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AEROSPACE INFORMATION REPORT

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STANDBY AUXILIARY POWER SOURCES FOR TACTICAL MISSILES

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Revised

1. PURPOSE AND SCOPE:

1.1 The purpose of this report is to present a brief summary of the experience gained to date with various types of power sources for use in standby auxiliary power systems for tactical missiles. The information covers general characteristics, areas of advantage and pitfalls that have been encountered in use, and areas where further development is needed.

2. GENERAL:

2.1 A substantial amount of work to advance the state-of-the-art is needed for the development of auxiliary power supplies of high reliability that are capable of long duration standby to be used with the tactical missiles of the United States Armed Forces. It will be necessary that many of these power supplies be capable of unattended standby under all manner of environmental conditions for a period of one year or possibly longer and then be capable of reliable operation with but a few seconds notice.

2.2 In advancing the state-of-the-art of long standby duration auxiliary power supplies for tactical missiles, one of the areas needing a great deal of work is power sources. Several types of power sources are being considered for use with auxiliary power supplies of the type described. The more prominently considered are:

1. Solid propellant gas generators to produce high pressure hot gas for powering a variety of devices.

2. Liquid monopropellants that can be decomposed to produce high pressure hot gas for powering the same types of devices as solid propellants.

3. Primary and secondary batteries for powering all variety of electric-consuming devices.

4. Flywheels which may be used to drive hydraulic and/or electrical power generating devices.

5. Non-circulating or blow-down systems which utilize stored high pressure gas as a power source.

3. SOLID PROPELLANTS:

3.1 Solid propellant gas generators are basically composed of three kinds of constituants. These are the oxidizer, the fuel, and additives. The number and quantity of additives will vary greatly with different propellants for different applications. The additives can be used as combustion catalysts, combustion stabilizers, diluents and many other functions. Two basic types of solid propellant gas generators have been used for auxiliary power work. The first type is the composite generator in which the oxidizer is mixed with a composite type fuel which also serves as the binder. The other type is the double based propellant. The prime double based propellants that have been used are the nitroglycerin-nitrocellulose propellants. Of the composite propellants that have been used, the ammonium nitrate composites have been most successful. Ammonium perchlorate composites have also been used; however, two of the products of combustion are hydrogen chloride gas and water. The combination of hydrogen chloride gas and water forms hydrochloric acid. This has resulted in many problems of etching and corrosion of auxiliary power components. For this reason the ammonium perchlorate propellants have generally been discarded for auxiliary power use. Due to their superior properties of burning rate temperature and cleanliness of gas generated, the ammonium nitrate composite solid propellants will be the only propellant considered here. Basically, ammonium nitrate composite propellants are manufactured by mixing finely divided ammonium nitrate salt with a fuel which will also serve as the binder. Some of the fuel-binders used are synthetic rubbers, acrylites, nitriles, urethanes and acetates. By varying the composition of the propellants, flame temperatures ranging from 950 F to 2400 F and burning rates ranging from 0.028 to 0.14 inch per second have been achieved with these propellants. Of great aid in varying the flame temperature has been the use of inert diluents such as ammonium oxilate. The following are some of the problem areas that have been encountered in the use of ammonium nitrate propellants.

3.1.1 Although the composition of a given propellant may be controlled exactly, the ballistic and physical properties of the resultant propellant can vary greatly due to variations in the manufacturing process and the conditions at the time of manufacture. In preparing the ammonium nitrate oxidizer, the size of the salt grains must be controlled very carefully since the burning rate of the propellant is a function of grain size. Also, variations in the polymeric cross linking due to variations in the conditions during curing have a decided influence upon the properties of the propellant. One of the most critical areas in manufacturing is the control of the amount of water absorbed by the ammonium nitrate. Ammonium nitrate is highly hygroscopic and will absorb water whenever exposed to the atmosphere. The amount of water absorbed by the ammonium nitrate will greatly vary the burning characteristics of the fuel. Initially, considerable trouble was encountered with the finished propellant grains absorbing water during storage. This problem has been solved through the development of impenetrable coatings for the propellant grains. In developing the better propellant coatings for the grains, additional problems were encountered in the effect of the coatings upon the ignition and burning of the grains. Coatings have now been developed which will adequately protect the grain from moisture and will aid in the ignition of the propellant.

