AGENT/SYSTEM COMPATIBILITY FOR HALON 1301 AVIATION REPLACEMENT

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ABSTRACT

This project has developed measurement methods and provided data for the appraisal of 12 USAF-specified candidate halon 1301 replacements for compatibility with flight systems, people, and the environment. The exposures of metals, elastomers and lubricants involve an initial temperature and pressure of 298 K (77 °F) and 4.1 MPa (600 psi), with a final temperature of 422 K (300 °F). These data and those from the companion project, "Agent Screening for Halon 1301 Aviation Replacement," will enable the selection by September 30, 1993 of 3 of the chemicals for full-scale testing by the Air Force. Longer-term testing will then be commenced to increase confidence in the preliminary results for materials compatibility. A final report will be delivered by September 30, 1995.

BACKGROUND

The Montreal Protocol of 1987 identified halon 1301 (CF_3Br) as one of a number of halogenated chemicals that were sufficiently deleterious to stratospheric ozone that their continued production and use required limitation. A recent amendment to the Protocol will cause new production of this chemical to cease by January 1, 1994.

Halon 1301 has been the agent of choice for fire suppression in engine nacelle and dry bay (avionics) spaces in most civilian and military aircraft. With its projected unavailability, the manufacturers, owners, and users of aircraft are in need of an alternative. Since it may take years to retrofit the large fleet of current aircraft, there is an urgency to identify one or more new chemicals soon.

The retrofit process will also likely be expensive. The bromine atom in halon 1301 is largely responsible for both the high fire suppression effectiveness and the ozone destruction. If, as is likely, the alternative chemicals do not contain a moiety like bromine and are less efficient suppressants, then new, larger agent storage and delivery components will need to be designed. To avoid costly design mistakes, extensive performance data regarding the compatibility of the alternatives with the delivery system and aircraft construction materials is essential.

Several Federal agencies have pooled resources to implement optimal replacements for in-flight fire suppression by 1996. A companion paper, "Agent Screening for Halon 1301 Aviation Replacement" [1] documents research to measure the fire-fighting effectiveness of 12 chemicals. This paper describes research on various aspects of the candidates' compatibility with aircraft construction materials,

delivery system materials, people and the environment. At the conclusion of initial studies on September 30, 1993, 3 chemicals will be selected for more extensive, full-scale testing. This includes 20-month exposures of metals, elastomers and lubricants to the 3 selected candidate suppressants. In addition, NIST will development of a predictive capability for HF and HCl formation during suppression and update of the environmental regulatory methods and compliance requirements.

The 12 chemicals identified by the U.S. Air Force as potential successors to halon 1301 that would be available in quantity by 1996 are:

Chemical	Formula
HFC-236	$C_3H_2F_6$
HFC-32/HFC-125	CH_2F_2/CHF_2CF_3 (azeotrope)
HFC-227	C_3HF_7
HCFC-22	CHF_2Cl
HFC-134a	CH_2FCF_3
FC-116	C_2F_6
HCFC-124	$CHFClCF_3$
HFC-125	CHF_2CF_3
FC-218	C_3F_8
FC-31-10	C_4F_{10}
FC-318	cyclo-C_4F_8
Sodium bicarbonate	$NaHCO_3$

The first eleven candidates are gases or volatile liquids; the twelfth is a powder.

RESEARCH TASKS

Seven tasks are designed to supply the needed compatibility data. These tasks include residue, storage stability of the chemicals, their degradation to harmful products during flame suppression, compatibility of the chemicals and their by-products with both metallic and polymeric materials, and definition of possible limitations for exposure of people and the environment.

The compatibility studies are for a range of storage conditions. Based on information supplied by the Air Force, it is presumed that the agent storage will be initially at 298 K (77 °F) and 4.1 MPa (600 psi). In flight, these could rise to 422 K (300 °F) and over 5.8 MPa (850 psi), depending on the vaporization of any liquid initially present in the bottle. Thus, the stability of a chemical and its potential damage to the storage vessel are examined under these conditions.

At present, the storage times on board aircraft are of the order of 5 years. In order to enable a selection of the most promising chemicals by September 30, 1993, only much shorter exposures (e.g., 1 month) were possible. A list of representative metals, elastomers, and lubricants likely to be used

in the storage systems was compiled by the Air Force. Phenomenological modeling, based on exposures at various time intervals, was pursued in some cases to increase confidence in the extrapolation to longer times. For those 3 chemicals selected for further testing, longer exposures year) will be performed to improve confidence in the extrapolations.

