

65.
GAS GENERATOR PROPELLANTS

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The properties of ammonium perchlorate have made it the oxidizer of choice for composite solid propellants for the past 20 years. Its ability to produce propellant compositions with high flame temperatures and densities has made it extremely useful to the missile propulsion industry. Recently, it has become possible to convert this versatile oxidizer to another missile system application, that of warm gas generator propellants.

Warm gas generator propellants are required for driving turbine-alternator systems for electrical power generation, for actuating jet-controlled attitude control systems, and for propelling torpedo propulsion units. Despite the advantages of ammonium perchlorate, it has been difficult to utilize it in these applications, because of the inherently high flame temperature (4500° to 5500°F) of propellants based on it. Because of the materials of construction used in warm gas generator systems, the flame temperatures of these propellants are limited to values in the region of 2200° to 2300°F.

In propellant technology, reduction of flame temperature is most conveniently obtained by reducing the oxidizer to fuel (O/F) ratio to a very low value, so that the composition is extremely fuel rich. In Figure 1 a plot is shown of flame temperature versus the weight percent of NH_4ClO_4 for a mixture of ammonium perchlorate and a typical low oxygen content, high fuel content polymeric hydrocarbon binder. Although aluminum powder is normally used as a fuel component in solid propellants, it has been omitted for two reasons: it increases flame temperature to still higher (and undesirable) values, while producing solid Al_2O_3 particles as an exhaust component. For most gas generator systems, the presence of solid particles in the combustion products is extremely undesirable because of the resultant clogging and erosion of the metallic portions of the system.

Examination of Figure 1 shows that the gradual reduction of the NH_4ClO_4 content from 90% to 70% reduces the flame temperature from 5000°F down to the desired level of 2200°F, simply by greatly reducing the oxidation ratio of the system. The oxidation ratio decreases from 4.33 down to 1.15 for these two compositions, where oxidation ratio is defined as:

$$\text{Oxidation Ratio} = \frac{\Sigma \text{O Atoms}}{\Sigma \text{C Atoms} + \frac{1}{2} \Sigma \text{H Atoms}}$$

Unfortunately, this reduction results in undesirably high levels of solid carbon in the combustion products when these are exhausted to the atmosphere. This can be seen in Table 1, where the level for the high fuel content binder is 6.45% solid carbon by weight. No carbon is found in the combustion chamber at 1000 psia, but expansion of the gases to 14.7 psia results in copious quantities of black smoke.

Two methods are applicable to the solution of this problem. The first of these involves substitution of much higher oxygen content binders for the polymeric fuel. In Figure 1 and Table I the results of substituting highly oxygenated polyester

polymers for the conventional fuel can be seen. Use of a carboxy-terminated polyester based on diethylene glycol and adipic acid, with an oxygen content of 37.0% results in almost a 50% reduction in solid carbon in the exhaust. The required amount of NH_4ClO_4 oxidizer for a 2200°F temperature is reduced to approximately 62%. For a 42.0% oxygen content binder, the amount of oxidizer for generation of 2200°F is reduced still further, to approximately 58%. Since one of the combustion products resulting from the use of NH_4ClO_4 is HCl, with its consequent erosivity of certain metals of construction, these reductions in oxidizer content are quite desirable, since they result in corresponding reductions in HCl content.

The second method of lowering flame temperature involves the addition of a third component to the system that is as low in energy content as possible and that has an internal oxidation ratio close to 1.0. Compounds with these high negative heats of formation and balanced stoichiometry are aptly designated as "coolants", since they are both poor fuels and poor oxidizers. A representative list of compounds of this type is shown in Table II. The oxidizers, ammonium perchlorate and ammonium nitrate, are included for comparison.

For each compound, the empirical formula, density, oxidation ratio, and heat of formation in kilocalories per gram are given. Because warm gas generating systems must be efficiently packaged, high density values are desirable. The advantage of possessing an oxidation ratio close to 1.0 has already been pointed out. Finally, since high flame temperatures result from either low negative or positive heats of formation, it is desirable that the value for $\Delta H_f/M$ be as large a negative number as possible, in order to produce low flame temperatures.

