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LIQUID PROPELLANTS FOR USE IN GUNS - A REVIEW

Nathan Klein

February 1985

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The use of liquid propellants in guns is reviewed both historically and in terms of the characteristics and properties required of such materials. The physical and chemical characteristics required of propellant formulations is strongly predicated on application in a particular weapons system and, based on such system requirements, the aqueous monopropellants consisting of the nitrate salts of hydroxylamine and an aliphatic, tertiary amine are shown to currently hold the greatest promise for use in a medium-to-large caliber

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artillery gun. Rationale for the selection of these compounds is described and the properties and reactions of these mixtures are discussed. The review does not discuss the gun systems considered but is limited to the propellants, their properties, and reactions.

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I. INTRODUCTION

The concept of a gun using liquid rather than solid propellant is attractive from both theoretical and practical considerations and has thus received serious attention to a greater or lesser degree since World War II.[1] Much of the incentive for consideration of liquids as propellants for guns derived from the greatly enhanced interest in rocketry that developed during and immediately after the war and a history of the development of gun liquid propellants parallels the search for suitable materials to be used in rocket motors.[2] Relatively little consideration was given to the sometimes profound differences between rockets and guns. The majority of the early work dealt with engineering studies of gun systems, attempted to establish ballistic properties, and in most cases were empirical and simply considered the fact that the liquid would contain substantially more energy per unit volume than would a solid propellant. A fair variety of gun concepts were studied, covering a range of complexity from the simple system of a cased liquid charge[3] to the rather esoteric, direct injection of a hypergolic bipropellant mixture into a gun chamber.[4] The usually inadequate consideration given to the properties and characteristics of the propellants in these early studies probably led to the failure of many of these concepts.

Rationale for the development of a liquid propellant gun, as with any new weapons system, must invoke some substantial improvement over systems already in existence. Historically, the use of caseless ammunition, a significant increase in muzzle velocity, and improved logistics, have been the incentives for development of this fairly radical gun concept. Caseless ammunition presents a number of potential advantages to the user since it is more versatile. For example, artillery zoning is controlled by the quantity of propellant metered into the gun rather than by the use of fixed bag charges and is thus infinitely variable. In addition, propellant is shipped and handled in bulk requiring substantially less space both in storage depots and in the vehicle that houses the gun. Commonality of propellant for guns of different caliber is readily obtained. In a vehicle, the propellant can be stowed in tanks of virtually any shape rather than in racks and, of course, cartridge case disposal is non-existent. As to increased muzzle velocity, a matter of considerable importance if the weapon system is to be either a tank or anti-aircraft gun, it was generally felt that the higher energy content available in a number of the propellant formulations considered would translate in some reasonably straight-forward way into increased muzzle

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[1] *W.J. Barr, E.J. Wilson, Jr., et al, "Liquid Fuel Catapult," Experiment, Inc., Richmond, VA, T.P.No.31, 1947.*

[2] *J.C. Clark, Ignition, Rutgers University Press, New Brunswick, NJ, 1972.*

[3] *C.R. Newman, "Investigation of Application of Liquid Propellants to 90 mm Tank Guns," Detroit Controls Corp., Redwood City, CA, Rpt. Nr. RC-184, 1956.*

[4] *B.A. Niemeier, D.L. Swanson, and H.B. Forney, "Liquid Propellant Small Caliber Gun With Repetitive Fire," Experiment Inc., Richmond, VA, T.P.No 58, 1953.*

velocity, an argument-by-analogy to solid propellants. Improved performance in general was frequently cited as an incentive for liquid propellant gun development, but such improvements are sufficiently vague that it could encompass virtually any characteristic considered important to a potential user and will not be addressed until specific propellant formulations are discussed.

Recent successes in gun technology and in the development of suitable propellants have been achieved and a review of these subjects at this time would appear beneficial to the gun community. Gun technology will not be discussed to any extent in this report although it is clearly understood that the liquid propellant for use in a gun is to be intimately linked with the gun system. Liquid propellant gun technology has been reviewed recently[5] and the reader is referred to that publication if detailed information on the subject is desired.

Since discussion is to be limited to gun propellants, two rather elementary constraints can serve to begin such discussion. First, all propellants are defined as self-contained, that is, all of the fuel and oxidizer must be present in the mixture at the time it is to be used, and second, gun propellants should be limited in composition to the elements C, H, O, and N. Although a propellant is self-contained in fuel and oxidizer, the fuel/oxidizer ratio is a major factor in its performance both in a gun and as a material that must be stored and handled. Energy content is near maximum when the ratio of fuel and oxidizer is balanced, that is, when neither material is present in excess, and such mixtures are called stoichiometric. The restriction regarding composition is imposed because the presence of other elements, notably the halogens, sulfur, or phosphorus, in significant concentration, will severely corrode the gun and unacceptably limit gun life. This restriction is not new nor is it unique to liquid propellants, but is of considerable importance in that it rather severely limits choices of propellant components.

One appears to have substantially more freedom in designing and formulating liquid propellants than one has with solids. For example, a bipropellant is a mixture in which the fuel and oxidizer are stored separately and are mixed only at the time of use, whereas a monopropellant is a material in which fuel and oxidizer are combined either as a single compound or as a mixture that, on at least a macroscopic level, is homogeneous. A bipropellant can, if desired, be hypergolic; that is, the mixture, upon its creation, promptly begins reacting so that no igniter is needed in order to fire the gun. Monopropellants cannot, of course, be hypergolic. Since solid propellants are premixed, all solid propellants are monopropellants. There are potential advantages to the use of bipropellants that have resulted in their serious consideration from time to time. Unplanned initiation in storage, either accidentally or as a result of enemy action, is usually a remote possibility and presents little hazard because neither component is

[5] *W.F. Morrison, J.D. Knapton, and M.J. Bulman, "Liquid Propellant Guns," in Gun Propulsion Technology, L.Stiefel, ed., Progress in Aeronautics and Astronautics Series, (in press).*

capable of releasing significant amounts of energy by itself. In contrast, unplanned initiation of a monopropellant, can be quite dangerous. The separation of fuel and oxidizer also permits consideration of mixtures with extremely high energy content. Comparable energy content in a monopropellant is beyond practical consideration because stability generally decreases as energy content increases. Hypergolic bipropellants consisting of hydrazine and hydrogen peroxide,[4] or hydrazine and nitric acid,[6] were examined in the 1950s, showing the strong dependence of this early work on rocketry and, not surprisingly, abandoned because the mixtures were exceedingly difficult to handle and control. Non-hypergolic bipropellants, consisting of nitric acid and various hydrocarbons, have been studied in greater detail and reasonably successful results obtained,[7] although this system was also eventually abandoned. The logistics of a bipropellant system are far more complex since two liquids must be stored, transported, and accurately pumped into the gun chamber and the extremely high energy content achievable is often through use of materials with sufficiently noxious properties as to be practical only in certain unique applications, usually ones in which operating personnel have no direct contact with the gun, such as an aircraft cannon. Although both bi- and monopropellants have been considered for use in liquid propellant guns, the logistic and engineering difficulties associated with bipropellant use are such that present emphasis in liquid propellant development centers almost exclusively on monopropellants and, therefore bipropellants will not be discussed further.

The development of propellants has been evolutionary with understanding slowly acquired as a result of past failures or partial successes. It would seem doubtful at this time that a universal propellant, suitable for use in a number of diverse gun systems, that is, systems with different principles of operation, can be developed in the near future. Active research is presently underway in the area of liquid propellant development and characterization and, although the material presented will be current, it is far from complete.

II. BACKGROUND

Compounds of the elements C,H,O, and N to which discussion is to be restricted, must be considered in terms of their use either as fuel or as oxidizer, or possibly, as both. Carbon and hydrogen are exclusively fuels since any reasonable compound of either of these elements in a propellant composition can only be in form such that both carbon and hydrogen would be oxidized. Oxygen itself can serve as oxidizer either in the form of molecular O_2, an impractical substance in a liquid propellant gun because of the cryogenic requirements associated with the use of O_2 as a liquid, or as hydrogen peroxide which, because of stability constraints and difficulties in handling, is also not a practical material. Thus, the element nitrogen is left as the sole oxidizer source.

