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## **HAZARD ASSESSMENT OF PERSONAL PROTECTIVE CLOTHING FOR HYDROGEN PEROXIDE SERVICE\***

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### **ABSTRACT**

Selection of personal protective equipment (PPE) for hydrogen peroxide service is an important part of the hazard assessment process. But because drip testing of chemical protective clothing for hydrogen peroxide service has not been reported for about 40 years, it is of great interest to test new protective clothing materials with new, high-concentration hydrogen peroxide following similar procedures. The suitability of PPE for hydrogen peroxide service is in part determined by observations made when hydrogen peroxide is dripped onto swatches of protective clothing material. Protective clothing material was tested as received, in soiled condition, and in grossly soiled condition. Materials were soiled by pretreating the material with potassium permanganate ( $\text{KMnO}_4$ ) solution then drying to promote a reaction. Materials were grossly soiled with solid  $\text{KMnO}_4$  to greatly promote reaction. Observations of results including visual changes to the hydrogen peroxide and materials, times to ignition, and self-extinguishing characteristics of the materials are reported.

### **INTRODUCTION**

#### PPE FOR HYDROGEN PEROXIDE SERVICE

The need for chemical protective clothing for hydrogen peroxide service was identified years ago, based primarily on the corrosive properties of the fluid and vapors.<sup>1,2</sup> Additionally, the reactivity of hydrogen peroxide with chemical protective clothing, including catalytically-enhanced reactivity, was deemed an important aspect in the selection process. This is because clothing material, which is otherwise relatively inert toward hydrogen peroxide exposure, could ignite and burn if sufficient heat is generated by the decomposition of hydrogen peroxide due to soiling with catalytic impurities. The hazards of soiled or unsoiled protective clothing that burns or decomposes (or decomposes the fluid when exposed to hydrogen peroxide), must be assessed prior to the selection of PPE and the corresponding training provided to the personnel who wear them.

Some of the recent test methods employed in the evaluation of chemical protective clothing include American Society for Testing and Materials (ASTM) methods F739 and F1383.<sup>3,4</sup> The primary objective of these methods is to obtain data concerning the permeation resistance of clothing materials under conditions of continuous or intermittent contact with the test fluid, respectively.

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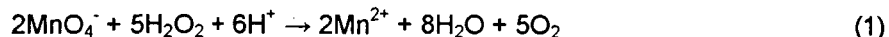
\* In-house document. WSTF RD-WSTF-0972-001-03. *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide*. 2004.

The method that was used in the past to test chemical protective clothing materials for hydrogen peroxide service was a gross compatibility test described by FMC in 1966.<sup>2</sup> This test used 90 percent Becco<sup>®</sup> electrolytically-produced hydrogen peroxide. However, the electrolytic process is no longer used to produce hydrogen peroxide and was replaced by the anthraquinone process. We used a modification of the FMC method to test various chemical protective clothing materials because as far as we could determine, the test has not been performed for many years and we were interested in its utility in testing materials with recently-produced 98 percent propellant-grade hydrogen peroxide.

The purpose of the original studies with chemical protective clothing included finding materials that would not ignite when they were soiled with catalytic dirt.<sup>2</sup> "Soiled" referred to the pre-immersion in 0.005 M KMnO<sub>4</sub> then drying. An important hazard that was studied was whether a worker's clothing could ignite if hydrogen peroxide were spilled on it. Secondly, examining the effect of the material on the fluid was part of the original studies. Some of the original reactivity tests were classical active oxygen loss (AOL) determinations made on the fluids immersing the clean materials at 30 °C and 66 °C.

The FMC procedure for "Inflammability Tests" or "Drip Tests" described shaping a swatch of material into a cup and fastening it over the mouth of a 400-mL beaker.<sup>2</sup> Next, 90 percent hydrogen peroxide was dripped from a burette onto the cupped material at a rate of 4 mL/min for 1 hr. During this time, any changes such as melting, deforming of the surface, smoking where hydrogen peroxide contacts the material, sparking, and igniting were noted. Tests with soiled materials were similarly performed, but time to ignition and whether the material supports combustion when removed from the dripping hydrogen peroxide were also noted.