Examination of the compounds in Table II shows materials ranging from low oxidation ratio fuel-like compounds such as oxamide and azodicarbonamide, to more evenly balanced materials such as ammonium oxalate hydrate, oxalohydroxamic acid, and hydroxylammonium oxalate. Ammonium dihydrogen phosphate theoretically appears to be an oxidizer, like ammonium nitrate, and ammonium perchlorate; however, in actuality it serves only as a coolant, since the phosphate portion of the molecule is extremely stable at elevated temperatures, and is not a source of oxygen, unlike the nitrate and perchlorate structures.

As might be expected, the compounds in the middle of the list are the most desirable and useful coolants; in particular, oxalohydroxamic acid (also sometimes referred to as dihydroxyglyoxime-DHG) is of particular interest. Its high density, balanced stoichiometry and negative heat of formation are of importance in this regard.

Table III points out still another important factor in the selection of an effective coolant. A good coolant is thermally stable, but not too stable. Oxalohydroxamic acid is quite satisfactory in this respect, showing no endotherm or exotherm in differential thermal analysis below 300°F, but it completely fumes off at the slightly higher temperature of 338°F (dec.). Its ammonium salt, on the other hand, exhibits its first exotherm at a lower temperature than 300°F, but it is not completely decomposed until 400°F is reached. The other coolants shown are more stable in a thermal sense, but this frequently means that the amounts that can be added to a propellant formulation are limited to low levels because of difficulty in achieving combustion.

The effect of adding various amounts of coolant to typical warm gas generator propellant compositions is shown in Figure 2. At the same binder content of 26.5%, larger amounts of oxalohydroxamic acid (DHG) are required to reduce the flame temperature of the 4% oxygen content binder to the 2200°F level than for the 37% oxygen content binder. The more negative heat of formation of hydroxylammonium oxalate makes it possible to reach the 2200°F level with even less coolant. The

overall effectiveness of these coolants is realized when the flame temperatures of the same compositions without coolant are compared, for these are 4250°F and 3900°F, respectively, for the 42% and 37% oxygen binders. Hydroxylammonium oxalate (HAO) is especially effective in improving the cleanliness of the exhaust for only 22% of this coolant produces a 2278°F flame temperature with no solid carbon in the exhaust products.

In addition to the foregoing methods of reducing carbon in the exhaust products, it is also possible to effect a reduction by reducing the pressure at which the combustion reaction is carried out. An indication of the extent of this factor can be seen in Figure 3, where the weight percent of solid carbon formed in the Exhaust is plotted as a function of the combustion pressure for a single composition over the pressure range of 100 psia to 20,000 psia. At 20,000 psia, the carbon content of the exhaust is over 5% by weight, while at pressures below 500 psia, 0% carbon results. A reduction in flame temperature also results, with the value of 2374°F for the 20,000 psia level decreasing to 2058°F at 100 psia.

In addition to the formation of solid carbon, it is also possible for ammonium chloride to condense in solid crystalline particles during the reduction of flame temperature resulting from expansion of the combustion gases through a nozzle or turbine system. The presence of chlorine in the ammonium perchlorate leads to the formation of HCl as one of the combustion products; this in turn reacts with traces of NH₃ in the composition products to form NH₄Cl when the temperature of the system falls below the value at which the vapor pressure of NH₄Cl is equal to the pressure of the system. A plot of the vapor pressure - temperature relationship for NH₄Cl is shown in Figure 4. If the temperature and pressure of the system fall above the line, solid NH₄Cl will not form; when either the temperature or the pressure or both are reduced sufficiently to fall below the line, formation of solid particles will occur. In general, the higher the pressure in the system, the less likely it is that NH₄Cl will deposit on cold walls or surfaces in the system.

Another problem resulting from the presence of HCl in the combustion products is the reaction of small amounts of this acid with the metallic materials of construction in systems using warm gas generators of this type. The metal chlorides formed from these reactions are undesirable for two reasons: changes in the dimensions of the attacked metal surfaces result from a volatilization of the chlorides, and later on deposition of metal chloride particles can occur in unwanted locations as the temperature of the gas is reduced.