[6] *T.M. Broxholm, L.C. Elmore, and W.H. Giedt, "Liquid Propellant Gun Systems," Detroit Controls Corp., Redwood City, CA, RC No. 170, 1955.*

[7] *H.D. Mallory, J. Ballistics, Vol 5, p 1113, 1981.*

A. Nitrogen Chemistry

Nitrogen exists in a total of eight oxidation states in, more or less, stable form, examples of which are shown in Table 1.

TABLE 1. OXIDATION STATES OF NITROGEN

Oxidation State	Examples
−3	NH_3, NH_4^+
−2	N_2H_4, $N_2H_5^+$, $N_2H_6^{++}$
−1	NH_2OH, NH_3OH^+
0	N_2
+1	N_2O, $N_2H_2O_2$
+2	NO
+3	HONO, NO_2^-
+4	NO_2, N_2O_4
+5	HNO_3, NO_3^-, NO_2^+, $R\text{-}NO_3$

With the exception of the −3 and +5 states, nitrogen is capable of both oxidation and reduction. It can, therefore, serve as fuel or as oxidizer as conditions warrant, thereby producing an extremely rich and complex chemistry. As can be seen from the Table, the +5 state, either in its ionic forms as NO_3^- or NO_2^+, or as the nitrate ester, $R\text{-}NO_3$, is readily available to serve as oxidizer. The oxidation states between 0 and +4 present compounds that are either gaseous or not especially stable.

It is not fortuitous that nitrate is the oxidizer of choice since this property causes nitric acid, the parent compound from which the nitrates are made, to be one of the basic industrial chemicals with annual production of 6.9 million tonnes in 1982 in the United States.[8] A variety of HNO_3 concentrations are available, oxidizing ability increasing with increasing concentration. The reason that nitric acid is a powerful oxidizer and that oxidizing ability increases with concentration is because of the dissociation leading to the formation of nitronium ion:

$$HNO_3 \rightarrow NO_2^+ + OH^- \quad . \qquad [1]$$

This dissociation is in competition with the more commonly known acid dissociation:

$$HNO_3 \rightarrow H^+ + NO_3^- \qquad [2]$$

which produces nitrate and accounts for the acidic properties of the acid. The reaction shown in equation [2] is oversimplified and is, in fact, incorrect. The hydrogen ion, commonly written H^+, is always associated with some solvent, usually water, and is never observed as a free proton under conditions in which chemical reactions are usually considered. The equilibrium that is the combination of reactions [1] and [2] is strongly

[8] *Chem. and Eng. News, American Chemical Society, Washington, DC, Vol. 61, No. 18, p 11, 1983.*

influenced by the type and quantity of other materials. The presence, in nitric acid, of a base. of which water is an example, strongly favors reaction [2] whereas the presence of acids, such as H_2SO_4 or P_2O_5, favors reaction [1], a matter that will repeatedly be stressed in much of the discussion of propellant chemistry that will be presented. The corrosivity of the acid is due, in part, to both reactions [1] and [2] with one or the other being dominant under specific circumstances.

Nitric acid itself, although an excellent oxidizer, has virtually no potential for use in a functioning gun propellant. The requirements that it would impose on the system because of its extreme corrosivity to equipment, and the hazard it would pose to personnel is such that its use is essentially dismissed. Nitrates, either as ions, or as nitrate esters in nonionic media are, therefore, the sole potential oxidizers in a liquid propellant formulation.

B. Nitrate Ester Containing Formulations

As previously stated, monopropellants are homogeneous liquids that contain both oxidizer and fuel. The oxidizer of choice is nitrate and the mixture may or may not be miscible with water. Considerations begin with those monopropellants that ar immiscible with water. In such case, the nitrate is present as the nitrate ester of some relatively simple, organic molecule. Molecular weight must be kept low because the material is to be a liquid over a fairly broad temperature range. Examples of the liquid range of several nitrate esters are presented in Table 2.[9]

TABLE 2. PROPERTIES OF SELECTED NITRATE ESTERS

Compound	Molecular Weight	Melting Point (C)	Boiling Point (C)
CH_3-NO_3	77	-82	65 d
$CH_3-CH_2-NO_3$	91	-94	88
$CH_3-CH_2-CH_2-NO_3$	105	---	111
$(CH_3)_2-CH-NO_3$	105	-82	102
$CH_3-CH_2-CH_2-CH_2-NO_3$	119	97	136
$(CH_3-CH_2)(CH_3)CH-NO_3$	119	---	124
$(CH_3)_2-CH-CH_2-NO_3$	119	---	123
$(CH_3)_3-C-NO_3$	119	---	21 (5 mm)
$CH_2(OH)-CH_2-NO_3$	107	<-20	91 (20 mm)
$(CH_2-NO_3)_2$	152	-22.8	199 d
$CH_2(OH)-CH(OH)-CH_2-NO_3$	137	54	155
$(CH_2-OH)_2-CH-NO_3$	137	58	155
$CH_3-CH(NO_3)-CH_2-NO_3$	166	-42	92 (10 mm)
$CH_2-(CH_2-NO_3)_2$	166	-38	108 (10 mm)
$CH_2(OH)-CH(NO_3)-CH_2-NO_3$	182	---	146 (15 mm)
$CH(OH)-(CH_2-NO_3)_2$	182	26	146 (15 mm)
$CH(NO_3)-(CH_2-NO_3)_2$	227	13.5	145 d

[9] *"Encyclopedia of Explosives and Related Items," PATR 2700, U.S. Army Armaments Research and Development Command, Dover, NJ, 1983.*

The nitrate esters do not exhibit the corrosivity of the acid because they are not ionic although the energy of the nitrate group is, to a large extent, retained. This well recognized property leads to their use in solid propellants, liquid and solid explosives, and to their early consideration as liquid propellant ingredients [10,11] As seen from the Table, a limited number of nitrate esters exhibit both sufficiently low freezing point and high boiling point to be used as the pure compounds and most of the formulations considered[12] were mixtures.

Many of the nitrate esters are readily detonable, a trait far less common in ionic nitrates. Possibly, the fact that nitrate esters are unimolecular, covalent compounds relates to their tendency toward detonability. Discrete species migration and combination, both requiring a finite time for completion, is not needed for reaction of these compounds as it is with ionic nitrates. In any case, these materials must be either fairly fuel rich, thus decreasing their sensitivity, or diluted with more or less inert organic material, or both, in order to be used. Either of these courses of action lowers the energy content of the propellant and make this type of material less than an ideal choice for the use intended. In addition, the nitrate esters are physiologically active causing profound changes in cardiovascular function and, in fact, compounds closely related to materials that have been considered are used as drugs. The toxicity of nitrate esters is avoided as a practical matter in solid propellants, in which they are the major, energetic components, either because vapor pressures are extremely low or because the charge is packaged in such manner that the propellant is not handled directly by operating personnel. Since the method of employment envisioned for liquid propellants is fundamentally different, i.e., the use of caseless ammunition, toxicity considerations are far more restrictive and nitrate ester containing mixtures can not be seriously considered as candidate propellants. They have been extensively used in test fixtures, however, because of their ready availability, non-corrosivity, and the fact that many of the parameters that must be determined in detail in the working gun can be determined using this type of formulation. Thus, the propellant OTTO II, which contains propylene glycol dinitrate as a major component, has been employed rather extensively in gun development studies.[13] This mixture is fuel rich in order to decrease detonability and thus does not burn cleanly. Based on the results obtained, it would appear doubtful that a non-aqueous monopropellant could be used in a fielded weapon system.

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[10] *"Evaluation of New Propellants For Liquid Propellant Gun Systems," Redel Inc., North Hollywood, CA, Contract Report No. CPR-4, 1955.*

[11] *"Investigation of Propellant Reactions For Liquid Propellant Gun Systems," Redel Inc., Anaheim, CA, Report on Contract NOrd-12148, 1956.*

[12] *"Discussion of a Cool Burning Flashless Liquid Monopropellant for Fixed Ammunition," Experiment Inc., Richmond, VA, TM-814, 1956.*

[13] *J. Mandzy, I. Magoon, W.F. Morrison, and J.D. Knapton, "Preliminary Report on Test Firing of a 105 MM Regenerative Fixture," Proceedings of 20th JANNAF Combustion Meeting, CPIA Pub. 383, Vol II, p 161, 1983.*

A summary of the discussion to this point indicates that there seems little potential application for either bipropellants or for monopropellants containing significant quantities of the nitrate esters in a liquid propellant gun. This essentially leaves one class of propellants to be considered, namely, the ionic mixtures in which miscibility with water is the common feature. The oxidizer of choice remains nitrate and, in subsequent discussion, the choice of counter-ions for nitrate will be reviewed.

