COMPATIBILITY OF HALON ALTERNATIVES DURING STORAGE

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Mark R. Stoudt and William K. Waldron, Jr.
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

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Chapter 12

Compatibility of Halon Alternatives During Storage

Richard G. Gann[1], Carlos R. Beauchamp[2], Thomas G. Cleary[1], James L. Fink[2], Richard H. Harris, Jr.[1], Ferenc Horkay[2], Gregory B. McKenna[2], Thomas P. Moffat[2], Marc R. Nyden[1], Richard D. Peacock[1], Richard E. Ricker[2], Mark R. Stoudt[2], and William K. Waldron, Jr.[2]

[1]Building and Fire Research Laboratory, Fire Science Division and [2]Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899–0001

A key facet of the evaluation of new fire suppressants is their behavior under pressure and at elevated temperature in a metal storage container with an elastomer seal. In this study, 13 candidate chemicals have been examined: C_2F_6, C_3F_8, C_4F_{10}, cyclo-C_4F_8, CH_2F_2, C_2HF_5, CH_2F_2 (60%)/C_2HF_5 (40%), $C_2H_2F_4$, C_3HF_7, $C_3H_2F_6$, CHF_2Cl, C_2HF_4Cl, and $NaHCO_3$. This paper presents the results of testing for thermal stability in the presence of various metals, corrosion of those metals, and effects on selected elastomers and lubricants.

Under the Montreal Protocol of 1987 and its subsequent amendments, production of new halon 1301 (CF_3Br) has been curtailed and now halted. However, the need for fire suppressants still exists for in-flight fires aboard aircraft. There, halon 1301 is now stored for up to 5 years in a metal container which is sealed with a lubricated elastomer. For high temperature applications, a metal gasket is used. The storage pressures are typically 2-4 MPa, and the temperature of the container (or bottle) during flight can range from -70 °C to +150 °C. Deleterious interaction between the chemical and the materials in the storage container could lead to leakage of the suppressant and/or failure of the container. Interaction between the chemical or its combustion by-products could also lead to weakening of downstream parts of the aircraft following a fire. Discussions with military and civilian maintenance personnel indicate that there has been no significant leakage of halon 1301 from its storage system, nor has there been evidence of significant agent deterioration during long-term storage. To avoid costly design errors, it is important that a replacement chemical be similarly stable and that the system remain intact.

Most of the chemicals under consideration (Table 1) are aliphatic halocarbons of low or zero ozone depletion potential that are being manufactured for other applications. Most were recommended by Zallen [1], considering past investigations

[2],[3],[4],[5]. His list was modified by the sponsors, the results of early testing, and a solicitation of additional chemicals.

Table 1. Core chemicals examined

Chemical Formula	Designation	IUPAC Name
C_2F_6	FC-116	hexafluoroethane
C_3F_8	FC-218	octafluoropropane
C_4F_{10}	FC-31-10	decafluorobutane
cyclo-C_4F_8	FC-318	octafluorocyclobutane
CH_2F_2	HFC-32	difluoromethane
C_2HF_5	HFC-125	pentafluoroethane
CH_2F_2 (60%)/C_2HF_5 (40%)	HFC-32/125	-
$C_2H_2F_4$	HFC-134a	1,1,1,2-tetrafluoroethane
C_3HF_7	HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane
$C_3H_2F_6$	HFC-236fa	1,1,1,3,3,3-hexafluoropropane
CHF_2Cl	HCFC-22	chlorodifluoromethane
C_2HF_4Cl	HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane
$NaHCO_3/SiO_2$ (1%)	-	sodium bicarbonate/silicon dioxide

This paper describes procedures developed for obtaining agent stability and materials compatibility data under conditions well-related to those during use [6]. It was determined that the agent storage would be initially at 25 °C and 4.1 MPa. In flight, these could rise to 150 °C and 5.8 MPa. The experimental approaches followed from an earlier study [7]. The facilities developed and knowledge gained go well beyond the specific applications to aircraft, and advance the fire suppression technology in general.

Corrosion of Metals

There are 6 forms of potential concern for the storage, distribution, and post-deployment corrosivity of fire suppressant agents on aircraft: **general corrosion,** the result of reactions over the entire exposed surface, resulting in metal thinning, reduced mechanical strength, and an altered surface appearance; **pitting corrosion**, which results in an accelerated corrosion rate in a small spot on the surface of a material; **crevice corrosion**, which occurs where the local environment does not freely mix with the bulk environment and could result in failure of joints; **intergranular corrosion**, rapid deterioration between the microcrystals formed during melt solidification of the metal, resulting in reduced mechanical strength; **environmentally-induced fracture**, crack formation at levels well below those due to mechanical stress, leading to catastrophic fracture; and **dealloying**, selective leaching of an alloying element, resulting in serious loss of mechanical strength.

