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Chemical Oxygen Supplies

RATIONALE

This document has been determined to contain basic and stable technology which is not dynamic in nature.

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FOREWORD

Generation of breathing oxygen from chemicals has been practiced since the 1930's. Two primary sources are used. The first is thermal decomposition of alkali metal chlorate slugs, called "chlorate candles" because they are solid grains that generate oxygen at a hot reaction zone that travels the length of the "candle". The second is alkali metal superoxides or peroxides that produce oxygen by reaction with moisture and remove carbon dioxide by reaction with the hydroxide produced in the first step.

Chlorate candles are compounded and shaped for desired oxygen production characteristics, and do not remove carbon dioxide. They are used primarily in submarine service and in aircraft, or as the oxygen supply in personal breathing equipment. When used in a closed cycle system, a method of carbon dioxide removal is required. Potassium superoxide is used in rebreathers, taking advantage of the control of oxygen generation by moisture from the breath to adjust to work rate of the wearer: carbon dioxide is absorbed after the moisture reaction step. The material is packaged for specific applications, taking into account chemical performance changes as the reactions progress with use time. Applications of superoxide include damage control, rescue operations, and closed habitat atmosphere control.

Chemical oxygen supplies are of interest because of storability and oxygen density of the chemicals. As emergency oxygen supplies, they require no storage inspection, do not lose oxygen on storage, and have long shelf life. Given sealed container storage, shelf life is basically unlimited; packaged units have been activated after 25 years and performed as designed. Potassium superoxide contains 34% by weight available oxygen: a cubic foot of chlorate candle will deliver 85% as much oxygen as a cubic foot of liquid oxygen. This document treats general information on both materials, but with emphasis on chlorate candles since they are used for emergency passenger oxygen supply in aircraft. Specific design information is not given; each application requires appropriate sizing, heat management, gas purification, compounding, etc.

1. SCOPE:

Solid chemical oxygen supplies of interest to aircraft operations are "chlorate candles" and potassium superoxide (KO_2). Chlorate candles are used in passenger oxygen supply units and other emergency oxygen systems, such as submarines and escape devices. Potassium superoxide is not used in aircraft operations but is used in closed-cycle breathing apparatus. Characteristics and applications of both are discussed, with emphasis on chlorate candles.

2. REFERENCES:

Air Revitalization Using Superoxides, Ames Research Center, NASA Technical Briefs, January 1988.

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Mausteller, J. W., Oxygen Generation Systems, Kirk-Othmer Encyclopedia of Chemical Technology, V16, 3rd Ed., pg 673, John Wiley and Sons, 1982.

Mausteller, J. W., Review of Potassium Superoxide Characteristics and Applications. Presented at ASME Meeting, November 15, 1982.

Volnov, I. I., Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals. Monographs in Inorganic Chemistry, Ed. by E. G. Rochow, Plenum Press, 1966.

3. CHLORATE CANDLES:

Candles are composed of sodium chlorate, a fuel, perhaps a material to remove contaminants and a binder as necessary. Iron is the fuel most commonly used, although cobalt and sodium monoxide have also been used. Once started, reaction is self-sustaining, the fuel being oxidized by oxygen from thermal decomposition of the chlorate, the heat from the oxidation then promoting more thermal decomposition. The overall reaction is generically shown in Equation 1:

$$NaC10_3 + Fe = NaC1 + Fe_xO_y + O_2 + heat \quad \text{(Eq. 1)}$$

Iron concentration is 4-11% by weight. Sodium chlorate is 85% and up. Barium peroxide is sometimes used to remove chlorine or chlorine compounds, and is 1-3% of the total. Binders are most frequently glass fibers or fibrous iron, running 2-5%.

Reaction is initiated by a preformed "cone" or starting button, generally of the same ingredients as the body of the candle. The iron content is increased to perhaps 30% and is of high purity to assure ignition. Ignition is accomplished thermally, using a cartridge firing onto the cone, electric squib, fuse wire, or similar means.

