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The Use of Halons as Fire Suppressants—A Literature Survey

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The literature on the use of halons as fire suppressants is reviewed. Specific areas covered are:

- The decomposition of halons thermally and catalytically in fire situations;
- The effects of fire, halon concentration, and environmental factors such as temperature and humidity on corrosion rates;
- The corrosion effects of halons on diesel engines, sensitive instruments, electronic components, and computer materials.

A bibliography on the toxicology of halons is included in the report.

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CONTENTS

THE USE OF HALONS AS FIRE SUPPRESSANTS – A LITERATURE SURVEY

INTRODUCTION

This report is a survey of literature concerned with the use of halons as fire suppressants. The project is sponsored by the United States Coast Guard and supplements the Navy's experimental Fire Extinguishant Program. The purpose of the report is to outline the work which has been done on specific problems involved in the use of halons to control fires. This compilation, when combined with a listing of current projects, will show the areas which have been studied and will be an aid in the selection of problems to be investigated in the future.

HALON NOMENCLATURE

Halogenated hydrocarbons or halons are designated in a number of different ways. In addition to their chemical names and formulas, they can be designated by proprietary names and numbers and by halon numbers. The halon system which was devised by the U.S. Army Corps of Engineers provides a convenient way to refer to fire extinguishing agents and will be used in this report. The first digit in the halon number refers to the number of carbon atoms in the molecule of the compound. The second, third, and fourth digits refer to the number of fluourine, chlorine, and bromine atoms, respectively. It is assumed that hydrogen satisfies the valence requirements not accounted for by the number. For example, bromochloromethane (CH_2BrCl) is halon 1011.

As used in this report, the term "decomposition products" refers to the compounds which result from reactions of the halon, and the term "combustion products" refers to the compounds which result from reactions of fuel molecules. In the ordinary fire situation the products may be either of these types or a combination of both. Generally it is impossible to differentiate between the two types.

SCOPE

There are a very great number of halogenated hydrocarbons, but only a few have been used as fire extinguishants. In the past, halons 1040 (carbon tetrachloride), 1011 (bromochloromethane), and 1001 (methyl bromide) have been so used, but they are now considered to be too toxic for such use. According to Jensen [26]*, at present four halons are potentially useful as fire extinguishants. They are halon 1202 (dibromodifluoromethane or CBr_2F_2), halon 1211 (bromochlorodifluoromethane or $CBrClF_2$), halon

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*References are listed in alphabetical order according to author or identifying name.

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1301 (bromotrifluoromethane or $CBrF_3$), and halon 2402 (dibromotetrafluoroethane or $CBrF_2$-$CBrF_2$). However, the National Fire Protection Association has adopted no standards for halons 2402 and 1202 and only tentative standards for halon 1211. Standards have been adopted for halon 1301, which is the only halogenated fire extinguishing agent currently being applied on a wide commercial scale in the United States [26]. It is classified by the National Fire Protection Association as being less toxic than carbon dioxide [39].

This review of literature on halons used as fire extinguishants covers the following specific subjects:

- The decomposition of halons thermally and catalytically in fire situations.
- The effects of fire, halon concentration, and environment (temperature, humidity, and ambient oxygen content) on corrosion rates.
- Corrosion effects of halons on diesel engine parts, sensitive instruments, electronic components, and computer materials.

In addition, a bibliography on the toxicity of halons used as fire extinguishants is included.

In this survey the authors reviewed the material already on hand at the Naval Research Laboratory; this included various government and industrial reports and technical manuals of E. I. du Pont de Nemours & Company, Underwriters' Laboratories, Inc., and the National Fire Protection Association. Also included were the proceedings of a symposium on "An Appraisal of Halogenerated Fire Extinguishing Agents" held at the National Academy of Sciences in Washington, D.C., on April 11-12, 1972. These proceedings presented an assessment of the status of halons as fire suppressants and included many references. It is thought that the NRL material on hand, with its references, covers most of the significant work which has been done in the field before 1972.

In addition to the literature described above, that listed below was searched with the aid of the Naval Research Laboratory library's information retrieval service:

1. *Chemical Abstracts* was searched from 1972 to present.

2. COMPENDEX was searched from 1972 to present. This index, prepared by Engineering Index, Inc., provides world-wide coverage of engineering literature.

3. SCISEARCH was searched from 1974 to present. SCISEARCH published by the Institute for Scientific Information, is an index to the literature of science and technology.

4. National Technical Information Service (NTIS) was searched from 1964 to present. NTIS has announcements covering all the research of over 240 government agencies.

From all of these sources more than 350 references were collected. This list was reduced to approximately 100 by reading the reports, or their abstracts, and eliminating those outside the field of interest. This reduced list of documents includes 43 which are reviewed below and 58 which comprise the bibliography on the toxicology of halogenated fire suppressants.

DECOMPOSITION TEMPERATURE OF HALONS

A number of sources have published information on the thermal decomposition of halon fire extinguishants (halon 1301, for the most part) under various conditions. The decomposition temperature of halon 1301 is given as approximately 950°F (510°C) by Jensen [26]. For halon in contact with hot surfaces or flames this temperature is given as above 900°F (482°C) by NFPA Bulletin No. 12A-1971 [39]; and as above 950°F (510°C) by Ford [22] and by Du Pont Bulletin No. B29C [11]. Du Pont Bulletin No. S-35A [13] reports this decomposition temperature as above 1000°F (538°C) for halon in contact with hot surfaces or flames. Engibous and Torkelson [14] show that the decomposition of halon 1301 in contact with stainless steel starts at 1022°F (550°C) and that of halon 1211 under the same conditions at 932°F (500°C).