Potassium permanganate solution was used to soil the protective clothing presumably because it was easily prepared in the laboratory and is known to be highly reactive with hydrogen peroxide. In fact, aqueous solutions of permanganate salts in combination with hydrogen peroxide have been used as propellant mixtures. The technique of spraying an aqueous solution of a permanganate salt with hydrogen peroxide into a decomposition chamber was used in Germany for catapult launching and for steam generation to drive the pumps of the V-2 rocket.<sup>1</sup> The basis for this reaction is oxidation of hydrogen peroxide by permanganate. A balanced equation for the reaction of hydrogen peroxide with permanganate is as follows:



Sources of protons (H<sup>+</sup>) for Reaction (1) are hydrogen peroxide and its water impurity. In addition to Reaction (1), there may be other reactions that occur as incomplete reduction of permanganate can form other oxides of manganese, such as manganese dioxide (MnO<sub>2</sub>). Additionally, MnO<sub>2</sub> is a common impurity in permanganate and can form by the partial reduction of permanganate. This is notable because MnO<sub>2</sub> is highly catalytic and sustains hydrogen peroxide decomposition. Consequently, initial reaction of hydrogen peroxide with KMnO<sub>4</sub> can be followed by catalytic decomposition with the oxides of manganese that subsequently form.

The procedure employed in our study differed from the FMC procedure as follows, in part due to safety considerations and in part due to lack of detail published in the original procedure:

- A peristaltic pump was used to deliver hydrogen peroxide to the test sample rather than a burette. Materials that ignited were not removed from the dripping hydrogen peroxide; rather, the flow of hydrogen peroxide was stopped via switching off the peristaltic pump.
- Some samples were dusted with KMnO<sub>4</sub> powder to produce a gross soiled effect. This was because some of the materials are not wetted by KMnO<sub>4</sub> solution and subsequent exposure to hydrogen peroxide would not fully represent a truly "soiled" material, such as one that was rubbed against a surface mechanically transferring catalytic impurities to adhere to the material surface.

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\* All trademarks are cited after the reference section.

- Tests were performed in a fume hood with an aluminum tray for secondary containment and behind a safety shield
- Active Oxygen Loss (AOL) determinations were not performed on post-test fluids

## OBJECTIVE

The objective of this work is to present the results of testing of representative chemical protective clothing materials using a modification of the FMC procedure. These tests were performed to screen candidate materials for gross reactivity and not to obtain permeation resistance data.

## EXPERIMENTAL

### CHEMICAL PROTECTIVE CLOTHING MATERIALS

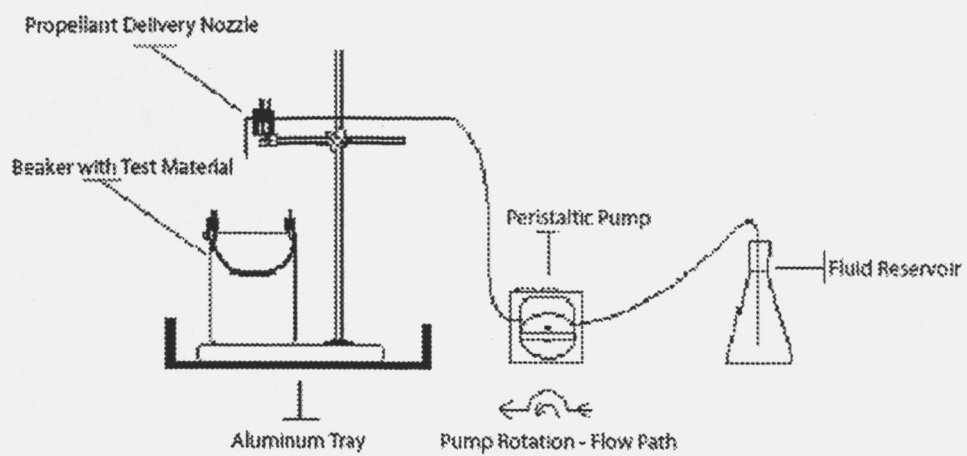
Chemical protective clothing materials were:

