

TAMPERE POLYTECHNIC UNIVERSITY OF APPLIED SCIENCES

Paper technology

Final thesis

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DISPERSING OF KAOLIN SLURRY IN A LABORATORY ENVIRONMENT

Thesis supervisor

Arto Nikkilä (MSc)

Commission of thesis by

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Järvenpää Tuomo Dispersing of kaolin in a laboratory environment

Thesis work 47 pages + 3 appendices

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ABSTRACT

The main target of this thesis work was to study the flow characteristics of kaolin pigment slurries and how these characteristics are affected by dispersing, dispersant dose and pH being the main variables.

The tests were carried out using three different dispersing agents at four different doses and in pH-values of 7 and 8. The dispersing agents were Kemira's Fennodispo A41, A48, and A55. The pigment used was Imerys' Supragloss95-kaolin.

The main focus was set on determining the affects these variables had on viscosity at both low and high shear rates and on water retention. The viscosity test methods included Brookfield viscosity tests and high shear rate tests on an ACAV-viscometer. The water retention tests included Åbo-academi's static water retention tests and ACA Systems' dynamic water retention tests.

TIIVISTELMÄ

Työn tarkoituksena oli tutkia kaoliinilietteen virtaus ominaisuuksia ja miten nämä ominaisuudet riippuvat dispergoinnista. Päämuuttujina työssä olivat dispergointiaineen annostelu ja pH.

Tuloksia etsittiin käyttämällä kolmea eri dispergointiainetta neljällä eri annostelulla ja pH-arvoilla 7 ja 8. Dispergointiaineet olivat Kemira Oy:n Fennodispo A41, A48 ja A55. Kaoliinina käytettiin Imerys Oy:n Supragloss 95:a.

Tutkittavina kohteina olivat edellä mainittujen muuttujien vaikutus viskositeettiin alhaisilla ja korkeilla leikkausnopeuksilla, ja vesirentioon. Alhaisten leikkausnopeuksien viskositeettia tutkittiin Brookfield-testeillä, ja korkeiden leikkausnopeuksien tutkimiseen käytettiin ACA-viskometriä. Vesirention tutkimiseen käytettiin Åbo-Academin staattista vesirentio testiä ja ACA-Systems:n dynaamista vesirentio testiä.

PREFACE

This thesis work was carried out in the paper laboratory at Tampere Polytechnic University during spring 2006. The actual writing process and data-analysis was done in Rauma and Tampere during 2006 and the spring of 2007. I would like to thank Arto Nikkilä, Ulla Häggblom-Ahnger and the rest of the laboratory staff for their support and professional assistance. Also I am grateful for Kemira LTD and Omya LTD as they provided the necessary pigments and dispersants.

TABLE OF CONTENT

ABSTRACT.....	2
TIIVISTELMÄ.....	3
1. PIGMENT COATING.....	6
1.1. General.....	6
1.2 Coating color.....	6
1.3 Coating process.....	7
2. KAOLIN.....	8
2.1. General.....	8
2.2 English kaolin.....	9
3. RHEOLOGY.....	10
3.1 General.....	10
3.2 Terms used in rheology.....	11
3.3 Viscosity and viscoelasticity.....	11
3.4 Newtonian and non-newtonian fluids.....	12
3.5 Shear thinning and shear thickening.....	13
3.5.1 Shear thinning.....	13
3.5.2. Shear thickening.....	14
3.6. Extensional viscosity.....	15
3.7 Water retention.....	15
4. DISPERSING.....	17
4.1. General.....	17
4.2 Wetting.....	18
4.3 Disruption of particle clusters.....	18
4.4 Stabilization.....	19
4.5 Dosing of the dispersant.....	21
4.6 PH and stabilization.....	22
5. TEST METHODS.....	24
5.1. Brookfield.....	24
5.2.1 Viscosity measurements.....	25
5.2.1.1 Formulas.....	27
5.3 Water retention measurements.....	30
5.3.1 Dynamic water retention.....	32
6. DATA ANALYSIS.....	33
6.1. Viscosity.....	33
6.1.1. Brookfield viscosity.....	33
6.1.2. High shear rate viscosity.....	36
6.2 Water retention.....	39
6.2.1. Static water retention.....	39
6.2.2 Dynamic water retention.....	42
7. CONCLUSIONS.....	44

1. PIGMENT COATING

1.1. General

The reason for coating paper lies in improving its optical properties, making the printed image more appealing to the eye. Basically, this is done by filling the porous structure of the paper and calendering it to highest possible smoothness. Figure 1. illustrates the affect of coating. [12]

In the top image the fibers are seen clearly and in a printing paper this would show as a rough surface. It is obvious that the amount of coating color has a huge affect on the properties achieved. A larger amount of coating gives a nice glossy surface. [12]

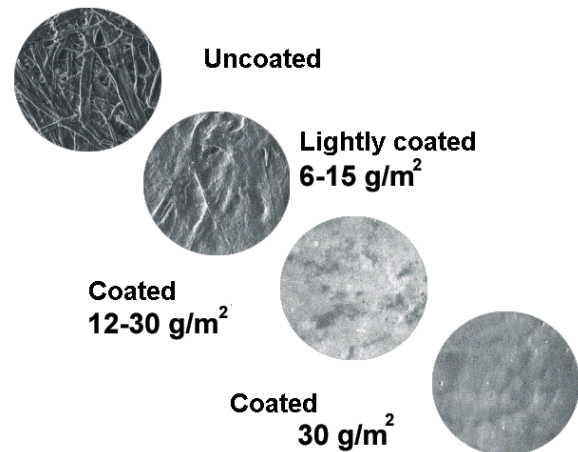


Figure 1. Affects of coating [12]

1.2 Coating color

The coating color consists of four main components: pigments, binders, thickeners and additives. When thinking about optical properties of the paper, the main affecting components are the pigments. Their main function is to fill the paper's porous surface and improve its optical properties. [12]

The main task of binders is to attach pigments to the paper surface and to one another. They can also affect runability and water retention. Thickeners are used to bring the viscosity to a desired level and to control water retention. Additives are normally used in very small doses. They can have numerous functions in almost all areas of paper making. [12]

In this work the main focus is on dispersing of kaolin clay. Both kaolin and dispersing agents will be discussed later.

1.3 Coating process

The coating process is a complex process where the coating color goes through a variety of conditions. The coating color must function well in all parts of the process. The coating process at its simplest consists of mixing of the coating color, application, metering and drying. Mixing will be discussed later in chapter 4. Figure 2 illustrates the application and metering of the coating color. [12]

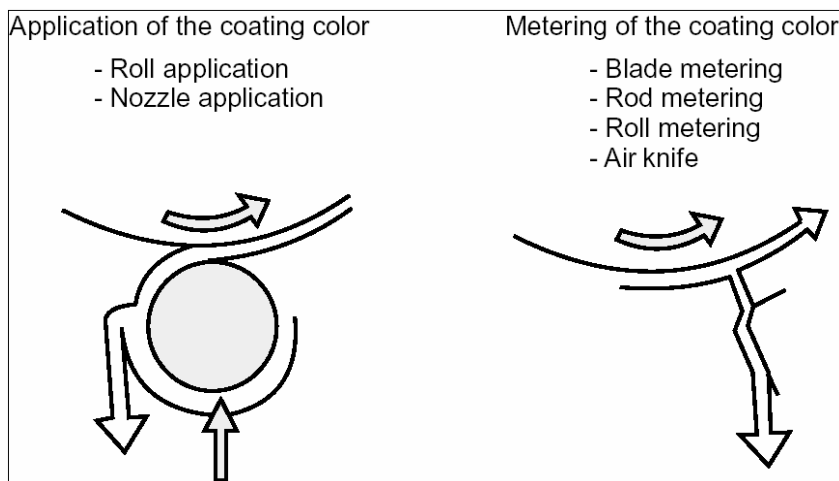


Figure 2. Application and metering of coating color. [12]

During the coating process the coating color goes through a wide variety of circumstances. Coating color acts differently in different circumstances. In the metering of coating color the shear forces rise to a very high level and in other parts of the process the flow of the coating color is more gentle and slower. There are many different ways to apply the coating color to the paper surface but they all have one thing in common, and that is the high shear forces up to a magnitude of 10^6 1/s that the coating color goes through. In order to get the best end result coating color must function well in these circumstances and at stages of the process where the flow of the coating color is less violent. [12; 8]

2. KAOLIN

2.1. General

Kaolin is an important pigment for the paper industry because of its plate-like shape, good color (white or near white) and the relative ease with which it can be processed. Kaolin is one of the most widely occurring minerals. Its most important commercial deposits occur in Georgia in the United States, in southwest England and in Brazil. Kaolin deposits are usually classified as primary or secondary. Primary deposits are found where they are formed by the alteration of the source granite; secondary deposits have been transported by water and laid down as sediments. This results in slightly different compositions and different characteristics. In this thesis work English kaolin was used. The next section will take a closer look at its characteristics. [2]

Kaolinite crystal with the unit cell chemical composition $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ consists of alternating layers of silica tetrahedra and alumina octahedra, and each kaolinite particle consists of several sheets of twin layers held together with hydrogen bonds. There is a significant charge difference between the basal plane and the edge of the particles due to the difference between their chemical composition. Kaolin edges contain both silica- and alumina-like charge sites but the faces contain only silica-like charge sites, which are negatively charged. The edges are positively charged. [11]

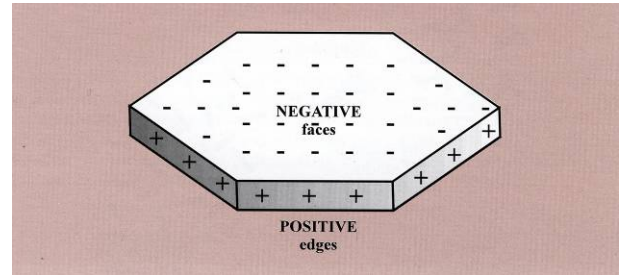


Figure 2. Electrical charges of a clay particle [5]

2.2 English kaolin

Supra Gloss 95 is an English kaolin from a typical primary deposit. English kaolin is highly plate-like and so it gives a very good coverage and print gloss. Figure 1. is a micrographic picture of an English kaolin. Figure 1 clearly illustrates that the particles have a large aspect ratio. Average aspect ratios can vary between 10:1 and 80:1, and generally increases as the particle size decreases. Rheologically speaking, a large aspect ratio leads to increased viscosity and improved water retention. [2]

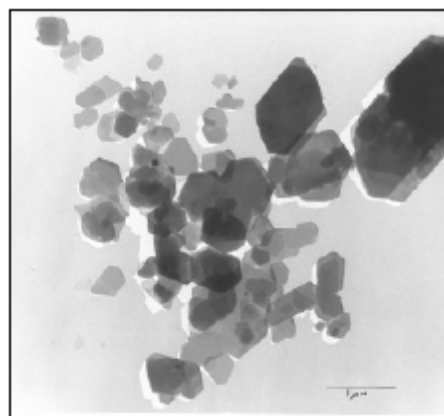


Figure 1. English kaolin [2]

3. RHEOLOGY

3.1 General

Rheology is defined as a branch of science that studies the deformation of flow and matter, which means how materials respond to the stress applied to them. Traditionally, there are two types of deformation: elastic, or reversible deformation, in which the internal structure remains intact, and flow deformation, or irreversible deformation, in which the internal structure is destroyed. Some materials, such as coating colors, can have characteristics from both deformations. They are called viscoelastic materials. For these materials, there is a limited degree of recovery once the stress is removed. [3; 8]

The duration and the type of stress have a significant affect on the rheology of coating colors. Prolonged mixing can break down structures in the coating color and result in lower viscosity over time. Coating colors go through a wide range of different stresses and different durations of stress, and all these affect the rheology of the coating color. [3; 8]

