OKLAHOMA TRANSPORTATION CENTER

ECONOMIC ENHANCEMENT THROUGH INFRASTRUCTURE STEWARDSHIP

SENSOR TECHNOLOGY FOR HAZARDOUS CARGO TRANSPORTATION SAFETY

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OTCREOS11.1-01-F

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16. ABSTRACT

The overall goal of this research project was to develop oxidant vapor detection devices that can be used to ensure the safety of hazardous freight transportation systems. Two nanotechnology-based systems originally developed for improvised explosive detection systems will be adapted to this application. The first of these are dark-blue nanometric tungsten or molybdenum hydrogen bronzes that are sensitive to all strong oxidants. The second is a titanium oxide nanoparticle-based system that is extremely sensitive and selective to hydrogen peroxide and organic peroxides. Our hypothesis, based on preliminary studies, was that we can use the dramatic color change or change in the electronic properties of hydrogen bronze nanoparticles or titania nanoparticles when exposed to strongly oxidizing vapors to produce a variety of products for improving the security of hazardous materials transportation systems. The specific technologies that were targeted were: (1) stick-on color-changing sensors that will passively detect strong oxidants (2) hand-held sensitive electronic sensors that detect strong oxidants (3) an electronic "area sensor" that utilizes color changes to identify the presence of strong oxidant leaks.

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SI (METRIC) CONVERSION FACTORS

Approximate Conversions to SI Units

Symbol	When you know	Multiply by	To Find	Symbol
		LENGTH		
in	inches	25.40	millimeters	mm
ft	feet	0.3048	meters	m
yd	yards	0.9144	meters	m
mi	miles	1.609	kilometers	km
		AREA		
in²	square inches	645.2	square millimeters	mm
ft²	square feet	0.0929	square meters	m²
yd²	square yards	0.8361	square meters	m²
ac	acres	0.4047	hectares	ha
mi²	square miles	2.590	square kilometers	km²
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft³	cubic feet	0.0283	cubic meters	m³
yd³	cubic yards	0.7645	cubic meters	m³
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.4536	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
		TEMPERATURE (exact)		
°F	degrees Fahrenheit	(°F-32)/1.8	degrees Celsius	°C
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.448	Newtons	N
lbf/in²	poundforce per square inch	6.895	kilopascals	kPa

Approximate Conversions from SI Units

Symbol	When you know	Multiply by	To Find	Symbol
		LENGTH		
mm	millimeters	0.0394	inches	in
m	meters	3.281	feet	ft
m	meters	1.094	yards	yd
km	kilometers	0.6214	miles	mi
		AREA		
mm²	square millimeters	0.00155	square inches	in²
m²	square meters	10.764	square feet	ft²
m²	square meters	1.196	square yards	yd²
ha	hectares	2.471	acres	ac
km²	square kilometers	0.3861	square miles	mi²
		VOLUME		
mL	milliliters	0.0338	fluid ounces	fl oz
L	liters	0.2642	gallons	gal
m³	cubic meters	35.315	cubic feet	ft³
m³	cubic meters	1.308	cubic yards	yd³
		MASS		
g	grams	0.0353	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.1023	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	degrees Celsius	9/5+32	degrees Fahrenheit	°F
		FORCE and PRESSURE or STRESS		
N	Newtons	0.2248	poundforce	lbf
kPa	kilopascals	0.1450	poundforce per square inch	lbf/in²

Acknowledgements

Sensor Technology for Hazardous Cargo Transportation Safety

Final Report

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Executive Summary

The hazardous material carried by all modes of transportation through the Nation's transportation network in 2007 was estimated to be 2.2 billion tons and the value of these shipments was $1,448 billion. The category of hazardous materials that were the target of this investigation, Hazardous Class 5, Oxidizers and Organic Peroxides, totaled almost 15 million tons and had a value of approximately $6.7 billion in 2007. The amounts of these materials and the distance that they were shipped (an average of 361 miles) led to a total of over 7 billion ton-miles. This research project targeted several devices that will markedly increase the safety of transportation of hazardous materials that consist of volatile, strongly oxidizing chemicals. These compounds constitute a significant risk to the public, transportation workers, and emergency responders. Many of these materials have been involved in numerous transportation-related catastrophes so that methods to identify leaks before they become serious, or, when an accident does happen are highly warranted. These sensors will be an extremely simple colorimetric detectors that can be viewed a distance to see if any oxidant is leaking.

