Pigment dispersion processing, optimization for higher pigmentation

By

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Acknowledgments

Abstract

One way to make a UV curable ink is to mix a pigment dispersion with monomers, oligomers, photoinitiators and additives. Creating a pigment dispersion is in many cases the first processing step of making a UV curable ink and is of large importance. To process pigment dispersions of Pigment red 2 and Pigment red 122 a premixing step with a dissolver is used followed by a grinding step employing a three-roll mill. The components for the dispersions are a monomer/oligomer blend of acrylates, pigment and a dispersing agent. The optimal monomer/oligomer blend of acrylates were determined by the Daniel flow point method. When processing using a three-roll mill the process time becomes of great importance, alongside with the final viscosity of the dispersion. Each dispersion was passed three times over the three-roll mill and the passing times were recorded to get the processing time. To find a correlation between processing time and viscosity a design of experiment was conducted for the two different pigments. The design of experiment model was of the extreme vertices design type which allows setting upper and lower boundaries for the input variables. From the design of experiment an expected viscosity and processing time could be estimated. For Pigment red 2 the model suggested a processing time of 14.47 grams/min and a viscosity of 44.58 Pa*s. The actual processing time came out as 16.46 grams/min with a viscosity of 49.10 Pa*s. For Pigment red 122 the estimated processing time was 24.35 grams/min with a viscosity of 43.04 Pa*s. The results were a processing time of 22.98 grams/min with a viscosity of 43.80 Pa*s. The use of the Daniel flow point method combined with design of experiment allows for an efficient way of screening new pigments and monomer/oligomer optimums for UV curable inks.

Sammanfattning

Ett sätt att göra en färg som går att härda med UV-ljus är att blanda en pigmentdispersion med monomerer, oligomerer, photoinitiatorer och andra additiv. Skapandet av en pigmentdispersion är i många fall det första processteget för att göra en färg som härdas av UV-strålning och blir därför ett viktigt steg. För att processera pigmentdispersioner av Pigment röd 2 och Pigment röd 122 användes ett förblandningssteg med en dissolver vilket sedan följdes upp av processering i en vals med tre valsar. Komponenterna som ingår i dispersionerna är en monomer/oligomerblandning av akrylater, pigment och ett dispergeringsmedel. Det optimala monomer/oligomerförhållandet var tagna från en metod känd som "The Daniel Flow Point Method". När ett valsverk med tre valsar används för processering blir processtiden väldigt viktig och därför får även viskositeten på pigmentdispersionen en viktig roll. Varje dispersion passerade över valsen tre gånger och processtiden togs för varje pass för att få den totala processeringstiden. För att hitta en korrelation mellan processeringstid och viskositet användes en så kallad "design of experiment" för de två olika pigmenten. Modellen som användes i "design of experiment" sattes till "extreme vertices design", vilken är en typ av modell som tillåter övre och undre gränser av ingångsvariablerna. Från "design of experiment" resultaten kan man sedan approximera framtida resultat för viskositet och processeringstid. För Pigment röd 2 föreslog modellen en processeringstid på 14.47 gram/minut och en viskositet på 44.58 Pa*s. Den verkliga processeringstiden blev 16.46 gram/minut med en viskositet på 49.10 Pa*s. För Pigment röd 122 blev den estimerade processeringstiden 24.35 gram/minut med en viskositet på 43.04 Pa*s. Resultaten blev en processeringstid på 22.98 gram/minut med en viskositet på 43.80 Pa*s. Användandet av "The Daniel Flow Point Method", kombinerat med "Design of experiment", är ett effektivt redskap för att undersöka nya pigment till nya pigmentdispersioner för UV härdade färger.

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1 Introduction

1.1 UV-curable inks

Inks cured by ultraviolet (UV) light were originally introduced in the 1960's and have during the last decades been widely adopted in many industries. UV curing now constitutes approximately 4 % of the industrial coatings market. UV curing has grown by more than 10% per year, a lot due to increased productivity and product quality compared to conventional water and solvent-based thermal drying processes [1]. UV curable flexo printing systems are very suitable for packaging printing as it is very reliable at high printing speeds [2]. Due to the many applications of UV curable inks there are also several other printing techniques applicable, such as UV letterpress, UV Screen and UV offset.

All UV curable inks have one thing in common and that is that ultraviolet light initiates a cascade of chemical reactions which cures the ink leaving a cured film behind. A photoinitiator blend in the ink responds to the UV light and initiates crosslinking reactions resulting in a thermosetting polymer film.

One way to make UV-curable inks is to mix acrylates and photoinitiators with a pigment dispersion. The pigment dispersion is, when comparing to the finished ink, a highly viscous fluid consisting of pigment, binder, monomer and dispersing agent. The goal when processing pigment dispersions is to achieve a smaller particle size distribution. The pigment dispersion will have different properties depending on which and how much of each separate component is used. One important property that is of high interest is the processing time. A sufficient model capable of estimating processing time also needs to take note of the amount of pigment in the dispersion, as a dispersion that has a lower processing time but also a lower pigment content could have a lower output of processed pigment than a dispersion with a higher processing time but with a higher pigment content. There are several common ways to process pigment dispersions, a few will be mentioned but the focus will be on the three-roll mill.

1.2 Acrylates

The acrylates in the ink can, when exposed to the free radicals generated by the photoinitiators start a crosslinking reaction. Each acrylate group can react with another acrylate group and then form a high molecular weight polymer. Typical acrylate chemicals used for UV-curable inks have in between 1-6 acrylate groups per molecule, this is often referred to as the functionality of the chemical. The acrylate compounds with six functional groups create a high cross-linking density, while the compounds with one functional group create a low cross-linking density. The high-functional acrylates usually have a higher reactivity compared to low-functional acrylates, however most of the high functional acrylates have a higher viscosity. Therefore, a blend of different acrylates are used to get the properties desired from the cured ink. The acrylate functional group can be seen in *Figure 1.1*
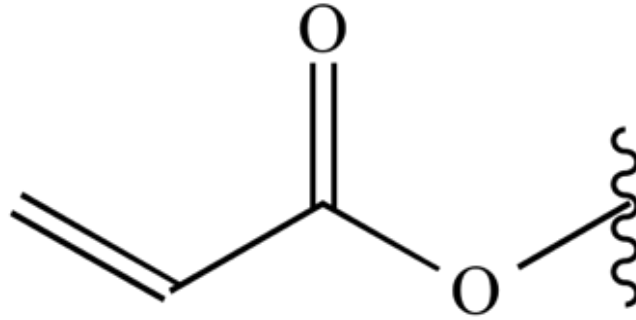
Figure 1.1: The acrylate group [3].

1.3 Screening for new pigment dispersions

Today screening for new pigment dispersions, especially dispersions containing new pigments, is a time consuming process. As pigment with the same pigment index can have very different properties a 1:1 replacement is often not possible. This leads to a lot of time going into trial and error. A lot of time spent in trial and error is due to the struggles that can be seen in the processing of pigment dispersions. As the dispersion has few components each component has a significant impact on the dispersion. One very important aspect of the dispersion is the rheology, this as the rheology in many cases decide which processing equipment is used.

1.4 Criteria for a good pigment dispersion

For a pigment dispersion to be classified as good it needs to work in the production but also in the final ink. For production purposes the pigment dispersion should preferably be of a viscosity where the dispersion is free flowing, i.e. it is pourable. There are several dispersions which are of low viscosity but are still not pourable, and this in turn can lead to production difficulties such as build up on the knife table on a three-roll mill. For the final ink the dispersion should preferably be of low viscosity as it opens up more opportunities for high viscous ingredients. Low viscosity dispersions are preferred but, in many cases, low viscosity dispersions give low output on some specific equipment, such as the three-roll mill. Another aspect for a good pigment dispersion is long term stabilization which is an affect from the dispersing agent. The dispersing agent needs to suit the pigment well in order to give good stabilization but also good rheology. In summary a good pigment dispersion has a low viscosity with a low processing time, it is free flowing and has a good long-term stabilization.

1.5 Typical information from the supplier of the dispersion components

The technical information from the supplier comes in the form of a technical data sheet. For monomers and oligomers these datasheets usually contain the viscosity, molecular weight, theoretical functionality, which type of acrylate it is, for example polyester acrylate and which properties the chemical shows in the cured ink. For monomers and oligomers there is quite a lot of information on these datasheets, for pigments however the datasheets can vary a lot in between suppliers. In many cases the datasheets contain the oil absorption of the pigment, the specific surface area, the lightfastness, specific gravity and chemical resistances.

2 Aim and limitations

Flint Group AB in Trelleborg are continuously developing new UV curable inks and therefore new pigment dispersions are developed simultaneously. The aim of this study is to improve the efficiency of the process for testing new pigments as well as improving the processing time for two specific pigments, Pigment red 2 and Pigment red 122 on a three-roll mill.

To optimize pigment processing time in the processing of pigment dispersions, the aim is to use design of experiment as a tool. To get a good starting point for the recipe of the dispersion the Daniel flow point method was used to investigate optimum vehicle compositions for a specific pigment. Once these optimum vehicle compositions have been found, boundaries around these compositions for the design of experiment were set up using the software Minitab 17. The three components used as input variables were pigment, dispersing agent and monomer/oligomer(s) mixture. The processing time variables which were of interest were viscosity and processing time of pigment.

Production of a ready to use UV-curable ink requires additional formulation work and will not be covered in this study.

3 Theory

3.1 Pigment dispersion processing

When a pigment is processed by a milling method to form a pigment dispersion three physical-chemical processes are usually described. The three processes taking place when dispersing a pigment are; wetting, separation and stabilization. For any good pigment dispersion all these three steps need to work efficiently.

3.1.1 Wetting

Wetting refers to the displacement of gases such as air and other contaminants from the pigment particles. This is done by the wetting medium adsorbing to the pigment particles surface, replacing the gases and contaminants which were in contact with the particle. Even if the conditions are favorable the wetting process is slow, however this can be sped up by mechanical separation of the agglomerates [4, p.217]. Wetted agglomerates require much less energy for de-agglomeration than dry agglomerates, as the wetting media reduces the attractive forces acting between the particles [5].

The penetration of liquids into dry pigment can be described by the Washburn Equation [6]:

$$v_p \propto [\tau \frac{\gamma cos\theta}{\eta}]^{0.5} [time]^{0.5} \tag{3.1}$$

Where v_p is the penetration rate, τ average radius of pores, γ surface tension of liquid, η viscosity of liquid and θ the contact angle of liquid on the pigment. This can further be developed to that the slope of mass^2 over time from sorption of resin in a powder column can be correlated to the wetting behavior. The pure slope can be used for comparison in between mixtures, *see Equation 3.2*.

$$\frac{m^2}{t} = \frac{c*\rho^2*\sigma*cos\theta}{\eta} \tag{3.2}$$

where c is the capillary constant (packing of powder), ρ is the liquid density, σ is the liquid surface tension, θ is the contact angle and η is the liquid viscosity. This slope when evaluated is called the sorption method.

The average pore size for cylindrical pore geometry can be estimated by *Equation 3.3*.

$$r_p = \frac{2*V_{liq}}{S} \tag{3.3}$$

Where r_p is the average pore size radius, V_{liq} is the volume of nitrogen in the pore and S is the specific surface area. The volume of nitrogen in the pore (V_{liq}) is derived from the amount of vapor adsorbed at a relative temperature close to unity [7].

Monomer surface tension has a great influence on pigment dispersion rheology; a lower surface tensions leads to better wetting of the pigment and therefore a better dispersion rate [6]. This is because the wetting process is driven by the differences in surface tension between the

pigment surface and the resin. For most resins the typical surface tensions are between 30-40 mN/m at 150°C [8].

The surface boundary between two liquids or a liquid and a solid result in an effect called interfacial tension. The ultimate geometric form for achieving the lowest surface tension is a droplet due to that it captures the maximum volume for a minimum surface. The surface tension is usually expressed as the force acting along a unit length of surface (N/m) and can be viewed in *Equation 3.4*.

$$\sigma = F/L \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3.4)$$

Where σ is the surface tension, F is the acting force and L is the length. The liquid surface tensions and the free energy residing in a unit area of liquid surface are equivalent quantities. For the wetting or non-wetting of a solid surface the contact angle θ is used. This angle ranges from 0-180 ° where ideal wetting occurs at the angle of 0° [4, p233].

Surface tension forces determine the size of the contact angle. There are three surface forces acting at the edge of the liquid/solid interface. Two forces act to pull the drop inward and away from the surface. These two are the surface tension of the liquid and the interfacial tension between the solid and the liquid. The third force that acts is the solid surface which pulls the edge of the liquid/solid interface in a direction exactly opposite to that of the interfacial tension force. When this is at equilibrium *Equation 3.5* arises [4, p.235]:

$$\sigma_s = \sigma_{sl} + \sigma_l cos\theta \qquad\qquad\qquad\qquad\qquad\qquad (3.5)$$

Where σ_s is solid surface tension, σ_l is the liquid surface tension and σ_{sl} is the interfacial surface tension.

3.1.2 Separation

Processes are designed to separate pigment aggregates into individual primary particles. In many cases the primary particle sizes are never reached due to the amount of energy that is required. The separation takes place when agglomerates are hit and are hit hard enough to rupture. For the maximum efficiency of separation, the mill base should have as high viscosity as possible that the machinery can handle [9, p.436]. For the three-roll mill the tackiness of the mill base influences rupture of the agglomerates. If the mill base exhibits low tackiness and the agglomerates are tightly bound together the pigment agglomerate will simply rotate like a ball bearing under the streamline forces. If the mill base exhibits a high degree of tackiness the agglomerates will be torn apart, sending the pieces of agglomerates into two different streamlines in the three-roll mill.

3.1.3 Stabilization

Once the agglomerates have been broken up into smaller particles, the particles tend to re-agglomerate if there are no molecules with a stabilizing effect present. Common stabilizers to achieve long term stabilization in UV-curable pigment dispersions are polymeric, hence using steric hindrance to stabilize the dispersion. Why these stabilizers are used is because conventional surfactants which are mono-functional can be outcompeted by the large amount of solvent molecules. The polymeric dispersants tend to have polar ends with many functional groups followed by a less polar tail that is soluble in the medium and have a sufficient length

to provide a surface layer that is at least 10 nm thick [9, p441-443]. Ideally a single dispersant that could anchor firmly to all pigments would be desired, this is however not the case but most polymeric dispersants are broadly effective and then reduce the number of tests required to find a good stabilizer for a specific pigment. In many cases a combination of stabilizing dispersing agents alongside oligomeric binders are used to achieve good stabilization.

3.2 Oil absorption

The oil absorption is a practical measure of the surface and morphology of a pigment. The higher the oil absorption value of the pigment the more binder is required to bind the pigment. Today there are many different pigments with many different oil absorption values, however in general they all fall roughly into a subset of categories. Ultra-low oil absorption, 5-15 g oil/100g, normally very regularly shaped particles with a low particle size. Low oil absorption, 15-30g oil/100g, normally very fine but regularly shaped pigment particles. Medium oil absorption, 35-70g oil/100g, this is the normal range for irregular shaped, but ultrafine pigment particles. High oil absorption, 75-160g oil/100g, normally very fine irregular shaped/structured pigment particles. Ultra-high oil absorption, greater than 160g oil/100g, very low particle sizes (nanometer range), especially carbon blacks fall into this category [10].

The critical pigment volume content (CPVC) of a system represents the densest packing possible of pigment particles. At the CPVC there is just enough binder molecules present to fill out the voids between the particles in a dry paint film. Above the CPVC there is not sufficient binder present and below the CPVC there is an excess of binder molecules. There is a correlation between the oil absorption value and the CPVC, however to establish a more exact correlation a different term for oil absorption is used which is measured in milliliters of oil/milliliters of pigment instead of grams of oil/grams of pigment. The relationship between oil absorption and the CPVC is found in *Equation 3.6*.

$$CPVC = \frac{100}{1+OA_m} \tag{3.6}$$

Where OA_m stands for the oil absorption in milliliters of oil/ milliliters of pigment [4, p.186].

3.3 Equipment for dispersion processing

For dispersing pigments there are several types of machinery that can be used. For UV curable pigment dispersions, it is common to use high-speed impellers, basket and three-roll mills.

3.3.1 High-speed impeller

High-speed grinding equipment often refers to an impeller apparatus. The rotary blade hits the pigment particles and breaks them apart. One key factor for the impeller efficiency is the diameter (D) of the rotary blade. A rolling doughnut flow is observed when the high-speed impeller is operating efficiently. Cylindrical tanks free of baffles and blind corners should be used. For satisfactory pigment dispersions a peripheral edge velocity of at least 4000 ft/min, however preferably one of 5000 ft/min (25.4 m/s) should be considered. The peripheral velocity can easily be calculated by *Equation 3.7*. The optimum tank dimensions should be a diameter of 2.8-4.0D. The impeller blade should be positioned between 0.5-1.0D on the vertical axis and the initial depth of charge should be in between 1-2D. High-speed impeller apparatus can also be used for pre-mixing purposes to get a good mix between the mill-base and the pigment before using other processing equipment such as the three-roll mill.

$$V = \frac{r*2*\pi*RPM}{60}$$
(3.7)

If thixotropic agents are part of the mill base composition, it may sometimes be expedient to postpone their introduction until the main part of the pigment dispersion action has been completed [4, p.329]. This due to that they may interfere with the doughnut flow pattern and the mixture might start clinging to the edges of the tank.

3.3.2 Three-roll mill

The three-roll mill is an extremely common machinery in the paint and ink industry, see *Figure 3.1*. This machinery consists of three-rolls; the feed roll, the center roll and the apron roll. The feed mill base is added between the space of the feed roll and center roll. A small portion is carried through the feed nip and the rest is rejected and flows back upwards. Extremely high shear is achieved in the feed nip. The medium after the feed nip is then split between the feed roll and center roll. The part that goes to the center roll then enters the apron nip and then in turn is split up between the center roll (returning to the feed bank) and the apron roll. A knife is then pressed against the apron roll to scrape of the medium.

Figure 3.1: A pilot scale three-roll mill used at Flint group.

