPF/Hz Propellants Using an 0.026-inch Diameter Unlike Impinging Stream Orifice Pair Element

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Figure 10. Single-Element, Unlike-Doublet Performance Characteristics Under Blowapart Conditions (Ref. 17)



Figure 11. Effect of Mixing Uniformity on Blowapart (Ref. 13)

-21-

Note that similar results were observed for the full-scale injector as were observed with the single element. However, due to a lack of adjacent elements in the single-element configuration, inter-element mixing is minimized and, consequently, the loss in c\* performance is considerably greater. It should be pointed out that the propellant combination for both of these studies was  $N_2O_4/A-50$ . The interpretations of these results are supported by the results obtained using  $ClF_5/N_2H_4$  (see Fig. 9) wherein steady-state separation occurred until the mixing uniformity index ( $E_M$ ) was changed from 0.5 ( $E_M = 1/1+\phi$ ) to 0.38.

Clayton (Ref. 18) studied the effects of jet momenta on popping for  $N_2O_4/A-50$  propellants and found that the maximum pop rate occurred at equal oxidizer-to-fuel stagnation pressure which for equal jet sizes also corresponds to the Rupe optimum mixing criteria condition. These results would tend to support the findings of Nurick and Cordill (Fig. 11) where hot-fire test data suggest that maximum disturbances occur when the mixing is optimum.

#### <u>Contact Time</u>

Contact time is defined as the time required for a "packet" of mixed propellants to travel from the point of initial contact between the oxidizer and fuel jets (i.e., the impingement point) to a position one orifice diameter downstream (Eq. 2). The appropriateness of this definition relies on geometric similarity of the mixing distance as defined by the orifice diameter as well as a physical relationship to blowapart. Kushida's definition (Ref. 4) suggests that the transverse mixing is linearly dependent on jet diameter resulting in equal reactor volumes when the contact times defined by  $d_j/V_j$  are equal. Several experimental studies have been conducted over limited ranges in contact time (Ref. 7, 19, 16, 10, and 11) and have clearly illustrated that  $d_j/V_j$  has a strong influence on RSS. Cyclic blowapart has also been shown to be affected by contact time. One of the more detailed studies on popping illustrating the influence of  $d_j/V_j$  on pop rate is that conducted by Houseman (Ref. 19) using  $N_2O_4/N_2H_4$  propellants. A summary of his results is provided in Fig. 12. Note that for these results the pop rate increases with increasing contact time.





-23-

#### Pressure

The results of Houseman (Ref. 10) discussed above (see Fig. 3) illustrate that the chamber pressure, independent of any-other parameter, also has a strong effect on RSS. His results show that for a fixed value of contact time of 100 µsec  $(d_j/V_j)$ , chamber pressures above approximately 60 psia will tend to produce reactive stream separation. These results are indirectly supported by hot fire data obtained in Ref. 17 using N<sub>2</sub>O<sub>4</sub>/A-50 propellants as well as the current Rocketdyne OME study (Ref. 20) using N<sub>2</sub>O<sub>4</sub>/MMH propellants. Using a single-element unlike-doublet and throttling up in chamber pressure produced the c\* performance characteristics shown as the solid curve in Fig. 13.

The dashed line in the figure represents the results obtained with a selfatomizing fan injector element (this element is not ordinarily subject to blowapart) during the same program. Note that for the unlike doublet, c\* performance initially increased, reached a maximum, then decreased rapidly to a minimum. The self-atomizing fan performance characteristics, however, continually increased (as would be predicted) as the chamber pressure was increased. These results indirectly support the contention that increasing chamber pressure above about 60 psia increases the tendency for blowapart; however, in that study it was not clear whether popping and/or RSS are occurring. The full-scale injector results obtained on the OME study with  $N_20_4$ /MMH propellants show the same tendency; however, because inter-element mixing occurs with this multi-element injector the overall loss in c\* performance is not as great (~3 percent).

In a separate study by Houseman (Ref. 19), it has been demonstrated that in some cases increasing chamber pressure tends to result in a decrease in the pop rate. Clayton (Ref. 18) conducted most of his tests at 100-psia chamber pressure although he did conduct one test at 300 psia. Clayton contends that for this specific case the higher chamber pressure decreased popping. The effect of chamber pressure on popping is discussed in more detail in a later section.

