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ATTACHMENT #13

CHEMISTRY OF PYROTECHNICS

Basic Principles and Theory

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forming potassium chloride and oxygen gas. This reaction has a slightly exothermic value of -0.68 kcal/mole [2] and produces substantial oxygen. The active oxygen content of $KClO_4$ — 46.2% — is one of the highest available to the pyrotechnician.

Because of its higher melting point and less-exothermic decomposition, potassium perchlorate produces mixtures that are less sensitive to heat, friction, and impact than those made with $KClO_3$ [2]. Potassium perchlorate can be used to produce colored flames (such as red when combined with strontium nitrate), noise (with aluminum, in "flash and sound" mixtures), and light (in photoflash mixtures with magnesium).

Ammonium Perchlorate (NH_4ClO_4)

The "newest" oxidizer to appear in pyrotechnics, ammonium perchlorate has found considerable use in modern solid-fuel rocket propellants and in the fireworks industry. The space shuttle alone uses approximately two million pounds of solid fuel per launch; the mixture is 70% ammonium perchlorate, 16% aluminum metal, and 14% organic polymer.

Ammonium perchlorate undergoes a complex chemical reaction on heating, with decomposition occurring over a wide range, beginning near 200°C. Decomposition occurs prior to melting, so a liquid state is not produced — the solid starting material goes directly to gaseous decomposition products. The decomposition reaction is reported by Shimizu [2] to be

$$2\ NH_4ClO_4 \xrightarrow{heat} N_2 + 3\ H_2O + 2\ HCl + 2.5\ O_2$$

This equation corresponds to the evolution of 80 grams (2.5 moles) of oxygen gas per 2 moles (235 grams) of NH_4ClO_4, giving an "active oxygen" content of 34% (versus 39.2% for $KClO_3$ and 46.2% for $KClO_4$). The decomposition reaction, above 350°C, is reported to be considerably more complex [9].

$$10\ NH_4ClO_4 \xrightarrow{heat} 2.5\ Cl_2 + 2\ N_2O + 2.5\ NOCl + HClO_4 + 1.5\ HCl + 18.75\ H_2O + 1.75\ N_2 + 6.38\ O_2$$

Mixtures of ammonium perchlorate with fuels can produce high temperatures when ignited, and the hydrogen chloride (HCl) liberated during the reaction can aid in the production of colors. These two factors make ammonium perchlorate a good oxidizer for colored flame compositions (see Chapter 7).

Ammonium perchlorate is more hygroscopic than potassium nitrate or potassium chlorate, and some precautions should be

taken to keep mixtures dry. The hygroscopicity problem can be substantial if a given composition also contains potassium nitrate, or even comes in contact with a potassium nitrate-containing mixture. Here, the reaction

$$NH_4ClO_4 + KNO_3 \xrightarrow{H_2O} KClO_4 + NH_4NO_3$$

can occur, especially in the presence of moisture. The exchange product, ammonium nitrate (NH_4NO_3) is *very* hygroscopic, and ignition problems may well develop [2]. Also, ammonium perchlorate should not be used in combination with a chlorate-containing compound, due to the possible formation of unstable ammonium chlorate in the presence of moisture.

Magnesium metal should also be avoided in ammonium perchlorate compositions. Here, the reaction

$$2\ NH_4ClO_4 + Mg \rightarrow 2\ NH_3 + Mg(ClO_4)_2 + H_2 + heat$$

can occur in the presence of moisture. Spontaneous ignition may occur if the heat buildup is substantial.

Under severe initiation conditions, ammonium perchlorate can be made to explode by itself [10]. Mixtures of ammonium perchlorate with sulfur and antimony sulfide are reported to be considerably more shock sensitive than comparable $KClO_3$ compositions [2]. Ammonium perchlorate can be used to produce excellent colors, with little solid residue, but care must be exercised at all times with this oxidizer. The explosive properties of this material suggest that minimum amounts of bulk composition should be prepared at one time, and large quantities should not be stored at manufacturing sites.

Strontium Nitrate [$Sr(NO_3)_2$]

This material is rarely used as the *only* oxidizer in a composition, but is commonly combined with potassium perchlorate in red flame mixtures. It is a white crystalline solid with a melting point of approximately 570°C. It is somewhat hygroscopic, so moisture should be avoided when using this material.

Near its melting point, strontium nitrate decomposes according to

$$Sr(NO_3)_2 \rightarrow SrO + NO + NO_2 + O_2$$

Strontium nitrite — $Sr(NO_2)_2$ — is formed as an intermediate in this decomposition reaction, and a substantial quantity of the nitrite can be found in the ash of low flame temperature mixtures [2]. At higher reaction temperatures, the decomposition is