For three-roll milling the velocity ratio between the rolls are extremely important for the fractional transfer of mill base. The transfer fractions are more or less fixed from a knowledge of the velocity ratio [4, p.317]. The three-roll mill production rate is influenced by several key variables. For any given mill five of these variables are set by the original mill design (K, D, L, RPM and n), where K is a constant specific to the original mill design, D is the diameter of rolls, L is the effective length of the rolls, RPM is the revolutions per minute of the feed roll and n is the velocity ratio of roll speeds.

The other factors that influence the three-roll mill production rate are the force (F) pushing the rolls together and the average mill base viscosity (η). The influence of these parameters can be viewed in *Equation 3.8*.

$$Q_m \left(\frac{gal}{hr} \right) = \frac{0.00047 * K * D * L^2 * RPM * (1+n) * c * a * \eta}{F} \tag{3.8}$$

Premix preparation that has shown effective is loading pigment on top of the vehicle medium, at a ratio of 2:1 and after a few minutes the remaining vehicle is added to get the premix into a suitable viscosity range for the three-roll mill. [4, p.322-323]

3.3.3 Basket mill

Basket mills are suitable for the processing of low- to medium viscous fluids [11], see *Figure 3.2*. The construction is very similar to the high-speed impeller with the exception that a basket is mounted above the impeller blade. This basket contains grinding media (beads) which are responsible for the grinding, once the fluid flows up in a doughnut type flow from the impeller blade and into the basket chamber, the beads then impact the pigment particles inside the chamber and break them into smaller agglomerates and/or primary particles. The basket mill has an advantage that the pre-dispersion as well as the grinding can be carried out in the same container. For the intense circulation needed for the processing, the dissolver blade sometimes is not sufficient, and an integrated pump wheel can be added. There are also basket mills which have a double walled grinding basket which allows cooling or heating of the dispersion under operation [12]. The grinding media is often dense and of high quality, preferred materials are zirconium silicate and stabilized zirconium oxide [13]. Lower quality glass or ceramic media can suffer from fractures and are worn down at a higher rate.

Figure 3.2: picture of a regular basket mill [14].

3.4 Rheological properties of pigment dispersions for UV-curable inks

The ideal case for a pigment dispersion is to follow a Newtonian behavior, i.e. the viscosity is independent of the shear rate. For most pigment dispersions where there are a lot of interactions between particles and macromolecules anomalous flow properties are observed. The viscosity of Newtonian or ideal fluids is a material constant only dependent on temperature and to a negligible extent pressure [15, p.90-91]. For non-Newtonian fluids a variable like shear time can influence the viscosity, especially for pigment dispersions.

3.4.1 Pseudoplastic flow behavior

The type of flow behavior for systems containing coiled molecules, micelles or flocculates is pseudoplastic flow behavior. The viscosity value for pseudoplastic flow at any given shear stress is called an apparent viscosity. This term is used due to that the viscosity at this one point cannot be applied by other shear stress- shear rate conditions. Pseudoplastic flow behavior is characterized by that the fluid appears thinner when submitted to shear forces. The relationship between shear stress and shear rate is not linear as it is for Newtonian fluids and is therefore termed non-Newtonian. This viscosity decrease arises due to structural changes which arise when shear forces act on the fluid. Examples of structural changes are alignment of thread-shaped molecules, stretching of coiled molecules and breakdown of flocculates and micelles [15, p.92-93].

3.4.2 Thixotropy

The word thixotropy is derived from two Greek words and means "change by touch". The flow behavior of a liquid or gel that shows a degree of thixotropy changes when the sample is subjected to the same shear rate under a period of time. Thixotropic behavior is due to breakdown of a loosely built up structure that is resident in the liquid, when the shear stress is removed the structure is rebuilt over a period of time. To evaluate thixotropic liquids a thixotropic loop can be used where the shear rate is gradually increased, then held constant and then gradually decreased. The degree of thixotropy is often decided by the area inside the thixotropic loop, see *Figure 3.3*. During the run the temperature is held constant and the part where the shear rate remains constant should be held constant long enough to ensure breakdown of the structure residing in the liquid.
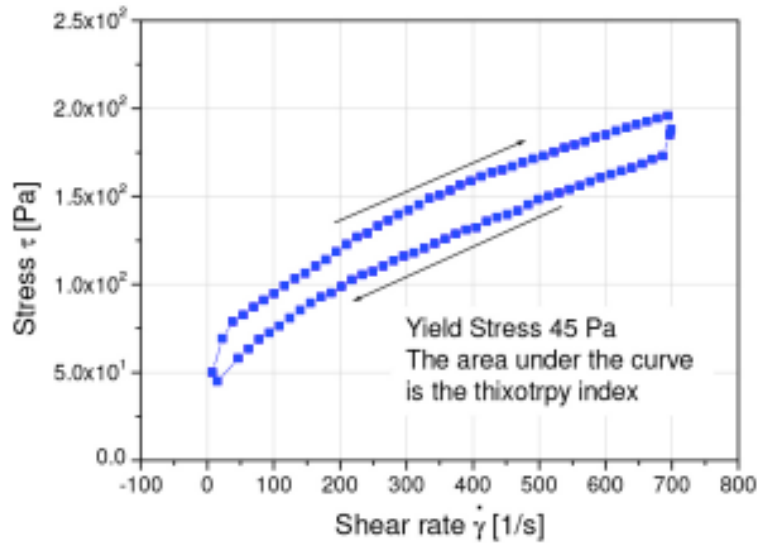
Figure 3.3: Thixotropic loop for a material showing thixotropy [16].

The rheology of many systems is very sensitive to temperature fluctuations. An increase in temperature tends to reduce the thixotropic behavior and at high enough temperatures eliminate it [17].

3.5   Daniel flow point method

The Daniel flow point method is used to estimate the most appropriate binder concentration to use with a particular pigment. One makes a series of solutions with different binder concentrations. Then it is determined the amount of each solution that must be added to a weighed amount of pigment so that when it is dispersed by blending with a spatula the resulting dispersion has a viscosity just low enough to flow readily off it. One plots the volume or mass of each solution needed for flow against the concentration of that solution. The point at which the dispersion flows readily off the spatula is called the flow point. Determining the flow point requires some experience, but the outline is as follows: When the pigment is blended with the spatula the content is a paste in the beginning. When more vehicle is added and mixed in, the resistance of the content becomes very small. At this time the spatula is lifted straight above the dispersion. If the liquid adhering to the spatula remains as a thin film, the last few drops fall at intervals of 1-2 second, and the liquid feels sticky, the flow point has been reached [18]. For good test with the Daniel flow point method a U-shaped curve with a distinct minimum is seen. This minimum is the optimal ratio and the dispersion is stabilized. To the left of this minimum the dispersion is not completely stabilized and to the right it is stabilized but the viscosity increases which leads to a higher flow point.

When a liquid is worked into a pigment by a vigorous kneading action with a spatula, a good dispersion will display a strong resistance to strong or sudden pressure. With further liquid addition, the mixture will suddenly reach a point where a transformation to a smooth glossy mass is observed. This dispersion is then characterized as a dispersion by deflocculated particles. If the shear stress applied is low, the particles are allowed sufficient amount of time to slip by each other resulting in a low viscous resistance. If the shear stress is high, particles will ram into each other resulting in high viscous resistance [4, p.284-287].

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If liquid is incorporated in a poor dispersion by vigorous kneading of a spatula the dispersion mixture will remain dull in appearance and adhesive in consistency. When more liquid is incorporated into the mixture the consistency will proportionally become softer. Finally, a stage is reached when the mixture drops from its own weight from a vertically held spatula. Physically, this type of dispersion represents a flocculated system. A low shear stress will then result in high viscous resistance and a high shear stress will result in a low viscous resistance. This low viscous resistance is a result of that the high shear stress, if high enough, has the ability to break up the flocculates [4, p284-287].

3.6   Design of experiment using Minitab 17

Minitab is a statistical software which allows easy set-ups for doing a design of experiment (DOE). There are several different types of design of experiments, which makes it important to choose the design that fits the experiment at hand. The DOE's available in Minitab 17 are factorial, response surface, mixture and Taguchi. A design of experiment does an analysis of a few input variables, in the case for pigment dispersions, pigment, dispersing agent and mixture of monomer/oligomer and correlates them to the output variable(s). The analysis of these input variables is conducted by varying the variables and checking which effect they have on the output variable. Correlations can also be found in between the variables, if they act synergistically or against each other. In general, a good starting point is to use factorial design to find the few significant factors out of a large group of potential factors. Full factorial designs often become very large and sometimes a design called fractional factorial design can be used instead.

In some cases, the factors can have limits, such limits are then set by upper and lower boundaries. When these cases appear, other designs could be better applicable to investigate the response. To analyze components with upper and lower boundary constraints there is a design called Mixture design – Extreme vertices design. This design allows investigation of a small portion of the simplex, see *Figure 3.4.*
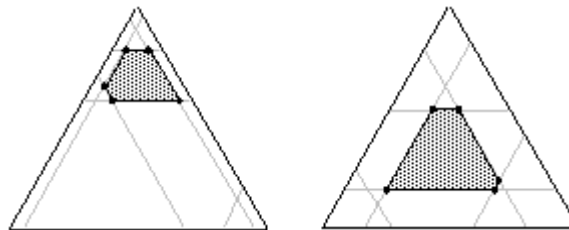
Figure 3.4: Extreme vertices design where the grey area represents the design space [19].

In this case the simplex can be seen as a triangle where each corner is one component. A good example of why this design is used is to think of baking, it would be hard to make a good dough using 100% flour and no other ingredients.

3.6.1   Mixture design of experiment - Extreme vertices design

In the case of pigment dispersion processing a factorial design could be used to find potential significant factors such as pressure or temperature. However, for evaluating the mixture of components, which are included to make up the dispersion, a mixture design is more suited.

The input variables for a pigment dispersion could be dispersing agent, pigment and mixture of monomer/oligomer(s).

Mixture design is a special class of response surface experiments where the product is made up out of several ingredients. In mixture experiments the amount of the different components add up to a common total. The response variable(s) in mixture designs are assumed to depend on the relative proportions of the components and the process variables. The process variables are parameters such as temperature or pressure which are not part of the mixture [20].

3.6.2 Interpreting data

For extreme vertices design it is possible to analyze the data collected by using a method called forward selection. Minitab then gives the estimated regression coefficients, the standard error of these coefficients, the p-values for the experiment as well as how well the model fits the data given in terms of S and R-sq.

The p-values in mixture designs are given for the interaction parameters but not for the individual (linear) parameters due to that the components must sum up to a fixed amount or proportion and altering with a single component forces a change in the others [21]. The p-value is one of the most important value in the results for a design of experiment. This is because it determines if the terms and the response have an association which is statistically significant. A significance level of 0.05 is usually used and if the p-value is lower or equal to the significance value the term has a statistical association with the response.

S-values given by Minitab represent the average distance that the observed values are from the regression line. This is a very convenient measure due to that the S-value is given in the units of the response term.

The R-sq values are always between 0-100 % and give an indication of how well the data fits the regression line. The definition of R-sq can be seen in *Equation 3.7*.

$$R_{sq} = \frac{explained\ variation}{Total\ variation} \qquad (3.7)$$

In most cases the higher the R-sq value is the better the model fits the data.

Pseudo-components are often used for designs which have upper and/or lower bounds. These variables are used to simplify the design construction and reduce correlation between component bounds in constrained designs. Pseudo-components are a rescaling of the original components to make them more measurable against each other [22]. To transform the values of the components *Equation 3.8* can be used [23].

$$x_i' = \frac{(x_i - L_i)}{(Total - L)} \qquad (3.8)$$

where x_i' stands for the pseudo-component, x_i stands for the original component value, L_i for the lower constraint limit of component i and L stands for the sum of all lower constraints.

To make an example of pseudo-components imagine that there are two components, X_1 and X_2, which make up a mixture of 50 ml. X_1 has a lower bound of 20 which makes the upper bound of X_2 to 30. *Table 3.1* shows a few data points transformed [22].

Table 3.1: Example of a two-component system transformation into pseudo-components.

Amounts		Proportions		Pseudo-components	
X_1	X_2	X_1	X_2	X_1	X_2
50	0	1.0	0.0	1.0	0.0
20	30	0.4	0.6	0.0	1.0
35	15	0.7	0.3	0.5	0.5

To analyze which subset of terms are significant to the model stepwise regressions can be used. The method specified can be further selected into forward selection. Forward selection starts with an empty model or includes terms that are specified to be included in the initial model. Afterwards, Minitab adds the most significant term for each step, stopping when all variables not in the model have p-values that are greater than the specified alpha to enter value [24].

Large standardized residuals are addressed by Minitab as unusual observations. These observations deviate from the rest of the data and can in some cases lead to producing misleading results. Unusual observations are when the standardized residuals are outside of the interval between -2 and 2 [25]. It is however expected to get a few unusual observations.

3.6.3 Mixture contour plot

Mixture contour plot divides the experimental area in different contours depending on how the response is. It is possible to add more contours to make it more precise and from the mixture contour plot it is easy to interpret what the expected response is from a given mixture.

4 Materials

4.1 Mill-base Chemicals

For the formulation of pigment dispersions containing acrylates there are several different monomers and oligomers that can be used. Oligomers with different functionality and different properties can all come into play when formulating a good dispersion. For the chemicals used in this study, see *Table 4.1*. Note that binders, oligomers and resins are used interchangeably and refer to the same types of chemicals.

Table 4.1: Mill base chemicals used for making pigment dispersions.

	Molecular weight (g/mole)	Theoretical functionality	Viscosity
Monomers			
Tripropylene Glycol Diacrylate (TPGDA)	300	2	10-20 mPa*s (25°C)
Oligomers/binders			
Four Functional Polyester acrylate	1100	4	1500-2100 mPa*s (23°)
Modified bisphenol A epoxy diacrylate	850	2	3300-5000 mPa*s (65.5°)
Fatty acid modified hexa-functional polyester acrylate	1200	6	9000 mPa*s (23°)
Dispersing agents			
Structured copolymer with pigment affinic groups	No data	No data	8600 mPa*s (50°)
Polyacrylate with pigment affinic groups	No data	No data	No data

TPGDA is the only monomer used in this study due to that is a good diluent with a low surface tension of 34 mN/m at 25℃ [26].

4.2 Pigments

The pigments used for the Daniel flow point method and the design of experiment were Pigment red 2 and Pigment red 122. Pigment red 2 also goes under the name 4-[2,5Dichloro-phenyl) azo]-3-hydroxy-N-phenylnaphthalene-2-carboxamide and can be seen in *Figure 4.1* [27]. The oil absorption for the Pigment red 2 that was used is 52 grams oil/100grams.
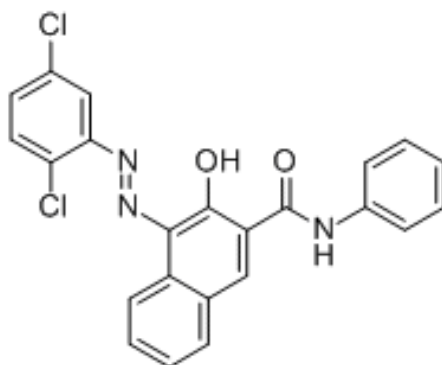

Figure 4.1: Chemical structure of Pigment red 2 [28].

Pigment red 122 goes under the chemical name 2,9-dimethyl-5,12-dihydroquinolino[2,3-b] acridine-7,14-dione and can be seen in *Figure 4.2* [29]. The oil absorption for Pigment red 122 that was used is 40-60 grams/100grams.
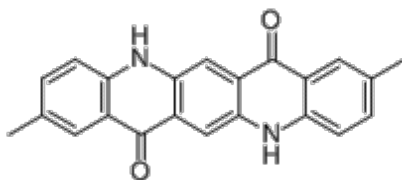

Figure 4.2: Chemical structure of Pigment red 122 [30].

5 Methods

5.1 Daniel flow point method

The Daniel flow point method was applied to two different pigments, Pigment red 2 and Pigment red 122 using three oligomer binders, a modified bisphenol A epoxy diacrylate, a four functional polyester acrylate and a fatty acid modified hexa-functional polyester acrylate. The monomer used in all Daniel flow point tests was TPGDA.

The resin concentrations used when applying the Daniels flow point method was between 10-60 %, at 10 % intervals. The rest of the solution constituted of TPGDA. The amount of pigment used was 20 g which was added to a 250 ml container. Typically, a 100 ml container is used, however a 250 ml container was used for pigment red 2 and Pigment red 122 due to that the bulk density is very low and the dry pigment therefor did not fit in any smaller container. The resin solution was then added carefully, first 20 g followed by 2 g additions until the flow point was observed. In between each addition the sample was stirred vigorously by using a stainless steel spatula. The optimum ratios where then further used in the design of experiment.

5.2 Design of experiment

For the design of experiment, the differences between the experiments of pigment red 2 and pigment red 122 are the boundaries of the different components, which each can be viewed in their separate sections.

5.2.1 Design of experiment using Pigment red 2

For the design of experiment of pigment red 2 dispersions a mixture design of the type extreme vertices was used. In this design three components where set up with upper and lower constraints, see *Table 5.1*.

Table 5.1: Upper and lower bounds of the design of experiment for Pigment red 2.

Component	Lower bound (g)	Upper bound (g)
Mixture of monomer/oligomer(s)	125	150
Pigment	80	100
Dispersing agent	12.5	25

The mixture of monomer/oligomer(s) are a direct result from the optimum mixtures found from the Daniel flow point method. For the exact ratios for the mixture see Section 6.1.3. The dispersing agent used was the structured copolymer with pigment affinic groups mentioned in *Table* 4.1.