-24 -



Figure 13. Effect of Chamber Pressure on c\* Performance Under RSS Conditions (Ref. 17)

#### Orifice Size

Zung (Ref. 8) contends that the orifice size affects cyclic blowapart, independently of contact time. Data published in Ref. 8 shows that for a given chamber pressure a minimum orifice size exists below which no popping will occur. Increasing orifice size beyond this value will result in operating in the popping regime. (His data are presented for constant contact times.) Lee and Houseman (Ref. 16) have shown that the value of contact time producing zero pop rate is dependent on the orifice size, decreasing with decreasing orifice size.

#### Propellant Temperature

Photographic studies by Zung (Ref. 8) and Nurick (Ref. 13) have conclusively demonstrated that if the injected propellants are at or near their boiling temperature, then RSS will occur. The liquid jets in fact will not even contact each other but will veer away from each other before the impingement point is reached (in a manner similar to that shown in Fig. 9). Also, Clayton (Ref. 18) has shown experimentally, that for  $N_2O_4/A$ -50 operating at a chamber pressure of 100 psia, popping is sensitive to propellant inlet temperature. Interestingly, he found that for fixed injection conditions, raising the temperature should first increase the popping rate until a maximum is reached and then further increases in temperature will result in a decrease in pop rate.

A propellant temperature effect on c\* performance has also been observed. The most recent example is the Rocketdyne OME study (Ref. 21) where the fuel temperature was increased from 70 to 200 F and c\* performance decreased slightly. This loss is thought to be related to increased reaction rates as well as the fact that there is less sensible heat rise required to achieve propellant boiling (pressure was constant). In other investigations, fuel temperature has also been shown to result in a decrease in c\* efficiency. During the Rocketdyne research and development program (Ref. 20) subscale OME unlike-doublet and triplet elements were evaluated over a wide range in MMH fuel temperature, 55 to 220 F. The injectors incorporated from three to five elements. A summary of the results is presented in Fig. 14. Note that over the range in fuel temperature from 50 to 220 F a decrease of about 10 percent in c\* efficiency occurred. High-speed instrumentation also showed that the combustion was very rough, suggesting that popping was occurring. In all probability at the higher propellant temperatures RSS was also occurring.









#### CHEMICAL REACTION STUDIES

#### Heat Release Rate

The relative importance of liquid phase reactions to blowapart mechanisms can be related to the extent and rate of the accompanying heat release. The maximum rates for this release was determined under forced-mixing conditions for the  ${\rm HNO}_3/{\rm N_2H_4}$  and  ${\rm HNO}_3/{\rm UDMH}$  combinations by Somogyi and Feiler (Ref. 2) and for the  $N_2O_4/N_2H_4$  combination by Lawver and Tkachenko (Ref. 5) in similar constant volume calorimeters. Mixing was accomplished by the impingement of two directly opposed jets at the top of a small mixing cup. The reacting liquids are in turn forced into a water quench pool at the bottom of the cup. Heat release and gaseous product evolution (assumed limited to the cup) was determined by measurement of quench pool temperature and pressure rise. An alternate approach was used by Breen and  $\cdot$  co-workers at Dynamic Science (Ref. 22) to determine the rate of N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>H<sub>4</sub> liquid phase reaction. They diluted the hypergolic reactants in the inert solvents, chloroform and benzene, and measured the reduced reactive rates in a tangential mixing device. The maximum heating rates measured in these experiments are compared in Table 1 to the previously-mentioned measurements

Table	1.	Maximum Heat Release Rates for HNO <sub>2</sub> /Amine
		and N <sub>2</sub> O <sub>4</sub> /Amine Liquid Phase Reactions Under
		Jet Mfxing Conditions

Reference	Reactant Combination	Mixing	Heat Release (kcal/mol oxidizer/sec)
2	HNO3/N2H4	А	$8.3 \times 10^4$
2		А	4.8 x $10^4$
5	N <sub>2</sub> O <sub>4</sub> /N <sub>2</sub> H <sub>4</sub>	Α	$6.5 \times 10^4$
22	N <sub>2</sub> 0 <sub>4</sub> /N <sub>2</sub> H <sub>4</sub>	В	$4 \times 10^{4}$
6	N204/N2H4	C	$4 \times 10^4$

A - Mixed jet stream confined by cup

B - Diluted tangentially mixed streams

C - Mixed jet stream unconfined

-28-

with  $N_2O_4/N_2H_4$  by Rodriguez and Axworthy (see p 15) in which the mixing was accomplished by impingement of unconfined jets at an angle of  $60^{\circ}$ . In general, all the data represent approximately the same order of chemical reaction rate. Of interest is the fact that Somogyi and Feiler (Ref. 2) concluded that the reaction was mixing limited and that the heating rate should be expressed in the form

$$\dot{Q} = k F(M)e^{-E/RT}$$
(19)

where F(M) is the fraction of the propellants that is mixed. They also hypothesize that the reaction and mixing occur at the interfacial surfaces between fuel and oxidizer and are related to the interfacial area. Under these circumstances, it may be more reasonable to assume a zero order reaction rather than the first order reaction assumed by Lawver in the development of his ignition delay model (see p 8).

