

# Challenges in flame retardant wood coatings

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Turku, Finland, 2020

## Abstract

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**Keywords**

*Flame retardant, emulsion polymerization, wood coating, defoaming*

This thesis was carried out with the scope to better understand the underlying challenges of developing novel environmentally friendly flame retardant wood coatings and to find possible solutions for overcoming such challenges. Several different wood types were treated with specialty coating formulations containing various flame retardant additives in order to obtain wood species exhibiting excellent flame retardant properties together with other desired properties such as weathering durability and visual appearance.

Emulsion polymerizations were conducted in order to obtain acrylic waterborne core-shell dispersions having small particle sizes and high tolerance towards electrolytes. Such dispersions might be suitable for exterior and/or interior wood coatings.

One deficiency most wood coatings have is excessive foaming. Excessive foaming can cause problems, especially during industrial application of coating. A test method was developed, and five different antifoaming additives were tested for their defoaming efficacy and their storage stability. DF-2 was found to be suitable for the dispersion, as low amounts of DF-2 had a strong decreasing effect on foaming as well as positive impact on long-term storage stability.

Cone calorimeter tests were performed on several coated wood samples in order to determine the viability of different flame retardant additives. All additive-containing coatings showed improved performance compared to the reference samples. Due to the varying nature of wood samples, the cone calorimeter tests results are indicative and may not fully correspond with full scale fire tests such as SBI.

## Acknowledgements

I would like to express my gratitude to Professor Carl-Eric Wilén for his supervision, support, and expertise during this project. My thanks also go out to Industrial partner for giving me the opportunity and trust to carry out this project, and for their support during its course. A special thanks goes out to Taru Huokuniemi for her help, patience, and expertise.

To my colleagues at the Laboratory of Polymer Technology, you all have my gratitude. Throughout my studies and during this project, the laboratory has always provided a welcoming working environment with knowledgeable and pleasant coworkers. Teija Tirri deserves praise for her tireless work in the laboratory, always being there to help when needed.

Finally, I would like to thank Åbo Akademi University and the Faculty of Science and Engineering for providing me with the knowledge and confidence to tackle this project and for giving me a stable platform from which I can confidently step out into working life.

André Båssar

Turku, November 2020

## Nomenclature

ATR	Attenuated total reflectance
CLT	Cross laminated timber
CMC	Critical micelle concentration
DLS	Dynamic light scattering
DSC	Differential scanning calorimetry
EHC	Effective heat of combustion
FTIR	Fourier transform infrared spectroscopy
Glulam	Glued laminated timber
HRR	Heat release rate
LDE	Laser doppler electrophoresis
LVL	Laminated veneer lumber
MAHRE	Maximum average rate of heat emission
MDF	Medium density fibreboard
MFFT	Minimum film forming temperature
MLR	Mass loss rate
OSB	Oriented strand board
SBI	Single burn item
T <sub>g</sub>	Glass transition temperature
UV	Ultraviolet
VOC	Volatile organic compounds
ZP	Zeta potential

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Swedish summary – Svensk sammanfattning

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# 1. Wood and wood-based materials

Wood has always played an important role as a construction material for housing and tools. During humanity's early days, the choice of material was mostly based upon availability and workability, and our knowledge of wood was reliant purely on experience. Even as society formed and eventually evolved into everything we see today, our close relationship with wood never ceased. Today we possess a much greater knowledge of wood, based on science and research – and its use has evolved into a complex material capable of enhancing human life (Youngs, 2009).

While society and the industry, having during the industrialization period neglected the implications of non-sustainable practices, the time of ignorance has now long been passed. The United Nations 2030 Agenda (United Nations, 2015) places a strong focus on sustainable development and urgent action against climate change and in the EU's roadmap for 2050 a goal is set to reduce carbon emissions by 80% (European Commission, 2011). These goals require environmentally sustainable materials for construction and production, and wood could be just such a material.

## 1.1. Wood composition

In general, the composition of wood can be split into four different parts. *Cellulose* is a polysaccharide of combined glucose monomers resulting in a high molecular weight linear polymer. The cellulose content of wood is around 40%. Present along with cellulose is *hemicellulose*, which is a shorter, branched polymer with lower molecular weight and containing different monomers. The structure and amount of hemicellulose varies with different tree species, but they generally make up 25% of the wood.

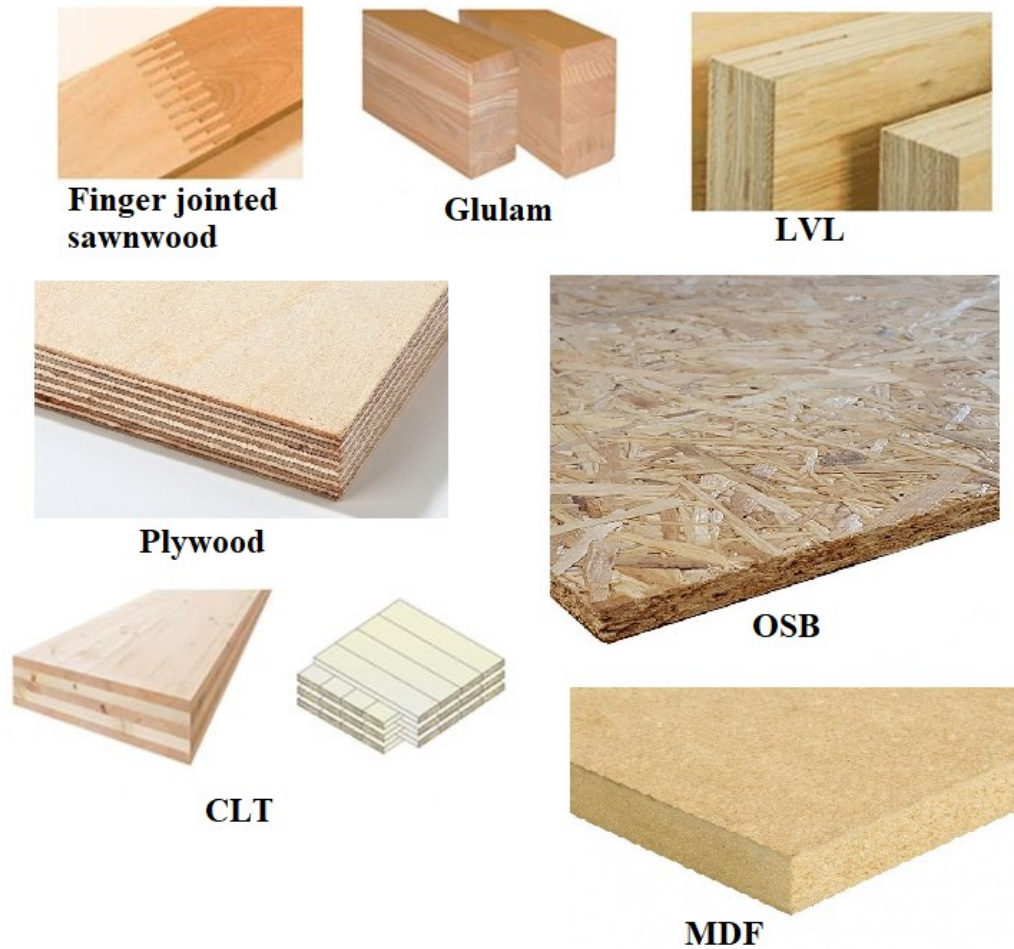
*Lignins* are another major component of wood, accounting for around 30% of wood composition. Lignin acts as the glue that binds the cellulose and hemicellulose,

creating a composite system in the wood. Lignin, like both cellulose and hemicellulose, is composed of carbon, oxygen, and hydrogen, but also contains other elements due to further reactions with other molecules found in the wood itself.

*Wood extractives* is the fourth and final part of wood. The term wood extractives does not specify any one compound but it is, instead, a general term for different low molecular weight compounds found in the porous structure of wood fibers. The extractives found varies greatly between the different species but generally make up around 5% of the wood composition. (Stevanovic, 2016)

## **1.2. Wood products**

It is widely known that in Finland and large parts of the world, sawn timber is the main structural component of everyday domestic housing. One big issue with sawn timber is the waste that is caused by cutting square boards out of round wood. In larger scale projects, such as industrial construction or commercial high-rises, the needs that must be met are much higher and the issues more complex than in a domestic house. To meet these demands and to mitigate the issues of sawn timber, engineered wood products (EWPs) have been developed. The list of different EWPs is very long as the applications and their needs vary on a case-by-case basis, and new EWPs are constantly in development to meet the needs of the future (Milner & Woodard, 2016).



*Figure 1.* Different EWPs

The following EWPs are chosen to give an example of widely used EWPs and the list is by no means exhaustive.

### 1.2.1. Glued laminated timber, Glulam

Glulam is often used in structural applications for example as a replacement for large structurally supportive beams that earlier would have had to be sawn from large trees or made out of metal. Instead of using one single beam, glulam is made by adhesive bonding and jointing several laminates. In other words, sawn timber is dried and then finger jointed together with other boards to an appropriate length. The

jointed board is then glued together with others of the same length to reach the needed width and height (Milner & Woodard, 2016).

### 1.2.2. Plywood

Plywood is based on veneer, i.e. thin slices of wood being glued together at an angle towards each other. The advantage of using veneer instead of normal sawn wood is that waste is minimized due peeling thin slices instead of cutting wide squares. This is especially true for expensive types of wood, which would otherwise not be economically viable. In plywood the number of veneer sheets are always uneven and the wood grain direction of two adjacent sheets being in a 90-degree angle. Due to the uneven number of sheets, both the top and bottom sheet will have the same grain direction.

Plywood is mostly used in construction in the paneling, flooring and roofs of houses. As well as in furniture like chairs and tables, or as a packaging material for more valuable items (Hughes, 2015).

### 1.2.3. Laminated Veneer Lumber, LVL

LVL is very similar to plywood, as it is made by glue-laminating sheets of veneer together. The main difference between LVL and plywood is that, in the case of LVL, the grain direction is oriented in the same direction. This lowers the production time and labor needed, making LVL a very economical EWP. The low cost and consistent properties make LVL a popular material choice in a wide variety of wooden furniture (Sasaki, 2001)

#### 1.2.4. Oriented Strand Board, OSB

OSB has been developed as a replacement for plywood usage in housing applications such as roofing, panels, and floors. It was developed in the 1960s and has since then soared to a 75% market share of structural panels as of 2014. To make OSB the logs are debarked and then sliced into thin *strands*. Resin is applied to the strands that are then oriented and formed into a sheet, which is then glued to another sheet with perpendicularly oriented strands (Nishimura, 2015).

#### 1.2.5. Cross laminated timber, CLT

CLT is one of the newer EWPs, developed in Switzerland and Austria in the 1990s to find a better use for the outer parts of logs that otherwise would be deemed to have low economic value. CLT consists of at least three perpendicularly glued laminates. In other words, it is very similar to glulam, but in the case of CLT each layer is at a 90-degree angle to the next whereas in glulam the grain of each layer is parallel. This tradeoff gives CLT a more rigid structure while giving up the flexibility of glulam (Harris, 2015).

#### 1.2.6. Medium density fibreboard, MDF

MDF was developed as a way to make use of waste wood from other wood production. The wood is fed to a chipper to make wooden particles of less than 50mm in diameter. Because the origin of the wood may vary, the particles need to be washed before they continue through the process. They are then subjected to high temperatures and pressure before being mixed with resins. This mixture can then be

formed into a mat and pressed into the desired thickness. This produces a cheap panel with even density throughout.

Applications for MDF panels are for example flooring or furniture. The uniform structure of MDF makes it a good choice for complicated and decorative structures. However, there are drawbacks as well, as MDF has very poor moisture resistance as well as health risks related to breathing in resins when working with the material (Ormondroyd & Stefanovski, 2015).

## **2. Coatings for wood and products thereof**

As previously discussed, wood is a very diverse material with many potential applications. Houses big and small, indoor panels, doors, furniture, and much more are often built out of wood. While using wood comes with many benefits such as renewability, overall favorable life cycle, low VOCs and carbon dioxide emissions in comparison to off-gasses from aluminum, steel, concrete and plastics, high mechanical strength there are also some drawbacks of wood. Being a natural product, wood requires protection from the impact of moisture, microbes and UV irradiation. To solve these issues, most if not all wood used in any type of construction is coated with a wood coat chosen based on the intended end application. The large number of different uses for wood subsequently leads to many different wood coatings, ensuring sufficient protection for even every niche use. The following chapters will compare the different types of wood coatings and their uses.

### **2.1. Solvent-borne coatings**

Wood coatings can generally be split into two categories based on the medium in which all the building blocks of the coat are diluted. The two mediums are water or organic solvents, the latter will be discussed in this chapter. While solvent-borne

coatings generally provide better performance than its water-based counterparts do, increasingly stringent regulations on the emission of Volatile Organic Compounds (VOC) in the EU and the world limit the future viability of this type of coating (Anderson & Daniels, 2003). The way coatings cure is by the evaporation of the solvent (Guo, Chang, Sparks, & Fortmann, 1999), it is then obvious from an environmental point of view that evaporating water into the air is always going to be preferable to any other kind of solvent. Although the future may look bleak for solvent-borne coatings, today the technology is still in wide use in several applications.

One of the main advantages of solvent-borne coatings over waterborne coatings is the ability to achieve very high solid content coatings. As solvents and water especially, are in the eyes of the industry an unwanted expense in terms of both storage and added weight, higher solid content in the final product is usually desired. This combined with the fact that an increase in solid content simultaneously decreases the solvent content, leading to a lower total VOC and lower environmental impact gives hope for future use of solvent-borne coatings (Weiss, 1997)

## **2.2. Waterborne coatings**

Waterborne coatings has been the coating industries answer to stricter environmental regulations. Using water as the medium in the coat comes with several advantages over its solvent based counterpart, such as reduced VOC and especially important in the case of this thesis: reduced flammability. Waterborne coatings come in many different forms, but the general definition is a coating where the resin is dispersed in water.