III. WATER MISCIBLE MIXTURES

The aqueous monopropellants are generally ionic mixtures. Nitrate remains the oxidizer of choice but is now used as the nitrate ion, NO_3^-. The nitrate-nitronium equilibrium, discussed earlier, applies to the nitrate ion in much the same way as it does to the acid. A variety of cations can be considered as the counter-ion for NO_3^- with other substances present to give the desired physical and chemical properties to the completed mixture. Since much of the discussion that follows deals with various ionic compounds, it is well to present a brief description of ionic materials in water at this point.

A. Solution Structure

A single crystal of ice at atmospheric pressure is a well ordered structure with an extensive network of hydrogen bonds linking an unshared electron pair of an oxygen atom to one of the hydrogen atoms of a neighboring water molecule. Because of the unshared electron pairs on the oxygen atom, a higher electron density resides in its vicinity and results in a significant dipole moment for the molecule. These hydrogen bonds are substantially weaker than the covalent bonds of the water molecule but are strong enough to profoundly affect the physical properties of the crystal. As the ice crystal is warmed and melts, the hydrogen bonding network is not promptly destroyed but is instead reduced to small groups of molecules called clusters. These clusters give liquid water its unique and rather unusual physical properties. Incidentally, hydrogen bonding is not a phenomenon unique to water and is seen in many organic compounds, accounting, for example, for the relatively high boiling points of alcohols and carboxylic acids.

If ionic material is added to water, the molecules in the immediate vicinity of the ions rotate, orienting either positive or negative dipoles toward the ion depending, of course, on the ion's charge. This arrangement of ions surrounded by dipole oriented water molecules is the structure that one finds in dilute, aqueous solutions. In some cases the attraction of the ion for the solvent water causes disruption of the hydrogen bonding network of the water clusters without creating a more highly organized network. Such ions are called "structure breaking." In other cases, the arrangement of the hydration sphere involves larger numbers of water molecules than existed in the clusters and such ions are commonly called "structure making."[14] As the concentration of ionic material increases, insufficient water remains available to maintain this process and the properties of the mixture change,

[14] *J.L. Kavanaugh, Water and Solute-Water Interactions, Holden-Day Inc., San Francisco, CA, 1964.*

making it difficult or impossible to describe the properties of concentrated solutions by extrapolation from dilute solution data. Much of presently accepted solution theory is based on extremely dilute solutions and fails to account for observed properties of concentrated salt-water mixtures.

If a salt with adequate thermal stability is heated, the salt melts, forming a liquid. Such molten salts routinely have vastly different properties from those of their aqueous solutions. Combinations of molten salts frequently form eutectic mixtures with properties that are not simply the sum of those of their pure components. If a molten salt has a sufficiently low melting point then eutectic mixtures with water can be obtained. In such cases one often can obtain liquids over almost the entire composition range from pure water to pure salt, the liquid state being retained at temperatures well below the freezing points of both pure components.

B. Acid-Base Reactions

Returning now to the aqueous monopropellants, the nitrate anion, serving as oxidizer, must be coupled with one or more suitable cations. Available cations are hydronium and ammonium, either as such or as one of its numerous homologs. The coupling of the nitrate ion with hydronium results in nitric acid, already discussed and dismissed as too corrosive for use in an application that involves the close proximity of operating personnel. Ammonium as the coupling cation produces, in the simplest case ammonium nitrate, NH_4NO_3.

The ammonia molecule contains three covalent N-H bonds and a lone pair of electrons. Protonation of the lone electron pair produces the ammonium ion, NH_4^+. The three covalent bonds are capable of undergoing substitution for the hydrogen, thus producing a variety of compounds, many with chemical and physical properties markedly different from those of ammonia. Replacement of one or more of the hydrogens with carbon results in the amines, a large family of organic compounds, most of which are basic. In addition, an N-H bond can be replaced by N-N forming the hydrazines, or by an N-O forming the hydroxylamines. The limitation that only the elements C,H,O, and N be used in propellant formulation thus still leaves a fair number of compounds to serve as candidates.

A simple description of the reactions of acids with certain types of bases involves the dissociation of the acid:

$$HA + H_2O \rightarrow H_3O^+ + A^- \qquad [3]$$

and the reaction:

$$H_3O^+ + B \rightarrow HB^+ + H_2O \qquad [4]$$

The bases, B, considered in reaction [4] are ones in which an unshared pair of electrons are available for reaction with the hydrogen ion, as, for example, ammonia and its homologs. The ease with which the electron pair attracts the proton is a measure of the strength of the base and the ease with which the acid dissociates is a measure of the strength of the acid. Equilibrium constants exist for both reactions [3] and [4] and the constant pertinent to

equation [4] is defined as:

$$K_b = \frac{[HB^+]\ [H_2O]}{[B]\ [H_3O^+]} . \qquad [5]$$

The species HA, B, and their ions are in equilibrium and the concentrations of the various entities in solution under a given set of conditions is a result of such equilibria. For convenience, the equilibrium constants are often given as pK, where pK = -log K. A list of such values, pertinent to the discussion at hand is given in Table 3.

TABLE 3. BASICITY OF VARIOUS AMINES[15]

Compound	pK_b
$(CH_3-CH_2)_2-NH$	3.07
$(CH_3-CH_2)_3N$	3.28
CH_3-NH_2	3.38
$CH_3-CH_2-CH_2-CH_2-NH_2$	3.39
$(CH_3-CH_2)(CH_3)CH-NH_2$	3.44
$(CH_3)_3C-NH_2$	3.54
$(CH_3)_2CH-CH_2-NH_2$	3.59
$(CH_3)_3-N$	4.20
NH_3	4.76
NH_2-NH_2	6.06
$(CH_2(OH)-CH_2)_3N$	6.24
NH_2-OH	8.04

The table is arranged in order of decreasing basicity. One sees that all of the simple, aliphatic amines are more basic than is ammonia, differences being due primarily to steric effects. The presence of an OH group on the beta carbon of the amine causes triethanolamine, $(CH_2(OH)-CH_2)_3N$, to be 30 times less basic than ammonia and replacement of an amine hydrogen by an OH group causes hydroxylamine, NH_2OH, to be almost 2000 times less basic than ammonia.

A strong acid when reacted with a strong base, results in a mixture that consists almost exclusively of the salt, HB^+A^-. If either the acid, the base, or both are weak, then the result of their mixing could contain significant quantities of the original materials at the expense of the desired salt. Considering that the physical and chemical properties of the starting materials are usually quite different from those of their salts, this latter point becomes far from trivial. Ammonia and its homologs are basic, although to different degrees. Thus, all of these compounds are capable of forming salts with acids and, except for hydroxylamine, these salts would be expected to be stable even if the acids were fairly weak. Since hydroxylamine is a

[15] *"Lange's Handbook of Chemistry," 12th ed., J.A. Dean, ed., pp 5-15, Mc Graw Hill Book Co., New York, 1979.*

very much weaker base than are the other compounds,[16] stable salts would be formed only with strong acids. Attempts to produce the hydroxylammonium salts of the carboxylic acids, for example, fail to give stable products even with formic acid,[17] the strongest acid in this group. All of the bases listed in Table 3 would, however, be expected to yield the appropriate nitrates and, indeed, this is the case.

C. Nitrate Salts as Oxidizers

Resuming the discussion of the nitrates of ammonia and its inorganic homologs, the first of which, the ammonium ion, NH_4^+, leads to NH_4NO_3. This salt melts at 170 C and forms solutions with water to a maximum concentration of approximately 10 mole/liter,[18] the melting point of the salt being too high to permit the formation of eutectic mixtures that are liquid at or near room temperature. At 10 Molar, the concentration of nitrate is not sufficiently high to permit consideration of ammonium nitrate as an oxidizer in the application under discussion.

Turning next to hydrazinium nitrate, $N_2H_5NO_3$, we find a melting point of 62 C,[19] almost adequate for the use being considered, although water-$N_2H_5NO_3$ mixtures would probably solidify at too high a temperature[20] to satisfy requirements for an operational gun propellant. An additional drawback to consideration of $N_2H_5NO_3$ is the fact that it is fairly easily detonated[21] a most undesirable trait. The combination of melting point and detonability would discourage consideration of hydrazinium nitrate as a propellant oxidizer.

