CHALMERS

Examination of the factors determining the degree of gloss in paint films

Diploma work in the program Chemical Engineering

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Göteborg, Sweden, 2012

Abstract

Water borne latex paints are complicated systems and they contain several different ingredients such as thickener, latex, dispersing agent, pigment, surfactants etc. In order to examine which of these ingredients contribute to the degree of gloss and also how the use of cellulosic thickeners and synthetically manufactured thickeners affect the gloss of a paint film, different paints were studied. These paints were produced with different thickeners, latexes, dispersing agents and different amounts of pigment.

Cellulosic thickeners are used in flat, satin and semi-gloss paints but are known not to be suitable in high-gloss paints. This study is of importance to gain knowledge in why the natural polymer cellulose is not suitable in gloss paints. To examine this, four different cellulosic thickeners, one synthetic thickener and also mixes of the different thickeners were studied. In total, 23 varied samples were mixed and examined.

The different samples were prepared and analyzed with the most relevant test methods to provide information on their properties. Tests such as rheology measurements were performed and when comparing these to the results of the fluent tests, sagging and leveling, we gained an understanding in why some paints are more fluent than other paints. There were also tests performed to understand the paints ability to coat a surface and to find out their degree of gloss. A few of the samples were studied with the help of scanning electron microscopy, SEM, which proved to be a good method to understand how the surfaces actually looked like.

Like expected, the tests showed that paints based on the synthetic thickener obtain higher gloss and that the gloss decreases as the pigment concentration increases. The cellulosic thickeners did not show any gloss according to standard. Paints containing the synthetic thickener are in general more fluent and therefore showed a better leveling as well as a lower sagging resistance. This result was consistent with the results of the rheology measurements. When changing to another dispersing agent as well as latex it showed a relatively small difference in degree of gloss but still it had a small influence. The main factors determining the degree of gloss were the thickener and also how smooth and even the surface of the paint film was.

Sammanfattning

Vattenbaserad färg är ett komplicerat system som innehåller många olika ingredienser som till exempel förtjockare, latex, dispergeringsmedel, pigment, tensider etc. För att undersöka vilka faktorer som bidrar till glansen av en färg och även förstå hur användandet av cellulosaförtjockare och syntetiskt framställda förtjockare påverkar glansen, studerades olika förtjockare, latex, dispergeringsmedel samt olika mängder av pigment.

Cellulosaförtjockare används i matta, halvmatta samt halvglansiga färger men är kända för att ej vara lämpliga i hög-glansiga färger. Denna studie är av betydelse för en större lärdom i varför den naturliga polymeren cellulosa inte är lämplig i glansiga färger. För att undersöka detta, studerades fyra olika cellulosa förtjockare, en syntetisk förtjockare såväl som blandningar av de olika förtjockarna. Allt som allt blandades och analyserades 23 varierade färgprover.

De olika proverna förbereddes och analyserades med de mest relevanta testmetoder för att erhålla information om deras egenskaper. Tester som reologimätningar genomfördes och jämfördes med resultatet av flytegenskaperna, leveling och sagging, för att ge oss en förståelse för varför vissa färger är mer flytande än andra. Det genomfördes även tester för att undersöka färgens förmåga att täcka en yta och tester för att mäta färgens glans. Några färgprover studerades med hjälp av svepelektronmikroskopi, SEM, vilket visade sig vara en bra metod för att ge en tydligare bild av hur ytorna faktiskt ser ut.

Som väntat, visade testerna att färger baserade på den syntetiska förtjockaren uppnår högre glans och glansen sjunker med ökande pigmentkoncentration. Cellulosaförtjockarna visade ingen glans enligt standard. Färger som innehåller syntetisk förtjockare är generellt mer flytande och därmed visade de bättre flytegenskaper vilket innebär en högre leveling och då även lägre saggingmotstånd. Detta resultat överensstämde med resultatet ifrån reologimätningarna. Utbyte av dispergeringsmedel samt latex visade relativt små skillnader på uppvisandet av glans men de har en liten påverkan. Huvudsakliga faktorer som påverkar glansen är förtjockare samt även hur jämn färgytan är.

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1. Introduction

AkzoNobel is the largest global paints and coatings company in the world and a major producer of specialty chemicals. The business unit Performance Additives develops and produces cellulosic thickeners which can be used as rheological modifiers in for example paint.

Paint is a complicated colloidal system and consists of several different ingredients. There are ingredients such as thickener, latex, dispersing agent, pigment, surfactants etc.

In terms of visual appearance, gloss is one of the key features of paints and therefore of great importance. AkzoNobel Functional Chemicals produce a key ingredient in paint, the thickener. The thickener they produce is made from the natural polymer cellulose and it helps the paint with rheological features. It is well known that when using these cellulose thickeners it is difficult or even impossible to obtain glossy paints but when using synthetic thickeners this is not a problem. This diploma work is made for AkzoNobel to gain knowledge on the subject and understand why the problem occurs. The aim of this diploma work is to do an examination of the factors determining the degree of gloss on paint films and also to study why it is not possible to obtain high gloss paints with the use of cellulosic thickeners.

To examine this problem, 23 different samples of paint were prepared and analyzed. Four different cellulosic thickeners and one synthetic thickener were studied in combination with varied amounts of pigment. To gain further understanding, the impact of different dispersing agents and latexes were studied. There have been previous studies made on the correlation between ingredients in paint and their impact on gloss. In the article written by Saeed Farrokhpay it is discussed how the dispersing agent contributes to the gloss and that it is of great importance to choose the right kind. [7]

In order to investigate what factors contribute the most to the degree of gloss, samples of paint containing variations in type of thickener, amounts of pigment, dispersing agent and latex were prepared. While keeping the rest of the components in the formula constant, one can understand the varied components effect on the gloss. As a final step in this study, paints containing a mixture of cellulosic thickener and synthetic thickener were prepared.

The samples were analyzed with the most relevant test methods. Tests were run to measure the gloss of the paints and an examination of the paints ability to coat the surface was done. Moreover, tests were performed to understand how fluent the paint was.

With the use of a rheometer, a picture of its rheological profile was given and the use of SEM showed how the paints actually look on the surface.

2. Theory

2.1 Paint

There are many different kinds of paint. In this paper, water borne latex paints have been studied. Paint is most commonly used to protect, color or provide texture to objects. It is also used for communication purposes. Paint is applied to a surface and then converted to a solid film.

Water borne latex paints are complicated systems and they contain several different ingredients. It mainly consists of binder, thickener, filler, pigment, dispersing agent and surfactants. For the paint to function optimally, it is important that the particles included are well stabilized.

Paint can be produced with different PVC, that is, different Pigment-Volume-Concentration. PVC is the volume fraction of pigment in the total volume of dry paint. Dry paint mainly consists of pigment, binder and extender. As the amount of pigment increases, the PVC increases. Since pigment has a higher refractive index than binder (polymer), the gloss will decrease with increasing amount of PVC. The range of PVC covers gloss to flat formulations.

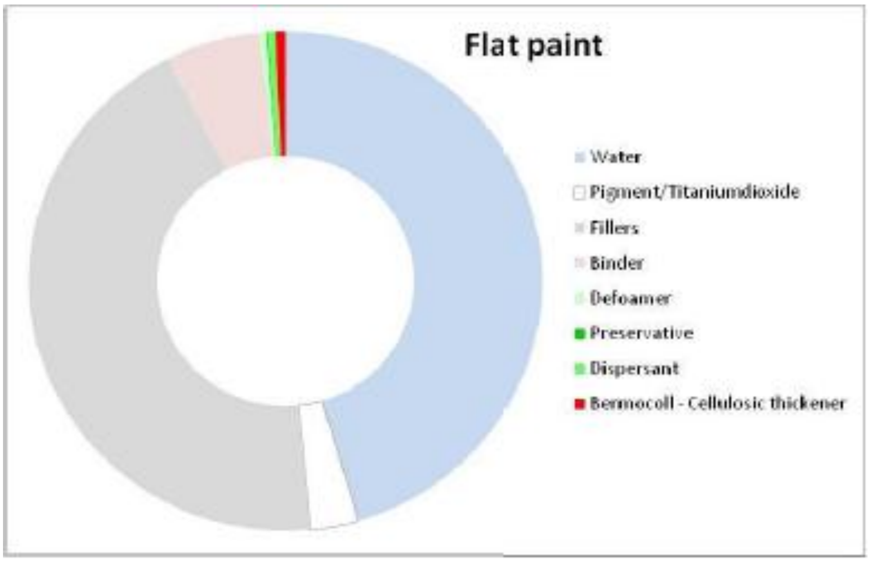

Figure 1: Illustration of the ratio between different ingredients in a flat paint.

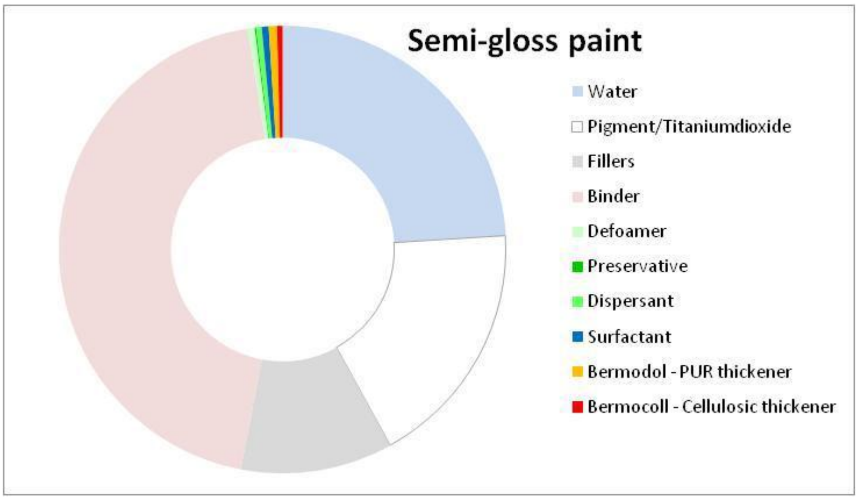

Figure 2: Illustration of the ratio between different ingredients in a semi-gloss paint.

A diluent or solvent is another ingredient used to produce a paint and it is included to dissolve all the polymers and to adjust the viscosity. But because of its volatile property, it is not an ingredient of the dried paint film. The ingredients can vary depending on the desired properties of the paint but the binder is always included. It is the film-forming component of paint. It imparts adhesion and strongly influences properties such as gloss and flexibility. As shown in the Figures 1 and 2, the greatest difference between a gloss and flat paint is the amount of filler, binder and pigment. Pigments and fillers are granular solids. Pigments are incorporated in the paint to contribute to the color and to provide opacity, i.e., hiding power. Fillers are incorporated to impart texture, to give the paint special properties, to improve its hiding power or to reduce the cost of the paint. Fillers are generally larger in size compared to pigment and when included in the paint, it will have an even greater impact on the decreased gloss.

The thickeners are polymers and they have a great affect on the paint, although it constitutes a very small part of a paint. Its function is to obtain a thickening effect, help achieve rheology control, and stabilization. Cellulosic thickeners also have an impact on the water retention.

In this study, cellulose thickeners have been examined. EHEC is a group of non-ionic cellulose ethers produced by AkzoNobel under the trade name Bermocoll. Cellulose ethers are not known to be suitable in high gloss paints and therefore, when a high gloss paint is desired the thickener is often of the polyurethane type.

2.2 Latex

The binder is the film-forming component of paint and is therefore the most important ingredient. In water borne paint formulations, latex is often used as a binder and imparts adhesion and has a great impact on properties such as gloss, flexibility and toughness.

Latex is a colloidal system where small polymer particles are dispersed in water. After the paint has been applied, the water starts to evaporate which leads to the particles getting closer. The space between the particles experience increased capillary forces and this creates high pressures. The pressures counteract the repulsion forces and this makes the particles merge together. The polymer particles are then joined in the tightest packing possible and when the water has disappeared the particles deform to fill up all the space.