In Minitab 17 these lower and upper bounds were inserted, the number of components being three. The runs where randomized meaning that there was no specific order in running the data collection and Minitab 17 provided the run order. The degree of the design was set to two, which allows fitting a quadratic regression to the model. The initial design space had 16 data points for collection of data, however five additional points and two replicates where

added to fill in some gaps of the design space. The design space is represented in a simplex design plot in *Figure 5.1*.
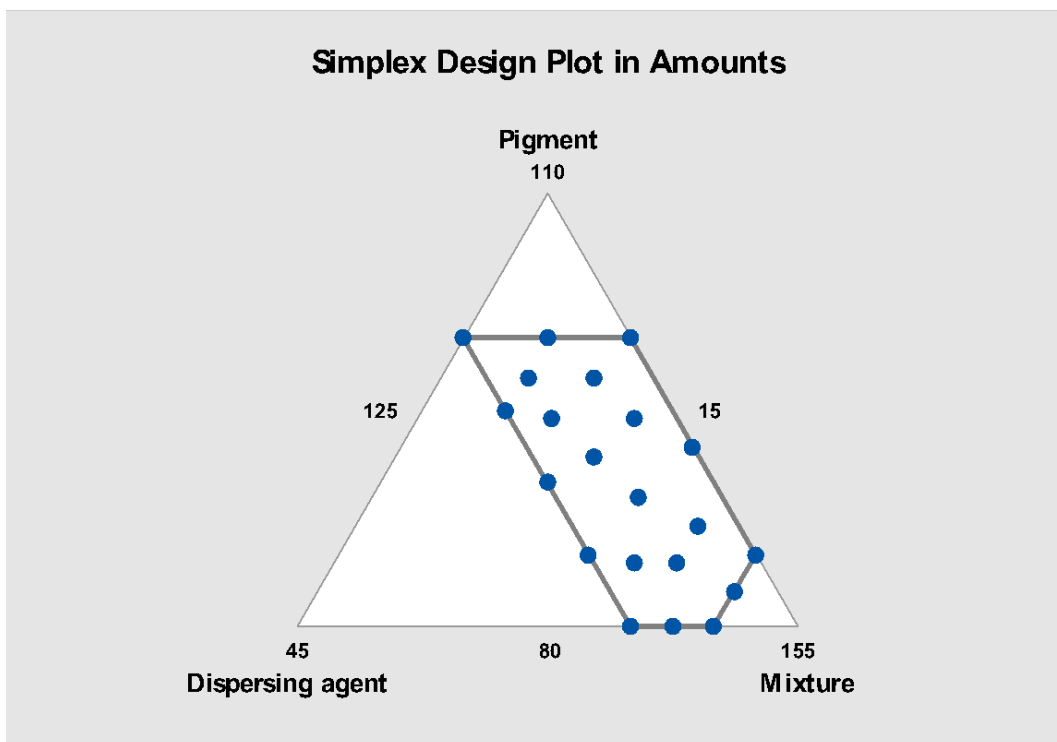

Figure 5.1: Simplex design plot of the design of experiment for Pigment red 2. Each circle represents a data collection point.

In the simplex design plot there are a total of 21 blue circles which represent the points from where data is collected. The grey lines are bound together by the upper and lower boundaries for each component. These 21 data collection points are represented in Appendix 10.2.1.

The processing time variables where the processing time of pigment processed in the three-roll mill in grams/min and the viscosity of the processed dispersion at a shear rate of $50s^{-1}$. The processed dispersion was also checked with a grind gage, see Section 5.4, to ensure a high quality dispersion.

5.2.2 Design of experiment using Pigment red 122
For the design of experiment of pigment red 122 dispersions a mixture design of the type extreme vertices was used. In this design three components where set up with upper and lower constraints, see *Table 5.2*.

Table 5.2: Upper and lower bounds of the design of experiment for Pigment red 122.

Component	Lower bound (g)	Upper bound (g)
Mixture of monomer/oligo-mer(s)	125	150
Pigment	80	95
Dispersing agent	20	30

The mixture of monomer/oligomer(s) are a direct result from the optimum mixtures found from the Daniel flow point method for Pigment red 122, see Section 6.2.3. The dispersing agent used was of the polyacrylate type dispersing agent mentioned in *table* 4.*1*.

In Minitab 17 these lower and upper bounds where inserted and just as for the Pigment red 2 design of experiment the runs were randomized. The degree of the design was set to two, just as for the Pigment red 2 design of experiment. The design space had 13 data points for collection of data. The design space is represented in a simplex design plot in *Figure 5.2*.
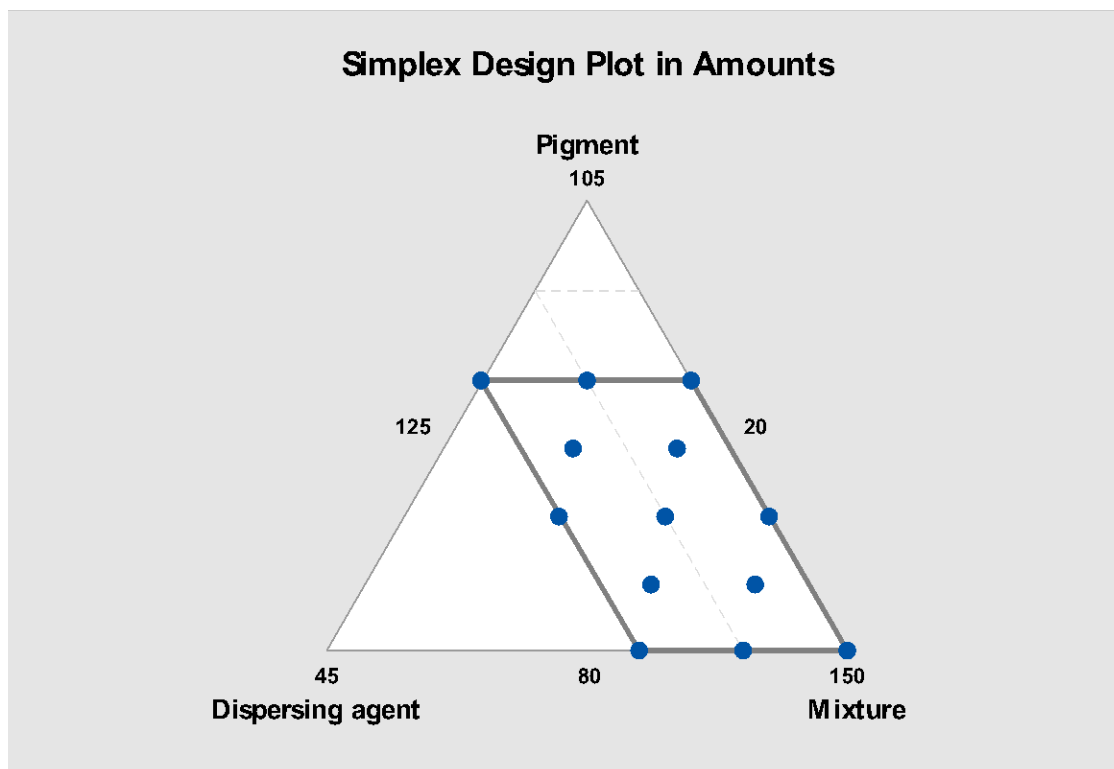
Figure 5.2: Simplex design plot of the design of experiment for Pigment red 122.

In the simplex design plot there are a total of 13 blue circles which represent the points from where data is collected. These 13 data collection points are represented in Appendix 10.2.2.

The processing time variables where the processing time of pigment processed in the three-roll mill in g/min and the viscosity of the processed dispersion at a shear rate of $50s^{-1}$. The processed dispersion was also checked with a grind gage, see Section 5.4 to ensure a high quality dispersion.

5.3 Premixing and three-roll milling

The sample size for pre-mixing and three-roll mill was 250g. The samples where weighed up according to the recipes in Appendix 10.2.1 and 10.2.2. For pre-mixing a dissolver blade, see *Figure 5.3*, with a diameter of 0.06 m was used. The dissolver was then run at 1400 RPM for 15 minutes to get a good pre-mix before loading to the three-roll mill. The peripheral velocity at 1400 RPM can be calculated according to *Equation 3.6* to 4.398 m/s.

Figure 5.3: High speed disc impeller used for pre-mixing of pigment dispersions.

After premixing the samples were processed using a three-roll mill with rolls having a diameter of 150 mm and a length of 300 mm. The revolutions per minute (RPM) of the different rolls where the following: 34.1 RPM for the feed roll, 101 RPM for the center roll and 212 RPM for the apron roll. These RPM values where measured using a tachometer. The pressure applied between the rolls was 13 bar and the knife pressing against the apron roll was pressed with a pressure of 10 bar. The dispersion was passed three times through the three-roll mill to ensure a dispersion of high quality.

5.4 Grind gage

Once the pigment dispersion had been processed through the three-roll mill the quality of the dispersion was checked using a grind gage, see *Figure 5.4*. Using a spatula, a sample is placed at the deep end of the grove (25µm) and then, by using a scraper, the sample is drawn down to the minimum depth of the grove. The grind gage is the held up so that oversized particles can be viewed. Characteristic lines are formed where the oversized particles start dragging against the grind gage.

Figure 5.4: Grind gage which can show particles from 0-25 μm.

5.5 Viscosity measurements

The measurements of rheological properties were measured using an Anton Paar Physica MCR101 cone and plate rheometer. The cone used was a CP25-1 cone which is a cone with a diameter of 25 mm and a degree of 1°. The measurement position used was 0.048 mm as indicated by the supplier. During the measurements the temperature was held constant at 23 °C with a tolerance of ±0.1 °C.

The sample was loaded onto the plate and the initial shear rate was 0 s^{-1}. The shear rate was then ramped up to 50 s^{-1} over a period of 50 s, where data points were collected every second. Once a shear rate of 50 s^{-1} was reached, constant shear rate was applied over 120 s and data points collected every 6 s. The shear rate was then ramped down back to 0.1 s^{-1} over a period of 50 s where data points were taken every second.

The samples were all rested for 24 hours before subjected to the viscosity measurements, this to ensure that accurate results of the thixotropy could be observed. Due to the high shear forces in the three-roll mill performing a measurement directly after grinding could interfere with obtaining the correct thixotropic loop.

5.6 External testing of pigment and resin with the sorption method at Krüss

For the testing of the rate of sorption, pigment red 2 was tested using TPGDA and a solution containing 80% TPGDA and 20% of the four functional polyester acrylate. These tests were conducted externally at Krüss where they used a force tensiometer.

6 Results

6.1 Daniel flow point method results for Pigment red 2

The Daniel flow point method was applied to three different resins, see method Section 5.1. There were quite large differences between the three resins, especially for the six functional fatty acid polyester acrylate, which showed no sign of stabilization of the pigment, see Appendix 10.1. For the two and four functional acrylates there are signs of stabilization and these were further used in the design of experiment.

6.1.1 Daniel flow point method with modified bisphenol A epoxy diacrylate

The results for the Daniel flow point method using the modified bisphenol A epoxy diacrylate gives the optimum monomer/oligomer ratio close to 40 wt. % oligomer, see *Figure 6.1*.

Figure 6.1: Daniel flow point method using a modified bisphenol A epoxy acrylate and pigment red 2.

From *Figure 6.1* it is clear that the optimum lies close to 40 wt. % oligomer, for the design of experiment a ratio of 45% is used due to the high stabilization effect coming from this resin. The curve forms a U-shape character which is typical if the resin has a stabilizing effect.

6.1.2 Daniel flow point method with a four functional polyester acrylate

The results when using a four functional polyester acrylate are quite different from the modified bisphenol A epoxy diacrylate, see *Figure 6.2*.

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Figure 6.2: Daniel flow point method using a four functional polyester acrylate and Pigment red 2.

From *Figure 6.2* it is hard to say where the optimum lies due to small variations between 20-60 wt. %. There is also no increase in solution needed at higher concentrations as it was for the modified bisphenol A epoxy diacrylate which is why no U-shape curve can be observed. There is however a decrease in grams of solution needed to reach a flow point and therefore 20 wt. % is used in the design of experiment. A higher concentration is not used due to the increase in mill-base viscosity.

6.1.3 Optimum oligomer ratios for design of experiment Pigment red 2

The mixture used in the design of experiment is a direct result from the Daniel flow point method results for the modified bisphenol A epoxy diacrylate and the four functional polyester acrylate. These ratios were then combined to give the final composition of the mixture, see *Equation 6.1*.

$$\frac{A}{A+B} = 0.45 \text{ And } \frac{C}{C+B} = 0.20 \tag{6.1}$$

Where A is the modified bisphenol A diacrylate, B is TPGDA and C is the four functional polyester acrylate.

6.2 Results Daniel flow point method Pigment red 122

The Daniel flow point method was applied to three different resins, the same resins as with pigment red 2, see method Section 5.1. There were differences between the three different resins, however not as large as for Pigment red 2. The six functional fatty acid polyester acrylate showed no sign of stabilization of pigment red 122, see Appendix 10.1. For the two and four functional acrylates there are signs of stabilization and these were further used in the design of experiment.

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6.2.1 Daniel flow point method with modified bisphenol A epoxy diacrylate

The results for the Daniel flow point method using the modified bisphenol A epoxy diacrylate gives the optimum monomer/oligomer ratio of 40 wt.% oligomer, see *Figure* 6.3.
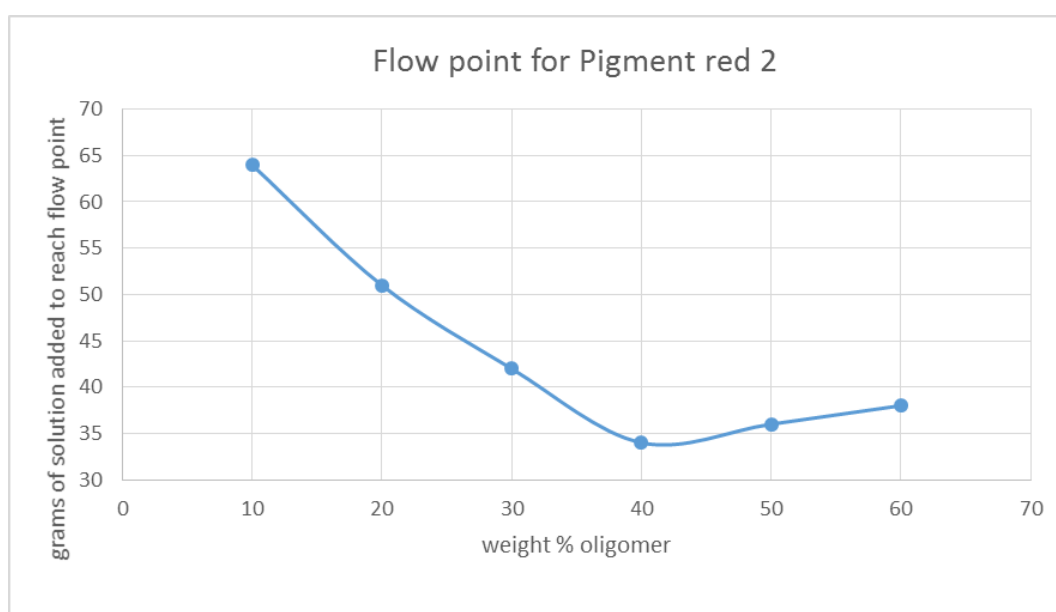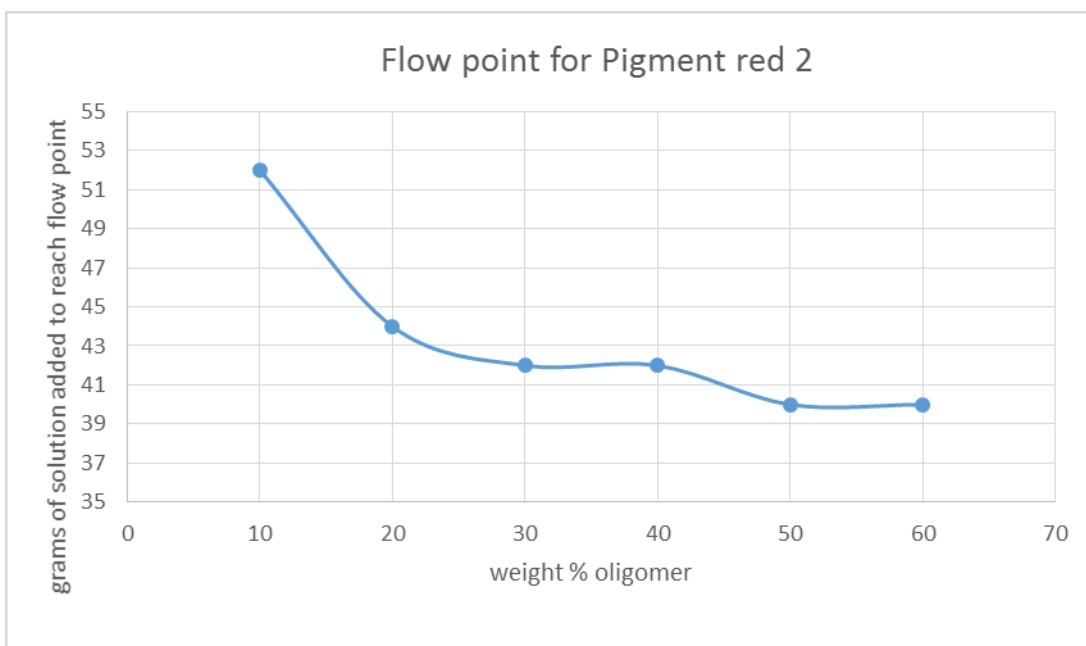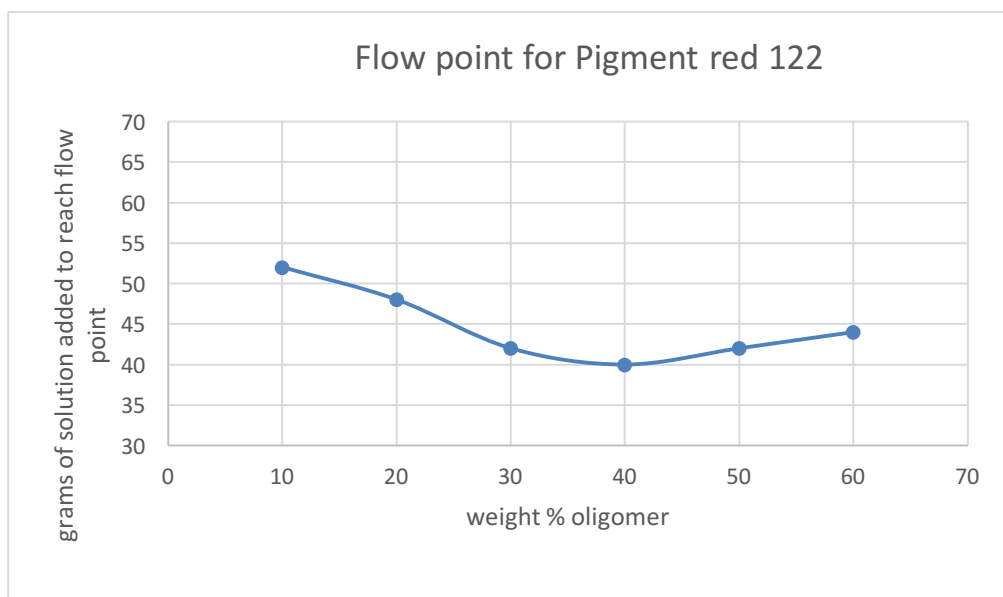

Figure 6.3: Daniel flow point method using a modified bisphenol A epoxy diacrylate with Pigment red 122.

