

# **Synthesis of Alkyd Resins and the Viscosity-Gloss Relationship of their waterborne coatings**

*Synthese van Alkydharsen en de Viscositeit-Glans Relatie van hun watergedragen coatings*

Jasper F. van den Hoek  
Institute for Life Sciences and Chemistry  
Hogeschool Utrecht  
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Supervisors: Amyke Veurink, Bert Hofkamp & Bart Reuvers  
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## 1. Summary

In order to build a better understanding of the influence of binder viscosity on after flow and gloss development of waterborne alkyd paints, various alkyd resins were synthesized with different oil lengths and molecular weights via three-step syntheses. Oil lengths were varied at a constant molecular weight between 35 % and 50 %, and molecular weights were varied at oil lengths of 38 % and 50 %. The alkyd resins were synthesized from phthalic anhydride, pentaerythritol, benzoic acid and soybean fatty acids. These alkyd resins were raised in acid value by post-modification with hexahydrophthalic anhydride, dissolved in acetone and chain extended with isophorone diisocyanate. The molecular weights and rheological properties of these alkyd resins were analyzed, and the alkyd resins were emulsified via solvent assisted dispersion.

A clear relationship between the viscosity and molecular weight, in correspondence to the relationship found by P.J. Flory in 1940<sup>2</sup>, was found for the alkyd resins with an oil length of 50 %. This relationship could not be applied to the alkyd resins with an oil length of 38 % with the same accuracy. Identical relationships were found between oil length and the logarithm of the viscosity and between oil length and glass transition temperature of the alkyd resins. The sizes of the emulsion particles were analyzed by particle size distribution analysis. A minimum particle size was found near a molecular weight of 30-40 kDa. The particle sizes increased when the neutralization grade approached 95 %, and the particle sizes decreased in general as the oil length of the alkyd resins increased. The gloss of the emulsified alkyd resin coatings was found to decrease at higher alkyd resin viscosities and oil lengths. An empirical equation has been found to describe these effects on the gloss.

The emulsions were stable at room temperature for several weeks up to months, but when stored at 50 °C some emulsions became unstable in as little as 24 hours. No emulsions were stable for longer than 7 days at 50 °C. This instability was due to the hydrolysis of hexahydrophthalic acid esters on the backbone of the alkyd resin, which decreases the amount of stabilizing carboxylic acid groups on the alkyd resin and increases the electrolyte concentration of the continuous phase of the emulsion. The activation energy of this acid catalyzed hydrolysis reaction was experimentally determined to be 67.85 kJ/mole.

## 2. Samenvatting

Om de invloed van harsviscositeit op de navloei en glansontwikkeling van water gedragen alkydverven beter te kunnen begrijpen, zijn er verschillende alkydharsen gesynthetiseerd met verschillende olielengtes en molgewichten via drie-staps syntheses. Olielengtes zijn gevarieerd tussen de 35 % en 50 %, en molgewichten zijn gevarieerd bij olielengtes 38 % en 50 %. De alkydharsen zijn gesynthetiseerd uit ftaalzuuranhydride, pentaerythritol, benzoëzuur en sojaboon vetzuren. Deze alkydharsen zijn gemodificeerd met hexahydroftaalzuuranhydride om het zuurgetal te verhogen. Vervolgens zijn de alkydharsen opgelost in aceton en zijn de polymeerketens verlengd met isoforondi-isocyaan. De molecuulgewichten en rheologische eigenschappen van de alkydharsen zijn bepaald, waarna de alkydharsen zijn geëmulgeerd via solvent assisted dispersion.

Er was een duidelijke relatie zichtbaar tussen de viscositeit en het molgewicht van de alkydharsen met een olielengte van 50 % die overeen kwam met de relatie die gevonden is door P.J. Flory in 1940<sup>2</sup>. Deze relatie kon niet met de zelfde precisie toegepast worden op de alkydharsen met een olielengte van 38 %. De relatie tussen de olielengte en het logaritme van de viscositeit van de alkydharsen was identiek met de relatie tussen de olielengte en de glastransitietemperatuur. De deeltjesgrootte van de emulsies zijn geanalyseerd met particle size distribution analysis. Een minimale deeltjesgrootte werd verkregen bij een molgewicht van 30-40 kDa. De deeltjesgrootte werd groter bij neutralisatiegraden rond de 95 %, en de deeltjesgrootte werd over het algemeen kleiner als de olielengte van de alkydharsen toenam. De glans van de alkyd emulsie coatings nam af bij hogere alkydhars viscositeit en olielengtes. Hiervoor is een empirische vergelijking gevonden.