3.1.2 Many applications require that the gas generated be essentially free of solid particles. It has been found that the prime source of solid particles in the exhaust gas is the inorganic combustion catalysts used in the propellants. These organic combustion catalysts may appear in the exhaust in the form of either small liquid droplets or soft solid particles. In either phase, they are highly detrimental to the operation of many devices. The carbonaceous particles also found in the combustion gases arise from incomplete combustion of the binder or stabilizers used in the propellant.

3.1.3 The burning rate of ammonium nitrate propellants are sensitive to both the pressure at which combustion takes place and the temperature of the grain prior to combustion. The higher the grain temperature prior to combustion the greater the burning rate. Also, the higher the pressure of combustion the greater the burning rate; and the burning rate varies in relation to the absolute pressure to approximately the 1/2 power. Due to this sensitivity of the propellant, both the grain temperature and the combustion pressure must be controlled carefully or the grain must be sized such that it will be adequate for the design under all conditions of temperature and pressure that might be encountered.

3.1.4 Ammonium nitrate, the oxidizer fuel, also has the undesirable tendency of undergoing changes in the crystaline state of the compound at various temperatures. This results in expansion and contraction of the crystals which can cause crumbling of the propellant grain. Through careful selection of the binder-fuel material, the possibility of damage to the propellant due to this change in grain size can be greatly decreased. Over the normal military temperature range for operation, ammonium nitrate undergoes three changes in grain size. Starting at -65 F and increasing the temperature, the first appears as a very sharp decrease in grain size at 32 F. At 96 F the rate of grain expansion with temperature increases sharply. At 140 F the rate of grain expansion with temperature decreases sharply. Between the temperatures of -65 F and +170 F, the volume of an ammonium nitrate composite solid propellant will vary about 4% due to recrystallization alone, not considering the cubic coefficient of expansion of the propellant. This phenomenon of the ammonium nitrate crystals is similar to the grain growth encountered in certain alloys of steel. Due to the marked change in the volume of the propellant, it is very important that care be taken to choose a relatively soft and pliable inhibitor which can compensate for these changes in the volume of the fuel, within the confines of the gas generator case.

3.1.5 Although the inhibitors used with ammonium nitrate solid propellants must, by the nature of the fuel itself, be soft, pliable materials, a strong bond strength must exist between the fuel and the inhibitor. This is necessary to prevent separation of the fuel from the inhibitor under conditions of shock and acceleration. If a gap does appear between the fuel and the inhibitor, burning of the flame front will move into the crack, thus increasing the total burning area of the grain with a resultant increase in pressure and burning rate and possibly resulting in an explosion.

3.1.6 Care must be taken to insure that metal particles from the igniter do not become imbedded in the surface of the grain. Metallic particles imbedded in the surface of the grain will increase the rate of heat transfer into the grain in the immediate area of their location with the result that the burning rate at these points is increased. Therefore, metal particles in the surface of the grain will cause tunnels to burn into the grain, thus developing pits in the surface of the grain and increasing the overall burning area. The ammonium nitrate propellants are also sensitive to acceleration during operation. Combustion of the ammonium nitrate propellants takes place in the gaseous phase with the propellant changing from the solid phase to the liquid and then to the gaseous phase as a result of radiation from the flame front back to the propellant. Under acceleration the flame front due to its mass, can be drawn far enough from the propellant that the back radiation level decreases sufficiently to result in insufficient vaporization of the grain. This condition will lead to flame-out of the grain. Under lateral acceleration, the liquid and gaseous phases of the flame front can be forced to one side of the grain, thus increasing the burning rate on that side and resulting in uneven burning of the grain.

3.2 Further work is needed to develop solid propellant grains that can maintain an even burning rate and gas generating rate during long durations of operation. To date, considerable trouble has been encountered in achieving even burning characteristics for long periods of burn.