From *Figure 6.3* the optimum lies at 40 wt. % oligomer, and this ratio is then used for the design of experiment. It is possible to see the trend of a U-shape curve, however slightly, for the modified bisphenol A epoxy acrylate.

6.2.2 Daniel flow point method with a four functional polyester acrylate
The results when using a four functional polyester acrylate are quite different from the modified bisphenol A epoxy diacrylate, see *Figure 6.4*.

Figure 6.4: Daniel flow point for the four functional polyester acrylate and Pigment red 122.

From *Figure 6.4* it is hard to say where the optimum lies, just as it was for pigment red 2. The grams of solution needed decrease slightly with increasing concentration. A concentration of 40 wt. % is used in the design of experiment of pigment red 122, as a higher concentration would lead to a higher increase in mill base viscosity.

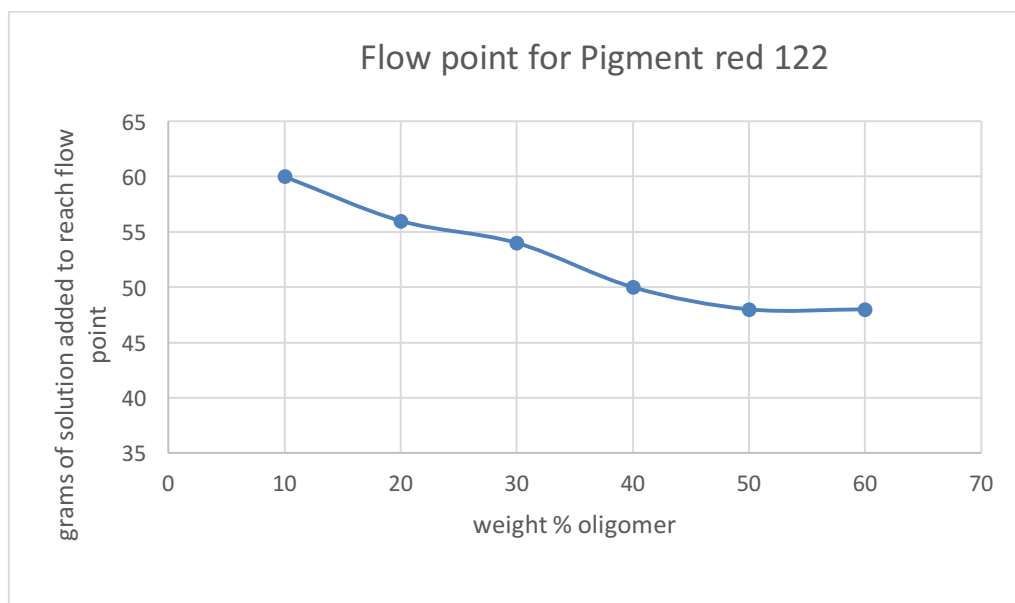### 6.2.3   Optimum oligomer ratios for design of experiment Pigment red 122

As the case was for Pigment red 2, the six functional fatty acid polyester acrylate showed no sign of stabilization and therefore the modified bisphenol A diacrylate and the four functional polyester was used for the design of experiment of Pigment red 122. The ratios can be viewed in *Equation 6.2*.

$$\frac{A}{A+B} = 0.40 \text{ And } \frac{C}{C+B} = 0.40 \qquad\qquad (6.2)$$

Where A is the modified bisphenol A diacrylate, B is TPGDA and C is the four functional polyester acrylate.

6.3   Results Design of experiment for Pigment red 2

Once all the collection of data was completed analyzation of the results in Minitab 17 was done to evaluate the influence of the components to the processing time variables. To run the analysis, the components where analyzed in their pseudo components and the model fitting method was set to forward selection. To enter the model, the components needed to achieve an alpha-level of 0.25. Once the regression had been done the p-values, R-sq, R-sq (pred), and the residual plots where evaluated to see if any terms were insignificant. The insignificant terms were then eliminated from the model to obtain the final fitting.

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6.3.1 Processing time model for Pigment red 2

The results for the processing time experiment done with the mixture design of pigment red 2 gave a model that can then be illustrated by using a mixture contour plot, see *Figure 6.5*.
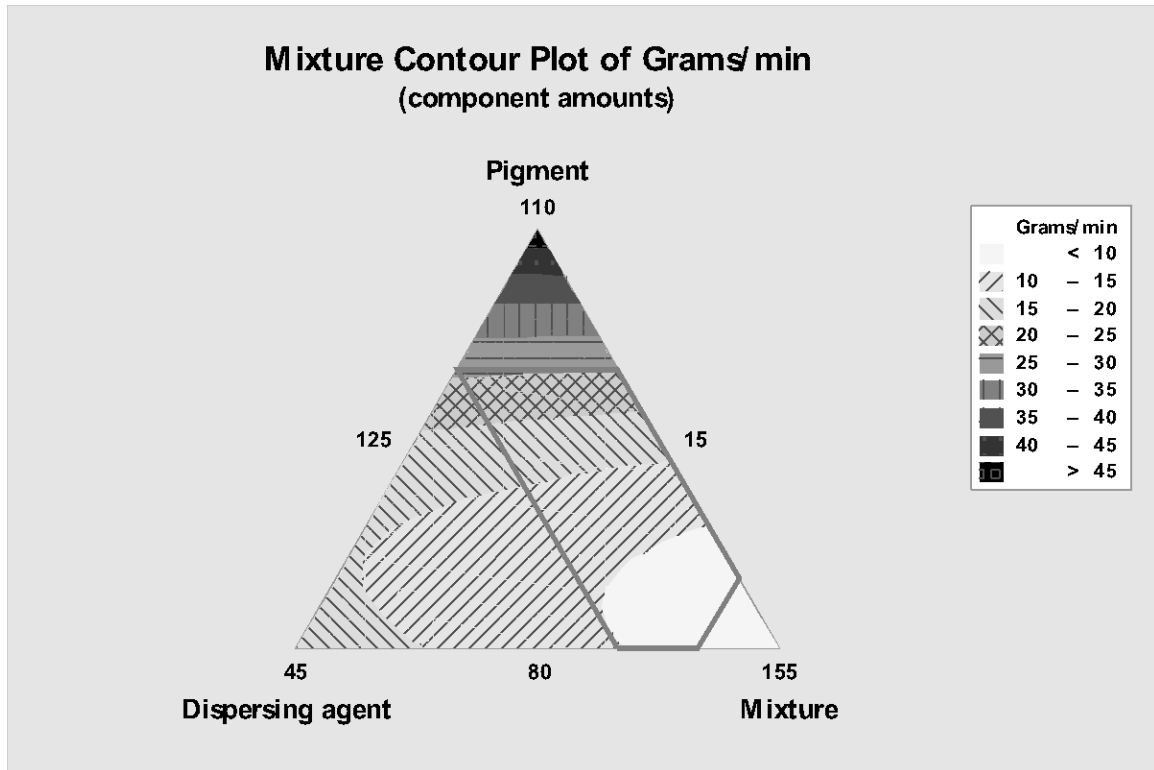
Figure 6.5: Mixture contour plot for the design of experiment, showing processing time in grams/min.

From the surface of the mixture contour plot it is clearly visible that increasing pigmentation level increases the processing time. There are however other factors that need to be taken into consideration such as how the dispersions rheology is. Too high pigmentation leads to higher thixotropy and eventually to build up on the knife *table*, which is an unwanted effect.

The following results for the P-values of the terms that entered the model and giving the best fit can be seen in *Table 6.1*.

Table 6.1: Terms that entered the model for processing time.

Component	P-value
Pigment*dispersing agent	0.1140
Pigment*mixture	0.04000

It is clear that Pigment*Mixture is a significant term in the model. The term Pigment*Dispersing agent has a p-value which is above 0.05, it is however kept in the model due to the fact that it contributes with a better model fit, and the residuals suggest that it is kept in the model.

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To see how well the model fits the collected data the model fitting values can be found in *Table 6.2*.

Table 6.2: *Model fitting values for processing time, design of experiment for pigment red 2.*

S-value	3.659
R-sq	76.79%
R-sq(pred)	63.95%

The model fitting values from *Table 6.2* suggest that we have a decent fit to the collected data points. The residuals for the analyzation can be viewed in Appendix 10.3. It is also significant to check the residuals with a normality test, see *Figure 6.6*, to see if the residuals follow a normal distribution or not.
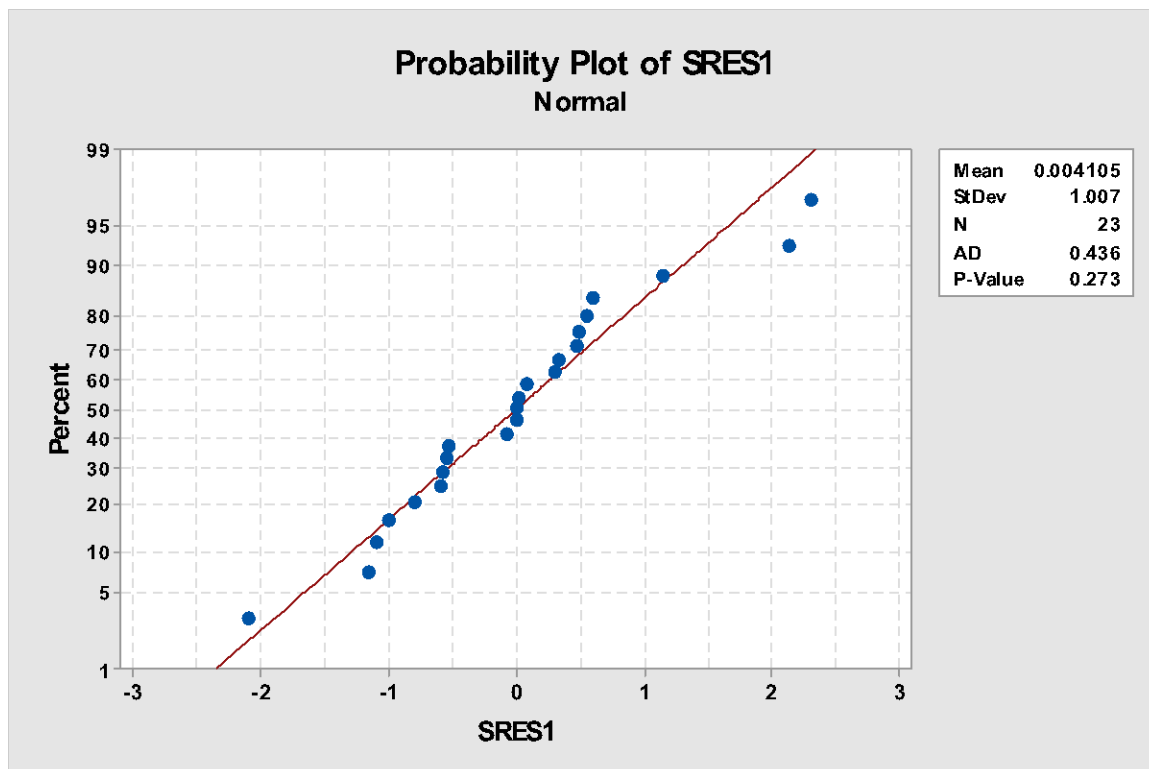
Figure 6.6: Normality test done in Minitab 17 for the processing time residuals.

From the normality test in *Figure 6.6* a p-value of 0.273 is obtained. The null-hypothesis for this test is that the residuals are normally distributed. As this p-value is >0.05 the null-hypothesis can not be discarded, and therefore the residuals can still be normally distributed.

From the residuals Minitab flags three of these for being unusual observations, these can also be seen in *Figure 6.6* and are just outside the interval between -2 and 2.

6.3.2   Viscosity model for Pigment red 2

The design of experiment viscosity results for pigment red 2 can just as with the processing time easily be visualized with a mixture contour plot, see *Figure 6.7*.

26
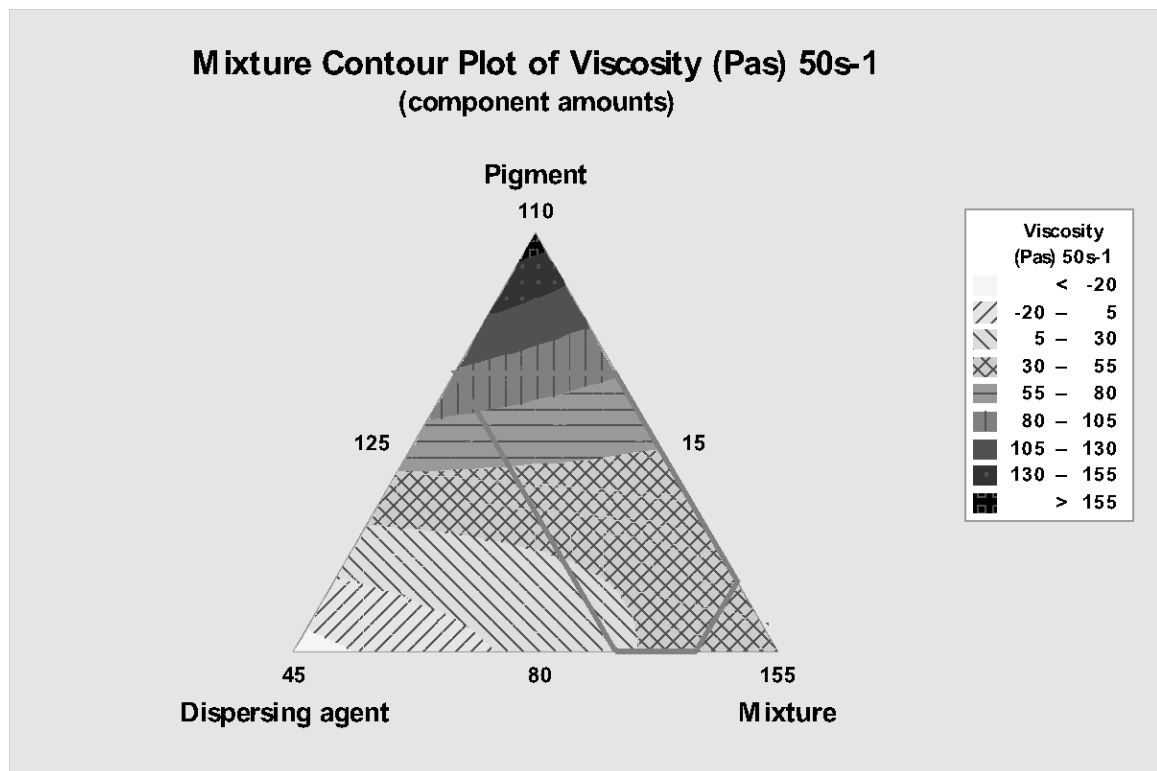
Figure 6.7: Mixture contour plot for the design of experiment, showing viscosity in Pa*s at a shear rate of 50 s⁻¹.

As in the case for processing time the increase of pigment also increases the viscosity. It is however favorable to have a low viscosity with high pigment concentration to allow greater flexibility when formulating the final ink. It is then necessary to determine what suits best for the final ink and how the formulation of the dispersion should look like to give both acceptable viscosity and processing time.

The following results for the P-values of the terms that entered the model and giving the best fit can be seen in *Table 6.3*.

Table 6.3: Terms that entered the model for viscosity.

Component	P-value
Pigment*mixture	0.000

From *Table 6.3* it is very clear that the Pigment*Mixture component is highly significant.

To see how well the model fits the collected data the model fitting values can be found in *Table 6.4*.

Table 6.4: Model fitting values for viscosity, design of experiment Pigment red 2.

S-value	8.917
R-sq	86.61 %
R-sq(pred)	79.65 %

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The model fitting values for the viscosity results have a better fit than the ones for the processing time. The residuals for the viscosity results can be seen in Appendix 10.4. Results from the normality test for the viscosity residuals can be viewed in *Figure 6.8*.
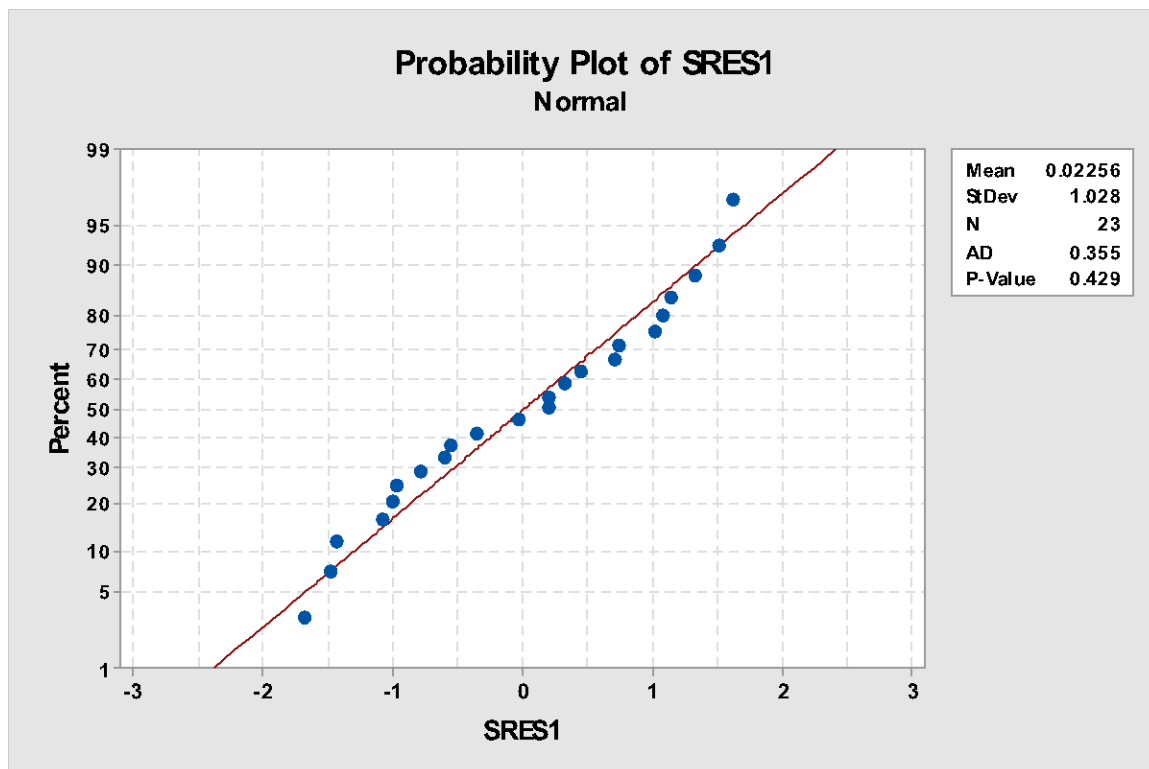
Figure 6.8: Normality test for the viscosity residuals.