3.2 Terms used in rheology

Figure 1. shows a fluid undergoing simple shear between two parallel plates. Shear stress is defined as a force applied on a certain area. Shear rate is defined as the change in velocity (dU) across the gap (d). Shear rate increases as the velocity of the upper plate increases and as the gap narrows. The fluid between the plates resists the movement of the upper plate, and this resistance to the flow is determined by the viscosity (η) of the fluid. [8]

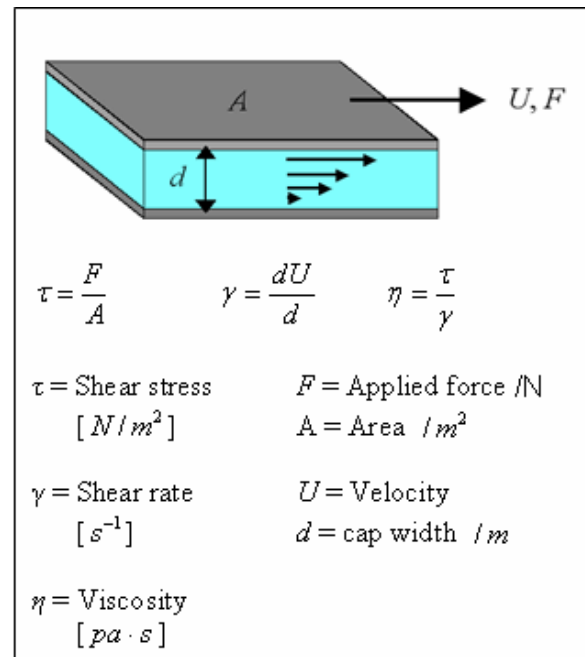


Figure 1. Terms used in rheology [8]

3.3 Viscosity and viscoelasticity

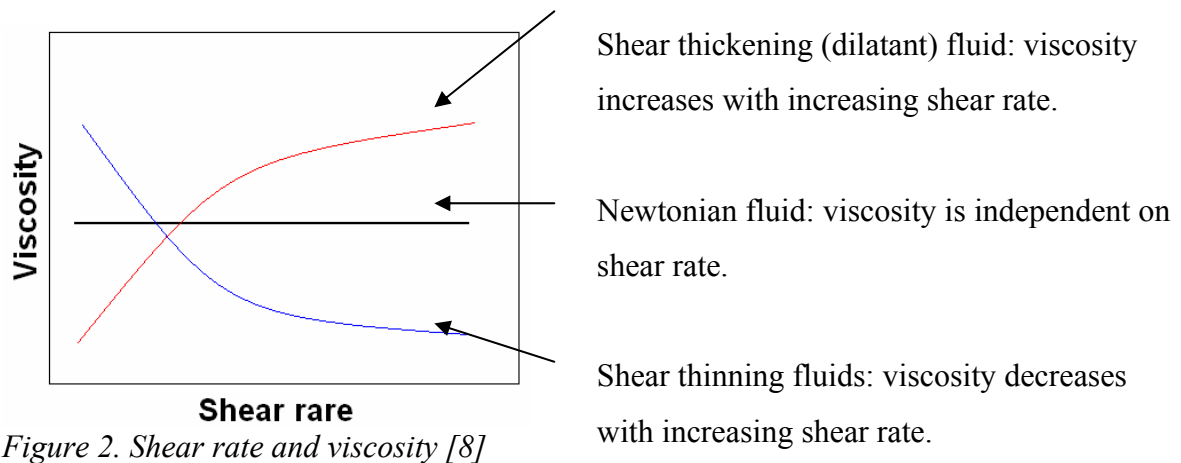
Viscosity is a value that describes the ability of a fluid to resist change. It is commonly known as thickness of a fluid. Viscosity is internal friction of a fluid, which is defined as the ratio between shear stress and shear rate. If the geometry (A, d) in figure 1 remains constant, shear stress is dependent on force F , and shear rate is dependent on the velocity U . Therefore doubled viscosity would need twice as high a force to obtain the same flow rate/velocity. And doubled force would result in twice as high flow rate/velocity. [8]

Coating colors however do not behave this way. They are viscoelastic in nature; they are non-Newtonian. At low shear rates coating colors are highly elastic and at high shear rates they are viscous. The unit of viscosity Pas is too great and mPas is used instead. [8]

3.4 Newtonian and non-Newtonian fluids

Fluids are usually divided into Newtonian and non-Newtonian fluids. A fluid is Newtonian if it doesn't have viscoelastic properties and its viscosity is not dependent on shear rate or shear time. For example water, glycerol and some oils are close to ideal Newtonian fluid. however no fluid is entirely Newtonian. [8]

It is important to remember that viscosity is not a number but a curve. Viscosity of most materials, including all coating colors, is dependent on shear rate. Figure 2 illustrates the relationship between shear rate and viscosity. [8]



3.5 Shear thinning and shear thickening

Shear thinning behavior is more common than shear thickening behavior. Coating colors are commonly shear thinning, but they can have shear thickening areas (figure 3.). Viscosity decreases first as the particles align with the flow until it reaches a point where the particles can flow past one another freely. When shear rate is increased further, the flow is disturbed and particles cause more friction between one another. After a certain point the viscosity does not increase further. [8]

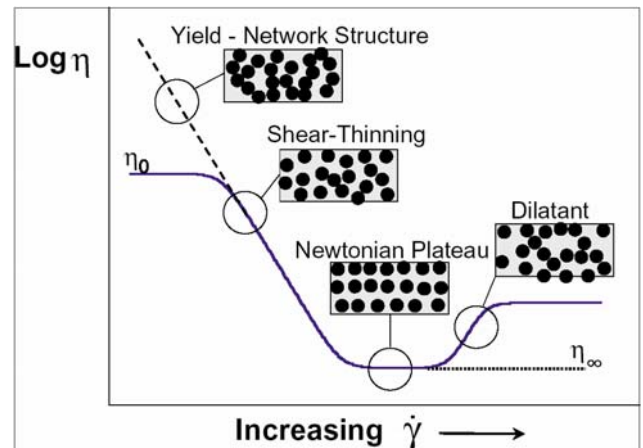


Figure 3. General flow curve for a suspension. [3]

3.5.1 Shear thinning

One of the reasons for shear thinning behavior lies in the alignment of particles with the flow of the slurry, as stated before. Figure 4 illustrates this phenomenon.

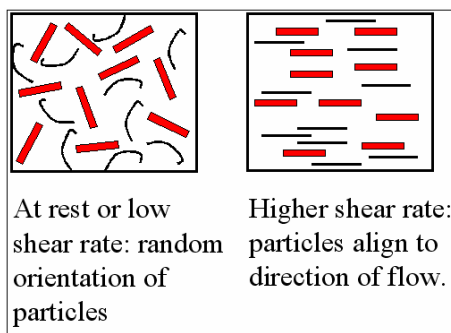


Figure 4. Alignment of particles [8]

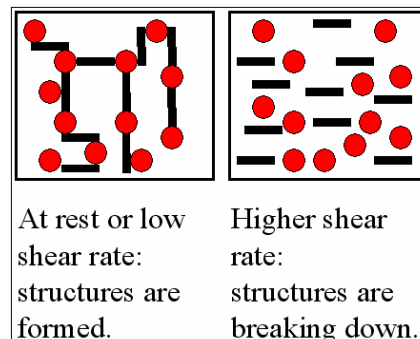


Figure 5. Breaking down of particles [8]

Breaking down of structures is another important reason for shear thinning (figure 5). Because of electrical charges, pigment particles tend to form structures. Resistance to flow of particles is lower than that of structures. Also water phase can be partly locked inside the structures. When freed, this water lubricates the flow, decreasing viscosity. [8]

3.5.2. Shear thickening

If the concentration of pigments in the slurry is too high, dispersion may turn into shear thickening. In high solids content pigment slurries, particle layers can't flow past one another (figure 6,a); the particles are packed too closely and there is not enough space for them to move freely. The pigment particles need more space in higher shear rates (figure 6,b). The structure of the particles dilates (dilatant), so the amount of water is insufficient to lubricate the flow. Another reason for shear thickening is the disturbance of the flow. In very high shear rates the orientation of the particles is disturbed (figure 3). [3; 8]

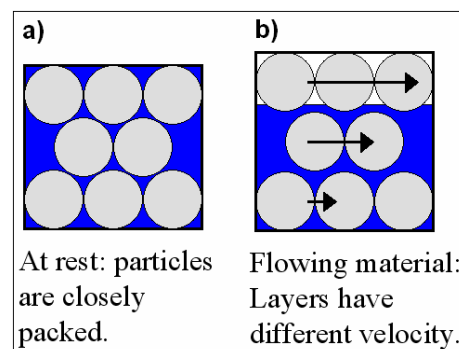


Figure 6 packing of particles[8]

Rotation of asymmetric particles can increase viscosity. Rotation of particles is connected to the geometry of the flow channel. For example if the symmetry of the flow channel changes suddenly, this may give rise to the rotation of particles and mixing of the fluid layers. [8]

3.6. Extensional viscosity

Viscosity (or shear viscosity) is resistance to steady flow. Extensional (or elongational) viscosity is resistance to accelerating flow. The flow velocity increases when a fluid enters a narrow gap. Figure 7 illustrates this phenomenon and how it affects viscosity.

As the flowing speed increases in the contracting flow channel, polymer chains are stretched in the accelerating flow. The resistance to

this stretching increases viscosity.

Extensional viscosity is normally associated with thickeners, but since dispersants are also polymers and they are flowing free in the waterphase if they are used in excess volumes, extensional viscosity must be taken into consideration.

[8]

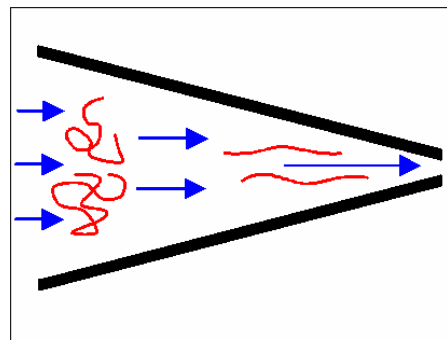


Figure 7. Extensional viscosity [8]

3.7 Water retention

Consolidation of coating layer is the process in which the liquid coating layer transforms into an immobilized (dry) coating layer. This occurs in two stages: first as the aqueous phase penetrates into the paper, and later, due to evaporation in the drying section. In this study the main focus is on the first and how different variables affect water retention. [4]

Figure 7 demonstrates what happens during dewatering. At first the dewatering rate is constant and rather fast. But quite rapidly a filtrating layer of pigment particles form on the paper surface. This hinders further dewatering. [8]

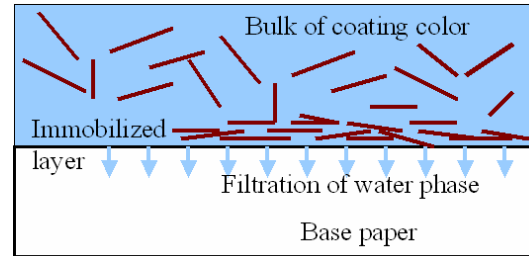


Figure 7. Dewatering [8]

The equation in figure 8 is used to predict the amount of water filtrated into the base paper. The square root is in the equation to simulate the filtrate cake forming on the paper surface. Base paper absorbs some water even when there is no pressure pulse. The typical absorption potential of a base paper is about 0,1 bar. As a comparison table 1 illustrates conditions in a typical coating station that has a roll application and blade metering. [8]

$$\frac{m}{A} = \sqrt{C \cdot \Delta p \cdot t}$$

m = mass /g
 A = functional area /m²
 C = Constant depending on the properties of the paper and coating color
 Δp = Pressure difference /Pa
 t = Duration of pressure /s

Figure 8. Dewatering equation

Phase	Pressure	Duration	$\Delta p \cdot t$ (of total)
Application nip	2 bar	2 ms	55 %
Free contact	0,1 bar	30 ms	41 %
Blade nip	10bar	30 μ m	4 %

Table 1. Conditions; roll application and blade metering

From table 1 it can be seen that most of the dewatering occurs before the blade. Even though Δp 's ads up to 100% the coating layer is still wet. Table 1 illustrates the amount of dewatering which happens by absorption.