By use of jet mixing devices similar to those described above and noting the delay between initial liquid contact and initial pressure rise, Kilpatrick and Baker (Ref. 23) and Bernard and Dufour (Ref. 24) measured ignition delay times of 3.1 and 7-12 milliseconds for the  $HNO_3/N_2H_4$  combination. The difference in results maybe due to differences in impingement techniques. The short time was measured with directly opposed jets while the longer delay time was measured with a triplet injector element.

#### Gas and Condensed Phase Reaction Products

Sawyer (Ref. 25, 26) and Lawver (Ref. 27, 28) have investigated the reactions of  $N_2O_4/N_2H_4$  in either the gas phase or as the combustion of liquid hydrazine in  $N_2O_4$  vapor. Their data generally agree with a two-flame front combustion model in which hydrazine decomposition is the primary reaction in a fuel-rich zone and oxidation of hydrazine decomposition products by  $NO_2$  is the principal reaction in the second zone. The products of these reactions are also gases,  $H_2O$  and  $N_2$  together with either  $H_2$  or  $O_2$  in the oxidation zone (depending on mixture ratio), and  $NH_3$  and  $H_2$  in the hydrazine decomposition zone. The products of condensed phase

reactions are more complex and, because of their low stability, are also difficult to isolate at ambient temperatures. Researchers at the U.S. Bureau of Mines (Ref. 15, 29) mixed frozen  $N_2O_4$  granules with frozen  $N_2H_4$ , MMH, UDMH and Aerozine-50 at  $LN_2$  temperatures. When these mixtures were allowed to warm up to -130°C, the various amine nitrates could be detected by IR spectroscopy. When the solid mixtures were further warmed to approximately  $-55^{\circ}$  to  $-60^{\circ}$ C, they underwent violent exothermic reactions including detonations. TNT equivalents of approximately 160% were determined for mixtures of  $N_2O_4$  with the various amine fuels. Saad, et al, (Ref. 30) reacted  $N_2O_4$  with  $N_2H_4$ , MMH and UDMH in a chilled (-20<sup>O</sup>C) inert diluent, carbon tetrachloride. Infrared spectrographic analysis indicated a complex product mixture including hydrazinium nitrate and the substituted amine analogs RN-NH2 HNO3, together with the various nitrosamines, RNHNO. Formation of a cloudy precipitate (probably hydrazinium nitrate) in liquid hydrazine drops burning in gaseous  $N_2O_4$  was also observed by Lawver (Ref. 27). Hydrazinium nitrate salts were also identified in the residue of a dilute vapor phase reaction of  $\mathrm{N_2O_4/HNO_3}$  (Ref. 31) and have been prepared in models of rocket thrust chambers under near vacuum ignition conditions (Ref. 15). Seamans, et al, (Ref. 32) have also shown that  $N_2O_4$  and MMH can react in the vapor phase to give MMH nitrate in good yields if the pressure is sufficiently low to prevent ignition.

In summary, the formation of condensed phase products (principally the  $RN-NH_2$   $HNO_3$  salts) has been established in a sufficient variety of condensed and gas phase reactions to justify inclusion in a model of impingement point chemistry. Because of the unstable nature and high energy of these compounds (Ref. 15), formation and subsequent detonation of nitrate intermediates becomes a plausible popping mechanism.

# DEVELOPMENT OF IMPROVED MODELS

The foregoing discussion indicates that the existing experimental data are at best limited and in some cases appear to be inconsistent. The apparent inconsistencies are probably the result of a lack of understanding of the governing mechanisms so that seemingly minor differences in operating conditions or geometry are not minor in terms of their effect on blowapart. It is also apparent from the data that clear limits have not been established defining mixing, RSS and/or popping regimes. Lastly, not been a clear establishment of cause and effect (i.e., lowered there has not been a clear establishment of cause and effect (i.e., lowered formance being the result of RSS or cyclic blowapart) between the performance studies and the photographic studies so that rational limits can be defined. Review of the above described models and experimental data suggest the more comprehensive models discussed below.