- Cloropel.<sup>®</sup> Plasticized chlorinated polyethylene material from a chemical protective suit.
- TyChem<sup>®</sup> QC. Polyethylene-coated high density polyethylene (HDPE) fiber sleeve-apron material.
- Respirax.<sup>®</sup> Rubberized (bromobutyl rubber-coated NOMEX<sup>®</sup>) gray chemical protective suit material.
- Sawyer-Tower Gore.<sup>®</sup> Chemical protective suit material comprising an outer layer of texturized polyester oxford (plain weave), a center layer of expanded polytetrafluoroethylene, and an inner knit polyester layer of polyester.
- WearGuard.<sup>®</sup> Laboratory coat material composed of 80 percent polyester and 20 percent cotton.
- PYLOX<sup>®</sup>/ V-20 polyvinylchloride (PVC). Glove material.
- North B324 butyl rubber. Glove material.
- NOMEX. HT90-40 heat-resistant and flame-retardant aromatic polyamide cloth.
- Cotton fabric. 100 percent cotton.
- TWOTAN.<sup>®</sup> Cowhide leather glove (the portion tested was the russet suede back).

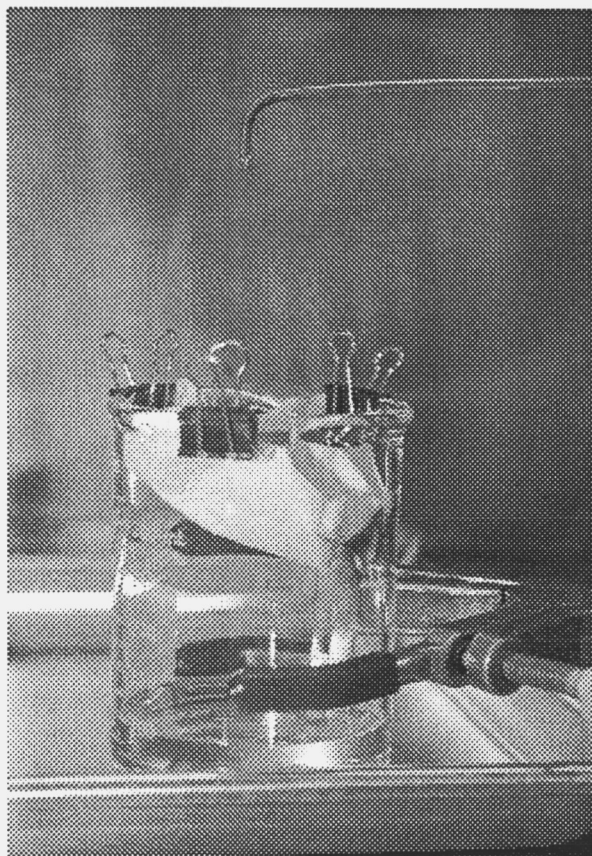
All chemical protective materials were cut into 4 in. by 4 in. swatches using ordinary scissors. The materials' thicknesses were determined using a Mitutoyo<sup>®</sup> type IDC-1012ME dial indicating gage and were measured in mil units (1/1000 of an in.).

### REAGENTS AND APPARATUS

Potassium permanganate was Baker-Analyzed grade obtained from J.T. Baker.<sup>®</sup> Deionized (DI) water was used to prepare a 0.005 M KMnO<sub>4</sub> solution. Propellant-grade hydrogen peroxide (98 percent) was obtained from FMC. Glassware was borosilicate glass and was cleaned sequentially with detergent (Alconox<sup>®</sup>), Baker Analyzed nitric acid (J.T. Baker), and 35 percent hydrogen peroxide (Mallinckrodt<sup>®</sup>) prior to use. A peristaltic pump using Viton<sup>®</sup> pump tubing was calibrated to deliver hydrogen peroxide at a rate of 4 mL/min. A 1-L borosilicate glass erlenmeyer flask was used as the fluid reservoir. Polytetrafluoroethylene (PTFE) tubing, 1/8-in. outer diameter, was slip-fitted into each end of the Viton pump tubing. One end of the PTFE tube was submersed in the hydrogen peroxide through a holed-rubber stopper in the fluid reservoir. The other end of the PTFE tube was swaged to a stainless steel delivery nozzle. The nozzle assembly was clamped to a ring stand and allowed the fluid to flow by drops directly onto the test material. The nozzle could also be swiveled to avoid contact with flames. A 400-mL beaker was used to hold the test material and to contain the fluid that was dripped on it. All components were cleaned with detergent (Alconox), Baker Analyzed nitric acid (J.T. Baker), 35 percent hydrogen peroxide (Mallinckrodt), and DI water prior to use. Binder clips were used to fasten a test material to the mouth of the beaker and were obtained from Sparco.<sup>®</sup> A schematic of the test apparatus is shown in Figure 1. A photograph of a test material below the propellant delivery nozzle is shown in Figure 2.