Most of the waterborne coatings are polymer dispersions and can be divided into categories based on different criteria. One such criteria is the particle size of the dispersed polymers which can range from as small as 1 nm to over 1 000 nm. The most commonly used way is to categorize the coatings based on the type of resin that is dispersed, e.g. acrylic dispersions.



Some examples of waterborne coatings are waterborne alkyd-based systems either as the only resin or in a hybrid system combined with an acrylic dispersion. But by far the most common type of waterborne coating used today are acrylic dispersions. Acrylic dispersions are the product of emulsion polymerization and can be tailor-made by the choice of monomer, the choice of stabilizer and the customization of the particle morphology (Prieto & Kiene, 2018).

### **2.3. Indoor coatings**

Another distinct difference in wood coating technology and requirements is between coatings intended for indoor versus outdoor use. Twenty years ago, there was a clear distinction between the types of coatings used in Southern Europe compared to Northern Europe. The southern countries preferred different types of polyurethane coatings while the north leaned towards acid curing coatings. The stricter regulations across the EU as well as the growing interest in environmental sustainability have since then united Europe in a move towards sustainable coating technologies, such as UV-coatings or waterborne coatings.

The requirements of indoor coatings vary widely depending on end use. The demands of stress resistance in a coating for a chair or flooring is, for example, much higher than that of a picture frame. Some general requirements of indoor coatings would be good wettability and low roughening of the wood as well as the finished coat being uniform in its appearance, as even a slight deviation in appearance is easily noticed indoors (Prieto & Kiene, 2018).

### **2.4. Outdoor coatings**

In outdoor coatings, we are seeing the same trend as in indoor coatings, i.e. a move towards sustainable coatings. However, the demands on outdoor coatings are

substantially different from those of indoor coatings. Roughly 95% of outdoor wood coatings are used in liquid form, which means that there is a solvent involved in the process. This sets an even stronger focus on lowering the VOCs in the coating. Other demands on outdoor coatings include uniform aesthetics, protection against moisture and UV radiation and protection against microbes such as fungi. Furthermore, the coating must withstand severe weather conditions for prolonged periods of time without deterioration. In the case of larger municipal buildings or high rise buildings, the coating must also provide sufficient protection against fire, a requirement that often interferes with the previously demanded low VOC content (de Meijer, 2001)

## **2.5. Opaque coatings**

Opaque coatings are what most people mean when they say “paint”. While there are many different types of opaque coatings based on different solvents and techniques, they all completely cover the wood grain. This means that, in terms of protectiveness, opaque coatings are better than transparent coatings because the wood is covered by pigment and therefore is not in contact with any UV-light.

Other advantages of opaque coatings are, for example, greater protection against surface erosion as well as access to more colors, as the underlying wood will not affect the color of the coat. A disadvantage of opaque coatings is the high amount of pigment used, as this can negatively affect long-term storage stability as the solid content of the coating increases (Feist, 2006).

## **2.6. Transparent coatings**

While opaque coatings offer a wider variety of colors, there are many cases where one would want to keep the appearance of the wood while still protecting it from the environment and even adding a hint of color. Transparent coats, especially for

outdoor use, do not perform to the same level as their opaque counterparts. The main issue is the low amount or even lack of pigment, which in opaque coatings provides important UV protection (Evans, Haase, Shakri, Seman, & Kiguchi, 2015).

Transparent coatings are also more prone to discoloration as time progresses, which is significantly more noticeable when the wood is coated with a low-pigmented coating. However, with the right combination of protective additives and particle morphology it is possible to make a durable transparent coat, enhancing the wood's own natural features (Prieto & Kiene, 2018).

### **3. Application processes for wood coatings**

Finding the right coating for a given project is not the only step needed for a successful result. Another equally important step is the application of the coating from its various containers onto the wood. In individual projects such as private houses, the application is often done by hand, but as the scale of the project grows, automation becomes a necessity.

Many factors need to be considered when choosing an application system. These include but are not limited to application rate, transfer efficiency, quality of the final product, and cost. Application rate is the amount of coating needed to create a film of a desired thickness. Transfer efficiency expresses the ratio between coating applied to the surface versus total coating consumed during the process. The final coating should be of high quality and of the lowest possible cost.

In general, for liquid coatings the application methods can be divided into two main categories. Contact methods involve the application system, coating and wooden surface all being in contact with each other. Atomizing methods are the other type and involve droplets of the coating being applied at the surface without the applicator and surface coming into contact with each other (Bulian & Graystone, Chapter 9 - Operational Aspects of Wood Coatings: Application and Surface Preparation, 2009).

### **3.1. Roller coating**

Roller coating is a simple method of application in which a suitable roll is chosen, and a coating is distributed on its surface. The application of coating is carried out by direct contact of the roll rotating on the wooden surface. Movement of the wood through the process is also done by rollers. Any excess coating not applied to the wood is scraped off the roll using a doctor blade before new coating is applied to the roller. The number of rollers and the material covering them, as well as the direction of their rotation versus the substrate can be varied to adjust the end result.

Roller coating can only be utilized on completely flat surfaces, as the uniformity of the coating relies on the wood being fed through a fixed gap. Multi component coatings or coatings with low working life are not suitable for roller coating, whereas for single component coatings, high viscosity and high solid content coatings, roller coating offers many advantages.

Transfer efficiency in roller coating is very high, as unused coating is recirculated back into the process. The systems themselves are often automated and require minimal manual labor. Roller coating also allows for precise regulation of the application rate as well as excellent film thickness and uniformity with high viscosity and high solid content coatings (Bulian & Graystone, Chapter 9 - Operational Aspects of Wood Coatings: Application and Surface Preparation, 2009).

### **3.2. Curtain coating**

Curtain coating is another flat surface application system. The coating is either pressed or allowed to fall using gravity through a head which forms it into a thin curtain. A conveyor belt below moves the wooden surface through the curtain which applies the coating to the surface. Any excess coating can be gathered and recycled back into the system.

Curtain coaters suffer from many of the same shortcomings as the roller coaters. These include the need for a flat surface, issues with multi component systems and problems coating the edges of the wood. As for multi component systems, this issue can be solved using several heads, combining the different components of the system immediately on the surface. Another limitation of curtain coating is a sensitivity to air draught disturbing the flowing curtain.

The main advantage of curtain coating is the ease and efficiency of its use. The speed of the conveyor belt pushing the wood can reach up to 100 meters per minute with application rates of up to 300g per square meter. Curtain coating can also be combined with roller coating for complex two component coats (Bulian & Graystone, Chapter 9 - Operational Aspects of Wood Coatings: Application and Surface Preparation, 2009).

### **3.3. Dipping**

Dipping is a fast and cheap way to apply low viscosity coating. Mainly used when the surface needing to be coated is uneven or otherwise difficult to coat. This method is simply done by dipping the wooden surface into an open tank of coating and withdrawing it at a set rate to reduce sagging. Nevertheless, even with precautions in place, dipping is not the method of choice for products with a demand for high quality finishes. The method is also not suitable for solvent-borne or high VOC coatings as the evaporation from the open tanks pose both environmental and health hazards (Bulian & Graystone, Chapter 9 - Operational Aspects of Wood Coatings: Application and Surface Preparation, 2009).

### 3.4. Spray coating

Spray coating is an example of an atomizing coating method. Conventional spray coaters are a three-part system composed of a body filled with coating, a head acting as the air intake to increase the pressure, and a nozzle which shapes the coating into droplets before pressing them out into the air.

One of the advantages of using spray coating is the ability to create a uniform film on most surfaces. Multi-component coating systems can also be kept separately, and then mixed in the head, thereby allowing easy application. The main drawback of spray coating is its poor transfer efficiency, sometimes as low as 30%.

Environmental and health regulations limit the usability of a system that could waste 70% of the coating. The lacking transfer efficiency has been mitigated by automatization and new technologies, such as hydraulic atomization, but no spray coating method can reach the near 100% transfer efficiency seen in contact coating methods (Bulian & Graystone, Chapter 9 - Operational Aspects of Wood Coatings: Application and Surface Preparation, 2009).

## 4. Polymers and emulsions

Polymers are a chain of repeating units of molecules or molecule groups.

Repeating unit refers to the covalently bonded monomers that are combined to make a long chain, i.e. the polymer. While most polymers have a high molecular weight, it is possible to steer the reaction to control the molecular weight, as well as many other parameters, that determine the final properties of the material. By, for example, changing the ratio of monomers, reaction conditions, or reaction techniques, one can tailor make the final characteristics of the polymer.

Characteristics that are important to control are, for example, the molecular weight and the molecular weight distribution, chemical composition, crosslinking, particle morphology, and chain configuration, as these determine the final properties of the polymer (Mandal, 2013).

## 4.1. Emulsion polymerization

Emulsion polymerization is the reaction of free radicals with monomer molecules that have been dispersed in an appropriate medium. The two types of emulsion polymerizations are waterborne and solvent-borne, of which the waterborne is the more common type. Waterborne refers to the monomers as the hydrophobic 'oil', and water as the dispersion medium. The result is a colloidal system with insoluble polymer particles finely dispersed in an aqueous medium, typically called a latex. The properties of the final latex vary, depending on reaction time, reaction rate, monomer composition, temperature, and so on. It is therefore very important to be able to control the reaction process, so as to achieve a latex suited for the specific end use.

The controllability of the process is one of the strengths of emulsion polymerization. Another advantage that emulsion polymerization has over other common polymerization methods, is that the polymerization rate and the molecular weight is not inversely proportional, as it often is in other methods. Emulsion polymerization also offers better heat dissipation and viscosity control compared to, for example, bulk polymerization. This means that by using emulsion polymerization, it is possible to achieve a high rate of polymerization, as well as a high molecular weight (Szycher, 2013).

### 4.1.1. Free radical polymerization

Polymerization reactions are divided into step-growth and chain polymerizations; free radical polymerization is a sub-category of the latter. These types of polymerizations are often exothermic and have high propagation rates. The lifetime of a polymer chain in these reactions is less than one second.

Free radical polymerization is divided into three or four simultaneously occurring reactions. These reactions are the initiation reaction, wherein the radicals are continuously generated, the propagation, which causes the growth of the polymer

chain by the addition of monomers, and the termination, where two radicals react and consume each other (Kiparissides, 1996). The fourth reaction is a separate chain transfer reaction that controls the molecular weight of the produced polymer chains (Soroush & Grady, 2019).

#### 4.1.2. Typical emulsion polymerization

An emulsion polymerization is typically carried out by emulsifying monomers in an aqueous medium after which the initiation reaction is started by an added water-soluble initiator, e.g. KPS (potassium persulfate). The resulting polymers are not miscible with water and therefore need stabilizers to ensure the stability of the colloidal system. For this purpose, different types of surfactants can be added at different stages of the reaction and even afterwards.

The emulsion polymerization takes place mainly in the formed micelles. A mixture of monomers and surfactants are introduced to the initiator, which thermally decompose to free radicals that initiates the polymerization process and gives raise to particle embryos. This short nucleation is very important as it heavily affects the finished latexes properties such as particle size and its distribution.

If sufficient amount of surfactant is present in the mixture the critical micelle concentration (CMC) is reached, meaning that monomer-swollen micelles are present in the aqueous medium. These micelles have a much larger surface area to the medium than conventionally dispersed droplet-type monomers. This means that when the initiator is added, the micelles and the droplets compete to react with the free radicals but due to the much larger area of the micelles they are more likely to be the winner in this scenario, this is called *heterogeneous nucleation*. Even the radicals, which do react with the dispersed monomers will in time, increase their hydrophobicity as the reactions continue until they find themselves hydrophobic enough and precipitate. The polymer is then stabilized by the surfactants and monomers can continue to diffuse into the organic phase, this is called *homogeneous nucleation* (Chern, 2008).



## 4.2. Emulsion mechanisms

The mechanism of emulsion polymerization is generally divided into three intervals. In the first interval an aqueous solution is mixed with an amount of surfactant exceeding the CMC. This produces the needed micelles as well as stabilizes the monomer droplets in the solution. The free radicals generated from the initiator gives raise to oligomeric radicals which in turn diffuse into the micelles and thereby nucleating the particle. This continues until all the micelles have been transformed into growing polymer particles or consumed as stabilizers for polymer particles. If no coagulation occurs, the number of particles formed in this step will be constant throughout the whole polymerization process.

The second interval starts when the micelles in the solution have all either seeded by monomer radicals or been used for stabilization of the other particles. The remaining monomers in the solution continue to diffuse into the polymer particles created in step one. The polymerization rate depends largely on the solubility of the monomers in water, but since the number of particles remain constant – so will the reaction rate of this interval.

When the monomers have all been diffused into the polymer particles and no monomer droplets are left in the solution, interval three is initiated. It is during this interval that the termination of the polymerization reaction occurs. The remaining monomers in the solution will be consumed, causing the reaction rate to decrease in proportion to the decreasing number of monomers left in the solution. When the monomers decrease, so will the rate of mass transfer which when it nears zero means that the reaction is terminated. (Harkins, 1947)

## 4.3. Emulsion polymerization processes

There are three different processes widely used for production of latexes. These are batch, semi batch and continuous reactors. In a laboratory scale, batch reactions are often used to study different phenomena and develop new latexes. In a larger scale,

batch reactors come with too many problems such as temperature control to be of any real use. In the industrial world semi batch or continuous reactors are the preferred methods (Schork, 2014).

#### 4.3.1. Batch reactors

In a batch reactor the monomers and surfactants are dispersed in an aqueous medium in one batch. The surfactants are there to adsorb onto the monomer droplets to stabilize the system while any excess surfactant create micelles. The reaction is often started with the help of thermal initiators such as KPS at temperatures ranging between 75 to 90 degrees Celsius. If higher initiation rates or lower temperatures are needed for the reaction, Redox systems could be used. During the nucleation stage when the polymers are formed, monomer droplets, monomer swollen micelles and polymer particles coexist in the batch reactor, competing for the radicals. As time goes on the amount of monomer and micelles will decrease as they are transformed into polymers. This corresponds to interval I in Harkin's theory. Intervals II and III then proceed as described earlier (Schork, 2014).

