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THE EFFECTS OF COMPOSITION VARIATION AND  
NITRIC ACID ON THE STABILITY AND REACTIVITY  
OF THE HAN-BASED LIQUID PROPELLANTS

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JANUARY 1991

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## 1. INTRODUCTION

The hydroxylammonium nitrate (HAN) based liquid gun propellants, LGP1845 and LGP1846, are homogeneous, aqueous mixtures of the salts HAN and triethanolammonium nitrate (TEAN). The HAN:TEAN molar ratio is 7, the value required for  $N_2$ ,  $CO_2$  stoichiometry, and the equation describing the overall reaction of either propellant mixture is:



A molar ratio of 7 is identical to a weight ratio of 3.17. Thermochemical calculations using the BLAKE code (Freedman 1982) show that impetus is dependent both on water content and on HAN:TEAN ratio. The effect of water content on the impetus of HAN-TEAN stoichiometric mixtures is shown in Figure 1.

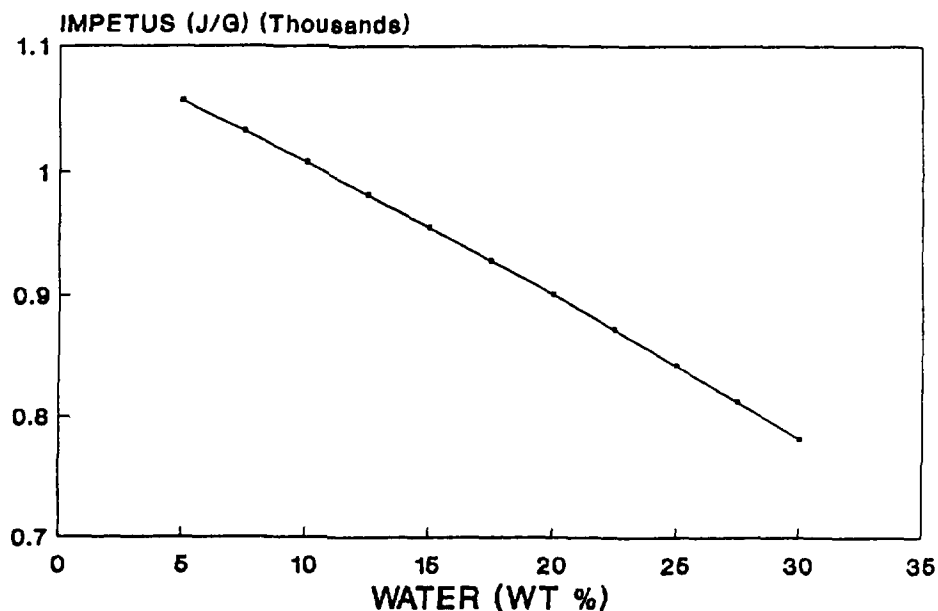


Figure 1. The Effect of Water Content on Impetus of HAN-TEAN Mixtures.

The data points at 16.8 and 20.0 wt.-% water with impetus values of 934.3 and 898.7 J/g, correspond to the nominal compositions of LGP1845 and LGP1846, respectively. The effect of HAN:TEAN ratio on the impetus of mixtures containing 20 wt.-% water, is shown in Figure 2. The data point at 3.17 corresponds to the 20% water point in the previous figure and is the nominal composition of LGP1846.

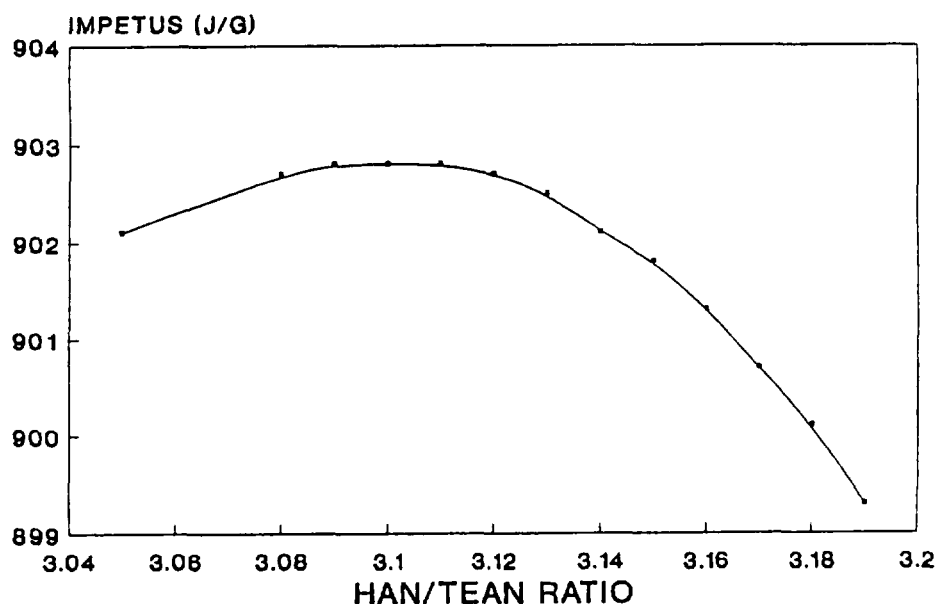


Figure 2. The Effect of HAN:TEAN Ratio on Impetus of Mixtures Containing 20% Water.

Maximum impetus is obtained for mixtures that are TEAN-rich, although the effect is small. Comparing Figures 1 and 2 reveals that water content more strongly affects impetus than HAN:TEAN variation. The propellants in use are stoichiometric mixtures, sacrificing maximum impetus in order to avoid the secondary muzzle flash that would result from the ignition of CO and H<sub>2</sub>, two of the gaseous products of combustion of TEAN-rich mixtures.

The propellants are ionic, somewhat acidic, and contain both oxidizing and reducing species. They are quite corrosive, reacting with a wide variety of inorganic and organic materials such as

metals and their alloys, plastics, greases and lubricants, and many other materials with which they make incidental or intended contact. These materials are often damaged as a result of such contact, their properties degrading to where they can no longer be used for their intended purpose (Feuer, Rodriguez, and Teets 1988). The result of contact with materials with which the propellant reacts can, in many cases, damage the propellant (Hansen, Backof, and DeGreiff 1990). Both damage to materials and to propellant must be considered in the choice of materials that will maintain long-term contact, such as storage containers and pumping hardware. Short-term contact, as would occur in gun components during the firing cycle, should not pose as severe a problem, although corrosion could affect the close tolerances of precisely machined components.

Although perfectly precise compositions can be used for computational purposes, the manufacture, storage, and shipment of propellant samples introduces some variability in both composition and purity. The extent to which such variability must be controlled in order to assure predictable and reproducible gun performance is one of the factors used for establishing manufacturing specifications and for the design of storage containers and handling procedures. The practicality of the weapon system and its cost is directly related to the tolerance levels used in such controls. One step in evaluating such costs is assessment of gun performance as propellant composition is varied. Since the expense of such an experimental investigation would be extremely high, a computational study was carried out in order to determine the magnitude of the effect.