Musick [37] detected no sign of decomposition of halon 1301 in contact with stainless steel at 698°F (370°C) nor of halon 1211 at 600°F (316°C) [36].

THERMAL DECOMPOSITION OF HALONS

The theoretical decomposition products of halons are listed and described by NFPA Bulletins Nos. 12A-1971 [39] and 12B-T [40], Du Pont Bulletins Nos. B-29C [11] and S-35A [13], and by Engibous and Torkelson [14]. These products are the free halogens (except for fluorine, which, because of its high reactivity, probably would not be found in its free state), the halogen acids, and the carbonyl halides. For example, if a halon molecule contained one or more atoms of chlorine (Cl_2), its decomposition products could include Cl_2, hydrogen chloride (HCl), and carbonyl chloride or phosgene ($COCl_2$) in addition to analogous compounds of any other halogen atom present in the molecule.

When halon 1301 is applied to cellulosic fires, the flames (gas-phase reactions) are promptly extinguished, but the deep-seated combustion (glowing or gas-solid reactions) may continue, as is shown by Fielding, Woods, and Johnson [17]. Toxic carbon monoxide (CO) is produced by the deep-seated combustion because the halon 1301 inhibits the oxidation of the CO.

Treon, et al. [42] and Du Pont Bulletin No. S-35A [13] give the concentrations of the thermal decomposition products produced when purified halon 1301 was passed through an Inconel tube at 1300°F (704°C) and 2000°F (1093°C). Concentrations of 2% and 0.75% halon 1301 in air were used, and total bromides as HBr, total oxidants as Br_2, and total carbonyl halides as $COBr_2$ were measured. The method of analysis was not given by Ref. 13, and the original report [42] was not obtainable. However, the method of reporting suggests that the concentrations were measured by means of wet chemical analysis.

The concentrations of the decomposition products as reported in Refs. 42 and 13 are given in Table 1.

Engibous and Torkelson [14] measured the percent of decomposition of five halogenated fire extinguishants over a range of temperature of 617°F (325°C) to 1472°F (800°C). The five compounds were halon 1011 (CH_2BrCl), halon 1202 (CBr_2F_2), halon 1211 ($CBrClF_2$), halon 1301 ($CBrF_3$), and halon 2402 ($CBrF_2$-$CBrF_2$). In this work, a

Table 1 — Concentrations of Decomposition Products for Halon 1301

Decomposition Product	0.75% Halon 1301 at 1300°F (704°C) (ppm)	2% Halon 1301 at 2000°F (1093°C) (ppm)
HBr	8	151
HF	34	2725
Br_2	11	1466
$COBr_2$	5	1955

mixture of 2.5 vol% of the halon in dry air was passed through a stainless steel pyrolysis tube. The most stable of the five compounds was halon 1301, which began to decompose at about 1022°F (550°C) and was 70% decomposed at 1454°F (790°C). The analyses were made by wet chemical methods; the gases were absorbed in appropriate solutions and titrated for chloride and bromide ions. It is possible that the products, or their amounts, would differ markedly in the presence of moist air.

MacEwen [32] reports the concentrations of "pyrolysis" products generated by the "pyrolysis" of halon 1011 and halon 1301 in a hydrogen-oxygen flame at 1472°F (800°C). The atomizer-burner assembly of a hydrocarbon analyzer was used, and the temperature was controlled by adjusting the fuel ratio. Halon 1011 at a concentration of 2000 ppm produced 380 ppm of hydrogen chloride (HCl) and 23 ppm of hydrogen bromide (HBr), whereas in another measurement, 3000 ppm of the halon produced 45 ppm of bromine (Br_2). Halon 1301 at a concentration of 3800 ppm "pyrolized" to produce 2370 ppm hydrogen fluoride (HF), 160 ppm HBr, and 236 ppm Br_2. MacEwen gives little information on the methods of analysis used. In one table of data, he indicated that bromine was analyzed by both a volumetric method and a spectrophotometric method.

Typical maximum concentrations of the combustion and decomposition products which result from the use of halon 1301 in fire tests are given by Ford [23] as 200 to 300 ppm of HF and 40 to 50 ppm of HBr.

Class A fires of paper, cotton, and nylon sheeting in a 216-ft^3 (6100-ℓ) chamber were extinguished by total flooding with halon 1301, a result reported by Kuchta, Cato, Martindill, and Spolan [30] and by Botteri, Cretcher, and Kane [1]. A 6% halon concentration was adequate for rapid extinguishment of the fires at fuel loadings of 0.018 to 0.07 oz/ft^3 (0.018 to 0.07 g/ℓ). Toxic products (HF, HBr, and CO) varied with preburn time, combustible loading, and extinguisher discharge mode. The highest concentrations of toxic products (HF and HBr) occurred with paper sheeting, which burned at the highest rate and produced the largest fires. A paper loading of 0.035 oz/ft^3 (0.035 g/ℓ) produced 800 ppm HF and 190 ppm HBr. Samples of the combustion gases were absorbed in water, and the HF and HBr concentrations were determined electrometrically by means of ion-specific electrodes. Other combustion products (carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen, and methane) were analyzed by conventional gas chromatographic techniques. Similar data from small-scale experiments with halon 3800 (C_3F_8 or perfluoropropane) in a 12-ft^3 (340-ℓ) chamber are presented by Kuchta, Cato, Martindill, and Spolan [30].

