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Assessing the Impact of Fire Extinguisher Agents on Cultural Resource Materials

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Abstract. Portable fire extinguishers and their associated fire extinguishing agents play an important role in reducing the impact of fire on cultural resource collections. These may be valuable collections or the structure housing the resources which itself may be of cultural significance. A fire which can be suppressed with an extinguisher in its incipient stage will not grow to threaten adjacent materials. A range of extinguishing agents are commonly used in museums and libraries, including water, clean gaseous agents, dry chemicals, and foam. Their effectiveness in combating fires has been studied and is well-understood, but their effects on collection materials have not been adequately studied. What is less well understood is what effect these agents might have on the cultural heritage materials that are exposed to them. The primary goals of this project were to study the effects of portable fire extinguisher agents on cultural heritage materials, establish a repeatable test protocol, and assess potential cleaning methods. Eleven tests were conducted, which evaluated the following variables: exposure with and without fire, extinguisher type, material type, and sample exposure (direct vs. indirect). Thirteen materials were evaluated, which represented a wide range of the materials that can be found in cultural heritage buildings. The established test method was found to be adequate for exposing a large number of materials to the effects of extinguisher agents. These affects have been assessed on a wide range of cultural resource materials. The results indicated that, there was no single extinguisher which had no effect on all of the materials tested, even the clean agents. In fact, the corrosive effects of the thermal decomposition products from the clean agents were more pronounced in the fire tests. Several cleaning methods were also evaluated. None of the cleaning methods worked for all materials, but some worked better for certain materials. It was found that damage to samples was immediate and did not appear to progress incrementally with time. This suggests that in some cases (i.e., exposure to water mist, Halotron I and FE-36) immediate remediation may not be necessary. It is the intent that the data in this paper could be used as the foundation of an extinguisher selection matrix to be included in NFPA standards.

Keywords: Cultural resources, Cultural resource materials, Extinguisher, Extinguishing agents

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1. Background

Portable fire extinguishers and their associated fire extinguishing agents play an important role in reducing the impact of fire on cultural resource collections. These may be valuable collections or the structure housing the resources, which itself may be of cultural significance. A fire that can be suppressed with an extinguisher in its incipient stage will not grow to threaten adjacent materials. A range of extinguishing agents is commonly used in museums and libraries, including water, clean gaseous agents, dry chemicals, and foam. Their effectiveness in combating fires has been studied and is well-understood, but their effects on collection materials have had limited study. Scheffey and Forssell [1] conducted an extensive literature review regarding the effects of fire and thermal decomposition products from extinguishing agents on a range of materials. While conservators are well versed in the effects of moisture and water on collections, little data is available on the effects of other extinguishing agents, with the exception of a limited study conducted in Norway [2]. The potential collateral damage from agent overspray, potential misuse of extinguishers in spraying collection materials, and the byproducts of the agent when used to extinguish a fire is of interest. Particularly, short- and long-term exposure to extinguishing agents needs to be quantified. This article is a condensed version of the full report [3].

2. Objectives

The primary goal of this project was to study the effects of portable fire extinguisher agents on cultural heritage materials. This goal was achieved by establishing a reproducible test protocol that could be used for future testing and that would permit the reporting and assessment of comparable test results by disparate testing entities. The responses of a range of selected materials were evaluated when exposed to the most commonly used portable fire extinguisher agents over both the short and long-terms. In addition, the efficacy of commonly utilized techniques employed to clean heritage materials after exposure to portable fire extinguisher agents was examined.

3. Approach

Two types of tests were performed in this work: non-fire (neat agent) tests and fire tests. The non-fire (neat agent) tests were exposures of representative materials directly and indirectly exposed to the extinguisher spray. The intent was to assess the impact of an agent which is discharged accidentally or maliciously in the absence of a fire. The fire tests were exposures of representative materials within and outside of the extinguisher spray pattern while using the extinguisher to fight a fire. The intent was to assess the impact of agent byproducts resulting from the extinguishment process.

Each test was conducted with each type of extinguisher. The following sections describe the test parameters and general approach of each type of test. Scoping

tests were performed to refine the specific test parameters. The effect of a fire alone on the representative materials was not evaluated.

3.1. Materials Evaluated

The aging of cultural heritage materials is subject to a number of variables, including but not limited to: the composition of the material, the way in which it was exhibited, stored, or used, the amount of light it received, as well as the ambient temperature (T) and relative humidity (RH) it experienced and the degree to which they fluctuated. As a result, it can be difficult to identify a large number of replicate samples that have all aged naturally and under the same conditions. For this particular investigation the task was more difficult because of the number of samples needed for the project. In addition to the 780 samples needed for the neat and fire tests combined, additional samples were needed to serve as control sets and for scoping tests. Consequently, the project team decided to use modern materials in all the tests. It was thought that these materials were the best options for enabling subsequent replication and/or extension studies.

