Performance studies and char characterizations of hydrocarbon intumescent coatings

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Preface and Acknowledgement

This thesis is the outcome of three years PhD project carried out in collaboration among the CoaST (Hempel Foundation Coatings Science and Technology) research group under the department of Chemical and Biochemical Engineering at the Technical University of Denmark, and the coating supplier Hempel A/S. Financial support from the Hempel Foundation to CoaST is gratefully acknowledged.

The completion of this thesis is thanks in great part to many people who have supported me along the way. I am tremendously grateful to my supervisors, Associated Professor Søren Kiil, Ph.D Claus Erik Weinell, Professor Kim Dam-Johansen, and Louise Ring from Hempel A/S. My main supervisor, Søren Kiil, has been dedicated to inspire my research and improve the paper work including the manuscript and the thesis with his wise comments and thoughtful suggestions. Claus Erik Weinell has always been an encouraging people that approve of my research endeavor and spur me to keep going. It was a very pleasant experience to work with him. Kim Dam-Johansen, who offered me the opportunity to conduct this project, has squeezed time to improve my manuscripts despite his overwhelming schedule. And my co-supervisor from Hempel, Louise Ring, has shared her great depth of knowledge concerning the industrial application of intumescent coatings and helped to arrange my relevant research in Hempel. I sincerely appreciate all the efforts made by my supervisors, as these are invaluable and pivotal to the proceeding of the three years project and the development of the dissertation.

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Ying Zeng

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Lyngby
Summary

Hydrocarbon intumescent coatings are an efficient way to protect steel structures during fires in high-risk environments such as offshore oil rigs. The fire-resistance performance evaluation of a hydrocarbon intumescent coating, according to standard hydrocarbon fire test methods (e.g. UL 1709), is typically conducted using industrial furnaces, because regular laboratory equipment, such as Bunsen burners, gas lamps, or cone calorimeters, cannot provide the required fast heating curves. These constraints of experimental facilities have greatly limited the understanding of the behavior of hydrocarbon intumescent coatings at conditions of industrial relevance. Consequently, in the present PhD project it is has been one of the goals to develop a laboratory-scale setup that can simulate the standard fire test curve UL 1709. Using this setup, a mapping of the performance of hydrocarbon intumescent coatings as a function of the concentration of coating ingredients has been undertaken.

The first ingredient studied was zinc borate and the fire-resistance experiments showed that the best performance (i.e. longest critical times of coated steel plates to reach 400 and 550 °C) was obtained when using a hydrocarbon intumescent coating with 15 wt.% zinc borate. Due to the strong influence of zinc borate on the rheological behavior of the coatings, increasing the level of zinc borate resulted in a more uniform, but less expanded char layer. The compositional profiles of the char layers indicated that the yield of phosphates (especially BPO$_4$) was enhanced by raising the zinc borate content. Analyses on thermal degradation of the coatings suggested that zinc borate can improve the thermal stability of the epoxy binder and the anti-oxidation properties of the char layer.

Before proceeding the investigation further to other ingredients, the initial laboratory-scale setup was upgraded with better insulation to the backside of steel plates to give a more clear distinction between different performances of the coatings. The reliability of the upgraded version was evaluated by comparing its performance in assessing five selected hydrocarbon intumescent coatings to those exposed to an industrial fire test furnace. A good agreement between these two setups was found for the temperature responses of the coated steel plates, and the physical appearance (relative expansion
and morphological structure) and chemical composition (crystalline phases) of the char layers.

With the confirmed reliability, the upgraded laboratory-scale furnace was applied to study the effects of various ingredients (ammonium polyphosphate, melamine, titanium dioxide, calcium carbonate, and vitreous silicate fiber) on the performance of selected zinc borate (ZB)-containing and ZB-free intumescent coatings. The results showed that increasing the content of ammonium polyphosphate (APP) or decreasing the content of melamine (MEL) in the ZB-containing coatings generally enhanced the critical times of the steel substrates and the physical appearance of the chars. Among the investigated formulations, the coatings with 25 wt.% APP or 5 wt.% MEL obtained the best performance. With respect to titanium dioxide (TiO$_2$), calcium carbonate (CaCO$_3$), and vitreous silicate fiber, varying their levels barely had an effect on the performance of the ZB-containing coatings, but the critical times and char appearance were strongly affected for the ZB-free intumescent coatings. The interaction of zinc borate with other ingredients such as APP and epoxy binder, which significantly influenced the viscosity of incipient chars, probably limited the room for these three inorganics to show an effect in the ZB-containing formulations. The ZB-free coating with 1.5 wt.% TiO$_2$, 2.5 wt.% CaCO$_3$, or 5 wt.% fiber had the longest critical times.

Taking advantage of a pool of experimental data from the ingredient studies, the relationship between the char properties and the critical times was further explored. A strong correlation was found between the critical time and a so-called integrated parameter, which combines the relative expansion and the insulation efficiencies of the three distinct char phases observed (i.e. sponge-like, macroporous and compact). The correlation confirms the assumptions regarding the insulation efficiencies of the different char phases and captures the desired char morphology (preferably macroporous and compact phases) for obtaining a good performance of a coating. The dynamic viscosity minimums of the corresponding coatings were measured and showed an exponential relationship with the physical appearance of the chars. It suggests that manipulating the rheological behavior of hydrocarbon intumescent coatings may lead to a targeted char appearance (e.g. moderate char expansion with macroporous and compact phases with a dynamic viscosity minimum in the range of 10 to 100 Pa·s).
With this desirable appearance, the good performance of the coating could be anticipated owing to the correlations between the char properties and the critical times.

In summary, the present thesis study has proposed a promising laboratory-scale for investigation of hydrocarbon intumescent coatings at conditions of industrial relevance. Moreover, the ingredient studies contribute to an understanding of the fundamental properties of hydrocarbon intumescent coatings and provide a scientific basis for formulation optimization or replacement of compounds with health risks.
Dansk Resumé


Inden yderligere undersøgelser af andre ingredienser blev igangsat, blev det oprindelige laboratorie-skala setup opgraderet med bedre isolering af bagsiden af stållader til at give en mere klar adskillelse mellem forskellige præstationer af belægningerne. Pålideligheden af den opgraderede version blev evalueret ved at sammenligne dens resultater af fem udvalgte kulbrinte intumescerende coatings mod tilsvarende resultater fra en industriel brandtestovn. En god overensstemmelse mellem disse to opsætninger
blev fundet for temperatur respons af de belagte stålplader, samt karakten (relativ ekspansions og morfologisk struktur) og den kemiske sammensætning (krystallinske faser) af kokslaget.


koksekspansion for makroporøse og kompakte faser med et dynamisk viskositetsminimum i intervallet 10 til 100 Pa·s). Med dette ønskede udseende kunne den gode ydeevne af belægningen forudses ud fra korrelationen mellem kokseegenskaberne og de kritiske tider.

Sammenfattende har den foreliggende afhandling på den ene side foreslået et lovende laboratorieskala setup for undersøgelse af kulbrinte intumescerende coatings ved betingelser af industriel relevans. På den anden side bidrager ingrediensundersøgelserne til en forståelse af de grundlæggende egenskaber af kulbrinte intumescerende coatings og udgør et videnskabeligt grundlag for optimering af formuleringer eller udskiftning af kemikalier med sundhedsrisici.
Contents

1 Introduction ................................................................................................................................. 1

1.1 Objectives of the project ........................................................................................................ 2
1.2 Outline of the thesis ................................................................................................................ 3

2 Literature review on passive fire protection with intumescent coatings ............................... 7

2.1 Introduction to fire protection of structural ......................................................................... 7
  2.1.1 Fire conditions .................................................................................................................. 8
  2.1.2 Strategies for fire protection ............................................................................................ 14
2.2 Intumescent coatings .............................................................................................................. 15
  2.2.1 Intumescent ingredients and binder ................................................................................. 17
  2.2.2 Functional fillers .............................................................................................................. 21
  2.2.3 Intumescence mechanisms .............................................................................................. 28
2.3 Performance evaluation of intumescent coatings ................................................................... 30
  2.3.1 Simulated fire-resistance tests ......................................................................................... 31
  2.3.2 Critical times in fire-resistance tests .............................................................................. 35
  2.3.3 Heat transfer parameters ............................................................................................... 38
2.4 Characterization of intumescent chars ................................................................................... 40
  2.4.1 Mechanical strength ......................................................................................................... 40
  2.4.2 Chemical properties ......................................................................................................... 42
2.5 Models for mapping intumescence ......................................................................................... 46
2.6 Conclusions ............................................................................................................................. 49

3 Hypotheses of the project ........................................................................................................... 51

3.1 Hypotheses related to the design of novel laboratory-scale setup ..................................... 51
3.2 Hypotheses related to the investigation of coating ingredients ........................................... 52
3.3 Hypotheses related to constructing correlations between performance parameters .......... 53

4 Effects of zinc borate on the properties of hydrocarbon intumescent coating chars .... 55

4.1 Introduction ............................................................................................................................. 56
  4.1.1 Performance requirements of intumescent coatings ......................................................... 57
  4.1.2 Objective and strategy of the present work .................................................................... 58
  4.1.3 Previous investigations on intumescent coatings containing functional fillers ............ 58
4.2 Experimental .......................................................................................................................... 60
  4.2.1 Coating materials and application .................................................................................. 60
4.2.2 Furnace experiments with standard hydrocarbon fire curve ........................................ 61
4.2.3 Scanning electron microscopy and digital microscopy recordings of the char structure... 62
4.2.4 Rheological measurements of the incipient intumescent char .................................. 63
4.2.5 Crystalline phases of the intumescent char identified with X-ray diffraction .......... 63
4.2.6 Thermal reactivity of formulations .............................................................................. 63
4.3 Results and discussion ................................................................................................. 64
4.3.1 Effects of zinc borate on the performance of hydrocarbon intumescent formulations .. 64
4.3.2 Clues to alternatives to zinc borate ............................................................................ 80
4.4 Conclusions ................................................................................................................. 82

5 Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings ......................................................... 83

5.1 Introduction .................................................................................................................. 84
5.2 Experimental ................................................................................................................ 87
  5.2.1 Coating materials and application ........................................................................... 87
  5.2.2 Fire-resistance experiments ..................................................................................... 87
  5.2.3 Thermal degradation of hydrocarbon intumescent coatings ...................................... 90
  5.2.4 Identification of crystalline phases of intumescent coating chars with X-ray diffraction... 90
  5.2.5 Digital microscope recordings of the intumescent coating char structure ................. 91
5.3 Results and discussion ................................................................................................. 91
  5.3.1 Effects of the furnace heating rate on the behavior of hydrocarbon intumescent coatings 91
  5.3.2 Performance of the laboratory-scale furnace .......................................................... 94
  5.3.3 Correlations between coating performance in the laboratory-scale fire-resistance experiments and the industrial fire tests ................................................................. 96
5.4 Conclusions ................................................................................................................. 110

6 Effects of various coating ingredients on the thermal properties of intumescent chars ................................................................................................................. 113

6.1 Introduction .................................................................................................................. 114
6.2 Experimental ................................................................................................................ 116
  6.2.1 Coating materials and application ........................................................................... 116
  6.2.2 Fire-resistance experiments following the UL1709 curve ....................................... 119
  6.2.3 Digital microscope recordings of intumescent char structures .................................. 120
6.3 Results and discussion ................................................................................................. 120
  6.3.1 Zinc Borate (ZB)-containing intumescent coatings .................................................... 120
  6.3.2 Zinc borate (ZB)-free intumescent coatings ............................................................... 130
6.4 Conclusions ................................................................................................................. 139
7 Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties ............................................... 141

7.1 Introduction ........................................................................................................ 142
7.2 Experimental....................................................................................................... 144
  7.2.1 Coating materials and application ................................................................. 144
  7.2.2 Rheological measurements of incipient intumescent chars ...................... 147
7.3 Results and discussion ........................................................................................ 148
  7.3.1 Influence of the char expansion on the critical times ................................. 148
  7.3.2 Correlation between critical times and integrated parameter of intumescent char .... 152
  7.3.3 Coupling of the rheological behavior of the intumescent coatings and the char parameters .............................................................................................................................. 156
7.4 Conclusions ........................................................................................................ 164

8 Conclusions and future work .............................................................................. 165

8.1 Conclusions ........................................................................................................ 165
8.2 Suggestions for future work ............................................................................ 168

Reference ................................................................................................................ 171
The protection of structural steel upon exposure to a fire has become paramount to prevent the loss of lives and assets. Structural steel retains only 60% of its original strength when its temperature reaches a critical value and thus loses weight bearing ability under full design load [1,2]. For regular loaded structural components, such as onshore platforms, the critical temperature is 538 °C, while for heavily loaded structural components, such as offshore platforms, the critical temperature is 427 °C [1]. In association to this, the time to reach the critical temperature in the event of a fire is termed the critical time. An efficient way to protect the building structure and prolong the critical time is by application of intumescent coatings to the surface of structural steel. At elevated temperatures, intumescent coatings swell to a multicellular char layer, which acts as an insulation barrier to slow heat transfer between hot gases and the underlying substrate. The integrity of the steel structure can therefore be maintained for 1-3 h under severe fire scenarios (e.g. with gas temperatures of more than 1100 °C) [3].

Depending on the source of fuel, fires can be roughly classified into so-called cellulosic (wood and plastics fuels) and hydrocarbon fire (oil or natural gas). Intumescent coatings designed to resist these two types of fires are correspondingly called cellulosic and hydrocarbon intumescent coatings. Regardless of the category, intumescent coatings generally consist of three essential ingredients (acid source, carbon source, and blowing agent) for the basic chemistry of intumescence and a polymeric binder for forming a continuous film throughout the coating. Other synergistic ingredients (e.g. metal oxides, composite fibers) are incorporated into the formulation as well to improve the thermophysical properties of the char layer. Proper manipulation among the chemical reactions of the ingredients is crucial to a good performance of an intumescent coating.

The fire-resistance performance of cellulosic or hydrocarbon intumescent coatings is commonly evaluated with standard fire test curves for which the fixed temperature-
time responses are imposed in order to roughly simulate the evolution of natural fires and meanwhile facilitate the normalization of fire test procedure. Standard cellulosic fire test curves are characterized with a moderate temperature rise (e.g. 60 min to around 925 °C as defined in ISO 834), while the heating rates specified in standard hydrocarbon fire test curves are much more critical (e.g. 5 min to 1093 °C as in UL 1709) and thereby difficult to fulfill with regular laboratory equipment, such as Bunsen burners, gas lamps, or cone calorimeters [4]. Due to the limitation in experimental facilities, relevant research regarding hydrocarbon intumescent coatings is rather rare in literature. This has slowed the development of hydrocarbon intumescent coatings which are, however, of great interest to growing demand across power, oil & gas, and refinery industries. Therefore, this project has been carried out to develop a laboratory-scale setup that can simulate the temperature-time relationship stated in standard hydrocarbon fire test curve UL 1709. With the benefit of the setup, the fundamental properties of hydrocarbon intumescent coatings can further be investigated to stimulate the progression of hydrocarbon fire protection.

1.1 Objectives of the project

This project aims to map the mechanisms behind the performance of hydrocarbon intumescent coatings. To be more specific, the main objectives are:

- Develop a laboratory-scale setup for evaluating the fire-resistance performance of hydrocarbon intumescent coatings according to the temperature-time response defined in standard UL 1709.

- Validate the reliability of the laboratory-scale setup by comparing with an industrial fire test furnace in the aspects of fire-resistance performance of hydrocarbon intumescent coatings (i.e. temperature response and critical times of coated steel plates) and the physical and chemical properties of the chars formed.

- Study the effects of various ingredients, including zinc borate, ammonium polyphosphate, melamine, titanium oxide, calcium carbonate, and vitreous silicate fiber, on temperature response of the coated steel plate, rheological behavior of the
intumescent coating, and physical appearance (i.e. relative expansion and morphological structure) of the intumescent char.

- Explore the correlations between the critical times of the coated steel plates and the properties of the intumescent chars such as relative expansion, char morphology, and dynamic viscosity of the incipient char.

The research presented in the thesis will boost the development of hydrocarbon intumescent coatings via constructing the convenient and reliable laboratory-scale setup for coating evaluation. Moreover, the experimental results regarding the effects of the coating ingredients will contribute to comprehensive understanding of the behavior of hydrocarbon intumescent coatings and provide guidance on optimization of coating formulations. In particular, it is of interest to understand the mechanisms behind the positive effects of zinc borate to provide a scientific basis for the replacement of boron compounds.

1.2 Outline of the thesis

This thesis includes eight chapters. The content of each chapter is briefly summarized as follows:

**Chapter 1 Introduction**

A general introduction to the project and the structure of the thesis.

**Chapter 2 Literature review on passive fire protection with intumescent coatings**

The application of intumescent coatings in passive fire protection for structural steel is introduced. Literature on intumescent formulations, testing methods of intumescent coatings, properties of intumescent chars, and mathematical models for mapping intumescence mechanisms is reviewed to guide the investigations of the project.

**Chapter 3 Hypotheses of the project**

This chapter describes the scientific and practical hypotheses behind the research carried out in the thesis.
Chapter 4 Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

This chapter presents the effects of zinc borate on performance of hydrocarbon intumescent coatings. The fire-resistance performance of the coatings exposed to fire test curve UL 1709 was investigated with the initial version of a developed laboratory-scale setup. The char formation influenced by zinc borate was analyzed with rheology measurement, X-ray diffraction, and flash-pyrolysis thermogravimetric analyses coupled with infrared spectroscopy.

Chapter 5 Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

In this chapter, the modified laboratory-scale setup is described and its reliability is discussed by comparing the results from the fire-resistance experiments performed with the setup (including critical times of the coated steel plates, physical and chemical properties of the chars formed) to those with an industrial fire test furnace.

Chapter 6 Effects of various coating ingredients on the thermal and mechanical properties of intumescent chars

This chapter presents the influences of various coating ingredients (ammonium polyphosphate, melamine, titanium oxide, calcium carbonate, and vitreous silicate fiber) on fire-resistance performance of hydrocarbon intumescent coatings (with and without zinc borate), and relative expansion and morphological structures of the intumescent chars formed.

Chapter 7 Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

With the abundance data obtained from the research presented in chapter 5 and 6, the correlations between intumescent char properties (relative expansion, morphological structure) and fire-resistance performance of intumescent coatings (i.e. critical times of coated steel plates) are investigated and presented in this chapter. The relationship between the char properties and rheological behavior of the coatings is mapped as well.
Chapter 8 Conclusions and future work

This chapter summarizes the main conclusions of the project and provides suggestions for further work.
2

Literature review on passive fire protection with intumescent coatings

A literature study on application of intumescent coatings in passive fire protection for structural steel is presented in this chapter. Intumescent formulations including various functional fillers formulated to improve performance of intumescent coatings are introduced. The performance evaluation of coatings, characterizations of char layers, and mathematical models for mapping intumescence mechanisms are reviewed to provide a basis for the research of the thesis.

2.1 Introduction to fire protection of structural

Uncontrolled fires are a serious threat that takes many human lives every year and destroy assets. To reduce the risk, there is much focus on fire protection research, which involves the study of the behavior and the suppression of fires, as well as the development, production, testing, and application of fire protection system [5,6]. In particular, attention has been drawn to fire protection of structural steel due to the increasing use of steel as a material for both modular and multistory buildings [4]. Steel is inherently non-combustible, but its strength and stiffness are, however, significantly reduced in the event of a fire.

Figure 2-1 shows the change of yield strength of structural steel according to the test by Outinen et al., the standard models of Eurocode 3, and the ECCS (The European Convention for Constructional Steelwork) [7–9]. Even though the data sets in these models are slightly different from each other, they are in good agreement with respect to the decreasing trend for the yield strength of the structural steel. When the temperature reaches 500 °C, the reduction factor for the yield strength has decreased to approximately 0.5, meaning that the structural steel has lost 50% of its load bearing
capability and will probably collapse under its full load design. Consequently, fire protection systems are necessary to delay the collapse of steel structures and thereby prevent the loss of lives and assets.

Figure 2-1 Reduction factor for yield strength of structural steel as a function of temperature (unity corresponds to the steel strength at room temperature). Curves based on data taken from [7–9].

2.1.1 Fire conditions

To provide sufficient fire protection, it is necessary to gain a general understanding of different fire conditions that steel constructions might be exposed to [10]. Fires happen with different characteristics and result in different complicated temperature-time responses depending on compartment size, type of compartment, available combustible material, and air supply available for combustion [11]. These compartment fire conditions are known as natural fires or parametric fires in standard EN 1991-1-2 [11,12]. Apart from the realistic fires, standard fires with a fixed temperature-time relationship are also widely applied in fire tests of structural elements and fire
protection materials [5]. Owing to the reproducible temperature-time relationship, these standard fires can unify the fire test procedures for different experimental facilities.

**Natural fires**

Natural fires typically spread until the fuel is consumed, and then the temperature in the compartment gradually decreases over time. The development of these fires, as shown in Figure 2-2, can be divided into three stages: pre-flashover (also known as growth period), post-flashover (fully developed fire), and decay period [11].

![Figure 2-2 The phases of a fully developed natural fire](image)

As the combustion is typically restricted to small areas at the stage of pre-flashover, the overall temperature rise during this period is very small and no obvious sign of fire can be observed [11]. If there is insufficient fire load or ventilation for air supply, the pre-flashover will stop at some point and cannot develop into the next stage. However, if the local phenomenon of fire in the pre-flashover is able to spread to all available fuels, the increased heat release rate from the combustion of these fuels can result in widespread flames and rapid increase of the temperature in the compartments. The transition from the local fire into widely propagated flames is called flashover [11].
After flashover, i.e. entering into the post-flashover period, structural elements are faced with the risks of collapse or loss of integrity due to the rapid temperature rise throughout the compartment. When the rate of fuel combustion becomes limiting, the temperature rise slows down and eventually leads to the highest temperature during the whole period of natural fires. Reaching this peak temperature that can be higher than 1000 °C is denoted as the sign of the end of post-flashover \[11\]. After that, the fire goes into a decay phase where the temperature in the compartment starts to decrease.

The models used to represent temperature-time responses in natural fires usually take the fire load in the compartment, openings in the walls and roofs, and nature of the enclosure into consideration \[5,13,14\]. For example, the equation below (Eq. 2-1), defined by Eurocode \[EN 1991-1-2, 2002\], shows the temperature of a compartment as a function of parametric time during the temperature rise phase in natural fires \[12\]. The parametric time is the time influenced by the conditions of the openings and enclosure of the compartment.

\[
T_g = 20 + 1325(1 - 0.324e^{-0.2t^*} - 0.204e^{-1.7t^*} - 0.472e^{-19t^*}) \quad \text{Eq. 2-1}
\]

\[
t^* = t \cdot \Gamma \quad \Gamma = \frac{(O/b)^2}{(0.04/1160)^2} \quad O = \frac{A_V\sqrt{h_{eq}}}{A_t} \quad b = \sqrt{\left(\rho c\lambda\right)}
\]

where \(T_g\) is the gas temperature in a compartment \([K]\); \(t\) is time \([h]\); \(A_V\) and \(A_t\) are the total area of vertical openings and enclosure (including openings), respectively \([m^2]\); \(h_{eq}\) represents the weighted average of vertical opening height \([m]\); \(\rho\), \(c\), and \(\lambda\) are the density, specific heat, and thermal conductivity of the enclosure, respectively \([J/(Kg \cdot K)]\).

The time \(t_{max}^*\) at which the temperature begins decreasing is a function of the fire load:

\[
t_{max}^* = 0.00013 \frac{q_{t,d}\Gamma}{O} \quad \text{Eq. 2-2}
\]

where \(q_{t,d}\) is the fire load density in the compartment.
Standard fires

As described above, the temperature-time response in natural fires is significantly dependent on the combustion of available fuels and the conditions of compartments. It is therefore difficult to apply this complex temperature-time relationship to a fire testing method of materials. To roughly simulate the evolution of natural fires and meanwhile facilitate the normalization of fire testing procedure, standard fires with fixed temperature-time responses have been defined. There are mainly two types of standard fires: cellulosic and hydrocarbon fire. The standard cellulosic fire simulates the natural fires that are fueled with cellulosic combustibles widely distributed in buildings (such as wood, paper, and textiles), while standard hydrocarbon fires represent the cases fueled by oil or natural gas which may happen to off-shore structures [4]. The simulation of standard fires based on the source of fuel is due to the fact that the fuel species has the most significant effect on the temperature-time response in the event of a natural fire [15].
Figure 2-3 shows the gas temperature of a natural fire inside a compartment fueled by cellulosic and hydrocarbon combustibles [15]. The temperature rise in the case with mainly hydrocarbon fuel (polypropylene blended with wood) is much faster than the one with cellulosic material (wood). Based on this feature, standard like ISO 834 define the temperature-time curve for cellulosic fire with a slow temperature rise to 927 °C after about 60 min [4,5,16,17], while the standard UL 1709 for hydrocarbon fires gives
a rapid temperature rise to 1093 °C within 5 min [4,5,16,18]. Jet fire is a special case for hydrocarbon fires, which is characterized with fuel expelled from an orifice under high pressure. Standard ISO 22899-1 specifies a 3 kg·s⁻¹ natural gas jet fire impinging on a full scale specimen, which would show a sharp temperature increase to 1350 °C within 5 min [4,19]. Apart from the extremely fast temperature rise, jet fire can cause severe problems of erosion to the elements exposed to the high pressure of explosion [4].

Figure 2-4 shows the standard temperature-time curves frequently used in fire testing method of materials: UL 1709, ISO 22899-1, and ISO 834. Compared with Figure 2-3, the standard fire curves capture the main difference between the natural fires fueled with cellulosic and hydrocarbon combustibles (i.e. different rates of temperature rise). The standard fire curves have been widely adopted in the investigation of fire protection systems and owing to the standardized testing curves, the classification of fire protection materials has become possible [4,20,21].

![Figure 2-4 Temperature-time curves defined in standard UL 1709, ISO 22899-1, and ISO 834.](image-url)
2.1.2 Strategies for fire protection

Two types of fire protection systems, active fire protection and passive fire protection, are usually used as the strategies against fire. Active fire protection includes human actions and automatic devices such as sprinklers, alarms, and gas release systems [4,5,11]. These can be highly effective and efficient to control and extinguish fires if they are activated timely. However, active fire protection involves considerable expenses and requires regular maintenance of the complex devices, and automatic devices have little effect when a large scale fire is developed. Human actions also require time to respond and even a very short delay will greatly increase the risk of fire loss. Therefore, in order to reduce fire damage to its utmost extent, passive fire protection is usually used along with active protection system [22].

Passive fire protection is a localized insulating system on the surface of the element that needs protection or mixed with bulk materials. It works via inhibiting heat transfer and mass transfer from a fire to the protected substrate or preventing combustion of flammable materials [5]. Passive fire protection can respond instantly to fire scenarios and has an advantage in limiting fire spread and delaying structural failure. Two types of passive fire protection products are widely used: conventional non-reactive inorganic materials and thermally reactive organic products. The former includes concrete, brick, tile, mineral fiber, and lightweight cementitious products [4,5,16]. These materials, which serve as thermal insulators, have been quite prevalent owing to their relatively low cost [23]. However, they have some notable drawbacks, such as poor aesthetic quality, vulnerability to spalling, health-related issues (e.g. problem with mineral fiber asbestos), space-consuming, and labor-intensive application [4,5,11,23].

With respect to thermally reactive organic products, it mainly includes halogenated fire retardant coatings, ablative/subliming coatings, and intumescent coatings [10]. Halogenated fire retardant coatings were the most prevalent fire protection materials from 1970s to 1990s [5,16]. It works via releasing fire retardant chemicals (e.g. halogen acids and metal halides) that can inhibit fuel combustion when exposed to fires. However, obscuring, toxic, and corrosive smokes would also release during the process. Considering the impact of the smoke on the environment, the application of halogenated fire retardant coatings has been limited [24]. An ablative/subliming coating
is a depletable insulation layer applied to substrates. In the event of a fire, the solid coating can turn into gas phase through endothermic reactions, which thereby prevent heat transfer from environment to the underlying material [23]. However, as the protection provided is based on the premise of coating consumption, the application of ablative/subliming coating is undesirable when the duration of fire exceeds the designed exposure period of the coating [5]. The disadvantages of the halogenated fire retardant coatings and ablative/subliming coatings make the third option, i.e. intumescent coatings, more and more favored by passive fire protection market [4].

2.2 Intumescent coatings

Intumescent coatings have been widely used to protect building structures, particularly steel-framed buildings, for over 30 years [25]. Increasing attention has been given to intumescent coatings as it has attractive architectural appearance and good performance in fire protection [16]. Upon heating, intumescent coatings undergo a series of physical and chemical reactions, making the original coating swell and form a multicellular char layer [1,4,25]. Intumescent coatings can swell up to 100 times of its initial dry film thickness [16,25]. Figure 2-5 shows an example of a swelled intumescent coating, adopted from the work of Nørgaard et al. [26].

Figure 2-5 Example of an intumescent coating after testing with standard cellulosic fire curve (ISO 834) [26].

The process of swelling and charring can reduce oxygen diffusion and passage of combustible volatiles inside the intumescent char formed with the coating (particularly
important for wooden substrates) [27]. Moreover, the char has low thermal conductivity and thereby acts as an insulating barrier to significantly slow heat transfer between gas and condensed phase [4,25]. The insulating barrier can prolong the time before the underlying steel reaches the temperature to collapse. Longer time means bigger chance to evacuate people and assets in buildings and enable active fire protection system and other emergency services to control fires.