De emulsies waren bij kamertemperatuur voor enkele weken tot maanden stabiel, maar wanneer de emulsies bij 50 °C bewaard werden, werden deze al in sommige gevallen binnen 24 uur onstabiel. Geen van de emulsies bleef bij 50 °C meer dan een week stabiel. Deze instabiliteit werd veroorzaakt door de hydrolyse van hexahydroftaalzuur esters aan de backbone van de alkydhars, wat de hoeveelheid stabiliserende carbonzuren op het alkydhars verminderd en de elektrolytconcentratie in de continue fase van de emulsie doet toenemen. De activeringsenergie van deze zuur gekatalyseerde hydrolyse reactie is volgens experimentele bepaling 67.85 kJ/mol.

### 3. Abbreviations

APC	Advanced Polymer Chromatography
AV	Acid Value
DMTA	Dynamic Mechanical Thermal Analysis
HHPA	Hexahydrophthalic anhydride
IPDI	Isophorone diisocyanate
KOH	Potassium hydroxide
Oil %	Oil length as a percentage of total mass of the alkyd resin
PL-PSDA	Polymer Laboratories - Particle size distribution analysis
SAD	Solvent Assisted Dispersion
W/O & O/W emulsions	Water in Oil & Oil in Water emulsions

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## 5. Introduction

In the past decade, increasing concerns for health and environment have led to the restriction of organic solvent-based coatings. As a result, the demand for environmentally friendly water-based products has greatly increased. These new water-based products are expected by consumers to meet the performance standards of their solvent-based counterpart, most importantly in terms of storage stability, hardness, gloss, and drying times. Because alkyd resins are truly versatile, their properties can be fine-tuned to meet these standards. However, the influence of the chemical properties of alkyd resins on their coating properties is not yet fully understood.

Gloss on rough substrates is one of the most important of these coating properties, and is thought to be mainly dependent on the viscosity of the alkyd resin. The rationale behind this is that a lower viscosity alkyd resin allows for more leveling before chemical drying immobilizes the coating.<sup>1</sup> Another property that has a large influence on the gloss of a coating is the drying time. Longer drying time allows for more time for a coating film to level out, raising the gloss. However the demand for fast drying times in coatings make this an impractical method of tailoring the gloss.

There are several ways to tailor the viscosity of alkyd resins. One which is to change the molecular weight of the alkyd resin.<sup>2,3</sup> Increasing molecular weights increases the entanglement of the polymer chains, raising the viscosity and, to a certain extent, raising the glass transition temperature. A second way to tailor the viscosity is to change the oil length of the alkyd resin. Fatty acids are one of the key ingredients used to synthesize alkyd resins. Fatty acids are what gives alkyd resins the ability to undergo chemical drying with oxygen and the amount and type of fatty acids influences many of the properties of an alkyd resin. The oil length is the mass percentage of fatty acid molecules, calculated as their triester derivatives with glycerol, which were used to synthesize the alkyd resin, even if the polyol used in the synthesis is not glycerol.<sup>4</sup> A higher oil length means that more long aliphatic chains, which have a high degree of free movement, were used in the synthesis of an alkyd resin. This causes a linear decrease in the glass transition temperature and an exponential decrease in viscosity.

The oil length of an alkyd resin coating influences the drying time of a coating in two ways. Raising the oil length increases the rate of chemical drying, which occurs in the double bonds of the fatty acids on the backbone of the alkyd resin, and it also lowers the viscosity which results in a longer drying time before the coating has built up sufficient hardness. For commercial coatings oil lengths ranging from 30 % to 80 % are being used depending on the desired properties of the coating.<sup>4</sup> Increasing the oil length increases yellowing rates, which is the color change of coatings that happens over a long period of time, as well.

Another key property of alkyd resins is the possibility to emulsify them in water. The formed emulsion particles can be stabilized by non-ionic and ionic means.<sup>5</sup> Non-ionic stabilization is often achieved by using polyethylene glycol as one of the reagents, which results in partly hydrophilic polymer to assist the formation of an emulsion. A popular strategy of obtaining ionic stabilization is by synthesizing an alkyd resin with a relatively large concentration of free carboxylic acid groups. These are then partly or fully neutralized with a base, often triethylamine or potassium hydroxide, which provides the necessary ionic stabilization to form an emulsion in water.