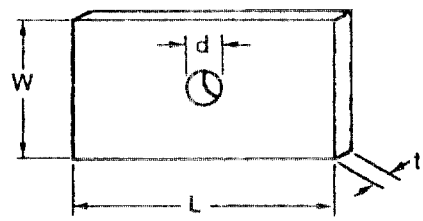
'able 2.Composition of the alloys in weight percent

Element	Nit 40	Al 6061	In 625	304 SS	CDA 172	13-8 Steel	AM 355	AISI 4130
Ni	7.1	--	61.39	8.26	0.06	8.4	4.23	0.08
Cr	19.75	0.04	21.71	18.11	0.01	12.65	15.28	0.98
Mn	9.4	0.15	0.08	1.41	--	0.02	0.8	0.51
Mg	--	i	--	--	--	--	--	--
Si	0.5	0.4	0.09	0.49	0.08	0.04	0.16	0.23
Mo	--	--	8.82	0.17	--	2.18	2.6	0.16
Nb	--	--	3.41	--	--	--	--	--
N	0.29	--	--	0.03	--	0	0.12	--
C	0.02	--	0.02	0.06	--	0.03	0.12	0.32
Be	--	--	--	--	1.9	--	--	--
Co	--	--	--	0.11	0.2	--	--	--
Zn	--	0.25	--	--	--	--	--	--
Cu	--	0.15	--	--	97.9	--	--	--
Fe	bal	0.7	3.97	bal	0.06	bal	bal	bal
Al	--	bal	0.23	--	0.04	1.11	--	0.04
g/cm^{3a}	7.83	2.70	8.44	7.94	8.23	7.76	7.91	7.85
kg/m^3	7,830	2,700	8,440	7,940	8,230	7,760	7,910	7,850

[a]Nominal Density

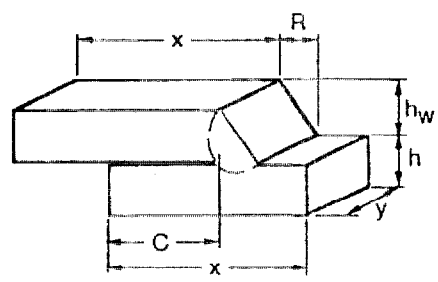
Very little is known about corrosion under elevated pressures and tempera-ures, the corrosivity of most of these agents to the metals used for aircraft storage :ontainers, or the potential for significant corrosion damage to aircraft structural :omponents by residual suppressant or by suppressant combustion products (*e.g.*, HF, NaOH). Therefore, the effects of the agents on 8 metals most typically used in ;uppressant storage vessels and fittings were examined. Their compositions are given n Table 2. Several different types of experiments were performed to evaluate the /arious forms of corrosion.

Exposure Tests. 25-day exposure tests were conducted to determine the change in nass and, in turn, to assess the rate of formation of corrosion scales or the rate of 'emoval of metallic species by corrosion. Visual and optical microscopic examination of these samples before and after exposure allowed for the evaluation of the occur-'ence of pitting, intergranular corrosion and dealloying. The samples were flat, smooth, and clean surface coupons as shown in Figure 1(a) [8].



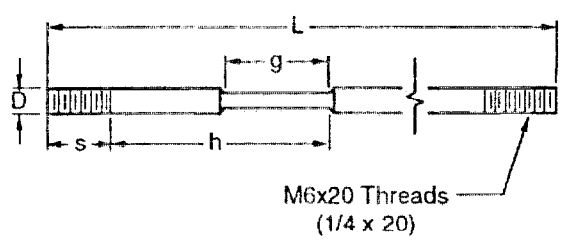
W= 25.4 mm (1.0 in)
L= 50.8 mm (2.0 in)
t= 1.6 mm (0.0625 in)
d= 6.7 mm (0.265 in)

(a) General corrosion coupon design (ASTM G-01).



x = 50.8 mm (2.0 in)
y = 50.8 mm (2.0 in)
R = 4.75 mm (0.1875 in)
C = 31.75 mm (1.25 in)
h = 3.2 mm (0.125 in)
h_W = 3.2 mm (0.125 in)

(b) Weld/crevice corrosion coupon design.



D = 19 mm (0.25 in)
L = 178 mm (7 in)
g = 25.4 mm (1 in)
h = 57 mm (2.25 in)
s = 19 mm (0.75 in)

(c) Slow strain rate tensile sample design (ASTM E-8, G-49).

Figure 1. Design of samples used in immersion and slow strain rate tensile tests.