Since surface roughness is the most important parameter affecting gloss, it is necessary in high gloss paints to choose a type of binder which produces as smooth film as possible.

2.3 Pigment

Titanium dioxide are white pigments with optical effects. The primary function of titanium dioxide in a paint is to produce opacity. Studies have shown that surface defects which are of the order of 0.1µm or more in height will affect the degree of gloss. Since the size of titanium dioxide particles are approximately 0.2 µm its presence could decrease the gloss. An increase of the PVC in a paint will lead to lower gloss because of the presence of a larger amount of pigment on the surface.

2.4 Dispersing agent

The function of the dispersing agent is to enhance the dispersion process and to ensure a fine particle size in order to stabilize the pigments in the solution. The dispersing agent is consistent of polymers and can be acrylic or have a different character. Since titanium dioxide has a major part in influencing the gloss of a paint, it is very important to ensure that the pigment is as well dispersed as possible in the dried film. This is important to keep surface irregularities at a minimum. The process when the pigment is dispersed consists of three stages. It starts with the wetting where the pigment-air interface is replaced by a pigment-medium interface. A force is then applied to help the wetting and to break down the titanium dioxide agglomerates. With the help of a dispersing agent, the pigment is stabilized by either electrostatic or steric repulsion. The stabilization is very important in order to prevent flocculation. To obtain high gloss, pigment flocculation should be kept at a minimum.

Therefore it is of great importance to choose the most suitable kind of dispersing agent. Depending on kind of dispersing agent and also the amount of dispersing agent, the pigments are wetted and stabilized to different extents.

2.5 Thickeners

Thickeners are added to the paint to have a rheological effect i.e. thickening the paint to the wanted viscosity. There are different kinds of thickeners such as synthetic ones, for example poly urethane based (HEUR) and natural ones, cellulosic ethers (EHEC). In this study these thickeners are examined closer.

2.5.1 EHEC

EHEC or Ethyl hydroxyethyl cellulose is a group of non-ionic cellulose ethers which are available in a wide range of viscosities and also in a variety of modified grades. EHEC is a water-soluble cellulose derivative. The water solubility is due to the presence of hydrophilic ethylene oxide substituents distributed along the cellulose backbone. Also ethyl groups are substituted onto the polymer. For an illustration of the EHEC molecule see Figure 3.

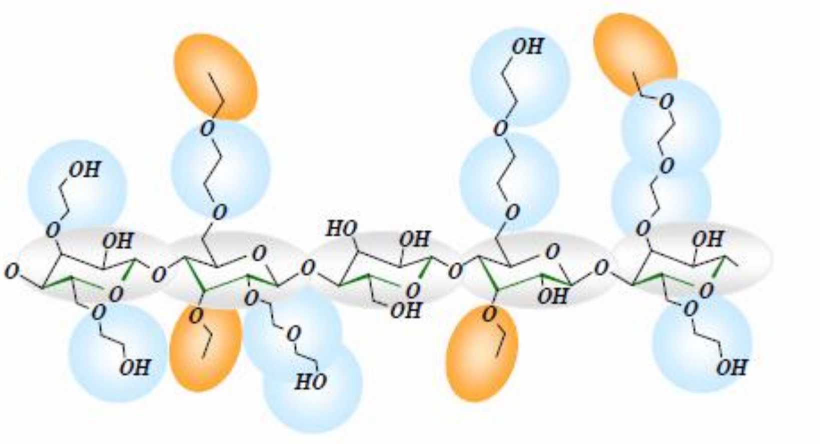

Figure 3: Possible structure segment of an EHEC molecule.

Cellulose is a polysaccharide built up from 1,4-anhydroglucose units, (AHG). Before it is possible to use the cellulose as a thickener, it needs to be modified to be soluble. The modification starts with an alkalization step. The process starts with introducing charges into the hydroxyl groups of the glucose units. This step makes the cellulose chains accessible for the chemical reaction, i.e. reaction with added ethylene oxide and ethyl chloride, see Figure 4.

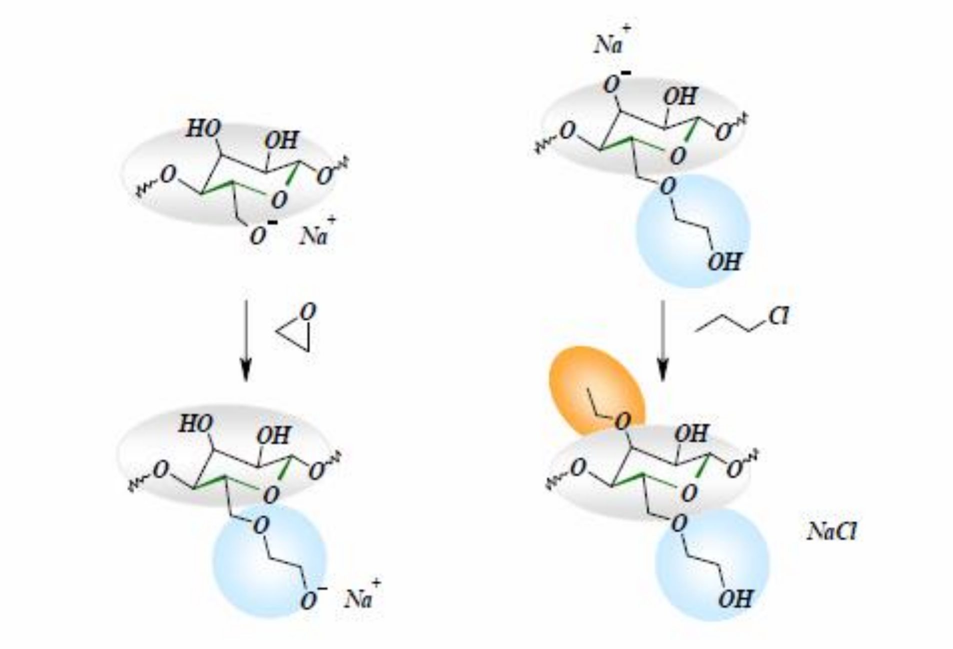

Figure 4. The reaction of ethylene oxide to alkalized cellulose (left). The reaction of ethyl chloride to alkalized hydroxyethyl cellulose (right).

The main thickening mechanism of EHEC is chain entanglements. As the polymer concentration increases, the polymer molecules are forced closer together and start entangling with each other, see Figure 5. The result is an increase in the viscosity of the polymer solution.

The thickening mechanism of hydrofobically modified EHEC, (HM-EHEC), contains contributions both from chain entanglements and hydrophobic interactions. Along the EHEC backbone, the HM-EHEC has hydrophobic substituents attached. The hydrophobic groups will try to minimize the contact with water in an aqueous solution and instead they associate to each other. These hydrophobic interactions together with the entanglements result in a significant increase in viscosity, see Figure 5. In a paint formulation the hydrophobic groups also interact with other hydrophobic entities, such as the latex particles, which contributes to the thickening efficiency.

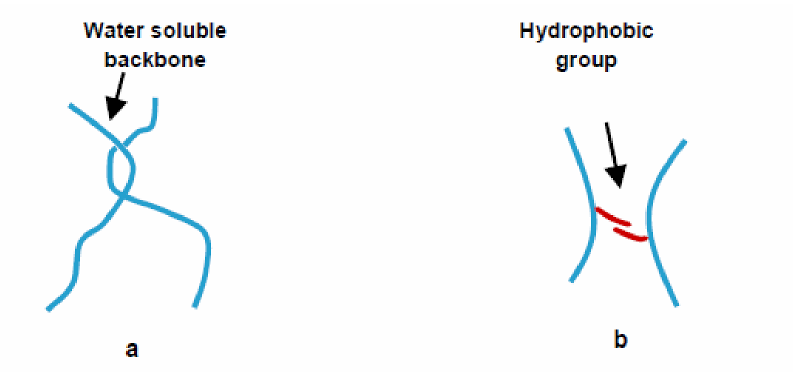

Figure 5. Schematic illustration of the thickening mechanisms of EHEC and HM-EHEC. (a) chain entanglements and (b) physical cross-links via hydrophobic interactions.

Cellulose ethers can be incorporated into the paint in different ways and also at several stages during the manufacturing process. The main addition method is as a stock solution although it can also be added as a slurry or as dry powder.
Four different cellulosic thickeners and one synthetic thickener were used in the examination.

Table 1: The four examined cellulosic thickeners.

Thickener	Property	Viscosity [mPa*s]	Approx. Mw
A	Low Mw	260-360 (2%)	300 000
B	Hydrophob. mod.	200-450 (1%)	200 000
C	High Mw	1700-2400 (1%)	1 500 000
D	High Mw	3000-4000 (1%)	1 500 000

2.5.2 HEUR

Hydrophobically modified ethoxylated urethane (HEUR) thickeners increase the viscosity of water based paints. It is a synthetic thickener which consists of a hydrophilic polyethylene glycol segment in the middle with hydrophobic groups attached at both ends. These hydrophobic groups interact with other hydrophobic groups. They also interact with one another, contributing to an increase in viscosity. In a paint formulation the hydrophobic groups also interact with other hydrophobic entities, such as the latex particles. Since the thickening effect relies mainly on hydrophobic associations, and entanglements are expected to be of very small importance, it makes it suitable to create Newtonian behavior.

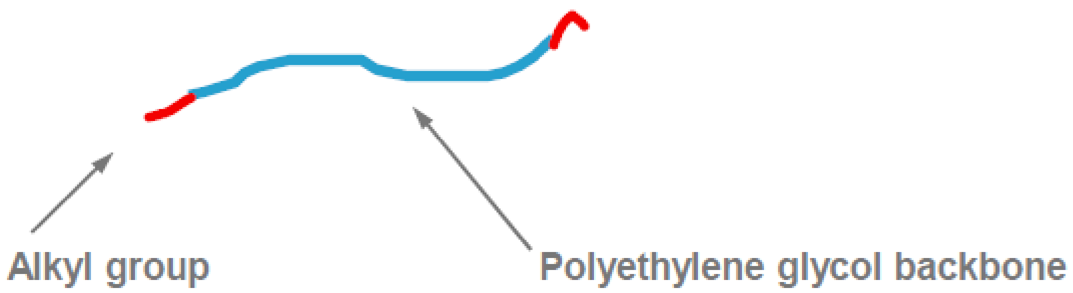

Figure 6: Illustration of the synthetic HEUR thickener.

2.6 Gloss

Gloss is a very important feature of a paint and it is also a term to express the capacity of surfaces to reflect directed light. When a beam of light of intensity is incident on an air-film interface, a percentage of the light is refracted into the body of the film and the remaining percentage is reflected. The refracted light, which is partly absorbed by the titanium dioxide and is responsible for the specular gloss, contributes to the opacity and color of the film.

Figure 7: Illustration of gloss measurement.

This degree of gloss, which is varied according to how the paint exhibit specular reflection, is divided into the categories full gloss, semigloss and flat. For an ideal flat surface, the light is scattered and reflected equally in all directions. The scatter of the reflected rays around the specular angle can be measured with a glossometer and the choice of angle on measurements depends on what standard one wants to use and also on the gloss of the film.

ISO 2813 specify values of 20°, 60° or 85°.[3] The 20 geometry is intended to be used on high gloss paints. The 60 geometry is used on paint films which do not have a very high gloss or a very low one and the 85 geometry on low gloss paints.

The gloss of a paint film is depended on how the surface looks like and very small changes are required before the gloss is affected. A rough surface will cause the specular light to decrease in intensity but this only occurs when surface irregularities are of the order of the wavelength of light. If surface defects are greater in size, then the total energy of the reflected beam remains unaltered but it is spread over a wider angle in accordance with the law of reflection which says that for each light ray, the angle of incidence is equal to the angle of reflection.