Table IV shows the deposition temperature (melting point) for several of these metallic chlorides at a pressure of 1000 psia (68.05 atmospheres). They are arranged in order of increasing volatility. Although the rate of erosion of surfaces of most of these metals is extremely slow, as shown by the data on loss rate, the amounts of the chlorides formed are still of concern in some applications. The use of carbon steel is undesirable, but some stainless steels are satisfactory due to the protective action of chromium and nickel. The use of molybdenum and its alloys results in good erosion resistance and volatile chlorides for the reaction products.

Finally, it should be pointed out that a general correlation exists for a great many of the specific compositions described in this paper between theoretical flame temperature and % solid carbon in the exhaust. This can be seen in Figure 5, for with a few exceptions, all of the compositions previously discussed fall within a single band. Above a flame temperature of approximately 2550°F, no carbon forms; while below this temperature the amount formed is inversely related to the temperature.

In summary, two general methods of obtaining low flame temperature propellant compositions have been described that do not result in the production of large (over 6%) quantities of solid carbon in exhaust products. These are the use of highly oxygenated polyester binders and the use of "coolant" compounds with large negative values of $\Delta H_f/M$ and oxidation ratios close to 1.0. Two useful compounds of this type are oxalhydroxamic acid and hydroxylammonium oxalate.

The effects of varying combustion pressure over the range of 100 to 20,000 psia have been described. Effects related to the presence of HCl in the system, including the conditions controlling solids such as NH_4Cl and various metallic chlorides in the system have also been discussed.

