EFFECT OF ADDITIVES AND PARTICLE SIZE ON THE HYDROLYSIS OF ALUMINUM AT 100° TO 110°C

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ABSTRACT

The reaction of aluminum powder with water at 100^{0} to 110° C was carried out in glass pressure bottles and was followed by the change in gas pressure as a function of time. It was observed that as the particle size of aluminum found to react under conditions used in solid propellant degradation was of minor significance. Hydrogen was involved, however, in sufficient quantity to form explosive mixtures with air and to raise the pressure of closed systems by an atmosphere or more. In the presence of oxidizing salts some of the hydrogen was oxidized and chloride was formed from ammonium and potassium perchlorates. Nitrates were reduced to ammonia. The proportion of these salts reduced was small, however, and was a linear function of the concentration of the additive.

The effect on the hydrolysis rate of aluminum by perchlorate and halide salts solution appeared to correlate with the ionic radius of the additive cation when the anion was held constant and with the additive anion when the cation was held constant. As the radius decreased the hydrolysis rate increased.

The effect of some oxidants on the hydrolysis rate of aluminum appeared to depend upon the final pH of the solution; the rate increased in highly basic solution and decreased in slightly acidic or neutral solution compared to water alone. A slight reaction of aluminum powder with alcohols was observed at 100° C. The rate of reaction increased as the dielectric constant of the alcohol increased.

INTRODUCTION

The hydrolysis reaction of aluminum in the temperature range of 100° to 110° C was investigated in a closed system. This study was undertaken to provide information needed in our program on the utilization and disposal of solid propellants and explosive waste (1). Acids and bases are used in the solvolytic degradation of propellants. In the subsequent recovery of propellant ingredients such as aluminum, ammonium perchlorate, and cyclotetramethylene tetranitramine it was necessary to determine if these ingredients singly or in combination react with the solvents and additives used in the degradation process.

The present investigation is concerned only with the effect of additives, particle size, concentration, temperature and pH on the hydrolysis of aluminum powder. Additives included: ammonia, perchlorates, halides, nitrates, permanganate, chromate, dichromates, sulfates, phosphates, iodate, periodate, alcohols, and ethanolamine.

EXPERIMENTAL

Method:

The hydrolysis reactions of aluminum were carried out in Fischer-Porter pressure bottles (280 ml volume). After the aluminum, additive, and solvent (usually water) were added, the bottles were evacuated until the solvent boiled. The bottles were equipped with calibrated pressure guages (0 to 100 psi above atmospheric pressure) and automatic safety release valves which were set at 75 psi. Pressure data were taken as psi above atmospheric, to obtain the absolute pressure of gaseous products 14.7 psi must be added and then the vapor pressure of water at the particular temperature subtracted. The pressure bottles were immersed in a constant temperature bath set at 100° , 105° and 110° C. Zero time was taken as one minute after the bottles were placed in the bath.

Materials:

Reagent grade samples were used. The volume of solvent was ll2 ml. The aluminum concentration was held constant at 6.88%. The concentration of additives was varied from 1.4 to 22.5%. The particle sizes of aluminum were 27, 69, and ll6 \pm 2 microns. The particle size distribution of aluminum was determined with a Sharples Micromerograph.

Analysis:

The concentration of reduced species from the hydrogenation of additives was determined using standard analytical procedures. (2) Chromate was analysed by iodometric titration with 0.1N sodium thiosulfate. Permanganate was determined by adding a excess of a standard solution of 0.1N arsenious oxide and back-titrating with 0.1N potassium permanganate. Ammonia was determined by adding an aliquot to 0.1N hydrochloric acid and back-titrating with 0.1N sodium hydroxide. Chloride and iodide were analyzed by titration with 0.1N silver nitrate using a silver/sulfide electrode as an indicator. An Orion digital pH meter, model 801 was used to determine the pH of the solutions.

