



New Technologies and Materials for Enhanced Damage and Fire Tolerance of Naval Vessels

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Defence R&D Canada – Atlantic

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Abstract

Emerging technologies for fire and damage detection, abatement and suppression on board naval vessels are reviewed. These include point and volume fire and damage sensors and systems, smoke control (ejection) systems, smart valves, water mist and gaseous agent fire suppression systems, and aerosol fire extinguishing agents. Technology readiness levels (TRL) of these technologies are assigned based on the criteria developed by the United States Department of Defence.

Several approaches to enhancing the fire and flammability properties of non-metallic (polymeric) materials used on naval vessels are also reviewed. The approaches include the selection of polymeric materials with inherent fire resistance, the use of flame retardant additives including nanoparticles, the incorporation of molecules into the polymer backbone that have flame retardant properties, and the use of intumescent coatings to protect the underlying substrate. Standards and test methods that are used to evaluate the fire performance of non-metallic materials are discussed.

Résumé

De nouvelles technologies pour la détection, la réduction et la suppression des incendies et des avaries à bord des bâtiments navals font l'objet d'un examen. Elles comprennent des systèmes de capteurs ponctuels et en volume des incendies et des avaries, des systèmes de contrôle (d'évacuation) des fumées, des valves intelligentes, des systèmes d'extinction d'incendie par la vapeur et par des agents gazeux, et des agents extincteurs d'incendie de type aérosol. Leurs niveaux de préparation de la technologie (NPT) sont déterminés selon les critères mis au point par le United States Department of Defence (le ministère de la défense des États-Unis).

Quelques mesures pour améliorer les propriétés de combustion et d'inflammabilité de matériaux non métalliques (polymères) employés à bord des bâtiments navals font aussi l'objet d'un examen. Elles comprennent la sélection de matériaux polymères qui ont une résistance inhérente au feu, l'utilisation d'additifs ignifuges qui comprennent des nanoparticules, l'incorporation de molécules qui ont des propriétés ignifuges dans la chaîne principale du polymère et l'utilisation de revêtements intumescents pour protéger le substrat sous-jacent. Les méthodes normalisées et d'essai qui sont employées pour évaluer la résistance au feu des matériaux non métalliques font l'objet de discussions.

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Executive summary

New Technologies and Materials for Enhanced Damage and Fire Tolerance of Naval Vessels

John A. Hiltz; DRDC Atlantic TM 2010-306; Defence R&D Canada – Atlantic; February 2011.

Introduction: Developments in technologies applicable to fire and damage control on naval vessels continue to be made. These technologies have the capability to enhance fire and damage detection, abatement and suppression on board naval vessels. A major challenge is to successfully move these systems from the laboratory/prototype stage to installation on operational naval vessels. In addition to the detection and abatement or suppression of damage and fires, the fire and flammability properties of non-metallic (polymeric) materials required for shipboard applications are critical in minimizing risks associated with their combustion. New fire and damage control technologies and approaches to minimizing hazards associated with non-metallic materials are reviewed and discussed in this memorandum.

Results: Advances in point and volume fire and damage sensors and systems, smoke control (ejection) systems, smart valves, water mist and gaseous agent fire suppression systems, and aerosol fire extinguishing agents are reviewed and discussed. Technology readiness levels (TRL) of these technologies are assigned based on the criteria developed by the United States Department of Defence. In many instances the components of systems, for instance the detectors used in point and volume sensors, have already been used on naval vessels. However, their incorporation into fire and damage control systems has not progressed past the prototype/demonstrator phase.

Approaches to enhancing the fire and flammability properties of non-metallic (polymeric) materials used on naval vessels are also reviewed. The approaches include the selection of polymeric materials with inherent fire resistance, the use of flame retardant additives including nanoparticles, the incorporation of molecules into the polymer backbone that have flame retardant properties, and the use of intumescent coatings to protect the underlying substrate. Standards and test methods that are used to evaluate the fire performance of non-metallic materials are discussed.

Significance: The technologies reviewed have the potential to not only enhance fire and damage control on naval vessels but also to automate certain fire and damage control tasks presently carried out by crew members. Materials with improved fire tolerance will reduce the risk associated with their use on board naval vessels. Materials that are more difficult to ignite and release less heat, smoke and toxic gases contribute to improved fire safety.

Future plans: Defence R&D Canada – Atlantic has acquired a prototype volume sensor system and will pursue opportunities to trial this system on an operational naval vessel.

Sommaire

New Technologies and Materials for Enhanced Damage and Fire Tolerance of Naval Vessels

John A. Hiltz; DRDC Atlantic TM 2010-306; Recherche et développement pour la défense Canada – Atlantique; février 2011.

Introduction : On continue d'élaborer des technologies pour lutter contre les incendies et les avaries à bord des bâtiments navals. Elles permettent d'y améliorer la détection, la réduction et la suppression des incendies et des avaries. Faire franchir le stade de prototypes en laboratoire à ces systèmes pour les installer avec succès sur des bâtiments navals opérationnels représente une grande difficulté. Tout aussi importantes que la détection, la réduction et la suppression des incendies et des avaries, sont les propriétés de combustion et d'inflammabilité des matériaux non métalliques (polymères) utilisés à bord des bâtiments navals, qui sont essentielles pour réduire au minimum les risques associés à leur combustion. De nouvelles technologies et mesures de lutte contre les incendies et les avaries, dont le but est de réduire au minimum les risques associés aux matériaux non métalliques, font l'objet d'un examen et de discussions dans le présent document.

Résultats : Des progrès en matière de systèmes de capteurs ponctuels et en volume des incendies et des avaries, de systèmes de contrôle (d'évacuation) des fumées, de valves intelligentes, de systèmes d'extinction d'incendie par la vapeur et par des agents gazeux, et d'agents extincteurs d'incendie de type aérosol font l'objet d'un examen et de discussions. Les niveaux de préparation de la technologie (NPT) de ces systèmes sont déterminés selon les critères mis au point par le United States Department of Defence (ministère de la défense des États-Unis). Dans bien des cas, les composants des systèmes, par exemple les types de détecteurs employés dans les capteurs ponctuels et en volume, ont déjà été utilisés à bord des bâtiments navals. Toutefois, on n'a pas encore réussi à créer un prototype fonctionnel qui les incorpore aux systèmes de lutte contre les incendies et les avaries.

Des mesures pour améliorer les propriétés de combustion et d'inflammabilité de matériaux non métalliques (polymères) employés à bord des bâtiments navals font aussi l'objet d'un examen. Elles comprennent la sélection de matériaux polymères qui ont une résistance inhérente au feu, l'utilisation d'additifs ignifuges qui comprennent des nanoparticules, l'incorporation de molécules qui ont des propriétés ignifuges dans la chaîne principale du polymère et l'utilisation de revêtements intumescents pour protéger le substrat sous-jacent. Les méthodes normalisées et d'essai qui sont employées pour évaluer la résistance au feu des matériaux non métalliques font l'objet de discussions.

Importance : Les technologies examinées ont non seulement le potentiel d'améliorer la lutte contre les incendies et les avaries à bord des bâtiments navals, mais aussi d'automatiser certaines tâches connexes qui sont pour l'instant exécutées par des membres de l'équipage. Des matériaux qui ont une meilleure résistance au feu réduiront les risques associés à leur utilisation à bord des bâtiments navals. Les matériaux qui s'enflamment moins facilement et qui libèrent moins de chaleur, de fumée et de gaz toxiques que d'autres contribuent à une meilleure protection contre les incendies.

Perspectives : Recherche et développement pour la défense Canada – Atlantique a fait l'acquisition d'un prototype de système de capteur en volume et procédera à des mises à l'essai à bord de bâtiments navals opérationnels.

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Table of contents

Abstract	i
Résumé	i
Executive summary	iii
Sommaire	iv
Table of contents	vii
List of figures	ix
List of tables	x
1 Introduction.....	1
2 Technologies.....	2
2.1 Fire and damage sensors and sensing systems	2
2.1.1 Point sensors and systems	2
2.1.2 Volume sensors and systems.....	3
2.2 Smoke control.....	4
2.2.1 Positive pressure ventilation	5
2.2.2 Smoke ejection system.....	5
2.3 Smart valves	6
2.4 Fire suppression agents and systems	6
2.4.1 Water mist.....	6
2.4.2 Gaseous fire suppression agents.....	8
2.4.3 Powdered aerosol extinguishing systems.....	9
3 Technology readiness levels (TRL).....	13
3.1 Sensors and sensor systems	14
3.1.1 Point sensors and systems	14
3.1.2 Volume sensors and systems.....	14
3.2 Smoke control.....	14
3.3 Smart valves	14
3.4 Fire suppression systems	15
3.4.1 Water mist systems	15
3.4.2 Dual agent systems.....	15
3.4.3 Powdered extinguishing agent technologies	16
4 Materials	17
4.1 Enhancing fire performance	17
4.1.1 Inherently flame retardant materials	17
4.1.2 Chemically modified polymers	18
4.1.3 Polymers containing flame retardants	19
4.1.4 Intumescent materials.....	20

4.1.5	Nanoparticles	21
4.1.6	A multi-faceted approach to improved flammability properties	21
4.2	Standards	22
5	Summary and Conclusions	28
	References..	30
	Annex A .. Test methods used to evaluate the fire and flammability properties of non-metallic materials.....	35
	Distribution list	41

List of figures

Figure 1. Front view of the Canadian Demonstrator Prototype volume sensor suite (VSS) showing the apertures for the various sensors.....	4
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List of tables

Table 1. Manufacturers of water mist systems and associated technologies.	8
Table 2. A list of powdered aerosol agents used in total flooding fire suppression applications. Environmental Protection Agency (EPA) conditions or restriction for their use and manufacturer trade name are also listed.	11
Table 3. Definitions of Technology Readiness Levels (TRL)[39].	13
Table 4. Fire Safety Requirements for Some Marine Products- Fire Test Procedures Code (FTP Code) IMO Resolution MSC.61(67).....	23
Table 5. US Naval standards for fire and flammability.....	24
Table 6. A summary of MIL-STD-1623E specifications for fire tests.....	25
Table 7. Summary of British Defence Standards (Def Stan) related to fire and flammability testing of materials	26
Table 8. Two of the thirty one test methods listed in Def Stan 07-247 for evaluation of the fire and flammability properties of materials.....	27

1 Introduction

The ability to float, move and fight is essential for a naval vessel to carry out its mandate. To maintain these abilities requires that an ongoing 'internal battle' be waged by the vessels' crew. This internal battle involves all activities necessary to ensure that the vessel does not sink, that power for propulsion and combat systems is maintained, and that these capabilities can be restored should they be lost due to damage or fire onboard the vessel.

