Quantifying Safe HF Exposure Limits for Sensitive Materials in Museums and Archives

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Agenda

• Problem Definition
  • Halocarbon clean agents and products of thermal decomposition
  • Need for quantification of effects of HF for halon replacement, new installations
  • Compatibility testing
  • Results and Conclusions
  • Acknowledgements, Q&A
Problem Definition

• Lack of understanding potential of thermal decomposition product (TDP) effects on museum materials.

• For halocarbon based systems, level of HF generated in a fire directly correlated not only the size of the fire but the room volume as well. \( (\text{kW}_{\text{fire}}/\text{m}^3_{\text{room}}) \). Significant data set available...
  • Ditch, 2002, WPI, others

• Advanced detection technologies detect to control fire to a certain size, thus limiting resultant HF to a specified level.

• **Bottom line:** Advantageous to determine a safe, maximum level of HF that will not adversely affect sensitive content materials that are typical to museums or archives.
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Peatross, et al ‘98 and Ditch ‘02

- Plotting HF produced to normalized fire size – $kW_{\text{fire}} / m^3_{\text{room}}$
Ditch TDP thesis work

Thermal Decomposition – the reality

• Fire size to room volume ratio all important. Keep fire small relative to room volume.
  • Smaller fire size to room volume ratios result in less chance to develop high thermal decomposition concentrations.

• Fires below 4 kW readily detectable in museums with current industry technology used.

TDP in a 1.28 m³ test room – LARGE $kW_{fire}/m^3_{room}$

Figure 8, Effect of Fire Size on Apparent HF Production for C₄ F-ketone. Agent concentration at 4.2% v/v and a 7 s discharge.

Data from Masters Thesis - Ditch, BD, Thermal Decomposition Products Testing With 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one (C₆ F-ketone) During Fire Extinguishing. WPI, Worcester MA USA, December, 2002.
Ditch TDP thesis work

Thermal Decomposition – the reality

• Fires down to 0.1 kW readily detectable in museums with current fire industry detection technology.

• Bottom line; engineer system to limit TDP below level known to be safe for museum artifacts.

TDP extrapolated to “Museum” sized rooms – SMALL $\text{kw}_{\text{fire}}/m^3_{\text{room}}$
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The State Hermitage Museum

New construction for “Open Storage” concept realization and expanding of exhibition area in historical buildings of Winter Palace:

- First stage commissioned in 2003 (Halon-1301)
- Second stage commissioned in 2012 (Inert gas)
- Third stage progressing

HF exposure limits in museums and archives
The State Central Museum of Musical Culture

Courtesy of Russia 1 Television Network
Background on museum research work

• To date, a “no effect” level for HF had not been experimentally quantified for museum occupancies.

• Determine and recommend reasonable maximum level of HF that...
  • Is not harmful to exposed museum/archive materials
  • Gives important guidance to specifying FPEs.

• Working with industry, a major museum and a national library have determined useful design parameters for the use of halocarbon based clean agent systems that can inform relevant occupancy standards (ie: NFPA 909 and 914).
Test Protocol

1. The following test protocol is used for HF testing.
2. Record a baseline paint sample reading with the Spectrophotometer.
3. Remove aluminum test chamber lid, place paint sample inside, replace lid. Tighten the four locks securely.
4. Open the ball valve for the nitrogen and purge for 1-2 minutes if necessary to remove HF from a previous test. Close the nitrogen ball valve.
5. Open the ball valve for the vacuum pump. Pull vacuum to approximately -20 psi (-1.4 atm). Close vacuum ball valve.
6. Set HF cylinder regulator standard to 15 psi (1.02 atm).
7. Open HF ball valve. Close HF valve when flow stops. Hold HF concentration for 10 minutes with a slight flow of HF if necessary. To visually confirm HF presence, a pH strip will be placed inside the test chamber during the test.
8. After 10 minutes, open ball valve on nitrogen supply line and open exit ball valve to purge HF for up to 5 minutes.
9. Remove test vessel lid. Record sample piece Spectrophotometer data in Excel per X-Rite specified procedures.
10. Place new sample piece in container and repeat the process, noting that multiple samples may be tested simultaneously.
11. Repeat.
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Trials at 3M St Paul Laboratory

- 71 samples prepared together with the Hermitage lab
- Paints (oil, tempera, gouache, watercolor) by historical recipes
- Most acid sensitive pigments were selected
- Paper samples circa 16th Century to 2000s
- Exposure to different levels of HF

HF exposure limits in museums and archives
Test Apparatus

- Certified gravimetrically mixed HF standards
- N2 for purging test vessel
Test Fixture

- Clear acrylic test cylinder
- Aluminum top and bottom, PTFE protected

HF exposure limits in museums and archives
Spectrophotometer – X-Rite SP60 Series

- Measures color reflectivity $\Delta E$ of sample
- Calibrated via standard traceable to NIST
- Baseline measurement before each use

Data recorded via Windows based laptop computer/software

HF exposure limits in museums and archives
Trials at 3M St Paul Laboratory

Samples on rack in test vessel located in safety laboratory hood

pH strip to verify HF presence

Individual sample placed beneath meter for measurement scan:
- Validate reflectivity before
- Measure reflectivity post HF exposure to determine $\Delta E$
- Gloves used to protect samples

HF exposure limits in museums and archives

Spectrophotometer
Delta E for all TDP levels tested

All but one sample tested at
- 50 ppm
- 200 ppm
below a Delta E of 2.0.

All but one sample tested at
- 2000 ppm
below a Delta E of 6.0.
Delta E for TDP levels of 50 ppm and 200 ppm tested

All but one sample tested at

• 50 ppm
• 200 ppm

below a Delta E of 2.0.

Industry color standards

• Delta E of 2.0-3.0 essentially undetectable to the human eye
Conclusions from this testing

• Current fire protection technology can detect fires less than 4kW to as low as 0.1kW.

• A fire of that size in a “normal”(ie: >100m3) size museum storage room would produce an average concentration of HF < 25ppm.

• Lab testing has demonstrated for HF exposures of 10 minutes or less, typical select museum articles safe below 200ppm
  • Delta E color reflectivity 3 or less for all but one sample.
  • Delta E of 2-3 essentially undetectable to the human eye.

• Halocarbon clean extinguishing agents can safely be specified for museum applications

• These test data can provide rationale to industry standards committees(ie: NFPA 909/914) for establishing performance based design limits.
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Questions

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