Due to the large number of samples required for testing and the surface area required to test the cleaning techniques, the size of the sample materials was selected to be nominally 10 cm (4 in.) by 10 cm (4 in.). The small sample size also facilitated the use of direct mass measurement of the deposition on the exposed material. The thirteen materials that were exposed in this test program and their associated test designation include: Black iron sheet [1.57 mm (20 gauge) thick], Material #1; Copper sheet (1.08 mm [0.042 in.] thick), Material #2; Aluminum sheet (3.15 mm [0.12 in.] thick), Material #3; Vegetable tanned leather (Bovine leather with mimosa tan; 1.87 mm [0.073 in.] thick), Material #4; Tulip poplar wood, unvarnished (simulating secondary wood; 6.43 mm [0.25 in.] thick), Material #5; Cherry wood, varnished with a shellac (0.57 kg [1.25 lb]) varnish (simulating primary wood; 6.43 mm [0.25 in.] thick), Material #6; Linen canvas, oil primed and painted with stripes of flake white, ivory black, chromium oxide, and red ochre paints with bare canvas between the color stripes (0.46 mm [0.018 in.] thick), Material #7; Cotton canvas, acrylic primed and painted with cadmium red, phthalo green yellow, titanium white, and mars black paints with bare canvas between the color stripes (0.46 mm [0.018 in.] thick), Material #8; Travertine tile, tumbled finish (9.75 mm [0.38 in.] thick), Material #9; Marble tile, tumbled finish (10.06 mm [0.41 in.] thick), Material #10; White-tailed deer fur (4.17 mm [0.16 in.] thick), Material #11; Unglazed terracotta tile (14.52 mm [0.57 in.] thick), Material #12; and Glazed ceramic tile (6.90 mm [0.27 in.] thick), Material #13. All samples were prepared by the Colonial Williamsburg Foundation in Williamsburg, VA and were transported to the test facility in sealed containers conditioned to 50% relative humidity using silica gel bags.

Three arrays of samples were exposed during each test, with two samples of each material on each sample array. One array was exposed directly in the spray pattern of the portable extinguisher while the other two arrays were exposed indirectly outside of the spray pattern (see Sect. 3.3). The materials directly exposed and on one of the indirectly exposed arrays were used for assessment and cleaning

by the conservators on the research team. For one of the indirectly exposed arrays, one sample was used as an uncleaned reference sample and the other was held for possible future analysis. At the time of this article, analysis of the held samples has not been conducted.

Two additional, identical sets of materials were prepared. These served as controls. Both of these sets were handled in the same manner as the test samples and traveled to the test facility under the same conditions as the other samples, but were not exposed to extinguisher agents. One of these sample sets was cleaned using the same techniques as used on the exposed samples to evaluate the effects of the cleaning methods. The remaining set served as an unexposed reference for relative measurements of the effects of the exposures.

The sample materials were mounted on plywood sample arrays using Velcro®. The hook portion of the Velcro was attached to the plywood and the loop portion of the Velcro was attached to each sample. One sample of each material was located near the center of the sample array, and one was located near the perimeter of the sample array. The test sample array included 26 samples (2 × 13 materials), with the center column containing six samples with reduced vertical spacing between samples. The total exposed area was approximately 56 cm (22 in.) wide by 67 cm (26.5 in.) tall. A photograph of a typical sample array is shown in Fig. 1. The samples were placed in the same locations for each test.

Figure 1. Typical sample array (for direct and indirect arrays) for exposure tests showing two samples of each material in a grid layout.

3.2. Extinguishers Evaluated

There are many types of extinguishers available to combat various fire hazards. The portable extinguishers evaluated were those applicable for use in a museum/cultural heritage type application. These extinguishers had a minimum UL 711 2A rating for A:B:C or A:C fires. The following five extinguisher agents were used: ABC dry chemical (monoammonium phosphate) [Amerex Model B456]; Water mist [Amerex Model B272NM]; HCFC blend B (Halotron I) [Amerex Model 398]; HFC-236fa (FE-36) [Ansul Cleanguard Model FE13]; and ABC dry chemical [Amerex Model B456] and Water mist [Amerex Model B272NM].

The combined ABC and water mist scenario was representative of water application from a sprinkler or water hose after unsuccessful application of an ABC powder extinguisher. The water mist extinguishers were filled with de-ionized water provided by the manufacturer. De-ionized water is typically used in the extinguishers. As carbon dioxide (CO_2) does not have a Class A rating it is generally not applicable to many museum/cultural heritage scenarios and was not included in these tests.

3.3. Test Enclosure

Cultural resource materials are commonly exhibited in rooms, display areas, and galleries. It was important to establish an appropriate fire size to room volume ratio. Keeping this ratio low is consistent with the typical application of portable extinguishers in museums and historic buildings, i.e., small fires in large spaces. The neat agent tests were conducted in a large test room with internal dimensions of 10 m (33 ft) wide by 10 m (33 ft) deep by 3 m (9.8 ft) high. The fire exposure tests were performed at a separate facility with an enclosure constructed in a similar fashion to the neat agent test enclosure but was slightly smaller. The interior dimensions were 9.1 m (30 ft) wide by 9.1 m (30 ft) deep by 3 m (9.8 ft) high.

3.3.1. Extinguisher Separation: Neat Test Scoping Results Through scoping tests, the optimal extinguisher separation distances were determined to be between 75% and 90% of the maximum effective range identified in the manufacturer specifications. These distances were established such that the extinguisher would provide relatively full coverage of most of the direct sample array. The following separation distances were established: ABC dry chemical (monoammonium phosphate): 4.3 m (14 ft); Water mist: 3.0 m (10 ft); HCFC blend B (Halotron I): 4.9 m (16 ft); and HFC-236fa (FE-36): 4.3 m (14 ft).

Through scoping tests, the locations of the indirect arrays were established. The indirect sample arrays were placed 1.5 m (5.0 ft) in front of the directly exposed array (and between the direct array and the extinguisher nozzle) and offset 1.8 m (6.0 ft) from the center of the direct array as shown in Fig. 2. These locations provided some exposure to the indirect samples, which was notably less than for the directly exposed sample array. It was decided to establish this criterion for both the non-fire and fire tests.