One device that was developed uses a color-changing material that will be in the form of a stick-on decal that can be placed on rail cars, tankers, trucks, freight containers, and cargo crates, or boxes that are being used to transport volatile hazardous materials that are oxidants. For example the device could be part of the warning placards or labels that are used when transporting such materials. The decals were designed to give a clear message even to unfamiliar members of the public that a hazard exists by changing color when exposed to oxidant vapors. Two types of decals were targeted, one that detects a broader range of oxidant materials (DOT Class 5.1 and toxic or corrosive oxidants such as chlorine, bromine, nitrogen oxide, and nitric acid) while the second one was specific for DOT Class 5.2 materials (organic peroxides). The project resulted in the development of the necessary sensing materials and production of the initial prototypes. Testing for durability and for the sensing of several key hazardous chemicals is expected to provide a strong foundation for the commercialization of the hazard materials sensor decals. These are expected to be

fairly inexpensive but they will have a dramatic impact on the safety of transportation of hazardous materials.

The other device that was developed to the stage of a prototype with proven ability to sense oxidants was a more sophisticated and sensitive electronic hand-held or mounted sensor that could be used to check for leaks, determine the presence of oxidant vapors in the case of an accident where release of volatile oxidants is suspected, and ensure safety during the loading and unloading of such hazardous cargo. We foresee that the handheld sensor could be used by transportation personnel to check for leaks and to ensure that they are not being exposed to dangerous vapors when loading or unloading operations. It would also be highly useful to first responders, hazmat teams, firefighters, and other emergency workers that are responding to an accident involving the hazardous materials targeted in this investigation. Mounted sensors would be useful for monitoring train yards, cargo depots, transportation warehouses, ship holds, etc. for oxidant vapors. This would provide the means to detect leaking containers but could also thwart the potential use of the transportation systems by terrorists to deliver nitric acid-based or peroxide-based improvised explosives to target sites or to detect terrorist attacks on the transportation systems themselves.

Introduction

Problem

According to a 2011 report from the Research and Innovative Technology Administration (RITA), the hazardous materials carried by all modes of transportation through the Nation's transportation network in 2007 was estimated to be 2.2 billion tons and the value of these shipments was $1,448 billion.[1] The category of hazardous materials that were the target of this investigation, Hazardous Class 5, Oxidizers and Organic Peroxides, totaled almost 15 million tons and had a value of approximately $6.7 billion in 2007. The amounts of these materials and the distance that they were shipped (an average of 361 miles) led to a total of over 7 billion ton-miles. Oxidizers are materials that can, generally by yielding oxygen, cause or enhance the combustion of other materials while organic peroxides are any organic compounds containing oxygen an oxygen-oxygen (–O-O–) bond and which may be considered derivatives of hydrogen peroxide, where one or more of the hydrogen atoms have been replaced by organic radicals. Not listed with these materials are other oxidants such as halogens and nitric oxide that are placed in other classes due to their toxicity and substances such as nitric acid that are listed with corrosive materials. The oxidizers present special challenges and hazards to first responders, hazmat teams, and firefighters in the event of a leak, spill, or fire.[2] The main hazards posed by organic peroxides are their fire and explosion hazards but they can also be toxic or corrosive.[3]

In a comprehensive assessment of hazardous materials transportation incidents and accidents, Battelle estimated that the average annual en route hazardous materials accident frequency to be 2,484 accidents, the release accident frequency to be 768 per year, the average annual en route leak incidents to be 1,455 and loading/unloading incidents to be 10,746 per year.[4] Of these, oxidizers and organic peroxides, experienced an estimated 56 accidents 27 of which were release accidents, two of which resulted in fires. The totals costs were about $23 million in the portrait year used by Battelle. Unfortunately, there was not a sufficient breakdown to determine the number of incidents that involved other oxidants (chlorine, bromine, nitric acid, nitrogen dioxide and dinitrogen tetroxide) that were also the focus of this investigation. However, there have been many dangerous spills leading to injuries and fatalities due to these substances.[5-7] These incidents delineate the need for the development of simple, preferably inexpensive, devices that can warn of leaks as a means to protect transportation workers, the public, first responders, hazmat teams, and firefighters. While the present

investigation will focus only on volatile oxidizing chemicals, future research would address other classes of hazardous materials.

