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CHLORATES AND PERCHLORATES
THEIR CHARACTERISTICS AND USES (U)

Prepared by
Department of Chemistry and Chemical Engineering
Southwest Research Institute

Contract NOrd 18471

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[redacted]

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CHLORATES AND PERCHLORATES
THEIR CHARACTERISTICS AND USES (U)

Prepared by
Department of Chemistry and Chemical Engineering
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DEPARTMENT OF THE NAVY
BUREAU OF NAVAL WEAPONS

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FOREWORD

NAVORD REPORT 7147, Volume 2, is concerned with the characteristics and uses of chlorates and perchlorates and their compounds and is classified CONFIDENTIAL. Volume 1 which is concerned with the manufacture, properties, and use of these compounds is unclassified.

An attempt has been made in Volume 2 to include all compounds which are being used as propellant ingredients or have potential usefulness in the defense program.

The report is transmitted for information purposes only.

Volume 2 of this two-volume series was prepared for the Bureau of Naval Weapons, Navy Department, by the Department of Chemistry and Chemical Engineering of Southwest Research Institute. The project was begun under the broad direction of Dr. Eugene P. Whitlow, Department Director, and completed under the direction of the present director, Dr. William E. Thompson.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF TABLES (Cont'd)

CHAPTER 1. CHLORATES AND PERCHLORATES IN NATIONAL DEFENSE

CHAPTER 1. CHLORATES AND PERCHLORATES IN NATIONAL DEFENSE

Introduction

Most of the information pertaining to the characteristics, methods of manufacture and applications of chlorates and perchlorates does not lie within the realm of national defense and therefore is not subject to the restrictions of military security regulations. Such material comprises the contents of Volume I of this two-volume series on "Chlorates and Perchlorates." There is, however, a certain amount of information on these compounds which is concerned with national defense. It is such material which makes up the contents of Volume II. In order to effect continuity in these two volumes, however, it has been necessary to include some unclassified information in Volume II.

The perchlorates have assumed considerable importance in the last few years because of their use as oxidizers in solid propellants. Chlorates are not used as an ingredient in these propellants but are important as constituents of pyrotechnics and igniter materials. They are also an important intermediate product in the production of perchlorates. The role of chlorates and perchlorates in national defense is an important and interesting one.

Historical

The use of perchlorates as the oxidizer in solid propellants is relatively new in this country, having been used for the first time probably about 1942. However, the use of inorganic oxidizers (e. g., potassium nitrate in black powder) dates back at least to the 13th century when the Chinese are reported to have battled their Tartar enemies with "fire arrows".(1)

Although Berthollet had discovered potassium chlorate as early as 1786 (see Volume I, Chapter 1) his unsuccessful attempt to incorporate it in a new gunpowder formulation in 1788 resulted in a lapse of some forty years before it was used again in pyrotechnic mixtures. According to Davis(2) when Berthollet attempted to prepare his new gunpowder in a stamp mill, the mixture exploded, killing two of the guests who had been invited to witness the manufacture of this new propellant. Because of their inherent sensitivity the chlorates have now been almost entirely replaced in pyrotechnic compositions by the less active perchlorates.

It is believed that chlorates first appeared in pyrotechnic mixtures about 1830.(2) An article by a Prussian artillery captain contained formulas for several compositions which were used in signal rockets. From this article it is apparent that the English at that time were using colored rockets for signalling at sea. The solid propellant rocket was also used by the English to carry lines used in sea disaster rescues. Rocket stations for this purpose were established all about the British Coast. Since 1870 they have saved over 13,000 lives.(3) (Additional information on pyrotechnics is given in Volume I, Chapter 4.) The application of chlorate compounds in signalling devices is still one of their chief military uses.

Although the development of the rocket has taken place principally on the basis of ultimate military use, there have been times when the military would have little to do with such devices. Early in the 15th century writings appeared by military experts suggesting the use of rockets in warfare. (1) In the book "Bellifortis," by Konrad von Eichstadt, in 1405, there is discussion of the use of rockets for military communications. In 1420 the Italian, Joanes de Fontana, proposed rocket propelled marine torpedoes. However, the more accurate cannon forced the rocket into the minor role of fireworks and signalling. This situation persisted in England at least for nearly three centuries.

Real emphasis on extended scientific study of solid propellant rockets developed in England, following a series of British defeats in 1770 around and about Seringapatam, India. Instrumental in defeating the British, was the large, well equipped rocket corps of Tippu Sahib's Indian Army. (5)

Under General Desaguliers and later Sir William Congreve, very effective development work was carried out at the Royal Military Laboratories at Woolwich, which resulted in English rocket supremacy during the Napoleonic Wars. The value of the English rockets was seen during the critical defeats suffered by Napoleon at Leipsig, and later at Waterloo. Even more spectacular was the almost total destruction of Copenhagen in 1807 by some 30,000 rockets fired from the British fleet. These same Congreve rockets were also immortalized by the lines in the Star Spangled Banner referring to the "rockets' red glare" during the British bombardment of Fort McHenry, at Baltimore in the War of 1812.

Ordnance rocket work began in the United States about 1932, about the time when Leslie Skinner began private studies which lead ultimately to the development of the bazooka. It was under Dr. Hickman, a physicist at the Bell Telephone Laboratories who had worked with Dr. Goddard as a graduate student in 1918 that development work began in earnest.(4) His activities under the sponsorship of the National Defense Research Committee were aided by the efforts of Army Capt. L. A. Skinner.(5)

In 1936 the Guggenheim Aeronautical Laboratory of California Institute of Technology, (GALCIT), was founded under the direction of von Kármán and Frank J. Molina. The Jet Propulsion Laboratory also founded by von Kármán and Molina was closely connected with this facility. Here emphasis was on development of small artillery rockets during World War II. However, one signal success in vehicular propulsion was achieved by GALCIT. This was the development of jet assisted take-off units (JATO) for heavily loaded aircraft.(1)

Dr. C. C. Lauritsen of Cal Tech was able to persuade the Navy at the same time to undertake the development of a variety of barrage and aircraft rockets, first at Cal Tech (Eaton Canyon facility) and later at the vast Mojave Desert installation of the U. S. Naval Ordnance Test Station.

In 1941 a rocket laboratory was established at the Naval Powder Factory, Indianhead, Maryland. The two Navy facilities shared in the development of Minnie Mouse, an anti-submarine rocket depth charge, and Tiny Tim, an 11.75-inch diameter aircraft rocket. (1) The first JATO units used in the U. S. were those developed at JPL and GALCIT and fired in 1941 in a successful aircraft take-off. Pressed black powder charges were used. (5) This propellant was difficult to manufacture, the large grains easily fractured, and the specific impulse developed was low.

GALCIT then turned to cast propellants, which were already being used in Germany. A composite propellant formed of granulated potassium perchlorate dispersed in an asphalt binder was prepared by heating the asphalt to 350° F, stirring in the perchlorate, casting in molds, then cooling. This propellant was a great improvement over the pressed black powder. Bigger grains, having better physical properties, could be made. Production was much simpler, and longer burning times with higher specific impulses were attainable. (5)

There were drawbacks to the new propellant, however. The charges deformed under elevated temperature storage. Operation at a high chamber pressure was necessary to maintain stable combustion, and the exhaust from this propellant contained dense clouds of white smoke, which in many cases was a nuisance to vision.

In 1846, the American, William Hale, made the decided improvement of spin stabilization of the rockets, which had been stabilized by Congreve only by the drag of a long stick. Nevertheless, rockets faded from military importance in the latter half of the nineteenth century due to the much greater accuracy achievable with cannon after the introduction of rifled barrels. (1)

For the next eighty years military interest in rockets was slight; the most spectacular use during World War I being that of solid propellant air-to-air rockets launched by French Nieuports against German observation balloons. Interest in rockets was kept alive, however, by a growing consideration of them as vehicular propulsive devices, both on the earth and for possible interplanetary voyages.

In 1903 Konstantin Ziolkowski, the father of Russian Astronautics, published a competent technical monograph, "The Exploration of World Space by Reaction Apparatus". (1) This was followed in 1918 by data published by the American Professor Goddard, under sponsorship of the Smithsonian Institute. This data, by inference, supported the practicability of a rocket flight to the moon. (3) Throughout the twenties and into the early thirties Goddard carried on valuable experiments with liquid fuel rockets.

In 1927 the "Space Travel Club" was formed in Breslau, Germany, and conducted some useful work until 1936 when all of the German activity was taken under the Nazi wing, and the research center at Peenemünde was established. (1) Sparked by Professor Hans Oberth and Werner von Braun, Germany undertook a rocket program at Peenemünde comparable in size to the later Manhattan project in the United States. Although major emphasis was placed on liquid fuel rockets, culminating in the famed V-2, a great deal of work was also done on solid propellant missiles.

A large four-stage (including booster) artillery rocket became operational in 1943. This "Rheinbote" was propelled by a solid mixture of nitrocellulose and diethyleneglycol dinitrate. 1290 pounds of this propellant brought the final stage to a velocity of 5380 ft/sec, and hurled it 136 miles with an 88-pound warhead. At the end of the war, Professor Oberth had in the design stage a three-stage solid propellant missile that was to carry a 3300-pound payload 200 miles, developing a total impulse of 3,190,000 pounds sec. This was more than competitive with the V-2.

Although German developments were paramount, all of the major belligerents of World War II developed rocket weapons. In Russia, emphasis was on massed short range artillery rockets, such as the Katysusha, which were used in tremendous quantities at Stalingrad. Russian cordite, composed of nitrocellulose-nitroglycerin and dinitrotoluene, was a favored solid propellant.

The most striking contribution of the Japanese was the manned solid propellant rocket plane, the Baka, which had a range of 55 miles after launching from a parent aircraft.

At the end of 1944 an Aerojet-General research rocket, called the Private A, flew eleven miles, powered by a motor that delivered 1000 pounds of thrust for 30 seconds. (5) Development work has continued, however, to the present time, when solid propellants provide the propulsion for such systems as the Polaris, the Pershing, and the Minute Man. Solid propellants are also playing their part in the space flight program. The three upper stages of the Jupiter-C, carrier of the Explorer satellites, are driven by solid propellants. (1) The third stage of the Vanguard also contained solid propellant.

Propellants

Up to World War II, most solid propellant rockets employed a simple black powder, which is a mixture of saltpeter (potassium nitrate), charcoal (carbon), and sulphur. Black powder in its usual condition, however, is a fine, granular material. The great surface-to-mass ratio for such a granulated material leads to very fast burning times, which are incompatible with the requirements of rockets for vehicular propulsion units. To slow the burning times, large, specially shaped grains of black powder, formed under high pressure, were developed for the JATO application.

Although nitrocellulose-containing compositions have been used in many rockets and missiles, composite propellants, having perchlorate oxidants, have been playing increasingly significant parts in the development of solid propellant rockets, ever since the early days of the GALCIT program when potassium perchlorate/asphalt was substituted for the pressed black powder initially used in the JATO application. These perchlorate systems have provided propellants with good physical properties, temperature stability, and fairly high specific impulses.

At first the perchlorates, potassium and later ammonium perchlorate, were combined with simple everyday materials as fuels. Thus asphalt, pitch, felt, and rubber, all were used in different applications. As these combinations revealed their various weaknesses, more unusual fuels were employed.

Plastic resins, polyvinyl chloride plastisol, polyurethane and polysulfide polymers have all enjoyed prominence as fuel binders for the perchlorates, along with the great number of plastic, resinous or elastomeric materials that were tried on at least an experimental basis.

In the continuing attempts to increase propellant specific impulses, so-called high-energy binders (fuels containing nitro or nitrate groups in their molecules) were mixed with the perchlorates. In some of these mixes, nitrocellulose was used, and sometimes nitroglycerine is added.

Nitroglycerin is a monopropellant in its own right, having adequate fuel and oxidant in each one of its molecules and is a liquid. A number of nitropolymers have been studied.

Recently the use of metals in quantities exceeding that normally thought of as typical of an additive, has resulted in a new class of metallized propellants, with exceptionally good specific impulses. Many different metals have been employed, with aluminum playing a leading part so far. The metal boron and its compounds are also being studied.

Perchlorates employed have not been restricted to potassium and ammonium. Some work has been done with sodium perchlorate, and even with barium, magnesium and aluminum perchlorates. Lately, lithium perchlorate has been gaining a great deal of prominence in experimental work. A small amount of study has been devoted to the possibilities of complex organic perchlorates, but generally these are undesirably unstable.

Until recently the use of perchlorates in propellant systems has been restricted to composite type solid propellants. Some new research and development programs are showing interesting results with (1) solid solution propellant and (2) stable slurries. In the first system a perchlorate (e.g., lithium perchlorate) which is soluble in a particular monomer is dissolved in this solvent. Upon polymerization of the monomer a solid system results. The second system consists of the formation of a stable gel in which the perchlorate particles are uniformly dispersed. This gel can be pumped as are liquid propellants, but it has nearly the density of a solid propellant and it is a very stable monopropellant.

Energy Sources

In addition to their use in solid propellants, the perchlorates (and chlorates) find other military applications. These include (1) signal devices, (2) initiators (or squibs), (3) igniters, (4) explosives and (5) miscellaneous items. Compared to propellants the quantities used are extremely small.

The use of chlorate and perchlorate compounds in the pyrotechnic mixtures of which most signal devices are composed has already been discussed. (See Volume I, Chapter 4.) Most signal devices have been adopted from the equivalent civilian units and are not, therefore, subject to security restrictions.

The initiators or electric squibs which are usually used to start the functioning of an igniter have been adapted from the explosives detonator field. Early units contained such explosive materials as mercury fulminate or lead azide. In order to obtain improved storage stability there has been a general shift to chlorate- or perchlorate-containing mixtures.

Black powder has been the universal igniter material since the days of Roger Bacon. In recent years certain new solid propellant compositions have become difficult to ignite with black powder. By incorporating a metal-oxidant mixture either wholly or in part as the igniter material, igniters **which operate successfully over relatively wide temperature ranges and high altitude have been achieved. The greater stability and lower sensitivity of perchlorate** mixtures have led to their more general acceptance over the chlorates as the oxidizing material in such mixtures.

The general use of chlorates and perchlorates in explosives has already been discussed (Volume I, Chapter 4). There is one area, however, which concerns the class of explosives designated as MOX, which is still classified. The compositions and characteristics of these compounds are, therefore, contained in this volume.

New Developments in Manufacturing

When it was realized in the late 1940's that the shift from nitrocellulose-based propellants to the newer composite-type systems was imminent there was deep concern over what to do about the tremendous demands for the perchlorates that this would create. There was serious doubt at that time that there was either sufficient electrical power or enough available platinum to permit full-scale production of these important compounds. As a result the military (primarily the Navy) sponsored several programs aimed at alleviating both or either of these problems.

These programs were carried out generally under Office of Naval Research guidance. Some of them have been reported in the open literature and are discussed in Volume I, Chapter 2. The more speculative programs and ideas which have not been given a release from security restrictions are discussed in this volume.

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CHAPTER 2. PROPELLANT SYSTEMS

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Introduction

Of the two classes of compounds, chlorates and perchlorates, only the perchlorates are used in solid propellants. The particular propellant compositions containing the perchlorates are called "composite" propellants. In these systems the inorganic compound in a finely divided form is uniformly dispersed in a resinous, plastic or elastomeric binder material. The oxidizer content is usually between 75 and 85 percent by weight. (61)

In addition to the usual composite systems there have recently been developed two modifications. One system takes advantage of the unusually high solubility of perchlorate compounds in organic solvents. The propellants of this type are called solid-solution propellants. In preparing them, the perchlorate (presently lithium perchlorate) is first dissolved in a monomer after which the solution is polymerized. The resulting solid propellant has quite different characteristics from the normally heterogeneous nature of the composite propellant.

The second modified system consists of a slurry. In this propellant the perchlorate is uniformly dispersed in a gel. The resulting slurry can be pumped in the same way the fuel or oxidizer is in a liquid propellant rocket. For convenience these last two systems have been placed in a separate section of this chapter, entitled "Other Propellant Systems."

In presenting information on the properties of particular propellant compositions, only general, pertinent data are tabulated. For more complete details the reader is referred to SPIA Manual M2. (43)

Solid Propellant Systems

Nonmetallized Systems

General Considerations. The two principal perchlorate compounds used in solid propellants are potassium and ammonium perchlorate. The early compositions all contained the potassium salt, but its undesirable smoke characteristics led to its subsequent replacement by the ammonium compound. Lithium perchlorate is the third perchlorate which has been used in propellants, but its use is still very small. Some work was also done with sodium perchlorate, but this was early in composite propellant history.

Up until recent times solid propellant compositions contained very little in the way of metallic compounds. In some compositions a metalo-organic compound in small quantities (2-4 percent) served as a ballistic modifier. The new, high-energy systems, however, all contain appreciable quantities of powdered metals, such as aluminum. For purposes of ease in presentation the nonmetallized systems will be discussed first and the effect of powdered metal will be introduced last.

$KClO_4$ Systems. The majority of early work on composite propellants was carried out with potassium perchlorate as the oxidizer. A review of some of these studies presents a historical summary of propellant development. Potassium perchlorate is seldom used today in any appreciable quantity.

The first composite propellant used in a rocket system in this country was the Asphalt-$KClO_4$ system employed in the JATO units developed by GALCIT. This system was later adopted by the then Aerojet-Engineering Corp. for use in their 14AS-1000,JATO units. The general composition and characteristics of this propellant are given in Table 2-1.

Alphalt has a melting point around 212° F and becomes brittle at moderately low temperatures. Consequently, this system had a very narrow safe-operating temperature range. (61) It was replaced by other binder materials.

In the mid 1940's there was an accelerated effort to find means to incorporate potassium perchlorate into a propellant system. Some of these methods might seem primitive if it were not that similar approaches are being followed again today.

One particular effort was directed toward the fabrication of a propellant utilizing sponge or felt saturated with a slurry consisting of 36 percent diesel fuel and 64 percent $KClO_4$. (57) Another composition contained 20. 2 percent gasoline, 1. 5 percent sodium palmitate, 0. 5 percent aluminum stearate, 2 3 percent fuel oil, and 75. 5 percent $KClO_4$. Such a mixture was loaded into a 1/2-inch pipe motor with a 0. 116-inch diameter nozzle and fired by means of hot wire ignition. It burned for 302 seconds and then blew up.

A water slurry of potassium perchlorate and ammonium nitrate was absorbed into a sponge resulting in a propellant of 16. 6 percent sponge, 33.3 percent $KClO_4$ and 50.1 percent NH_4NO_3. These sponges were submitted to solar drying; however, "the California sunshine proved a little too damp for satisfactory drying." The propellant was never burned successfully.(57)

In some later developments a mixture of Paraplex P-10 fuel and potassium perchlorate was studied.(48) This propellant yielded a specific impulse of about 199 lb-sec/lb, but the P-10 monomer was rather hard to handle because it had a flash point of 90°F. Nevertheless, this system was studied further and was found to produce a propellant charge with physical properties superior to the asphalt base propellants being used then in JATO units.(47) The paraplex propellants exhibited no tendency to flow or deform appreciably under high stresses at temperatures of 150°F or more. Their impact strength at low temperatures was good. This propellant was easier to mix and cast than the asphalt propellant and was somewhat safer to handle because of ignition difficulties at atmospheric pressure. The performance characteristics of the two propellants were about the same. A typical composition with its characteristics is given in Table 2-2. This system served as the basis for a whole series of propellant compositions in which ammonium **perchlorate later replaced the potassium salt and which are still being used.**

Because of the problems encountered at low temperatures as a result of the brittle behavior of the propellant, attention was turned to elastomeric materials. One of the early systems investigated was a propellant containing potassium perchlorate in a Vistanex (polyisobutylene) binder (60) A mixture of 76 percent potassium perchlorate and 24 percent Vistanex had an autoignition temperature above 900° F. It would not detonate under a 2 kg weight dropped from 100 cm and at 40° F it would not shatter when "thrown forcibly against a concrete wall." The physical properties were "good" over the temperature range from -40° F to 140° F.

Since rubber appeared to possess the near-ideal properties, it was also used as a binder with $KClO_4$. Various methods for preparing a system were studied. In one case a propellant composed of 26 percent neoprene casting cement and 74 percent potassium perchlorate was prepared.(53) This propellant had a low tensile strength (40 psi ultimate). The burning rate was 0.7 in./sec at 1000 psi and yielded a specific impulse of 170 lb-sec/lb. The propellant would not burn stably above 800 psi. Because of the bad physical qualities, further work was suspended on this neoprene casting cement-$KClO_4$ propellant.

Other methods of incorporating the $KClO_4$ into the rubber were investigated.(53) Two in particular were:

(1) Coagulation of rubber to occlude oxidizer from a rubber latex - oxidizer slurry, followed by filtering, drying and pressing into a charge.

(2) Milling the oxidizer and rubber together on a differential-roll mill, cutting discs from the resultant sheets and pressing them together.

These methods failed to produce as acceptable grains as the casting-cement method which was attractive because of its simplicity and the lower hazards involved. In spite of the hazards involved in rolling material containing $KClO_4$, some additional compositions were made. A sucessful propellant was prepared with neoprene as fuel-binder by incorporating $KClO_4$, cottonseed oil (plasticizer), micronex (carbon black), calcinated magnesia, neozone A (phenyl-alpha-naphthylamine as an antioxidant), zinc oxide, and stearic acid, using a differential-roll mill.(42) The burning rate for this propellant was .57 in./sec at 1000 psi with a pressure exponent of .60. However, this method of preparation was soon dropped and has not been used except for systems which utilized the less sensitive oxidizer, ammonium nitrate.

The $KClO_4$ systems became of interest to rocketry primarily because they were made by a casting process and, therefore, there were no known restrictions on charge size. At that time the only competitive systems were the nitrocellulose-base or homogeneous propellants. Since this latter class of propellants was at that time formed into charges by means of an extrusion process, it very definitely had a size limitation. When comparative firing of the two types of propellants were made, the very undesirable feature of the tremendous clouds of smoke which were generated by the $KClO_4$ propellants became apparent.

This factor forced the replacement of $KClO_4$ by the smokeless compound NH_4ClO_4.

Aside from the smoke problem, the $KClO_4$ propellant system had a number of desirable characteristics. Of course, there were also a few additional undesirable ones. For comparative purposes, a typical $KClO_4$ composition might be compared with a typical nitrocellulose-base system. For example, AK-14(Mod 1) is compared with JPN in Table 2-3.

One early composition containing $KClO_4$ has managed to survive. In the early 1940's it became necessary to improve the performance (especially at low temperatures) of the propellant used in the Bazooka rocket. The results of research efforts was a composition containing about 8 percent $KClO_4$. This composition was called M7 (now T-4). The characteristics of this propellant are given in Table 2-4.