**Figure 1. Schematic of the Test Apparatus**



**Figure 2. A Test Material Below the Propellant Delivery Nozzle**

## PREPARATION OF SOILED MATERIALS

Four-in. square swatches of each material were soiled by immersing in 0.005 M  $\text{KMnO}_4$  solution for 30 sec. Excess solution was removed by shaking and then drying material overnight in an oven at approximately 110 °C. These materials were referred to as "soiled." Four samples of soiled NOMEX were prepared for repeatability testing.

Four-in. square swatches of selected materials were dusted lightly with approximately 100 to 200 mg of  $\text{KMnO}_4$  after they were fastened in place in the test apparatus and prior to the application of hydrogen peroxide. These samples were referred to as "grossly soiled."

## EXPERIMENTAL PROCEDURE

A swatch of chemical protective clothing material was formed into a cup and fastened to the mouth of the 400 mL borosilicate glass beaker so that liquid could pool in the cupped material without contacting the clips and would overflow into the beaker. Approximately 100 to 200 mg of solid  $\text{KMnO}_4$  was placed directly on selected swatches of material once they were cupped and clipped to a beaker. The time that hydrogen peroxide was being delivered until the time the flow was stopped was recorded. If a flame was observed the fluid flow was stopped, the propellant delivery nozzle was swiveled away from the flame path, and the self-extinguishing characteristics of the material were noted. The duration of each test was 1 hr unless the material ignited before that time. Each test was terminated after the flames extinguished with the following exceptions:

- In one test with soiled NOMEX, the position of the beaker containing the test material and the propellant delivery nozzle was adjusted to allow hydrogen peroxide to drip onto an obviously soiled portion of the material after 1 hr had lapsed.
- In one test with grossly soiled TyChem QC, the position of the propellant delivery nozzle was adjusted to allow hydrogen peroxide to drip onto another portion of the material approximately 17 sec after the test began.

A JVC®-model GY-DV500 digital video camcorder was used to record some of the material tests; others were observed visually and times were measured with a laboratory timer. All times were noted as closely as possible based on visual observations using the camera frame counter or laboratory timer.

Post-test materials were rinsed with water and dried in air.

## **RESULTS AND DISCUSSION**

Some of the protective clothing materials did not wet well when immersed in the 0.005 M  $\text{KMnO}_4$ . These materials were:

- Cloropel
- TyChem QC
- Respirax
- Sawyer-Tower Gore
- PYLOX/ V-20
- North B324 butyl rubber
- TWOTAN Cowhide

Because these materials did not wet well, sufficient  $\text{KMnO}_4$  may not have adhered to these materials to induce reaction with hydrogen peroxide in the soiled condition.

The sample identification, sample thickness, and results of testing the as-received materials, the soiled materials, and the grossly soiled materials are summarized in Table 1 and discussed below.

**Table 1. Drip Test Evaluation of Protective Clothing  
With FMC 98 Percent Hydrogen Peroxide After 1 Hr**

SAMPLE	THICKNESS	EFFECT OF FLUID ON MATERIAL		
		Clean	Soiled	Grossly Soiled
Cloropel	21 mil	None observed	None observed	Ignited
TyChem QC	8.3 mil	None observed	None observed	Ignited <sup>a</sup>
Respirex (gray)	89 mil	None observed	None observed	Ignited
Sawyer-Tower Gore	23 mil	None observed	None observed	Ignited
WearGuard	16 mil	None observed	Ignited	Not tested
PYLOX/ V-20	19 mil	None observed	None observed	Ignited
North B324 Butyl Rubber	31 mil	None observed	None observed	Ignited
NOMEX	13 mil	None observed	Ignited <sup>b</sup>	Ignited
Cotton Fabric,	12 mil	Hardened, fused	Hardened, fused	Ignited
TWOTAN Cowhide	58 mil	Ignited	Ignited	Not tested

<sup>a</sup> Initially, a hole melted through the material. Subsequently, the propellant delivery nozzle was moved to another portion of the material and the material ignited.

<sup>b</sup> There were 4 tests conducted with soiled NOMEX. Ignition of soiled NOMEX occurred within 1 hr with 3 samples and did not occur within 1 hr with 1 sample.