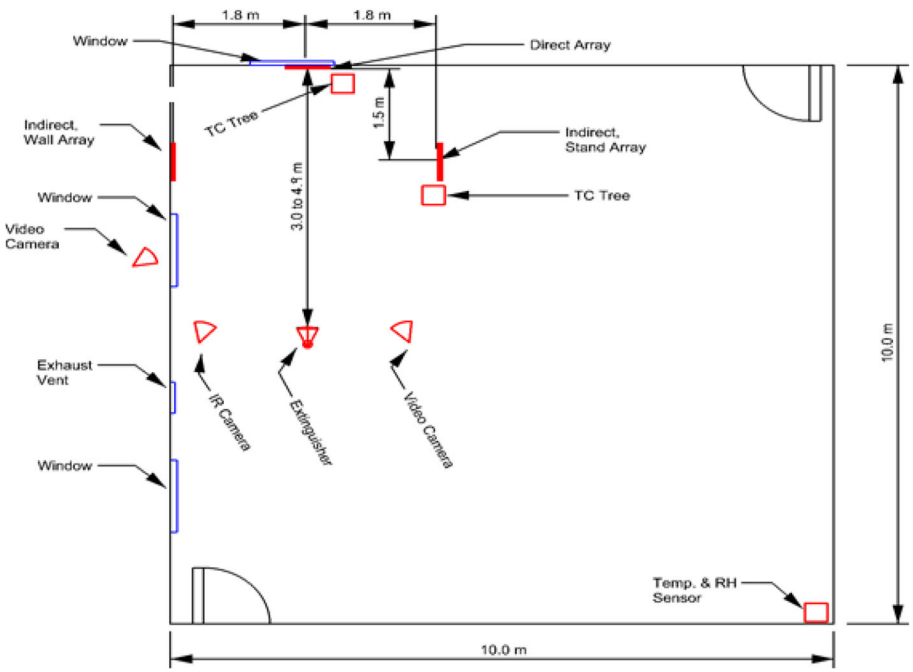

Figure 2. Non-fire test enclosure plan view showing sample array locations, extinguisher location, and instrumentation locations.

3.4. Instrumentation

The instrumentation for the fire and non-fire tests was largely the same. Figure 2 is a schematic of the test enclosure with instrumentation for the non-fire tests. Figure 3 is a photograph of the test setup for the fire tests. The test setup for the non-fire tests was the same, except with the wood crib removed. The instrumentation employed during these tests included a scale to measure the deposition on the exposed samples. The scale was able to measure mass with a resolution of 0.001 g (2.2×10^{-6} lb). A scale with a larger resolution (0.1 g [0.0002 lb]) was used for samples weighing over 300 g (0.66 lb).

In the test enclosure, the temperature and relative humidity were monitored. Temperatures were recorded at two locations using vertical trees of five, evenly spaced type-K thermocouples at heights of 0.3 m, 0.9 m, 1.5 m, 2.1 m, and 2.7 m (1 ft, 3 ft, 5 ft, 7 ft, and 9 ft) above the floor. One was installed 0.45 m (1.5 ft) from the center of the indirectly exposed sample array and 2.5 cm (1.0 in.) in front of the indirect array. The second was installed 0.45 m (1.5 ft) from the center of the directly-exposed sample array and 2.5 cm (1.0 in.) in front of the direct array. In addition, a thermocouple was installed in the center of the directly-exposed sample array so that the thermocouple bead was flush with the sample surface. This thermocouple was installed from behind the sample array.

Figure 3. Fire exposure test setup showing installation of sample arrays and wood crib in test enclosure.

A relative humidity and temperature sensor (Omega model HX92AV) was installed in a corner of the enclosure 1.5 m (5 ft) above the floor. All data was recorded at a rate of 1 Hz using National Instruments data acquisition hardware and software.

Two video cameras were used to capture the extinguisher activation and spray during the test. One was located outside of the spray area behind the extinguisher, approximately 6.1 m (20 ft) away from the direct sample array, looking at the direct sample array. The second video camera was located outside of the test enclosure looking through a window perpendicular to the spray. The window was located near the indirect sample array mounted on the wall, approximately 4.3 m (14 ft) away from the direct sample array. An infrared camera (FLIR Model T440) was located inside of the test enclosure, behind the extinguisher approximately 6.1 m (20 ft) away. It was directed at the direct sample array to assess the extinguisher agent impact area. Photographs of the test setup, sample mounting, and extinguisher were taken.

3.5. Fire Source Scoping Test Results

The objective of the fire exposure tests was to evaluate the effects of the combination of the agents, decomposition products and fire effluent on representative materials. Fires in ordinary (Class A) combustibles appear to be the most common and representative fire threat. The use of standard extinguisher test methods (that is, the use of repeatable wood crib fires as the Class A source) was adopted, with the realization that a fire on the order of 200 kW to 500 kW would likely be used. Also, it was decided that the fire should not be of sufficient magnitude to thermally damage exposed materials. This would allow for better assessment of agent effects.

Scoping tests were conducted to determine the sizes of the wood crib and associated ignition pan fire that could be readily extinguished by all of the extinguishers. Scoping tests were also conducted to establish the separation distance between the wood crib and the directly exposed sample array. The three criteria that were

used to evaluate the scoping fires were: (1) the fire had to be easily extinguished, so that all flaming was extinguished well before the agent was totally expended; (2) agent exposing the direct sample array had to pass through and around the fire source; and (3) agent overspray and smoke/soot must be deposited on the directly exposed sample array without thermally damaging the sample array.

Two standard wood cribs were evaluated: a UL 1A crib [12 layers of 6 pieces per layer of 3.8 by 3.8 by 50.8 cm (1.5 by 1.5 by 20 in.) wood] [4] and a UL 1715 wood crib (10 layers of 5 pieces per layer of 3.8 by 3.8 by 38 cm [1.5 by 1.5 by 15 in] wood) [5]. The UL 1A crib was readily extinguished by all of the extinguishers tested. Only the FE-36 extinguisher was used on the UL 1715 crib and readily extinguished the fire. This crib produced a lower flame height and less smoke than the UL 1A crib and was deemed an appropriate incipient fire source for the fire tests.