Intumescent coatings can generally be classified into cellulosic and hydrocarbon intumescent coatings depending on the fire scenario under consideration. Cellulosic intumescent coatings are usually thin films with dry film thickness of 1-3 mm, while hydrocarbon intumescent coatings are normally thick films/mastics with dry film thickness of 3-30 mm [4]. The required thickness of coating is dependent on the size of structural elements and conditions of environment [5]. Three forms of intumescent coatings can be supplied: waterborne intumescent coating, solvent-based intumescent coating, and two-part epoxy system (solvent-free or low solvent) [4,5]. Waterborne and solvent-based coatings are commonly seen in the cases of cellulosic intumescent coatings. The former is mostly used for interior structures as it has less odor and less tolerance towards humidity and low temperature, while the solvent-based form is frequently seen in external applications used against complex weather and temperature variations. The two-part epoxy system is particularly suitable for the case against hydrocarbon fires and therefore quite common in hydrocarbon intumescent coatings [23].

The application of intumescent coatings on a steel element can be done with airless spray, brush, or rollers. Prior to application, the target surface should be coated with a primer that can act as adhesion promotor and corrosion inhibitor and thereby prolong lifetime of the upper intumescent coating [26]. Apart from a primer, a topcoat is maybe required to cover the intumescent coating and protect it against harsh environments [26].
2.2.1 Intumescent ingredients and binder

*Intumescent ingredients*

Intumescent coatings are typically composed of three intumescent ingredients: acid source, char former, and blowing agent. Acid sources are inorganic acids or compounds that can generate mineral acids. Char formers are carbon-rich polyhydric compounds with numerous esterifiable sites such as hydroxyl groups. Blowing agents usually refer to organic amines, organic amides, or other compounds that can yield incombustible gases. Table 2-1 lists some examples of the intumescent ingredients.
Table 2-1 Examples of ingredients in an intumescent coating system (both cellulosic and hydrocarbon type)

<table>
<thead>
<tr>
<th>Intumescent ingredient</th>
<th>Examples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid source</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus-containing</td>
<td>Phosphoric acid</td>
<td>[28]</td>
</tr>
<tr>
<td>compound</td>
<td>Ammonium phosphate/polyphosphate</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Melamine phosphate</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>Guanidine phosphate</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Alkyl phosphate</td>
<td>[32]</td>
</tr>
<tr>
<td>Boron-containing</td>
<td>Boric acid</td>
<td>[33]</td>
</tr>
<tr>
<td>compound</td>
<td>Ammonium pentaborate</td>
<td>[34]</td>
</tr>
<tr>
<td>Sulphur-containing</td>
<td>Sulfuric acid</td>
<td>[35]</td>
</tr>
<tr>
<td>compound</td>
<td>Ammonium sulfamate</td>
<td>[36]</td>
</tr>
<tr>
<td><strong>Char former</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>Mono-, Di-, Tri-pentaerythritol</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Sorbitol</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>Methylol melamine</td>
<td>[10]</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>Starch</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>β-cyclodextrins</td>
<td>[38]</td>
</tr>
<tr>
<td>Other polymers</td>
<td>Poly(amide) 6, poly(amide) 11</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>poly(amide) 6/ montmorillonite nanocomposite</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Poly(urethane)</td>
<td>[41]</td>
</tr>
<tr>
<td><strong>Blowing agent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amine</td>
<td>Melamine</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Melamine-formaldehyde resins</td>
<td>[43]</td>
</tr>
<tr>
<td>Amide</td>
<td>Urea</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>Urea-formaldehyde resins</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>Dicyandiamide</td>
<td>[46]</td>
</tr>
</tbody>
</table>

The interactions between intumescent ingredients result in the swelling and charring of intumescent coatings. Upon heating, the acid source firstly releases inorganic acid at its decomposition temperatures. At slightly higher temperatures, the inorganic acid will react with the char former through esterification, yielding esters that can then decompose into a carbon-rich substance through dehydration and carbonization [47]. Gases decomposed from the blowing agent can cause the ester and carbon-rich
substance to expand. The sequence of these reactions, e.g. esterification, dehydration, and decomposition of blowing agent, is crucial to the occurrence of intumescence.

The development of the intumescent ingredients is mainly regulation-driven. One aspect of regulation changes concerns the banning of chemicals or elements due to environmental and toxicological issues, which push the field to seek more renewable and eco-friendly alternatives. For instance, halogen-based acid sources were popular owing to its superior performance in reducing flammability with release of hydrogen halides and forming a carbonaceous layer through dehydration. However, the toxic effluents especially hydrogen halides from the reactions of halogen compounds have turned the market to less hazardous phosphorus-based compounds, as the examples shown in Table 2-1.

Another regulation effect is the increasing demand for better coating performance to resist specific fire scenarios and various aging scenarios before being exposed to heat. Nowadays, ammonium polyphosphate (APP) is widely used as an acid source for/in intumescent coatings due to its good thermal stability at temperatures below 200 °C [47]. It also serves as a blowing agent by decomposing into polyphosphoric acid and ammonia (gas form) [48]. However, APP has poor hydrolytic stability, which makes it non-resistant to weathering or moisture circumstances [16,29]. Likewise, the same problem exists in the case of pentaerythritol (PER), which is the most prevailing char former compared with other compounds such as polysaccharides (see Table 2-1), owing to its best compromise between two important parameters of an effective char former: carbon content and number of reactive hydroxyl sites [4]. However, the high degree of water solubility of PER limits its application in conditions of high humidity. Some efforts like surface treatment and microencapsulation were made to conquer the humidity-related issues of these compounds [4,16]. Moreover, some relatively new intumescent ingredients, such as melamine phosphate, ammonium pentaborate, poly(urethane), and poly(amide) 6 (see Table 2-1), have been developed to replace the traditional acid sources (e.g. APP) and char formers (e.g. PER).

With respect to blowing agent, the challenge is to develop compounds that can release large quantities of non-flammable gases at proper temperatures. For example, melamine
(MEL) is the most common blowing agent used with APP and PER, because the decomposition temperature of MEL corresponds to the temperature of esterification between APP and PER. Some researchers also proposed using two blowing agents with slightly different decomposition temperatures in an intumescent coating formulation, to improve the performance of the coating via extending gas-release period and facilitating intumescent char expansion [49].

It is noteworthy that an intumescent ingredient (e.g. APP as mentioned above) can be multifunctional regarding its role in the system of acid source, char former, and blowing agent. In fact, many efforts have been put on synthesis of all-in-one intumescent molecule that incorporates the characteristics of acid source, char former, and blowing agent into one molecule (e.g. melamine salt of pentaerythritol phosphate) [50]. However, up to now, instead of being used in intumescent coatings, this kind of all-in-one intumescent ingredient is presently more common as fire retardants for polymeric materials.

**Binders for intumescent coatings**

The binder, in the form of colloids, polymers or reactive oligomers, is another essential component for intumescent coating formulations [4]. It should soften and melt prior to or during the esterification of acid source and char former. This process is crucial to obtaining sufficient viscosity and enough flexibility for char expansion and consequently the form of a uniform multicellular structure throughout the char [31]. When the reactions between intumescent ingredients are nearly completed, the continuous substance formed with binder or its derivatives would also influence gelation and final solidification of incipient intumescent char [47]. Therefore, the selection and development of a binder with suitable properties are of significance to improve fire-resistance performance of intumescent coatings.

Traditional binders used in intumescent coatings are organic polymers, such as thermoplastic acrylic resins for cellulosic intumescent coatings and thermosetting epoxy resins applied to hydrocarbon intumescent coatings. It is noted that an epoxy resin cured with amide or amine is rich in hydroxyl groups (-OH), therefore it is not only a regular binder but also acts as a char former through esterification with acid
source. Except for the traditional binders, silicon-based inorganic binders with high strength of Si-O-Si bond have recently attracted much attention due to their better anti-oxidation properties compared to traditional organic polymers [55–58]. Yew et al. investigated the efficiency of intumescent formulations with ammonium polyphosphate/pentaerythritol/melamine (APP/PER/MEL) as intumescent ingredients and silica fume as a binder [51]. Thermogravimetric analyses (TGA) showed that silica fume improved the residual weight and thermal stability of the coatings. Their lab-scale furnace experiments, according to the natural fire defined in the EN 1991-1-2, confirmed the positive effects of silica fume on the thermal stability of the coatings, char expansion, surface structure of the intumescent chars, and adhesion of the chars to steel substrate. Dong et al. studied the influence of silicone emulsion on the insulating performance of waterborne intumescent coatings [52]. The formulations were composed of typical intumescent ingredients (APP/PER/MEL), TiO$_2$, kaolin, and a binder of polyacrylate emulsion blended with different proportions of silicone emulsion. Silicon emulsion improved the anti-oxidation and residual weight of the coatings. However, a proper amount of silicon emulsion is required to guarantee an even dispersion of silicon in the binder and thereby ensure a uniform pore (cell) size in the intumescent chars.

2.2.2 Functional fillers

Intumescent chars formed with binder and intumescent ingredients (e.g. APP/MEL/PER) usually have deficiencies in the aspects of morphological structure, mechanical strength, and thermal stability [53]. Therefore, apart from intumescent ingredients and binder, other compounds are also formulated into intumescent coatings to improve its fire-resistance performance or obtain additional properties such as resistance to weathering, corrosion, and smoke release. These kinds of compounds include a wide range of materials, such as metal oxides (e.g. TiO$_2$, Fe$_2$O$_3$) [4,16,54], hydroxides (e.g. Al(OH)$_3$, Mg(OH)$_2$) [55–57], industrial minerals (e.g. kaolin clay, wollastonite) [33,58–60], and fibers (e.g. glass fiber, carbon fiber) [61–63]. There is no unified way to describe these compounds; many terms like pigment, filler, and synergist have been used in the literature [47,51,64]. To avoid confusion, the term functional fillers are used,
in the present context, to define all the solid materials in intumescent formulations that actively influence coating performance (excl. acid source, char former, and blowing agent).

**Metal oxides**

Metal oxides such as TiO$_2$ and Fe$_2$O$_3$ mainly serve as color providers in regular coating products [65]. However, in intumescent systems, these oxides can take effects on the performance of intumescent coatings through its chemical reactions with intumescent ingredients (mainly phosphate derivatives of acid source). For example, TiO$_2$ can react with APP or phosphoric acid decomposed from APP, forming a glassy inorganic layer on the surface of intumescent chars [16,29,66]. This inorganic layer can play a major role in reducing thermal radiation and maintaining mechanical strength of the char at the later stages of fire protection (> 500 °C) [16,29]. Li et al. investigated the effects of Fe$_2$O$_3$ and MoO$_3$ on the thermal stability of solvent-based intumescent coatings with APP/PER/MEL as intumescent ingredients and a mixture of acrylic resin and amino resin as binder [67]. By means of thermogravimetric analyses (TGA), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM), they found that Fe$_2$O$_3$ and MoO$_3$ can increase the residual weight of the coating and improve the outer surface and inner structure of the intumescent char layer, resulting in the enhanced thermal stability of the coatings. The conversion of Fe$_2$O$_3$ and MoO$_3$ into Fe(PO$_3$)$_2$ and MoO$_2$ through their reaction with phosphate species (derived from APP) and NH$_3$ (released from APP and MEL), respectively, was confirmed according to the results from X-ray diffraction (XRD).

**Industrial minerals**

Industrial minerals are geological materials, used after beneficiation as additives in a wide range of coating industries [68]. Typical examples of industrial minerals are limestone, clays, kaolin, silica, and talc [47,68]. Zia-ul-Mustafa et al. investigated the synergistic effects of industrial minerals, kaolin clay and wollastonite, on the heat-shielding performance of intumescent coatings [58]. The formulations consist of APP, MEL, Bisphenol-A epoxy, boric acid, expandable graphite (EG), and a mixture of kaolin clay and wollastonite (50:50) from the range of 0 to 5 wt.%. Figure 2-6 shows
the variation of the backside temperature of the coated steel plate during the fire test with a Bunsen burner.

![Graph of backside temperature](image)

Figure 2-6 Backside temperature of the steel plate coated with the intumescent fire retardant coatings (IFRC) [58]. The symbol C or the number following the IFRC term represents 0 or 1–5 wt.% industrial minerals in the formulation.

The intumescent coating with 5 wt.% industrial minerals performed best as it obtained the lowest substrate temperature after a 60 min fire test. According to characterizations like TGA and XPS, the formulation with the industrial minerals can increase the carbon content and residual weight of the intumescent char up to 51% and 46%, respectively. They concluded that the presence of the kaolin clay and wollastonite favored the formation of boron phosphate, silicon phosphate oxide, and aluminum borate, which increased the char integrity and thermal protection of the intumescent coatings.
**Nanocomposites**

Nanocomposites containing nano-dimensional particles have shown great enhancement of the fire-resistance performance and durability of intumescent coatings even with a low loading in the formulation. It is an important advantage over their counterparts, micro-sized fillers, from an industrial and economic perspective [4]. Wang et al. investigated the effects of nanosilica on the corrosion-resistance and fire-resistance performance of APP-PER-MEL intumescent coatings [69]. They suggested that the nanoscale Si-O-Si network could effectively shield penetration of corrosive mediums into the coating and thereby greatly enhance the corrosion resistance of the coating during the salt spray test. This Si-O-Si network along with the ceramic-like layer formed by nanosilica particles also improved the anti-oxidation and fire resistance of the intumescent char during the standard cellulosic fire test (ISO 834).

It is noteworthy that good dispersion of nanocomposites in intumescent coatings is crucial to get the expected improvement on the performance of the coating. However, nanoparticles have a strong tendency to agglomerate due to its high oil absorption value, which therefore makes it a great challenge to disperse nanoparticles in intumescent formulations. Wang et al. studied the performance of APP-PER-MEL intumescent coatings with the addition of 0, 0.5, 1.0, 1.5, 2.0, 3.0, or 5.0 wt.% of nano-montmorillonite [59]. The SEM results showed the poor dispersion of nano-montmorillonite when its concentration exceeds 1.0 wt.%. The coating with 1 wt.% well-dispersed nano-montmorillonite performed much better than those with other levels of nano-montmorillonite in the aspects of water resistance, corrosion resistance, and thermal stability.

**Fibrous materials**

Fibrous materials have been used in a diverse range of coatings bringing improvement in plenty of physical properties, such as density, thermal conductivity, and electrical and magnetic properties [4]. In the field of intumescent coatings, the most prominent effect of fibrous materials is its reinforcement in properties of intumescent chars [64]. Canosa et al. evaluated the effects of four fibrous materials (alumina, carbon, aramid, and glass fiber) on the performance of intumescent coatings comprised of APP, PER, melamine sulfate, Al(OH)₃, Mg(OH)₂, TiO₂, and a specific resin (chlorinated rubber...
resin, phenolic resin, or epoxy resin) [61]. The results from thermal conductivity tests, two-foot tunnel, OI cabin, UL 94 horizontal-vertical chamber, and TGA trials showed that the reinforcement effect of these fibers follows the rank of:

Alumina fiber > Carbon fiber > Aramid fiber > Glass fiber

The thermal stability of the fibers and a stable physical or chemical link between the fibers and the matrix of intumescent chars is very important to block heat penetration throughout the chars [64]. A similar conclusion was made by Ahmad and his coworkers through their investigations on glass fiber, ceramic wool fiber, and basalt fiber [62,63,70]. With the introduction of these fibers, a strong network was formed in the intumescent char and to some degree protected the underlying steel substrate from the temperature rise in the event of a fire. Duquesne et al. studied the influence of mineral fiber (trade name Rockforce® MS603-Roxul®1000) on the fire protection of intumescent coatings [71]. They found that the use of the fiber brought better performance of the coatings, presumably due to the fiber maintained the char integrity for a longer time. However, it was also noted that the mineral fiber retarded char expansion, especially when a high load of the fiber was used.

**Flake fillers**
Flake fillers particularly refer to minerals with flake or layered structures, such as flake glass, expanded vermiculite, and expandable graphite [29,53,72,73]. Owing to their distinct morphological structures, these functional fillers can help to trap the nonflammable gases released from blowing agents inside the intumescent char and thereby facilitate char expansion [29]. Xue et al. studied the effects of expanded vermiculite on fire protection performance of intumescent coatings [53]. They suggested that the flaky structure of expanded vermiculite prevented the nonflammable gases from escaping and resulted in an increase of the expansion ratio of the coating. This structure could also slow down the diffusion rate of oxygen into the char layer and therefore reduce oxidation. However, the study pointed out that the excessive amount of expanded vermiculite may lead to uneven diffusion of the non-flammable gases and an inferior structure of the intumescent char.
The effects of expandable graphite (EG) are relatively complicated among the flake fillers, as it acts like an intumescent ingredient rather than an ordinary functional filler. Figure 2-7 shows the structure of expandable graphite, which is usually formed via intercalating sulfuric acid and/or nitric acid into the gap of parallel carbon planes of a crystalline graphite [16]. It was proposed that the intercalated acids will react with graphite through a redox reaction, releasing non-flammable gases like CO$_2$, H$_2$O, and SO$_2$ [4]. These gases force the graphite layers to expand to a great degree (about 100 times of the original thickness) and thus provide insulation to the underlying materials.

![Figure 2-7 The structure of an expandable graphite intercalated with sulfuric acid](image)

It seems that the expandable graphite alone can replace the traditional intumescent ingredients to form an intumescent char. However, the expanded char layer generated from graphite can easily detach from substrates due to its poor adhesion and low mechanical strength. This limitation makes the expandable graphite mainly used as a supplement to the traditional intumescent ingredients [75]. For instance, expandable graphite is often used with APP to produce a synergistic fire protection effect to hold the expanded char together [4].
**Other compounds**

Apart from the main categories mentioned above, other functional fillers such as boron compounds, sulfur compounds, and transition metal compounds are found to be effective for improving the thermal shielding, anti-oxidation, and smoke resistance performance of intumescent coatings \[4,16,76–78\]. Gillani et al. evaluated the influence of nano-sized zinc borate on the thermal degradation of intumescent fire retardant coatings and the gaseous products release from the degradation \[79\]. Ullah et al. developed different formulations (based on expandable graphite, APP, MEL, boric acid, and Bisphenol A epoxy resin) to study the effects of boric acid on the performance of the intumescent coatings \[33,80,81\]. All of these studies ended up with the same conclusion that boron compounds would convert into borophosphate via its reaction with APP, resulting in superior fire protection performance, thermal stability, and mechanical resistance of intumescent chars \[16\]. However, the mechanism behind the positive effects of boron compounds is probably more complex than this. Unlu et al. added different levels of boron compounds (boric acid, zinc borate, or melamine borate) into the intumescent formulation comprised of merely Bisphenol A epoxy resin and APP \[77\]. With the amount of boron compounds increasing, the fire-resistance performance of the intumescent coating decreased due to the reduced char expansion. They suggested that the benefits brought by boron compounds may result from its synergistic effects with other intumescent ingredients and functional fillers apart from with APP.

Wang et al. investigated the influence of transition metal chelates, CuSAO, CoSAO, and NiSAO, on the fire-resistance performance of intumescent systems (APP/PER/melamine phosphate) \[78\]. The open porous intumescent char produced from the sample without chelate turned into the compact and tough char layers after the introduction of CuSAO, CoSAO, or NiSAO to the formulation. They speculated that transition metal chelates could catalyze the reactions such as release of phosphoric acid, dehydration, crosslinking between the coating ingredients, and the graphitization of char. This conclusion is in agreement with the work of Song et al., who investigated the positive effect of Zn- and Cr- chelate on the intumescent system with poly(4,4-diamino diphenyl methane-O-bicyclicpentaerythritol phosphate-phosphate) (PDBPP)
According to the measurement of limited oxygen index (LOI) values and cone calorimeter tests, the presence of the metal chelates considerably enhanced the fire retardant performance of the intumescent system. The metal chelates could promote the decomposition of PDBPP and react with its product, polyphosphoric acid, to form a crosslinked network and compact char layer, which was therefore responsible for the improved thermal and flame retardancy properties of the system [76].

2.2.3 Intumescence mechanisms

A detailed study on the chemical reactions between intumescent ingredients, binder, and functional fillers is of significance to understand the intumescence mechanisms of intumescent coatings. As mentioned earlier, the primary reactions involved in the process is that between intumescent ingredients. With the typical intumescent ingredients (APP/PER/MEL) as an example, the intumescence process would be triggered by decomposition of APP into acidic phosphoric groups and ammonia at around 200 °C [47]. Simultaneously, the binder of the coating (e.g. acrylic resin) partly melts to create a viscoelastic substance. The acidic phosphoric groups, e.g. orthophosphate and phosphoric acid, can react with PER via esterification, yielding the mixture of esters. The decomposition of APP and esterification are illustrated in Figure 2-8 and Figure 2-9. The number of repeating unit in APP has a range of 700 to more than 1000.

Figure 2-8 Scheme for decomposition of APP [26].
At higher temperatures (280 to 350 °C), the esters would go through carbonization process that involves complicated free radical reactions and Diels–Alder reactions [47,72]. Thermal pyrolysis of the binder also contributes to the formation of carbonaceous substance. Detailed scheme for carbonization can be found in the work of Wang et al. [72]. The decomposition of MEL (shown in Figure 2-10) usually proceeds along with or slightly lags behind the process of esterification and carbonization. The ammonia decomposed from MEL and APP, along with other gaseous products released from polymeric compounds (e.g. binder), would cause the mixture of the esters and carbonaceous materials to swell up, forming an incipient multicellular char. At around 430 °C, gelation and solidification of the incipient char would occur and cease the expansion of the material [47]. The final step is the degradation of intumescent chars mainly caused by oxidation of carbonaceous materials at temperatures higher than 540 °C [72]. The degradation would increase thermal conductivity of the char layer and therefore reduce the protection of the char to the steel substrate.
Functional fillers may also participate in reactions of intumescence process due to the active reactivity of the derivatives of APP (e.g. phosphoric acid). Oxides can easily react with phosphoric acid yielding P–O–X species (X = Ti, B, Mg ...) [82]. Figure 2-11 and Figure 2-12 depict a series of mechanism reactions between functional fillers (titanium dioxide and zinc borate) and phosphoric acid decomposed from APP [83,84]. The phosphates formed from the reactions, such as titanium pyrophosphate (TiP₂O₇) and boron phosphate (BPO₄), can serve as a ceramic-like protection layer, leading to an improved mechanical strength and anti-oxidation properties of intumescent chars.

\[
(NH₄PO₃)ₙ \rightarrow nH₃PO₄ + NH₃ ↑ + 2 H₂O ↑
\]

\[
TiO₂ + 2 H₃PO₄ \rightarrow TiP₂O₇ + 3 H₂O ↑
\]

\[
4 H₃PO₄ \rightarrow P₄O₁₀ + 6 H₂O ↑
\]

\[
2 TiO₂ + P₄O₁₀ \rightarrow 2 TiP₂O₇
\]

Figure 2-11 Reactions between TiO₂ and APP [83].

\[
2ZnO, 3B₂O₃, 3H₂O \rightarrow 2ZnO, 3B₂O₃ + 3H₂O
\]

\[
10(HPO₃)ₙ + 2ZnO, 3B₂O₃ \rightarrow 6BPO₄ + (n – 6)/4 P₄O₁₀ + 2ZnO + n/2 H₂O
\]

Figure 2-12 Reaction mechanism between zinc borate and polyphosphoric acid, proposed by Samyn et al. [84].

2.3 Performance evaluation of intumescent coatings

Different testing methods (e.g. simulated fire-resistance tests) have been used to evaluate fire-resistance performance of intumescent coatings. The present section is devoted to introducing these testing methods and their corresponding performance parameters. The performance parameters, such as temperature-time response of steel
substrate, is of significance to estimate the performance of the coating in a real fire scenario.

2.3.1 Simulated fire-resistance tests

With a simulated fire-resistance test in which a steel sample coated with an intumescent coating is exposed to a specific heating condition, the temperature-time response of the steel substrate would be obtained. The rate of temperature rise would reflect the fire protection performance of the coating towards the substrate. A wide range of simulated fire-resistance tests with equipment like furnaces, radiators, and gas burners have been used and classified into standard and non-standard fire-resistance tests.

Standard fire-resistance tests refer to evaluation of intumescent coatings with exposure to the temperature-time relationship defined in standard fires. Figure 2-13 shows an industrial furnace for standard fire-resistance tests and the example of intumescent coating samples mounted on the furnace door [1]. Owing to its gas-fueled heating method, industrial furnaces are capable of tackling various temperature-time relationships including standard cellulosic fires with relatively low heating rates (e.g. ISO 834) and standard hydrocarbon fires with extremely high heating rates (e.g. BS 476). Standard fire-resistance tests performed with an industrial furnace are required for a third-party approval of intumescent coatings. However, the construction and operation of this kind of furnace is space- and cost-consuming.

Figure 2-13 (a) Industrial furnace with a chamber volume of 1.5 m³ for fire-resistant tests; (b) intumescent coating samples mounted on the furnace door [1].
Non-standard fire-resistance tests of intumescent coatings performed with laboratory equipment, such as electrically heated furnaces [85,86], gas burners [29,42,59,81,87], and radiators [1,71], are more common in the literature. These devices usually cannot follow the temperature-time relationship defined in standard fires, due to either uncontrolled flame temperature (gas burners) or limitation in heating power to meet a required heating rate and temperature (e.g. electrically heated furnaces). Nevertheless, these testing methods can serve as an initiatory screening of intumescent formulations in laboratories.

Bunsen burner is one of the typical gas burners fueled with liquid natural gas, methane, or butane [42,58,88]. During experiment, the steel plate coated with an intumescent coating is placed with a certain distance to the nozzle of a Bunsen burner (see Figure 2-14) [63]. Thermocouples are usually attached to the backside of the steel plate to record its temperature. The flame temperature can, theoretically, be adjusted by changing the fuel composition of the burner. However, the notable thing for the tests with Bunsen burners is the requirement of well-ventilated conditions and precautions for the operator.

Figure 2-14 A Bunsen burner for fire-resistance experiments of intumescent coatings [63].
Figure 2-15 shows an example of setups that use a radiator as heat source to investigate fire-resistance performance of intumescent coatings [1]. The side of a steel plate coated with an intumescent coating is exposed to the radiator and the temperature response of the steel plate is monitored by an infrared pyrometer. Unlike the convective heat transfer in other testing methods, the setup with a radiator mainly heats samples up through radiation. The incident heat flux imposed by a specific radiator is usually fixed. Therefore, these radiators may not able to heat samples to a temperature as high as that in regular furnaces (e.g. 1000 °C) due to the limitation of the incident heat flux [1]. Moreover, it is hard to control/adjust the temperature rise experienced by samples with the fixed incident heat flux.

In general, the non-standard fire-resistance tests with these laboratory devices could be an option to investigate fire protection performance of intumescent coatings, considering the low availability and high cost of standard fire-resistance tests with industrial furnaces. Nevertheless, more and more researchers have pointed out that intumescent coatings evaluated under different heating conditions (mainly heating rate and temperature) may exhibit different performances [89,90]. Therefore, developing
laboratory-scale setups for standard fire-resistance tests is an ongoing topic in the field of intumescent coatings. Several research groups have successfully designed testing methods to replace the industrial standard cellulosic fire tests [1,82,83,91,92]. For instance, Mariappan et al. developed a bench-scale furnace to simulate the standard cellulosic fire curve ISO 834 [83]. However, the standard hydrocarbon fire curves, e.g. UL 1709 that require a high heating rate (more than 200 K/min) to 1093 °C, is still a great challenge to tackle with a laboratory-scale setup.

Elliott et al. designed a novel setup, called heat-transfer rate inducing system (H-TRIS), to conquer the problem brought by the constant incident heat flux of radiators and therefore perform fire-resistance tests according to different cellulosic and hydrocarbon standards [91]. The configuration of the H-TRIS setup is shown in Figure 2-16. The radiant heater is installed in a mobile support and thereby the distance between the sample and the radiant heater can be adjusted to control the heat flux absorbed by the sample over time to meet the profile of standard temperature-time curves. Nevertheless, the maximum output of the radiant heater is enough to follow cellulosic standards like ISO 834, but it failed to meet the required temperature-time relationship defined in a hydrocarbon standard.

Figure 2-16 Heat-Transfer Rate Inducing System (H-TRIS) [91].
2.3.2 Critical times in fire-resistance tests

As mentioned in Section 2.1, structural steel would lose its load bearing capability with the temperature of the steel increasing. The temperature at which only 60% of the original strength remains is called critical temperature of the steel [1]. The critical temperature is 538 °C for regular reinforcing steel and 427 °C for heavily loaded structural steel [1]. Once the critical temperature is reached, the structural steel would lose its integrity and collapse. With the protection of intumescent coatings, the time, specifically called critical time, for the coated steel sample to reach its critical temperature can be prolonged. Clearly, the critical time is directly linked to the fire protection performance of intumescent coatings and therefore identified as the most important parameter in industry [1].

For the majority of the non-standard fire-resistance tests, the steel sample cannot reach its critical temperature due to the restricted heating conditions. Therefore, the parameter of critical time is not accessible according to the temperature-time response obtained from these testing methods. Instead, they would usually define their own assessment parameters, for example, the temperature after a certain time of test (e.g. 60 min [54,81]). Further details are not provided considering the complexity of these disjunctive parameters. With respect to standard fire-resistance tests, the critical time can be easily read from the temperature-time response of a coated steel sample. It has to be noted that standard fire-resistance tests widely select 500 (or 550) and 400 °C as critical temperature for regular reinforcing steel and heavily loaded structural steel (offshore platforms), respectively [1,16]. They are slightly different from the critical temperatures mentioned above.