NH_4ClO_4 Systems. The vast majority of the composite-type solid propellants used today contain ammonium perchlorate as the major ingredient. Other oxidizers may excel in either available oxygen content, insolubility or other properties, but they lack the over-all capabilities of NH_4ClO_4. The extensive use of this oxidizer in present propellant composition is largely because of the following reasons: (1) good stability, (2) reasonably high density, (3) availability, (4) results in high performance compositions with metal additives, (5) low moisture affinity, (6) propellants generally have low pressure exponents and low temperature sensitivities.(22)

1. Comparison With $KClO_4$. The replacement of $KClO_4$ in propellant compositions with NH_4ClO_4 helped eliminate the smoke problem and made other helpful changes in propellant processing and performance characteristics. A comparison of some of these characteristics is made in Table 2-5.(13)

The main difference between the two perchlorates lies in the generally higher burning rates (with higher pressure exponents) and lower specific impulses obtained with $KClO_4$. It has been shown(15) that the replacement of potassium perchlorate by ammonium perchlorate in polyvinyl plastisol formulations decreases the burning rate by a factor of about one half. Also the burning rate-pressure exponent decreases at the same time. Figure 2-1 compares the burning rate curves for the two types of propellants. It is postulated that the higher burning rate for the $KClO_4$ composition is due to the decomposition of this perchlorate to give KCl which acts catalytically.(44) The fact that the pressure exponent is also higher with $KClO_4$ propellants must not be overlooked. Because of this factor, it should be possible to have a faster burning rate with the $KClO_4$ propellant at moderate and high pressures, but to have a slower burning rate at low pressures. For example, the substitution of potassium perchlorate for ammonium perchlorate in "C" rubber formulation in order to increase the burning rate of this composition produced a decrease in burning rate and an appreciable increase in the pressure exponent.(10) This propellant was generally inferior to NH_4ClO_4 propellants.

A comparison has been made of the effect of replacing $KClO_4$ with NH_4ClO_4 on the calculated specific impulse.$^{(6)}$ The particular binder used was a polyvinyl chloride-dibutyl sebacate plastisol. Figure 2-2 shows that increased specific impulse is obtained with all equivalent contents of NH_4ClO_4.

When ammonium perchlorate replaces ammonium nitrate a much greater change in performance characteristics takes place. For example, when a portion of the NH_4NO_3 oxidizer in a butadiene-methylvinyl pyridine copolymer propellant was replaced with NH_4ClO_4, there was a noticeable increase in c* value and burning rate.$^{(41)}$ The NH_4ClO_4 also appeared to reduce the tensile strength of a propellant while increasing the elongation.

2. Binder Variations. Although the oxidizer is the major consitituent of a composite propellant system, it is the binder which determines many of its characteristics. On the basis of binder alone it is possible to divide the composite propellant systems into several classes. Even though the subject of this volume pertains to chlorate and perchlorate compounds and not to propellant binders, it is of interest to divide the many compositions into such classes in order to examine the different characteristics of the propellants which are produced.

There are innumerable materials which have been used as binders in composite propellants. Most are plastic, resinous or elastomeric materials. For convenience they may be divided into the following categories: asphalt-oil; resins; elastomers; and high-energy binders (e.g. nitrocellulose).

a. Asphalt-oil. The asphalt-ammonium perchlorate propellant was one of the first of the composites. Its use was limited almost entirely to JATO units. Because the asphalt became extremely brittle at moderately low temperatures, it was mixed with an oil. This, however made the composition soft at elevated temperatures. This was true for either the $KClO_4$ or NH_4ClO_4 types. The NH_4ClO_4 composition was, of course, smokeless and it had good chemical stability. Typical specific impulse values quoted for these compositions were about 211 lb-sec/lb. (54)

b. Resins. A wide variety of resinous materials can be used as binders for NH_4ClO_4 propellants. Resins used have included the polyesters and acrylates.

Polyester resins are of interest because they can be easily cured in a simple casting operation. For example, the acrylate-polyester resins have excellent low-temperature properties as well as high specific impluse. The styrene-polyester propellants are still being made. (16) A representative composition is given in table 2-6. (43) The burning rate of these compositions may be varied within

relatively wide limits by adjusting the concentration of the burning-rate catalysts ethyl ortho silicate and ammonium dichromate.(16)

c. Elastomers. The search for the binder which would give the best physical (mechanical) properties at low temperatures has led to the adoption of certain elastomeric materials.

Natural rubber has found little use in propellants. Types of synthetic elastomers that have found considerable use are: (1) the polysulfide polymers, and (2) the plasticized vinyl chloride polymers and copolymers of butadiene-methyl vinyl pyrdine, polyurethanes and polybutadiene-acrylic acid.

One of the early groups of propellants investigated by the British were the plastic propellants. These contained polyisobutylene, a plastic with rubbery characteristics. Recent efforts have been concentrated on a group of elastomers made from the reaction between a diol and an isocyanate with a triol used as a cross-linking agent. These compounds called polyurethanes have many interesting characteristics.

1) Polysulfide Propellants. A large number of compositions have been made with ammonium perchlorate in a matrix of polysulfide rubber. Three basic types of polysulfide prepolymers are recognized. These are: (1) ethyl formal polysulfide (LP-33), (2) butyl formal polysulfide (LP-205), and (3) butyl ether polysulfide (ZL-270)(23) The most commonly used is the LP-33. One of the attractive properties of polysulfide propellants is their good low-temperature flexibility. The composition and characteristics of a typical polysulfide propellant are given in Table 2-7.

Ferric oxide is commonly used as a burning rate modifier in polysulfide propellants. Magnesium oxide is sometimes used to improve the tensile strength. Aluminum (about 2 percent) is occasionally added as an antiresonance agent. (58)

2) Vinyl Propellants. The vinyls have found relatively wide usage in the "Plastisol" type propellants. For these compositions the resin (usually polyvinyl chloride) has been completely polymerized prior to mixing with other ingredients. A plastisol propellant then is a fluid suspension of polymer particles in a nonvolatile plasticizer containing large quantities of inorganic oxidizer, which, on the application of heat, fuses into a single solid-phase mass. (14)

The characteristics of a typical propellant are shown in Table 2-8.

One of the attractive features of this type of propellant is its physical properties which provide good performance over a relatively wide temperature range.

The use of conventional burning rate catalysts in polyvinyl chloride plastisol has little or no effect on the burning rate. Burning rates may be controlled by varying the size and percent ammonium perchlorate. A wide variation in burning rate may also be obtained by adding varying amounts of $KClO_4$ to the oxidizer. (14) Higher burning rates have been effected by the use of small diameter wire embedded in the propellant. (7)

Ammonium perchlorate has also been used with polyvinyl ether as a binder. This formulation appeared to have good physical characteristics even with an oxidizer concentration as high as 90 percent and was simple to process. Grains were extruded in finished form with no additional curing or drying required. (49) This propellant has not received much use as yet.

3) Polyurethane Propellants. One of the newer propellant systems, polyurethane propellants, utilizes ammonium perchlorate as the oxidizer. Because of the fundamental linkage mechanism of the polymer network, there exists an almost endless array of possibilities for obtaining desirable propellant properties. (23) The polyurethane which serves as the fuel and binder, consisting of a diol, (e. g. , polypropylene glycol), a cross-linking triol (e. g. , glyceryl monoricinoleate) and an isocyanate (e. g. , tolylene diisocyanate). Because the more recent, interesting propellant compositions contain metal, details on their characteristics will be discussed under Metallized Systems.

The composition and some of the characteristics of a polyurethane propellant are given in Table 2-9.

In manufacturing some of these propellants a wetting agent, such as lecithin, is added to the propellant mixture in order to permit casting of the high-solids formulations. (4)

Polyurethane propellants seem to have lower pressure exponents and temperature sensitivities compared to other classes of composite propellants. (23)

4) Other Elastomers. Plastic propellants developed by the English consist of ammonium perchlorate and ammonium picrate in a polyisobutylene binder. The burning rate of these propellants may be increased up to 100 percent by the use of catalysts such as Ci_2O_3 or TiO_2. The specific impulse is about 240. Plastic propellant burning rates are generally insensitive to temperature in the range -40° to 140°F. Lecithin is used as a wetting agent in processing. Considerable study has been made relating the specific surface of the oxidizer to the burning rate. (5) This class of propellant has not been studied very much in this country. Table 2-10 shows a typical composition. **For one synthetic rubber-ammonium perchlorate propellant composition it has been reported that high burning rates and good physical properties were obtained.(8) The binder in this particular propellant composition was a modified polybutadiene elastomer. Burning rates of well over 2 in./sec at 1000 psi and $70^{\circ}F$ were obtained. The use of MgO as an additive increased the burning rate slightly while it greatly increased the tensile strength.(11) An experimental composition is shown on the following page.**

Ingredients			Wt %
Binder	Modified polybutadiene	83.33	14.55
	Stearic acid	16.67	
Ammonium perchlorate			83.79
Silan S			1.00
Mg O			.66

Silon S, a high surface area silica pigment, serves as a burning rate catalyst. (11) The use of copper chromite as a burning rate catalyst, while giving excellent ballistic properties, caused considerable instability of both physical and ballistic properties during subsequent aging. (11) The use of oleic acid as a softener in place of stearic acid gives much improved physical properties as the oxidizer level is increased. (9)

A polybutadiene-acrylic acid copolymer (PBAA) **is currently being evaluated as a propellant binder.** (25) **The PBAA binder is being used by several organizations developing new formulations of propellants.** (26) This system was developed to provide a polymer with a combustion enthalpy comparable to the best hydrocarbon fuels. For best use, aluminum is added. A typical composition is TRX-H 606.

Constituent	Wt %
NH_4ClO_4	74.00
PBAA	18.00
Aluminum	8.00

Burning rate at 100 psi and 70° F = 0.295
Temperature coefficient = .11
Specific impulse (1000 psi) = 240

d. High-energy Binders. The desire to increase the energy content of composite propellant systems has stimulated research on high-energy binders. The most common approach is to use materials containing nitro or nitrate groups. Nitrocellulose is a readily available nitrated compound. Other considerations include nitro-polyacrylate, petrin (pentaerythritol trinitrate) acrylate, polyglycidal nitrate, nitro polyurethane A new group of compounds - the fluorocarbon polymers - are also being given consideration.

1) Nitrocellulose. The use of perchlorates in nitrocellulose composition dates back to the 1940's when the M-7 (J4) composition was developed for the Bazooka rocket. A relatively small amount (about 8%) of $KClO_4$ was used (see $KClO_4$ propellants). Solventless-type propellants did not incorporate NH_4ClO_4 in their compositions because of the danger of detonation during the rolling operation. Later when cast compositions were developed, it has become easier and less hazardous to use NH_4ClO_4.

The interest in composite-type propellants using nitrocellulose as a binder had not been very strong until metallized systems were developed. Early work produced some experimental compositions containing nitrocellulose without an explosive plasticizer. For example, single-base polymer propellants have been formulated using nitrocellulose plasticized with EPON 562 (glycidal glycerate) as a binder for ammonium perchlorate oxidizer. Triacetin is added to aid in colloiding the mix. M-phenylenediamine is the curing agent. The following composition has been studied:(52)

Ammonium perchlorate	60%
Nitrocellulose	18%
Triacetin	2%
Epon 562	20%
M-phenylene diamine	14 parts/100 parts resin

This composition cures readily to give a hard tough propellant. The thermal stability is very good. Burning rate for milled strands was 0.55 in./sec at 1000 psi.

In some other experimentation a propellant containing nitrocellulose, triethylene glycol trinitrate, and ammonium perchlorate was investigated in an attempt to find a propellant with good low-temperature characteristics and improved physical properties.(51) Charpy impact tests at -40° C indicated a slight improvement in the strength of this formulation over some standard double-base compositions.

The current interest, however, lies with two systems. One is the cast double-base system and the other is the nitrocellulose plastisol system. A discussion of both of these will be given in the section on Metallized Systems.

2) Other Nitro-compounds. The use of high-energy binders other than nitrocellulose with ammonium perchlorate has been accelerated by the requirements for higher and higher specific impulse. In most instances development studies have been undertaken directly with the

metallized systems. Consequently a detailed discussion of most of these systems will be left for the section on metallized systems.

Of interest here is the work done with nitroacrylates. Nitropolyacrylate propellants using ammonium perchlorate as an oxidizer were studied as part of a program to formulate a nitropolymer grain of high performance. (1) The binder material consisted of dinitropropylacrylate-acrylic acid copolymer plasticized with dinitropropyl nitrazopentanoate. In these formulations, the ammonium perchlorate content was less than 70 percent. Zinc oxide was added as a cross-linking agent. The degree of crosslinking, and therefore the physical properties, were determined by the percent ZnO present. CaO and MgO were also studied as possible cross-linking agents.

Burning rates of nearly 2.5 in./sec at 1000 psi have been obtained using cupric oxide or ammonium dichromate as catalysts.

Another interesting study was concerned with the substitution of polyglycidal nitrate for polypropylene glycol in polyurethane binder formulations and the incorporation of nitric ester groups in the plasticizer for an ammonium perchlorate/polyurethane propellant of high theoretical performance. (20) The mechanical properties of the resulting resin were closely related to polypropylene-polyurethane resins which have good low-temperature elongations. However, the desirability of using nitric ester binders with ammonium perchlorate oxidizer is somewhat questionable. (21) A typical experimental formulation (JPLX560) is shown on the following page.

Constitutent	Wt %
Polyglycidal nitrate	18.5
G-3F- crosslinker	1.27
Hexamethylene diisocyanate	4.73
1, 4 Butylene glycol dinitrate	10.50
Ammonium perchlorate	65.00

Calculated specific impulse for this formulation is 251.9 lb-sec/lb.

Sodium Perchlorate. The use of sodium perchlorate as an oxidizer in solid propellant formulation has been studied.(36) $NaClO_4$ is attractive in that it is an intermediate in the production of $KClO_4$ and NH_4ClO_4; hence, it would be less expensive. $NaClO_4$ also contains more available oxygen than either $KClO_4$ or NH_4ClO_4. Incorporating $NaClO_4$ in a polysulfide fuel matrix results in a propellant with a tensile strength much greater than those using $KClO_4$ or NH_4ClO_4. However, this propellant picks up moisture both in storage and in processing due to the hygroscopicity of NaClO4. It is also very difficult to ignite. Because of these undesirable characteristics sodium perchlorate has never been used to any great extent in solid propellant compositions.

Lithium Perchlorate. Lithium perchlorate has a number of advantages over other perchlorates as an oxidizer in solid propellant formulations.(18) This compound has a high-oxygen content (on a weight basis) resulting in propellants with lower salt contents than ammonium perchlorate propellants. The lithium perchlorate propellants are reported to have better physical properties, are more easily processed, and are less sensitive to impact because of this lower salt content. A higher burn-out velocity is obtained in some propellant compositions using lithium perchlorate due to its high density, although the specific impulse is lower. The autoignition temperature and detonation properties of these propellants are very similar to those of potassium perchlorate.

Lithium perchlorate propellants produce a large amount of white smoke which might be objectionable. However, the development of metallized systems in the search for higher impulse propellants also results in smoky exhaust.

The first experimental studies with lithium perchlorate were carried out in a butyl rubber fuel matrix.(30) The resulting compositions were characterized by very difficult ignition, high autoignition temperature, high impact sensitivity, and high burning rate-pressure exponents. It has been found that the burning rate-pressure exponent increased with an increase in oxidizer particle size.(33) The calculated specific impulse for this composition was 245 lb-sec/lb(34), giving promise of a high-performance propellant.

Similar studies with lithium perchlorate were carried out in other rubber-base propellants.(46) The compositions where lithium perchlorate was the sole oxidizer were characterized by difficult ignition and irregular burning. By using ammonium perchlorate as a co-oxidizer, better ignition and burning were obtained. However, satisfactory propellants were not obtained until the ammonium perchlorate was increased to the major portion of the oxidizer. The addition of small amounts of lithium perchlorate to ammonium perchlorate/rubber-base propellants was also found to decrease the impact sensitivity.

A propellant with good physical properties was prepared with lithium perchlorate in a polysulfide fuel matrix.(30) Density, tensile strength, elongation, and impact sensitivity were improved and the burning rate was raised with the addition of carbon black.(32) The specific impulse for this propellant is about 225 lb-sec/lb and the volume impulse is approximately 15.7 lb-sec/in.^{3}. A burning rate of 0.76 in./sec at 1000 psi and a pressure exponent of 0.44 have been obtained. An increase in burning occurs with the addition of powdered aluminum.

The use of lithium perchlorate as an oxidizer in polyurethane propellant formulations has also been investigated.(30) The resultant propellant was found to be thermoplastic at temperatures above 180° F. In this formulation, a reaction between $LiClO_4$ and polypropylene glycol to form a hard mass necessitated a change in the methods of processing.

Magnesium Perchlorate. Extensive work has been carried out to evaluate several high-density perchlorates as oxidizers in an effort to increase the performance of propellants utilizing some of the more suitable polymer binder-fuels.(30) From a theoretical view magnesium perchlorate shows much promise as an oxidizer. Its density of 2.6 g/cm^3 is much higher than ammonium perchlorate (1.95 g/cm^3) and it has more available oxygen.

This would enable the total amount of solids to be reduced, thus improving the physical properties. $Mg(ClO_4)_2$ was found to be reactive with aromatic diisocyanates (polyurethane ingredient) when heated. Polysulfide/magnesium perchlorate propellants were eliminated because of unsuccessful efforts in obtaining a castable material.(32) Magnesium perchlorate was incorporated into butyl rubber using a roller mill. The hygroscopicity of the $Mg(ClO_4)_2$, however, made processing difficult and resulted in a propellant that was low in oxidizer content and badly laminated.(30)

Barium Perchlorate. Barium perchlorate, while being rather low in available oxygen [$Ba(ClO_4)_2$ = 38.1, NH_4ClO_4 = 54.7], has the highest density of all the oxidizers investigated. With this oxidizer, it was hoped to obtain a propellant with a high volume specific impulse.

A plastisol-barium perchlorate propellant was made using Elastomer 105 (Furane Plastics, Inc., Los Angeles, Calif.). This propellant cured readily, but was not castable even at low oxidizer concentrations.(30)

It was next attempted to use barium perchlorate as an oxidizer in a polyurethane binder.(44) The mix was easily processed; however, the mix began to harden before the catalyst (ferric acetylacetanate) was added. The reaction was such that a satisfactory casting could not be obtained.

A propellant with physical properties comparable to other propellants in its class was prepared using $Ba(ClO)_4$ in a polysulfide binder-matrix. The specific impulse for this propellant was 185 lb-sec/lb compared to a similar one using ammonium perchlorate giving specific impulse of 235 lb-sec/lb^{-1}. However, the volume impulse of the former is 16.2 lb-sec/in.^{3} against 15.1 lb-sec/in.^{3} for the ammonium perchlorate propellant.(31) Burning rates of about 2 inches per second at 1000 psi have been obtained; however, the burning rate-pressure exponent was unacceptably high.(32)

Aluminum Perchlorate. The use of aluminum perchlorate as a possible additive to obtain propellants of high impulse has been investigated.(59) The use of this material, however, was discontinued because of the instability of combinations with certain binder systems.

Metallized Systems.

General Considerations. Investigations have been made on the effect of the addition of powdered metals in propellant compositions. The use of these metals boosts the specific impulse by increasing the flame temperature and decreasing the average molecular weight of the exhaust gases.(19) The most common approaches to increasing performance in the development of high impulse propellants have been: (1) to increase the oxidizer content, and (2) to introduce nitro groups into the polymer structure.

Increasing the oxidizer content of a propellant causes many problems in casting the grains in addition to causing a loss in physical properties. Also, increasing the oxidizer beyond a point will result in high molecular weight oxides, producing an exhaust gas of high average molecular weight, thus offsetting any gain in impulse due to a higher flame temperature. Resonant burning in high oxidizer content propellants also becomes a problem.

The introduction of nitro groups into the polymer structure increases castability by reducing the oxidizer requirement. However, the impact sensitivity of the binder increases as more oxygen is added.

The increase in the flame temperature of aluminum-containing propellants causes severe erosion to conventional steel nozzles. This has been largely overcome by the use of temperature resistant materials. (2) A reduction (of about 5 %) in the total quantity of solids required when aluminum is used, also results in improved physical properties.

At the present time interest lies in obtaining solid propellants with specific impulses of between 250-275 lb-sec/lb. The ultimate requirement, in order to be competitive with liquid propellant systems, is for specific impulse values of 275 and above. Such high specific impulses are to be obtained, of course, with the same high reliability possessed by the present lower-energy systems.

The high-energy systems receiving the most attention now are the following:

(1) Metallized Nitrasol

(2) Metallized Double Base-Composite

(3) Metallized Nitropolyurethane

(4) Metallized Petrin Acrylate

(5) Metallized-Elastromers with Ammonium Perchlorate

In addition to the above consideration is being given to the use of fluorocarbon polymers as binders in propellant systems.

Nitrosol Propellant. The incorporation of nitrosol-grade nitrocellulose, petrin (pentaerythritol trinitrate), ammonium perchlorate and aluminum into a single composition has resulted in a propellant with very high performance characteristics. (20 Experimental values in excess of 250-lb-sec/lb have been obtained. In addition the system has excellent casting properties, a long pot life, a short cure time and good physical properties. The composition and characteristics of a typical composition are given in table 2-11.

Double Base-Composite Propellant. In order to increase the specific impulse values for the cast double-base systems, it has been necessary to add ammonium perchlorate and aluminum.(54) A number of these compositions have been made and evaluated. Calculated specific impulse values range from 260 to 275 lb-sec/lb. Experimental values in excess of 250 lb-sec/lb have been obtained. Numerous metallic salts have been used to increase the burning rate. The following are some of the compounds tried:(5)

(1) Vanadium pentoxide
(2) Cobalt stannate
(3) Tri-mol
(4) Cuprous oxide
(5) Cuprous chloride
(6) Iron phosphate
(7) Lead acetate
(8) Titanium lactate

Other studies have shown that the addition of magnesium oxide (1%) increases the stability of these compositions.(38) The characteristics of a typical double-base composite propellant are summarized in Table 2-12.

Nitropolyurethane Propellant. From the reaction of nitrodiisocyanates with nitrodiols in the presence of nitroplasticizers and using nitrotriols as a cross-linking agent a series of high-energy binders has been prepared.(24) These nitropolyurethane binders have characteristics which lead to propellants with interesting properties, including: (1) high specific impulse, (2) improved mechanical properties, and (3) great latitude for inclusion of other ingredients, including aluminum, without adversely affecting castability or mechanical properties. Although not yet produced in large quantities, these propellant compositions appear to show promise. The characteristics of a typical composition are summarized in Table 2-13.

Petrin Acrylate Propellant. Petrin acrylate, ammonium perchlorate and aluminum have been combined to produce another high-energy propellant. This type of propellant has a combination of desirable properties, including excellent castability, high-specific impulse, adjustable physical properties, and good case-bonding characteristics.(50) The petrin acrylate binders usually consist of petrin acrylate monomer, a comonomer, a cross-linker, a plasticizer, and a stabilizer. A polymerization catalyst is not required for curing as is the case with most binders.(17) Table 2-14 contains a summary of the pertinent characteristics of a typical petrin acrylate propellant.

Fluorocarbon Propellants. Propellant compositions utilizing fluorocarbon polymers as oxidizer binders for ammonium perchlorate (also lithium perchlorate) and thermogenic metals (fuel) are characterized by unusual physical properties and high specific impulse. (27) One extraordinary feature of this type of propellant is the use of a normally chemically inert fluorocarbon polymer as an oxidizer fuel. Metal halides are formed as reaction products while the inorganic oxidizer is used to oxidize the carbon present to carbon monoxide. Compositions of this type are being investigated only on an experimental scale.

Lithium perchlorate may be used as an auxiliary oxidizer in experimental fluorocarbon propellants because of its high oxygen content, desirable density, absence of hydrogen, and insensitivity to impact. (39, 40) The organic fluorocarbon polymers used so far in these studies have included Viton A (hexafluoropropylene-vinylidene fluoride copolymer) and Teflon (tetrafluoroethylene). A metal fuel such as lithium, aluminum, or silicon is also incorporated into the propellant. The occurence of hairline cracks in compression-molded specimens of this propellant has presented serious problems.