The separation distance between the wood crib and the directly exposed sample array was also evaluated during this scoping test. A separation distance of 0.66 m (26 in.) between the wood crib and the direct array allowed for fire products and agent deposition on the direct array without any thermal effects. It was determined visually from the firefighting procedures that the indirect target locations used in the neat tests were also appropriate for the fire tests. At these locations, it was determined that the indirect arrays would be exposed to some fire products and agent deposition, but notably less than the direct array.

4. Test Matrix

A total of 5 non-fire and 6 fire tests were conducted during this test program. Each extinguisher type was evaluated for each type of test; the matrix of tests conducted is shown in Table 1. Test 6B was conducted with only the direct sample array. This repeat test was conducted to utilize surplus material samples.

Table 1
Test Matrix for Non-fire and Fire Exposure Tests

Test number	Exposure	Extinguisher
1A	Non-fire	ABC dry chemical
2A	Non-fire	Water mist
3A	Non-fire	HCFC blend B (Halotron I)
4A	Non-fire	HFC-236fa (FE-36)
5A	Non-fire	ABC dry chemical and water mist
1B	Fire	ABC dry chemical
2B	Fire	Water mist
3B	Fire	HCFC blend B (Halotron I)
4B	Fire	HFC-236fa (FE-36)
5B	Fire	ABC dry chemical and water mist
6B	Fire	ABC dry chemical and water mist

5. General Test Procedures

Except for the water mist extinguishers, all of the extinguishers came from the vendor in a charged and ready condition. The water mist extinguishers were charged in accordance with manufacturer's instructions. All extinguishers were weighed prior to discharge.

Materials were conditioned to a temperature of 21°C ± 4°C (70 °F ± 8 °F) and a relative humidity of 50% ± 10% for a minimum of 5 days prior to the exposure tests. Prior to any testing, the test samples were visually assessed. A condition report detailing their pre-exposure condition was written up and any anomalies, such as knot holes (in the wood sample), scratches (in the metal and stone samples), and scars (in the hide layer of the fur samples and in the leather samples), were noted. The samples were photographed and weighed. Nitrile gloves were worn during all sample handling, both pre- and post-exposure, to avoid transferring oils, salts or other contaminants onto the samples. Velcro® was applied to the back of each sample. The samples were then labeled, weighed and mounted on one of the sample arrays.

Doors to the enclosure were shut during all tests. For fire tests, natural ventilation was provided by a 0.45 by 0.45 m (18 in. by 18 in.) louvered vent in the ceiling. The louvered vent was located away from the fire in the opposite corner of the fire. No ventilation was provided for the non-fire tests.

The data acquisition system in the test enclosure was activated, and, after 1 min, the sample arrays were mounted in their appropriate locations. Both video cameras and the infrared camera were then activated.

5.1. Non-fire Exposure Procedures

For the non-fire tests, after 30 s of background video, the extinguisher was discharged by the firefighter and aimed at the center of the directly exposed sample array from the fixed desired separation distance. The fire extinguisher was discharged until it was completely empty. The end of discharge time was recorded. For the ABC plus water mist test, the extinguishers were sequentially discharged, first the ABC unit, then the water mist unit.

5.2. Fire Exposure Procedures

The wood crib was placed in its stand above the ignition pan. Both video cameras were activated. The pan was then filled with 300 ml (0.08 gal) of commercial grade n-heptane.

After 30 s of background, the ignition pan beneath the wood crib was lit, and the doors to the enclosure were shut. The wood crib was allowed to burn for 4 min. The firefighter then began to suppress the fire with the portable extinguisher, starting from a distance of 1.8 m (6.0 ft), aligned with the directly exposed material array. The firefighter was allowed to advance on the crib and move toward either side of the crib, the top and bottom as necessary to cause extinguishment. The firefighter was not allowed to attack the crib from behind (nearest the directly exposed array). The firefighter fully discharged the fire extin-

guisher onto the wood crib. Where both the ABC and water mist extinguishers were used, the water mist extinguisher was fully discharged on to the wood crib after the ABC extinguisher was fully discharged.

5.3. Post-exposure Procedures

For both test series, 5 min after the conclusion of the extinguisher discharge, the sample arrays as a whole were removed from the test enclosure by the firefighter and transported to an examination room. This 5 min ''soak period'' allowed any agent dispersed throughout the test enclosure to settle onto the sample arrays.

The process of removing and transporting the sample arrays to the examination was accomplished within 1 min. Once all sample arrays were removed, both doors to the test enclosure were opened and the test enclosure was purged using the ventilation system. The enclosure floors, walls, and ceiling were vacuumed and/or cleaned as necessary to remove agent before conducting the following test. Each sample was then weighed and photographed before being packaged for transportation to the conservator assessment facility. Individual samples were handled by personnel wearing nitrile gloves.

5.4. Sample Assessment and Cleaning

A detailed condition assessment was carried out on each sample within 1 week of testing. The samples were reassessed after 6 months, 12 months, and 18 months of exposure. The samples were photographed at each of these times and a visual assessment was conducted under both ambient and raking light. The assessment noted individual condition issues, such as cockling, surface accretions, staining, corrosion, and visible color change. This last criterion was noted by comparing the sample against other non-exposed samples. Due to the normal color variation in all the samples, it was primarily useful for determining whether exposure to ABC dry chemical had resulted in a color shift. Estimates as to the degree of surface change considered exposure to the face of the sample only. Changes to the back of the sample were noted but not quantified.

The directly exposed samples and the indirectly exposed samples from the wall array were divided into two groups, one of which underwent immediate cleaning and the other of which was stored for 6 months and then cleaned. The rationale for this division was to assess whether prolonged exposure to the extinguishing agents resulted in additional damage and/or made it more difficult to remove the extinguishing agent from the surface. The 6-month delay was selected as being reflective of the delay some institutions might face while lining up resources, whether funding or staffing, prior to mitigating any exposure.