From the normality test in *Figure 6.8* the p-value comes out as 0.429. The null-hypothesis for this test is that the residuals are normally distributed. As this p-value is >0.05 the null-hypothesis can not be discarded, and therefore the residuals can still be normally distributed.

From *Figure 6.8* it is also clear that all the residuals are in between the interval -2 and 2 which means that for the viscosity there are no unusual observations.

6.3.3   Pigment red 2 - Future prediction of model and thixotropic loops

To test the prediction of new data from the model a 1kg sample was tested. The formulation for 250g can be seen in *Table 6.5* and this recipe was multiplied by a factor 4.

Table 6.5: Formulation of the predicted sample from the design of experiment.

Component	Amount (g)
Pigment	91.20
Dispersing agent	25.00
Mixture monomer/oligomer(s)	133.8

From the fitted model the expected viscosity comes out to 44.58 Pa*s and the expected processing time to 14.47 grams/min. After the same processing procedure as for all other dispersions the viscosity ended up at 49.10 Pa*s, with the processing time of 16.46 grams/min. These values are slightly higher than the predicted ones, however they are both within the limits of the corresponding S-value for the models.

The thixotropic loop measurements were conducted on all samples, however the most interesting one is the predicted sample. Alongside the predicted sample it is also of interest to look at a sample showing high thixotropy and one showing low thixotropy, sample 4 and 14 respectively. These thixotropic loops can be viewed in *Figure*s *6.9* and *6.10*.
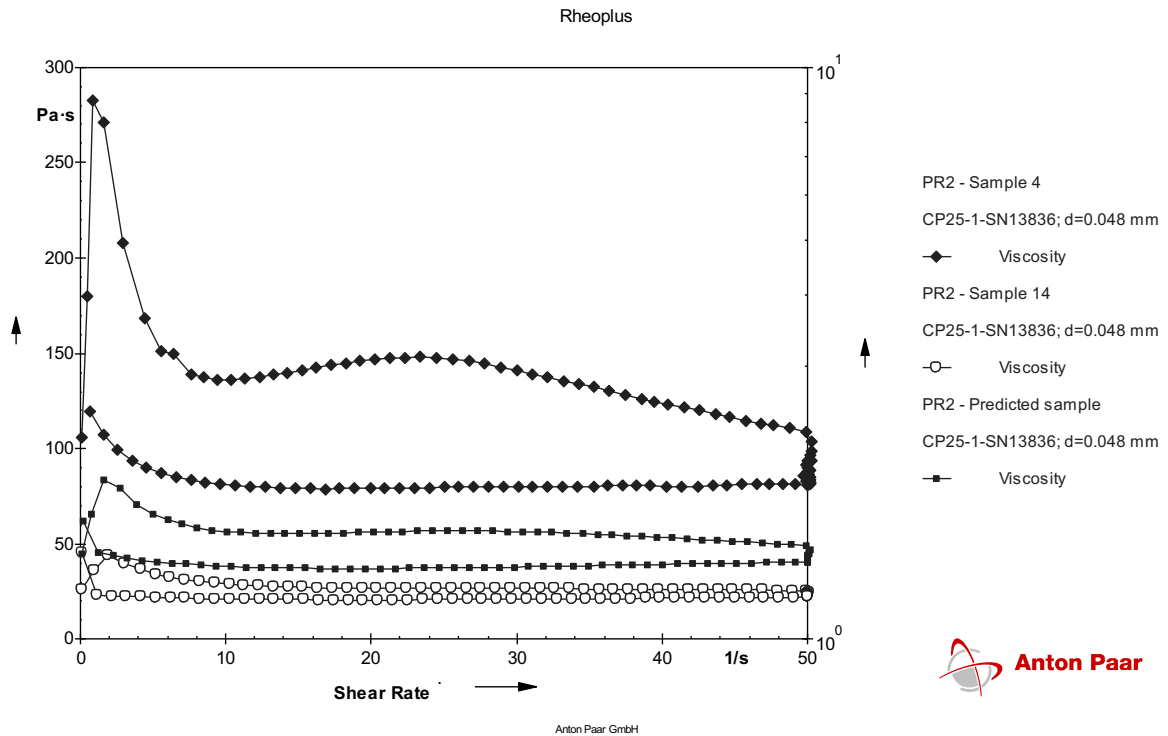
Figure 6.9: Thixotropic loop, shear rate vs viscosity, for three different samples, sample 4, predicted sample and sample 17. Shear rate given in the unit s^{-1} and viscosity given in Pa*s.
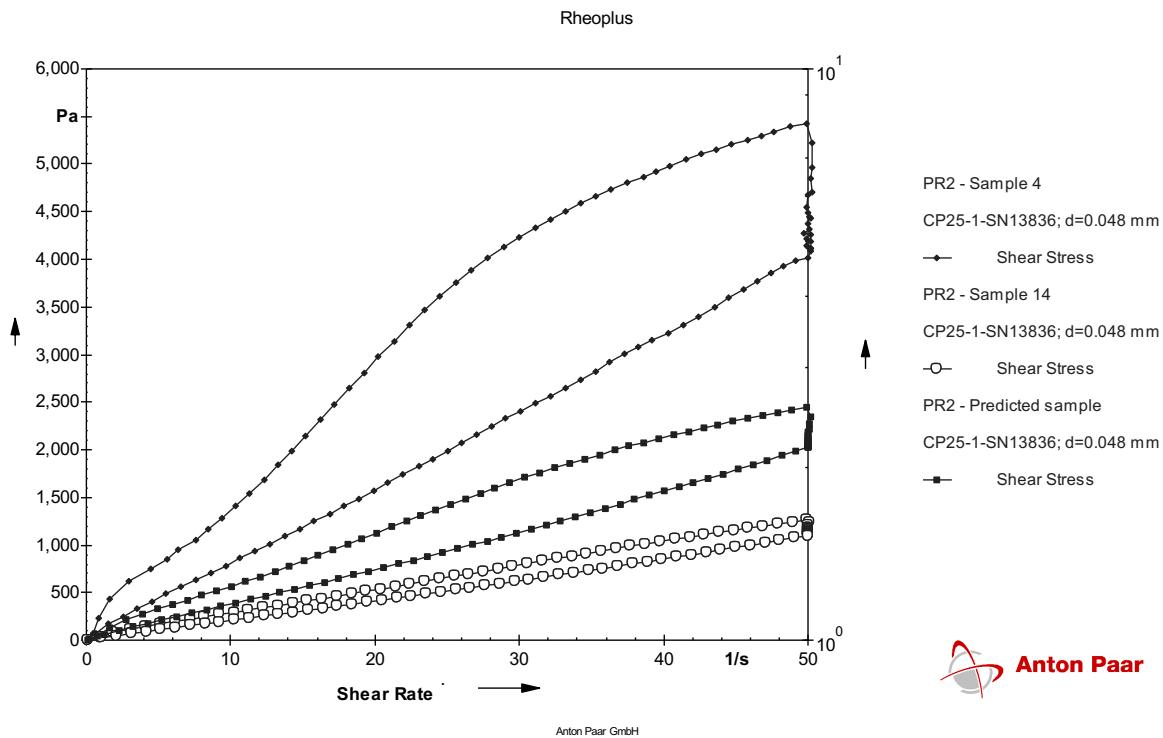
*Figure 6.10: Thixotropic loop, shear rate vs shear stress, for three different samples, sample 4, sample predicted and sample 17. Shear rate given in the unit s^{-1} and viscosity given in Pa*s.*

From *Figures 6.9* and *6.10* it is clear that sample 4 has the highest thixotropy followed by the predicted sample and then sample 14. For the viscosities and processing time for all the samples, see Appendix 10.5.

6.4   Results design of experiment Pigment red 122

Once all the collection of data was completed analyzation of the results in Minitab 17 was done to evaluate the influence of the components to the processing time variables. To run the analysis the components where analyzed in their pseudo components and the model fitting method was set to forward selection. To enter the model, the components needed to achieve a α-level of 0.25. Once the regression had been done the p-values, R-sq, R-sq (pred) and the residual plots where evaluated to see if any terms were insignificant.

6.4.1   Processing time model for Pigment red 122
The results for processing time from the mixture design of pigment red 122 are illustrated by a mixture contour plot, see *Figure 6.11*.
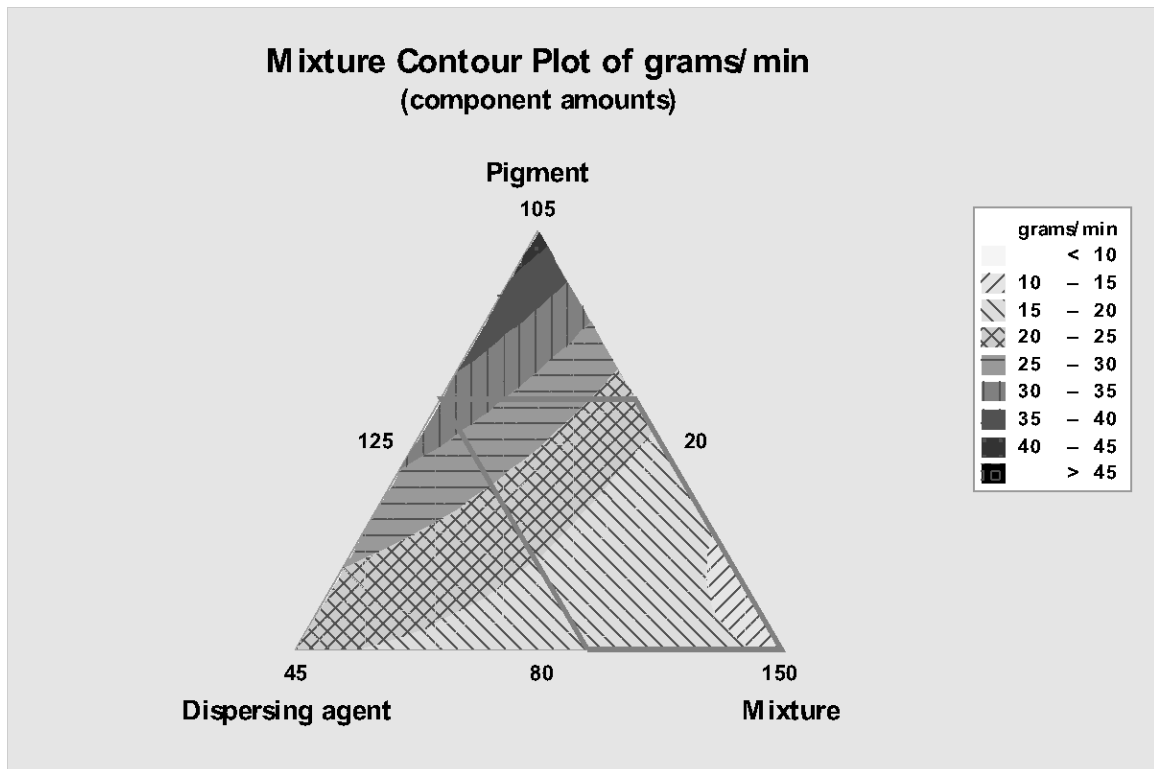
Figure 6.11: Mixture contour plot for the processing time in grams/min for the design of experiment on Pigment red 122.

From the surfaces of the mixture contour plot it is clearly visible that by increasing pigmentation level the processing time increases, just as the case was for pigment red 2. Just as with the pigment red 2, too high pigmentation levels lead to bad rheology. There is also a trend from *Figure 6.11* that increasing the dispersing agent level increases the processing time for pigment red 122. This could have to do with that a different dispersing agent was used that was more viscous than the one used for Pigment red 2.

The following results for the P-values of the terms that entered the model and giving the best fit can be seen in *Table 6.6*.

Table 6.6: P-values for the components that entered the model.

Component	P-value
Pigment*mixture	0.033

It is clear that Pigment*Mixture is a significant term in the model. The term Pigment*Dispersing agent which entered the Pigment red 2 model does not enter the pigment red 122 model. This could be because a different dispersing agent was used.

To see how well the model fits the collected data the model fitting values can be found in *Table 6.7*.

Table 6.7: Model fitting values for processing time of Pigment red 122.

S-value	2.759
R-sq	84.98%
R-sq(pred)	73.13%

The model fitting values from *Table 6.7* suggest that we have a decent fit to the collected data points. These values are better than the ones for the Pigment red 2 model. The residuals for the analyzation can be viewed in Appendix 10.6. It is also significant to check the residuals with a normality test, see *Figure 6.12*.
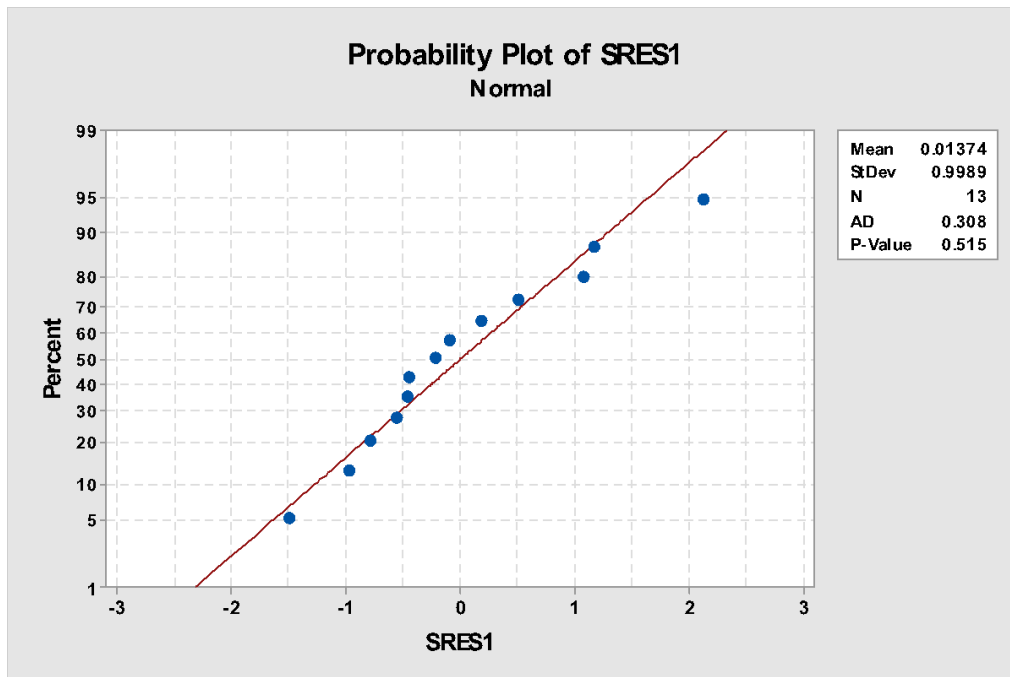
Figure 6.12: Normality test of the processing time residuals for Pigment red 122.

From the normality test in *Figure 6.12* a p-value of 0.515 is obtained. The null-hypothesis for this test is that the residuals are normally distributed. As this p-value is >0.05 the null-hypothesis can not be discarded, and therefore the residuals can still be normally distributed.

From the residuals Minitab flags one of these for being unusual observations, this point can be seen in *Figure 6.12* and is the point laying just outside the value 2 on the x-axis.