In addition to compositional variation, the propellant manufacturing process is also a possible source of impurities. Trace impurities such as metal ions could be incorporated into the formulations. If these trace impurities act as decomposition catalysts and have an activation energy for reaction that is substantially lower than that of the propellant itself, they will adversely affect the thermal stability of the mixture. Both catalysis and a lower activation energy are required for a measurable lowering of thermal stability. If the trace impurity does not act as a decomposition catalyst, its concentration will quickly be reduced by reaction to a point where no further degradation will take place. In a similar vein, if the activation energy of the trace impurity reaction is not significantly lower than that of the pure propellant, no decrease in thermal stability will be observed. The ferric ion, FeIII, is an excellent example of a catalytic impurity that lowers thermal stability (Klein and Wellman 1976) although the effect is more complicated than it would appear from a casual appraisal. FeIII is reduced by  $\text{HA}^+$  to

FeII which is promptly reoxidized by nitrate so that the effect seen is the catalytic destruction of HAN. The rate of HAN disappearance follows the rate law:

$$-d[\text{HAN}]/dt = k[\text{HAN}][\text{FeIII}]^2.$$

The rate constant,  $k$ , is temperature dependent:

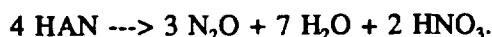
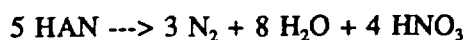
$$k = 1.01 \times 10^{12} \exp (-24,900/1.987T).$$

If temperature is in Kelvin, the constants result in a rate of disappearance in  $\text{M}\cdot\text{s}^{-1}$ . The more usual units for trace concentrations are part per million, 1 ppm FeIII being  $2.59 \times 10^{-5}$  mol/l of propellant. HAN is 9.19 M in LGP1846, and storage of propellant containing 5 ppm FeIII for 20 years at  $65^\circ \text{C}$  will reduce HAN concentration 0.085%, an apparently insignificant amount. Products of the FeIII-HAN reaction are  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{HNO}_3$  and the role played by the acid in affecting propellant reactivity will be discussed subsequently. The effect of contact with iron metal or its alloys is somewhat different. The propellant first reacts with the metal to produce FeIII which then reacts as described above. In the immediate vicinity of the metal, FeIII concentration can exceed 1 mol/l and its reaction with HAN will proceed rapidly. Damage to both the metal and the propellant will occur and such contact should be avoided.

Another plausible impurity may be one of the starting materials used in propellant synthesis. The physical and chemical properties of nitric acid and triethanolamine, the starting materials from which propellant is produced are quite different from those of the propellant itself and the presence of either could adversely affect stability and performance. HAN is prepared by the electrolysis of nitric acid (Barnatt, Dotson, and Leistra 1988), a process that results in a dilute product that, although free of impurities, does contain excess nitric acid. This excess acid is removed (Klein, Leveritt, and Wojciechowski 1990) and the dilute HAN concentrated to approximately 80 wt.-% by removal of water under vacuum. TEAN is prepared by reaction of triethanolamine with nitric acid, an acid-base neutralization, followed by isolation and recrystallization. Both HAN and TEAN should be pure and free of starting materials before propellant compounding is undertaken although inadvertent noncompliance with processing procedures creates the possibility that some small amount of either nitric acid or triethanolamine could be present in a given lot of propellant. Both acid and amine

cannot simultaneously contaminate the propellant mixtures because they would react until only the compound present in excess would remain. Of the two potential impurities, nitric acid poses the more serious problem.

The first step in the thermal degradation of the HAN-based propellants is the thermal decomposition of HAN (Klein, Sasse, and Travis 1976; Klein et al. 1977). The gases  $N_2$  and  $N_2O$  are produced as is nitric acid, the quantity of the products being a function of reaction path as follows:



The presence of nitric acid lowers the activation energy for HAN decomposition and, when sufficiently concentrated, is capable of initiating the propellant decomposition sequence at ambient temperature (Klein and Sasse 1980). Thus, it would seem reasonable to suspect that the presence of nitric acid in propellant, either from improper manufacture or as a result of some slight degradation in storage, could affect storage stability and possibly gun performance. The effect of nitric acid on the physical properties of the propellant mixtures is an additional cause for concern because many aspects of liquid propellant gun performance are dependent on the properties of the propellants. An experimental investigation was therefore undertaken, the purpose of which was to assess the effect of this plausible impurity on propellant properties and performance.

## 2. THE EFFECT OF COMPOSITIONAL VARIATION ON GUN PERFORMANCE

The nominal composition of LGP1846 by weight is 60.81% HAN, 19.19% TEAN, and 20% water. A detailed study of the effect of water content on propellant performance was conducted since the data in Figures 1 and 2 indicate that propellant impetus would be most strongly affected by variation in water content. Any compositional variation must affect the concentration of at least two of the components and the impetus surface generated by permitting water to vary 0.5 wt.-% contiguous to its nominal composition is shown in Figure 3.

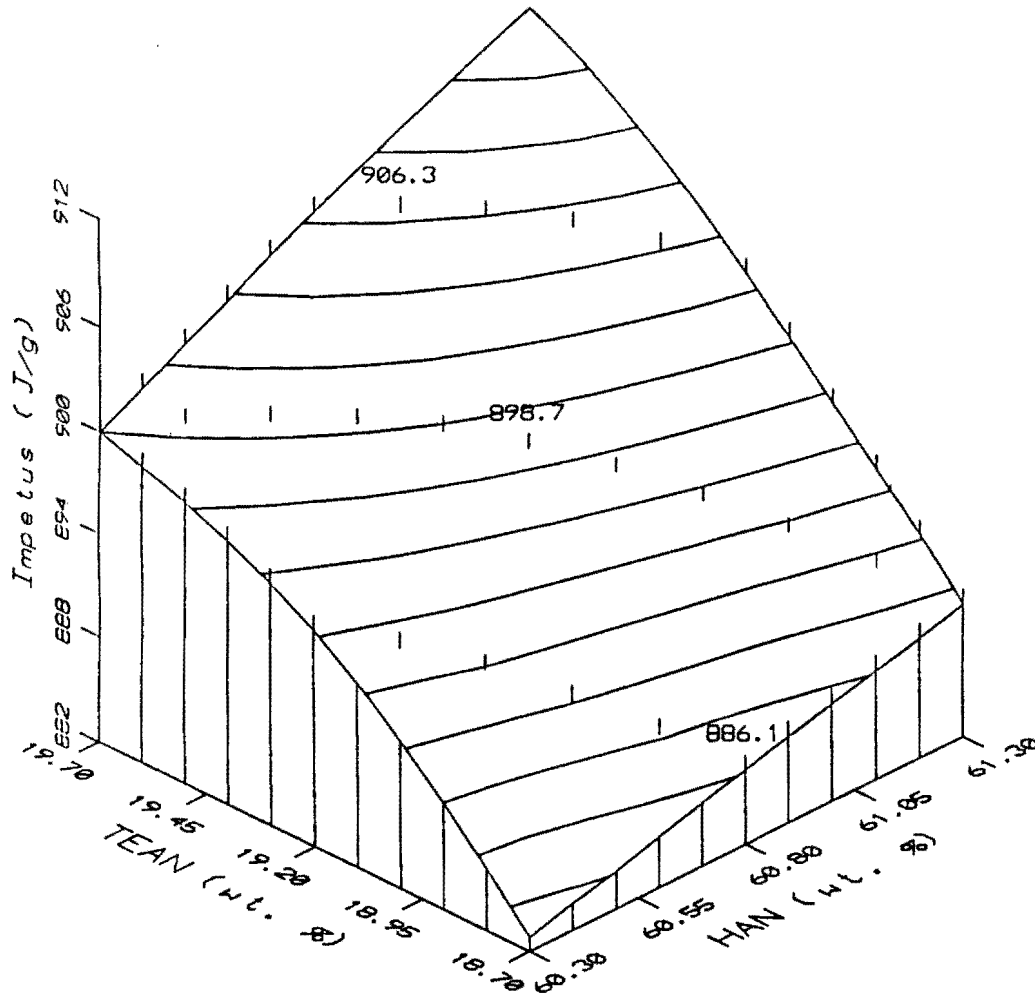


Figure 3. The Effect of HAN and TEAN Concentration on Impetus of Mixtures Containing  $20 \pm 0.5\%$  Water.