No information on approaches to cleaning materials exposed to fire extinguishers was found in the conservation literature; however, there are several papers detailing cleaning after exposure to soot and/or fire. The most commonly utilized cleaning techniques were vacuuming combined with light brushing [6, 7]; cleaning with a soot eraser [8–10]; and cleaning using aqueous mixtures [8]. A fourth method, brushing with soft brushes, has been used by some institutions but not published. Each sample was divided into four 2.5 × 2.5 cm (1 × 1 inch) quad-

rants, and each of the quadrants was cleaned by one of the four methods (see Fig. 4). To ensure that the cleaning was conducted in a manner that was comparable from sample to sample, overlapping passes were made left to right from the top to the bottom of the sample quadrant, then up and down from left to right, then left to right from top to bottom and once more from top to bottom moving across the sample left to right. To ensure that material was not carried from one sample to the next the brushes were cleaned between each sample and the end of the soot eraser was cut off to ensure a fresh surface was used.

6. Results

The individual observations associated with each test series are detailed below, but a few generalizations may be made about the overall test set up. The lower set of samples on the direct sample array tended to get the greater exposure of the two direct sets. Although the two indirect samples were situated at the same lateral distance from the extinguisher, there was a difference in the agent deposition between the two. The wall-mounted array tended to get more exposure than the floor stand array. Typically, the floor stand samples got very little exposure. Some of the heavier samples, such as the terracotta tile and the marble, fell off the direct array during the water mist tests, which resulted in breakage of some of the samples. It is possible that the adhesive failure on the Velcro® was a mechanical one

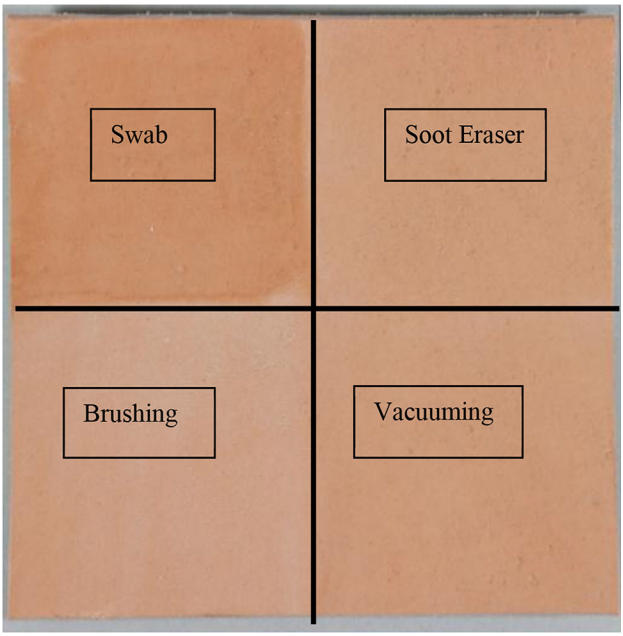

Figure 4. Leather sample showing the four cleaning divisions demarcated, typical for all materials.

due to increased sample weight as a result of the exposure to water; however, it is also possible that the failure was a chemical one, produced by the interaction between the adhesive and the water and possibly augmented by the stress (weight) the adhesive was under.

6.1. Direct Array Temperature: Non-fire Tests

Prior to the agent discharge, the temperatures in the test enclosure were nominally 20°C. There was some minor variation (generally less than 1°C). The minimum temperatures reached at the center of the direct array are shown in Table 2. For the ABC dry chemical test, the temperature at the center of the direct array did not change as a result of the discharge. For the tests with water mist extinguishers, including the combined ABC and water mist test, the temperature at the center of the direct array decreased slightly from the ambient temperature.

The most significant temperature changes came from the gaseous agents. FE-36 had the lowest temperature reached – 41°C; Halotron I was slightly higher at – 23°C. These large decreases in temperatures were expected for the gaseous agents because they are in a liquid state within the extinguisher, due to the high cylinder pressure. As Halotron I and FE-36 were discharged, the liquids rapidly evaporated and the temperature decreased dramatically. For the gaseous agents, the temperatures remained at the low values for approximately 1 min after the end of discharge before returning to ambient. This was likely due to the presence of liquid agent or frost (from water in the air) that remained on the direct array after the end of discharge. Although the thermocouple temperatures returned to ambient levels within approximately 1 min after discharge, there was visible frost remaining on some of the samples at least 6 min after discharge as shown in Fig. 5 (i.e., when samples were photographed in the examination room).

6.2. Temperature and Relative Humidity: Fire Tests

Table 3 contains the temperature and relative humidity test data for the fire exposure tests. It should be noted that all of the extinguishers extinguished the test fire in less than 6 s, but the extinguishers were discharged until empty. The total discharge times for the individual extinguishers were comparable to the data pre-

Table 2
Direct Sample Array Minimum Temperature During Discharge and Extinguisher Discharge Times for Non-fire Tests

Test no.	Agent	Extinguisher discharge time (s)	Minimum direct sample array temp. during discharge (°C)
1A	ABC dry chem.	29 ± 2	20 ± 1
2A	Water mist	78 ± 2	14 ± 1
3A	Halotron I	15 ± 2	− 23 ± 1
4A	FE-36	13 ± 2	− 41 ± 1
5A	ABC and water mist	ABC: 33 ± 2 Water: 85 ± 2	15 ± 1