**CLOROPEL**

**Clean:** The fluid decomposed mildly on the surface of the material. The fluid in the beaker was colorless and free of bubbles. The material did not appear changed.

**Soiled:** Fluid decomposed mildly on the surface of the material. The fluid in the beaker was colorless and contained bubbles. The material did not appear changed.

**Grossly soiled:** The material ignited after 16 sec and the flame self-extinguished 6 sec after the flow of fluid stopped. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

**TYCHEM QC**

**Clean:** The fluid did not decompose on the surface of the material. The fluid in the beaker was pale yellow and did not contain bubbles. The material did not appear changed.

**Soiled:** Fluid decomposed mildly on the surface of the material. The fluid in the beaker was pale yellow and did not contain bubbles. The material did not appear changed.

**Grossly soiled:** The material ignited after 6 sec and a hole burned through it. The flame self-extinguished very rapidly. When the fluid was subsequently directed towards another portion of the material, ignition occurred again after approximately 10 sec and this time the material burned almost to completion after 14 sec. The remaining burned edges were partially melted, warped, charred, and stiff.

**RESPIREX (GRAY)**

**Clean:** The fluid decomposed mildly on the surface of the material. The fluid in the beaker was colorless and contained bubbles. The material did not appear changed.

**Soiled:** Fluid decomposed vigorously on the surface of the material. The fluid in the beaker was colorless and contained bubbles. The material did not appear changed.

**Grossly soiled:** The material ignited after 108 sec and the flame self-extinguished after 7 sec. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

### SAWYER-TOWER GORE

Clean: The fluid decomposed mildly on the surface of the material. The fluid in the beaker was pink and contained bubbles. The material did not appear changed.

Soiled: The fluid decomposed on the surface of the material. The fluid in the beaker was pink and contained bubbles. The material did not appear changed.

Grossly soiled. The material ignited after 17 sec and the flame self-extinguished after 20 sec. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

### WEARGUARD

Clean: The fluid did not decompose on the surface of the material. The fluid in the beaker was colorless and contained bubbles. The material did not appear changed.

Soiled: The material ignited after 6 sec and the flames self-extinguished after 3 sec, but the material continued to smolder. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

Grossly soiled. This test was not performed.

### PYLOX/ V-20

Clean: The fluid did not decompose on the surface of the material. The fluid in the beaker was pale yellow and contained bubbles. The material did not appear changed.

Soiled: The fluid decomposed mildly on the surface of the material. The fluid in the beaker appeared slightly milky and contained bubbles. The material did not appear changed.

Grossly soiled: The material ignited after 9 sec and the flame self-extinguished after 8 sec. A hole burned through the material, which became warped, and the adjacent areas were charred and stiff.

### NORTH B324 BUTYL RUBBER

Clean: The fluid decomposed mildly on the surface of the material. The fluid in the beaker was colorless and did not contain bubbles. The material did not appear changed.

Soiled: The fluid decomposed vigorously on the surface of the material. The fluid in the beaker was colorless and contained bubbles. The material did not appear changed.

Grossly soiled: The material ignited after 74 sec and the flame did not self-extinguish. The material burned for 7 min and 14 sec until it was virtually all consumed. Only the corners of the material that was clipped to the beaker remained, and these were tarry remnants.

### NOMEX

Clean: The fluid did not decompose on the surface of the material. The fluid in the beaker was colorless and did not contain bubbles. The material did not appear changed.

Soiled: Four samples of this material were tested. In the first test, the material ignited after 18 sec and self-extinguished, but the time to self-extinguish was not recorded. In the second test, the material ignited after 11 min and 51 sec and the flame did not self-extinguish; the material burned almost to completion after 21 sec. In the third test, the material did not ignite after 1 hr. The fluid in the beaker was slightly yellowed and contained bubbles. However, after the 1-hr test observation was made, the hydrogen peroxide stream was directed to an obviously soiled portion of the material and the material

ignited after 2 sec and the flame did not self-extinguish; the material burned almost to completion after 20 sec. In the fourth test, the material ignited after 7 sec and self-extinguished after 14 sec. For those samples that burned, holes were burned through them, all of the materials wetted by hydrogen peroxide were consumed, the flames did not reproducibly self-extinguish, and adjacent unburned areas were charred and stiff. A summary of times to ignition is shown in Table 2.