Following dispensing, the suppressant chemical would decompose while in and near the flames, leading to the production of potentially harmful by-products. The potential for these by-products to damage the airplane materials was examined under potential post-fire conditions. A list of representative materials likely to be exposed to the by-products was compiled by the Air Force.

These measurements and their interpretation are at or beyond the state-of-the-art. Therefore, the tasks were pursued with the utmost scientific care to maximize their validity. Discussions were held with both manufacturers of the twelve chemicals and manufacturers and users of current fire suppression systems to obtain background information.

1.   Agent Residue

As manufactured, halon 1301 is a "clean" suppressant, that is, it leaves no residue in the fire environs. For the candidate alternatives, a residue could result from either a high boiling point of the chemical itself or of the impurities contained in the storage cylinder.

The 11 gaseous or volatile liquids were obtained from commercial manufacturers when possible and from a custom synthesizer otherwise. They present a wide range of boiling points from 195 K to 277 K (-108° F to 39° F). Each of these was delivered into a small copper cooling coil immersed in a low temperature bath at a temperature that allowed the compound to be delivered as a liquid. Small, tared crucibles containing 1 mL liquid samples were warmed to allow evaporation of the liquid without excessive boiling (bumping) and then weighed. This is similar to a previously-developed screening procedure [2].

Eight of the chemicals vaporized completely during the test procedure. There were yellow-brown, oily residues observed from commercial HCFC-22, HCFC-124, and HFC-134a. The manufacturer of these chemicals has identified the residue as an oil deposited on the inside of the metal containers to protect against rusting. It is presumed that oil-free chemical could be obtained.

$NaHCO_3$ is a solid under all test conditions. Thus, its removal from the fire zone would only result from flushing by a high air flow. This process was not evaluated.

2.   Instability Under Storage

Halon 1301 is presumed to be stable in metal containers for many years. Any by-products do not affect its fire suppression effectiveness or result in an unacceptable residue. For candidate replacement chemicals, we obtained comparable data, reflecting the storage conditions of elevated temperature and pressure.

NIST Technical Note 1278 [2] details a screening test for the stability of chemicals, with the purity of the chemical determined by infrared spectral analysis. Following this concept, nine samples of each of the eleven fluids were stored in separate 1-liter teflon-lined stainless steel cylinders for 30 days at 423 °C and 5.8 MPa (850 psi). [It was presumed that $NaHCO_3$ is stable under the likely storage

temperatures and pressures.] For each chemical, one cylinder contained only the chemical. Each of the other 8 contained pieces of a metal of which future suppressant bottles might be fabricated:

Nitronic-40 (21-6-9 stainless steel)
304 Austenitic stainless steel
4130 alloy steel
13-8 molybdenum alloy
Inconel 625
6061-T6 aluminum alloy
CDA172 copper-beryllium alloy[1]

The surface area of the metal pieces was comparable to the interior surface area of the 1-liter bottle.

Both before and after the incubation, samples of the chemical were analyzed at rom temperature by Fourier Transform Infrared (FTIR) spectroscopy. None of the samples showed any degradation with any of the metals present.

For those 3 chemicals selected for further study, aging tests of 20 months will be performed at 423 K and 5.8 MPa.

3. Combustion By-Products

The degree of combustion-induced decomposition of the suppressant will depend on its chemical nature, its suppression efficiency, and the time/temperature history of the suppressant in the fire. The latter includes both transport effects and chemical effects.

The most harmful products likely to be formed from the 11 gaseous/liquid suppressants are HF and HCl, when chlorine atoms are present in the parent chemical. CF_3H is a candidate propellant for the suppressant, and was included as a 12th chemical. All of these chemicals are less efficient suppressants than halon 1301, and several have been shown to produce far higher halogen acid yields during suppression. It is important to predict these yields under in-flight suppression conditions in order to assess their potential effects on metals corrosion and elastomer deformation. [$NaHCO_3$ powder is itself an undesirable suppression leftover. The production of NaOH is also likely. However, its prediction is not now part of this project.]

This task is underway, with completion planned for September, 1995. The general approach is to obtain global information on the final products in simple burners that allow operation over a range of conditions simulating those in dry bay and engine nacelle fires.

The first burner is a common cup burner, here using JP-8 and propane as fuels. Steady-state acid yields have been determined for agent concentrations in air of 50% and 90% of that needed for flame extinction.