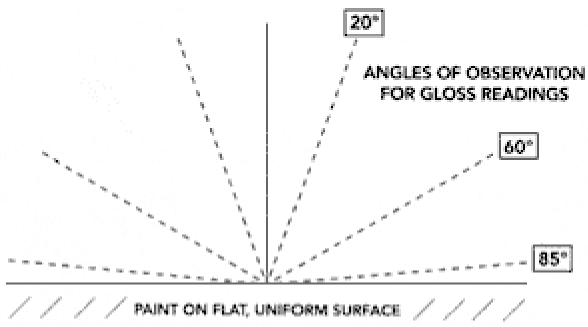

Figure 8: Illustration of the law of reflection.

There are different factors contributing to a rough surface and decreased gloss. Studies tell that how well the thickener interacts with the components dispersing agent, latex and pigment can decide the degree of gloss in paint films[4] and hence, to obtain a high gloss paint it is important to choose the right types of components. The pigment is a component that should when incorporated in a paint be chosen with much consideration. This is due to its particle size and also the distribution of the pigment in the medium. This distribution contributes significantly to the development of the optical properties.

The pigment used in this study is titanium dioxide and it is the pigment with the greatest scattering power of all white pigments

2.7 Pigment Volume Concentration (PVC)

The PVC in paint is the ratio of the total volume of pigments and extenders to the volume of the dried paint film in percent by volume. The range of PVC covers gloss to flat formulations.

$\%PVC = 100 * (V_{pigment} / (V_{pigment} + V_{binder} + V_{extender}))$

Table 2: Approximate relation between gloss level and PVC

Gloss	PVC 15-25
Semi-gloss	PVC 25-40
Flat	PVC 40-85

3. Experimental

3.1 Materials

The following components were used to formulate the paints: the different thickeners A, B, C, D and HEUR were provided by AkzoNobel Functional Chemicals, Stenungsund. The latex Joncryl was given from BASF (trade name Joncryl 8225), and the latex Mowilith from Celanese (trade name Mowilith LDM 7411), a defoamer from BYK Chemie (trade name Byk 022), a preservative from Angus Chemie GmbH (trade name Canguard), a TiO_2 pigment from Kronos AS (trade name Kronos 2190), a dispersing agent from Rohm and Haas (trade name Orotan 731, 25%), a dispersing agent from BASF (trade name Dispex N40, 25%), and 1,2-propanediol from Emplura.

3.2 Paint

The manufacture of a paint which contained cellulosic thickener differed from the procedure to prepare a paint based on a synthetic thickener. In a paint with a cellulosic thickener, the cellulose is added in the first step, before undergoing dispersing step. When it is desired to include a synthetic thickener in the paint, it is added after the dispersing, right before adding the latex.

Table 3: Formulation of included components in a paint based on a cellulosic thickener, amounts in (g).

Grind		
1.	Water+cellulose thickener	Approx.80+3.5
2.	A few drops of ammonia	1
3.	Defoamer	2
4.	Dispersing agent	15.5
5.	Preservative	1
6.	Propylene glycol	32
7.	TiO2 pigment	434
Let down		
8.	Latex(50%)	410
9.	Defoamer	2
10.	Water	19
	Total	1000

Cellulose powder was added to water and mixed. A few drops of ammonia were added to make the cellulose soluble. When the cellulose was dissolved, 3-7 was added and dispersed for 20 minutes with the speed of 3000 rpm using a Diaf lab dissolver for paint production.

Under stirring with the use of an impeller stirring device and with the speed of approximately 700 rpm, 8-9 was added. If it was desired to add the cellulose as a slurry, it was done as the last step together with the water and this process was done with the speed of approximately 700 rpm during an hour.

Table 4: Formulation of included components in a paint based on a synthetic thickener, amounts in (g).

Grind		
1.	Water	79.5
2.	Defoamer	2
3.	Dispersing agent	15.5
4.	Preservative	1
5.	Propylene glycol	32
6.	TiO2 pigment	434
7.	Potassium hydroxid	1
Let down		
8.	Synthetic thickener	4
9.	Latex (50%)	410
10.	Water	19
11.	Defoamer	2
	Total	1000

1-7 was dispersed with the speed of 3000 rpm for 20 minutes using a Diaf lab dissolver for paint production. To produce the let down, 8-11 was added under stirring with an impeller stirring device. The solution was then mixed during an hour at a speed of approximately 700 rpm.

3.3 Methods

3.3.1 Gloss

The paint is applied to a glass plate and spread to a thickness of 600 µm using an applicator (BYK) and is then left to dry. After 7 days the paints ability to reflect light is measured with a glossmeter. The gloss is measured at three different angles which are 20°, 60° and 85°.

3.3.2 Leveling

Leveling is a test to determine the paints ability to flow out after application. It is a desired property of paints because of its ability to provide even surfaces. If the paint has a low leveling ability, it will show irregularities such as brush marks during the process of application. A sample of 60 ml paint is pre-sheared 30 seconds before applied to a chart, with the Leneta leveling test blade, with the speed of 500 mm/s. The draw-down is then left to dry in a horizontal position. The results are compared with standard charts and are judged on a scale 1-10 with 10 as the most fluent.

Figure 9: Illustration of a leveling test.

3.3.3 Sagging

Sag resistance is a procedure made on aqueous coatings to comprehend how fluent the paint is. Sagging is considered a paint defect because of its dripping which results in an uneven coating. With an applicator, at a speed of 150 mm/s, a drawdown is made on a black and white chart. The applicator will form streaks of various thicknesses. After the drawdown is performed, the chart is immediately placed in a vertical position with the thinnest stripe at the top. Gravity will cause an overloaded area of paint to droop or sag in a horizontal line. When the paint has dried, the sag pattern is analyzed. The sagging is compared against the notch numbers on the Anti Sag Meter and the lowest or thickest stripe that has resisted any sagging is decided. A higher number corresponds to a higher ability to resist sagging.

Approximately 60 ml paint is pre-sheared 30 seconds at 1300 rpm and then applied to a chart with Anti Sag Meter with 4-24 mils clearance range.

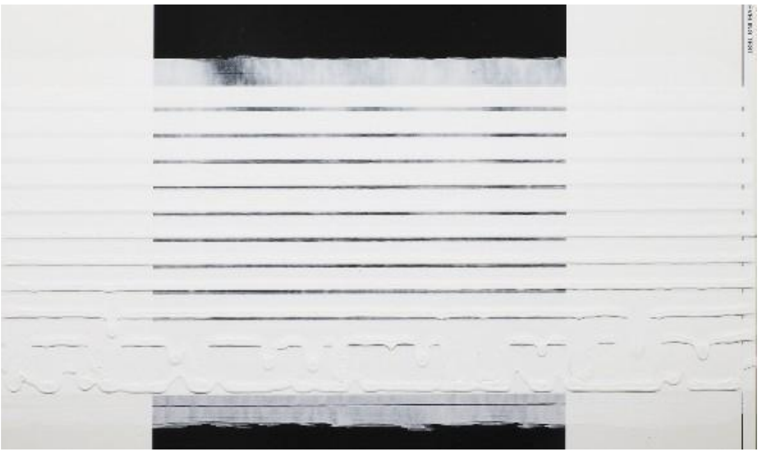

Figure 10: Illustration of a sagging test.

3.3.4 Hiding power

Hiding power is a test which tells how good the paint covers the surface. A contrast card is painted and then evaluated on its hiding power. The hiding power of a paint is decided by its ICI viscosity. The higher ICI viscosity the paint has, the better it will cover the surface. This test provides an indication of the possibility of pigment flocculation in the paint. If there is, the contrast card would not be well coated. The results are judged on a scale 1-10 and a 10 would mean the surface is completely coated.

Approximately 60 ml paint is pre-sheared 30 seconds before applied to a contrast card with an applicator, 2 (0.05 mm) The draw-down is made with the speed of 150 mm/s.

Figure 11: Illustration of a hiding power test.

3.3.5 Stormer/ICI

The Stormer viscosity is resembled to pouring the paint and the ICI viscosity is comparable to when the paint is sprayed or rolled. These viscosity values are very important for the application behavior and performance of the paint. In this examination, all paint samples had a Stormer viscosity between 97-102 KU.

3.3.6 Rheology

Rheology is the science of deformation and flow of materials. Every material is influenced by external forces. Gravitational forces influence phenomena such as leveling and sagging. The rheology of a paint is of great importance and rheological additives influence properties such as viscosity, consistency, leveling and gloss. Measurements were made to understand the paints rheology profile. The tests are made to give a deeper understanding on the phenomena sagging and leveling and to find possible correlations to gloss results.

During the measurement a defined shear stress was applied and the resulting flow or deformation, i.e. the viscosity of the paint sample, was recorded. A 4° cone with the diameter of 40 mm was used.

There is a great difference in the rheology behavior of a paint made of a cellulosic thickener compared to the behavior of a synthetic thickener based paint, see Figure 12. The cellulosic thickener paint show a more shear thinning behavior whereas the paint with the synthetic thickener show a Newtonian behavior.

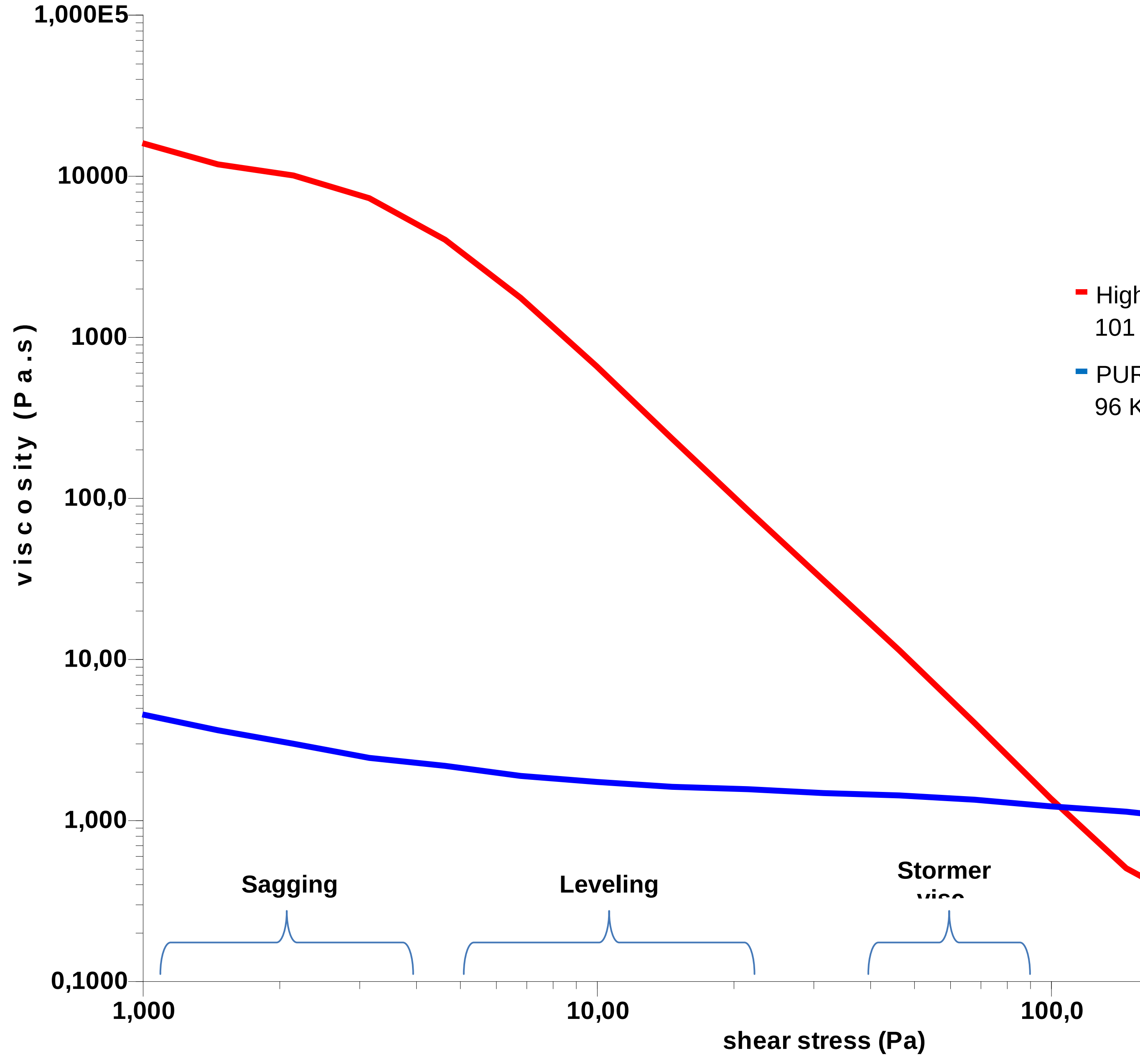

Figure 12: Flow curves of a characteristic synthetic thickener and a characteristic cellulosic thickener. In the picture the shear stresses corresponding to sagging, leveling, Stormer viscosity, brushing, and rolling are indicated.