Other Propellant Systems

Solid Solution Propellants

The unusually high solubility characteristics of the perchlorates in organic solvents have been the basis of considerable research on these compounds. At the present time a study is underway to find monomers in which the perchlorate is soluble.(55) The resulting solutions upon being polymerized would give a solid material having the perchlorate much more uniformly distributed and in a much smaller state of subdivision than in the ordinary composite propellants. Of the systems studied, lithium and ammonium perchlorate are the most promising of the oxidizers. Strand-burning-rate tests with material prepared from 29 percent coprolactam and 71 percent lithium perchlorate gave a burning rate of 1.46 in. when burned at 1000 psi pressure.

In some later work(56) the possibility for using several types of condensation polymers and even some vinyl monomers seemed good. Of interest is the observation that mixed (fused) lithium perchlorate/ammonium perchlorate in proportions approaching those of the eutectic composition is more soluble in diamines than either perchlorate alone. Diamines dissolve up to 1300 percent of their own weight of the mixed perchlorate. Solution is effected at 185° F (85° C) but all remain dissolved or supersaturated at room temperature. The solutions can be poured at room temperatures. When reacted with diisocyanates at room temperature the reaction proceeds readily. The product is obtained with properties varying from hard to rubbery. The perchlorate sppears to remain in solid solution.

The solubility of lithium perchlorate in diamines is much less than was obtained with the eutectic mixture. In vinyl monomers, the solubility is even less than in the diamines. However, it is felt this is compensated for by the need for a lower amount of perchlorate in order to provide complete combustion. It is not known whether the amount of perchlorate needed to obtain the desired high specific impulse can be dissolved in the monomer.

Polymerization of vinyl monomers in the presence of lithium perchlorate appears to vary from very moderate to instantaneous, depending upon the pi electron density of the monomer.

Slurries.

The possibility of development a monopropellant which possesses the stability and storage characteristics of a solid propellant but which can be pumped like a liquid has been considered for some time. Some studies were made a number of years ago in connection with the development of wakeless underwater propulsion.(37) In this investigation a slurry of potassium perchlorate, magnesium and fluorokerosene was prepared by mixing the potassium perchlorate with the fluorocarbon and then introducing the metal into the system. The reaction of a typical formulation is:

$$C_{14}F_{30} + 15\ Mg + 7KClO_4 \longrightarrow 15\ MgF_2 + 7KCl + 14CO_2$$

This paste is safe to handle; it will not detonate in the standard impact tester nor will it detonate when ignited in a pipe with blasting cap and booster charge. It is noninflammable at ordinary pressures, has a low freezing point, and has a high boiling point. Toxicity is reported to be negligible. The composition and characteristics of several experimental compositions are shown in Table 2-15. These systems were examined as possible materials for either liquid or solid rocket propellant, but nothing definitive has ever been done with them.

Some recent investigations have brought slurries back into the propellant picture. The development of what are called heterogeneous liquid monopropellants is underway.(35) The particular propellant mixture being studied consists of a heavy liquid slurry of inorganic oxidizers and other high-energy ingredients in a gelled liquid. An oxidizer such as ammonium perchlorate and powdered aluminum metal are dispersed in an organic liquid fuel which has been modified by the incorporation of suitable gelling agents and catalysts. The resulting mixture is in the form of a dough or paste which can be pumped, but still holds its shape in the burner. Lithium perchlorate-aluminum -hydrocarbon systems have also been studied.

One of the preliminary formulations had the following composition:

NH_4ClO_4	78 wt percent
Triocetin	20
Nitrocellulose*	1
Copper chromite	1

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*gelling agent

A burning rate of 0.044 in./sec at atmospheric pressure was observed with this mixture. Studies of these systems are continuing.

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CHAPTER 3. USE AS ENERGY SOURCES

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General Considerations

The chlorates and perchlorates have found extensive use in a number of so-called high-energy systems. The role of perchlorates as the major ingredient in composite solid propellants has been discussed in Chapter 2 of this volume. In Volume I a description has been given of the uses of both chlorates and perchlorates in the chemical and agricultural industries in Chapter 4. The general reactions which accompany the decomposition of these compounds or their combination with other substances have been discussed in detail in Chapter 3. It is of interest now to consider the explicit role of these compounds as sources of energy for propulsive and related devices.

Propulsive devices of today depend upon the release of energy from chemical reactions occurring with one or more substances. The motion of shells and rockets takes place as a result of the rapid chemical reactions of certain selected compounds. The advent of jet propulsion has been achieved by the controlled development of gases at high pressures and temperatures which can be released at high velocities. Most of these reactions are combustion or oxidation processes. Since it is the speed at which a reaction occurs which determines the type of propulsion device in which it is used, it is necessary to consider the chemical kinetics of such reactions. Studies of chemical reactions reveal that their speed is affected by such factors as temperature, pressure, compositions of the reactants, and also the presence or absence of other substances including surfaces.

The reactions involving chlorates and perchlorates in propulsive devices pertain primarily to solid and solid-gas reactions. It is these types of reactions for which the kinetics are less well developed than for other chemical processes. In studies concerned with the burning of solid propellants considerable progress has been made in developing fundamental theories to describe the chemical reactions and kinetics which take place. The ultrafast reactions leading to gaseous products which are characteristic of explosive compounds have also been examined and provide additional information of considerable interest. For purposes of clarity in presentation, this information on energy release is being presented under the following four major headings: (1) Energy Release in Propellants, (2) Energy Release in Explosives, (3)Energy Release in Ignition Systems, and (4) Energy Release in Other Systems. Illustrations of the use of chlorates and perchlorates in these various systems is also given.

Energy Release in Propellants

The class of solid propellants which contain perchlorates is called composite and, as has been pointed out previously, is composed of the inorganic oxidizer dispersed in a finely divided state throughout a plastic, resinous or elastomeric matrix. The system contains sufficient oxygen within its structure to permit its transformation into gaseous products. The combustion process which occurs releases a large amount of heat and, when the reaction takes place within an enclosed space, also develops considerable pressure.

The most important of the oxidizer ingredients are potassium and ammonium perchlorate. Although considerable work has been done in studying the decomposition reactions for these compounds, they are still not well understood. In Chapter 3, Volume I, the presently available information on the thermal decomposition of these compounds has been discussed. The mechanism of thermal decomposition and deflagration of these compounds and of mixtures of the salts with other materials is discussed here again on the basis of its direct relationship to the burning of propellants.

Thermal Decomposition

The thermal decomposition of potassium perchlorate has already been discussed (see Volume I, Chapter 3). It is to be recalled that decomposition occurs at about 500° C. The reaction is described as unimolecular over the temperature range 536° to 617° C and takes place as follows:(32)

$$KClO_4 \rightarrow 2O_2 + KCl$$

On the basis of this reaction the rate of decomposition can be expressed by(31, 39)

$$k = 10^{14.0} e^{-60.800/RT} \text{sec}^{-1}$$

The normal frequency factor and high activation energy point to the good stability of this compound at low temperatures. It has been shown that the decomposition can be catalyzed by such substances as manganese dioxide and ferric oxide.(5, 31)

The decomposition of ammonium perchlorate is relatively complex and admittedly not completely understood (see Volume I, Chapter 3). Geckler(21) considers the following approximate reaction as being representative:

$$10\ NH_4ClO_4 \longrightarrow 6O_2 + 4N_2O + 2NOCl + 2Cl_2 + HClO_4 + 3HCl + 18H_2O(g)$$

The rate of decomposition is not easily determined because of the variety of reactions taking place at different temperatures. Decomposition starts at about 200°C, is slow enough to measure at 450°C, but a change in reaction is observed at about 300°-350°C. There also is a change in crystal structure occurring at 240°C.

The decomposition of potassium perchlorate occurs with the release of only about 4 cal/g.(21) On the other hand, ammonium perchlorate decomposes with the liberation of 256 cal/g.(21) The ammonium salt thus differs remarkedly from the potassium salt in the highly exothermic nature of its decomposition reaction. In addition, ammonium perchlorate behaves like a monopropellant which makes it possible to study its actual deflagration without the presence of interfering substances. This is not possible with potassium perchlorate.

Friedman et al(19, 20) conducted burning-rate studies with pressed strands of pure ammonium perchlorate. In their initial work(19) they showed an apparent upper-pressure limit of deflagration at about

250 atm. (This was later disproved.) Also there was a surprisingly large increase in burning rate caused by the addition of catalysts such as copper chromite, ferrous oxide, and manganese dioxide under certain conditions.

More recent work(20) showed that the apparent upper-pressure limit was caused by convective cooling which becomes increasingly effective with increasing pressure. The rate measurements were extended to 340 atm (limit of apparatus) by wrapping the strands with asbestos. There was still a lower limit at about 22 atm. These data showed a burning rate of about 0.31 in/sec at 1000 psi (77° F) for the pure material. The addition of as little as 1 part in 20,000 of copper chromite to the perchlorate raised the lower pressure limit fourfold. The deflagration rate was unaffected by additions up to one part per thousand but increased rapidly thereafter. The addition of about 5 percent catalyst increased the deflagration rate fifteen times.

Additional studies of surface temperatures and other effects coupled with the work on deflagration led these investigators to establish a tentative model of the deflagration process. They envision the ammonium perchlorate decomposing into ammonia and perchloric acid vapors. Heat generated above the surface in an exothermic gas-phase oxidation reaction results in a final temperature of 930° C (1203° K) and a surface temperature some 200° cooler. Heat is conducted back through a thin surface layer to supply the heat required to decompose the crystalline material. The rate of propagation is governed by the rate of heat generation in the gas phase and the thermal conductivity of the gaseous layer just above the surface.

It is further postulated that the flammability limit at the lower pressures is caused by radiative heat loss to the surroundings while the high-pressure limit is caused by connective heat loss which can be eliminated by proper insulation. The increase in rate by addition of catalyst is explained on the assumption that the particles project from the surface into the thin gas-reaction layer and produce local accelerations of rates. At low concentrations the catalyst acts primarily to reduce flammability by increasing the emissivity of the surface and thence the radiation heat loss rate.

Propellant Burning

When the perchlorates are mixed with a fuel material the mixture becomes the familiar composite propellant. It has been shown that the addition of a solid fuel such as carbon black to potassium perchlorate causes the decomposition to occur at a much lower temperature (about 320° to 385°C) and at a rate much faster than would be expected.(40) It is such a direct reaction between fuel and oxidizer which presumably may occur in composite propellants and add complications to the over-all reaction mechanism.

In early studies by Crawford(9) and Rice(48) stoichiometric mixtures of potassium perchlorate and carbon were introduced into a double-base matrix. Strand burning-rate measurements showed a marked increase in burning rate in the pressure range 100 to 300 psi.(31) As the pressure was increased the burning rates appeared to approach that of the matrix asymptotically. At the very low pressures (less than 100 psi) the perchlorate acted as a diluent causing the burning rate to fall below that of the matrix. Finely ground perchlorate crystals were found to be more effective than coarse crystals in lowering the burning rate at these low pressures. This would suggest that although the crystals do not reach equilibrium in the surface zone, the finer crystals approach it more closely.

Photographs of burning strands showed flashes of flame originating from perchlorate crystals. This suggested that the crystals decompose releasing streams of oxygen which can react with the binder or binder decomposition product in the flame. Rice estimated the surface temperature of the crystals at 1100°K - much higher than the probable surface temperature of the double-base matrix.

The concept of the stream of oxygen arising from the decomposing perchlorate crystals and being surrounded by a stream of decomposition products from the matrix has led to an early theory of burning. The rate of reaction in this theory is believed to be controlled by the rate of mixing of the reactants. A large number of small oxygen sources will be created when finely divided perchlorate is used. This would promote mixing by diffusion and hence would decrease the mixing distance and hence increase the burning rate. Since the diffusion process will tend to compensate for the increase in mixing distance caused by an increase in pressure, Rice further postulated that the perchlorate should provide a propellant with a low pressure exponent. Although the exponents are lower than for some double-base systems, they are still high.

Chaiken and Anderson(6) in reviewing contemporary combustion theories also point out this discrepancy in the Rice hypothesis. They also refer to the work of Lawrence and Geckler(21), Summerfield et al, (52) Penner(41) and Nachbar and Parks. (38) In applying Zeldovitch's and Kamentsky's methods for describing the deflagration of gases and solids to composite propellants, Lawrence and Geckler concluded that the only important heat flux through the burning surface affecting burning rate was that from the oxidizer-binder gas-phase reactions.

Summerfield and his co-workers have assumed that the burning rate is primarily dependent upon the rate of heat transfer from the high-temperature gas reaction between oxidizer and binder to the propellant surface. (52) They believe the chemical reaction itself to be rate controlling at the low pressures while the mixing by diffusion of the oxidizer-binder gases is controlling at the higher pressures. The two reactions are expressed by simple analytical expressions. These are then coupled together by adding the diffusion time to the chemical reaction time to produce a total combustion time.

As Chaiken points out(6) this hypothesis has met with some success in correlating some limited experimental data. However, such a relationship cannot predict absolute burning rates nor can it account for the monopropellant characteristics of ammonium perchlorate.

From Penner's application of the Shvab-Zeldovitch procedure to the preliminary treatment of composite propellant burning it was concluded that a pure diffusion-flame model was not sufficient to lead to significant predictions of various important variables of combustion thoery.(41) Although Nachbar and Parks extended the initial work of Penner,(38) Chaiken does not believe that suitable quantitative results can be obtained from such a treatment.(6)

After reviewing the early combustion theories, Chaiken(6) emphasizes the importance of the "Two-Temperature" theory of Schultz and Dekker(50) and his own thermal layer theory. According to the "Two-Temperature" theory, the decompositions of the solid oxidizer and binder occur as independent processes. At equilibrium burning, the average linear rate of regression of the oxidizer surface is equal to the average linear rate of regression for the binder surface. These rates are also equal to the mean linear burning rate of the propellant. These rates can all be expressed by conventional Arrhenius rate equations. Because the respective rate factor and activation energy terms will in general be different for the oxidizer and binder decompositions it is evident that the mean surface temperatures for the oxidizer and binder during burning are also different. Because of the complex geometry of the oxidizer-fuel mixture, it is quite possible to have specific local temperatures vastly different from the average temperatures. Although this makes the structure of the burning surface time-dependent, for convenience in handling steady-state conditions are assumed to prevail.

The "Two-Temperature" theory, according to Chaiken, was developed and utilized in the treatment of the burning of ammonium nitrate propellants. The analysis of ammonium perchlorate propellant burning is still incomplete. However, he postulates, on the basis of the work of Friedman et al, (19) that initially the ammonium perchlorate probably evolves NH_3 and $HClO_4$. These reaction products would then react to establish a redox flame close to the propellant surface. He feels that this reaction is further complicated by an exothermic solid-phase decomposition reaction which occurs in certain small regions (e. g. the so-called intermosaic crystal structure) of the crystals. Then, even though the desorption of NH_3 and $HClO_4$ would still be the rate-controlling step in surface pyrolysis, the over-all endothermicity of the oxidizer surface gasification step would be lowered by these exothermic surface or presurface reactions. The particular crystal structure of ammonium perchlorate (e. g. orthorhombic to cubic transition at 240°C - see Volume I , Appendix A) could also influence the kinetics of the solid-phase reaction. Since the solid-phase decomposition probably occurs by electron transfer, additives which influence electron transfer (e. g. ballistic modifiers or binder catalysts) could affect the over-all propellant burning.

The Chaiken thermal layer mechanism is based on the "Two-Temperature" theory. Although originally developed for the ammonium nitrate system, it is also applicable to ammonium perchlorate. It considers the decomposition of oxidizer separately from that of the binder. It further assumes that the solid-phase reaction occurs as a consequence of the transfer of heat from a flame zone or thermal layer surrounding the oxidizer particle. This flame zone is the result of the gas-phase redox reaction between the oxidizer pyrolysis products.

According to this concept, for the case of ammonium perchlorate propellants, the $NH_3(g) + HClO_4(g)$ redox reaction occurs at such a rate that the binder would gasify near the surface of the oxidizer particle and the flame zone would completely cover the binder surface. Consequently, all or part of the binder gas would diffuse into the flame zone. The presence of binder decomposition products in the thermal layer could influence the rate of the gas-phase redox reaction and the effective temperature of the flame zone. Since it is not known how much of the binder products enter nor the rate at which they react, it is not possible to characterize completely the over-all reaction.

Chaiken examines one of several possible situations and concludes that in the ammonium perchlorate system the binder, which plays only a minor role in ammonium nitrate propellants, has a significant influence on the burning characteristics of the propellant. He thus feels that any study of the burning mechanism must include consideration of the diffusion and reaction of oxidizer and binder decomposition products near the propellant surface.

The respective works of Chaiken and his associates and Friedman and his co-workers which are still incomplete represent two of the very few existing programs (outside of possibly Dr. Summerfield's studies) directly concerned with the mechanism of burning of composite propellants. Although considerable progress has been made in recognizing the possible reactions occuring in or near the surface of the burning propellant, much additional study and experimentation is needed before a satisfactory theory of burning can be established.

Effect of Additives

Since the early days of solid propellant development attempts have continually been made to find an ingredient which, when added to the propellant, will give it the desired performance characteristics. Quite by accident it was found that lead-organic compounds gave double-base propellants interesting and useful burning characteristics. A large number of chemical compounds were then examined as possible additives to the homogeneous propellant compositions. A few were found to be useful.

Although a similar approach (i. e. trial and error) has been tried with composite propellants, no such spectacular change in burning characteristics which had been found for double-base systems was ever discovered. The search has continued for the ideal additive. Recently a summary or "Handbook" was prepared listing the effect of a wide variety of additives on the burning characteristics of several composite propellant compositions. (24) Because of the interest in the effect of additives on the reactions involving perchlorate compounds, those data pertaining to compositions containing either ammonium perchlorate, potassium perchlorate or both have been summarized in Table 3-1. Because of the lack of control data in many instances and differences in preparation techniques in others direct comparison between compositions is almost impossible. However, the trends which occur in each particular propellant group do offer reliable information regarding the probable effects of these many additives. The authors of the "Handbook" readily admit to the limitation in the number of reports abstracted. In spite of this, much data of value has been assembled.

Use of Released Energy

The burning of composite propellants is seen to result in the evolution of a large quantity of high-temperature gases which, when they are confined, bring about the development of high pressures. It is by control of the development and release of these high-temperature gases that the operation of the various propulsive devices is accomplished. For the purposes of this analysis it is believed sufficient to divide such devices into the following three major categories:

(1) Constant-volume, closed-vessel systems
(2) Constant-volume, vented-vessel systems
(3) Variable-volume, closed-vessel systems

Constant-volume, closed-vessel systems.

1. Fundamental Relationships. The closed chamber is one of the simplest of propellant-operated devices. Of course, if such an apparatus were used as a propulsive device, no work would be accomplished. Actually

the volume does not remain exactly constant, but the change is small enough that it can be neglected. An example of such a device would be a thruster in which piston movement would be relatively small, but the force exerted could be great.

In a closed chamber the properties of the gas resulting from the burning of the propellant can be described by the equation of state for an ideal gas.

$$PV = nRT \tag{1}$$

where P, V, and T are the pressure, volume and temperature of the gas, n is the number of moles of gas and R is the universal gas constant. This relation can be modified to include the mass of propellant burned, C, by using the relationship

$$n = \frac{C}{M} \tag{2}$$

where M is the average molecular weight of the propellant gases.

For condition of maximum pressure this pressure can be defined by

$$P_{max} = \frac{C}{V}\,\frac{RT_v}{M} \tag{3}$$

where T_v is the flame temperature at constant volume. This relationship can be further simplified to give

$$P_{max} = \Delta\lambda \tag{4}$$

where $\Delta = C/V$ is the density of loading and $\lambda = RT_v/M$ is the impetus. The impetus is relatively constant for any propellant composition so that once determined it can be used to predict the maximum pressure for any loading density.

When high pressures are used (e. g. greater than 5000 psi) a correction must be applied for the volume occupied by the molecules, themselves. This is accomplished by using the co-volume correction, η thus

$$P_{max} = \frac{\Delta \lambda}{(1 - \eta\Delta)} \qquad (5)$$

This last relationship can be used to determine experimentally the values for impetus and co-volume (a convenient approximation is to let $\eta = 1/\rho$, where ρ = propellant density). These values can then be used in designing devices to provide a prescribed maximum pressure.

2. Applications. The main use for the constant-volume closed-chamber type of system is in initiators and thrusters. Initiators are small, constant-volume chambers within which a propellant charge is burned to provide high-temperature gas under high pressure. The energy of these compressed gases is by pneumatic or hydraulic means brought to bear on a piston or firing mechanism to accomplish a desired function. In thrusters this same compressed gas acts on a piston which, on moving, does work on some object such as a latch or disconnect pin. Initiators and thrusters form an important part of the integrated escape systems presently used in high-speed aircraft. These integrated systems by means of a series of properly sequenced operations automatically prepare the pilot for ejection and eject him from the disabled plane. At the present time composite propellants are

not being used in initiators or thrusters, but there is no particular reason why they should not be used.

Constant-volume, vented-vessel systems.

1. Fundamental Relationships. This system is the conventional rocket and it provides thrust in a direction opposite to that of the gas exhausting from its vent or nozzle. The magnitude of thrust is determined by the momentum change of the gas particles as they leave the nozzle.

In a solid propellant system two processes are taking place; (1) the gases are being generated at a given rate and (2) gases are exhausting out of the nozzle at a given rate. When these two rates are equal, the rocket is in equilibrium and the pressure existing within the chamber is called the equilibrium pressure.

The rate at which gas is generated from a solid propellant charge is dependent upon the amount of surface available for burning and the rate at which the surface recedes, that is

$$\dot{m} = Sr\rho \tag{6}$$

where

$\dot{m}$ = mass rate of gas flow (i. e. development)

S = available surface area

r = linear burning rate of propellant (normal to burning surface)

ρ = propellant density

The flow of gas out of the nozzle is described by the conventional flow-rate equation(54)

$$\dot{m} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \left(\frac{\gamma}{nRT_c}\right)^{\frac{1}{2}} \cdot A_t \; P_c = C_D A_t P_c \tag{7}$$

where

γ = ratio of specific heat of gases

n = number of moles of gas

R = Universal gas constant

T_c = gas temperature in the chamber

P_c = gas pressure in the chamber

C_D = discharge coefficient

At equilibrium the two flow rates are equal so that the following relationship between the variables S, r and P_c results:

$$S r \rho = C_D A_t P_c \tag{8}$$

To obtain the design parameters for a given thrust, it is necessary to consider the basic thrust relationship which is

$$F = \dot{m} v_e + A_e(P_e - P_a) \tag{9}$$

where

v_e is the effective velocity of the gas

A_e is the area of the exit of the nozzle

P_e and P_a are the pressure at the exit and atmospheric pressure, respectively. From a one-dimensional flow model it can be shown that(54)

$$v_e = \left\{ \frac{2\gamma}{(\gamma - 1)} \quad nRT_c \left[1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma - 1}{\gamma}} \right] \right\}^{\frac{1}{2}} \tag{10}$$

so that

$$F = \left\{ \frac{2\gamma^2}{(\gamma - 1)} \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma + 1}{\gamma - 1}} \left[1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma - 1}{\gamma}}\right]\right\}^{1/2} \cdot A_t P_c + A_e(P_e - P_a) \quad (11)$$

Since the thrust is now seen to be proportional to the throat area and pressure in the chamber this relationship can be simplified to(54)

$$F = C_f A_t P_c \quad (12)$$

where

$$C_f = \left\{ \frac{2\gamma^2}{(\gamma - 1)} \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma + 1}{\gamma - 1}} \left[1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma - 1}{\gamma}}\right]\right\}^{1/2} + \frac{P_e - P_a}{P_c}\left(\frac{A_e}{A_t}\right) \quad (13)$$

By integrating the thrust equation the relationship for $\int$ Pdt is defined for a given total thrust. From either $\int$ Fdt or $\int$ Pdt the functioning time can be determined. Thus Equations (8) and (12) are sufficient for defining the basic design parameters.