The surface contours in Figure 3 are lines of constant impetus and the 898.7 J/g value is obtained for the nominal LGP1846 composition. The points posted on the impetus surface correspond to composition extremes with an additional set describing HAN:TEAN ratio variation at 20% water. Impetus is reduced 1.4% in a composition that is 60.8% HAN, 18.7% TEAN and 20.5% water and is raised 0.8% in a composition that is 60.8% HAN, 19.7% TEAN and 19.5% water, the extreme values possible within the compositional constraint used. The extent to which such variation affects the performance of a 155-mm regenerative liquid propellant (RLP) howitzer was computed using the RLPGUN code developed by Coffee (1985). Three zone/velocity levels were simulated: a low

(305 m/sec), medium (680 m/sec), and high (1000 m/sec) zone. The low zone case corresponds to about zone 4 in the 155-mm solid propellant (SP) howitzer; the medium zone corresponds to about zone 8; and the high zone is a "super zone" corresponding to an experimental high performance 155-mm SP howitzer now under development. Overall gun configuration was kept the same for all zones and barrel lengths, combustion chamber volume, and maximum liquid propellant chamber volume were chosen so that 1,000 m/sec could be attained with the M549 projectile (43.545 kg). This required a maximum projectile travel of 8.14 m and a combustion chamber volume of 4.975 liter. Injector design was the General Electric Concept VI, an in-line, annular piston injector. Reservoir volume and vent area were adjusted in order to obtain the desired muzzle velocity. The maximum propellant reservoir pressure was constrained to 514 MPa. The volume of the propellant reservoir and vent area required to achieve desired performance with nominal LGP1846 is listed in Table 1.

Table 1. Reservoir Volume and Vent Area Requirements

Zone	Reservoir Volume, Liter	Vent Area, cm <sup>2</sup>	Muzzle Velocity, m/sec
Low	1.434	6.529	304.8
Medium	5.032	24.205	680.3
High	15.236	38.189	1,000.6

Vent area during injection was assumed to be constant and the liquid propellant burned instantly to combustion product gases upon injection. Instant combustion after injection eliminates the effect of propellant composition on burning rate. All of the compositions were run parametrically at each zone level using appropriate reservoir volume and vent area values. Values of density, chemical energy, specific heat ratio, molecular weight, and covolume for each composition were needed for the RLPGUN code. Thirty-nine composition variations were considered for each zone for a total of 117 separate computations.



The largest increase in liquid pressure (1.73%) and in combustion chamber pressure (1.75%) with composition is obtained in the high zone calculations whereas the largest increase in muzzle velocity (1.52%) is obtained for the low zone case. A variation of 1.5% in muzzle velocity exceeds the performance specifications normally associated with this type of gun. Since propellant will be metered into the gun and the amount delivered controlled in small increments, a suitable adjustment based on propellant composition is readily envisioned. The muzzle velocity-composition surface in Figure 4 is the high zone result and covers the same composition variation used in Figure 3. The surface contours are lines of constant muzzle velocity.

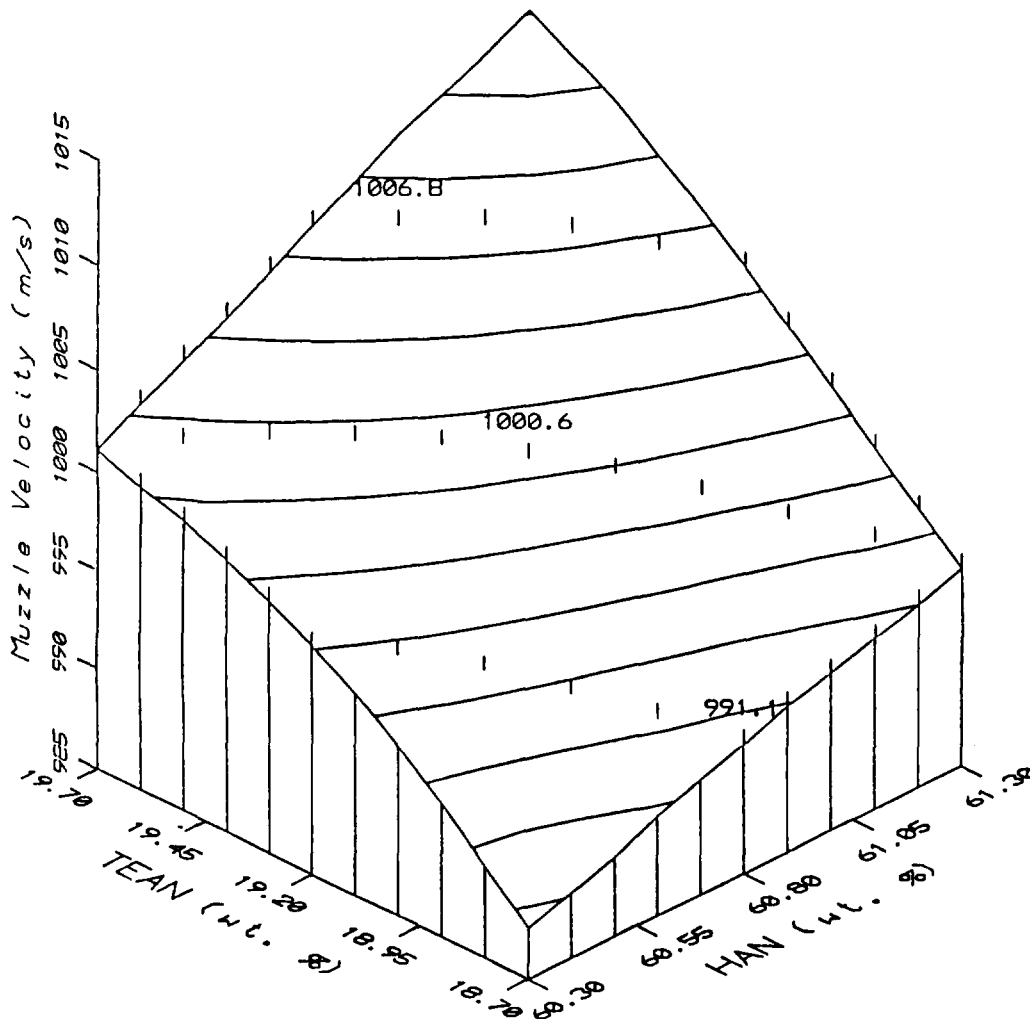


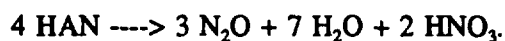
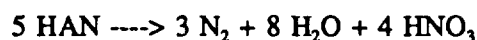
Figure 4. The Effect of Propellant Composition on Muzzle Velocity.

Quite obviously, muzzle velocity varies in much the same way as impetus and neither change drastically over the composition range studied.

### 3. EXPERIMENTAL INVESTIGATIONS

The nitric acid content of propellant that had been released from a production facility would be small. Massive nitric acid contamination that was the result of improper production control would pose a problem only if the resulting mixture was so unstable as to present a hazard at the production facility. Assay, required prior to packaging and shipment, would detect excess acid and nullify the possibility that such material could leave the manufacturing facility and enter the logistic system. Qualitative experiments showed that nitric acid at concentrations of up to 5% did not lower thermal stability to the extent that short term storage under controlled conditions presented an unacceptable risk and attention was then directed to either the formation of nitric acid as a result of propellant degradation in storage or the presence of acid in small amounts in manufactured material.