Solid propellants are the simplest type of gas generator that is available for auxiliary power supply use. The operation of a solid propellant gas generator requires only an ignition signal. Solid propellants have one prime disadvantage, however, in that the rate of gas generation cannot be effectively varied to match the changes in requirement of the item being supplied. Therefore, solid propellant gas generators must be sized to continuously supply the maximum power requirement that will occur during the mission rather than the average power requirements. For those missions that entail brief periods of high activity interspersed with periods of low activity, this will result in a very great weight penalty.

4. <u>LIQUID MONOPROPELLANTS</u>:

4.1 Liquid monopropellants have also been very successfully used for the generation of high pressure hot gas for powering auxiliary power supplies. The liquid monopropellants do not require oxidizers since they generate gas through the decomposition of the compound into simpler compounds or into elements. The prime advantages of the liquid monopropellants are the ability to vary their rate of gas generation in order to match the actual requirement and their ability to supply high pressure hot gas for extended periods of time. The rate of gas generation of all monopropellants can be varied by several orders of magnitude by simply modulating or pulsing the flow of the monopropellant into the gas generator. Unlike the solid propellant they are not effectively limited to a maximum duration of operation of approximately ten minutes. The basic disadvantage of liquid monopropellants is their instability. For a compound to be a useful monopropellant, it must incorporate some basic instability, thus making easy decomposition possible. This instability, however, often manifests itself in poor storage characteristics and explosive hazards.

4.2 Three categories of liquid monopropellants have been successfully used for auxiliary power applications. These three basic types of fuel are ethylene oxide (C_2H_4O), hydrazine (N_2H_4), and hydrogen peroxide (H_2O_2). The latter two can be used in their pure state or in mixtures with other chemicals.

4.2.1 Ethylene Oxide:

4.2.1.1 The principal advantages of ethylene oxide (ETO) are: low freezing points, high auto-decomposition temperature, insensitivity to shock, availability (one of ten major chemicals produced in U.S.A.), and low cost. Its principal disadvantages are: a tendency to polymerize during very long-term or high temperature storage or a contamination and coking of gas generators during long duration operation (carbon particles from the exhaust collecting in the gas generator or turbine nozzle). Ethylene oxide has been successfully stored at temperatures as high as 160 F for periods of up to one year in clean, Type 302, stainless steel drums incorporating teflon seals. If contaminated, particularly with a metallic oxide, ETO may polymerize rapidly during storage. ETO is decomposed thermally by injection into a gas generator that has been preheated thermally to approximately 1300 F. Once initiated, the decomposition is self-sustaining. Many of the initial problems encountered in the electrical preheating of ETO gas generators have been solved by the use of small solid propellant charges to provide the heating required for decomposition initiation. From the standpoint of safety, ETO is only moderately toxic. Its toxic properties closely parallel those of most volatile organic solvents and are very similar to those of high-test aviation gasoline. Both ETO and its decomposition products are flammable and must be treated accordingly. Neither ETO liquid nor vapor is shock sensitive. ETO decomposes in an exothermic reaction producing methane, carbon monoxide, and heat. Part of the methane formed by decomposition dissociates, releasing carbon and hydrogen. It is the carbon thus released that causes coking of the gas generators. The amount of dissociation can be controlled to some extent through gas generator design. This is one of the prime areas in which work with ethylene oxide is required since coking of gas generators has been the main deterrent to the use of ETO in applications requiring power for more than approximately ten minutes.