Grossly soiled: The material ignited after 19 sec and the flame did not self-extinguish but burned for 18 sec. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

#### COTTON FABRIC

Clean: There was no decomposition of the fluid on the material. The weave of the wetted portion of the sample hardened and fused together, causing the material to stiffen. The fluid in the beaker was colorless and contained no bubbles.

Soiled: The fluid decomposed on the surface of the material. The fluid in the beaker was pale yellow and contained bubbles. The weave of the wetted portion of the sample hardened and fused together causing the material to stiffen.

Grossly soiled: The material ignited within 1 sec and the flame did not self-extinguish. The flame diminished after 15 sec then continued to smolder. A hole burned through the material, the material warped, and the adjacent areas were charred and stiff.

#### TWOTAN COWHIDE

Clean: The material ignited after 1 min and 50 sec. The flame self-extinguished after the accumulated fluid was consumed. A green ring of color was visible over the darkened, burned material. The material warped, and the adjacent areas were stiff.

Soiled: The material ignited after 2 sec and the flame self-extinguished after 9 sec. The material warped, and the adjacent areas were charred and stiff.

Grossly soiled. This test was not performed.

**Table 2. Ignition Times for Soiled NOMEX With 98 Percent Hydrogen Peroxide**

TEST NUMBER	TIME TO IGNITION
1	18 sec
2	11 min, 51 sec
3	Did not ignite after 1 hr <sup>a</sup>
4	7 sec

<sup>a</sup> After the 1-hr test observation was made, the hydrogen peroxide stream was directed to an obviously soiled portion of the material. Ignition occurred after 2 sec and the flames did not self extinguish. The material burned almost to completion after 20 sec.



## OBSERVATIONS ON THE TEST METHODOLOGY

The use of a peristaltic pump to deliver hydrogen peroxide to the test material seemed a practical improvement over the use of a glass burette from both a safety and a quality perspective. The remote location of the pump allowed the fluid flow to be shut off by its switch in a timely manner when ignition was observed. In contrast to the historical method, shutting off fluid flow from a glass burette directly over a flaming material or moving the material out of the fluid flow as was implied in the original procedure would require less desirable and perhaps delayed or inconsistent manipulations. The propellant delivery nozzle clamped to a ring stand in our configuration was easily rotated out of the flame path within the protection of the safety shield. Additionally, our configuration avoided the potential consequences of a fire under a glass burette filled with hydrogen peroxide, because our entire nozzle volume was approximately 0.4 mL and only a fraction of that was exposed to heat before it could be rotated out of a flame path.

Despite being able to safely rotate the propellant delivery nozzle away from flaming materials, soot and spattered material occasionally deposited on it. Because material that was potentially catalytic toward hydrogen peroxide decomposition and was deposited on the propellant delivery nozzle might have an effect on delivered propellant, the tip of the propellant delivery nozzle should be periodically cleaned by rinsing and wiping with deionized water. This must be performed with caution (after emptying the propellant delivery nozzle of hydrogen peroxide to avoid contact of the wiping media with hydrogen peroxide).

## ADDITIONAL TEST OBSERVATIONS

Leaching of red color from the Sawyer-Tower Gore fabric (red surface), and yellow from the TyChem C and PYLOX/ V-20 (both yellow surface) materials into the hydrogen peroxide was somewhat unexpected, although the post-test materials did not appear to have been bleached. The clean cotton fabric also imparted a yellow color to the hydrogen peroxide, although the clean cotton fabric was off-white.

The inflammability drip tests repeated with NOMEX yielded interesting information. The observation that the ignition times of the soiled material varied from almost instantly to not within 1 hr suggested that the uniformity of soiling, the proximity of higher concentration soil to the hydrogen peroxide drip stream, and possible wicking effects of the fluid toward areas of higher soil concentration play a role in whether the material ignites. This was highlighted by the test in which, after no ignition occurred after 1 hr, the fluid stream was directed toward an obviously heavily soiled area and ignition occurred immediately.

