Flexible polyurethane in fire investigation: detection of hydrogen cyanide and time until flashover.

by

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For…

Lorraine Grimwood, who shaped me in her absence;

Michael Dawson, who believed in my ability even when I did not; and

Neil Barnett, who reminded me about the healing qualities of white light.

What matters most is how well you walk through the fire.

Charles Bukowski

Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

Kate Grimwood

31/03/2014

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This tangible product of blood, sweat and a good deal of tears would never have come to fruition if not for those who inspired me to *be* better and to *do* better. For that I thank all of you, sincerely.

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Abbreviations

%RSD	Percent standard deviation
ADG Code	Australian Code for the Transport of Dangerous Goods by Road and Rail
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
CFD	Computational Fluid Dynamic
CMS	Chip Management System
CN^-	cyanide ion
CNS	Central Nervous System
CO	carbon monoxide
COHb	carboxyhaemoglobin
DNP	2,4-dinitrophenylhydrazine
EPM	Embedded Piezoresistive Microcantilevers
ESEM	Environmental Scanning Electron Microscopy
FFFD	Fergus Falls Fire Department
FIA	flow injection analysis
FMV	fair market value
FRNSW	Fire and Rescue New South Wales
FTIR	Fourier Transform Infrared spectroscopy
GC-MS	Gas Chromatography Mass Spectrometry
gm	grams
HCN	hydrogen cyanide
HPLC	High Performance Liquid Chromatography
HRR	Heat Release Rate
HS	Head Space
IAAI	International Association of Arson Investigators
IC	Ion Chromatography
IQR	interquartile range
IRS	Internal Revenue Service

ISE	Ion Selective Electrode
KCN	potassium cyanide
kg	Kilograms
KOH	potassium hydroxide
kW	Kilowatts
LEAA	Law Enforcement Assistance Administration
LOD	Limit of Detection
LOQ	Limit of Quantitation
m	meters
MALDI-MS	Matrix-Assisted Laser Desorption Ionization Mass Spectrometry
MDI	methylene diphenyl diisocyanate
MFD	MN Fire Department
mL	Millilitres
mm	Millimetres
MN	Minnesota
MQH	McCaffrey, Quintiere and Harkleroad
mV	Millivolt
N	Hardness
n	Number
N_2	Nitrogen
NaOH	sodium hydroxide
NBS	National Bureau of Standards
NFPA	National Fire Protection Association
NFPA 921	NFPA 921 Guide for Fire and Explosion Investigations
$Ni(OH)_2$	nickel hydroxide
Ni^{2+}	Nickel ion
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance spectroscopy
O_2	Oxygen
OH-	Hydroxide ion
PPE	personal protective equipment
PU	Polyurethane
Py-GC-MS	Pyrolysis gas-chromatography mass spectrometry
QCESA	Queensland Combined Emergency Services Academy

S&S	Signs and Symptoms
SCBA	self contained breathing apparatus
SCN-	Thiocyanate ion
sec	Seconds
SS	Stainless steel
STD	standard deviation
STEL	Short term exposure limit
SUT	Swinburne University of Technology
TDI	toluene diisocyanate
TGA	Thermogravimetric analysis
The Code	Internal Revenue Code
TWA	Time weighted average
UL	Underwriters Laboratories
UP	ultra-pure
USA	United States of America
USFA	United States Fire Administration
UTS	University of Technology, Sydney

Abstract

Although the majority of fires attended by Fire and Rescue NSW (FRNSW) originate in the kitchen, most fatalities occur in the lounge and bedrooms. These rooms have a comparatively higher proportion of polyurethane (PU) and hence this project sought to focus on the role of PU during the progression of a fire.

The research presented here is a significant addition to the existing body of knowledge and, for the first time, investigates whether the time until flashover is proportional to the amount of PU in a cell. Additional research was undertaken to determine the lowest temperature that hydrogen cyanide (HCN) could be detected in effluent produced from the degradation of polymeric materials, specifically flexible PU.

Thirty large scale burns, which were fuelled with PU-containing furniture, were conducted at three different sites in the United States of America (USA) and Australia between 2007 and 2010. After significant method optimisation (that concentrated on the standardisation of the majority of the experimental parameters) the time until flashover based on the amount of PU in the cell was successfully determined.

Gas analysis was run in parallel to the large scale burns. To facilitate gas sampling an apparatus was developed to remotely trap effluent produced during the progression of a fire, by drawing it through potassium hydroxide (KOH) solution from directly inside the fire cell. The system was used in conjunction with a novel HCN detection method using Ultraviolet Visible (UV-Vis) spectroscopy. The method involved adding nickel (Ni^{2+}) solution to the KOH + fire effluent solution and analysing the resultant solution using UV-Vis spectroscopy. The positive presence of HCN in the fire effluent could be shown by the presence of the tetracyanonickelate (II) complex with a characteristic absorbance at 267 nm. The presence of HCN in fire effluent was quantitatively determined in the pre-flame and at an interval of 30 minutes post suppression in the large scale burns conducted in Australia. In addition a commercially available Ion Selective Electrode (ISE) specific to HCN was used to analyse the KOH + fire effluent solution; though it and was found that this technique was best suited to qualitative, rather than qualitative, work.

In a controlled laboratory environment the detection of HCN between 171 °C – 203 °C was investigated. Using a modified version of the method used to detect HCN at the large scale test burns, PU foam was heated in an oven between 171 °C – 180 °C and 184 °C – 203 °C and the resultant effluent was drawn through KOH solution at different time intervals. An amount of Ni^{2+}solution was added to each of the collected sample solutions. The presence of the characteristic absorbance caused by the combination of CN^- and Ni^{2+} to form tetracyanonickelate (II) complex was determined using UV-Vis spectroscopy. In some cases the fire effluent was found to contain HCN after heating PU foam for 30 minutes and 50 minutes at both temperature ranges.

The data presented in this body will provide insight to fire investigators when determining the origin and cause of fires, when flashover is suspected to have occurred. This research will certainly benefit the occupant as it provides data to inform the development of a self egress plan that acknowledges the presence of PU in a fire, and its potential hazards. Emergency services members can use the information described in this work to further inform the level of respiratory personal protection equipment (PPE) required when they attend the post suppression scene of a PU fuelled fire. Finally, the research undertaken in this work regarding time until flashover has the potential to inform fire brigades, such as FRNSW, at a strategic level when developing their response time isochrome map (the time taken for an engine to respond to a fire at the furthest point within their area.