6.4.2 Viscosity model for Pigment red 122

The design of experiment viscosity results for pigment red 122 can just as with the processing time easily be visualized with a mixture contour plot, see *Figure 6.13*.
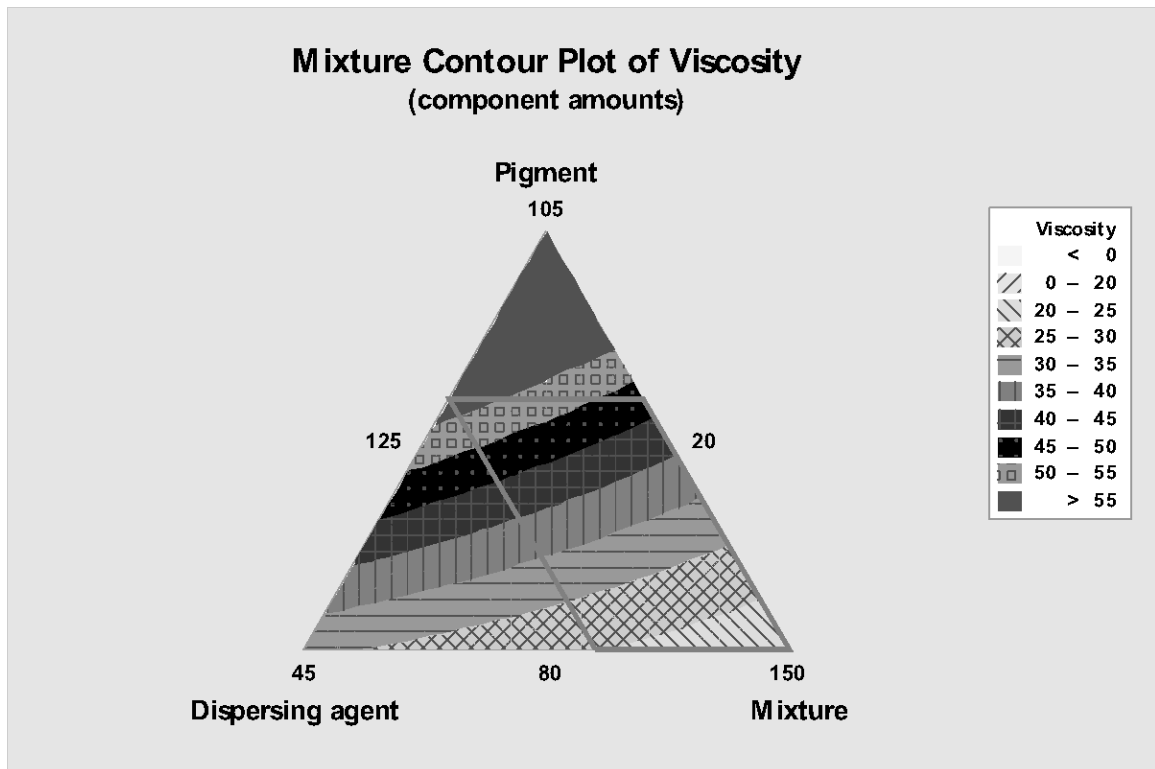
Figure 6.13: Mixture contour plot for Pigment red 122 with the response variable viscosity in Pa*s at a shear rate of 50 s^{-1}.

As in the case for processing time the increase of pigment also increases the viscosity. An interesting fact is that a higher processing time for pigment red 122 is observed when comparing to the same viscosity for pigment red 2. This could be due to the fact that the chemical composition of the pigments are different but also with differences in tackiness of the mill-base.

The following results for the P-values of the terms that entered the model and giving the best fit can be seen in *Table 6.8*.

Table 6.8: P-values for components that entered the model for pigment red 122.

Component	P-value
Pigment*mixture	0.059

From *Table 6.8* the Pigment*Mixture component is the only one close to a p-value of 0.05 and is therefore kept in the model.

To see how well the model fits the collected data the model fitting values can be found in *Table 6.9*.

Table 6.9: Model fitting values for the response variable viscosity for Pigment red 122.

S-value	2.245
R-sq	97.30%
R-sq(pred)	94.64%

33

The model fitting values for the viscosity have higher accuracy than for the processing time fitting values, just as the case was for pigment red 2. The residuals for the viscosity results can be seen in Appendix 10.7. Results from the normality test for the viscosity residuals can be viewed in *Figure 6.14*.
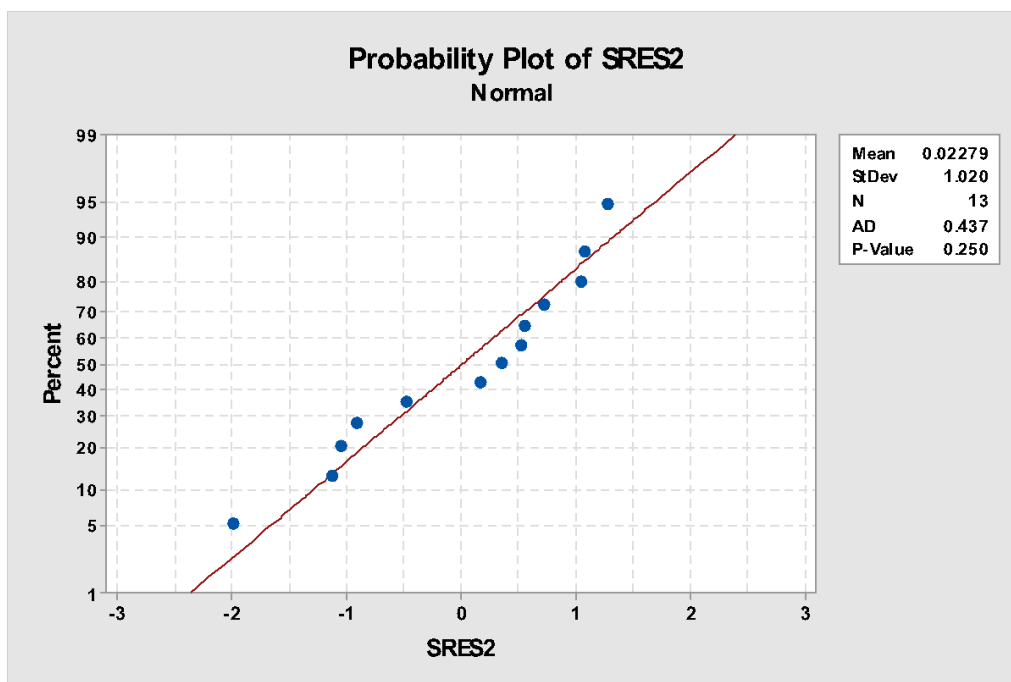

Figure 6.14: Normality test for viscosity residuals for Pigment red 122.

From the normality test in *Figure 6.14* the p-value comes out to 0.250. The null-hypothesis for this test is that the residuals are normally distributed. As this p-value is >0.05 the null-hypothesis cannot be discarded, and therefore the residuals can still be normally distributed.

From *Figure 6.14* it is also clear that all the residuals are in between the interval -2 and 2 which means that for the viscosity residuals of pigment red 122 there are no unusual observations.

6.4.3   Pigment red 122 – Future prediction and thixotropic loops
To test the prediction of new data from the model a 1kg was tested. The formulation for 250g can be seen in *Table 6.10* and this formulation was then multiplied by a factor 4.

Table 6.10: recipe for the predicted sample of Pigment red 122.

Component	Mass (g)
Pigment	89.50
Dispersing agent	30.00
Mixture monomer/oligomer(s)	130.5

From the fitted model the expected viscosity comes out to 43.04 Pa*s and the expected processing time to 24.35 grams/min. After the same processing procedure as for all other dispersions the viscosity came out to be 43.80 Pa*s, with the processing time of 22.98 grams/min. The value for the viscosity is slightly higher and the value for processing time slightly lower, however they are both within the limits of the corresponding S-values for the models.

The thixotropic loops for Pigment red 122 all show some degree of thixotropic behavior, just as the case was for Pigment red 2. Three thixotropic loops for Pigment red 122 dispersions can be viewed in *Figures 6.15* and *6.16*.
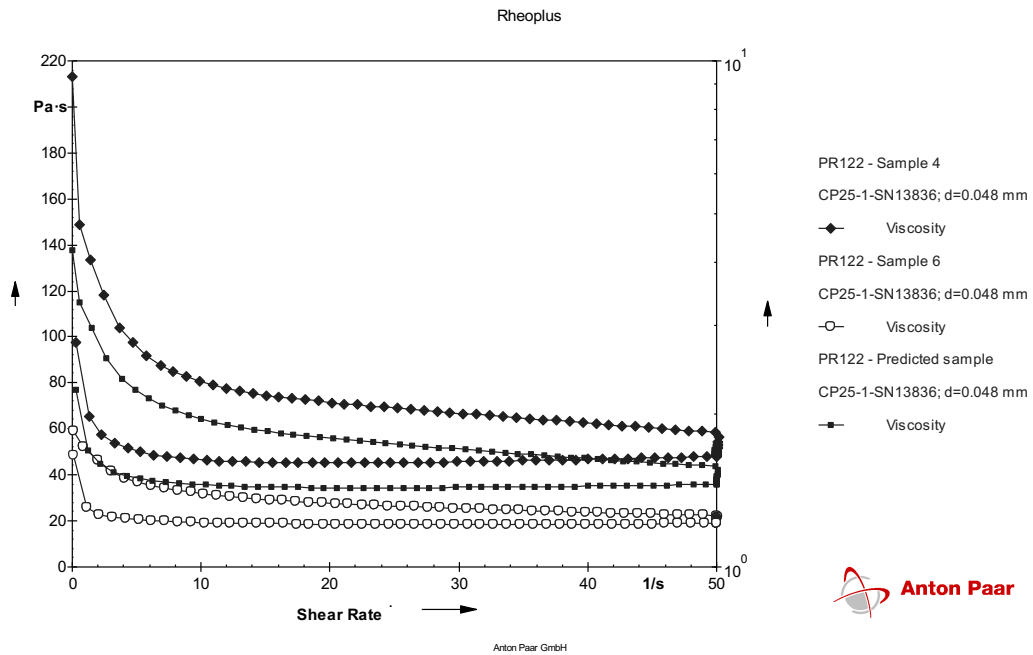
Figure 6.15: Thixotropic loops showing shear rate vs viscosity for Pigment red 122 dispersion samples 4, 6 and predicted. Shear rate given in the unit s^{-1} and viscosity given in Pa*s.
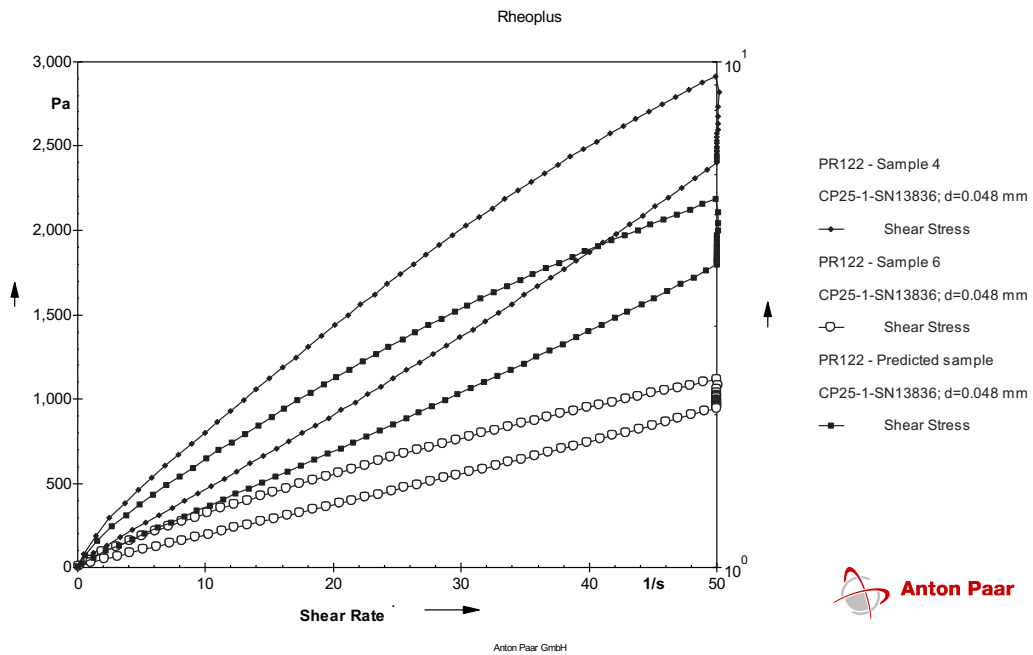
Figure 6.16: Thixotropic loops showing shear rate vs shear stress for Pigment red 122 dispersion samples 4, 6 and predicted. Shear rate given in the unit s^{-1} and viscosity given in Pa*s.

The predicted sample shows a medium degree of thixotropy while sample 6 shows a low degree and sample 4 shows a high degree. The thixotropic behavior increases with pigment load and decreases with the amount of dispersion agent. For the processing time and viscosity results for all samples, see Appendix 10.8.

6.5 External results from Krüss with a force tensiometer

The external results from Krüss on Pigment red 2 can be seen in Figures 6.17-6.18.
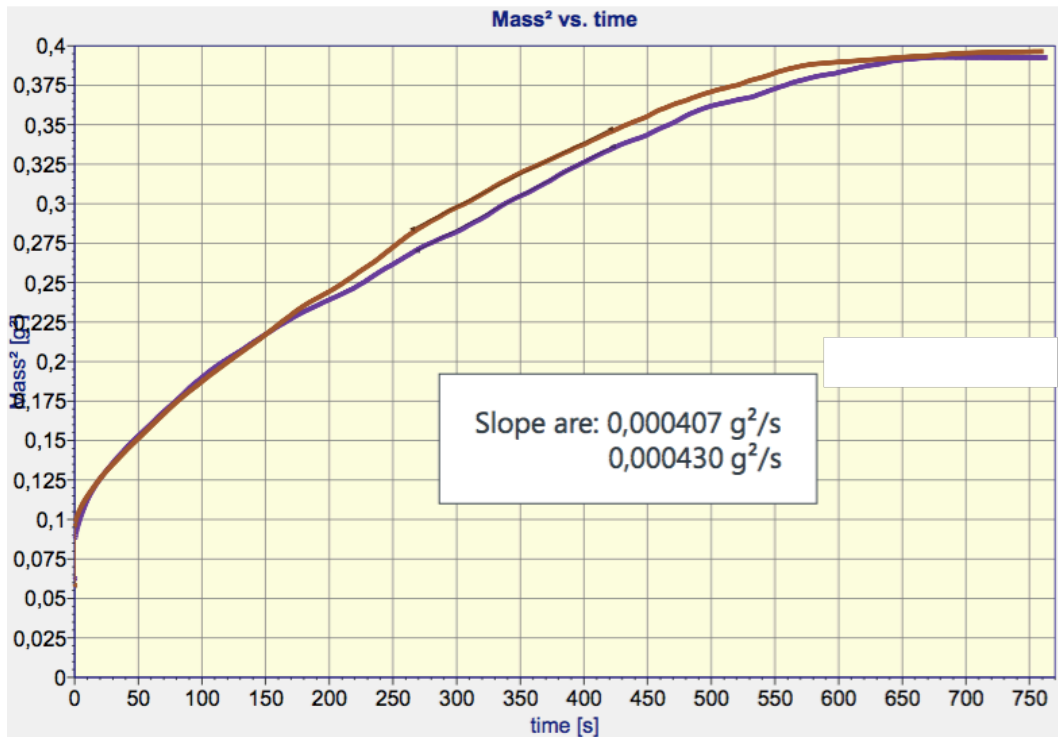
Figure 16.17: slopes of the sorption for Pigment red 2 using 100% TPGDA.
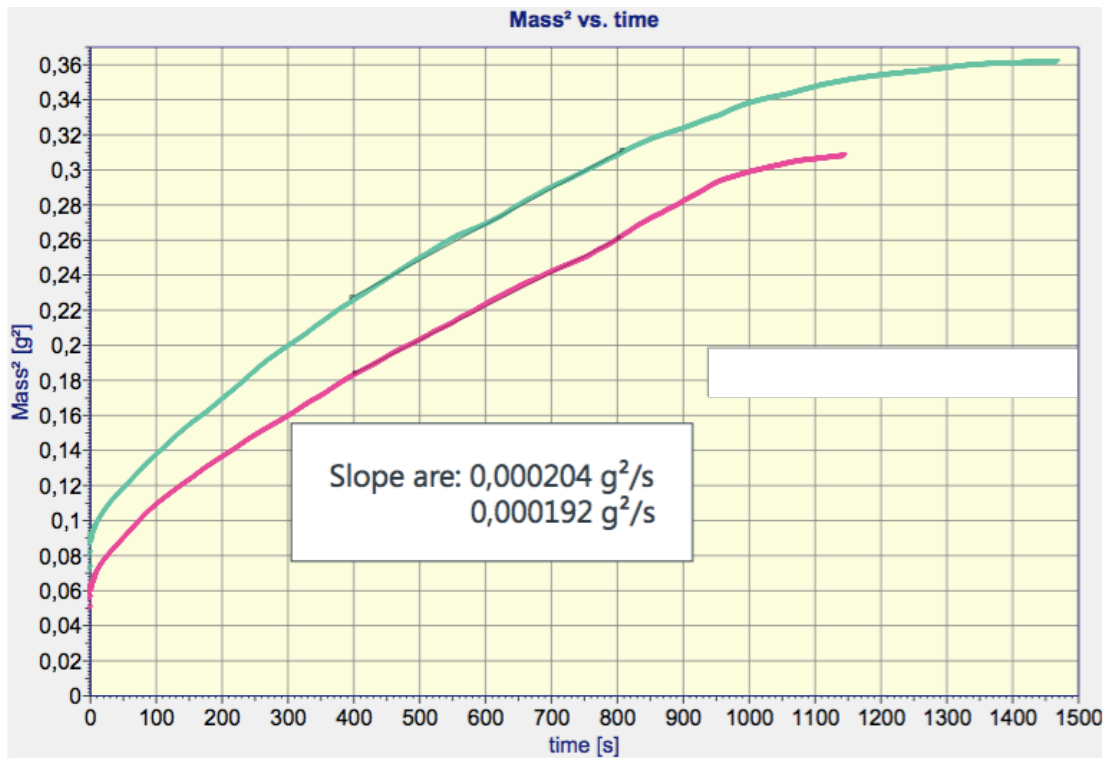
Figure 16.18: slopes of sorption for Pigment red 2 using a mixture of 80% TPGDA and 20% of the four functional polyester acrylate.

The average slope from *Figure 16.17* comes out as 0.0004185 g^2/s and the average slope from *Figure 16.18* comes out as 0.000198 g^2/s. The ratio in between these two mixtures is then 2.114. The viscosity for the pure TPGDA was measured to 14.1 mPa*s, and the mixture of 80% TPGDA and 20% of the four functional polyester acrylate was measured to 32.3 mPa*s. The viscosity ratio then comes out to 2.291.

7 Discussion

7.1 Comparing Daniels's flow point method of Pigment red 2 and Pigment red 122

As the Daniel flow point method was conducted on two different pigment it is interesting to see which kind of differences can be observed. For Pigment red 2 the amount of solution that needed to be added to reach to flow point was lower than for Pigment red 122 when it came to the resins that showed a stabilizing behavior. The reason for that this is observed could have to do with that the oil absorption value as it differs for Pigment red 122 and Pigment red 2, 40-60 grams oil /100 grams against 52 grams oil/100 grams respectively. The specific surface area could also be different between the two different pigments, the one with higher surface area then needs more resin molecules to stabilize the dispersion.