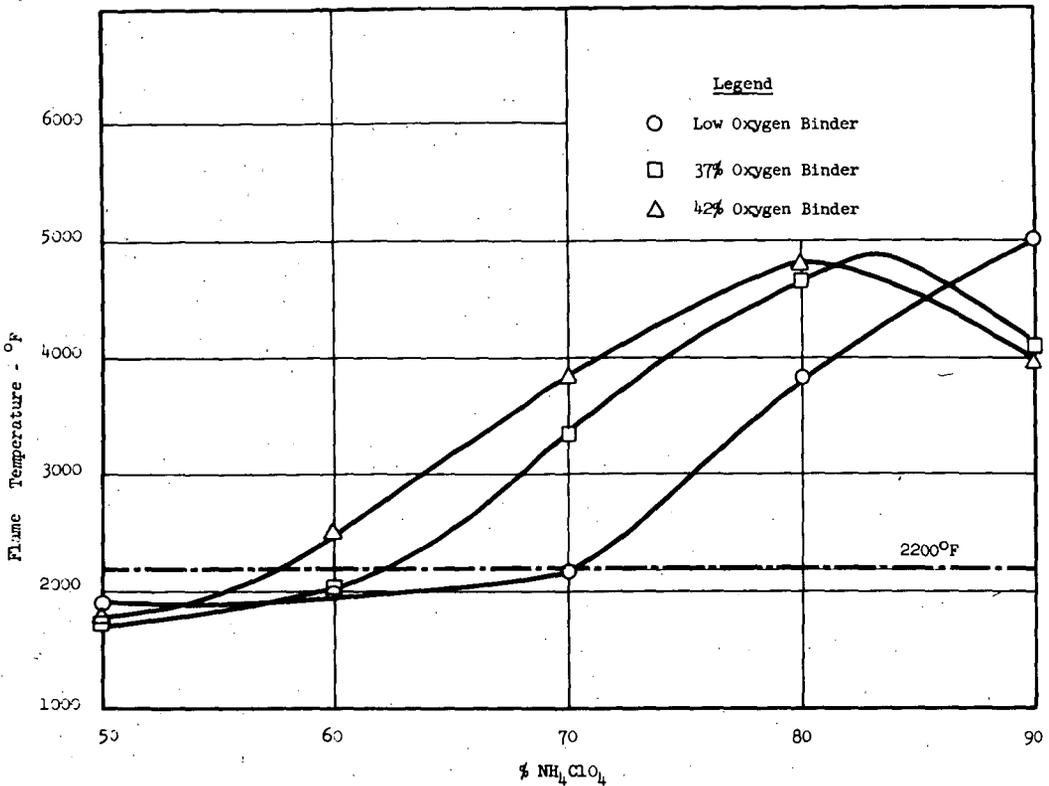


Figure 1. Effect of Oxygen Content on Flame Temperature

Table I
Reduction of Carbon Content
of
Combustion Products

<u>Binder</u>	<u>Wgt. % Oxidizer/Coolant</u>	<u>Flame Temp. (°F)</u>	<u>Oxidation Ratio</u>	<u>Wgt. % C(s) in Exhaust</u>
Low Oxygen Content	70/0	2186	1.15	6.45
37% Oxygen Content	60/0	2028	1.56	3.52
37% Oxygen Content	43.5/30	2138	1.69	1.99
42% Oxygen Content	37.5/36	2175	1.74	1.88

Table II

Coolants

<u>Compound</u>	<u>Empirical Formula</u>	<u>Density (g/cc)</u>	<u>Oxidation Ratio</u>	<u>$\frac{\Delta H_f}{M}$ (kcal/g)</u>
Azodicarbonamide	$C_2H_4O_2N_4$	1.63	0.5	-0.60
Oxamide	$C_2H_4O_2N_2$	1.667	0.5	-1.375
Ammonium Oxalate Hydrate	$C_2H_{10}O_5N_2$	1.50	0.715	-2.40
Oxalohydroxamic Acid	$C_2H_4O_4N_2$	1.85	1.0	-1.138
Hydroxylammonium Oxalate	$C_2H_8O_6N_2$	1.60	1.0	-1.85
Ammonium Dihydrogen Phosphate	$NH_4H_2PO_4$	1.803	1.33	-3.02
Ammonium Nitrate	NH_4NO_3	1.725	1.5	-1.09
Ammonium Perchlorate	NH_4ClO_4	1.95	2.0	-0.60

Table III
Differential Thermal Analysis
of Coolants

<u>Coolant</u>	<u>Endotherm (°F)</u>	<u>Exotherm (°F)</u>	<u>Fumes (°F)</u>
Oxalohydroxamic Acid	None	311.0	338.0
Ammonium Oxalohydroxamate	None	266.0	401.0
Hydroxylammonium Oxalate	271.4	348.8	399.2
Azo-dicarbonamide	None	372.2	451.4
Ammonium Oxalate Hydrate	192.2 + 413.6 (dec.)	None	None

Table IV
Formation and Deposition of Metallic Chlorides

<u>Metal</u>	<u>Milligrams of Loss per 10 grams</u>	<u>Highest Melting Chloride</u>	
		<u>Chloride</u>	<u>Melting Point (°C)</u>
Cr	0 (1)	CrCl ₃	1150
Ni	---	NiCl ₂	1001
Fe	3.6	FeCl ₂	670-674
Ti	2.7	TiCl ₃	dec. 440
Zr	---	ZrCl ₄	437
W	---	WCl ₆	275
Nb	0	NbCl ₅	204.7
Mo	0	MoCl ₅	194