4. DISPERSING

4.1. General

Pigment particles tend to form clusters (figure 1.). Some of these clusters are packed more tightly than others. These are called aggregates (a). The more loosely attached clusters, which normally consist of aggregates and primary particles or other aggregates, are called agglomerates (b). Clay particles form these clusters because of their attracting forces created by the difference in electric charge between the edges and the faces of the particles. [1]

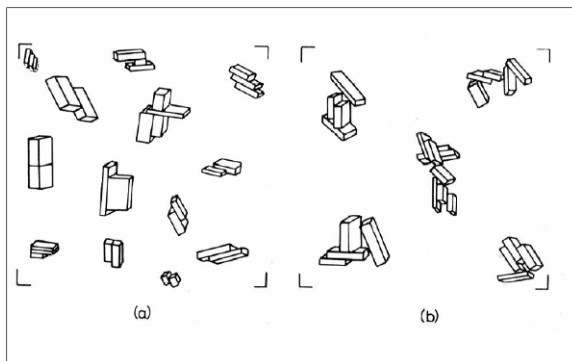


Figure 1. (a) Aggregates, (b) agglomerates [1]

The idea of dispersing is to break down these pigment particle clusters into individual particles (figure 2.) in order to reach the best coating results with a given pigment. In general the process of dispersing pigment slurries consists of three stages: wetting, disruption of particles clusters and stabilization of the slurry. [1,7]

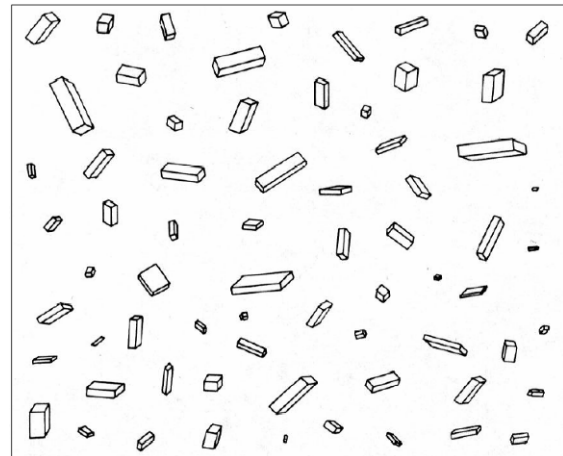


Figure 2. Ideal dispersion [1]

4.2 Wetting

Wetting the pigments means that all the external surface of the particles must come into contact with water. All air must also be removed from the internal surfaces between particles and particle clusters. Wetting is important because dispersing agents are water-soluble and complete wetting allows the dispersants to affect all surfaces. It is important that the pigment is introduced to the process slowly enough, so that every particle comes into contact with water. If the pigment is added too fast and in too large doses, the particle clusters don't have enough time to break down; only the surface of the cluster is wetted and air and dry pigments stay inside. [1]

4.3 Disruption of particle clusters

The breaking down of particle clusters can be divided into three categories: Mechanical thrust, collision of particles and shear forces. Mechanical thrust occurs for example when a particle cluster comes into contact with a mixer blade. [1]

Shear forces mean the affecting forces between particle clusters and the dispersion medium. The best affect in this case requires a somewhat high concentration of pigment in the slurry. Figure 3 illustrates the different forces in disruption of the pigment clusters. [1]

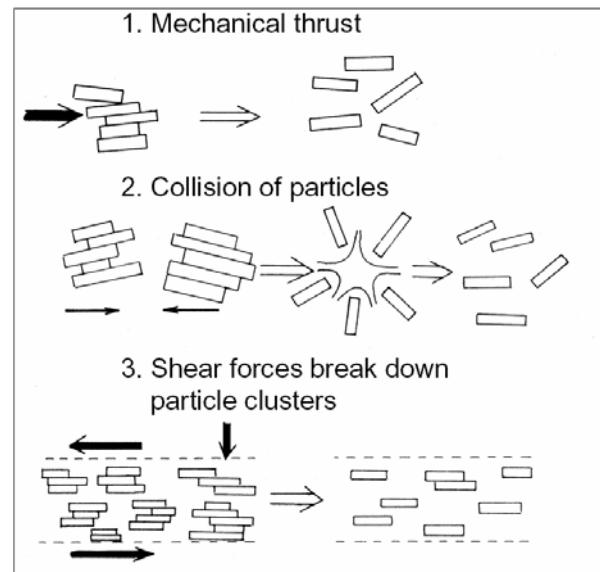


Figure3. Disruption of pigment clusters [1]

4.4 Stabilization

After the pigment clusters are broken down the surface area of the pigment increases. This means that there is more surface area for particles to interact with. This results in rapidly increasing viscosity. And after the mixing is stopped and no more shear forces are induced to the slurry, the pigments start to form new clusters (reagglomeration). Both these problems can be avoided by using dispersants. Dispersants should be added into the water before pigment in order to achieve the best outcome. It is important that the dispersant can function from the first moment on and all pigment is affected. [1]

The idea is to keep the particles far enough from each other. Two main principles are considered as stabilization mechanisms: electrostatic and steric stabilization. These methods are illustrated in figures 4 and 5. [1]

In electrostatic stabilization the surface energy of the pigment is altered. The dispersant adheres to the surface of the pigment and causes a highly localized charge. In this case the charge is negative (anionic dispersant). The dispersant attaches itself on the positive edges of the particle making the whole particle negatively charged. The negative surface charge attracts positive counter ions from the water. This cloud of positive ions (so-called “electric” or “ionic” double layer) surrounding the particles works as a repulsing force field between individual particles keeping them apart from one another. The thicker the double layer is the better the stabilization. The typical thickness of the double layer is a few nanometers. [1]

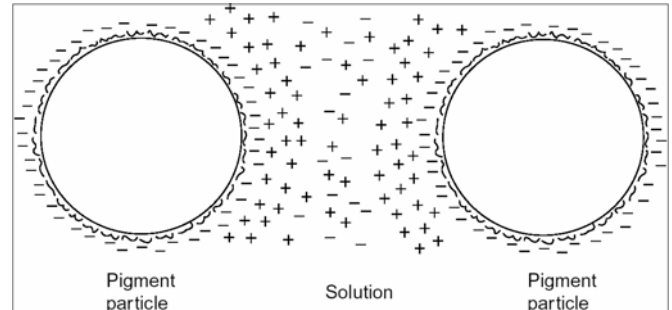


Figure 4. Electrostatic stabilization [1]

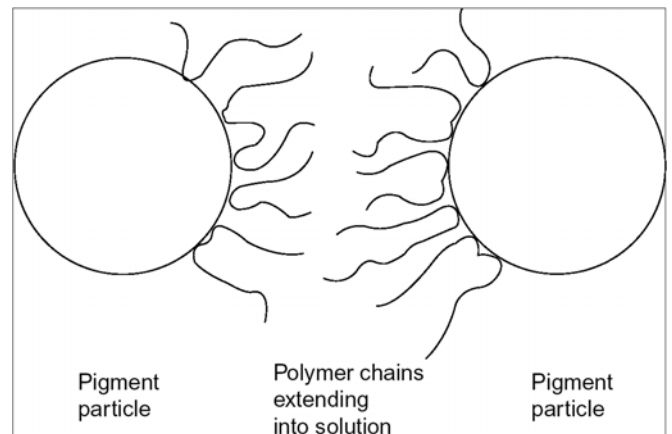


Figure 5. Steric stabilization [1]

In steric stabilization the particle surfaces are covered with long-chained uncharged polymers, which extend into the water (figure 5). Two polymer covered particles can not come too close to each other because the extending polymer chains would overlap, and this is not entropically favorable.[1]

In the case of electrostatic stabilization anything that makes the double layer thinner destroys the stabilization. In the best case the positive counter ions are totally monovalent cations. Monovalent counter-ions have nothing but repulsive forces between them and that makes them pack more loosely, and this makes the double layer thicker. Multivalent counter-ions tend to have some attracting forces between each other and they pack more closely. And this results in a thinner double layer. Cationic polymers can have drastic affects on stabilization, even in low concentrations. [1]

4.5 Dosing of the dispersant

Figure 6 gives an idea of how viscosity is affected by the amount of dispersant used.

At low concentrations viscosity remains quite high. But when the dispersant dose is increased, viscosity decreases rapidly at first and reaches a minimum level. If dosing is increased further, viscosity increases slowly. Viscosity decreases at first due to the increased stability of the slurry. With higher amounts, viscosity increases because dispersant can not all adhere to the surface of the pigments and the excess dispersant remains in the water phase increasing the electrolyte concentration and decreasing stabilization. [1]

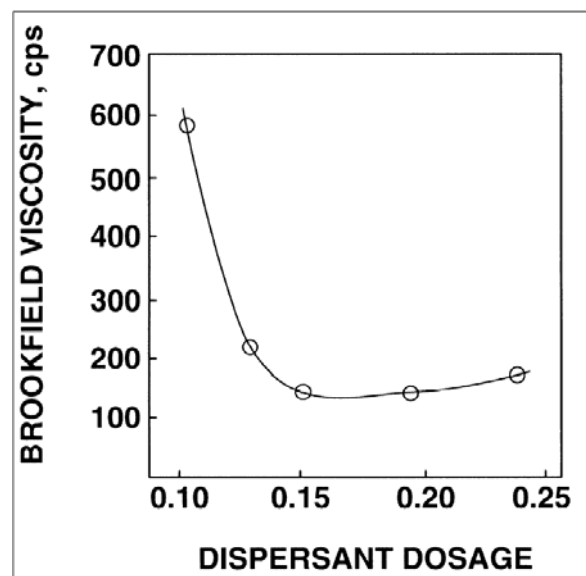


Figure 6. Dispersant dosage curve [1]

The amount of dispersant needed for good stability is dependent on many things. Pigment type and particle size, dispersant type, pH, and all additional components affect the dispersant dosage required. The easiest and recommended way to check the right dosage is to measure a viscosity curve as illustrated in figure 6. Even though Brookfield viscosity doesn't correspond directly with the conditions of the coating station it gives an estimate of what the dosage should be. [1]

4.6 PH and stabilization

Higher pH means increased anionization in polyacrylate salt dispersions. Anionization increases between pH's 4 and 9, after which it stays the same. Increased pH also increases anionicity or at least decreases cationicity in mineral pigments. Therefore it can be said that higher pH favors stabilization, when anionic dispersants are used. [1]

However, increasing pH with alkali increases electrolyte concentration in dispersion, and so it decreases stabilization when anionic dispersants are used. For some pigments, absorption of anionic dispersant increases and for some pigments decreases when pH increases. In the case of kaolin clay, absorption of anionic dispersant decreases when pH increases. Therefore it could be predicted that stability in clay dispersions will be best at low pH. however with the same amount of dispersant, viscosity in clay dispersions is lower at high pH. Figure 7 illustrates this peculiarity. [1]

Figure 7 shows that lower viscosity can be reached at lower pH. But in order to have good stability at low pH, a larger dose of dispersant is needed. In practice this is a compromise between quality and costs. For technical purposes the stability reached with higher pH is sufficient. [1]