Table 2-2 and Table 2-3 lists some examples of intumescent formulations and their corresponding critical times. The selected intumescent formulations were tested under the same standard temperature-time curves (ISO 834 in Table 2-2 and UL 1709 in Table 2-3). Standard cellulosic fire curve ISO 834 is for coatings used in common interior buildings, while standard hydrocarbon fire curve UL 1709 is usually adapted to test intumescent coatings for exterior application such as offshore platform. Therefore, the critical time for the tests with ISO 834 and UL 1709 are corresponding to the critical
temperature of 500 °C and 400 °C, respectively, unless otherwise specified. In Table 2-2 and Table 2-3, some ingredients of the formulations are not available in the literature due to proprietary issues.

Table 2-2 Examples for intumescent formulations evaluated with standard cellulosic fire curve ISO 834.

<table>
<thead>
<tr>
<th>Intumescent formulation for cellulosic fire</th>
<th>Critical time (min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>APP, PER, MEL, acrylic resin</td>
<td>40</td>
<td>[93]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic resin, nano-SiO₂, glass fiber, TiO₂, butyl acetate, dimethyl benzene</td>
<td>131 (300 °C)</td>
<td>[69]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic emulsion</td>
<td>57.2 (538 °C)</td>
<td>[94]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic resin, pigment, filler</td>
<td>30.4</td>
<td>[95]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic resin, glass fiber, TiO₂, butyl acetate, dimethyl benzene, nanoclay</td>
<td>87 (300 °C)</td>
<td>[96]</td>
</tr>
<tr>
<td>APP, MEL, di-PER, acrylic resin, nano-SiO₂, TiO₂, sodium silicate, sodium tetraborate, polymethylsilane latex, borosilicate glass, calcite</td>
<td>90 (300 °C)</td>
<td>[97]</td>
</tr>
<tr>
<td>APP, di-PER, MEL, ethylene benzene–acrylic resin</td>
<td>31.4</td>
<td>[93]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic resin, glass fiber, TiO₂, Al₂O₃, dimethyl benzene, butyl acetate</td>
<td>70 (300 °C)</td>
<td>[72]</td>
</tr>
<tr>
<td>APP, PER, MEL, acrylic resin, glass fiber, EG, rutile-TiO₂, Al₂O₃, dimethyl benzene, butyl acetate</td>
<td>&gt;100 (300 °C)</td>
<td>[72]</td>
</tr>
<tr>
<td>APP, MEL, di-PER, acrylic emulsion, expanded vermiculite</td>
<td>60 (450 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td>APP, MEL, di-PER, acrylic emulsion</td>
<td>60 (367 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td>Silicone matrix, EG, calcium carbonate, clay</td>
<td>&gt;66.7</td>
<td>[98]</td>
</tr>
</tbody>
</table>

Nearly all the formulations listed in Table 2-2 comprise the three typical intumescent ingredients (i.e. APP, PER (or di-PER), and MEL), and acrylic resin as binder. As mentioned in Section 2.2.1, the performance of the intumescent coating with merely these typical ingredients is limited (e.g. ref [93] in Table 2-2). Therefore, diverse functional fillers have been incorporated into intumescent formulations, to improve fire-resistant performance of intumescent coatings and properties of intumescent char.
As seen in Table 2-2 the critical time was greatly increased by the introduction of functional fillers such as silica, fibers, and expandable inorganics.

### Table 2-3 Examples for intumescent formulations evaluated with standard hydrocarbon fire curve UL 1709.

<table>
<thead>
<tr>
<th>Intumescent formulation for hydrocarbon fire</th>
<th>Critical time (min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{BO}_3$, APP, epoxy, silicate fiber, calcium carbonate, TiO$_2$</td>
<td>38.1</td>
<td>[3]</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$, APP, MEL, epoxy, EG, 50% clay/50% wollastonite</td>
<td>&gt;60</td>
<td>[58]</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$, APP, MEL, epoxy, EG, ceramic wool fiber</td>
<td>&gt;60</td>
<td>[63]</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$, APP, MEL, epoxy, EG, nano-TiO$_2$, barite</td>
<td>&gt;60</td>
<td>[87]</td>
</tr>
<tr>
<td>APP, MEL, epoxy, TiO$_2$, filler</td>
<td>12.1</td>
<td>[82]</td>
</tr>
<tr>
<td>Silicone resin (Ti catalyst), EG</td>
<td>9.3</td>
<td>[20]</td>
</tr>
<tr>
<td>Silicone resin (Ti catalyst), EG, organoclay</td>
<td>16.7</td>
<td>[2]</td>
</tr>
<tr>
<td>Silicone matrix, organoclay, EG, fibers</td>
<td>16.1</td>
<td>[99]</td>
</tr>
</tbody>
</table>

Compared with the case of the standard cellulosic fire curve ISO 834, available data for intumescent coatings tested with standard hydrocarbon fire curves is rare (see Table 2-3). The setups, as mentioned previously, that can meet the harsh requirements of standard hydrocarbon fires are quite few in literature. Except for the silicon-based intumescent coatings, almost all the formulations in Table 2-3 include the combination of APP and boron compound. The interactions between these two ingredients have been widely investigated [3, 63, 87, 100]. Boron compounds can be degraded into boron oxide, which is a glasslike material that can increase the viscosity of melted intumescent coatings and prevent the escape of gases decomposed from blowing agent. Boron oxide can also react with polyphosphoric acid decomposed from APP at about 300 °C, forming borophosphate that is thermally stable up to 1200 °C [58]. The thermal stability of borophosphate can benefit thermal resistance of the char at elevated temperatures [33]. Moreover, boron compound can improve sintering and crosslinking among various ingredients of intumescent formulations, retaining more substance in intumescent chars [77]. Therefore, the presence of boron compounds can greatly enhance the performance of intumescent coatings against severe fire scenarios such as
hydrocarbon fires. However, the problem related to the use of boron compound is its potential hazard to human health [101]. Remove potential toxic ingredients and meanwhile improve fire-resistant performance are big challenges for development of intumescent coatings for hydrocarbon fires. The group of Bourbigot et al. have made a lot of efforts on developing silicon-based intumescent coatings, out of consideration of thermal stability of Si-O-Si network and ceramic-like layer formed by silica [2,20,99]. However, as shown in Table 2-3, the critical times of the steel samples coated with the silicon-based intumescent coatings, are still not comparable to those of boron-containing coatings.

2.3.3 Heat transfer parameters

Apart from evaluating temperature-time response and critical time of coated steel plates according to simulated fire-resistance tests, there are also some small-scale testing methods developed to evaluate the heat transfer parameters of intumescent coatings [1]. The typical equipment is cone calorimeter, as shown in Figure 2-17 [102]. The standard for using a cone calorimeter is described in ISO 5660-1, which specifies that an intumescent coating sample with an area of 100 mm × 100 mm is supported on a load cell and exposed to the cone heater with a heat flux of 10 to 100 kWm⁻² [102].

Figure 2-17 Cone calorimeter [102].
A sparker igniter placed above the sample is used to ignite flammable gases produced from thermal degradation of the sample. The mass loss of the sample during the test can be recorded by the load cell. An exhaust hood positioned over the cone heater collects all the effluents and transport them to pass through a thermocouple, pressure sensor, smoke measurement system, and sample probe. Cone calorimeter can obtain parameters such as heat release rate, time to ignition, smoke production, and weight loss of the sample. These properties are very important especially for mathematical models aiming to map the mechanism of intumescence [102].

Cone calorimeters also exhibit some shortcomings. The dry film thickness (DFT) and expansion ability of the sample tested with cone calorimeters have to be limited to a certain value, to prevent the cone heater being damaged by the expanding intumescent char layer. Moreover, the samples may not be fully volatilized or oxidized, due to the insufficient heat flux of cone calorimeters. Therefore, a new type of calorimeter named pyrolysis combustion flow calorimetry (PCFC) has been developed to deal with those problems. An illustration of a PCFC is shown in Figure 2-18.

![Figure 2-18 Schematic of flaming combustion and pyrolysis combustion flow calorimetry](image)

Figure 2-18 Schematic of flaming combustion and pyrolysis combustion flow calorimetry [103].
Samples are loaded into the pyrolyzer and heated in an inert atmosphere to separate the solid state and gas phase. The volatile gas products swept from the pyrolyzer are further burned at flame temperatures (about 900 °C) in the combustion chamber for complete oxidation [47]. Then the combustion products would flow through the flow meter and analyzers. Total heat release (THR), peak of heat release rate (PHRR), heat release capacity (HRC), and mass loss are measured as the main results from the PCFC.

2.4 Characterization of intumescent chars

The good fire protection performance of an intumescent coating would rely on the properties of the intumescent char. Characterization techniques such as texture analyzer, SEM, XRD, and FTIR have been applied to identify physical (e.g. mechanical strength) and chemical (e.g. chemical composition) properties of intumescent chars. The results help understand the performance of intumescent coatings and map the intumescence mechanism.

2.4.1 Mechanical strength

Among various physical properties, mechanical strength of intumescent chars is the most important one, especially for drastic fire scenarios such as hydrocarbon fires. The turbulence like heat shock, blowing, or even blast in hydrocarbon fires would easily remove or destroy a mechanically weak char, leading to the loss of fire protection to the steel substrate. Therefore, strong mechanical strength of intumescent char is crucial to passive fire protection against hydrocarbon fires.

Some lab-made setup, texture analyzer, and rheometer were used to measure mechanical stability of intumescent chars [2,3,63,86,89,98,104–107]. Amir et al. studied the mechanical strength of intumescent chars at room temperature, by observing the height reduction of the char after applying with a predetermined weight load [86]. The chars were produced from intumescent coatings reinforced with different fibers (glasswool fiber, rockwool fiber, ceramic wool fiber, and mineral fiber & Al₂O₃/SiO₂ fiber). Figure 2-19 shows the setup for the char mechanical resistance test (left) and the performance of different samples (right). It can be seen that compared with other fibers
investigated, the addition of ceramic wool fiber in the intumescent coating can benefit the reinforcement of char strength most.

![Experimental setup for char mechanical resistance test](image1)

**Figure 2-19** Left: experimental setup for char mechanical resistance test; right: char height reduction after the resistance test (GWFRIC: glasswool fiber; RWFRIC: rockwool fiber; CWFRIC: ceramic wool fiber; C7: mineral fiber & Al$_2$O$_3$/SiO$_2$ fiber; Control: without fiber) [86].

Muller et al. investigated the mechanical resistance of intumescent chars on a rheometer with a parallel-plate configuration at room temperature [106]. The chars were produced from cone calorimeter test or tubular oven test. The results showed that the heating type (convection in tubular oven or radiation in cone calorimeter) would not modify the mechanical strength of the intumescent chars, while the heating temperature and heating rate did play a key role in the char resistance to mechanical force. Higher temperature and heating rate resulted in the weaker chars.

Apart from the measurement at room temperature, Muller and his coworkers also examined the mechanical strength of intumescent chars at a high temperature with a furnace rheometer [3, 106]. By comparing the results measured at the maximum operating temperature of the furnace rheometer (500 °C) and at room temperature, they found that the char is more resistant when tested at 500 °C than that at room temperature. This observation is in accordance with the fact that intumescence is a dynamic process, therefore char morphology and composition may be modified during a cooling down process [106].
Knowing that the temperature at which the mechanical strength of an intumescent char was measured would make a difference, it is clearly more practical to perform the measurement during the fire-resistance tests of intumescent coatings. However, it is a great challenge to quantify the mechanical strength of intumescent chars in a hot furnace or other test equipment. The furnace rheometer mentioned above usually has a maximum operating temperature at around 500 °C, while the temperature in a regular fire scenario can reach up to 1100 °C. Jimenez and her coworkers designed an air-jet setup to roughly estimate mechanical properties and cohesion of intumescent chars during the process of fire-resistance tests (at in-situ temperature) [2,89,105]. The scheme for the setup is shown in Figure 2-20. An airflow is introduced into the setup to simulate air turbulence or wind perturbation in real fire scenarios. The response of the intumescent chars to the turbulence can, therefore, be seen to evaluate the char resistance to flow impact during the fire-resistance tests.

![Figure 2-20 Schematic setup to determine cohesion properties of the char](image)

**2.4.2 Chemical properties**

The thermal stability (e.g. char yield in thermogravimetric analyses) and chemical composition (e.g. carbon and oxygen content) of intumescent chars is closely related to
the fire protection performance of intumescent coatings. Generally, a high char yield means more substance retained to construct the protective char layer, and a high ratio of carbon to oxygen content indicates the better anti-oxidation of the intumescent char. Table 2-4 lists some ingredients that have been investigated regarding their effects on improving char yield and carbon content and reducing oxygen content of intumescent chars. The grid with tick indicates a positive effect on the specific parameter, while the blank grid refers to an uncertain case. It can be seen that the chemical properties of intumescent chars can be improved with a wide range of compounds.

These compounds make an effect in different ways. Some of them would react with other ingredients of the formulation, forming thermally stable substances to improve the char yield and anti-oxidation properties of the char (e.g. formation of phosphate via reactions between oxide and APP) [33,67,87,100]. Some compounds, such as silicone (forming inorganic silica layer under heat) and flake fillers (e.g. EG and montmorillonite), may serve as a physical thermal barrier, delaying heat transfer and oxygen penetration in the char and thereby reducing char degradation [52,59,72].
<table>
<thead>
<tr>
<th>Additive</th>
<th>Formulation</th>
<th>Char yield</th>
<th>CC</th>
<th>OC</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketone-aldehyde resin</td>
<td>APP, triazine polymer, zinc borate, modifying resin, fluororubber</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[100]</td>
</tr>
<tr>
<td>MoO₃</td>
<td>APP, PER, MEL, acrylic resin</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[67]</td>
</tr>
<tr>
<td>Ceramic fiber</td>
<td>Commercial intumescent coating</td>
<td>✓</td>
<td></td>
<td></td>
<td>[108]</td>
</tr>
<tr>
<td>Boric acid</td>
<td>APP, MEL, EG, bisphenol A, polyamide amine</td>
<td>✓</td>
<td></td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>Dolomite clay</td>
<td>APP, MEL, EG, boric acid, bisphenol A, tetra ethylene tetraamine</td>
<td>✓</td>
<td></td>
<td></td>
<td>[42]</td>
</tr>
<tr>
<td>Alumina fiber</td>
<td>APP, PER, melamine sulfate, chlorinated rubber resin, Al(OH)₃, Mg(OH)₂, rutile-TiO₂</td>
<td>✓</td>
<td></td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>APP, PER, melamine sulfate, chlorinated rubber resin, Al(OH)₃, Mg(OH)₂, rutile-TiO₂</td>
<td>✓</td>
<td></td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td>EG</td>
<td>APP, PER, MEL, acrylic resin, glass fiber, TiO₂, Al₂O₃, dimethyl benzene, butyl acetate</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[72]</td>
</tr>
<tr>
<td>Expanded vermiculite</td>
<td>APP, MEL, di-PER, acrylic emulsion</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[53]</td>
</tr>
<tr>
<td>Glass fiber</td>
<td>APP, MEL, EG, boric acid, bisphenol A, polyamide amine</td>
<td>✓</td>
<td></td>
<td></td>
<td>[62]</td>
</tr>
<tr>
<td>Glass flake</td>
<td>APP, PER, MEL, Kaolin/TiO₂, bisphenol A, waterborne amine</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>APP, PER, MEL, TiO₂, epoxy emulsion, waterborne amine</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>[59]</td>
</tr>
<tr>
<td>Silicone emulsion</td>
<td>APP, PER, MEL, Kaolin/TiO₂, self-crosslinking polyacrylate emulsion</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[52]</td>
</tr>
<tr>
<td>Nano-TiO₂</td>
<td>APP, MEL, EG, boric acid, barite, bisphenol A, polyamide polyamine</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[87]</td>
</tr>
<tr>
<td>Clay and wollastonite</td>
<td>H₃BO₃, APP, MEL, EG, bisphenol A</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>[58]</td>
</tr>
</tbody>
</table>
Nevertheless, the improvement in the char yield and carbon content (and/or reduction of oxygen content) not always guarantee better fire protection performance of intumescent coatings. The proper amount of the target component in the formulation is crucial to enhance those chemical properties of the char and meanwhile improve the performance of the coating.

Xue et al. investigated the effects of expanded vermiculite on performance of intumescent coatings and properties of intumescent chars [53]. The coating formulations comprise of APP, MEL, di-PER, acrylic emulsion, and different amounts of expanded vermiculite (0, 3, 5, 7, 9, and 11 wt.%). The results showed that the char yield and ratio of carbon to oxygen content in the char were improved by increasing the amount of expanded vermiculite. However, as shown in Figure 2-21, the performance of the intumescent coating in fire-resistance tests started decreasing once the amount of expanded vermiculite was high than 7 wt.% (F3). They explained that the excessive amount of expanded vermiculite would bring an uneven and loose char structure due to the non-uniform diffusion of gases in the melting char, and therefore lead to inferior performance of the coating [53].

![Figure 2-21 Temperature–time curves for intumescent coatings [53]. F0-F5 represent the intumescent coating formulations with 0, 3, 5, 7, 9, and 11 wt.% expanded vermiculite, respectively.](image-url)
2.5 Models for mapping intumescence

Mathematical models validated with experimental data are useful tools to predict the response of intumescent coatings to a certain type of fire scenarios and thereby facilitate the performance-based fire engineering design such as optimization of intumescent coatings for industrial standard fire tests. Table 2-5 lists some mathematical models describing intumescent coating behavior. Except for the work of Cirpici et al. [25], which focused on bubble growth in incipient char and estimated transient char expansion, the output data from the rest of the models are the temperature of the steel substrate.
Table 2-5 Examples of mathematical models of intumescent coatings.

<table>
<thead>
<tr>
<th>Model</th>
<th>Year</th>
<th>Validation</th>
<th>Exp. time (min)</th>
<th>Fire curve/Max. heat flux</th>
<th>Output</th>
<th>Chemical reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lucherini et al. [109]</td>
<td>2019</td>
<td>Lab-scale radiator</td>
<td>30</td>
<td>Non-standard (70 kW/m²)</td>
<td>Substrate temperature</td>
<td>N/A</td>
</tr>
<tr>
<td>Tian et al. [110]</td>
<td>2018</td>
<td>Cone calorimeter</td>
<td>25</td>
<td>Non-standard (50 kW/m²)</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
<tr>
<td>Nørgaard et al. [66]</td>
<td>2016</td>
<td>Pilot Furnace</td>
<td>180</td>
<td>ISO 834</td>
<td>Intra-char temperatures</td>
<td>1, 1st order</td>
</tr>
<tr>
<td>Cirpici et al. [25]</td>
<td>2016</td>
<td>Pilot Furnace; Cone calorimeter</td>
<td>60</td>
<td>ISO 834</td>
<td>Char expansion</td>
<td>N/A</td>
</tr>
<tr>
<td>Mouritz et al. [111]</td>
<td>2013</td>
<td>Lab-scale Radiator</td>
<td>100</td>
<td>Non-standard (50 kW/m²)</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
<tr>
<td>Zhang et al. [112]</td>
<td>2012</td>
<td>Cone calorimeter</td>
<td>60</td>
<td>Non-standard (65 kW/m²)</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
<tr>
<td>Staggs et al. [113]</td>
<td>2012</td>
<td>Pilot Furnace; Mass-loss calorimeter</td>
<td>50-66</td>
<td>EN 1991-1-2(^a) Non-standard (75 kW/m²)</td>
<td>Substrate temperature</td>
<td>1, 1st order</td>
</tr>
<tr>
<td>Zhang et al. [114]</td>
<td>2012</td>
<td>Pilot Furnace</td>
<td>60</td>
<td>ISO 834</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
<tr>
<td>Staggs et al. [21]</td>
<td>2010</td>
<td>Pilot Furnace</td>
<td>60</td>
<td>EN 1991-1-2(^a)</td>
<td>Substrate temperature</td>
<td>N/A</td>
</tr>
<tr>
<td>Griffin et al. [115]</td>
<td>2009</td>
<td>Cone calorimeter</td>
<td>30</td>
<td>Non-standard (90 kW/m²)</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
<tr>
<td>Gillet et al. [116]</td>
<td>2007</td>
<td>Solar furnace</td>
<td>5</td>
<td>Non-standard (870 °C)</td>
<td>Substrate temperature</td>
<td>1, 1st order</td>
</tr>
<tr>
<td>Blasi et al. [117]</td>
<td>2001</td>
<td>Lab-scale Radiator</td>
<td>10-16</td>
<td>Non-standard (157 kW/m²)</td>
<td>Substrate temperature</td>
<td>3, 1st order</td>
</tr>
</tbody>
</table>

\(^a\) Standard hydrocarbon fire curve

Figure 2-22 shows the substrate-intumescent coating system used for model derivation.

Three states of the intumescent coating are defined: unreacted coating, reacting zone (where physical and chemical reactions occur), and char residue (relatively stable char...
after the reactions). By setting up an energy balance equation for the steel substrate, the steel temperature can be obtained with parameters of intumescent char (e.g. thermal conductivity, char expansion) and heat transfer coefficients in the system (e.g. convective heat transfer from hot gas flow to char surface). Depending on the specific model, some terms in the expression of energy balance can be neglected, for example, the terms related to convective heat transfer in the models applicable to fire-resistance tests with a cone calorimeter [118]. The parameters of an intumescent char can be determined with characterization techniques or estimated with classic models.

![Schematic illustration of substrate-intumescent coating system.](image)

In general, almost all the models for intumescent coatings are one-dimensional. The coating thickness change (i.e. char expansion and shrinkage) is assumed to be normal to the surface of a char layer. Three-dimensional models are still not mature due to insufficient knowledge of rheological dynamics during char expansion [47]. Moreover, as shown in Table 2-5, the models for the behavior of intumescent coatings in standard fires are rare due to lack of corresponding experimental data. Therefore, further work concerning mathematical models of intumescent coatings should emphasize dynamical, rheology, and chemistry aspects in the intumescent mechanism [47]. More data of
Literature review on passive fire protection with intumescent coatings

Intumescent coatings tested under standard fires (especially hydrocarbon fires) is needed to thoroughly understand intumescent behavior and thereby facilitate better assumption and creditable validation for mathematic models.

2.6 Conclusions

This chapter presents a review of intumescent coatings in the aspects of intumescent formulations, performance parameters of intumescent coatings and corresponding testing methods, properties of intumescent chars, and mathematical models for mapping intumescence mechanisms. Numerous intumescent coatings have been developed and investigated in the literature. Various functional fillers have been added to the formulations to improve fire protection performance. Nevertheless, most testing methods applied to evaluate the fire protection performance of intumescent coatings did not follow the standard fire testing curves, especially the standard hydrocarbon fire curves. This limits the understanding of effects and reaction mechanisms of coating ingredients, such as the intumescent components and functional fillers, and therefore impedes the development of intumescent formulations orientated towards special fire scenarios (e.g. hydrocarbon fires). Moreover, the lack of data on standard fire testing of intumescent coatings limits the development of mathematical models describing intumescent coating behavior.
The hydrocarbon fire risk faced by offshore industries such as gas and oil exploration calls for the development of hydrocarbon intumescent coatings. According to the literature review, the understanding of hydrocarbon intumescent coatings and the effects of various coating ingredients has been greatly limited by the lack of convenient and reliable experimental facilities for performance evaluation in laboratories. Therefore, the research presented in this project aims at developing a laboratory-scale setup that can simulate the standard hydrocarbon fire test curve UL 1709. The setup is subsequently used for mapping of the mechanisms behind the behavior of hydrocarbon intumescent coatings comprising a collection of typical intumescent ingredients (ammonium polyphosphate, melamine, epoxy resin) and functional fillers (zinc borate, calcium carbonate, titanium dioxide, and vitreous silicate fiber). The hypotheses underlying the research are summarized in this chapter.

3.1 Hypotheses related to the design of novel laboratory-scale setup

The motivation for constructing a laboratory-scale setup that can follow the standard fire test curve is that the performance of hydrocarbon intumescent coatings evaluated with a limited heating rate (cone calorimeter and radiator) or an unstable/excessive flame temperature (Bunsen burner) may remarkably differ from the industrial counterpart. Therefore, the setup developed in this project is expected to reveal the coating performance that can be correlated to those with an industrial fire test furnace. It has to be noted, however, that getting the exact same temperature response of the coated steel plates as observed for industrial fire tests is not possible and not the intention with the laboratory-scale setup. Instead, the relations between the results from the setup and the industrial furnace in the behavior of hydrocarbon intumescent coatings
and the properties of the char formed, are of interest. Therefore, the hypotheses of this part of the work are:

- The properties of the char formed are significantly influenced by the heating conditions (mainly heating rate and dwell temperature) applied to evaluate hydrocarbon intumescent coatings.

- The fire-resistance experiments performed with the laboratory-scale setup and an industrial furnace fit a correlation in terms of the thermal behavior of hydrocarbon intumescent coatings and the associated temperature response and critical times of the coated steel plates.

- The physical properties (including relative expansion and morphological structure) of the chars formed in the fire-resistance experiments using the laboratory-scale setup, are comparable to those observed in the industrial furnace tests.

- The chemical compositions of the chars formed in the laboratory-scale setup and in the industrial furnace are very similar.

3.2 Hypotheses related to the investigation of coating ingredients

The most general hypothesis regarding the ingredient studies is clearly that the target ingredient would have notable effects on the fire-resistance performance of hydrocarbon intumescent coatings (i.e. temperature responses and critical times of coated steel plates) and/or the properties of the intumescent chars. Moreover, varying the levels of different ingredients would expect different kinds and extents of influence on the coatings. The hypotheses are:

- Zinc borate: the presence of zinc borate affects a range of coating performance parameters, such as the relative expansion, the char structure, and the thermal degradation of the coating, through its reactions with other ingredients (e.g. ammonium polyphosphate), and hence influence the temperature response of the coated steel plates during fire-resistance experiments.
Hypotheses of the project

- Ammonium polyphosphate (APP): increasing the content of APP prolongs the critical times of the coated steel plate, as more substances (e.g. phosphoric acid esters and phosphates) produced from the reactions of APP increase the yield of the intumescent char.

- Melamine (MEL): increasing the content of MEL in the formulation may benefit the expansion of the coating.

- Titanium oxide (TiO$_2$): intumescent char properties, such as morphological structure and anti-oxidation, may be influenced by the reaction of TiO$_2$ with APP forming titanium phosphate.

- Calcium carbonate (CaCO$_3$): the effects of CaCO$_3$ are similar to those of TiO$_2$. Nevertheless, along with the yield of calcium phosphate, the reaction between CaCO$_3$ and APP would release CO$_2$ as well. Therefore, increasing the content of CaCO$_3$ may also benefit char expansion.

- Vitreous silicate fiber: this mineral fiber reinforces the structure of an intumescent char, through physically constructing the char layer and chemically interacting with other active ingredients (e.g. APP).

3.3 Hypotheses related to constructing correlations between performance parameters

The fire-resistance performance of an intumescent coating depends on quite a few properties of the intumescent char, such as relative expansion, morphological structure, and chemical compositions. Figuring out the coupling of these char properties is crucial in order to identify the contribution of each char parameter to the fire-resistance performance, and to give clues to optimization of intumescent coating formulations. With the aplenty data obtained from the ingredient studies, the correlations between fire-resistance performance and char properties can be explored. The hypotheses behind the exploration are:
The correlation between a single parameter (e.g. char expansion) and the fire-resistance performance (i.e. critical times of coated steel plate) is influenced by other parameters such as the morphological structure of the char.

The char properties can be combined into a single parameter, which can be correlated to the critical times of the coated steel plates.

The behavior of the intumescent coating, such as rheological aspects, controls the parameter derived from the combining of the char properties and thereby influence the critical times.
4

Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

This chapter describes the investigations on the effects of zinc borate. The content is presented with a paper published in the journal *Progress in Organic Coatings*.


Noted that the furnace used for the fire-resistance experiments in the paper is the initial version of the laboratory-scale setup developed in this project.

**Nomenclature**

- APP = ammonium polyphosphate
- MEL = melamine
- ZB = zinc borate
- EB = pure epoxy binder
- TGA = thermogravimetric analyses
- FTIR = Fourier transform infrared spectroscopy
- XRD = X-ray diffraction
- W = residual weight of a component or mixture, wt.%
- xZB = weight fraction of zinc borate in a coating, dimensionless
Abstract

Hydrocarbon intumescent coatings are an efficient means to passive fire protection of steel structures in high-risk environments such as petrochemical plants and offshore platforms. In the present study, the effects of zinc borate on the performance of hydrocarbon intumescent coatings were investigated. The analyses include steel temperature-time relationships and char expansion, as well as structural investigations and compositional profiles of the char. Furthermore, transient rheological coating behaviors and thermal degradation of the coatings were measured and analyzed. Results of furnace experiments, conducted under a standard hydrocarbon fire curve (UL1709), showed that a formulation containing 15 wt.% zinc borate gave the best performance. Fully expanded char measurements and the associated rheological recordings, evidenced that adjusting the zinc borate content from 0 to 20 wt.% increased the dynamic viscosity minimum of the incipient char from 6.2 to 5671.4 Pa·s. The increased dynamic viscosity resulted in a more uniform, but less expanded char layer. Compositional profiles of intumescent chars, measured using X-ray Diffraction, showed an increasing phosphate (especially BPO$_4$) content with increasing levels of zinc borate in the intumescent coatings. Finally, the thermogravimetric analyses revealed that zinc borate can help to reduce epoxy binder degradation and oxidation of the carbon-inorganic residue. Due to the health risks associated with borate and its compounds, there is a requirement to find alternatives. The present work has mapped out some of the beneficial properties of zinc borate, and the results may provide some insight as to how to formulate without these compounds in the future.