Fire is a major, if not the greatest, threat to a ship's ability to carry out its mandate. It requires an immediate and coordinated effort by the crew to ensure that the ship can continue to perform its duties. If a fire cannot be controlled it will ultimately result in the loss of the ship. As a result, improvements in fire detection technology, fire suppression equipment, fire fighting techniques and command and control systems that assist the crew in minimizing the damage arising from a fire will result in a diminished threat from fire.

There are other technologies that can have an important role to play in enhancing fire suppression capabilities onboard ships. One is ventilation control. It can be used to isolate a space where a fire is burning and reduce the spread of smoke and toxic gases to other areas of a ship. The ability to remove smoke and improve visibility assists fire fighters in finding and extinguishing a fire. Another technology is automatic or smart valves that can sense a loss of pressure due to pipe ruptures and redirect the fluid the pipe was carrying to bypass the rupture. If the pipe is carrying water for fighting the fire or chilled water for cooling a component of a combat system, this will have a profound effect on how rapidly the ship can extinguish a fire or restore its combat systems.

Materials that are inherently better from a fire and flammability perspective will also lessen the hazards associated with a fire onboard a naval vessel. Many of the materials used onboard ships are non-metallic and will burn. The combustion of these materials contributes to the hazards associated with a fire such as the generation of heat, smoke and toxic gases. Improvements in the fire performance of non-metallic materials reduce their threat in a fire situation.

Materials are also being developed to reduce the vulnerability of naval vessels to weapons and blast effects or to reduce the signature of the ship. Some of these are polymeric and if introduced onto a ship could increase the amount of flammable material considerably.

In this Memorandum new technologies and materials that may enhance damage and fire control on naval vessels will be discussed. The discussion will focus on technologies developed to improve fire detection and suppression and new materials with improved fire and flammability performance.

2 Technologies

2.1 Fire and damage sensors and sensing systems

The best damage and fire sensors on a ship are its crew. However, the crew cannot be everywhere at all times. Therefore a need exists for sensors and sensing systems on a ship that alert the crew to damage and fire. The more rapidly incidents can be detected, the more rapidly damage control actions can be initiated. Rapid response can be the difference between bringing the incident under control and the incident becoming a threat to the safety of the crew and ultimately the survival of the ship. As navies move to ships with reduced crewing levels, sensors and sensing systems will become even more important in damage and fire detection and the reduction of risk associated with undetected damage and fire incidents.

2.1.1 Point sensors and systems

There are two types of sensors. The first are referred to as point sensors. A point sensor monitors a parameter, for instance smoke, temperature or carbon dioxide concentration, at one location in a space. If there is a fire in a space remote from the sensor, it cannot detect the fire until the parameter it is measuring changes. In a large space this may take a considerable time. During this time the fire can grow and spread to adjacent spaces and make the extinguishment of the fire a more difficult task.

The obvious solution is to install more sensors in a space. Then if there is a fire the chance that a sensor is close to it is greater and the time before the sensor measures a change indicative of a fire will be reduced. The actions required to deal with the fire can then be started sooner which increases the probability that the damage will be minimal and reduces the chance that the fire will spread.

The limitation of any point sensor is that it cannot differentiate between, for example, an increase in temperature resulting from a fire and one resulting from welding or cutting being carried out near to it. Similarly, a smoke detector cannot differentiate between smoke resulting from a fire in a Galley and smoke from a piece of toast burning. This can result in false alarms. In the worst case scenario the sensor will be disabled or its response ignored.

To address false alarms, research into the use of suites of point sensors and data fusion has been carried out by the Naval Research Laboratory (NRL), Washington, DC [1-7]. The aim of this research was to develop an early warning fire detection (EWFD) system with increased detection sensitivity, decreased detection time, improved reliability and an improved capability to differentiate between real fires and nuisance sources such as toast burning in the galley, welding, torch cutting and grinding of steel, and the operation of a diesel powered vehicle on the ship. Input from several different point sensors is processed and compared to inputs from actual fires and nuisance events using a probabilistic neural network (PNN). Four point detectors were used in the studies conducted by the NRL.

This multi-criteria fire detection technology has been commercialized by System Sensors. The commercial system uses a photoelectric (light-scattering) particulate sensor, an electrochemical

carbon monoxide (CO) sensor, a daylight-filtered infrared sensor and solid state thermal sensor(s) rated at 135°F (57.2°C). The EWFD system developed by the NRL was hardened for shipboard use and military specification (MIL Spec) tested. It has not been installed on US Naval vessels to date [8].

2.1.2 Volume sensors and systems

Volume sensors differ from the more traditional point fire sensors in that they have the ability to monitor a space for indications of the presence of fire even when the fire is distant from the sensor. The ability to monitor a space is important because early detection allows the damage control personnel to address the situation in a timely manner and reduces the chance of damage (or fire) spreading from the initiation site.

As was indicated for point sensors and sensors suites, it is important that volume sensor systems be designed to minimize false alarms arising from nuisance events. The nature of nuisance events that can be detected will depend on the types of sensors used in the volume sensor suite. Many of the nuisance sources are the same as those discussed in the preceding section, such as toast burning in the galley, welding, torch cutting and grinding of steel and the operation of a diesel powered vehicle on the ship. However, a volume sensor can also handle nuisance sources such as a camera flash and the use of an aerosol in the vicinity of the detector suite. The minimization of false alarms is critical because they lead to the operator losing confidence in the sensing system. This can result in real fire and damage events being ignored on the ship or the system being turned off. In either case this severely compromises ship safety.

The NRL has developed a volume sensor system (VSS) [9-15]. The system consists of infrared, near infrared, ultraviolet, long wavelength infrared video, video, and acoustic detectors, software to acquire and process the data from the detectors, software to fuse the acquired data and decide whether or not the input is indicative of a fire and or flooding event or a nuisance type event. The data fusion and decision aid software is critical to the usefulness of this system as it has been developed to minimize the occurrence of false positive alarms arising from nuisance events.

DRDC Atlantic has purchased a prototype VSS. The front view of the Canadian prototype VSS showing the apertures for the various sensors is shown in Figure 1. Testing of this system on the ex-USS SHADWELL, the NRL fire test ship located in Mobile Bay, Alabama, was completed in September 2010. An opportunity to carry out an operational evaluation of the system on a Canadian Forces (CF) ship will be pursued.



Figure 1. Front view of the Canadian Demonstrator Prototype volume sensor suite (VSS) showing the apertures for the various sensors.

2.2 Smoke control

Smoke generated by a fire reduces visibility. This negatively impacts the ability of crew to get out of a space and away from the fire. It also hinders the efforts of fire fighters to find and extinguish a fire and assist crew in leaving a space. Toxic and acid gases are also produced by the combustion process. Toxic gases can affect the crew at locations remote from the area of the fire. Acid gases can also affect materials and components, such as circuit boards, remote from the fire. Therefore the control or management of the spread of smoke and toxic gases on a ship during a fire is critical to the successful fighting of that fire.

Klote [16] defines smoke management as “the application of all methods to modify smoke movement for the benefit of occupants and fire fighters, as well as, the reduction of property damage”. Smoke management or control on board a ship can be afforded by either zone pressurization or air flow. Zone pressurization works by creating higher air pressures in zones surrounding a fire zone. As the pressure is higher outside the fire zone, air will flow into the fire zone and prevent smoke from escaping. Air flow is applicable to fires in a space with an opening. It works by forcing air into the fire zone through the opening and preventing movement of smoke out of the opening.

Smoke control systems on board a ship can either be dedicated or non-dedicated systems. A dedicated system incorporates a separate air moving and distribution system and is used only in the event of a fire. A non-dedicated system uses components of the heating ventilation and air conditioning (HVAC) systems already in place. A dedicated system requires more space and is more costly than a non-dedicated system. However, the controls of a non-dedicated system are more complicated than those for a dedicated system.

Positive pressure ventilation and the use of the ship board HVAC trunking to control the spread of smoke and toxic gases are discussed in the following sections.

2.2.1 Positive pressure ventilation

The control of smoke improves visibility and reduces its spread to areas of a ship away from the fire. This is important for both crew attempting to escape from a space and firefighters attacking the fire in a space. The creation of positive pressure can be used to control smoke. The positive pressure can be created using either the ship's HVAC system or a fan. The positive pressure forces the smoke and toxic gases from the space and out of (off of) the ship. This requires that a route from the space where the fire is burning to the exterior of the ship can be established. The technique can also be used to create a positive pressure in a passageway, for instance, and prevent or slow significantly the ingress of smoke and combustion products into it.

The use of the Collective Protection System (CPS) in conjunction with the HVAC system and dampers has been investigated as part of an automated smoke ejection system on ships [17]. This is discussed in the next section.