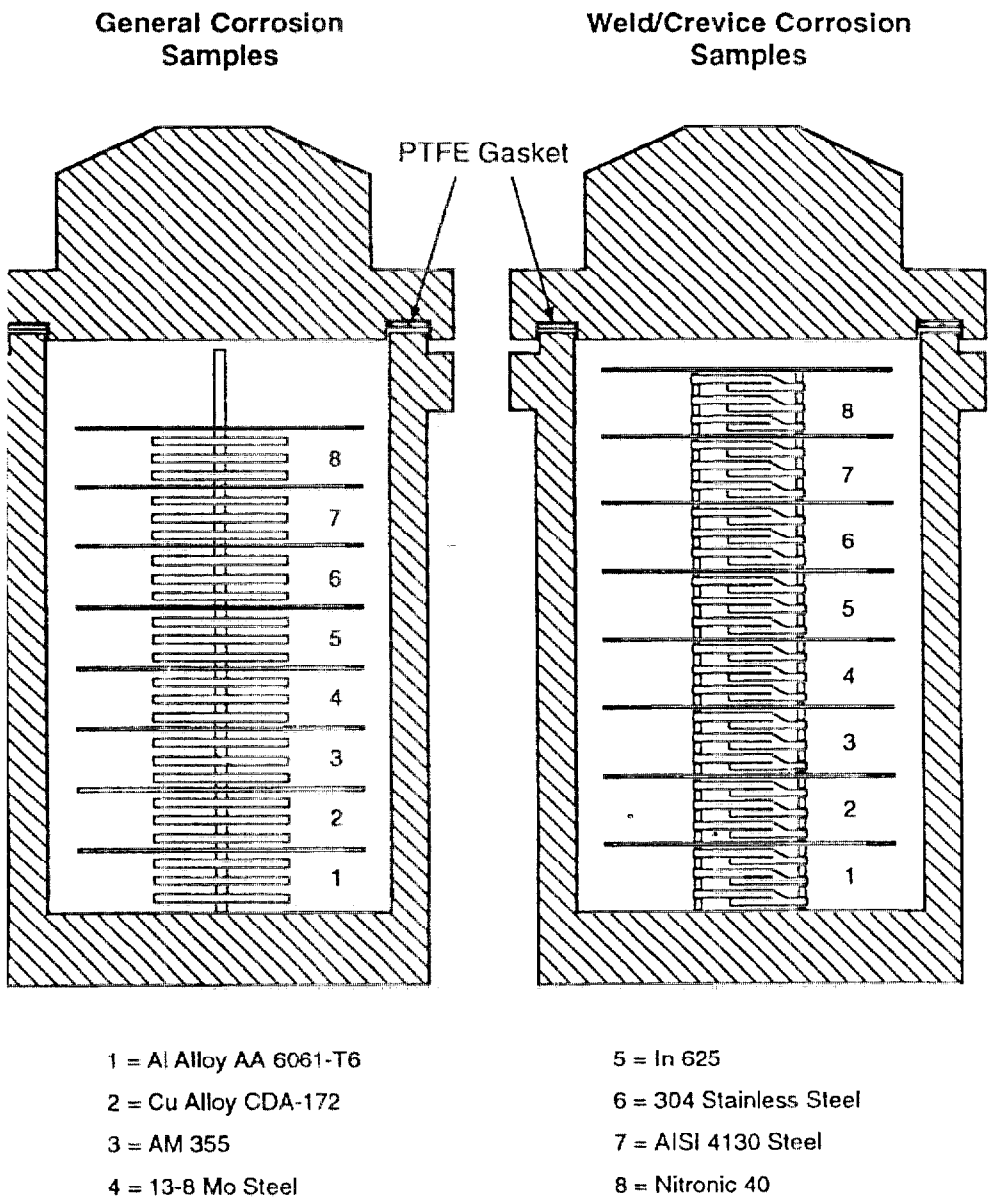


Figure 2. Immersion testing chamber used for general corrosion coupon tests and weld/crevice corrosion coupon tests.

In each exposure test, 3 pre-weighed coupons of each of the 8 alloys were mounted on a polytetrafluoroethylene (PTFE) rod with PTFE spacers between the triplicate samples as shown in Figure 2. This both separated the samples and eliminated galvanic coupling effects. The samples were placed in a PTFE liner and charged into a 2000 ml stainless steel pressure vessel. Each vessel was charged with enough neat agent to achieve a final pressure of ≈5.86 MPa at 150 °C. At the conclusion of the testing period, the coupons were extracted from the cooled vessels and re-weighed.

All of the mass changes were found to be relatively small and most were mass increases. Visual examination confirmed the presence of very thin surface films on many of the samples as noted by a color change.

Similar experiments were conducted to evaluate crevice corrosion, weld zone attack, and intergranular attack in the heat-affected zone. The geometry of these samples is shown in Figure 1(b) and the test chamber is shown in Figure 2.

At the end of the 25-day test period, the samples were removed from the test chambers and split along the fusion boundary. The corrosion damage within the crevice region of the 3 samples for each agent/alloy combination was then evaluated visually and statistically [9]. Seven of the agents had an alloy that showed no visible evidence of attack and all of the agents had at least three alloys with only light discoloration of the surface. Thus, the crevice/weld immersion experiments show that while there is a clear difference in the corrosivity of the agents, one can find container alloys for each of the candidates. The agents were then ranked based on the appearance of the corrosion damage in the crevice region for each alloy. The results showed the same general trend as the first analysis. Sodium bicarbonate received distinctly poor ratings here. Third, the alloys were graded based on their performance in all agents. Again, the results were consistent.

Tensile Testing. The stress corrosion cracking susceptibilities of the 8 alloys in the replacement candidates were evaluated using the slow strain rate (SSR) tensile test technique. A test involves slowly increasing the strain on the sample until failure occurs. The result for each agent is then compared to that strain required to cause failure in an inert environment.

The samples used for these experiments were machined with the tensile axis parallel to the rolling direction of the plate stock (Figure 1(c)). The vessels were 250 ml volume autoclaves similar to those used for the exposure testing, except that for these vessels, a load could be applied to the tensile specimen *in situ* under constant environmental conditions (5.86 MPa at 150 °C). The number of moles of agent was held constant for all tests.

After failure, the fracture surfaces were cut from the broken SSR samples for analysis. Scanning electron microscopy was used to evaluate the mechanism of crack propagation based on the fracture morphology. The test results were analyzed using the maximum load observed during the tensile test, the total strain to cause failure, and the reduction in area of the fracture surface. Each of these three parameters were considered relative to the value from an inert environment.