#### 4.3.2. Semi continuous and continuous reactors

Semi continuous reactors work in a similar way to the batch reactor but in this case the monomers, surfactants, initiators, and water are continuously added into the reactor. The trick is that the rate of polymerization should be higher than the rate at which the monomers are added to the reactor. If this is not the case, monomer droplets will instead be formed which will hinder the controllability of the reaction and product properties.

Continuous reactors work in the same way as semi continuous except for an extra step in which the product is also extracted from the reactor continuously as opposed

to the semi continuous case where the product is extracted at the end of the reaction. Other than the obvious differences in the mechanical steps, both the semi and the continuous reaction's processes are the same as the batch reactions. One added bonus of these continuous systems is the added control over the reaction and of the ratio between homogeneous and heterogeneous nucleation. (Schork, 2014)

#### **4.4. Components of emulsion polymerization**

While many components can be included in an emulsion polymerization that influence the properties of the final product, a few key components make up the base of any emulsion polymerization. These are water, monomers, surfactants, and initiators. Controlling the properties and ratios of these key components is the recipe for success for any emulsion polymerization.

The medium of the emulsion polymerization is water, being the obvious choice for dispersing monomers as they most often have a low solubility in water. Water is easy and cheap to work with, but this also means that transportation of water is not economical. The key to a successful emulsion is to have the highest solid content possible without affecting the stability of the final product (Anderson & Daniels, 2003).

##### **4.4.1. Monomers**

The choice of monomer is an important part of the process of planning a latex. The properties of the final product are mostly determined by the selection of monomers used in the emulsion. Additionally, there can be requirements such as cost or health concerns that must be taken into consideration. Common monomers used in latexes are for example styrenes, acrylics and methacrylics.

While emulsion polymerization can be carried out using only a single monomer type, most commercial latexes use a combination of two or more as this allows for easier control of the final properties. By changing the ratio of different monomers one can control the glass transition temperature, mechanical properties and much more (Anderson & Daniels, 2003).

#### 4.4.2. Initiators

The initiator is the trigger of the whole polymerization process. Its purpose being to generate free radicals and allow for the nucleation of particles. Most initiators used in emulsion polymerization are water soluble, for example different persulfates. Another added bonus of persulfate initiators are their ionic nature as it helps stabilize the system by giving the latex an anionic surface charge (Anderson & Daniels, 2003).

#### 4.4.3. Surfactants

Surfactants, sometimes referred to as emulsifiers are another important decision in the polymerization planning process. There are many kinds of surfactants that can be used to make a latex, and as the surfactants largely determine the particle size and final stability of the system. An insufficient amount of surfactant can lead to coagulation of the final product while an excessive amount can lead to unwanted nucleation, foaming and worsened properties of the final film.

The three main kinds of surfactants are anionic, cationic, and nonionic. Oftentimes the latex recipes contain a combination of several surfactants, mixtures of anionic and nonionic being the most common as the anionic surfactant contributes greatly during the nucleation stage while nonionic surfactants help stabilize the final product (Anderson & Daniels, 2003).

Any ionically stabilized emulsion must be stabilized using the same type of electrical charge. Combining anionic and cationic surfactants will only lead to problems in stability (Goldschmidt & Streitberger, 2018).

#### **4.5. Evaluating emulsion stability**

Emulsions used for coatings and in several other industries are often mixed with other additives and stored for months or even years. When selling a commercial product, the producer cannot fully control transportation nor storage conditions of painting companies. This places great importance on the long-term stability of the emulsion both in terms of long-term storage under a wide range of conditions and in terms of stability against added additives, for example electrolytes.

There are many different factors affecting the stability of a colloidal system. Initially scientists believed that the balance between van der Waals forces and electrostatic repulsion was the two key factors. It has been shown that other factors such as steric repulsion, hydration, oscillatory surface forces and so on also impact the stability of a colloidal system.

There are four ways an emulsion might become unstable. Creaming occurs when two liquids with different densities separate, leading to the lighter liquid gathering on top. Flocculation means that the droplets in the emulsion start aggregating to each other to form bigger structures, but without direct contact. This can be either reversible or irreversible depending on the cause of the flocculation. Coalescence is similar to flocculation but in this case the drops completely mix together to form a single drop. And finally, Ostwald ripening is the chemical potential difference between two different sized drops resulting in molecular diffusion from the small drop to the larger one (Petsev, 2015).

One way to gain insight to the stability of an emulsion is to measure its zeta potential. Zeta potential is a measurement of the repulsion between charged particles in a dispersion. A high value in either positive or negative direction means that the

particles in the dispersion are highly charged, leading to electrostatic repulsion and a stable emulsion.

While measurements of zeta potential are a good indicator of emulsion stability, a high ZP value does not equal a stable emulsion, as other factors also affect stability. A low ZP value could however indicate that the emulsion will coagulate during storage (Samimi, Maghsoudnia, Eftekhari, & Dorkoosh, 2019). By storing emulsions and continuously measuring their zeta potential, the rate of decrease in zeta potential could however be used to monitor emulsion stability (Bhatt, Prasad, Singh, & Panpalia, 2010).

#### **4.6. Anti-foaming agents**

Foam can cause issues in the industrial application of wood coatings. To combat this issue, many wood coating producers add anti-foaming agents to their recipe. However, there are many different types of foams, and consequently many different route causes. To effectively remove excessive foam from a wood coating, one must first understand the underlying cause of the foaming.

Some foams, especially in low viscosity liquids, are not an issue and will quickly disappear. Nevertheless, as the viscosity rises, the speed at which the foam escapes slows down. Combined with surfactants that stabilize the bubbles, this can become a problem. The two main types of foam in wood coatings are microfoam and spherical bubbles. Microfoam is air trapped inside the coating itself, while spherical bubbles are larger bubbles on the surface of the coating.

In a liquid without any surfactant, the air will simply rise until it reaches the surface, and the liquid lamella will burst, letting the air escape. In wood coatings, these lamellae are stabilized by surfactants, both on the inner and outer walls of the bubble. The repulsive forces between the surfactants on the inner and outer walls of the bubble create a film that is thick enough to withstand the pressure of the air without bursting. This effect is enhanced by the fact that if the lamella is stretched in any way, the surface tension caused by the sudden lack of surfactants will restore the

bubble to its original position. To counteract this, the defoaming agent must induce non-uniformity in the surface tension, allowing the bubble to burst.

A defoaming agent should be tiny droplets, insoluble in the coating substance. These droplets attack the foam lamellae, creating irregularities and eventually bursting them. Because defoamers are by design incompatible with the solution, they must not be included unnecessarily or in excess. Excessive amounts of defoamers can cause issues both in storage and in the final coated product. Ladder studies are therefore needed to ensure that an optimal amount of defoamer is added to the formulation (Goldschmidt & Streitberger, 2018).

#### **4.7. Structure-property relationships**

Binders are the polymer particles that form the film on the surface. The binder determines the mechanical properties of the coating during all stages of its life. There are several demands placed on the final properties of any modern wood coating, especially exterior coatings, and it is by tuning the binder these demands can be met. For example, the binder needs to have good enough weather stability, the right ratio between elasticity and hardness, good adhesion while retaining sufficient blocking resistance, sufficient blushing resistance, good water repellency, and so on. All these demands must be met while remaining low on VOC and being economically viable to produce.

In acrylic binders, these properties are achieved through the careful formulation of the recipe and the reaction technique, allowing the control of several parameters, including polarity, glass transition temperature ( $T_g$ ), surfactant amount and type, particle size, morphology, and more. The control of these parameters is of great importance, especially in the case of wood coatings since wood as a construction material requires careful protection against the environment and the life forms therein. The complex structure of wood puts further demands on the binder, as it must be able to penetrate the wood structure to provide enough adhesion and sufficient protection to the wood (Baumstark & Tiarks, 2002).

#### 4.7.1. Particle size and distribution

Particle size and distribution are important properties in any latex as they determine the usability of the end product. For example, the particle size will affect the rheology of the dispersion which in turn determines how to apply the coating. Particle size in wood coatings also impact how deep the particles will penetrate into the wood.

Distribution of the particle size varies between different latexes. Particle sizes within an emulsion might be monodisperse, bimodal or multimodal. The length of the nucleation period in relation to the length of the entire reaction is the determining factor in the distribution of particle sizes. (Anderson & Daniels, 2003).

Most emulsions for wood coatings have particle sizes ranging from 5 nm to 1000 nm and can therefore be called colloidal dispersions. There are exceptions with extraordinarily small or large particle sizes outside of this range but these are no longer colloids (Poth & Müller, 2011).

#### 4.7.2. Core-shell binders

In most cases, the T<sub>g</sub> of the binder is the factor that determines the film formation temperature (MFFT), final hardness and elasticity of the formed film. Higher T<sub>g</sub> means lower elasticity and harder film, while lower T<sub>g</sub> means the opposite. For wood coatings a T<sub>g</sub> of between 0 to 10 °C is usually preferred. Here lies a problem, acylates with such a low T<sub>g</sub> do not in turn give the final film enough blocking resistance to be an ideal wood coating. These properties can be tuned by crosslinking, but this solution is often expensive and can also have other adverse effects on other film properties.

Another solution is to create a binder with a core-shell morphology. This means that several polymers are present in the dispersion at once but separated into different



phases. For wood coatings a soft polymer with a low  $T_g$  in the core provides the elasticity and wanted film properties, while a hard shell containing a high  $T_g$  polymer acts as a high blocking resistance barrier. By changing the ratio between core and shell, and monomer compositions in both, one can fine-tune the  $T_g$  and final film properties of the binder (Baumstark & Tiarks, 2002).

#### 4.7.3. Blocking resistance

One issue in industrial coating is the stacking of coated wood onto each other or other surfaces. The term blocking refers to coated surfaces being in contact and under load, for example stacked on each other, causing unwanted adhesion. Sufficient blocking resistance means that after a reasonable amount of time has passed, the coated surfaces should be able to be stacked on top of each other without being damaged when separated (Bulian & Graystone, Chapter 6 - Properties of Wood Coatings – Testing and Characterisation, 2009).

Achieving a sufficiently elastic and simultaneously blocking resistant wood coat by only varying the monomer types and ratios is nearly impossible. The industrial way of solving this issue is either to introduce cross-linking agents or by changing the morphology of the particles, e.g. the earlier mentioned core-shell dispersions (Prieto & Kiene, 2018).

## 5. Coloring

The color and finish of a wooden construction is an important element for how people experience the building. Gloss levels also range from matte to very glossy and the combination of gloss and color must be decided at the design stage of any new construction. Older buildings, found in so-called “old towns”, had coats that aged considerably with time, changing the gloss and tone along with it. Newer coats have

considerably improved in this area with better application techniques and improved pigments, leading to a uniform and protective coat, but at the cost of the charm of the living old towns (Arnkil, 2013).

### **5.1. Wood stains**

Wood stains are the coatings of choice when the goal is to darken the wood while keeping an emphasis on the grain. A wood stain has a lower solid content than most other coatings, at around 20%. To provide sufficient protection, the components of the wood stain must penetrate deep into the wood. Solvent-borne wood stains accomplish this more easily due to their waterborne counterparts causing swelling of the wood. To accomplish similar penetration in a waterborne wood stain, the binder's particle size should be small and the amount of binder in the formulation should also be kept as low as possible while providing enough stability for the pigments.

While wood stains do incorporate fungicides and preservatives in their formulation, some application methods, such as normal brushing, will not apply enough pressure for the stain to penetrate deep into the wood. This means that the preservatives will remain on the surface and, if subjected to harsh weather conditions, may be washed away or simply be insufficient. In cases like this, pre-treating the wood with preservatives before applying the wood stain is needed (Bulian & Graystone, Chapter 7 - Market Needs and End Uses (1) – Architectural (Decorative) Wood Coatings, 2009).

### **5.2. Organic dyes**

Dyes are soluble colorants that can be incorporated into a coating formulation. In the wood coating industry, most dyes are synthetic organic dyes originally used in the

textile industry. Some common dyes used in wood stains are acid dyes and metal complex dyes (Prieto & Kiene, 2018).

Acid dyes are, as their name suggests, applied under acidic conditions. The main advantages of acid dyes are ease of application and a wide choice of colors. Within the category of acid dyes, they are further categorized based on the fastness properties, pH and migration of the dye. The different types of acid dyes require specific application methods and cannot be combined with each other (Richards, 2012).

Metal complex dyes are acid dyes with a metal atom incorporated into the structure. The ratio of metal to dye usually ranges from 1:1 to 1:2. Similarly to acid dyes, the metal complex dyes will require different application methods depending on this ratio. Compared to acid dyes, the metal complex dyes feature greater fastness while losing some brightness (Richards, 2012).

### **5.3. Pigments**

Pigments are split into organic and inorganic pigments. Organic pigments are hydrophobic and offer a wider range of colors with greater saturation compared to inorganic pigments. They do however require complex synthesis, which makes them significantly more expensive than inorganic pigments. Inorganic pigments, while cheaper, are also denser and more opaque. They are also hydrophilic and have low surface energy, which necessitates a larger amount of inorganic pigment in a formulation, which in turn can lead to wetting and stability issues.

Although the main function of any pigment is to add color to the coating, they also provide several other positive improvements. Pigments protect both the coating and the underlying surface from UV-light and, in some cases, even infrared heat, which could be useful during industrial drying. Some pigments, such as the industry staple titanium dioxide, can even provide fire retardant properties.

Controlling the properties of the pigment is very important since the physical properties of the pigment will affect how the coating performs during storage, application, and as a coated surface. All extra molecules in a coating formulation can affect the stability and coating properties of the product, and sufficient compatibility between the pigment and the formulation must be ensured. The particle size and distribution of the pigment also influence the optical properties of the coated product, as the hue of the color shifts depending on these variables. Analyzing the refractive index of the pigment is important in transparent coatings since a mixture of binder and pigment with similar refractive indexes will seem more transparent to the human eye (Bulian & Graystone, Chapter 4 - Raw Materials for Wood Coatings (2) – Solvents, Additives and Colorants, 2009).