(1) 304 Stainless Steel

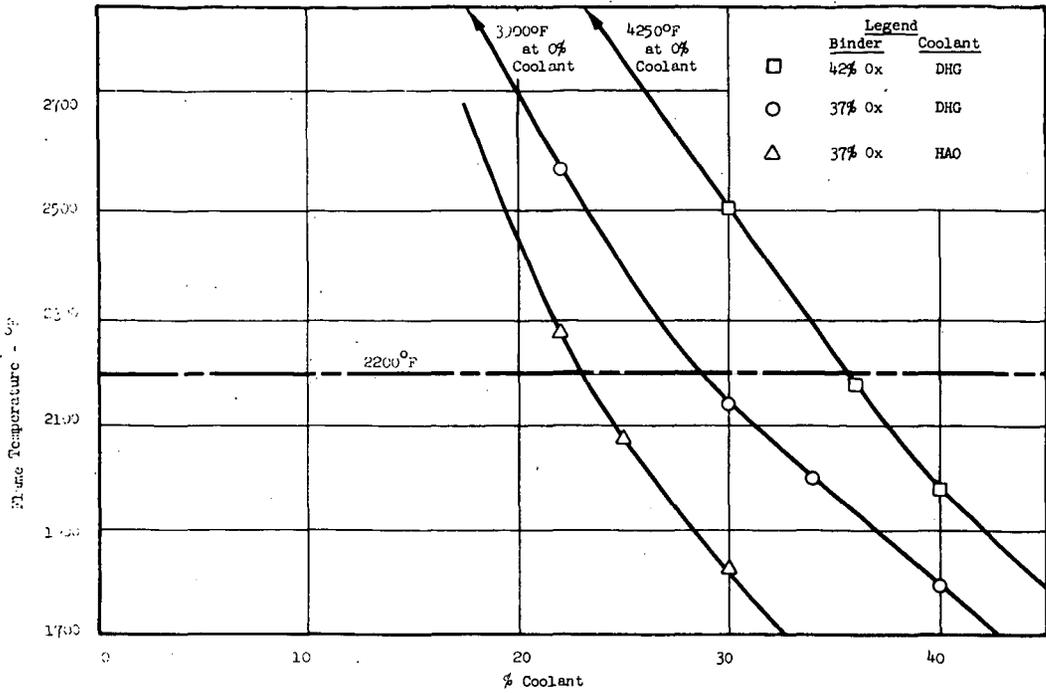


Figure 2. Effect of Percentage of Coolant on Flame Temperature

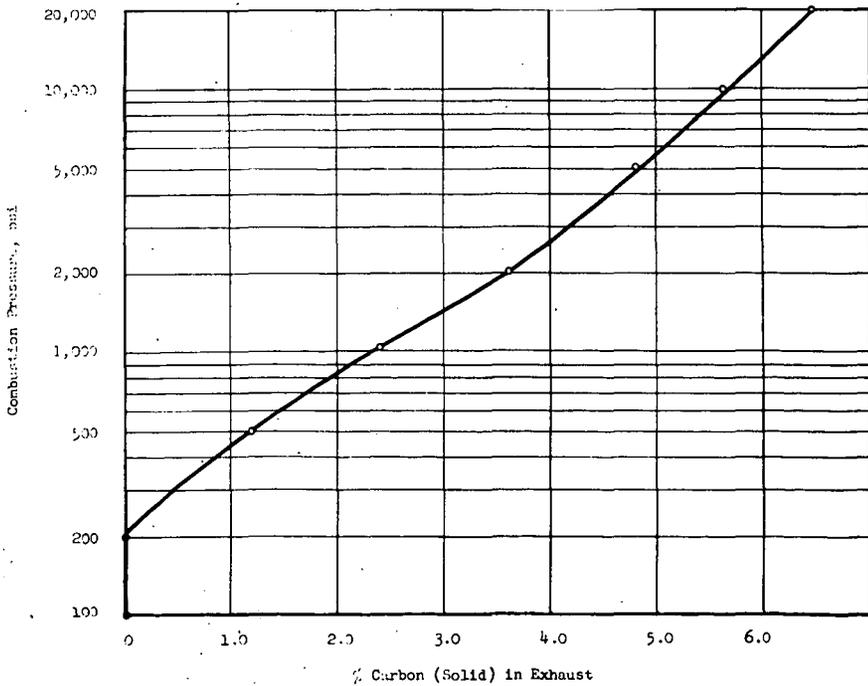


Figure 3. Effect of Pressure on % Carbon(s)

