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**Proceedings of HOTWC-2002 12th
Halon Options Technical Working
Conference, Albuquerque, NM,
April 20 – May 2, 2002**

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Building and Fire Research Laboratory*

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U.S. Department of Commerce
Donald L. Evans, Secretary

Technology Administration
Phillip J. Bond, Under Secretary for Technology

National Institute of Standards and Technology
Arden L. Bement, Jr., Director

DEVELOPMENT AND TESTING OF GOODRICH 244 FIRE SUPPRESSANT

Dr. Donald E. Olander
Goodrich Corp.
25401 N. Central Ave.
Phoenix, AZ 85027-7899
623/516-3340
don.olander@goodrich.com

Abstract

Goodrich has developed an active non-ozone depleting replacement for Halon®. It is intended primarily for critical applications such as aircraft cargo holds, maritime engine and equipment rooms, etc, as a total flooding agent. Fire suppression tests have been performed in full-scale test devices rather than using laboratory tests. The surprising result show that the weight of the new suppressant needed is 7% of that of Halon® 1301 in the identical tests. The stored volume of the suppressant is approximately 3% of that required for Halon 1301. For fire suppression lasting longer than 30 minutes, 2-1/2 pounds of suppressant agent for each 1000 cubic feet of enclosure is recommended.

Goodrich 244 is a solid propellant using potassium bromate as the principal oxidizer. Approximately 47% of the effluent is potassium bromide, the active fire suppressant. The gaseous products are water, carbon dioxide and nitrogen. The bromine atom is in a solid ingredient both before and after use. Therefore, the Ozone Depletion Potential is zero. The only global warming agent in the effluent is carbon dioxide, which constitutes 24% of the effluent. Therefore, the global warming potential is 0.2. Because the Acute Inhalation Test (“rat test”) show no gross abnormalities after a 4 hour exposure followed by 2 weeks observation and necropsy, the SNAP approval is for limited times in inhabited spaces.

The fire suppressant data were obtained by testing in a chamber, which is a surrogate of a cargo bay in the DC-10 aircraft. It is agreement with the design published by the FAA.

Instrumentation includes 45 thermocouples, FTIR analyses, oxygen concentration meter, and aerosol chemical concentration equipment, visible and IR videos and two pressure transducers.

Other applications for the technology are listed.

Introduction

Goodrich started a development program with the premise that a halide active suppressant that is a solid before and after use would be equivalent to Halon®1301 in suppression and would still not be an Ozone Depletion Agent nor would it be an excessively Global Warming Agent. The test results of the new suppressant showed that:

- The new suppressant, in full-scale tests, was an order of magnitude more effective than Halon®. We believe that this is caused by the release of bromine as an ionic compound

instead of a covalent structure, such as Halon®, that must be modified by the flame before it is effective.

- Through the elimination of fluorine in the suppressants, the solid halide suppressants have been found to be essentially non-toxic.
- We find that the new type of suppressant can extinguish fires that Halon® cannot.
- The use of a solid generant, instead of liquefied gas, simplifies and reduces the weight and cost of storage and ancillary equipment.

Description of Goodrich 244 and Method of Fire Suppression

Goodrich 244 is a composite solid propellant whose principal oxidizer is potassium bromate.² Upon reaction, the potassium bromate is reduced to potassium bromide. Because both the bromide and bromate are solids, no halide containing compound can pollute the upper atmosphere. The Ozone Depletion Potential is, therefore, zero.

In northern Europe the Global Warming Potential (GWP) is almost as important as the Ozone Depletion Potential. That is because of the apparently logical presumption that as the polar ice cap melts, it may form a layer of fresh water that will intersect the warm saline water of the Gulf Stream. If the Gulf Stream sinks below the lighter fresh water it could trigger a new European ice age.