2.2.2 Smoke ejection system

The ex-USS SHADWELL is a fire and damage control test ship operated by the US NRL, Washington, DC. It is located in Mobile Bay, Alabama. The ship has a smoke ejection system (SES) conformation that involves the use of the CPS for smoke ejection. The SES has numerous supply and exhaust fans for air movement and thirty one motorized dampers to control flow direction. There are two types of dampers, smoke control dampers (SCD) and smoke purge dampers (SPD). Under normal conditions the system is configured in the CPS mode where the seventeen SCDs are open and the fourteen SPDs are closed. When a fire is detected, the system is reconfigured to provide smoke control. This is accomplished by the flipping of an electrical switch that closes the SCDs and opens the SPDs.

The development of an automated system is described in reference 16. An integral part of this development was the writing of software that would take data from the sensors (temperature sensors and optical density meters (ODM)) and use it to control frequency drive speeds (exhaust fans), the turning on and off of fans, and the alignment of actuators. The experimental system consisted of eight sensors, ten actuators and two frequency drives. The goal of the tests was to explore the use of ventilation system reconfiguration to maximize a ship's ability to control smoke. The software to control the systems could be used in one of four modes; the CPS mode, the SES mode, the DC-ARM mode and the AUTO mode.

The CPS and SES modes mimic the modes of the manual smoke ejection system on the ex-USS SHADWELL. These modes are not sensory reactive. The DC-ARM mode is what amounts to an automated CPS and SES ventilation system. The ventilation system is changed from the CPS to the SES mode based on damage indication. Damage indication was determined from critical set points; thermocouple temperature 43.3°C (110°F) and ODM 25% obscuration (75% visibility). When these set points are exceeded the system is activated. The AUTO mode is also sensory reactive but uses different damper alignments and variable frequency drive speeds. The ventilation technique used in the AUTO mode is also different from the DC-ARM mode. For instance, the AUTO mode uses only exhaust ventilation to remove smoke and heat from a space. The damper alignment and frequency drive operations are compartment independent. If fire is indicated in a space then only the ventilation in that space is turned on. The other components of the system do not activate until there are fire indications in the space where they are located.

2.3 Smart valves

The fire main and chilled water systems are critical to the safe operation of a ship. The fire main system provides water for fire fighting. It is designed in such a way that small sections of the system can be isolated using valves. This is to ensure that a rupture or ruptures do not disable the whole system. The fire main system or a separate seawater system may also be used to supply water for cooling combat systems and auxiliary equipment. The chilled water system is a critical system as it supplies cooling water to combat, surveillance and communications systems. If heat is not removed from the electronic components of these systems they will shut down within a few minutes and may even fail. In a combat situation it is essential that ruptured piping be isolated and the flow of chilled water to these systems be restored. Smart valves provide a means of restoring flow in fire mains and chilled water systems without damage control crew being directly involved.

As part of the DC-ARM Program, the US Navy developed a reflexive smart valve system [18-20]. This is an assembly of valve and control components for fire main, chilled water, and fuel systems. It was designed to reduce the time to detect and isolate ruptures and leaks thus reducing workload for the ship's crew. An experimental smart valve was tested on the ex-USS SHADWELL and successfully isolated pipe ruptures in between 15 and 90 seconds. The results of the testing indicated that the smart valve concept is applicable to a variety of valve designs. Differential pressure sensing was deemed to be sufficiently accurate for both leak and rupture detection in valve designs with a reduced size seat. However, for valves with high flow coefficients (such as gate and full port ball valves) the range of flow detection may be limited.

2.4 Fire suppression agents and systems

2.4.1 Water mist

Water mist (fog) is regarded as an effective fire suppression agent. It extinguishes fires by fuel surface cooling, flame cooling, and oxygen depletion and displacement [21]. Water mist refers to fine water sprays in which 99% of the droplets are less than 1000 microns in diameter [22]. The water mist droplet size distributions are defined in the National Fire Protection Association (NFPA) Standard 750 as Class 1 (90% of the volume of spray with diameters of 200 microns or less), Class 2 (90% of the volume of spray with diameters of 400 microns or less), and Class 3 (90% of the volume of spray with diameters greater than 400 microns).

Enclosure effects are extremely important for naval applications of water mist systems. In confined spaces with poor ventilation, a water mist system can be effective for obstructed fires. However, as the level of ventilation increases or the fire size with respect to the size of the space decreases then the system becomes less effective. Fire size, large or small, is defined in terms of how the fire effects the temperature and oxygen concentration in the space. In a large fire the temperature of the space increases and the oxygen concentration decreases. Both increase the effectiveness of water mist and therefore decrease extinguishment times relative to small fires. The mode of extinguishment for water mist is different for large and small scale fires. In a large fire the primary mechanism is oxygen depletion while for a small fire the primary mechanism is cooling.

Water mist can be generated using a number of nozzle types [23]. Impingement nozzles work with a single fluid and consist of a large diameter orifice and a deflector at low (12.0 bar or less) and intermediate (12.0 to 43.0 bar) pressures. Pressure jet nozzles also work with a single fluid and consist of small diameter orifices (0.2 mm to 0.3 mm) or swirl chambers. Operating pressures can range between 5.1 bar and 272 bar. Twin fluid nozzles operate with a compressed gas (usually air) and water and consist of a water inlet, a compressed gas inlet and an internal mixing chamber. The pressures of the gas and water are controlled separately and are in the low pressure region (between 3 bar and 12 bar).

Water mist fire suppression systems have been used for the protection of machinery spaces, turbine enclosures, and other spaces where there are flammable liquid hazards [24]. Water mist fire suppression systems are effective in extinguishing a number of exposed and shielded hydrocarbon pool, spray and cascading fires. They are also effective for combined Class A (ordinary combustible materials including wood, paper, cloth, rubber and many plastics) and Class B (flammable or combustible liquids and gases, greases and similar materials) fires. The time to extinguishment of fires with water mist systems is longer than that for gaseous agents. However, water mist cools the space and controls levels of carbon dioxide and carbon monoxide.

Testing of water mist systems indicates that the effectiveness of these systems is very dependent on fire size, degree of obstruction of the fire, ventilation, and compartment geometry. Larger fires were extinguished more rapidly than small fires, fires under obstructions were very difficult to put out [25-26], and fires in large spaces and/or spaces with high ceilings were very difficult to extinguish [27]. This was attributed to the inability of the system to deliver sufficient water mist to the fire location. The systems were also affected by openings in the test space although an increase in the number of doorway nozzles (from 2 to 4) was found to mitigate the effect of the opening. US Navy full scale testing [28] indicated that the effect of openings on performance of water mist systems is dependent on the size of the fire. For small fires, openings increased extinguishment times while for larger fires there was no effect on extinguishment times.

The placement and number of water mist nozzles in a compartment has been investigated [29-30]. Full scale testing indicated that the ability of the system to extinguish fires was enhanced by placing nozzles at two heights in the compartment. High pressure single fluid nozzles were found to perform better than low pressure single fluid and twin fluid systems [30-31]. The improved performance was attributed to characteristics of the water droplets, specifically their small size and high momentum, produced by the high pressure nozzle. Low pressure nozzles used at higher flow rates and that produced larger water droplet sizes were found to be effective against large pool fires and unshielded class A fires. The US Navy has identified a modified high pressure nozzle (70 bar) as the most effective for water mist systems while the Royal Navy has focused testing on low pressure nozzles (up to 7 bar) [32] with and without 1% aqueous film forming foam (AFFF). The test results indicated that fine water mist produced with low pressure nozzles extinguished large obstructed spray and pool fires by oxygen depletion and extinguished some unobstructed spray fires at high oxygen content by cooling. The low pressure nozzles using 1% AFFF extinguished unobstructed pool fires at high oxygen content, prevented fuel in bilges from igniting and contained small obstructed pool and spray fires. The low pressure water mist system was found to improve the maintainability and survivability of the space whether or not the fire was extinguished and also provided boundary cooling.

Manufacturers of water mist systems, pumps and nozzles are shown in Table 1.

Table 1. Manufacturers of water mist systems and associated technologies.

TECHNOLOGY	MANUFACTURERS
Water Mist Suppression Systems	Chemetron Fire Systems, Matteson, Illinois, USA Ansul (Tyco Fire and Security), Pennsylvania, USA Securiplex LLC, Mobile, Alabama, USA CAFS Unit Inc., Ottawa, Ontario Nanomist Systems LLC, Warner Robins, Georgia, USA Marioff North America, Ashland, Massachusetts Fike, Blue Springs, Missouri, USA Ultra Fog AB, Sweden Fogtec, Brandschutz GmbH, Cologne, Germany
Water Mist Pumps	Edwards, Pentair Pump Group, Illinois, USA
Water Mist Nozzles	Chemetron Fire Systems, Matteson, Illinois, USA Grinnell Corporation, Cranston, Rhode Island, USA Tyco Engineered Products and Services, USA Spraying Systems Co., Illinois, USA BETE Fog Nozzle, Greenfield, Massachusetts, USA Lechler Nozzles North America, St. Charles, Illinois, USA Hago Manufacturing Co., Mountainside, New Jersey, USA

2.4.2 Gaseous fire suppression agents

The US Environmental Protection Agency (EPA) maintains a directory of suitable gaseous fire suppression agents for replacement of Halon 1301 in total flooding fire suppression applications [33]. This initiative is referred to as the Significant New Alternatives Program (SNAP). The alternative agents are reviewed on the basis of their ozone depletion potential (ODP), global warming potential (GWP), toxicity, flammability and exposure potential. Gaseous agents on the list deemed feasible for use in normally occupied spaces include HFC-227ea (heptafluoropropane), HFC-227ea with 0.1% d-limonene, HFC-23 (trifluoromethane), and HCFC Blend A (a mixture of HCFC 22 (chlorodifluoromethane), HCFC 123 (dichlorotrifluoroethane), and 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)- 3-pentanone (Novec[®] 1230)). One of these agents, HFC-23, has a GWP of 11,000 which is greater than the upper level of 3450 accepted by the Canadian Department of National Defence (DND).

