ALKALI METAL SALT AEROSOLS AS FIRE EXTINGUISHANTS

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1. INTRODUCTION

Salts of alkali metals (such as sodium and potassium bicarbonates) in powder form have been employed in fire and explosion suppression for many years - a brief history is given below - but interest in their use for applications which would previously have been served by Halons has naturally grown recently. As for many of the proposed Halon replacements and alternatives, significantly more attention must be devoted to optimising the formulation of the agent and to the selection and design of the distribution means than was typically needed previously; however, provided the necessary care is taken, these powders can be extremely effective.

The mechanisms by which these materials act are discussed, and the importance of particle size – the smaller the particles, the better the performance - will become apparent. Examples of recent experimental work on the engine compartments of military vehicles and on arresting detonations in pipelines illustrate the demanding applications to which "conventional" powder systems can be extended. However there are practical and commercial limitations on the fineness of powders which can be manufactured and applied in such systems; a new approach - the use of pyrotechnic compositions to generate an extremely fine aerosol - is outlined, and an indication given of the high efficacy of such an agent in preliminary small scale total flood tests.

2. HISTORY

The use of alkali metal salts as fire extinguishants is very far from new. Sodium bicarbonate, in particular, has been employed in hand extinguishers since at least the early 1940s, the first NFPA standard was issued in 1955, and off-road vehicles have been protected using these agents since the early 1960s. More recently, during the 1980s, alkali metal salt powders were introduced in industrial explosion protection to replace existing (but less digestible) agents such as monoammonium phosphate, particularly in protecting food processing plant; they have since become much more widely used.

3. MECHANISMS

Three principle mechanisms account for the fire suppression performance of alkali metal salts. The first is thermal: cooling due to the intrinsic thermal mass of the cold material injected into the flame is augmented by endothermic decomposition reactions, for instance:

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O\uparrow + CO_2\uparrow$$
$$T > 150^\circ C \qquad \Delta H^\circ = 47 kJ/mol$$

$$K_2CO_3 \rightarrow K_2O + CO_2\uparrow$$
$$T > 1000^\circ C \qquad \Delta H^\circ = 394 kJ/mol$$

$$K_2O \rightarrow 2K + \tfrac{1}{2}O_2\uparrow$$
$$T > 1500^\circ C \qquad \Delta H^\circ = 363 kJ/mol$$

The standard heat absorbed as a result of these reactions amounts to 4.2kJ/g for potassium bicarbonate and 5.5kJ/g for potassium carbonate. The second mechanism is chemical: active flame-propagating species such as the hydrogen, hydroxyl and oxygen radicals may recombine (heterogeneously) on the surface of the particles or (homogeneously) as a result of gas phase reactions catalysed by alkali metal atoms. Thirdly, the water and carbon dioxide produced in the reactions shown above act as local oxygen diluents or inertants.

Two of these essential mechanisms - heat absorption and heterogeneous catalysis - are surface effects (and the other two - homogeneous catalysis and inerting - are dependant upon heat absorption and thermal decomposition to generate the gaseous species which bring them about): the greater the area of surface available, the more rapidly they will proceed and the better the fire suppression performance will be. Smaller particles have a greater surface area per unit mass of material, and have been shown to be more effective fire suppressants (ref 1).

An additional advantage of smaller particles is that, once dispersed, they remain airborne for longer. The terminal velocity of a spherical particle of a typical potassium salt with a diameter of 10μm is approximately 5mm/s; with a diameter of 1μm, approximately 0.05mm/s. The former would therefore be expected to remain airborne for a few minutes, the latter for many hours. Aerosols of very small particles thus behave much as gases, and long term inerting becomes possible.

4 AFV ENGINE BAYS

Fire suppression in the engine bays of armoured fighting vehicles presents a particular challenge because of the very high airflows which are typically encountered - anything up to 90 air changes per minute. An experimental programme has been carried out to determine the effectiveness of non-Halon agents in this application.