APPLICATION OF DATA TO MECHANISMS THAT CAN CONTROL POPPING

As is the case with any physical mixing process, time is required to accom-Mixing Limited Induction Time plish liquid propellant mixing at an injector element impingement point. As a consequence, it is possible that this mixing time could be the limiting factor for impingement disturbances. If this were the case, the pop rate for all propellants would be similar at equivalent operating conditions. To investigate this possibility, a comparison was made of the overall popping rates measured in Ref. 13 with the  $N_2O_4/N_2H_4$ ,  $N_2O_4/Aerozine-50$ , and RFNA/UDMH propellant combinations. These data are presented in Fig. 15 together with the  $N_2O_4/N_2H_4$  data of Lee and Houseman (Ref. 16). Comparison is made on the basis of the familiar contact time parameter. Figure 15 shows that no significant difference exists among the rates obtained with the various propellants. Because all the combinations had the same rate regardless of propellant reactivity, it is therefore possible that the induction time required for the initiation of the disturbance could be limited by mixing time. (Although similar popping rates were observed, it should be noted that the amplitudes of the





-32-

detonations varied considerably among the propellants. With  $N_2O_4/N_2H_4$ , popping was primarily of the powerful Class A level. With the other propellants, Class B and C pops also occurred.)

For two impinging jets, the maximum available mixing time is dependent on the sheet length and velocity. The sheet length has been determined for equal diameter jets and the previously defined expression for the maximum possible time for reaction to occur is:

$$t_{lig} = L/V = K d/V^2$$

where

K = 200 ft/sec

The data of Houseman (Ref. 16) were used to determine independently the value of  $t_{lig}$  corresponding to the induction time for the above operating conditions and to verify that popping will not occur if the "contact" length of the sheet results in insufficient stay time to produce "ignition" within the sheet. This occurs if:

tlig > tind; popping will occur

Calculated ligament times for Houseman's data are plotted in Fig. 16 versus the popping interval (i.e., the inverse of the pop-rate). The results show that the pop-rate approaches zero as:

 $d/V^2 \rightarrow 0.8 \ \mu sec^2/ft$ 

Using Eq. (12), the resulting threshold ligament time is:

 $t_{lig} = 0.8 \times 10^{-6} (200) = 160 \,\mu\text{sec}$ 

(12)



Figure 16. Determination of the Induction Time for  $NTO/N_2^{H}$  Propellants at 14.2 psia

-34-

This induction time criterion applies at atmospheric pressure and a 40<sup>o</sup>F injection temperature for unlike doublets designed to provide optimum cold flow mixing characteristics.

The reality of the above induction time requirement is indicated by the results of separate experiments made with  $N_2O_4/N_2H_4$  in the Rocketdyne study of Ref. 13. In that study, high speed streak movies were taken of the flow from the impingement point to a location approximately 3-inches downstream which recorded the location of a disturbance. The film was oriented as shown in Fig. 17. The average film speed was 4200 frames/sec while the liquid sheet velocity was 50 ft/sec. A pressure of 13.7 psia, propellant injection temperatures of  $40^{\circ}$ F together with a mixture ratio that gives maximum cold flow mixing efficiency made the experimental conditions equivalent to those of Fig. 15.



Figure 17. Orientation of Film with Respect to Injector Fan

-35-

An enlarged photograph of a typical disturbance pattern is shown in Fig. 18. Note that the high-velocity luminous disturbance fronts appear in pairs, noted in the figure as "initial" and "secondary" disturbances. (The initial and secondary waves are separated in time by about 0.2 millisecond.) Reduction of the time/distance characteristics recorded on this photograph shows that the initial disturbance originates just slightly downstream of the impingement point. The location of initial disturbance is determined by the minimum slope shown in the photograph. There is a minimum because the disturbance is traveling both upstream and downstream at the point of initiation. This origin of the initial disturbance is about 0.1 inch downstream of the jet impingement point. The wave speed of the disturbance was calculated to be 5150/sec indicating that the disturbance was an explosive deflagration wave. Based on the location of the disturbance, the liquid sheet velocity, the induction time is:

 $t_{ind} = \frac{0.1}{12(50)} = 166 \ \mu sec$ 

The correlation between this experimental induction time (166 µsec) and the ligament time resulting in zero pop-rate (160 µsec) clearly supports the hypothesis that popping occurs when sufficient contact time is available for mixing-induced ignition and can be prevented by proper injector geometric and hydraulic design. That is, once the induction times for a given propellant combination are determined over the particular range of operating conditions (i.e.,  $P_c$ ,  $T_{o,f}$ , d), then injector design criteria for avoidance of popping can be defined quantitatively.