Although these agents may be effective fire suppressants, two things must be considered when they are used. The first is that the effective concentration of the gas does not exceed the concentration at which it becomes hazardous to humans if the system is used with humans in the space. The second is that both hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) will decompose in a fire and produce acid and toxic gases. If ventilation cannot be controlled these will affect both crew and equipment remote from the fire. These gases also impact the time fire fighters must wait before it is safe to re-enter a space.

The US Navy Technology Center for Safety and Survivability investigated the optimum fire suppression hold time prior to venting of a compartment and the effectiveness of a water spray cooling system in reducing compartment temperature and concentration of acid decomposition products in real scale tests of gaseous agents [34]. A low pressure water spray cooling system was found to be very effective in reducing compartment temperature. Heptafluoropropane was tested in a real scale test and the results compared to data for Halon 1301 [35]. A number of parameters, including fire extinguishment times, oxygen depletion, and hydrogen fluoride (HF) production, were monitored. Compartment re-entry following the fire was noted as the most critical and potentially the most dangerous part of a fire fighting event when gaseous agents are used.

Director Maritime Ship Systems (DMSS)-4, in conjunction with the National Research Council of Canada National Fire Laboratory, has evaluated a combination of a gaseous agent (Novec 1230[®]) and a water mist system for fire suppression in large machinery spaces on HMC Submarines. Dual systems have the potential to extinguish fires that water mist alone cannot and the water mist should mitigate the effects of thermal decomposition by-products produced by Novec 1230[®]. Using Novec 1230[®] alone to suppress a fire resulted in an average HF concentration of ~750 ppm. The scenarios tested all had the water mist system on one minute prior to, during and four minutes after the Novec 1230 system was activated. This resulted in HF concentrations of ~75 ppm. The water mist was left on four minutes after the Novec 1230[®] to increase the pH (reduce the acidity) of the water used in the suppression through dilution. For instance, the pH increased from less than 1 to between 5 and 7 when the water mist was left on four minutes. The testing indicated that the use of water mist in conjunction with Novec 1230[®] not only reduces the concentration of HF in the compartment after a test but also reduces temperature and allows fire fighters to re-enter the space more rapidly.

The report notes that it is important to keep the Novec 1230[®] concentration below 10%/volume which is the no observed adverse effect level (NOAEL) for this fire suppression agent. The NOAEL is the concentration below which a gaseous agent has no adverse effects on humans. To meet this requirement, the system was specified to produce a concentration of 6.5%/volume plus 10% when discharged.

2.4.3 Powdered aerosol extinguishing systems

Powdered aerosol extinguishing systems produce solid particle aerosol fire suppressants. There are two types of powdered aerosol systems, dispersed and condensed. In a dispersed system the powder forming the aerosol is stored in a pressurized cylinder containing a carrier gas such as a halocarbon or an inert gas. When the system is activated the aerosol is introduced into a space through a delivery system similar to that used for gaseous agents. In a condensed system the aerosols are produced pyrotechnically using a solid compound in the generator. The aerosol particles are released in the exhaust of the burning compound along with the degradation products of the pyrotechnic compound such as nitrogen (N₂), oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂) and water (H₂O). Potassium salts are generally used to produce the aerosol particles.

There are several types of powdered agents used to produce the aerosols. These include Powdered Aerosol A, Gelled Hydrocarbon/Dry Chemical Suspension with additives (formerly Powdered Aerosol B), Powdered Aerosol C, Powdered Aerosol D and Powdered Aerosol E [36].

Powdered Aerosol A produces approximately 60% gaseous products (CO_2 , N_2 , O_2 and H_2O) and 40% solids (potassium chloride (KCl), potassium oxide (K_2O) and potassium carbonate (K_2CO_3)). It extinguishes a fire by inhibiting the radical chain reaction in the flame zone. This is accomplished through the removal of hydrogen (H), oxygen (O) and hydroxyl (OH) free radicals that propagate the reactions that result in combustion. Powdered Aerosol A is effective against Class A, Class B and Class C fires and is used in engine enclosures, computer rooms, aircraft nacelles, electronics cabinets, telecommunications enclosures, flammable liquid and gas storage areas, and sub floor wiring enclosures. It has a shelf life of greater than 10 years.

Gelled hydrocarbon/dry chemical suspension, which was formerly known as Powdered Aerosol B, can be used on Class A, Class B, and Class C fires. These agents are a blend of several halocarbons (hydrofluorocarbons (HFCs)) and additives such as sodium bicarbonate (NaCO_3) or ammonium polyphosphate ($(\text{NH}_4)_3\text{PO}_4$) that reduce the amount of hydrogen fluoride (HF) released when the HFCs decompose in the fire. The release of the agent is activated by heat. This agent is used to provide fire suppression in air cargo areas, ship compartments, engines and enclosed spaces.

Powdered Aerosol C is a polymer formulation containing potassium nitrate (KNO_3) and plasticized nitrocellulose. The aerosol produced by this agent is primarily micron sized K_2CO_3 and potassium bicarbonate (KHCO_3) particles and N_2 , CO_2 , and H_2O . The agent interferes with the combustion process by inhibiting the radical chain reaction in the flame zone, cuts the flame off from the combusting material, and absorbs heat. It is effective against Class A, Class B, Class C, and Class K (cooking) fires. It is used to protect pumping stations, mining equipment, power substations, electrical distribution systems, aviation and marine cargo holds, and helicopters.

Powdered Aerosol D consists of alkaline metal nitrates that are released following a pyrotechnic reaction. It is used in total flooding fire suppression and for explosion suppression applications. It is effective against Class A, Class B, and Class C fires. It is used in warehouses, industrial facilities, flammable liquid storage areas, turbine enclosures, marine engine rooms, and aircraft engines.

Powdered Aerosol E consists of K_2CO_3 , N_2 , CO_2 , and H_2O . The K_2CO_3 forms potassium radicals in the presence of heat. These act as radical scavengers and interfere with the reactions that are responsible for the combustion process.

A list of powdered aerosol agents used for total flooding fire suppression applications, comments, conditions or restrictions placed on their use by the Environmental Protection Agency (EPA) and manufacturer trade names are shown in Table 2.

Table 2. A list of powdered aerosol agents used in total flooding fire suppression applications. Environmental Protection Agency (EPA) conditions or restriction for their use and manufacturer trade name are also listed.

Powdered Aerosol Type	Comments	Conditions or Restrictions	Trade Name
Gelled Hydrocarbon/dry chemical suspension with sodium bicarbonate	Use of this agent should be in accordance with the safety guidelines in the latest edition of NFPA 2001 Standard for Clean Agent Fire Extinguishing Systems, and the latest edition of the NFPA 2010 standard for Aerosol Extinguishing Agents	Use of whichever hydrofluorocarbon gas (HFC-125, HFC 227ea, or HFC-236fa) is employed in the formulation must be in accordance with all requirements of acceptability (narrowed use limits) of that HFC under EPA's SNAP program	Envirogel B25 + 36
Gelled Hydrocarbon/dry chemical suspension with ammonium polyphosphate additive	Use of this agent should be in accordance with the safety guidelines in the latest edition of NFPA 2001 Standard for Clean Agent Fire Extinguishing Systems, for whichever hydrofluorocarbon gas is employed		Envirogel
Gelled Hydrocarbon/dry chemical suspension with any additive other than ammonium polyphosphate or sodium bicarbonate	Use only in normally unoccupied areas.	Use of this agent should be in accordance with the safety guidelines in the latest edition of NFPA 2001 Standard for Clean Agent Fire Extinguishing Systems, for whichever hydrofluorocarbon gas is employed	Envirogel
A	For use in unoccupied areas only		SFE
C	For use in unoccupied areas only		PyroGen, Soyuz
D	For use in normally unoccupied areas only	Use of this agent should be in accordance with the safety guidelines in the latest edition of the NFPA 2010 standard for Aerosol Extinguishing Agents	Aero K, Stat X
E	For use in normally unoccupied areas only	Use of this agent should be in accordance with the safety guidelines in the latest edition of the NFPA 2010 standard for Aerosol Extinguishing Agents	Fire Pro

NFPA – National Fire Protection Association

SNAP – Significant New Alternatives Policy

The US Coast Guard has evaluated three commercially available aerosol extinguishing systems (AES) against the International Maritime Organization (IMO) test protocol (MSC/Circ. 1007) for approving AES for machinery space applications [37]. The systems tested were effective against Class B fires but had difficulty extinguishing Class A fires and therefore did not pass the IMO test protocol.

Parameters such as visibility, temperature, and gas concentrations following the discharge of the systems were also monitored. The results indicated that visibility in the test space was reduced to ~0.3 m immediately after discharge. The reduction in visibility would make exiting the space difficult. The discharge of the systems also caused an increase in the temperature in the space, from 17°C to 25°C above ambient, depending on the system. It was noted that discharge resulted in much higher temperatures in the immediate vicinity of the aerosol generators. The temperatures were high enough that persons should not be within 0.9 to 1.5 m of the generator, depending on the system, when the system was activated.