The overall goal of this research project was to develop oxidant vapor detection devices that can be used to ensure the safety of hazardous freight transportation systems. Two nanotechnology-based systems originally developed for improvised explosive detection systems will be adapted to this application. The first of these are dark-blue nanometric tungsten or molybdenum hydrogen bronzes that are sensitive to all strong oxidants. The second is a titanium oxide nanoparticle-based system that is extremely sensitive and selective to hydrogen peroxide and organic peroxides. Our hypothesis, based on preliminary studies, is that we can use the dramatic color change or change in the electronic properties of hydrogen bronze nanoparticles or titania nanoparticles when exposed to strongly oxidizing vapors to produce a variety of products for improving the security of hazardous materials transportation systems. The specific targets that we will research include: (1) stick-on color-changing sensors that will passively detect strong oxidants (2) hand-held sensitive electronic sensors that detect strong oxidants (3) an electronic "area sensor" that utilizes color changes to identify the presence of strong oxidant leaks.

The proposed research fits several areas of importance to the Oklahoma Transportation Center. It will increase the security of the movement of freight, assist in emergency response preparedness, and provide important support tools for enhanced safety of hazardous freight shipping. It is likely that the sensors produced in this investigation could even prevent serious incidents through early detection of leaks, protecting transportation personnel and the travelling and non-traveling public. In the future, the sensors could also be adapted to detection of peroxide-based explosives that might be used in terrorist attacks on public transportation systems or terrorist's use of transportation systems for delivery of improvised explosives to a target site. The technology could also thwart attempts to utilize hazardous cargo as a weapon.

Professor's Apblett and Materer are co-founders of a Stillwater-based company called XploSafe, LLC that will provide an avenue for the transfer of the new technology to the transportation industry. XploSafe is currently marketing related improvised-explosive sensing materials and devices. It is expected that the company will license the inventions that are forthcoming from the proposed research and aggressively market the oxidant vapor sensors.
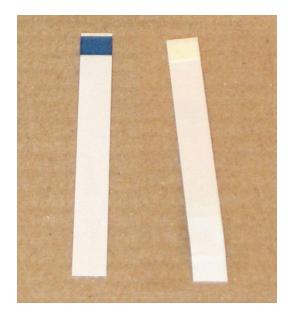
Background and Proposed Technology

An earlier investigation, funded by the Memorial Institute for the Prevention of Terrorism, uncovered reagents that can neutralize both peroxide-based improvised explosives under ambient conditions in a reaction that results in a remarkable change in color.[8] These reagents are based on molybdenum or tungsten trioxide and are referred to as hydrogen bronzes. They are derived from reduction of molybdenum or tungsten trioxide with hydrogen or a hydrogen source such as an alcohol.[9] They are highly-colored blue compounds that contain pentavalent metal centers with attached hydroxides. In this form, the hydrogen is completely non-flammable but still capable of behaving as a reducing reagent.[10] This is a result of the fact that the transfer of the hydrogen ion to a substrate is usually accompanied by electron transfer and reoxidation of the metal ion to the hexavalent state. In some respects, the bronze can be considered to be a convenient storage medium for reactive hydrogen.[11] Since removal of the hydrogen by reaction with a sufficiently strong oxidizer causes a dramatic color change from dark blue to white or pale yellow, they are suitable for colorimetric detection of strong oxidant vapors. As an example these reagents could work by reducing (Reaction 1) the peroxide groups of an organic peroxide to alcohol groups and water. This reduction occurs rapidly at room temperature. Figure 1 shows the dramatic color change obtained after exposure to hydrogen peroxide within a few minutes of exposure to peroxide vapors above a 10% hydrogen peroxide solution.

$$2\ Mo_2O_5(OH) + ROOH \rightarrow 4\ MoO_3 + ROH + H_2O \quad (1)$$

The molybdenum hydrogen bronze can be synthesized by a reaction of molybdenum trioxide with butanol resulting in a brilliant blue suspension of molybdenum hydrogen bronze nanoparticles. For the peroxide based explosives, these brilliant blue nanoparticles turn to a light yellow color as they react. It was this material that was utilized to form the colorimetric test strips shown in Figure 1. When exposed to hydrogen peroxide vapors, the blue color rapidly fades as the bronze nanoparticles are oxidized to colorless molybdenum trioxide

Figure 1: Test Strips for Explosive Detection. The strip on the left is the as-prepared strip while the one on the right was exposed to hydrogen peroxide vapors above a 10% solution