DISCUSSION

The overall hydrolysis reaction of aluminum is assumed to be:

$$2A1 + 6H_20 - 2A1 (0H)_3 + 3H_2$$

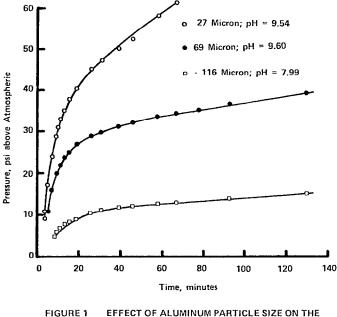
or
$$2A1 + 3H_20 - A1_20_3 + 3H_2$$

The hydrogen generated may reduce many of the additives present in solution such as perchlorate to chloride, iodate to iodide, nitrate to ammonia, permanganate to manganese ((IV), chromate to chromium (III) etc. The reaction of aluminum powder with water was carried out in glass pressure bottles and was followed by the change in gas pressure as a function of time at a constant temperature. The pressure versus time curves show an initial acceleratory region where there is a rapid increase in pressure followed by an inhibiting region where there is only a gradual increase in pressure. The latter region is probably caused by the formation of a passivating layer of hydrous alumina on the metal particle which inhibits the hydrolysis reaction.

Effect of Particle Size and Proportion of Aluminum

The effect of the particle size of aluminum on the hydrolysis reaction at 100° C is shown in figure 1. The pressure generated increased as the particle size decreased. The final pH of the solution containing 27 and 69 microns aluminum were nearly the same (9.6) and greater than that for 116 micron (8.0). The initial pH was 6.8. The reason for the increase in pH is not known. It took place in Teflon containers as well as in glass. The initial pH of the distilled water was 6.6 to 6.8. Water boiled in the glass bottles for two hours had a pH of 7.0 to 7.5 at ambient temperatures. Addition of some neutral salts to the water before boiling in glass containers in the absence of aluminum had only a slight effect on the pH. Perhaps the increase in pH is caused by trace amounts of other metals present in the aluminum which then may react with water to form hydroxide at elevated temperatures. The total metal impurity content in the aluminum used is 0.2% and includes silicon (0.11%), iron (0.05%) and smaller amount of seven other metals.

The amount of 27 micron aluminum powder in a constant volume of water was varied at 100° C with increases in pressure as shown in figure 2. The final pH of the solutions was above 9.



HYDROLYSIS REACTION OF ALUMINUM (6.88%) AT 100°C



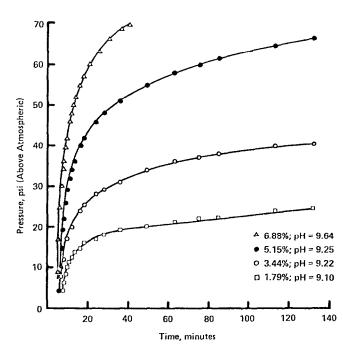
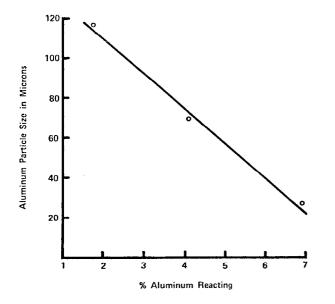


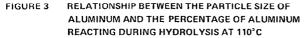
FIGURE 2 EFFECT OF THE PROPORTION OF ALUMINUM ON THE HYDROLYSIS REACTION OF 27 MICRON ALUMINUM POWDER AT 100°C

Proportion of Aluminum Reacting

The application of the ideal gas law permits the calculation of the number of moles of aluminum reacted since the pressure, volume, and temperature of the system are known. These values are given in Table I. Figure 3 shows that there is an inverse relationship between the proportior of aluminum reacted and the particle size of aluminum. As the particle size of aluminum increased, the percentage reacted decreased. Since the fraction of aluminum reacted is known, it is possible to calculate the reduction (Table I) assuming no Al_203 or Al(OH)3 remain on the surface. The calculation reveals that the diameter of the particles was reduced only by 1-3%. The maximum proportion of aluminum reacting was only about seven percent. Such a reduction in yield can be tolerated in a plant process. If oxide is formed on the surface, however, burning rates of propellant made with the aluminum may be affected.