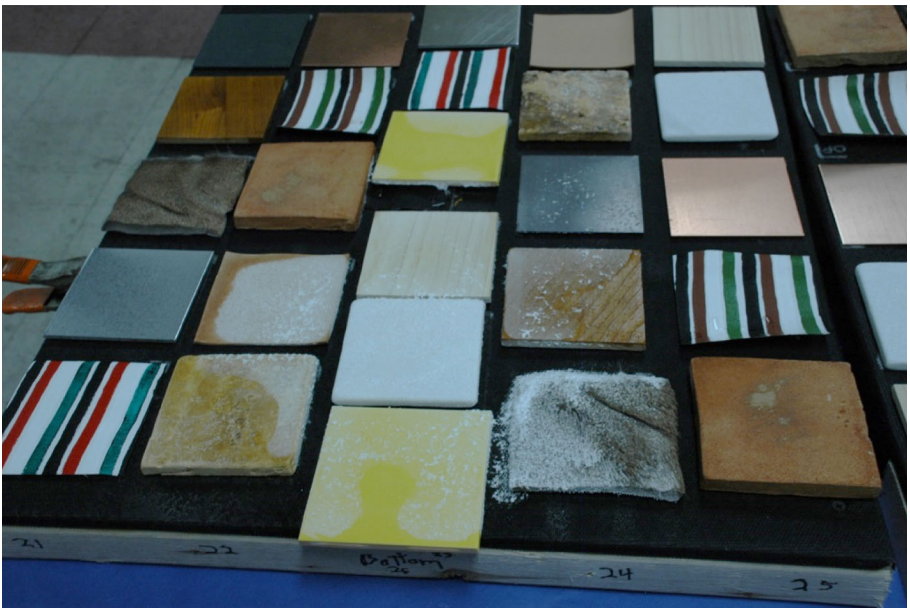

Figure 5. Example of frosting of samples on the direct sample array due to FE-26 exposure (from Test 4A).

sented in Table 2. During the fire there was a general increase in relative humidity in the test enclosure. The increase in relative humidity varied widely between tests; from 1% RH for Test 4B (FE-36) to 21% for Test 2B (water mist). After the extinguishers were discharged, the relative humidity spiked to nearly 100% RH for every test. The increase in relative humidity was expected, due to the release of water vapor by the combustion process, and can be an added threat to cultural resource materials via smoke from the fire.

Prior to the agent discharge, the temperatures in the test enclosure were nominally 25°C; this was slightly higher than for the non-fire exposure tests but still in the range of what is considered normal indoor ambient temperatures. The direct sample array temperatures were notably higher for the fire tests compared to the non-fire tests. In general, direct array temperatures from the fire exposure tests were between 17°C and 59°C higher than for non-fire exposure tests. None of the fire tests with the clean agents resulted in frost on the direct array as was observed for the non-fire tests.

6.3. Conservator Assessment Results

The results of the conservator assessments are summarized in Table 4 (non-fire tests) and Table 5 (fire tests). Within the parameters of these tests, damage was both less diverse and less dramatic than expected. Many samples exhibited no visible changes at all. Although there was individually significant damage to samples, the types of damage noted tended to be within the scope of the known risks for

Table 3
Post-discharge Direct Sample Array Temperatures and Pre-discharge Relative Humidity, Maximum Relative Humidity During Fire, and Maximum Relative Humidity Post-discharge Data for Fire Tests

Test no.	Agent	Pre-discharge enclosure RH (%)	Post-discharge direct sample array temp. (°C)	Maximum enclosure RH during fire (%)	Maximum enclosure RH post-discharge (%)
1B	ABC dry chemical	70 ± 2	55 ± 1	80 ± 2	100 ± 2
2B	Water mist	51 ± 2	31 ± 1	72 ± 2	93 ± 2
3B	Halotron I	74 ± 2	− 3 ± 1	88 ± 2	98 ± 2
4B	FE-36	78 ± 2	18 ± 1	79 ± 2	98 ± 2
5B	ABC and water mist	83 ± 2	58 ± 1	94 ± 2	100 ± 2
6B	ABC and water mist	84 ± 2	61 ± 1	88 ± 2	98 ± 2

Table 4
Summary of All Extinguisher Discharge Effects on All Materials for Non-fire Tests

	Extinguisher				
Material	Water mist	Halotron I	FE-36	ABC	ABC + water mist
Glazed ceramic tile	N/A	Surface residue noted	Surface residue noted-10% to 25%	Heavy layer of powder-100%	Surface accretions-100%
Terracotta	N/A	N/A	N/A	Heavy layer of powder-100%	Surface accretions-100%
Marble	N/A	N/A	N/A	Heavy layer of powder-100%	Surface accretions
Travertine	N/A	N/A	N/A	Heavy layer of powder-100%	Surface accretions
Iron	Limited corrosion (spotting) 2% of surface	Corrosion	N/A	Heavy layer of powder-100%	Corrosion 2% to 5%; surface accretions-100%
Copper	Limited corrosion (spotting) 5% of surface	Corrosion—100% of surface	Slight corrosion 1% to 2%	Heavy layer of powder-100%	Corrosion 1% to 5%; surface accretions—100%
Aluminum	Limited corrosion (spotting) 2% of surface	Corrosion—75%	Slight corrosion 1% to 2%	Heavy layer of powder-100%	Corrosion; surface accretions-75% to 100%
Leather	Surface darkening	Surface darkening	Surface darkening	Heavy layer of powder-100%	Surface accretions
Acrylic paint	Planar distortions	Planar distortions; paint damage	N/A	Heavy layer of powder-100%	Surface accretion
Oil Paint	Planar distortions	Planar distortions	Planar distortions	Heavy layer of powder-100%	Planar distortion; surface accretion
Fur	N/A	N/A	N/A	Heavy layer of powder-100%	Surface accretion; fur matted
Varnished wood	Surface spotting	Surface residue noted	N/A	Heavy layer of powder-100%	Surface accretion
Unvarnished wood	Surface spotting	N/A	N/A	Heavy layer of powder-100%	Surface accretion

Where a percentage range is present it represents the effects seen on both samples; *N/A* no observable change

that material. For example, it was expected that the water mist extinguisher would cause staining or discoloration of the organic samples, and similarly that it might cause the painting samples to cockle.