#### **5.4. Volatile organic compounds, VOC**

Volatile organic compounds or VOC are, according to ISO: ‘any organic liquid and/or solid that evaporates spontaneously at the prevailing temperature and pressure of the atmosphere with which it is in contact’ (International Organization for Standardization, 2014). Solvent-borne coatings having more VOC have been mentioned several times in this thesis. Since the solvent is designed to evaporate to allow the coating to form a film, a solvent being an organic liquid would then be a VOC per se. In the past, this was not a problem since coating quality and ease of application were the main criteria for a successful coating product. Due to stricter regulations on VOC, the need for lower amounts of solvent is clear.

Waterborne coatings have taken over the market largely because using water as a solvent eliminates the VOC issue in its entirety. Broadly speaking this is true, but most coatings are not simply a mixture of polymers and solvent, they also include other additives and pigments, which in turn introduce VOC back into the formulation. Mineral spirits and formaldehyde are examples of common ingredients in many pigments, and the VOC levels must be calculated when using such additives, so as not to exceed the current legal limits. Good practice is to always try to reduce the VOC content in any coating product, if not for environmental reasons alone, then

for future-proofing the product against ever-stricter EU regulations (Prieto & Kiene, 2018).

## **6. Flame retardant wood**

While wood has many advantages as a construction material, such as versatility, sustainability, and overall appearance, its flammability and contribution as fuel to an ongoing fire holds wood back from its fullest potential as the construction material of choice for any new building. While increased interest in wood as a construction material has been noted due to the rise in environmentally sustainable solutions, there are restrictions concerning flammability and ignitability placed on any construction material used for industrial or commercial construction, and this includes wood. To meet these demands flame retardant coatings and systems are being continuously developed to suppress the flammability of wood to a degree that is acceptable in modern society (Mariappan, 2017).

### **6.1. Different flame retardant systems**

Combustion of wood is a three-stage process taking place in both the gaseous and the solid phase. In the first stage, water will evaporate by absorbing heat in an endothermic process. Only when the moisture content of the wood approaches zero will the temperature of the wood itself rise above 100 °C.

When all the water has been evaporated, the temperature rises sharply and volatile gases are produced. This second stage can further be divided into primary and secondary combustion. Primary combustion, ranging from 280 °C to 480 °C, will release large amounts of energy and unburned gases, as large molecules start to decompose into char. A large amount of the potential heat in wood is contained in these gases. As temperatures continue to rise above 500 °C, the reaction reaches secondary combustion, and the gases start to combust.

After all the gases have been driven from the wood, stage three begins. During this stage, the remaining carbon chains of cellulose and lignin will continue to burn slowly as charcoal. This stage has a much lower heat output compared to the second stage but can continue for a long time depending on oxygen supply (Garrett, 1981), (Iwuozor, 2019).

Flame retardants work by changing the parameters of this process to limit the combustion process in favor of other reactions. Important factors that can be influenced by flame retardants are time to ignition, heat release rate, mass loss, smoke release rate, flame spread rate and fire resistance. They must also be non-toxic and non-harmful to humans and the environment before combustion and preferably also during combustion. The flame retardants must also be stable during storage and when coated, as many otherwise effective flame retardants are prone to crystallizing on the coated surface or leaching, especially under moist outdoor conditions (Popescu & Pfriem, 2019).

#### 6.1.1. Halogen-based flame retardants

Halogen-based flame retardants are widely available and used in many flame retardant wood coatings today. These types of flame retardants most often act in the gas phase as free radical scavengers. Which means that they bond with the free radicals created by the combustion of wood and, therefore, slow down the reaction kinetics.

Flame retardants based on halogens have long been known to be an effective and cheap solution but have recently been losing ground to other solutions, since they have been identified as widespread environmental contaminants that can be found in alarmingly high and increasing concentrations in human tissue, including blood, fat tissue and breast milk, as well as wildlife from Europe, Japan, North America and even Arctic regions. In addition, during combustion the brominated flame retardants will release toxic and corrosive substances that persist in the environment and that are harmful to all life (Popescu & Pfriem, 2019), (Janssen, 2005).

### 6.1.2. Salt-based flame retardants

Inorganic salts are often used in synergy with other flame retardants in a coating formulation. These salts, phosphates, sulfates, hydroxides, and carbonates offer thermal stability and low smoke release while being environmentally sustainable. They are, however, highly soluble in water which limits their use for outdoor coatings, and as standalone flame retardants the load required to achieve sufficient fire retardancy to pass various fire tests is too high.

Different salts may provide different flame retardant properties. Some common compounds used in flame retardants are magnesium hydroxide and calcium carbonate. During combustion, these compounds will decompose endothermically, absorbing heat and releasing water and/or CO<sub>2</sub>. This will inhibit the combustion process while releasing no toxic material into the environment (Tang, et al., 2017).

### 6.1.3. Boron-based flame retardants

Boron-based flame retardants are another widely used flame retardant solution. Boron compounds have high thermal resistance, however, they have also been included in the list of Substances of Very High Concern within the EU (European Chemicals Agency, 2010). A boron-based system is often made by combining boric acid and sodium borate, as both compounds flame retardant properties complement each other.

Boric acid will increase dehydration of cellulose leading to increased charring and lower VOC emissions. Sodium borate will instead work to reduce the spread of the fire. Borium salts can also be used and work by releasing water while also enhancing dehydration of cellulose. Boron-based compounds also create a protective layer on

the wood surface when exposed to high heat. These compounds have also been combined with other flame retardants with good results (Popescu & Pfriem, 2019).

#### 6.1.4. Phosphorous-based flame retardants

Phosphorous-based flame retardants are a promising alternative to replace the halogen-based systems in use today. These compounds, like in the case of halogens, can act in the gas phase as radical scavengers, or in the condensed phase, by promoting charring and slowing down the pyrolysis, or even insulating the material to a point of self-extinguishing (Schartel, 2010).

Flame retardants based on phosphorus compounds may be partially toxic and can by themselves be irritating, or even dangerous, to vulnerable individuals. These compounds also raise the moisture content of the wood, increasing the need for biocides and fungicides, which in turn might contain VOC (Popescu & Pfriem, 2019).

#### 6.1.5. Nitrogen-based flame retardants

Melamine  $C_3H_6N_6$  is the most commonly used nitrogen-based flame retardant. Upon sublimation, at around 350 °C, melamine will endothermically absorb large amounts of heat. When the temperature rises further, melamine will decompose several times, eliminating ammonia at each step and acting endothermically.

Melamine can also be combined with phosphates, where the intumescent properties of the phosphorous, and the endothermic effects of the melamine, work together to effectively suppress the combustion reaction. The disadvantage to using nitrogen-based flame retardants is the release of ammonium into the environment, as well as some ammonium salts being potentially toxic (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009)



#### 6.1.6. Silicon-based flame retardants

Silicon-based flame retardants work by forming a protective layer of silica on the wood surface, isolating it from heat. These types of compounds can be combined with phosphorous-based flame retardants to enhance the intumescent properties of both. Combinations with other flame retardant systems, such as boronic acid, have also shown great promise. Silicon-based flame retardants are environmentally sustainable and are therefore an attractive alternative as an enhancing additive to other flame retardant systems (Popescu & Pfriem, 2019).

#### 6.1.7. Nanocomposite-based flame retardants

Nanocomposites have been proven to protect the oxidation of the char structure in combusting wood. This property alone is not enough to provide sufficient suppression of the combustion reaction, but the small particle sizes of nanocomposites mean that very low concentrations can be added together with other flame retardant systems to enhance their properties. Nanosized versions of silicates, titanium dioxide, and silicon dioxide have all been shown to promote the flame retardant properties of wood (Popescu & Pfriem, 2019).

### **6.2. Fire standards for wood**

In industrial wood coatings, there are always standards that must be met. Especially when the matter at hand is flame retardancy, the ability to prove a coatings efficiency is essential since failure could result in death. In Europe, these standards are EN ISO

1182, EN 13823 and EN ISO 11925-2. Combined, these standards are used to classify the flammability of any wooden construction material in accordance to the EU standard EN 13501-1 (The British Standard, 2007). In a laboratory, a cone calorimeter can also be used to analyze the combustion properties of a small wood sample.

### 6.2.1. Cone calorimeter

A cone calorimeter is used to study the combustion properties of a small sample, such as a coated wood piece. The sample is placed on a scale and subjected to a set heat flux, most often  $35 \text{ kW/m}^2$  or  $50 \text{ kW/m}^2$ . During the test, the machine will continuously measure heat release, smoke release, mass loss, CO and CO<sub>2</sub> levels and other gases, as well as the time to ignition and total flame time (Rowell & Dietenberger, 2012). This gives a quick insight into the efficiency of the flame retardants, especially if there are references to other flame retardants that have passed the standardized testing of the EU.

### 6.2.2. Combustability testing

Non-combustibility testing is done to show whether a test piece is combustible. A test piece 45 mm in diameter and 50 mm high is placed into a cylindrical furnace at  $750 \text{ }^\circ\text{C}$ . The temperatures of the furnace, on the surface of the test piece as well as the center of the test piece, are continuously measured. The duration of visible flames as well as mass loss of the test piece are also noted. For a test piece to be non-combustible it must fulfill three criteria: The furnace temperature should not rise more than  $50 \text{ }^\circ\text{C}$ , the mean duration of visible flames should not exceed 20 seconds and the average mass loss should not be more than 50% of the original sample (International Organization for Standardization, 2010)

### 6.2.3. Single burn item test

Single burn item test, or SBI, is an important test to pass for coated wooden materials. SBI tests are used to determine the fire hazard of all non-floor construction materials. A specimen consisting of two walls no thicker than 200 mm, one measuring 500 mm x 1500 mm and the other 1000 mm x 1500 mm, are attached into an L-shape. The constructed corner wall is then exposed to a propane burner placed at the bottom of the corner with a heat output of 30.7 kW. Once the burner is on, the sample will be continuously analyzed for 20 minutes where heat release, smoke production and total volume flow will be measure automatically. Additionally, flame spread and falling flame drops will be observed visually (The British Standard, 2010)

### 6.2.4. Ignitability test

Ignitability is tested by attaching a 250 mm x 90 mm test piece to a specimen holder. This test piece is subjected to a propane gas flame of 20 mm at an angle of 45°. Depending on the classification sought after, the flame application time is varied from 15 seconds to 30 seconds. A filter paper is placed below to ignite in case of any falling debris. The test measures the flame spread, and visually observes the occurrence of flaming or glowing on the test piece (International Organization for Standardization, 2020).

### **6.3. Durability of coatings**

Treating a piece of wood with flame retardant coating will surely better the results in flame retardant related testing. But merely passing flame retardant standards shortly after coating is not enough for a product that is likely to be subject to the environment for ten years or more. Therefore, there is a need to test how these coated products perform after being subjected to humid conditions and UV-light for prolonged periods of time.

There are two recognized methods of accelerating the weathering for durability testing. In the first method the test specimens are subjected to one-week cycles of 96 hours of water followed by 72 hours of drying, repeated for twelve weeks. The second method is a 24-hour cycle of 4 hours of wetting followed by 4 hours of drying, repeated once for 16 hours total, followed by 8 hours of rest. This cycle is then repeated for 1000 hours.

After the weathering is completed, the test pieces are subjected to the same flame retardant tests that gave them their original flame retardant classifications. Since SBI-tests require a large construction to be carried out, this classification can be verified using a cone calorimeter (European Committee for Standardization, 2014)

## **7. Methods of analysis**

### **7.1. Solid content**

Gravimetric analysis was used to measure the solid content of the polymer dispersions. A diamond weighing boat measuring 85 mm by 65 mm was weighed when empty and its weight noted. Samples of ca 2 grams were pipetted onto the weighing boat and left to evaporate. When all the water had evaporated, the weighing boat was weighed again, and the mass loss noted. Dividing the mass of the resulting film by the original sample mass and multiplying by 100 yields the total solid content

percentage of the sample. This was done twice for each dispersion and the total evaporation of water was verified using ATR-FTIR.

## **7.2. FTIR analysis**

To confirm that all the monomers have reacted in the emulsion polymerization and to verify that all the water has evaporated from the film used for solid content analysis, FTIR analysis was used, specifically, ATR-FTIR - Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. An infrared beam is shot at a transparent crystal with a high refractive index in contact with the sample film. The sample will alter the wave which then bounces back into the spectrometer's detector and is used to generate an infrared spectrum (Gregoriou, 2000).

## **7.3. Glass transition temperature**

Differential scanning calorimetry (DSC) was used to measure the glass transition temperature of the polymer dispersions. This is a thermoanalytical analysis method in which a small sample of ca 5 mg is cut from the solid film obtained during the solid content analysis. The sample is placed into a pan and placed into the DSC along with an empty reference pan. For this analysis, a set Heat-Cool-Heat program in which the samples are heated to 100 °C, cooled to -40 °C and reheated back to 100 °C with a speed of 10 °C per minute was used. The heat flow required to keep the sample heated at the same rate as the reference pan is measured, and the glass transition temperature is obtained from the inflection point of the curve.

#### **7.4. Particle size**

Particle size was measured using a Malvern Zetasizer Nano ZS using dynamic light scattering. The polymer dispersion samples were diluted with ionized water to 2% solid content and a sample was placed in a disposable cuvette custom made for the Zetasizer. A laser passes through the solution and measures the scattering of light as a function of time. Due to Brownian motion, smaller particles will diffuse faster than larger particles, the link between light scattering and particle size is used to calculate the particle size of the solution (Raval, et al., 2019).

#### **7.5. Zeta potential**

Zeta potential was also measured using the Malvern Zetasizer Nano ZS but using Laser Doppler Micro-electrophoresis. The polymer dispersion samples were further diluted to 0.5% solid content and pipetted into appropriate cuvettes. An electric field is applied to the sample, which will initiate movement of the dispersed particles in relation to their zeta potential. By measuring the velocity of the particles, the Zetasizer can then calculate the zeta potential of the sample.

The goal of the analysis is to measure the effect on zeta potential when adding a salt to the diluted dispersions. Samples of the diluted dispersions were therefore thoroughly mixed with different amounts of salt, the resulting mixtures were analyzed in the Zetasizer and the results were compared to each other.