Average Particle Diameter, Micron	Mols H ₂ at 200 minutes	Percentage Al reacting	Calculated Al Particle Diameter after reaction Micron		
27	0.0293	6.9	26.3		
69	0.0175	4.1	68.1		
116	0.0079	1.8	115.3		





Effect of Temperature Change

Figure 4 shows that as the temperature increased, the hydrolysis rate of aluminum increased. The time-temperature dependence of the hydrolysis of 27 micron aluminum is shown in figure 5 by plotting the time it takes to reach a given value of pressure/temperature at different temperatures. At constant volume the moles of hydrogen measured is proportional to pressure/

Reaction of Aluminum Powder (6.88%) with Water at 110⁰C

Table I

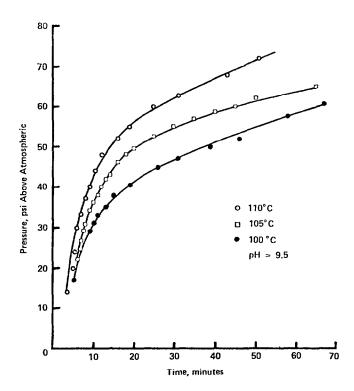


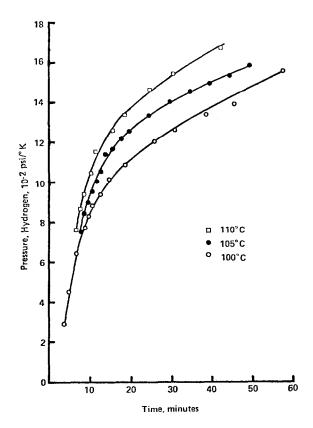
FIGURE 4 EFFECT OF TEMPERATURE ON THE HYDROLYSIS REACTION OF 27 MICRON[®] ALUMINUM POWDER (6.88%)

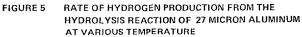
temperature. A correction was made for the excess vapor pressure of water at $105^0\ \text{and}\ 110^0\text{C}$.

Activation Energy for Hydrolysis

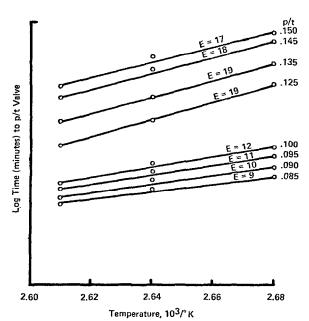
Kinetic data for the hydrolysis of aluminum may be obtained from isothermal studies by means of the equation: $\log F(C) = \log A + \log t - E/2$. 3RT where F(C) is a function of the conversion which in this experiment is the pressure, A is the frequency factor, t is the time, E is the activation energy, R is a constant, and T is the temperature in degrees Kelvin.

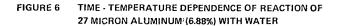
The activation energy may be calculated directly from the equation or from the slope of a plot of log time at various pressure/temperature values versus the reciprocal of the absolute temperature. The activation energy is only approximate because as the value of pressure/temperature increases, the activation energy apparently increases. However, within the limits of the experiment, two values for the activation energy may be obtained from the data corresponding to acceleratory (E_1) and inhibiting





 (E_2) regions for the pressure-time curves for the hydrolysis reaction. These values are given in figure 6 and Table II. The average activation energy values for the hydrolysis of 27 and 69 micron aluminum are the same namely 10 and 18 kcal/mole corresponding to E1 and E2. However as the particle size increases to 116 microns the activation energy apparently increased to 16 and 27 kcal/mole for E1 and E2 respectively. One would expect that if the only change in the aluminum is particle size, the activation energy would be the same for all three samples. During the course of a single reaction, however, a coating of hydrous alumina would form on the surface and the activation energy might increase. There is unfortunately an uncertainty in the zero time of the reaction which could have a large effect on activation energy calculations at the beginning of the reaction. As a consequence one cannot say for certain that the inhibiting effect has actually been observed.





<u>Table II</u>

Activation Reacti	Energ	ies for	the H	lydrolysis
Reacti	on of	Alumin	um (6.	.88%)

Numinum Particle	Activation Energy, Kcal/mole			
fize in Microns	Е ₁ *	E2**		
27	10 ± 2	18 ± 1		
69	10 <u>+</u> 2	18 <u>+</u> 1		
116	16 <u>+</u> 3	27 <u>+</u> 2		
27 + 22.5% AP	13 <u>+</u> 1	16 <u>+</u> 1		

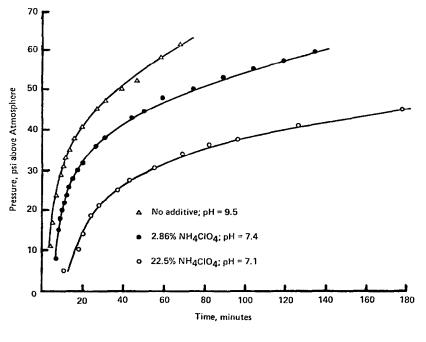
* Acceleratory region which is the vertical portion of pressure vs time curve.