The inflammability drip tests with TWOTAN Cowhide leather also gave interesting results. The clean leather accumulated about 8 mL of hydrogen and after it ignited it burned until the accumulated hydrogen peroxide was consumed. The soiled leather ignited and the flame extinguished almost immediately. Therefore, the fire damage was significantly greater to the clean leather than to the soiled leather. However, observation that flame was sustained only in the presence of hydrogen peroxide suggests that burning leather requires an oxygen source greater than ambient air (such as hydrogen peroxide) to sustain a flame. Observations of the behavior of cowhide leather may be complicated by the likelihood that the leather was tanned using a chromium process. The chrome tanning process typically uses chromium(III) sulfate, which is predicted to be catalytic toward hydrogen peroxide decomposition. Therefore, the "clean" leather may have been catalytically enhanced to begin with. The lack of wetting of specified materials is likely to play a role in limiting the amount of soil that a material absorbs. For this reason, we employed gross soiling to extend our pre-treatment of materials beyond the FMC soiling procedure in order to assess a relatively extreme condition of material ignition promoted by catalysis of hydrogen peroxide decomposition.

All of the grossly soiled chemical protective clothing materials that were tested ignited. This suggests that sufficient heat is generated by the reaction of hydrogen peroxide with  $\text{KMnO}_4$  or its catalytic decomposition products to induce ignition. Whether the flame self-extinguished or sustained itself after removal of the source of hydrogen peroxide varied with the material.

The self-extinguishing characteristics of the burning materials varied widely. When ignited, the halogenated materials (Cloropel (plasticized chlorinated polyethylene), Respirax (gray, bromobutyl covered NOMEX), Sawyer-Tower Gore (polyester/PTFE), and PYLOX/ V-20 (PVC)), self-extinguished quickly after the flow of hydrogen peroxide was stopped. Halogenated materials are typically flame resistant or flame retardant, although they obviously did burn at least briefly under the conditions of the experiments with grossly soiled materials. When ignited, the simpler hydrocarbon-based materials, TyChem C (polyethylene), North B324 Butyl Rubber (butyl rubber), WearGuard (cotton/polyester), and cotton (cellulose-based material) did not self extinguish. NOMEX, an aromatic polyamide, is generally considered heat-resistant, flame retardant,<sup>5</sup> inherently flame resistant, won't melt, drip, burn or support combustion in air,<sup>6</sup> but when ignited the flames consumed the hydrogen peroxide-wetted fabric and some of the adjacent fabric. The failure of a material that is normally considered flame retardant to self-extinguish may in part be due to the materials' being wetted with hydrogen peroxide and thus having a readily-available oxygen source in intimate contact with it. Leather (a proteinaceous material), is generally considered heat-resistant, being widely used in welding, forging, and other operations requiring handling of hot objects. However, the observation that the leather flame self-extinguished after the accumulated hydrogen peroxide had been consumed also suggests that its ability to sustain a flame depends on the proximity to the hydrogen peroxide oxygen source.

Our observations on the self-extinguishment of flames on the materials in the hydrogen peroxide drip tests are generally consistent with the observation that combustion efficiency decreases in the order:<sup>7</sup>

Aliphatic > Aromatic > Aliphatic/Aromatic > Highly halogenated species (2)

#### HAZARD ASSESSMENT OF PERSONAL PROTECTIVE CLOTHING FOR HYDROGEN PEROXIDE SERVICE

The hierarchy of PPE selection using OSHA guidelines includes the following:<sup>8</sup>

- Assessing the hazards
- Selecting the PPE
- Training the personnel
- Documenting the above

The hazards must be assessed based on the particular operation. For example, the hazards associated with handling small quantities of hydrogen peroxide in the laboratory, performing a railcar to tank fluid transfer, moving drums of fluid in a storage area, or responding to a spill or fire where hydrogen peroxide is present are different and must be assessed accordingly.

Some desirable features of protective clothing include, as appropriate:

- Prevent contact of the fluid and vapors with the body
- Provide protection of the skin from contact with heavy, sharp or abrasive objects
- Provide heat and fire resistance

It was outside the scope of this work to determine the permeation resistance of protective clothing to hydrogen peroxide. Permeation resistance may be obtained from the suppliers or by performing ASTM tests. Permeation resistance should be considered in the selection of protective clothing.<sup>3,4</sup>