For particular charge geometries for solid propellant devices which will give satisfactory performance it is necessary to consider many factors, most of which are beyond the scope of this text. Suffice it to say that each charge is characterized by a certain surface-distance burned relationship. This means that when the desired surface area and burning distance (based on total duration and burning rate of the propellant) have been determined, the basic parameters of the charge have been established.

2. Applications. The vented vessel is one of the most useful of the propellant-actuated devices. All of the devices are essentially gas generators. However, the term "gas generator" is usually restricted to those devices where the gas issuing from the nozzle is used to produce work on the basis of pressure exerted on a piston or the change in momentum in a turbine. Devices developing thrust as a result of the change in momentum of the gases expelled from the nozzle are considered as rockets.

a. Gas Generators. Gas generators are a source of auxiliary power used to actuate servomechanisms, operate seat ejection catapults, supply electrical or hydraulic power, generate heat, and other miscellaneous uses.

In many of today's air-to-air rockets with their various guidance systems it is necessary to have power of some sort for the servomechanisms. This power can be obtained by using a gas generator. This generator normally may be required to function for a relatively long period or a short period of time. The demand of the unit the generator is serving dictates the demands of the generator fuel. For a servomechanism that must operate throughout the flight of a missile it is necessary to have a slow-burning fuel. Such a fuel rarely contains chlorate or perchlorate oxidizers; however, when faster rates are necessary these oxidizers are used.

Gas generators are often programmed to accomplish a series of jobs such as the generator for a seat ejection catapult. When the pilot of a disabled jet aircraft finds it necessary to escape he fires a gas generator. This generator furnishes the necessary power to fire cartridge-actuated devices which in turn (1) stow the aircraft controls, (2) eject the canopy, and (3) eject the pilot.

Generally speaking, gas generator fuels are developed to meet the requirements of the specific unit for which they are designed. In this development the engineers must take into consideration the function of the unit. In the development of the SPARROW missile, for example, the following requirements were set up for the fuel by the demands of the unit.(3)

Propellant Burn Time at 130°F	18 sec
Propellant Burn Rate at 2000 psi	.26 in./sec
Length	5.20 in.
Diameter	1.58 in.
Gas Flow Rate	20 in.^{3}/sec
Burn Rate Pressure Exponent at 2000 psi	0

With these requirements in mind the following fuel was developed:

Ingredient	Weight %
NH_4ClO_4 (unground)	51.51
NH_4ClO_4 (3450 rpm in Bantam Micropulverizer)	22.08
Polyvinyl chloride	12.43
Dibutyl sebacate	4.14
Calcium carbonate	1.0
Ferro 1203	.50
Carbon black	.05

There are a large number of compositions which can be used in gas generators. As indicated , however, few contain appreciable quantities of the perchlorates. This is because of the need for low flame temperatures, no corrosive products in the gas stream, and no solid particles which might cause plugging of the very small orifices used in these devices to control gas flow. Such conditions are difficult to meet when perchlorates are used.

b. Rocket Systems. The composite propellants find their widest use in rocket systems. The types of rockets are many. A general list might include the following:

Air-to-air
Air-to-ground
Ground-to-air
Surface-to-surface
Underwater
Intermediate Range Ballistic Missiles (IRBM)
Intercontinental Range Ballistic Missiles (ICBM)
Space Probes
Boosters for other rocket systems
Sustainers for other systems
Sled Boosters
Others

At one time it appeared that one propellant composition might be developed which would be suitable for most applications. Today, however, it is evident that the stringent requirements for each rocket are so high that a large portion of the performance must be built into the propellant.

As a consequence, propellant development follows closely the development of the rocket or missile and a new composition is evolved for each new application.

In Chapter 2 of this volume the characteristics of most of the composite propellant systems have been summarized. It is known that new compositions are being developed as this text is being written. Therefore, it is not possible to have a complete, up-to-date summary of the latest propellant compositions. It seems safe to say, though, that ammonium perchlorate will be used as a major ingredient in the majority of compositions for several years to come.

Variable-Volume, Closed-Chamber Systems.

1. Fundamental Relationships. The variable-volume systems include guns and catapults. The establishment of fundamental ballistic relationships to describe the functioning of such devices is made more complex than the constant-volume or vented-vessel system because of the change in chamber volume.

The simple ballistic model for a typical seat-ejection catapult can serve to illustrate the types of relationships needed to describe such a device. For simplicity, heat losses are neglected and the expansion of the telescoped system is assumed to occur without a change in internal cross-sectional area.

The equation of state for such a system can be given by

$$P = \frac{nRT}{V_o + xA_i} \tag{14}$$

where

V_o = initial volume of chamber

x = tube displacement

A_i = internal area of telescoped tube sections

The moles of gas will be

$$n = \frac{CG}{M} \qquad (15)$$

where

C = charge mass

G = fraction of charge mass burned

= $(1 - f)(1 + \theta f)$ = form function

f = fraction of web remaining

θ = form factor, dependent upon charge shape

M = average molecular weight of gases

The temperature in the chamber can be approximated by taking an arithmetic average over the length of the chamber (and expanded tube) so that

$$T = 1/2(T_v + T_b) \qquad (16)$$

where

T_v = isochoric adiabatic flame temperature

T_b = gas temperature at end of tube (must be calculated from heat-loss and expansion considerations where they are considered)

The new equation of state then becomes

$$P = \frac{CGR(T_v + T_b)}{2M(V_o + xA_i)} \tag{17}$$

One additional relation must be established. This concerns the motion of the load being moved by the catapult. This can be writted as

$$PA_i = m\left(\frac{d^2x}{dt^2} + g\right) \tag{18}$$

where

m = mass to be ejected

g = acceleration of gravity

In the simplified form presented here, solution of the ballistic performance of the catapult can be effected by use of Equations (17) and (18). This assumes that either charge mass is known or desired acceleration characteristics of catapult are given. To establish grain shape would require additional relationships for burning characteristics of the propellant and definition of burning distance or web. Such detail is not believed necessary here.

2. Applications. The two systems which depend upon an expanding volume are (1) guns and (2) catapults. Guns have not found much application for propellants containing the perchlorates. Catapults, however, have used such compositions to a limited extent.

a. Guns. Although conventional guns do not use perchlorate-containing propellants, there is a report which refers to a new concept in gun propellants which has utilized a composite propellant consisting of ammonium perchlorate in a double-base matrix. This concept, called the "Langweiler Principle", is supposed to give higher muzzle velocities than conventional rounds with the same propellant-to-projectile weight ratio. During firing, according to this principle, the propellant remains attached to the projectile. To attain the hypervelocities believed necessary with this principle the burning rate of the propellant would have to be extremely high. To achieve the desired burning rate and velocity a standard cannon charge would be used to bring the projectile to a predetermined velocity, then the double-base-perchlorate traveling charge would be ignited. For the sake of accuracy this charge must be consumed prior to the projectile leaving the gun, hence the reason for a high burn-rate. A typical experimental composition which has been developed as part of a study of this principle(18) is as follows:

NH_4ClO_4	60%
Nitrocellulose (12.6% N)	23.4
Nitroglycerine	12.0
Triacetin	4.1
Ethyl Centralite	0.4

The true utilization of the "Langweiler Principle" has has not yet been accomplished. Its study does present an interesting challenge to the interior ballistician.

b. Catapults. The small size and weight required for storage of the chemical energy of solid propellants together with the simplicity of operation, have made the use of propellant-actuated devices attractive in escape systems for high-speed aircraft. One of the first such devices was a seat-ejection catapult for use in pilot escape systems and standardized as Catapult, Personnel, M1. It was employed to eject a pilot from a crippled fighter plane and saw service in the Korean War. Since then several types of personnel ejection catapults have been developed. The catapult usually consists of two or three concentric, telescoped tubes which expand axially under the pressure of the propellant gases.

Following the success of the catapult, similar devices were developed for other uses. Two-and three-tube telescoping mechanisms were designed for removal of aircraft canopies just prior to seat ejection. These are called removers.

Lately, integrated escape systems for large aircraft, such as the B-52, have been developed. These involve initiators, removers, catapults and work devices called thrusters, which are merely propellant-actuated devices that move a piston, the thrust of which does some desired work. These integrated systems perform automatically, and in proper sequence, the operations needed to evict the entire crew of a plane.

Now propellant-actuated devices are finding applications in missiles, where they have been used for separating missile stages, and for pressurizing missile hydraulic systems. Many new uses for these convenient energy sources will arise in the space craft soon to be developed.

So far, perchlorates (or chlorates) have rarely been used in propellants for such devices. Most propellant formulations for these applications have been double- or single-base types. However, in 1954, Aerojet-General Corporation studied the use of rubber-base perchlorates for the propellant in a Cockpit Ejection System.(12) Burning rates and pressure exponents are given below for six formulations that were tested.

Composition No. 1

86.5%	Ammonium Perchlorate
11.0%	Butyl Rubber and Circo oil
2.0%	Ammonium Dichromate
0.5%	Silon F

Burning rate at 1000 psi and 60°F = 1.9 in./sec
Pressure exponent = 0.5

Composition No. 2

86.0%	Ammonium Perchlorate
11.5%	Butyl Rubber and Circo oil
2.0%	Ammonium Dichromate
0.5%	Silon F

Burning rate at 1000 psi and 60°F = 1.5 in./sec
Pressure exponent = 0.77

Composition No. 3

86.5%	Ammonium Perchlorate
11.5%	Butyl Rubber and Circo oil
2.0%	Ammonium Dichromate

Burning rate at 1000 psi and 60°F = 1.26 in./sec
Pressure exponent = 0.65

Composition No. 4

86.0% Ammonium Perchlorate
12.0% Butadiene-Styrene and Sundex oil
2.0% Ammonium Dichromate

Burning rate at 1000 psi and 60° F = 1.25 in./sec
Pressure exponent = 0.52

Composition No. 5

88.0% Ammonium Perchlorate
10.0% Butadiene-Styrene and Sundex oil
2.0% Ammonium Dichromate

Burning rate at 1000 psi and 60° F = 2.22 in./sec
Pressure exponent = 0.62

Composition No. 6

86.0% Ammonium Perchlorate
11.0% Butadiene-Styrene and Sundex oil
2.0% Ammonium Dichromate
1.0% Carbon

Burning rate at 1000 psi and 60° F = 2.12 in./sec
Pressure exponent = 0.56

A glance at these data show how sensitive burning rate is to minor changes in composition.

In the continuation of this program various other ammonium perchlorate-rubber formulations were considered for use in the seat-ejection system.

Ammonium perchlorate was also tested in connection with resin binders. Six compositions of this type, with their burning rates and pressure exponents are shown in Table 3-2.

Some consideration was given to potassium perchlorate with A-20: Acrylate and with A-20: Styrene.(13) The following are two compositions investigated:

82.0% Potassium Perchlorate
17.0% Genpol A-20: Styrene
1.0% Carbon black

Burning rate at 1000 psi and 60° F = 0.96 in./sec
Pressure exponent = 0.67

82.0% Potassium Perchlorate
17.0% Genpol A-20: Acrylate
1.0% Carbon black
1.0% Ethyl Silicate
0.15% Copper Chromate

Burning rate at 1000 psi and 60° F = 1.04 in./sec
Pressure exponent = 0.76

In 1956, under a continuation of this program, further work with perchlorates for oxidants in a propellant for a personnel ejection catapult was done. A major objective was to develop a propellant that would burn so fast that a single grain could be used for the propellant. Various formulations were found that would meet this requirement.

Oil-extended butyl rubber was selected over butadiene-styrene because it yielded propellants with higher burning rates and improved physical properties. Ammonium and potassium perchlorates were found to produce about the same burning rates when in high concentrations.(23) Of the oxidizer variables studied, particle size seemed to be most effective in varying burning rates. Short strands of copper or aluminum wire were the most striking burning-rate additives employed.

Theoretical specific impulses as high as 256 lb-sec/lb were calculated for rubber-ammonium perchlorate-aluminum formulations.

Below is an example of the compositions that gave the highest burning rates.(23)

83.0% Ammonium Perchlorate
9.6% Butyl Rubber and Oil
4.0% Copper Chromite
3.0% (.002 x 1/4 in.) Cu wire

Burning rate at 1000 psi and 60° F = 7.00 in./sec
Pressure exponent = 0.46

The burning rate proved sensitive to the diameter of the wire additives, increasing with decreasing diameter. There was also considerable batch-to-batch variation in results with presumably identical propellant.

Energy Release in Explosives

General Considerations

Both chlorates and perchlorates have been used as explosives or explosive ingredients as far back as 1788.(10) In Volume I, Chapter 4 a review has been presented of such utilization of these materials. Although most of the chlorate explosives were used in industrial and mining application, some were even used by the French in World War I for grenades, mines and trench mortar bombs. The Germans used perchlorates in an explosive, Perdit, which they used in trench mortar bombs. Perchlorates also found use in explosives for French 75-mm shells and 58-mm trench mortar bombs.(10)

In recent times interest has been aroused in a series of explosive compositions called MOX-type high explosives. These consist of a mixture of ammonium perchlorate with powdered metal and an explosive such as tetryl, RDX or TNT. It has been estimated(7) that 5 percent of the current (1959) 20-mm shell loadings contain the MOX-26 composition.

Explosive Characteristics of Ammonium Perchlorate

A recent report by Anderson and Chaiken on the detonability of solid composite propellants contains an interesting discussion of the physicochemical parameters associated with the detonation of ammonium perchlorate.(2) The initial part of the discussion leans heavily on the concepts attributed to Chaiken in the earlier section of this chapter on propellant burning.

The same concept of surface-decomposition kinetics used in considering the burning of ammonium perchlorate is applicable to the detonation or explosive deflagration phenomenon. The authors point out the importance of the discovery that the rate-controlling mechanism of surface decomposition of certain solids is different from the decomposition in the bulk phase. This has been proven true with ammonium nitrate and is believed to be true also for ammonium perchlorate.

In another recent paper Anderson and Chaiken(2) suggested that "low velocity detonation in granular explosives is propagated by the same rate-controlling chemical reactions which occur during their deflagration." They refer to Eyring's "grain-burning" theory where in a detonating explosive the reaction to individual grains consists of a surface burning in which a layer of molecules is not ignited until the previous layer is consumed. The theory implies that the detonation reaction zone consists of a finite region in which the decomposition of the explosive granules occurs at the surface in a layerwise manner. Initiation at the surface is presumed to occur by a "hot spot" mechanism.

According to Anderson and Chaiken the time required to complete the reaction in the steady-state detonation zone is dependent upon the time required for the reaction to traverse the grain radius.(2) An expected high detonation pressure means that the surface temperature of the reacting explosive will be nearly the same as the gas temperature in the reaction zone. Therefore, one unique rate-controlling reaction exists, and it should be equal to the linear pyrolysis rate of the explosive particle. The reaction time of grain-burning detonation was postulated to be given by

$$t = \frac{\bar{R}_g}{B} \text{ sec} \qquad (19)$$

where $\bar{R}_g$ is the average radius of the explosive particle and B is the linear pyrolysis rate. This rate term can be expressed by the usual Arrhenius type equation.

Preliminary data on the linear-pyrolysis rate of ammonium perchlorate give the following relationship(2)

$$B = 5.88T_s \exp(-20,000/RT_s) \text{ cm/sec} \qquad (20)$$

In the discussion on burning of ammonium perchlorate it was shown that the reaction which occurs is probably the following

$$NH_4ClO_4(s) \longrightarrow HClO_4(g) + NH_3(g) \qquad (21)$$

The probability of a solid phase exothermic reaction occurring in the so-called intermosaic lattice was also indicated. Rates for the two different crystal structures follow:

Orthorhombic crystal, temperature below 513°K

$$B = 1.5 \times 10^8 \exp(-31,500/RT_s) \text{ cm/sec} \qquad (22)$$

Cubic crystal, temperatures above 513°K

$$B = 25 \exp(-16,200/RT_s) \text{ cm/sec} \qquad (23)$$

On the basis of Equations (19) and (20) detonation reaction times were calculated for the steady-state detonation of ammonium perchlorate for particle radii of 7 and 120 microns. A value of 2160°K was selected for T_s.

The results follow for pure ammonium perchlorate:

$\bar{R}_g$	Reaction time, microsec
7μ	5.6
120μ	96.4

To estimate the minimum (critical) charge diameter (d_c) at which steady-state detonation can propagate, use was made of the curved-front theory. The function for uncased charges is given by

$$D/D_i = 1 - a'/d \tag{24}$$

where D_i is the ideal (infinite diameter) detonation velocity, and a' is the reaction zone length given by

$$a' = \frac{V}{V_o} tD \simeq 0.8\, tD \tag{25}$$

From these relationships it follows that the critical diameter is given by

$$d_c = \frac{0.8\, D_i C_o t}{D_i - C_o} \tag{26}$$

where

C_o is the velocity of sound = D

This gives a minimum calculated value for critical diameter.

In addition to the above, consideration must also be given to the velocity of sound in the reaction zone (C_1). This wave could cause failure of the detonation wave by quenching it within the reaction-time period. An upper limit to the critical diameter can be expressed by the equation

$$d_c = 2C_1 t \tag{27}$$

Anderson and Chaiken indicate that the results from Equations (26) and (27) differ only by the factor 1.54. They thus utilize an arithmetical average to arrive at the following value for pure ammonium perchlorate:

$\bar{R}_g$	Estimated Minimum Critical Diameter, in.
7μ	0.3
120μ	5.5

The values for C_o and C_1 were approximated by the conventional expressions

$$C_o = \sqrt{\frac{E}{\rho_o}} \tag{28}$$

$$C_1 = \sqrt{\gamma \frac{RT}{M}} \tag{29}$$

where E is Young's modulus, ρ_o the charge density, γ the ratio of specific heat and M is the average molecular weight of the detonation products.

Applications

The use of chlorates and perchlorates in explosives has been discussed in Volume I, Chapter 4. There are several military applications which should be considered in this volume. In particular the information on MOX explosives should be presented.

Historical Interest. According to Davis(10) explosives containing potassium chlorate were used by the French during World War I for grenades and in mines. In particular he mentions the composition Minelito B which was used under the designation O No. 6B and had the following composition:

Potassium chlorate	90 wt %
Vaseline	3
Paraffin	7

A similar composition but having the potassium salt replaced with the sodium compound was used in grenades and mortar shells.

When aromatic nitro compounds are used in chlorate explosives higher detonation velocities and greater "brisance" is obtained. A small amount of nitroglycerin increases the detonation velocity even more. During World War I the Germans developed the following brisant explosives of this type(10)

<u>Gesteinskoronit, T1</u>

Sodium chlorate	72.0	wt %
Vegetable meal	1.0-2.0	
Di-and tri-nitrotoluene	20.0	
Paraffin	3.0-4.0	
Nitroglycerin	3.0-4.0	
Heat of Explosion	1219 cal/g	
Detonation Velocity	5000 m/sec	

There has been even more interest in the perchlorate explosives. Because of the scarcity of military explosives in Germany during World War I, use was made of such perchlorate explosives as PERDIT which contained

Potassium perchlorate	56 wt %
Dinitrobenzene	32
Dinitronaphthalene	12

The perchlorate explosives are somewhat less sensitive to initiation than chlorate explosives. According to Davis(10) a small amount of nitroglycerin aids materially in progapating the explosive wave.

The French used two ammonium perchlorate compositions in World War I, the first(I) in 75-mm shells, the second(II) in 58-mm trench mortar shells. Their compositions were as follows:

	I	II
Ammonium perchlorate	86	61.5
Sodium nitrate		30.0
Paraffin	14	8.5

For the most part, though, chlorate and perchlorate explosives have not seen very extensive use.

Current Interest. The use of perchlorates in explosives in recent years has been limited primarily to experimental work. The most interesting of these have been mixtures containing such explosives as TNT and RDX with ammonium perchlorate and aluminum. In one particular study, these were examined as possible underwater explosives with the hope that they would have qualities superior to the existing explosives.(27) Unfortunately, the increased sensitivity of the mixture was such that it was not considered suitable. Potassium perchlorate has been substituted for ammonium perchlorate in certain of these mixtures with a resultant decrease in sensitivity. The loss in explosive power, though, is such as to decrease its usefulness.

Increased blast effects have been observed in mixtures of aluminum-potassium perchlorate and tetryl.(16) When tetryl is mixed with stoichiometric amounts of aluminum and potassium perchlorate it yields an energy content of 2.63 KCal/gram compared to TNT which has an energy content of 0.990 KCal/gram. There are other advantages in that the materials are cheap and supply is plentiful. This explosive is safe to handle at normal pressures and temperatures because it is relatively difficult to initiate.

Probably the most extensive use of perchlorate explosives in recent times has been the MOX systems which are used, for example, in 20-mm shells. According to a recent report(7) 5 percent of the current (1957) shell loadings for 20-mm guns contained MOX-26 composition. These compositions, which were developed in 1950(35), consist of mixtures of ammonium perchlorate and RDX or TNT with added aluminum or magnesium and a plasticizer such as calcium stearate to aid in the pressing operation. Graphite is added as a lubricant. Two typical compositions and their respective characteristics are shown in Table 3-3.(51)

Energy Release in Ignition Systems

General Considerations

The utilization of chlorates and perchlorates in igniters and ignition systems has increased considerably in the last few years. The original igniter material, black powder, after several hundreds of years of continued use is gradually being replaced.

Black powder has served well as an igniter material for several reasons. First, it is readily ignited at any pressure. Its burning rate is not appreciably changed by pressure (i. e., it has a relatively low pressure exponent). It is relatively inexpensive. Unfortunately its flame temperature is low (about 2500°K).* It is very hygroscopic and extremely sensitive to friction and static electricity. When composite propellants were first introduced it was found that they were very difficult to ignite compared to the nitrocellulose propellants. As a result a search began for igniter materials with higher flame temperatures.

The pyrotechnic mixtures of a metal and a chlorate or perchlorate create compositions which have very high flame temperatures. Generally, unless organic binders are used, these mixtures give off little gas. This is sometimes desirable, especially in cases where black powder systems have produced excessive pressure peaks. In general, black powder transfers heat to the propellant during the ignition process by convection and radiation. With a metal-oxidant system heat can be transferred by (1) condensation of vapors on the surface, liberating the heats of vaporization and fusion, (2) impingement of solid particles on the propellant surface and (3) improved radiation due to the high emissivity of the particles.(34)

There are several igniter compositions which have been developed and which are used in some cases extensively, in others only occasionally. In addition several new igniter systems or ignition concepts have evolved from the use of these chlorate or perchlorate-containing materials. These are examined in the following sections.

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* There are considerable differences of opinion regarding this temperature. Davis(14) gives a calculated value of 2420°K.