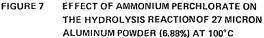
** Inhibiting region which is the more horizontal portion of the pressure vs time curve.

Effect of Ammonium Perchlorate and Ammonia

Figure 7 shows the effect of the concentration of ammonium perchlorate on the hydrolysis of 27 micron aluminum at $100^{\circ}C$. As the concentration of ammonium perchlorate increased, the observed final pressure decreased. The ammonium perchlorate underwent a hydrogenation reaction whereby the perchlorate ion was reduced to chloride. This result is shown in figure 8 where there is a linear relationship between the chloride ion concentration produced in ppm and the percentage of ammonium perchlorate daded. The perchlorate ion is much more readily reduced in ammonium perchlorate than in potassium perchlorate (figure 7, Table III). This is believed to be caused by the pH of the solution and by the potassium ion. The pH was 7.2 after reaction in the case of the ammonium perchlorate solution and over 9 for the potassium perchlorate solution.

Figure 9 shows the effect of ammonium perchlorate and of 3N ammonium hydroxide on the hydrolysis of 27 micron aluminum at 100° C. Ammonia increases the rate of the hydrolysis reaction. The addition of 22.5% ammonium perchlorate to 3N ammonium hydroxide decreases the rate of hydrogen formation but is still faster than in water alone. The ammoniacal solution from this hydrolysis reaction contained 66ppm chloride as a result of the reduction of perchlorate. This amount is half of that





Additive	Slope (3) ppm/%	pH(4)	Analyzed for
K10 ₃	5,492	9.5	I (1)
KMn04	2,753	12	Mn (VII)
KNO3	1,572	12.5	NH3
K ₂ Cr0 ₄	499	12.7	Cr (VI)
кс104	۱	9.5	C1 (1)
NH4N03	16	8.4	NH3
NH ₄ C104	6	7.2	C1 (1)

Т	a	b	1	e	I	I	I

Relative Slope Values from the Hydrogenation of Additives (1) in the Hydrolysis Reaction of 27 Micron Aluminum Powder (2) at 100°C

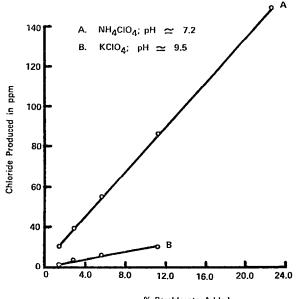
(1) Additive concentration is 1.4 to 22.5%

- (2) Aluminum is 6.88%
- (3) Slope obtained from a plot of concentration in ppm of analyzed species versus percentage of additive in solution
- (4) pH of solution at end of reaction

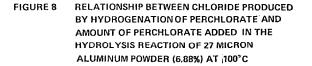
found after reaction in aqueous ammonium perchlorate, and much more than that found in aqueous potassium perchlorate solutions even though both the ammoniacal and potassium perchlorate solutions have approximately the same pH. Thus the cation influences the hydrogenation of the perchlorate ion. The activation energies for the hydrolysis of 27 micron aluminum in an aqueous solution containing 22.5% ammonium perchlorate was found to be 13 and 16 Kcal/mole respectively for E1 and E2 (Table II). Thus ammonium perchlorate had a slight effect on the activation energy in the acceleratory region during the hydrolysis of aluminum.

Effect of Perchlorate Salts

The effect of perchlorate salts on the hydrolysis of aluminum at 100° C is shown in figure 10. The hydrolysis rate increased in the order lithium>tetramethylammonium>>sodium>potassium>magnesium>cesium>ammonium. Compared to water alone, the addition of cesium and ammonium perchlorate decreased the rate and the others increased the rate. With lithium perchlorate the solution foamed. The generation of hydrogen approached runaway conditions with lithium and tetramethyl ammonium perchlorate.