The ignition properties of soiled protective clothing demonstrate the need to keep PPE clean. Keeping PPE sanitary, properly maintained, and in reliable condition is not only an OSHA requirement but is a practice that must be strictly adhered to when working with or around hydrogen peroxide.<sup>8</sup> The worker must be aware that activities which contaminate PPE can be detrimental to its use as protective equipment with hydrogen peroxide. For example, laboratory workers who contaminate their lab coats or gloves with  $\text{KMnO}_4$  should take extreme care to change them before working with hydrogen peroxide. Another example is field personnel who might contaminate their protective clothing on rusty objects; they

should not engage in any hydrogen peroxide handling activities until their protective clothing is changed. Fire and emergency services personnel similarly must take extreme caution, as airborne debris that may be catalytic to hydrogen peroxide contamination may adhere to protective clothing. Combination PPE, such as a steel-toed boots composed of a suitable outer material but with a steel toe and possibly a steel metatarsal guard must be carefully evaluated prior to use, because if the outer material was damaged it might be possible for hydrogen peroxide to come into contact with an incompatible steel that could induce hydrogen peroxide decomposition with potentially undesirable consequences.

There is not one kind of chemical protective clothing that will protect the worker from multiple hazards. For example, leather work gloves that are normally ideal for protecting the hands when moving drums in general may not be appropriate for moving drums of hydrogen peroxide. Alternative materials must be sought by personnel performing the hazard assessment for such activities. Similarly, a normally sufficient protective material that becomes soiled or grossly soiled may burst into flame with potentially disastrous results. Fire and emergency services personnel must be made aware of these hazards.

### CONCLUSIONS

Tests with protective clothing materials and propellant grade 98 percent hydrogen peroxide were performed using a modification of a test method that has not been performed for approximately 40 years. A newer grade of hydrogen peroxide was tested with newer materials. Insight on the test methodology, its limitations, and possible improvements were gained.

Ten chemical protective clothing materials were evaluated with propellant grade 98 percent hydrogen peroxide. The materials were tested clean, soiled with  $\text{KMnO}_4$ , and grossly soiled with  $\text{KMnO}_4$ . In tests with clean materials, only leather ignited. In tests with soiled materials, only WearGuard (polyester/cotton blend lab coat material), and NOMEX (aromatic polyamide) ignited and the flames did not rapidly self-extinguish. In tests with grossly soiled materials, all of the materials ignited although the flame self-extinguishing time varied greatly. For example, halogenated materials self-extinguished almost immediately, and polyethylene and butyl rubber materials burned to completion. Materials that could be wetted by hydrogen peroxide were also more prone to ignition and soiling by  $\text{KMnO}_4$  solution; wetting is a hydrophilic or hydrophobic characteristic of the material and the weave. On the other hand, gross soiling is a purely mechanical occurrence and none of the materials avoided gross soiling.

The results of the tests conducted in this work suggested that screening of candidate chemical protective clothing materials for hydrogen peroxide flammability hazards include the following considerations:

- The material should not ignite on contact with hydrogen peroxide.
- The material should resist wetting by hydrogen peroxide. Wetting appears to cause the material, if it ignites, to sustain a flame longer than if it was not wetted. This may be attributed to accumulated hydrogen peroxide providing an oxygen source.
- The material should be clean and free of chemical reactants and catalytic impurities
- The material should have flame self-extinguishing characteristics. The order of self-extinguishment of the materials tested appeared to follow the general order:

Halogenated > Aromatic/aliphatic > Aliphatic

(3)

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#### TRADEMARKS

<b>Trademark</b>	<b>Company Name</b>	<b>Company Location</b>
Alconox	Alconox, Inc.	New York, NY
Becco	Buffalo Electro-chemical Co.	Tonowanda, NY
Cloropel	ILC Dover	Frederica, DE
J.T. Baker	J. T. Baker	Phillipsburg, NJ
JVC	Victory Company of Japan	Yokohama City, Japan
Mallinckrodt	Mallinckrodt TMH Corp.	Las Vegas, NV
Mitutoyo	Mitutoyo Manufacturing Co.	Tokyo, Japan
NOMEX	E. I. du Pont de Nemours	Wilmington, DE
PYLOX	Pioneer Company	Willard, OH
Respirex	Diemolding Corp.	Canastota, NY
Gore	W. L. Gore & Associates, Inc.	Newark, DE
Sparco	Sparco Corp.	Torino, Italy
TWOTAN	Red Steer Glove Co.	Brooks, OR
TyChem	E. I. du Pont de Nemours	Wilmington, DE
Viton	E. I. du Pont de Nemours	Wilmington, DE
WearGuard	WearGuard Corp.	Norwell, MA