The flow point minimum is a dispersion which is in balance that it is stabilized, which to the left of the minimum the stabilization fails and to the right where it is stabilized but the viscosity increases. For the case of the four functional polyester acrylate where the minimum cannot be observed the stabilization effect is clearly not ideal. This resin is however still used in the design of experiment due to that the resin shows good curing properties of the final ink. There is also a decrease in the solution needed which is a sign of some stabilization. The main stabilizing effect should come from the dispersing agent and not the grinding resin, however if the grinding resins show a small stabilizing effect the rheology of the processed dispersion might be improved due to the resin.

In this study three different grinding resins are tested which all have different functionalities. It might be the case that the two functional grinding resin shows the best stabilizing effect due to that the molecule itself is more linear and has a longer length which creates a layer on the surface of the pigment particle that is longer than the other resins. This could be why the six functional fatty acid polyester acrylate shows no sign of stabilization.

7.2 How viscosity and other factors affect the processing time on the three-roll mill

The processing time on the three-roll mill varied greatly between the two different pigments. The main factor affecting the processing time on each pigment independently was the viscosity. There were however severe differences between the two pigments, even at roughly the same viscosity, and this could have to do with the tack and chemical composition of the pigment.

7.2.1 Viscosity and how it influences processing time on the three-roll mill

From *Equation 3.8* viscosity is a factor on the processing time on the three-roll mill. Increasing the viscosity increases the processing time, mostly due to that the clearance between the rolls increases with increasing viscosity. When comparing the processing time results of two dispersions with similar viscosity, one containing Pigment red 2 and one with Pigment red 122, there are however large differences. For example, Sample 2 for pigment red 122 had a viscosity of 42.5 with a processing time of 18.88 grams/min whereas sample 20 for Pigment red 2 had a viscosity of 42.0 with a processing time of 12.23. This suggests that viscosity is a factor on processing time but there are other factors as well which cannot be described by *Equation 3.8*.

7.2.2 Tackiness of mill base and how it influences processing time on the three-roll mill

One of the other factors which is not described by *Equation 3.8* but still has an influence on the processing time is the tackiness of the mill base. Due to that the clearance between the rolls is kept constant, the size of the particles need to be below this clearance level. If the tack increases of the mill-base the breakdown of the agglomerates will be more efficient allowing more particles to be below the clearance level, which in turn speeds up the transfer.

The chemical composition of the pigment could also have a big part in this due to that some pigment agglomerates from a certain pigment will have less chemical forces holding it together while another pigment will have higher chemical forces.

7.3 Residuals for the design of experiments

The residual evaluation for the design of experiments which can be seen in Appendix 10.3-10.4 for Pigment red 2 and Appendix 10.6-10.7 for Pigment red 122 indicate that the distribution could be normal. As in many cases to get a true normal distribution more samples would need to be measured. The models containing 13 and 23 samples are just not enough to truly evaluate if they follow a normal distribution. The processing time residuals for both Pigment red 2 and Pigment red 122 seem to follow the normal distribution better than for the viscosity residuals. This could however be a coincidence.

7.4 Design of experiment, limitations and possibilities

The use of design of experiment is quite time consuming, however there are several ways to make it more efficient, reducing the time needed to evaluate new pigment dispersions. As the case of Pigment red 122 where the number of samples could be reduced to 13. By knowing how the software works, and for the case of extreme vertices design how the boundaries reflect the number of samples needed to set up the model, the experiment can be made less time consuming. One of the best possibilities by using design of experiment is that it is possible to predict future samples and how they will behave. In many cases the data collection points do not give the optimum ratios in the mixture, but due to this function it is easy to set up which ratios should be used to get in a close range of the results that are sought.

7.5 Krüss results

The results from Krüss gave a sorption ratio of 2.114 and the viscosity ratios in between the two mixtures were 2.291. This means that from *Equation 3.2* this must depend on differences in the contact angle of the liquid and the surface tension of the liquid. As this ratio is higher the term $\sigma*\cos\theta$ must be higher than it is for the 100% TPGDA solution. As the liquid surface tension gets lower the term $\cos\theta$ gets higher and the term σ becomes lower, however with the term $\cos\theta$ having the most impact, hence the higher ratio. This is a probable explanation as the binder should have a lower surface tension than the monomer.

8 Conclusions

This thesis investigated the optimal monomer/oligomer blends with the Daniel flow point method followed by investigation of processing time and viscosity using design of experiments. Evaluating new pigments from scratch is in many cases a time-consuming process due to that a 1:1 replacement is not often possible.

The results from the Daniel flow point method showed to be effective, however it is a very crude method and due to that the results are evaluated by experience, results may vary greatly. Even though the optimums where found for Pigment red 2 and Pigment red 122 for different blends, these might not in fact be the true optimums. The oligomers that were found effective for both pigments were the modified bisphenol A epoxy diacrylate and the four functional polyester acrylate. The fatty acid modified hexa-functional polyester acrylate showed no sign of stabilization.

The results from the design of experiment has shown to work well for Pigment red 2 and Pigment red 122 and the prediction of the models for both processing time and viscosity are within the frames of the error given by the model.

From the technical data sheets on pigments all the data necessary is not always available. A great help to improve the time it takes to develop a pigment dispersion would be to always have the data for oil absorption, specific surface area, pore size and surface treatment. Surface treatment is something that is never mentioned in the datasheets, most likely due to company secrets, but would be of great value for the formulator. For the monomer and binder datasheets most information is there, however a value of the surface tension of the liquid would help immensely when choosing the appropriate binder and monomer. Alongside with the Daniel flow point method the knowledge of the surface tensions of, especially the binders could help in making the flow point method more efficient by excluding binders with high surface tension.

For UV curable inks the viscosity is often rather low, especially for UV flexo inks. This can in some cases make it quite difficult to process the dispersions on a three-roll mill, as the three-roll mill processing time increases with viscosity but at the same time the viscosity of the dispersion is wanted as low as possible. For some pigments which are processed favorably in a three-roll mill, the viscosity can still be kept relatively low with an acceptable processing time. For low viscosity dispersions a different type of processing equipment seems more suitable.

There were a few limitations to this study, such as the time needed to investigate a broader range of pigments and to investigate a different processing equipment, such as the basket mill.

9 Future work

In this study design of experiment was conducted on two different pigments. It would be of great interest to increase the number of pigments investigated to be able to compare the factors affecting processing time more thoroughly. An interesting thought would to be to run the design of experiment with the same oligomer/monomer blends for two different pigment showing the same core chemical composition. This to gain knowledge on how much influence the processing of the dry pigment has on the processing time on the three-roll mill.

Investigation by this method with different processing equipment such as a basket mill or bead mill could be of interest. If possible to use the combination of the Daniel flow point method and design of experiment with a bead or basket mill it could be possibly to process low viscosity dispersions. This is one of the limiting factors with the three-roll mill and for the final ink a low viscosity dispersion would be of great help to reduce the viscosity of the final ink.

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11 Appendix

11.1 Daniel flow point appendix

The *Figures 10.1* and *10.2* are the experiment for the Daniel flow point method with the fatty acid modified hexa-functional polyester acrylate.
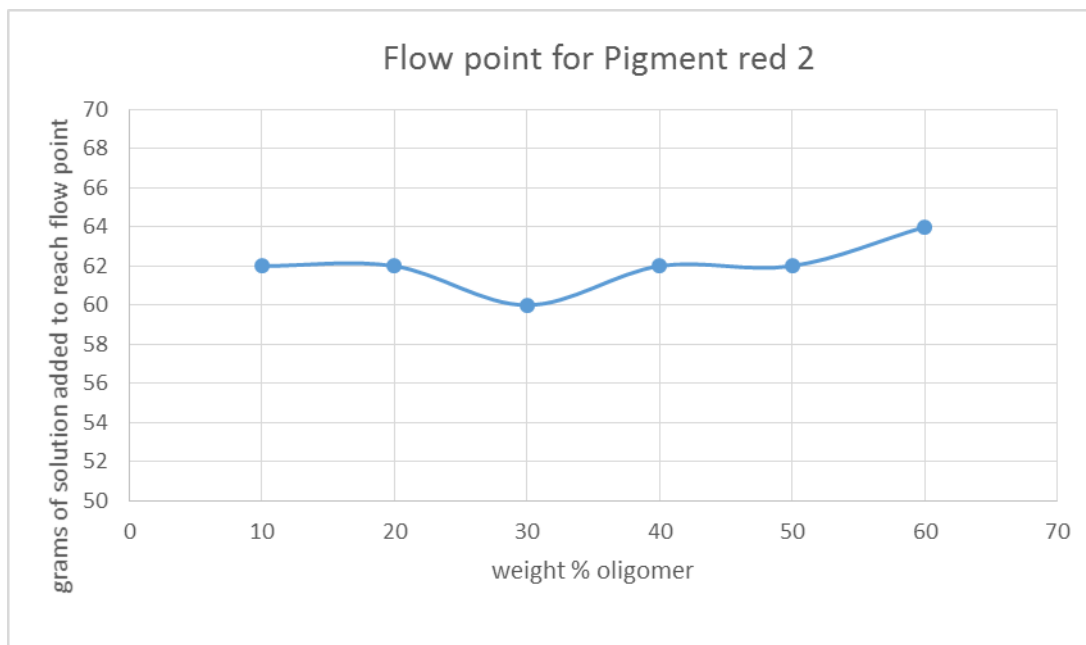

Figure 10.1: Daniel flow point method for the fatty acid modified hexa-functional polyester acrylate and pigment red 2.
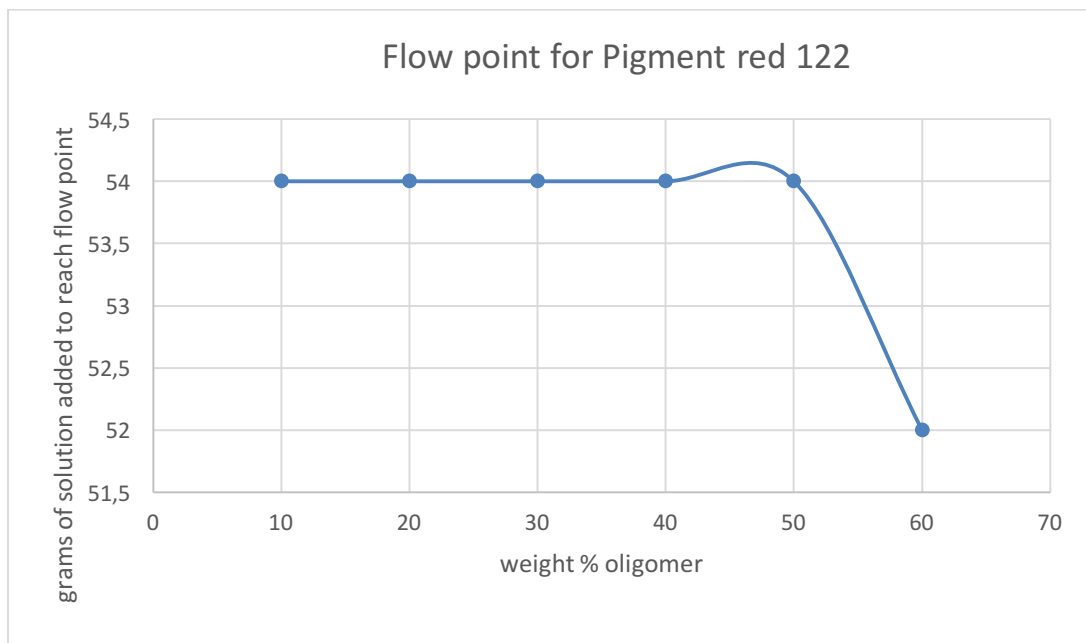

Figure 10.2: Daniel flow point method for the fatty acid modified hexa-functional polyester acrylate and pigment red 122.

11.2 Data collection points in design of experiment

11.2.1 Pigment red 2 data collection points

Table 10.1: Data collection points for the design of experiment of Pigment red 2.

Sample	Pigment (g)	Dispersing agent (g)	Mixture monomer/oligomer(s) (g)
1	89.00	20.00	141.0
2	92.50	15.00	142.5
3	85.00	15.00	150.0
4	100.0	25.00	125.0
5	80.00	25.00	145.0
6	94.50	17.50	138.0
7	84.50	22.50	143.0
8	100.0	20.00	130.0
9	90.00	25.00	135.0
10	100.0	15.00	135.0
11	94.50	22.50	133.0
12	80.00	20.00	150.0
13	82.50	17.50	150.0
14	80.00	22.50	147.5
15	84.50	20.00	145.5
16	87.00	17.50	145.5
17	90.00	25.00	135.0
18	94.50	22.50	133.0
19	85.00	25.00	140.0
20	91.75	21.25	137.0
21	97.25	18.50	134.3
22	95.00	25.00	130.0
23	97.25	22.50	130.3

11.2.2 Pigment red 122 data collection points

Table 10.2: Data collection points for Pigment red 122 in the design of experiment.

Sample	Pigment (g)	Dispersing agent (g)	Mixture monomer/oligomer(s) (g)
1	95.00	20.00	135.0
2	91.25	22.50	136.3
3	83.75	27.50	138.8
4	95.00	30.00	125.0
5	87.50	25.00	137.5
6	80.00	25.00	145.0
7	87.50	30.00	132.5
8	80.00	30.00	140.0
9	95.00	25.00	130.0
10	91.25	27.50	131.3
11	80.00	20.00	150.0
12	87.50	20.00	142.5
13	83.75	22.50	143.8

11.3 Residuals for processing time, Pigment red 2

The residuals for processing time for pigment red 2 can be viewed in *Figure*s *10.3-10.5*.
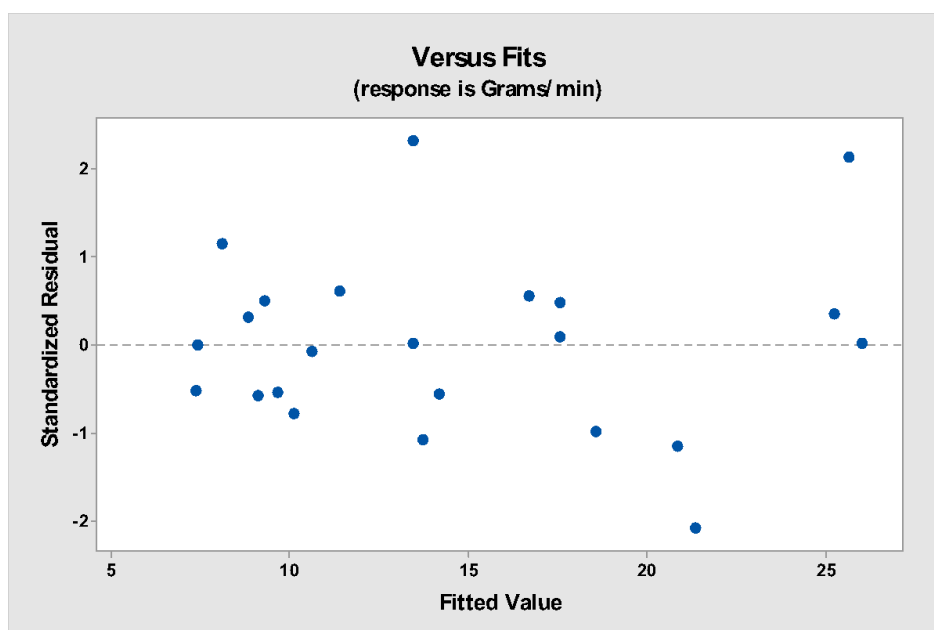

Figure 10.3: Standardized residuals vs fitted value for the response grams/min, in the design of experiment of pigment red 2.
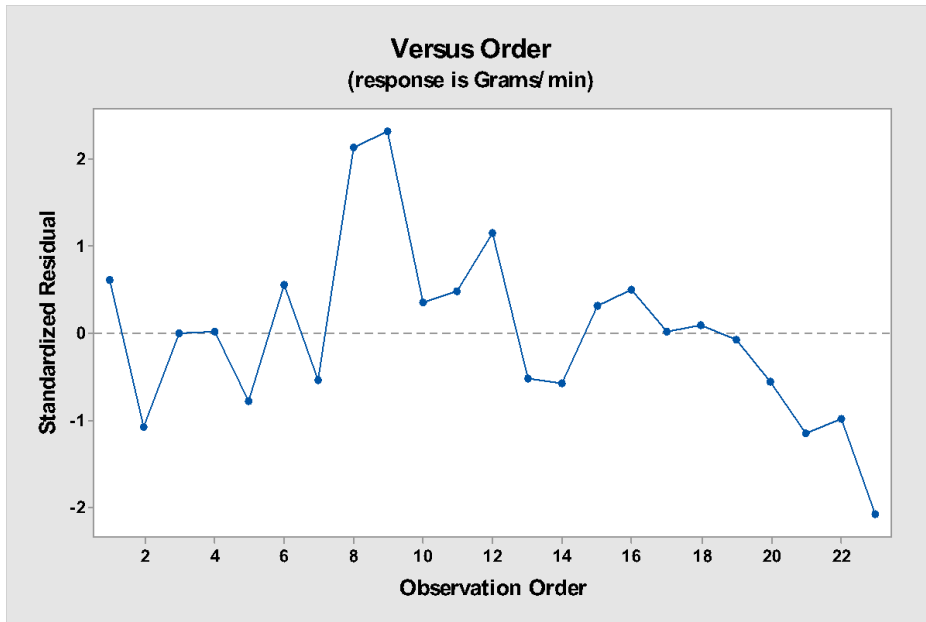
Figure 10.4: Standardized residuals vs observation order for the response grams/min, in the design of experiment of pigment red 2.
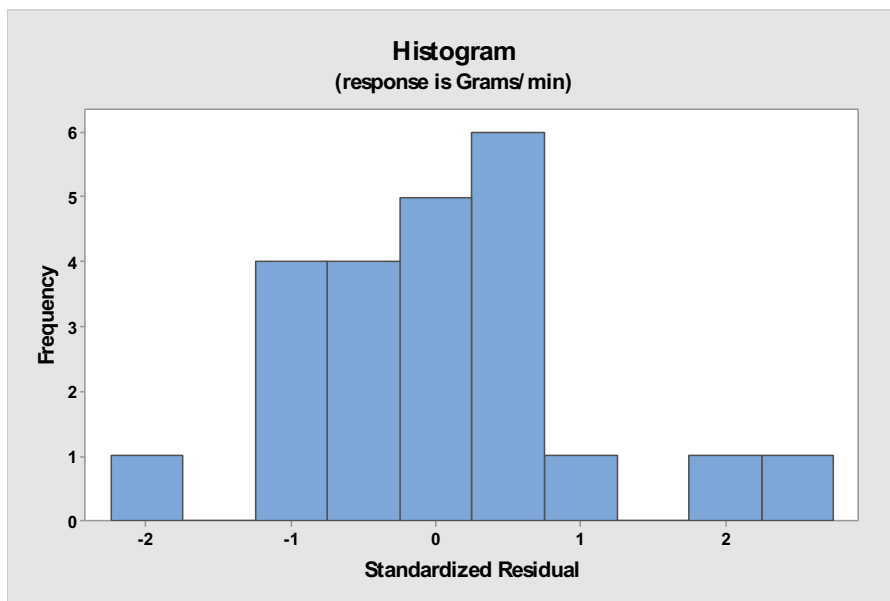

Figure 10.5: Histogram of the standardized residuals for the response grams/min, in the design of experiment of Pigment red 2.