The products of combustion of the fire suppressing propellant are as follows:

Potassium Bromide	46.6%
Potassium Carbonate	21.5%
Water	9.4%
Carbon Dioxide	20.0%
Nitrogen	2.5%

The only global warming compound is carbon dioxide, whose GWP is defined as 1. The global warming potential is therefore 0.2. The effluent of Goodrich 244 is therefore environmentally benign. At the isochoric temperature and a pressure of 100 psia, all products of combustion are gasses. Immediately after dispersion into the atmosphere, the solids sublime. SEM photographs shown that the vast majority of the solids are in the form of nearly perfect cubic crystals of one-micron average size. Imperfections are present as parts of the crystals missing at the shear planes. The gasses produced disperse the solids without creating excessive pressure in the test cell.

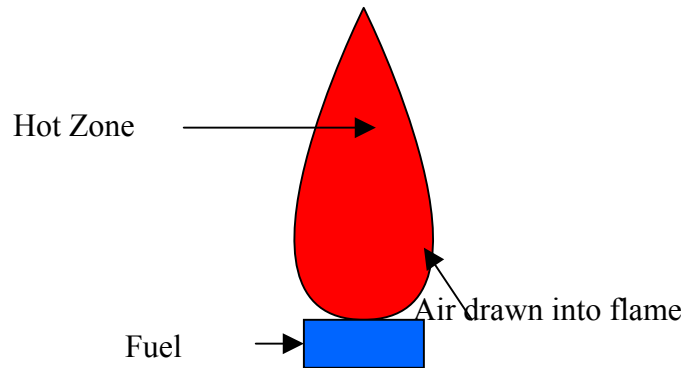
Because Halon® and many Halon® substitutes contain fluorine, toxic compounds are produced when the suppressant comes in contact with the flame. The worst of the toxic compounds are hydrogen fluoride and volatile fluorine containing compounds.³ On the other hand, the effluent of Goodrich 244 does not react, except catalytically, in the flame. The toxic gasses produced by Goodrich 244 have been measured using the FTIR. Hydrogen bromide (the most toxic expected by-product) has not been identified in any test. (The limit of detection is 1 ppm.) In tests without fire, the maximum concentration of carbon monoxide is 10 ppm. Nitrogen oxides are somewhat less, but are variable. Of course, when the products of combustion of the fire are added the concentration of carbon monoxide is much higher.

The solid aerosol components have been used medically for many years. Therefore it should not be surprising that there were no inhalation toxicity limits. Because of the possibility of accidental discharge cargo bays are considered inhabited spaces for Halon® replacements. Because no data existed we performed an acute inhalation study on ten rats. They were exposed to the effluent at a concentration of 2 milligrams per liter for 4 hours. Then they were observed for two weeks. No adverse effects were noted during the observation period or during necroscopy. The effluent is therefore considered safe for at least 5 minutes.

Mechanism of Active Flame Suppression

Flame suppressants are frequently classified as either active or passive suppressants. Most suppression agents are passive. They either blanket the burning material to deprive it of oxygen, or they dilute the oxygen in the environment to below the point that can sustain the flame or they cool the burning surface below its ignition temperature. However, this type of suppressant does not react chemically with the flame. Examples of such agents are water, carbon dioxide, sand, and sodium carbonate. Gaseous passive agents cannot be used as total flooding agents in occupied spaces because they must reduce the oxygen content below the amount that will sustain life. This is especially true for carbon dioxide because it also interferes with human respiration.

Active Suppressants interfere with the chemistry within the flame.



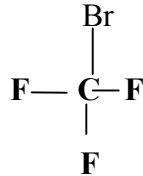
Let us look at the sketch of a typical flame. The majority of the heat is generated near the top of the flame. Heat is radiated in all directions from all portions of the flame. The amount of the heat radiated is proportional to the fourth power of the absolute temperature. The amount radiated downward is over two orders of magnitude greater than that which is radiated upwards from the fuel. Obviously, a reduction of temperature in the upper part of the flame has a disproportionate (approximately to the fourth power) reduction to the radiation downward. Because the flow of the material is upwards, there is no heat transfer downwards by means of conduction or convection.