#### **7.6. Defoamer efficiency analysis**

To analyze the efficiency and viability of defoamers, an original test method had to be created. The method was based on the British Standard (The British Standard, 2002). A 200 ml beaker was filled with 50 g of polymer dispersion and a set amount

of defoamer was added. A bladed stirrer was applied at 2000 rpm for 2 minutes after which 35 g was poured into a 100 ml glass cylinder. The volume of the dispersion was measured continuously for 15 minutes. Knowing the volume and mass in relation to time, the density can be calculated as a function of time.

The mixtures were then bottled and left to stand for two weeks. During this time, the samples were visually examined for any signs of separation or flocculation. Any sample that passed the two-week stability requirement was retested using the same test method as before. The results were then compared to the initial test results.

### **7.7. Cone calorimeter analysis**

To analyze the fire retardant properties of wood coatings, a cone calorimeter was used. Coated wood samples of approximately 10x10x2 cm were placed at a distance of 25 mm from the cone. The cone was then heated to around 700°C to produce a heat flux of 35 kW/m<sup>2</sup> on the wood surface. An igniter assists in igniting the wood sample and the time to ignition is noted. During the time between ignition and flame out several variables such as heat release rate, effective heat of combustion and total smoke production are continuously measured.

## **8. Performing the emulsion polymerization**

The polymer dispersion is an acrylic polymer dispersion based on two monomers, here referred to as monomer A and monomer B. Three different surfactants were also used, referred to as surfactant X, Y and Z. Furthermore, several additives which will not be named were used in different stages of the reaction. A solution of initiator and water is used to initiate the polymerization reaction.

Every emulsion polymerization was performed in a fume hood, using a 500 ml glass reactor vessel and accompanying glass lid with 5 necks. The lid was sealed and securely tightened to avoid any evaporation. A reflux condenser and thermometer were fitted through the necks, as well as two input tubes and a stirrer. The monomer and initiator solutions were fed to the reactor using two mechanical pumps. A circulating bath pumped heated water through the reactor vessel's walls to maintain the temperature of the reactor.

First, two surfactants are mixed with water and additives and added to the reactor. The temperature is set to 80°C and the stirrer to 200 rpm. While this mixture is heating, two other mixtures are prepared. In one beaker the two monomers are combined with an additive and in another the initiator is mixed with water. These mixtures are left to stir while the temperature in the reactor rises. When the temperature has reached 80°C, the reaction is initiated by adding some of the monomer mix and initiator solution to the reactor. This starts the polymerization of the monomers and creates the base on which all further polymerization reactions will occur. The initial reaction is allowed to proceed for 15 minutes after which the rest of the monomer mix and initiator solution is added slowly, during 4 to 5 hours. When both the initiator solution and monomer mix beakers have been emptied, an additive is added to the reactor and the temperature raised to 90°C for 45 minutes, to ensure the complete reaction of all monomers. Finally, the temperature is lowered to 40°C after which the product is filtered, and its pH adjusted to 8 using an ammonia solution.

It was observed that a simple emulsion polymerization did not achieve sufficient film properties and the recipe was adjusted to a core-shell type emulsion polymerization to allow for greater control of the T<sub>g</sub> and therefore the film properties. Recipes can be found in Appendix A.



## 9. Results and discussion

The purpose of this thesis was to study fire retardant waterborne wood coatings and the challenges involved with their manufacturing and use.

### 9.1. Synthesis and characterization of acrylic binders

In wood coatings the penetration of the binder is largely dependent on the particle size of said binder (Bulian & Graystone, Chapter 7 - Market Needs and End Uses (1) – Architectural (Decorative) Wood Coatings, 2009). Another important factor is Tg which correlates to the MFFT, often being a few degrees higher than the corresponding MFFT. Any coating must have a low enough Tg to allow film formation in the temperature range where it will be applied, but still high enough to give sufficient film hardness (Jones, Nichols, & Pappas, 2017).

The goal was to synthesize a binder with a lower Tg and particle size that would simultaneously provide high storage stability and colloidal stability even in the presence of electrolytes. Monomers were chosen based on the requirements of the final product.

Table 9.1. *Synthesized binders and their corresponding Tg and S.C*

Binder	B1	B2	CS1	CS2	CS3	CS4	CS5	CS6	CS6Z	CS7
Tg (°C)	-	-	-	-	-7.9	-21.7	-11.5	+4.0	+4.0	-7.7
Solid content (%)	32.4	34.0	32.6	32.8	33.0	34.2	35.5	33.5	33.7	38

A total of 10 different acrylic binders were synthesized as shown in Table 9.1. B1 and B2 were prepared according to conventional emulsion polymerization given

homogeneous particles, after which the strategy shifted to core-shell type of polymerization as can be noted by the name changing to CSx. No further testing was done on the B-range, as well as the visually lackluster CS1 and CS2, which explains the lack of Tg values.

By changing the ratio of core to shell and the ratio of monomer A to monomer B in both core and shell, the Tg value could be optimized. CS6 and CS6Z produced visually uniform films, while the films of CS5 and CS7 both had minor defects but were still used in further analysis. This indicated that a core to shell ratio of 80:20 was optimal. As CS5 had minor defects, the recipe for CS6 softened the core which raised the Tg and resulted in a uniform film. In CS7 the core was softened further to compensate for a harder shell, but the film forming properties immediately deteriorated. Such a hard shell seemed to hinder the film forming even if compensated for in the core. It was determined that CS6 was the optimal recipe and CS6Z was promptly synthesized analyze the effect of changing the anionic surfactant to another. Appendix B shows the DSC analysis of CS6.

#### 9.1.1. Zetasizer analysis

One goal was to lower the particle size of the binders. To see if this was accomplished the binders were analyzed using DLS, the results are shown in Table 9.2 and Appendix C.

Table 9.2. *Particle sizes of binders*

Binder	A0	CS5	CS6	CS6Z	CS7
Particle Size (nm)	213.6	87.1	88.9	137.5	67.6

As is clear from Table 9.2, all synthesized binders had lower particle size compared to the provided commercial binder. Using surfactant Z raised the particle size

compared to the original CS6 based on surfactant X, but this was still an improvement over A0. Every synthesized binder was close to 100 nm in particle size, which is widely used in binders for exterior use (Friel, 1995).

For the purpose of the industrial partner, the binder needs to retain its colloidal stability when mixed with large amounts of salt. One milliliter diluted sample of every binder was mixed with increasing amounts of the salt N and the samples zeta potential was measured in the zetasizer. The amount of salt N needed to reach the cutoff point of -25 mV can be found plotted in appendix D and estimated below in Table 9.3. To ease in understanding, the results have been converted as if the solid content of the binder was 30%.

Table 9.3. *Milliliters of salt added to 1 ml of binder at -25 mV*

Binder	A0	CS5	CS6	CS6Z	CS7
Salt N (ml)	12	55	55	32	65

While zeta potential is not a definitive tool for measuring colloidal stability, the results strongly indicate that the synthesized binders are more resistant to salts than their commercial counterpart. Surfactant Z negatively impacted the salt resistance compared to the surfactant X-based binders.

The goal of developing a superior binder for was accomplished. Binders CS6 and CS6Z both had appropriate film properties and T<sub>g</sub> for wood coating use, but surfactant X-based CS6 yielded greater results in the particle size and zeta potential analyzes. CS6 also had similar results to CS5 and CS7 in these tests. It was therefore concluded that CS6 was the optimal recipe for the purpose of this thesis.

## 9.2. Defoamer optimization

One issue most waterborne wood coatings face is foaming. Foaming can cause issues during application, especially in industrial application when the rate of application is high and the machinery is automatic and depends on consistent flow rates. While

surfactants are needed for multiple purposes, they often increase the amount of foaming. One way to reduce excessive foaming in coatings is by adding defoamers or surface modifiers. The purpose of this part of the thesis was to find a suitable defoamer.

Five different products, three defoamers and two surface modifiers, were added to the recipe in various amounts and the effect on foaming was observed. The results are presented as density over time in grams per milliliter compared to a reference sample of non-defoamed product. Defoamers are referred to as DF-1, 2 and 3, while surface modifiers are referred to as SM-1 and SM-2.

All additives reduced the amount of foaming when added to the product. The bigger challenge was long-term stability. The product contains large amounts of salt which, negatively impacts the long-term stability of most colloidal systems. Further modifying the surface properties of such a product could push the system over the edge into instability. This was seen during the study as four out of five additives did not pass the two-week stability test when added even at very low amounts.

DF-2, when added at levels below those specified in the technical data sheet, did remain stable during storage while still improving the foaming properties. When the tests were redone after two weeks, the defoaming capabilities had not deteriorated. The optimal amount of DF-2 was determined to be ca 0.15% by weight, as this showed similar results as 0.5% which in turn separated in storage. It was also determined that adding as low as 0.05% of DF-2 had a noticeable impact on foaming and could be considered for non-industrial applications. Density over time for various levels of DF-2 can be seen in Appendix E, the other additives are omitted as none were stable in storage.

### **9.3. Cone calorimeter analysis**

During the thesis, several cone calorimeter analyses were performed as an indicative test to see how a specific formula impacted the fire properties of wood. Coated wood pieces measuring 10x10x2 cm were analyzed. By comparing the results of these tests

with wood pieces coated by the reference product, one can gain insight into how various additives impact the flame retardant properties of the reference coating. The additives tested were FR1, 2 and 3 as well as a mix of FR1 and FR2, all added to the reference product totaling 0.5% of active substance.

Table 9.4. *Cone calorimeter results for various additives*

Additive	FR1	FR2	FR3	FR-Mix	Reference
Time to ignition (s)	18.5	18	18.5	21	21
Peak HRR (kW/m <sup>2</sup> )	107	110	123	127	183
Peak EHC (MJ/kg)	53	60	69	65	72
Peak MLR (g/s)	0.13	0.16	0.16	0.15	0.17
Total heat release (MJ/m <sup>2</sup> )	83	84	83	89	106
Total oxygen consumed (g)	63	65	64	68	77
Total mass lost (g)	75	76	75	78	87
Average specific MLR ((g/m <sup>2</sup> )/s)	5.65	5.80	5.85	5.77	6.25
Total smoke release (m <sup>2</sup> /m <sup>2</sup> )	100	100	70	102	162
Total smoke production (m <sup>2</sup> )	0.99	1.00	0.70	1.02	1.56
MAHRE (kW/m <sup>2</sup> )	63	65	69	66	73

As can be seen from Table 9.4 all additives improved the flame retardant properties compared to the reference product. FR1 and FR2 yielded the lowest peak of heat release rate and similar results throughout the analysis, while their mixture produced worse results. Smoke production was significantly lower in the case of FR3 compared to all others. Since gaining a specific flame retardant certification requires low values in several of these categories these results help in choosing the right additive to add to a formula needing to improve its heat release or smoke release properties.

While these results give a clear indication that flame retardant properties improve by adding these additives, inconsistencies are a fact due to the varying properties of different wood pieces. The results may therefore not be fully conclusive as the inherent variations in composition in the wood samples that were burned could have impacted the results. Therefore, these results should be used only as a guideline until further SBI testing is performed. Another important aspect to take into consideration when adding any additive to a formula is the ease of incorporation that may vary from additive to additive. One additive that produces great results could cause difficulties in storage, during mixing or after application that is not noted by cone

calorimeter testing but should be taken into consideration when choosing which additive to use.

## 10. Conclusions

Wood-based constructions are gaining popularity and regulations are opening doors for new types of wood constructions. While Finland has long had a trend of wooden constructions in personal households, wooden multistory constructions and industrial constructions are increasingly being made out of wood (Toppinen, Röhr, Pätäri, Lähtinen, & Toivonen, 2018). This combined with the global trend of sustainability creates a demand on new, sustainable flame retardant wood coatings. This thesis has studied the challenges in creating such a coating and furthered the understanding of several challenges faced in developing environmentally friendly flame retardant coatings for wood.

Acrylic core-shell type of emulsions having small particle sizes that exhibit high stabilities even in the presence of electrolytes have been successfully synthesized. The optimized emulsion showed good film properties having suitable T<sub>g</sub>s for use in wood coatings. As for the CS6 emulsion, while promising, further studying is nonetheless needed. Its behavior when used in actual coating production, as well as drying properties, wood penetration and weather stability is still unknown.

Another part of the thesis was to find a suitable defoamer for a given dispersion. A test method was developed and used to test five different additives. The challenging composition of the product makes the addition of surface modifying additives challenging. Out of the five additives, only one was found to be stable, and only when added at very small amounts. Defoaming capabilities at this range was however acceptable and a viable option for defoaming the product was found. The commercial market of defoamers can change in the future, and there is no guarantee for the price and availability of the suitable defoamer. Further studies to find other alternatives could lower the cost, improve performance, or provide a sense of security for the future.

Cone calorimeter analysis was done on several coated wood samples with the goal of determining the viability of different flame retardant additives. All additives improved flame retardant performance compared to the reference coated samples.

While the results of FR-1 and FR-2 were different from FR-3, the magnitude or even existence of this difference is not certain since the wood properties themselves could have been a significant factor. Although not conclusive, the results clearly show that all additives had improved performance over non-additive containing coating. In the case of these additives, the decision on which one to use should instead of performance fall on pricing, availability, and ease of use. To gain more conclusive results, the analysis would need more samples and for the coating to be carefully applied on more uniform wood samples.

## Swedish summary – Svensk sammanfattning

### Utmaningar med flamskyddande träbeläggning

Trä har alltid varit ett viktigt byggnadsmaterial både för hus och verktyg. Genom historiens gång, fram till att mänskligheten utvecklats till det vi ser idag, har träet alltid varit med oss. Med en allt större fokus på hållbarhet och miljövänlighet har intresset av trä som en lösning på framtidens hållbarhetsproblem ökat drastiskt.

EU sätter stor press på dess medlemsländer att minska på sina koldioxidutsläpp i framtiden. Nutidens kunskap om trä och dess egenskaper öppnar nya dörrar för att lösa detta problem. En sådan lösning vore att använda trä som byggnadsmaterial i större byggen och höghus. För att möjliggöra detta måste säkerheten säkerställas, detta innebär att byggnader av trä måste hålla samma standarder som sådana som byggts av andra byggnadsmaterial.