The size of the alkyd resin particles in water are influenced by various properties, of which the neutralization grade, molecular weight, and oil length of the alkyd resins are the most influential. Generally a decrease in particle size results in a higher viscosity of the emulsion and a decrease of the rate of sedimentation and coagulation of the emulsion.

In order to methodically study the influence of oil length and molecular weight of alkyd resins on their viscosity, and the influence of viscosity on the gloss of the alkyd emulsion coatings, a series of polymers with varying molecular weight and oil length was synthesized. Other variable properties in the synthesis of the alkyd resins, such as the acid value and OH-value, were kept at a constant value.



## 6. Theory

The development of a waterborne alkyd coating can be divided in the synthesis of an alkyd resin, the emulsification of an alkyd resin, and the analysis of the coating properties.

### 6.1. Alkyd resins<sup>4</sup>

Alkyd resins are hyperbranched polyesters that are applied in the paint industry as a solution in an organic solvent or as an emulsion in water. The most common way of producing an alkyd resin is by polycondensation of polybasic acids and polyols at 150-280 °C. Glycerol and pentaerythritol are commonly used polyols; phthalic anhydride is the most commonly used polybasic acid. In the production of alkyd resins different polybasic acids or polyols are sometimes chosen to obtain certain desired properties of the alkyd resin.

Commonly used polyols include:

- Ethylene glycol (1,2-ethanediol)
- 1,6-hexanediol
- Neopentylglycol (2,2-dimethyl-1,3-propanediol)
- Propyleneglycol (1,2-propanediol)
- Sorbitol
- Trimethylpropane (2-ethyl-2-(hydroxymethyl)-1,3-propanediol)

Commonly used polybasic acids include:

- Adipic acid
- Fumaric acid
- Isophthalic acid
- Maleic acid or Maleic anhydride
- Terephthalic acid
- Trimellitic anhydride

In most cases monobasic acids like benzoic acid and various fatty acids are used to further tailor the properties of the alkyd resin. The oil length of an alkyd resin is the mass percentage of the fatty acids used in the alkyd resin synthesis, calculated as the triglyceride derivate of the fatty acids, even if a different polyol than glycerol is used.

In the synthesis of an alkyd resin the ring-opening reaction of the anhydride and a primary alcohol takes place at around 150 °C. At roughly 170 °C the esterification reactions of the carboxylic acid and alcohol groups start taking place. In this reaction water is formed, which has to be removed from the reaction mixture to ensure high conversion rates, because the synthesis of an alkyd resin is an equilibrium reaction. Even though this polycondensation reaction is usually performed at temperatures as high as 200 to 280 °C, at which water has a high vapor pressure, removing trace amounts of water from the reaction mixture can be difficult. The reasons for this are that the solubility of water in organic compounds is higher at such high temperatures, and water vapor may condense on the sides of the reaction flask and return into the mixture. For these reasons an azeotropic component is often used to ease the removal of water from the reaction mixture. An aromatic compound like benzene, toluene or xylene is highly effective for this purpose. Because of the relatively low toxicity, xylene is the most popular choice. A Dean-Stark apparatus is used to separate the xylene and water, which allows the xylene to return into the reaction mixture.

An alkyd resin composed of phthalic anhydride, pentaerythritol, benzoic acid and fatty acids could, depending on the ratio of the components, have the molecular structure as shown in the figure below. In this figure the  $C_xH_y$  groups present the aliphatic tail of a the fatty acids.