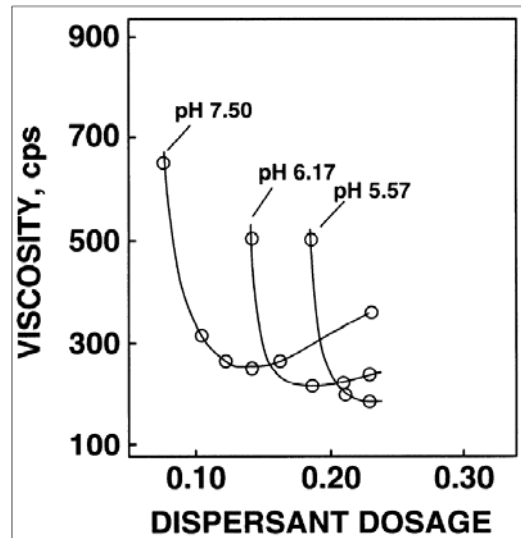


Figure 7. pH and dispersant dosage [1]

5. TEST METHODS

5.1. Brookfield

As stated earlier viscosity of pigment slurry is highly dependent on shear rate. Therefore there must be different methods to measure viscosity. Figure 1 shows the shear rate ranges of different viscometers and the shear rates that different processes generate. It is clear that a Brookfield viscometer doesn't give an accurate picture of what happens in a coating station. However Brookfield testing is still widely used in the paper industry because the equipment is cheap and easy to use. It does not exactly simulate the actual coating process but it can be easily used as a reliable indicator of change in the process. The 100 RPM of the Brookfield viscometer is equal to shear rate of 30 1/s. [10]

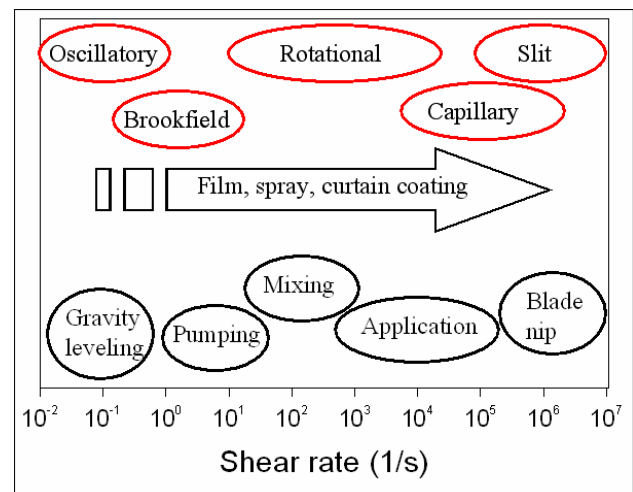


Figure 1. Process and viscometer shear rates [10]

5.2. ACAV A4

The ACAV A4 High Shear Viscometer was designed for testing coating materials. It uses a piston-driven mechanical principle to provide a complete and precise shear rate analysis ranging from 10 000 1/s to 10 000 000 1/s. It is used in the paper industry both for quality control and R&D. [7]

5.2.1 Viscosity measurements

When measuring viscosity with ACAV A4, the idea is to force under controlled circumstances the coating color through a small capillary or slit (figure2). Figure 1 illustrates how these two tools overlap one another in the shear rate chart, so with these two tools it is possible to examine viscosity over quite a wide range of shear rates. [6]



Figure 2. Capillary and slit

The principle is to measure the flow rate, and the pressure required to maintain it. With the dimensions of the capillary or slit known, shear stress, shear rate, and viscosity can be calculated. In addition, the density of the slurry is needed for the kinetic correction. [6]

The capillary is made of glass and when in use it is incased in a steel holder (figure 3). After screening the slurry with a filtering bag or pouch, the slurry is put into the tube on the left side of the picture. The piston comes from above and into the tube forcing the slurry through the capillary in the capillary holder. The computer calculates the viscosity and shear rate at desired pressures and draws a viscosity-shear rate graph. [6]

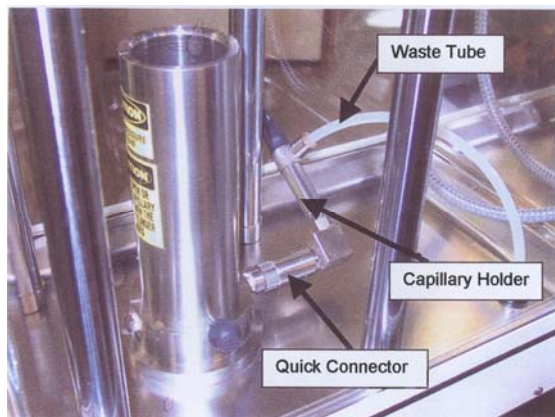
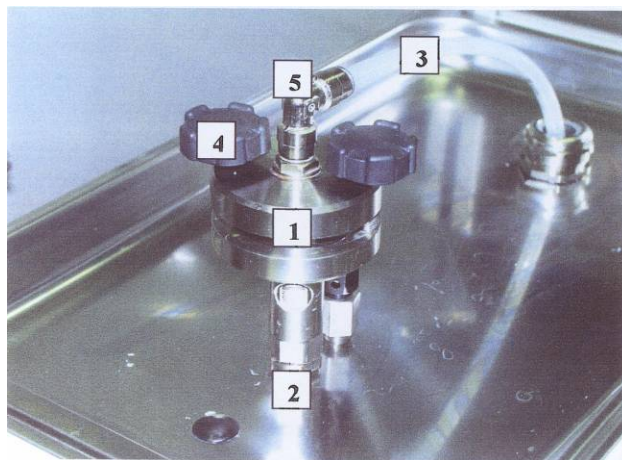


Figure 3. Capillary tool installed [6]

The slit is made of steel and it is placed between two “plates” in a sealed holder (figure 4). The slurry is forced through the slit and through calculations a viscosity-shear rate graph is formed. [6]



1. Slit holder
2. Quick connector
3. Outlet tube
4. Finger nut
5. Waste tube holder

Figure 4. Slit tool installed [6]

5.2.1.1 Formulas

Since the flow characteristics of pigment slurries are complex, the flow doesn't always follow the simple equations of shear stress, shear rate and viscosity. Certain corrections have to be made concerning shear stress and shear rate. The symbols used in these equations are listed below:

P	Measured (uncorrected pressure) / Pa	L	Length of the capillary / m
Q	Volumetric flow rate / ml/s	w	Width of the slit / m
γ	Shear rate / m^{-1}	h	Height of the slit / m
τ	Shear stress / N/m^2	l	length of the slit / m
η	Viscosity / Pas	v	average flow velocity / m/s
ρ	Density / g/m^3	ζ	Couette correction coeff.
R	Radius of the capillary / m	m	Kinetic energy correction coeff.

Flow velocity of the fluid suddenly increases when the slurry enters the narrow capillary/slit. Therefore a certain part of the extrusion (measured) pressure turns into kinetic energy of the fluid. Kinetic energy correction subtracts this pressure from the measured pressure. Because the geometry of the capillary and slit are different, also the correcting equations are different. [6]

Kinetic correction for the capillary:

Kinetic correction
$$p_{kin} = m\rho\left(\frac{Q}{\pi R^2}\right)^2$$

Corrected pressure
$$p_{cor} = p - p_{kin} = p - m\rho\left(\frac{Q}{\pi R^2}\right)^2$$

Corrected shear stress $\tau_{cor} = \frac{p_{cor}R}{2L}$

Corrected viscosity $\eta_{cor} = \frac{\tau_{cor}}{\gamma}$

Default value for coefficient m is 1, but it can be altered.

Streamlines of the flow contact the entrance of the capillary/slit. Therefore there is a small viscous pressure lost outside the capillary tube. Instead of the physical length of the capillary/slit, “effective length” is used to compensate this pressure lost. Couette correction is insignificant in the case of the capillary since the length of the capillary is so much larger than the radius. [6]

Couette correction for the capillary:

Effective length $L' = L + \zeta R$

Corrected shear stress $\tau_{cor} = \frac{pR}{2(L + \zeta R)}$

Corrected viscosity $\eta_{cor} = \frac{\tau_{cor}}{\gamma}$

Default value for coefficient ζ is 1. [6]

Kinetic correction for the slit:

Shear rate (at the wall) is $\gamma = \frac{6Q}{wh^2}$

Shear stress $\tau = \frac{ph}{2l}$

Viscosity $\eta = \frac{\tau}{\gamma}$

Kinetic correction $p_{visc} = p_{meas} - m\rho v^2 = p_{meas} - m\rho \left(\frac{Q}{hw}\right)^2$

The kinetic energy correction coefficient m is 0.8 for slit (in case of capillary it was 1).

After kinetic correction shear stress is $\tau = \frac{p_{visc}h}{2l} = \frac{\left(p_{meas} - m\rho \left(\frac{Q}{hw}\right)^2\right)h}{2l}$. [6]

Couette correction for the slit:

is calculated in the same way as for the capillary. Real shear stress is calculated by using effective length instead of physical length.

Effective length $l' = l + ch$

Shear stress after kinetic and coquette correction is defined as:

$$\tau = \frac{P_{visc}}{2l'} = \frac{\left(P_{meas} - m\rho \left(\frac{Q}{hw} \right)^2 \right) h}{2(l + ch)} \quad [6]$$

5.3 Water retention measurements

The water retention of the slurry was measured in two ways. In the static water retention tests (Åbo Akademi) the slurry was stationary and in the dynamic water retention test (ACAV-viscometer) the slurry was flowing. The two methods are so different that the values between the methods cannot be compared; however, the changes between the different slurries can.

Static water retention was studied with Åbo Akademi's water retention test.

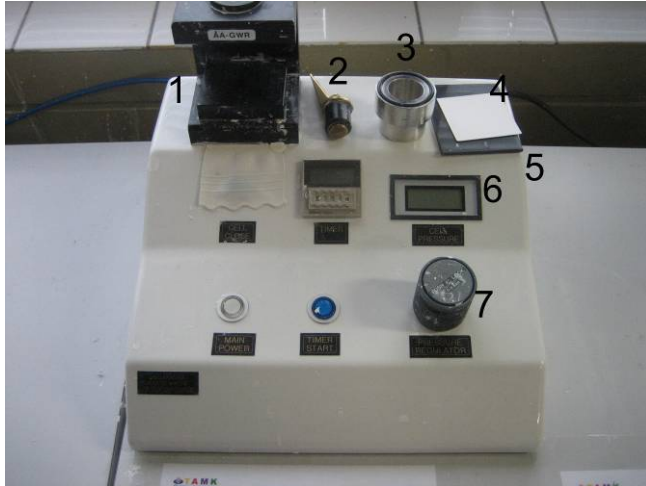


Figure 5. WR-test, ÅBO Akademi

The water phase from the slurry is absorbed through a polycarbonate filter into the absorption carton (4). The carton and the filter are placed on a plate (5) and the container (3) is placed on top of them. The whole system is put into the holder (1), and 10 ml of well-blended slurry is poured in. The top of the container is sealed with a plug (2). The pressure has to be 0.5 bar throughout the test. The

pressure is controlled manually (7) and observed from the pressure display (6).

The duration of this test was 90s. The absorption carton was weighed before and after the test. The radius of the container is 21.22 mm. The weight difference must be multiplied by 1500 to get the result in g/m^2 . As the pressure is controlled manually, the results are not as reliable as in dynamic water retention tests. Therefore the tests were repeated 10 times per sample. Since the unstable circumstances were similar for all samples, the multiple testing should minimize errors.

5.3.1 Dynamic water retention

Dynamic water retention was measured with the ACAV A4 viscometer. In the static water retention test the pressure had to be maintained manually but with ACAV A4 the pressure is maintained automatically, which makes the dynamic retention test more reliable. Figure 6 shows the test apparatus.

The idea is to feed the slurry from below (1) against a polyacrylate filter (2) at a constant pressure of 1 bar (4. pressure sensor). On the other side of the filter is a piece of paper (2) into which the water is absorbed. The slurry is disposed of through the waste tube (3). The whole package is sealed with a cap (5). The duration of this test was 6 seconds and the paper was weighed before and after the test. The effective diameter is 41 mm.