The considerations that caused elimination of $N_2H_5NO_3$ also eliminate the dinitrate of hydrazine, $N_2H_6(NO_3)_2$, which has an even higher melting point of 80 C and is more easily detonated than is the mononitrate. This leaves hydroxylammonium nitrate, NH_3OHNO_3, (HAN), as the only remaining inorganic nitrate salt containing only the elements H,O, and N. HAN melts at 48 C,[22] and forms salt mixtures with water that are liquids at room temperature covering a concentration range from almost pure salt to pure water. In addition, HAN-H_2O mixtures show no tendency to detonation covering a range of

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[16] *R.A. Robinson and V.E. Bower, J. Phys. Chem., Vol 65, p 1279, 1961.*

[17] *N. Klein and E. Freedman, "A New Class of Improved Liquid Gun Propellants," Proceedings 1984 JANNAF Propulsion Conference, CPIA Publication (in press).*

[18] *"Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed., M. Grayson, ed., Vol 2, p. 525, J.Wiley Sons, New York, 1978.*

[19] *L.F. Audrieth and B.A. Ogg, The Chemistry of Hydrazine, J.Wiley Sons, New York, 1951.*

[20] *R.P. Seward, J. Am. Chem. Soc., Vol 77, p 905, 1955.*

[21] *L. Medard, Memorial de Poudres (Paris), Vol 34, p 147, 1952.*

[22] *M. Berthelot and B. Andre, Compt. Rendues, Vol 110, p 830, 1890.*

stimuli that exceeds what might reasonably be expected in a gun application.[23] The potential of HAN as a major propellant component is great enough that substantial investigation has been devoted to it.

IV. THE HYDROXYLAMMONIUM NITRATE PROPELLANTS

The use of a HAN-based aqueous system as a gun propellant was first proposed by personnel at the Naval Ordnance Station, Indian Head, Md. Such systems had been developed originally for other applications and the proposed use was not the result of an analysis of the characteristics required but was essentially empirical. The system was sufficiently promising that detailed studies were undertaken. As an understanding of the system developed, modifications and improvements were made based on desired properties and characteristics. At present, properties and reactions of HAN-based propellants are sufficiently understood that mixtures, to a large degree, can be tailored for specific purposes.

HAN, the nitrate salt of hydroxylamine, possesses many of the chemical properties of its parent compounds, although few, if any, of their physical properties. Hydroxylamine is ammonia with one of the hydrogens replaced by OH. The electronegativity of the hydroxyl group, relative to the hydrogen it replaces, accounts for the markedly decreased basicity of hydroxylamine. This decreased basicity causes HAN-water mixtures to be considerably more acidic than are NH_4NO_3 mixtures of comparable concentration. Hydrogen-bonding between the OH group and solvent water may also contribute to the extremely high solubility of HAN.

Hydroxylamine can be viewed as a cross between hydrazine, NH_2-NH_2, and hydrogen peroxide, HO-OH, and indeed, its chemical properties are much as one would expect from such a hybrid, having some of the oxidizing character of the peroxide and some of the reducing character of hydrazine. NH_2-OH is a much weaker oxidizer than is nitrate and reactions of NH_3OH^+ and NO_3^- show oxidation of NH_3OH^+ and reduction of NO_3^-. HAN-water mixtures are, therefore, monopropellants:

$$NH_3OHNO_3 \rightarrow N_2 + 2H_2O + 2O_2 \qquad [6]$$

although rather poor ones because of their excess oxygen content and additional fuel is needed to extract the energy available from the system. Equation [6] does not represent the chemistry of the system. Products obtained from various experimental studies include all of the oxides of nitrogen as well as NH_4^+ and indicate an extremely complex sequence of reactions.

The fuel selected for use with HAN should not compromise the excellent physical properties of the HAN-water system and be totally compatible with it. Compounds of choice for this purpose are the nitrate salts of simple,

[23] *W.J. Cruice, "Classification of Liquid Gun Propellants and Raw Materials for Transportation and Storage," ARBRL-CR-00454, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, Md., 1981. (AD A100 729)*

aliphatic amines. Since such amines are somewhat more basic than ammonia, their nitrate salts are expected to be highly ionized and not subject to hydrolysis to any significant extent. Saturated, aliphatic functional groups are also sufficiently insensitive to oxidation that their presence would not be expected to compromise the stability of the mixture under normal handling and storage conditions.

A. Thermochemistry of the HAN Propellants

Thermodynamics has been applied to the study of propellants for many years[24,25] and plays a major role in interior ballistics modelling. Since discussion is to be limited to propellants and their properties, only a portion of such models, namely the closed chamber approximation, will be used, where it is assumed that a sample of propellant is placed in a chamber of known volume and burned. Impetus, flame temperature, pressure, the chemical composition of the products and their average molecular weight, among other valuable data, are calculated. The HAN-based propellants have all been evaluated using the BLAKE code.[26]

The ratio of fuel-to-oxidizer in any propellant is a major factor in its performance and such is also the case for the HAN-based propellants. An example calculation of the effect of varying this ratio on impetus, where the fuel is an aliphatic ammonium nitrate, is presented in Figure 1. The Figure also shows the effect of varying water content. Maximum impetus is obtained on the fuel-rich side of stoichiometry. The use of HAN and the nitrate salt of an aliphatic amine results in stoichiometry according to the following general equation:

$$\left(\frac{3n-1}{2}\right) N_2H_4O_4 + C_nH_{(2n+4)}N_2O_3 \rightarrow nCO_2 + \left(\frac{3n+1}{2}\right) N_2 + (4n+1)\ H_2O \qquad [7]$$

where n is the number of carbon atoms in the aliphatic amine. It occurs in the example calculation when the HAN/fuel ratio is 4 because the value of n used was 3.

[24] *C. Cranz, Lehrbuch der Ballistik, Vol 2, J.Springer Verlag, Berlin, 1926.*

[25] *J. Corner, Theory of the Interior Ballistics of Guns, pp 35-129, J.Wiley and Sons, New York, 1950.*

[26] *E. Freedman, "BLAKE, a Ballistic Thermodynamic Code Based on TIGER," Proceeding of International Symposium on Gun Propellants, 1973.*

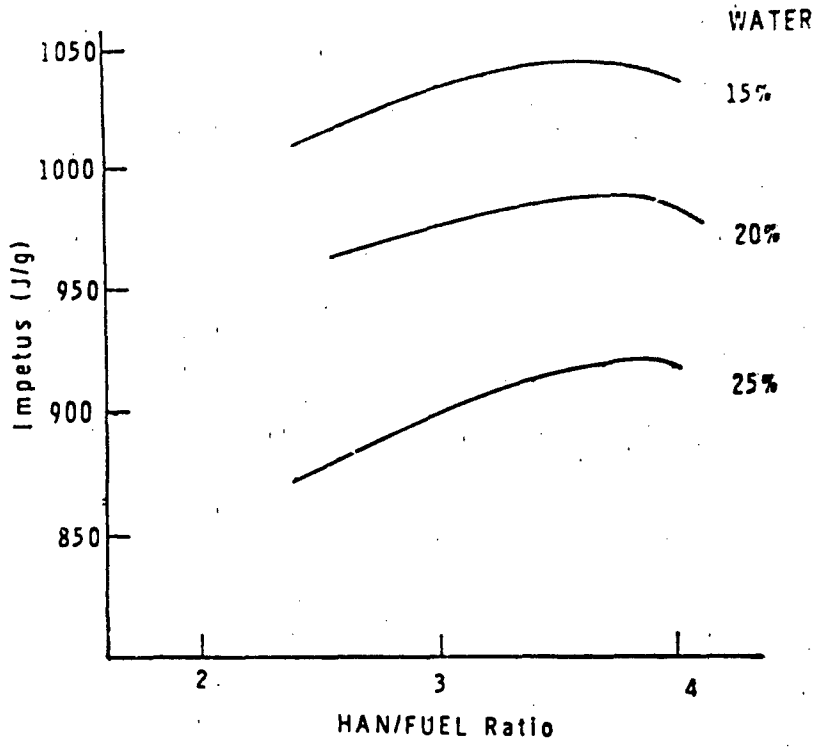

Figure 1. Calculated Impetus As A Function Of Stoichiometry And Water Content

Although not shown in the Figure, the calculations also indicate that propellants formulated in accordance with equation [7] will have essentially the same flame temperature and impetus regardless of the structure of the amine used or of the value of n. Impetus is proportional to the pressure, volume, and temperature of the product gases. It thus follows that a propellant that generates hotter gases, or gases with a lower average molecular weight will produce higher impetus values. The matter is substantially more complex than would be inferred from this rather simple statement. One observes from the calculation that impetus values are strongly dependent on water content. For the most part, the water is considered in the calculation as in inert diluent so that it would be reasonable to expect that impetus decreases with increasing water content. A more critical inspection of the data reveals that not only is maximum impetus always obtained when the mixture contains a slight excess of fuel, but that the fuel/oxidizer ratio at maximum impetus is also dependent on water content. One can assume that a decrease in oxidizer/fuel ratio causes a decrease in the average molecular weight of the product gases because fuel-rich mixtures favor the production of carbon monoxide and hydrogen, rather than carbon dioxide and water (the "water-gas" reaction), and thus, maximum impetus appears on the fuel rich side of stoichiometry for these, as for almost all, propellants. This, however, should not cause the location of the maximum impetus value in Figure 1 to be water dependent. The water apparently plays a larger role than that of an inert diluent, acting possibly as a heat absorber and thus lowering the