Cato, Martindill, and Kuchta [5] reported that 10 to 12 vol% halon 3800 was required to extinguish fires of cotton and paper sheeting in the 216-ft^3 (6100-ℓ) chamber and produced up to 2500 ppm of HF. In another study, Martindill, Spolan, and Kuchta [33] measured the concentrations of HF and HBr resulting from the decomposition of halon 1301 used in extinguishing fires of cotton sheeting and expressed them as functions of preburn time.

Gassmann and Marcy [24] report the concentrations of toxic gases produced in tests of halon 1301 used to extinguish fires of polyurethane seat foam and wool drapery in a closed 640-ft^3 (18,000-ℓ) insulated enclosure simulating an airplane cabin. Using colorimetric tubes, they measured gas concentrations as high as 150 ppm HCl, 15 ppm HF, 10 ppm HCN, 20 ppm NH_3, 8 ppm Cl_2, 50 ppm Br_2, and 1.5 ppm $COCl_2$.

Ford [21,22] reported a fire test program in which four different companies (the Ansul Company, Cardox—a Division of Chemetron Corporation—Du Pont Corporation, and Ferwal, Inc.) participated to test halon 1301 as an extinguishant for computer room fires. Concentrations of HF and HBr produced by both surface and deep-seated fires of stacked printout paper, polyester-base magnetic tape, polyethylene and polystyrene components, paper punch tape, shredded paper, and data tabulating cards in various configurations were measured. Also, concentrations of HCl from fires of polyvinyl chloride were measured. Surface fires of polyethylene and polystyrene produced HF and HBr concentrations below 100 ppm, and fires of stacked printout paper, extinguished with 5.1 vol% of halon 1301, produced less than 20 ppm each of HF and HBr. For deep-seated fires of polyester-base magnetic tape, printout paper, tabulating cards, and paper punch tape, maximum individual HF and HBr concentrations in all tests did not exceed 150 ppm. Concentrations of HF, HBr, and CHl were determined electrometrically by measuring with ion-specific electrodes.

Jensen [26] reports the results of tests made by the Ansul Company to acquire data concerning the extinguishment of fires involving computer materials. In these tests 5.1% to 21% of halon 1301 was used to extinguish the fires, and 0-33 ppm HF and 0-26 ppm HBr were produced. These appear to be the same tests as those reported by Ford [22].

Cholin [6] reports the results of 24 tests in which halon 1301 was used to extinguish Class A and B fires in enclosures of 336-ft^3 (9500-ℓ) and 2000-ft^3 (57,000-ℓ) volume. Measurements of concentrations of HF and HBr in the post-extinguishment atmospheres from fires of alcohol, cotton, fur, and several types each of paper, wood, and plastic were made. Except for one fire which was allowed to burn itself out, the maximum concentrations of decomposition and combustion products measured were 38 ppm HF and 79 ppm HBr. The methods of analyses were not reported.

Carey and Haas [3] measured the HF and HBr concentrations resulting from using halon 1301 to extinguish Class A and B fires of shredded newspaper, bond paper, carbon paper, and alcohol in a 2100-ft^3 (60,000-ℓ) room. Measured concentrations varied from 2 to 116 ppm HF and 2 to 38 ppm HBr. The analyses were made by measuring the fluoride and bromide ion concentrations in buffered aqueous solutions of samples of the gas. These same tests are also reported by Cholin [7].

Practical fire extinguishment tests in which gasoline, ethyl alcohol, and wood fires were extinguished with halon 1301 applied from a portable extinguisher were conducted at Underwriters' Laboratories and are reported by Dufour [9] and in Du Pont Bulletin No. S-35A [13]. The amount of halon 1301 applied to the fires varied from 0.4 to 2.5 lb., and the time to extinguish the fires ranged from 3 to 10 min. Concentrations of HF as high as 289 ppm, HBr 9 ppm, Br_2 7 ppm, and carbonyl halides 34 ppm were measured. The methods of analyses are not given by Ref. 13, and the original report [9] was not available.

Floria [19] and Ford [21] report studies to determine the effects of fire size, fire preburn time, and agent discharge time on the quantities of decomposition and combustion products formed by a fire. They used halon 1301 to extinguish n-heptane fires in a 1695-ft^3 (48,000-ℓ) enclosure. Minimum HF and HBr concentrations were realized when the fire pan size and preburn time were minimized and the fires were extinguished rapidly. No bromine was detected in any of the tests. Analyses were made by determining the concentrations of the fluoride and bromide ions electrometrically and the concentration of bromine by titration.

Floria [18,20] also used halon 1301 on n-pentane fires to study the relationship between quantities of decomposition and combustion products produced and the halon discharge rate. Halon acid concentrations increased irregularly to a maximum (215 to 230 ppm HF and 20 to 27 ppm HBr) in 18 to 24 s, after which they decreased with time. These concentrations were measured electrometrically with ion-specific electrodes.

Yamashika [43] analyzed the results of a series of fire extinguishing tests with halogenated agents applied to both open and enclosed fires. He used a formula expressing the relationship between the application rate of the extinguishant and the extinction time of the fire. Fuels were hexane, wood crib, charcoal, paper, rubber, and plastics, and extinguishants were halons 1011, 2402, 1301, and 1211. The concentrations of hydrogen halides produced decreased as the application rate of the extinguishant increased. Gas chromatography was used to analyze halons and carbon oxides, whereas the titration method was used to analyze the hydrogen halides.