The Canadian Coast Guard has installed a commercial powdered aerosol product, STAT-X, in unmanned machinery spaces on its air cushioned vehicle (ACV) Mamilossa. Although STAT-X, a Type D powdered aerosol, is not a Transport Canada approved product for marine applications, the Coast Guard obtained a Board exemption for the installation. The exemption was based on the small volume of the four unmanned machinery spaces[38]. It should be noted that powdered aerosol agents A and C are for use in unoccupied spaces only and that powdered aerosols agents C and D are for use in spaces that are normally unoccupied.

3 Technology readiness levels (TRL)

A number of technologies were discussed in Section 2. Some of these are in use on naval vessels, others are in use on commercial ships, while others still are in the developmental process. The technology readiness level (TRL) of these technologies will be discussed in this section. The current Technical Readiness Level Assessment used by the US Department of Defence (DoD) consists of nine TRLs, varying from the observation of basic principles to the in-service validation of a system which utilizes the technology [39]. The TRLs are defined in Table 3.

Table 3. Definitions of Technology Readiness Levels (TRL)[39].

Technology Readiness Level	Description
1	Basic principles observed and reported. Lowest level of technology readiness. Scientific research begins to be translated into applied research and development. Examples might include paper studies of a technology's basic properties.
2	Technology concept and/or application formulated. Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative and there may be no proof or detailed analysis to support the assumptions. Examples are limited to analytic studies.
3	Analytical and experimental critical function and/or characteristic proof of concept. Active research and development is initiated. This includes analytical studies and laboratory studies to physically validate analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative.
4	Component and/or breadboard validation in laboratory environment. Basic technological components are integrated to establish that they will work together. This is relatively "low fidelity" compared to the eventual system. Examples include integration of "ad hoc" hardware in the laboratory.
5	Component and/or breadboard validation in relevant environment. Fidelity of breadboard technology increases significantly. The basic technological components are integrated with reasonably realistic supporting elements so it can be tested in a simulated environment. Examples include "high fidelity" laboratory integration of components.
6	System/subsystem model or prototype demonstration in a relevant environment. Representative model or prototype system, which is well beyond that of TRL 5, is tested in a relevant environment. Represents a major step up in a technology's demonstrated readiness. Examples include testing a prototype in a high-fidelity laboratory environment or in simulated operational environment.
7	System prototype demonstration in an operational environment. Prototype near, or at, planned operational system. Represents a major step up from TRL 6, requiring demonstration of an actual system prototype in an operational environment such as an aircraft, vehicle, or space. Examples include testing the prototype in a test bed aircraft.
8	Actual system completed and qualified through test and demonstration. Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental test and evaluation of the system in its intended weapon system to determine if it meets design specifications.
9	Actual system proven through successful mission operations. Actual application of the technology in its final form and under mission conditions, such as those encountered in operational test and evaluation. Examples include using the system under operational mission conditions.

The TRL of components and the systems that they may be used in may also vary considerably. This will be discussed where it is pertinent.

3.1 Sensors and sensor systems

3.1.1 Point sensors and systems

Point sensors such as the ionization smoke detector, the photoelectric smoke detector, carbon monoxide (CO) and carbon dioxide (CO₂) detectors and temperature sensors have a TRL of 9. They are widely used on naval vessels. Sensing systems involving suites of point sensors, data fusion and probabilistic neural networks, such as the NRL early warning fire detection (EWFD) system, have not been used on naval vessels. However, the system has been tested on the ex-USS SHADWELL and has been hardened and passed Military Specification (MIL-Spec) testing. This system has a TRL of 8.

3.1.2 Volume sensors and systems

Many of the components of a volume sensor system, such as infrared, near infrared, ultraviolet, long wavelength video, video, and acoustic detectors have been used on naval vessels and have TRLs of 9. The use of these detectors might require that they are hardened to ensure they will stand up to the more rigorous requirements of naval applications.

The volume sensor system has a TRL of 6. It has been tested under fire and damage conditions on the ex-USS Shadwell. DRDC Atlantic has obtained the latest version of the system with the detectors housed in a single sensor unit. Data fusion and decision aid software can distinguish between real fire and damage events and those arising from shipboard activities that could lead to false alarms when conventional point sensors are used. No effort has been made to harden the system for use on naval vessels. Opportunities to trial/test the system on an operational naval vessel will be pursued.

3.2 Smoke control

The use of fans and the HVAC system to desmoke spaces on ships is well established. These are examples of non-dedicated desmoking systems and have a TRL of 9.

The US NRL has also studied the development of a smoke ejection system (SES) that uses the collective protection system (CPS) of the ship for smoke ejection. The system requires that supply and exhaust fans and dampers be built into the system to move smoke in the event of a fire. There are both smoke control and smoke purge dampers that are controlled remotely. During normal operations the smoke control dampers are open and the smoke purge dampers are closed. When a fire is detected the system is reconfigured to enable smoke control. This technology has a TRL of 6. Although an SES could be retrofitted to a ship, the design of a new ship that includes a SES would ensure optimized performance of the system.

3.3 Smart valves

The components of a smart valve, that is, the valve, sensor and automated actuator are available commercially and have a TRL of 9.

Smart valves have been evaluated by the US NRL onboard ex-USS SHADWELL and were found to respond to pipe ruptures in 15 to 90 seconds. The US Navy is developing a chilled water automation system (CWAS). It will use programmable automated valves (smart valves) and flow sensors to detect and isolate pipe ruptures within the closed loop system. A facility to support testing of the system has been constructed at the Naval Surface Warfare Center (NSWC) land-based engineering site in Philadelphia, Pennsylvania. Fairmount Automation was contracted to design, develop and integrate a control and monitoring system for the CWAS [40]. This technology has a TRL of 6.

The Netherlands has modeled the use of smart valves as part of a two zone chilled water system. Each computing node (controller) is placed as close as possible to the component in the system such as a pump or a valve that it controls. Therefore if the component is damaged the likelihood that the computing node is also damaged is high. Further research and development is planned to determine if the robust automation concept is scalable to larger systems composed of many components, to develop the small computing nodes so that they can be used on naval ships, and to build a full scale demonstrator. This technology has a TRL of 4-5.

3.4 Fire suppression systems

3.4.1 Water mist systems

Water mist fire suppression systems are in service on naval and commercial ships in total flooding and non-total flooding applications. This technology has a TRL of 9. The Canadian Navy uses a water mist system in diesel engine enclosures on its patrol frigates. Water mist systems can be purchased as low, medium or high pressure systems. The US NRL determined that a system with a modified high pressure (70 bar) nozzle is the most effective for fire suppression while the UK research has focused on low pressure (<7 bar) systems. The US Navy requires that any systems used on their ships be commercially available. High pressure systems pose a problem as the high pressure piping required by the US Navy is not available as part of a commercial package from water mist system suppliers.

Rules societies, such as the International Maritime Organization (IMO), have prescribed test requirements for the approval of total flooding water mist systems in shipboard spaces such as machinery spaces and cargo pump rooms (MSC/Circ.1165) prior to installation. Therefore depending on how a system is specified, full scale testing of the system may have to be conducted in a space that is similar in size to that where it will be used.

3.4.2 Dual agent systems

Dual agent total flooding systems, such as the system described in Section 2.4.2 that use both water mist and a gaseous agent such as Novec 1230[®], have a TRL of 8-9. The low pressure water mist and Novec 1230[®] systems used in the dual agent system each have individual TRLs of 9. However, evaluation of the most effective way to use the dual system is ongoing. Novec 1230[®] produces acid gas when it thermally degrades. Activating the water mist systems for 30 seconds to a minute prior to the release of the Novec 1230[®] has been found to substantially reduce the

levels of acid gases in the space. Running the water mist system for several minutes after the gaseous agent has been released also reduces the pH (acidity) of the residual water in the space.

3.4.3 Powdered extinguishing agent technologies

The powdered aerosol agents discussed in Section 2.4.3 have a TRL of 9. They are all commercially available. Their use must take into consideration the conditions and restrictions listed in Table 2.

4 Materials

A range of organic (carbon-based) materials, most of them polymers, are used on CF vessels. These materials include coatings (paints), electrical and communication cable sheathing, thermal and acoustic insulation, furnishing, bedding, mattresses, flooring, and wood fibre (paper and cardboard) and plastic packaging materials. Coatings provide corrosion protection; polymeric electric and communication cable sheathings are non-conductive and provide insulation against electric shock and shorts; foamed polymers are used for thermal and sound insulation, and furnishings and bedding are used for their comfort and warmth. Although the use of composites has not been prominent on CF ships, requirements for the reduction of weight or radar signature may result in an increase in their use on new vessels.

All organic materials will burn. From a fire and flammability perspective the best approach is to limit the use of flammable materials on ships. However, many of these materials are used because they have unique properties that cannot be provided by other materials or alternative materials with improved fire and flammability properties are so expensive that they are cost prohibitive to use.

There are several approaches to minimizing the fire hazards involved with the use of organic materials on ships. These include the selection of materials that are inherently safer, that is, less susceptible to fire, the chemical modification of the material to improve its fire performance, the use of additives such as flame retardants that improve the performance of a material in a fire, and the protection of the flammable substrate with a non-combustible material that physically separates it from sources of heat and flame. These approaches will be reviewed below.

4.1 Enhancing fire performance

4.1.1 Inherently flame retardant materials

Inherently flame retardant (FR) polymers are defined as polymers with a continuous operating temperature from 180°C to 300°C (or higher) that will not thermally degrade below 350°C [41]. Polyimides, used as foamed thermal insulation on CF ships, are an example of inherently FR polymers. They cannot be ignited and incandesce in the presence of a flame. Poly(*p*-phenylene terephthalamide), commonly known as Kevlar® or Twaron®, and poly(*m*-phenylenediamine isophthalamide), commonly known as Nomex®, are other examples of FR polymers that are used by the Canadian Forces. Nomex®, for instance is used for firefighting gear and in navy work dress because of its excellent resistance to fire.