#### Role of Nitrate Intermediates

The verified presence of unstable nitrate intermediate compounds in the combustion of N2O4/Amine propellants (Ref. 15, 29, 30) makes them suspect as the prime cause of popping. The detonation of nitrates may be produced by either impact shock or by thermal ignition. If the detonations are caused by ignition explosions of the nitrate intermediates, then the induction time alone would control popping. If, however, the detonations are initiated by impact, then the popping limits would be controlled by both an induction time and an impact force.

-36-



where:

k = calibration of film (inches of flowfield/inches of film)
D = film distance

 $\Delta T = time$ 

Figure 18. Section of Streak Photograph Showing Disturbances and Description of Events If the explosions are triggered by thermal ignition, they might be expected to have many of the classical detonation characteristics including the pressure-temperature explosion limit curve representing the competition between the reactions which form and remove intermediate species.(Ref. 33, 34). These characteristics are represented qualitatively in Fig. 19. Pressure and induction time are shown in this graph rather than the usual P-T relation. Such a transformation of variables is possible because the induction time represents a heat-up period as well as a mixing period; consequently the induction time represents a  $\Delta T$  above a fixed inlet propellant temperature. Of particular interest is that these characteristics suggest that increasing chamber pressure could either increase or decrease pop rate depending on the  $P_{c}$  range covered. From the data of Houseman, where chamber pressure was varied, several values of induction time for different pressures could be determined. The results are presented in Fig. 20. Note that these results could be interpreted as corresponding to the second, third, and fourth legs of the theoretical induction time characteristics as schematically shown above.\*

These results suggest that, over the range in  $P_c$  studied, increasing  $P_c$  should initially result in a decrease in the pop rate (increasing induction time). Then with further increases in  $P_c$  the pop rate should increase up to a chamber pressure of about 150 psia. Increasing  $P_c$  beyond this point should again result in decreasing the pop rate. Zung (Ref. 8) reports popping frequency as a function of chamber pressure in the 100 to 200 psia range. His data show that the popping is a maximum (~45 pops/sec) around 100 psia and drops rapidly to about 8 pops/sec at 200 psia.

The above result is particularly interesting when considered in terms of c\* efficiency characteristics with chamber pressure. If the maximum pop rate produced minimum time averaged c\* performance, then based on the above described

-38-

<sup>\*</sup>One possible reaction contributing to Region 2 of Fig. 19 is the highly exothermic and pressure dependent recombination 2 NO<sub>2</sub>  $\neq$  N<sub>2</sub>O<sub>4</sub> which might be expected at the impingement point of an injection element.



Figure 19. Theoretical Induction Time as a Function of Ambient Pressure for Ignition Explosions



Figure 20. Comparison of the Data of Reference 16 with the Theoretical Prediction of Induction Time

-39-

characteristics, the maximum performance should occur at about 60 to 70 psia, and minimum performance at about 100 psia. Inspection of Fig. 13, presented previously, shows these identical trends in c\* efficiency with increasing chamber pressure. This result suggests that the detonations are ignition initiated. It is believed that the detonations result from rapid liquid-phase combustion of nitrate intermediates which are formed in liquid-phase reactions but are not found in gas-phase reactions between propellant vapors. Consequently, if the nitrate intermediates are going to enter into a detonation then they require (1) liquid/liquid contact, and (2) sufficient time for the liquid phase reactions to occur. A third requirement supported by the mixing limited induction time results is that sufficient mixed volume must exist to support a detonation. In addition, studies at Atlantic Research Corporation (Ref. 35) have shown that agitation and forced intimacy of the oxidizer with the fuel is also necessary for detonation. Their study has experimentally shown that when  $N_2O_4$  and Hz are brought into contact without forced mixing (i.e., touching of the interfaces), then no detonation will occur, although violent vapor evolution does result causing separation of the liquids. However, when turbulent mixing of the propellants is forced, and delay times are sufficient to obtain liquid-phase reactions, then an explosion will occur, depending on whether a mixed region of adequate size is achieved. This latter requirement suggests that spontaneous spray detonations should not be possible since liquid-phase reactions do not occur in the mixed spray, where droplets are decomposing due to droplet heatup and vaporization. However, in a rocket engine, the mixed sprays can of course amplify a detonation and sustain an instability. In addition, for unlike-impinging elements, the mixing is dependent on the element design and operating conditions so that the pop rate should be maximized when optimum mixing occurs. This conclusion is supported by the results presented in Fig. 10, which shows minimum performance at the optimum mixing design condition.