3.3.7 SEM

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a well used method to achieve high-resolution images of objects. This analysis was performed to show how the paints actually look on the surface.

The method uses a focused beam of high-energy electrons to generate signals at the surface of a solid sample. The accelerated electrons in SEM carry a great amount of kinetic energy and this energy is dissipated as a variety of signals when the electrons interact with the atoms in the sample. The signals reveal information about chemical composition, crystalline structure and orientation of materials included in the sample. To be able to use SEM, the samples need to be electrically conductive at the surface to prevent accumulation of electrostatic charges. Secondary electrons and back-scattered electrons are two types of signals produced during a SEM analysis and these signals provide high-resolution images.

The samples were examined using a Leo Ultra 55 FEG SEM, equipped with an Oxford Inca EDX detector. Typically the images were recorded with a secondary electron detector at an accelerating voltage of 5 kV and a working distance of approximately 5.5 mm.

The samples needed to be electrically conductive and were therefore coated with a 30 nm thin layer of gold which was deposited on the sample by low-vacuum sputter coater from JEOL Fine COAT, JFC-1100E, Ionsputter.

4. Results

In this section the results from the tests operated are presented. Some comments concerning the results will also be given. In Table 5, the results from the gloss, leveling, sagging and hiding power tests are presented.

Table 5: Following are the results from the tests of gloss, leveling, sagging and hiding power.

	Thickener	Gloss* (60°)	Leveling#	Sagging^	Hiding power¤
1.	HEUR PVC 15	90.7	10	12	4
2.	HEUR PVC 20	87.2	10	10	7
3.	HEUR PVC 25	83.2	10	10	7
4.	HEUR PVC 30	80.5	10	10	7
5.	HEUR PVC 40	76.2	10	10	7
6.	A PVC 15	31.4	7	›24	4
7.	A PVC 20	28.3	6	›24	3
8.	A PVC 25	27.9	6	›24	3
9.	A PVC 30	24.8	6	›24	3

10.	A PVC 40	20.7	6	›24	3
11.	C PVC 15	13.3	8	18	3
12.	B PVC 15	47.0	9	20	3
13.	D PVC 15	13.8	9	10	2
14.	HEUR + C(90:10)PVC 15	84.7	10	14	3
15.	HEUR + B(90:10)PVC 15	89.7	10	12	3
16.	HEUR + D(90:10)PVC 15	79.8	9	10	3
17.	HEUR + A(90:10)PVC 15	89.4	9	14	4
18.	HEUR + A(75:25)PVC 15	78.9	10	16	6
19.	HEUR + A(50:50)PVC 15	72.9	7	20	5
20.	Dispex N40 + A PVC 15	21.4	8	22	3
21.	Dispex N40+ HEUR PVC 15	85.6	10	14	3
22.	Mowilith + A PVC 15	70.2	3	›24	4
23.	Mowilith + HEUR PVC 15	77.2	10	14	4

* The values of gloss are presented from the measurements of 60°.
# The leveling is judged on a scale 1-10 with 10 as the most fluent.
^The sagging is rated from 4-24 by deciding the thickest stripe that has resisted any sagging. As the number increase, the sagging resistance improves.
¤ The hiding power is judged on a scale 1-10 with 10 as the value corresponding to a completely coated surface.

4.1 Gloss

According to standard Norm DIN EN 13300[3], for a paint to be considered glossy, it should reach values above 60 when measuring from a 60° angle. Like expected, the results show that the samples containing HEUR are gloss paints and that the gloss decreases as the PVC increases. The cellulosic thickeners do not show any gloss according to standard but B is the one with the highest gloss value. It is interesting that when mixing a sample (90:10) in both cases A and B, the paint keeps its high gloss. When mixing as much as (50:50) A+HEUR the gloss is decreased but is still considered a gloss paint according to standard.

Another interesting result is that when using the latex Mowilith together with A, the paint obtains gloss but when using the same latex together with HEUR, the gloss is decreased.

Dispex N40 did not prove to be the best choice when a gloss paint is desired. Orotan 731 would be the better choice in that aspect.

4.2 Leveling

The results tell us that paints with HEUR included have the best leveling and these are also the samples that appear glossy.

When changing latex, dispersing agent or PVC, almost all samples maintain similar grades of leveling and that means, the thickener is the factor determining the grade of leveling. One interesting observation is that the change of latex has a great impact on the cellulosic thickener A. When changing the latex from Joncryl to Mowilith the leveling is decreased from 7 to 3 which is a quite large difference.

The samples containing HEUR mixed with thickener A show good results of leveling. The HEUR+A (90:10) as well as the (75:25) show excellent results of leveling. The (50:50) show that the degree of leveling is reduced but only to 7 so it is still acceptable. The results make it clear that good leveling is a criterion to obtain gloss paints.

4.3 Sagging

It is well shown that the samples with cellulosic thickeners, except from D, have very good or relatively good sagging resistance. The samples containing the synthetic thickener are more fluent and therefore have a lower sagging resistance. When analyzing the results, we realized that the alternative latex and dispersing agent did not have any remarkable impact on the sagging resistance.

Neither did the PVC influence the sagging. When analyzing the sample with a (50:50) mixture of HEUR and A, it shows that the sagging resistance stays relatively good. Disregarding thickener D, we can draw the conclusion that the samples with the lower sagging resistance are the same samples that show gloss.

4.4 Hiding power

As the results show, the samples containing thickener HEUR have the best hiding power but PVC 15 show a reduced ability to coat the surface compared to the higher PVC-grades of this thickener. Disregarding the HEUR PVC 15 sample, a clear trend is that a lower hiding power is related to a lower gloss.

4.5 Rheology

Samples containing the synthetic thickener, HEUR, show a curve more similar to a Newtonian fluid. That is, the viscosity is more or less independent of the shear stress. Samples containing cellulose show a more shear thinning behavior, see Figure 13.

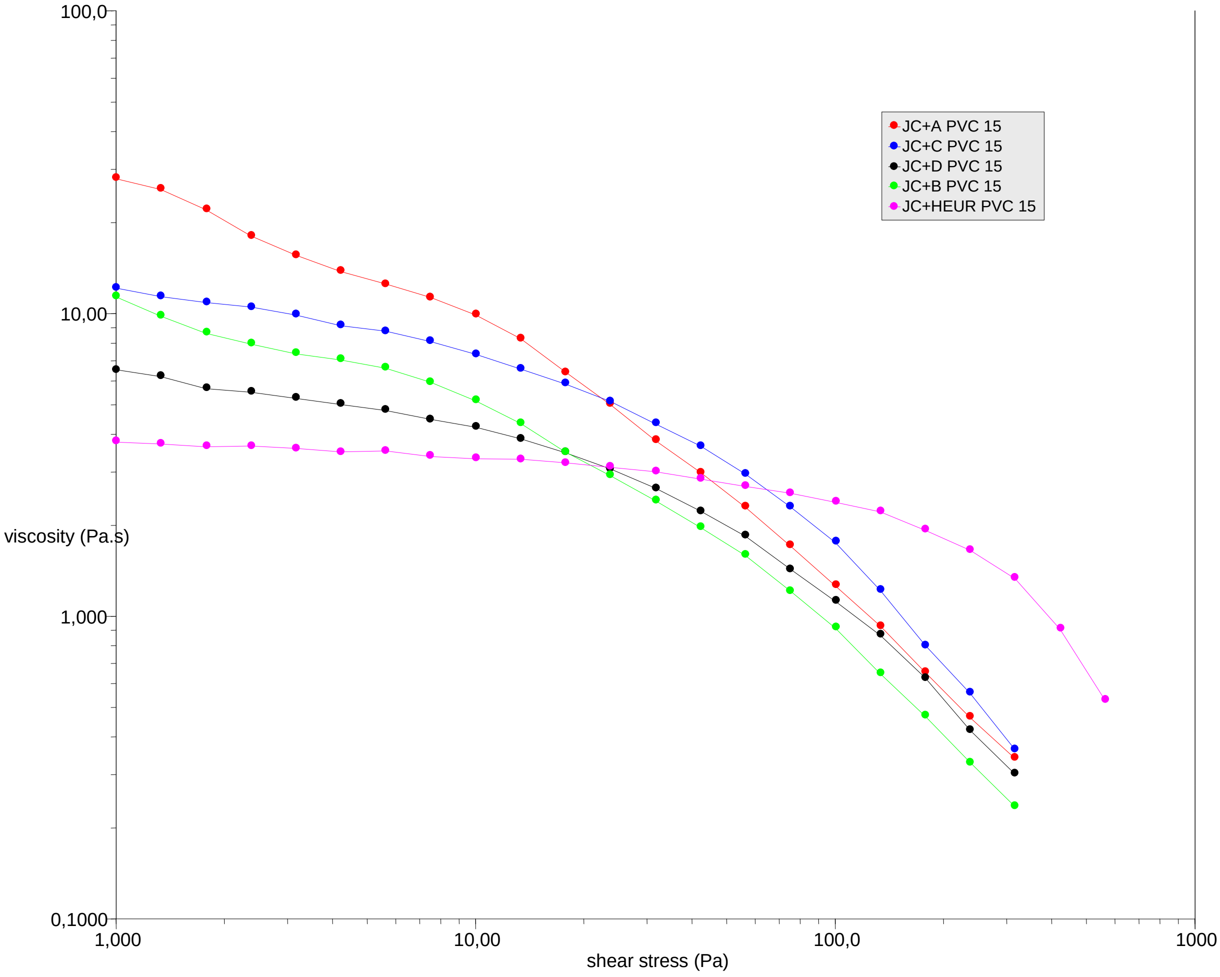

Figure 13: Flow curves of paints produced with the five different thickeners examined in this study.

The curves related to the four different cellulose thickeners show the same pattern and they are all shear thinning. The low molecular weight thickeners A and B show curves of similar shapes and high molecular weight thickeners C and D show similar curves. The obvious difference is that the curves are offset.

Comparing the curve of the synthetic thickener to the cellulosic thickeners a great difference is shown in the region of shear forces which corresponds to those experienced during sagging and leveling i.e. at around 5 Pa and 10 Pa, respectively.

The cellulose based thickeners have higher values on both sagging and leveling and it tells us that they are therefore not as fluent as the samples with HEUR. Therefore the results from the rheology are consistent with the results from the sagging and leveling.

When analyzing the curves, we observe the significant difference in especially the sagging area. The viscosity at the shear stress corresponding to sagging for the cellulosic thickeners is approximately a decade higher than the viscosity related to the synthetic thickener in the same area.

4.6 SEM micrographs

The images obtained from the SEM analysis gave a deeper understanding on how the paint surfaces actually look like. This technique was made to show if there were any irregularities on the surfaces such as flocculation. HEUR PVC 15 and PVC 40 look very similar. They have a smooth surface and no irregularities, see Figure 14.