Figure 6. Dynamic water retention test

6. DATA ANALYSIS

6.1. Viscosity

6.1.1. Brookfield viscosity

Chart 1 illustrates the affect of *Fennodispo* A41 dispersant on Brookfield viscosity as a function of dose and pH. The slurry was prepared into a dry content of 65 %.

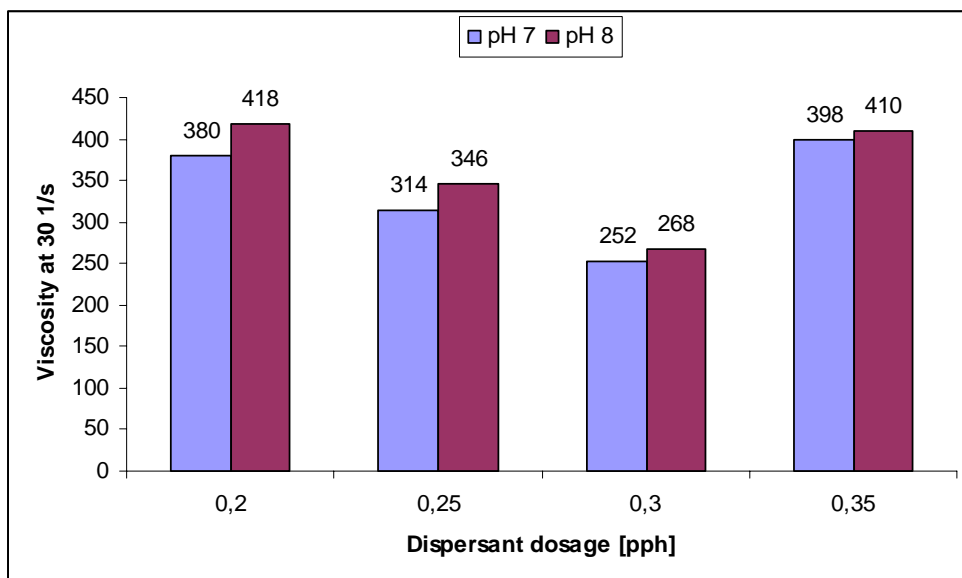


Chart 1. *Fennodispo* 41.

First thing that stands out is the fact that higher pH results in higher viscosity at low shear rates. (The same result was found with all the samples). This is the result of higher electrolyte concentration in the slurry. Increasing pH with alkali increases electrolyte concentration. With kaolin pigments this results in decreased absorption of dispersants. More negatively charged dispersant polymers remain in the water phase making the ionic double-layer thinner. As the repulsing field between the particles is thinner, they are able to move closer to one another. This increases interaction between the particles and results in higher viscosity. [3]

Increased dose seems to reduce the affect of pH on the dispersion. The rise in pH at the highest dose increased viscosity only 1/3 of what it did at the lowest dose. This could be because with higher dispersant doses there are more negatively charged dispersant polymers in the water phase. These polymers already hinder the stability of the slurry. The affect of the additional OH⁻-ions is smaller as the stability of the slurry has already been compromised.

Dispersant dose affects viscosity in two ways, first decreasing it and then increasing it. Viscosity decreases first because the dose of 0.2 pph is insufficient to cover all pigment surface. At the dose of 0.3 pph viscosity reaches its minimum (chart 1.). At this point, all or almost all dispersant polymers have been absorbed by the pigment with very small amount of polymers remaining in the water phase. The particles are now highly anionic. When dispersant dose is increased the excess polymers remain in the water phase decreasing cationicity in the water phase. This makes the ionic double-layer thinner and decreases stability.

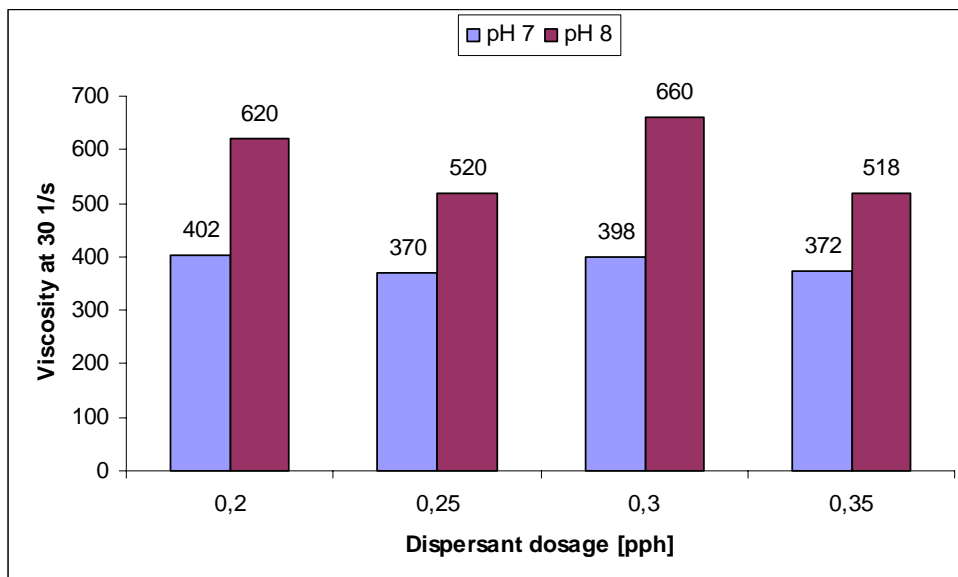


Chart 2. Fennodispo 48.

When looking at the affects of *Fennodispo 48* (chart 2), it seems that it is more sensitive to changes in pH. The differences are enormous compared to those of *Fennodispo 41*, almost 10 times higher. Dispersant being the only variable, it can be concluded that the reason for this lies within the chemical composition of the dispersing agent. But since no additional information was available, further examination was impossible.

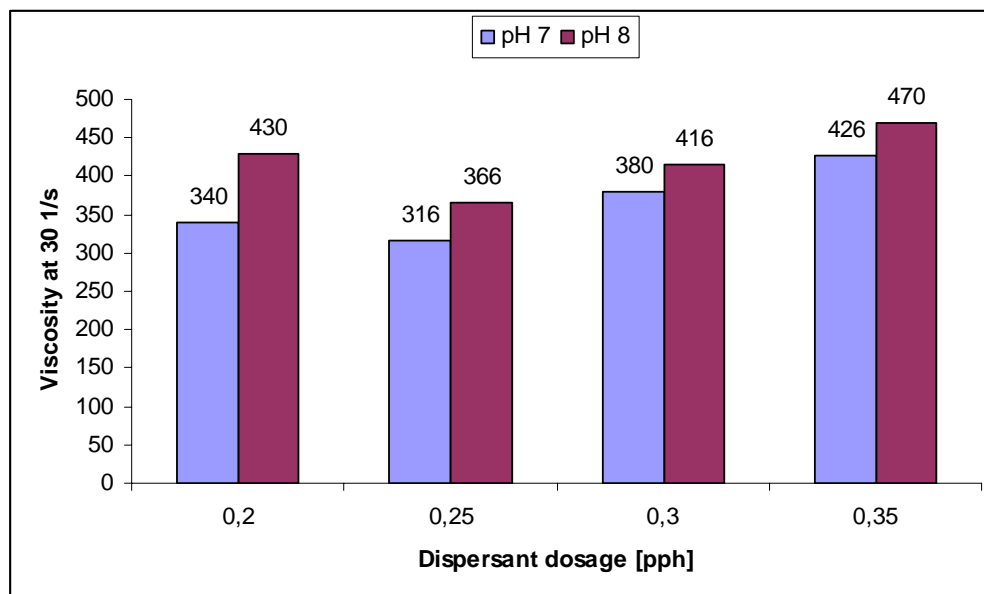


Chart 3. *Fennodispo 55*.

Fennodispo A55 and *Fennodispo A41* have similar affects regarding pH. The differences are of the same magnitude and they seem to decrease with increased dose. *Fennodispo 41*, however, reaches the minimum viscosity at a higher dispersant dose at 0,3 pph. Chart 4 illustrates the differences between the dispersing agents at pH 7.

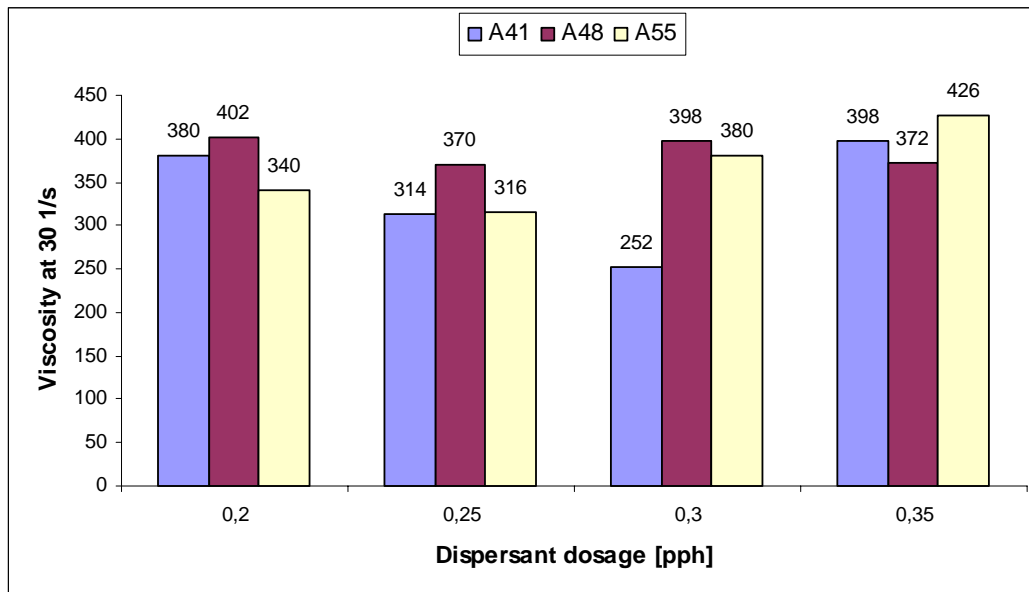


Chart 4. Comparison of dispersing agents as a function of dose.

Chart 4 shows that the lowest Brookfield viscosity can be achieved with Fennodispo A41 at the dose of 0,3 pph. Apart from this dose, A41 and A55 seem to act similarly.

6.1.2. High shear rate viscosity

Along with the high shear rate viscosity measurements came the first problems in this thesis work. Unfortunately, the shear rates reached in this study do not fully simulate the actual conditions of a coating station. This is because the slit used in the measurements had become worn in use. The actual height of the slit was 0,078 mm instead of the 0,05 mm used in the calculations. This problem arose after the measurements had been taken and there was not enough time to do them again. The correct height was fed into the calculations and the measurements were corrected. However this led to another problem. Because of the new

calculations the shear rates achieved in the measurements are slightly lower than in actual mill conditions.

High shear viscosity could not be measured with capillary tests. The slurry became totally dilatant as it entered the capillary. The reason for this must lie in the geometry of the capillary and the dimensions of the clay particles. The high aspect ratio clay particles need to orientate in clear flow layers to move freely past one another. The round geometry of the capillary does not allow this to happen and viscosity increases dramatically.