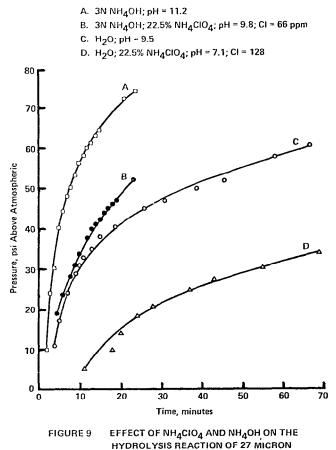




In comparing the pH of the different perchlorate solutions after the hydrolysis reactions, it was found to be between 6.9 and 7.9 except for potassium perchlorate where it was over 9. Thus pH does not appear to play a predominant role with perchlorate solutions in the hydrolysis reaction of aluminum.

The hydrogenation of perchlorate salts as measured by the amount of chloride ion produced showed that the most chloride ion was formed from magnesium and ammonium perchlorate (35 ppm chloride) and the least from tetramethyl ammonium perchlorate (3 ppm chloride). Initially a relationship was assumed between the amount of chloride produced and the hydrolysis rate i.e., the more chloride produced, the slower the hydrolysis rate and vice versa. However there does not appear to be any correlation between the amount of chloride produced produced not be the amount of chloride produced.

The effect of the lithium perchlorate concentration on the hydrolysis rate of aluminum at 100° C was determined. As the concentration increased from 5.6% to 22.5% the hydrolysis rate decreased. This was observed also with ammonium perchlorate. The pH of the lithium perchlorate solutions after the reaction was lower at the higher concentration, namely 6.5 compared to 7.8.

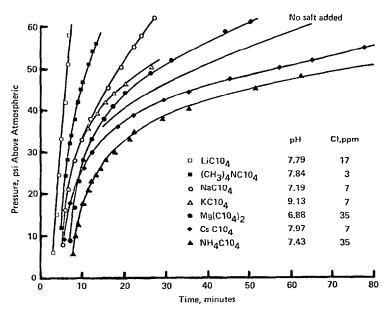


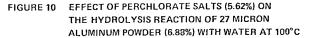
ALUMINUM POWDER (6.88%) AT 100°C

The order of the alkali and alkaline earth perchlorates on the hydrolysis of aluminum cannot be explained on the basis of the pH of the solution or the amount of reduced species (chloride) produced. However, since the anion is held constant in this series the order of increasing the hydrolysis rate appear to parallel the position of the additive cations in the Periodic Table.

Effect of Nitrates

Figure 11 shows that potassium nitrate increased the rate of production of gas from aluminum compared to water alone and that ammonium nitrate markedly decreased the rate of hydrogen production. After the hydrolysis reaction the potassium nitrate solutions had a very high pH (12) while the ammonium nitrate solutions was only 8.5. The color of the aluminum in the potassium nitrate solution turned white as the reaction proceeded.





A marked concentration effect in potassium nitrate solution was observed on the hydrolysis reaction of aluminum. As the concentration of potassium nitrate increased tenfold from 1.7% to 17%, its pressure-time curve became exponential resulting in a rapid increase in pressure with time after an induction period.

Eigure 12 shows a linear relationship between the ammonia produced in 10^3 ppm by hydrogenation of potassium nitrate and the percentage of potassium nitrate added in the hydrolysis reaction of 27 micron aluminum at 100° C. The behavior of ammonium nitrate was anomalous, there was a slight decrease in the concentration of ammonia produced as the percentage of ammonium nitrate increased.

Further Effects of Additive Salts

Aside from perchlorates and nitrates a number of other salts were added to water and 27 micron aluminum powder and the rate of production of hydrogen and reduced salts was followed at 100^{9} C. The aluminum content was 6.88% and the concentration of salts varied from 1.43% to 5.62%. The salts included potassium and ammonium halides, and several oxidizing agents, potassium permanganate, potassium chromate, potassium iodate, and potassium periodate, and some acidic salts, ammonium sulfate, ammonium dihydrogen phosphate, and ammonium monohydrogen phosphate.

As in the case of the perchlorates and nitrates, the production of hydrogen increased over that in water alone in some cases and decreased in others. When a decrease was observed there was in some cases no possibility of reduction of the salt by hydrogen. Among the halides as with the perchlorates, the position of the anion in the Periodic Table appeared to play a role. As the ionic radiu of the anion decreased, its effect on the hydrolysis rate of aluminum increased.

In comparing the effect on the hydrolysis rate of aluminum by potassium and ammonium salts of perchlorates, nitrates, halides, and sulfates; the potassium salts increased the hydrolysis rate and the ammonium salts decreased the rate compared to water alone. The pH of the potassium salt solutions was over 9, and the ammonium salt solutions around 7.