A very important part of most igniters is the initiating element or electric squib (sometimes a percussion element is used, but this rarely uses chlorate or perchlorate compounds). Several new squibs make use of chlorates. Their characteristics are discussed.

Igniter Materials

General. There are a number of pyrotechnic mixtures which are being used as igniter materials. Studies are being continued at several activities to determine the characteristics of different compositions. The results of sensitivity tests on some such compositions are shown in Table 3-4.(53)

The true effectiveness of an igniter material is difficult to evaluate. During the past few years an attempt has been made by an Ignitability Panel of the Joint Army-Navy-Air Force Solid Propellant Group (JANAF) to develop a standard ignitibility test. Considerable progress has been made but a truly standard test still remains to be developed. Some data have been made available from a particular ignitibility test apparatus developed at the Ordnance Missile Laboratory, Redstone Arsenal.(34) These are summarized in Table 3-5.

Ammonium perchlorate has not been used extensively in igniter materials as yet, but it has been considered. Some calculations of heat of explosion for combinations of this oxidizer with various metals is shown in Table 3-6.(37)

An experimental composition containing potassium perchlorate has been developed by the Ordnance Missile Laboratory, Redstone Arsenal.(36) This mixture, called "Tichloral," consists of titanium, aluminum, potassium perchlorate and polyisobutylene. These ingredients are mixed in various percentages to fulfill the ignition needs of a given rocket. Tichloral embraces a family of igniter mixtures that can be used in pelleted igniters, coated igniters or powdered igniters. A typical mixture is:

Tichloral 1A	Wt %
Titanium	13.2
Aluminum	20.4
Potassium perchlorate	62.9
Polyisobutylene	3.5

Some characteristics of this igniter mixture are:

(1) Impact Sensitivity (50% probability) with Bu Mine apparatus - 105 cm compared to 87 cm for A-5 black powder.

(2) Heat Stability - No apparent effects after 4 hours at 120°C.

(3) Hygroscopicity measurements at 25°C -

	Relative Humidity	
Time, hrs	52%	88%
2	0.00	0.02
25	0.00	0.05
96	0.01	0.06

(4) Constant-density pellets are obtained when pressed to pressures in excess of 100,000 psi.

(5) Heat of explosion is 1965 cal/gm.

A new approach in the preparation of igniter materials is being investigated under Bureau of Naval Weapons sponsorship.(17) The procedure is based upon small-arms propellant processing techniques and the principle that many of the burning characteristics of igniter materials can be controlled by the use of granules of specific, controlled geometric shape. As a result mixtures of potassium perchlorate, metals and other ingredients are incorporated into a nitrocellulose matrix. The mixture is then extruded and cut to a specific shape.

A typical igniter composition is as follows:

Nitrocellulose	36.61%
Nitroglycerin	24.86
Potassium Perchlorate	7.95
Ethyl Centralite	0.56
Magnesium Oxide	.04
Magnesium Stearate	.04
Titanium	29.94

Standard Mixtures. There are only two compositions containing either chlorates or perchlorates which have been standardized. These are ALCLO and RH1M-1.

ALCLO is a mixture of aluminum and potassium perchlorate. This composition which is pressed into pellet form has been made with a number of different variations in quantities of the same ingredients. The following is believed to represent the standard composition: Newer experimental composition contain lead in addition to potassium perchlorate and aluminum (44)

	Wt %
Potassium perchlorate	64.0
Aluminum	35.0
Vegetable Oil	1.0

Aluminum is Alcoa standard No. 606, unpolished flake, nominal 100 mesh, low grease, 2% 100 mesh and 90% through 325 mesh. (22)

Potassium perchlorate is from American Potash and Chemical. Reground to 81.7% through 325 mesh. (22)

The mixture is pressed to the desired dimensions under pressures approximating 100,000 psi.

ALCLO is usually pressed into pellets having a diameter of 0.375 in. and a length of 0.20 in. The end surfaces are convex to prevent compact loading in the igniter.

The burning characteristics for ALCLO with lead are shown in figure 3-1. It is to be noted that at pressures above 100 psia the pressure exponent increases greatly. Because of the high pressure exponent ALCLO pellets are generally used in a plastic-coated wire basket-type igniter container. With this type of loading arrangement pressures above 100 psi are avoided.

Other characteristics of ALCLO are:

Heat of combustion, cal/g	2490
Ignition temp, °F	1050
Burning rate (100 psi), in./sec	0.59
Shear strength, psi	74
Impact sensitivity (2 Kg wt), cm	35
Specific heat, cal/g/°C	0.198
Flame temp, °K	38.00
Density, g/cm^3	2.448
lb/in.^{3}	0.089

ALCLO pellets are safe to handle and can be safely stored within a -40°F to +175°F temperature range.

The composition identified as RH1M-1 was developed by Rohm and Haas Company as a replacement for black powder.(49) This mixture has been used extensively in standard igniters used in solid propellant devices developed by this company. It has the following composition:

	Wt %
Potassium perchlorate	25
Magnesium	60
Barium nitrate	15

Pertinent properties of this material are (compared with black powder):

	RH1M-1	Black Powder
Heat of explosion, cal/g	1600	700
Impact sensitivity (50%/2 Kg wt) in.	32.8	24.7

Special Igniters. One of the newest concepts for an ignition system is the conductive film igniter. The principles of printed circuitry have been combined with pyrotechnics to produce this ignition system for solid rocket propellants. The conductive-film igniter consists of interlocking grids of igniter mixture and conducting surfaces. The conducting igniter mixtures are metal-oxidant type usually a combination of boron and potassium perchlorate in a binder such as polyisobutylene. The solution is sprayed onto the propellant grain.(30) When current is applied to the film, the heat caused by its resistance ignites the film and causes ignition over the entire grain simultaneously. In this type of system there is no energy loss from a driving force to bring the ignition energy to the grain surface. Although it is still in an experimental stage, the system has many attractive features. One of the difficulties is in not being able to separate the ignition system from the propellant after fabrication. This is often desirable from a safety point of view.

Another new-type ignition system is the "Jelly Roll Igniter."(11) This igniter consists of a metal-oxidant composition evenly coated on one side of a rectangular base sheet. The coated base sheet is rolled into a cylinder and an electric squib is centered inside the cylinder. The cylinder is wrapped with a protective covering of aluminum foil or plastic film and the two ends of the igniter sealed with rubber caps. This type igniter is placed inside the propellant grain and held securely to it.

The principal igniter materials used in this system are magnesium, titanium and boron with potassium perchlorate and a binder, usually polyisobutylene. The binder is dissolved in a solvent (hexane or toluene) and a slurry is made with the metal and oxidant. The slurry is coated on the base sheet and the solvent is evaporated. A variety of compositions have been used. By varying the chemical composition of the mixture and the physical form of the igniter, a wide variety of performance characteristics can be obtained.

A modification of this type of ignition system is found in the "Rolled-tube" igniter.(29) In this system a sheet of cotton broadcloth, coated with a metal-potassium perchlorate-binder igniter material, is rolled around a multi-perforated thin-wall paper tube. Inside the tube at one end is the squib or initiator. This type of igniter can be made up into any length and number of wraps. However, as the length of the tube is decreased the performance approaches that of the jelly roll igniter. In experimental studies it was found that the rates of pressure rise were inversely proportional to the length of the igniter. The longer the igniter the slower the pressure rise. This type of igniter is very useful in reducing shock from high pressure built up by the igniter.

A further modification of the "Jelly-Roll" igniter is the "coated-tube" igniter.(29) This type of ignition system makes use of a perforated plastic tube 1/2 in. OD x 10 in. long, coated inside and outside with an igniter mixture of boron or magnesium and potassium perchlorate with a binder and inserted in a plastic bag for protection. Typical formulations are: (1) 20.4% boron, 73.6% potassium perchlorate, and 6% ExBM (Polyvinyl ether) and (2) 66% magnesium, 28% potassium perchlorate and 6% Vistanex (Polyisobutylene). The coated tube igniter shows increased performance over the jelly roll in some cases. This is probably due to the increased distribution and decreased confinement of the igniter mixture.

The perchlorate-containing igniter material can also be used in the so-called "Shotgun" igniters.(29) This type of igniter was developed to ignite large propellant grains. The igniter is appropriately named, since it looks and operates much like a shotgun shell. The igniter material, generally metal-oxidant pellets, is ignited and ejected into the propellant chamber by the initiator charge. The igniter material presumably is consumed before it traverses the length of the propellant chamber. A small propellant charge of black powder or metal-oxidant powder is generally used to burst the crimped cartridge. A wide variety of compositions and designs are used for particular applications.

One of the newer problems in igniter design is concerned with high altitude ignition. Studies were carried out at the Ordnance Missile Laboratories to observe the effects of high altitude (i. e., low pressure) on metal-oxidant igniter mixtures such as those containing potassium perchlorate and aluminum, boron, titanium, or zirconium.(25) These materials were pressed into flares and ignited under a pressure of 5 mm of mercury (Hg) (0.097 psia). It was found that the pyrotechnic mixtures were extremely hard to ignite even when the oxidizer ratio was increased. It was discovered in these investigations that the candle power of a flare decreased linearly with the pressure. At 15 mm of Hg the candle power was reduced to 1.5% of the sea level value and the burning time was increased by a factor of four.

In connection with this problem, researchers at the Naval Ordnance Test Station have developed a high-altitude igniter composition that appears to be very effective.(46) The igniter mixture, consisting of ammonium-perchlorate and poly-2-methyl-5-vinyltetrazole, has been used to ignite propellants at pressures as low as 25 mm of Hg (0.48 psi).

Potassium and ammonium perchlorates have also been used by the Naval Ordnance Laboratory in the development of an ignition system for the combustible cartridge case ammunition to be used in the 30-mm aircraft gun.(26) The igniter must gain satisfactory ignition without leaving residue from either cartridge case or the primer after firing in order for this system to be effective. One of the methods studied was the use of a consumable primer. The primer body was molded from a composition containing 78.4% ammonium perchlorate and 21.6 expoxy resin binder. The primary composition for the igniter consisted of 98% n-lead styphnate and 2% nitrocellulose The igniter extension tube was filled with 0.3g of a mixture of 47.3% potassium perchlorate, 47.3% zirconium and 2.4% epoxy resin binder.

This formulation proves successful except for the wide variations found in firing current. There was no residue found in the breech or down range from the muzzle. Experimental work on this primer system is still in progress.

Squibs. The electric squib can be defined as a small charge of chemicals, activated by an electrical resistance wire, and used to provide the energy needed to initiate the reaction of a larger charge of propellant. In most applications of squibs in the rocket field, the squib sets off the reaction in a larger igniter charge, which in turn initiates burning of the propellant. This is not invariable practice, however, for in the 2.36 - in. Bazooka rocket a squib ignites the propellant directly. In general, one might say that the use of an intermediary igniter is governed by the size scale between the squib and the working charge in question. Where the gap is large, an igniter stage must be used.

The customary devices used as squibs before the advent of modern rocketry were simple detonators borrowed from the explosives industry. In general these devices used a finely ground black powder charge, ignited by a bridge wire. This material has not been adequate for the new exacting conditions, so many other squib charges have been investigated. Most suitable results have been found in the combination of metal powders with inorganic oxidants. Among these oxidants, potassium chlorate has found wide application.

Information concerning the chemical constitution of squib charges is not usually given on many manufacturer's data sheets. Performance characteristics may be given, but the material is referred to only by a manufacturer's code number. The composition seems to be considered proprietary.

The four following squibs are known to contain potassium chlorate so their characteristics are of interest:

(1) M1A1 Squib (Army)

(2) M2 Squib (Army)

(3) MK1 Mod O Squib (Navy)

(4) MK113 Squib (Navy)

1. M1A1 Squib. This squib is an Army device which has had a relatively long history.(8) Its charge composition is as follows:

	Wt %
Potassium Chlorate	60
Diazodinitrophenol	20
Charcoal	15
Nitrostarch	5

This composition has a flame temperature of 1870°K.

The squib body is 0.26 in. diameter and 0.45 in. long. The charge is sealed in with a polyethylene plug. Lead wires to the squib are 22-gauge tinned copper, with polyethylene insulation. The approximate electrical resistance of the squib, including the lead wires, is 1 ohm. Additional property data are summarized in Table 3-7.

2. M2 Squib. This is another Army squib of the same size as the M1A1 but with a different composition which gives it a somewhat longer

reaction time.(8) Its charge consists of the following:

	Wt %
Potassium chlorate	44
Lead thiocyanate	36
Charcoal	20

This squib is also of 0.26 in. diameter and 0.45 in. length, sealed with a polyethylene plug and assembled with 22-gauge tinned copper lead wires. Over-all electrical resistance is 1 ohm. Additional details are summarized in Table 3-8.

3. MK1 Mod O Squib. This is an unusually complex squib. It has a three-stage charge.(8) A minute charge consisting of a mixture of potassium chlorate and diazodinitrophenol surrounds the bridge wire. Around this is placed a 45-grain charge of black powder. Below this is another 45-grain charge of black powder. The bridge wire (80/20 platinum-iridium) and lead assembly are molded into a mineral-filled phenolic plug. A metal case encloses the entire assembly and is crimped to the phenolic plug to provide hermetic sealing. Either aluminum or copper is used for the case. The wall thickness is 0.008 in. while the base is 0.003 in. thick. The assembly has a diameter of 0.285 in. with a length of 0.435 in. Some characteristics of this squib are summarized in Table 3-9.

4. MK113 Squib. This is another Navy squib (the MK 114 has characteristics nearly the same as the MK113) which is similar in construction to the MK1 Mod O.(8) It has a charge composition of

	Wt %
Potassium chlorate	25
Diazodinitrophenol	75

The squib has a 0. 281 in. diameter and a 0. 435 in. length. The charge is retained with a bakelite plug. The bridgewire is of 60/28/12 nickel/chromium/iron composition. The over-all resistance of the squib is 2 to 7 ohms. A minimum firing current of 70 to 90 milliamps will fire the squib. The maximum nonfiring current is 50 milliamps.

Energy Release in Other Systems

One area of Ordnance research and development which has found a place for perchlorates has been the combustible cartridge case program The objective has been to develop a light weight material to replace the metallic case which would be consumed within the breech. After firing ideally there should be no residue and the next round could be rammed home without delay. The advantages to be gained from such an accomplishment are as follows:(47)

(1) A reduction in Ordnance requirements for strategic materials.

(2) A reduction in weight of ammunition with consequent tactical and logistical advantages.

(3) Elimination of ejection mechanism in automatic weapons with consequent decreases in gun weight and possible increase in rates of fire.

(4) Elimination of problems associated with the storage, transportation, and disposal of used cartridge cases.

(5) Possible decreases in cost of manufacture of guns and ammunition.

In these studies many different types of high-energy polymers have been investigated as possible binders in the cartridge case. One such study has led to the development of a fabric cartridge case made of surgical gauze impregnated with ammonium perchlorate, resin binder, and plasticizer.(15) This particular case was prepared by dissolving Bakelite VYHH (a polyvinyl chloride-acetate copolymer) in methyl ethyl ketone (MEK) and making a slurry of finely ground ammonium perchlorate. The slurry was used to coat a strip of cotton gauze. While the gauze was still damp it was wrapped uniformly over a mandrel of the desired shape, dried and heat sealed.(1)

The ammunition loaded from these combustible cartridges was fired under accepted test procedures and the ballistic performance was found to be comparable with that of standard service ammunition. However, the excessive amount of smoke from the combustible cartridge cases and the corrosion effects from the hydrogen-chloride gas evolved prevented general acceptance of the cases.(15)

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CHAPTER 4. MILITARY USES

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General Requirements

In the first three chapters of this volume attention has been given to particular areas within the defense structure where chlorate and perchlorate compounds have found application. It should be evident from the material in these chapters that the solid propellant field is the major consumer of perchlorates. In Volume I, Chapter 4, where industrial uses for chlorates and perchlorates were discussed, it was shown that the main use of chlorates was for bleaching and for matches. From the military point of view the compounds of chief concern are the perchlorates with ammonium perchlorate the single compound of major interest. The chlorates also play an important but a much less extensive role.

An examination of the solid propellant field reveals that at the present time and almost certainly for several years to come the Federal Government is and will be the chief purchaser, either directly or indirectly, of solid propellants. Up to the present the Government's interest in propellants has been centered in the Department of Defense. With the present interest in space exploration and study a considerable portion of this interest is now being invested in the National Aeronautics and Space Agency (NASA). For the purposes of this text, however, no distinction is being made between these two agencies.

Although the end use of the rocket, missile or device may be different, its present design or basic characteristic pertaining to chlorates or perchlorates is considered to be the same. Therefore, whenever the term military is used in the following sections, the requirement or use may be applicable as well to NASA.

In examining the over-all military use of chlorates and perchlorates consideration is given first to a review of the quantities of these compounds involved in the military programs. The particular end uses are then discussed in general terms as they apply to each of the following categories:

(1) Rockets and Missiles

(2) Jatos and Booster Units

(3) Igniters and Signals

(4) Miscellaneous

Capacities and Uses for Perchlorates

The plant capacities and uses for chlorates have been given fairly extensive coverage in Volume I, Chapters 2 and 4. The manufacturing processes and some general production data on the perchlorates was also included. However, it was felt that a discussion of production and end use figures should be left for this classified volume.

The complexity of the procurement system of the Federal Government plus the inability to obtain a clear distinction between research, development or production in regard to end use for perchlorate compounds make the development of realistic figures difficult. From a variety of sources it has been possible to arrive at some figures which are believed to be reasonable.

As has been shown in Volume I, Chapter 2, there are at present four companies producing ammonium perchlorate, namely:

(1) American Potash and Chemical Corp.

(2) HEF, Inc. (i. e., Hooker-Foote Mineral)

(3) Pennsalt Chemicals Corp.

(4) Pacific Engineering Corp.

It has been estimated(3) that the present total capacity of these plants is about 4,000,000 lb/month. [Lithium Corporation also has a plant (still in pilot plant stage) for lithium perchlorate production.] However, the Business and Defense Services Administration (BDSA), Department of Commerce estimates that total production for 1959 will be 29,000,000 lb (or an average production rate of 2,400,000 lb/month).

There were no data readily available concerning the actual amounts of ammonium perchlorate purchased by the government. A reasonable estimate based upon present programs being conducted under Navy, Army or Air Force sponsorship places the current use rate at about 2,000,000 lb/month.

With the exception of probably less than 1 percent of the above figure all of the ammonium perchlorate will be used in the production of solid propellants. The extent to which solid propellants will be used in the large missiles and space vehicles during future years is not known. There seems to be a strong feeling that solid propellants will be used almost exclusively for military applications, while liquid propellants will be used principally for astronautical exploration. (1)

Lithium perchlorate which is still used only in experimental quantities is being produced only in limited amounts. From the present military point of view the use of this compound is not of importance. However, if its use in propellants will show improved performance at some future time, then requirements for it will increase. None of the other perchlorates are being used by the military at present.

Capacities and Uses for Chlorates

Because most of the uses for chlorates are for nonmilitary applications, it was possible to include considerable detail on plant capacities and production rates for the chlorates in Volume I (see Chapters 2 and 4). It was shown, for example, that the U. S. production of sodium chlorate for 1959 is expected to be 80, 000 tons (representing a production rate of 13, 300, 000 lb/month).(3) Of this total amount about 26% will be converted into perchlorates and other chlorates (mainly potassium chlorate). The military will be the main purchaser of the perchlorates.

The demand for potassium chlorate has remained fairly constant at 7500 tons/year(6) - as was indicated in Volume I (Chapter 4) the match industry utilizes most of this material (80 percent) with the government requiring only a small amount. Uses for the other chlorates is of little consequence.

Applications

The changing requirements of the military and the constant replacement of one particular weapon model by an improved model make the presentation of detailed listings of specific end items a seemingly useless task. Instead, it seems desirable to indicate types of devices which utilize the chlorate and perchlorate compounds. In this way it will be possible to determine the extent to which their use has spread throughout the military organization.

A request was made to the Office of Assistant Secretary of Defense for Supply and Logistics for a listing of military end items which utilize perchlorates. The results of this inquiry are summarized in Table 4-1. (2)

Examination of this table reveals a wide variety of devices. For convenience these items can be divided into the four categories mentioned previously. These are (1) rockets and missiles, (2) jatos and boosters, (3) igniters and signals and (4) miscellaneous.

Missiles and Rockets

The interest in rockets and missiles has increased at a significant rate during the past few years. The use of solid propellants to provide the propulsive power for these devices has also increased. This has been a result of the improvements in performance characteristics for the propellants and the high reliability exhibited by these systems.

In considering the accomplishments which have been made in the solid propellant field, Katcher(9) presents the following impressive list:

(1) Demonstrated age life up to ten years

(2) Smokeless operation

(3) Unstable burning eliminated by additives or mechanical methods

(4) Long duration - up to nine minutes of operation

(5) Case bonding effected for improved loading density

(6) Temperature sensitivity reduced from 0.25%/°F to 0.04%/°F

(7) Demonstrated resistance to temperature changes

(8) Demonstrated high performance in air launching

(9) Demonstrated safety in handling and in shipboard storage.

(10) Demonstrated 99+ percent reliability in field use

(11) Demonstrated low cost

(12) Demonstrated specific impulse from 235 to 258 lb-sec/lb

(13) Demonstrated high (200°F) and low (-85°F) temperature capability

As an example of the relative amounts of ammonium and potassium perchlorates used in a rocket, some simple computations were made for three early rockets.(8) The results are summarized in Table 4-2. The oxidizer requirement is seen to increase as the size of the rocket becomes greater. (The potassium perchlorate shown in the table has now been replaced almost entirely by ammonium perchlorate.)

The number of missiles and rockets which are operational or under development in the Department of Defense Arsenal is large. Solid propellants have found use in many of these. There are several ways by which these devices can be classified. A common method is by location of the launching point and of the target.(11) On this basis there are the following four systems.

Air-to-Air Systems (AAM). These are missiles and rockets used by fighters and bombers (and eventually by missile-carrying missiles) against enemy aircraft or missiles. They are small in size, light in weight and man-handled on the ground. They usually are powered by solid propellants. Many contain their own guidance system; others are controlled from the mother plane.

Examples: Falcon, Mighty Mouse (2.75 in. FFAR), Sidewinder.

Antiaircraft Systems (SAM). The surface-to-air missiles are used against enemy aircraft or missiles. They are somewhat larger than the AAM systems but are still in the small class. Although most are propelled with liquid propellants, many use solids. Some have self-contained guidance systems, while others are radar controlled.

Examples: Nike Hercules, Terrier, Nike Zeus.

Air-to-Surface Systems (ASM). These missiles are bombs to which have been added power plants, intelligence, and, in some cases, wings. They are presently carried either internally or externally by fighters or bombers and, eventually, will be carried by missiles. These systems are usually small in size and have self-contained intelligence. Solid propellant systems are becoming of greater interest.

Surface-to-Surface Systems (SSM). These missiles include artillery, bombing, antitank, antipersonnel, intermediate-long range and intercontinental range missiles. A wide variety of sizes and types of missiles are found in this class. The Army uses short-range systems to replace artillery while the Air Force uses long-range devices to replace bombers. The Army devices follow ballistic trajectories while the Air Force "birds" behave more like conventional aircraft. Solid propellants are used frequently in artillery and anti-tank missiles and only recently are they being tried in large units.