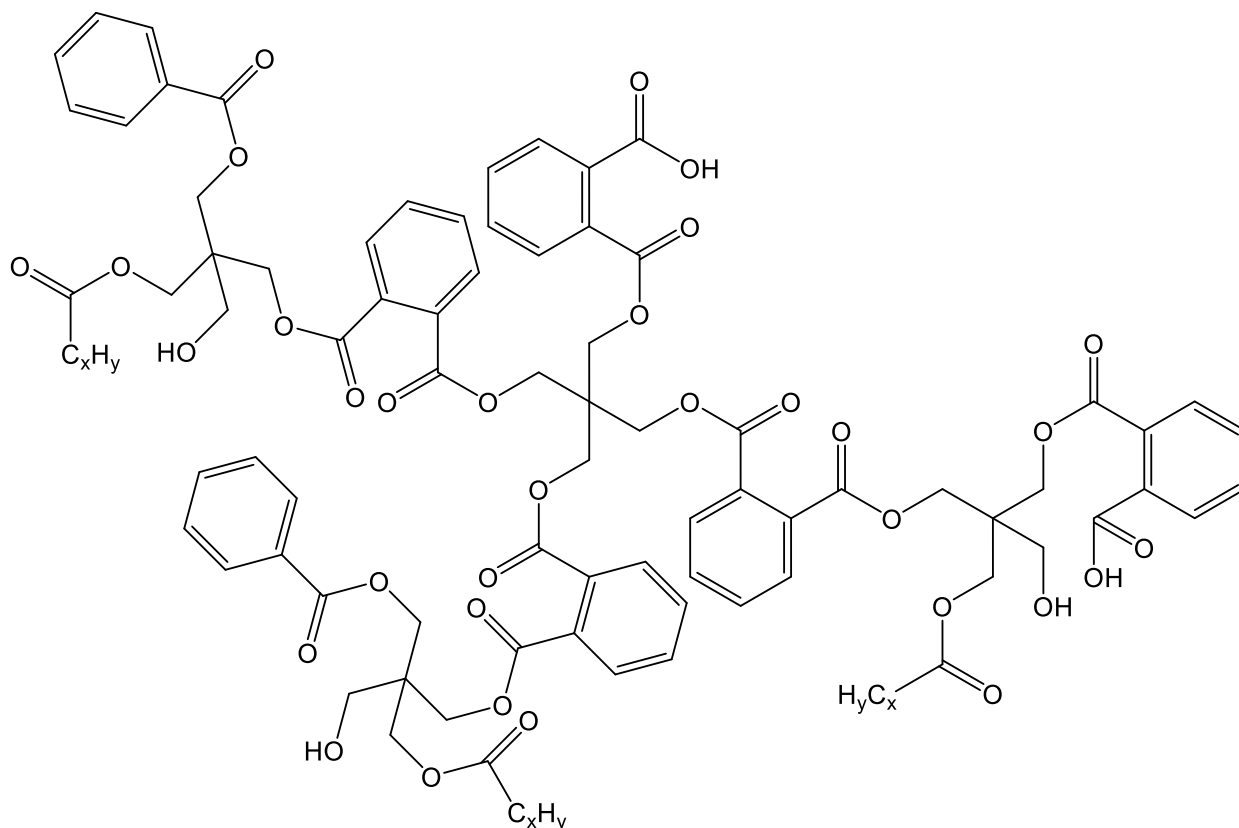


Figure 1 Molecular structure of an alkyd resin

### 6.2. Emulsifying alkyd resins<sup>5</sup>

Two popular methods of obtaining alkyd resin emulsions are the inversion process and the solvent assisted dispersion (SAD) process. In the inversion process, water is slowly added to melted alkyd resin which contains a surfactant or a base. At the start of the water addition a water in oil (W/O) emulsion is formed, but as the addition of water continues a point is reached at which the emulsion is about to invert from a water in oil emulsion (W/O) into an oil in water emulsion (O/W). At this inversion point the viscosity of the system rises significantly, which is used to obtain high shear forces and lower the particle size of the emulsion. After the desired homogenization is acquired the emulsion is further diluted with water to obtain the desired solids content of the emulsion.

In the SAD-process, sometimes called the acetone process when the solvent of choice is acetone, the alkyd resin is dissolved in a low boiling solvent to lower the viscosity and decrease the temperature at which the emulsification can take place. A surfactant or base is added to the alkyd resin solution after which water is slowly added to the mixture. With this method, the increase of viscosity during the addition of water is much less extreme, however much smaller particle sizes can be obtained compared to the inversion process. After the addition of water the solvent is removed from the system by distillation at reduced pressure until all the solvent has been removed and the desired solids content is obtained.

### 6.3. Coating properties

The main difference between waterborne and solvent-borne alkyd resin coatings is their film drying behavior. Solvent-borne alkyd resin coatings are able to level out the unevenness of the film's surface while the solvent is evaporating from the film, and after the solvent has evaporated the alkyd resin can keep leveling out the unevenness until chemical crosslinking with oxygen immobilizes the film.

Waterborne alkyd resin coatings do not possess the ability to level out film unevenness while water is evaporating.