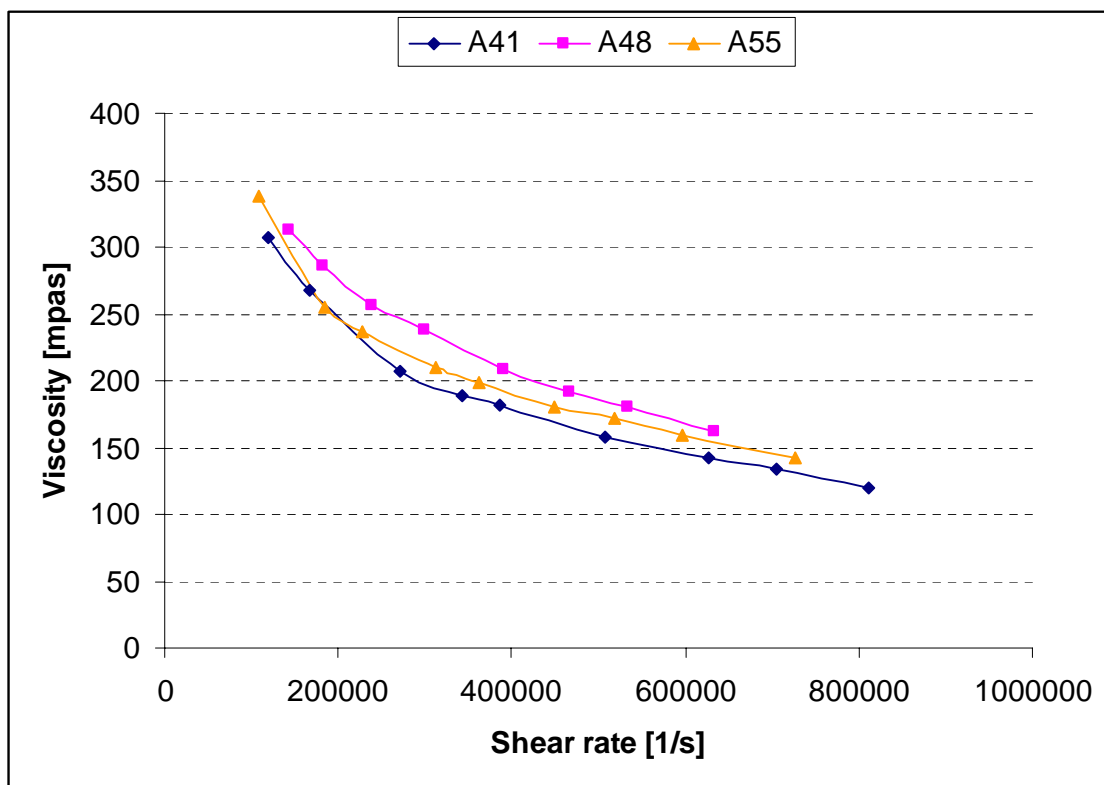


Figure 1. Comparison of dispersants at pH7

The test results reveal the fact that pigment slurries are viscosity-wise indeed dependent on shear rate (figure 1). The viscosity-shear rate curves illustrate clearly how viscosity decreases with increased shear rates. The main reasons for this are the alignment of pigment particles along with the flow and breaking down of structures [8]. Even though the slurry has been effectively dispersed, there is some forming of clusters when the mixing stops and

the slurry remains undisturbed. When the slurry is again introduced to high shear rates, the clusters break down and this decreases viscosity. Figure 1 also suggests that the use of A41-dispersant seems to result in the lowest viscosity.

The tests performed with the ACAV-viscometer also reveal that at higher shear rates the slurry does not need as much dispersant as it did at lower shear rates in order to work properly. The minimum dose of 0,2 pph resulted in the lowest viscosity with practically every sample (figure 2). In the Brookfield tests the results were different. The minimum dose was not enough to reach sufficient stabilization.

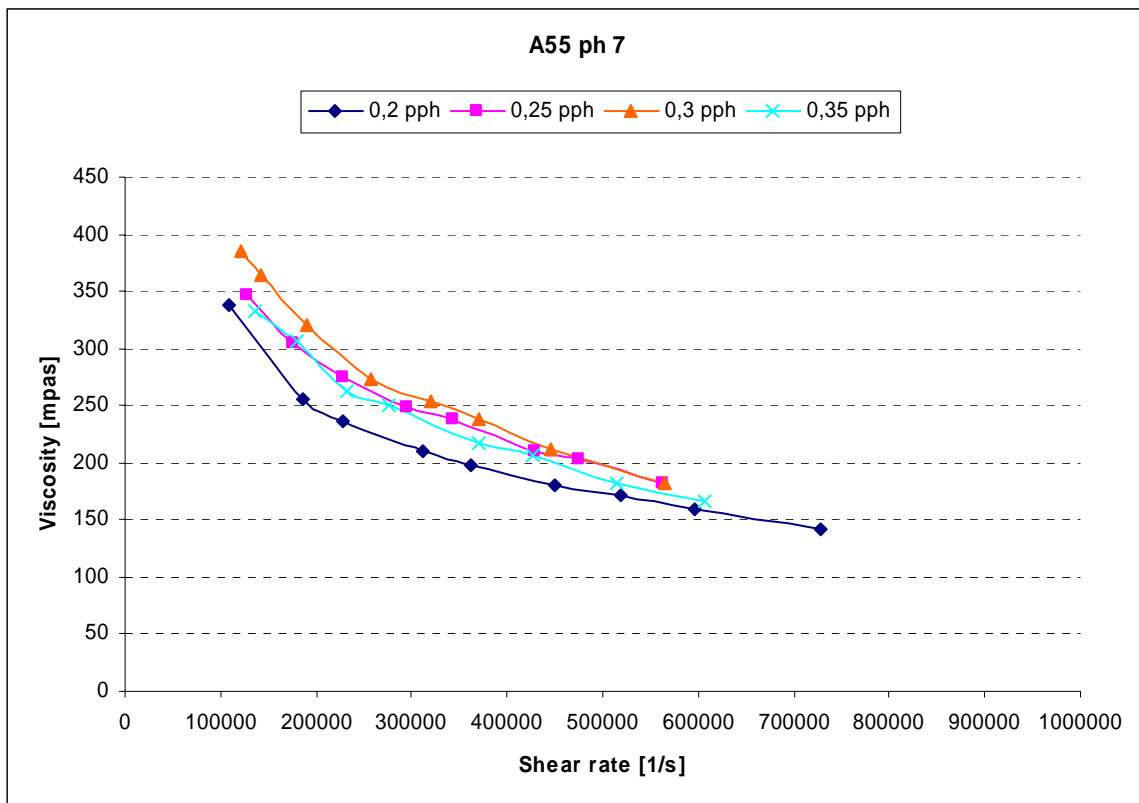


Figure 2. The affect of dispersant dosing at high shear rates.

Testing the samples at different pH values revealed that increased alkalinity of the slurry had the opposite affect on viscosity when comparing to the results achieved in the Brookfield tests. At low shear rates the rise in pH resulted in higher, viscosity but at high shear rates higher pH decreased viscosity. These results are illustrated in the appendix section (appendices 1-3). Dispersant A41, however, seemed to be less pH-sensitive at both low and high shear rates. Hardly any difference can be seen at high shear rates. The viscosity of the slurries with dispersants A48 and A55 in turn were highly affected by the rise in pH-value. It would seem that the narrowing of the ionic double layer doesn't have as great an effect at high shear rates as it does at low shear rates. It is possible that the attracting forces between pigment particles are not great enough to hinder the stabilization of the slurry at high shear rates.

6.2 Water retention

6.2.1. Static water retention

Charts 5-7 illustrate the affects of dispersant dose and pH on static water retention. The differences are so small that finding a definite pattern is hard. Especially the differences between different doses seem to be random.

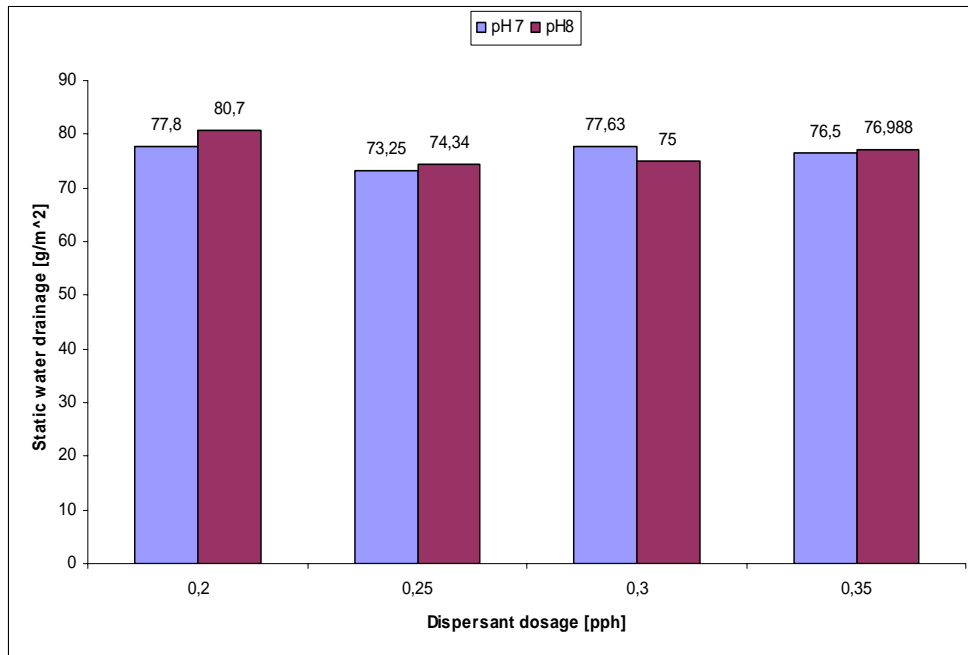


Chart 5. Static water drainage as a function of dose and pH
(Dispersant: Fennodispo A41)

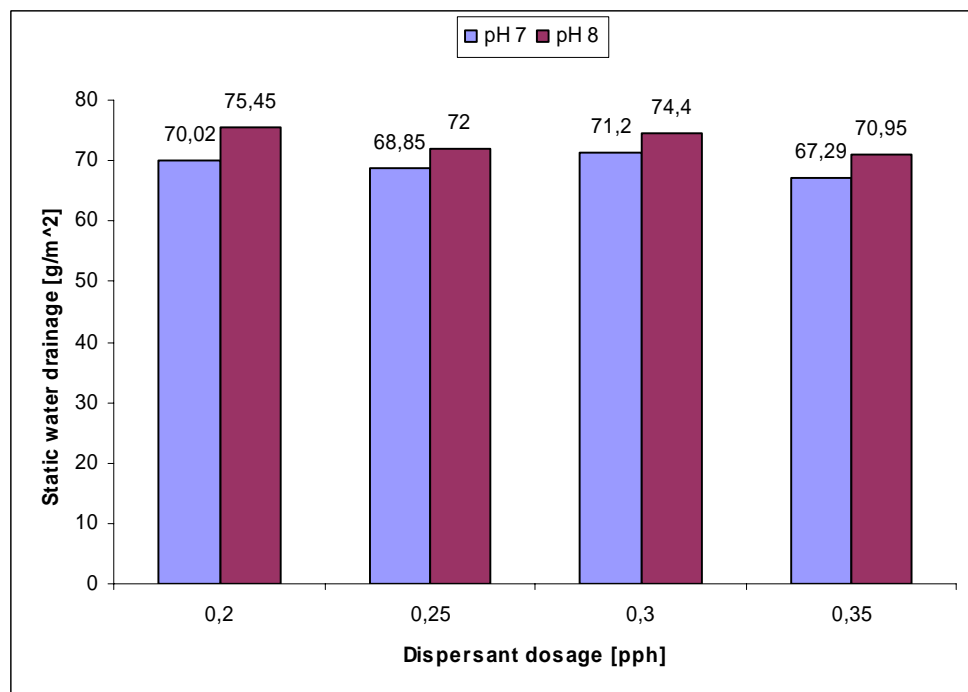


Chart 6. Static water drainage as a function of dose and pH
(Dispersant: Fennodispo A48)