4.1 Introduction

Structural steel is a widely used construction material for multi-story buildings, process equipment, and offshore platforms. Though inherently non-combustible, the load bearing capability of steel decreases severely at elevated temperatures [119]; at a critical point of 500 °C, approximately 50% of the original strength is lost [7–9]. When this happens, the structure may, due to the large mass involved, collapse. An efficient way to prolong the integrity of the structural steel in the event of a fire is to apply intumescent coatings to exposed surfaces. At elevated temperatures, these type of
coatings will swell to a multicellular char layer that acts as a physical barrier, which will lower heat transfer rates and thereby prolong the time (1-3 hours) before the critical temperature of the substrate is reached [1,57]. The extended time to structure collapse will allow people longer escape time.

4.1.1 Performance requirements of intumescent coatings

Industrial fire testing of intumescent coatings employs standard fires with a preset temperature-time relationship. Depending on the source of “fuel”, most of the standard fires are classified into two types: cellulosic fire (e.g. ISO 834) and hydrocarbon fire (e.g. UL 1709). Their corresponding intumescent coatings are called cellulosic intumescent coatings (mostly acrylic types with dry film thicknesses of 0.2 - 5 mm) and hydrocarbon intumescent coatings (typically epoxy-based with dry film thickness of 2 - 40 mm). The essential parameter of the industrial fire tests is the critical temperature at which the structural steel retains 60% of its original strength [1]. For regular loaded components, such as onshore platforms, 550 °C is generally selected as the standard critical temperature, while for heavily loaded components, such as offshore platforms, a temperature of 400 °C has been selected as the standard [1,5].

The chemistry involved in industrial fire tests of intumescent coatings is interactions between the so-called intumescent ingredients, i.e. acid source, char former, and blowing agent. A typical example is a system of ammonium polyphosphate (acid source), pentaerythritol (char former), and melamine (blowing agent) [4,16,47]. In the temperature range of 180 to 280 °C, ammonium polyphosphate and its degradation products (orthophosphates, PO₄³⁻, and phosphoric acid, (HPO₃)n) react with hydroxyl groups of pentaerythritol through esterification, yielding an ester mixture [47]. At higher temperatures (280 to 350 °C), the esters are further converted into a carbonaceous mass via dehydration and carbonization. The low viscosity of the esters and the carbonaceous mass enable an expansion of the system by trapping gases released from decomposition of melamine and ammonium polyphosphate. Above 350 °C, gelation and consolidation of the expanded mixture occur, giving rise to a multicellular char with a low thermal conductivity (e.g. for an epoxy-based coating
below 0.4 W·m$^{-1}$·K$^{-1}$ [66]). At still higher temperatures, thermal degradation of the char (mainly oxidation of carbon) takes place.

### 4.1.2 Objective and strategy of the present work

This investigation deals with characterization of hydrocarbon intumescent coating chars formed according to the temperature-time curve of the UL 1709 standard, which has been widely adopted industrially for evaluating the effects of hydrocarbon-based fires in the petrochemical industry. Focus is on zinc borate, a functional filler (in this work specifically 2ZnO·3B$_2$O$_3$·3.5H$_2$O) well known in the coatings industry to have beneficial effects on the mechanical and thermal properties of intumescent coating chars. Zinc borate, for instance, can act as a flame retardant and in hydrated form it promotes the formation of a protective, cellular, and vitreous char layer. In addition, endothermic dehydration and evaporation of crystal water provide cooling effects [79]. Unfortunately, boron compounds also have some undesired effects on human health and reproduction [120], and the industry could face a ban on the use of these compounds in future years. Therefore, it is of interest to understand the mechanisms behind the positive effects of zinc borate to provide a scientific basis for the replacement of boron compounds.

The strategy of the investigation has been to evaluate the effects of zinc borate on the fire-resistance performance of selected coatings, when exposed to the fire curve UL 1709, and to characterize the chars being formed. Analyses techniques used for studying the process from virgin coatings, over melt states, to the formation of highly porous char layers are X-ray diffraction, rheology measurements, and flash-pyrolysis thermogravimetric analysis coupled with infrared spectroscopy.

### 4.1.3 Previous investigations on intumescent coatings containing functional fillers

The investigation of this work is concerned with hydrocarbon intumescent coatings and the use of zinc borate as a functional filler. Consequently, it would be relevant to focus on a discussion of past work on these coatings. However, quite often, the type of intumescent coating (cellulosic or hydrocarbon) used in an analysis is not stated directly [33,55,57,59,60,80,81,121,122]. Only in a limited number of papers (e.g. [2,20], where the effects of organoclay and expandable graphite were investigated in silicone-based
Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

binders) is it explicitly stated, that a standard hydrocarbon fire curve was followed. Therefore, this short review will include studies with a focus on the importance of filler materials, irrespective of the type of intumescent coating employed. However, it must be emphasized, that the use of a standard or standard-like fire curve can be rather critical, especially when it comes to hydrocarbon intumescent coatings. The high heating rate (more than 200 K/min) and dwelling temperature (in excess of 1100 °C) required for hydrocarbon fire curves are difficult to fulfill with regular laboratory equipment, such as Bunsen burners, gas lamps, or cone calorimeters, even though these devices are the most common alternatives for the investigation of intumescent coatings [16,70,123]. The concern is that the fire-resistance performance and the intumescent char obtained with a setup of low or uncontrollable heating rate could be dramatically changed under the severe heating conditions of a hydrocarbon fire curve [2,109,124].

Ullah and his coworkers studied the effect of fillers (e.g. kaolin, boric acid, basalt fiber, and zirconium silicate) on the thermal performance of intumescent coatings with the aid of a Bunsen burner and a Carbolite furnace (heating rate of 10-20 K/min) [33,60,70,80,81,121]. Wang et al., on the other hand, constructed a Gaslamp to evaluate the influence of epoxy binder, glass flakes, montmorillonite, and silicone emulsion, respectively, on fire protection of waterborne intumescent coatings [29,52,59,125].

Yew et al. investigated interactions between flame-retardant fillers (eggshell, Mg(OH)2, and Al(OH)3) and an intumescent coating system (ammonium polyphosphate/pentaerythritol/melamine) with a Bunsen burner [55,57]. Using thermogravimetric analyses, X-ray diffraction, and scanning electron microscopy, these investigations proved that thermal stability and char structure could be improved by adjusting the level of target filler in the intumescent formulations. For the cases of phosphate derivatives (e.g. ammonium polyphosphate) as the acid source, a probable reaction is that fillers can yield phosphates, such as zinc phosphate and boron phosphate, by consuming the acid source [47,77,122,126]. Often, these phosphates are assumed to reinforce the structure of the intumescent chars, although, due to insufficient investigations (particularly, the rheological aspect of a hydrocarbon intumescent coating), the mechanism behind the reinforcement is not fully understood. Gillani et al. [79] experimented with nano-sized zinc borate as a substitution of boric acid for thermal
degradation and gaseous products in expandable graphite-based intumescent coating systems. The heating source used was a Bunsen burner. They found that nano-size zinc borate promotes more continuous and compact char layers, less toxic gases, and that a zinc-based glassy intumescent “shield” can form that strengthens the char. It was not stated if the coating used was a hydrocarbon or cellulosic type (an epoxy binder was used, but the fire test applied, ASTM E-119, is for cellulosic coatings).

In summary, functional fillers can have a strong influence on the char formation and properties. Comprehensive investigations on the physical (e.g. char expansion and strength and rheological behavior) and chemical (e.g. thermal reactivity and anti-oxidation) properties are essential to understand the intumescent mechanisms of a hydrocarbon intumescent coating formulated with functional fillers.

**4.2 Experimental**

**4.2.1 Coating materials and application**

An intumescent coating with different contents of zinc borate was formulated with a two-component (base and curing part) epoxy system. The base part was composed of a bisphenol A epoxy resin (Hexion B.V.), a diluent (ICL-IP B.V.), and several fillers: ammonium polyphosphate (Clariant GmbH), zinc borate (Borax Ltd.), calcium carbonate (Reverté Minerales S.A.), and silicate fibers (Rockwool B.V.). For the zinc borate powder used, the maximum-, minimum-, and mean volume-based (D [4;3]) diameter was measured to respectively, 22.40, 0.40, and 9.62 µm. The curing agent was a mixture of an amide and a catalyst from Air Products B.V., formulated with melamine (OCI Nitrogen B.V.) and titanium dioxide (Huntsman Ltd.). The carbon source of the coating was the epoxy binder itself (no additional carbon source was added). The composition of the intumescent coatings used and the name assigned to the various formulations are listed in Table 4-1. To adjust the level of zinc borate, the binder content was varied accordingly. The influence introduced by the change in binder content (e.g. char expansion and thermal degradation of coating) will be taken into account later when discussing the effects of zinc borate. A high-speed disperser (800 rpm, 300 rpm after addition of fibers) was used for mixing (and dispersion) of the various ingredients. The temperature of the mixture was kept below 50 °C during dispersing.
Table 4-1 Composition of the series of intumescent coatings (in wt.%), APP = ammonium polyphosphate, MEL = melamine.

| Name | APP | MEL | CaCO₃ | Fiber | TiO₂ | Zinc borate | Epoxy binder
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB0</td>
<td>15.79</td>
<td>12.63</td>
<td>1.44</td>
<td>10.18</td>
<td>3.44</td>
<td>0.00</td>
<td>56.52</td>
</tr>
<tr>
<td>ZB5</td>
<td>15.79</td>
<td>12.63</td>
<td>1.44</td>
<td>10.18</td>
<td>3.44</td>
<td>5.00</td>
<td>51.52</td>
</tr>
<tr>
<td>ZB10</td>
<td>15.79</td>
<td>12.63</td>
<td>1.44</td>
<td>10.18</td>
<td>3.44</td>
<td>10.00</td>
<td>46.52</td>
</tr>
<tr>
<td>ZB15</td>
<td>15.79</td>
<td>12.63</td>
<td>1.44</td>
<td>10.18</td>
<td>3.44</td>
<td>15.00</td>
<td>41.52</td>
</tr>
<tr>
<td>ZB20</td>
<td>15.79</td>
<td>12.63</td>
<td>1.44</td>
<td>10.18</td>
<td>3.44</td>
<td>20.00</td>
<td>36.52</td>
</tr>
</tbody>
</table>

* Total amount of epoxy resin, diluent, amide, and catalyst.

Application of intumescent coatings was initiated by mixing two parts (base and curing agent) according to a specific amide/epoxy stoichiometric ratio of 0.867. For the furnace experiments, a coating thickness of 6 ± 0.2 mm was applied to the surface of a grit-blasted steel plate (area of 60x60 mm² and 3 mm thickness) using first a spatula and then a roller. No mesh was used to reinforce the coating. A circular PVC frame (diameter of 25 mm and 2 mm height) or a petri dish was used to cast free liquid films of the coating for rheological measurements and thermogravimetric analysis, respectively. All samples were cured for 24 h at room temperature before use.

4.2.2 Furnace experiments with standard hydrocarbon fire curve

Furnace experiments were carried out with an oven (LHT 01/17D from Nabertherm GmbH) that can simulate the temperature-time curve defined by the standard hydrocarbon fire test UL1709. In Figure 4-1a, the dashed lines are the experimental UL1709 curves mimicked by the laboratory oven, which show few differences compared with the standard UL1709 curve (solid black line). The coated steel plate, held in place with a tailor-made insulating cap (Figure 4-1b), was put inside the oven chamber during the furnace experiment. Ventilation of the chamber was controlled (on a scale from fully open to closed) by adjusting a fresh air lever, placed at the front panel of the oven. To qualitatively simulate the rather low oxygen concentration in the local gaseous environment of an industrial furnace, the lever was adjusted to an intermediate position.
A thermocouple (type K, -50 – 1200 °C) was attached to the backside of the steel plate to record its temperature versus time response. To make sure that the temperature response of the steel plate results from heat transfer through the intumescent coating only, the sides and the backside of the steel plate were insulated with cap and oven insulation material, respectively. Once the temperature of the steel plate reached 550 °C, the oven was turned off. Repeatability was assessed using a 3-fold repetition of the furnace experiments with a model intumescent coating. Results are shown in Figure 4-1a. It can be seen that the temperature-time repetition curves for the coating overlap. The relative standard deviations of the time to reach the critical temperatures (400 and 550 °C) are less than 1%. Given the good repeatability, the furnace experiments with the five target formulations were only performed twice, unless a considerable deviation was found, in which case at least three repetitions were conducted.

Figure 4-1 (a) Transient measurements of steel substrate temperatures during three repetitive furnace experiments with an intumescent coating (b) an insulating cap for support of intumescent coatings during experimentation (the grey part, barely visible in the middle is the top of an intumescent coating char after an experiment).

4.2.3 Scanning electron microscopy and digital microscopy recordings of the char structure

The morphology of char structures was analyzed with a scanning electron microscope (Inspect S, from FEI) operated at an accelerating voltage of 20 kV and a digital
Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

microscope (VHX-6000, from KEYENCE) with the lens VH-Z20T, which can magnify up to 200 times.

4.2.4 Rheological measurements of the incipient intumescent char

The dynamic viscosity (also termed the complex viscosity) of a viscoelastic material as a function of temperature was measured on a rheometer DHR-2 (TA Instruments) with a disposable parallel-plate configuration. The free circular films of intumescent coating (Ø25 mm x 2 mm height) were placed between the plates and an oscillation temperature ramp with a heating rate of 50 °C/min, a displacement of 5·10⁻⁵ rad (5·10⁻³ rad for low viscous phases), and a frequency of 5 Hz was applied for measurements from 30 to 600 °C. A low axial force adjustment (0±0.1 N) was activated so that the gap between the plates was continuously adjusted to accommodate the intumescence (expansion) during heating.

4.2.5 Crystalline phases of the intumescent char identified with X-ray diffraction

The Crystalline phases of the intumescent coating chars, produced in the furnace experiments, were identified on a Huber G670 powder diffractometer with CuK(α)1 radiation (λ=1.54058 Å, 40keV, 40mA) using a focusing primary monochromator, in transmission mode in the range 3 to 100 degrees in 2(θ) for 30 minutes.

4.2.6 Thermal reactivity of formulations

Thermogravimetric analyses of the hydrocarbon intumescent coatings were performed at 213 °C/min in a flow of N₂ (79 mL/min, purity grade 5) and O₂ (21 mL/min, purity grade 5), using a Netzsch Jupiter F1 STA coupled with a Fourier transform infrared spectroscopy (FTIR). The powdery samples (approximately 45 mg), ground from the free films of the intumescent coatings, were put in alumina crucibles and heated from room temperature to 1000 °C. Gases released during heating were transported to the FTIR chamber and detected according to the absorption of the FTIR beam (650 - 4200 cm⁻¹). The temperature of the absorption chamber was kept at 200 °C.
To assess the interactions between zinc borate and other ingredients in the formulations, the “theoretical” residual weight ($W_{\text{theo}}$, in the unit of wt.%) after exposure at the specific heating rate (213 °C/min) was calculated using equation (Eq. 4-1).

$$W_{\text{theo}}(T) = W_{ZB0}(T) + x_{ZB}[W_{ZB}(T) - W_{EB}(T)]$$  \hspace{1cm} (Eq. 4-1)

Here, $W_i$ is the residual weight of substance $i$ (unit is wt.%), $i = ZB0$ (coating ZB0), ZB (pure zinc borate), or EB (pure epoxy binder); $x_{ZB}$ is the weight fraction of zinc borate in the target coating. The second term on the right-hand side of eq (1) accounts for zinc borate replacement of binder in the formulations containing zinc borate.

The theoretical residual weight represents the case when zinc borate does not interact with other coating ingredients. $W_{ZB}$ and $W_{EB}$ can be read from separate mass loss curves of pure zinc borate and pure epoxy binder. Considering the possible interactions between the epoxy binder and other ingredients in the formulation ZB0, two boundary conditions (maximum and minimum decomposition of the epoxy binder in ZB0) were calculated and used as the deviation from the theoretical residual weight.

4.3 Results and discussion

4.3.1 Effects of zinc borate on the performance of hydrocarbon intumescent formulations

4.3.1.1 Fire-resistance performance

The temperature versus time curves obtained from the furnace experiments are shown in Figure 4-2a. For the sake of clarity, results from duplicated experiments are not provided (repeatability of the curves is excellent, as shown in Figure 4-1a). Exposure times to reach critical temperatures (400 and 550 °C) are provided in Figure 4-2b. The critical times are averages (± standard deviation) of the repetitive furnace experiments.
Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

Figure 4-2 (a) Temperature versus time curves for the intumescent coatings (ZB = zinc borate). The response of the uncoated steel plate is included for comparison. (b) Average exposure times to reach critical temperature of steel substrate (based on repeated furnace experiments). Error bars correspond to the standard deviation.

The bare steel plate reaches its critical temperature within only 7.5 minutes. When intumescent coatings were applied, this time was observed to exceed 30 minutes (550 °C). All coatings showed almost the same temperature-time response from 0 to 20 mins, except for the formulation with a very high concentration of zinc borate (20 wt.%, ZB20). Thereafter, the curves diverged leading to differences in critical times. The critical times presented in Figure 4-2b represent the fire-resistance performance of the coatings. The best performing formulation is ZB15 (15 wt.% zinc borate), which has the longest critical time for both 400 and 550 °C, while the worst performance changed from ZB0 to ZB5 when the critical temperature increased from 400 to 550 °C. The trends in Figure 4-2b clearly demonstrate that zinc borate can improve the fire-resistance performance of hydrocarbon intumescent coatings, even though the absolute difference between the critical times of the formulations is surprisingly small.

The degree of expansion of the intumescent chars was estimated by averaging the height measurements of the (cooled) chars produced from the repetitive furnace experiments. The results are plotted in Figure 4-3, which shows that the expansion of the chars is dramatically constrained with zinc borate in the formulation. According to the work of Canosa et al. [61], the level of expansion is directly proportional to the pigment volume concentration, or, equivalently, the binder content. However, the disproportional change seen in Figure 4-3 points to a more active role of zinc borate in
limiting the char expansion because the level of zinc borate was adjusted in the formulations by a proportional reduction of the binder content.

Figure 4-3 Coating char expansions (measured at room temperature) relative to the initial coating thickness as a function of zinc borate in the coatings. Error bars represent the standard deviation.

It can be seen, from a comparison of Figure 4-2 and Figure 4-3, that the higher expanded chars did not bring a better fire-resistance protection of the substrate. The reason for this is that the chars with high expansions may suffer from an inferior internal structure. For instance, a soft and fragile char with defects (e.g. delamination) can compromise the thermal heat conductivity [3].

Figure 4-4 and Figure 4-5 show the physical appearance and inner structure of the fully expanded intumescent coating chars.
Figure 4-4 Top line: intumescent coatings (in the form of char) after furnace experiments; Bottom line: corresponding cross-sections of the chars (after use of a scalpel) with the big voids (width >5 mm) highlighted in red. The blue squares indicate the approximate positions where the corresponding SEM images (shown in Figure 4-5) were recorded.
Figure 4-5 SEM images of the inner char structures: (a) ZB0, (b) ZB10, and (c) ZB20. Note that the magnifications in the left-hand images are not the same.

The fluffy char with a thin-film structure seen for formulation ZB0, cannot provide sufficient protection, regardless of this char having the highest degree of expansion. This undesirable structure is improved with zinc borate in the coatings. Specifically, zinc borate results in more uniform chars with less and smaller voids (cells) as seen in...
Figure 4-4 and 4-5. Overall, with increasing levels of zinc borate, the images in Figure 4-5 show a transition from filaments, to a foam-like structure, to a dense phase. The dense structure is optimal with respect to insulation properties of the char. The char ZB0 has a distinct light-yellow layer in the top structure, which is a typical result of oxidation of the intumescent char. It suggests that zinc borate may also play a role in reducing char oxidation. This observation is further discussed in the section on thermogravimetric analyses.

In spite of the benefits, a high level of zinc borate in the hydrocarbon intumescent formulation can introduce delamination and cracks in the char structure. The former was found in the case of ZB15 and ZB20 (top part of the shell in Figure 4-4). The partly detached upper part of char ZB15 was connected with the rest of the char structure after the furnace experiments, its damaged structure only became visible when the char was cross-sectioned. The char ZB20, on the other hand, presents a delaminated shell that is completely detached from the rest of the char. Moreover, the char ZB20 shows cracks on the surface below the detached shell.

The positive (e.g. homogenizing the char structure) and negative (e.g. limited char expansion and introducing cracks) effects of increasing zinc borate content in the hydrocarbon intumescent coatings may be the cause of the threshold value (15 wt.% zinc borate) of the fire-resistance performance presented in Figure 4-2.

**4.3.1.2 Viscoelastic behavior of incipient chars**

Structure and apparent expansion of chars are closely related to rheological properties of the intumescent coatings. Figure 4-6a shows the dynamic viscosity of the intumescent coatings as a function of temperature.
All formulations show a similar dynamic viscosity change that can be roughly divided into three stages. The first stage lasts until a temperature of around 235 °C, characterized by a small peak in the dynamic viscosity before 100 °C and a subsequent moderate growth. The dynamic viscosity change during this stage mainly results from the temperature dependence and crosslinking reactions of the thermoset epoxy [127].

The second stage refers to the dynamic viscosity drop during the temperature change from 235 to 375 °C, taking the coating to a dynamic viscosity minimum. The subsequent rise in dynamic viscosity pushes the coating into the third stage.

In summary, the three stages correspond to crosslinking, melting (viscoelastic substance), and charring. Figure 4-6b shows the gap change of the parallel-plate configuration during the dynamic viscosity measurement. Owing to the axial force
adjustment of the rheometer, the gap varies with the expansion of the intumescent coating. The obvious increase of the gap (i.e. the expansion of the coating) was observed during the temperature range of 235 to 375 °C for all the formulations, which matches the temperature range for the second stage in Figure 4-6a. This result supports the conclusion reported by Jimenez et al. [3]; that a positive correlation exists between the dynamic viscosity of the viscoelastic material (i.e. the second stage) and the expansion of hydrocarbon intumescent coatings.

In Figure 4-6a, the second stage shows that the extent of dynamic viscosity drop was reduced with increasing levels of zinc borate in the formulations. The changes in the dynamic viscosity of the viscoelastic substance coincide with the results of the char expansion discussed in section 4.3.1.1. The highest expansion after the furnace experiment was obtained with the formulation ZB0, which formed the viscoelastic substance with the lowest dynamic viscosity minimum (6.2 Pa·s) at the end of the second stage. The highest dynamic viscosity minimum (5671.4 Pa·s) is in the case with the highest amount of zinc borate (ZB20), which corresponds to the lowest char expansion after the furnace experiments.

The mechanism behind the correlation of the dynamic viscosity minimum and the char expansion can be explained by the diffusion of the gases in the incipient char. To get an appropriate multicellular char, the gases released from the intumescent ingredients (mainly blowing agent) need to be trapped and subsequently diffuse slowly in the viscoelastic material [3]. For the coating without zinc borate (ZB0), the dynamic viscosity during this stage is too low to ensure proper entrapment of gases in the matrix and a high expansion with large voids is expected. If the dynamic viscosity is increased by enhancing the amount of zinc borate in the formulation, the viscoelastic material is able to accommodate the pressure from the evolving gas, and to create a more uniform and firm char. However, if the dynamic viscosity is too high, the viscoelastic mass will slow down gas evolution and limit diffusion, leading to a rigid and thin layer with a high level of internal stress. In this case, cracks easily form and propagate [3], which explains the inferior structure (cracks and delamination) in the char ZB20.
4.3.1.3 Chemical composition profiles of intumescent chars

The chemical composition of the intumescent chars produced from the furnace experiments was analyzed with depth profiles using X-ray diffraction (XRD). To enable this, the chars were divided into three zones, based on color and structure, as shown in Figure 4-7 for the cross-section of ZB15.

![Cross-section view of three-layer structure in intumescent coating char](image)

Figure 4-7 Cross-section view of three-layer structure in intumescent coating char (ZB15 from the furnace experiment as an example).

The crystal phases identified in each layer of the chars are presented in Figure 4-8. For ZB0, the main characteristic peaks are AlPO$_4$ and Ti$_4$P$_6$O$_{23}$ (top and middle and top) and TiO$_2$ (bottom). For the formulations with zinc borate, on the other hand, the main crystal phases identified in the layers change from Ti$_4$P$_6$O$_{23}$ (top), to BPO$_4$ and Ti$_4$P$_6$O$_{23}$ (middle), and to TiO$_2$ and BPO$_4$ (bottom). The composition change from top to bottom layers is probably related to the temperature gradient inside the char during the furnace experiment. The higher temperatures of the top layers increase reaction rates and allow an earlier conversion of reactants into products, thereby resulting in peak diminishment (e.g. TiO$_2$ and BPO$_4$) and peak growth (e.g. Ti$_4$P$_6$O$_{23}$ and AlPO$_4$).
Figure 4-8 XRD patterns of the three layers (see Figure 4-7) of the intumescent chars ZB0 - ZB20.
The difference of the compositions between the formulations is revealed by comparing the patterns of the same layer. With the introduction of zinc borate, the main crystal phase of the char is changed from Ti$_4$P$_6$O$_{23}$ to Ti$_4$P$_6$O$_{23}$ and BPO$_4$, especially in the middle layers. The intensity of the characteristic peak of BPO$_4$ ($2\theta=40.0^\circ$) and Ti$_4$P$_6$O$_{23}$ ($2\theta=32.4^\circ$) are enhanced with increasing contents of zinc borate. It suggests that high levels of zinc borate cannot only facilitate the formation of BPO$_4$, but may also enhance the conversion of TiO$_2$ into Ti$_4$P$_6$O$_{23}$. This may be explained by interactions between TiO$_2$ and ZnO, the latter being a product of zinc borate. Upon heating, the TiO$_2$-ZnO system can form non-stable compounds like Zn$_2$Ti$_3$O$_8$ [128]. These compounds may serve as intermediates in the conversion of TiO$_2$ to Ti$_4$P$_6$O$_{23}$, providing a reaction path with a lower energy barrier. The inorganic layer (e.g. BPO$_4$ and Ti$_4$P$_6$O$_{23}$) of chars contributes to improved mechanical properties and better resistance to thermal radiation and oxidation [47,126].

Considering the fact that BPO$_4$ is dominant in the bottom layers of the char, it can be speculated that the reaction between zinc borate and polyphosphoric acid may start at a lower temperature, at least lower than the formation temperature of Ti$_4$P$_6$O$_{23}$, which is rich in the top layers. Bourbigot et al. [84] reported that zinc borate reacts with the degradation products of APP between 300 and 415 °C, which falls into the temperature range of the melting stage (expansion region) in Figure 4-6. With increased zinc borate contents, a larger fraction of liquid polyphosphoric acids is converted into crystalline BPO$_4$. The increased yield of BPO$_4$ gives a more solid-like char during the melting stage and may, therefore, contribute to a smaller drop in dynamic viscosity as seen in Figure 4-6.

The positive effect on the yield of the crystal phases BPO$_4$ and Ti$_4$P$_6$O$_{23}$ was reduced when the content of zinc borate was increased to 20 wt.% (ZB20). Instead of forming more crystal phases, the evident broad peak between $2\theta=13.0^\circ$ and $2\theta=25.0^\circ$ in the patterns of ZB20 (especially in its middle and top layers) indicates that the formulation ZB20 yielded a considerable amount of amorphous phases in the char. This inference agrees with the observation of an abundance of non-porous glass-like spheres on the surface of the ZB20 char, which was barely seen on the surface of the other chars, e.g. ZB15 (Figure 4-9). The composition of these amorphous phases is not clear yet, but
they may be formed from phosphates such as BPO$_4$, Ti$_4$P$_6$O$_{23}$, and Zn$_3$(PO$_4$)$_2$. This is in agreement with results of Bourbigot et al. [84], who found a yield of amorphous B$_2$O$_3$ due to a reaction between BPO$_4$ and Zn$_3$(PO$_4$)$_2$. In fact, they used this reaction to explain the disappearance of BPO$_4$ during the high-temperature treatment (800 °C for 3 h in air) of APP and zinc borate. According to our XRD results, the disappearance of BPO$_4$ is also found in the patterns of the top layers (high-temperature region of the char), which may therefore also be attributed to this reaction.

![Digital microscopy images of the outer surface of the chars formed from ZB20 and ZB15 coatings.](image)

**4.3.1.4 Thermal degradation of the formulations**

The thermal degradation of the formulations and the reactivity between ingredients were evaluated by thermogravimetric analyses coupled with gas detection using a Fourier transform infrared spectroscopy (TGA-FTIR). The mass loss and its first derivative with respect to time are plotted in Figure 4-10 as a function of temperature.
The residual weights of the coatings increased from 24.59 (ZB0) to 45.58 wt.% (ZB20) by raising the level of zinc borate in the formulation. Three peaks are identified in the curves of the mass loss rate. The first one started around 200 °C and can be assigned to the decomposition of the epoxy, yielding mainly CO\textsubscript{2}, H\textsubscript{2}O, and aromatic species [129,130]. The second, with its maximum located at 380 °C, is the most significant and complicated one, as the main reactions of intumescence are taking place in this range. According to the results of the thermogravimetric analyses on the individual ingredients (not shown here for brevity) and literature data [131,132], the decompositions of APP and MEL start around 300 °C. The polyphosphoric acid derived from APP can thereby react with the epoxy binder (and its derivatives), which are rich in hydroxyl groups (-OH), via esterification. Zinc borate, TiO\textsubscript{2}, and CaCO\textsubscript{3}, at these temperatures, are available for reaction with the phosphoric acid as well [26,84]. The ammonia decomposed from APP and MEL is trapped and can diffuse to expand the material. The
Effects of zinc borate on the properties of hydrocarbon intumescent coating chars

third peak in Figure 4-10b is quite typical for the gradual oxidation of the intumescent char. The appearance change of a char from black to light grey (e.g. ZB0) usually occurs at this stage depending on how prone the coating is to oxidation.