The heat in the flame is produced by the reaction of fuel fragments with the oxygen in the air that is drawn into the flame. The heat that is absorbed by the fuel decomposes the fuel into the aforesaid fragments, which are carried upwards by the motion within the flame. Without suppression the fuel reacts with the oxygen that is drawn into the flame. The heat of this reaction radiates in all directions, including downward, continues the cycle. If a more reactive material, such as a halide or alkali metal ion or radical, whose reaction is less exothermic, intervenes the

temperature in the hot portion of the flame is lowered, the radiation downward is reduced, thereby potentially suppressing of the flame.

Reaction of Halon® with Flames

Halon® 1301 is bromotrifluoromethane. Its structure is:



Obviously, this is a covalent, not the ionic or free radical structure expected for an active fire suppressant chemical. However, when it burns or when it enters a hydrocarbon flame it can react to become hydrogen bromide, bromine radicals and hydrogen fluoride or one of a series of hydrocarbon fluorides. Hydrogen bromide is a strong fire suppressant agent. Unreacted Halon does not appear to be a significant fire suppressant. If it were, it would be more efficient in full-scale tests. In contrast, potassium bromide is active at the time of release from the aerosol generator.

Initial Intended Use and Test Protocol

Goodrich is basically an aerospace company. Since commercial aircraft is one of the “critical applications” exempted by the Montreal Protocol and is a high value application, the initial thrust of the demonstration and evaluation of the new suppressant was aimed at commercial aircraft cargo holds.

By international agreement, the test protocol entitled “Minimum Performance Standards” is the standard used for evaluating new fire suppressants.¹ This document is still in draft form, because of suggested changes. It is doubtful that complete agreement will ever be obtained. Some organizations wish to match the performance of a new suppressant exactly with that of Halon® 1301; even though the database is not extensive enough to justify such exactness any more than the realities of the fire suppression task demand it. Others want to modify such tests because their preferred solution to the problem will not pass the current tests. To the credit of the large aircraft manufacturers they have stated that they will not accept such changes. (An example of such requested test change is the modification of the test for an aerosol can test that cannot be suppressed by a water mist system.)

The tests under this protocol are performed in a surrogate DC-10 cargo hold, with the liner replaced with 18 gauge mild steel. Its volume is 2000 cubic feet. There is a minimum of 40 thermocouples and two pressure transducers that are precisely located. There is also a requirement for monitoring of gasses. There is a surrogate cargo door leak at 50 cubic feet per minute. Make-up air is through seams in the ceiling of the test cell.

There are four tests defined. These are 1) the bulk load test, 2) the LD3 container test, 3) the fuel fire test and 4) the aerosol can test.

The bulk load test The test chamber is loaded with 178 18-inch cube corrugated paper boxes. This amounts to two layers of boxes. Each box contains 2 to 2-1/2 pounds of shredded paper. One of the bottom boxes is vented. It is electrically ignited. After the fire is established, the temperature is measured at all forty points. There are maximum temperature and maximum time-temperature integral for 30 minutes.

LD3 Container Test This is a hidden fire test. An LD3 container is loaded with 33 boxes identical to those in the bulk load test. Two empty containers are used to further block the suppressant from the fire. Test limits are similar to those of the bulk load test.

Fuel Fire Test A pan of jet fuel plus gasoline is positioned near the ceiling. After the fire is established for a prescribed time the fire suppressant is released. There are time of and temperature limits for 15 minutes.

Aerosol Can Test A device which simulates a 16 ounce aerosol can is loaded with propane, alcohol and water. After the minimum design concentration of the suppressant is established the nozzle of the simulated aerosol can is opened. The effluent impinges on sparking electrodes. There can be no explosion or other pressure rise.

Significant Test Results

The quantity of Halon® that is needed to suppress a fire is usually given as volume percent. However, when the volume percent is converted into pounds for a 2000 cubic foot cargo hold, it is obvious that the weight of Halon® is considerable. The amounts needed are shown in Table 1.