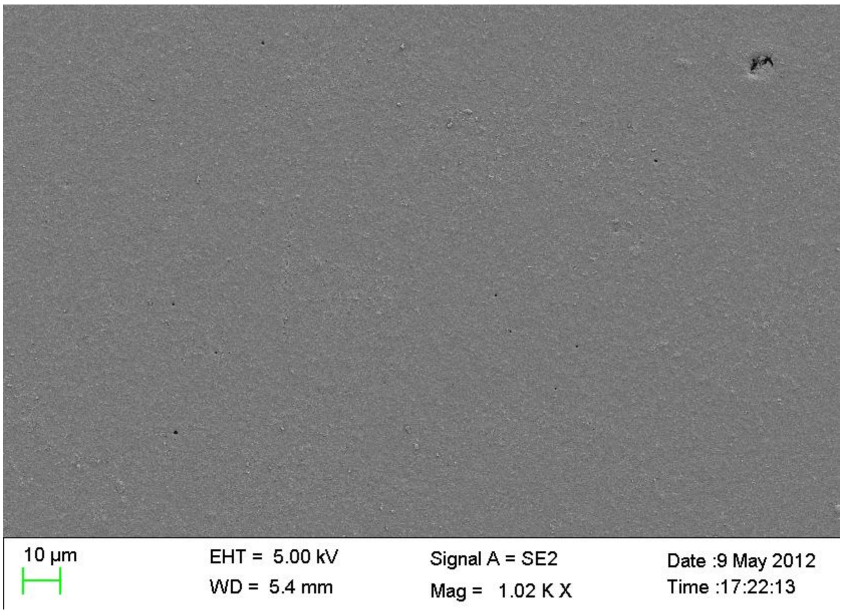

Figure 14: SEM micrograph of paint HEUR PVC 15.

There is a difference in the images of HEUR PVC 15 and HEUR PVC 40 and the difference lies in their amounts of pigment which is shown in the pictures. PVC 40 shows a lot more pigment but it looks well dispersed and the surface appears smooth and shows no irregularities.

The images of the cellulose containing paints were different from the HEUR paints in that they all exhibited holes. The diameter of the holes ranged from 1 µm to 25 µm. The depth of the holes was not possible to determine using SEM.

Figure 15 shows a representative image of the quite small holes, 1-1.8 µm, observed on all images related to the cellulosic thickeners A and B.

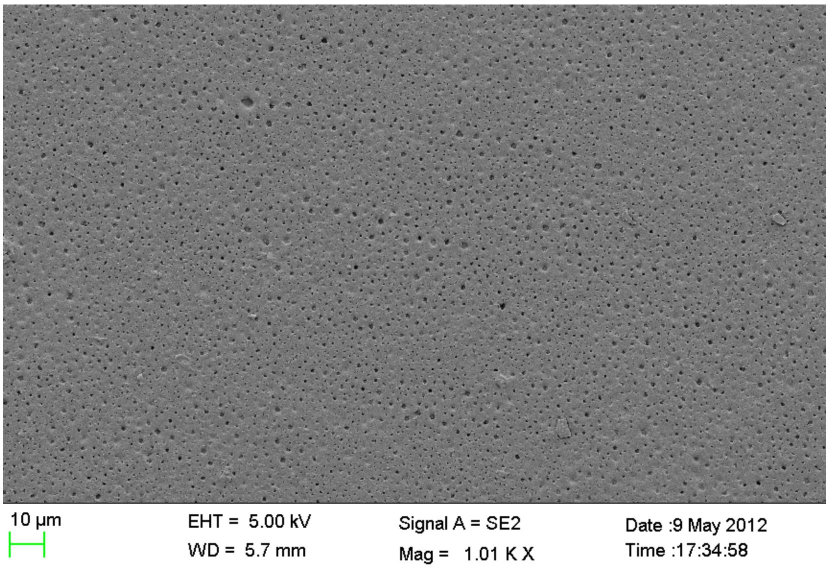

Figure 15: SEM micrograph of paint containing thickener B, PVC 15.

The paints containing cellulose thickener C and D were also quite similar in that they had fewer holes but the holes were larger in size, ~25 µm. Compared to the images of HEUR there is a resemblance in that the surface between the holes is extremely smooth and even, see Figure 16.

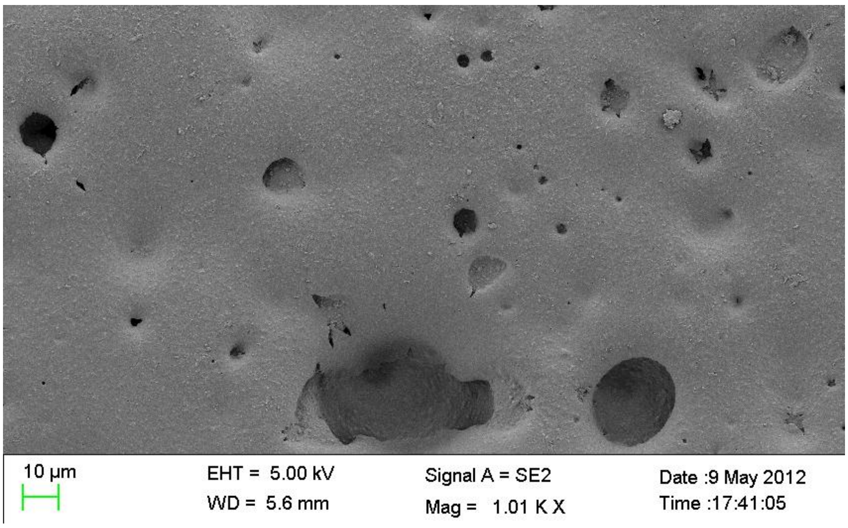

Figure 16: The paint based on cellulosic thickener D, PVC 15. A representative image of the quite large holes observed on all images related to the cellulosic thickeners C and D.

With an enlargement of the picture C (30 k X) it is shown that a possible flocculation of the pigment has occurred, see Figure 17.

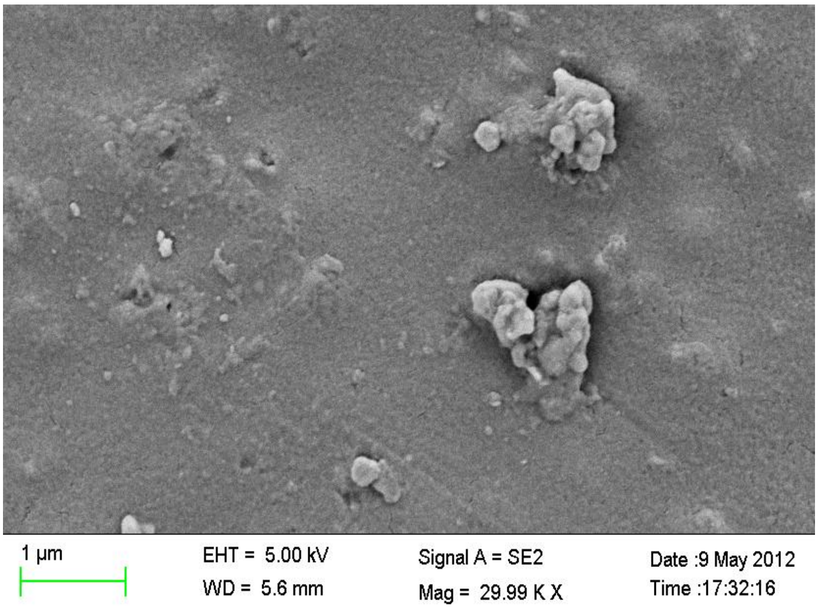

Figure 17: Image of the paint based on thickener C. This micrograph show possible flocculation of titanium dioxide particles.

5. Discussion

This study was made to examine what factors contribute to the gloss of a paint film. Another aim was to understand why it is difficult to obtain glossy paints with the use of cellulosic thickeners. Paint is a very complicated system which makes it very challenging to understand the different components interactions and behavior. This work has provided further knowledge on the factors influencing the degree of gloss but there have been some difficulties operating the study. The most challenging part was the research on determining appropriate paint formulations. It was very difficult to find out the amounts of thickener that needed to be added into the paint for it to obtain the desired Stormer viscosity between 97-102 KU. Paints based on cellulosic thickener A and B needed a larger amount of thickener to reach the wanted viscosity and this made it extremely difficult to incorporate it into the paint due to the small amount of water available in the formulations. Different ways were tried out and it was decided to add a part of the thickener as a slurry.

Regarding the results, the application tests performed provided relevant information on this subject of gloss. As expected, both types of thickener showed that the gloss decreased as the PVC increased and this because of the larger amount of pigment incorporated into the paint. Mixes of 90:10 between the two different types of thickener, cellulose and HEUR, were successful for the low molecular weight cellulose thickeners, A and B. They retained their gloss but this was not the case for the high molecular weight cellulose thickeners, C and D.

Leveling and sagging are techniques which tell how fluent a paint is. While leveling is a desired property of paints, sagging is considered a paint defect. It is difficult to obtain a paint with excellent sagging behavior as well as excellent leveling behavior. The synthetic thickener showed excellent leveling while the cellulosic thickeners A, B and C show excellent sagging resistance. The results from the sagging and leveling tests together with the results from the rheology test show that the samples containing HEUR are more fluent and also glossier.

Studying the curves, a significant difference in the thickeners viscosity profiles is noticed. The paint sample containing thickener HEUR is more Newtonian and the curves related to paints with cellulose thickener show a more shear thinning behavior. HEUR, the synthetic thickener, has the lowest viscosity and it is close to 4 Pa*s at the shear stress of 1.0 Pa. Following is cellulosic thickener D with the viscosity of 7 Pa*s. Thickeners B as well as C are around 12-13 Pa*s and the highest viscosity belongs to thickener A which has a value as high as 30. The low shear viscosity of the cellulosic thickeners is very high and this leads to poor leveling.

It is showed in the results of the flow curves that when analyzing the cellulosic thickeners, the viscosity increases as the molecular weight of the thickener decreases. This is a strange result and in pure aqueous systems it should be the other way around because the shorter the molecule, the lower the viscosity. However, these measurements were performed on paints which are complicated systems with many different components interacting with the thickeners. Moreover, the paints were prepared to show a Stormer viscosity between 97-102 and to obtain this Stormer viscosity different amounts of thickener were added to the paint. This quite small differences in thickener amounts can still show a quite large difference in rheology curves.

Thickeners C and D are both of a rather high molecular weight but they differ due to a slight differens in substituents. This does not influence their viscosities in any strange way.

The gloss test showed, like expected, that the paint samples containing HEUR will show gloss. Regarding cellulose thickeners A, B, C and D, according to standard they were not considered gloss paints. Low molecular celluloses A had a value of 31 on its gloss and cellulose B had the value of 47. Cellulose C as well as D showed the least gloss and that was around 13. This was reflected in the results of sagging which showed that A and B were the least fluent. The leveling tests indicated that all four thickeners are more or less fluent. An interesting result is that the gloss of cellulosic thickener B reached 47. It is not high enough to be considered a gloss paint but it is a value higher than the gloss values shown with the paints containing cellulosic thickener A, C or D. It would be very interesting to look into a mix between this thickener and a HEUR to see how much of the B could be mixed with a HEUR and still be considered a gloss paint.

It was very interesting to see the results of the gloss test when using the latex Mowilith together with cellulosic thickener A. The gloss result obtained is 70.2° which is over the limit of gloss paints. There is a possibility that they interact in a way that makes the paint appear glossy. Another possibility could be that something went wrong with the preparation of this paint sample.

The change of dispersing agent from the hydrophobic Orotan 731 to the hydrophilic Dispex N40 did not give any extreme differences in the results of the different application tests. A minor decrease in gloss was observed.