During the course of Oklahoma Transportation Center funded research aimed at preparation of titanium oxide coatings the Apblett research group discovered a facile method for the synthesis of stable aqueous suspensions of titania nanoparticles. The procedure involves producing a metastable solution of aqueous titanyl sulfate and then aging it at 60°C so that hydrolysis takes place to produce titania nanoparticles with a size of approximately 15 nm. Previously Apblett, Materer, and Khan found that depositing titanium ions on the surface of the tungsten bronze treatment makes it a more reactive sensing material for nitrotoluene (a surrogate for TNT).[12] Therefore, scientists at XploSafe, LLC investigated the reaction of the nanoparticulate suspension with solid HMTD. A dramatic color change from colorless to orange occurred when a drop of the suspension was added to solid HMTD. Furthermore, application of the suspension to the pad of a blank test strip produced a test strip that underwent a dramatic color change when exposed to peroxides in organic solvents, aqueous hydrogen peroxide, and hydrogen peroxide or TATP vapors. Unfortunately, the sulfuric acid in the suspension was incompatible with the test strip pad so that the test strip developed an unacceptable tan color before use. Therefore, titanium isopropoxide was used to deposit titanium oxide nanoparticles on the test strip pad. As shown in Figure 2,

these are extremely successful for detecting peroxides. This approach will be useful for producing sensors that are specific for hydrogen peroxide and organic peroxides

Figure 2: Test Strips for Peroxide Detection. The strip on the top is the as-prepared strip while the one on the bottom was exposed to hydrogen peroxide vapors above a 10% solution.

Objectives and Scope

The research activities targeted several devices that will markedly increase the safety of transportation of hazardous materials that consist of volatile, strongly oxidizing chemicals. The compounds targeted for sensing constitute a significant risk to the public, transportation workers, and emergency responders. Many of these materials have been involved in numerous transportation-related catastrophes so that measures are highly warranted that identify leaks before they become serious, or, when an accident does happen, to be able to examine a colorimetric detector from a distance to see if any oxidant is leaking. The specific technological objectives of this research project were: (1) stick-on color-changing sensors that will passively detect strong oxidants (2) sensitive electronic sensors that utilize the change in resistance of a hydrogen bronze film to detect oxidant vapors (3) an electronic "area sensor" that utilizes color changes to identify the presence of strong oxidants.

One device that was targeted is a color-changing material that will be in the form of a stick-on decal that can be placed on rail cars, tankers, trucks, freight containers, and cargo crates, or boxes that are being used to transport volatile hazardous materials that are oxidants. For example the device could be part of the warning placards or

labels that are used when transporting such materials. The decal can be designed to give a clear message even to unfamiliar members of the public that a hazard exists when oxidant vapors cause the sensing material to change color. Two types of decals were targeted, one that detects a broader range of oxidant materials (DOT Class 5.1 and toxic or corrosive oxidants such as chlorine, bromine, nitrogen oxide, and nitric acid) while the second one is specific for DOT Class 5.2 materials (organic peroxides). The intention was that the research would result in the development of the necessary sensing materials and production of the initial prototypes. Testing for durability and for the sensing of several key hazardous chemicals will provide a strong foundation for the commercialization of the hazard materials sensor decals. These are expected to be fairly inexpensive but they will have a dramatic impact on the safety of transportation of hazardous materials. Not only will these materials provide clear indication of danger in the case of an accident but they will also provide the ability for transportation personnel to detect minor leaks that might occur in transit.

The other devices that were developed to the stage of prototypes with proven ability to sense oxidants are more sophisticated and sensitive electronic hand-held or mounted sensors that could be used to check for leaks, determine the presence of oxidant vapors in the case of an accident where release of volatile oxidants is suspected, and ensure safety during the loading and unloading of such hazardous cargo. We foresee that the handheld sensor could be used by transportation personnel to check for leaks and to ensure that they are not being exposed to dangerous vapors when loading or unloading operations. It would also be highly useful to first responders, hazmat teams, firefighters, and other emergency workers that are responding to an accident involving the hazardous materials targeted in this investigation. Mounted sensors would be useful for monitoring train yards, cargo depots, transportation warehouses, ship holds, etc. for oxidant vapors. This would provide the means to detect leaking containers but could also thwart the potential use of the transportation systems