Six full-scale tests in which halon 1301 was used to extinguish fires of diesel fuel in the 100,000-ft^3 (2,800,000-ℓ) machinery space of a ship (M/V *Rhode Island*) are described by McDaniel [35]. Halon concentrations varied from 3.39 to 5.65% and discharge times from 7 to 28 s. Temperatures in the compartment ranged from 212°F (100°C) to 2084°F (1140°C). For all the tests except the one using the 28-s discharge time, maximum HF concentration measured was 12 ppm, and maximum HBr concentration was 3 ppm. In the 28-s discharge test, concentrations of 230 ppm HF and 68 ppm HBr were measured. Halon 1301 was analyzed by gas chromatography, and HF and HBr by a method using ion-specific electrodes to measure the concentrations of fluoride and bromide ions.

Browne and Szczepanski [2] measured the concentrations of HF, HBr, and Br_2 in the stack gases resulting from feeding air containing up to 7.5% of halon 1301 into the firebox of a marine DDG-15 main propulsion boiler. The results of the gas analyses varied widely (36 to 89,000 ppm of HF, 17 to 20,000 ppm of HBr, and 153 to 1260 ppm of Br_2), possibly because the stack gases were not well mixed. The method of analysis was not given but was to be treated in a separate report.

The smokes generated by burning Aerozine-50 propellant [51 wt% of hydrazine (N_2H_4) and at least 47 wt% unsymmetrical dimethylhydrazine (UDMH)] in a halon 1301-air atmosphere were analyzed by Kuchta and Burgess [29]. The smokes were collected on glass cloth filters and analyzed for carbon, hydrogen, nitrogen, fluorine, and bromine. A substantial amount of fluoride was present in the smokes. Gas chromatography and x-ray diffraction were used in making the analyses.

Sayers [41] gives the concentrations of decomposition and combustion products produced when 3 pounds of halon 1211 were used to extinguish a 2.5-ft^2 (0.23 m^2) fire of n-heptane in a 2500-ft^3 (71,000-ℓ) room. They were 2 ppm of HCl and HBr, 0.5 ppm of HF, less than 0.1 ppm Cl_2 and Br_2, and less than 0.25 ppm of $COCl_2$. The methods of analyses were not described.

Matson and Dufour [34] report the results of tests made to determine the decomposition and combustion products of chlorobromomethane in the presence of hot iron surfaces, electric arcs, gas flames, and fires of gasoline, ethyl alcohol, and wood. In all cases, significant quantities of halogen acids and carbonyl halides were produced, and, in some cases, free chlorine and bromine were also detected. For example, 5% by volume of chlorobromomethane in air in contact with an iron surface at 1022°F (550°C) produced 2709 ppm HCl, 1267 ppm HBr, 1298 ppm Cl_2, 38 ppm Br_2, and 33 ppm carbonyl halides. The analyses were made by wet chemical methods.

A few typical tests selected from the considerable number reviewed above are summarized in Table 2. In all of these tests, Class A or B fires were extinguished by the application of halons (halon 1301 in most cases). In tests where analyses of decomposition and combustion products were made at different locations and different times, the maximum concentrations measured are presented in the table. Although the conditions of the tests vary, these variations do not adequately explain the wide variations in the concentrations of the decomposition and combustion products. Further, as shown by the blank spaces in the table, some of the test reports do not specify some of the important test conditions.

In expressing the yields of decomposition products, it should be pointed out that ppm means little unless precise experimental conditions, such as ventilation rate, room size, burning rate, and fuel consumed, are known. If these parameters are known, then ppm data can be translated from one fire situation to another but not rigorously, as we do not know enough about scaling such parameters. A better way to present these data is by milligrams of specific contaminant vs grams of fuel consumed. The contaminant concentration is still markedly dependent on fire conditions, but the latter units make it easier to translate from one experiment to another.

CATALYTIC DECOMPOSITION OF HALONS

The resistance to catalytic decomposition of a fire extinguishant is important if it is to be used in an atmosphere which is treated by a catalytic burner. Any halon vapor in such an atmosphere would be subjected to strong catalytic action. The Naval Research Laboratory has investigated the catalytic decomposition of a number of halons, most of which are not considered to be fire extinguishants, but no information on this subject from other sources was found.

Table 2 — Summary of Results of Typical Tests of Halon Extinguishants on Class A and B Fires