4.2.2 Hydrazine:

4.2.2.1 Hydrazine has been used extensively in accessory power work. The principal advantages of hydrazine are: high energy release, clean products of decomposition (the gases are non-corrosive and contain no carbon or other solid particles), ease of decomposing and low flame temperature of decomposition products. The principal disadvantages of hydrazine are: high freezing point of the anhydrous liquid, decomposition during high-temperature storage (low autodecomposition temperature), shock sensitivity of the vapor phase, and toxicity. The use of hydrazine in tactical applications has been severely handicapped by its high freezing point, 35.5 F. A considerable amount of work has been done on freezing point depressants for hydrazine; however, to date, no completely acceptable depressants have been found. Many solutions of hydrazine with other chemicals, however, do have lower freezing points. Hydrazine and its decomposition products are both highly toxic, having properties equivalent to those of concentrated ammonia and should be handled with care. Also, hot hydrazine vapor may explode (diesel) if suddenly pressurized. Several minor explosions have been reported of hydrazine vapor exploding in ejector nozzles under the conditions described. During long-term storage hydrazine has a tendency to slowly decompose. Hydrazine has successfully been stored out of doors in aluminum and stainless steel containers for periods of one year with changes in volume (decomposition) of less than 1%. The decomposition rate is a function of temperature and contamination. Hydrazine can be decomposed either thermally or catalytically. In most applications it has been found advantageous to use the combination of thermodynamic and catalytic decomposition in a single chamber. Hydrazine decomposition takes place as two separate but simultaneous chemical reactions. First, hydrazine decomposes exothermically to form ammonia and hydrogen. Secondly, some of the ammonia dissociates endothermically to form nitrogen and hydrogen. Through gas generator design it is possible to control the percentage of ammonia dissociation that takes place. Through this control of ammonia dissociation, it is possible to vary the flame temperature of the hydrazine over a moderate band. Hydrazine decomposition with approximately 70% ammonia dissociation results in a gas of approximately 1500 F. Hydrazine has the additional advantage of having a relatively low average molecular weight of the decomposition products. For the 70% ammonia dissociation reaction, the average molecular weight of the decomposition products is 12.3, as compared to 22.0 for ethylene oxide.

4.2.2.2 Unsymmetrical Dimethyl Hydrazine (UDMH) has also been considered as a possible monopropellant. Both the physical and ballistic characteristics of UDMH are very similar to those of hydrazine. The advantages of UDMH as compared to hydrazine are: lower freezing point (-71 F), stability at high temperatures, shock stability, and superior storage characteristics. The main disadvantage of UDMH is that it has bad toxicity characteristics. Very little work has been done with UDMH as a monopropellant. The work done indicates that there may be some trouble in initiating and sustaining decomposition.

4.2.3 Hydrogen Peroxide:

4.2.3.1 Several solutions of hydrogen peroxide have been used or experimented with for accessory power applications. Three of the more common solutions of hydrogen peroxide are: a solution of 90% hydrogen peroxide and 10% water; 99.6% pure hydrogen peroxide and 0.4% water; and a solution designated BMP-DEG, consisting by weight of 67.8% hydrogen peroxide, 6.6% diethylene glycol, and 25.6% water. The hydrogen peroxide fuels are all non-toxic and non-inflammable, having non-toxic and non-inflammable products of decomposition. The principal advantage of the hydrogen peroxide fuels are ease of initiating and maintaining decomposition, clean products of decomposition (water and oxygen), and high liquid density. The 90% hydrogen peroxide and 10% water solution has the additional advantage of presenting a low flame temperature, approximately 1800 F. The principal disadvantages of the hydrogen peroxide monopropellants are the storage instability of all the propellants, their low auto-decomposition temperature, and, in the case of all the propellants but BMP-DEG, high freezing point (11.3 F). If stored in compatible materials at 86 F (room temperature) the hydrogen peroxide monopropellants have an auto-decomposition rate of approximately 1% per week. If stored in non-compatible materials or contaminated, particularly by an oxide of iron, they will decompose at a very rapid rate, and in extreme cases, explode. The hydrogen peroxide monopropellants are considered to be unsafe for many applications and present an explosive hazard when heated to temperatures in excess of 240 F.

4.2.3.2 All of the hydrogen peroxide monopropellants are decomposed catalytically and require no decomposition chamber pre-heating. The decomposition reaction is exothermic, yielding water and oxygen.