Examples: (1) Artillery: - Honest John, Sergeant
(2) Long Range: - Pershing, Polaris
(3) Intercontinental: - Minuteman
(4) Antitank: - Dart, Heller

Jatos and Boosters

The jet-assist-take-off (JATO) rocket was developed to assist heavily-loaded aircraft in taking off from a short runway. As has been pointed out earlier, the first composite solid propellant was used in such a device. Since that time a large number of such rocket systems has been developed. A number use double-base cast propellant while many use composite propellants. The potassium perchlorate of the early compositions has now been replaced by the smokeless ammonium perchlorate. The SPIA JATO Manual(12) summarizes the characteristics of the several accepted JATO units.

The development of the large missiles created a need for first-stage boosters. A large number of different systems have been produced. For example, Regulus I uses a 2.2 KS 33,000 booster. Such a unit develops a thrust of 33,000 lb per 2.2 sec.

A third use for boosters is in high-speed sled work. A variety of solid propellant booster rockets are used to create high accelerations on the supersonic tracks used for testing missiles, rockets and escape systems under simulated operational conditions.

The JATO units which have been used or are currently being used are made in a variety of sizes and contain a variety of propellant compositions. A summary of the perchlorate requirements for some typical units is given in Table 4-3.(8) At the time these data were obtained potassium perchlorate was still being used. It has now been almost entirely replaced by ammonium perchlorate.

Igniters and Signals

The composition of igniter materials and squibs used in ignition systems has been discussed in Chapter 3. A compilation of the various igniters which use these materials is beyond the scope of this text. However, it is understood that an igniter handbook is in preparation under Bureau of Ordnance sponsorship and should be available shortly.

A wide variety of signals and signalling devices contain either chlorates or perchlorates. In recent times the more stable perchlorates have replaced the chlorates in most flare compositions. Davis(4) presents considerable information on compositions used for industrial and military applications.

From correspondence with several of the pyrotechnic, match and igniter manufacturers some information was obtained on the use of chlorate and perchlorate compounds in igniter and certain other pyrotechnic-containing devices for military applications. These devices can be divided into (1) squibs, (2) primers, (3) igniters and (4) flares.

Squibs. The exact composition of most squibs (with the exception of those discussed in Chapter 3) is usually proprietary. However, information from some of the manufacturers reveals that potassium chlorate is a common ingredient in most electric squibs, blasting caps and detonators.(5, 7, 14) For example, the squibs listed in Table 4-4 all contain this compound as an ingredient. Only small quantities are used. It is estimated(14) that in a production lot of 150, 000 squibs only 2 to 3 lb of potassium chlorate would be required. This is also true for blasting caps and other detonating devices.

Primers. Potassium chlorate also finds use in gun primers. Several have been developed/for the military. Examples of Navy primers which use this material follow:(7)

Primer MK 112 Mod O

Primer MK 113 Mod O

Primer MK 114 Mod O

Primer MK 114 Mod 1

Primer MK 114 Mod 2

Primer MK 115

Primer MK 116

Primer MK 117

Primer MK 121 Mod O

Primer MK 139 Mod O

With the requirements for operation at higher temperatures becoming more important, there is a general tendency to replace the potassium chlorate with materials which have better heat stability. (7)

Igniters. Special igniters have been developed which resemble closely the common safety match. Of particular interest are the "pull-wire" igniters. The normal "book-match" composition has from 45 to 50 percent potassium chlorate. The pull-igniters use a variation of these formulas. For example, Fire Starter M-1 uses a match head mixture V according to MIL-Std-M-S585. (13) Match-head mixture MIL-Std-M-569 is used in the igniter pellet for the M-1 portable flame throwers. A striker strip or coated pin whose active ingredient is red phosphorus is usually provided in all military or commercial devices of this type. Where no separate striker is necessary the active ingredient, phosphorus sesquisulfide, is incorporated with a chlorate mixture. (13)

The use of chlorates and perchlorates in specific igniter material compositions has already been discussed in Chapter 3 under "AlClO".

Certain other igniter materials contain these ingredients to some extent(14) but potassium nitrate still serves as the oxidizer in many of these mixtures.

Although pyrotechnic igniters are usually thought of in connection with solid propellants, they also find extensive use in liquid propellant rockets. When nonhypergolic liquid propellants are used, a small, metal-oxidant containing igniter has been found to be most effective in promoting ignition. In many cases such devices are superior to glow plugs or hot-wire ignition systems. Either ammonium or potassium perchlorate or both have been used in particular ignition compositions for such igniters.(10) Since each rocket has its own particular ignition system, there is no "standard" igniter for general use.

Closely allied with the igniters are the delay elements used in many ordnance items. It has been pointed out(13) that potassium perchlorate serves as a burning-rate regulator in such systems. Several compositions have been developed which contain, for example, zirconium-nickel alloy, barium chromate and potassium perchlorate. The necessity for high reliability and extremely close control of burning rate is paramount in such elements.

Flares. Signal flares play an important role in most military operations. These devices come in a variety of colors and color combinations. Illuminating flares produce high candle power without reference to color. The flares are also supplemented by colored smokes. These are also used for signalling.

In recent years potassium perchlorate has replaced the chlorate in colored lights and illuminating flares.(10) Potassium chlorate is commonly used in fireworks while military signals require use of potassium perchlorate. Numerous colored lights contain, for example, potassium perchlorate with either barium or strontium nitrate.(13) Occasionally, ammonium perchlorate can be used as a burning-rate regulator and to volatilize the barium or strontium salts, but usually the ammonium compound is shunned by the military because of its greater sensitivity to accidental explosion.

The most common of signal compositions is that used in illuminating devices. In particular, photo flash powder, MIL-P-466A, consists of potassium perchlorate, barium nitrate and aluminum powder.(13) This finds wide application in illuminating flares and signals.

Although the potassium salts are used almost extensively in flares, at one time barium chlorate served in a "star" composition as both an oxidizer and as a source of the green color. In another application, strontium and barium perchlorates were dissolved in alcohol and used to saturate a cotton mass which contained finely divided magnesium.(10) Such applications are rare.

Smokes usually contain an organic fuel, aniline dye and either chlorate or perchlorates as oxidizer.(10, 13) Potassium chlorate is generally used with lactose or sucrose in such compositions. A wide variety of brilliant colors are possible with the selection of the proper stable organic dye.(13)

Miscellaneous

There are numerous other applications for chlorate and perchlorate compounds by the military. The total amount of material utilized for such purposes is actually very small. It is of academic interest principally, to illustrate the extended use of these compounds, that examples of miscellaneous usage are presented. It is not the purpose of this text to cover every possible application.

One particularly interesting application for potassium chlorate is in the pyrotechnic whistling compounds used in the M-119 Simulator, Booby-trap, Whistling. This composition contains the chlorate with gallic acid and red gum. Another application is in railroad torpedoes. Such devices are used both by the railroad companies and by the military. A mixture of potassium chlorate, sulfur, abrasive material and a binder create an explosive sound when crushed between the wheel and rail. (13)

Potassium chlorate is also used in combination with red phosphorus in antipersonnel mines. The so-called "Armstrong's Mixture" is extremely sensitive to explosive reaction on slight disturbance if the ingredients are in the dry state. (13)

Of a somewhat different requirement is the use of sodium chlorate as a weed killer. However, the military uses this compound to keep down the growth of weeds around storage magazines, munitions dumps and operating buildings for handling hazardous materials.

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CHAPTER 5. NEW MANUFACTURING DEVELOPMENTS

CHAPTER 5. NEW MANUFACTURING DEVELOPMENTS

General Considerations

As has been indicated in earlier chapters the chlorates and perchlorates were originally made by chemical rather than electrolytic methods. The greater economy found in the electrical methods, however, soon forced their over-all adoption by the industry. The anticipated increased demands for the perchlorates inparticular in the early 1950's focused attention again on the chemical processes. Interest in these methods was further stimulated by the desire to produce the perchlorates without being completely dependent upon two commodities: (1) platinum for electrodes and (2) economical electrical power.

Chemical Processes

Support for research and development in the areas of new methods for producing perchlorates was given for the most part through the Office of Naval Research, starting about 1951.(4) As a result of this support four separate chemical processes were evaluated at the laboratory stage. Through further support from the separate military services, some of these methods were studied even at the pilot plant stage. The four processes evolved were:

(1) thermal process

(2) lead dioxide chemical process

(3) acid disproportionation process

(4) ozone process.

In addition to the methods mentioned on the preceding page considerable effort was expended to develop nonplatinum anodes for the electrolytic process for manufacturing perchlorates (See Volume I, Chapter 2). The use of massive lead dioxide anodes has shown promise of being a good substitute for platinum.

Although there is still an interest in these chemical manufacturing processes, activity on particular research and development programs is practically nil at the present time. Because the majority of the work completed on these processes was classified and much has still not been declassified, it has been necessary to place the discussion of these programs in Volume II. In the following sections a brief review is given of these processes.

Thermal Process

The manufacture of perchlorates in large quantities has never been undertaken by the thermal process. However, such a method for the manufacture of sodium perchlorate was patented(2) and its procedure has been described in Volume I, Chapter 2. Basically, this process consists of thermally decomposing sodium chlorate continuously into sodium perchlorate. The unreacted sodium chlorate is recycled. The sodium perchlorate formed is extracted in a water crystallization process.

Reference is made(5) to the thermal conversion of chlorates and perchlorates by a method developed by Oldbury Electrochemical Company at Niagara Falls, N. Y. No details have been found concerning this process.

Examination of the thermal process reveals that although this process requires no electrical power for conversion of chlorate to perchlorate, it does consume about 1.5 lb of chlorate for the production of 1.0 lb of perchlorate.(3) This means that the over-all saving in electrical power in going from chlorine to perchlorate would be no more than about 10 percent. For this reason very little further work has been done with this process.

Lead Dioxide Chemical Process

Under ONR sponsorship considerable work was done in developing a process for producing ammonium and sodium perchlorate from sodium chlorate, using lead dioxide.(3) This process offered a means for producing the perchlorate with no electrical power required in the conversion of chlorate to perchlorate. Because of the attractive features of this process, additional development activity at the pilot-plant level was sponsored by the Bureau of Ordnance.(1, 9, 10)

Under the "Perch Project" a pilot plant was constructed for the production of ammonium perchlorate from sodium chlorate by the lead dioxide chemical process.(9) This process consisted of the oxidation of sodium chlorate to the perchlorate in the presence of lead dioxide, a powerful oxidizing agent(8), and some perchloric acid. A one-step process was used initially with sulfuric acid added to the reaction. The resulting mixture then contained the perchlorate as perchloric acid. After filtering and neutralizing with ammonia the desired ammonium perchlorate was obtained.

To make the process economical the lead salts had to be recovered and reused. This was accomplished by first neutralizing the lead sulfate produced during the formation of the perchlorate with sodium carbonate or hydroxide and then exposing the solution to chlorine.

In the final modification of the process, the oxidation was carried out as a two-step operation in order to improve the yield.(1) Thus the sodium perchlorate was recovered by crystallization. This material was then converted to a crude perchloric acid solution with sulfuric acid. Neutralization of the resulting solution with ammonia gave the desired ammonium salt. The recovery of the lead salts in the recycling step was also made easier by substituting sodium hydroxide for the sodium carbonate; undesirable frothing was thus eliminated. Data for use in designing a full-scale plant were obtained in this program. A preliminary product cost estimate for a 10,000 ton/year plant was $0.43 per lb (current selling price is $0.28 per lb). It is probably this higher estimated cost which has curtailed further exploration of this process.

Acid Disproportionation Process

Another method for producing ammonium perchlorate from sodium perchlorate was the acid disproportionation process. This process was investigated under ONR support by several companies.(3) In general, strong acids such as sulfuric, phosphoric and perchloric were used.(5) Very little information was generally available on this work. However, it was concluded that there was no particular saving in electrical power to be realized by utilizing this process. (3)

In connection with the work carried out under the Perch Project a novel process of the above type was considered. (9) This consisted of reacting sodium chlorate with perchloric acid to form sodium perchlorate and chlorine dioxide. The make-up sodium chlorate was made from sodium hydroxide, chlorine and the recovered chlorine dioxide. Perchloric acid was prepared by treating part of the sodium perchlorate with hydrochloric acid. The economics of this process were not given.

The Ozone Process

In a review of the possible methods for producing ammonium perchlorate, it was pointed out that chemical oxidizing agents had not been very successful in converting chlorates to perchlorates. (3) Possible exceptions, however, were the oxidation of the chlorate with lead dioxide and the use of ozone with the hypochlorites. Reference is made(5) to the direct oxidation of chlorates by ozone to pure perchlorates. As far as it is known no ammonium perchlorate has been made in quantity by the use of ozone. Nevertheless, it is of interest to examine the possible ways in which ozone could be used.

It has been suggested(6) that ozone might be used to produce perchlorates without requiring platinum. This suggestion was based largely on calculation of heats of reaction which were in turn based on available (or estimated) heats of formation data. Three methods have been suggested:

(1) Direct combination of ozone and chlorine

(2) Direct oxidation of hypochloric acid with ozone

(3) Direct oxidation of sodium hypochlorite with ozone.

Direct Combinations of Ozone and Chlorine. The direct reaction of ozone with chlorine would form chlorine heptoxide which could be subsequently hydrated to give perchloric acid. The acid could then be readily neutralized to the desired ammonium or sodium salt.

The reaction between ozone and chlorine can be shown as

$$3Cl_2(g) + 7O_3(g) \longrightarrow 3Cl_2O_7(l) + 15.9 \text{ kcal/mol of product} \qquad (5\text{-}1)$$

According to Byrns and Rollefson(2) chlorine heptoxide has been obtained experimentally from the reaction of ozone and chlorine under "blue light." In this reaction it appears that chlorine trioxide is produced first and is later oxidized to the heptoxide. Chlorine heptoxide was first produced by action of P_2O_5 on $HClO_4$.(7) It is a colorless oil which melts at -91.5°C and boils at 82°C. It is soluble in cold water in which it hydrolyzes to give $HClO_4$.

The reaction represented by Equation (5-1) is believed to offer a possible means for producing perchlorate on a commercial scale. Chlorine with an excess of ozone would be passed through a cooled reaction zone illuminated with the proper wave length of actinic light. The reaction products would be passed through water to absorb the chlorine heptoxide formed and to remove the unused excess ozone. The reaction should be facilitated by increased pressures.

Direct Oxidation of HOCl with Ozone. The oxidation of hypochlorous acid with ozone should give perchloric acid according to the following reactions:

$HOCl\ (400\ m) + O_3\ (g) \longrightarrow HClO_4\ (dil) + 37.27$ k cal/mol of product (5-2)

An exothermic reaction is indicated with the ozone acting on an aqueous solution of HOCl. This reaction should be accelerated by high pressures. The HOCl may be prepared in a 25% aqueous solution by acidifying a solution of NaOCl and distilling. The HOCl solution may also be prepared by reacting Cl_2 with NaOH and continuing the chlorination. This procedure will yield a solution of HOCl containing NaCl, but this latter material should not interfere in the process.

Direct Oxidation of NaOCl with Ozone. The oxidation of NaOCl with ozone should give $NaClO_4$ according to the reaction:

$NaOCl\ (dil) + O_3\ (g) \longrightarrow NaClO_4\ (dil) + 48.0$ k cal/mol of product (5-3)

This reaction should be exothermic and should be accelerated by light and high pressure. The NaOCl solution may be made (as in the previous method) by chlorinating a NaOH solution. This reaction leaves NaCl in solution, but that is not believed to be harmful.

The three methods described above have never been tried experimentally, so far as it is known, to determine whether they would be suitable for making production quantities of potassium or ammonium perchlorate. The exact nature of the ozonation reaction used in converting chlorates directly to perchlorates referred to earlier(5) is not known. Since the use of ozone does not appear to offer a saving in electrical power or in over-all production costs, it has not received very much attention. It is quite probable that future increases in production of ammonium perchlorate will arise from expansion of present plant facilities rather than the introduction of a new manufacturing process.