Rigid-rod polymers such as polyoxazoles and polythiadiazoles are other examples of inherently FR polymers. Although these polymers are difficult to synthesize and process and the resulting high cost has limited their use, they do have low flammability. The *p*-phenylene-based rigid rod and extended chain polymers have been developed with excellent mechanical properties at high temperature, low flammability and excellent heat resistance. These include poly(*p*-phenylene-2,6-benzobisthiazole) (PBZT) and poly(*p*-phenylene-2,6-benzobisoxazole) (PBO). M5, a high-modulus and high-strength fibre made of poly(2,6-diimidazo[4,5,4',5'-e]-pyridinylene-1,4(2,5-

dihydroxy)phenylene) or PIPD [42], has exceptional fire protection properties when compared with PBO, Twaron®, Kevlar® and Nomex® fibres. A PIPD fibre, designated PIPD-HT, has a modulus greater than 300 GPa and a strength greater than 5 GPa. Its fire performance index (FPI) value is similar to PBO and it produces less smoke. The FPI is defined as the ratio of the time to ignition of a sample (seconds (s)) to its peak rate of heat release (kilowatt per meter squared (kWm^{-2})) and has the units $\text{sm}^2\text{kW}^{-1}$. A larger FPI is related to improved fire performance.

4.1.2 Chemically modified polymers

A second approach to preparing polymers with improved fire and flammability properties is to incorporate compounds into the polymer backbone or graft compounds onto the polymer chain that improve fire performance. The driving force for this approach is the reduction in the weight of fire retardant additives that must be mixed with a polymer to affect improved flammability properties. High levels of additives often negatively affect the desirable properties of the polymers to which they are added. Chemically modified polymers may also be used to replace halogen containing additives that release acid gas when exposed to heat and flame.

There are a number of examples of the incorporation of phosphorus containing compounds into polymers to improve fire and flame resistance. Epoxy resin precursors and curing agents have been synthesized that contain phosphorus [43]. Flame resistance of the epoxy resin was observed at a phosphorus concentration of 1.5% and fire resistance at a phosphorus concentration of 3%. The reduction in flammability of these polymers was attributed to charring caused by the phosphorus in the polymer. As the phosphorus compound was not consumed in the char forming reaction, it acted to catalyze the formation of char.

Phosphorus containing compounds have also been incorporated into thermoplastics [44]. This has resulted in the synthesis of a halogen free, flame retardant poly(sulfone) and a poly(ether-ether ketone) with improved thermal stability. Phosphorus modified poly(sulfone)s have been evaluated as flame retardants in epoxy resins [45]. The improved flammability properties were attributed to char formation in the condensed phase of the resin promoted by the phosphorus in the modified poly(sulfone).

Polymers with silicon and boron compounds incorporated into their backbone have also been synthesized [46], [47]. The polymers containing silicon showed a marginal increase while the boron containing polymers showed a significant increase in flame retardancy.

More recently, polyureas with portions of the organic backbone replaced by phosphorus and silicone-based compounds have been synthesized and their flammability properties determined [48]. Polyureas are of interest because of their potential use as explosion resistant coatings. However, the fire and flammability properties of polyureas without additives are poor. Three polyureas with flame retardant compounds incorporated into the polymer backbone were studied. The first used a diisocyanate prepolymer with a portion of its backbone made up of a phosphorous polyol (S1), the second sample used an amine terminated polydimethylsiloxane (S2) and the third sample combined the phosphorous polyol with the amine terminated polydimethylsiloxane (S3). Cone calorimetry indicated that three samples exhibited a marked decrease in the peak heat release rate (PHRR) relative to base polyurea, i.e., the polyurea without the phosphorus and silicon-based components. The base polyurea had a PHRR of 1252kW/m^2 ,

while samples S1, S2, and S3 had PHRR of 286.3, 542.4, and 351.9 kW/m² respectively. Sample S3 yielded the best results for lowering smoke production and increasing time to ignition compared to the base polyurea. It is believed that the phosphorous polyol and polydimethylsiloxane have a synergistic effect in improving the flammability properties of the polyurea.

In another part of this study, sample S3 (phosphorous polyol/ polydimethylsiloxane based polyurea) was used as the base formulation and various combinations of flame retardant additives were incorporated in an attempt to further improve the flame properties. Cone calorimetry indicated that the best combinations of additives was sodium phosphate, ammonium polyphosphate (APP)/triisocyanurate 3:1, treated graphite, urea, zeolite and melamine. The PHRR for this compound was 164.1 kW/m².

4.1.3 Polymers containing flame retardants

Flame retardants are effective in altering the fire performance of polymeric (organic) materials because they interfere with the combustion process. Some fire retardants act via a physical mechanism, that is, they cause physical changes to the combusting material, while others act via chemical mechanisms.

There are a number of ways in which a flame retardant can act physically. These include the formation of an insulating (barrier) layer on the surface of the combusting polymer. This reduces heat transfer from the flame back to the material's surface. This in turn slows the degradation of the material and reduces the release of degradation products that fuel the fire. The fire will eventually go out if there is insufficient fuel to maintain the combustion process. Some retardants cool the combusting material via endothermic reactions, that is, reactions that take heat out of the fire. Once the substrate is cooled below the temperature required to sustain the combustion process it will extinguish. Inert substances, such as talc (hydrated magnesium silicate) and chalk (calcium carbonate), dilute the concentration of fuel available in the solid phase. Other additives when heated release inert molecules that dilute the concentration of flammable gases in the flame zone. A reduction in the availability of flammable degradation products reduces the intensity of the fire and leads to its extinguishment.

Chemical reactions that interfere with the combustion process can take place in the condensed phase of the burning material or in the gas phase in the vicinity of the burning material. In the condensed phase, the retardant can accelerate the degradation of the polymer. This causes the polymer to flow. If the polymer moves (flows) away from the flame, this can result in the fire going out. Retardants can also promote the formation of a layer of carbon or an inorganic material on the surface of the polymer. This isolates the polymer from the flame and slows thermal degradation processes that provide fuel to the fire.

In the gaseous phase, the fire retardant or its degradation product(s) interferes with the chemical reactions taking place in the flame that produce the heat required for the continued burning of a material. The reactions in the flame involve radical chain mechanisms and the retardant or its degradation products interfere with these. This reduces the heat generated by the flame which in turn reduces the generation of flammable degradation products and the fire eventually goes out.

4.1.4 Intumescent materials

Intumescent materials are materials that expand (swell) when heated and form a porous (foamed) material that acts to insulate the substrate below them. The composition of the char forming component of these materials can be either organic or inorganic based.

Organic intumescent materials consist of an inorganic acid or a component that releases acidic species, an organic char forming material, and a compound that releases a gas or gases (blowing agent) at a temperature and a time that cause the char to expand. Typical inorganic acid sources include phosphoric, sulfuric and boric acids, ammonium salts of phosphoric, polyphosphoric, boric, polyboric, sulfuric or halogen acids, phosphates of amines or amides, and organophosphorus compounds such as tricresyl phosphate and alkyl phosphates. The char forming constituent is a polyhydric compound such as starch, dextrin, sorbitol, mannitol, the monomer, dimer or trimer of pentaerythritol, phenol formaldehyde resins or char forming polymers such polyamide 6. The blowing agent can be urea, urea - formaldehyde resins, dicyanamide, melamine or a polyamide.

The constituents of an intumescent are chosen so that the formation of the intumescent foam takes place at a temperature where minimal damage is done to the underlying substrate. Typically the release of acid is activated at temperatures between 100°C and 250°C. The acid esterifies the char forming material at or slightly above the acid release temperature and the mixture melts. The esterified char forming material decomposes to form a residue (char). The blowing agent then decomposes and the gaseous degradation product(s) cause the char residue to foam and expand. The foamed residue then gels and solidifies. The resulting porous material insulates the underlying substrate from degradation, either physical or chemical, resulting from the heat generated by the fire. As the char forming constituents in an organic intumescent is organic, it can contribute to smoke and toxic gases when activated.

Inorganic intumescent materials have also been developed [49]. These materials are based on alkali silicates. These materials intumesce through the release of water from the alkali silicates when they are heated. The resulting foam is hydrated silica. As water vapour is the only gas released, these intumescent compounds do not release toxic gases and smoke that are associated with intumescent compounds containing organic char forming compounds. However, alkali silicates have some limitations. They are sensitive to atmospheric carbon dioxide and may eventually lose their ability to intumesce. Problems with the adhesion of these coatings to underlying substrates have also been observed [41]

Intumescent compounds are generally applied as part of a coating formulation or incorporated into polymeric materials to improve their resistance to fire. If an inorganic intumescent material is used in an organic coating or polymeric material, then the advantage gained from the use of inorganic foam forming agent is lost. The coating or polymeric material will release gaseous degradation products and smoke. However, the incorporation of an inorganic intumescent material into a coating or polymeric matrix will lessen the rate at which carbon dioxide will affect the ability of the material to intumesce.

4.1.5 Nanoparticles

In the discussion of the use of additives to improve fire performance it was indicated that a drawback to their use was the weight percent filler that was required to enhance the fire property of interest. The high levels of fillers (30 to 40 weight percent) that are often required can have a negative effect on other properties of the polymer. Nanoparticles are defined as particles with diameters between 1 and 100 nanometers (nm). It has been observed that nanoparticles can be added at much lower levels to polymers than conventional flame and fire retardants and have an effect on the flammability properties of the resulting nanocomposites. Their effectiveness is directly linked to their dispersion in the polymer.

