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A LITERATURE REVIEW OF THE IMPACT OF THERMAL DECOMPOSITION PRODUCTS GENERATED BY HALON REPLACEMENTS ON ELECTRONIC EQUIPMENT

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1.0 INTRODUCTION

Following the ban on halon production by the Montreal Protocol, some halocarbons are being considered as halon replacement agents for use in protecting electronic facilities in telecommunication industry. However, research carried out by NRC and other research organizations [1-4] indicated that current halocarbon replacement agents were less effective than Halon 1301 and produced greater quantities of thermal decomposition products (TDP), such as hydrogen fluoride (HF), hydrogen chloride (HCl) and carbonyl fluoride (COF_2), than Halon 1301 for the same fire challenge. These thermal decomposition products are toxic and corrosive. They can pose a health hazard to people in the protected space and cause potential corrosion damage to the facilities that are protected by the agents [3, 4]. For some facilities with limited access, corrosion damage will be further increased where the thermal decomposition products cannot be vented quickly from the compartment after fire extinguishment.

This literature review provides information on the impact of thermal decomposition products generated during fire suppression by halon replacements on electronic facilities. It includes a review of the thermal decomposition products formed during fire suppression and the potential corrosive damage to electronic facilities caused by halon replacements. The factors that contribute to the corrosive damage to electronic facilities, such as the concentration of corrosive species, the exposure period, the nature of the combustible materials involved in the fire, the temperature and humidity in the compartment, and the type of equipment exposed, are identified. Previous experimental studies on the impact of HF corrosion to the electronic equipment, including laboratory-scale and full-scale tests, are also reviewed and discussed. Based on this review, recommendations are provided for minimizing HF corrosive damage to the electronic equipment and some issues for further study are identified.

2.0 THERMAL DECOMPOSITION PRODUCTS GENERATED FROM HALON REPLACEMENTS

Fires can be extinguished by either physical or chemical mechanisms. Fire suppression can be achieved by the physical removal of any of three elements (heat, oxygen or fuel) from the fire, i.e., the standard fire triangle. Fires can also be extinguished through chemical means: when OH and O free radicals from fuel combustion are chemically consumed by the free radicals (e.g., bromine (Br), Cl, F free radicals) released from halons and halon replacements to form the stable combustion by-products (e.g., hydrogen bromide (HBr), HCI and HF), resulting in the termination of the chain reactions of the fuel-air mixture [5-7].

Fire suppression with halogenated fire suppressants containing Br is more effective than with agents containing chlorine (Cl) or fluorine (F) [8]. Over the last two decades, halogenated fire suppressants, such as Halon 1301 (CF_3Br), have been widely used. Br atoms from halogenated fire suppressants, however, have been identified as a factor responsible for ozone depletion [9]. In an effort to improve the global environment, the Montreal Protocol has identified the need to phase out the use of halon agents containing Br atoms.

Over the years, significant efforts have been made to develop halon-like replacements. These halon replacements include perfluorocarbons (PFCs or FCs), hydrofluorocarbons (HFCs), hydrochlorocarbons (HCFCs), hydrobromofluorocarbons (HBFCs), and fluoroiodocarbons (FICs) [4, 10]. These halon replacements contain a large number of F atoms per molecule. During fire suppression, the F atoms trap H atoms from fuel combustion and form stable HF combustion by-products. The HF does not participate in any known catalytic process during fire suppression. Most of the current halon replacements extinguish fire by physical means (i.e., cooling and fuel vapour dilution). Because of this, high agent concentrations (typically a factor of two) are required to extinguish a fire, compared to Halon 1301 [4, 11-13]. This requirement, together with the large number of F atoms per molecule contained within the current halon replacements, results in the formation of large quantities of HF during fire suppression.

Table 1 summarizes data on thermal decomposition products produced by the current halon replacements under various test conditions, including small-scale, intermediate-scale and full-scale tests [10, 14]. The thermal decomposition products generated by the current halon replacements include HF, COF_2 and HCl. Among these thermal decomposition products, HF, which is both toxic and corrosive, is the predominant product generated. The current halon replacements produce 5 to 10 times more HF than Halon 1301 for the same fire challenge. In the full-scale tests carried out by the U.S. Coast Guard (Table 1), halocarbon agents, FC-3-1-10, HFC-23 and HFC227ea produced 4,500 ppm, 1,200 ppm and 2,000 ppm of HF, respectively, whereas Halon 1301 only produced 300 ppm HF under the same fire conditions. Therefore, there is a concern that the large quantities of HF generated by current halon replacements could cause serious corrosion damage to the electronic equipment.

3.0   POTENTIAL DAMAGE TO ELECTRONIC FACILITIES USING HALON REPLACEMENTS

During a fire, smoke and fire effluents are generated. Common fire effluents are carbon monoxide, carbon dioxide and water. Fire effluents released from fires involving polymeric materials used in electronic equipment may also contain chloride, hydrogen cyanide, HCl, sulphur oxides and nitrogen oxides [15]. Solids present in smoke may include particles of carbon (soot), metals and salts. These smoke and fire effluents can adversely affect electronic equipment. In the short-term, they can lead to circuit bridging due to smoke depositing onto the electronic components, and in the long-term, they will cause a direct corrosion damage to the electronic components [16-18]. Investigations of recent accidents in telecommunication facilities, computer centres and nuclear power plant equipment have revealed that 95% of the damage to electronic equipment in a fire results from smoke and fire effluents [16-20].