The ease of hydrogenation of some of the oxidizing salts is compared quantitatively in Table III. The concentration of reduced species was determined as a function of the concentration of oxidizer. See for instance Figures 8 and 12. The slopes of the curves in ppm of reduced species divided by percent oxidizer is given in Table III. The higher the slope

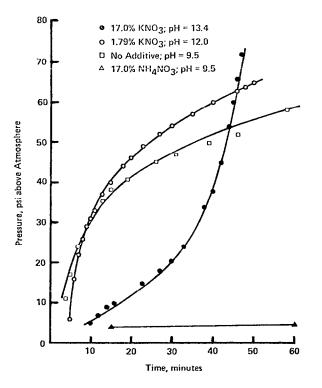
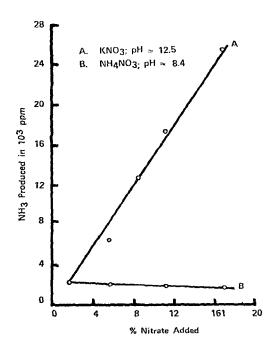
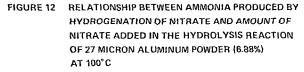


FIGURE 11 EFFECT OF KNO₃ AND NH₄NO₃ ON THE HYDROLYSIS REACTION OF 27 MICRON ALUMINUM POWDER (6.88%) AT 100°C





values the more readily the anion is reduced under the conditins (e.g. pH) which exist in these experiments. Thus the nitrate ion in potassium nitrate is more readily reduced than in ammonium nitrate, and the perchlorate ion in ammonium perchlorate is reduced more readily than in potassium perchlorate. The iodate ion is the easiest to reduce while the perchlorate ion is the hardest.

Effect of Ethanolamine and Alcohols

One of the solvent systems employed in degrading propellant is ethanolamine in equal volumes of toluene and propanol. Consequently we wished to determine if the alumpinum and ammonium perchlorate underwent any changes with this solution at 110° C. It is known (3) that ammonium perchlorate reacts with amines releasing ammonia and forming compounds which when dry are sensitive to an impact test. The solubility of ammonium perchlorate in the mixed solvent above is around 3% and the resulting ethanol ammonium perchlorate is more soluble in this solvent. A dilute solution of the substituted ammonium perchlorate is insensitive to an impact test. Figure 13 illustrates the effect of addition of aluminum and/or ammonium perchlorate to lm. solutions of ethanolamine in equal volumes of toluene and n.-propanol at 110° C. One can conclude:

- Addition of aluminum to the ethanolamine solution caused a slight but definite increase in pressure, i.e.-hydrogen evolved.
- Addition of ammonium perchlorate to the solution lead to evolution of a gas - ammonia. A tenfold increase in ammonium perchlorate concentration causes only a slight increase in pressure because the solubility of ammonium perchlorate in the solvent is exceeded.
- 3. Addition of both aluminum and ammonium perchlorate to the solution caused only a slight increase in pressure over that found with ammonium perchlorate alone. In this case 10 ppm of chloride was found which could have been formed from H₂ and perchlorate or possibly from a direct reaction between aluminum and perchlorate.

The ethanolamine solution was analyzed also for free amine content. The system aluminum and ethanolamine does not cause a change in amine concentration.

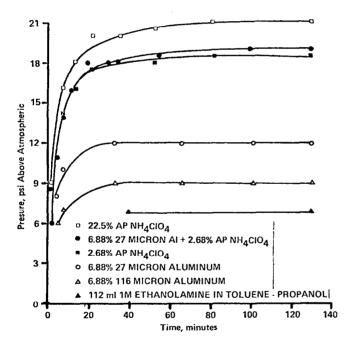


FIGURE 13 PRESSURES DEVELOPED IN A CLOSED SYSTEM OVER TOLUENE-PROPANOL CONTAINING ETHANOLAMINE WITH VARIOUS ADDITIVES AT 110°C

The addition of ammonium perchlorate to the ethanolamine solution with/without aluminum causes the amine concentration to decrease by 5%. Thus both the aluminum and ammonium perchlorate react with ethanolamine; the aluminum with the hydroxyl group and the ammonium ion being replaced by the amine group.