Typical nanoparticles that have been studied are organoclays, polyhedral silsesquioxanes (POSS) and carbon nanotubes. Two mechanisms have been proposed to describe the improved flammability performance of polymers containing nanoparticles. The first mechanism proposes that the nanoparticles form a carbonaceous silicate multilayer structure when the polymer is heated [50]. The resulting structure acts as a barrier layer to protect the underlying substrate from further degradation. The second mechanism proposes that radicals formed during thermal degradation are confined within the nanoparticles and this leads to a number of bimolecular reactions that suppress the combustion process [51].

Although nanoparticles have been observed to reduce the peak heat release rate of nanocomposites, other properties such as limiting oxygen index and time to ignition can be adversely affected. The incorporation of nanoclays (Cloisite 30B – a natural montmorillonite modified with methyl, tallow, bis-2-hydroxyethyl ammonium chloride), multiwall carbon nanotubes (at 0.5 weight %), and POSS (at 5 weight %) were found to reduce the PHRR of a polyurea by 33%, 45% and 73% respectively. The reduction in PHRR observed for the conventional flame retardants expandable graphite (10 weight %), ammonium polyphosphate (15 weight %) and zinc borate (5 weight %) were 88%, 79% and 41% respectively. The addition of nanoparticles into polyureas containing conventional flame retardants improved the flammability properties of polyureas slightly over that achieved without the nanoparticles. However when ammonium polyphosphate, cloisite or expandable graphite were added at concentrations that resulted in the maximum reduction in PHRR, a significant reduction in tensile strength, effective modulus of elasticity and elongation at break of the polyureas was observed.

4.1.6 A multi-faceted approach to improved flammability properties

Often to develop a polymeric material with improved fire and flammability properties requires a multi-faceted approach. It should be noted that in the example discussed below, it is required that the material maintain a certain percentage of the mechanical properties that it was selected for in the first instance. Polyureas were discussed in Section 3.1.2. Significant improvements in PHRR were realized through the incorporation of phosphorous and silicone – based compounds into the polyurea backbone [48]. A continuation of this work has investigated the use of additives and protective (intumescent) coatings in addition to modifying the polymer through a change in starting materials or the use of starting materials that incorporate inorganic materials into the polymer backbone [52]. The work consisted of investigating the effect of a) increasing the aromatic content of the polymer backbone of the polyurea formulation in an effort to improve the inherent fire retardant properties, b) the use of two sizes of treated graphite at various

concentrations on the flammability of polyurea, c) adding both graphite and flame retardants [48] to polyurea formulations and d) coating polyurea formulations with flame resistant coatings to increase time to ignition of the polyureas.

An increase in the aromatic content of the polyurea resulted in a marked improvement in the PHRR (449 kW/m² versus 1252 kW/m²). The PHRR was further reduced, from 449 kW/m² to 101 kW/m², through the addition of 22 weight percent large particle graphite (LPG). This effect was observed for several polyurea formulations, i.e., those with and without increased aromatic backbone content, which all had PHRR of ~100 kW/m². The addition of conventional flame retardants to the LPG filled polyureas resulted in an increase in the PHRR of the polyurea formulations. This was attributed to the inability of the LPG to expand and produce the protective char responsible for the observed decrease in PHRR. An intumescent coating (Paint to Protect DC333) was found to significantly increase the time to ignition from ~32 seconds to 134 seconds.

4.2 Standards

The selection of non-metallic materials, from the fire and flammability perspective, requires that the performance of the materials be evaluated. Standards, specifications, test methods and apparatus for the evaluation of fire performance of materials are discussed in this section. These have been developed to minimize the risk associated with the use of non-metallic (organic) materials on board naval vessels.

There are a number of standards for the fire performance of non metallic materials. These standards include those of the International Maritime Organization (IMO) and the International Standards Organization (ISO), US military specifications (Mil Spec) and Royal Navy Defence Standards (Def Stan) and associated British Standards (BS) and Naval Engineering Standards (NES). These standards, in turn, reference a large number of methods and apparatus for the evaluation of fire and flammability properties of non-metallic materials. The methods include ASTM (American Society for Testing and Materials), Underwriter's Laboratories (UL), ISO, and NES fire performance standards. The testing apparatus are referenced in the standards.

Standards, methods and apparatus for the testing and evaluation of the fire performance of non-metallic materials have been reviewed [53]. For instance, the fire safety requirements for certain materials used on ships required by the Fire Test Procedures Code (FTP Code) of IMO Resolution MSC.61(67) are shown in Table 4. Materials must meet these standards to show compliance with the safety of life at sea (SOLAS) regulations.

The US Navy has written or adopted fire standards for non-metallic materials that are to be used on naval vessels. These are listed in Table 5 and cover material selection requirements, composite materials for topside applications, thermal and acoustic insulation, fire and toxicity tests for composites to be used on submarines, and fire performance requirements for interior finish materials and furnishings.

Table 4. Fire Safety Requirements for Some Marine Products- Fire Test Procedures Code (FTP Code) IMO Resolution MSC.61(67)

FTP Code	Type of test	Referred test method	Similar test method
Part 1	Non-combustibility Test	ISO 1182	-
Part 2	Smoke and Toxicity Test	ISO 5659-2	-
Part 3	Fire Resistance Test for Fire Resistant Divisions	IMO A.754(18)	ISO 834-1
Part 4	Fire Resistance Test for Fire Door Closing Mechanisms	-	-
Part 5	Surface Flammability Test	IMO A.653(16) IMO A.687(17)	ISO 5658-2
Part 6	Test for Primary Deck Coverings	IMO A.653(16)	ISO 5658-2
Part 7	Flammability Tests for Curtains and Vertically Suspended Textiles and Films	IMO A.471(XII) IMO A.563(14)	ISO 6940/41 EN 1101/02
Part 8	Test for Upholstered Furniture	IMO A.652(16)	BS 5852-1 ISO 8191-1/-2 EN 1021-1/-2
Part 9	Test for Bedding Components	IMO A.688(17)	EN 597-1/-2
	Fire restricting-materials for High Speed Craft	IMO Res. MSC.40(64)	ISO 9705 ISO 5660

Military Standard MIL-STD-1623 E "Fire Performance Requirements and Approved Specifications for Interior Finish Materials and Furnishings" in turn specifies the tests used to determine the surface flammability, vertical fire resistance, tests for incombustibility and fire endurance of these materials. The specifications are shown in Table 6.

The United Kingdom has also established a number of Defence Standards (Def Stan) applicable to the smoke and toxicity of gases produced by materials, the selection of materials based on their fire characteristics, and fire hazards associated with sheathing for wire, chords and electrical cables used on ships. These are shown in Table 7.

Def Stan 07-247 Part 1 lists 32 test methods for the evaluation of fire and flammability performance of non-metallic materials. These test methods cover a wide range of properties including combustibility, flame spread, fire propagation, ignitability, rate of heat release, oxygen index, and the minimum temperature at which a material will continue to burn under specified conditions. Two of the test methods, their purpose, description, and how the test data is interpreted are given in Table 8

Table 5. US Naval standards for fire and flammability.

Material Selection Requirements, NAVSEA Technical Publication, T9074-AX-GIB-010/100	This document defines the Material Selection Requirements (MSR) that must be met by each design activity responsible for the selection of materials for ships and their systems.
ABS Naval Vessel Rules (NVR)	The NVR was recently developed by ABS & the U.S. Navy to allow the Technical Authority (U.S. Navy) to periodically update Technical Instructions for design and construction of naval vessels. The NVR covers structural aspects of Topside applications.
ABS Guide for High Speed Craft (HSC)	All structure of composite high speed craft are covered in the ABS HSC Guide
Composite Materials, Surface Ships, Topside Structural and Other Topside Applications – Fire Performance Requirements, Design Data Sheet DDS 078-1	This DDS provides the fire performance requirements for various Fiber Reinforced Plastic (FRP) composite materials used in the construction of U.S. Navy surface ship topside structures, and other topside applications.
Insulation, High Temperature Fire Protection, Thermal and Acoustic, MIL-PRF-32161	Addresses passive fire protection for steel decks and bulkheads with stiffeners. (Refer to IMO A.754 (18) for more guidance with composite divisions)
Military Standard ``Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used in Hull, Machinery, and Structural Applications Inside Naval Submarines" (MIL-STD-2031(SH))	Establishes the fire and toxicity test methods, requirements, and the qualification procedure for composite materials and composite material systems to allow their use inside naval submarines.
Military Standard MIL-STD-1623 E "Fire Performance Requirements and Approved Specifications for Interior Finish Materials and Furnishings"	Covers fire performance requirements for bulkhead sheathing, furniture & bedding, deck coverings, and thermal insulation.

Comparison of Tables 4, 6 and 7 indicates that the IMO FTP Code specifies ISO test procedures, the MIL-STD-1623E specifies ASTM, UL and other test procedures, and that the Def Stan specifies British Standards (BS) tests that have been adopted as European (EN) standard tests by the ISO. A more complete listing of test methods for the evaluation of the fire and flammability properties of non-metallic materials is found in Annex A.

It has been noted that “Proper fire protection decisions result from a combination of fire experience and fire testing. As new products formulations arise with little fire experience, fire testing becomes of great importance” [54]. This is prudent advice when selecting materials for use on naval vessels. However, the large number of test methods and apparatus that can be used to evaluate the combustion properties of materials can lead to confusion and uncertainties regarding the interpretation of results. The large number of tests may also make it difficult to select those that will provide the ‘best’ information concerning the performance of a material in a fire.

Table 6. A summary of MIL-STD-1623E specifications for fire tests.