Olika träprodukter har utvecklats för att möta dessa behov. Glulam kan byta ut stora stödjande balkar som traditionellt byggs av metall, medan OSB idag äger 75% av marknaden för huspaneler. Det alla träprodukter har gemensamt är att de behöver beläggas för att skydda träet från miljön och skydda träet från eld. För att åstadkomma detta används träbeläggningar.

Träbeläggningar kan kategoriseras utgående ifrån hur beläggningsens alla byggstenar är utspädda. Lösningsmedelsbaserade beläggningar, där byggstenarna är utspädda i ett lösningsmedel, har varit det alternativ som erbjudit bäst prestanda. När beläggningsen torkar och bildar en film kommer lösningsmedlet att evaporera, vilket i en lösningsmedelsbaserad beläggning innebär utsläpp i miljön. På grund av detta har det andra alternativet, nämligen vattenbaserade beläggningar, vuxit i popularitet. Det ökade fokuset på vattenbaserade beläggningar har snabbt förbättrat prestandan i dessa produkter och idag hittas vattenbaserade beläggningar med liknande prestanda som sina lösningsmedelsbaserade motsvarigheter.

De flesta vattenbaserade beläggningarna består till del av ett bindemedel gjort med hjälp av emulsionspolymerisation. En emulsionspolymerisation är en kontrollerbar reaktion som producerar en slutprodukt bestående av olösliga polymerpartiklar



utspädda i vatten. Reaktionen kan styras för att ändra på egenskaperna hos dessa partiklar och därmed egenskaperna hos emulsionen och slutligen beläggningen. För en lyckad träbeläggning måste flera egenskaper tas i beaktande. Beläggningen måste penetrera tillräckligt djupt in i träet och där bilda en stark men ändå elastisk film. Filmen måste skydda mot väder, mikrober och i många fall eld.

En emulsionspolymerisation består av tre intervaller. I det första intervallet blandas en vattenlösning med surfaktanter till en nivå över den kritiska micellkoncentrationen (eng. critical micelle concentration). Detta innebär att miceller med mycket stor ytareal existerar i lösningen. Monomerer samt en initiator adderas sedan till lösningen. Initiatorn kommer att radikaliserar monomererna som i sin tur binder sig till micellerna. Reaktionen fortskrider tills alla miceller antingen transformerats till polymerer eller används för att stabilisera andra polymerer.

När det första skedet framskridit till sin slutpunkt kommer resterande monomerer att binda sig själv till polymererna som skapades i steg ett. Det betyder alltså att det första skedet är den avgörande faktorn i hur många polymerer som kommer att finnas i slutprodukten. Då största delen av monomererna har reagerat kommer reaktionen att påbörja terminering och reaktionshastigheten sakta minska tills inga monomerer finns kvar och reaktionshastigheten nått noll.

I denna avhandling utfördes flera sådana emulsionspolymerisationer med målet att utveckla ett bindemedel med bra egenskaper för flamskyddande träbeläggning. De egenskaper som eftersträvades var en låg partikelstorlek, glasomvandlingstemperatur mellan 0 och 10°C, och hög stabilitet även när den blandas med salt. Snabbt upptäcktes det att en kärna-skal-struktur (eng. core-shell) behövdes för att tillfredsställa dessa krav. Sammanlagt syntetiserades tio olika emulsioner med olika förhållanden mellan kärna och skal, samt olika monomerproportioner i både kärnan och skalet. Genom analys med FTIR, DSC, DLS, LDE hittades ett optimalt recept. Detta recept syntetiserades även med en annan stabiliserande surfaktant, men utan förbättring. Det optimala receptet kallades CS6 och hade en partikelstorlek på 89 nm, T<sub>g</sub> på 4°C och bildade fina filmer under torkning. Jämfört med ett kommersiellt referensbindemedel påvisade även CS6 elektrostatisk stabilitet vid högre mängder salt. Emulsionernas recept och analys hittas i Appendix A till D.

Skumdämpande av träbeläggningar undersöktes i denna avhandling. Skum kan orsaka stora problem vid applikation av träbeläggningar, speciellt vid industriell applikation där appliceringshastigheterna är höga och processen automatiserad. För att minska skumbildningen kan skumdämpare tillsättas till beläggningsrecept. Dessa skumdämpare är små olösliga droppar som attackerar bubblornas lameller och spräcker dem. Eftersom skumdämpare på grund av deras funktion måste vara olösliga kan de skapa problem både vid applikation, lagring och på ytan av den slutliga produkten. Därför är det viktigt att mängden skumdämpare hålls så låg som möjligt.

För att hitta en passande lösning utvecklades en testmetod för att utvärdera olika skumdämpares och ytmodifierares prestanda och lagringsstabilitet. Additivämnen i olika mängd lades till ett bindemedel och utsattes för omrörning under en bestämd tid. Efter omrörningen mättes blandningens densitet under 15 minuter, där en högre viskositet innebar mindre skum. Blandningarna lagrades i två veckor varefter de blandningar som fortfarande var stabila utsattes för samma omrörning igen och resultaten jämfördes med de första resultaten. Av de fem analyserade additiverna var det endast ett ämne, DF-2, som klarade lagringskravet. DF-2 uppvisade inga defekter under längre lagring och hade dessutom en minskande effekt på skum även när det adderades i väldigt låg andel. Resultaten hölls även på acceptabel nivå efter två veckors lagring. Den optimala mängden DF-2 fastställdes till 0,15% av blandningen i vikt. Resultaten av dessa analyser hittas i Appendix E.

Konkalorimeteranalys utfördes på flera träbitar behandlade med olika beläggningar. Detta gjordes för att utvärdera effekten av olika flamskyddande additivämnen. Samtliga additivämnen hade en positiv inverkan på beläggnings flamskyddsförmåga jämfört med referensen. Noggrannare jämförelser mellan de olika additivämnena försvårades av låg sampelmängd kombinerat med träbitarnas naturliga variation. För att noggrannare jämföra de olika additivämnena skulle en större sampelmängd behövas.

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# Appendices

## Appendix A

Emulsion polymerization recipe.

Table Appendix - 1. *Emulsion polymerization recipe*

Binder	Core		Shell		Surfactants			Additives		H <sub>2</sub> O
	Monomer A	Monomer B	Monomer A	Monomer B	X	Y	Z	K	P	
B1	40	30	-	-	2.5	1	-	No	No	80
B2	40	30	-	-	2.5	1	-	Yes	Yes	80
CS1	28	7	7	28	2.5	1	-	Core only	Core only	80
CS2	28	7	7	28	2.5	1	-	C&S	C&S	80
CS3	24.5	10.5	10.5	24.5	2.5	1	-	C&S	C&S	80
CS4	39.2	9.8	4.2	16.8	2.5	1	-	C&S	C&S	80
CS5	39.2	16.8	4.2	9.8	2.5	1	-	C&S	C&S	80
CS6	33.6	22.4	4.2	9.8	2.5	1	-	C&S	C&S	80
CS6Z	33.6	22.4	4.2	9.8	-	1	3	C&S	C&S	80
CS7	36.4	19.6	2.8	11.2	2.5	1	-	C&S	C&S	80

## Appendix B

DSC analysis of CS6, showing inflection point.

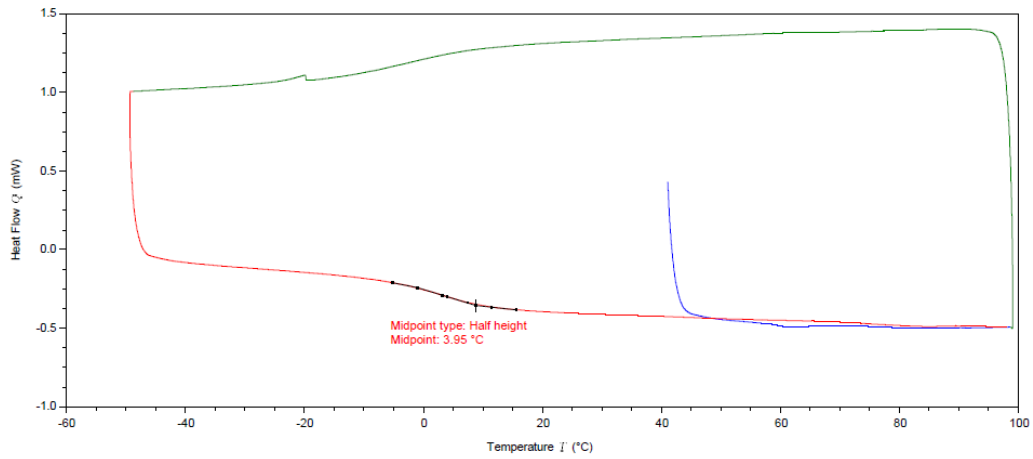


Figure Appendix - 1. DSC analysis of CS6.

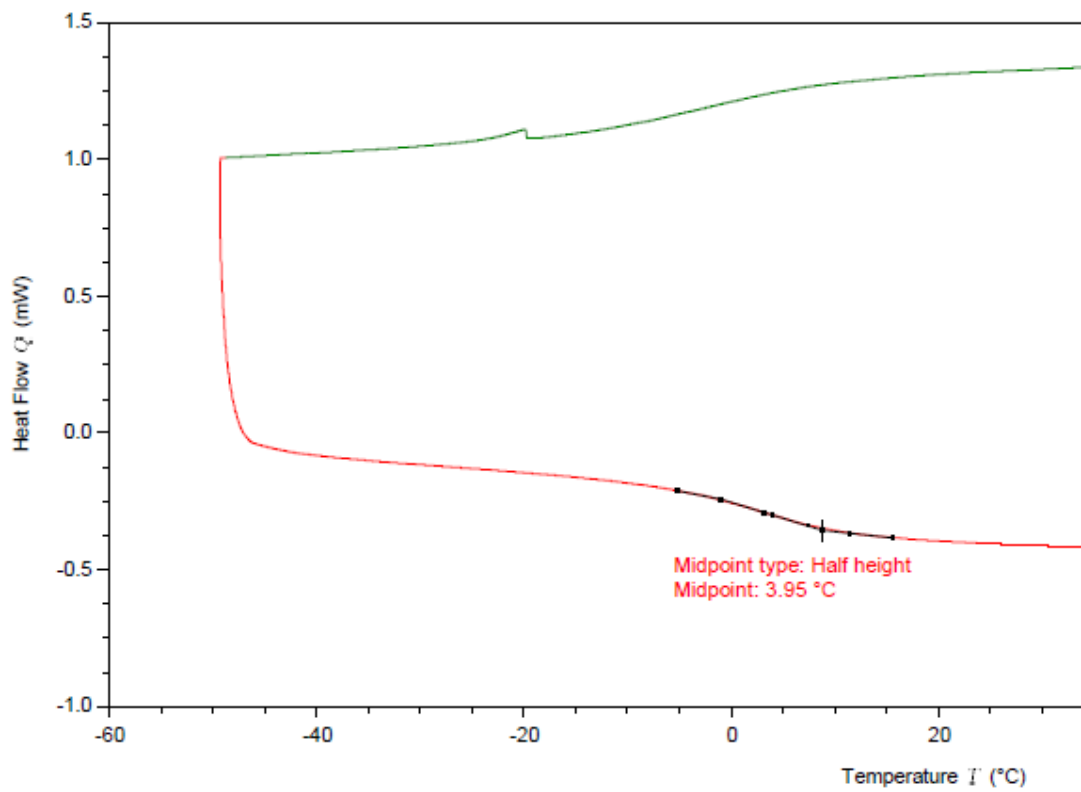
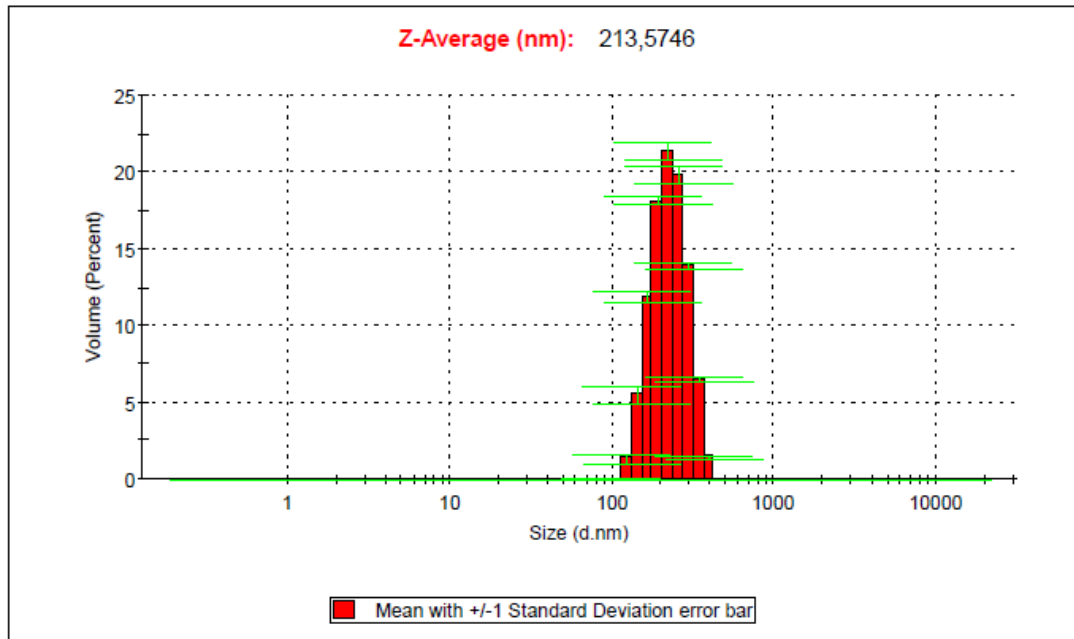


Figure Appendix – 2. Cropped DSC analysis of CS6.