The increased residual weight from formulation ZB0 to ZB20 can be attributed to the interaction between zinc borate and other ingredients, which might retain more substances in the residual char by exhibiting a stabilization behavior on the degradation of the coating (e.g. decomposition of the epoxy binder or oxidation of the char). The stabilization behavior is clear in Figure 4-11 by comparing the actual residual weights and the theoretical residual weights of a formulation with zinc borate at 310, 600, and 1000 °C. The temperatures selected, agree with the position of the ends of the peaks in Figure 4-10b.

![Figure 4-11 Comparison of actual (black solid points) and theoretical residual weights (red hollow points) of the coatings with zinc borate at 310, 600, and 1000 °C.](image)

Compared with the theoretical value, all the formulations with zinc borate show an increased residual weight at 310 °C. The biggest improvement is found in the formulation ZB15, which corresponds to the most effective coating for stabilizing the epoxy in the early stage of thermal degradation. The stabilizing behavior becomes,
however, less conspicuous at 600 °C, except for the case of ZB5. At 1000 °C, the notable difference appears between the actual and the theoretical residual weights of the formulations. Due to the reactions between 600 and 1000 °C being assigned to oxidation of the chars, the increased difference from 600 to 1000 °C may demonstrate the positive effect of zinc borate on the anti-oxidation of the chars. The anti-oxidation property is rooted in the chemical compositions of the intumescent chars. According to the results of X-ray diffraction (Section 4.3.1.3), the increased yield of BPO$_4$ and Ti$_4$P$_6$O$_{23}$, caused by formulating with more zinc borate in the coating, were found. These phosphates, converted by consuming (poly)-phosphoric acids that can sublimate through dehydration to P$_4$O$_{10}$ higher than around 600 °C, are thermally stable and can resist the high temperature of a hydrocarbon fire. Therefore, the increased yield of phosphates may contribute to the anti-oxidation of the chars by serving as the inorganic layers with the function of limiting oxygen diffusion inside the char [81]. Besides, more phosphate radicals retained by BPO$_4$ and Ti$_4$P$_6$O$_{23}$ also favor the increment of the final residual weights.

The gas evolution during the thermogravimetric analyses was monitored by the TGA-FTIR. The absorbance spectrum of the volatiles (in the form of a gas at 200 °C) was collected continuously and the main characteristic peaks observed on the spectra corresponds to NH$_3$ (800cm$^{-1}$-1100cm$^{-1}$), CO$_2$ (2200cm$^{-1}$-2400cm$^{-1}$), and some aromatic species (1100cm$^{-1}$-1700cm$^{-1}$, 2800cm$^{-1}$-3200cm$^{-1}$). The absorbance (the area of characteristic peak) of NH$_3$ and CO$_2$ for the formulations are illustrated in Figure 4-12a and Figure 4-12b as a function of temperature.
The NH$_3$ absorbance appeared at around 300 °C for the formulations in Figure 4-12a. It coincides with the temperature at which APP and MEL initiate decomposition and releasing of NH$_3$. The decreased NH$_3$ absorbance is seen when increasing the level of zinc borate, especially from ZB10 to ZB15. It probably results from the high load of zinc borate, which constrained the decomposition of APP, MEL, or the amide group of the cured epoxy, as these are the sources of NH$_3$ reported in the literature [47,133]. In Figure 4-12b, the absorbance of CO$_2$ is observed at almost the same temperature as the decomposition of epoxy started in Figure 4-10. All formulations presented a similar evolution of CO$_2$ until the temperature reached about 600 °C. The CO$_2$ absorbance after 600 °C dwindles significantly as a function of zinc borate content, which supports the statement regarding the effect of zinc borate on improving the anti-oxidation of the chars.

With respect to aromatic species, the characteristic peak area is too complex to be determined by the FTIR software. Therefore, the evolution of the aromatic species is merely presented in Figure 4-13 by the spectrum of a formulation that showed the strongest absorbance signal of the phenolic group.
The characteristic peaks of the aromatic species diminish with the increased content of zinc borate and nearly disappear when it comes to ZB15. According to the results in Figure 4-11 at 310 °C, zinc borate shows a stabilization behavior on the thermal degradation of the epoxy binder. With reduced polymer degradation, the release of the low-molecular-weight aromatic species (derived from the epoxy binder) is expected to decrease. The interaction between zinc borate and the epoxy binder is probably, as mentioned elsewhere, that boron compounds can minimize the polymer decomposition and the evolution of the volatiles by promoting crosslinking of the polymeric materials [81,134]. It is noted that this interaction might also support the reduced dynamic viscosity drop during the melting stage of the formulations and improve the anti-oxidation of the intumescent chars, as more cross-linked polymer materials usually bring increased dynamic viscosity and enhance the ability to resist oxidation [135].

4.3.2 Clues to alternatives to zinc borate

Overall, zinc borate influences almost all the relevant physical (expansion, viscosity) and chemical (char composition, thermal degradation) properties of the intumescent...
coatings. This complex effect gives improved fire-resistance performance when increasing the level of zinc borate in the formulation up to 15 wt.%, even though the absolute difference between the critical times is small. Among these, the most prominent role of zinc borate is that it can significantly change the morphological structure of the intumescent char. The fluffy and soft char, formed with the zinc borate-free formulation, not only disfavors the heat shielding (as shown in Figure 4-2) but more importantly also cannot resist the turbulent flame of a hydrocarbon fire or even gravitational force. The risk of the latter is not evaluated with our furnace experiments, as the coatings were exposed horizontally with static-electrical heating. However, a partial or complete detachment of the intumescent char from the substrate is expected in an industrial hydrocarbon fire test due to the inferior structure, leading to loss of the fire-protection role of the char. Therefore, it is clear that the effect of zinc borate on improving the char structure is important for intumescent coatings exposed to a hydrocarbon fire scenario, even though the introduction of zinc borate limits the char expansion.

Nevertheless, the positive effects of zinc borate on making a uniform char structure should be the paramount factor taken into account when seeking an alternative to zinc borate. In other words, the alternative is expected to show at least the comparable behavior on improving the char structure. It would be better if the alternative can present less impact on char expansion. Instead of checking many formulations with time-consuming fire tests, the strong correlation between the char structure and the rheological properties suggests an easier way to predict the effect of an alternative chemical on the char structure by looking into the dynamic viscosity drop during the melting stage (expansion region) of an intumescent coating. According to the studies on the chemical composition of the chars and the thermal reactivity of the formulations, the effect of zinc borate on reducing the dynamic viscosity drop might relate to the increased yield of BPO$_4$ and a stabilization behavior in the decomposition of the epoxy binder. The formation of BPO$_4$, on the one hand, starts at the melting stage of the coatings and takes an active role in changing the dynamic viscosity drop of the incipient char. On the other hand, BPO$_4$ is quite stable even at a temperature higher than 1200 °C [80], which can effectively retain phosphorous oxide and serve as the protection
layer for anti-oxidation. With respect to the stabilization behavior of zinc borate in the decomposition of the epoxy binder, it was not fully investigated in this work how zinc borate affects polymer degradation. According to earlier work [81,134], most boron complexes are Lewis acids and can promote crosslinking reactions and minimize decomposition of polymeric materials.

4.4 Conclusions

Zinc borate has been investigated with respect to its effect on the performance of the hydrocarbon intumescent coatings. Furnace experiments, according to the UL1709 curve, were carried out to assess the fire-resistance performance of the coatings with different levels of zinc borate. The use of 15 wt.% zinc borate in the coating was the most efficient formulation, with the longest critical time for both 400 and 550 °C. The chars produced from the furnace experiments show that zinc borate can lower the cell (void) size and promote a uniform char structure even though a high char expansion is sacrificed. The effect of zinc borate on the char structure and the char expansion can be explained by the dynamic viscosity change during the intumescent process. Increasing the zinc borate content, significantly increases the dynamic viscosity of the viscoelastic material that forms during the expansion. A moderate dynamic viscosity can accommodate the pressure from the evolving gas and create a more homogeneous and firm char. However, excessively high viscosities may lead to a rigid char with defects such as cracks and delamination. X-ray diffraction studies of char layers demonstrated increased yields of phosphates (especially BPO₄) as the level of zinc borate rises in the formulation. The thermogravimetric analyses and the gas evolution during the degradation of the coatings suggest that zinc borate can improve the residual weight of the char by stabilizing the epoxy binder and improving the anti-oxidation property. The effect of zinc borate on the yield of BPO₄ and on reducing the thermal degradation of the coatings is related to the increased dynamic viscosity of the formulations during the melting stage (expansion region).
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

The modified laboratory-scale setup and the discussion on its reliability are presented in this chapter. It is written in a manuscript format and to be submitted to a peer-reviewed journal. The authors to be included in the manuscript are Ying Zeng, Claus Erik Weinell, Kim Dam-Johansen, Louise Ring, and Søren Kiil.

Nomenclature

\[
\text{XRD} \quad = \quad \text{X-ray diffraction}
\]

Abstract

Due to increasing demands for fire protection in high-risk environments, such as petrochemical processes and offshore platforms, so-called hydrocarbon intumescent coatings are increasingly used to protect structural steel in the event of a hydrocarbon fire. For these coatings, the fire-resistance performance is typically evaluated in a series of costly experiments with industrial-scale (i.e. 1-10 m$^3$) furnaces, programmed to follow a standard hydrocarbon fire test curve. In the present work, we propose a laboratory-scale furnace for coating evaluation, which can simulate the conditions of a typical hydrocarbon fire curve, i.e. the standard UL1709. In a case study with five hydrocarbon intumescent coating formulations, the correlation between the laboratory- and the industrial-scale furnace was investigated and a good agreement was found for
the temperature progression of the coated steel plates. The physical and chemical properties of the intumescent coating chars were also similar for the two furnaces. In summary, the low-cost, time-efficient laboratory-scale furnace can provide reliable screening of hydrocarbon intumescent coatings, and is recommended as a complementary tool for industrial fire tests.

5.1 Introduction

In the event of a fire in buildings, infrastructure (e.g. airports or skyscrapers) or at onshore or offshore oil rigs, the temperature of unprotected steel constructions may rapidly reach a critical value (around 500 °C), where the probability of equipment or building collapse becomes prohibitively high. To avoid such incidents, so-called intumescent coatings can be used as passive fire protection of the steel structures [4]. Under the influence of heat, an intumescent coating, swells to up to 100 times its original thickness and forms a multicellular char layer [4,91,136]. The high degree of expansion and the low-density structure make the char layer an insulating barrier that can prolong the time (1-3 h) for safe evacuation of people [1].

A real fire has a rather complex temperature-time response; it depends on the structure dimensions, the amount and type of combustible materials, and the air available for combustion [11]. On the other hand, to simulate the evolution of realistic fires and meanwhile, unify the fire test procedures for different experimental facilities and conditions, standard fire test curves with fixed temperature-time responses have been defined [5]. Depending on the primary “fuel” for the anticipated fire scenario, standard fire test curves are divided into a cellulose (e.g. ISO 834) and a hydrocarbon (e.g. UL 1709 and BS 476) temperature-time relationship. In Figure 5-1, three such examples, of which further details can be found elsewhere [1,4], are provided. In general, the transient temperature rises of the hydrocarbon curves are much faster than those of the cellulose type (Figure 5-1).

The essential parameter of industrial fire tests is the critical temperature at which the structural steel retains only 60% of its original strength [1]. For regular loaded components, such as onshore platforms, a temperature of 550 °C is generally selected as the standard critical temperature, while for heavily loaded components in high-risk
environments, such as petrochemical complexes and offshore platforms, a temperature of 400 °C is normally selected as the standard [1,5]. In accordance with the classification of the standard fire test curves, intumescent coatings are grouped into cellulosic- and hydrocarbon intumescent coatings. The former is typically a water- or solvent-based acrylic coating with a dry film thickness of 0.2 - 5 mm, while a two-component (solvent-free) epoxy system, that permits a film build of 2 - 40 mm, is particularly suitable for intumescent coatings for hydrocarbon fires.

Industrial fire tests, which are required for third-party approval, are costly to perform and have significant footprints when installed in-house [1,91,137,138]. Moreover, the coating application is labor-intensive (typically four coated steel plates are required for a single experiment) and the testing itself, due to hour-long cooling times of the furnaces, is time-consuming. In addition, the repeatability of the results is often rather...
poor [1,91]. As a consequence, accelerated methods are needed for screening of intumescent coatings and for this engineers and scientists use devices like the Bunsen burner [42,81,87], the Gaslamp [59], and the cone calorimeter [71,110,139]. However, a serious limitation of these devices, due mainly to the limited heating rate (cone calorimeter and radiator) or the unstable/excessive flame temperature (Bunsen burner), is that they cannot meet the requirements of the heating curves defined in the standards (Figure 5-1). This is a challenge for hydrocarbon intumescent coatings in particular. Moreover, the coated steel plates used in these testing devices often have insufficient or no insulation at all for the sides, allowing heat to dissipate to the surroundings [42,58,59,81,87,139]. The intumescent coating chars formed under the lower heating rates and temperatures may exhibit incomparable morphological structures and chemical compositions, as well as uncorrelated fire-resistance performance [89,90,140]. The design and construction of reliable laboratory-scale furnaces, which can meet the standard fire curves and thereby boost the development of intumescent coatings, such as the rapid screening of formulations and the mapping of the underlying mechanisms, are therefore highly needed.

Several research groups have designed novel testing methods to replace the industrial cellulosic fire tests [1,82,83,91,92]. For instance, for simulation of the standard cellulosic test curve ISO 834, a Heat-Transfer Rate Inducing System (H-TRIS) was developed by Elliott et al. [91,138] and Mariappan et al. [83] developed a bench-scale furnace. However, the hydrocarbon testing curve, which exhibits a high heating rate (more than 200 K/min) to a temperature in excess of 1100 °C, is still a great challenge for laboratory-scale ovens. As an example, the heating curve for the H-TRIS, due to the limited maximum incident heat flux of the radiant heaters in the system, deviates significantly from the desired temperature-time relationship [91]. Only in the investigations conducted by the group of Bourbigot were it specified that the lab-scale fire-resistance experiments met the requirements of the UL1709 curve [2,20,82,89,99,105]. However, none of these works included validating comparisons with industrial fire tests.

In the present work, a laboratory-scale furnace, which can assess the efficiency of intumescent coatings exposed to a standard hydrocarbon fire curve, is presented. To
validate that the furnace allows for a representative approach, fire-resistance experiments (including char expansion) with the setup were carried out and the results, including the physical and chemical properties of the chars formed, were compared to those of an industrial furnace.

5.2 Experimental

5.2.1 Coating materials and application

Five hydrocarbon intumescent coating formulations (F1 – F5) were used in the fire-resistance experiments. The ingredients of the two-component formulations can be found in our previous work [141] and, for the sake of brevity, the details regarding the compositions are not provided as they are not necessary for discussion. The coating application was initiated by mixing binder and curing agent according to an amide/epoxy functional group stoichiometric ratio of 0.867. The coating thickness was targeted to 6 ± 0.2 mm and the substrate used was a grit-blasted steel plate (area of 60x60 mm² and 3 mm thickness for the laboratory-scale fire-resistance experiments; area of 200x300 mm² and 5 mm thickness for the industrial fire tests). Plates of 5 mm thickness are the standard for the industrial fire tests, while the dimension of the steel plates for the laboratory-scale furnace experiments has to be fixed to precisely match with a tailor-cut insulation material (described in the section below). To benefit a long-term investigation with the laboratory-scale furnace and allow comparison with earlier laboratory work (e.g. refs [2,77,89,142]), the most common and accessible steel plate thickness, i.e. 3 mm, was selected. No mesh was used to reinforce the coatings. All samples were cured for 24 h at room temperature before use.

5.2.2 Fire-resistance experiments

Fire-resistance experiments were performed with a laboratory-scale furnace (in the following referred to as “laboratory-scale fire-resistance experiments”) and an industrial-scale furnace (termed “industrial fire tests” in what follows). Although the use of the same hydrocarbon fire curve would be beneficial for a direct comparison, the laboratory-scale fire-resistance experiments and the industrial fire tests were conducted
with two different standards (UL1709 and BS476, respectively) due to the limitations of the setups. The industrial furnace was not capable of following the temperature-time profile of UL1709, while the laboratory-scale furnace could not tackle the rapid temperature rise (more than 700 °C/min) during the first minute of the BS476 curve. Considering that both standards are industrially-recognized for evaluating the effects of hydrocarbon fires, it was therefore assumed that the performance of hydrocarbon intumescent coatings is comparable when exposed to the two fire curves. Such an approach was also used by Jimenez et al. [1], who disregarded the difference between the targeted curve (UL1709) and the experimental curve (similar to BS476) performed with a gas-fueled bench-scale furnace.

5.2.2.1 Laboratory-scale furnace
A compact furnace (LHT 01/17D from Nabertherm GmbH), modified with an opening in the furnace door for installation of samples, was used to perform the laboratory-scale fire-resistance experiments. A photo and a schematic diagram of the modified furnace are shown in Figure 5-2. Prior to an experiment, a coated steel plate is mounted vertically with a tailor-cut insulation material (50 mm) between the plate backside and the accessories that immobilize the coating and the insulation material in the furnace door opening. This particular arrangement ensures that the sample is well insulated on its unexposed surfaces. The temperature rise of the furnace was measured by a B-type thermocouple (labeled as 2 in Figure 5-2b) and simulated the temperature-time curve as defined by the UL1709 standard. The temperature-time response of the steel plate was recorded by a copper-disk thermocouple (K-type, 0 – 700 °C) attached to the central area of the non-coated backside of the steel plate. Once the temperature of the steel plate reached 550 °C, the furnace heating was turned off, the transient experiment thereby covering both of the critical temperatures, 400 and 550 °C. For each of the five hydrocarbon intumescent coating formulations (F1 – F5), a repetition of the laboratory-scale fire-resistance experiment was performed.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

Figure 5-2 (a) Laboratory-scale furnace for fire-resistance experiments and (b) Schematic diagram of the furnace (seen from above): 1. heating elements of the furnace; 2. thermocouple wrapped with ceramic cap (for monitoring the gas temperature of the furnace chamber without influence of radiation); 3. built-in insulation material of the furnace; 4. tailor-cut insulation material (VIP12-HT from Skamol A/S); 5. the intumescent coating; 6. the steel plate; 7. contact point of a copper-disk thermocouple (for measuring the steel temperature); 8. metal accessories for immobilization of samples.

5.2.2.2 Industrial fire tests

Industrial fire tests were performed according to the BS476 hydrocarbon fire standard. The furnace applied has a chamber volume of 7.5 m$^3$ and the furnace door is equipped with four wall penetrations (200 x 300 cm) (Figure 5-3, right). Covering each penetration is a steel plate with intumescent coating, the coating facing the furnace chamber. Two copper-disk thermocouples (K-type, 0 – 700 °C) were attached to the non-coated side of the plate. For insulation of the backside of the steel plate, a fiber blanket (around 5 cm in thickness) was used, and fixation of a sample in the door was secured with a support panel and tools as shown in Figure 5-3 (right). Four plates at a time were used for experimentation. The temperature-time response of each plate was the average recorded by the two thermocouples attached (the maximum deviation at any time was less than 30 °C). Once the temperature of all four plates reached 550 °C, the furnace was shut down. To evaluate the uncertainties involved, the industrial fire tests of each hydrocarbon intumescent coating were repeated four times.
Figure 5-3 The industrial gas-fired furnace (left) and the outside of the furnace door (right). The steel panels with fixation tools, seen on the right, are not the actual coated steel plates, but merely support panels for the coated steel plates and backside insulation material placed in the door penetrations. The white material framing the support panels is insulation material (fiber blanket).

5.2.3 Thermal degradation of hydrocarbon intumescent coatings

Thermogravimetric analyses of the hydrocarbon intumescent coatings were performed at 213 °C/min or 21 °C/min in a flow of N\textsubscript{2} (79 mL/min, purity grade 5) and O\textsubscript{2} (21 mL/min, purity grade 5), using a Netzsch Jupiter F1 STA. The powdery samples (approximately 45 mg), ground from the free films of the intumescent coatings, were put in alumina crucibles and heated from room temperature to 1000 °C.

5.2.4 Identification of crystalline phases of intumescent coating chars with X-ray diffraction

The crystalline phases of the intumescent coating chars, produced in the laboratory-scale fire-resistance experiments and the industrial fire tests, were identified on a Huber G670 powder diffractometer with Cu-K\textsubscript{α1} radiation (λ=1.54058 Å, 40keV, 40mA) using a focusing primary monochromator, in transmission mode in the range 3 to 100° in 2Theta for 30 minutes.
5.2.5 Digital microscope recordings of the intumescent coating char structure

The morphology of the char structures was analyzed with a digital microscope (VHX-6000, from KEYENCE) with a VH-Z20T lens, which magnifies up to 200 times.

5.3 Results and discussion

In the following sections, the experimental results are described and discussed. To address the challenges of developing the laboratory-scale furnace to simulate the standard hydrocarbon fire test curve, the effects of heating rate on intumescent char structures are first considered. Then follows an investigation of the performance of the laboratory-scale furnace and its correlation with the industrial counterpart in terms of assessing fire-resistance properties of hydrocarbon intumescent coatings.

5.3.1 Effects of the furnace heating rate on the behavior of hydrocarbon intumescent coatings

In the literature, laboratory- and industrial-scale furnaces typically employ rather different heating rates. This process parameter is therefore an important point to consider when comparing data from the two scales of operation. However, only in a few studies were the influence of heating rate on the fire-resistance performance and development of the morphological char structure of intumescent coatings considered. Lucherini et al. [109,124] used the so-called Heat-Transfer Rate Inducing System (H-TRIS) test method and found that the onset of swelling of intumescent coatings is directly influenced by the heating conditions at the exposed surface. Nørgaard et al. [107] found that, unlike the case in regular fire testing, the mechanical resistance of cellulosic intumescent coating chars formed under rapid heating rates (shock heating in a muffle oven), cannot meaningfully be correlated to the degree of char expansion.

As a consequence of these findings, it is essential to consider the effects of heating rate on the behavior of hydrocarbon intumescent coatings, prior to presenting the performance of the laboratory-scale furnace in comparison to the industrial-scale counterpart. For the purpose of demonstration, formulation F3 was selected for the investigation of the possible influences caused by different heating rates. Figure 5-4
shows the char cross-sections of the coating F3, formed in laboratory-scale furnace experiments using the UL1709 standard (i.e. approximately 210 °C/min from ambient temperature to 1093 °C) and a non-standard (i.e. 21 °C/min from ambient temperature to 1093 °C) fire curve, respectively. The experiments were halted when the temperature of the steel plate reached 350 °C. At this temperature, it is reasonable to assume that the very bottom layer of an intumescent coating has gone into the melting stage (temperature interval of the expansion) and that the intumescent coating has fully expanded [141]. The chars formed in the laboratory-scale furnace experiments were taken out for observation when the furnace had cooled to room temperature. It was found that the relative expansion of the coating (i.e. the average height of an intumescent char relative to its initial coating thickness) evaluated with the heating rate of 210 and 21 °C/min is 6.4±0.5 and 5.7±0.4 mm/mm, respectively, which are comparable to each other. However, as shown in Figure 5-4 (and repetitions not shown), the low heating rate conditions give a denser and more lamellar char structure compared with the UL1709 curve.

Figure 5-4 Hydrocarbon intumescent coating chars (formulation F3) formed in a laboratory-scale furnace experiment under different heating conditions: (a) according to the UL1709 curve (i.e. a heating rate of around 210 °C/min from ambient temperature to 1093 °C), and (b) a heating rate of 21 °C/min from ambient temperature to 1093 °C. The significant voids formed, in particular for the conditions underlying the left-hand figure, are emphasized with red markings.
The structure of a fully developed intumescent coating char is mainly a result of the intumescence process, which occurs at temperatures of around 235 to 375 °C, and is characterized by a distinct dynamic viscosity drop of the coating [90,141,143]. The different interior char structures shown in Figure 5-4 may, therefore, be explained by the impact of heating rate on the intumescence process. A high heating rate leaves a short time for the intumescence to take place, whereby gases from blowing agents are released at an extreme rate, leading to a structure with big voids (Figure 5-4). Slower (desired) heating rates may lead to a homogenous structure with small cell volumes.

The heating rate may also influence the thermal decomposition (e.g. gas release of blowing agents) and the chemical composition of an expanding char. Figure 5-5 shows the chemical degradation of the intumescent coating F3 during the thermogravimetric analyses performed under different heating rates. Even though the residue weights (Figure 5-5a), at the end of the analyses, are more or less the same, regardless of the different heating rates, the rates of mass loss (Figure 5-5b) clearly indicate that the thermal degradation steps are strongly related to the heating conditions applied. It seems plausible that different chemical degradations of an intumescent coating (especially during the intumescence process) can make a difference for the char structure, although the explicit relationship between the degradation and the char structure is not yet known in any details.
Figure 5-5 Mass loss curves (a) and the corresponding mass loss rate (b) for the intumescent coating F3 under different heating rates. Note that the two y-axis for the rate of mass loss curves in (b) are different because the time scale for the measurements varied with the heating rate.

In summary, the results demonstrate that the choice of heating rate selected for the fire-resistance evaluation of hydrocarbon intumescent coatings, especially for formulations that form crumbly chars with big cells under a high heating rate (e.g. F3 in Figure 5-4), is crucial. These fragile char structures are not expected to resist the strong turbulence in a hydrocarbon fire scenario [16,56,144]. However, the denser structures formed under too low heating rates may, on the other hand, lead to a wrong assessment of the performance of these coatings.

5.3.2 Performance of the laboratory-scale furnace

For the laboratory-scale furnace to be a reliable tool for evaluation of fire-resistance performance of intumescence coatings, the ability of the furnace to simulate the standard hydrocarbon fire curve and replicate the fire-resistance experiments must be ensured. Figure 5-6 presents the ability of the laboratory-scale furnace to follow the gas temperature of the UL1709 curve. It can be seen that the experimental curve performed by the laboratory-scale furnace is in very good agreement with the standard (an average temperature of $1093 \pm 56 \, ^\circ C$ must be reached within the first 5 min [18]).
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

Figure 5-6 Comparison between the standard and the experimental (laboratory-scale furnace) hydrocarbon curve UL1709.

The repeatability of the furnace was assessed with repetitions of the laboratory-scale fire-resistance experiments with the five hydrocarbon intumescent coatings (F1 – F5). In general, the exposure time of coated steel plates to reach the two critical temperatures (400 and 550 °C) are repeatable to a relative standard deviation of 3 %. Figure 5-7 shows examples of the temperature-time response for the bare steel plate and the steel plates coated with intumescent coating F1, F3, and F5. The deviation is seen to be negligible, confirming the good repeatability throughout a laboratory-scale fire-resistance experiment.
5.3.3 Correlations between coating performance in the laboratory-scale fire-resistance experiments and the industrial fire tests

The potential for using the laboratory-scale furnace for accelerated screening and development work of hydrocarbon intumescent coatings was studied by comparing the two furnace scales with respect to the insulating behavior of the coatings (F1 - F5), as well as the physical and chemical properties of the chars formed in the fire-resistance experiments. In the following paragraphs, the results and correlations obtained are presented and discussed. It is noted that the five intumescent coatings serve as a case study for the potential correlations between the laboratory-scale and the industrial furnace. The mechanisms underlying the different performances of the coatings have not been the focus of the present work and therefore they are not discussed in great detail.

5.3.3.1 Fire-resistance performance of intumescent coatings

The insulating behavior of the hydrocarbon intumescent coatings was examined in fire-resistance experiments with both the laboratory- and industrial-scale furnace. The temperature-time curves of the coated steel plates, each an average of the results from
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

repetitive experiments, are shown in Figure 5-8. In the case of formulation F3, the measurements from the industrial fire tests showed large uncertainties in the critical times to 550 °C (the temperature where the fire-resistance experiments were halted), and the average temperature-time response was therefore not available after times longer than 71.6 min (or temperature higher than 500 °C).

A high consistency can be observed in the temperature-time curves of each coating obtained with the laboratory-scale furnace and industrial furnace. All the curves are composed of two arched parts, connected by a transition point at a temperature of approximately 280 °C (marked with dashed lines in Figure 5-8). These very similar arched parts suggest that the coated steel plates, in the two setups, generally experienced the same exposure conditions.

Figure 5-8 Steel temperature-time curves (industrial and laboratory scale, respectively) for the five coating formulations. The dashed line indicates the approximate transition point of the two arched parts of the curves.
The temperature development is emphasized in Figure 5-9 where the first derivatives of the temperature-time curves are plotted with respect to time. For the laboratory-scale furnace experiments, the curves show two distinct peaks. The origin of these peaks can be attributed to the major temperature-related actions of hydrocarbon intumescent coatings: intumescence (from 235 to 375 °C) and char degradation (mainly thermal oxidation, from around 540 °C to the temperature at the end of the experiments) [26,66,112,141,143,145]. It is generally acknowledged that the intumescence (i.e. the foaming process) limits the rate of increase of the substrate temperature as a result of the insulating char and the associated endothermic reactions [146]. Therefore, after a more or less linear temperature rise in the first 5 min (dictated mainly by the flow pattern and the external heat transfer coefficient of the furnace [38]), the intumescence process significantly reduces the heat conduction to the underlying substrate, thereby slowing down the temperate rise of the steel plate.