4.2.3.3 The use of monopropellants for the generation of high pressure hot gas is a little more complicated than the use of solid propellants in that, rather than simply maintaining a grain which is ignited and thus produces hot gas, it is necessary to store monopropellants, pressurize them at the time of use, inject them into a decomposition chamber which may or may not require pre-heating, and control their flow into the decomposition chamber in order to control the rate of gas production. This latter point, however, leads to the main advantage of monopropellants, this being the capability to accurately match the rate of gas generation to a varying demand. This ability to vary the rate of gas generation makes possible the most efficient use of the fuel since only enough fuel need be carried to match the average demand, not the peak demand for the full period of operation. Two areas require additional work in the field of liquid monopropellant; either one of which if satisfactorily solved would lead to the desired propellant system. First, additional work needs to be done on the decomposition of ethylene oxide to eliminate the coking problem encountered during long duration decomposition. The second approach is to develop monopropellants which have the favorable storage characteristics of ethylene oxide but yet do not contain solid particles in the decomposition gases. Work is also needed on expulsion devices for transferring the monopropellant from the storage tank to the decomposition chamber. The expulsion method that has recently shown the most promise is the storage of the monopropellants in bladders contained inside pressure vessels.

5. BATTERIES:

5.1 Batteries used in missile accessory power applications must be capable of high-rate discharges within specified voltage limits for durations in the order of seconds to one-quarter hour or more. Usually batteries must be capable of delivering this performance at high altitude while in any attitude of position and while undergoing severe environmental conditions of shock, acceleration, vibration and temperature.

5.2 Three basic batteries are presently being used in missile accessory power systems. Two of these batteries are of the secondary type; that is, they are capable of repeated charge-discharge cycles. The number of times these batteries can be recycled is a function of their electro-chemistry. Batteries falling into this class are the sintered plate nickel-cadmium and the zinc-silver oxide. The remaining battery, the automatically activated zinc-silver oxide, is a primary type battery. This means that once activated and discharged, it cannot be recharged; it is therefore commonly referred to as a "one-shot" battery.

6. SINTERED PLATE NICKEL-CADMIUM SECONDARY BATTERY:

6.1 The sintered plate nickel-cadmium secondary battery has been the most extensively used missile battery to date. The reliability of this battery is high when adequate quality control is exercised in its manufacture and relatively simple maintenance procedures are followed prior to use.

The battery as received from the manufacturer normally contains electrolyte, but is uncharged; electrolyte handling problems are therefore minimized. The batteries may be stored in this condition for several years; standard charging methods are used to place the battery in service. The "ready" life of the battery in the missile is at least two years if kept on a continuous float charge, and provided excessive temperatures are not encountered. In order to obtain full output capacity within the required voltage limits at temperatures below approximately 32 F, heat must be applied to the battery from an external source. This is usually accomplished by providing electrical heater wires within the battery package.

6.2 The nickel-cadmium secondary battery is capable of perhaps one thousand charge-discharge cycles. Charge-discharge or recycling capability is of importance during the earlier phases of missile development when considerable time may be spent in testing the missile and its components on the ground since it allows battery replacement to be held to a minimum.

6.3 The cost of the sintered plate nickel-cadmium secondary battery is less than that of the zinc-silver oxide secondary battery. When charging equipment and maintenance are taken into account, it is probable that either of these batteries will cost more than the automatically activated zinc-silver oxide battery.

7. ZINC-SILVER OXIDE SECONDARY BATTERY:

7.1 The zinc-silver oxide secondary battery has seen limited missile use to date. Although the output per unit weight and volume of this battery is the highest of any battery presently available (its watt-hour per pound capacity is approximately three times that of the sintered plate nickel-cadmium battery, and it occupies only about one-third as much space), its sensitivity to charging abuses, shorter life and greater maintenance requirement makes it less desirable for many applications. Also, the change in voltage which occurs when load is first applied is more pronounced in this battery than in other types. The reliability of this battery is high if the special maintenance procedures required are followed.

7.2 Because of the relatively short wet stand life of the zinc-silver oxide secondary battery, it is normally shipped in the dry condition. A storage life of several years can be expected if stored dry, provided temperatures in excess of 90 F are not encountered for an appreciable period of time.