The use of halon replacements for fire suppression may result in increased damage to the electronic equipment. First, the use of halon replacements for fire suppression will generate large quantities of HF that cause direct corrosion damage to the electronic equipment. Second, the discharge of halon replacements will introduce a pronounced and very abrupt cooling effect in the compartment.

As shown in the full-scale testing carried out by NRC, local temperatures even in areas that are far from the discharge nozzles can abruptly drop from 20°C to -10°C during the discharge period due to agent vaporization [1, 2]. This can lead to water vapour condensation and the formation of moisture droplets, or even frost, on the surface of the electronic equipment. The condensation will enhance the conductivity of smoke deposits on the components and scavenge acid gas molecules from fire effluents, resulting in circuit bridging faults and corrosive damage [17, 18]. HF gases will also react with moisture to form hydrofluoric acid on the surface of the electronic equipment. The combination of HF gas and acid with smoke deposits and fire effluents will cause extensive and synergistic damage to the exposed electronic equipment.

There are three types of corrosion in electrical and electronic equipment caused by HF, smoke and fire effluents [21, 22]:

1. Metal loss due to electrolytic and chemical attacks on metal;

2. Electrical current leakage due to increased surface conductance; and

3. Increased contact resistance due to the deposit of combustion products and subsequent chemical reactions.

The loss of metal due to corrosion reduces the strength of structural components and increases the electrical resistance of exposed metal parts. Some metals (for example, galvanized zinc or zinc chromalized finishes that represent a major portion of the structural components of telecommunication and computer equipment), can form electrically conductive solutions, when exposed to acid gases. These electrically conductive solutions can move, drip or run onto equipment, resulting in serious electrical shorting problems [16, 20]. The second type of corrosion results from the deposit of combustion products onto electronic circuit boards. This may lead to an increased electrical current leakage and cause shorts. These shorted electrical signals then cause the electronic equipment to receive false data, resulting in system failure [17, 23]. The third type of corrosion influences the electrical resistance between contacts for relays and switches. Corrosion causes a drop in the

resistance between the contacts because of increased surface conductance by the deposit of combustion products and subsequent chemical reactions [23, 24].

The corrosion damage caused by HF, smoke and fire effluents may involve other areas in the building. During or after fire suppression, HF, together with other fire effluents, can be carried away by the buoyant smoke or circulated by the ventilation system and cover the external and internal surfaces of walls, floors and equipment. The corrosive gases can spread at more than 5 times the rate of the smoke particulate [20]. Since they produce no optical density change, their movement is not always detected until substantial equipment damage has occurred. Thus, corrosion damage not only occurs in those facilities that are directly exposed to the fire or are close to the fire, but it can also occur in remote equipment.

The corrosive effect on electronic equipment can be both short-term and long-term. For some materials, flash rusting may occur within hours. When such short-term corrosion attacks small circuit traces, particularly if the attack is in the form of "pitting" corrosion rather than general surface corrosion, short-term loss of circuit functionality will occur [17, 25]. In general, however, the damage caused by corrosion is long-term and it may become evident after weeks, months or years. The corrosion process to the electronic equipment will not stop after the fire is out [20]. Some fire effluent salts or the initial products of flash rusting may be hygroscopic and retain moisture which enhances corrosion [15]. Soot particles may also absorb ions and retain acidic condensates for considerable periods of time. These result in corrosion to the electronic equipment over a long period of time.

4.0   FACTORS AFFECTING CORROSIVE DAMAGE TO ELECTRONIC EQUIPMENT

Corrosion is an electrochemical process and requires an electrolyte and a material that is susceptible to corrosion by that electrolyte. A number of factors are involved in controlling the corrosive damage to electronic facilities. These factors can be summarized as follows [15, 22, 26]:

- The concentration of corrosive species;

- The nature of the combustible material involved in the fire;

- The duration of the exposure to corrosive species;

- The temperature and relative humidity of the room or building during the fire and immediately after the fire and during the corrosion process; and

- The characteristics of the exposed equipment, such as the type of materials, the location of the equipment in the space, and the sensitivity of the equipment to damage.

4.1   Concentration of Corrosive Species

The concentration of corrosive species is a very important factor in determining the corrosion rate of materials [15]. In general, corrosion rates increase with the concentration of corrosive species, but this is not always the case. Some materials may corrode slowly under certain concentration regimes and rapidly under others. The corrosion rate may also dramatically decrease at high concentrations if the corrosion product provides a protective layer, or if a transition occurs from "active" to "passive" behaviour. For example, at room temperature (20°C), the corrosion rate of copper increases with the concentration of hydrofluoric acid, but decreases when HF acid concentration is higher than 60% [27].