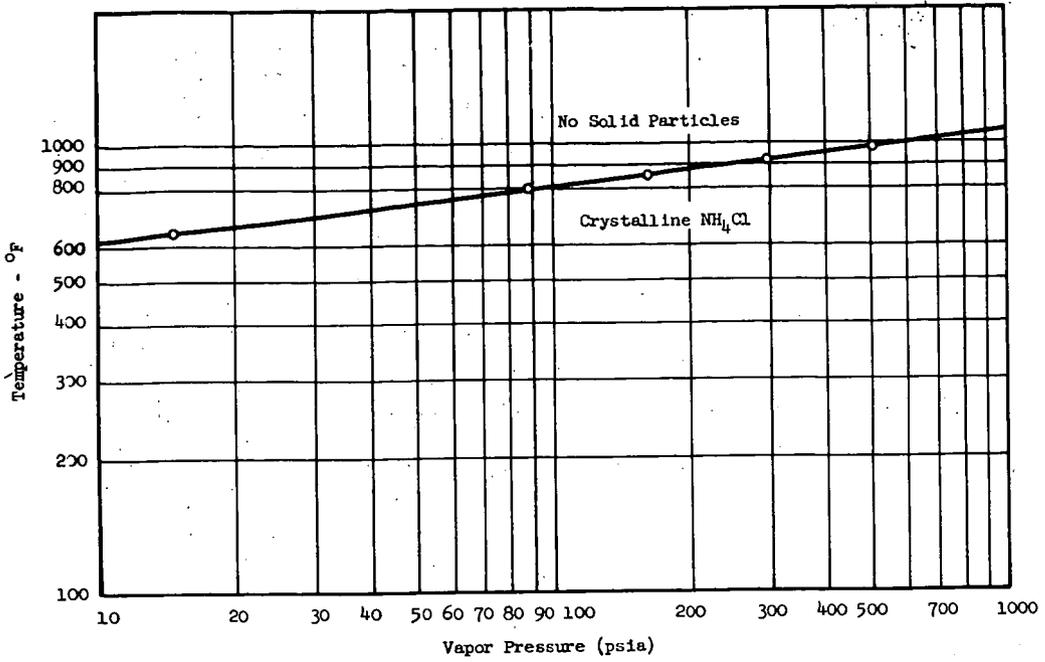


Figure 4. Vapor Pressure of NH₄Cl

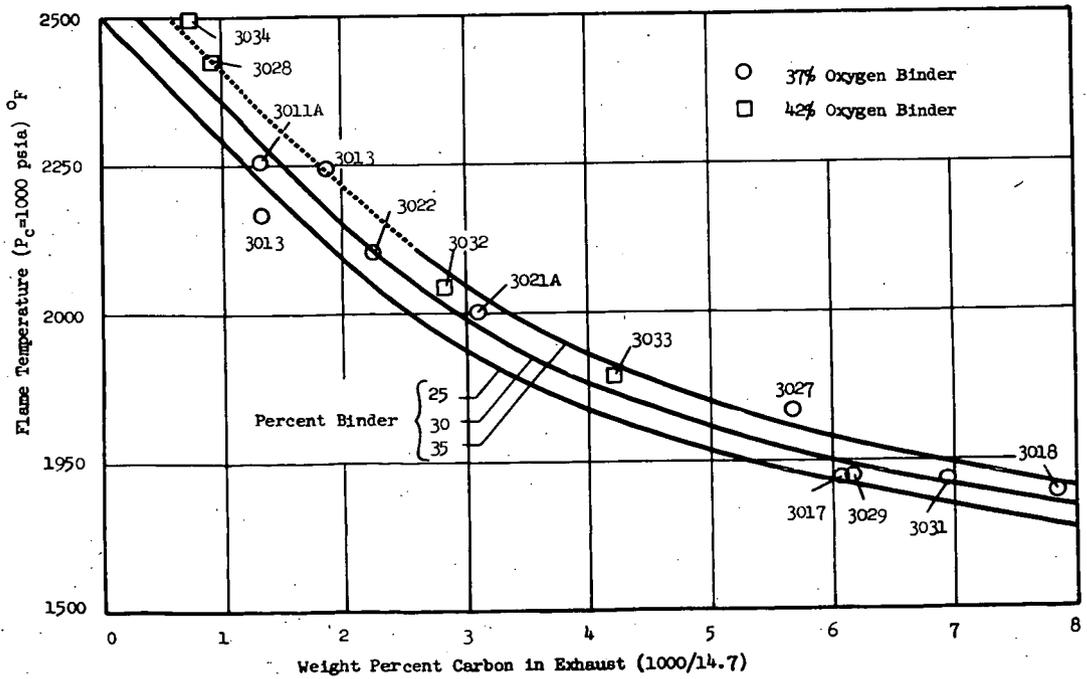


Figure 5. Temperature vs. Carbon Content of Q Series DEQ-AP Propellant Compositions