Author and Ref. No.	Class of Fire	Type Halon	Fuel		Encl. Vol. (ft^3)	Halon Application		Exting. Time (s)	Maximum Concentration (ppm)					Method of Analysis
			Type	Load		Amt. Vol%	Time (s)		HF	HBr	HCl	Br_2	$COCl_2$	
Carey, et al. (3)	B	1301	Alcohol	2.5 ft^2	3,200	3.7	7	7	116	38	—	—	—	Electrometric
Cholin (6)	A	1301	Wood	50 pc 2" X 2" X 19"	336	5 *	—	—	14.7	9.8	—	—	—	—
Cholin (6)	A	1301	PVC	—	2,000	3.8	—	—	2.3	1.5	—	—	—	—
Dufour (9)	B	1301	Gasoline	—	—	2.3*	104	104	230	2	—	1	16(1)	—
Floria (19)	B	1301	n-Heptane	1 ft^2	1,695	4	13.5	12.6	243	41	—	< 0.3	—	Electrometric and titration
Ford (22)	A	1301	Polystyrene	—	1,536	3	1.2	—	29	27	—	—	—	Electrometric
Ford (22)	A(2)	1301	Paper	—	1,729	5.1	2	—	14	5	—	—	—	Electrometric
Gassmann, et al. (24)	A	1301	Urethane	10 lb	640	—	—	—	8	—	75	5	0.8	Detector tubes
Kuchta, et al. (30)	A	1301	Paper	0.035 oz/ft^3	216	6	—	—	700	80	—	—	—	Electrometric
Kuchta, et al. (30)	A	1301	Cotton	0.035 oz/ft^3	216	6	—	—	60	4	—	—	—	Electrometric
McDaniel (35)	B	1301	Diesel Fuel	—	100,000	4.4	7	—	9.6	2.6	—	—	—	Electrometric
Cato, et al. (5)	A	3800	Paper	0.035 oz/ft^3	216	11.9	—	0.6	1470(3)	—	—	—	—	Electrometric
Matson, et al. (34)	A	1011	Wood	0.85 lb	735(4)	2.5	—	—	—	251	969	< 1	34(1)	Wet chemical
Sayers (41)	B	1211	n-Heptane	2.5 ft^2	2,500	3 *	—	—	0.5	1(5)	1(5)	< 0.1(6)	< 0.25	—

(1) Analysis includes all carbonyl halides
(2) Deep-seated fire
(3) Total fluorides reported as HF
(4) Unit of volume in $in.^3$
(5) Analyzed as 2 ppm total halides
(6) Analyzed as total free halogens
A dash indicates that the report did not present this information.

*Pounds

Christian and Johnson [8] measured the extent of decomposition of halon 2402 ($CBrF_2$-$CBrF_2$) in addition to that of several other halons of less interest to this survey. When mixed with air and passed over hopcalite* at 315°C, the halon 2402 was decomposed to the extent of 30%. The analyses were made by gas chromatography.

Johnson and Gammon [27] studied the catalytic decomposition of four halons, and Johnson and Musick [28] studied eleven others, but none of these compounds are considered to be potential fire extinguishants.

The decomposition of halon 1301 by hopcalite catalyst at 700°F (370°C) was reported as 3% or less [37] and that of halon 1211 by hopcalite at 600°F (316°C) as 5% or less by Musick [36]. These measurements were made by gas chromatography.

Some of the above work on catalytic decomposition is reported by Carhart and Fielding [4], and all of it is summarized by Musick and Williams [38].

THE EFFECTS OF HALONS ON CORROSION RATES

Du Pont Technical Bulletin B-4 [12] reports corrosion tests in which steel, brass, and aluminum were separately exposed to both wet and dry halon fire extinguishing liquids at 248°F (120°C) for 260 days. The extent of decomposition was determined by measuring the penetration of the metal and by observing the deterioration of the liquid during the test. The results of the tests indicate that the relative stabilities of the halons fall in the following order from the most stable to the least stable: halon 1301, halon 1211, halon 1202, halon 2402, halon 1040, halon 1001, and halon 1011. Reference 12 also reports corrosion tests run by the Aerojet Engineering Corporation in which copper, 1020 steel, 302 stainless steel, 24S-T3 aluminum, and 61S-T6 aluminum were tested with halogenerated agents for corrosion. The metals were immersed in halons both dry and wet (3 vol% water added) for 7 days at room temperature. When halons 1301, 1202, and 1011 were tested, the data showed halon 1301 to be least corrosive. It had no observable effect on any of the metals except for the 1020 steel, which rusted in air after the exposure to wet halon 1301.

Fielding [15,16] reports some of the results described in Ref. 12.

Engibous and Torkelson [14] report three different sets of corrosion tests of metals exposed to halons: the Du Pont tests [12] reviewed above, Purdue Research Foundation tests, and Dow Chemical Company tests. In the Purdue tests, the corrosion of copper, aluminum, and iron in halons 1301, 1011, and 2402 was investigated. Strips of the metals were sealed in glass ampoules with the halons and subjected to a temperature of 392°F (200°C) for 30 days. Under these conditions, only halon 1301 was stable in the presence of all three metals. Halon 2402 was then subjected to a similar but less severe test of 200°F (93°C) for 30 days and found to be stable with copper, aluminum, iron, and brass.

In the Dow Company tests, aluminum, brass, copper, iron, magnesium, Monel®, nickel, stainless steel, tin, and zinc were tested with halons 1011, 1202, and 1301. Here, the

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*A coprecipitate of copper and manganese oxides.

metal strips were sealed in glass ampoules with halons both dry and wet (1 wt% water) at 86°F (30°C) for 30 days. The results of these tests showed that most of the metals could be used with any of the halons if they were dry and that the corrosion-resistant metals (Monel®, nickel, and stainless steel) did not appear to be adversely affected even in the presence of water. In a wet aluminum system halon 1301 had a high degree of stability, which the other halons did not have.