During fire suppression, the amount of HF generated depends on many factors, such as the fire scenario, the type and concentration of the agent used for fire suppression and discharge and extinguishing times [28, 29]. As shown in Table 1, under similar test conditions, the concentrations of HF gas generated vary substantially from one agent to another. This is because the formation of HF during fire suppression varies with the agent's chemical composition (its hydrogen to fluorine ratio) and the concentration required for fire suppression [29]. Some halon replacements (e.g., hydrofluorocarbons (HFCs), and hydrochlorocarbons (HCFCs)) contain both fluorine and hydrogen atoms. For other halon replacements (e.g., perfluorocarbons (PFCs or FCs)), the agent contains fluorine only and hydrogen is derived from the hydrocarbon fuels and water vapour in the air [28, 30, 31].

Agents decompose and generate HF only when they come into contact with the fire or with hot surfaces [26, 32]. Therefore, a large fire caused by a fast fire growth and delayed fire detection or

longer agent discharge period, results in high HF generation. A long extinguishing time also contributes to the generation of a high HF concentration [33-35]. There is a linear relationship between the amount of HF generated from fire suppression and the extinguishing time.

The enclosure conditions, such as the volume of the space with respect to the fire size, the ventilation conditions and the presence of surfaces for acid gas condensation will also affect the peak and average concentrations of HF in the compartment [29]. Test results have shown that the quantity of HF gas generated in fire suppression increases linearly with the ratio of fire size to room volume [33-35].

The degree of ventilation in the compartment will affect not only the quantity of fire effluent produced but also the distribution of the fire effluents in the space. Test results showed that, in a space with partial ventilation, the HF gas produced during fire suppression is much greater than that with minimal ventilation, because the influx of fresh air from partial ventilation results in a more intense fire and longer extinguishing time [36]. However, the concentration of HF gas decreases more rapidly with partial ventilation than with minimal ventilation during the post fire period.

4.2   **Nature of Combustible Materials**

The nature of the combustible materials involved in a fire determines both the properties of the fire effluents and the combustion mode. This affects the amount of HF gas generated during fire suppression. Combustible materials present in electronic facilities are liquid fuels, transient fuels (e.g., general trash, paper waste, wood, plastics, etc.) and in situ solid fuels (e.g., cable insulation and jacketing materials) [17, 25]. Liquid fuels used in pumps, hydraulic-operated equipment and other equipment requiring lubrication usually result in open flames with large fires and high temperatures. High HF concentrations will be produced, when halon replacements are used to extinguish such fires.

While the fire effluents generated from transient fuel fires may contain a variety of chemical species, fires involving such fuels will generally be limited in both extent and duration. HF concentrations generated in extinguishing these types of fires are relatively low.

The most significant corrosion threat to the electronic equipment caused by burning materials will be associated with in situ solid fuels. The compounds of in situ solid fuels encountered in the electronic equipment may include cross-linked polyolefin (XLPO), polyvinyl chloride (PVC), ethylene-propylene rubber (EPR), chlorosulfonated polyethylene (CSPE or Hypalon), teflon and silicone [25]. Fires involving such materials are typically inefficient and generate many intermediate combustion products that contain acid and dense compounds, such as hydrogen cyanide, HCl and sulphur oxide. These products themselves may cause corrosive damage to the electronic equipment [17, 25]. In addition, these types of fires may involve deep seated combustion. In order to extinguish such fires, a long contact time of the suppressant with the fire may be needed, which may result in the production of high HF concentrations during fire suppression. As shown in tests conducted at Sandia National Laboratories involving electrical cable insulation materials [37], if the suppressant concentration is not maintained for 15-20 min, the fires will re-flash to open flaming on venting of the space.

4.3   Exposure Time

The exposure time to corrosive species can be addressed in two stages [17, 25]. The first exposure period includes the time required to detect and suppress the fire and the time required to remove smoke and HF gases from the compartment. The second exposure period is the post-fire recovery time required to clean the equipment and restore the operation after a fire event. Corrosive damage to electronic facilities increases substantially with both exposure periods.

The first exposure period determines the amount of smoke and HF gases generated during fire suppression and the duration during which the electronic equipment is actually exposed to smoke and HF. In order to reduce HF levels and exposure time, the fire must be detected and suppressed at an early stage. After fire extinguishment, the time required to remove the smoke and HF gas from the compartment will mainly depend on the enclosure characteristics, such as the compartment volume and ventilation conditions. The full-scale tests carried out by NRC showed that HF concentration in a well-sealed compartment without ventilation decreased very slowly after fire extinguishment [1, 2]. Proper ventilation after fire extinguishment is required to remove the smoke and HF gases quickly from the compartment and minimize the impact on the equipment.

Even after the removal of smoke and HF from the enclosure, corrosion on the electronic equipment may continue. For some materials, the consequences of corrosion may not become apparent for months or years after the exposure to corrosive species if surface contaminants are not removed. Hence, the extent and timing of the post-fire recovery action can have a major effect. Cleaning the equipment quickly after fire suppression can minimize the extent of corrosion damage.