From the SSR data, every agent had at least one alloy demonstrating good erformance and all but two agents had more than one. However, no alloy was naffected by all of the agents and no agent left all the alloys unaffected. Since the loys have different chemical compositions, surface films and corrosion susceptibili-es, this is not surprising, but it indicates the importance of conducting experiments of is type.

Finally, the data from all of the tests were combined into a single matrix, which ›pears as Table 3. It is clear from these compiled results that there are metals that are ›mpatible with each of the agents under consideration. Some of the metals, espe-ally the aluminum and copper-beryllium alloys and the 355 and 4130 steels, appear skier to use than the others. The range of choice is more limited for sodium bicar-›nate than for the other agents.

ost-Deployment Corrosion. An additional set of experiments appraised the effects deposits of a suppressant and its byproducts on potential aircraft metals. The mples were the same as in Figure 1(a) without the hole in the center.

These agents can be classified into two categories: those that will produce ılogen acids (of which HF is usually the worst) and those that contain sodium carbonate. Sodium bicarbonate will decompose on heating to form sodium carbon-e (Na_2CO_3), and on combustion to form sodium hydroxide (NaOH).

To produce a surface film rich in fluoride ions, the surfaces of the samples ere first sprayed with ASTM artificial seawater (a worst-case wet environment) then ›rinkled with sodium fluoride (NaF) powder while the surface was still wet. A :cond surface film was simulated by spraying with the ASTM seawater and sprin-ing with a 50/50 mixture of sodium bicarbonate/sodium carbonate. A third set of mples was sprayed with the ASTM seawater and then sprayed with a 0.1 M solution f NaOH. Samples of alloys with the 3 treatments were then stored for 30 days at 3 ifferent fixed relative humidities (RH): 20%, 52%, and 93%.

The samples were weighed between the cleaning and the surface pre-treatment eps, after the application of the ASTM artificial seawater, and after application of the ›rrosive salt(s). Following the exposure, the coupons were weighed, then rinsed in ›uble distilled water, dried and reweighed. Finally, they were weighed again after ıemical removal of the corrosion product films.

For most of the alloys the mass changes were quite small, no particular surface retreatment was consistently worse than the others, and there was no clear trend in ıe magnitude of the mass change with relative humidity. For three alloys (aluminum 061-T6, AISI 4130 steel, and Cu-Be CDA-172), the mass changes were somewhat rger. Of particular importance is the large effect of $NaHCO_3/Na_2CO_3$ on the alumi-ım alloy, which comprises most of the aircraft surface. Cleaning these surfaces soon fter discharge of the $NaHCO_3$ fire suppressant would be a very beneficial practice 0],[11],[12],[13].

Table 3. Interactions of Metals During Storage. Worse of Slow Strain Rate and Weight Loss tests

NAME	NITRONIC 40	AL ALLOY 6061-T6	INCONEL 625	304 STAINLESS	CU-BE CDA 172	13-8 STEEL	AM 355 STAINLESS	AISI 4130 STEEL
HFC-236fa	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	GOOD	GOOD
HFC-32/125	GOOD	FAIR	GOOD	GOOD	FAIR	FAIR	FAIR	FAIR
HFC-227ea	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	GOOD	GOOD
HCFC-22	FAIR	FAIR	FAIR	GOOD	FAIR	GOOD	GOOD	FAIR
HFC-134a	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	FAIR	GOOD
FC-116	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	FAIR	FAIR
HCFC-124	FAIR	FAIR	GOOD	GOOD	FAIR	GOOD	FAIR	GOOD
HFC-125	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	FAIR	FAIR
FC-218	GOOD	FAIR	GOOD	GOOD	FAIR	GOOD	FAIR	FAIR
FC-31-10	GOOD	FAIR	FAIR	FAIR	FAIR	FAIR	FAIR	FAIR
FC-318	GOOD	FAIR	GOOD	GOOD	FAIR	FAIR	GOOD	GOOD
$NaHC0_3$	FAIR	FAIR	GOOD	GOOD	FAIR	BAD	GOOD	FAIR

GOOD: NO SIGNIFICANT INTERACTION FAIR: MAY BE AN INTERACTION BAD: POSSIBLE PROBLEM

Storage Stability

Storing chemicals under high temperature and pressure accelerates both homogeneous reactions and heterogeneous interactions with the metal storage cylinders. These can promote the evolution of undesirable products and a concomitant loss of fire suppression effectiveness.

The most reliable way to assess storage stability of a chemical is by monitoring its degradation in the actual storage environment. Cylinders made of some of the metals were unavailable or extremely costly. Accordingly, in this project samples of each of the candidate agents were evaluated in pressurized, PTFE-lined, 1000 ml carbon steel cylinders. To simulate the interactions with actual storage bottle materials, each test cylinder contained 30 pieces (10.2 cm x 0.8 cm x 0.2 cm) of one of the 8 metals. The combined surface area of the pieces was comparable to the inside of a 1000 ml bottle. New metal pieces were used for each test. Blanks with no metal added were also run. While the 12 fluids in Table 1 and halon 1301 were studied, $NaHCO_3$ was not tested because it is stable under these storage temperatures and pressures. CF_3I was added to the test list.