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ILLUSTRATIONS

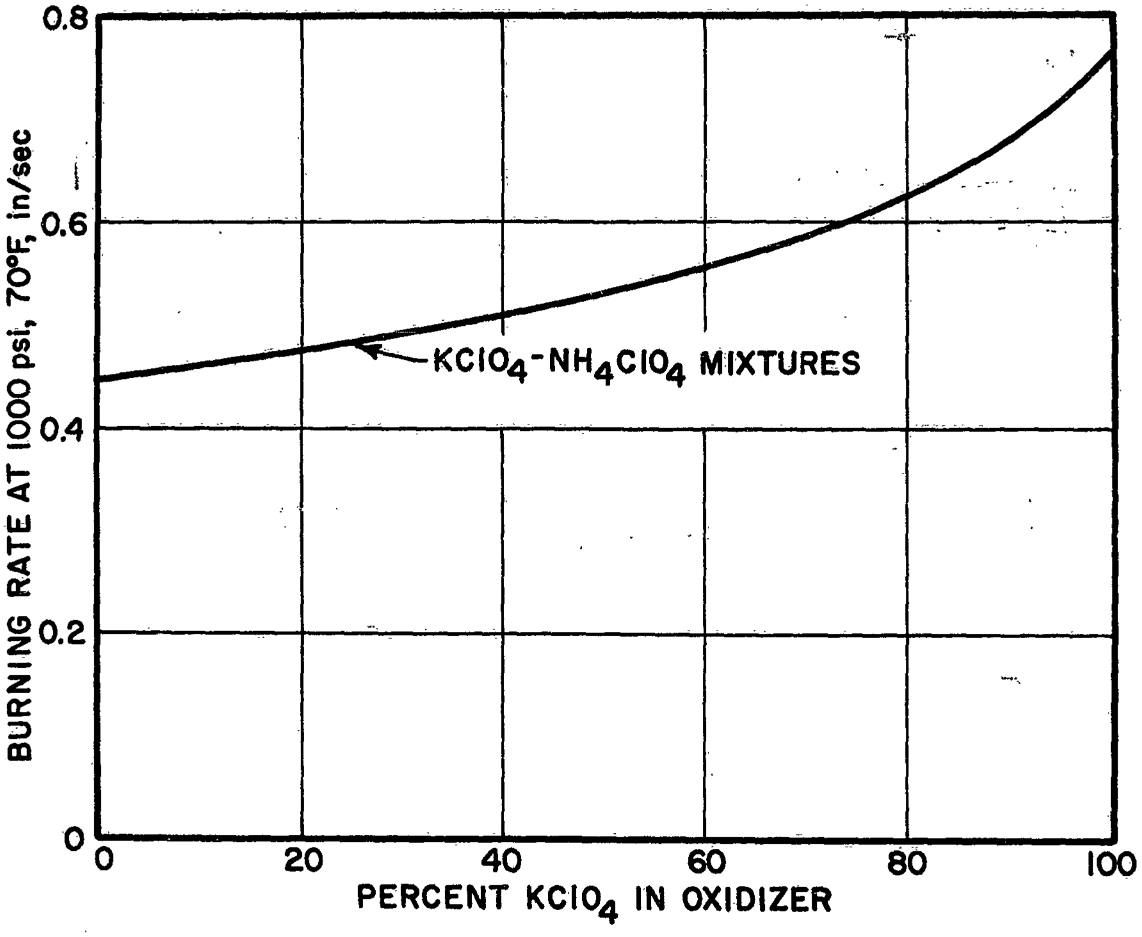

FIGURE 2-1. EFFECT ON BURNING RATE OF REPLACING NH_4ClO_4 WITH $KClO_4$

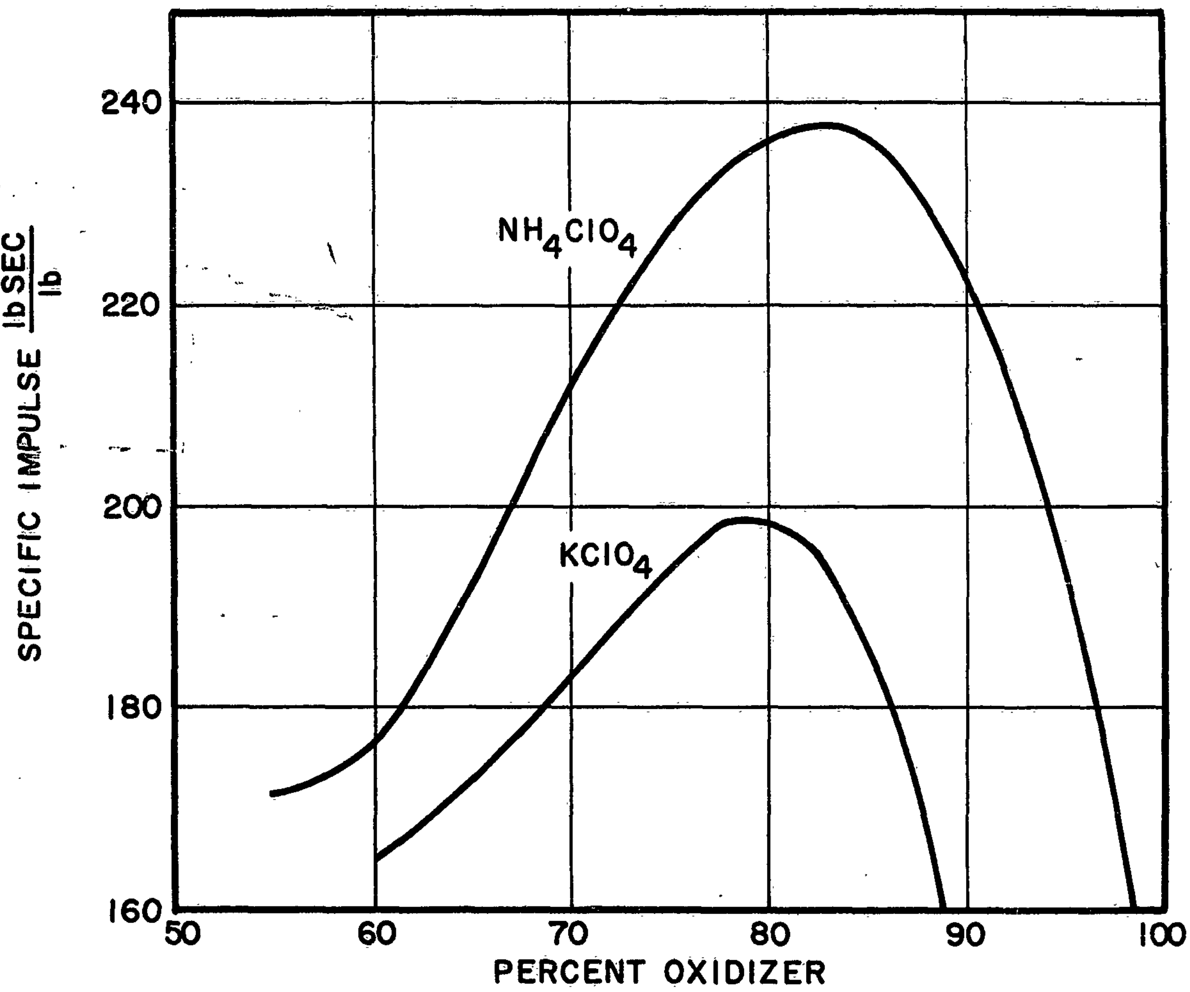

FIGURE 2-2. EFFECT ON CALCULATED SPECIFIC IMPULSE OF REPLACING $KClO_4$ WITH NH_4ClO_4

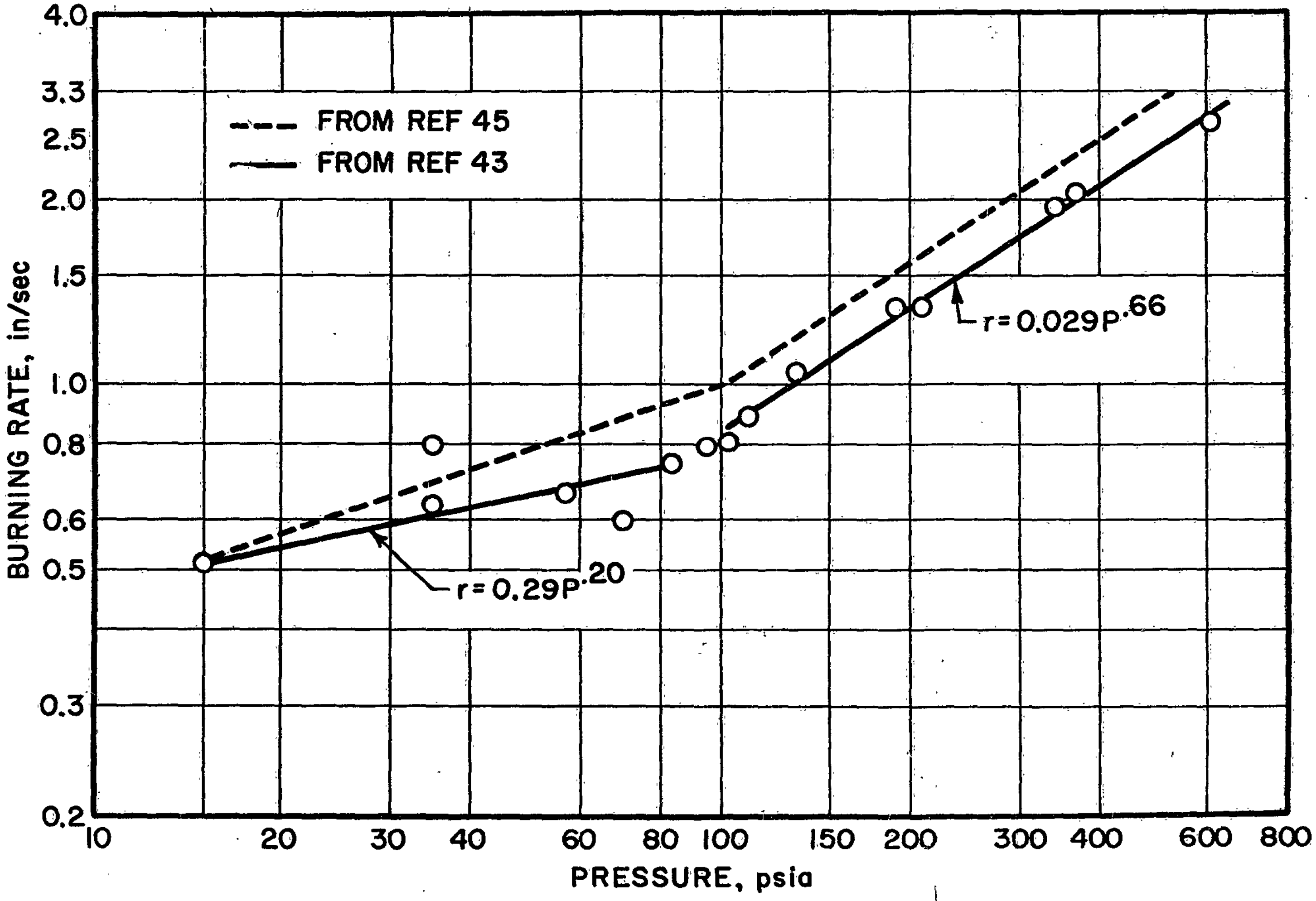

FIGURE 3-1. BURNING RATE - PRESSURE RELATIONSHIP FOR AlClO (AlClO + 13% LEAD)

TABLES

TABLE 2-1 COMPOSITION AND CHARACTERISTICS OF $KClO_4$-ASPHALT PROPELLANT (ALT-161)(43)

1. Composition	Wt %
Potassium perchlorate	76.50
URSA P-10 oil	9.40
TA-567 Asphalt	9.40
T-18 Asphalt	4.70

2. Burning	
Burning rate at 1000 psi and 60° F, in/sec	0.93
Pressure exponent	.745
Temperature coefficient, π_K	.41
Discharge coefficient	.00883
Specific impulse, (2000 psi, $\epsilon = 6.75$), lb-sec/lb	186

3. Physical	
Density, $lb/in.^3$	0.064
g/cm^3	1.78

4. Mechanical

no data

5. Thermodynamic	
Heat of explosion, cal/g	--
Heat capacity, C_p, cal/g/° C	--
Specific heat ratio	1.27
Flame temperature, T_p, ° K	2034

TABLE 2-2. COMPOSITION AND CHARACTERISTICS OF A $KClO_4$-RESIN PROPELLANT (AK-14 MOD 1)(43)

1. Composition	Wt %
Potassium perchlorate	74.00
P-10 resin	24.75
Cumene hydroperoxide	.25
P-33 carbon black	1.00
Cobalt octoate	*

2. Burning	
Burning rate (1000 psi, 60° F), in./sec	0.72
Pressure exponent	.741
Temperature coefficient, π_K	.36
Discharge coefficient	0.00889
Specific impulse (1000psi, ϵ = 5.3)	177
3. Physical	
Density, lb/in.^{3}	0.068
g/cm^3	1.89
4. Mechanical	
Ultimate tensile strength at 60° F, psi	1301
5. Thermodynamic	
Heat of explosion, cal/g	967
Heat capacity, C_p, cal/g/° C	0.248
Specific heat ratio	1.164
Flame temperature, T_p, °K	1950

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*As required for desired gel time.

TABLE 2-3 COMPARISON OF A $KClO_4$ PROPELLANT WITH A NITROCELLULOSE-BASE PROPELLANT(43)

1. Composition

AK-14(Mod 1)		JPN	
Constituent	Wt %	Constituent	Wt %
Potassium perchlorate	74.00	Nitrocellulose (13.25% N)	51.40
P-10 resin	24.75	Nitroglycerin	42.90
Cumene hydroperoxide	0.25	Diethylphthalate	3.23
P-33 carbon black	1.00	Ethyl centralite	1.00
Cobalt octoate	as required	Potassium sulfate	1.25
		Carbon black	.20
		Candelilla wax	.02

2. Burning

	AK-14	JPN
Burning Rate, (1000 psi), in/sec	0.72 (60° F)	0.60 (70° F)
Pressure exponent, n	.741	.69
Temperature coefficient (π_K)	.36	.75
Discharge coefficient, C_d	.00889	.00661
Specific impulse, I_s, lb-sec/lb	177	236

3. Physical

Density, lb/in.^{3}	0.068	0.059
g/cm^3	1.89	1.62

4. Mechanical

Stress at rupture (77° F), psi	1736	1276
Tensile strength, psi	1301 (60° F)	775 (77° F)

5. Thermodynamic

Heat of explosion, cal/g	967	1220
Heat capacity, C_p, cal/g/° C	0.248	0.341
Specific heat ratio	1.164	1.217
Flame temperature, T_p, ° K	1950	3010

TABLE 2-4 COMPOSITION AND CHARACTERISTICS OF A $KClO_4$-NITROCELLULOSE PROPELLANT (M7 or T-4)(43)

1. Composition

Constituent	Wt %
Potassium perchlorate	7.80
Nitrocellulose (13.15% N)	54.60
Nitroglycerin	35.50
Ethyl centralite	.90
Carbon black (dry)	1.20

2. Burning

Burning rate (1000 psi and 70° F), in./sec	0.695
Pressure exponent	.77
Temperature Coefficient, π p/r	.77
Discharge coefficient	--
Specific impulse (1000 psi, $\epsilon = 8$), lb-sec/lb	240

3. Physical

Density, lb/in.^{3}	0.061
g/cm^3	1.69

4. Thermodynamic

Heat of explosion, cal/g	1280
Heat capacity, C_p, cal/g/° C	--
Specific heat ratio	1.21
Flame temperature, T_p, ° K	3160

TABLE 2-5. RESPECTIVE ADVANTAGES OF $KCLO_4$ AND NH_4CLO_4 PROPELLANTS(13)

$KClO_4$ Propellants	NH_4ClO_4 Propellants
Lower material cost	
High oxygen balance for a given percentage of oxidizer	Higher c* for a given percentage of oxidizer.
Better castability for a given percentage of oxidizer.	
Higher density for a given percentage of oxidizer.	
Higher burning rates (especially desirable for short burning time applications).	Lower burning rates obtainable (especially desirable for such applications as sounding and long-range rockets).
Lower temperature coefficient of burning time.	Lower temperature coefficient of steady-state pressure and hence less variation in rocket-motor performance over the operating temperature range. Much lower pressure exponents.
No HCl produced in the exhaust with resultant corrosion problem.	No solid particles (i. e., KCl) from combustion with resultant nozzle erosion problem.
Lower hygroscopicity.	
No NH_3 evolved during curing with dipenyl guanidine as an accelerator in polysulfide propellants.	
	Lower combustion limit.
	Easier ignition and hence less chance for ignition delay.

TABLE 2-6. COMPOSITION AND CHARACTERISTICS OF A TYPICAL AMMONIUM PERCHLORATE/POLYESTER RESIN PROPELLANT (ANT 623)(43)

1. Composition

Constituent	Wt %
Ammonium perchlorate	83.00
n-Butyl acrylate	6.06
A-20 resin	3.37
Methyl methacrylate	2.69
Methyl acrylate	1.35
Ammonium dichromate	2.00
Ethyl orthosilicate	1.00
Lecithin	0.2
CHP	0.3
Tetraethylene pentamine	0.03

2. Burning

Burning rate (1000 psi 60° F), in./sec	0.99
Pressure exponent	.51
Discharge coefficient	.0067
Specific impulse (1000 psi), lb-sec/lb	255

3. Physical

Density, lb/in.^{3}	0.0635
g/cm^3	1.76

4. Mechanical

None

5. Thermodynamic Properties

Heat capacity, C_p, cal/g/° C	0.0066
Specific heat ratio	1.21
Flame temperature, T_p, ° K	3025

TABLE 2-7. COMPOSITION AND CHARACTERISTICS OF A TYPICAL AMMONIUM PERCHLORATE/POLYSULFIDE PROPELLANT (T-13E1)[43]

1. Composition

Constituent	Wt %
Ammonium perchlorate	66.98
Liquid Polymer (LP-33)	29.99
Paraquinone dioxime (GMF)	2.00
Diphenylguanidine (DPG)	1.00
Sulfur, flowers of	.01
Butyl carbitol adipate	.02

2. Burning

Burning rate (1000 psi and 70° F), in. /sec	0.35
Pressure exponent	.216
Temperature coefficient, π_K	.175
Discharge coefficient	--
Specific impulse, (1000 psi, $\epsilon = 7.94$), lb-sec/lb	208

3. Physical

Density, lb/in.^{3}	0.0598
g/cm^3	1.66

4. Mechanical

Ultimate tensile strength (77° F), psi	40

5. Thermodynamic

Heat of explosion, cal/g	--
Heat capacity, C_p, cal/g/° C	--
Specific heat ratio	1.254
Flame temperature, T_p, °K	2314

TABLE 2-8. COMPOSITION AND CHARACTERISTICS OF A TYPICAL AMMONIUM PERCHLORATE/VINYL PROPELLANT (ARCITE 251)(43)

1. Composition

Constituent	Wt %
Ammonium perchlorate	73.63
Geon 121*	12.44
Flexol dioctyl phthalate	6.22
GE 2557	6.22
Calcium carbonate	.99
Ferro 1203-X**	.50

2. Burning

Burning rate (1000 psi and 70° F)	0.255
Pressure exponent	plateau
Temperature coefficient, π_K	0.18
Discharge coefficient	0.0069
Specific impulse (1000 psi, $\epsilon = 7.5$), lb-sec/lb	222

3. Physical

Density, lb/in.^{3}	0.059
g/cm^3	1.639

4. Mechanical

Ultimate tensile strength (77° F)	127

5. Thermodynamic

Heat of explosion, cal/g	--
Heat capacity, C_p,cal/g/° C	--
Specific heat ratio	1.233
Flame temperature, T_p, ° K	2360

---

*polyvinyl chloride plastisol
**stabilizer

TABLE 2-9. COMPOSITION AND CHARACTERISTICS OF A TYPICAL AMMONIUM PERCHLORATE/POLYURETHANE PROPELLANT (ANP2541CD PROPELLANT)(43)

1. Composition

Constituent	Wt %	
Ammonium perchlorate	81.5	oxidizer
Polyurethane fuel	16.00	fuel-binder
Copper chromite	0.50	burning rate accelerater
Aluminum oxide	2.00	resonance suppressor

2. Burning

Burning rate, 1000 psi at 60° F, in./sec	0.50
Pressure exponent	.33
Temperature coefficient, π_K	(.15)
Discharge coefficient	0.0067
Specific impulse, (1000 psi) lb-sec/lb	229

3. Physical

Density, lb/in.^{3}	0.0616
g/cm^3	1.81

4. Mechanical:

No data

5. Thermodynamic

Heat of explosion, cal/g	--
Heat capacity, C_p, cal/g/° F	--
Specific heat ratio	1.19
Flame Temperature, T_p, °K	2890

TABLE 2-10. COMPOSITION AND CHARACTERISTICS OF A TYPICAL AMMONIUM PERCHLORATE/POLYISOBUTYLENE PROPELLANT (R. D. 2304)(43)

1. Composition

Constituent	Wt %
Ammonium perchlorate	70.5
Ammonium picrate	15.0
Polyisobutylene (B14)	12.5
Lecithin	1.0
Titanium dioxide	1.0

2. Burning

Burning rate, 1000 psi at 70°F, in./sec	0.60
Pressure exponent	.45
Temperature coefficient	.0025
Discharge coefficient	--
Specific impulse (1000 psi, $\epsilon = 7.5$), lb-sec/lb	197

3. Physical

Density, lb/in.^{3}	0.061
g/cm^3	1.682

4. Mechanical

No data

5. Thermodynamic

Heat of explosion, cal/g	935
Heat capacity, C_p, cal/g/°C	0.395
Specific heat ratio	1.28
Flame Temperature, T_p, °K	2350

TABLE 2-11. COMPOSITION AND CHARACTERISTICS OF AN AMMONIUM PERCHLORATE-NITRASOL PROPELLANT (H-3515)(43)

1. Composition

Constituent	Wt %
Ammonium perchlorate	35.00
Pentaeyrthritol trinitrate	35.00
Nitrocellulose (12.6% N)	14.25
Aluminum	15.00
N^1, N^1-diphenyl-diethyl urea	0.75

2. Burning

Burning rate (1000 psi and 70°F), in./sec	0.42
Pressure exponent	.68
Temperature coefficient, $\pi_{p/r}$	.22
Discharge coefficient	--
Specific impulse (1000 psi, ϵ = opt.), lb-sec/lb	255

3. Physical

Density, lb/in.^{3}	0.064
g/cm^3	--

4. Mechanical

Stress at max. strain (77°F), psi	164

5. Thermodynamic

Heat of explosion, cal/g	1700
Heat capacity, C_p, cal/g/°C	--
Specific heat ratio	--
Flame temperature, T_p, °K	3450

TABLE 2-12. COMPOSITION AND CHARACTERISTICS OF AN AMMONIUM PERCHLORATE - DOUBLE BASE PROPELLANT (BSQ)(43)

1. Composition	Wt, %	Casting Powder (ABL 1346. 3)	Solvent
Nitrocellulose (13. 15% N)	21. 5	33. 0	--
Nitroglycerin	26. 3	--	75. 0
Ammonium perchlorate	21. 4	33. 0	--
Aluminum	21. 4	33. 0	--
Triacetin	8. 4	--	24. 0
Nitrodiphenylamine	1. 0	1. 0	1. 0

2. Burning	
Burning rate (1000 psi at 70°F), in. /sec	0. 71
Pressure exponent	. 57
Temperature coefficient	--
Discharge coefficient	--
Specific impulse (1000 psi), lb-sec/lb	251
3. Physical	
Density, lb/in.^{3}	0. 0628
g/cm^3	--
4. Mechanical	
Ultimate tensile strength (77°F), psi	52
Modulus	1500
% Elongation	8. 4
5. Thermodynamic	
Heat of explosion, cal/g	--
Heat capacity, C_p, cal/g/°C	0. 3937
Specific heat ratio	1. 1
Flame temperature, T_p, °K	4415

TABLE 2-13. COMPOSITION AND CHARACTERISTICS OF AN AMMONIUM PERCHLORATE - NITROPOLYURETHANE PROPELLANT (ANP 2599CD MOD B)(24,45)

		Wt %	
1.	**Composition***		
	3-nitraze-1, 5-pentane-diisocyanate (XIII)	8.96	
	2, 2 -dinitro-1, 3-propane-diol (A)	6.71	
	Tris (hydroxymethyl)-nitromethane	0.35	
	4-nitrazapentanonitrile (NPN)	16.02	
	Ammonium perchlorate (AP)	66.00	
	Aluminum powder	1.96	
2.	**Burning**		
	Burning rate (1000 psi at 60°F), in. /sec		0.371
	Pressure exponent		--
	Temperature coefficient		--
	Discharge coefficient		.0063
	Specific impulse (1000 psi opt. exp.), lb-sec/lb		233
3.	**Physical**		
	Density, lb/in.^{3}		0.0623
	g/cm^3		--
4.	**Mechanical** (Based on ANP-2599CO Mod A)		
	Ultimate tensile, 60°F, psi		55.1
	Secant Modulus, 60°F, psi		171
	Elongation at break, 60°F, %		46.9
5.	**Thermodynamic**		
	Heat of explosion, cal/g		--
	Heat capacity, C_p, cal/g/°C		.50(est.)
	Specific heat ratio		1.167
	Flame temperature, T_p, °K		3184

---

* In addition to the listed ingredients, the propellants contain variable quantities of ferric chloride catalyst, added as a 2-wt % solution in part of the NPN. These may be some CAO-6 (Catalin Corporation of America), which is 2, 2-thiobis(4-methyl-6-tert-butylphenol). CD is the oxidizer-blend designation for 70% ground at 2200 rpm in Micro-Pulverizer
30% ground at 9600 rpm in Micro-Pulverizer

TABLE 2-14. COMPOSITION AND CHARACTERISTICS OF AN AMMONIUM PERCHLORATE - PETRIN ACRYLATE PROPELLANT (OY_d)(43)

1.	**Composition**	**Wt %**
	Ammonium perchlorate	62.2
	Petrin acrylate	14.6
	Triethylene glycol dinitrate	17.5
	Polyester 920	0.9
	2-Ethylhexyl acrylate	1.6
	Aluminum	3.0
	Ethyl centralite	0.2
2.	**Burning**	
	Burning rate (1000 psi and 70° F), in. /sec	0.596
	Pressure exponent	0.40
	Temperature coefficient, π_K	0.178
	Discharge coefficient	--
	Specific impulse (1000 psi), lb-sec/lb	247
3	**Physical**	
	Density, lb/in.^{3}	0.0618
	g/cm^3	1.565
4.	**Mechanical**	
	Ultimate tensile strength (75° F), psi	32.6
	% elongation (75° F)	20
5.	**Thermodynamic**	
	Heat of explosion, cal/g	1445
	Heat capacity, C_p, cal/g/° C	--
	Specific heat ratio	1.19
	Flame temperature, T_p, ° K	--

TABLE 2-15. COMPOSITION AND CHARACTERISTICS OF SOME POTASSIUM PERCHLORATE-METAL-FLUOROCARBON SYSTEMS(37)

Mix No.	Composition		Density, g/cm^3	Heat of Explosion cal/g	77° F Burning Rate, in/sec		Detonation Using No. 8 Cap.
	Constituent	Wt, %			Rate	Pressure	
1.	$C_{12}F_{26}$ Magnesium $KClO_4$	37.7 17.7 46.6	2.12	1997	0.214	500	No
2.	$C_{14}F_{30}$ Magnesium $KClO_4$	39.1 15.3 45.6	2.15	1730	.54	1000	No
3.	$C_{14}F_{30}$ Magnesium $KClO_4$	41.7 21.2 36.1	2.08	2000	.316	700	No
4.	$C_8F_{16}O$ Magnesium $KClO_4$	38.3 18.6 43.1	--	--	--	--	Yes
5.	$C_{14}F_{30}$ Magnesium Aluminum $KClO_4$	45.6 4.1 6.2 44.1	2.16	1488	.34	700	No
6.	$C_{14}F_{30}$ Aluminum $KClO_4$	42.6 11.8 45.6	2.28	1458	.091	700	No
7.	$C_{14}F_{30}$ Magnesium Boron $KClO_4$	46.4 4.6 5.4 43.6	2.16	1559	.17	700	No
8.	$C_{14}F_{30}$ Silicon Magnesium $KClO_4$	46.3 10.6 4.6 38.5	2.15	1565	.092	700	No

TABLE 3-1. EFFECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS(24)

Additive	Propellant System	General Effect on Burning Rate	General Effect on Pressure Exponent	General Effect on Temperature Coefficient	Remarks	Reference
Aluminum	Polyacrylate/AP	1. 14 - . 46	little change	slight decrease	1. 01 wt%, particle size varying from 16. 5 - 104. 0μ	R & H Rept. P-58-9, May '58
	Polyurethane/AP/PP	. 436 - . 457 . 436 - . 767	. 079 - . 134 . 079 - . 294	. 18 - . 30 . 18 - . 25	Al pdr, . 0 - . 50 wt% Al wire, . 0 - . 50 wt%	AGC Rept. No. 1270
	Thiokol/AP				3 grades spherical Al pdr Finer grades gave more castable propellant	Thiokol Rept. E-16-55
Ammonium dichromate	NC/AP	. 37 - . 48	. 43 - . 47	. 30 - . 38	0, 1, 3 wt%	NOTS 1880 TPR 201
	Polystyrene/AP	. 245 - . 296	. 44 - . 37	. 26 - . 15	. 0 - . 50 wt%	AGC Rept. 1270
	Polyurethane/AP/PP	65% increase	--	22% increase	. 5 wt%	AGC Rept. 1270
	Rubber/AP	. 23 - . 33	. 70 - . 45	no change	0 - 8 parts	Phillips Rept. 308-67-54R
Ammonium halide	Polystyrene/AP	slight increase	--	no change	NH_4Br, NH_4Cl increased r slightly, no affect π_K NH_4I inhibited propellant cure	AGC Rept. 507
Ammonium tungstate	Polystyrene/AP	no change	--	slight lowering	1 wt%	AGC Rept. 507
Boron	NC/AP	. 59 - . 52	--	. 41 - . 22	1 wt%, 2 wt% made little change.	ABL/QPR-1 January 1959
	Polyurethane/AP	. 30 - . 79 . 38 - . 75	unchanged --	unchanged . 15 - . 07	0 - 6 wt% strands 0 - 10 wt% motors (Is increased)	AGC Rept. 1441
	Polyurethane/AP/PP	--	--	reduced to . 05	1. 42 wt% selected by box method.	AGC Rept. 1630
Boron nitride	NC/AP	slight change	. 43 - . 50	. 30 - . 25	0 - 3 wt%	NOTS 1880 TPR 201

TABLE 3-1. EFFECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS[24] (Cont'd)