temperature of the product gases, or possibly, that the water-gas equilibrium is disturbed by the presence of additional water. The combination of these various effects is neither readily predicted nor easily explained.

In addition to making near maximum impetus available, stoichiometry provides a number of other desirable characteristics. Since no excess fuel is present in the mixture, the combustion products venting from the gun are not combustible and therefore little or no secondary muzzle flash and blast is expected. There has been a rather severe penalty for attempting to achieve stoichiometry in solid propellant formulations, or in liquid formulations containing nitrate esters, namely that such formulations tend to be shock sensitive and detonable. Since shock sensitivity or detonability are not, a priori, conditions associated with stoichiometry for all systems, there is no reason to require that aqueous liquid propellants be fuel rich. Indeed, HAN-based, stoichiometric, formulations give no indication of detonability under conditions that could reasonably be expected in a gun environment.[23]

B. Fuel Components

Mixtures of HAN with specific fuels can be easily prepared since the components are miscible in almost all proportions. Stoichiometry fixes the oxidizer/fuel ratio but the water content is determined by the desired properties of the mixture. A water content below 5% by weight is generally not considered practical because the temperature range over which the mixture will remain liquid will be too small. Virtually any amine can be used as the fuel source. Aromatic amines are not sufficiently reactive to be seriously considered and the quaternary ammonium salts have been found to be almost totally unreactive in formulations of the HAN type. Heterocyclic amines could potentially serve as fuels but have not been thoroughly investigated at this time. The aliphatic amines, the basis of the formulation described in equation [7], have been investigated and are the fuels of choice at present. These compounds form stable nitrate salts only if the molecular weight of the amine is fairly low. As the number of carbon atoms in the aliphatic chain increases, the salts tend to become thermally unstable, undergoing internal oxidation-reduction and producing tars and heavy oils. There is no reason, a priori, to restrict the presence of functional groups on the aliphatic amine. In fact, a formulation containing the nitrate salt of triethanolamine is currently in use. Equation [7] is, of course, not applicable if such functional groups are present.

There are no physiological hazards presented from the HAN-based propellants other than by ingestion, a rather minor risk in that it would seem reasonable to discount the probability that operational personnel would drink these liquids. The propellants are miscible with water in all proportions and are biodegradable[27] so that disposal presents no unique problem.

[27] *D.L. Kaplan, D.J. Emerson, P. Riley, and A.M. Kaplan, "Decomposition of Four Ammonium Nitrate Propellants," NATICK/TR-83/045, U.S. Army Natick Research and Development Center, Natick, MA, 1983.*

The required characteristics of propellants are determined by their intended use and physical properties must be consistent with these characteristics. The physical properties themselves, however, are determined by the materials that comprise the formulation and cannot be changed unless the formulation is changed. Thus, it becomes necessary to identify a specific formulation before its physical properties can be described. Some general statements relevant to all HAN-based formulations can, however, be made. The presence of the OH group in the hydroxylammonium cation will encourage hydrogen bonding with the water present thus increasing the "structure" of the mixture. This, in turn, should increase miscibility with water and discourage crystallization at low temperature producing instead, amorphous glasses, if the temperature is low enough. A disadvantage associated with such hydrogen bonding would be an increase in viscosity, a point to be seriously considered if OH groups are also to be present in the aliphatic amines that comprise the fuel.

A second, general point, is that formulations sufficiently energetic for practical application will have insufficient water to permit the formation of normal hydration spheres around the ions present and therefore result in properties unpredictable from studies of the same ions in dilute solution. In fact, salt concentrations will be high enough that a proper description of the system will be a low temperature salt melt rather than a solution. Since hydrolysis of the salts is not expected, the concentration of nitric acid or of the free amines will be vanishingly small and the vapor pressure of the mixtures is expected to be approximately equal to the partial pressure of the water present, a prediction that is confirmed experimentally.

V. PROPELLANT CHEMISTRY

Generally, propellant chemistry means the reactions and products of three aspects of decomposition: ignition, combustion, and thermal stability, each with pertinent subdivisions. Ignition is usually the sequence of events that makes decomposition self-sustaining. It often leads to combustion which results in the final products observed. The majority of the energy is released during combustion and both chemical and physical processes are drastically different from those found during ignition. The ignition phase involves a liquid of chemical composition similar to that of the starting material, whereas combustion involves primarily gases that contain significant concentrations of unstable transient species. Physically, the ignition phase involves pools, droplets, or sprays with reaction taking place at or near the surface, since a definable surface still exists at these early stages of reaction and heat transfer from the reaction zone back into the propellant is an important means of reaction rate control. In contrast, combustion is probably controlled by species diffusion in hot gases at rather high pressures. When increasing pressure accelerates reaction rates, reaction zones become smaller and the complexity of the reacting system makes even qualitative descriptions nebulous at best. An important part of the ignition process (or processes) is often reaction initiation, the stimulus that starts an observable chemical change. Initiation differs from ignition in that the requirement for self-sustaining decomposition is absent. This seemingly small difference is quite important from an experimental viewpoint because reaction quenching either by dilution or by cooling can permit reaction products to be isolated and identified. Initiation studies also make possible detailed investigation of activation energy, the minimum input stimulus required for

reaction. If such stimulus is thermal, then initiation studies provide information relating to thermal stability.

A. Experimental Studies

One fairly simple method to investigate initiation processes and study the effects of compositional changes on the ignition of HAN mixtures is by use of a small, high-pressure hydrogenation apparatus consisting of a 50 cm^3 ANSI 316 stainless steel bomb, a furnace, and associated gas handling hardware. Propellant sample size is restricted to 2 ml or less because maximum safe operating pressure of this bomb is approximately 69.9 MPa (10,000 psi). The furnace is capable of heating the bomb and sample uniformly to about 250 C at rates up to 10 C/min. Although the apparatus creates a set of experimental conditions quite far removed from those to be found in a gun, the conditions are highly reproducible and readily selected, thus simplifying data collection and evaluation. The bomb is normally equipped with a piezoelectric pressure gauge which records the rate of gas evolution when the sample has been heated to reaction initiation temperature. Reaction products, either gases, liquids, or solid residues can be sampled for analysis, and mass accountability obtained. The effect of reactant concentration on reaction initiation temperature, obtained with this apparatus, is shown in Figure 2.