-40-

The above described data suggests that popping is controlled by:

- 1. Forced mixing and agitation
- Sheet length which must provide sufficient time:
   a. To achieve an adequate volume of mixed propellant
   b. For liquid phase reactions to occur
- 3. The tendency of propellants to produce unstable condensed phase intermediate products (ordinarily nitrates) whose formation and decomposition rates are temperature and pressure dependent.

Based on the above discussion, no single model is likely to completely describe popping limits. This possibly explains the inability of past investigators to extrapolate their findings to other operating conditions and the apparent inconsistency of results from differing studies. An example of a consistent set of models describing popping limits is shown in Fig. 21. First consider the orifice size limits below which insufficient mixed volume exists to support a detonation (Fig. 21a). The minimum orifice limits should be a function of chamber pressure and temperature as those parameters are related to reactivity and induction time. The various curves are determined by varying both orifice size and contact time until an orifice size is obtained which will not pop regardless of contact time. The limits are described for a given pressure and propellant temperature. A designer could simply enter this curve to determine the maximum allowable orifice to ensure that popping will not occur. However, based on injector face diameter and orifice size limitations the maximum allowable orifice size as specified above may be unacceptable. In that case, the designer would then enter Fig. 21b, which gives the induction time limits for the specific engine operating conditions. Induction time is then related to injector design parameters by:

 $t_{ind} < K d_j / V_j^2$  for no popping

The constant K has an assigned value of 200 for equal diameter unlike doublets. Differing values may be appropriate for doublets with differing orifice diameters or for other types of injector elements.

Ν



 Maximum Allowable Orifice Size Providing Insufficient Mixed Volume for Detonation



(b) Induction Time for Detonation if Sufficient Volume Available for Detonation

Figure 21. Schematic of Popping Limits

-42-

Injection  $\Delta P$  and therefore injection velocity limits are generally bounded by both feed system coupled instability ( $\Delta P_{min}$ ) and system requirements ( $\Delta P_{max}$ ). Based on these values the range in orifice size consistent with overall design conditions which will not produce popping can be determined. If this value is consistent with orifice size fabrication, plugging, or other limits then the designer may proceed to the RSS model to determine if the injector can be designed to provide both popping and RSS free operation.

#### APPLICATION OF DATA TO MECHANISMS THAT CAN CONTROL RSS

A corollary to the above discussion could be interpreted to state that reactive stream separation will occur when sufficient contact time is available for gas-phase reactions but when the mixed volume is insufficient to support a detonation. This suggests that a minimum orifice size probably exists where the mixed volume will always be insufficient for popping but could produce RSS. In this regard, it should be noted that under conditions when the contact time is insufficient for popping (i.e., not enough time for liquid-phase reactions) mixing would be expected to occur since gas-phase reactions should require greater times. However, if the heat transfer to the propellants before impingement is sufficient to cause some vaporization, gas-phase reactions would produce RSS, thereby inhibiting liquid/liquid contact. This result requires propellant jets that are initially popping or mixing to eventually operate in the RSS region as the propellant temperatures are increased unless the free jet length before impingement is reduced. Since the saturation temperature is dependent on pressure then  $P_{\rm c}$  should also have an effect where RSS occurs.

A schematic illustrating RSS limits is shown in Fig. 22. For ease in interpretation, this schematic is presented for a single propellant temperature and orifice diameter. It is important to note that even if the design will be pop-free, the injector could still operate in the RSS region. If the orifice diameter,  $d_1$ , was selected based on minimum mixed volume for a detonation then the injection velocity must be sufficient to insure operation

-43-



Contact Time

Figure 22. Schematic of Reactive Stream Separation

-44-

in zone 1 rather than zone 3. If a larger diameter  $d_3$  is chosen, then the injection velocity must be chosen to prevent operation in either zone 2 or 3. As shown in Fig. 22, there is little that can be done in terms of element orifice diameter or injection velocity to prevent separation by the flashing mechanism in zone 4.