Du Pont Bulletin B-29C [11] reports corrosion tests of halon 1301 with 11 different types of metals. The halon 1301 and test strips of the metals were sealed in glass tubes and stored at 250°F (121°C), 130°F (54°C), and room temperature for periods up to 44 months. Samples of the halon, both dry (2 ppm water present) and wet (about 70 ppm water present) were tested under identical conditions. The conclusion was that all of the following metals were suitable for use with halon 1301: type 302 stainless steel, 1020 CR steel, 321 stainless steel, 1100 aluminum, 2024 aluminum, 6061 aluminum, yellow brass, A2-91C magnesium, commercial titanium, and AllOAT titanium. In additional tests, three different types of steel (Inconel®, type 316 stainless steel, and mild steel) were exposed to halon 1301 in sealed tubes at 600°F (316°C) for 25 hours. These tests showed that Inconel® was the best of the three materials for use with halon 1301, both from the standpoint of low metal corrosion and of minimum decomposition of the halon. The second best of the three metals was the type 316 stainless steel.

Edwards and Grabski [10] immersed a specimen of naval brass in halon 1301 at 160°F (71°C) for 7 days. The brass was slightly discolored but not substantially affected by the halon.

In the corrosion tests discussed above no information on the presence or absence of oxygen was found. Apparently, the test samples were completely immersed in the liquid halons and not exposed to a halon-air interface.

Le Pera and Sonnenburg [31] tested four metals (CR steel, automotive cast iron, aluminum alloy, and chrome alloy steel) with diesel fuel containing 5% halon 1011 additive. The metals were tested in diesel fuel-halon 1011 mixtures, both dry and wet (0.5 vol% distilled water added). It was found that, with trace water present, all the metals reacted with the fuel-halon mixture.

THE EFFECTS OF FIRE-HALON ENVIRONMENTS ON CORROSION RATES

Ford [22] reports a series of tests in which halon 1301 was used to extinguish fires of electronic data processing (EDP) materials; the tests were carried out by the Ansul Company, the Cardox Company, Du Pont Corporation, and Fenwal, Inc. The conditions of these tests varied widely, but in many of the tests 4-6% of halon 1301 was used to extinguish a fire of 5 lb of EDP material in a test enclosure of 1500-1700-ft^3 (42,500-48,000 ℓ) volume. In addition, a series of tests was run specifically to generate high concentrations of HF and HBr to test the corrosion resistance of metals. In the tests using 4-6% halon 1301, surface fires produced HF and HBr in concentrations of 100 ppm each or less. Deep-seated fires produced HF and HBr in concentrations not exceeding 150 ppm each. Special concentrations generated for corrosion tests were as high as 1700 ppm HF and 810 ppm HBr. HF and HBr were analyzed by measuring the specific ion concentration in a sample by a device similar to a pH meter. Nine metals, which were representative of the metals used in EDP equipment, were tested for their resistance to corrosion. The metals were copper, coin silver, phosphor bronze, 1020 steel, solder (60/40 tin-lead), "Kovar" (iron, nickel, cobalt alloy), cadmium plating over steel, silver plating over copper, and gold plating over nickel plating over copper. Coupons of these metals were attached to plaques on the walls of enclosures where the fires of EDP materials (computer printout paper, data tabulating cards, paper punch tape, polystyrene tape, polyester-base magnetic tape, polyethylene tape, and polyvinyl chloride) were extinguished with halon 1301. The relative degrees of corrosion of the metals were measured electrically as contact resistance.

After the initial evaluation of the amount of corrosion, the metal coupons were subjected to accelerated aging, a repetitive cycle of temperature and humidity conditions to which an exposure of 1000 h is rated as equivalent to about 10 yr of exposure in a normal environment at 70°F (21°C) and 50% relative humidity (RH). Extent of corrosion was measured again after periods of accelerated aging of 1 week, 1 month, and 6 months. The contact resistance of most metals was not significantly affected immediately after exposure to halon 1301 decomposition products. Gold and silver surfaces were not significantly affected by exposure to even high concentrations of HF and HBr either initially or following aging. Steel and "Kovar" exposed to either fires or extinguishment atmospheres showed marked increases in contact resistance upon aging. Copper-containing metals (copper, phosphor bronze, and coin silver) were not greatly affected by exposure to even high concentrations of HF and HBr initially after exposure but showed moderate increases in contact resistance with aging.

THE EFFECT OF HALONS AND HALON EXTINGUISHMENT ATMOSPHERES ON ELASTOMERS AND PLASTICS

Du Pont Bulletin B-4 [12] reports tests of nine elastomers (Hycar OR-15, Perbunan 26, Neoprene GN-A, Hypalon E-7, GR-S, Natural Rubber, Butyl, Thiokol FA, and Silicone 23) with five halons (halons 1211, 1202, 1301, 2402, and 1011). In addition, "Kel-F" and red vulcanized fiber were tested in halon 1301, and Resistoflex, nylon, and polyethylene were tested in halon 1202. In these tests, strips of the elastomers were sealed in glass tubes with the agent, and the amount of swelling of the elastomer was determined by measuring its increase in length. Reference 12 reports similar tests made by the Aerojet Engineering Corporation in which eight elastomers (Neoprene, Buna N, Hycar, Polyethylene, Saran, Vinylite, Tygon, and Silastic) were tested with three halons (halons 1301, 1202, and 1011). The Aerojet tests were made at room temperature for 7 days with both dry halons and halons containing 3 vol% water. The results of these tests are reported as percent change in volume of the elastomers. Maximum swelling of the elastomers was observed to occur in about 3 days. There were wide differences in swelling caused by the action of different agents on different elastomers. However, in nearly every case a satisfactory elastomer for use with a particular agent was found. Halon 1301 was found to be far superior to the other halons in regard to its effect on elastomers, causing little or no swelling in all cases except that of the Silicone 23. The work reported in Ref. 12 is summarized by Fielding [16] and by Engibous and Torkelson [14].