4.4   Humidity and Temperature in the Enclosure

Humidity in the environment is one of the most important factors affecting the corrosion rate [15, 18, 25]. It affects the surface insulation resistance of electronic components and leads to corrosion when HF and fire effluents dissolve into condensed moisture films.

During a fire event, the humidity level in an enclosure will be increased due to the formation of water vapour during combustion. Condensation will occur during the discharge of halon replacements due to sudden cooling by the agent vaporization. As a result, in order to reduce corrosion damage, it is important to control the relative humidity of the room immediately after the fire is extinguished.

The enclosure temperature will also increase even for a relatively small fire. This is because, during a fire event, most ventilation supply and exhaust systems are designed to shut down to contain the spread of smoke and fire in the enclosure [25]. In general, corrosion rates increase with temperature. For example, at 6% HF acid concentration, the corrosion rate of copper will increase from 0.20 mm/year to 0.69 mm/year, when the temperature increases from 20°C to 80°C [27]. Furthermore, exposed to high temperatures, the electronic components will also become more vulnerable to be attacked by corrosion in a synergistic manner [25].

4.5   Properties of Equipment Exposed

The amount of corrosion that can be tolerated will be dependent on the size, function and sensitivity of equipment components. In certain cases, such as on aesthetic surfaces or on conducting wires with small cross-sections, minor corrosion may be tolerated. In other cases, even small corrosion on electrical/electronic connector surfaces may result in considerable function impairment [15].

Since corrosion is specific to particular combinations of materials and corrosive species, corrosion to the electronic equipment is dependent on the properties of materials used. Some materials may be resistant to oxidizing acid conditions such as nitric acid, but will corrode severely under acidic fluoride conditions. The presence or absence of oxygen can also influence the corrosion rate of certain materials in specific environments.

There are many types of materials used in computer and telecommunication equipment. The common materials used in computers and telecommunication equipment and their functions are as follows [15, 38]:

Metals

1. Copper for power cables (covered in PVC) and printed circuit boards (lacquer coated);

2. Gold-plated copper for high quality and low voltage semi-conductor connections;

3. Gold flash over nickel-plated copper alloy for terminal port connections;

4. Lead-tin solders for electrical connections;

5. Platinum/platinum alloys for relay contacts;

6. Phosphur bronze for spring loaded contacts;

7. Electrolytically nickel-plated steel for blanking plates and electroless nickel-plated through holes on printed circuit boards;

8. Nickel or cadmium plated screws;

9. Palladium and rhodium for electrical contacts and coatings on printed circuit boards;

10. Aluminum, silver and tantalum capacitors;

11. Aluminum diecast fans and aluminum for compact discs; and

12. High strength steel circlips.

Nonmetals

1. Ceramic or glass mounted microprocessors;

2. Ceramic capacitors;

3. Glass for VDU screens and glass windowed EPROMS;

4. Filled epoxy resin for mounting circuit boards;

5. PVC for insulation of wires; and

6. ABS plastic for molded cases.

The corrosion of these materials depends on the composition of the materials, the concentration of HF, and the temperature and humidity in the enclosure. The corrosive behaviour of these common materials exposed to HF is briefly summarized in Table 2 [24, 35, 38-40].

The table shows that HF gas and acid should not cause appreciable corrosion to gold-plated semi-conductors and terminal post connections, platinum relay contacts, palladium and rhodium electrical contacts. However, other components, such as aluminum and tantalum capacitors, compact discs fabricated from aluminum, glass mounted microprocessors, glass VDU screens, as well as components made of copper, silicon, tin and zinc are likely to be affected by HF acid. Corrosion damage to other components made of ceramic, such as ceramic capacitors and ceramic mounted microprocessors could also occur, depending on the type of ceramic used. For some components, such as lead-tin solders for electrical connections, their compatibility with HF gas and acid is uncertain, although some corrosion can be expected.

As shown in Table 2, the information available in the literature on corrosivity of materials used in telecommunication equipment with HF mainly refers to whether or not materials will be affected, rather than providing information on how they are corroded under given operating conditions.

5.0 PREVIOUS STUDIES ON HF CORROSION OF TELECOMMUNICATION EQUIPMENT

5.1 Experimental Studies on HF and HBr Corrosive Damage Involving Halon 1301

The research on the potential damage to computers and electronic equipment, caused by thermal decomposition products generated from fire suppressants, can be traced back to the 1960s, when Halon 1301 was introduced into the telecommunication industry. There was a concern that the HF and HBr, generated by Halon 1301 during fire suppression, might present a risk to the electronic equipment.

5.1.1 Laboratory-Scale Studies

There were a number of laboratory-scale studies conducted involving electronic components, such as printed circuit boards and their raw materials [41-43]. Musick and Williams [32] have summarized the studies conducted by Du Pont (1962, 1969), U.S. Atomic Energy Commission (1969), Advanced Safety Systems (1970), Safety First Products (1971) and IBM (1971). The fires used in these tests included Class A, B and C fires. Concentrations of Halon 1301 used in the tests varied from 3.7% to 7.2%. The HF concentrations generated in these tests ranged from 3 ppm to 294 ppm, and HBr concentrations ranged from 1.5 ppm to 39 ppm. The exposure time in these tests was approximately 30 min. These early studies indicated that fire extinguishment by Halon 1301 did not produce an atmosphere that interfered with computer operations, and data on recorded magnetic tape was unaffected. Printed circuit cards (NAND logic gates) exposed in these tests operated satisfactorily immediately after the tests and again after a subsequent accelerated aging test under temperature (24°C) and humidity (50% RH) conditions rated as equivalent to several years.