#### NOMENCLATURE

- a speed of sound
- A frequency factor
- B empirical exponential reaction coefficient
- C concentration
- C<sub>p</sub> specific heat
- d diameter
- $\mathcal{B}$  detonation parameter
- E activation energy
- F(M) fraction mixed
- $g_c$  conversion factor
- ∆H enthalpy change
- J conversion factor
- k modified frequency factor
- L length

Υ,

- n number of moles
- p,P pressure
- Q heat release rate
- r reaction rate
- S injector element spacing
- t time
- T temperature
- V velocity
- wweight flow rate
- X constant relating mixing length to jet diameter
- Y lumped reaction constant

Ŷ	impingement angle
δ	gas film thickness
η	mixing efficiency
£	explosion energy
ρ	density
τ	delay time

## Subscripts

₽,

b	boiling
f,F`	fuel
g	gas
ind	induction
ign	ignition
inj	injection
j	jet
L	loss
lig	ligament
mix	mixing
0	initial
ox	oxidizer
R	reaction
V	vaporization

-47-

#### REFERENCES

- Elverum, G. W., Jr., and P. Staudhammer, <u>The Effect of Rapid</u> <u>Liquid-Phase Reactions on Injector Design and Combustion in</u> <u>Rocket Motors</u>, Progress Report 30-4, Jet Propulsion Laboratory, Pasadena, California, August 1959.
- Somogyi, D., and C. E. Feiler, <u>Liquid-Phase Heat Release Rates of</u> <u>the System Hydrazine-Nitric Acid and Unsymmetrical Dimethylhydrazine -</u> <u>Nitric Acid</u>, NASA TN D-469, September 1960.
- Beltran, M. R., et al, <u>Liquid Rocket Engine Combustion Instability</u> <u>Studies</u>, AFRPL-TR-66-125, Final Report Contract AF04(611)10542, Dynamic Science Corp., Monrovia, California, July 1966.
- 4. Kushida, R., and J. Houseman, <u>Criteria for Separation of Impinging</u> <u>Streams of Hypergolic Propellants</u>, Tech. Memorandum 33-395, Jet Propulsion Laboratory, Pasadena, California, July 15, 1968.
  - Lawver, B. R., and E. A. Tkachenko, <u>Heat Release Rate for the Liquid</u> <u>N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>H<sub>4</sub> Reaction by Somogyi and Feiler's Method</u>, Final Report SN-114, Dynamic Science, Monrovia, California, April 1968.
  - Rodriguez, S. E., and A. Axworthy, <u>Liquid Phase Reactions of Hypergolic</u> <u>Propellants</u>, R-8374, Rocketdyne, a division of Rockwell International, Canoga Park, California, December 1970.
  - Lawver, B. R., and B. P. Breen, <u>Hypergolic Stream Impingement Phenomena -</u> <u>Nitrogen Tetroxide/Hydrazine</u>, NAS-CR-72444, Dynamic Science Division, Marshall Industries, Monrovia, California, October 1968.
  - Zung, L. B., "Hypergolic Impingement Mechanisms and Criteria for Jet Mixing or Separation," paper presented at the 6th ICRPG Liquid Propellant Combustion Conference, Chicago, Illinois, <u>CPIA Publication</u> No. 192, Vol. 1, December 1969.
  - Dickerson, R., et al, <u>Correlation of Spray Injector Parameters with</u> <u>Rocket Engine Performance</u>, AFRPL-TR-68-17, Final Report, Rocketdyne, a division of Rockwell International, Canoga Park, California, June 1968.

- 10. Houseman, J., "Jet Separation and Popping with Hypergolic Propellants," paper presented at the 7th JANNAF Combustion Meeting, <u>CPIA Publication</u> No. 204, Vol. 1, February 1971.
- 11. Lawver, B. R., "A Model of the Hypergolic Pop Phenomena," J. of <u>Spacecraft and Rockets</u>, 9, 4, 225, April 1972.
- Hines, W. S., et al, <u>Extension of a Thrust Chamber Compatibility Model</u>, AFRPL-TR-72-19, Final Report for Air Force Contract F04611-70-C-0056, Edwards AFB, California, March 1972.
- Nurick, W. H., and J. Cordill, <u>Reactive Stream Separation Photography</u>, R-8490, Final Report Contract NAS7-720, Rocketdyne, a division of Rockwell International, Canoga Park, California, May 1972.
- 14. Rupe, J., D. Dipprey, R. Kushida and R. Clayton, "The Stability Criterion for Impinging Jets and its Impact on Combustion," paper presented at the 6th ICRPG Combustion Instability Conference, Chicago Illinois, <u>CPIA Publication No. 192</u>, Vol. 1, December 1969.
- Christos, T., et al, "Combustion Characteristics of Condensed-Phase Hydrazine-Type Fuels with Nitrogen Tetroxide," <u>J. of Spacecraft and</u> <u>Rockets</u>, <u>4</u>, 9, 1224, September 1967.
- 16. Lee, A., and J. Houseman, "Popping Phenomena with N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>H<sub>4</sub> Injectors," presented at the Western States Section Meeting of the Combustion Institute of Stable Combustion of Liquid Propellants at JPL, Pasadena, California, October 26-27, 1970.
- 17. Nurick, W., and R. McHale, <u>Noncircular Orifice Holes and Advanced Fabri-</u> <u>cation Techniques for Liquid Rocket Injectors</u>, Phase I Final NASA Contract Report CR-108570, Rocketdyne, a division of Rockwell International, Canoga Park, California, November 1970.
- Clayton, R. M., <u>Experimental Observations Relating the Inception of</u> <u>Liquid Rocket Engine Popping and Resonant Combustion to the Stagnation</u> <u>Dynamics of Injection Impingement</u>, TR 32-1479, JPL, Pasadena, California, 15 December 1970.