3. (Continued):

The reaction zone proceeds through the candle at a rate dependent upon candle density, formulation, operational pressure, and thermal insulation. The latter is important because enough heat must be conserved to permit the heat released by fuel oxidation to maintain the chlorate at the decomposition temperature. A nominal reaction rate is 1/4 in/min (0.6 cm/min). Oxygen production is a function of the cross section of the candle; the greater the cross section, the greater the quantity of oxygen produced per unit time (at the same linear burn rate).

Heat generated is approximately 1000 Btu/lb O_2 (2325 kJ/kg). Temperature of the reaction zone is about 1200 °F (650 °C). Temperature of the gas produced can be controlled by providing heat exchange surface in the plumbing to the user. Temperature of the case housing the candle is a matter of design: insulation is used, along with standoffs and/or heat sink materials.

3.1 Applications:

Candles have been used since the early 1940's as "quick starts" in superoxide canisters for rebreathers. Because of the almost instantaneous oxygen evolution upon activation, a 10 L oxygen candle is used to provide oxygen rapidly at low temperature, since the superoxide requires several breaths to begin working satisfactorily.

The Navy uses large candles (120 ft^3 of oxygen generated in 45 min). These are packaged as raw candles, removed from the shipping container, and used in a burner. After reaction is complete, the "ash" remaining is a solid clinker, which is then removed and discarded.

In the 1940's there was interest in a walk-around candle unit for aircraft, and demonstration units were tested. There was no further interest until the mid-1960's, when a unit was furnished for removable palletized seats for military aircraft. By this time candle technology had been further developed and a variety of designs was possible with tailored flow rates as a function of time, better control of exterior surface temperatures, improved gas purity, and the like. Further work resulted in aircraft passenger oxygen units ranging from 1 to 4 people served. These units are started by mechanical or electrical igniters.

Figure 1 shows a schematic arrangement of parts for one type of oxygen supply unit. The candle is shaped to provide the specified oxygen flows over the use period. Here the initial flow is 3.6 L/min within 2 s after actuation, sustained for 1 min. Over the next 7 min the flow drops linearly to 0.9 L/min, holds for 4 min, and then drops to 0.2 L/min over the final 3 min. The housing for the candle is generally stainless steel. The candle is held at top and bottom for vibration and shock resistance and to give room for insulation between the candle and the housing shell. A cup at the cone end prevents splattering as the cone burns. Oxygen flows across the candle and through a gas conditioning section that provides particulate filtration and control of carbon monoxide and residual chlorine compounds. A relief device in the housing prevents overpressurization. Variations in configurations, use times, flows, and packaging are possible.