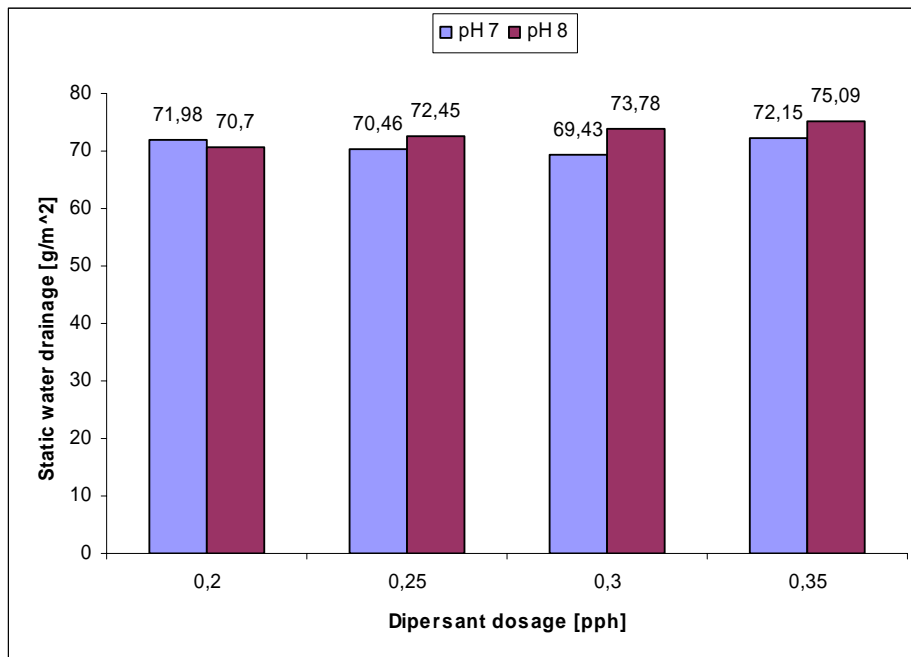


Chart 7. Static water drainage as a function of dose and pH

(Dispersant: Fennodispo A55)

When observing the results from a pH-point of view, a pattern emerges. Disregarding a few measurements, in all cases increased pH led to a slightly higher dewatering. Increased OH^- concentration leads to a compact and thin ionic double layer and stability of the slurry decreases. Decreased stability in turn reduces water retention. [4]

When comparing the three dispersing agents, the differences again are small. Fennodispo A41 results in slightly higher dewatering with the average of all samples being $76,5 \text{ g/m}^2$. The use of dispersants A48 and A55 led to almost similar dewatering, with averages of $71,2 \text{ g/m}^2$ and 72 g/m^2 .

6.2.2 Dynamic water retention

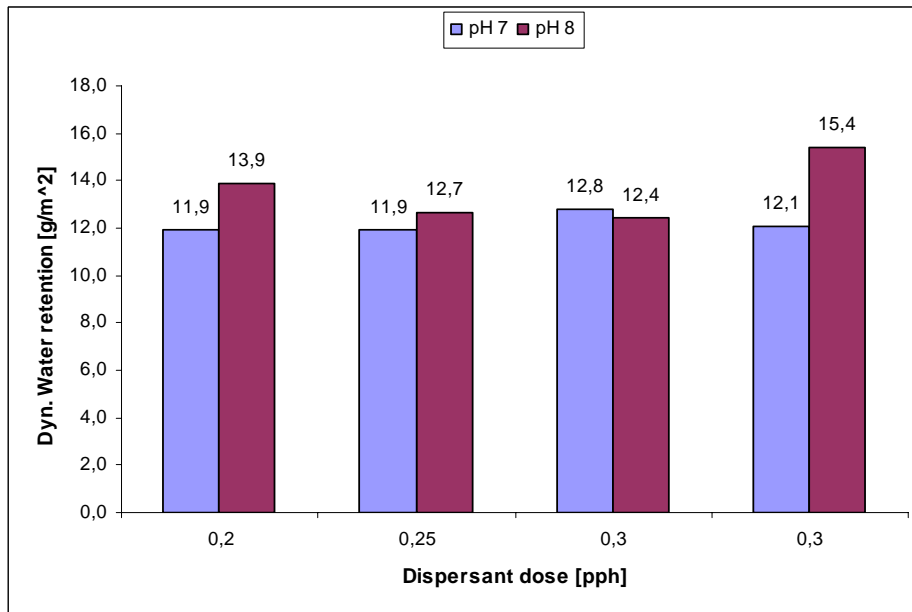


Chart 8. Dynamic water drainage as a function of dose and pH
(Dispersant: Fennodispo A41)

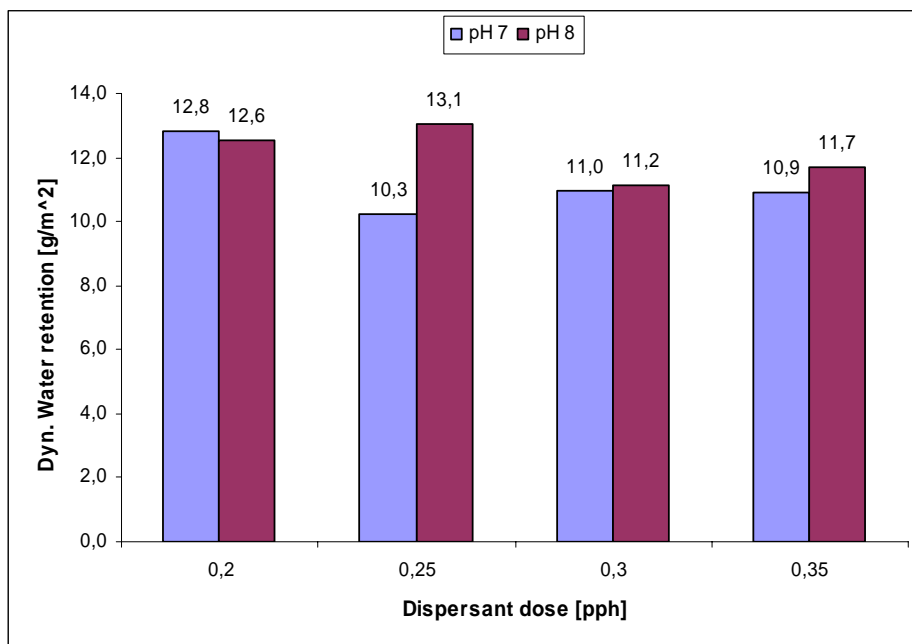
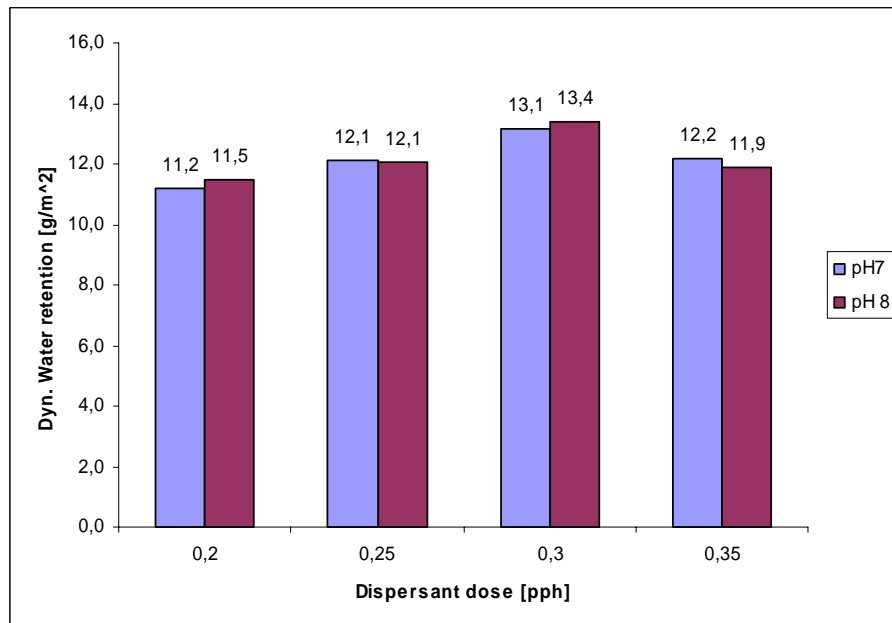


Chart 9. Dynamic water drainage as a function of dose and pH
(Dispersant: Fennodispo A48)



*Chart 10. Dynamic water drainage as a function of dose and pH
(Dispersant: Fennodispo A55)*

The dynamic water retention tests show similar data as the static water retention tests. Again, the choice between dispersants doesn't reveal any significant patterns. In most cases, increased pH leads to slightly higher dewatering (similar as in static tests). Again this is the result of higher alkalinity. The variations, however, are on a slightly larger scale. And as in the static tests, A41 led to the highest drainage and A48 and A55 follow close behind.

All in all, these measurements reveal that differences in dispersing agents, their dosage and pH have very little effect on water retention. Of these three factors, dosing had the smallest if any effect. Variations between different doses can be seen, but due to their random nature no scientific assumptions can be made.

However using dispersant will significantly affect water retention as opposed to not using any. The samples without any dispersant were so thick that they couldn't even be measured; they were totally immobilized. This suggests that dewatering without dispersant would be very low.

7. CONCLUSIONS

Initially the slurry was intended to be prepared to a dry content of 67%. However this proved to be impossible. The shear forces induced by the mixer were not strong enough to fully disperse the slurry. After all the pigments were added to the slurry the slurry was totally immobilized and it was impossible to perform any measurements on it. The dry content was decreased to 65 % and the difference was enormous. At 65 % dry content the slurry behaved much more like a fluid than at 67 % dry content.

The water retention tests show slight difference between the three dispersing agents. All dispersants had similar effects on dewatering. Increase of pH resulted in slightly increased dewatering with all samples. These differences were greater for dynamic water retention. The effect of dispersant dose was very low on water retention. These results can be seen in both static and dynamic water retention.

The only actual difference between the dispersing agents was that the dispersing agent Fennodispo A41 had a slightly higher dewatering value than A48 and A55. The effects of A48 and A55 were almost identical.

Viscosity of the slurry was more affected than water retention by all variables. Increased dispersant dose of the kaolin slurry led to slightly different results at low and high shear rates. At low shear rates the minimum dose of 0,2 pph was not enough to create sufficient stabilization. Stabilization was reached at 0,25 and 0,3 pph. At high shear rates, however, the minimum dose led to lowest viscosities in almost all cases.

The comparison of different dispersing agents revealed that the use of Fennodispo A41 led to lowest viscosities at high shear rates, reaching 100 mPas at 1000 000 1/s. The use of A48 and A55 led to almost similar results with slightly higher viscosities than A41. At low shear rates A48 resulted in higher viscosities than with other dispersants. The minimum viscosity reached was 370 mPas at 30 1/s with a dispersant dose of 0,25 pph at neutral pH.

Fennodispo A55 reached its minimum viscosity of 316 mPas with a dose of 0,25 pph. A41

reached the lowest viscosity of 252 mPas, but at the higher dose of 0,3 pph. The choice between different dispersants in this case would be a compromise between quality and costs.

At low shear rates high pH gave high viscosity with all samples. At high shear rates, the high pH led to low viscosity. The measurements with different pH-levels also revealed that a slurry dispersed with Fennodispo A41 is less pH-sensitive than the other samples, especially at high shear rates.

High shear viscosity could not be measured with capillary tests. The slurry became totally dilatant as it entered the capillary. The reason for this must lie in the geometry of the capillary and the dimensions of the clay particles.