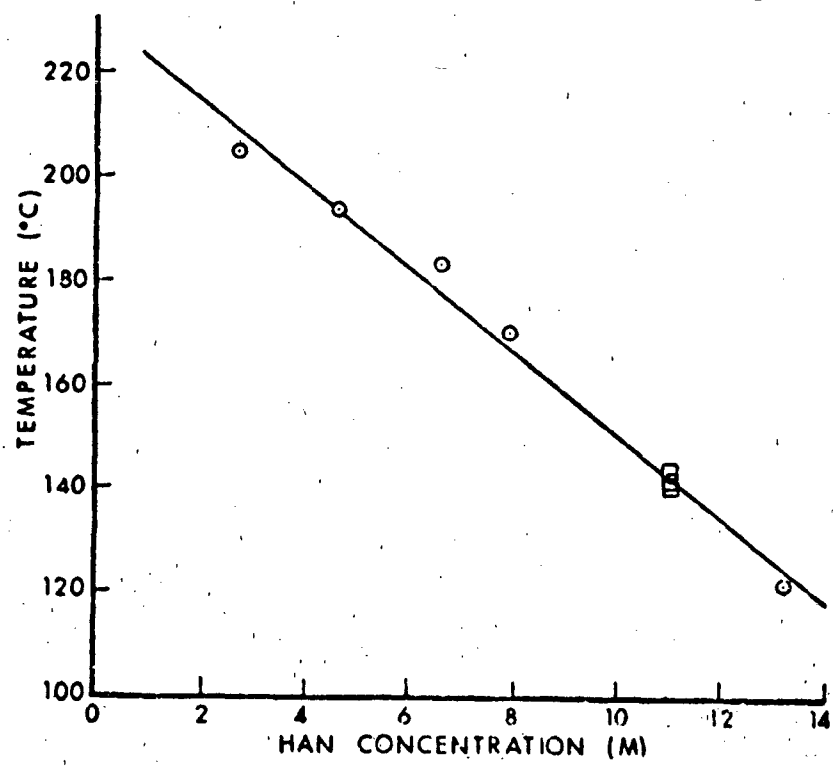

Figure 2. Reaction Initiation Temperature Of HAN Solutions

The Figure presents the initiation temperature of HAN-water mixtures as a function of concentration. Although the data seem to indicate that initiation temperature decreases linearly with increasing HAN concentration, it would be doubtful that this is the case, there being no basis in theory to support a linear relationship. The relationship is probably exponential, linearity

appearing as an excellent approximation over the range of concentrations studied. In fact, initiation temperature is a function not of HAN, but of nitrate concentration, since propellants containing various aliphatic ammonium nitrate salts begin to decompose at precisely the same temperature as does HAN of equal nitrate content. Ignition is more complex than reaction initiation since the observation of self-sustaining reaction is also dependent on a number of physical phenomena such as droplet concentration, residence time, heat transfer, etc.

The nitrate-nitronium equilibrium, first mentioned in equations [1] and [2] appears to be the critical parameter in the initiation of HAN-based propellants and any method whereby the nitronium concentration is increased, caus s initiation of the reaction sequence. The critical NO_2^+ concentration is essentially independent of formulation but is dependent on the experimental conditions employed so that extrapolation to different conditions is difficult. Since the nitrate-nitronium equilibrium can be shifted by a wide variety of stimuli, such stimuli can be used, either singly or in combination, as propellant igniters. A number of materials such as NO_2, P_2O_5, and concentrated H_2SO_4 drive the equilibrium toward NO_2^+ and can thus cause ignition without thermal input. Stable nitronium salts exist and the addition of small quantities of such salts as nitronium flouorophosphate or fluoroborate very effectively ignites the propellant. An increase in temperature increases the nitronium concentration and, when a critical level is attained, decomposition becomes self-sustaining, since the decomposition is exothermic.

A special comment regarding initiation by NO_2 is called for since it ralates directly to the storage stability of these formulations. The oxides of nitrogen, including NO_2 and NO, are decomposition products of HAN and NO is promptly converted to NO_2 in the presence of air. Thus, decomposition of these mixtures, when stored in sealed containers, will accelerate unless some means are provided for the removal of these gases.

The passage of an electrical current through these conducting mixtures causes, in addition to the expected ohmic heating of the mixture, ion migration, with NO_3^- moving to the anode. In the vicinity of the anode, NO_3^- concentration increases thus causing an increase in NO_2^+ and, as might be expected, reaction initiation is observed.[28] If electrical energy is supplied as a high-current pulse, a plasma arc forms and the interaction of propellant with the plasma arc results in a variety of rather complex physical and chemical processes,[29] a number of which are presently under investigation. The plasma arc presents a high temperature, high pressure stimulus to the propellant in addition to the chemical changes induced by the passage of the electrical current, and the combined stimuli produce dramatically different

[28] *N. Klein, F.J. Weinberg, and F.B. Carleton, "Ignition Phenomena in Energetic Liquids," ARBRL-TR-02514, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1983. (AD B077 357L)*

[29] *N.Klein, "Liquid Propellant Ignition Studies," Proceedings of 20th JANNAF Combustion Meeting, CPIA Pub. 383, Vol 1, p 473, 1983.*

effects from those observed when the stimuli are delivered singly. Ignition of propellant by pulsed plasmas is currently being considered for use in a liquid propellant gun[30] because it offers a number of advantages over other techniques. Pressure, in the absence of heating, does not induce reaction, even at values greater than 700 MPa.[31]

B. Effect of Fuel Structure on Reaction Rate

A second set of data, obtained with the small pressure vessel, is shown in Figure 3 which presents the rate of gas evolution from a group of HAN-aliphatic ammonium nitrate (AAN) mixtures that differ only in the chemical structure of the aliphatic amine used.

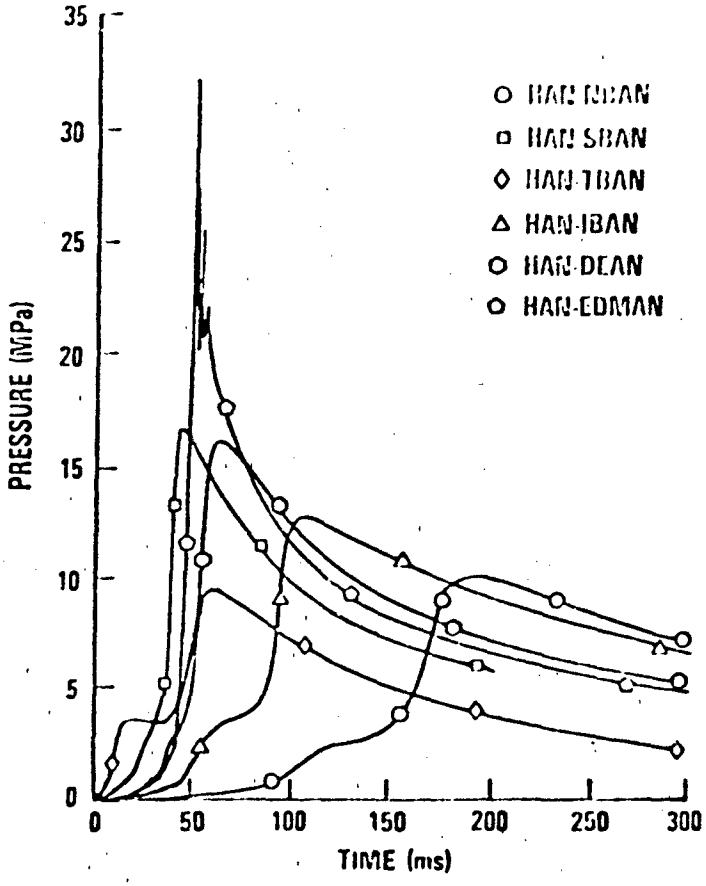

Figure 3. Gas Evolution Rates For HAN-C_4AAN Mixtures

[30] *N. Klein, F.B. Carleton, and F.J. Weinberg, "Methods for Evaluation of Ignition Stimuli for Liquid Propellants," Proceedings of 19th JANNAF Combustion Meeting, CPIA Pub. 366, Vol 1, p505, 1982.*

[31] *C.A. Van Dijk, "Characterization of Hydroxylammonium Nitrate at Various Pressures and Temperatures," Geo- Centers, Inc., Newton Upper Falls, MA, Rpt GC-TR-83-266, 1983.*

The mixtures used to obtain the Figure 3 data all are 11 Molar in nitrate concentration, are stoichiometric, and consist of HAN, water, and one of the AAN salts that have the empirical formula $C_4H_{12}N_2O_3$, of which eight exist.[32] The amines that produce these salts are listed in Table 4.