In 1985, NASA conducted a project to study the corrosion of typical orbiter electronic components exposed to thermal decomposition products generated by Halon 1301 [38]. During the tests, the targets, including metallic and nonmetallic electronic components, PC boards and CPU boards, were not exposed under actual fire/post-fire conditions, but exposed to mixtures of HF and HBr vapours in a polyethylene chamber of 190 L volume. The concentration of HF and HBr mixtures used ranged from 500 ppm HF and 200 ppm HBr, up to the theoretically-calculated worst case of

50,000 ppm HF and 20,000 ppm HBr. The humidity in the enclosure during the tests varied from 50% to 100%. The exposure periods ranged from 15 min to nine days.

The NASA tests showed that many electronic components, their raw materials and conformal coatings degrade physically and functionally when exposed to the pyrolysis products generated by Halon 1301 in a confined space. The amount of degradation was dependent upon the concentration of HF and HBr and the length of exposure period. The majority of the test items were severely degraded, when subjected to a atmosphere of 50,000 ppm HF and 20,000 ppm HBr for extended periods of time. The surface resistance of all four conformal coatings that were used to coat circuit boards dropped rapidly. Powered CPU boards failed without recovery of function after 49 min of exposure to 50,000 ppm HF and 20,000 ppm HBr, with each type of board showing significant corrosion. The powered CPU boards also failed after 210 to 306 min of exposure to 5,000 ppm HF and 2,000 ppm HBr, and showed significant corrosion and coating damage. However, two of the four boards recovered their function after four days. With a concentration of 500 ppm HF and 200 ppm HBr, all the coatings of the CPU boards showed some damage, and the resistance of conformal coatings was reduced by five orders of magnitude after 48 h of exposure. One CPU board showed appreciable corrosion at the end of the test, but none of the CPU boards malfunctioned.

The NASA test results confirmed that thermal decomposition products, such as HF and HBr generated by Halon 1301, could potentially degrade the performance of the electronic equipment. However, since NASA did not conduct tests in the post-fire atmosphere, neither the actual concentration of HF and HBr generated during fire extinguishment nor the long-term effects of lower concentrations of HF and HBr on electronic systems are known. NASA recommended long-term full-scale simulation testing to fully assess the effects of thermal decomposition products of fire extinguishing agents on electronic systems.

5.1.2   Full-Scale Studies

There were also some early full-scale studies carried out on corrosion damage involving Halon 1301 [44-46]. During these studies, computers and computer support equipment were exposed to post-fire environments. In 1972, a joint test program of Safety First Products Corp., Du Pont and Underwriters' Laboratories Inc. [44, 45] was carried out to study the performance of Halon 1301 for real computer installations. Class A and B fires in a 57 m^3 room containing a computer (NCR 315-101 Central Processor Unit and NCR 316-3 Memory Unit) were extinguished with 3.7% of Halon 1301 in four tests. The maximum HF and HBr concentrations generated in the tests were 116 ppm and 38 ppm, respectively. There was a 30 min soaking time before the door was opened. Afterwards, the change in the performance of the electronic equipment was tested at certain time intervals during a several day period. In these tests, no failure in the performance of the electronic equipment was observed after 14 days.

In 1982, the U.S. Air Force carried out a series of tests to determine immediate and long-term effects of exposure of sensitive electronic equipment and stored data to a fire suppression environment involving Halon 1301 [46]. Controlled deep-seated Class A fires in a facility housing an operational electronic data processing system were extinguished by 5.6% of Halon 1301. During the tests, the concentrations of both HF and HBr were below 30 ppm and the electronic equipment was exposed to a 30 min soaking time. Test results showed that Halon 1301 did not produce an atmosphere that interfered with the operation of the electronic data processing systems, and data recorded on magnetic tape was not affected by exposure to these conditions. Also, printed circuit boards showed no degradation in performance immediately after the tests. Also, the circuit boards performed normally when checked at regular intervals for up to 18 months after exposure.

5.2   Experimental Studies on HF Corrosive Damage Involving Halon Replacements

In comparison with Halon 1301, current halon replacement agents generate more HF gases during fire suppression. However, there are only two published experimental studies on HF corrosive damage to the electronic equipment by current halon replacements. In 1993, Bryan [47] carried out research on the effect of HF on Input/Output (I/O) cards, produced by Halon 1301 and halon

replacements. During the tests, six Relialogic CA8202 Input/Output cards were used. The following components were attached to the card:

- 2 Goldstar GM16C450 9234;

- 1 UMC UM82C11;

- Goldstar drivers (GD75189A, GD75188);

- 20 Capacitors;

- 13 Resistors;

- 1 C820 microchip;

- 1 Parallel connection; and

- 1 Serial connection.