SEM micrographs gave a good image of the paint surfaces and they showed in particular one significant difference in surface structure of a paint with synthetic thickener compared to a paint with cellulosic thickener. The difference that these images showed was that all paints made from cellulosic thickeners have holes on the surface and this was not a problem in the case when synthetic thickeners were used. In paint there are many surface active ingredients as e.g. surfactants and there is a possibility that during SEM, which is run under vacuum, the surfactants, or another substance not included in the film formation, have evaporated and left are the holes. Another explanation regarding the holes could be that cellulosic thickeners are surface active and have an ability to stabilize air bubbles in a much higher degree than what synthetic thickeners are able to. This could be a reason there are air bubbles shown on the images of the cellulosic thickeners.

A possible reason that these airbubbels might have formed was that due to the small amounts of water available in the formulas it was difficult to add all the cellulose in the first step and therefore, when preparing paint C and D, an amount of cellulose was added as a slurry in the final step. When the cellulose is added as a slurry it is of great importance that the paint is stirred properly and enough. Because of this, they were stirred much longer than the paints with thickener A and B and the longer the paints are stirred, the higher are the chances that air bubbles are formed. Another interesting observation is obtained when comparing the images of the paint made from cellulosic thickeners. Thickener A and B who showed similar images with SEM also have similar values on their gloss. The holes showed on the surface of thickener B look smaller than those on thickener A. The gloss result of thickener A is 31.4° and 47.0° of thickener B. It appears that the smaller the holes are the higher gloss is obtained.

Comparing thickener C to D show similarities in their images. They have larger holes and possible flocculation on their surfaces. The holes and the aggregated systems result in a very low gloss value of around 13° for both the thickeners. It is clear that irregularities such as holes and aggregates have a significant influence on the gloss.

Comparing results from the hiding power with the results of SEM, there is a correlation that the synthetic thickener, HEUR PVC 40, had a relatively high hiding power and the SEM image showed a very even surface with no irregularities. Surfaces with irregularities such as flocculation will contribute to a decreased hiding power as well as decreased gloss.

6. Conclusions

The study showed that paints containing HEUR are gloss paints and none of the cellulosic thickeners showed any gloss according to standard. The results of the rheology compared to results of sagging and leveling are consistent. The synthetic thickener is more fluent and showed the best results of leveling. At low shear stresses, paints containing HEUR show a low viscosity. The paints with cellulosic thickener have higher values on both sagging and leveling and are therefore not as fluent as the samples containing HEUR. One can say that there is a strong correlation between leveling and gloss but there is surely more to it. As seen in the results, good leveling is not an assurance when a gloss paint is desired.

The surface structure is a very important factor when a gloss paint is desired. The images from SEM analyses showed that paint surfaces of the synthetic thickener are smoother and more even while surfaces of paints with cellulosic thickeners have more irregularities. Another factor contributing to the gloss is PVC. Less pigment means lower PVC and hopefully a higher gloss. It is also very important that the pigment in the paint is well dispersed and therefore the dispersing agent is of great importance when it is desired to obtain a high gloss paint.

The latex is another component contributing to the gloss. Other crucial criteria to obtain glossy paints are that the paints need to be fluent and also show an even surface with no or minimum amounts of irregularities.

The paint made from hydrophobe modified thickener B is the one that displays the highest gloss value. Because of its hydrophobic properties a smaller amount of thickener needed to be incorporated to reach a Stormer viscosity of 97-102, compared to thickener A. It is possible that this smaller amount could help the paint reach a higher gloss.

It was possible to do a mix with the synthetic thickener and cellulose A and B of (90:10) and still obtain a paint with almost no decrease in gloss or deterioration of other properties. The (90:10) mixes with the synthetic thickener and cellulose C and D did not prove to be successful due to the quite large decreases in gloss.

Due to the holes shown on the SEM micrographs it is difficult to say how trustworthy the results obtained in this study actually are. For it to be possible to produce a paint with this large amount of cellulose together with a very small amount of water, and still not need to add parts of it as a slurry, the methodology of the paint production needs to be improved. It would be a great advance if there were a possible way to incorporate the thickener into the paint without any excessive need of stirring.

7. Future Work

For further knowledge on the subject of paint films and gloss there are different studies to look into. A few ideas would be:

- To look deeper into what kind of mechanism that lies behind the reduction of gloss in use of cellulosic thickeners.
- To further investigate the possibility to mix cellulosic thickeners with synthetic thickeners yet still obtain high gloss paints.
- It would be interesting to do analyses of the surface topography of the paint films to gain further knowledge on the surfaces. It would also give a deeper understanding on the roughness on the surfaces and how the gloss reduces as the irregularities enlarges.
- To look further into if it is possible to obtain glossy paints when using cellulosic thickener A with latex Mowilith.
- To further examine cellulosic thickener B which showed the highest gloss of the cellulosic thickeners studied. It would be interesting to know to what grade this thickener can be mixed with a synthetic thickener and still obtain a gloss paint.

8. Acknowledgements

I would like to thank my supervisor at AkzoNobel, Maria Stjerndahl for all her help and support through this. Her contribution and interesting inputs made this work the best it could possibly be.

I also wish to thank Leif Karlson for this opportunity.

Furthermore I want to thank the rest of the staff at Performance Additives for helping me whenever needed and thank you Åsa Söderlund for all your help with the rheology.

Also thank you to Lars Nordstierna at Teknisk Ytkemi for interesting discussions and thank you to my examiner Martin Andersson for your help with SEM analyses.

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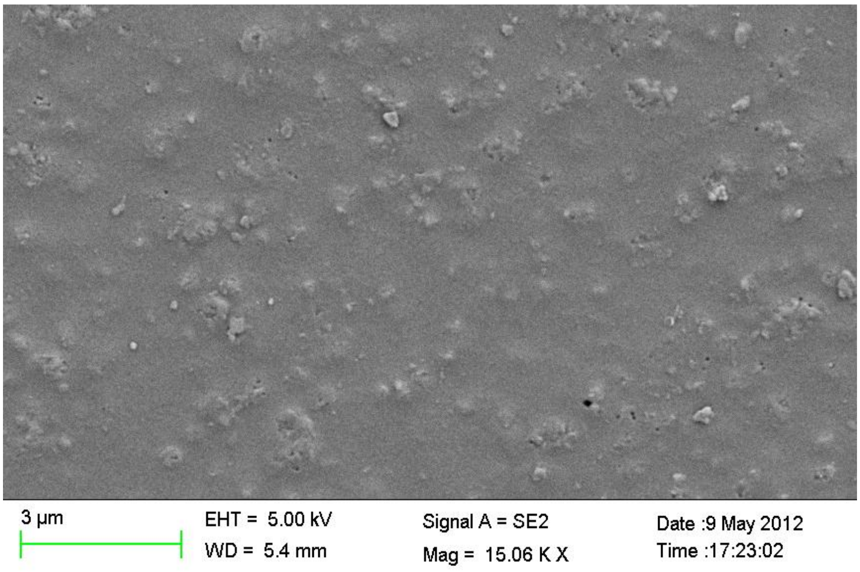
10. Appendix

Gloss

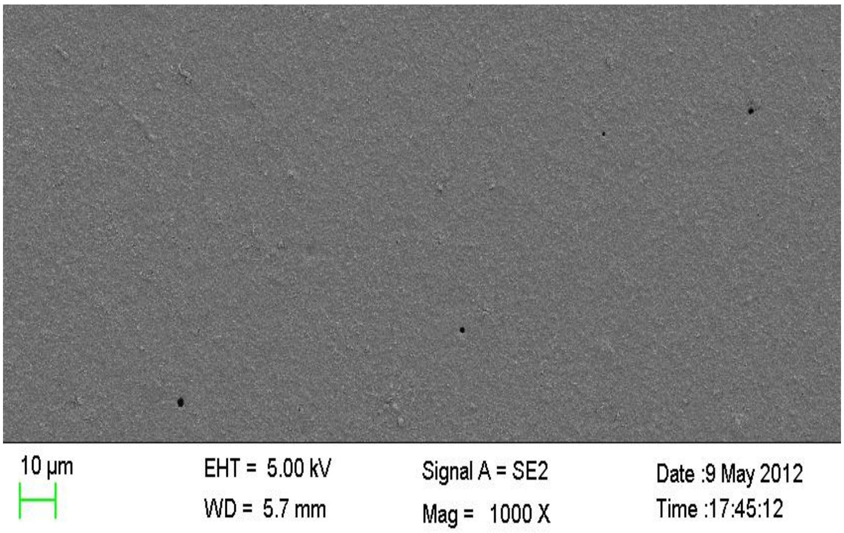
	Angle	20°	60°	85°
1.	HEUR PVC 15	60.6	90.7	102
2.	HEUR PVC 20	53.1	87.2	102
3.	HEUR PVC 25	44.7	83.2	101
4.	HEUR PVC 30	40.3	80.5	99.9
5.	HEUR PVC 40	30.7	76.2	98.2
6.	A PVC 15	6.40	31.4	88.1
7.	A PVC 20	5.10	28.3	87.8
8.	A PVC 25	4.90	27.9	86.7
9.	A PVC 30	4.20	24.8	85.4
10.	A PVC 40	3.10	20.7	84.4
11.	C PVC 15	2.80	13.3	24.6
12.	B PVC 15	12.7	47.0	93.8
13.	D PVC 15	2.60	13.8	28.8
14.	HEUR + C (90:10) PVC 15	49.5	84.7	101
15.	HEUR + B (90:10) PVC 15	60.3	89.7	102
16.	HEUR + D (90:10) PVC 15	41.0	79.8	98.5
17.	HEUR + A (90:10) PVC 15	59.7	89.4	102
18.	HEUR + A (75:25) PVC 15	49.7	78.9	95.5
19.	HEUR + A (50:50) PVC 15	38.4	72.9	95.2
20.	Dispex N40 + A PVC 15	3.10	21.4	83.4
21.	Dispex N40 + HEUR PVC 15	59.5	85.6	102
22.	Mowilith + A PVC 15	31.0	70.2	92.6
23.	Mowilith + HEUR PVC 15	49.4	77.2	97.8

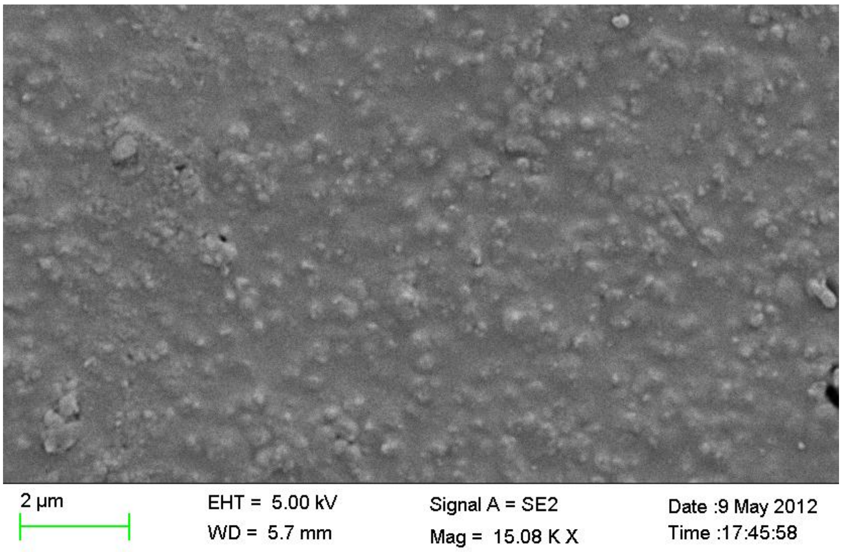
SEM

HEUR, PVC 15



HEUR, PVC 40




2 µm
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WD = 5.7 mm
Signal A = SE2
Mag = 15.08 K X
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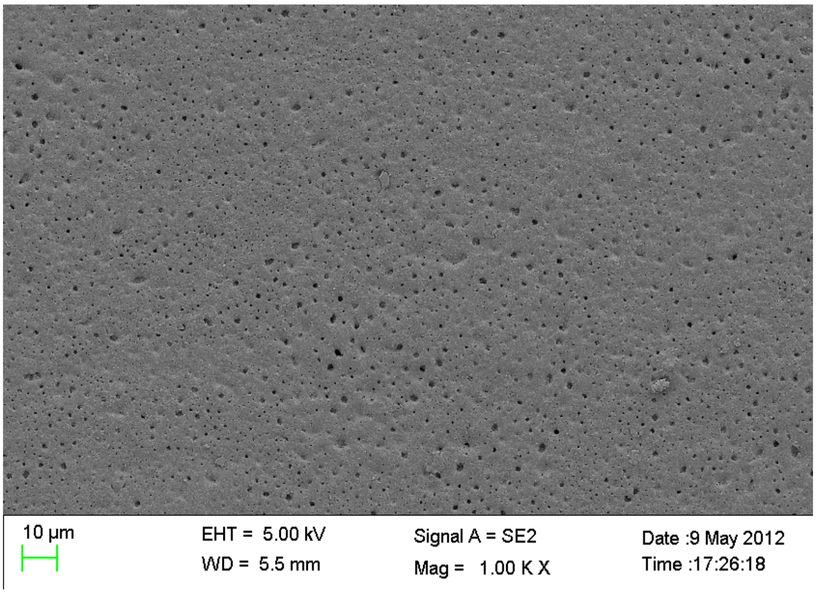
Time :17:45:58