Due to transition of the char structure from a closed-cell foam to an open-cell sponge induced by carbon loss, thermo-oxidation reactions can decrease the insulating properties of intumescent chars [141,143]. When the behavior of the intumescent coatings went from intumescence domination to that of thermo-oxidation, the alleviated temperature rise shown in the downhill of the first peak started to increase again (the second peak). At the later stage of the experiments, the main actions of the intumescent coatings were completed, yielding a relatively stable carbon-inorganic char. At this point in time, the temperature difference within the system of the steel plate, the residual char, and the furnace chamber (1093 °C) started to decrease, which made the temperature rise of the steel plate descent to a low value.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

The rate of steel temperature rise (i.e. the first derivative of the temperature-time curve) of coated steel plates with respect to time. The red arrows show the boundary between the first and second peak of each curve.

The results in Figure 5-9 clearly show that the temperature response of the steel plates in the industrial furnace experiments are driven by the same mode of actions as in the laboratory-scale furnace experiments. The laboratory- and industrial-scale furnace experiments have the boundary between the first and second peak (demonstrated with dashed arrows in Figure 5-9) at more or less the same temperature (280 °C). This temperature, corresponding to the term of “transition point” in Figure 5-8. The time to the transition point and the maximum of the second peak show the same sequence (ranking) of the coatings in both of the testing methods.

The correlations between the temperature responses obtained with the laboratory- and the industrial-scale furnace are emphasized in Figure 5-10. The dashed line indicates the approximate position of the transition point, which divides the curves into the
intumescence and thermo-oxidation region (see Figure 5-9). An almost linear relationship is evident in the intumescence region, which starts to deviate after going into the stage where the thermo-oxidation reactions dominate. At still higher temperatures, the slopes of the curves gradually recover to values comparable to those in the intumescence region.

Figure 5-10 Comparison of temperature responses of the steel plates coated with intumescent coatings obtained in the laboratory- and industrial-scale furnace. The dashed line indicates the transition point defined in Figure 5-8.

The deviation of the linear relationship observed at the beginning of the thermo-oxidation region, suggests that the thermo-oxidation in the laboratory-scale furnace may be more severe than that taking place in the industrial furnace, resulting in the much faster temperature responses and inclination of the curves towards the x-axis. Thermo-oxidation of intumescent coatings is affected by oxygen concentration which varies widely in a real fire scenario [145,147]. In a well-tuned industrial furnace chamber the oxygen concentration is around 4 mol % [26,145], while the counterpart in the laboratory-scale furnace chamber was plausibly higher, as the chamber was connected (through the exhaust in the roof of the furnace) to the atmosphere with 21 mol% of O₂. The difference in the oxygen level may account for the different thermo-oxidation conditions in the laboratory- and industrial-scale furnace experiments.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

Depending on the anti-oxidation properties of the coating, the more severe oxidation environment in the laboratory-scale furnace would have different impacts on the deviation of the curves. Therefore, as shown in Figure 5-10, the inclination degree of the curves after the transition point apparently differ for different formulations. Nevertheless, except for the case of F3, the curve progressions are highly consistent with each other and the sequence of the curves is generally constant within the temperature range. The exception observed with F3 for which the curve intersects with the case F5, was caused by surge of the temperature response in the industrial furnace due to detachment of the intumescent char.

As demonstrated above, the laboratory- and industrial-scale furnace experiments clearly show a strong correlation in terms of the thermal behavior of intumescent coatings and the associated temperature response of the steel plates. This is thought to be due to these two testing methods having similar heating conditions, including heating rate and dwell temperature of the fire curve, and the heat dissipation. Therefore, the performance of the coatings (i.e. the exposure time of the steel plate to critical temperatures) is expected to show a good connection between the laboratory- and industrial-scale furnace experiments. The average exposure times to reach the critical temperatures are collected in Figure 5-11. For each coating, the results from the laboratory- and industrial-scale furnace experiments are comparable. Apart from the cases of formulation F3 and F5 in Figure 5-11b, the average time to approach the critical temperatures (400 and 550 °C) in the laboratory-scale furnace experiments is moderately shorter than that in the industrial furnace. It is, as explained above, mainly related to the more severe thermo-oxidation conditions which speed up the temperature rise of the steel plates in the laboratory-scale furnace. The exceptions in the formulations F3 and F5 are related to char defects (e.g. detachments and/or cracks) formed in the industrial furnace and discussed in the next section. The most important observation in Figure 5-11 is that the intumescent coatings show the same ranking of exposure time to reach the critical temperatures in the laboratory-scale and industrial furnace experiments:

\[ F3 > F5 > F4 > F1 > F2 \]
Moreover, compared with the industrial furnace, a better repeatability with negligible standard deviation is seen in the results from the laboratory-scale setup. These results indicate that the laboratory-scale furnace can be an effective device to ranking of the fire-resistance performance of hydrocarbon intumescent coatings, and for studies of the underlying mechanisms.

![Graph showing critical times for coated steel substrate to reach 400 °C and 550 °C](image)

Figure 5-11 Average exposure times for the coated steel substrate to reach (a) 400 °C and (b) 550 °C. Error bars correspond to the standard deviation of repetitive furnace experiments.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

5.3.3.2 Physical appearance of intumescent chars

The intumescent chars from the furnace experiments were taken out for analyses once the furnace was cooled to room temperature. The aim was to study the interrelationship between the chars formed in the laboratory- and industrial-scale furnace experiments. The relative expansion of the intumescent coatings was first examined, because char thickness is usually one of the most crucial parameters for good protection performance [143]. The results for the relative expansion of the coatings are presented in Figure 5-12 with error bars given by standard deviation of the repetitive experiments.

Figure 5-12 Char expansions after furnace experiments, relative to the initial coating thickness. Error bars represent the standard deviations.

It can be seen that the expansion of the coatings in the laboratory-scale furnace experiments is less than those of the industrial furnace. The limited expansion is probably related to the edge effects introduced by the reduced sample size in the laboratory-scale furnace experiments. For a given coating sample, the edges were protected by the use of insulation materials during the furnace experiments (e.g. see schematic diagram of the laboratory-scale furnace in Figure 5-2). This configuration gives an arc-shaped intumescent char for which the expansion close to the edge can be
seen to be somewhat restricted. The restricted area apparently constitutes a higher proportion for the samples with a reduced size. The difference in char expansion among the coatings evaluated with the laboratory-scale furnace (except for formulation F3) is quite small as shown in Figure 5-12. However, the sequence of the relative expansions in the case of the laboratory-scale furnace, follows the same order as that of in the industrial furnace experiments:

\[ F_3 > F_1 > F_4 > F_5 \approx F_2 \]

The agreement in the relative expansion is another important advantage of the laboratory-scale furnace for assessment and development of hydrocarbon intumescent coatings, aside from the fire-resistance ranking described above. Nevertheless, it should be noted that many recent studies have pointed out the limitation of char thickness in predicting the performance of intumescent coatings, especially in the circumstance of hydrocarbon intumescent coatings [141,143]. Mechanical stability and thermal anti-oxidation of intumescent chars are increasingly emphasized as means to resist the high temperature and violent thermal shock of hydrocarbon fire scenarios. Figure 5-13 shows the cross-sections of the intumescent chars from the laboratory- and industrial-scale furnace experiments. No distinct differences were found between formulations F1 and F4 with respect to the cross-sectional structure (and also the relative expansion if the deviations in Figure 5-12 are taken into account). Therefore, the cross-section of F4 is taken as being representative. For better observation and comparison, the magnified images of the cross-sections were recorded with a digital microscope and the results are shown in Figure 5-14.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

(a) Industrial furnace

(b) Laboratory-scale furnace

Figure 5-13 The cross-sections of the intumescent coating chars formed in the industrial (a) and the laboratory-scale (b) furnace. For reasons of space, a photo of the F1 char is not shown (it looked very similar to the F4 char).
Figure 5-14 The structures of the char cross-sections magnified by a digital microscope (30 x magnification). The intumescent char F3 was very fragile and crumbly and could not be placed on the stage of the digital microscope without falling apart.
The cross-sections in the cases of the industrial furnace experiments (Figure 5-13a and 14a) show different characteristics depending on the varying formulations. A two-layered structure is observed in the chars from formulation F2 and F4. The top layer has a porous light grey appearance, and the bottom is a bulk of black dense char. The main difference between the chars F2 and F4 is in their top layers. Compared with char F4, char F2 exhibits smaller cell size in the porous structure and a particular yellow film on the char surface which is probably the result of severe oxidation. The Formulation F3 gave a fragile and fluffy char, which is challenging to maintain while performing the cross-sectional cutting and microscope recordings. The magnified image of char F3 is therefore not shown in Figure 5-14 because it fell apart. On the contrary, a tough and dense char with delaminated shell and white oxidized layer on the top was obtained with formulation F5. The tricky structures from formulation F3 (crumpled ashes) and F5 (cracks and delamination) bring large deviations in determining the relative expansion of the coatings, as seen in Figure 5-12.

The images in Figure 5-13b and Figure 5-14b clearly show that the chars formed in the laboratory-scale furnace experiments are rather similar to those developed in the industrial tests. One difference is that the structural defects (detachment and cracks) are more severe in the industrial furnace experiments due to its strong turbulent flow from gas combustion. The structural defects, especially the detachments, can significantly speed up the temperature rise of coated steel plates, which may explain the exceptions mentioned earlier in Figure 5-11b; the coatings F3 and F5, when exposed in the industrial furnace, exhibits a shorter time to 550 °C than in the laboratory-scale furnace. Nevertheless, the similarity in the relative expansion and morphological structure suggests that hydrocarbon intumescent coatings assessed in the laboratory-scale furnace can provide valuable information on the physical properties of the chars, comparable to those observed in the industrial furnace tests.

5.3.3.3 Crystalline phases in the intumescent char layers

Apart from the physical appearance, the chemical compositions of the chars were examined to comprehensively establish the correlations between the chars formed in the laboratory- and industrial-scale furnaces. The chars were divided into three zones
(layers), based on color and structure, as described elsewhere [141]. The crystalline phases in each layer were analyzed using X-ray diffraction (XRD) and the results are presented in Figure 5-15. The comparison in terms of formulation F1 was excluded due to its resemblance to F4 in fire-resistance performance and physical appearance of char. The objective here is to compare the diffraction patterns of the chars produced in the two furnaces, rather than to investigate the details of the crystalline phases in a sample. Therefore, instead of identifying all the peaks in the X-ray diffraction patterns, only the main crystalline phases are marked out.

Figure 5-15 shows that the diffraction patterns vary with the different formulations and layers of a char. Titanium phosphate and titanium dioxide (rutile crystal form) are the main phases in all the chars, while the diffraction signals of boron phosphate present in particular in the patterns of the char F4 and F5. The diffraction intensity of these main phases and other unidentified peaks varies with the depth of a specific char. This makes sense because thermal degradation of intumescent coatings is a continuous process which moves from the coating surface toward the layer just above a steel plate. Different layers of a char are at different stages of degradation, which therefore results in distinct chemical compositions.

When focusing on a specific formulation and a “layer”, for instance, the top layer of char F2, it can be seen that the patterns barely diverge, regardless of the furnace used for the experiments. The high affinity of the patterns implies that the chars produced from the laboratory- and industrial-scale furnace share not only the identifiable crystalline phases but also the non-recognized amorphous signals. A strong correlation is therefore demonstrated between the chemical compositions of the chars formed in the two furnaces.
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

<table>
<thead>
<tr>
<th>Laboratory-scale furnace</th>
<th>Industrial furnace</th>
</tr>
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**F2**

- Top layer
- Middle layer
- Bottom layer

- Titanium phosphate \( \text{Ti}_4\text{P}_6\text{O}_{23} \)
- Rutile \( \text{TiO}_2 \)

**F3**

- Top layer
- Middle layer
- Bottom layer

- Titanium phosphate \( \text{Ti}_4\text{P}_6\text{O}_{23} \)
- Rutile \( \text{TiO}_2 \)
Figure 5-15 X-ray diffraction patterns of the three layers of the intumescent coating chars.

5.4 Conclusions

A laboratory-scale setup, modified from a commercially available furnace, is proposed for the fast evaluation of hydrocarbon intumescent coatings in the laboratory. Taking advantage of the high heating rates of the furnace, the setup can perform fire-resistance
Comparison of a laboratory- and industrial-scale furnace for performance analysis of hydrocarbon intumescent coatings

experiments according to the standard fire test curve, UL1709. The reliability of the setup was examined by comparing its efficiency with an industrial furnace with respect to fire-resistance performance of coatings including physical appearance and chemical compositions of the chars. Temperature responses of the steel plates obtained in fire-resistance experiments showed a high repeatability, supporting the use of the laboratory-scale furnace for investigation and screening of hydrocarbon intumescent coatings.

As a case study, five hydrocarbon intumescent coatings were selected and assessed in the laboratory-scale and industrial furnace experiments, respectively. Owing to the similar heating conditions (dwell temperature, heating rate, and heat dissipation), the two types of furnace experiments showed a high consistency in their temperature response of steel plates coated with a specific coating. The exposure times to critical temperatures, obtained in the laboratory-scale furnace, showed the same ranking of the coatings as that in the industrial furnace. An investigation of the chars formed in the experiments, showed that the laboratory- and industrial-scale furnaces can be correlated for the physical appearance (relative expansion and morphological structure) and chemical composition (crystalline phases) of the chars, although the char defects (e.g. detachments and/or cracks), due to turbulence from gas combustion and scaled-up sample size, were much more pronounced in the gas-fueled industrial furnace. Nevertheless, these good correlations suggest that the laboratory-scale furnace is a promising tool to evaluate fire-resistance performance of hydrocarbon intumescent coatings and to provide a reliable indication of the char potential for thermal insulation.
Effects of various coating ingredients on the thermal properties of intumescent chars

This chapter shows the influences of various coating ingredients (ammonium polyphosphate, melamine, titanium oxide, calcium carbonate, and vitreous silicate fiber) on the performance of selected hydrocarbon intumescent coatings (with and without zinc borate). It is written in a manuscript format and the revised version will be submitted to a peer-reviewed journal. The authors to be included are Ying Zeng, Claus Erik Weinell, Kim Dam-Johansen, Louise Ring, and Søren Kiil.

Given the significant effects of zinc borate (ZB) on the intumescent char characteristics, a low content of 5 wt.% zinc borate was chosen as a representative of the ZB-containing system in this chapter, instead of using a level of 15 wt.% which showed the best performance in Chapter 4. By doing this, the influences of the target ingredients were expected to be more perceptible.

Nomenclature

\[
\begin{align*}
\text{APP} & = \text{ammonium polyphosphate} \\
\text{MEL} & = \text{Melamine} \\
\text{ZB} & = \text{zinc borate}
\end{align*}
\]

Abstract

Mapping of the performance of intumescent coatings as a function of concentration levels of ingredients is of great significance for formulation optimization. In this work, five classical ingredients, ammonium polyphosphate (APP), melamine (MEL), TiO₂,
CaCO$_3$, and vitreous silicate fiber, were investigated with respect to their effects on the fire-resistance performance of selected zinc borate (ZB)-containing and ZB-free hydrocarbon intumescent coatings. The fire-resistance experiments were carried out according to the temperature-time curve defined in the standard UL1709 for hydrocarbon fire testing. It was found, owing to the promoted interactions of APP with epoxy binder and zinc borate, that increasing levels of APP in the ZB-containing intumescent coatings enhanced the critical times for heating of the steel substrate and the physical condition of the char (including relative expansion and formation of macroporous and compact structures). In contrast, when increasing the content of MEL, the performance of the ZB-containing coatings was generally found to decline, but this effect was due mainly to the restricted char formation resulting from the decreased binder content. Among the investigated formulations, the coating with 25 wt.% APP or 5 wt.% MEL obtained the best performance. The oxides TiO$_2$ and CaCO$_3$, and the mineral fiber barely had any effects on the performance of the ZB-containing intumescent coatings, but the critical times and char appearance were strongly affected for the ZB-free intumescent coatings. Increasing the content of any of the three inorganic components led to a reduced expansion of the ZB-free intumescent coatings, but improved the chars with smaller pores and denser structure. A ZB-free formulation with 1.5 wt.% TiO$_2$, 2.5 wt.% CaCO$_3$, and 5 wt% vitreous silicate fiber showed the best performance (i.e. the longest critical times to reach 400 and 550 °C).

6.1 Introduction

Steel constructions, widely applied in modern architecture such as airports, oil rigs, and housing, are commonly specified to meet a given fire-resistance rating [14]. In general, this rating is determined by the time it takes the material to reach a certain critical temperature (often around 500 °C) in a standard fire test [12]. Depending on the primary “fuel” of the anticipated fire, the test can be of the so-called cellulosic or hydrocarbon type, of which the latter has a much faster transient temperature rise than the former [4]. A practical way to accomplish the thermal insulation of steel structures is the application of intumescent coatings. Upon heat exposure, these coatings swell up to 100 times their original thickness, whereby a multicellular char with a low thermal
Effects of various coating ingredients on the thermal properties of intumescent chars

conductivity is formed, which restricts the heat transfer from the hot gases of the fire to the underlying steel substrate. With the protection provided by intumescent coatings, the structural steel can attain a fire-resistance rating of 1-3 hours [1,57]. This greatly prolongs the time available for saving of lives and preservation of property.

Typically, intumescent coatings are composed of three fundamental ingredients: acid source, char former, and blowing agent. The acid source can be a mineral acid or a material which can generate acidic species upon heating. The char former, carbon-rich polyhydric compounds with numerous esterifiable sites (often hydroxyl groups), can cross-link with the acidic species through esterification reactions, thereby forming a mixture of esters. The intumescence of the mixture is accomplished by the release of incombustible gases from the blowing agent. The accurate coordination of acid generation, esterification, and gas release (as well as the viscosity reduction of the coating) is crucial to the working of an intumescent coating char [47,143]. Nevertheless, the chars formed with these three fundamental ingredients are generally vulnerable to the turbulent environments in fire scenarios. Therefore, to improve the fire-resistance properties (i.e. expansion, morphology, and thermal and mechanical stability) of the chars formed, diverse functional fillers, such as dolomite clay [42], titanium oxide [54,71,83,85,87], boric acid [33,80,81], kaolin [33,58,60], and montmorillonite [59,139,148], have all been added, in various concentrations, to intumescent coating formulations.

The studies of intumescent coatings were performed following either a temperature-time curve defined in the standard cellulosic fire test method with an adapted furnace [83], or non-standard curves using regular laboratory equipment, such as the Bunsen burner [33,42,54,58,60,80,81,87], the gas lamp [59], and/or the cone calorimeter [139]. However, none of the investigations comprehensively examined an epoxy-based intumescent coating system according to standard hydrocarbon fire test methods, such as the UL1709 or BS476 standards, where the gas temperature increases rapidly from room temperature to more than 900 °C within five minutes.

The standard or standard-like test conditions can be crucial, especially for the intumescent coatings orientated towards hydrocarbon fire protection; quite a few
studies have pointed out that the heating conditions directly affect the behavior of intumescent coatings in a complicated manner and thereby dramatically shape the fire-resistance properties of intumescent coating chars \([2,92,109,124,140,149–151]\). The present work is devoted to the study of the effects of five ingredients (ammonium polyphosphate, melamine, TiO\(_2\), CaCO\(_3\), and vitreous silicate fiber) on the fire-resistance performance of epoxy-based intumescent coatings, when exposed to the temperature-time curve defined by the standard hydrocarbon fire test method UL1709. Zinc borate, which is popularly formulated in hydrocarbon intumescent coatings owing to its efficiency in improving char structure, is expected to be replaced due to its health risks \([141]\). Therefore, two types of epoxy-based intumescent coating formulations (with and without zinc borate) were selected to represent the present commercial market and a potential boron-free future alternative.

### 6.2 Experimental

#### 6.2.1 Coating materials and application

The epoxy-based hydrocarbon intumescent coatings studied were formulated with a two-component (base and curing part) system. The base part contained a bisphenol A epoxy resin (Hexion B.V.) and a diluent (ICL-IP B.V.), and filled with ammonium polyphosphate (100 % pure, Clariant GmbH), zinc borate (>98.8 wt.%, Borax Ltd.), calcium carbonate (>99 wt.%, Reverté Minerales S.A.), and vitreous silicate fiber (95-100 wt.%, length of approx. 120 µm, diameter of approx. 5 µm, Rockwool B.V.). The curing part was composed of a polyamide (Air Products B.V.), a catalyst (Air Products B.V.), and filled with melamine (100 wt.%, OCI Nitrogen B.V.) and titanium dioxide (>90 wt.%, Huntsman Ltd.). The distribution of the solid materials was chosen to balance the pigment volume concentration in the two parts.

The compositions of the intumescent coatings with and without zinc borate (ZB) are listed in Table 6-1 and Table 6-2, respectively. According to our previous work \([141]\), zinc borate has a strong influence on coating performance. Therefore, a relatively low level of zinc borate, i.e. 5 wt.%, has been used in the ZB-containing intumescent coatings to presumably permit room for the target components to play a role. The components, ammonium polyphosphate (APP), melamine (MEL), titanium dioxide
Effects of various coating ingredients on the thermal properties of intumescent chars

(TiO$_2$), calcium carbonate (CaCO$_3$), and vitreous silicate fiber, were investigated individually in the hydrocarbon intumescent coating system. For a target component (e.g. TiO$_2$), its mass fraction was adjusted by varying the epoxy binder content accordingly, and the levels of all other components were constant. This was thought to be a sound way of studying and comparing the effects of these components, because the effects of the epoxy binder system, which have previously been thoroughly investigated in the literature [4,16,125,152,153], are supposed to be distinguished readily to identify the effects of the target component. The pigment volume concentrations of the coatings are below the critical value (50 %).

Dispersion of the base and curing part was done with a high-speed disperser at 1600 rpm (decreased to 400 rpm when vitreous silicate fiber was added to avoid breakage). The temperature of the mixture was below 50 °C during dispersion. The intumescent coatings were prepared by mixing the well-dispersed base and curing part according to an amide/epoxy functional group stoichiometric ratio of 0.867. For a fire-resistance experiment, the coating was applied to the surface of a grit-blasted steel plate (area of 60x60 mm$^2$ and 3 mm thickness) in a film thickness of 6 ± 0.2 mm. All samples were cured for 24 hours at room temperature before use.
Table 6-1 Composition of the series of zinc borate intumescent coatings (in wt.%), APP = ammonium polyphosphate, MEL = melamine, ZB = zinc borate.

<table>
<thead>
<tr>
<th>Coating name</th>
<th>APP</th>
<th>MEL</th>
<th>ZB</th>
<th>TiO₂</th>
<th>CaCO₃</th>
<th>Vitreous silicate fiber</th>
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⁹Corresponding to the total amount of the epoxy resin, diluent, amide, and catalyst. The ratio between these components was kept constant in all the formulations.
Effects of various coating ingredients on the thermal properties of intumescent chars

Table 6-2 Composition of the series of zinc borate-free intumescent coatings (in wt.%), APP = ammonium polyphosphate, MEL = melamine, ZB = zinc borate.

<table>
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<th>Coating name</th>
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<th>MEL</th>
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⁸ Corresponding to the total amount of the epoxy resin, diluent, amide, and catalyst. The ratio between these components was kept constant in all the formulations.

6.2.2 Fire-resistance experiments following the UL1709 curve

Fire-resistance experiments of the intumescent coatings were carried out with a compact furnace modified with an opening in the furnace door for sample placement (details are available elsewhere [151]). A steel plate coated with an intumescent coating was mounted vertically with a tailor-cut insulation material (VIP12-HT supplied by Skamol A/S, thickness of 50 mm) between the plate backside and the accessories that immobilize the sample. The temperature response of the steel plate during the fire-resistance experiment was recorded with a copper-disk thermocouple (K-type, 0 – 700
°C) attached to the central area of the backside of the steel plate. The thermocouple was connected to a data logger that recorded temperature with a time interval of 1 s.

The fire-resistance experiments were initiated by heating the furnace chamber according to the temperature-time relationship stated in the standard hydrocarbon fire test method UL1709. Once the temperature of the steel plate reached a critical value of 550 °C, the furnace was turned off. The value of 550 °C was selected because it covers both the standard critical temperature of 400 °C for heavily loaded structural steel components, and the standard of 550 °C for normally loaded components such as onshore platforms. The intumescent chars formed in the fire-resistance experiments were taken out for further analyses when the furnace had cooled down to room temperature. Key parameters of the fire-resistance experiment are the times that the steel plate takes to reach the critical temperatures of 400 and 550 °C (i.e. the critical times) as well as characterizations of the chars formed. For each of the intumescent coatings, a repetition of the fire-resistance experiments was performed and the average of the results (including the temperature response and the critical times of the steel plate) was used in the subsequent analysis.

6.2.3 Digital microscope recordings of intumescent char structures

A digital microscope (VHX-6000, from KEYENCE) with a VH-Z20T lens was used to observe the structures of the intumescent coating chars formed in the fire-resistance experiments.

6.3 Results and discussion

6.3.1 Zinc Borate (ZB)-containing intumescent coatings

The effects of the five components, APP, MEL, TiO₂, CaCO₃, and vitreous silicate fiber, on the fire-resistance performance of the intumescent coatings were studied in the systems with zinc borate. The results are presented in the following sections. The performance parameters including the temperature-time response and critical times of the coated steel plate, relative expansion and morphological structure of intumescent char are addressed.
6.3.1.1 Fire-resistance performance

The effects of the five components on the performance of ZB-containing intumescent coatings were first examined. Figure 6-1 shows the temperature-time responses of the steel plates obtained from the fire-resistance experiments. The curves are the average of the two repetition experiments and the standard deviation of the data points are in all cases within 4 min (not shown in the figure). Both the levels of APP and MEL exhibited certain influences on the fire-resistance performance of the ZB-containing intumescent coatings, while the cases of the inorganic components (TiO$_2$, CaCO$_3$, and vitreous silicate fiber) showed almost the same temperature progression, regardless of the levels and species of the target component.
Figure 6-1 Temperature versus time curves of the steel plates coated with ZB-containing intumescent coatings in the fire-resistance experiments. The coatings differ in the concentration levels of APP, MEL, TiO$_2$, CaCO$_3$, and vitreous silicate fiber.

Figure 6-2 summarizes the critical times of the coated steel plates to reach the critical temperatures (400 and 550 °C). The critical times are averages (± standard deviation)
Effects of various coating ingredients on the thermal properties of intumescent chars

of the repetition experiments. The most distinct change was displayed by increasing the mass fraction of APP for which the critical time was decreased first and then increased. The longest critical time to 400 and 550 °C was 40.5 and 73.0 min with the coating containing 25 wt.% APP. Similar variation in the critical times was observed when raising the level of MEL, although the changes were lessened and the best performance (38.5 and 64.3 min to 400 and 550 °C) was found with the coating comprising the lowest content of MEL (i.e. 5 wt.%). Regarding the inorganic components (TiO$_2$, CaCO$_3$, and vitreous silicate fiber), the critical times of the samples to 400 and 550 °C varied quite marginally from 35.5 to 37.8 min and from 57.7 to 62.1 min.

![Graph showing critical times vs. mass fraction of target components](image)

Figure 6-2 Average critical times of the ZB-containing intumescent coatings. Error bars correspond to the standard deviation.

The results show that increasing the content of APP or decreasing the content of MEL generally improved the fire-resistance performance of the ZB-containing coatings (aside from the anomalous value), while adjusting the levels of the inorganics, TiO$_2$, CaCO$_3$, and the fiber, barely presented notable effect. The performance of these inorganics is quite surprising, as it is in contradiction to results found in the literature. For example, Ahmad’s group from Malaysia has claimed that the content of TiO$_2$ has an active role in extending thermal protection time of intumescent systems with zinc borate and/or boric acid [54,85,87]. A possible explanation for the divergence is the different intumescent formulations and heating conditions of fire-resistance
experiments applied in the present work and the literature reports. Due to the possible interactions among the different ingredients being very complex, the influence of the actual formulations cannot be mapped here. However, with regard to the heating conditions, as discussed in the introduction part, these are certainly expected to have an effect on the fire-resistance performance of the intumescent coatings. Compared with the present work, the fire-resistance experiments in the relevant literature were performed under a more moderate temperature environment (e.g. fire protection tests with a Bunsen burner in Ahmad’s group), where the temperature progressions of the steel plates were sluggish and nearly flattened at temperatures below 300 °C [54,85,87]. In such cases, more substances, e.g. polyphosphoric acid that derives from ammonium polyphosphate and dehydrates to sublimate at around 550 °C [84], may be retained longer and can react with oxides such as TiO₂, increasing the probability of additional interactions.

6.3.1.2 Physical appearance of the intumescent chars
The effects of the five components on the expansion ratios of the coatings and the morphological structures of the chars were examined. Figure 6-3 shows the relative expansion of the ZB-containing intumescent coatings, which were estimated by dividing the average height of the chars formed in the repetition of fire-resistance experiments with the original dry film thickness of the coating. By increasing the level of APP, the relative expansion of the chars were first abruptly reduced to its minimum and then gradually increased. The highest relative expansion was found with the coating containing 10 wt.% APP (ZB-A10). In the case of MEL, the increased mass fraction resulted in a steadily decreasing char expansion. TiO₂, CaCO₃, and the fiber exhibited a limited influence on the expansion of the ZB-containing intumescent coatings, coinciding with their performance in the temperature responses and critical times in Figure 6-1 and Figure 6-2. The changes caused by adjusting these inorganics components are at the same level as the standard deviations of the experiments.
Effects of various coating ingredients on the thermal properties of intumescent chars

Figure 6-3 Char expansions, relative to the initial coating thickness, as a function of the content of the target component in the ZB-containing intumescent coatings. Error bars represent the standard deviation.