by terrorists to deliver nitric acid-based or peroxide-based improvised explosives to target sites or to detect terrorist attacks on the transportation systems themselves.
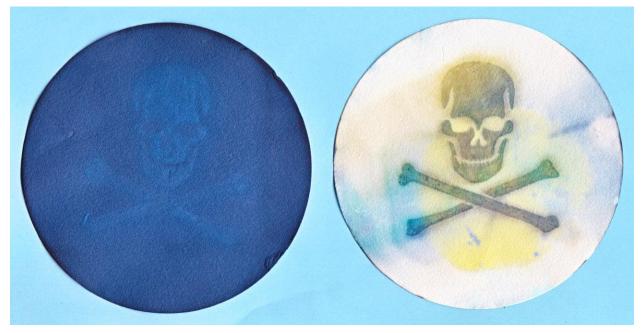
Accomplishments

Development of Color Changing Decals for Sensing Strong Oxidants

The plan for production of stick on sensors involved gluing an absorbent pad of cellulose onto a polyester plastic film. To develop a colorimetric sensor for a broad range of strong oxidants, cellulose pads were flooded with a butanol solution of molybdenum hydrogen bronze nanoparticles. The amount and concentration of the "ink" was optimized to give a uniform deep blue color. The papers were then air-dried and tested for their response to hydrogen peroxide vapor over a 30% solution of hydrogen peroxide. A rapid color change was observed from dark blue to pale yellow demonstrating that these pads will perform well for strong oxidant sensors. Next, in order to avoid the using of toxic organic solvents a water-based molybdenum (V, VI) gluconate ink was investigated. This was prepared by refluxing molybdenum trioxide with potassium gluconate in water in a 1:1 molar ratio. The "dye molecule" consists of a molybdenum(V)-molybdenum (VI) dimer. Since the redox state must be balanced, the synthetic procedure must be carefully controlled to maximize the color of the sensing dye. Experimentation required to efficiently and reliably synthesize the molybdenum gluconate ink was completed and test papers were prepared by flooding with the aqueous solution and then drying. These were found to respond rapidly (within 1 minute) to hydrogen peroxide, nitric oxide, bromine, and chlorine with a color change from blue to white or yellow. Examples of this response are shown in Figure 3. While this color change is extremely obvious, the objective of these decals was to clearly indicate the presence of a dangerous leak. Therefore, a stencil was used to draw a skull and crossbones on the paper substrate with an ink pen. Numerous inks were tested until one was found that matched the blue color of the sensing ink and did not interfere with the dyeing of the paper. The end result was the sensing paper shown on the left in Figure 5. When it was exposed to nitrogen dioxide fumes the sensing dye immediately bleached revealing the skull and crossbones warning sign as shown on the right in Figure 5. This would be an unmistakable sign of a dangerous leak even to a ley person. A similar response was observed for hydrogen peroxide vapors, chlorine gas, and

bromine vapors.

Figure 3: Paper with Blue Sensing Dye: As Manufactured (Left); Exposed to Hydrogen Peroxide Vapors (Middle); and Exposed to Nitrogen Dioxide (Right)

Figure 4: Sensing Paper with Skull and Crossbones: As Manufactured (Left) and Exposed to Nitrogen Dioxide (Right)

A second type of sensor paper that is meant for detection of peroxides was prepared by flooding cellulose pads with titanium isopropoxide. This yielded white sensing materials that turned dark orange when exposed to hydrogen peroxide. A second approach to this type of sensor utilized aqueous titanyl sulfate. We experimented with a variety of concentrations, acid catalysts, and non-volatile liquid solvents to maximize the rate and extent of the colorimetric response (white to orange).

The response to hydrogen peroxide approaches that which we achieved previously using a titanyl sulfate sensing dye but was not quite as good. The problem with the latter dye is it reacts with the cellulose substrate to give a grey color that interferes with the visibility of the color-changing sensors. Therefore, the substrate was switched to a glass fiber filter that is compatible with this dye. The picture of a paper treated with this dye and partially exposed to hydrogen peroxide is shown in Figure 5.
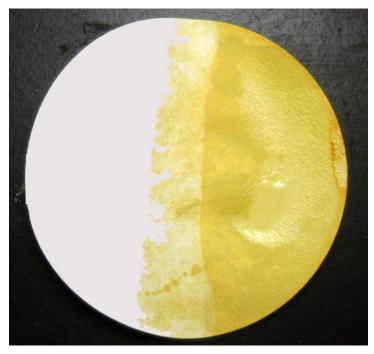

Figure 5: Paper Treated with Titanyl Dye and Partially Exposed to Hydrogen Peroxide

As for the blue sensing paper, there was still a need for the color change to provide a definite indication of a leak of toxic gases. Therefore, a stencil was used to create a skull and crossbones painting on the glass microfiber substrate with the titanyl ink. This gave a completely white substrate (shown on the left in Figure 6) that developed a yellow skull and cross bones when exposed to hydrogen peroxide vapor as shown on the right in Figure 6.