In general, during the evaporation of water the viscosity of the film will increase until most of the water has evaporated. Then the alkyd resin particles will coagulate and start leveling out unevenness while chemical drying is taking place. Therefore, waterborne coatings cannot level out for nearly as long as solvent-borne coatings, giving waterborne coatings a relatively low gloss. When an alkyd resin emulsion is applied as a coating on a substrate, the water will usually evaporate at room temperature within an hour. If no pigment is added to the emulsion a clear alkyd resin film layer will remain.

Depending on properties like the viscosity of the alkyd resin, coating thickness, type and amount of drying catalyst (usually a cobalt or iron complex), the film layer will level out the surface unevenness to a certain degree before oxidative crosslinking in the fatty acid chains will immobilize the film. The viscosity of the alkyd resin and the time until the film layer is immobilized by oxidative crosslinking are important properties of a coating. These properties impact the gloss, hardness, tacking and other factors that determine the quality of the coating. A proposed mechanism for the oxidative crosslinking is displayed in the figure below, in which cobalt acts as a catalyst.

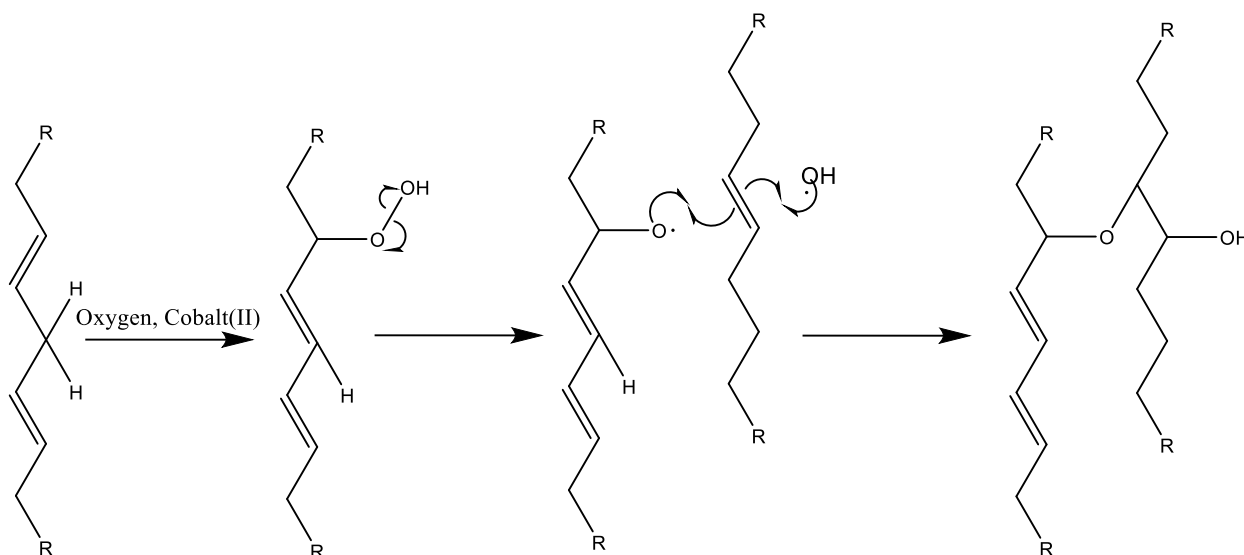


Figure 2 Proposed mechanism for the oxydative crosslinking in the fatty acid chains of alkyd resins<sup>4</sup>

The leveling equation<sup>1</sup> for an ideal striped pattern coating on a level substrate, after the evaporation of water, is given as follows:

$$\ln \frac{a_0}{a_t} = \frac{16\pi^4}{3} * \frac{\gamma x^3}{\lambda^4} * \int \frac{dt}{\eta} \quad (1)$$

In which  $a_0$  = amplitude of the unevenness at  $t = 0$  (cm)

$a_t$  = amplitude of the unevenness at  $t$  (cm)

$x$  = average coating thickness (cm)

$\lambda$  = wavelength (cm)

$\gamma$  = surface tension (dynes/cm)

$\eta$  = viscosity (poises)

$t$  = time (seconds)

Leveling can be seen as a stepwise process in which the amplitude becomes fractionally smaller in time. If for each fractional reduction of the amplitude average values are assumed, equation 1 can be rewritten as the required time,  $\Delta t$ , for such a reduction of amplitude to take place:

$$\Delta t = \frac{\log\left(\frac{a_0}{a_t}\right) \lambda^4 \eta}{226 \gamma x^3} \quad (2)$$