The cross-sectional structures of the intumescent chars were recorded with a digital microscope using 20 times magnification. Figure 6-4 shows the results obtained with the varied APP levels. All the chars present a two-layered structure: a foam-like macroporous structure with a grey color appears on top, while the black compact layer is placed at the bottom. By increasing the content of APP from 10 to 25 wt.%, the void (cell) size and thickness of the macroporous structure dropped and gradually increased. In contrast, the depth of the compact phase was consistently enlarged from 3.5 to 6.7 mm by formulating with more APP in the coatings. Comparing with the relative expansion shown in Figure 6-3, it can be seen that the highest relative expansion of the coating ZB-A10 (10 wt.% APP) resulted from its great depth of the macroporous structure, while the increased char expansion from the coating with 15 to 25 wt.% APP benefited from both the increased macroporous and compact phase. In general, except for the macroporous layer observed in the case of ZB-A10, the high levels of APP apparently presented positive effects on the foam of the macroporous structure and the formation of the compact phase.
Figure 6-4 Cross-sections of the chars formed with ZB-containing intumescent coatings containing different levels of APP. The images were recorded with a digital microscope magnified 20 times.

The well-expanded macroporous layer formed with the coating ZB-A10 certainly explains its good fire-resistance performance (i.e. long critical times of the steel plates) in the furnace experiments, although the reason for forming this structure is not yet clear. Nevertheless, aside from this exception, the positive effects of APP on the char appearance may be on account of its reactions in the system. With the present ZB-containing intumescent formulations, the main reactions of APP, occurring at similar temperatures, are releasing ammonia (T>250 °C [141]) to promote char expansion, and its derivative polyphosphoric acid reacting with the cured epoxy (T<280 °C [47]) and zinc borate (T≥300°C [84]). The stoichiometry molar ratio of the latter two reactions are APP (repeating unit): cured epoxy (hydroxyl group): zinc borate = 1: 0.5: 0.05 [26,84]. Facilitating these reactions (e.g. via increasing concentration of reactant APP unless a substantial stoichiometric excess is reached) improves the char structure, thermal stability of the coating, and the residual weight of the char [4,16,154]. However, in the present system, even with the coating ZB-A25, which has the highest content of APP and the lowest content of the epoxy binder, the molar ratio of APP to the hydroxyl group of the cured epoxy, and zinc borate is merely 1: 0.49: 0.05. It is just theoretically enough for the main reactions of APP and far less than a level of stoichiometric excess. Therefore, it seems reasonable that increasing the content of APP improves the char expansion (contribution from both the macroporous and the compact phase) and consequently the fire-resistance performance of the coatings.
The variation of the char structures caused by the different levels of MEL is illustrated in Figure 6-5. By enhancing the content of MEL from 5 to 15 wt.%, the char layer including the macroporous and compact phase became denser. Coinciding with the trend observed in the relative expansion, the thickness of the compact phase was reduced from 6.9 to 5.8 mm. These results are quite surprising, as the increase of the MEL level was expected to yield more ammonia to benefit char expansion.

This shows that it is important to ensure that a well-expanded char does not only rely on the amount of gases released from blowing agents, but also the amount of substances in the incipient char for foaming and the viscosity of the incipient char for trapping the gases [47,140,141,155]. By increasing the level of MEL, the content of the epoxy binder, which contributes to the yield of the incipient char, was decreased accordingly; the viscosity of the melted incipient char may increase due to the introduction of more solid particles (i.e. MEL) and thus generate higher internal stress for char stretching [155,156]. Moreover, the cured epoxy binder could serve as a blowing agent to some extent, as it decomposes plenty of gases such as CO$_2$, H$_2$O, and low-molecular volatiles during thermal degradation [129,141]. Therefore, the increment of gas release due to the increased level of MEL may partly be offset by the reduction of the binder content. In summary, all these factors could be responsible for the reduced char expansion (including the thickness of the macroporous and compact phase) and inferior fire-resistance performance observed with the coatings containing the high level of MEL.
However, a lower char expansion does not necessarily result in a poorer fire-resistance performance (especially when the variation of char expansion is within a narrow range), because a compact char structure could possess better insulation properties [141]. This may explain the results that the coating ZB-M15 with the lowest expansion and densest structure did not exhibit the worst fire-resistance performance. Furthermore, it has to be noted that the negative effects of decreasing binder content was not shown in the case of APP due mainly to that APP functions not only as a blowing agent like MEL does, but more decisively as an acid source that generally promotes the coating performance via interactions with other ingredients (see the earlier discussion).

With regard to the cases of TiO₂, CaCO₃, and vitreous silicate fiber, their influences on the morphological structures of the chars are quite similar to each other (see Figure 6-6). By increasing the mass fraction of these inorganic components, the most observable change was the gradually reduced voids (cells) size in the macroporous structure. The slightly varied structures may also relate to the decreased binder content. However, in contrast to the case of MEL, the amount of substances in the incipient chars would increase by raising the contents of these non-volatile compounds. This probably accounts for the fact that the char expansion was not evidently changed in the results of these inorganics.
Figure 6-6 Cross-sections of the chars formed with ZB-containing intumescent coatings containing different levels of (a) TiO$_2$, (b) CaCO$_3$, and (c) vitreous silicate fiber. The images were recorded with a digital microscope magnified 20 times.

Nevertheless, these types of inorganics are usually expected to affect the performance of an intumescent coating via their interactions with other active compounds in the formulation, e.g. TiO$_2$ reacting with APP, instead of simply their influences on binder content. As shown in Figure 6-6, some differences do exist between the effects of these three components. Specifically, the binder contents in the coatings with 2 wt.% TiO$_2$, 0.5 wt.% CaCO$_3$, and 10 wt.% fiber are almost the same. When the approximately equal amount of the binder was decreased (i.e. from 2 to 6 wt.% TiO$_2$, 0.5 to 5 wt.% CaCO$_3$, and 10 to 14 wt.% fiber), the extent to which the macroporous structure was affected is clearly different and depends on the type of the compound. Adjusting the level of the
fiber demonstrated more distinct change on the size of the voids compared with the cases of TiO$_2$ and CaCO$_3$. Nonetheless, compared to our previous work on zinc borate which can distinctly impact the performance of the intumescent coatings (including the fire-resistance performance and char structures) [141], the effects exhibited by TiO$_2$, CaCO$_3$, and the fiber are quite limited. Their insignificant effects on the physical appearance of the intumescent chars explain the similar temperature responses of the coated steel plates shown in Figure 6-1.

The restricted performance of TiO$_2$, CaCO$_3$, and the fiber is probably due to the presence of zinc borate, which actively reacts with APP and its derivatives with a strong influence on the viscosity of incipient chars [84,141]. The room for these three inorganics to show an effect may be small in the ZB-containing formulations. Therefore, from the perspective of formulation design, low contents of TiO$_2$, CaCO$_3$, and the fiber (only valid for the investigated ranges) could be used to permit a high level of other compounds that can effectively improve the performance of the ZB-containing intumescent coatings (e.g. APP, zinc borate).

6.3.2 Zinc borate (ZB)-free intumescent coatings

Due to the suspected toxicity of boron compounds, investigation of the behavior of ZB-free coatings is in line with the ongoing search for boron-free hydrocarbon intumescent formulations. With the studies of the ZB-containing intumescent coatings, it is plausible to assume that APP and MEL would take similar effects in ZB-free coatings, while TiO$_2$, CaCO$_3$, and vitreous silicate fiber may perform differently in the absence of zinc borate. Consequently, the effects of TiO$_2$, CaCO$_3$, and the fiber on the ZB-free intumescent coatings were studied and the results are presented in this section.

6.3.2.1 Fire-resistance performance

Figure 6-7 shows the average temperature-time response of the steel plate coated with a ZB-free intumescent coating in the repetitive fire-resistance experiments. Unlike the results observed with the ZB-containing intumescent coatings, the levels of TiO$_2$, CaCO$_3$, and vitreous silicate fiber in the ZB-free systems actively influence the temperature response of the steel plates.
Effects of various coating ingredients on the thermal properties of intumescent chars

Figure 6-7 Fire-resistance performance of ZB-free intumescent coatings with different levels of TiO$_2$, CaCO$_3$, and vitreous silicate fiber.

The exposure times of the steel plates to reach the critical temperatures are given in Figure 6-8. By adjusting the mass fraction of TiO$_2$ from 0 to 15 wt.% in the
formulations, the critical times of the steel plates to 400 and 550 °C were first increased and then gradually decreased. The best performance was found with the coating containing 1.5 wt.% TiO₂ (T1.5) for which the steel plates stood 51.6 and 87.7 min before reaching the critical temperatures of 400 and 550 °C, respectively. A similar trend was found in the ZB-free intumescent coatings with different levels of CaCO₃ and the fiber. Among the investigated formulations, the optimal mass fraction of CaCO₃ and the fiber are 2.5 and 5 wt.%, respectively. The corresponding critical times to 400 and 550 °C are 50.7 and 86.3 min for the coating with 2.5 wt.% CaCO₃ (C2.5) and 50.7 and 85.1 min for the coating with 5 wt.% vitreous silicate fiber (F5). Nevertheless, it is noted that significant uncertainties in some cases with long critical times were found, for example, the one without TiO₂ (T0) and the majority of the coatings in the case of the fiber. These uncertainties are the reason that some of the curves in Figure 6-7 were halted before 550 °C.

Figure 6-8 Critical times of ZB-free intumescent coatings with different levels of TiO₂, CaCO₃, and vitreous silicate fiber.
6.3.2.2 Physical appearance of the intumescent chars

The effects of TiO$_2$, CaCO$_3$, and vitreous silicate fiber on the physical appearance of the intumescent chars were further examined. Figure 6-9 shows the relative expansion of the chars produced from the ZB-free intumescent coatings. By increasing the content of TiO$_2$ or CaCO$_3$ in the ZB-free formulations, the relative expansion of the chars was gradually decreased. This trend is in accordance with the variation of the critical times shown in Figure 6-8, except for the coatings without TiO$_2$ or CaCO$_3$. With respect to the fiber, the relative expansion of the chars was first boosted and then reduced. This coincides with the effects of the fiber on the critical times of the coated steel plates. The char with the highest relative expansion (F5) was produced from the coating that obtained the longest critical times among the formulations with different levels of the fiber.

![Figure 6-9 Char expansions relative to the initial coating thickness as a function of the levels of TiO$_2$, CaCO$_3$, and vitreous silicate fiber in the ZB-free intumescent coatings. Error bars represent the standard deviation.](image)

The uncertainties on the relative expansion of the chars are rather noteworthy, especially for the coatings with 0 and 1.5 wt.% TiO$_2$ and the coatings with different
levels of vitreous silicate fiber. In all these cases, the top layers of the chars completely detached and actually fell off, disintegrating into smaller pieces. The occurrence or degree of detachment was not repeatable in the furnace experiments, and therefore a large uncertainty exists in the assessment of the expansion factor of these chars. The detachment of a char top layer could happen during the fire-resistance experiments, during the period of cooling down of the furnace, or during the process of removing the char from the furnace door. However, the latter two options only influence the measurement of the char expansion, while the former has a significant impact on the temperature response of the steel plate, (i.e. the fire-resistance performance of the coating). Therefore, the detachment during the fire-resistance experiments probably resulted in the large deviations seen for the critical times (e.g. T0 and F0 in Figure 6-8). In particular, the formulation with 0 wt.% vitreous silicate fiber had a relative expansion varied from 3.4 mm/mm down to nearly zero, corresponding to the case where the coating burnt out during the experiment, leaving a large and continuous cavity through the few persistent char residues. For this case, plenty of fragments of the char was found on the bottom of the furnace.

As it has been mentioned in the case of the ZB-containing intumescent coatings, char expansion would also relate to the epoxy binder content that was accordingly decreased with raising the levels of the target components. Therefore, to confirm the effects of TiO2, CaCO3, and the fiber, it is necessary to discuss the role of the binder system in the relative expansion of the ZB-free intumescent coatings. Figure 6-10 shows the relationship between the relative expansion and the content of the binder system in the coatings. It can be seen that the binder content seems to demonstrate some connections with the char expansion, however, the extent to which the relative expansion was affected clearly depends on the investigated inorganic components, i.e. TiO2, CaCO3, and vitreous silicate fiber.
Effects of various coating ingredients on the thermal properties of intumescent chars

Figure 6-10 Relative expansion of the intumescent chars as a function of the content of the binder system (including the epoxy resin, diluent, amide, and catalyst).

The cross-sections of the chars were investigated after cutting with a scalpel and the results are shown in Figure 6-11 (TiO$_2$), Figure 6-12 (CaCO$_3$), and Figure 6-13 (vitreous silicate fiber). In this case, the photos were taken with a digital camera (as opposed to the digital microscope), as most of these chars were too fragile to hold themselves together while placed horizontally on the stage of the digital microscope. TiO$_2$ and CaCO$_3$ bear a strong resemblance in how they affect the morphology of the chars. This is in good agreement with their effects on the critical times and relative expansion. A sponge-like phase, characterized with a light-yellow color (outcome of severe oxidation of char layers [140,141]), with a thin compact layer underneath was found in the formulation without TiO$_2$ or CaCO$_3$ (see Figure 6-11 and Figure 6-12). It is hard to maintain the integrity of the sponge-like phase and it detached to different degrees either during the fire-resistance experiments and cooling down of the furnace.
(e.g. the case with 0 wt.% TiO₂) or while the char was being transferred out from the furnace (e.g. the case with 0 wt.% CaCO₃). By increasing the contents of TiO₂ and CaCO₃ in the coatings, the sponge-like phase was gradually transformed into a less expanded and oxidized macroporous phase.

Figure 6-11 Cross-sections of the chars produced with the ZB-free intumescent coatings with different levels of TiO₂. The top layers in the case of 0 wt.% TiO₂ were partially detached.

Figure 6-12 Cross-sections of the chars produced with the ZB-free intumescent coatings with different levels of CaCO₃.
The improved morphological structures of the chars are probably on account of the interactions between the APP and TiO$_2$ or CaCO$_3$. Phosphoric groups of APP and its derivatives can react with TiO$_2$ and CaCO$_3$, forming titanium phosphate (e.g. TiP$_2$O$_7$) and calcium phosphate (e.g. Ca(PO$_3$)$_2$), respectively [26,157]. The formation of these phosphates can influence the chemical (e.g. anti-oxidation) and physical (e.g. morphological structure and emissivity of the surface) properties of intumescent chars [47,71,83]. Mariappan et al. investigated the effects of TiO$_2$ on the fire-resistance performance of cellulosic intumescent coatings according to standard cellulosic fire test curve (ISO834), and found that the ratio of APP to TiO$_2$ near to their stoichiometric reaction ratio (2 mol/mol) could benefit the performance of the intumescent coatings most [83]. Excess amount of TiO$_2$ was suspected to affect the char structure and inhibit the expansion of chars [71,83]. Considering that the reaction between CaCO$_3$ and APP is quite similar to the case of TiO$_2$, an optimal ratio for the stoichiometry between CaCO$_3$ and APP may also exist and influence the performance of the intumescent coatings. For the present study, the most prominent improvement on the char structures (disappearance of the oxidized sponge-like phase) arose when the content of TiO$_2$ or CaCO$_3$ was 5 wt.%. In these two coatings, the ratios of APP to the total amount of TiO$_2$ and CaCO$_3$ (see compositions in Table 6-2) are 1.8 mol/mol (D5) and 2.1 mol/mol (R5), which are quite close to the theoretical stoichiometric value (2 mol/mol).

With respect to the vitreous silicate fiber, its influence on the morphology of the chars is moderately different from that of TiO$_2$ and CaCO$_3$. As shown in Figure 6-13, the primary structures of the chars (i.e. a sponge-like phase at the top and a compact phase at the bottom) did not change even when the level of the fiber was increased to 20 wt.%. However, the char structure including the sponge-like and compact phase became denser with the content of the fiber increasing. Unlike the cases of TiO$_2$ and CaCO$_3$, the effect of the fiber is hardly related to its reactions with other active ingredients in the formulations, such as APP. In our earlier work, we only observed the crystalline phase of AlPO$_4$ in the top and middle layers of the char produced from an intumescent coating without zinc borate [141]. The shape of the fiber was maintained in the char layers regardless of the formation of AlPO$_4$. It suggests that the reactivity of this fiber is quite limited and only the very surface of the fiber can react with derivatives of APP.
at high temperatures. In fact, the rod-shaped fiber was more likely to play a role of physically reinforcing the network to keep the char integrity. Thus, without the support of the fiber (i.e. the coating with 0 wt.% fiber), the char was observed to be severely burnt, leaving penetrated cavities in the residual char and plenty of scattered pieces on the furnace chamber floor.

Figure 6-13 Cross-sections of the chars produced with the ZB-free intumescent coatings with different levels of vitreous silicate fiber.

The effects of TiO$_2$, CaCO$_3$, and vitreous silicate fiber on the physical appearance of the chars explains the temperature response of the coated steel plates observed in the fire-resistance experiments. The cases with the low content of TiO$_2$, CaCO$_3$, or vitreous silicate fiber resulted in the high relative expansion of the chars, which therefore gave more protection (long critical times) to the underlying steel plate. However, these high-swelled chars were mainly contributed by the sponge-like layers that are prone to detach from the bulk of the char (e.g. T0 and C0). Increasing the level of TiO$_2$, CaCO$_3$, or the fiber clearly improved morphological structures of the chars and reduced the probability of detachment. Therefore, the longest critical times to 400 and 550 °C were
shown when the char exhibited high expansion and relatively maintained its integrity (i.e. T1.5, C2.5, and F5). Nevertheless, it is probably hard to generalize the respective best performance found with the coating T1.5, C2.5, and F5 to cases of industrial hydrocarbon fire tests. Compared with the static-electrical heating applied in the present fire-resistance experiments, the turbulent flow exposed by the intumescent coating samples evaluated in industrial hydrocarbon fire tests is much more violent [151]. The sponge-like phases of T1.5, C2.5, and F5 that was barely enough to be intact in the present case may be completely damaged in the industrial fire tests, leading to inferior fire-resistance performance. Therefore, the char structures that were improved with a high content of TiO$_2$, CaCO$_3$, or the fiber, e.g. T5, C5, and F10, are probably more practical from the perspective of the application of ZB-free intumescent coatings in real hydrocarbon fire scenarios.

6.4 Conclusions

The effects of ammonium polyphosphate (APP), melamine (MEL), TiO$_2$, CaCO$_3$, and vitreous silicate fiber on the performance of selected ZB-containing and ZB-free intumescent coatings were investigated, using the fire-resistance experiments carried out with the temperature-time curve defined in the standard UL1709. Increasing the content of APP or decreasing the content of MEL generally benefited the performance of the ZB-containing intumescent coatings, in the aspects of critical times to 400 and 550 °C and physical appearance of the char (including relative expansion and formation of macroporous and compact structures). Among the investigated formulations, the best performance was found with the coating containing 25 wt.% APP or 5 wt.% MEL. The positive effect of raising the APP level was owing to the promoted interactions of APP with the epoxy binder and zinc borate, while the inferior performance of the coatings by increasing the content of MEL was related to the negative influence from the changes on the binder system. Varying the levels of TiO$_2$, CaCO$_3$, and the fiber barely had an influence on the performance of the ZB-containing coatings. Only the cell sizes of the macroporous layers in the chars were slightly reduced by increasing the content of TiO$_2$, CaCO$_3$, and the fiber in the formulations. The presence of zinc borate significantly constricted the room for these inorganic fillers to play a role.
More prominent effects of TiO$_2$, CaCO$_3$, and the fiber were observed on the performance of ZB-free intumescent coatings. The coating with 1.5 wt.% TiO$_2$, 2.5 wt.% CaCO$_3$, or 5 wt.% vitreous silicate fiber was found with the longest critical time to both 400 and 550 °C, among the investigation regarding TiO$_2$, CaCO$_3$, and the fiber, respectively. High content of TiO$_2$ or CaCO$_3$, on the one hand, inhibited the char expansion of the ZB-free intumescent coatings, but on the other hand, improved the char phases from a sponge-like - compact phase structure, which is vulnerable to detachment, to a more mechanically stable macroporous - compact phase structure. The trade-off between the decreased char expansion and the enhanced char morphology resulted in the optimal performance in terms of critical times. With respect to the vitreous silicate fiber, it mainly physically reinforced the internal network of the intumescent chars, and thereby affected their morphological structures.
Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

In this chapter, correlations between fire-resistance performance (i.e. critical times of coated steel plates) and char properties are investigated. Aimed at later submission for publication, the chapter is written in a manuscript format with the following author list: Ying Zeng, Claus Erik Weinell, Kim Dam-Johansen, Louise Ring, and Søren Kiil.

Nomenclature

\( \text{APP} = \) ammonium polyphosphate
\( \text{MEL} = \) melamine
\( \text{ZB} = \) zinc borate

\( I = \) insulation efficiency of a phase, \([\text{min}]\)
\( t = \) critical time to 550 °C, \([\text{min}]\)
\( x = \) dimension of a phase in the char divided by the original dry film thickness of the coating, \([\text{dimensionless}]\)
\( \text{P}_{\text{integ.}} = \) integrated parameter, \([\text{min}]\)

Subscript
\( i = \) target phase
\( s = \) sponge-like phase
\( m = \) macroporous phase
\( c = \) compact phase
Abstract

To optimize formulations and understand the performance of hydrocarbon intumescent coatings, it is of great industrial and scientific interest to establish relationships between the char properties and the critical heating times of coated steel plates. In this work, we use a pool of experimental data to explore such relationships. The strongest correlation between the char properties and the critical times was found with a so-called integrated parameter, which combines the relative expansion and the insulation efficiencies of the three distinct char phases observed (i.e. sponge-like, macroporous and compact). An approximate linear relationship was mapped between the integrated parameter of the chars and the fire-resistance performance of intumescent coatings (i.e. critical times to 400 and 550 °C). The relationship would facilitate understanding the coating performance and identifying the desired char properties (preferably a high thickness of the macroporous and compact phases). Owing to the exponential relationship found between the dynamic viscosity minimum and the char appearance, the required dynamic viscosity change of an intumescent coating can be pointed out to obtain the target char properties (e.g. macroporous and compact phases with a dynamic viscosity minimum in the range of 10 to 100 Pa·s). Thus, the performance of hydrocarbon intumescent coatings may be manipulated via the rheological behavior of the coatings and performance expectations provided with the methodology developed for the integrated parameters.

7.1 Introduction

Intumescent coatings are widely applied to protect the steel elements of buildings, infrastructure, and oilrigs during a fire. When exposed to high temperatures, intumescent coatings expand to form a multicellular char that thermally insulates the underlying steel substrate [109,158]. The performance of an intumescent coating depends on the various ingredients used in the formulation. A combination of an acid source (e.g. ammonium polyphosphate), a char former (e.g. pentaerythritol), and a blowing agent (e.g. melamine) are typically applied to ensure the basic intumescence process [47]. However, to improve the coatings fire-resistance performance, or to obtain properties such as resistance to weathering, corrosion, and smoke release, other
compounds, such as metal oxides (e.g. TiO$_2$, Fe$_2$O$_3$) [4,16,54], hydroxides (e.g. Al(OH)$_3$, Mg(OH)$_2$) [55–57], industrial minerals (e.g. kaolin clay, wollastonite) [33,58–60], and fibers (e.g. glass fiber, carbon fiber) [61–63], are also considered when formulating intumescent coatings.

The mechanisms by which these ingredients affect the fire protection behavior of intumescent coatings have been widely discussed in the literature [4,16,47,79,123]. Yasir et al. [70] investigated the effects of basalt fibers on the thermal properties of an epoxy-based intumescent coating; with 3 wt.% basalt fibers added to the formulation, the coating showed optimal thermal shielding of a steel substrate, and microstructure-, yield-, and anti-oxidation properties of the char layer were all improved. Mariappan et al. [83] studied the effects of TiO$_2$ on the fire-resistance performance of cellulosic intumescent coatings according to a standard cellulosic fire test curve (ISO834). They found that the presence of TiO$_2$ increased the thermal stability of an intumescent coating and a ratio of ammonium polyphosphate to TiO$_2$ close to their stoichiometric reaction ratio, benefitted the performance of the intumescent coatings the most. Lu et al. [159] evaluated the fire retardancy and thermal stability of intumescent coatings with additions of different sizes (1-2 μm, 2-5 μm, and 5-10 μm) of zinc borate; the coating with 2 wt% zinc borate (2-5 μm) showed the best performance in smoke production and the total heat release during burning, most likely due to an optimal specific surface area and dispersion of this particular zinc borate particle size.

In general, these investigations provide valuable information for application of chemicals in intumescent coatings. However, focus has mainly been on the effects of a specific ingredient on the individual performance parameters such as the intumescent coating char properties. What is needed is a discussion of the extent to which these parameters correlate with the actual fire-resistance performance of the coating (i.e. the critical time for a coated steel plate to reach a preset critical temperature during a given fire testing method). For example, char expansion is regarded as one of the significant parameters of intumescent coatings [74,81,143], but its influence on the fire-resistance performance of a given coating is, in many cases, not as expected. Many researchers have observed that a high expansion of the char resulted in a good fire-resistance performance of the coating [53,74,160], while others have pointed out that good
insulation of the coating cannot be guaranteed with a high degree of expansion alone [143]. The discrepancy between these investigations can be attributed to the fact that the fire-resistance performance of a coating is the result of several coupled properties of the char. The correlation between a single parameter (e.g. char expansion) and the critical times measured is influenced by other parameters such as the morphological structure of the char. Understanding the interactions and coupling of these parameters is crucial in order to identify the contribution of each char parameter to the fire-resistance performance, and to give clues to optimization of intumescent coating formulations.

The aim of the present investigation is to explore the potential correlations between intumescent char properties and fire-resistance performance of epoxy-based intumescent coatings (with and without the active filler material zinc borate). In our previous work, an abundance of data on the effects of five typical ingredients (ammonium polyphosphate, melamine, TiO₂, CaCO₃, and vitreous silicate fiber) on the performance of hydrocarbon intumescent coatings was generated [161]. Using these data, the potential correlations between temperature-time response of coated steel plates (exposed to standard hydrocarbon heating curve UL 1709), the relative expansion of the intumescent coatings (thickness of the intumescent char divided by the original dry film thickness of the coating), and the morphological structure of intumescent chars, are explored. Furthermore, to give a direction on how to ensure the desirable char properties identified in its correlations with the fire-resistance performance, the relationship between char properties and the dynamic viscosity of incipient intumescent chars is investigated.

7.2 Experimental

7.2.1 Coating materials and application

The epoxy-based hydrocarbon intumescent coatings studied were formulated with a two-component (base and curing part) system. The base part contained a bisphenol A epoxy resin (Hexion B.V.) and a diluent (ICL-IP B.V.), and filled with ammonium polyphosphate (100 wt.%, Clariant GmbH), zinc borate (>98.8 wt.%, Borax Ltd.), calcium carbonate (>99 wt.%, Reverté Minerales S.A.), and vitreous silicate fiber (95-
100 wt.%, length of approx. 120 µm, diameter of approx. 5 µm, Rockwool B.V.). The curing part was composed of a polyamide (Air Products B.V.), a catalyst (Air Products B.V.), and filled with melamine (100 wt.%, OCI Nitrogen B.V.) and titanium dioxide (>90 wt.%, Huntsman Ltd.).

The compositions of the intumescent coatings with and without zinc borate (ZB) are listed in Table 7-1 and Table 7-2, respectively. The base and curing part was dispersed individually with a high-speed disperser at 1600 rpm (the speed reduced to 400 rpm when vitreous silicate fiber was added). For rheological measurements, free films of the coating were prepared by mixing the well-dispersed base and curing part according to an amide/epoxy functional group stoichiometric ratio of 0.867, followed with casting the sample in a circular PVC frame (diameter of 25 mm and 2 mm height). All samples were cured for 24 hours at room temperature before use.
Table 7-1 Composition of the series of zinc borate intumescent coatings (in wt.%), APP = ammonium polyphosphate, MEL = melamine, ZB = zinc borate.

<table>
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<th>Coating name</th>
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<th>ZB</th>
<th>TiO$_2$</th>
<th>CaCO$_3$</th>
<th>Vitreous silicate fiber</th>
<th>Binder system$^a$</th>
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$^a$ Corresponding to the total amount of the epoxy resin, diluent, amide, and catalyst. The ratio between these components was kept constant in all the formulations.
Table 7-2 Composition of the series of zinc borate-free intumescent coatings (in wt.%), APP = ammonium polyphosphate, MEL = melamine, ZB = zinc borate.

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<td>12.63</td>
<td>3.44</td>
<td>5.00</td>
<td>10.18</td>
<td>52.96</td>
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<tr>
<td>C10</td>
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<td>12.63</td>
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<td>10.00</td>
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<td>47.96</td>
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<tr>
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<td>42.96</td>
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<tr>
<td>Vitreous silicate fiber</td>
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<tr>
<td>F0</td>
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<td>12.63</td>
<td>3.44</td>
<td>1.44</td>
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<td>3.44</td>
<td>1.44</td>
<td>20.00</td>
<td>46.70</td>
</tr>
</tbody>
</table>

²Corresponding to the total amount of the epoxy resin, diluent, amide, and catalyst. The ratio between these components was kept constant in all the formulations.