11.4 Residuals for viscosity results, Pigment red 2

The residuals for the viscosity results on Pigment red 2 can be viewed in *Figure*s *10.6-10.8*.
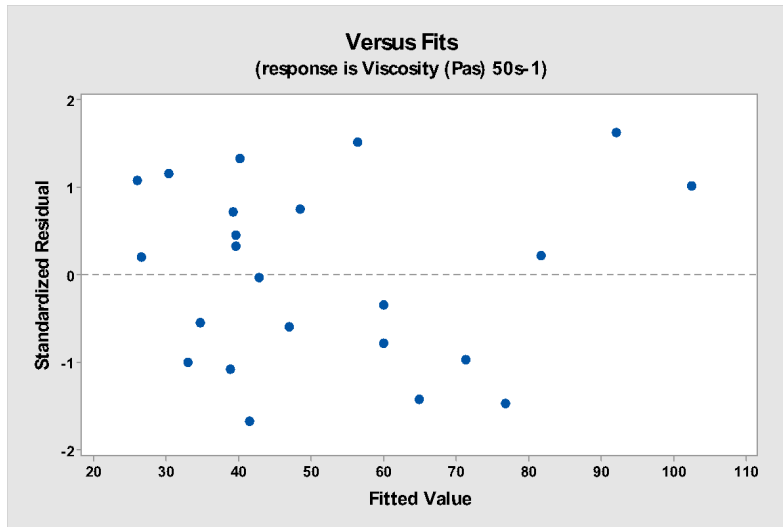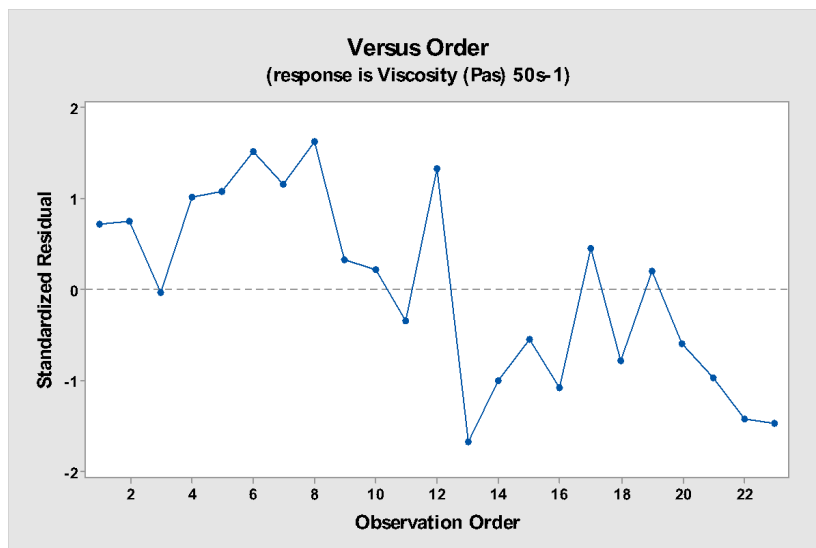

Figure 10.6: Standardized residuals vs fitted value for the response viscosity, in the design of experiment of pigment red 2.

Figure 10.7: Standardized residuals vs observation order for the response viscosity, in the design of experiment of pigment red 2.
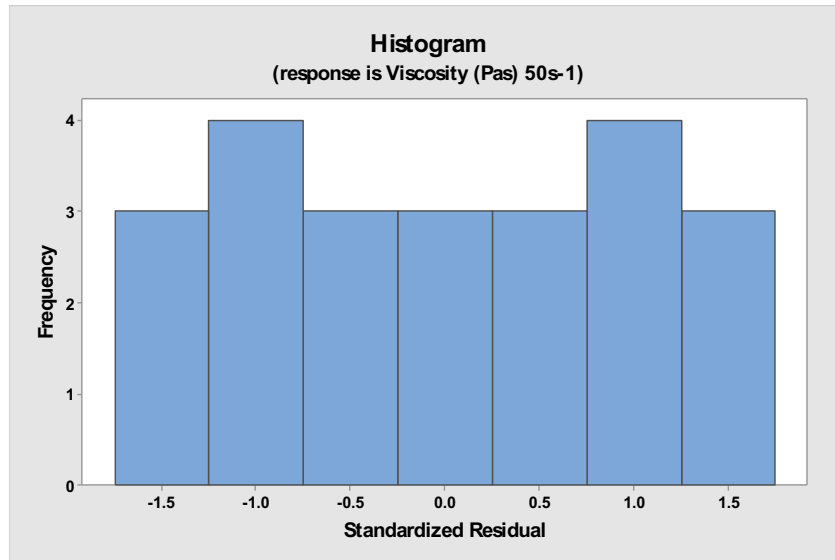
Figure 10.8: Histogram of the standardized residuals for the response viscosity, in the design of experiment of Pigment red 2.

11.5 Viscosity and processing time for all Pigment red 2 samples in the DOE

Table 10.3: Viscosity and processing time results for all samples in the design of experiment of pigment red 2.

Sample	Viscosity at 50s-1	Processing time in
1	45.50	13.52
2	54.50	10.28
3	42.70	7.45
4	109.0	26.09
5	34.70	8.00
6	69.20	18.59
7	40.30	7.80
8	105.0	32.43
9	42.50	21.18
10	83.50	26.09
11	57.20	19.22
12	50.30	11.71
13	28.40	5.76
14	25.30	7.33
15	30.20	9.94
16	29.90	10.99
17	43.50	13.50
18	53.50	17.86
19	28.50	10.41
20	42.00	12.23
21	63.20	16.91
22	53.20	15.28
23	64.60	14.23

11.6 Processing time residuals for Pigment red 122

The residuals for processing time on Pigment red 122 can be viewed in *Figure*s *10.9-10.11*.
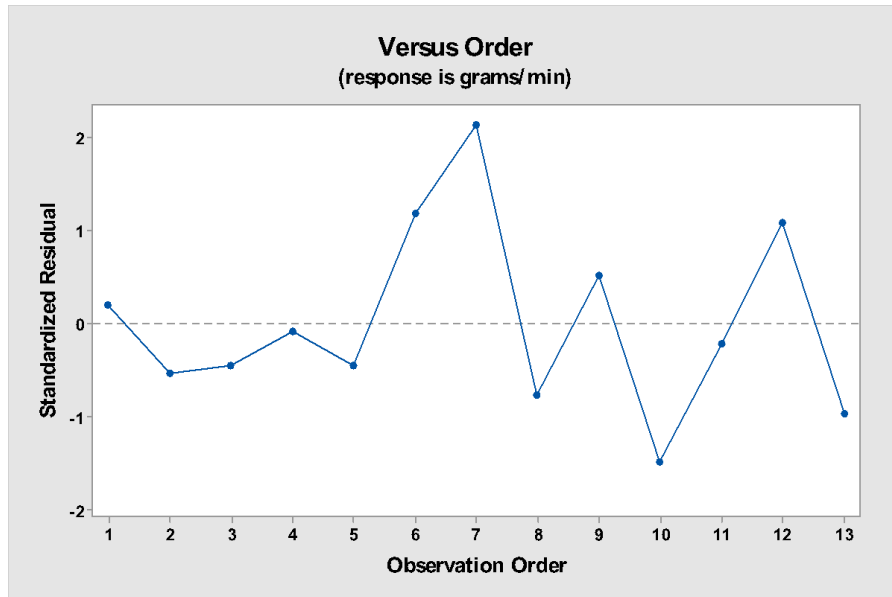

Figure 10.9: Standardized residuals vs observation order for the response grams/min, for the design of experiment of Pigment red 122.
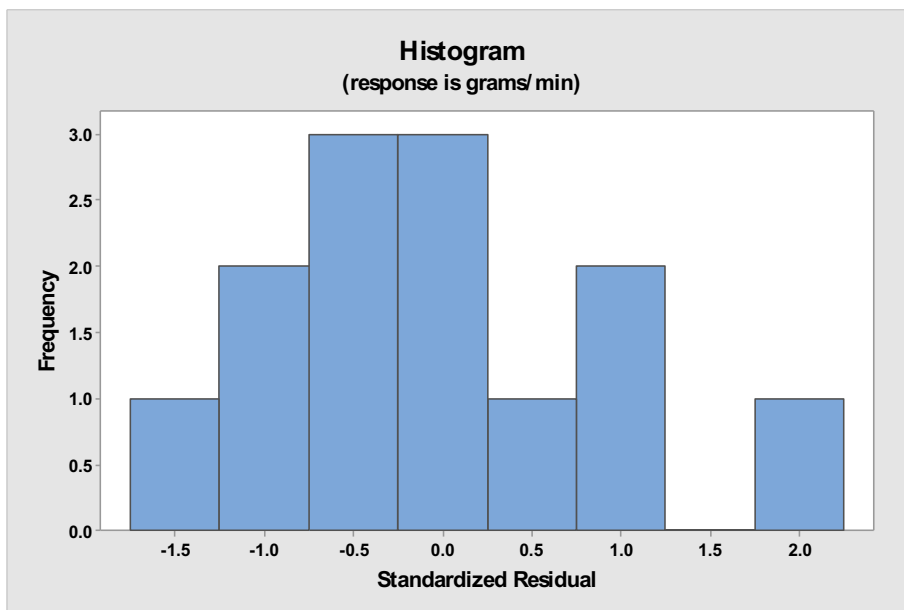

Figure 10.10: standardized residuals vs frequency for the response grams/min, for the design of experiment of Pigment red 122.
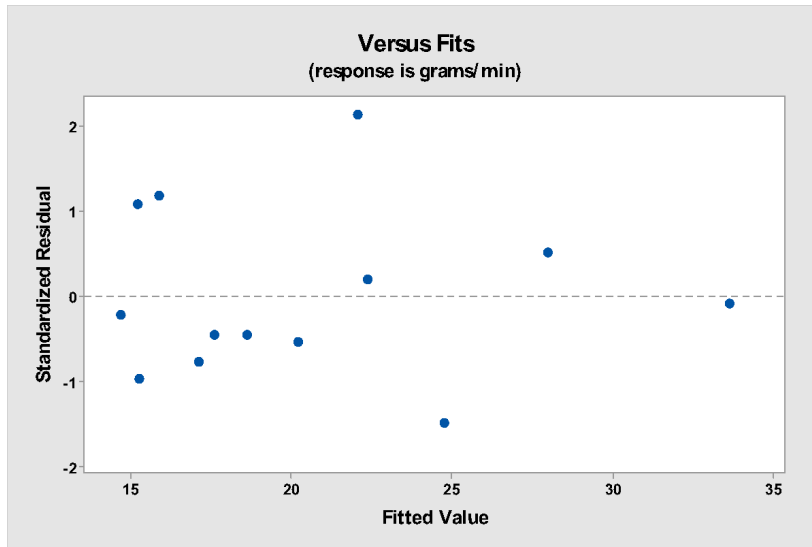
Figure 10.11: standardized residuals vs fitted value for the response grams/min, in the design of experiment of Pigment red 122.

11.7 Viscosity residuals for Pigment red 122

The viscosity residuals for Pigment red 122 can be viewed in *Figure*s *10.12-10.14*.
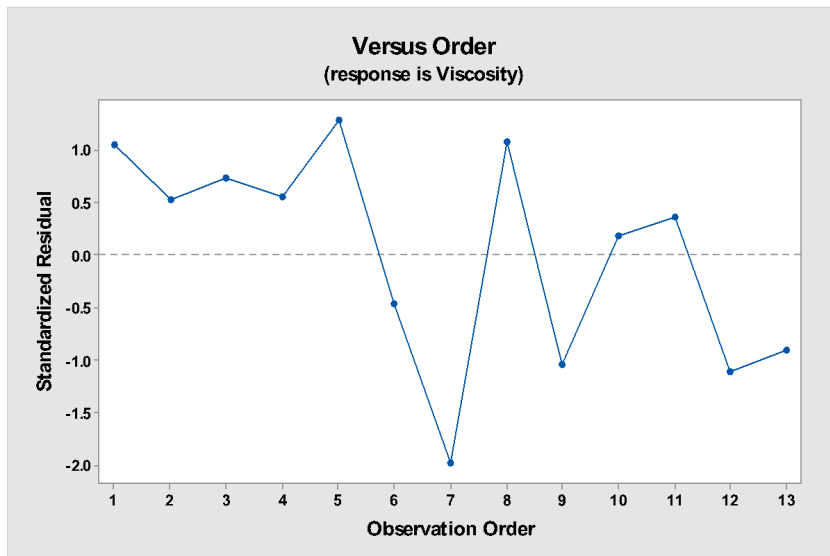

Figure 10.12: Standardized residuals vs observation order for the response viscosity, in the design of experiment of Pigment red 122.
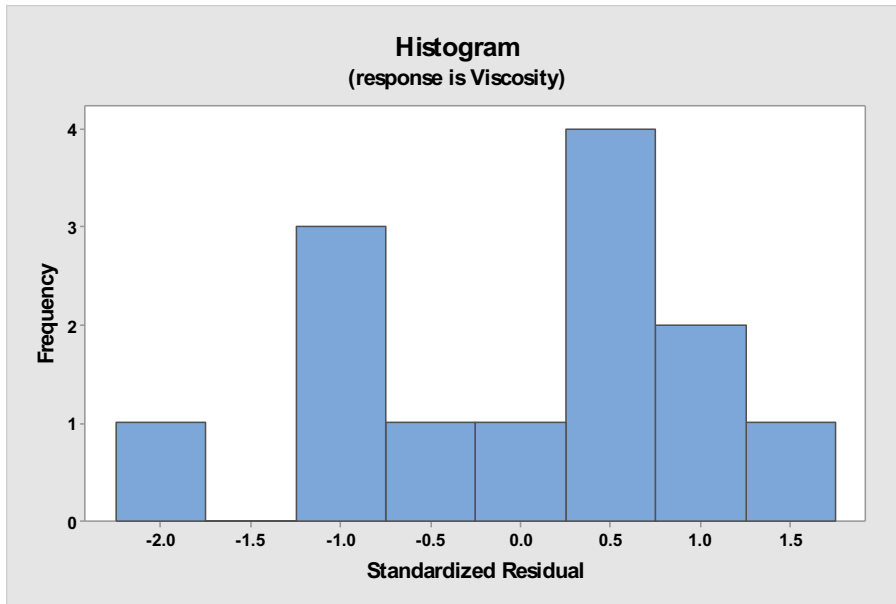
Figure 10.13: Standardized residuals vs frequency for the response viscosity, in the design of experiment of Pigment red 122.
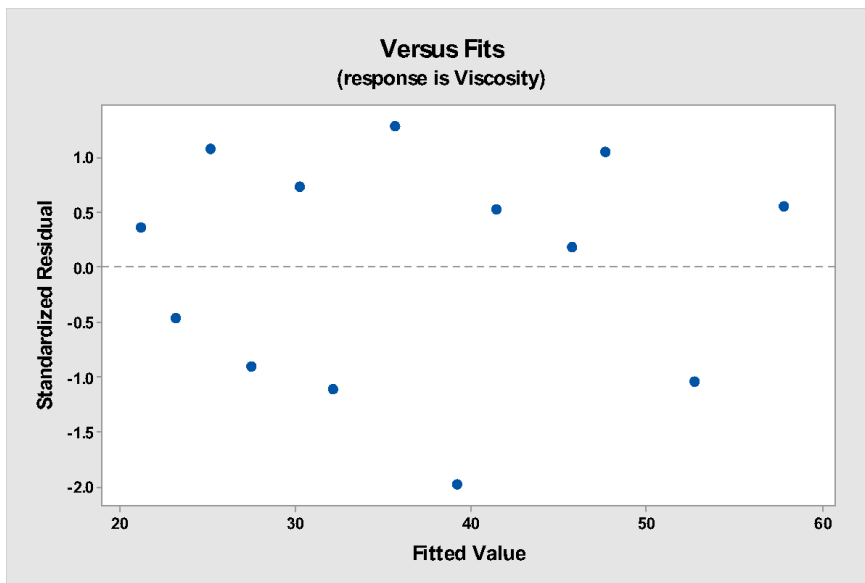

Figure 10.14: Standardized residuals vs fitted value for the response viscosity, in the design of experiment of Pigment red 122.

11.8 Viscosity and processing time for all Pigment red 122 samples in DOE

Table 10.4: Viscosity and processing time results for all the samples run in the design of experiment of Pigment red 122.

Sample	Viscosity at 50s-1	Processing time in
1	49.50	22.80
2	42.50	18.88
3	31.70	16.48
4	58.50	33.53
5	38.30	17.50
6	22.30	18.68
7	35.40	27.06
8	27.10	15.43
9	50.70	29.23
10	46.10	20.98
11	21.70	14.33
12	30.00	17.74
13	25.60	12.82