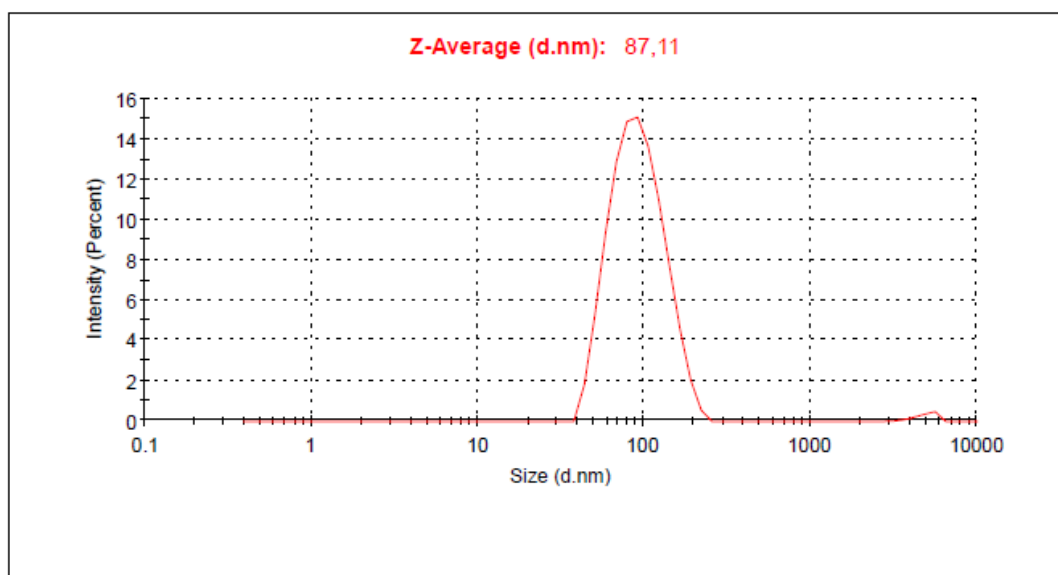
**Appendix C**

**(1/3)**

DLS analysis of binders.



*Figure Appendix – 3. DLS analysis of A0.*



*Figure Appendix – 4. DLS analysis of CS5.*

Appendix C

(2/3)

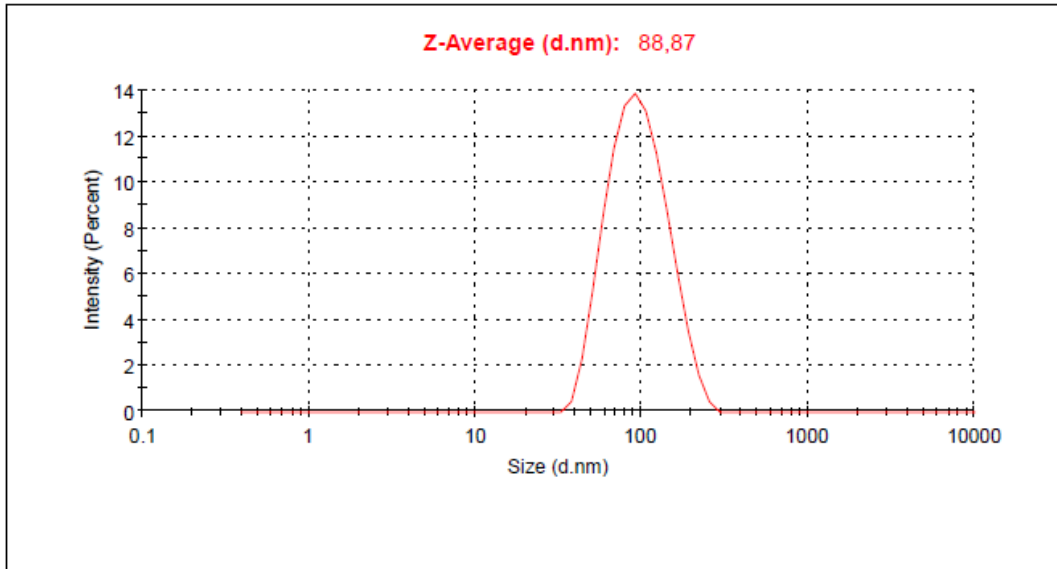


Figure Appendix – 5. DLS analysis of CS6.

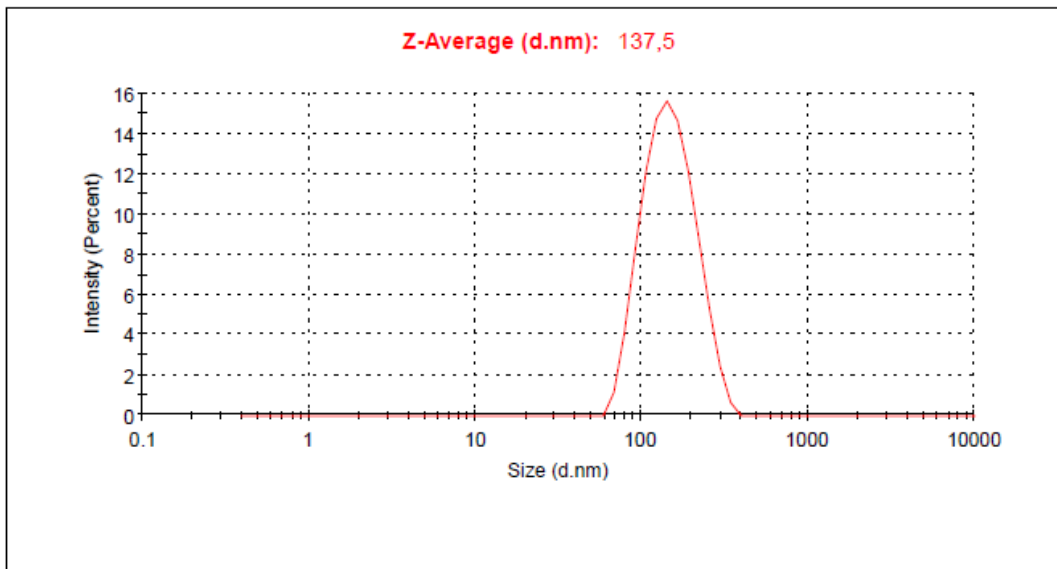


Figure Appendix – 6. DLS analysis of CS6Z.

Appendix C

(3/3)

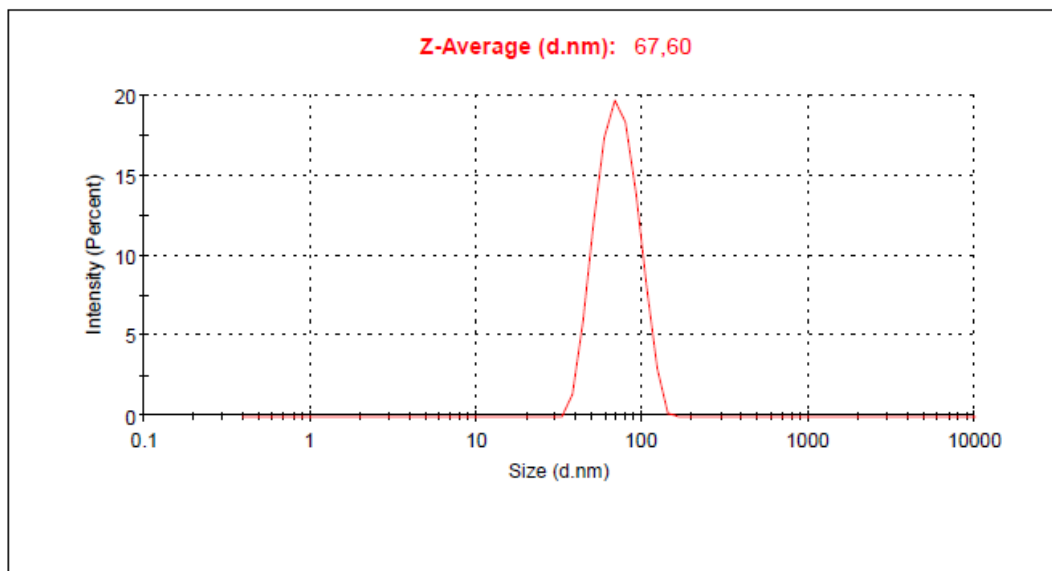


Figure Appendix – 7. DLS analysis of CS7.

**Appendix D**

**(1/3)**

Zeta potential as a function of salt N added to a 30% solid content binder.

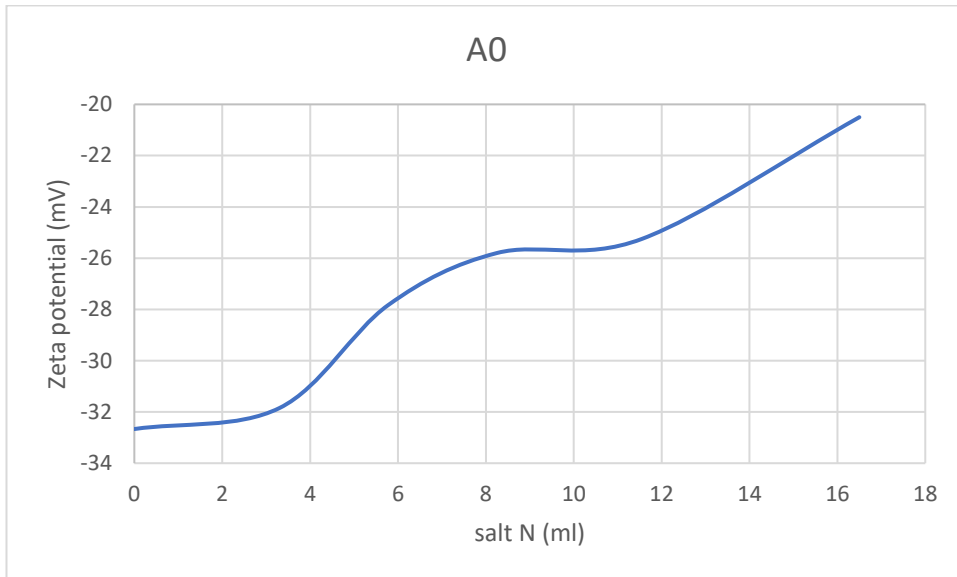


Figure Appendix – 8. Zeta potential analysis of A0.

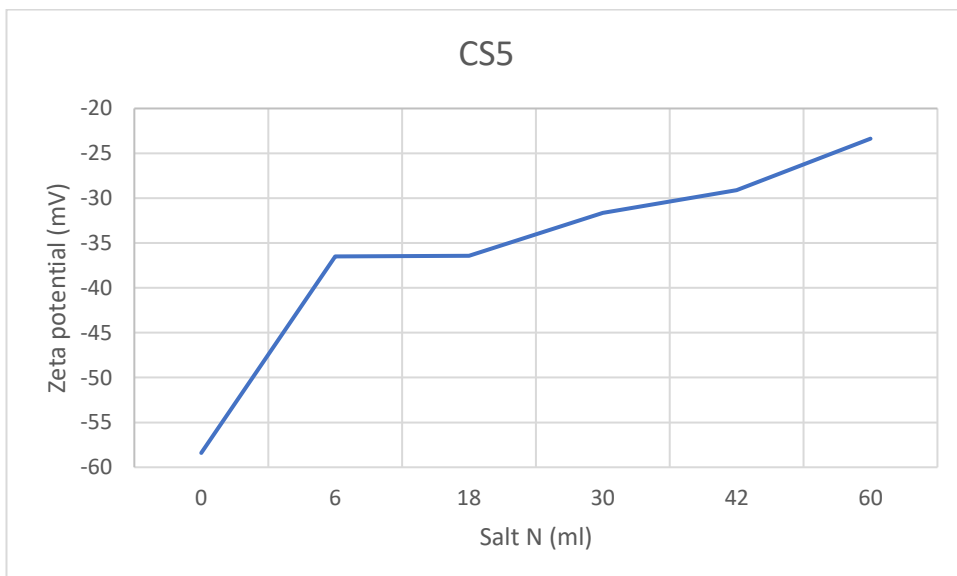
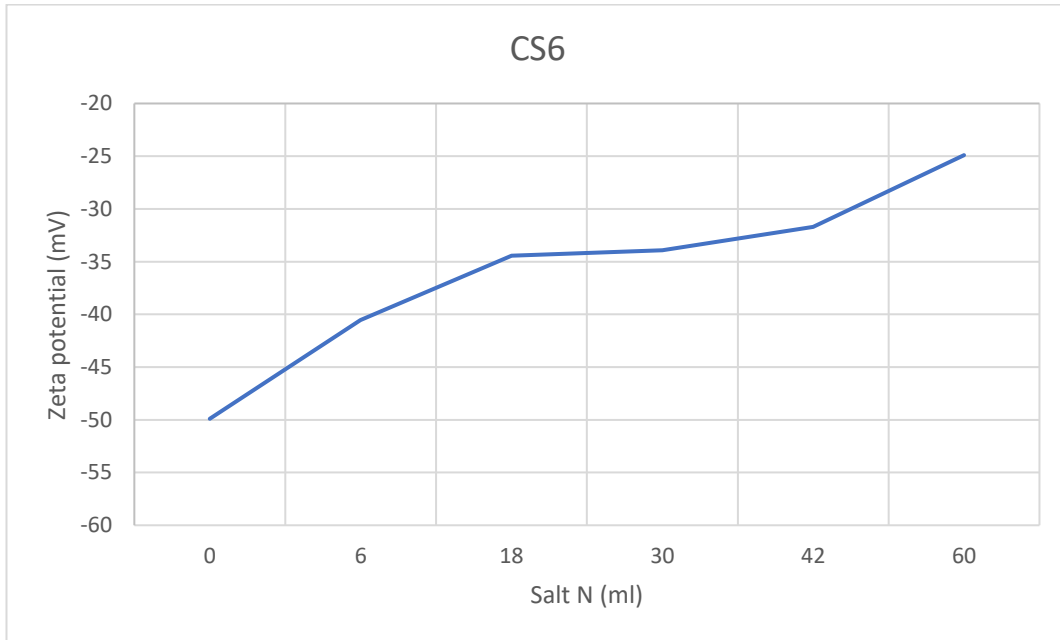


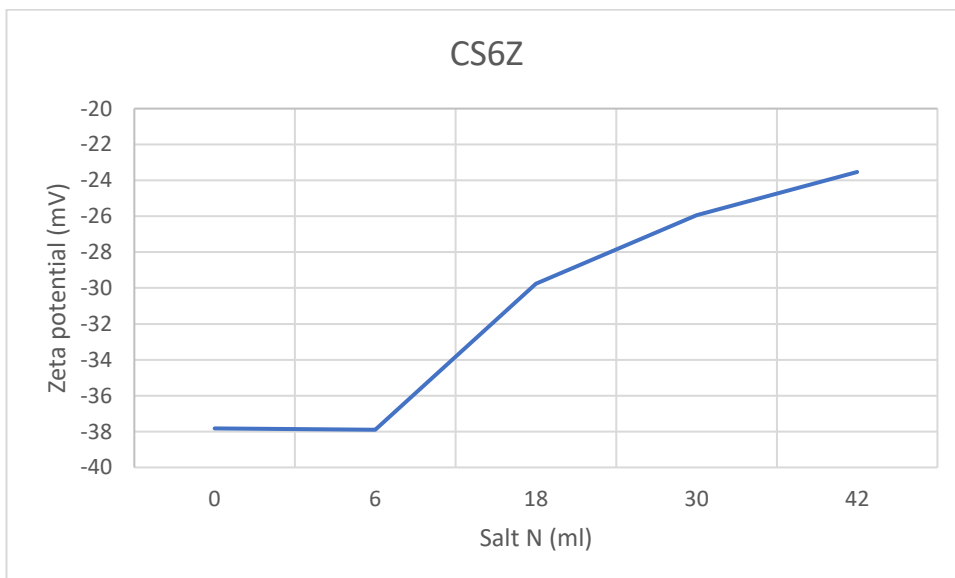
Figure Appendix – 9. Zeta potential analysis of CS5.