TABLE 4. THE C_4 ALIPHATIC AMINES

Amine		Density ($gm\ cm^{-3}$)	Boiling point (deg C)
$CH_3-CH_2-N-(CH_3)_2$	(EDMA)	0.67	36-37
$(CH_3)_3-C-NH_2$	(TBA)	0.693	44-46
$(CH_3)_2-CH-NH-CH_3$	(MIPA)	0.703	50
$(CH_3-CH_2)_2-NH$	(DEA)	0.704	55-56
$CH_3-CH_2-CH_2-NH-CH_3$	(MPA)	0.720	62-64
$(CH_3-CH_2)(CH_3)CH-NH_2$	(SBA)	0.724	63-65
$(CH_3)_2-CH-CH_2-NH_2$	(IBA)	0.773	67-69
$CH_3-CH_2-CH_2-CH_2-NH_2$	(NBA)	0.740	76-78

Ethlydimethylamine (EDMA) is a tertiary amine, diethylamine (DEA), methylpropylamine (MPA), and methylisopropylamine (MIPA) are secondary amines, and normal (NBA), secondary (SBA), tertiary (TBA), and isobutylamine (IBA) are primary amines. All form stable, white, crystalline, nitrate salts that are very soluble in water.

Reaction initiation temperature for the six mixtures shown in Figure 3 is constant and is the same as that required to initiate reaction in 11 Molar HAN under the same conditions. Although no differences are observed for reaction initiation, the results indicate significant differences in the ignition and combustion chemistry of propellants containing salts of tertiary amines compared with that observed in mixtures containing either primary or secondary amines. The fact that the AAN salt plays essentially no role in reaction initiation but is of considerable importance in determining the rate of energy release during combustion has profound consequences in designing propellant formulation since it becomes possible to tailor the rate of energy release without changing either the energy content of the mixture or the conditions required for ignition.

If reaction initiation is permitted to take place under conditions that do not permit a significant increase in pressure, then reactions usually do not continue to completion. The products and residues obtained indicate the reaction sequences that took place. At the earliest stages of reaction, gaseous products are exclusively nitrogen and its oxides NO_2, NO, and N_2O. No carbon containing products are obtained and all of the AAN salt is recovered from the liquid residue. These results indicate that only the HAN is undergoing decomposition, the reactions being both the internal oxidation-reduction of the hydroxylammonium ion, the oxidation of the ion by nitrate and

[32] *N. Klein, "Preparation and Characterization of Several Liquid Propellants," ARBRL-TR-02471, US Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 1983. (AD B071 589)*

the reduction of the NO_3^- ion. The residue from these early reactions is substantially more acidic than is the starting material, indicating formation of the hydronium ion as a reaction product. This is not surprising since the nitrate concentration originally present is sufficient for total oxidation of the mixture which, of course, has not yet occurred.

If reaction is permitted to proceed, the carbon containing ions become involved and a variety of organic products are obtained, the composition of which is dependent on the structure of the amines used originally. Primary amines are deaminated, producing the appropriate carbonium ion which then undergoes stepwise oxidation yielding first, alcohols:

$$R\text{-}NH_3^+ \rightarrow R^+ \rightarrow R\text{-}OH \quad . \qquad [8]$$

If the alcohol is on a primary carbon, the corresponding carboxylic acid is obtained:

$$R\text{-}OH \rightarrow (R\text{-}1)\ CHO \rightarrow (R\text{-}1)\ COOH \qquad [9]$$

whereas a secondary alcohol produces the expected ketone:

$$R_1\text{-}C\text{-}OH\text{-}R_2 \rightarrow R_1\text{-}CO\text{-}R_2 \quad . \qquad [10]$$

Both the acids and ketones are sufficiently unreactive that they can be recovered as intermediate products. When they finally become involved in the reaction sequence, conditions are usually sufficiently severe that reaction goes to completion and the only products obtained are N_2, CO_2, and H_2O. Tertiary amines cannot undergo deamination, although carbonium ions are formed, and early reaction products are instead the nitrosamines:

$$R_1R_2R_3NH^+ \rightarrow R_1R_2N\text{-}NO + R_3^+ \quad . \qquad [11]$$

Thus, trimethylamine produces dimethylnitrosamine, triethanolamine produces bis (2-hydroxyethyl) nitrosamine, and ethyldimethylamine gives both methylethylnitrosamine and dimethylnitrosamine. The carbonium ion, R_3^+, reacts according to Reaction [8]. Secondary amines appear to undergo deamination and the reactions observed are similar to those obtained with primary amines. The consequences of the difference in reaction path for the tertiary amines is important in terms of the rate of gas generation during the very early stages of combustion.

If the sample is contained, so that the evolved gases can cause a significant increase in pressure or, if the original sample container is at elevated pressure, the reaction sequence continues and the final combustion products are obtained. The mode of transition to the combustion phase and the rate of gas evolution are dependent on the structure of the AAN salt used in formulating the mixture since the nitrosamines and their oxidation products, the nitramines, are much less stable than are carboxylic acids and ketones and therefore decompose more readily. No build-up of intermediate products takes place resulting in a smoother rate of gas generation without the "steps" seen in the primary and secondary amine mixtures. This is clearly illustrated in Figure 3. Analysis of chamber residue and comparison of observed and calculated peak pressure both indicate that reaction proceeded to completion in the mixture containing the tertiary ammonium salt. This was not the case for the other mixtures.

A word of caution is in order regarding the use of thermodynamics for the prediction of propellant performance. Since energy content is the same for all of the mixtures shown in Figure 3, thermochemical calculations predict no difference in performance. The various thermochemical codes produce results based only on thermodynamics, kinetics of reaction not being considered. The weight assigned to such results should, therefore, be kept in proper perspective, to wit, negative findings bode badly for the system being evaluated but favorable results give little or no indication that the system will perform satisfactorily.

In addition to the example of the AAN isomers just presented, an example of historic interest is a propellant mixture consisting of hydrazine, hydrazinium nitrate, and water.[33] This formulation received a great deal of attention[34-36] because of its unique thermodynamic properties. The system is compounded to achieve stoichiometry, vis.:

$$4N_2H_5NO_3 + N_2H_4 \rightarrow 7N_2 + 12H_2O \qquad [12]$$

water being added to control the energy content and to create more acceptable physical properties. This propellant is unique among the monopropellants in that it contains no carbon. Normally, at stoichiometry, the only product gases from combustion of a propellant containing carbon would be N_2, H_2O, and CO_2, with CO_2 having, by far, the highest molecular weight. Since impetus is closely related to the average molecular weight of the product gases, it would be expected that N_2H_4-$N_2H_5NO_3$-H_2O mixtures be very efficient in transferring energy to a projectile. In addition, calculations indicated that these mixtures would have unusually low flame temperatures thus improving gun life. Unfortunately, the same mixture presented such poor performance with regard to the rate of energy release, in addition to poor thermal stability and extreme toxicity, that it could not be seriously considered.

Mention has been made of the fact that the HAN-based propellants do not react to completion unless pressurized. Thermal initiation temperature is the safe storage and handling limit of the mixture, which is 120 C when water content is approximately 20%. If the mixtures are stored and shipped in

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[33] *R.D. Dwiggins, H.M. Sternberg, and D. Bosco, "Investigations of Mixtures of Hydrazine, Hydrazine Nitrate and Water," NAVORD Report 2787, Naval Ordnance Laboratory, White Oak, MD, 1953.*

[34] *M.J. Evans, F.I. Given, and D.G. Doran, "Ignition and Combustion Properties of Liquid Monopropellants," Report for Contract DA 04-200-ORD-320, Poulter Labs, Stanford Research Institute, Menlo Park, CA, 1956.*

[35] *"Nozzle Erosion, Burning Characteristics, Covolume and Impetus of Liquid Propellants," Report on Contract DA 11-022-ORD-1157, Armour Research Foundation, Chicago, IL, 1955.*

[36] *S. Wise, G. Beichler, and J. Dykstra, "The Vulnerability of Hydrazine Based Liquid Monopropellants When Attacked By a 3.5 IN M28A2 Heat Round," BRLMR 1006, Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1956. (AD 101 031)*

containers that do not permit pressurization, then only a small portion of the available energy would be released if accidentally initiated, and thus hazards associated with propellant handling are greatly reduced. Numerous attempts to obtain combustion at atmospheric pressure, under a wide variety of conditions, have consistently failed to achieve more than a partial decomposition of the fuel component.

Attack by shaped charges or by hot spall fragments presents a hazard that is related to, but not the same as, thermal initiation. The rate at which energy is transferred to the propellant is markedly different in these cases, a matter of major importance. Presently available data are incomplete, but appear to indicate that the HAN-based propellants can be caused to undergo substantial decomposition when attacked in such manner although detonation has never been observed.