7.2.2 Rheological measurements of incipient intumescent chars

The rheological behavior of the intumescent coatings as a function of temperature was recorded on a rheometer DHR-2 (TA Instruments) with a disposable parallel-plate configuration. During a measurement, the free film of an intumescent coating (Ø25 mm x 2 mm height) was placed between the two plates and the program of an oscillation temperature ramp was set for the instrument. The program heated the samples in the range of 30 to 600 °C with a heating rate of 50 °C/min. The frequency of the oscillation
was 5 Hz. To record the rheological behavior of the coating at both the solid cured and low-viscosity state, the displacement of the oscillation was first set as $5 \cdot 10^{-5}$ rad and then changed to $5 \cdot 10^{-3}$ rad once the programmed temperature reached 290 °C. A low axial force adjustment (0±0.1 N) was activated to accommodate the expansion of the sample and meanwhile ensure the contact between the sample and the upper plate of the configuration.

7.3 Results and discussion

In the following, the relationships between fire-resistance performance of intumescent coatings (i.e. critical times to reach 400 and 550 °C), relative expansion of intumescent chars, and morphological structure of char layers are analyzed. The rheological behavior of the intumescent coatings was further investigated to explore its correlations with the char expansion and the char structure.

7.3.1 Influence of the char expansion on the critical times

The ZB-containing and ZB-free intumescent coatings with different contents of ammonium polyphosphate (APP), melamine (MEL), TiO$_2$, CaCO$_3$, and vitreous silicate fiber (see Table 7-1 and Table 7-2) were studied in previous work [161]. The data regarding the critical times and relative expansion are adopted here to examine the correlations between fire-resistance performance of intumescent coatings and char expansion. Figure 7-1 shows the critical times to 400 and 550 °C as a function of the relative expansion. The results generally present a positive relationship between the relative expansion and the critical times: with a higher relative expansion comes a longer critical time during the fire-resistance experiments. This supports the finding that char expansion is regarded as one of the most crucial parameters for good performance of intumescent coatings [143], which seems plausible, considering that the thermal conductivity of a homogeneous material is directly proportional to the thickness of the material. In fact, most of the detailed mathematical models developed for quantifying fire protection performance of intumescent coatings rely on a thickness measurement of the fully expanded intumescent coating char as model input and with this approach good agreements between simulations and experimental data have been found [66,90,115].
Figure 7-1 The critical time to 400 °C (a) and 550 °C (b) as a function of the relative char expansion of the ZB-containing and ZB-free intumescent coatings. Each point corresponds to the data from a specific intumescent coating. The error bars on the x- and y-axis are the standard deviation of the relative expansion and the critical times, respectively.
However, the results in Figure 7-1 clearly show some exceptions to the approximately linear relationship between the relative expansion and the critical times, especially in the region of the ZB-free intumescent coatings. For example, the intumescent coatings T0 and D0 both have a relative expansion higher than those of the coatings F10 and T1.5, but the critical times of these coatings are comparable. These exceptions are in agreement with the statement by Morys et al., that the thickness of a char residue is not all that matters; a high expansion does not guarantee a good performance of an intumescent coating [143].

The limited applicability of using the char expansion alone to correlate with the critical time is due to the fact that the complexity of the morphological structure and the composition of the char are not taken into account. The inner structure and chemical composition of the intumescent char directly influence the thermal conductivity of the layer and therefore play a significant part in determining the overall thermal insulation property of the char. Assuming that the intumescent chars have the same structure and composition, then the critical time of the coating is only affected by the degree of char expansion. This seems to be the case for most of the ZB-containing intumescent coatings for which the differences between the char structures were reported to be quite small [161]. Therefore, as shown in Figure 7-1, the critical times of the ZB-containing intumescent coatings are mainly clustered within a narrow range as a result of the minor variations of the relative expansion.

On the other hand, for the chars produced with the ZB-free intumescent coatings, the morphological structures were found to be more diverse, depending on the coating formulation considered [161]. For the sake of evaluation in the present work, the layered phases of the intumescent chars formed in the previous work are roughly grouped into three types: “sponge-like”, “macroporous”, and “compact”. Examples are shown in Figure 7-2.
Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

Figure 7-2 Illustration of three representative char phases. The examples on the left and right hand sides originates from the coating with 2.5 wt.% CaCO$_3$ (D2.5) and the one with 5 wt.% CaCO$_3$ (D5), respectively.

For a specific char, the contribution of each phase (if it exists) to the overall relative expansion was calculated from the measured height of the phase divided by the original dry film thickness of the coating. The results are given in Figure 7-3 as a function of the corresponding relative expansion. It can be seen that the char expansion demonstrates a clear linear relationship with the contribution from the sponge-like and macroporous phases, but it hardly relates to that of the compact phase. As concluded in the previous work, a compact char layer may possess better insulation properties (due to a low thermal conductivity) than those with sponge-like and discernible macroporous phases [141]. The relative expansion that cannot correlate with the contribution from the compact phase could cause deviations while connecting with the critical times of the coated steel plates (see the exceptions in Figure 7-1).
7.3.2 Correlation between critical times and integrated parameter of intumescent char

To establish a better correlation between the intumescent chars and the critical times, the relative expansion has to be “corrected” with a term containing the thermal conductivity, which is influenced by the morphology and chemical composition of the char. However, it is a challenge to quantify the thermal conductivity as it varies throughout the non-uniform char and is a function of temperature. Therefore, a parameter we term “insulation efficiency” of a char phase is introduced here and the assumptions underlying the calculations and the correlation development are:

- An intumescent coating char consists of a composite made up of the sponge-like, macroporous, and/or compact phases mentioned above.
- The sponge-like, macroporous, and compact phases are each homogeneous with respect to physical and chemical properties.
The individual phases (i.e. sponge-like, macroporous and compact) in different intumescent coating chars are assumed to be identical.

These assumptions are certainly not always reasonable. For example, the bottom layers of the chars shown in Figure 7-2 were visually classified into the same compact phase, while the properties of these two layers are not genuinely identical. However, the correlation approach targets the core factor (i.e. the existence of the three contrasting phases) which significantly influences the insulation properties of a char, whereby a method to crudely characterize complex intumescent coating chars in a quantitative way becomes available.

The insulation efficiency expresses the critical time of a steel substrate in minutes according to (Eq. 7-1):

\[ t = I_s \cdot x_s + I_m \cdot x_m + I_c \cdot x_c \]

(Eq. 7-1)

where the subscript s, m, and c stands for the sponge-like, macroporous, and compact phase, respectively. The symbol I is the insulation efficiency of a phase in minutes, and the dimensionless number, x, is the thickness of the target phase divided by the original dry film thickness of the coating.

Ideally, for an intumescent coating char with only one specific phase, equation (Eq. 7-1) can be simplified and rearranged to:

\[ I_i = \frac{t}{x_i} \]

(Eq. 7-2)

where i stands for the target phase (i.e. sponge-like, macroporous, or compact phase), and \( x_i \) is equal to the relative expansion of the char. Note that this expression does not suggest a specific physical condition of a char. Understanding its relation to physical properties, such as the thermal conductivity, was not attempted.

To apply the correlation expressed in equation (Eq. 7-1), the insulation efficiencies of the sponge-like, macroporous, and compact phases have to be determined a priori with data from at least three separate intumescent coatings. In our previous work, the coating F5, which produced a char with a compact phase only, was studied using the exact same fire-resistance experiments (a critical time of 79.8 min to 550 °C with an associated
relative expansion of 2.035 mm/mm was obtained) [151]. Therefore, it could be adopted to calculate the insulation efficiency of the compact phase using equation (Eq. 7-2), i.e. $I_c = 39.2$ min. Regarding the insulation efficiencies of the sponge-like and macroporous phase, chars containing only one of these two phases were not available. However, chars with a combination of the sponge-like and compact phases only (e.g. coating C2.5) or the macroporous and compact phases only (e.g. coating ZB-T2) were obtained [161]. With the thermal efficiency of the compact phase ($I_c$) known, the corresponding values for the sponge-like and the macroporous phases can therefore be calculated using equation (Eq. 7-1). For the coatings C2.5 and ZB-T2, the critical times to 550 °C and the thicknesses of the phases divided by the original dry film thickness of the coating (values plotted in Figure 7-3), the thermal efficiencies of the sponge-like ($I_s$) and macroporous ($I_m$) phases were calculated to 5.7 and 14.1 min., respectively.

By substituting the values of the thermal efficiencies into equation (Eq. 7-1), the right-hand side gives the integrated parameter as follows:

$$\text{Integrated parameter (P}_{\text{integ.}}) = 5.7 \cdot x_s + 14.1 \cdot x_m + 39.2 \cdot x_c$$  \hspace{1cm} (Eq. 7-3)

Here, $P_{\text{integ.}}$ has the unit of minutes.

The critical times as a function of the integrated parameter are presented in Figure 7-4. Compared to the implicit relationship with the relative expansion in Figure 7-1, the critical times show an approximate linear correlation to the integrated parameter that combines the relative expansion with the insulation efficiencies of the char phases. The results prove the rationality of the expression described in the equation (Eq. 7-1), and more specifically of the argument that taking the influence of different char phases into account can offset the inconsistency between the critical times and the relative expansion. Nevertheless, the good agreement between the critical times and the integrated parameter is apparently owing to the fact that the values of the thermal efficiencies calculated with the three individual intumescent coatings (F5, C2.5, and ZB-T2 mentioned above) represent the insulation performance of the corresponding char phases in the other ZB-containing and ZB-free intumescent coatings with a reasonable accuracy. This supports the assumption made earlier that each of the sponge-like, macroporous and compact phases are homogenous and identical in different
intumescent coating chars. However, it is not yet known if this assumption can be extrapolated to hydrocarbon intumescent coatings in general.

![Graph showing correlation between critical times and integrated parameter of char properties](image)

Figure 7-4 Correlation between the critical times and the integrated parameter of the chars formed from the ZB-containing and ZB-free intumescent coatings.

It has to be noted that the correlation described here is not for predicting the critical time of an intumescent coating with the char properties. Instead, it provides a straightforward way to understand and/or explain the fire-resistance performance obtained from fire tests with the characteristics of the char formed, and more crucially identifies the desirable char characteristics that one can aim for to obtain a good coating performance. According to the correlations between the critical times, the integrated parameter, and the thickness of the phases, optimizing the ingredients of intumescent coatings to form more of any of these phases can, at least theoretically, lead to longer critical times. However, due to its high insulation efficiency it is apparently more efficient to promote the formation of a thicker compact phase. Moreover, although the
cases with a high thickness of the sponge-like phase (e.g. T0 and F5) resulted in long critical times to 400 and 550 °C, the deviations they showed on both critical times and relative expansion are remarkable (see Figure 7-1). It was, as discussed in the previous work [161], caused by the partial detachment of the sponge-like layers observed in some of the fire-resistance experiments. In a real fire scenario, especially for a hydrocarbon type, the thermal shock induced by the fuel combustion and gas flow is more damaging than that in the fire-resistance experiments in our work [151]. The mechanical instability of the chars with the sponge-like phase would experience more severe detachment and gain critical times even shorter than their respective bottom limits of the uncertainties in Figure 7-4. Therefore, from the perspective of formulation development, the better performance of intumescent coatings in fire-resistance experiments should rely on the formation of the macroporous and compact phase, owing to their superior insulation efficiency and mechanical stability compared with the sponge-like phase with fragile films and large voids.

7.3.3 Coupling of the rheological behavior of the intumescent coatings and the char parameters

Having identified the integrated parameter of intumescent chars (especially the contribution of the macroporous and compact phase) as the key factor to influence the fire-resistance performance of intumescent coatings, the challenge is now to control this parameter, i.e. manipulating the formation of the char phases. The major actions that influence the properties of the intumescent residual chars are the intumescence process and the char degradation (mainly thermal oxidation) [143,151]. The former determines the overall appearance of the char, while the latter induces the gradual microstructure transition of chars from closed-cell foam to open-cell sponge (cell walls disappear through carbon loss) [92,143,146,151]. Due to the insulating protection from the top layers, the temperature progression of the bottom char layers (usually the compact phase) is relatively slow. The layers are marginally affected by char degradation due to the short exposure time to oxidation (starting from 540 °C or higher). Therefore, formulation wise, the intumescence process should be focused on controlling the development of the char phases. The intumescence process of an intumescent coating is significantly influenced by the dynamic viscosity change during
Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

its viscoelastic state [3,141,151]. It suggests that the rheological behavior of an intumescent coating can be used to discover its connection to the intumescent char and hence get inspiration for enhancing the integrated parameter of a char.

Figure 7-5 shows the dynamic viscosity of the ZB-containing intumescent coatings as a function of temperature. In the beginning, all the coatings experienced a relatively stable stage where the dynamic viscosity changes were moderate. However, when the temperature reached around 250 °C, the coatings showed a substantial viscosity drop to a dynamic viscosity minimum. The subsequent return of the curves drove the dynamic viscosity back to a value comparable or even higher than that of the original coating. The progression of the dynamic viscosity reflects the three different states of the coatings: temperature-dependent change of the epoxy binder (e.g. post cure cross-linking); softening as a viscoelastic substance; incipient charring of the substance [141]. The softening stage, characterized by the distinct dynamic viscosity drop, coincides with the temperature range where the blowing agents (e.g. melamine) release gases to cause the swelling of the viscoelastic substance. The dynamic viscosity change within this stage is therefore regarded as the key factor that influences the expansion of an intumescent coating and the morphological structure of an intumescent residual char [141].
Complex viscosity (Pa.s) vs. Temperature (°C)

(a) 10 wt.% APP
- 10 wt.% APP
- 15 wt.% APP
- 20 wt.% APP
- 25 wt.% APP

(b) 5 wt.% MEL
- 5 wt.% MEL
- 10 wt.% MEL
- 15 wt.% MEL

(c) Dynamic viscosity (Pa×s) vs. Temperature (°C)
- 2 wt.% TiO₂
- 6 wt.% TiO₂
- 10 wt.% TiO₂
Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

Figure 7-5 Dynamic viscosity changes for the ZB-containing intumescent coatings with different levels of (a) APP, (b) MEL, (c) TiO₂, (d) CaCO₃, and (e) vitreous silicate fiber.

With decreasing content of APP or increasing levels of the other investigated ingredients (i.e. MEL, TiO₂, CaCO₃, and vitreous silicate fiber), the extents of the dynamic viscosity drop were generally reduced. The dynamic viscosity minimums accordingly increased nearly with two orders of magnitude. These results are fairly plausible, considering that APP would decompose into ammonia and liquid polyphosphoric acids at the beginning of the softening stage of the coatings, conducing the dynamic viscosity drop of the coatings, while increasing contents of the other ingredients would bring a higher solid portion in the mixture and thereby raise the
dynamic viscosity of the viscoelastic ‘‘coating’’. It is noted that the effects of MEL on the rheological behavior of the coatings were grouped with TiO$_2$, CaCO$_3$, and the fiber, as the elimination of ammonia from MEL occurs consecutively at around 350 °C (later stage of the viscosity drop) and the co-product melam ([(H$_2$N)$_2$(C$_3$N$_3$)]$_2$NH) would convert into melem (C$_6$N$_7$(NH$_2$)$_3$) without passing through melting at higher temperatures [131,132]. As stated in our previous work [141], the high dynamic viscosity of a viscoelastic mass, originating from the reduced viscosity drop, can accommodate more pressure from the gas release of blowing agents and thereby suppress the expansion and form a more uniform char. It generally coincides with the results that the intumescent chars showed a decrease in the relative expansion and denser macroporous and compact phase with decreasing content of APP or increasing content of the other ingredients in the ZB-containing formulations [161].

Figure 7-6 shows the behavior of TiO$_2$, CaCO$_3$, and the fiber in affecting the dynamic viscosity of the ZB-free intumescent coatings. Analogous to that observed with the ZB-containing coatings, the dynamic viscosity drop was reduced by adding more TiO$_2$, CaCO$_3$, and the fiber in the ZB-free formulations. Nevertheless, with the absence of zinc borate, the dynamic viscosity minimum altered by the ingredients was limited by an order of magnitude. It agrees with the significant role of zinc borate in controlling the dynamic viscosity drop of viscoelastic substances and thereby the physical appearance of intumescent chars [141]. The good correlation between the dynamic viscosity drop and intumescent char properties was found in the investigation of ZB-free formulations as well. In accordance with the reduced dynamic viscosity drop, the chars were varied from the sponge-like-compact phase with high expansion to the general macroporous-compact phase with limited height by increasing the levels of TiO$_2$, CaCO$_3$, and the fiber in the ZB-free intumescent coatings [161].
Correlation study on fire-resistance performance of hydrocarbon intumescent coatings and char properties

Figure 7-6 Dynamic viscosity changes for the ZB-free intumescent coatings with different levels of (a) TiO$_2$, (b) CaCO$_3$, and (c) vitreous silicate fiber.
Overall, the results in Figure 7-5 and Figure 7-6 reveal the good correlation between the dynamic viscosity drop of the coatings and the intumescent char properties irrespective of the presence of zinc borate. Nevertheless, zinc borate does influence the order of magnitude of the dynamic viscosity minimum (1 and 2 for the ZB-free and ZB-containing coatings, respectively). More interestingly, although the relative changes of the dynamic viscosity minimum caused by TiO$_2$, CaCO$_3$, and the fiber are comparable in the formulations with and without zinc borate (e.g. around 80% between T$_{ZB}$-6 and T$_{ZB}$-10 and between T-1.5 and T-5), the corresponding difference in the intumescent chars is different. The relative expansion and char phases observed in the ZB-free cases are clearly more sensitive to the dynamic viscosity change.

Figure 7-7 plots the relative expansion of all the ZB-containing and ZB-free intumescent coatings as a function of the dynamic viscosity minimum. Some representative chars [161] are presented aside the figure to indicate the change of the char appearance with the dynamic viscosity increasing. As highlighted with a blue dashed line, the relative expansion of the coatings showed an exponential decrease with the elevated dynamic viscosity minimum. With the dynamic viscosity minimums lower than 10 Pa·s, the relative expansion varied tremendously. The intumescent chars are characterized by a high expansion with a contribution mainly from the sponge-like phase (e.g. T0 and D0). When the minimums are in the range of 10 to 100 Pa·s, the response of the relative expansion became relatively modest, and the macroporous and compact phase were gradually found to dominate in the chars (e.g. T5 and D5). After the dynamic viscosity minimum increased to 100 Pa·s or higher, the relative expansion started to stabilize at around 2.1, which seems to indicate the bottom limit of the char expansion. The sponge-like phase completely disappeared and only the thin layers of the macroporous and the compact phase were left in the intumescent chars (e.g. ZB-T6).
Figure 7-7 Relationship between the dynamic viscosity minimum and the relative expansion of the intumescent coatings. The temperature interval for which the dynamic viscosity minimums were observed is from 354 to 369 °C.

The results in Figure 7-7 indicate that the formation of the char phases can be controlled by adjusting the dynamic viscosity minimum of the intumescent coatings. For the intumescent coatings that showed a substantial viscosity drop to a minimum lower than 10 Pa·s, even though the integrated parameter of the chars were considerable, the poor mechanical stability of the sponge-like phase makes the coating undesirable. The coatings which have a dynamic viscosity minimum higher than 100 Pa·s may not be favored as well, as the char expansion is greatly restricted and the integrated parameter would be quite small. However, considering some extreme cases that have a high requirement for the mechanical strength of intumescent chars, such as jet fire scenarios, the compact chars formed at this range may be desirable. Nevertheless, for a regular hydrocarbon fire scenario, the preferable range of the dynamic viscosity minimum to obtain a good phase composition and high integrated parameter could be within 10 to 100 Pa·s.
7.4 Conclusions

In this work, the existence of correlations between the fire-resistance performance of intumescent coatings, relative expansion of intumescent chars, and the morphological structure of char layers were investigated. The intumescent coatings (i.e. zinc borate (ZB)-containing or ZB-free formulations with different levels of ammonium polyphosphate, melamine, TiO₂, CaCO₃, and vitreous silicate fiber) were evaluated under the standard hydrocarbon heating curve UL 1709. The relative expansion of the chars produced correlated reasonably well with the corresponding fire-resistance performance (i.e. the critical times of the coated steel plates to 400 and 550 °C). Nevertheless, due to the fact that the relative expansion cannot reflect the insulation properties of the intumescent char phases, limitations were observed. Therefore, a methodology based on a so-called “integrated parameter” that covers both the relative expansion and insulation efficiencies of the different char phases (i.e. sponge-like, macroporous, and compact phase) was developed. A better correlation was seen between the critical times and the integrated parameters. Owing to the relatively high insulation efficiencies of the macroporous (14.1 min) and compact (39.2 min) phase in the integrated parameter, their formation would be favored for formulation development wise. The dynamic viscosity change of the intumescent coatings showed a high correlation with the physical appearance (i.e. the relative expansion and morphology) of the chars. This suggests that manipulating the dynamic viscosity change of intumescent coatings can effectively control the integrated parameter and thereby obtain the desired performance of the coatings.
Conclusions and future work

A summary of the main conclusions from the thesis and suggestions for future work are summarized in this chapter.

8.1 Conclusions

This thesis has specifically focused on studying the fire-resistance performance of hydrocarbon intumescent coatings, when exposed to the standard fire test curve UL 1709, and on characterizing the intumescent coating chars being formed. The laboratory-scale furnace that can handle the severe heating conditions (a heating rate higher than 200 K/min up to 1093 °C) defined in the standard UL 1709, was developed to perform the fire-resistance experiments in the present study and provide a solution to the facility challenge generally faced with the performance evaluation of hydrocarbon intumescent coatings in laboratories. With the benefit of the device, the effects of typical ingredients (zinc borate, ammonium polyphosphate, melamine, titanium dioxide, calcium carbonate, and vitreous silicate fiber) were studied to comprehend the behavior of hydrocarbon intumescent coatings and guide the optimization of coating formulations.

Two versions of the laboratory-scale furnace have been sequentially constructed. The initial version was applied to investigate the effects of zinc borate on performance of hydrocarbon intumescent coatings. Results of fire-resistance experiments showed that, among the investigated levels (0 to 20 wt.% zinc borate) the use of 15 wt.% zinc borate in the coating was the most efficient formulation, with the coated steel plates obtaining the longest critical time for both 400 and 550 °C. The analyses on the intumescent chars formed from the fire-resistance experiments revealed that zinc borate can restrict char expansion but promote a uniform char structure with small cell (void) size. Rheological recording evidenced that increasing the zinc borate content distinctly increased the
dynamic viscosity of the coating during its viscoelastic state, which may explain the results found for the char expansion and the char structure. X-ray diffraction studies on the compositional profiles of the intumescent chars showed increased yields of phosphates (especially BPO$_4$) with increasing level of zinc borate in the formulation. Furthermore, the thermogravimetric analyses on the coatings suggest that zinc borate can improve the residual weight of the char by reducing epoxy binder degradation and oxidation of the carbon-inorganic residue. Overall, the results from these studies could be used to provide guidance as to replacements for raw materials that are classified or could become classified as hazardous. The zinc borate study is one such example.

Although the initial version of the laboratory-scale furnace has been successfully applied to the investigation of zinc borate, the furnace was further modified to make the differences between the steel temperature responses of different coatings more distinct. The reliability of the upgraded version was examined by comparing its performance with an industrial fire test furnace with respect to fire-resistance performance of coatings, and physical appearance and chemical compositions of chars. Five hydrocarbon intumescent coatings were selected and evaluated with the laboratory-scale and industrial furnace experiments, respectively. The two types of furnace experiments demonstrated a good agreement for the temperature responses and critical times of the coated steel plates. By examining the chars formed in the experiments, it was found that the laboratory-scale and industrial furnace can be correlated for the physical appearance (relative expansion and morphological structure) and chemical composition (crystalline phases) of the chars. These results proved that this laboratory-scale furnace is a promising tool to evaluate coating performance and reveal thermal properties of chars.

Supported by the validated reliability, the upgraded laboratory-scale furnace was further adopted to study the effects of various ingredients (ammonium polyphosphate, melamine, titanium dioxide, calcium carbonate, and vitreous silicate fiber) on the performance of selected zinc borate (ZB)-containing and ZB-free intumescent coatings. Increasing levels of ammonium polyphosphate (APP) or decreasing levels of melamine (MEL) in the ZB-containing coatings generally prolonged the critical times of coated steel plates and improved the physical conditions of the chars (including relative...
expansion and formation of macroporous and compact structures). The positive effects of APP were attributed to the promoted interactions of APP with the epoxy binder and zinc borate, while the results for MEL was probably accounted for by the negative influence from the binder content accordingly changed with level of MEL.

Varying the levels of titanium dioxide (TiO$_2$), calcium carbonate (CaCO$_3$), and vitreous silicate fiber barely had an effect on the performance of the ZB-containing coatings. In contrast, the levels of these three ingredients in the ZB-free intumescent coatings demonstrated significant influences on the critical times and the physical appearance of the chars. The ZB-free coating with 1.5 wt.% TiO$_2$, 2.5 wt.% CaCO$_3$, or 5 wt.% fiber showed the longest critical time to both 400 and 550 °C. By increasing the level of any of the three inorganic components, the char expansion of the coating was reduced but at the same time the char morphology was improved. The influences of TiO$_2$ and CaCO$_3$ on the ZB-free coatings are probably related to their reactions with APP. The mineral fiber affected the char structure mainly by physically reinforcing the internal network of the char layer.

The results from the ingredient studies are of great significance for understanding of hydrocarbon intumescent coatings and formulation optimization. Moreover, the large amount of experimental data from the investigations can be used to explore correlations between the critical time of a coated steel plate and the char properties. By plotting the critical times to 400 and 550 °C as a function of relative expansion (data from studies of APP, MEL, TiO$_2$, CaCO$_3$, and vitreous silicate fiber), a reasonable correlation was revealed. However, with defining a so-called integrated parameter that covers both the relative expansion and insulation efficiencies of the different char phases observed (sponge-like, macroporous, and compact phase), an approximately linear relationship was seen between the critical times and the integrated parameter. The results indicate that the fire-resistance performance of intumescent coatings would be improved by promoting the macroporous and compact phases due to their high insulation efficiencies in the integrated parameter. The rheological behavior of the corresponding coatings were examined and the dynamic viscosity minimum showed an exponential relationship with the relative expansion and morphology of the chars. Thus,
manipulating the rheological behavior and thereby the integrated parameter may effectively control the performance of a hydrocarbon intumescent coating.

8.2 Suggestions for future work

Future work to stimulate the development of hydrocarbon intumescent coatings could be mapping the mechanisms behind the formation of distinct char structures, developing methodologies for quantification of char properties, and exploring new ingredients for coating formulations.

In the present thesis study, the fire-resistance performance of an intumescent coating was significantly affected by the distinct char phases formed in the intumescent char layer, while the mechanism behind the formation of these phases is not explicit yet. Further investigations, for example, the influences of thermal conditions (e.g. temperature, heating rate), chemical reactions, and compression force (e.g. applied by the top part of the incipient char to the bottom part in the coatings with high dry film thickness) on the intumescence process of hydrocarbon intumescent coatings, may give more guidance to formulation optimization. Moreover, the char properties such as porosity and mechanical strength were qualitatively presented in the thesis by analyzing the morphological structure of the char layers. Establishing methodologies to quantify these char properties would give a better interpretation of performance of hydrocarbon intumescent coatings. The specific suggestions for the quantification of porosity and mechanical strength are presented as follows:

- **Porosity**: characterization of char porosity may take advantage of techniques such as X-ray computed tomography and microscopy. The former can provide a three-dimensional image of the inner structure of a char without manually cutting or destructing the sample. While the use of microscopy to characterize char porosity could start with mounting the sample in an epoxy resin to minimize structure damage, followed by observing the pieces cut from the casted sample with optical or electron microscopy. Clearly, with the images recorded with X-ray computed tomography or microscopy, work will be involved afterward to quantitatively distinguish the pores from the solid part of the char.
Conclusions and future work

- **Mechanical strength**: the mechanical disturbances in a fire scenario, especially hydrocarbon fire scenario, require good mechanical stability of the char layer to maintain its protection of the substrate. Therefore, a so-called quantified mechanical strength is a critical index of the performance of a hydrocarbon intumescent coating. To accomplish the quantification, efforts could be put on developing a specialized setup that can compress or penetrate the char layers (preferably during the fire-resistance experiments) and the forces used to destruct the char could be recorded with a sensor to represent the resistance of the char against mechanical disturbance.

Regarding the development work on coating ingredients, this involves the search for alternatives to hazardous raw materials, such as boron compounds or phosphate esters or modifying existing ingredients (e.g. APP and MEL, which are known for their poor resistance to a corrosive environment like seawater) to achieve better fire-resistance and weathering-resistance performance of a coating. To solve this problem, one option is to modify these hydrolysis-/chloride-sensitive ingredients. The suggestions to carry out these improvements are presented below:

- **Alternative raw materials**: as has been demonstrated in the thesis study, the positive effects of zinc borate were attributed to its reaction with phosphoric acids derived from APP during the viscoelastic state of the coating and its stabilization behavior on thermal degradation of the epoxy binder. Therefore, work may focus on seeking alternatives that can readily react with derivatives of APP, which then can make an influence on the dynamic viscosity drop of intumescent coatings, and promote crosslinking reactions of polymeric materials. The same method could be utilized to find alternatives for other hazardous raw materials.

- **Modification on hydrolysis-/chloride-sensitive ingredients**: methods such as surface treatment and microencapsulation could be used to modify the hydrolysis-/chloride-sensitive ingredients. These means have been successfully employed to solve the hydrolytic problem of APP while being applied in flame retardant polymers. Nevertheless, the application of these methods in hydrocarbon intumescent coatings is rather rare. Therefore, it is of interest to carry out research
on modifying ingredients with these techniques to improve the resistance of intumescent coatings to weathering causes.
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