A, PVC 15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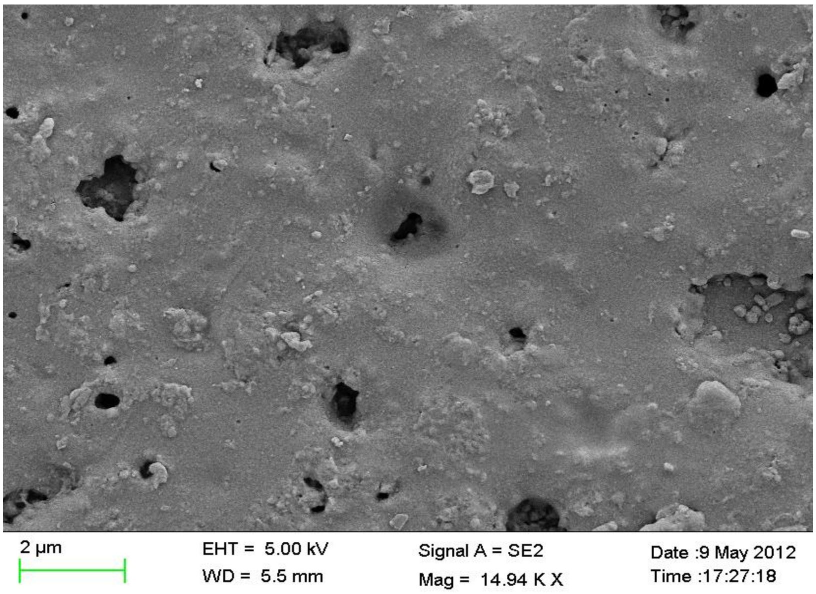
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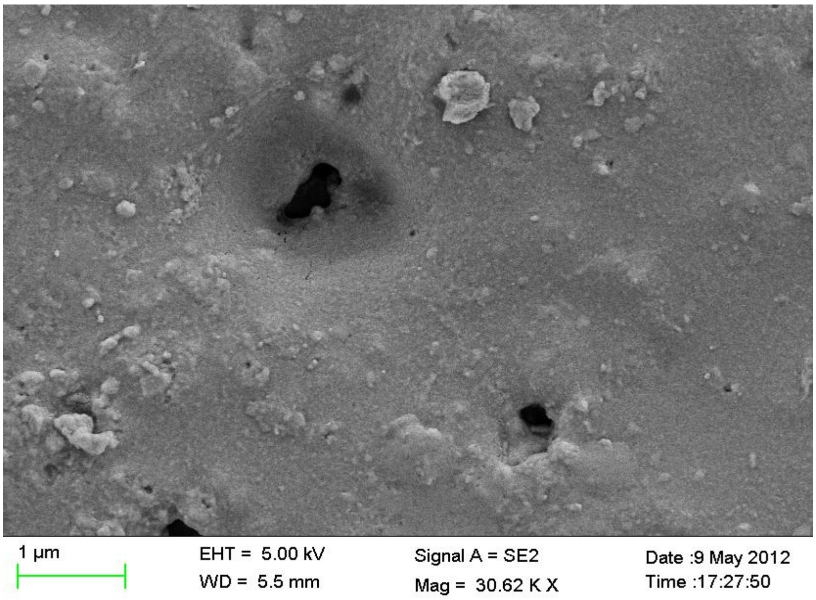
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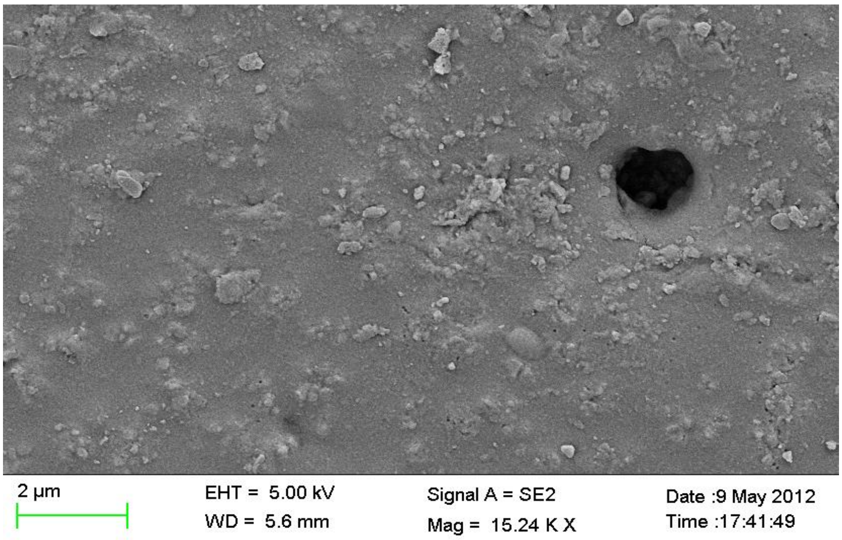
D, PVC 15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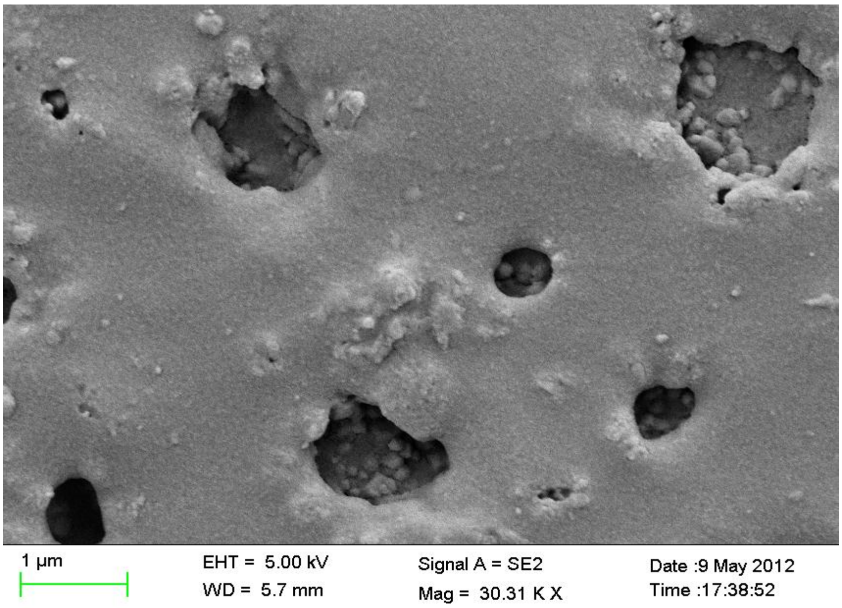
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EHT = 5.00 kV
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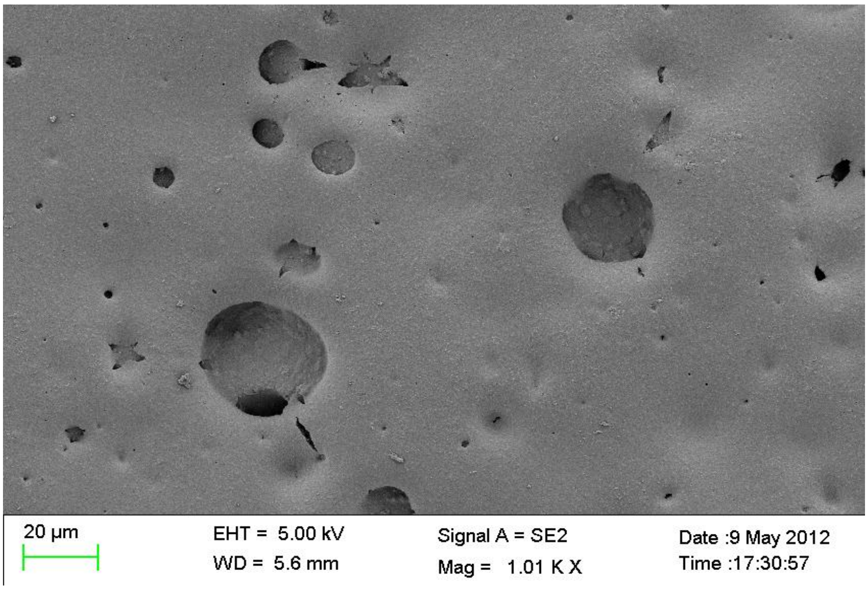
C, PVC 15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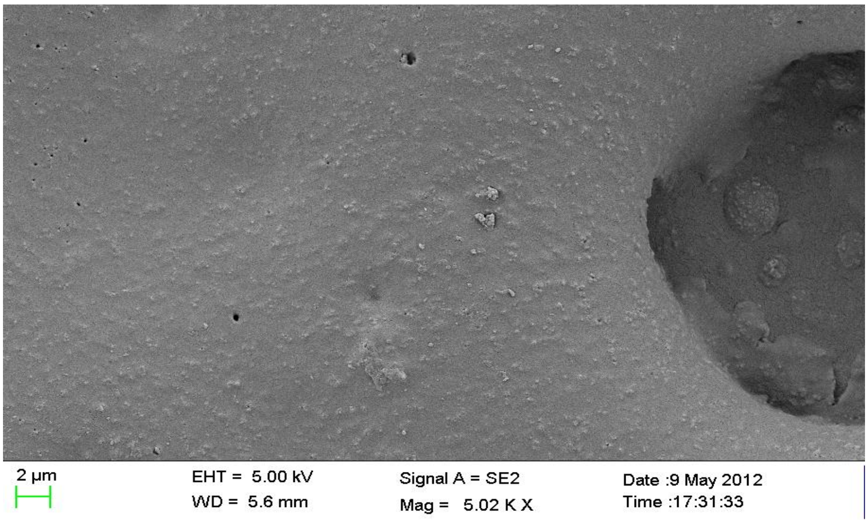
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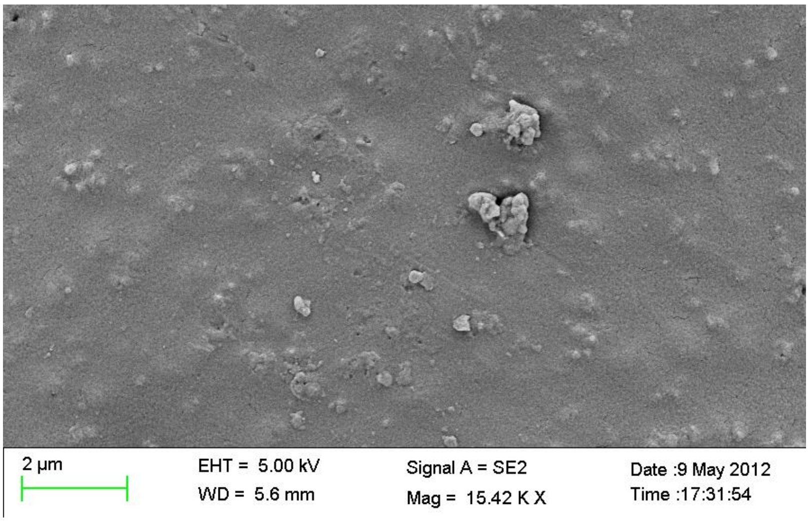
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EHT = 5.00 kV
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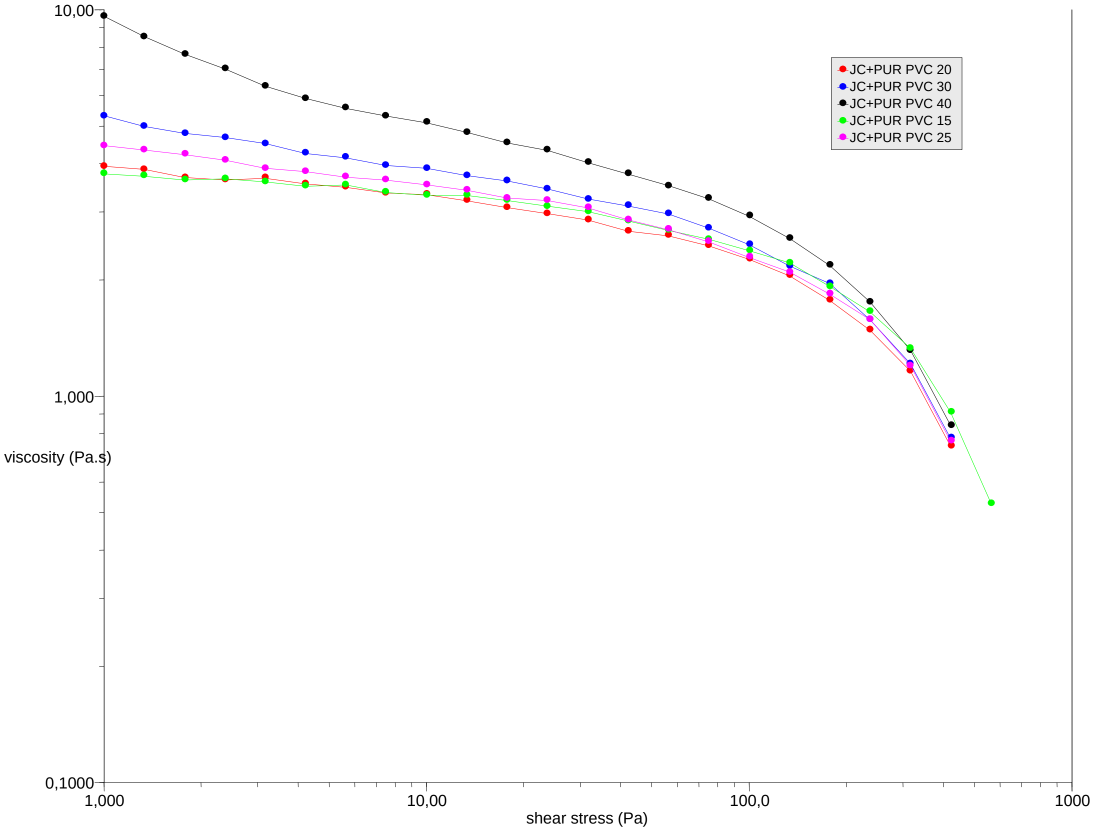
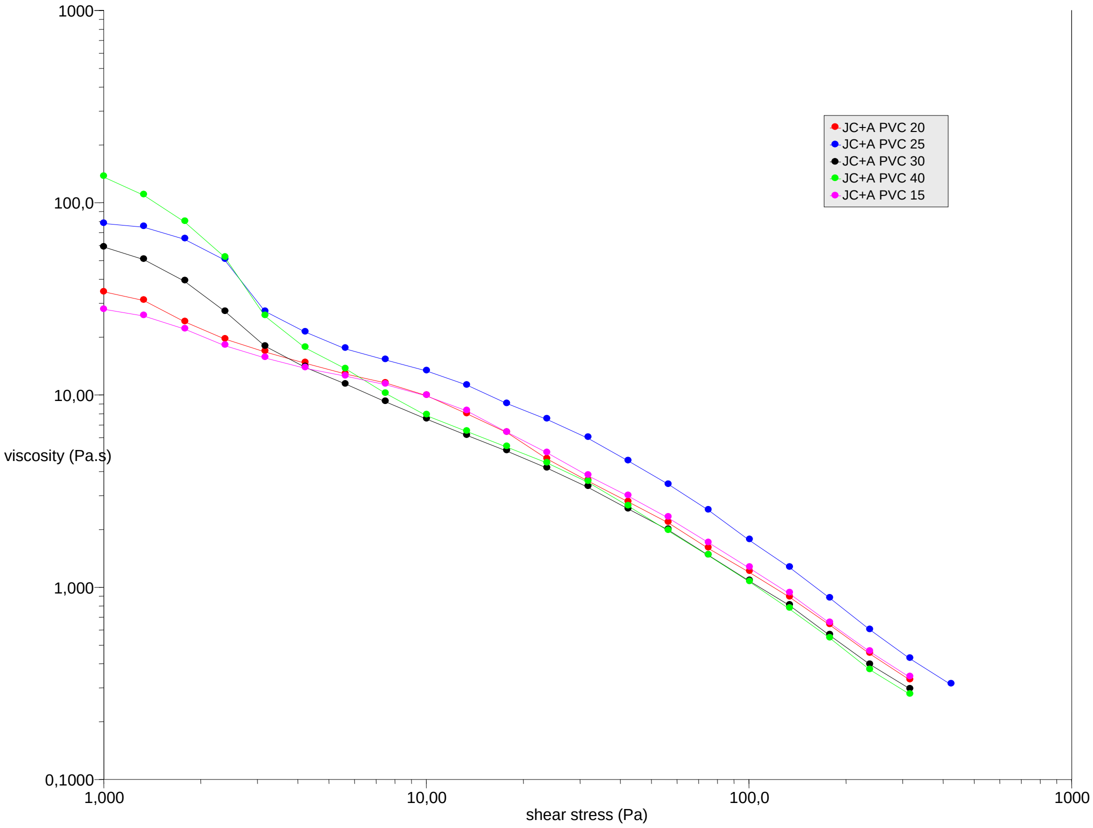
Time :17:31:54