C. Effects of Impurities on Stability

Thermal stability, as discussed to this point, applies to mixtures that, within detectable limits, are pure. An additional consideration that affects propellant stability is the role of impurities in initiating decomposition. One such impurity would be an acid since it has already been shown that the presence of acids drives the $NO_3^- - NO_2^+$ equilibrium toward NO_2^+ and hence facilitates reaction initiation. Thus, although the mixtures are somewhat acidic, the presence of excess acid would adversely affect stability.

HAN-based propellants are ionic and contain both oxidizing and reducing species. As would be expected, they react readily with a wide variety of materials many of which could find their way into the mixtures as impurities. Of cardinal importance in this regard are the salts of the transition metals, notably iron, copper, and nickel. The reactions of such salts should not be confused with the reactions of the metals themselves, although both are important. The effect of transition metal ions on the thermal stability of HAN-AAN mixtures has been studied[37] and, generally, the presence of such impurities in low concentrations tends to lower the stability of the mixture. The effects are quite complex, however, behavior being dependent on the particular metal present. The ferric ion, Fe^{3+}, acts as a catalyst, lowering the activation energy required for initiation of HAN decomposition. The reactions observed are the reduction of Fe^{3+} to Fe^{2+} by NH_3OH^+, followed by oxidation of the Fe^{2+} to Fe^{3+} by NO_3^-. Reaction products are N_2 and N_2O exclusively and reaction proceeds at a constant rate until essentially all of the HAN is destroyed.

In the case of the cupric ion, Cu^{2+}, both reaction mechanism and the products obtained are drastically different. This transition metal ion does not show catalytic action because, although Cu^{2+} is reduced to Cu^+ by NH_3OH^+, the complex ion formed is not reoxidized by NO_3^-. Thus, reaction rate decreases as Cu^{2+} is depleted and decomposition would eventually stop. It happens, however, that NO is a reaction product together with N_2 and N_2O. The

[37] *N. Klein, "Liquid Propellant Stability Studies," Proc. 15th International ICT Conference on Technology of Propellants and High Explosives, 1984 (In press)*

NO formed would be converted to NO_2 by reaction with air and then facilitate decomposition of the mixture even as the adverse effect of the Cu^{2+} impurity was decreasing by its removal.

The transition metal ions in question are always present in these mixtures as complexes and the reactivity of such complexes is strongly dependent on the ligands involved. As an example of such dependence, the tetraaquo complex of Cu^{+} is readily oxidized by nitrate whereas various amino complexes are sufficiently stable to resist such oxidation, an observation supported by the current data. The lability of the complex ions is also strongly dependent on the ligands involved, amines generally forming rather nonlabile complexes with the transition metal ions. This latter point would suggest that this type of impurity would not lend itself to removal from propellant mixtures by ion exchange or complexation techniques.

In addition to reaction with the ions of the transition metals, the HAN-based propellants react readily with the metals themselves and with many of their alloys. When exposed to copper or brass, HAN solutions turn blue and a brown gas is evolved, indicating the presence of NO_2. Reaction becomes more vigorous as it continues, eventually resulting in fume-off of the sample. In contrast, reaction of HAN with iron and many of the carbon steels produces a colorless gas and a yellow-brown solution. Reaction does not accelerate and eventually stops when essentially all of the HAN is depleted. The apparent similarity of reaction with the metals and with their respective ions could be deceptive since reaction mechanisms might be different.

Simply stated, HAN-based propellants are sensitive to impurities and are corrosive. Considerable care is required in selection of materials with which they will come in contact both from the standpoint of damage to the propellant and of damage to the materials. It is also possible that the presence of such impurities will influence reaction sequences after initiation and thus change the performance characteristics of the propellant in a gun. This effect, although not yet investigated, could present major problems if it does indeed occur.

VI. SUMMARY

The work presented is possibly best summarized by relating it to the characteristics required of a liquid propellant to be used in a gun. The characteristics required are intimately related to the gun system in which it is to be used which, for purpose of discussion, is to be a medium caliber, high performance, self-propelled cannon using caseless ammunition. It is reasonable to assume that the complete gun system will be substantially improved over what is presently in use in order to warrant the expenditure of effort for development and fielding of so radically different a system.

The concept of caseless ammunition presents a number of advantages to the user and several rather severe constraints to the developer. The advantages were described in Chapter I. Constraints concerning caseless ammunition center about the fact that the propellant will be pumped and is thus exposed to the possibility of contamination. The possibility of exposure of operating personnel to the propellant is increased requiring greater concern about toxicity.

A. Impetus:

Factors influencing propellant impetus are sufficiently complex and present ramifications to other aspects of the overall ballistic cycle such that no single value can usually be generated. In spite of this, a high performance gun generally requires an impetus of approximately 1 kJ/gm. Bearing in mind that a liquid will assume the shape of its container and that the HAN-based, aqueous monopropellants have a density of approximately 1.5 gm cm^{-3}, loading of propellant without void space will result in a volumetric impetus of 1.5 kJ cm^{-3}, a fairly high value compared with what is presently available.

B. Vulnerability:

Propellants are energetic materials and are inherently dangerous, the extent of the danger being closely related to the ease with which they can be induced to release the energy that they contain. Attack on systems with which the propellant is associated usually involves input of thermal or mechanical energy and vulnerability is reduced when the energy required for initiation of reaction is high. The ultimate in vulnerability reduction would be that reaction initiation not be possible until the propellant is properly loaded into the gun combustion chamber, a situation almost achieved in a non-hypergolic bipropellant because oxidizer and fuel are not in contact until that time. In the case of monopropellants, an alternative could be that the mixture, although capable of initiation, is not able to release the majority of the energy available unless some relatively high pressure is maintained in the combustion chamber, the situation that exists with the HAN-based propellants.

C. Stability:

The distinction between vulnerability and stability in the context of this discussion, is that stability refers to more benign circumstances over longer times. Reactions of the propellant with its storage containers and the role of trace impurities in accelerating decomposition must be carefully considered. The presence, in the propellant, of components with relatively high vapor pressure, such as hydrazine or the nitrate esters, could produce a serious stability problem in that such components could evaporate, if storage conditions permitted, thus changing the composition of the mixture. A stability problem of a special kind exists if the mixture contains components that separate at some low temperature. The separation or "freezing out" of such components causes a change in composition of the liquid and hence a change in propellant properties. It is possible that such change is temporary in that the components could redissolve as the temperature is raised, reforming the original mixture.

D. Toxicity:

The use of caseless ammunition increases the importance of propellant toxicity because of the increased possibility of exposure. This requirement is of special importance if the liquid is to contain nitrate esters of low molecular weight. Such compounds are, without exception, physiologically active to the extent that they would be considered toxic. The HAN-based propellants are possibly unique among candidate liquids as to their lack of toxicity.

E. Viscosity:

Caseless ammunition requires that the propellant be pumped into the combustion chamber at high speed. Since the gun must be operational over a broad temperature range, propellant viscosity should not vary severely with temperature. This is a rather difficult requirement to satisfy since liquids inherently become more viscous at lower temperatures.

The problem of propellant performance at various temperatures is not addressed in this summary in part because the problem is not unique to liquid propellants. Although specific, temperature dependence data are not yet available, it would not be surprising to find that performance is temperature dependent.

F. Cost and Producibility:

Since the liquids are homogeneous, mixing and blending operations become almost trivial and, obviously, casting or extruding is non-existent. Savings expected from the absence of these production steps should be considerable and should more than compensate for the increased handling and shipping costs associated with maintaining purity and compositional integrity while handling the propellant in bulk. The HAN-based mixtures contain no critical materials and are produced from raw materials for which a well established production base already exists.

G. Demilitarization and Disposal:

It is reasonable to expect that not all available propellant will be consumed by the weapon system and that demilitarization and disposal will be required. Burning is becoming an increasingly less viable method of disposal as more becomes known of the impact of such disposal on the environment and the use of a non-toxic and biodegradable propellant is certainly desirable.

H. Muzzle Flash and Blast:

Secondary muzzle flash and blast result from ignition of combustible gases that are products of propellant combustion, a situation not present if the propellant is stoichiometric.

In conclusion, it would appear that, based on what is presently known of the HAN-based propellants, they successfully address many of the requirements presented. A number of problems, such as variation of viscosity with temperature, corrosivity, and the deleterious effects of low concentrations of impurities on stability seem formidable at this time. It is assumed that as work continues and more becomes known about these interesting and rather unique materials, improvements in properties and performance will be realized.

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