As stated previously, the decomposition of HAN is the first result of thermal degradation of propellant (Klein, Sasse, and Travis 1976) and, in addition to nitric acid, the several oxides of nitrogen and nitrogen itself are produced. If NO is produced, it will spontaneously react with any air present in the container and be converted to NO<sub>2</sub>. If NO<sub>2</sub> is present, either as a result of the NO reaction or as a reaction product, it will rapidly react with the water in the remaining propellant, resulting in a mixture of nitrous and nitric acids. Nitrous acid reacts readily with HAN (Klein, to be published) producing N<sub>2</sub>O, water, and nitric acid. The only innocuous products of HAN decomposition that forms nitric acid are thus N<sub>2</sub> and N<sub>2</sub>O according to the following reactions:



In either case, HAN is depleted, water and nitric acid are formed, and the composition of the propellant changed although variation in HAN:TEAN ratio will depend on the HAN reaction chosen.

The decomposition of HAN and addition of nitric acid will affect the impetus of the mixtures. The composition and calculated impetus of LGP1845, a propellant that is nominally 11 Molar in nitrate ion, that decomposed via the  $N_2$  or  $N_2O$  route is given in Tables 2 and 3.

Table 2. Composition and Impetus of LGP1845 Decomposed to  $N_2$

	Concentration (wt.-%)				
Sample	Acid	HAN	TEAN	Water	Impetus, J/g
1845	0	63.23	19.96	16.81	934.3
0.1a	0.1	63.06	19.97	16.88	933.6
0.2a	0.2	62.89	19.97	16.93	933.1
0.5a	0.5	62.38	19.99	17.12	931.2
1.0a	1.0	61.53	20.03	17.44	928.2
2.0a	2.0	59.83	20.09	18.07	922.1
5.0a	5.0	54.76	20.29	19.95	903.8

Table 3. Composition and Impetus of LGP1845 Decomposed to  $N_2O$

	Concentration (wt.-%)				
Sample	Acid	HAN	TEAN	Water	Impetus, J/g
1845	0	63.23	19.96	16.81	934.3
0.1b	0.1	62.99	19.98	16.93	933.4
0.2b	0.2	62.75	20.00	17.05	932.4
0.5b	0.5	62.03	20.06	17.40	929.6
1.0b	1.0	60.84	20.17	17.99	924.4
2.0b	2.0	58.46	20.38	19.16	911.8
5.0b	5.0	51.30	21.01	22.69	865.8

The lowering of impetus with changing propellant composition for the most extreme case in Table 2 is less than 4%; the Table 3 worst case is less than 8%. The 5% acid compositions presented in the Tables are felt to be well beyond any practical case that would be encountered. Volumetric impetus is a better indicator of gun performance than gravimetric impetus because propellant is metered into the gun by volume rather than by weight, and a knowledge of sample density is required in order to estimate volumetric impetus.

LGP1845 was chosen as the propellant on which to conduct the majority of the experimental study because it is more reactive than LGP1846. This increased reactivity should accentuate the effects of acid and composition variation and simplify interpretation of the data. Since the fundamental propellant chemistry of LGP1845 and LGP1846 is the same, results obtained with LGP1845 should be applicable to LGP1846. Propellant samples with compositions as shown in the Tables were prepared from pure HAN, TEAN, water, and analytical grade nitric acid. In addition, samples of LGP1846 containing 0, 0.01, 0.02, 0.05, and 0.10%  $\text{HNO}_3$  were prepared. All of the samples prepared were analyzed (Sasse 1990) and their density determined using a Mettler-Paar Model DMA 55<sup>a</sup> density meter.

The effect of the compositional changes shown in Tables 2 and 3 on both storage stability and on reactivity was determined using an accelerating rate calorimeter (ARC) that had been modified specifically for use with the HAN-based liquid propellants (Klein and Leveritt 1988). Starting temperature for these reaction studies was 35° C, final temperature was 225° C, the temperature step used was 5° C, and the sensitivity for exotherm detection was 0.01°/min. Both the temperature of onset of exothermic reaction and the detailed nature of the exotherms observed were recorded. Onset temperature relates directly to thermal stability of the sample whereas details of the exothermic output relate to the performance of the mixtures once reaction has been initiated. Sample size was chosen to produce a loading density of 0.04 g/ml in order to avoid the possibility of sample bomblet rupture. The results of thermochemical calculations were available at this loading density so that a direct correlation of experimental results with thermodynamic predictions could readily be made. The majority of the reaction studies were conducted at atmospheric pressure because this would be the usual propellant storage condition. Since the effect of acid on propellant efficacy involves reaction at elevated pressure, a number of experiments were carried out under nitrogen at a pressure of about 30 atm.

---

<sup>a</sup>Anton Paar, KG, Graz, AUS.

3.1 Effect of Acid on Propellant Density. The density of the prepared mixtures, determined at 20° C, is shown in Table 4.

Table 4. Density of the HAN-TEAN-Acid Mixtures

Sample	Density, g/ml	Sample	Density, g/ml
LGP1845	1.4729		
0.1a	1.4713	0.1b	1.4683
0.2a	1.4700	0.2b	1.4660
0.5a	1.4684	0.5b	1.4619
1.0a	1.4626	1.0b	1.4554
2.0a	1.4610	2.0b	1.4507
5.0a	1.4581	5.0b	1.4232
LGP1846	1.4484		

The data shows that the density of the LPG1845 prepared for these studies to be 1.7% greater than that of the LPG1846. Previously reported work (Decker et al. 1987) obtained with lots of propellant manufactured for gun use showed a difference of 1.5%. The small difference in density values is due to uncertainty in the concentration of HAN and TEAN used to prepare the acid samples for this study, since no special effort was made to precisely duplicate the composition specifications that a manufacturer must meet. The experimental data obtained are not adversely affected by such small concentration variations (Klein, Speigel, and Messina 1987). Although the small differences in density between the prepared propellant samples and previously manufactured propellants are not considered important, the variation in density with composition within the set of samples is quite another matter and substantial effort was made to assure compositional consistency within the set of prepared samples.

The density of HAN-TEAN mixtures can be accurately estimated from the densities of their components using a semi-empirical additivity model (Sasse 1988; Sasse et al. 1988). This model was expanded to include nitric acid as a component assuming density additivity. The density of the

LPG1845 mixtures given in Tables 2 and 3 was calculated and are shown in Figure 5 together with the experimental values obtained (Table 4).

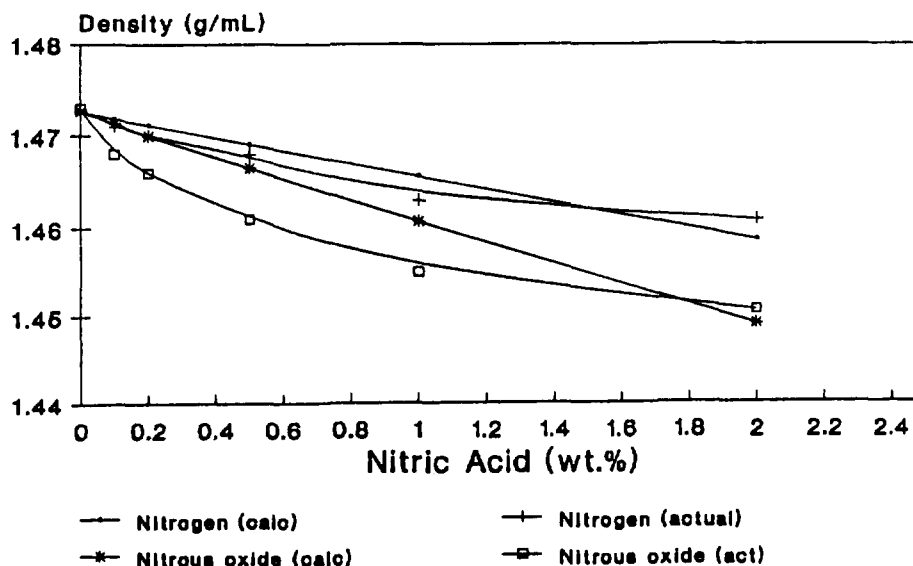


Figure 5. Density of LPG1845-Nitric Acid Mixtures.