In general, change was hardest to detect on the unvarnished wood, marble, and travertine samples. This was due in part to the light color of the samples and also to the matte appearance of the surface. Changes in gloss, for example on the glazed ceramic tile, acted as indicators of potential surface deposits. Change was also difficult to detect on the terracotta and the fur samples due to the texture of the surfaces. There were differences in exposure between the two samples of the same material on an array that made it difficult to compare the extent of damage. For example, one copper sample might tarnish over 100% of the surface and the other sample only over 75% of its surface. As noted earlier, these differences were due to the degree of exposure its location on the sample array received.

None of the extinguisher agents left the samples entirely damage free. All of them impacted at least some of the materials in the test group in some manner. The introduction of a fire scenario increased the extent of the extinguisher agents' impact on the sample materials. For example, light tarnish was noted on the copper after exposure to the neat Halotron I test, but in the fire scenario the tarnish was much more pronounced. This was expected as clean agents that contain fluorine are known to decompose during a fire and produce hydrogen fluoride, which is corrosive [1].

When damage did occur to a sample, it was immediate and did not appear to progress incrementally with time. This suggests that future testing can be shortened and does not need to be run out for the lengthy assessment period undertaken by this project. It also suggested that in some cases (i.e., exposure to water mist, Halotron I and FE-36) immediate remediation may not be necessary. In other words, some time can be bought. However, it must be noted that addressing exposure to ABC dry chemical should be a high priority because of the degree to which the material spreads, and the potential for it to be tracked to other galleries/spaces.

6.4. Cleaning Results

Some of the results from the cleaning tests are summarized in Table 6. None of the cleaning methods worked well for all of the materials, and individual methods worked better for certain materials. Although the soot eraser was effective at removing sooty and charred material from the stone and ceramic samples, it resulted in a matte or tarnished surface on the metal samples. This is most likely due to an interaction between the sulfur in the vulcanized rubber (the principal component of a soot eraser) and the metal surface. Brushing performed poorly overall. It had a tendency to smear soot into the surface, to abrade surfaces, and was not effective at removing particulates, such as the ABC dry chemical powder. Swabbing worked well on most samples, but did tend to cause darkening of the leather surfaces and swelling of the wood fibers in the unvarnished wood sample. Additionally, the wet cleaning created a slurry that was left behind on some of the samples with the heaviest layer of ABC dry chemical powder. This was most

Table 5
Summary of All Extinguisher Discharge Effects on All Materials for Fire Tests

	Extinguisher				
Material	Water mist	Halotron I	FE-36	ABC	ABC + water mist
Glazed ceramic tile	Soot 5%	Soot-60% to 80%	Soot-50% to 60%	Light layer of powder 100%	Surface accretions
Terracotta	Soot 10% to 20%; Breakage due to fall	Soot-70%	Soot-20%	Light layer of powder 100%	Surface accretions; breakage due to fall
Marble	Sooty streaks—1%	Heavy soot-80%	Soot-100%	Light layer of powder 100%	Surface accretions; Breakage due to fall
Travertine	N/A	Soot-10%	N/A	Light layer of powder 100%	Surface accretions
Iron	Limited corrosion (spotting) 2% to 10% of surface	Corrosion 80%; heavy soot-70%	N/A	Light layer of powder 100%	Corrosion-80%; surface accretions-100%
Copper	Limited corrosion (spotting) 5% to 10% of surface	Corrosion—100% of surface; soot—50%	Corrosion-100%	Light layer of powder 100%	Corrosion-60%; surface accretions—100%
Aluminum	Limited/spotting corrosion 2% of surface	Corrosion—70% to 80%; soot-1%	Corrosion—10%; soot 25%	Light layer of powder 100%	Corrosion; surface accretions-100%
Leather	Planar distortion; hardening; soot-60% to 70%	Soot = − 60%	Soot-80%	Light layer of powder 100%	Light layer of powder-100%; surface accretions-1%
Acrylic paint	Planar distortion; cracking of paint surface; soot 1% to 2%	Planar distortion; soot-40% to 50%	Heavy soot-50%	Light layer of powder 100%	Planar distortion
Oil paint	Planar distortion; rigidity	Planar distortions; soot 70%	Planar distortions; soot-70%	Light layer of powder 100%	Planar distortion; cracked paint; hardening
Fur	Planar distortion; slight rigidity	Small amounts of soot at ends of hairs	Soot in whiter fur; hairs loosened	Light layer of powder 100%	Surface accretions-100%; fur matted
Varnished wood	Surface spotting; darkening-100%	Soot-70%	Light soot-60%	Light layer of powder 100%	Light layer of powder 100%

Table 5
continued

Material	Extinguisher Water mist	Halotron I	FE-36	ABC	ABC + water mist
Unvarnished wood	Planar distortion; darkening	Heavy soot-70%	Soot–60% to 70%	Light layer of powder 100%	Light layer of powder 100%

Where a percentage range is present it represents the effects seen on both samples; *N/A* no observable change

Table 6
Partial Results from the Evaluation of Four Proposed Cleaning Methods for Removal of the Effects of Extinguisher Discharge