In practice the properties of a coating are tested by applying a coating with a constant coating thickness on a substrate with a constant roughness. After the evaporation of water from the coating the substrate roughness determines the amplitude of the film surface unevenness. Assuming the surface tension is the same in a series of similar coatings, the viscosity of the alkyd resin is the only influential variable on the speed of leveling. Thus, the equation can be simplified as follows, in which the constant  $C$  is dependent on the surface tension, substrate roughness, and coating thickness:

$$\Delta t \text{ (halving of amplitude)} = C * \eta$$

Given the fact that the gloss of a coating is inversely proportional to the surface roughness of the film layer<sup>21</sup>, an exponential relationship can be expected between the gloss of a coating and the viscosity of the alkyd resin. For this relationship it is assumed that the viscosity remains constant while the leveling is taking place, while in practice the viscosity of the alkyd resin increases as the oxidative crosslinking progresses.

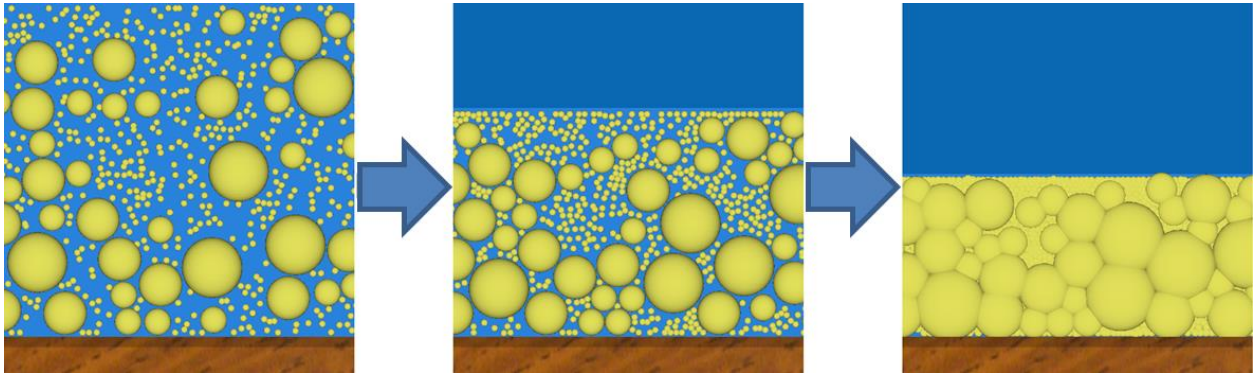


Figure 3 Evaporation of water in a waterborne coating

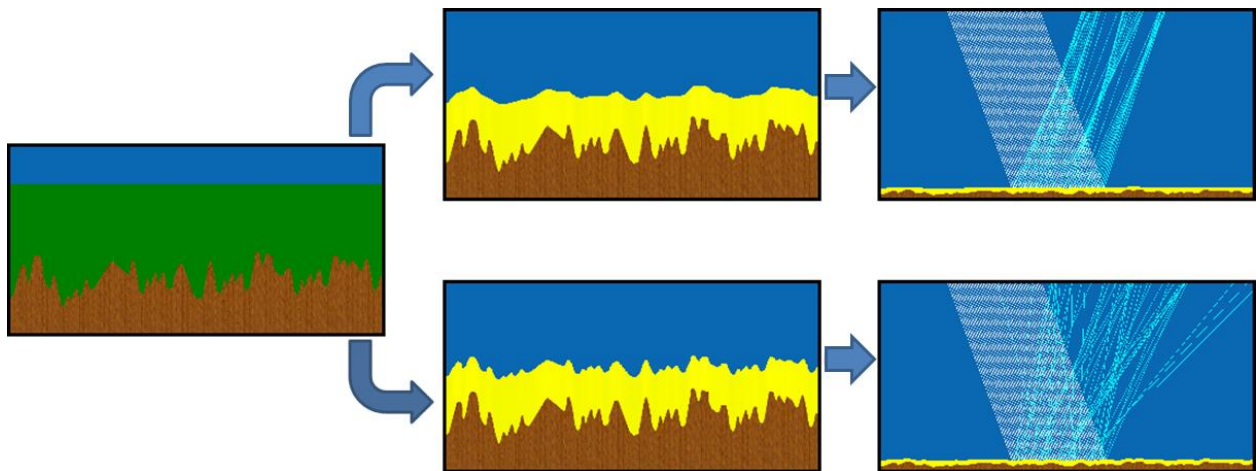


Figure 4 Film drying and light reflection. Top: low viscosity alkyd resin. Bottom: high viscosity alkyd resin

As illustrated in figure 4, the gloss is dependent on the degree of light scattering. The gloss of a surface is defined in Gloss Units, in which a polished black glass standard with a defined refractive index is used as a reference. This reference has a specular reflectance of 100 Gloss Units at the specified angle.