Each vessel was filled to the saturation vapor pressure of a liquid agent at 22 °C and then pressurized with nitrogen to an initial pressure of 4.13 MPa (600 psi). FC-116 was available as a high pressure gas, and two other agents (HFC-125 and the azeotrope of HFC-32 and HFC-125) had saturation vapor pressures somewhat higher than the other agents. Therefore, these three were were filled to a pressure approximating the mass filled for most of the other agents. All vessels were then stored in an oven for 28 days at 149 °C (300 °F). These tests simulate degradation that might be expected over a far longer storage time under typical use.

After cooling to ambient conditions, an infrared (IR) spectrum of the aged sample was compared to a spectrum of the original sample [14]. Degradation of the sample would be indicated by a systematic decrease in the absorbance of peaks attributable to the agent and/or the appearance of new peaks in the IR spectrum of the aged agent. The absolute signals varied between the two analyses due to sensitivity to the alignment of the Fourier transform infrared (FTIR) spectrometer. Thus, the key indicator of degradation was the formation of new compounds evidenced in the spectra.

For both the initial and final analyses before and after the exposrure, a cooled cylinder was connected to the inlet of the gas cell on the FTIR system. The agent/N_2 mixture was introduced into the gas cell to an absolute pressure of 1330 ± 10 Pa (9.95 ± .05 torr). Three 3 spectra were taken for each sample.

For all 13 agents examined, no new peaks were observed in any of the spectra. To determine whether the peaks of new compounds were being masked by the peaks from the original compound, we examined the peak heights and areas of selected peaks in the spectra before and after the 28 day storage. Again, no new compounds were identified in any of the spectra for any of the agents.

For CF_3I, an initial spectrum and two later (8-day and 28-day) spectra were available. The peak areas systematically decreased over the four-week exposure, but the changes were likely within the experimental measurement error. Since no new compounds were observed in the CF_3I spectra, the possible degradation of CF_3I deserves further examination.

The metal coupons were removed from the cylinders and examined. Changes in their appearance are given in Table 4. When the metals from the CF_3I cylinders were removed, a dark solid was apparent on the coupons, and then disappeared within seconds, perhaps solid I_2 which then sublimed. For the other metals, visual changes may be due to the prolonged heating of the metal or to interaction with the agent. For the former, effects would be observed for all of the agents (for example, the Cu/Be C82500 coupons). Interaction with the agents is far more common, with some metals affected by only a few agents and others effected by nearly all of the agents. HCFC-22 and CF_3I affected most of the metals, while for others, only the Cu/Be C82500 coupons were affected.

Table 4. Visible Changes in Metals After 28-Day Exposures at 149°C (300°F)

Agent	304 stainless steel	Nitronic-40 (21-6-9)	Inconel 625	6061-T6 aluminum	4130 alloy steel	AM 350 stainless	Cu/Be C82500	13-8 Mo stainless
HCFC-22	✓[a]	✓	✓	✓	✓		✓	✓
HCFC-124							✓	
HFC-125							✓	
HFC-32/HFC-125							✓	
HFC-134a					✓		✓	
FC-218		✓		✓	✓		✓	
HFC-227ea					✓		✓	
FC-31-10		✓		✓	✓		✓	✓
FC-116					✓		✓	
FC-318	✓				✓		✓	
HFC-236fa							✓	
halon 1301							✓	
CF_3I	✓	✓	--[b]	✓	✓	✓	--	✓

a - ✓ indicates visible change in metal appearance after exposure
b - data not available

These results indicate that for these chemicals, stability in long-term storage should not be a major deciding factor in selection of agents for further study. However, pending further study, CF_3I could be an exception.

Elastomer Seal Compatibility

Excessive swelling or deterioration of the elastomer seal (o-ring) and its lubricant in the fire suppressant storage container could lead to leakage of the agent, leaving the system unready to respond in case of fire. The elastomers and lubricants examined in this study (Tables 5 and 6) reflect the types likely to be considered for storage bottle use. Both crosslinked and uncrosslinked elastomers were studied.

Table 5. Elastomers used in swelling experiments

Elastomer	Vendor	Designation
Silicone	Colonial Rubber	Si
55% Butadiene-45% Acrylonitrile	Goodyear	N206
Fluorosilicone	Colonial Rubber	FSi
Viton E-60 Fluorocarbon	Du Pont	FKM
Neoprene	Colonial Rubber	CR
85% Butadiene-15% Acrylonitrile	Goodyear	N926

Table 6. Lubricants used in swelling experiments

Lubricant	Vendor	Designation
Krytox 240AC Fluorinated Grease	Du Pont	240AC
Braycote 600 Perfluoropolyether Grease, Low Volatility	Castrol	600
Braycote 807 Aircraft Grease MIL-G-27617, Type IV	Castrol	807

Two types of measurements were conducted to determine the proclivity of candidate agents to alter the properties of various elastomers and greases and thus assist in the identification of appropriate seals for suppressant storage containers.