The gaseous agents used in the tests included: Halon 1301 (3.34%), C_3HF_7 (FM-200, 6.58 - 8.12%) and C_4F_{10} (CEA-410, 5.62 - 5.86%). Heptane was used as the fuel for pan fires. The pan size varied from 250 mm to 380 mm.

During the tests, the maximum HF concentration ranged from 484 ppm to 2126 ppm, depending on the type of agent and concentration used. Each I/O card was exposed to the post fire environment for six minutes and then the exhaust fans in the test box were automatically turned on. The I/O card was taken out of the test box after 1.5 h and sealed in a ziploc bag. In the following days, each card was tested on a 286 IBM compatible computer. The testing period ranged from 18 to 54 days.

Test results showed that corrosion took place in several locations on the cards. The amount of corrosion that accumulated on the I/O cards was unknown and was not large enough to destroy any components. However, Bryan [47] reported that when average HF concentrations were greater than 600 ppm, the contacts had enough accumulated corrosion to cause the computer not to recognize that

the I/O card was installed. The shortest time for the occurrence of malfunction was 4 days after exposure to an HF concentration of 1523 ppm. The malfunction of the I/O cards mainly occurred in the tests involving halon replacements (C_3HF_7 and C_4F_{10}), because they produced higher HF concentrations during the tests.

In 1995, Hughes Associates carried out research to quantify the amount of HF formed under conditions similar to telecommunication equipment applications, and to assess the potential damage for electronics and data processing facilities exposed to the thermal decomposition products of FM-200^{TM} [48]. The tests were conducted in an enclosure with internal dimensions of 3.43 x 5.87 x 3.61 m. Four types of fires were used in the tests: wastebaskets with paper, printed circuit boards, electrical cables and magnetic tapes. The average fire size varied from 4 kW to 23 kW, depending on the type of fire employed. The design concentration of FM-200^{TM} in the tests was 7.0 % by volume. During the tests, Relialogic ISA I/O cards were exposed to the post-suppression environment for 30 min. The operation of the exposed I/O cards were then checked 1, 8, 20, and 30 days after the exposure.

During the tests, the maximum HF concentration (averaged over 10 min) ranged from 9 ppm to 970 ppm, depending on the fire size, the length of extinguishing time and discharge rate. HF concentrations in the enclosure decayed quickly with time. For example, in one test, HF concentration in the enclosure reduced from 1248 ppm to 385 ppm in 30 min. It was reported that no failure of the electronic components was observed 30 days following the exposure. The corrosion conditions on the I/O cards caused by HF gas and acid were not reported.

6.0   DISCUSSION

The current halon replacement candidates produce at least 5 to 10 times more HF than Halon 1301 under similar fire conditions due to the large number of fluorine atoms per molecule and high agent concentrations required for fire suppression. The large quantities of HF gases generated will cause direct corrosion damage to the electronic equipment. Furthermore, the use of halon replacements for fire suppression may cause water vapour condensation on the surface of the electronic equipment due to the sudden cooling by agent vaporization during the agent discharge, which will increase the damage of smoke and fire effluents to the electronic equipment and lead to the formation of hydrofluoric acid on the

exposed equipment with the reaction of moisture and HF gas. When HF gas and acid are combined with smoke deposits and fire effluents, extensive damage to the exposed electronic equipment may result. Therefore, the use of halon replacements may result in a risk to the electronic facilities that are protected by the agents.

Even in the case where there is no short-term effect on the electronic equipment by HF generated by halon replacements, there is a potential that HF corrosion may cause long-term damage. The corrosion process does not stop after the fire is out. Damage caused by corrosion may become evident only after a long period of time. It is difficult for loss adjusters to decide whether to approve equipment cleaning and/or replacement for items that may not be visibly affected, particularly shortly after the fire.

The degree of corrosion damage by thermal decomposition products depends on a number of variables. These variables include the concentration of corrosive species; the temperature and relative humidity of the room; the exposure period; the nature of the combustible material involved; and the properties of the equipment exposed. In general, corrosion rates increase with HF concentration, exposure period, temperature and humidity in the compartment.

The amount of HF corrosion that can be tolerated is dependent on the size, function and sensitivity of the electronic equipment. Many common materials and their components, such as aluminum and tantalum capacitors and components made of copper, silicon, tin and zinc, will be attacked by HF, whereas some components, such as gold-plated semi-conductor and platinum relay contacts, will not be affected by HF corrosion.