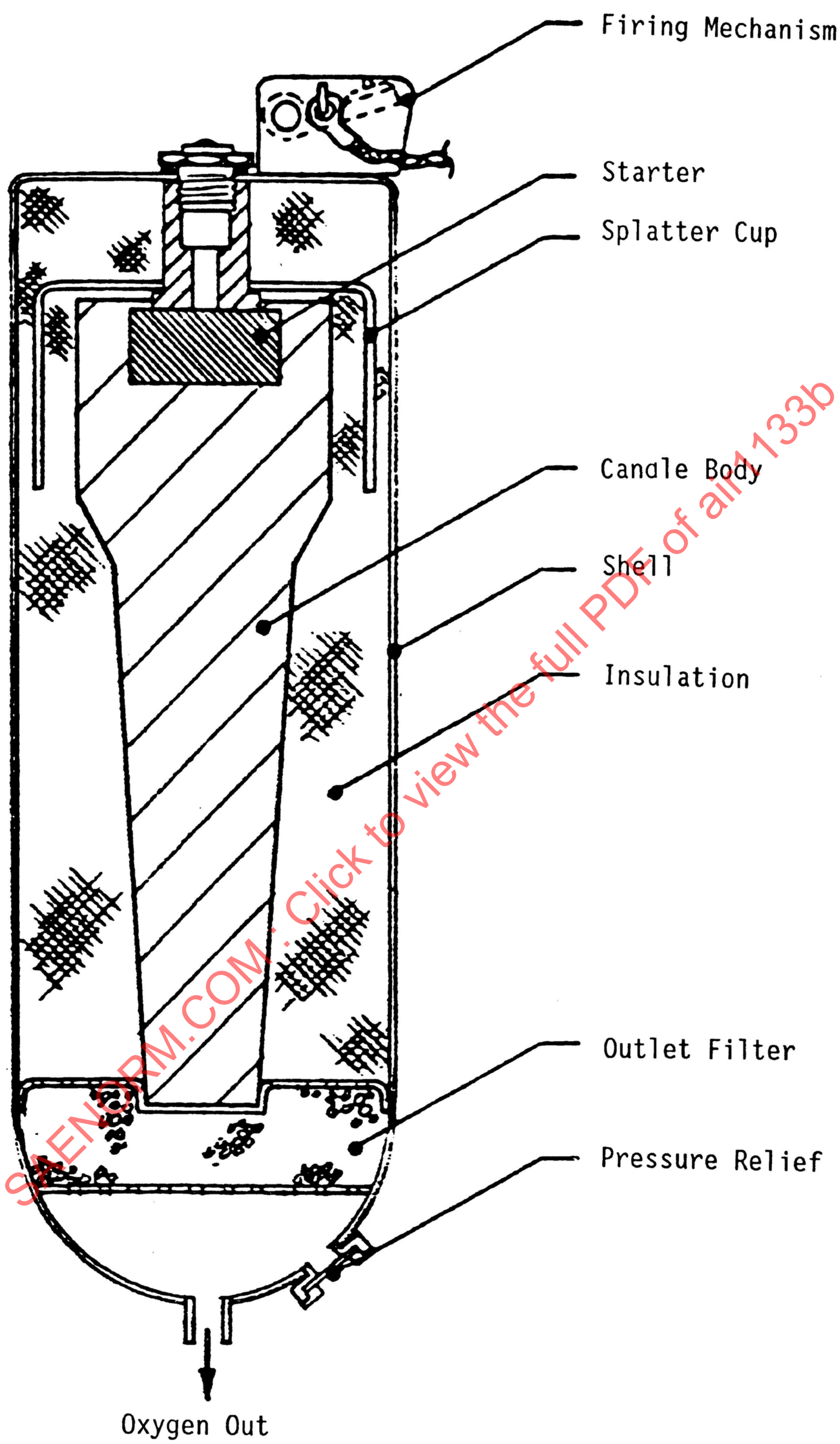

FIGURE 1 - Schematic of Chlorate Oxygen Candle

3.1 (Continued):

Generators are held in appropriately configured storage, which also provides touch protection. Walk-around units require standoff casings for thermal protection. Oxygen at the generator outlet is 200 to 300 °F (93 to 149 °C), which cools further through tubing to the mask.

Aircraft applications are primarily walk-around units and passenger supply during cabin decompression and emergency descent.

Oxygen candles for ejection seats in military aircraft have been proposed. In the latter case, the candles charge a reservoir at pressure sufficient to operate military pressure regulators.

3.2 Environmental Conditions:

Environmental testing has been done to commercial and to MIL-STD-810 specifications. Units can perform satisfactorily from -65 to +160 °F (-54 to 71 °C). Operation at altitude has been demonstrated, and performance is unaffected by generator attitude. Vibration and shock schedules have been passed successfully. The usual dust, salt fog, fungus, etc., tests present no problem.

3.3 Oxygen Purity:

Oxygen purity is of concern, and specifications have been met with the incorporation of a gas conditioning filter for both particulates and gaseous impurities. Typical specification ranges for oxygen contaminants in aircraft applications are:

a. Chlorine: 0.2 to 1.0 ppm
b. Carbon Monoxide: 15 to 50 ppm
c. Carbon Dioxide: 2000 to 5000 ppm
d. Water Vapor: 10 to 20 mg/L

These impurities can be reduced by appropriate conditioning filters to a total of about 1 ppm, excluding water vapor.

3.4 Reliability and Safety:

Reliability programs have been performed, and candles are acceptable in this regard. Factors investigated include ignition, time to full flow, maintenance of minimum oxygen flow profile, and container surface temperature.

Safety is acceptable and hundreds of thousands of candles have been used in all types of equipment. A major consideration is prevention of blockage of the gas exit, since the candle will continue to build up pressure and not be extinguished. Hence, a pressure release mechanism should be used. The candle residue is primarily sodium chloride, but the barium may dictate controlled disposal.