The effect of acid on propellant density is different from what is predicted. The presence of acid in relatively small amounts apparently modifies the molecular structure of the propellants (Klein 1990) and, in so doing, lowers density more than predicted by the simple model. Modification of propellant structure would be expected to alter a number of colligative and transport properties. The storage and use scenarios for the propellants are highly dependent on such properties as freezing point (or glass transition), viscosity, and thermal conductivity, among others, and modification of these properties could have far-reaching, practical consequences. Although the influence of propellant density on volumetric impetus is stressed because it is of major concern in this report, other effects should not be overlooked.

**3.2 Thermal Reactions.** The data produced by the ARC includes reaction initiation temperature and detailed thermodynamic and kinetics information about the reaction or reactions that were thermally initiated. In the case of burning propellant, rapid gas evolution is also accurately measured. Since reaction initiation temperature relates directly to propellant stability whereas the reaction rate information relates to the chemistry of ignition and combustion, the two will be treated separately.

3.2.1 Reaction Initiation. It had been observed (Sasse and Klein 1979) that thermal reaction initiation temperature varied inversely with the total nitrate concentration of acid-free HAN-fuel mixtures, decreasing linearly at approximately 8° per mole of additional nitrate at concentrations near those of the propellants. Although these observations were made under other experimental conditions, there is every reason to expect that a similar relationship will exist for ARC data. This was confirmed by comparing the reaction initiation temperature of acid-free LGP1845 and LGP1846. The former, with a nitrate concentration of 11.1 mole/l reacts at 118° C whereas LGP1846, in which nitrate is 10.5 M, reacts at 123° C, a difference of 8.3° per mole of additional nitrate ion. Since composition and density of all of the mixtures was known, molarity could be calculated and reaction initiation temperature predicted. These values, together with the temperature at which the onset of exothermic activity was detected, are presented in Table 5.

One sees from Table 5 that the modified LGP1845 samples begin reacting at significantly lower temperatures than would be expected if only total nitrate was the sensitive variable. Reaction onset temperature decreases with increasing acid concentration, reaches a minimum value at 1% acid, and then increases. The presence of 0.1% acid in the LGP1845 mixtures produces a drop of over 30° in reaction initiation temperature. The decrease in initiation temperature is less dramatic between 0.1 and 1.0% acid, although a ultimate difference of 70° in initiation temperature is observed.

The presence of nitric acid in LGP1846 samples in amounts up to 0.1% produces far less striking results. The acid appears to have little effect on reaction onset and a temperature decrease of only 4° is observed at 0.1% acid. It would appear that addition of very small amounts of acid possibly results in a slight increase in thermal stability, producing a maximum onset temperature at 0.02% acid. The experimentally observed temperature variations are small enough that they would be dismissed as mere statistical variability except that the same observation had been made (Hansen, Backof, and De Grief 1990) using an entirely different procedure for assessing propellant stability. The explanation for this behavior advanced by Hansen and co-workers is that the addition of very small amounts of acid inhibits the dissociation of HAN to hydroxylamine and nitric acid. HAN is the nitrate salt of hydroxylamine:

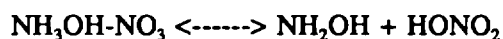


Table 5. First Observation of Heat Production

Sample	NO <sub>3</sub> -Molarity	Reaction Onset Predicted	Temperature Found (°C)
LPG1845	11.1	118.0	118
0.1a	11.1	118.0	85
0.2a	11.1	118.0	80
1.5a	11.0	118.8	64
1.0a	11.0	118.8	47
2.0a	11.0	118.8	62
5.0a	10.9	119.7	68
0.1b	11.0	118.8	84
0.2b	11.0	118.8	72
0.5b	10.9	119.7	54
1.0b	10.8	120.5	46
2.0b	10.7	121.3	50
5.0b	10.1	126.3	58
LGP1846	10.5	123.0	123
1846-.01	10.5	123.0	120
1846-.02	10.4	123.8	129
1846-.05	10.5	123.0	123
1846-.1	10.5	123.0	119

maintaining an acid-base equilibrium, as do all salts. The presence of acid drives the equilibrium to the left, reducing the probability of dissociation. Since hydroxylamine is far less stable thermally than is HAN, an increase in thermal stability is seen. The reaction sequence associated with reaction initiation is complex (Klein, to be published) and nitric acid plays a major role, a role quite different from the one suggested here.

The difference in behavior between LPG1845 and LPG1846 requires comment. Quite obviously, the higher salt content of LPG1845 affects the data obtained and although the only overlapping acid



concentration is 0.1%, the lowering of reaction initiation temperature 30° vs. 4° is beyond experimental uncertainty. The same general trend would be expected in either mixture because the chemical reactions taking place are the same although reaction rates should be higher in LGP1845. It would appear that some critical concentration of reactants is required for thermal decomposition to become measurable and relates directly to the total nitrate concentration of the mixture in acid-free propellants. This concentration is either lower or is more easily achieved in LGP1845. The presence of nitric acid superimposes an additional effect that is much more strongly concentration dependent. The stabilizing effect seen in LGP1846 at 0.02% acid would be expected in LGP1845 at some lower concentration and the destabilizing effect that produces a minimum initiation temperature at 1% acid in LGP1845 should produce a similar effect in LGP1846, although at a concentration above 1%. Further study of this phenomenon would be well beyond the scope of the investigation being addressed and has not been pursued.

3.2.2 Ignition and Combustion. Although reaction initiation is only slightly pressure dependent, the HAN-based propellants will generally not ignite and burn at atmospheric pressure (Klein et al. 1977). In order to assure that combustion will follow reaction initiation, pressurization is required and can be achieved either by charging with an appropriate gas prior to conduct of an experiment or by gas production that accompanies the early stages of thermal decomposition. In order that the latter case repeatably results in combustion, a sample loading density for LGP1846 of at least 0.05 g/ml is required. The required loading density for LGP1845 is somewhat lower because energy content is higher and reaction, once initiated, is more vigorous. Thus, at the 0.04 g/ml loading density used to obtain the Table 5 data, it would be reasonable to expect that LGP1846 and possibly LGP1845 not reproducibly exhibit complete combustion when reaction is initiated at atmospheric pressure.

Combustion in the ARC produces a sizable exotherm, involving a temperature rise of approximately 35° together with a rapid pressure increase of about 1 MPa (Klein and Leveritt 1988). When reaction initiation is not followed by ignition and combustion, a series of exotherms associated with decomposition of HAN at about 120°, decomposition of nitric acid at 180°, and the onset of decomposition of TEAN at about 220° are recorded. Both the rate of gas generation and the quantity of gas produced is, of course, much smaller when combustion does not take place.

The datum for LGP1845 in Table 5 shows the onset of an exothermic reaction at 118°. This reaction accelerates rapidly and at 122° the sample burns completely. The heat release rate associated

with this event so far exceeds the capacity of the ARC heaters that the gases generated are able to cool by expansion and heat transfer to the sample container producing a logarithmic cooling curve. A pressure curve obtained from one of these samples including its extrapolated cooling curve (log pressure) is shown in Figure 6.