There were a number of laboratory and full-scale studies [41-46] on the effect of HF and HBr corrosion damage to computers and electronic equipment, produced by fire suppression with Halon 1301. In the laboratory studies, only electronic components, such as PC boards and their materials, were tested, while in the full-scale experimental studies, computers and electronic equipment were exposed to a post-fire environment. During these studies, the quantities of HF and HBr gases generated were small because small fire sizes and low halon concentrations were used. In the laboratory-scale tests, no failure in the performance of electronic components was observed, when they were exposed to

HF and HBr concentrations of up to 300 ppm for 30 min. Full-scale tests also showed that the operation of computers and electronic equipment was not affected under post-fire conditions involving Halon 1301, when they were exposed to HF and HBr concentrations of up to 116 ppm and 38 ppm, respectively, for 30 min. However, studies carried out by NASA showed that, with increased HF and HBr concentrations and the length of exposure period, many electronic components, their raw materials and conformal coatings degraded physically and functionally. With concentrations of 500 ppm HF and 200 ppm HBr, all the coatings of the CPU boards showed some corrosive damage and the resistance of conformal coatings was reduced by five orders of magnitude after 48 h of exposure. When HF and HBr concentrations further increased, the amount of degradation increased significantly and the length of the exposure period for component failure became shorter. With concentrations of 5,000 ppm HF and 2,000 ppm HBr, the powered CPU boards showed significant corrosion damage and failed after being exposed for 210 min.

There are only two published experimental studies [38, 42] dealing with HF corrosion on electronic equipment by halon replacements. Both studies were laboratory-scale and were mainly involved with Input/Output cards. The maximum HF concentration generated in these tests involving C_3HF_7 (FM-200) and C_4H_{10} (CEA-410) was up to 2126 ppm. The corrosion damage to I/O cards was dependent on HF concentrations and test conditions, such as fire size and type, the properties of halon replacements and the length of the exposure period. A study carried out by Hughes Associates [48] showed that no short-term damage (less than 30 days) to I/O cards was observed when exposed to HF concentrations of up to 970 ppm HF (averaged over 10 min) for 30 min. On the other hand, the study carried out by Bryan [47] showed that the HF gas and acid generated from halon replacements caused corrosion in several locations on the I/O cards. With HF concentration greater than 600 ppm, and an exposure period of 6 min, there was enough corrosion accumulated on the contacts for the computer not to recognize the installed I/O cards.

The previous studies involving halon replacements were not carried out to systematically investigate the effect of HF corrosion on computer systems and electronic equipment under realistic fire situations. These studies do not provide sufficient information to establish the threshold value of HF concentration and the length of exposure that the electronic equipment could tolerate. Also, there is a

need for information on short-term and long-term effects of HF on electronic equipment. More studies in this area are needed.

Although adequate information on HF corrosion on electronic equipment is not available there are some measures which can be used to reduce potential HF corrosive damage to electronic equipment. These measures include:

- To choose a proper agent for fire suppression (which will produce low thermal decomposition products);

- To install a good fire detection system to extinguish a fire at its early stage;

- To control humidity and temperature in the enclosure immediately after a fire; and

- To vent the enclosure and clean the equipment quickly after a fire.

These measures will reduce the quantities of HF gas generated during fire suppression and the duration during which the electronic equipment is exposed to the post-fire environment, and control the formation of HF acid on the surface of the electronic equipment.

7.0   CONCLUSIONS

1. HF is the primary thermal decomposition product generated by the current halon replacement candidates. Under similar fire conditions, the current halon replacement candidates produce at least 5 to 10 times more HF than Halon 1301 during fire suppression.

2. Corrosion damage caused by HF gas and acid, smoke and fire effluents will lead to metal loss, electrical current leakage and increased contact resistance. These damages may result in serious electrical shorting or cause the electronic equipment to receive false data and upset electronic systems, leading to system failure.

3. The damages caused by HF, smoke and fire effluents not only occur in the equipment located close to the fire but also occur in remote equipment.

4. Even in cases where there is no immediate reaction on the electronic equipment from exposure to HF, it is possible that HF corrosion may cause long-term damage to the equipment. The corrosion process to the electronic equipment will not stop after the fire is out.

5. The degree of corrosion damage depends on HF concentration, the temperature and relative humidity in the enclosure, the length of the exposure period, the nature of the combustible material involved and the properties of the exposed equipment.

6. The amount of HF corrosion that can be tolerated depends on the size, function and sensitivity of the electronic equipment. Many common materials and their components, such as aluminum and tantalum capacitors and components made of copper, silicon, tin and zinc, will be affected by HF corrosion, while some components, such as gold-plated semi-conductor and platinum relay contacts, will not be affected by HF corrosion.

7. In laboratory-scale studies involving Halon 1301, no failure of electronic components was observed when they were exposed to 300 ppm HF and 40 ppm HBr for 30 min. However, many electronic components, their raw materials and conformal coatings degraded physically and functionally when they were exposed to 500 ppm HF and 200 ppm HBr for a longer exposure period (up to 48 h). With increased HF and HBr concentrations, the amount of degradation increased significantly and the length of exposure period for component failure was reduced.

8. There are only two published experimental studies on HF corrosion involving halon replacements (FM-200, CEA-410). In a study conducted by Hughes Associates [48], no failure of Input/Output cards was observed when they were exposed to 970 ppm HF for 30 min. However, in the Bryan [47] study, malfunction of Input/Output cards occurred when exposed to HF concentrations of greater than 600 ppm for 6 min.

9. Available information from previous studies is insufficient to establish a threshold value of HF concentration and the length of exposure that the electronic equipment can tolerate. More studies in this area are needed.