**Appendix D**

**(2/3)**



*Figure Appendix – 10. Zeta potential analysis of CS6.*



*Figure Appendix – 11. Zeta potential analysis of CS6Z.*

## Appendix D

(3/3)

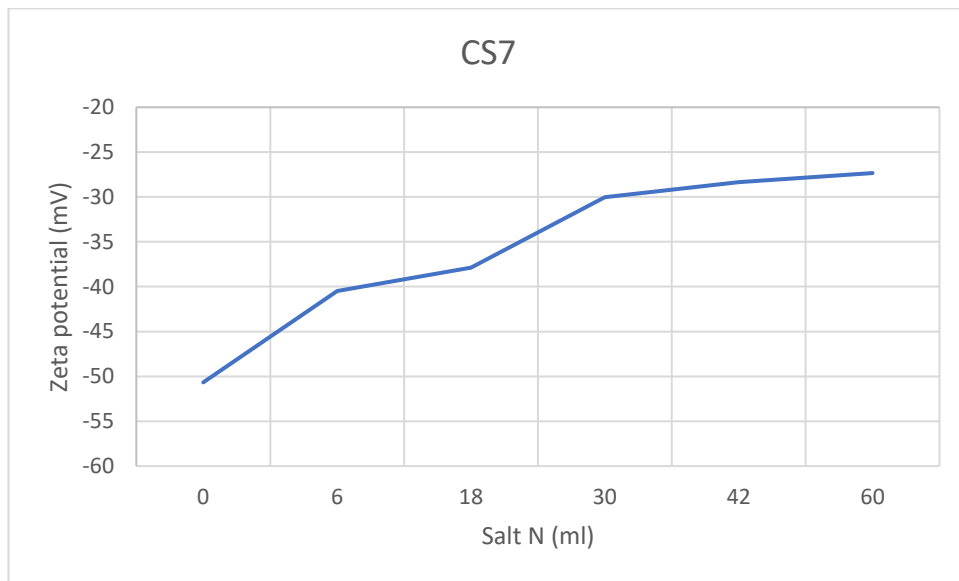


Figure Appendix – 12. Zeta potential analysis of CS7.



## Appendix E

(1/3)

Density measured over time for various amounts of DF-2 when added into a coating product and subjected to defoamer analysis.

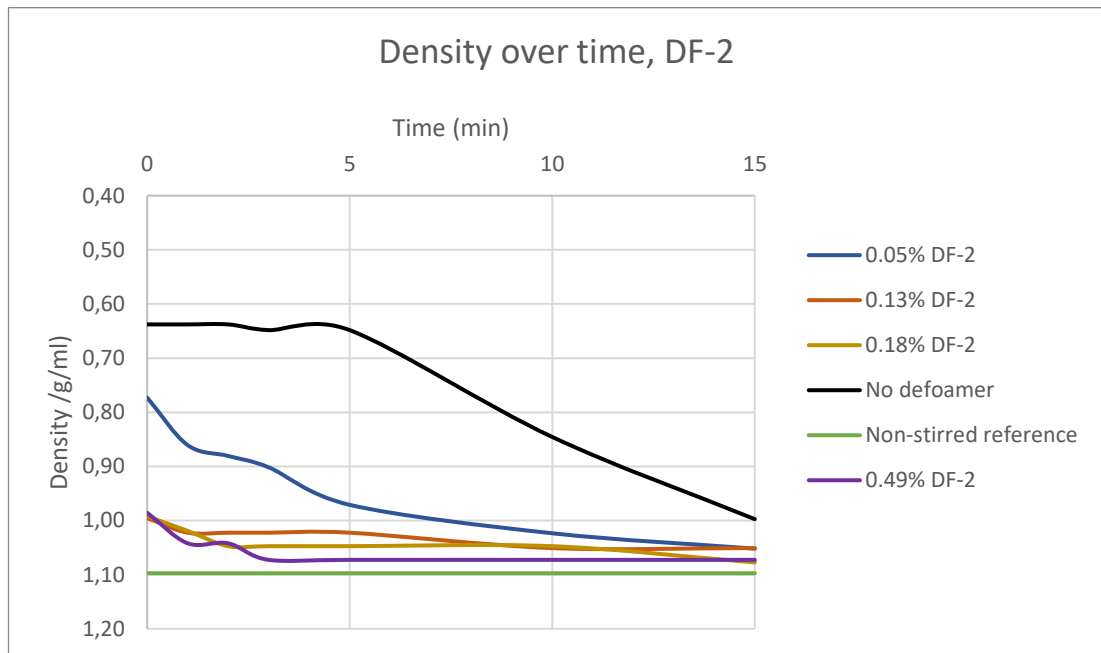


Figure Appendix – 13. Density over time during defoamer analysis for various amounts of DF-2.

**Appendix E**

**(2/3)**

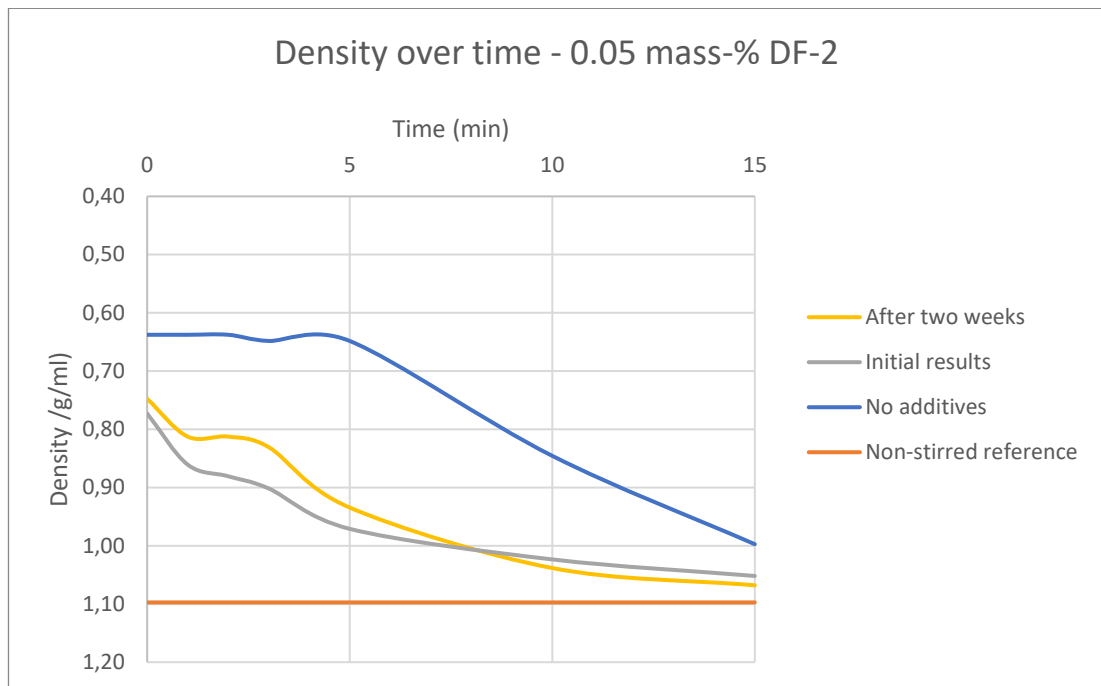


Figure Appendix – 14. Two-week comparison of DF-2 when added at 0.05% in weight.

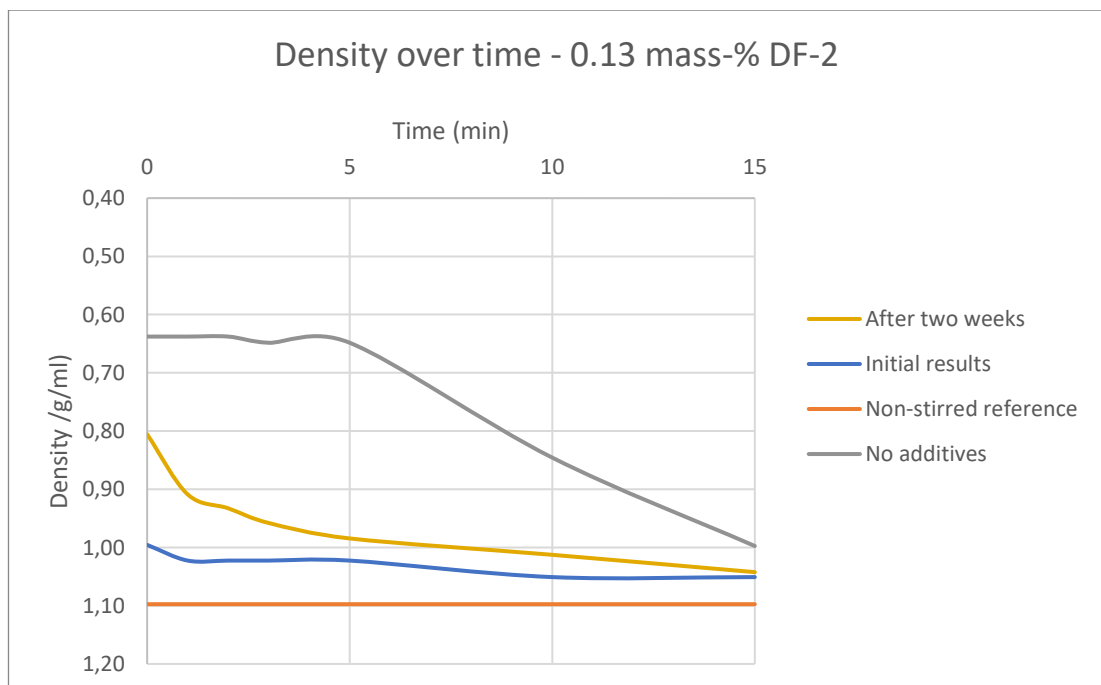
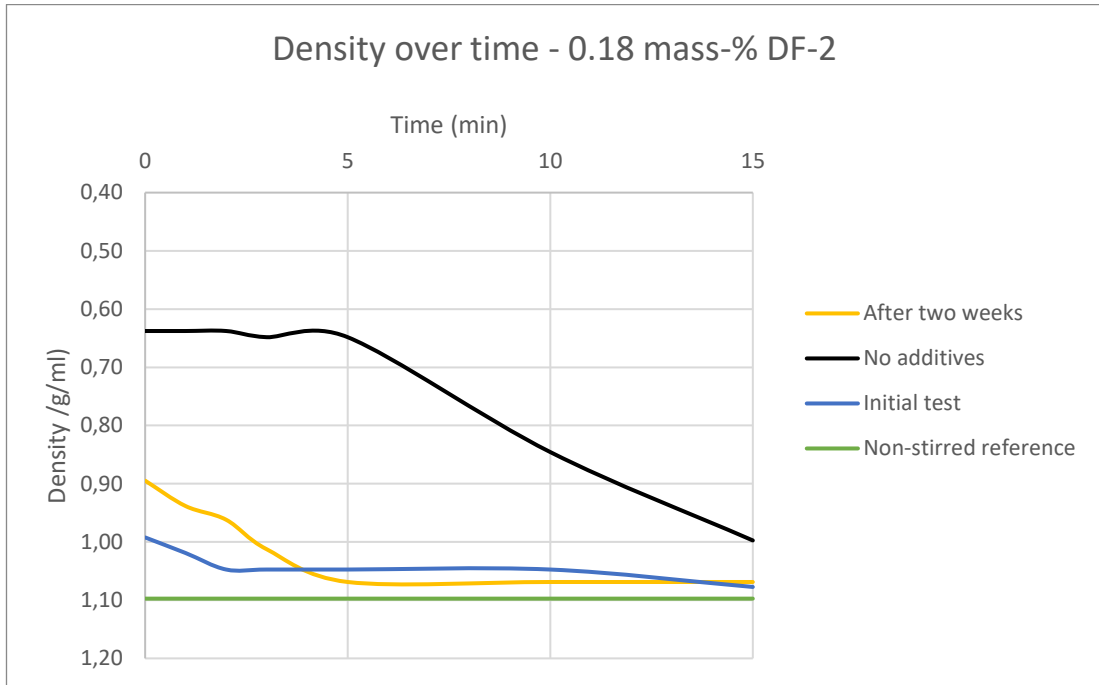


Figure Appendix – 15. Two-week comparison of DF-2 when added at 0.13% in weight.

**Appendix E**

**(3/3)**



*Figure Appendix – 16.* Two-week comparison of DF-2 when added at 0.18% in weight.