The final step in creating the sensor decals was finding a method to prevent the sesnors from deteriorating in moist conditions such as rainy weather. Several water proofing chemicals were tested and it was found that an inexpensive spray for water proofing

tents was quite successful in making the sensing decals waterproof while still preserving their ability to respond to strong oxidant vapors.

Figure 6: Response of Hydrogen Peroxide Sensing Paper with Skull and Crossbones to Hydrogen Peroxide

Electronic Sensor to Detect Strong Oxidant Vapors

Several sensor devices for peroxide vapors have been proposed and/or developed using a variety of methods including amperometric[13], colorimetric[14], biochemical[15], and chemiresistive[16] methodologies. One particularly promising colorimetric method utilizes a suspension of nanoparticulate molybdenum hydrogen bronze in butanol for the purpose of neutralization of peroxide-based explosives and for preparation of colorimetric test papers for the detection such explosives.[17]

Peroxide compounds are oxidizers and can be neutralized by sufficiently strong reducing agents. One such reagent is sodium molybdenum bronze, a non-stoichiometric compound produced by reduction of molybdenum trioxide. The bronze contains intercalated sodium and hydrogen ions that are associated with molybdenum (V) centers, see Figure 7. This compound is a reducing agents and is metallic in nature (*i.e.* it is brightly-colored, lustrous, and electronically conductive). The oxidation product is a sodium molybdenum oxides that is a non-conductive, essentially colorless solid. These properties make the sodium molybdenum bronze an ideal candidate as a "chemiresistive" sensor as well as a colorimetric indicator for oxidizing agents. It was these properties that suggested the development of the hydrogen peroxide vapor

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detector reported herein. The rationale for the sensor is that oxidation by peroxide vapor transforms the conductive bronze species into a non-conducting solid. The change in the electrical conductivity of the bronze material is of sufficient magnitude and rate, to allow the oxidizer to be easily detected by monitoring the ohmic resistance across the sensor. This type of sensor should then lend itself well for the purpose of detecting the presence of strong oxidant vapors such as peroxides, ozone, chlorine, chlorine dioxide, nitrogen dioxide. etc.
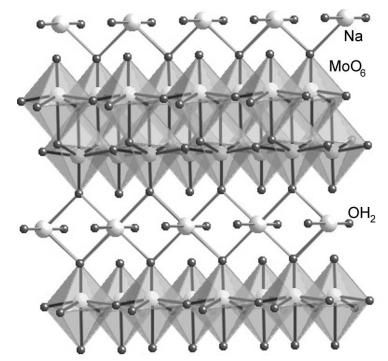

Figure 7: Structure of Sodium Molybdenum Bronze

The detector apparatus was constructed by attaching two flat gold plated leads[18] onto a glass microscope slide using a two-part epoxy glue. The separation between the two leads was 3 mm. The active material was prepared by mixing 1.60 g of Vycar® 660x14 vinylidene chloride copolymer latex with 3.26 g of the sodium molybdenum bronze[19] in a mortar and pestle to form a thick paste. This paste was then packed between the leads and allowed to dry forming the device shown in Figure 8. The conductivity of the sodium bronze material was determined to be 2.8 $m\Omega^{-1}m^{-1}$ using a pressed pellet method.[20]

The detector response was determined by connecting the detector device to a Keithley Model 2010 digital multimeter in resistance mode and placing it into the

reaction cell.[21] The reaction cell apparatus was set to provide a flow rate of 20 standard cubic centimeters per minute at a peroxide vapor concentration of 35 ppm.   The resistance of the device was read and noted at a one minute interval during the course of the experiment.

Figure 8: Sodium Bronze/Vycar Gas-Phase Peroxide Sensor.