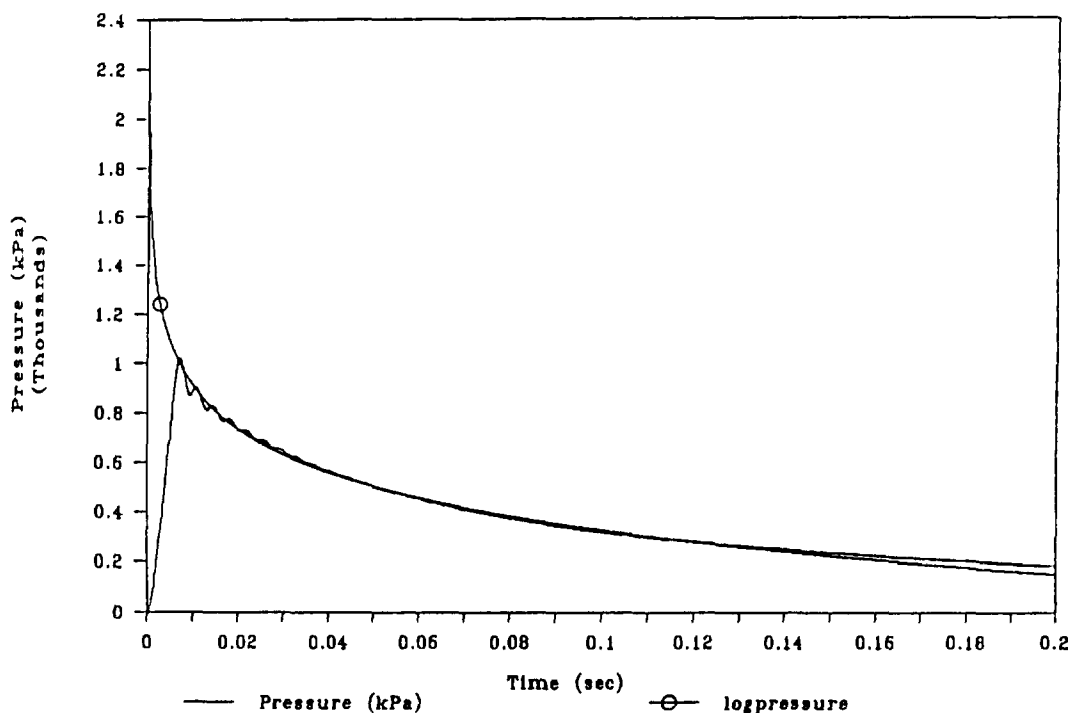


Figure 6. Filtered and Extrapolated Pressure History of the Reaction of LGP1845.

The experimental data shown have been filtered using a 28 Hz wide digital filter centered at 250 Hz (Klein and Leveritt 1988) in order to remove an acoustic resonance. The pressure observed derives from complete combustion of the sample and no additional heat output is measured after this sequence is completed because the contents of the ARC bomblet are  $N_2$ ,  $CO_2$ , and water.

All of the samples in Table 5 with an a or b suffix reacted differently than acid-free LGP1845. In addition to the onset of exothermic activity at a lower temperature, the nature of the exotherms observed reveal that reactions different from those observed in acid-free propellant are taking place. At acid concentrations higher than 0.2%, neither combustion nor the distinct reactions associated with

decomposition of HAN, nitric acid, and TEAN are seen in unpressurized samples. Instead, a low rate of heat production is detected that, in most cases, continues from onset temperature until system shutdown at 225° C. An example of such a reaction sequence is shown in Figure 7.

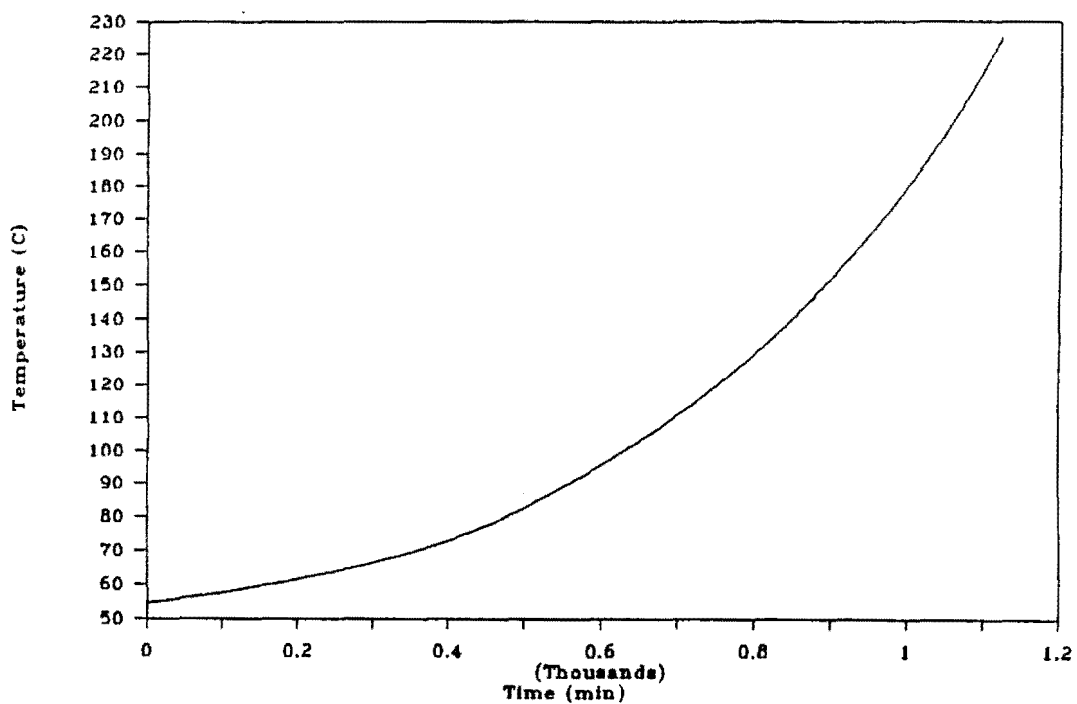
The liquid residues obtained from the samples contain materials in addition to water and it is perfectly apparent that the samples did not react completely. Samples containing 0.2% acid or less did burn when pressurized, although burning was erratic, often producing extended periods of gas generation. Extrapolation of the cooling curves resulted in pressures considerably different from the thermochemically predicted values also indicating that combustion was not complete. An example of such a pressure-time curve is shown in Figure 8.

Whereas the extrapolated pressure at  $t = 0$  in acid-free samples is in good agreement with the thermochemically predicted value, the extrapolated pressure in Figure 8 is clearly impossible because not enough propellant is used to achieve even half this pressure.