Engibous and Torkelson [14] also report work on elastomer swelling done at the Dow Chemical Company. In these tests, 16 elastomers (natural rubber, Neoprene GN, Tygon, Polyethylene, Resistoflex PVA, Butyl, Teflon, Nylon, Saran, Kel-F, and six types of Silastic) were immersed in halons 1301 and 1202 at 86°F (30°C) for 30 days. The elastomer swelling was then determined by visual observation. Silastic 152 was the only elastomer which swelled more than a slight amount in the halon 1301, whereas four elastomers swelled by a large or extreme amount in the halon 1202. The conclusion was that halon 1301 presents little problem in the selection of elastomers, while other halons must be used only with carefully selected elastomers.

Test strips of 11 elastomers and 17 plastics were sealed in glass tubes with liquid halon 1301 at room temperature for 2 weeks in tests reported in Du Pont Bulletin B-29C [11]. Maximum linear swelling and the changes in weight of the test pieces were measured, and the general condition of the material and the liquid observed at the end of the test. The test pieces were weighed again after drying for 2 weeks. The Du Pont conclusion was that all the elastomers tested except silicone rubber are suitable for use with halon 1301. Also, most of the commonly used plastics undergo little, if any, swelling in the presence of halon 1301, with the exception of ethyl cellulose and possibly cellulose acetate/butyrate. Fielding [15] summarizes these Du Pont tests and notes that an epoxy resin was not included in the plastics tested.

Edwards and Grabski [10] report that six plastics and eight elastomers were immersed in liquid halon 1301 at 160°F (71°C) for 7 days. In another experiment, six types of rubber were immersed in halon 1301 at 80°F (27°C) for 14 days. Of the 14 materials tested, only polystyrene, butyl rubber, and the two silicone rubber compounds were regarded as substantially affected by the exposures. The following materials were recommended for use with halon 1301 in the order listed: Thiokol, Neoprene, butadiene-styrene compounds, and natural rubber. Fielding [15] summarizes this work and again notes that an epoxy resin was not included in the plastics tested.

Le Pera and Sonnenburg [31] immersed test strips of eight elastomers in diesel fuel containing 5 volume-percent halon 1011 at 212°F (100°C) for 6 hours. They recommended further study to find an elastomer suitable for use with the fuel-halon mixture.

CORROSION EFFECTS OF HALONS ON DIESEL ENGINE PARTS

Grotsky [25] reports the test of a V-12, four-stroke cycle, Waukesha diesel engine, Model L1616 DSIN (rated 600 hp at 2000 rpm), which was run for a few minutes in an atmosphere containing 5 vol% of halon 1301. A bright orange smoke which "could have been bromine gas" appeared in the exahaust. The engine was operated continuously for 8 h after exposure to the halon and then disassembled for inspection. No damage was apparent, and it appeared that the halon decomposition products had acted as a cleaning agent and removed most of the carbon from around the piston and compression rings. The report recommended that no diesel engine be allowed to ingest halon 1301. The conclusion appears to contradict the results of the experiment. However, Grotsky did report that the acidity of the lube oil increased during the experiment, and he may be concerned about the long-term effects of this. Although he did not say so, the toxicity of the halon decomposition products may be another factor which led him to his conclusion.

Browne and Szczepanski [2] reported tests in which up to 7 vol% of halon 1301 was injected into the firebox of a DDG-15 main propulsion marine boiler. However, no corrosion studies were made.

CORROSION EFFECTS OF HALONS ON SENSITIVE INSTRUMENTS AND ELECTRONIC COMPONENTS

A series of tests run by four companies (the Ansul Company, Cardox Company, E. I. Du Pont de Nemours & Co., and Fenwal, Inc.) included some tests of electronic components in halon-fire atmospheres and is reported by Ford [22]. Reference 22 also reviews previous work done in this field; this may be summarized as follows:

1. In 1962 the Du Pont Company exposed electrical switch metals to fires extinguished by halon 1301 and carbon dioxide. There were no significant corrosive effects.

2. In 1969 the U.S. Atomic Energy Commission conducted two full-scale fire tests in an electronic instruments trailer and used halon 1301 to extinguish fires of wood and "electrical type fuel." This fuel is presumably insulating materials or the type of fuels which burn in a Class C fire. There was no damage to instruments and magnetic tapes exposed in the tests.

3. In 1969 the Du Pont Company exposed an energized computer (IBM data processing) unit for 30 min to a UL size 1A wood-crib fire which was extinguished with 5% halon 1301. There was no damage to the unit or interference with its operation.

4. In 1970 the Advanced Safety Systems Company gave two demonstrations of operating computer units (IBM and Honeywell) in an atmosphere in which flammable liquid fires covering 4 sq ft (0.37 m^2) were extinguished by halon 1301. There were no adverse effects to the computer units.

5. In 1971 the Safety First Products Company conducted six tests in which fires of a variety of combustibles were extinguished with halon 1301. The exposed electronic components suffered no significant damage that was attributable to halon 1301 decomposition. These appear to be the same six tests reported by Cholin [6].

6. In 1971 the IBM Corporation extinguished a variety of typical computer room combustibles with halon 1301 in five total flooding tests. An electronic tape reader exposed to the cumulative effects of all five tests was unaffected.