Swelling. The degrees of swelling of the greases and elastomers were each determined by measuring the displacement of a quartz spring using a cathetometer as in the

experimental arrangement illustrated in Figure 3. The 2.25 l pressure vessel had two 10.2 cm diameter glass view ports 180° apart for viewing and backlighting purposes. Inside was a stainless steel spring stand with 16 fused quartz spring and pan assemblies. Temperatures were maintained by immersing each vessel in a thermostatically-heated borosilicate jar filled with silicone oil.

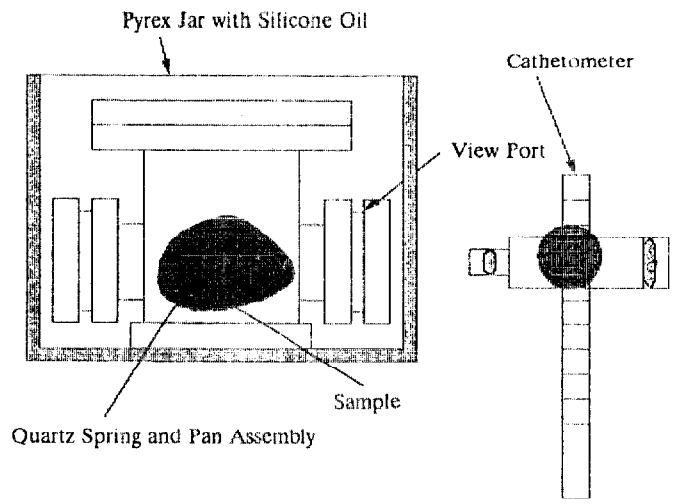


Figure 3. Schematic of the experimental apparatus for isopiestic swelling measurements

Swelling measurements were taken at four vapor pressures at 35, 70, 105, and 150 °C. FC-116 was also tested at 5 °C (p^o=2.133 MPa) because this fluid has a low critical temperature (T_c = 19.7 °C) and little swelling was observed at temperatures above T_c. The maximum pressure considered was 5.86 MPa. Saturation pressures for each temperature were determined using thermodynamic properties software [15],[16] or vendor-supplied data [17],[18],[19],[20].

The elastomer's or grease's mass uptake of the agent (solvent) was calculated from the relative displacement of the springs. Values of χ [21] for the various polymer/agent mixtures were then calculated from:

$$\ln(p/p^o) = \ln(1 - w_2) + w_2 + \chi_0 w_2^2 + \chi_1 w_2^3, \quad (1)$$

where p^o is the saturation pressure of the solvent, and w_2 is the polymer weight fraction [22].

The χ (= $\chi_0 + \chi_1$) values were used to characterize the compatibility of the solvents (agents) with the polymers (elastomers and greases). The maximum swelling occurred for exposures at 35 °C, and thus these data were used in the analysis. Small χ values correspond to good solubility or, for present purposes, bad compatibility.

Table 7. Compatibility of lubricants and crosslinked elastomers based on swelling measurements in various fluorocarbon agents at 35 °C

Agent	240AC	600	807	Si	N206	FSi	FKM	CR	N926
HFC-236fa	good[a]	good	good	fair[b]	fair	bad[c]	bad	bad	bad
HFC-32/125	good[f]	good	good[f]	fair	good[f]	good	good	good	good[f]
HFC-227ea	fair[e]	fair	fair[f]	fair[e]	good[f]	fair[e]	fair[f]	good[e]	bad
HCFC-22	fair	good	fair	fair	bad	fair	fair	good	bad
HFC-134a	good	fair	good	fair	good	fair	good	good[f]	good
FC-116[d]	fair	fair	fair	good[e]	good[f]	good	good	good[f]	good[f]
HCFC-124	good[f]	good[f]	good	bad[f]	fair[f]	fair[f]	fair[f]	fair[f]	fair[f]
HFC-125	fair	good	good	good	good	good	fair	good	good
FC-218	good[f]	good	good	good	good	good	good	good	good
FC-31-10	fair	bad	bad	fair	fair	good	fair	good	fair
FC-318	fair	fair	fair	good	good	good[e]	good	good	fair

[a] $\chi > 1.2$
[b] $0.9 \leq \chi \leq 1.2$
[c] $\chi < 0.9$
[d] measured at 5 °C
[e] $12.5 < CV < 20\%$ and $0.64 < \chi < 1.5$
[f] $CV > 20\%$

Ratings (Table 7) were defined based on the values of χ parameters obtained from swelling measurements at 35 °C, where the swelling was the largest. Good compatibility ($\chi > 1.2$, $w_1 < 0.22$) implies that an elastomer or lubricant is acceptable for use in the fire suppressant system. Bad compatibility ($\chi < 0.9$, $w_1 > 0.38$) corresponds to excessive swelling. For values of $0.9 < \chi < 1.2$, the agent was considered to have fair compatibility with the elastomer or grease and represents a marginally acceptable system.

Durability. These measurements produced data on residual mechanical (rheological) properties of the elastomers and greases, determining their ability to maintain their elasticity. Ratings were based on the results of compression set and tensile test measurements of the elastomers and viscosity measurements of the greases. These tests provide direct information on the physical and chemical damage to the samples at extreme conditions. It is important to note that the long term exposure response of these materials cannot be extracted from the tests as performed.