	Cleaning method			
Material	Swabbing with deionized water	Soot eraser	Brushing	Vacuuming and brushing
Glazed ceramic tile	Could create slurry with ABC powder	N/A	Did not remove ABC powder	Incomplete removal of ABC powder
Terracotta	Cotton fibers became caught on surface	N/A	Did not remove ABC powder; some abrasion of surface	Incomplete removal of ABC powder
Marble	Could create slurry with ABC powder	N/A	Did not remove ABC powder; did not remove soot effectively	Incomplete removal of ABC powder; did not remove soot
Travertine	Could create slurry with ABC powder	N/A	Did not remove ABC powder	Incomplete removal of ABC powder
Iron	Could create slurry with ABC powder	Caused tarnish	Did not remove ABC powder	Incomplete removal of ABC powder; no impact on active corrosion
Copper	Could create slurry with ABC powder	Caused tarnish	Did not remove ABC powder; some abrasion	Incomplete removal of ABC powder; no impact on active corrosion
Aluminum	Could create slurry with ABC powder	Caused tarnish	Did not remove ABC powder; some abrasion	Incomplete removal of ABC powder; no impact on active corrosion
Leather	Staining noted on all samples	N/A	Did not remove ABC powder; caused smearing of soot in some samples	Incomplete removal of ABC powder
Acrylic paint	N/A	N/A	Burnished paint surface; did not remove ABC powder; caused smearing of soot in some sample	N/A
Oil paint	N/A	N/A	Burnished paint surface; did not remove ABC powder; caused smearing of soot in some samples	Caused smearing of soot in some samples

Table 6 continued

Material	Cleaning method Swabbing with deionized water	Soot eraser	Brushing	Vacuuming and brushing
Fur	Caused hairs to clump together especially if ABC dry chemical present	Pulled hairs loose	Did not remove ABC powder; pulled hairs loose	N/A
Varnished wood	Could create slurry with ABC powder	N/A	Did not remove ABC powder	N/A
Unvarnished wood	Staining and swelling of wood	N/A	Did not remove ABC powder; did not remove soot effectively	Did not remove soot

N/A no observable adverse effect

noticeable on the samples with an impervious surface, such as the metal samples and the glazed ceramic tile, and may be due to the arbitrary cut off of the cleaning to ensure comparability. This would not be a factor if the cleaning were carried out to its conclusion. Swabbing was the most effective at dealing with the ABC dry chemical accretions that resulted from the combined ABC dry chemical and water mist tests. These accretions proved to be quite adherent and none of the other methods were able to address them well. None of the methods dealt with active corrosion on the metal samples effectively. The swabbing and the soot eraser performed best in this regard, most likely due to the mechanical action of the technique resulting in polishing.

Due to the degree to which the ABC powder spreads, the process of clean up after an intentional, accidental or malicious deployment is compounded. All of the materials in the room where the discharge of the extinguisher occurs should be cleaned and it would be worthwhile to inspect materials in adjoining galleries or rooms and to consider the possibility that the HVAC system could redeposit the powder in other spaces or that the powder could be tracked out of the room on shoes during assessment and recovery efforts. This will clearly impact the cost of remediation. Similarly, the ability of the ABC dry chemical powder to get behind the samples and to work its way into the fur structure suggests that multipartite artifacts may need to be disassembled in order to ensure that all of the surfaces are effectively cleaned. While both of these are negative aspects to the use and remediate of ABC dry chemical powder, there was a positive aspect. Examination of the swabs and soot eraser fragments used to clean the samples exposed to ABC dry chemical revealed that soot appeared to be universally absent from these materials. None of the swabs or soot eraser fragments had any of the blackening seen on those used to clean materials from the other tests.

As a technique for removing the ABC powder, vacuuming seemed to remove about 80% of the powder present on the surface. It is unlikely that the percentage would have gone up significantly if the number of passes had been increased as the first pass appeared to be the most effective. This raises the question of how clean is clean? Is this degree of cleaning sufficient to prevent future damage? Vacuuming was not as efficient at removing soot as the literature had indicated. In this case, it may have been because of the limits placed on the number of passes in this study or it may have been because of an interaction between the soot and the extinguishers. It is possible that the degree to which the extinguishing agents propelled the soot towards the sample may have an impact on the tenacity of the soot possibly because the soot was forced into the interstices of the material.

7. Conclusions

A reproducible test method for fire and non-fire exposures of cultural resource materials by extinguishing agents has been established. This simple test method is able to be used in future research and for practical evaluation of extinguishers for the materials contained in a specific cultural heritage building.

The effects of a number of extinguishers have been assessed on a wide range of cultural resource materials. Although, individual results may appear alarming, it is important to remember that, for most extinguishing agents the degree to which the agent spread, as evidenced by the impact seen on the indirect arrays, was limited. Overall, the results indicated that there was no single extinguisher which had no effect on all of the materials tested, even the clean agents. In fact, the corrosive effects of the thermal decomposition products from the clean agents were more pronounced in the fire tests. The results of this study can be used by fire protection engineers to select extinguishers for materials contained in a specific cultural heritage building in order to minimize the effects of the agents in the event that an extinguisher is discharged. It is the intent that these results will be used as the foundation of an extinguisher selection matrix to be included in NFPA standards. Additionally, it is important to remember that in an incipient fire situation, not using an extinguisher is likely to have more damaging repercussions than using an available extinguisher, even if it is not the ideal type.

Several cleaning methods were also evaluated. None of the cleaning methods worked for all materials, but some worked better for certain materials. It is unlikely that a single technique will ever be successful for 100% of materials and exposure circumstances. However, the results of this study can be used to inform conservators of the most efficient cleaning method for a range of materials such that remediation after an extinguisher discharge does not further damage materials. It was found that damage to samples was immediate and did not appear to progress incrementally with time. This suggests that in some cases (i.e., exposure to water mist, Halotron I and FE-36) immediate remediation may not be necessary. However, it must be noted that addressing exposure to ABC dry chemical should be a high priority because of the degree to which the material spreads, and the potential for it to be tracked to other spaces.

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