**Table 1
Weight of Halon® Needed in 2000 Cubic Foot Test**

Criterion	Percent by Volume	Weight needed for a 2000 cubic foot Volume
Suppression Threshold	3%	25 pounds
Minimum Design Concentration	4%	33 pounds
Initial Concentration	8%	66 pounds

These are the quantities needed to pass the FAA test, which requires suppression for 30 minutes. However, in the US the airlines for domestic flights require at least 45 minutes. For extended range flights (ETOPS) the requirements vary from 180 to 240 minutes. There is consideration that 540 minutes may be needed for trans polar flights. The weight of Halon® can become considerable. Some of the more significant test results using Goodrich 244 are given in Table 2

An examination of the results shows that the weight of Halon® needed to suppress to the level of Halon® 1301 is only 7% of the weight of Halon®. Because of the propellant's higher density the stored volume is 3 % of that of Halon®.

A significant difference is that it was found that Goodrich extinguishes fuel fire instead of only suppressing such fires. It is postulated that the reason for this fortuitous behavior is that after the initial suppression of the flames, there is a thin deposit of potassium bromide on the fuel. When

oxygen is supplied to the fuel, the heated areas around the fuel cannot ignite it because of the suppression effect of the potassium bromide. The fire therefore remains extinguished until there is no longer an ignition source.

Table 2
Significant Test Results

Test	Weight of Suppressant	Result	Typical Initial Concentration mg/liter
Fuel Fire	2,0 pounds	Extinguished	7.6
Bulk Load	0.8 pounds	Suppressed until test termination @46 minutes	6.8
Bulk Load	3.6 pounds	Suppressed until test termination @ 200 minutes	23
Aerosol Can Test	3.6 pounds	No pressure rise Oxygen content during test = 18.5%	13
Container Test	3.6 pounds	Suppressed for 16 minutes	13
Container Test	5 pounds	Suppressed until test termination @ 110 minutes	19
Container Test	1.7 pounds	Extinguishment Observed @ 540 minutes	6

Non-Technical Problems in Replacing Halon®

In Europe non-critical applications of Halon® must be eliminated by 2003. Critical Application (aircraft and maritime) must be eliminated by 2010 or before, if a substitute is found. There is no such requirement in the US. As a result European supplies were sold to the US at reduced prices. There is at least 5 years supply of Halon® in this country. There will be great resistance to the elimination of the use of Halon® until all supplies are used.

Aircraft substitutes for small hand held extinguishers and for lavatory extinguishers have been qualified. This is made possible by the fact that the increase in weight of a small unit is not significant. However, there are no sales of these products and the system paper work is dragging. Why? Because there is no regulation saying that the airlines must retrofit. The FAA does not take action because they expect the EPA to make such a requirement. There is also a reticence to spend money to retrofit aircraft by taking off an acceptably operating system and paying to have a new one installed.

The natural conservatism of regulating bodies to require changes to existing systems requires lengthy approval cycles.

Other Applications

Goodrich is seeking more immediate markets for this product. Currently under investigation are:

1. Fire fighter's protective devices,
2. Maritime uses,
3. Offshore oil production platforms.

Summary

Goodrich has developed a replacement for Halon® in the cargo holds of commercial aircraft. It is environmentally benign and is of extremely low toxicity. The low weight and small size of devices using the material will reduce life cycle cost of aircraft. Because of the lack of impetus in the US to eliminate Halon®, Goodrich is seeking out other opportunities, especially in Europe.

Acknowledgments

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References

³ *An Analysis of Halon 1301 Combustion Products Using GC-MS with a Wide-Bore, Porous Open Tubular (PLOT) Column: Stiebich, R., Rubey, R., Grinstead, R., Research Institute, University of Dayton, Dayton Ohio*

² *U. S. Patent Numbers 5,861,106; 6,019,177, 5,988,438 and 5,419,118, and additional US and international patent applications*

¹ *FAA Document "Minimum Performance Standards for Aircraft Cargo Compartment's Built-in Fire Suppression Systems*