7.3 Before the battery can be used in the missile, it must be put through an initial charge-discharge cycle or "Formation Procedure". The "ready" life of the battery in the missile is approximately six months, provided sustained temperatures in the range of 110 F-125 F or above are not experienced. In order to maintain the required capacity, the battery should be given a boost charge approximately every thirty days. While the battery could also be kept on either a float or a trickle charge, its life would be reduced below that which can be realized with the boost charge method. The zinc-silver oxide secondary battery, like the sintered plate nickel-cadmium battery is also temperature sensitive and requires power from an external source for heating during low temperature operation. This battery has a charge-discharge cycle life of 10 to 20 cycles.

7.4 The state of charge of the secondary zinc-silver oxide battery can be determined by checking the open circuit voltage. However, a reading of normal open circuit voltage indicates only that the battery is up to at least 70% of its charge capacity. This is a function of the state of oxidation (oxide or peroxide) of the silver. For this reason batteries which are to be maintained by the boost charge method must be overdesigned by 30%. Under this condition the performance of the zinc-silver oxide secondary battery is only twice that of the sintered plate nickel-cadmium battery on a weight and volume basis.

8. AUTOMATICALLY ACTIVATED ZINC-SILVER OXIDE BATTERY:

8.1 Of the batteries now available for missile use, the automatically activated zinc-silver oxide battery offers the best performance in all respects except reliability and temperature independence.

8.2 The principal advantages of the automatically activated zinc-silver oxide battery are high output per unit weight and volume, low maintenance and a shelf life of at least five years; its potential shelf life is unlimited.

8.3 The principal disadvantage of this battery is that it cannot be checked for output before use. This battery has not been used extensively in the past, but is presently scheduled for use in several missiles now being designed.

8.4 In this battery the electrolyte is not placed in contact with the plates until time of use. The electrolyte is stored in a separate reservoir and is transferred to the battery cells (activating the battery) when it is desired to use the battery.

8.5 The reliability of the battery can be reduced essentially to that of the system employed to transfer the electrolyte. Many such systems have been devised. In all of the systems, a common manifold is used to distribute the electrolyte to the cells. In the most successful scheme to date, the electrolyte is stored in a continuous metal tube coiled around the battery and sealed at both ends with metal foil diaphragms. One end of the tube is connected to a manifold for distributing the electrolyte to the cells. The other end is connected to a squib fired gas generator. For reliability, two squibs connected in parallel are used. When the squibs are ignited, the pressure generated causes both diaphragms to rupture. The gas pressure then forces the electrolyte out of the tube, through the manifold and into the battery cells. Once in the cells, the electrolyte is absorbed by pads located between the cell plates, and the battery is thus activated.

8.6 With this method of activation a pressure relief valve is placed in the opposite end of the distribution manifold from the electrolyte reservoir. By allowing excess gas from the gas generator to escape overboard the excess electrolyte in the manifold is swept overboard, thus purging and drying the manifold. This minimizes the possibility of short-circuits developing between the cells.

8.7 To further minimize the possibility of short-circuits developing between the cells, the distribution manifold is usually constructed of lucite, which is a non-conducting material. In addition, the interior surfaces of the manifold are sometimes coated with a silicon compound to prevent the electrolyte from "wetting" the manifold walls.

8.8 The initial high voltage experienced with nickel-cadmium and zinc-silver oxide secondary batteries will not occur in the automatically activated zinc-silver oxide battery if it is activated under load. Two simple checks can be made to determine whether the battery has been accidentally activated prematurely. If voltage is present, as indicated by a voltmeter reading, the battery is defective and should be rejected. Changes in the internal resistance of the battery as indicated by ohmmeter readings may also be cause for rejection.

8.9 This battery also requires external power to provide electrical heating for satisfactory operation at low ambient temperatures. Thermostatically controlled resistance heating wires are placed in the battery to maintain the electrolyte at a temperature above a set minimum. With the electrolyte so heated it is possible to achieve activation in less than two seconds.