In view of the results above, an attempt was made to determine if 27 micron aluminum undergoes an alcoholysis reaction at 110°C. The difference in pressure between the pure solvent and solvent + aluminum was found to be in the order methanol>ethanol>propanol. This is the order of decreasing dielectric constant in this series. The pH of the solution was 8.2 to 8.4. Figure 14 shows a linear relationship between the dielectric constant of the alcohols and the pressures developed in the reactions with aluminum. It is apparent that the alcoholysis reaction is much slower then the hydrolysis reaction with aluminum.

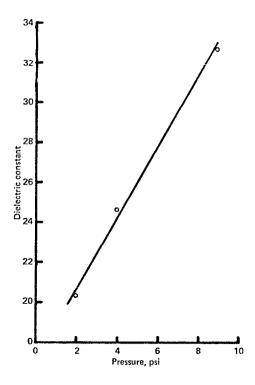


FIGURE 14 RELATIONSHIP BETWEEN DIELECTRIC CONSTANT OF ALCOHOLS AND PRESSURE IN REACTION OF 27 MICRON ALUMINUM AT 110°C

Hydrolysis Rates of Different Lots of Aluminum

Figures 15 and 16 show the differences in the hydrolysis rates at $105^{\circ}C$ of different lots of 27 and 69 micron aluminum powder. These differences are reproducible at other temperatures and also in the presence of ammonium perchlorate or ammonium hydroxide. These lots of aluminum passed specifications and lots of the same particle size are considered to be the same. The hydrolysis reaction provides a simple, quick, qualitative method of distinguishing between the reactivities of different lots of aluminum powder, and may help explain differences in the burning rates of propellants when different lots of aluminum are used.

Conclusion

The reaction of powdered aluminum with water alone and in the presence of ammonia and perchlorate and nitrate salts have been followed. The proportion of aluminum found to react under conditions used in solid propellant degradation was of minor significance. Hydrogen was evolved, however, in sufficient quantity to form explosive mixtures with air and to raise the pressure of closed systems by an atmosphere or more. In the presence of oxidizing salts some of the hydrogen was oxidized and chloride was formed from ammonium and potassium per-

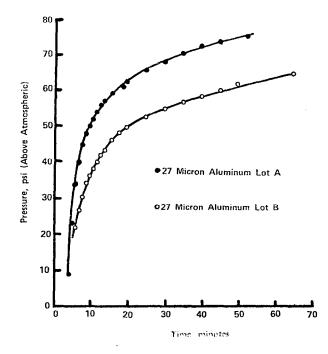
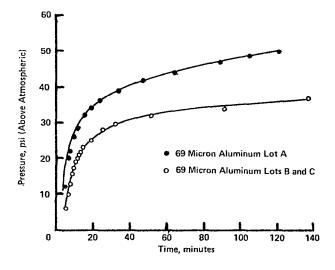
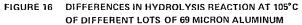


FIGURE 15 DIFFERENCES IN HYDROLYSIS REACTION AT 105°C OF DIFFERENT LOTS OF 27 MICRON ALUMINUM





chlorates. Nitrates were reduced to ammonia. The proportion of these salts reduced was small, however. Linear relationships were found for the concentration of reduced species produced by hydrogenation of an additive and the concentration of the additive.

The effect on the hydrolysis rate of aluminum by some oxidants was to increase the rate over that of water alone if the solutions were basic (pH 9.5), however if the solutions were slightly acidic or nearly neutral (pH 8), then the rate of hydrolysis decreased.

The effect on the hydrolysis rate of aluminum by perchlorate and halide salt solutions appeared to correlate with the ionic radius of the additive cation when the anion was held constant and with the additive anion when the cation was held constant. As the ionic radius decreased, the hydrolysis rate increased.

It has been reported (4) that (1) water rapidly oxidizes aluminum at 180° C, (2) basic solutions containing ammonia and ethanolamine do not attack aluminum, (3) alkali metal halides are more aggressive in dilute than in concentrated solutions, (4) alkali metal and alkali earth perchlorates, nitrates, and sulfur compounds in aqueous solutions do not attack aluminum, (5) phosphates may act aggressively on aluminum depending on the pH of the solution, and (6) oxidants tend to act as inhibitors in contact with aluminum by reinforcing the protective oxide film covering the metal. Thus what compounds attack or do not attack aluminum depends upon the meaning of the word "attack". Consequently our studies are in agreement with only some of the above statements.