The mechanical property measurements of the elastomers and greases were obtained after 1-, 2-, 4- and 6-week exposures to the agents at the extreme conditions of 150 °C and 5.86 MPa. The two pressure vessels were similar to those used for the swelling measurements, but without view ports. Inside each vessel was a compression set fixture with samples of the 6 elastomers, and a 2 ml vial for each of the three greases. The vessel was heated using a forced air oven. The o-rings used in this study were Parker size no. 2-214 and are listed in Table 8.

Table 8. Elastomers used in durability experiments

Elastomer	Vendor	Designation
Silicone	Parker	S604-70[a]
Nitrile (standard industrial)	Parker	N674-70
Fluorosilicone	Parker	L1120-70
Fluorocarbon	Parker	V1164-75
Neoprene	Parker	C1185-70
Nitrile (low temperature industrial)	Parker	N103-70

[a]The number following the dash in the designation (compound number) represents the Shore hardness of the elastomer.

The compression set tests were conducted per standard test methods [23],[24]. The compression set C_B was calculated using the average thickness readings before and after the exposure and was expressed as a percentage of the original deflection. Bad compatibility was defined as a condition when the compression set exceeded 90% after a 2 week exposure. Elastomers have good compatibility if the compression set was less that 90% after 4 weeks. Fair compatibility (marginally acceptable) meant that the compression set was less than 90% after 2 weeks but exceeded 90% after a 4-week

exposure. If a specimen was split or broken, the agent was considered to have bad compatibility with the elastomer.

Tensile tests were conducted per standard test methods [25]. For each agent, ultimate elongation, tensile stress, and modulus measurements were taken after 1-, 2-, 4-, and 6-week exposure times at 150 °C and 5.86 MPa. A type TT-B Instron tensile testing instrument was used for this purpose. The force F was recorded at rupture and at an elongation of 100% (if the ultimate elongation exceeded 100%). If the o-ring could not be installed without breaking the specimen because of embrittlement due to the high temperature exposure, the specimen was considered to have a 100% decrease in ultimate elongation.

The elastomers were then rated as follows. Bad compatibility was defined as

Table 9. Compatibility of elastomers and lubricants based on durability ratings (G = good, F = fair, B = bad)

Agent	240AC	600	807	S604-70	N674-70 (N206)	L1120-70	V1164-75	C1185-70	N103-70 (N926)
HFC-236fa	G[a]	G	G	G (F)[b]	B (F)	G (B)	B	B	B
HFC-32/125	G	G	G	G (F)	B (G)	B (G)	B (G)	F (G)	B (G)
HFC-227ea	B (F)	G (F)	G (F)	G (F)	B (G)	G (F)	B (F)	F (G)	B
HCFC-22	B (F)	B (G)	F	B (F)	B	G (F)	B (F)	B (G)	F (B)
HFC-134a	B (G)	B (F)	B (G)	G (F)	B (G)	G (F)	B (G)	F (G)	B (G)
FC-116	F	G (F)	G (F)	G	F (G)	G	B (G)	G	B (G)
HCFC-124	G	G	G	B	B (F)	G (F)	B (F)	B (F)	B (F)
HFC-125	G (F)	G	G	G	B (G)	B (G)	B (F)	G	B (G)
FC-218	B (G)	B (G)	B (G)	G	F (G)	G	B (G)	G	B (G)
FC-31-10	B (F)	B	B	G (F)	B (F)	F (G)	B (F)	F (G)	B (F)
FC-318	B (F)	B (F)	B (F)	G	F (G)	G	G	G	F

[a]If the ratings for compression set and tensile testing were different, the worse compatibility is listed
[b]If different, the rating for swelling compatibility (Table 7) is listed in parentheses

the decrease in ultimate elongation exceeding 65% after a 2 week exposure. Good compatibility meant the decrease was less that 65% after 4 weeks. If the decrease in ultimate elongate was less that 65% after 2 weeks but exceeded 65% after a 4-week exposure, the agent was considered to have fair compatibility with the elastomer and represents a marginally acceptable system.

The rheological properties of each grease were characterized using a Rheometrics Mechanical Spectrometer Model 800. The viscosity of the greases, when measurable, did not show systematic variation with exposure time, indicating that no significant chemical degradation occurred. However, mobile substances or fractions were extracted by some of the candidate fire suppressant fluids, resulting in the

greases becoming powder-like, *i.e.*, their viscosities were not measurable. Therefore, the ratings for the lubricant compatibility were based on the following criteria. Good compatibility meant the grease did not become powder-like after a 6 week exposure. Bad compatibility meant the grease became powder-like after a 4 week exposure. Fair compatibility meant the grease's viscosity was measurable after 4 weeks, but became powder-like after 6 weeks.

Table 9 shows the compiled compatibility of the elastomers and lubricants. It is clear from the results of the durability testing that the 150 °C condition is too severe, *i.e.*, property changes for the most part were extreme. Further testing at lower temperatures will be required to provide better estimates of elastomer and lubricant durabilities. However, the data show that there are elastomer materials and lubricants that are suitable for use with each tested suppressant.

Conclusion

Procedures have been developed for appraising the mutual stability of fire suppressant chemicals and the materials of their storage containers. These methods are capable of differentiating among chemicals, elastomers and greases, and metals on the basis of their performance in close simulations of actual storage. In general, there are storage materials available for any of the 13 tested candidate suppressants, although the choices are more restrictive for some of the chemicals.