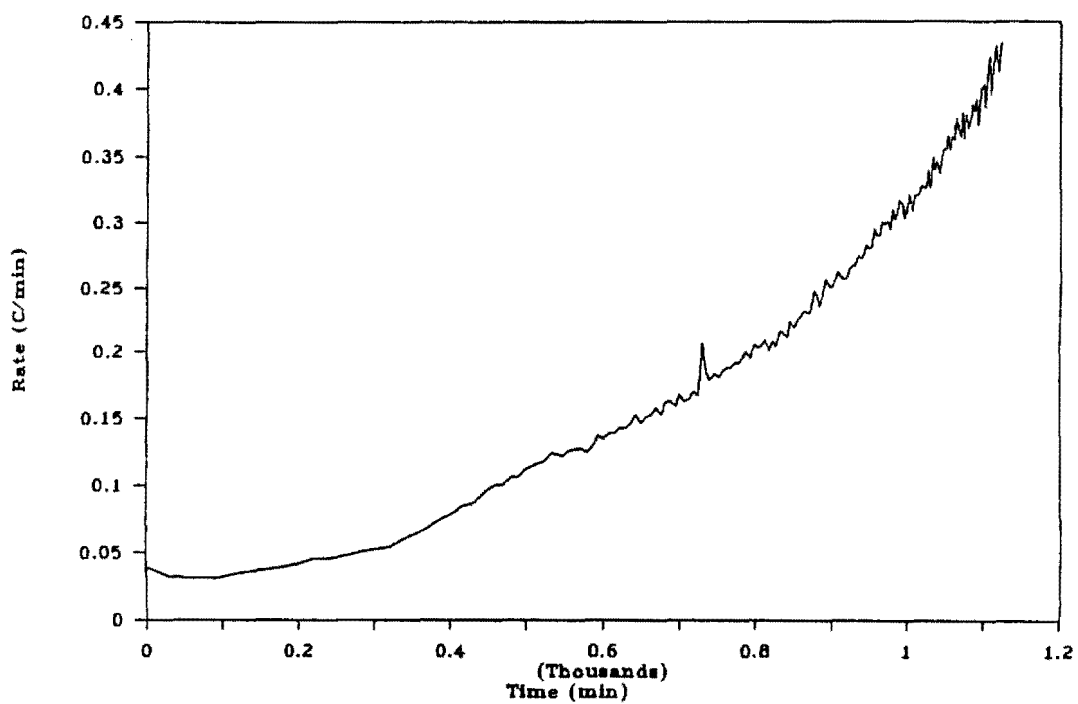
It is interesting to note that the calculations used to obtain the impetus values presented in Tables 2 and 3 indicate that only small changes would be expected when HAN, in part, is replaced by nitric acid. The disagreement between experimental findings and calculations illustrates the important role that reaction kinetics plays in the early stages of propellant decomposition since thermodynamics is independent of reaction path and the calculations assume thermodynamic equilibrium and do not include any kinetics effects.

The LGP1846 samples in Table 5 behave much the same as the acid-free samples. All of the samples produce essentially the same reaction history differing only slightly in reaction onset temperature. It would appear that the presence of very small amounts of acid in LGP1846 does not change reaction mechanism and possibly results in a slight increase in thermal stability. The difference in calculated impetus between an acid-free LGP1846 sample and one containing 0.1% nitric acid is shown in Figure 9. The compositional range is the same as in Figure 3.

The largest difference obtained is 1.5 J/g in approximately 900 J/g or 0.2%. It would appear that LGP1846 containing up to 0.1% nitric acid will be stable in storage and be indistinguishable from acid-free propellant in performance. In fact, the acid-containing propellant should be somewhat more stable.



(a)



(b)

Figure 7. Self-Heating (a) and Self-Heating Rate (b) for Sample 0.5b.

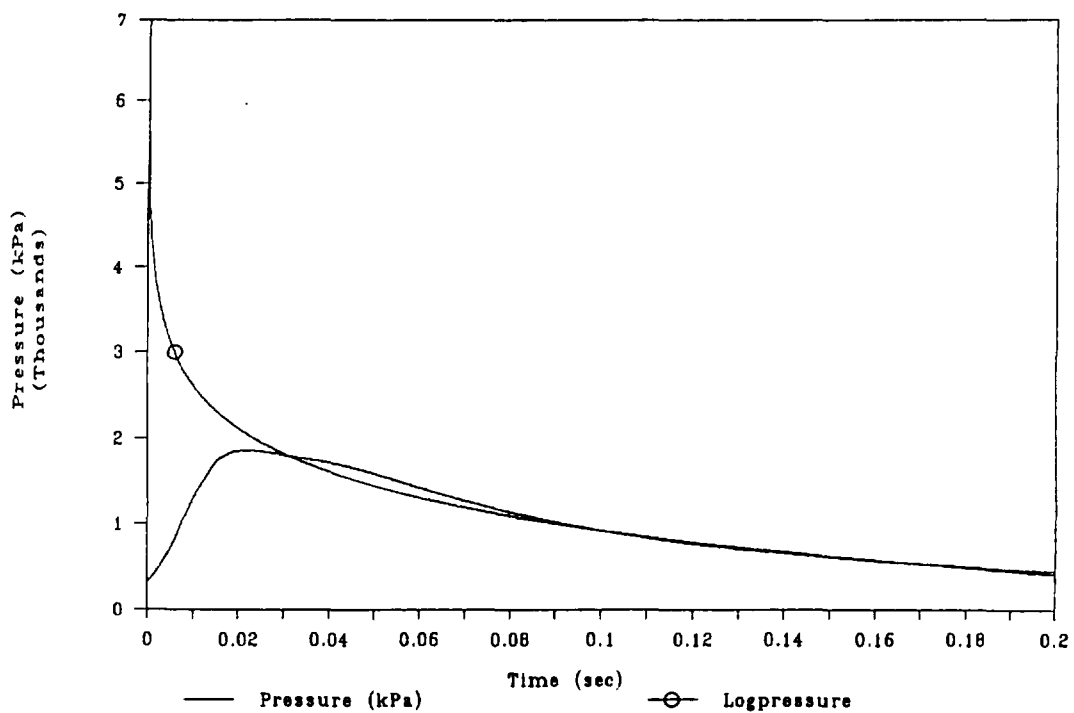


Figure 8. Filtered and Extrapolated Pressure History of the Reaction of Modified LGP1845 (Sample 0.2a).