The initial resistance value of the sensor device was determined to be around 44 kΩ.   Upon exposure to hydrogen peroxide in the test cell, the reaction proceeds increasing the resistance until it becomes constant at 100 kΩ. This suggests that as the conductive bronze is reacted to the nonconductive oxide, the density of conductive particles fall below the required percolation density such that the conductivity of the molybdenum bronze/Vycar material approaches that of the Vycar film (which is slightly conductive when saturated with water). In the first five minutes the detector resistance increased from 44000 ohms to 56000 ohms, which corresponds to a 27.2% increase in resistance.   In this region the response is quite linear and of sufficient magnitude to provide an unequivocal response that is illustrated in Figure 10.

The response of the peroxide detector was sufficiently fast and of high enough magnitude for this device to be used as a passive detector for peroxide vapors.

Furthermore this study exemplifies the practicality of sodium molybdenum bronzes as chemical sensors for a number of applications in which an oxidizing species needs to be detected. The conductance/resistance response lend itself well for interface with any number of monitoring devices, allowing these types of devices to be set up in several locations and monitored remotely.
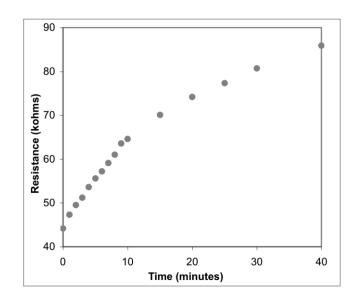

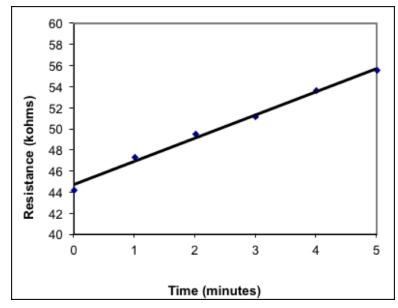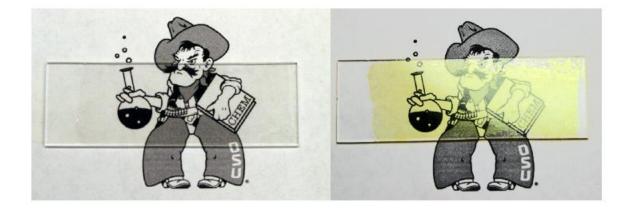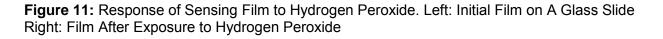**Figure 9:** Resistance-time Response of Peroxide Sensor to Peroxide Vapor.

Figure 10: Initial Linear Response of the Detector to the Peroxide Vapor

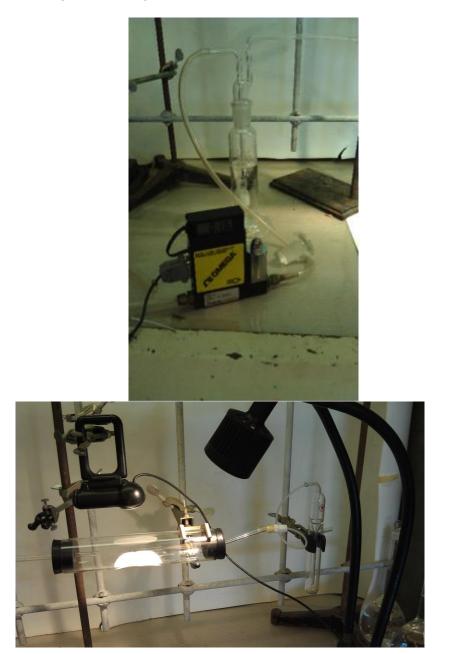## Colorimetric Area Sensor for Detection of Strong Oxidant Vapors

Experiments were performed to design a colorimetric area sensor that operated by changes in light transmission through sensing dyes using transparent plastic or glass slides as substrates. A sol-gel method that utilized titanium isopropoxide and hydroxyethyl cellulose was developed to prepare transparent colorless, flexible sensing films on plastic (polyester) substrates. Experiments were performed to maximize the titanium content and hence the colorimetric response of the films without sacrificing the flexibility. An example of the results is shown in Figure 11. The picture on the left shows the as-prepared film while that on the right shows the film after exposure to hydrogen peroxide.