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Table 1. Thermal Decomposition Product (TDP) Concentrations Generated by Halon Replacements (in ppm by volume) [10]

Scale		Laboratory-Scale Testing					Intermediate-Scale Testing					Full-Scale Testing				
Organization		FAATC	NMERI		3 M		Hughes Assoc. and NASA			NMERI		NRL		U.S. Coast Guard		
Analytical Method		MS	FTIR		ISEF		ISEF & FTIR			FTIR		Ion Chromatography		FTIR		
Enclosure Vol.		265 ml	Cup Burner	0.175 m^3	1.26 m^3		1.20 m^3	29 m^3		18.27 m^3		56 m^3		560 m^3		
Special Condition		@.7-.9 of ext. conc	@0.9 of ext. conc		ext. $\leq$ 8 seconds		8 s discharge	15 s discharge		5 s discharge, ext.< 7 s		$\leq$ 6 s discharge		10 s discharge		
Heptane Fire Size (Pan Size)		250 W[A]		390 mm^2	0.1 kW	3.7 kW	4.0 kW	78 kW	250 kW	370 cm^2	0.155 m^2	0.23 m^2	1.1 m^2	1.0 MW	2.5 MW	5.5 MW[B]
HF	FC-318		74000													
	FC-3-1-10	13000	46000	7	79	1546	1450	850	2200	30	800	2900		4500	3500	6000
	HFC-23	41900	60000	115	39	1199	1100			226	1300	3400	11000	1200	2600	7000
	HFC-125	10000	61000													
	HFC-134a		99000													
	HFC227ea	1800		3	96	2241	1400			26	700	2500	26000	2000	3500	9000
	NAF S-III															
	HCFC-124	22500	44000							80	1200				15000	
	HCFC-123	13600														

	HBFC22B1	2900	19000													
	CF$_3$I	2000	27000													
	Halon1301	1200	7900	0.1	8	157	250			10	80			300		
COF$_2$	FC-318		154000							12	84	600	1700			
	FC-3-1-10		4600													
	HFC-23		4900													
	HFC-125		5200													
	HFC-134a		12000													
	HFC227ea															
	NAF S-III															
	HCFC-124		5200													
	HCFC-123		2700													
	HBFC22B1		4200													
	CF$_3$I		1600													
	Halon1301															
HCl	HCFC-124	610														
	HCFC-123	2400														

	Halon 1301	140														

[A] methane   [B] diesel pan fire in the 5.5 MW fire

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Table 2:   The Corrosive Behaviour of Selected Common Materials with Hydrogen Fluoride and Hydrofluoric Acid [15, 27, 38-40]

Material	Corrosive Behaviour with Hydrogen Fluoride and Hydrofluoric Acid
Aluminum	Aluminum is corrosion-free with hydrogen fluoride. However, it is susceptible to corrosion by hydrofluoric acid. The corrosion rate of aluminum with relatively low concentration of hydrofluoric acid is higher than that with relatively high HF acid concentration. A high HF acid concentration produces a corrosion layer on the surface which reduces further corrosion of the aluminum.
Ceramic	Al_2O_3 is resistant to hydrofluoric acid, Fe_3O_4, TiO_2, ZrO_2 and SnO_2 are affected by hydrofluoric acid. No data is available for the corrosive resistance of BeO to hydrofluoric acid, but BeO is extremely resistant to hydrogen fluoride.
Copper	Copper reacts slowly with hydrogen fluoride but is considered unsuitable for use in contact with hydrofluoric acid, even when cold.
Gold	Gold is unaffected by hydrogen fluoride and hydrofluoric acid of any concentration.
Glass and Enamel	These materials are attacked by hydrofluoric acid but no corrosion rate data is available.
Irons	Hydrofluoric acid is corrosive to irons but its corrosive rate depends on the composition of the material.
Lead and Lead Alloys	Lead has good resistance to high hydrofluoric acid concentrations (52% - 70%) but is rapidly attacked by diluted acid. No data can be found for lead-tin solder exposed to hydrogen fluoride or hydrofluoric acid.

Magnesium	Magnesium is resistant to hydrofluoric acid attack.
Nickel	Nickel is resistant to hydrogen fluoride up to 800 K. Nickel has a low corrosion rate in hydrofluoric acid but its corrosion behaviour is highly dependent on the presence of oxygen.
Palladium	No data is available on the effects of hydrofluoric acid alone.
Platinum	Platinum is unaffected by hydrogen fluoride and hydrofluoric acid of any concentration.
Rhodium	No corrosion occurs in rhodium with 40% hydrofluoric acid at room temperature.
Silicon	Silicon is affected by hydrofluoric acid.
Silver	Silver corrodes rapidly in the presence of hydrogen fluoride and hydrogen bromide.
Steels	Both carbon steels and stainless steels have useful corrosion resistance to high concentrations of hydrofluoric acid (90%) but their corrosion in dilute acids is appreciable.
Tantalum	The corrosion of Tantalum by hydrofluoric acid is fast.
Tin	Tin is attacked by both hydrogen fluoride and hydrofluoric acid.
Zinc	Zinc is attacked by hydrofluoric acid.

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