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Literature Cited

1. Zallen, D.M., Halon Replacement Study, SBIR Report No. ZIA-92-001 to Aeronautical Systems Division, Wright-Patterson AFB, Zallen International Associates, Albuquerque, February 28, 1992.
2. Purdue Research Foundation and Department of Chemistry, Final Report on Fire Extinguishing Agents, AD 654322, Purdue University, West Lafayette, IN, July 1950.
3. Pitts, W.M., Nyden, M.R., Gann, R.G., Mallard, W.G., and Tsang, W., "Construction of an Exploratory List of Chemicals to Initiate the Search for Halon Alternatives," NIST Technical Note 1279, National Institute of Standards and Technology, Gaithersburg, MD, August 1990.
4. Sheinson. R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants," *Fire Safety Journal 15*, 437-450 (1989).
5. Tapscott, R.E., Moore, J.P., Lee, M.E., Watson, J.D., and Morehouse, E.T., Next Generation Fire Extinguishing Agent Phase III, ESL-TR-87-03, Air Force Engineering and Services Center, Tyndall AFB, FL, April 1990.
6. Grosshandler, W.L., Gann, R.G., and Pitts, W.M., eds., *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*, NIST Special Publication 861, National Institute of Standards and Technology, Gaithersburg, MD, 1994.
7. Gann, R.G., Barnes, J.D., Davis, S., Harris, J.S., Harris, Jr., R.H., Herron, J.T., Levin, B.C., Mopsik, F.I., Notarianni, K.A., Nyden, M.R., Paabo, M., and

Ricker, R.E., "Preliminary Screening Procedures and Criteria for Replacements for Halon 1211 and 1301," NIST Technical Note 1278, August 1990.

8. ASTM, Standard Practice for Laboratory Immersion Corrosion Testing of Metals, *Annual Book of ASTM Standards Section 3, Metals Test Methods and Analytical Procedures*, Phil., PA, 1993.
9. ASTM, Standard Guide for Applying Statistics to Analysis of Corrosion Data, *Annual Book of ASTM Standards Section 3, Metals Test Methods and Analytical Procedures*, Phil., PA, ASTM, 1993.
10. Romans, H. B., and H. L. C., Jr., "Atmospheric Stress Corrosion Testing of Aluminum Alloys," *Metal Corrosion in the Atmosphere*, Boston, MA, ASTM, 1967.
11. Scully, J. R., Frankenthal, R. P., Hanson, K. J., Siconolfi, D. J., and Sinclair, J. D., "Localized Corrosion of Sputtered Aluminum and Al-0.5% Cu Alloy Thin Films in Aqueous HF Solution: II. Inhibition by CO_2," *J. Electrochem. Soc.*, 137, 1373-1377, 1990.
12. Scully, J. R., Peebles, A. D., Romig, A. D., Frear, D. R., and Hills, C. R., "Metallurgical Factors Influencing the Corrosion of Aluminum, Al-Cu, and Al-Si Alloy Thin Films in Dilute Hydrofluoric Solution," *Metallurgical Transactions A* 23A, 2641-2655, September 1992.
13. Stoudt, M. R., Vasudévan, A. K., and Ricker, R. E., "Examination of the Influence of Lithium on the Repassivation Rate of Aluminum Alloys," *Corrosion Testing of Aluminum Alloys*, San Francisco, CA, ASTM, Phila., PA., 1990.
14. Willis. H.A., Van der Maas, J.H., and Miller, R.G.J. (eds.), *Laboratory Methods in Vibrational Spectroscopy*, John Wiley & Sons, New York, 1987.
15. Gallagher J., McLinden, M., Huber, M., and Ely, J., *NIST Standard Reference Database 23: Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 3.0*, U.S. Department of Commerce, Washington, DC (1991).
16. Allied Signal, Inc., *Thermodynamic Properties of Refrigerants (Genie)*, SML Services, Inc. (1989).
17. E.I. du Pont de Nemours and Co., Inc., *Thermodynamic Properties of "Freon" 116 Refrigerant*, (1968).
18. E.I. du Pont de Nemours and Co., Inc., *Thermodynamic Properties of HFC-236fa Refrigerant*, (1993).
19. Robin, M.L., *Thermodynamic and Transport Properties of FM-200*, Great Lakes Corporation (1992)
20. Wilson, L.C., Wilding, W.V., and Wilson, G.M., *Thermo-Physical Properties of Perfluorobutane*, Wiltech Research Company (1992).
21. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953).
22. McKenna, G.B. and Crissmann, J.M., "Thermodynamics of Crosslinked Polymer Networks: The Anomalous Peak in Swelling Activity Measurements," *Macromolecules 1992*, ed by J. Kahovec, VSP, Utrecht, The Netherlands, pp. 67-81 (1993).
23. ASTM, Designation D 395-89, "Standard Test Methods for Rubber Property - Compression Set," *Annual Book of ASTM Standards*, **09.01**, 24 (1989).
24. ASTM, Designation D 1414-90, "Standard Test Methods for Rubber O-Rings," *Annual Book of ASTM Standards*, **09.02**, 181 (1990).
25. ASTM, Designation D 412-87, "Standard Test Methods for Rubber Properties in Tensions," *Annual Book of ASTM Standards*, **09.02**, 100 (1990a).

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