- 19. Houseman, J., "Jet Separation and Optimum Mixing for an Unlike Doublet," paper presented at the 6th ICRPG Combustion Instability Conference, Chicago, Illinois, <u>CPIA Publication No. 192</u>, Vol. 1, December 1969.
- Yost, M. C., <u>OME Injector Evaluation</u>, ITR-73-069-C, Rocketdyne IR&D Technical Report, Rocketdyne, a division of Rockwell International, November 1973.
- Personal communication from R. D. Paster of Rocketdyne, Canoga Park, California.
- 22. Breen, B. P., et al, "Liquid Phase Kinetics for the Hypergolic Nitrogen Tetroxide Hydrazine System," paper presented at 3rd Combustion Conference, Cocoa Beach, Florida, <u>CPIA Publication No. 138</u>, Vol. 1, February 1967.
- 23. Kilpatrick, M., and L. L. Baker, "A Study of Fast Reactions in Fuel-Oxidant Systems," <u>Fifth Symposium (International) on Combustion</u>, Reinhold Publishing Corporation, New York, 1955, p. 156.
- 24. Bernard, M., and J. Dufour, "On the Existence of Detonation Conditions in the Combustion of Some Nitric Acid Propellants," <u>Fifth Symposium</u> <u>(International) on Combustion</u>, Reinhold Publishing Corporation, New York, 1955, p. 1074.
- 25. Sawyer, R. F., and I. Glassman, "Reaction Kinetics of the Hydrazine-Nitrogen Tetroxide Propellant System," paper presented at the 2nd Combustion Conference,
- 26. Sawyer, R. F., "The Hydrazine-Nitrogen Tetroxide Reaction, a Comparison of Experimental Observations," paper presented at the 3rd Combustion Conference, Cocoa Beach, Florida, <u>CPIA Publ. No. 138</u>, Vol. 1, February 1967.
- 27. Lawver, B. R., "Some Observations on the Combustion of N<sub>2</sub>H<sub>4</sub> Droplets," AIAA per No. 65-355 presented at the 2nd Annual AIAA Meeting, San Francisco, California, July 26-29, 1965.

- 28. Lawver, B. R., and B. P. Breen, "The Hydrazine/N<sub>2</sub>O<sub>4</sub> Flame Structure," paper presented at the 3rd Combustion Conference, Cocoa Beach, Florida, CPIA Publ. No. 138, Vol. 1, February 1967.
- 29. Perlee, H. E., et al, Hypergolic Ignition and Combustion Phenomena in <u>the Propellant System Aerozine-50/N<sub>2</sub>O<sub>4</sub></u>, Final Report, U. S. Bureau of Mines, Pittsburgh, Pennsylvania, March 31, 1967.
- 30. Saad, M. A., et al, "Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazine Under Non-ignition Conditions," <u>AIAA Journal</u>, <u>10</u>, 8, 1073, August 1972.
- 31. Saad, M. A., and M. B. Detweiler, "Analysis of N<sub>2</sub>H<sub>4</sub>/RFNA Reaction Product," <u>AIAA Journal</u>, 7, 8, 1588, August 1969.
- 32. Seamons, et al, "Development of a Fundamental Model of Hypergolic Ignition in Space Ambient Engines," <u>AIAA Journal</u>, <u>5</u>, 9, 1616, September 1967.
- Lewis, B., and G. von Elbe, <u>Combustion, Flames, and Explosions of Gases</u>, 2nd Edition, Academic Press, Inc., New York, 1961.
- 34. Williams, F. A., <u>Combustion Theory</u>, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1965.
- 35. Friedman, R., et al, <u>A Study of Explosions Induced by Contact of</u> <u>Hydrazine-Type Fuels with Nitrogen Tetroxide</u>, Report ASD-TDR-62-685, Tech. Documentary Report for Contract AF33(616)-6918, Atlantic Research Corporation, Alexandria, Virginia.