The results of the series of tests reported in Ref. 22 led to the following conclusions:

1. Extinguishing fires automatically with halon 1301 total flooding systems does not produce atmospheres that will interfere with computer operation.

2. Magnetic data on recorded magnetic tape are unaffected by exposure to HF doses (mean concentration multiplied by exposure time) of up to 294 ppm-h, to HBr doses of up to 39 ppm-h, and to HCl doses of up to 2425 ppm-h. These doses were the maximum produced in these tests.

3. Printed-circuit cards (NAND logic gates) exposed in these tests operated satisfactorily immediately after the tests and also after a subsequent accelerated aging test at temperature and humidity conditions rated as equivalent to two years at 75°F (24°C) and 50% RH.

Class A and B fires in a 2000-ft^3 (57,000-ℓ) room containing a computer (NCR 315-101 Central Processor Unit and NCR 316-3 Memory Unit) were extinguished by total flooding with halon 1301 in four tests reported by Carey and Haas [3]. These tests were also reported by Cholin [7]. The results showed that the halon-fire atmosphere did not adversely affect the operation of the central processor unit, memory unit, or exposed circuit boards. The computer operated normally during and after each extinguishment test. There was no apparent cumulative corrosion effect, since the computer functioned normally 17 days after the conclusion of the four tests.

Six tests in which Class A and B fires in 336-ft^3 (9500-ℓ) and 2000-ft^3 (57,000-ℓ) enclosures were extinguished by halon 1301 are reported by Cholin [6] and summarized by Ford [22]. Electronic components and prerecorded magnetic tape were exposed to the extinguishment atmospheres. Two weeks after the exposure tests, there was no significant change in contact resistance of the components or damage to the magnetic tape information.

Jensen [26] reports the conclusions resulting from tests run by the Ansul Company, apparently the same tests reported by Ford [22]. The conclusions were that halon 1301 produced no apparent corrosion of metals or equipment and did not impair the operation of electrical equipment.

CONCLUSIONS

The following conclusions have been drawn from this literature survey:

1. Halon 1301 is the most promising halon for use as a fire suppressant. Therefore, it is the halon that has been studied the most extensively.

2. Halon 1301 is classified by the National Fire Association as less toxic than carbon dioxide; furthermore, a 5 vol% concentration will extinguish most Class A and B fires unless they are the deep-seated or smoldering type.

3. Liquid and gaseous halon 1301 is compatible with many metals, plastics, and elastomers.

4. Liquid halon 1301 is more corrosive in the presence of water due to the compound decomposing to corrosive and toxic products when exposed to fire or hot surfaces.

5. A concentration of halon 1301 sufficiently high to extinguish flames has little or no effect on computers and their operations.

6. Very little work has been done on the corrosion effects of halon-fire atmospheres on diesel engine parts.

7. No reference concerned with the corrosion effects of halon-fire atmospheres on sensitive instruments other than computers was found.

8. Numerous tests of halon 1301 have been made. However, the data are phenomenological, and both test conditions and results vary widely. Concentrations are usually expressed in ppm, which are very difficult to apply to real situations.

9. In the reports of corrosion and compatibility tests, no information on the presence of oxygen is given. Apparently, the test samples were completely immersed in the liquid halons.

10. The reliability of the analyses of halon combustion products is questionable, partly because of the wide disparity of the results of different tests. In some cases the analytical method used was not described. Detector tubes are notorious for false readings due to interferences. Unreliable figures would be particularly likely in fires with the myriad of products being formed.

11. More work is needed to determine both the degree of decomposition of halon 1301 and the concentrations of toxic and corrosive products generated in fire situations. Testing must be done under realistic and well-defined conditions using reliable and precise methods of analysis.

RECOMMENDATIONS

As a result of this literature study, the following recommendations for additional work are proposed.

1. A series of fire tests using halon 1301 to extinguish Class A, B, and C fires with various application rates and preburn times should be made.

2. An in situ method of analysis of HF, HBr, and HCl employing noninterference techniques, such as laser spectroscopy, should be used in these tests.

3. A procedure should be developed for clean-up after test fires to insure that test conditions are standardized.

4. The effect of $CBrF_3$ and other proposed extinguishants on the upper atmosphere should be studied. See "The Effects of Bromofluorocarbons on Stratospheric Ozone," an NRL Report by D. J. Bogan, in preparation.

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Appendix A

THE TOXICOLOGY OF HALON FIRE SUPPRESSANTS—A BIBLIOGRAPHY

According to the literature reviewed in the above report, halon 1301 ($CBrF_3$) is the halon generally considered to be the best for use as a fire suppressant. One reason for this is its low toxicity. The National Fire Protection Association's standard on halon 1301 (39) places it in the least toxic group, which is designated as Group 6. Undecomposed halon 1301 has been studied in humans and found to produce minimal, if any, central nervous system effects at concentrations below 7 percent for exposures of approximately 5 minutes duration (39). Other fire suppressants including carbon dioxide, halon 1211, halon 1202, and halon 1011 are classified in groups of compounds which are more toxic than are those in Group 6.

The following references comprise a comprehensive bibliography on the toxicology of halon fire suppressants. A majority of the listed publications are concerned solely or largely with halon 1301 because it shows the most promise for use as a fire suppressant for a wide range of applications. In cases where a single publication covered the pertinent subjects, it is listed both with the literature reviewed above and in the bibliography below. The references are listed in alphabetical order.

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