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[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to document the results adequately. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment or material is necessarily the best available for the purpose.

While these data provide indicative information, the fires of interest are transient in nature. We wil attempt to measure transient acid gas yields with the cup burner. However, more direct knowledg will come from experiments using the turbulent jet burner described in [1] and a counterflow diffusion flame burner. The data obtained will be used to formulate, first, an empirical correlation of yield with chemical formula and concentration, fuel type and consumption rate, and flame characteristics Detailed chemical modeling [1] will also be used.

4.   Corrosion

There is the potential for agent-induced corrosion failure of the fire suppressant storage system (stored agent), the distribution system, and other aircraft systems (after deployment). A series of corrosion tests has evaluated the corrosion of storage container metals by the as-received agents and the corrosion of typical airframe metals by the combustion by-products.

In general, there are eight different forms of corrosion: general corrosion, pitting corrosion, intergranular corrosion, crevice corrosion, dealloying, environmental induced cracking (stress-corrosion cracking, etc.), galvanic corrosion, and erosion corrosion. The experiments of this program are designed to evaluate the potential for failure by all of these except for the last two. These two were not included in the test matrix because coupling of dissimilar metals in contact with a liquid phase is usually avoided in service, and the suppressants are usually stagnant except during deployment where erosion of the nozzles may occur.

Each of the metals listed above were exposed to each of the listed chemicals for 30 days at 422 K and a total pressure of 600 MPa (850 psi). After completion of the exposure test interval, the samples were weighed and examined by optical microscopy, scanning electron microscopy and metallography if warranted. Realizing that extrapolation from 1-month exposures to 5-year in-service life prediction introduces uncertainties, 20-month exposures will be performed for the 3 chemicals selected for further study.

In addition, *in situ* slow strain rate tests were performed on samples of each of the metals in each of the fluid chemicals. The crosshead speed was 25×10^{-6} mm/s (1×10^{-6} in/s). These experiments provided data on the susceptibility of the alloys to stress corrosion cracking in each of the agents.

A limited number of metal samples were exposed to aqueous solutions of HF and NaOH to evaluate the potential for post-deployment corrosion damage to exposed metals by the by-products of combustion that might stick to moist surfaces of metals and electronic components.

A complementary set of electrochemical experiments will improve the quality of corrosion ratings by helping to resolve the scientific uncertainties inherent in short-term exposure tests. These experiments enable assessment of the effects of variations in the exposure conditions that could cause rapid runaway corrosion that would otherwise be missed by the exposure test matrix due to the limitations of cost and time. In addition, these tests will enable assessment of the potential for galvanic attack and local breakdown of protective films to a level not possible with exposure tests. This type of testing is at the state-of-the-art. Standards have not yet been developed for predicting performance from these measurements and the relatively low conductivity of the suppressants will make measurement difficult. As a result, the first objective of the electrochemical experiments will be to establish whether or not different types of electrochemical measurements can be used to estimate the relative corrosion behavior. Then, once the validity of these measurements is

established, the objective will be to evaluate the influence of impurity levels, decomposition products and contaminants on the corrosivity of the compounds to the metals used in suppressant storage systems. The electrochemical testing has been started, and as part of the effort to improve the scaling of corrosive effects with time, will be completed September, 1995.

5. Elastomer Seal Compatibility

Deterioration of the gasket in the suppressant storage device (under high pressure) could result in leakage of the chemical, leaving the system unready to respond in case of a fire. Further, should the system be activated, the combustion by-products of the suppressant could damage other exposed polymeric materials in the aircraft. Research in two areas was performed to establish a data base relevant to the compatibility of the gaskets in the fire suppressant candidate fluids. First, a study based on solution thermodynamics was performed to ascertain the proclivity of six representative elastomers and three greases to swell in each of the suppressant fluids. Second, degradation of the physical properties of the elastomers could also be detrimental to system operation and a study was undertaken to measure the retention of strength, modulus and elasticity of representative elastomers after fluid exposure for times up to six weeks at 150 °C (300 °F). The viscosity behavior of the three greases was monitored for the same exposure conditions. The greases and elastomers tested are:

Greases:

> Braycote 600
> Krytox 240AC
> Braycote 807

Elastomers:

Type	Swelling Measurements	Residual Property Measurements
silicone	RS 383	S604-70
nitrile	Chemigum N926	N674-70
nitrile	Chemigum N206	N103-70
fluorosilicone	Sylon FX 11293	L1120-70
fluorocarbon	Viton E-60	V1164-70
chloroprene	Neoprene WRT	C1185-70

[Braycote is a trade name of Castrol, Inc.; Krytox, Viton and Neoprene are trade names of Dupont Company; Chemigum is a trade name of Goodyear Tire and Rubber Company; RS 383 is a designation of Rhone-Poulenc and Sylon FX 11293 is a trade name of 3M Company. All the designations for the samples tested for residual properties are from Parker Seal Group.]