Additive	Propellant System	General Effect on Burning Rate	 Pressure Exponent	 Temperature Coefficient	Remarks	Reference
Iron	Polyacrylate/AP	.392 - .387 - .350	--	.11 - .10 - .12	0, .25, 1.0 wt%	AGC Rept. 1270
Iron meta-vanadate	Polyurethane/AP/PP	.436 - .482 - .700	.079 - 000 - .217	.18 - .08 - —	0, .10, .50 wt%	AGC Rept. 1270
Iron oxide	Polyacrylate/AP	.392 - .486 - .473	.232 - .365 - .450	.11 - .11 - .10	0, .25, 1.00 wt% Fe_2O_3	AGC Rept. 1270
	Polystyrene/AP	.345 - .308 .373	--	.22 - .12 .24	1 wt% Fe_2O_3 1 wt% Fe_2O_3 + 1 wt% $MgCrO_4$	AGC Rept. 507
		.403		.17	1 wt% Fe_2O_3 + 1 wt% Cu-0202	
	Polyurethane/AP/PP	.436 - .533 - .750	.079 - .217 - .334	.18 - .17 - .17	0, 0.10, 0.50 wt%	AGC Rept. 1270
Isano Oil	Polyacrylate/AP	.396 - .662	.232 - .135	.11 - .07	0 - 3.63 wt%	AGC Rept. 1270
Magnesium	Polyurethane/AP (Al enriched)	increased	increased	decreased to .07	1.48 wt% obtained by box method of statistical analysis	AGC Rept. 1630
Magnesium chromate	Polystyrene/AP	.252 - .312 - .367	.39 - .10 - .35	0.26 - .14 - .16	0 - .25 - 1.0 wt%	AGC Rept. 507
Magnesium oxide	NC/AP	.37 - .39 - .40	.43 - .64 - .56	.30 - .46 - .49	0 - 1 - 3 wt% MgO	NOTS 1880 TPR 201
	Polystyrene/AP	.265 - .302	--	.24 - .24	0 - 1 wt% MgO	AGC Rept. 507
Magnesium stearate	NC/AP	.37 - .36 - .35	.43 - .52 - .58	.30 - .30 - .36	0 - 1 - 3 wt%	NOTS 1880 TPR 201
Manganese phosphate	Polyacrylate/AP	.392 - .471 - .450	.232 - .388 .392	.11 - .11 - .15	0 - .25 - 1.0 wt%	AGC Rept. 1270
Nickel oxide	Polystyrene/AP	.234 - .271 - .202 - .214	.44 - .44 - .00 - .09	.21 - .26 - .11 - .15	0, .05, 2.0, 4.0 wt%	AGC Rept. 410

TABLE 3-1. EFFECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS[24] (Cont'd)

Additive	Propellant System	General Effect on Burning Rate	General Effect on Pressure Exponent	General Effect on Temperature Coefficient	Remarks	Reference
Copper chromite	Al/AP	.87 - 1.80	--	? - .032	Pressed strands, 2 wt%	ARC Rept. QPR-31, 1957
	NC/AP	.37 - .50	.43 - .54	.30 - .41	0, 1, 3 wt%	NOTS 1880 TPR 201
	Polyacrylate/AP	.392 - .481	.232 - .136	.11 - .10	.50 wt% + .50 wt% calcium oxalate	AGC Rept. 1270
	Polyurethane/AP	? - .50	--	? - .22	1.0 wt% added	BFG Rept. G-56-4
	Polyurethane/AP/PP	.40 - .55	--	constant at .155	0.1 - 1.0 wt%(AP, 15-20μ)	
		.62 - .87	--	.15 - .04	0.1 - 1.0 wt% (AP, 45-60μ)	AGC Rept. 1270
	Polyurethane/AP (Al enriched)	.258 - .384 - .499	.157 - .361 - .244	.16 - .18 - .15	Reynolds Al #101, 0 - .5 - 2.0 wt%	AGC Rept. 1630
		.278 - .346 - .406	.291 - .254 - .281	.07 - .16 - .10	Reynolds Al #400, 0 - .5 - 2.0 wt%	
	Rubber/AP	1.37 - 1.82 - 2.13	.47 - .43 - .47	.11 - .08 - .12	0 - 2.0 - 5.0 wt%	Phillips Rept. 2056-58R
Copper oxalate	Polyurethane/AP	0.332 - .490	--	0.19 - .20	0 - 1 wt%	AGC QPR 2793-3
Copper oxide w/Fe_2O_3	Polyurethane/AP	increase	--	low to .05	1 wt% $CuO \cdot Fe_2O_3$	AGC Rept. 1441
		--	--	0.08	2 wt% $CuO \cdot Fe_2O_3$	
	Rubber/AP	1.37 - 1.46 - 1.21	--	.13 - .07 - .04	CuO at 1 part. NH_4ClO_4 varied from 87 - 83 parts	Phillips Rept. 1846-57R
Copper phosphate	Polyacrylate/AP	.392 - .514 - .595 - .318	.232 - .188 - .272 - .289	.11 - .10 - .16 - .15	0, .25, 1.0 wt% .5 + .5 $CaCO_3$	AGC Rept. 1270
	Polyurethane/AP/PP	.436 - .730	.079 - .485	.18 - .22	0 - 1.0 wt%	AGC Rept. 1270
Hopcalite (Cu x1709)*	Polyurethane/AP/PP	increase 20-70%	--	decrease 46-75%	0 - 1.50 wt%	AGC Rept. 1441
		increase 99%	--	decrease 78%	1 wt% Cu 0202	
		increase 56%	--	decrease 79%	1 wt% $CuO \cdot Fe_2O_3$	

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*Mixture of oxides of manganese (47.5%) and copper (16.3%) plus oxides of iron, nickel, silicon, aluminum, titanium, and magnesium.

TABLE 3-1. EFFECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS[24] (Cont'd)

Additive	Propellant System	General Effect on Burning Rate	General Effect on Pressure Exponent	General Effect on Temperature Coefficient	Remarks	Reference
Calcium aluminate	Polyurethane/ AP	.296 - .374	.20 - .238	.12 - .08	3 wt% added	AGC Rept. 1441
Calcium carbonate	Polyurethane/AP	--	reduction	reduction	varying amounts. Same with calcium oxalate	AGC Rept. 1441
	Polyurethane/AP (Al enriched)	--	--	reduced to .05	Box method of treating 5 variables. Best contained 2.73 wt% $CaCO_3$	AGC Rept. 1630
Calcium phosphate	Polyacrylate/AP	slight increase	--	slight decrease	1 wt% level best. Addition of .1 wt% ammonium dichromate gave greatest reduction	AGC Rept. 1270
	Polystyrene/AP	slight reduction	slight reduction	reduced to .14	1 wt% optimum	AGC Rept. 492
	Polyurethane/AP/PP	decreased increased increased	decreased increased decreased & increased	increased constant decrease	0.1 - .5 wt% .5 - 1.5 wt% 1.5 - 2.5 wt%	AGC Rept. 1270
Chromium III chromate	Polyacrylate/AP/PP	no systematic change	no systematic change	no systematic change	0 - 1.00	AGC Rept 1270
Chromium oxide	Polyacrylate/AP	.392 - .503	--	.10 - .07	.25 - 1.00 wt%	AGC Rept. 410
	Polyurethane/AP	no change	--	little change	0.1 wt%	AGC Rept. 410
Copper (wire)	Polyurethane/AP/PP	.456 - .759	--	.18 - .35	0.1 - .5 wt%	AGC Rept. 1270
Copper aluminate	Polyacrylate/AP	slight increase	--	some reduction	0.25 - 1.0 wt %	AGC Rept. 1270

TABLE 3-1. EFEECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS(24) (Cont'd)

Additive	Propellant System	General Effect on Burning Rate	General Effect on Pressure Exponent	General Effect on Temperature Coefficient	Remarks	Reference
Phthalo green	Polyurethane/AP	.66	--	.14	1.18 wt%	BFG Rept. G-55-2
Potassium dichromate	Polyacrylate/AP	.392 - .507 - .472	.232 - .344 - .337	.11 - —— - .18	0 - .25 - 1.0 wt%	AGC Rept. 1270
	Polyurethane/AP/PP	.436 - .522 - .705	.079 - .100 - .397	.18 - .20 - .11	0 - .10 - .50 wt%	AGC Rept. 1270
Potassium permanganate	Polyurethane/AP	.332 .683 .687	.377 .582 .438	.18 .18 .16	Control $KMnO_4$-SiO_2 2 wt% $AgMnO_4$-Al_2O_3 2 wt%	AGC Rept. 1441
	Polyurethane/AP/PP	.436 - .510 - .420	.079 - .008 - .021	.18 - .09 - .31	0 - .25 - .50 wt%	AGC Rept. 1270
	Polyurethane/AP (Al enriched)	.278 - .273	.291 - .309	.07 - .11	0 - 1.0 wt%	AGC Rept. 1630
Silver (wire)	Vinyl Plastisol/AP	.49 - 2.30 - 4.95	.45 - .34 - .41	.24 - .24 - .27	0 - 5-mil Ag - 5-mil AgC*	ARC Rept. QPR NO 30
Sodium barbiturate	Polyurethane/AP/PP	.436 - .409 - .452	.079 - .071 .094	.18 - .10 - .19	0 - .50 - 1.0 wt%	AGC Rept. 1270
Sodium barbital	Polyurethane/AP/PP	.436 - .410 - .415	.079 - .030 - .059	.18 - .24 - .23	0 - .50 - 1.0 wt%	AGC Rept. 1270
Sodium silicopolymolybdate (SSPM)	Rubber/AP	.540 - .438 - .424	.47 - .62 - .66	.09 - .07 - .06	0 - 10 - 12 wt%	Phillips Rept. 1969-57R
Tin (wire)	Polyurethane/AP	.332 - .370 - .381	.337 - .310 - .293	.18 - .09 - .08	0 - 2 - 3 wt%	AGC Rept. 1441
(powder)		.332 - .355 - .360	.337 - .205 - .148	.18 - .06 - .07	0 - 2 - 3 wt%	

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*5-mil Ag wire coated with 5-mil of 73% NH_4ClO_4, 5% polyvinyl chloride, 2% Hycar plasticizer, 20% aluminum powder and 0.5% copper chromite.

TABLE 3-1. EFFECT OF ADDITIVES ON THE BURNING CHARACTERISTICS OF COMPOSITE PROPELLANTS(24) (Cont'd)

Additive	Propellant System	General Effect on Burning Rate	Pressure Exponent	Temperature Coefficient	Remarks	Reference
Vanadium pentoxide	Polyurethane/AP/PP	.436 - .460 - .415	--	.18 - .10 - .15	0 - .10 - .50 wt%	AGC Rept 1270
	Rubber/AP	.540 - .405 - .522 .556	.47 - .42 - .59 .34	.09 - .16 - .05 .00	0 - 4 wt% V_2O_5 6/6 wt% V_2O_5/SSPM 4/4 wt% V_2O_5/SSPM	Phillips Rept. 1969-57R
Zinc vanadate	Polyacrylate/AP	.392 - .401 - .455	.232 - .253 - .206	.11 - .14 - .09	0 - .25 - 1.0 wt%	AGC Rept. 1270

NOTES

1. This material has been abstracted from "Handbook of Additives Of the Reduction of Temperature Sensitivity of Composite Solid Propellants." Aerojet-General Corp. Report No. 1631 (Special). Contract NOrd 18230, Task 3, August 1959.

2. Abreviations

ABL - Allegany Ballistics Laboratory
AGC - Aerojet-General Corp.
AP - Ammonium perchlorate
ARG - Atlantic Research Corp.
BFG - B. F. Goodrich Chemical Co.
NC - Nitrocellulose
NOTS - Naval Ordnance Test Station
Phillips - Phillips Petroleum Corp.
PP - Potassium perchlorate
R & H - Rohm and Haas Company

TABLE 3-2. COMPOSITION AND CHARACTERISTICS OF SOME AMMONIUM PERCHLORATE-RESIN BINDER COMPOSITIONS(13)

Ammonium Perchlorate	83%	83%	78%	83%	80%	80%
Genpol A-20: Acrylate	14	14	15	10.44		
Genpol A-20: Styrene					10.13	14.21
Ammonium Dichromate	2	2	2	2	0.1	0.1
Vinyl Pyrrolidone				2	8.62	4.54
Ethyl Silicate	1	1	1	1	1	1
Copper Chromite					0.15	0.15
Boron Powder		(0.5)	4			
Burning rate - in./sec	0.96	1.11	0.96	1.02	0.66	0.86
Pressure exponent	0.54	0.60	0.41	0.54	0.40	0.50

TABLE 3-3. COMBINATIONS AND CHARACTERISTICS OF TWO AMMONIUM PERCHLORATE EXPLOSIVES(51)

1. Composition	MOX-1	MOX-2B
Ammonium perchlorate, wt %	35.0	35.0
Aluminum, atomized, wt %	26.2	52.4
Magnesium, atomized, wt %	26.2	
Tetryl, wt %	9.7	
RDX*, wt %		5.8
TNT*, wt %		3.9
Calcium stearate, wt %	1.9	1.9
Graphite, artificial, wt %	1.0	1.0
2. Properties		
Heat of combustion, cal/g	4087	4484
Heat of explosion, cal/g	2087	1472
Gas volume, cm^3/g	212	221
Explosion Temperature, 5 sec at °C	285	375
Impact sensitivity (Picatinny Arsenal apparatus - 2kg wt)	22mg/13 in	24mg/12 in

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*Coated on ammonium perchlorate

TABLE 3-4. SENSITIVITY TESTS ON VARIOUS IGNITER MATERIALS(53)

Ingredients %						Pendulum Friction Test		Impact Test	Static Spark Test
						Type of Ignition		Maximum drop w/no Ignition (cm)	For no Ignition (Joules)
$KClO_4$	Mg	Ti	B	Vistanek	EXBM	Steel Shoe	Fiber Shoe		
28.0	66.0			6.0		Burning	None	55	6.25
48.1	48.1			3.8		Explosion	None	40	0.63
73.6			20.4	6.0		Explosion	None	50	0.125
72.5			21.5		6.0	Explosion	Burning	45	0.063
73.1			20.9	6.0		Explosion	Burning	50	0.063
83.1			10.9	6.0		Burning	Explosion	50	0.125
89.5			4.5	6.0		Explosion	None	35	0.25
72.3		14.8	6.9	6.0		Burning	None	55	0.63
61.8		32.2			6.0	Explosion	None	30	0.125
62.7		31.3		6.0		Crackling	None	50	0.63
67.2		26.8		6.0		Crackling	None	40	0.25
74.8		19.2		6.0		Crackling	None	30	0.25

TABLE 3-5. IGNITABILITY TESTS WITH VARIOUS IGNITER MIXTURES AND JPN PROPELLANT(33)

Fuel Type	Fuel Wt, %	Oxidizer Type	Oxidizer Wt, %	Measured Heat of Explosion, cal/g	Wt Required for 50% Probability of Ignition, mg	Measured Gas Volume at Standard Conditions cc/g
Magnesium	50	$KClO_4$	50	2158	131.5	13.1
Magnesium	45	$KClO_4$	55	2300	265.6	15.6
Magnesium	40	$KClO_4$	60	2203	105.5	27.7
Magnesium	37	$KClO_4$	63	2050	98.5	44.9
Boron	30	$KClO_4$	70	1323	114.5	40.8
Boron	25	$KClO_4$	75	1219	79.5	--
Boron	20	$KClO_4$	80	1148	75.5	--
Boron	15	$KClO_4$	85	1003	72.5	115
Titanium	50	$KClO_4$	50	1740	154.5	67
Titanium	55	$KClO_4$	45	1620	151.5	63
Aluminum	30	$KClO_4$	70	2250	98.5	--
Aluminum	35	$KClO_4$	65	2365	95.5	--
Aluminum	22.2	$KClO_4$	63.5	2167	--	50
Zirconium-Nickel*	50	$KClO_4$	50	1209	141.5	--
A-5 Black Powder	--	--	--	711	160.2	224
A-3 Black Powder	--	--	--	711	207.6	224

* 70/30 Zirconium/Nickel Alloy

TABLE 3-6. CALCULATED HEATS OF EXPLOSION OF METAL-AMMONIUM PERCHLORATE SYSTEMS(37)

Metal	Mol. Wt.	Assumed Oxide	Oxidizer/g metal	Heat of Explosion cal/g metal oxide
Lithium	6.94	Li_2O	3.386	2539
Beryllium	9.02	BeO	5.211	2629
Boron	10.82	B_2O_3	6.516	1947
Sodium	23.00	Na_2O	1.044	1201
Magnesium	24.32	MgO	1.932	2220.5
Aluminum	26.97	Al_2O_3	2.614	2138
Iron	55.85	Fe_2O_3	1.262	931
Zinc	65.38	ZnO	0.719	852
Lead	207.21	PbO	0.227	255

TABLE 3-7. SOME CHARACTERISTICS OF THE M1A1 SQUIB

1. Composition(8)

	wt%
Potassium chlorate	60
Diazodinitrophenol	20
Charcoal	15
Nitrostarch	5

2. Thermal Properties(42)

Heat of reaction, cal/squib	73.16
Flame temperature, °K	1870
Heat evolved, cal/mole of gas	26.05

3. Current vs Delay Time (Standard atmosphere)(8)

Number tested	Current, amps	Average delay
10	0.40	37.23 msec
10	0.50	16.20 msec
10	0.75	7.30 msec
10	1.00	4.80 msec
10	3.00	1.34 msec
10	5.00	1.00 msec

4. Storage Characteristics(8)

These squibs failed after storage for 7 days at 100% relative humidity and 130°F temperature They also failed after 17 days storage in ammonia gas at 30 psia.

TABLE 3-8. SOME CHARACTERISTICS OF THE M2 SQUIB

1. Composition(8)

	wt%
Potassium chlorate	44
Lead thiocyanate	36
Charcoal	20

2. Thermal Properties(42)

Heat of reaction, cal/squib	54.63
Flame temperature, °K	2925
Heat evolved, cal/mole of gas	74.01

3. Current vs Delay Time (Standard atmospheric pressure)(8)

	Average Delay Time, msec		
Current, amp	-70°F	70°F	160°F
0.40	--	49.89	--
0.45	--	39.33	--
0.50	32.15	27.15	22.26
0.75	14.85	13.56	12.60
1.00	11.04	10.13	8.67
3.00	6.37	6.30	6.16
5.00	5.22	5.71	5.33

(A minimum of 10 squibs was tested at each condition.)

4. Altitude vs Delay(8)

Number Tested	Altitude, ft	Pressure, mm of Hg	Temp., °F	Max Delay, msec	Min Delay, msec
10	0	760	60	5.71 msec (avg)	
8	30,000	220	60	10.01	6.34
9	40,000	140.6	-70	17.48	6.67
10	50,000	87.4	-70	22.75	8.48
10	60,000	54.2	-70	19.34	10.89
10	70,000	34.0	-70	23.60	9.75

TABLE 3-9. SOME CHARACTERISTICS OF THE MK1 MOD O SQUIB(8)

1. Composition

Stage 1: Mixture of potassium chlorate and diazodinitrophenol

Stage 2: Black powder, 45 grains

Stage 3: Black powder, 45 grains

Bridge wire: 80/20 platinum-iridium

2. Firing Current

Will not fire below 0.2 amp D.C. 100% firing above 0.3 amp.

3. Humidity Effect

After storage for 2 days at 130°F and 100% relative humidity, the average delay time for 10 squibs was 0.20 msec.

TABLE 4-1. MILITARY END ITEMS UTILIZING PERCHLORATES(2)

A. Ammonium Perchlorate

- Sustainers
- Boosters
- Thrust Vector Motors
- Track Jatos
- Explosives
- Smoke Generators

B. Potassium Perchlorate

- Cartridges (Ball, Spotter, Illumination)
- Projectiles, Illumination
- Rocket (Heat, Smoke, Practice)
- Flares
- Igniters
- Signals
- Simulator Projectile, Ground Burst
- Simulator, Booby Trap
- Grenades
- Smoke Generators
- Mines
- Bomb, Photoflash

C. Lithium Perchlorate

No end items (limited to research and development only)

TABLE 4-2. PERCHLORATE REQUIREMENTS FOR SOME TYPICAL AIRCRAFT ROCKETS(8)

	2.25 in. SCAR	2.75 in. FFAR	5.00 in. HVAR
Propellant weight, lb	2.28	6.0	29
Process yield, %	80	50	80
Oxidizer content, %	75	75	75
Oxidizer Requirement lb oxidizer/delivered wt	2.14	1.35/7.65	27.2
Oxidizer type	$KClO_4$	$KClO_4/NH_4ClO_4$	$KClO_4$

TABLE 4-3. PERCHLORATE REQUIREMENTS FOR SOME TYPICAL JATO UNITS(8)

	14 KS-1000	15 KS-1000	33 KS-2200	5 KS-4500	1.8 KS-7800	2.2 KS-11,000	2.2 KS-33,000
Propellant weight, lb	81	74	395	105	68.5	143	410
Process yield, %	74.7	80	50*	60	60	70	60
Oxidizer content, %	76.5	75	75	75	75	75	75
Oxidizer requirement, lb oxidizer/delivered wt	83.0	69.5	592	131.2	12.8 72.8	153	550
Oxidizer type	$KClO_4$	NH_4CLO_4	NH_4ClO_4	NH_4ClO_4	$KClO_4$ NH_4ClO_4	$KClO_4$	$KClO_4$

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*Low yield because of development status.

TABLE 4-4. POTASSIUM CHLORATE-CONTAINING SQUIBS AND DETONATORS

Type of Device	Identification	Manufacturer
Squib	M-100	Atlas Powder Co.
Squib	S-56	E. I. DuPont de Nemours & Co.
Squib	S-65	E. I. DuPont de Nemours & Co.
Squib	S-67	E. I. DuPont de Nemours & Co.
Squib	S-67M	E. I. DuPont de Nemours & Co.
Squib	S-68	E. I. DuPont de Nemours & Co.
Squib	S-68M	E. I. DuPont de Nemours & Co.
Squib	S-75	E. I. DuPont de Nemours & Co.
Squib	S-75M-1	E. I. DuPont de Nemours & Co.
Squib	S-77	E. I. DuPont de Nemours & Co.
Squib	S-79	E. I. DuPont de Nemours & Co.
Squib	S-84	E. I. DuPont de Nemours & Co.
Squib	S-85	E. I. DuPont de Nemours & Co.
Squib	S-86	E. I. DuPont de Nemours & Co.
Squib	S-87	E. I. DuPont de Nemours & Co.
Squib	S-88	E. I. DuPont de Nemours & Co.
Squib	S-89	E. I. DuPont de Nemours & Co.
Squib	S-90	E. I. DuPont de Nemours & Co.
Squib	S-91	E. I. DuPont de Nemours & Co.
Squib	S-92	E. I. DuPont de Nemours & Co.
Squib	S-93	E. I. DuPont de Nemours & Co.
Squib	USF-107	U. S. Flare Corporation
Squib	USF-207	U. S. Flare Corporation
Squib	USF-407	U. S. Flare Corporation
Blasting Caps	E-1A (No. 6)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-1A (No. 8)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-1B (No. 6)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-1B (No. 8)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-77	E. I. DuPont de Nemours & Co.
Blasting Caps	E-78	E. I. DuPont de Nemours & Co.
Blasting Caps	E-80 (No. 6)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-80 (No. 8)	E. I. DuPont de Nemours & Co.
Blasting Caps	E-81	E. I. DuPont de Nemours & Co.
Blasting Caps	E-83	E. I. DuPont de Nemours & Co.