Rheology

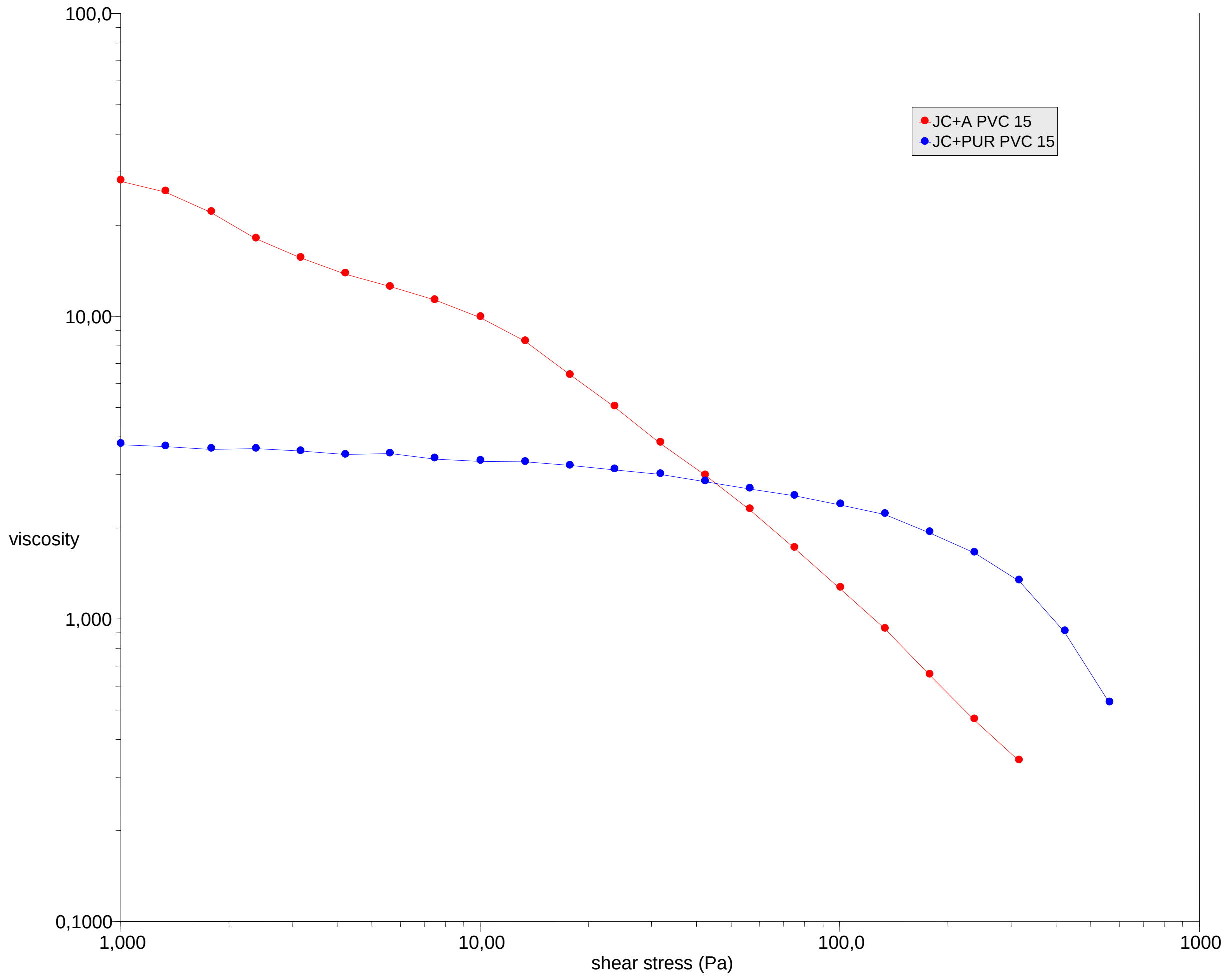
Flow curve of thickener HEUR with varied PVC



Flow curve of cellulosic thickener A with varied PVC



Flow curve of thickener HEUR and thickener A



Paint formulations used, amounts in (g).

Synthetic thickener + Joncryl
PVC 15

Water	28
Byk 022	2
Orotan	7
Canguard	1
Propylene glycol	32
KRONOS 2190	196
Potassium hydroxid	1
HEUR 2110	4
Latex (50%)	688
Water	39
Byk 022	2
Total	1000

Synthetic thickener + Joncryl
PVC 40

Water	79.5
Byk 022	2
Orotan	15.5
Canguard	1
Propylene glycol	32
KRONOS 2190	434
Potassium hydroxid	1
HEUR 2110	4
Latex(50%)	410
Water	19
Byk 022	2
Total	1000

Cellulosic thickener + Joncryl
PVC 15

Water+cellulose	72
A few drops of ammonia	
Byk 022	2
Orotan	7
Canguard	1
Propylene glycol	32
KRONOS 2190	196
Latex(50%)	688
Byk 022	2
Total	1000

Cellulosic thickener + Joncryl
PVC 40

Water+cellulose	102.5
A few drops of ammonia	
Byk 022	2
Orotan	15.5
Canguard	1
Propylene glycol	32
KRONOS 2190	434
Latex(50%)	410
Byk 022	2
Total	1000