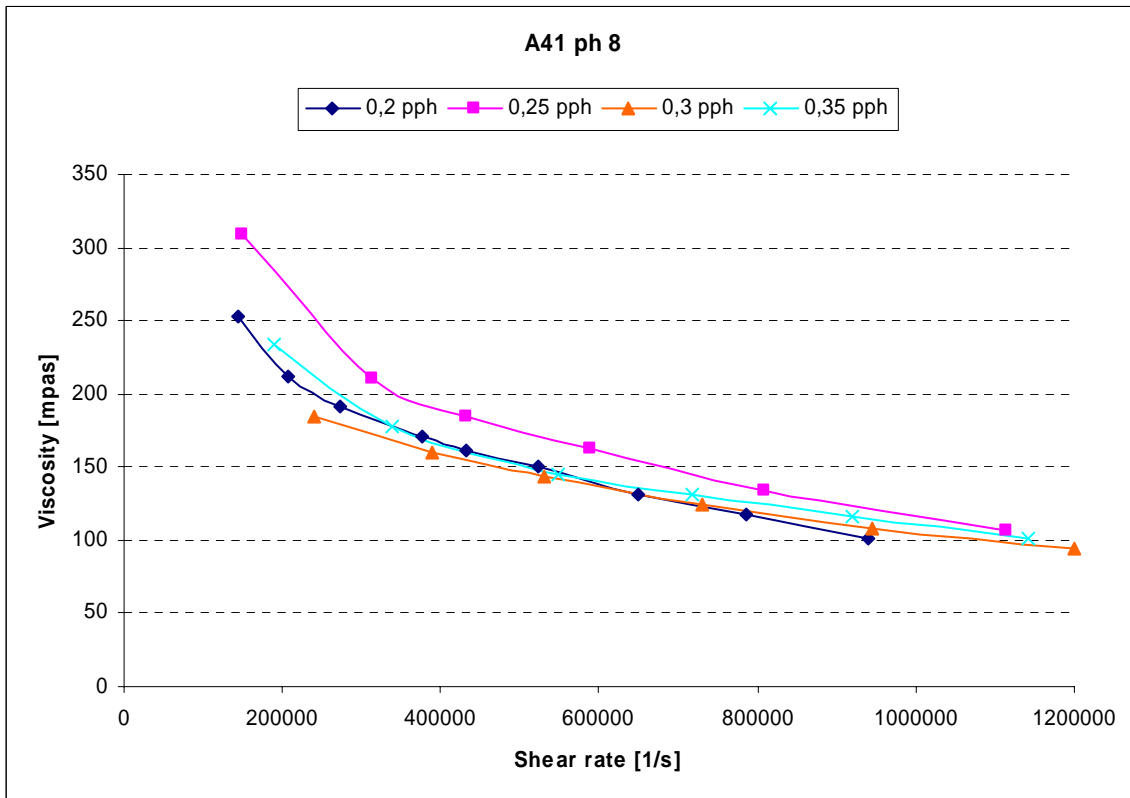
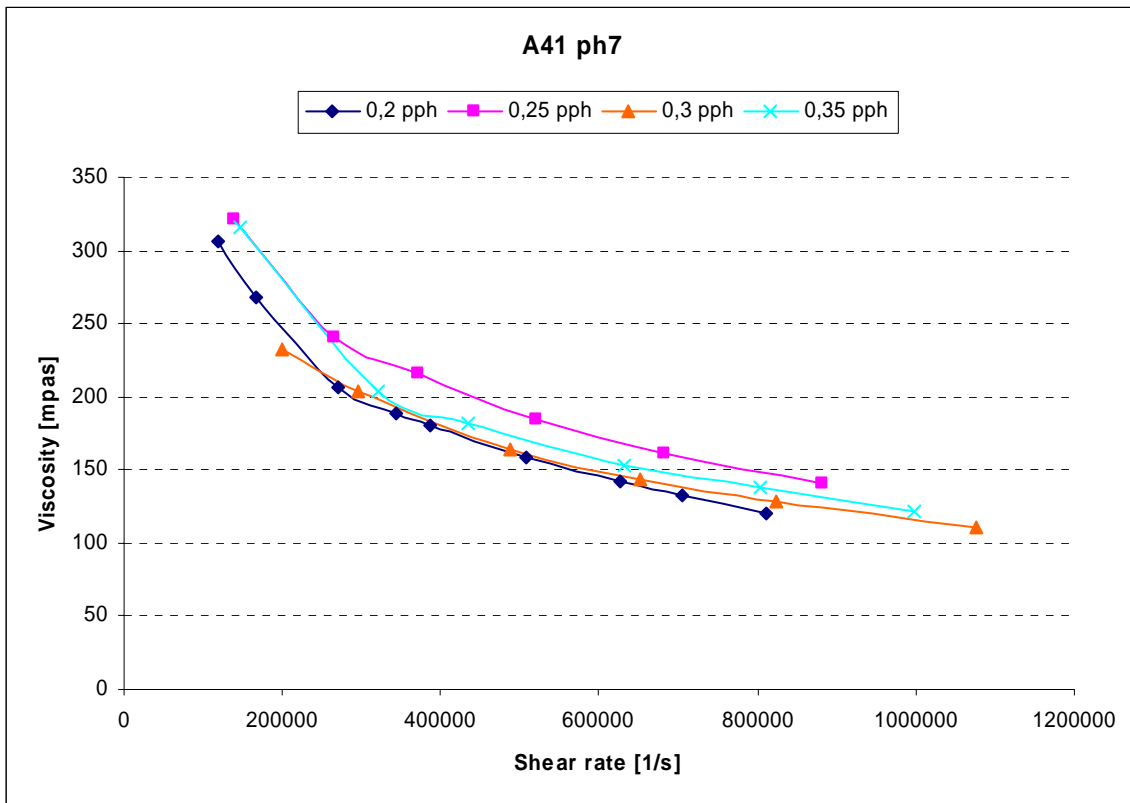
The test results indicate that Fennodispo A41 would be the best choice in a mill-scale coating station. It reached the lowest viscosity at high shear rates and can therefore be assumed to be the most effective product. Also its ability to withstand changes in alkalinity makes it less vulnerable to changes in the process.

Further studies could be made on even lower dispersant doses at high shear rates. Another possible study could be made to determine the highest possible solids content on a functional kaolin slurry.

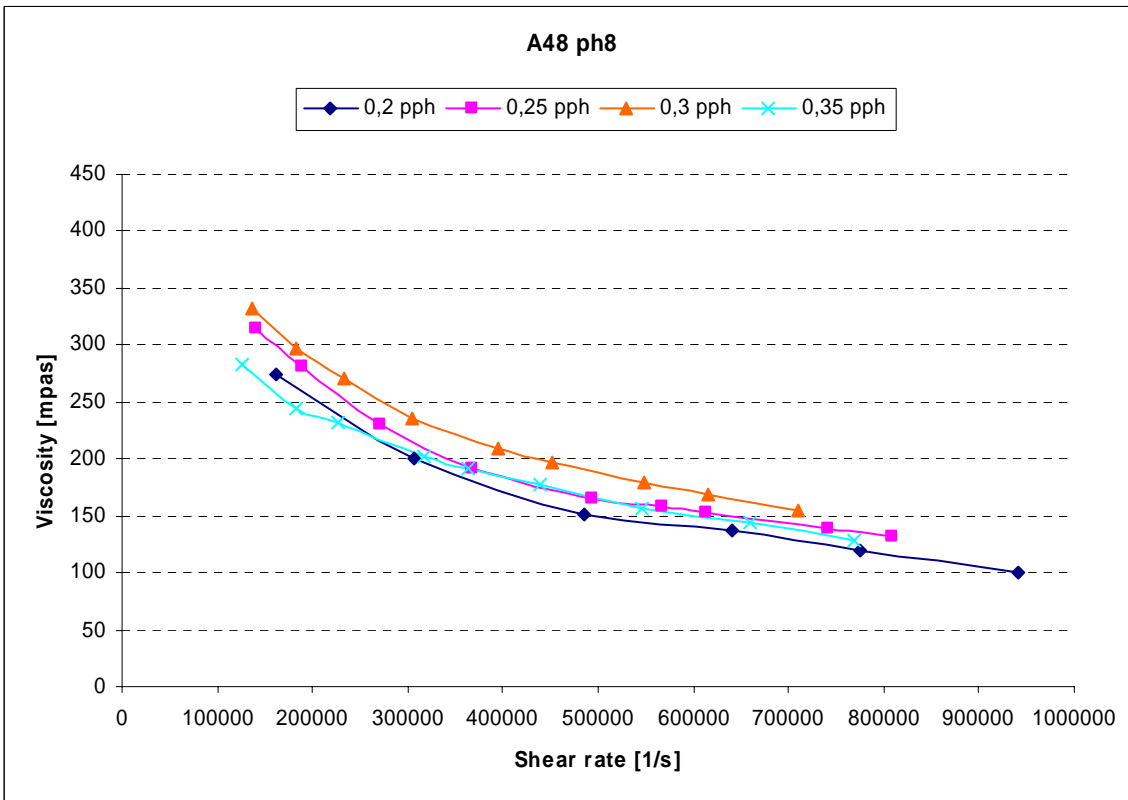
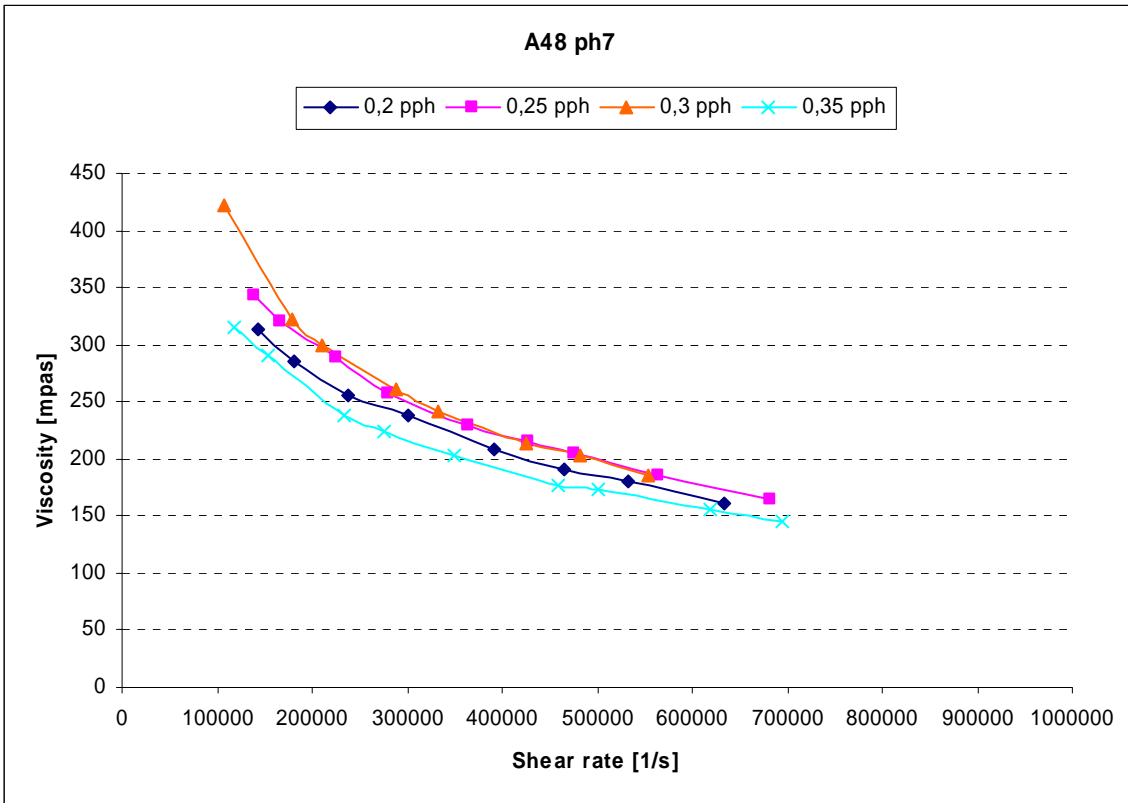
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APPENDIX 1



APPENDIX 2



APPENDIX 3