Specification	Description
<i>Surface Flammability</i>	
ASTM D635	Burn rate test
ASTM E84	Tunnel test
ASTM E162	Radiant Panel
ASTM E648	Floor radiant panel
FED-STD-501, Method 6411	Floor covering, fire resistance
UL 94	Flammability of plastics
<i>Vertical Flame Resistance</i>	
ASTM D6413*	Flame Resistance of textiles
<i>Smoke Generation</i>	
ASTM E84	Tunnel test
ASTM E662	Specific optical density of smoke
<i>Test for incombustibility</i>	
46 CFR 164.009	Heated tube test
<i>Fire endurance</i>	
NFPA 267**	Fire characteristics of mattresses
UL 1709**	Hydrocarbon pool fire exposure test

* A minimum of five specimens from each of the warp and fill directions on materials of the same lot shall be tested and their results averaged (arithmetic mean). ** Only one specimen.

Table 7. Summary of British Defence Standards (Def Stan) related to fire and flammability testing of materials

Standard	Description
Def Stan 02-711 (70)	Determination of the Smoke Index of the Products of Combustion from Small Specimens of Materials
Def Stan 02-713 (64)	Determination of the Toxicity Index of the Products of Combustion from Small Specimens of Materials
Def Stan 07-247 (14)	Selection of Materials on the Basis of their Fire Characteristics: <ul style="list-style-type: none"> • Part 1: Policy • Part 2: Structural Materials • Part 3: System Materials • Part 4: Habitability • Part 5: Paints • Part 6: Insulation Material • Part 7: Miscellaneous Materials • Part 8: Fire Characteristics database
Def Stan 61-12 “Wires, Cords and Cables Electrical - Metric Units”	<ul style="list-style-type: none"> • Part 0: Wires, Cords, Cables, Electrical General requirements and Test methods* • Part 9: Cables and Wires Electrical for Cables, Radio Frequency Including Limited Fire • Part No: 18: Equipment Wires Limited Fire Hazard • Part No: 25: Cables, Electrical Limited Fire Hazard, up to Conductor Size 10 mm² Cross-Sectional Area • Part No: 31: Sheaths-Limited Fire Hazard

* Part 0 contains several fire and flammability tests including: Flammability BS 3G 230 Test 28a, Flame Propagation BS 3G 230 Test 28a, Critical Oxygen index BS 2782 Part 1 Method 141, Smoke index Def Stan 02-711, Toxicity index Def Stan 02-713

Table 8. Two of the thirty one test methods listed in Def Stan 07-247 for evaluation of the fire and flammability properties of materials.

Test No.	REFERENCES	PURPOSE OF TEST	DESCRIPTION
1	BS 476 Part 4 Non-combustibility (See also BS EN ISO 1182)	Materials are classified as combustible or non-combustible by identifying those which make little or no thermal contribution to the heat of the furnace and do not produce a flame, and by calling the remainder “combustible”.	Tests carried out in a furnace. The furnace is heated to 750 ±10°C and stabilised for 10 min. The specimen is inserted and the furnace temperature is recorded for a further 20 minutes. The occurrence of any flaming in the furnace is noted.
	Interpretation of Test Data: The material shall be deemed non-combustible if, during the test, none of the three specimens either: (1) Causes the temperature in the furnace to rise by 50°C or more above the initial furnace temperature, or; (2) Is observed to flame continuously for 10s or more inside the furnace. Otherwise, the material shall be deemed combustible.		
2	BS 476 Part 6 Fire propagation	The test takes account of the combined effect of factors such as the ignition characteristics, the amount and the rate of heat release, and the thermal properties of the product in relation to their ability to accelerate the rate of fire growth. (Note this test is used in UK building (regulations.)	Test carried out in a combustion chamber. The face of the specimen is subjected to gas jets impinging on the bottom edge of the specimen for 20 min and radiant heat applied 2 min 45 sec after start of test.
	Interpretation of Test Data: The index of performance I is the summation of sub indices I1, I2 and I3 calculated from the funnel gas temperature/time curve. The smaller the index I the more acceptable the material. The value of the sub index I1 is a measure of the heat contribution of the material to the early stages of the fire		

5 Summary and Conclusions

The technologies discussed in Section 2 of this report; point fire sensors, the components of a volume sensor including video, long wavelength video, infrared, ultraviolet and acoustic sensors, positive pressure ventilation, ventilation dampers and fans, water mist systems, gaseous agent systems, and powdered extinguishing agents, are commercially available and are in use on sea going vessels. Their TRLs are 9.

However, the incorporation of these components into ship board systems that enhance damage and fire control capabilities has not been proven on operational naval vessels. In some instances this is due to the specific requirements of warships. High pressure water mist systems are an example of this. Commercial high pressure water mist systems are not available with piping that meets the requirements of the US Navy.

In other instances, research and development of systems that incorporate some of the technologies has not advanced past a TRL of 6. The volume sensor system is an example of this. It has been tested in a simulated operational environment and performed well. However, it has not, at this time, been tested on an operational ship. The incorporation of smart valves into fire main or chilled water systems also has a TRL of 6. Systems incorporating smart valves are under development in the US and the Netherlands. To date, a chilled water system incorporating smart valves has been tested in a simulated operational environment. No system utilizing smart valve technology has been installed on an operational naval vessel. Questions concerning the level of autonomy given to the smart valves in a system and how the system of smart valves should be designed to maximize survivability of the system if part of it is damaged must also be considered. The SES has a TRL of 6. The incorporation of a SES on an operational naval vessel has not been carried out. This would be more easily accomplished on a new build ship where the required fans, dampers and controls were designed for and built into the ship.

The fire suppressant systems and agents reviewed in this memorandum all have a TRL of 9. However, it is essential that the impact of the use of these systems or agents on how a fire is extinguished be considered. Whether or not a suppressant can be used with crew in a space may require a change in fire fighting tactics. For instance the selection of a powdered extinguishing agent must consider whether or not the space is manned or unmanned. The use of gaseous agents will also require the consideration of the production of acid or toxic gases. The re-entry time for fire fighters returning to the space in which the suppressant may be affected. Conversely, the use of water mist as a fire suppressant may allow fire fighters to re-enter the space in a much shorter time.

The fire and flammability properties of organic and primarily polymeric materials used on naval vessels can be enhanced in a number of ways. The use of polymers that have superior fire resistance, the incorporation of flame retardants, the incorporation of compounds that enhance fire resistance into the polymer itself, the use of nanoparticles in conjunction with traditional fire retardants, and the use of intumescent coatings on vulnerable substrates are approaches that reduce the fire risk involved with these compounds. The challenge is to use products that retain the properties that the material (polymer) was selected for in the first instance.

There are many fire standards and test methods that can be used to evaluate the fire performance of polymeric materials. US Military Specifications (MIL-Spec) and UK Defence Standards (Def Stan) are excellent sources of tests and procedures for the evaluation and certification fire properties of many polymeric (organic) materials used on ships. Rules societies, such as the IMO and UL, have also developed tests and procedures for the certification of the fire performance of polymeric materials. MIL-Specs, Def Stans, IMO and other rules societies can be used to specify the required fire performance of materials.

Attempts to scale the results of laboratory based test to in-service performance of materials have not met with great success. However, the two most important flammability properties of materials measured using laboratory tests are time to ignition and the peak heat release rate. These two properties are directly related to the ease of ignition of a materials and how much energy the material adds to a fire in a space.

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Annex A Test methods used to evaluate the fire and flammability properties of non-metallic materials.

ULC (Underwriter's Laboratories of Canada)

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ASTM (American Society for Testing and Materials)

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Emerging technologies for fire and damage detection, abatement and suppression on board naval vessels are reviewed. These include point and volume fire and damage sensors and systems, smoke control (ejection) systems, smart valves, water mist and gaseous agent fire suppression systems, and aerosol fire extinguishing agents. Technology readiness levels (TRL) of these technologies are assigned based on the criteria developed by the United States Department of Defence.

Several approaches to enhancing the fire and flammability properties of non-metallic (polymeric) materials used on naval vessels are also reviewed. The approaches include the selection of polymeric materials with inherent fire resistance, the use of flame retardants additives including nanoparticles, the incorporation of molecules into the polymer backbone that have flame retardant properties, and the use of intumescent coatings to protect the underlying substrate. Standards and test methods that are used to evaluate the fire performance of non-metallic materials are discussed.

De nouvelles technologies pour la détection, la réduction et la suppression des incendies et des avaries à bord des bâtiments navals font l'objet d'un examen. Elles comprennent des systèmes de capteurs ponctuels et en volume des incendies et des avaries, des systèmes de contrôle (d'évacuation) des fumées, des valves intelligentes, des systèmes d'extinction d'incendie par la vapeur et par des agents gazeux, et des agents extincteurs d'incendie de type aérosol. Leurs niveaux de préparation de la technologie (NPT) sont déterminés selon les critères mis au point par le United States Department of Defence (le ministère de la défense des États-Unis).

Quelques mesures pour améliorer les propriétés de combustion et d'inflammabilité de matériaux non métalliques (polymères) employés à bord des bâtiments navals font aussi l'objet d'un examen. Elles comprennent la sélection de matériaux polymères qui ont une résistance inhérente au feu, l'utilisation d'additifs ignifuges qui comprennent des nanoparticules, l'incorporation de molécules qui ont des propriétés ignifuges dans la chaîne principale du polymère et l'utilisation de revêtements intumescents pour protéger le substrat sous-jacent. Les méthodes normalisées et d'essai qui sont employées pour évaluer la résistance au feu des matériaux non métalliques font l'objet de discussions.

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Damage control, Fire suppression, smoke control, water mist, gaseous agents, propelled extinguishing agents, smart valves, sensor suites, volume sensor, fire performance non-metallic materials

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