The tests were conducted in a mockup of the engine compartment of an M1 Abrams battle tank; dimensions and airflow were closely simulated, and a simple "engine" was installed to give the correct free volume and to ensure that the complexity of the space was represented. Most of the experiments were performed using a large pan fire which covered substantially the whole lower surface of the enclosure, with a smaller number of tests on localised fires elsewhere within the rig. Halon 1301 was tested to establish a baseline performance, and tests were also carried out on the new halocarbons, both singly and in mixtures; on water, both with and without additives; on carbon dioxide; and on a sodium bicarbonate-based powder.

None of these agents performed as well as Halon when a simple spray bar distribution system similar to that currently installed was used; all required modified distribution and the introduction of nozzles of appropriate design. This having been done, the results set out in the table below show that dry powder is the most attractive of all the new agents.

Agent	Minimum Effective Quantity (litres)
Halon 1301	**0.2**
Dry Powder	**0.25**
Water with Additives	**0.3**
Best Halocarbon	0.6
Carbon Dioxide	1.3

4. DETONATION ARRESTING

Most explosions are deflagrative: a combustion wave propagates through a premixed fuel/air mixture at a typical velocity between 0.5 and 10m/s, generating overpressures in the range 8-lobar. In certain circumstances, however, such as in long pipelines, the combustion front may become coupled to the shock wave; it then propagates at the velocity of sound in the compressed medium which may be as high as **4km/s.** The axial pressures generated can be immense - up to 80bar - while radial pressures, though lower, can reach at least 20bar. Such events clearly represent a very serious potential hazard to, for instance, ship-to-shore pipeline systems. Passive countermeasures such as containment or the introduction of detonation arresters are effective but costly.

A test programme was undertaken at the UK Health and Safety Executive's Explosion Test Laboratory. Stoichiometric propane/air detonations were generated in a 147m length of 18" nominal bore duct. Terminal flame velocities of 2km/s were measured. Pressure detectors were used to activate two explosively opened High Rate Discharge suppressors each containing 16kg of a sodium bicarbonate-based extinguishant powder.

The results showed that the system successfully extinguished the flamefront and dramatically reduced axial overpressure. Radial pressures were reduced from 20 to 1-2bar. It is believed (ref 2) that the dense cloud of powder particles acts mechanically to decouple the combustion front from the shock wave, after which the fire extinguishing properties of the powder suppress the flame and prevent a deflagration from becoming re-established. The recommended system based on this work uses powder suppression in conjunction with a high speed gate valve closing in 20-40ms. Multiple detectors are recommended to ensure that all possible events, whether detonations or deflagrations and wherever their point of ignition, are dealt with effectively.

5. LIMITATIONS AND A NEW APPROACH

As has been seen, the applications of powder extinguishants continue - and undoubtedly will continue - to be extended by the introduction of improved detection (as in detonation arresting), improved distribution and formulation (as in A N engine bays) and very fast discharge (in both). Still greater improvements might be possible if powders with smaller particle sizes could be employed, but there are limitations on the fineness of powders which can practically be manufactured at a reasonable cost, difficulties in preventing agglomeration and.coagulation of such fine powders in storage; and problems of effectively discharging particles with such low momentum. An interesting new approach is currently under investigation.

Pyrotechnic compositions comprising a potassium-based oxidant and an organic binder which also acts as a fuel are well known as rocket propellants and were used for this purpose for many years. Slow burning versions of these compositions have been studied (refs 3 and 4, for example) as a means of generating a fire extinguishing aerosol. The high reaction temperatures mean that the salts produced are initially gaseous; as they cool, the particulates produced by condensation from the vapour phase are extremely fine. Preliminary experiments on such devices have involved total flood extinguishment in a laboratory test chamber of a small pan fire. Successful suppression was achieved at a mass concentration some 5-6 times lower than is required for Halon 1301. It seems very possible that this technology may provide an even more interesting future for alkali metal salt fire extinguishants.

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