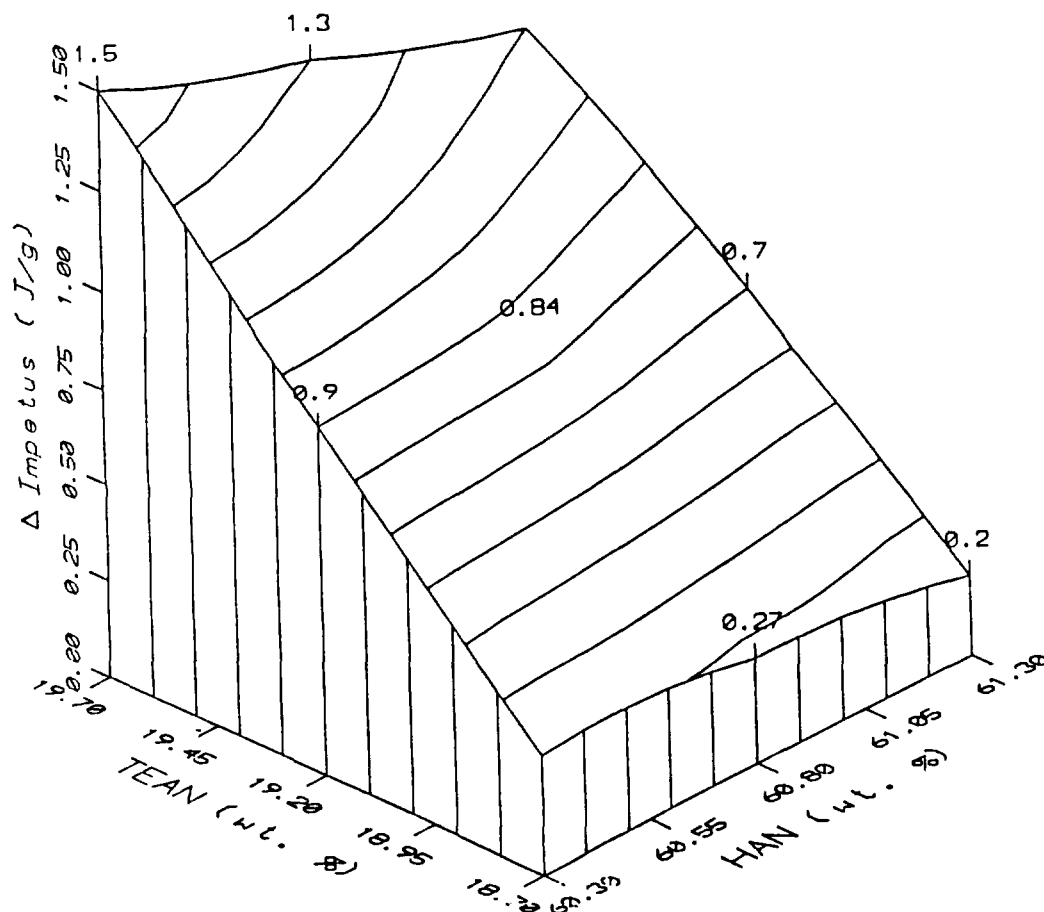


Figure 9. The Effect of 0.1% Nitric Acid on Impetus of Mixtures Containing 20 ± 0.5% Water.

#### 4. PROPELLANT SPECIFICATIONS

No formal compositional specification exists, as yet, for the propellants. The basis for propellant procurement has been essentially "as pure as possible," a clearly inadequate, qualitative specification constrained by analytical capability and cost. The development of a formal specification should, unquestionably, be evolutionary, changing as more complete data becomes available. The ability to analyze components and propellant with accuracy and precision is an intimate aspect of meaningful specification development since it is the basis for acceptance or rejection of the manufactured product.

**4.1 Analytical Capability.** Since a manufacturing specification is meaningless if the concentration of specified components cannot be determined accurately, a variety of analytical methods have been investigated in detail (Klein, Travis, and Biddle 1980; Decker, Klein, and Leveritt 1986; Klein and Wong 1986; Decker, Klein, and Freedman 1986; Decker et al. 1988; Hansen, Backof, and De Greiff 1990). HAN, TEAN, and nitric acid in propellant mixtures can be accurately determined by aqueous acid-base titrimetry. HAN and TEAN are acidic salts, HAN being the more strongly acid of the pair. The equivalence curve obtained upon titration with base does not have the strong inflection characteristic of strong acids and makes it difficult to detect separate endpoints for each of the salts. This limitation is removed by permitting the mixture to react with an excess of acetone prior to titration with base. HAN is thus converted quantitatively to acetoxime and nitric acid, the latter being readily determined titrimetrically. Under these conditions, the nitric acid and TEAN endpoints are sufficiently separated that interference is avoided. The dual titration with and without acetone addition permits accurate determination of HAN, TEAN, and nitric acid. Analytical precision of  $\pm 0.08$  for HAN and  $\pm 0.14$  for TEAN are obtained. Nitric acid in propellant can be determined to within  $\pm 0.003$  and water is accurately determined to  $\pm 0.20$  using Karl Fischer reagent (Sasse 1990). The compositional variations used in Figure 3 are all well within this analytical capability. Trace metal content can be accurately measured to  $\pm 0.1$  ppm using either atomic absorption or inductively coupled plasma spectroscopy.

**4.2 Recommended Composition.** The permissible concentration of trace metal ions in propellant mixtures generally cannot be stated with confidence because the various ions react differently. Ions that have only one stable oxidation state, such as the alkali and alkaline earth metals, will not affect the stability or reactions of the mixtures. Among the metal ions in which multiple oxidation states are common, the course of reaction is so varied that no generalization is possible. The rate of

disappearance of HAN is third order overall, first order in HAN and second order in FeIII, in the example cited in the Introduction. In contrast, the reaction with CuII is second order, first order each in HAN and CuII. In addition, the CuII reaction sequence is not catalytic whereas the FeIII reaction is. It would thus appear that the permissible concentration of CuII in propellant could be considerably higher than FeIII. From the data presented, FeIII in the ppm range will not significantly reduce HAN concentration in stored propellant. This statement is misleading because nitric acid is a reaction product and the 5 ppm FeIII, 65° C example cited will raise HNO<sub>3</sub> concentration 0.02% and could thus affect storage stability. The same reasoning must be applied to other transition metal ions and concentration limits can be relaxed only when the course of reaction is accurately known to be nondetrimental. As a result, it is suggested that the overall concentration of transition metal ions be limited to no more than 5 ppm.

Nitric acid in very small amounts enhances the stability of LGP1846. Great care is required in suggesting a nitric acid concentration since enhanced stability is bounded on both the low and high side. The complete absence of acid should be detrimental as will its presence in excessive amount. Based on the data presently available, a nitric acid concentration of  $0.10 \pm 0.05\%$  is recommended.

No significant change in gun performance should be expected if the water content of LGP1846 varies by 0.5%, a value well within presently available analytical capability. It is therefore suggested that the water content of LGP1846 be  $20.00 \pm 0.50\%$ . This limitation simultaneously establishes limits for the HAN + TEAN content of the mixture but does not limit HAN:TEAN ratio. It is recommended that both HAN and TEAN concentration be determined. Assay for HAN and TEAN individually is readily carried out in propellant mixtures and the resultant data produce both the HAN + TEAN sum and the HAN:TEAN ratio. The nominal HAN:TEAN ratio for LGP1846 is 3.17 and the value recommended is  $3.17 \pm 0.05$ . This range will not compromise performance and is readily obtainable. The set of analytical data obtained from HAN, TEAN, nitric acid, and water determinations is redundant and therefore provides important information regarding the purity of the mixture. Materials other than the four compounds mentioned can find their way into the propellant mixtures if quality control is not carefully maintained; ammonium nitrate is an example that comes to mind. Ammonium nitrate is a product of nitric acid electrolysis if cell voltage is not adequately controlled and its presence, in quantities greater than 0.1%, should have an adverse effect on the low temperature properties of the mixtures. The redundant assay procedure recommended will detect the presence of such an impurity although it will not necessarily identify the offending compound.

## 5. CONCLUSIONS AND RECOMMENDATIONS

Modelling of liquid propellant gun performance using the RLPGUN code provides a basis for specifying compositional limits for LGP1846. These limits are based on mixtures containing only the ingredients HAN, TEAN, and water and are a HAN:TEAN ratio of  $3.17 \pm 0.05$  and a water content of  $20.0 \pm 0.5\%$ .

The experimental data presented leads to the following conclusions:

- (1) The density of HAN-TEAN-water mixtures is affected by the presence of small amounts of nitric acid.
- (2) The presence of 0.02% nitric acid enhances storage stability and does not adversely affect ignition or combustion of LGP1846.
- (3) The presence of nitric acid in excess of 0.1% is deleterious. Thermal stability is reduced, the rate of heat evolution is lowered once reaction has been initiated, and, at higher acid concentrations, combustion is suppressed.

Although the procurement specifications in current use do not call for the presence of nitric acid in propellant and result in product that provides consistent gun performance, it is recommended that manufacturing specifications reflect the effect of small variations in acid content on both storage stability and performance. An acid content of  $0.1 \pm 0.05$  wt.-% is suggested.



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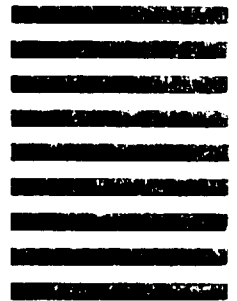


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