The swelling measurements were performed in custom-made pressure vessels with a view port and large enough capacity to admit quartz springs. Samples of crosslinked and uncrosslinked elastomer were placed on quartz pans and hung from the springs. An agent was introduced into a previously

evacuated chamber at pressures from sub-atmospheric to the saturation pressure of the suppressant for temperatures ranging from ambient to 150 °C (300 °F). Above the agent critical point, there is no saturation vapor pressure and the pressure was increased to 5.9 MPa (850 psi). The degree of swelling was determined by measuring the mass uptake of the solvent by the elastomers using a cathetometer to observe the displacement of the quartz springs [3].

The thermodynamics of the swelling agents in the elastomers was analyzed using classical Flory-Huggins [4],[5] theory of mixing and Flory-Rehner [6] theory of swelling of elastomers. The Flory-Huggins interaction parameter χ was determined for each elastomer/suppressant or grease/suppressant combination. This parameter provides a quantitative method of determining the solubility of the elastomer in the fire suppressant fluid. The higher the χ value, the lower the solubility. Hence for a system compatibility determination, high values of χ are desirable. In all cases, the fluids would be considered poor solvents because $\chi \geq 0.5$. Differentiation among fluids for a given elastomer and among elastomers for a given fluid is readily made through the measurement of χ.

For agent/seal or agent/grease compatibility above the agent critical point, the classical theories discussed above are inapplicable. We analyzed the data in terms of the Flory corresponding states theory [7]. The systems showed significantly less swelling under supercritical conditions than below the critical point. Thus, differentiation among elastomers, greases or sealants upon exposure to the suppressants is more logically made based upon the subcritical measurements.

Separate pressure vessels were built for the assessment of the residual properties of the elastomers and greases upon exposure to the suppressants at 150 °C (300 °F) and 5.9 MPA (850 psi). Materials were incubated for times of 1, 2, 4, and 6 weeks and then tested according to standard methodologies. For the elastomers, the samples were in the form of 'o' rings and the properties measured were breaking stress, breaking strain and modulus in experiments performed at room temperature at a cross-head separation rate of 51 mm/min (20 inches/min). The greases were tested in a cone and plate rheometer to determine the viscosity behavior.

A literature search was conducted to compile estimates of damage to classes of polymeric materials upon exposure to the post-deployment suppressant degradation by-products. Stability of the polymers to HF, HCl and NaOH was researched.

Upon selection of the 3 candidates fire suppressants for further evaluation, a limited number of elastomers and greases will be subjected to long term (1 year) exposures to ascertain appropriate scaling of material performance with time.

6.   Potential Human Exposures

Although these agents are typically employed in unoccupied sections of an aircraft, the possibility of human exposure still exists during handling, storage, and transport. Thus, it is important to know if the accidental release of the 12 agents in areas of typical occupancy would result in differing threats to life safety.

Room-scale experiments were conducted with those chemicals having the highest and lowest densities to determine the uniformity of distribution following an accidental discharge. Immediately following dispensing from a pressurized cylinder, FTIR measurements were made to determine whether spatial disproportionation of the chemical occurred. No people were exposed. Up to 30 minutes after discharge, no significant effects were observed. Thus, one can comfortably assume a uniform

distribution throughout the space.

A compilation of published toxicological results for chronic or acute exposure were summarized. This provides working guidelines (rather than definitive exposure limits) for safe exposures, thus placing the experimental results in context.

7. Environmental Requirements

There are a number of regulatory constraints that might affect the selection for further examination of each of the 12 candidates. Fortunately, the Environmental Protection Agency (EPA) is implementing its Significant New Alternatives Policy (SNAP), which becomes the definitive evaluation of chemicals intended to be used in place of ozone-depleting substances to approve their acceptability from a human health and environmental perspective. A database is being prepared containing the appropriate information on the chemicals listed above. The regulatory methods and the compliance requirements are likely to change during the course of this project. Thus, the database will be updated by September, 1995 to reflect new guidelines or regulations.

ACKNOWLEDGEMENTS

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