Figure 11: Response of Sensing Film to Hydrogen Peroxide. Left: Initial Film on A Glass Slide Right: Film After Exposure to Hydrogen Peroxide

The glass slides were washed with acetone and sonicated for 30 minutes in a 8 M HNO_3 bath, then rinsed with water and dried. Ten drops of the titanium sol/gel solution were applied to the surface and films approximately 10 mils thick were formed using a Gardco Wet Film Applicator. Films were dry and ready for use in approximately 15 minutes. The slides were then placed into a glass cell through which hydrogen peroxide vapor was passed (Figure 12). Ultra high purity nitrogen gas was fed though

an Omega FMA 5400 mass flow controller set at 350 sccm. The nitrogen was then bubbled through an H_2O_2 solution. By adjusting the H_2O_2 concentration, the concentrations of the peroxide vapors can be altered.

Figure 12: Apparatus for Measuring the Colorimetric Response to Hydrogen Peroxide

A Logitech Pro 9000 camera was used to record the slide during its exposure to H_2O_2 vapor. The effluent gas from the reactor was bubbled through a solution of $TiOSO_4$, which neutralizes the peroxide vapors and undergoes a color change that was

used to determine how much peroxide was present in the gas phase for the duration of the exposure. Placing a Leiz Wetzlar Blue BG 12 fluorescence filter between the cell and camera, allows the yellow spectrum to be quantifiable. Using this data, the rates of reaction for the slide may be determined. The graph below (Figure 13) is a plot of the natural log of the measured intensity versus time. With a high correlation coefficient for the linear regression ($R^2 \geq 0.99$), the reaction kinetics correlate very well to a first-order reaction with respect to the peroxide concentration.
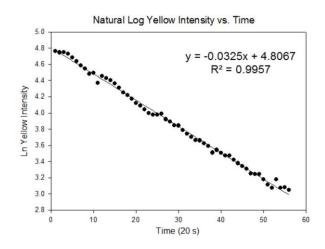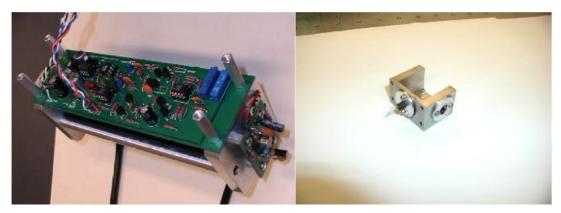

Figure 13: Colorimetric Response of Sensor to Hydrogen Peroxide

Based on the excellent results for the laboratory scale prototypes, a final colorimetric sensor will be designed and commercialized. This can be accomplished by placing the sensing film in a custom dual beam spectrometer using a blue LED as the light source. A metering air pump will provide a constant flow of the ambient air across the film. This will be based on a gas sensor platform previously developed by Drs Apblett and Materer for chlorine dioxide sensing. This gas is used for microbial decontamination and deodorization of commercial and residential real estate. The sensor is shown in Figure 14 along with the beam splitter on the right. In addition, the sensor in Figure 14 can be connected to an electronic platform to allow wireless monitoring. The first sensor will use a coated glass slide for proof-of-principle. After which, a coated ribbon will be utilized to provide a fresh detection surfaces at periodic intervals to eliminated issues such as dust collection on the film and to allow the sensor to detect another event without manual intervention.

Figure 14: Optical ClO$_2$ sensor developed by Drs Apblett and Materer. The beam splitter assembly showing the LED and photodiode.

Technology Transfer

Several OSU invention disclosures have been files on this research based on the molybdenum sensing materials. A patent was applied for that technology previous to the initiation of this research project and XploSafe, LLC has licensed the technology. We are working with XploSafe, LLC to build and market the more sophisticated electronic and colorimetric sensors.

Summary and Conclusion

Several sensors for detection of hazardous oxidant vapors including stick-on color-changing sensors that will passively detect strong oxidants , hand-held sensitive electronic sensors that detect strong oxidants, and an electronic "area sensor" that utilizes color changes to identify the presence of strong oxidant leaks. The sensing technologies developed in this project are expected to make a substantial contribution to increasing the security of the movement of freight, assisting in emergency response preparedness, and providing important support tools for enhanced safety of hazardous freight shipping. It is likely that the sensors produced in this investigation could even prevent serious incidents through early detection of leaks, protecting transportation personnel and the travelling and non-traveling public. In the future, the sensors could also be adapted to detection of peroxide-based explosives that might be used in terrorist attacks on public transportation systems or terrorist's use of transportation systems for delivery of improvised explosives to a target site. The technology could also thwart attempts to utilize hazardous cargo as a weapon.

The next step is scaled up production of the sensors and their placement in the field. We hope that these oxidant sensors will be used to increase the safety of hazardous cargo transportation and will eventually protect people and save lives.

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