## 7. Materials and methods

The properties of the raw materials used in the experiments met DSM criteria. These criteria are displayed in the table below.

Table 1 Criteria for the quality of the raw materials used in the syntheses

Compound:	Purity:	Melting point:
Phthalic anhydride	Min. 99.7 % (w/w)	130-133 °C
Benzoic acid	Min. 99.0 % (w/w)	121-123 °C
Hexahydrophthalic anhydride	Min. 99.0 % (w/w)	34-38 °C
Pentaerythritol	Min. 98.0 % (w/w)	Min. 250 °C
Soybean oil fatty acid	N/A	17-28 °C
Isophorone diisocyanate	Min. 99.5 %	N/A

### 7.1. Synthesis of alkyd resin<sup>6,7</sup>

A 6 liter round-bottomed flask was equipped with a stainless steel 5-necked lid, mechanical propeller stirrer, PT100 temperature probe, heating mantle, nitrogen inlet, and Dean-Stark apparatus with Dimroth condenser. The flask was kept under a nitrogen atmosphere for the duration of the reaction. The round-bottomed flask was charged with amounts of soy bean fatty acids, benzoic acid, pentaerythritol, and phthalic anhydride to a theoretical yield of 4500 g. The ratio of components was calculated using the proprietary calculation program Forest v1.52. The Dean-Stark apparatus was filled with xylene (mixture of isomers) and 40 to 60 mL xylene was added to the reaction mixture. During the reaction the mixture was kept in a nitrogen atmosphere. The reaction mixture was heated to 240 °C. During the heating process xylene started to evaporate between 140 and 190 °C. During and after the heating process xylene was added to or removed from the Dean-Stark apparatus to maintain an appropriate reflux rate.

Care was taken that no water accumulated on the sides of the distillation bridge of the Dean-Stark apparatus and that the xylene refluxed at a rate that causes no problems in the flow to the reaction mixture. The water that is formed during the reaction was collected from the bottom of the Dean-Stark and poured into a measuring cylinder, so it could be used as an indication for the conversion of the reaction. The acid value of the reaction mixture was measured every half hour. At an acid value of less than 9 mg potassium hydroxide (KOH) per gram resin the reaction mixture was cooled to 210 °C and the remaining xylene was removed from the reaction mixture at reduced pressure. The hot resin, with final acid value of 4-8 mg KOH/g resin, was poured into glass jars for storage. The acid values were determined with a method based on ISO 2114.

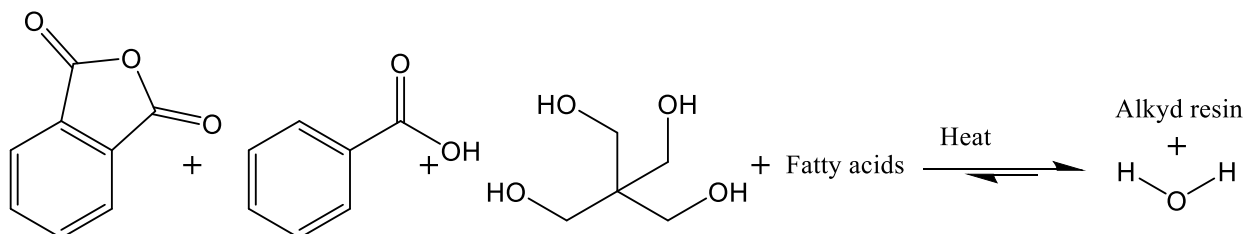


Figure 5 Reaction scheme of the synthesis of an alkyd resin

### 7.2. Post-modification of alkyd resin with hexahydrophthalic anhydride<sup>6,7</sup>

The acid value of 4-8 mg KOH/g resin obtained by method 7.1 does not provide sufficient ionic stabilization to obtain stable emulsions. Therefore, the acid value was raised by reacting the hydroxyl

groups with hexahydrophthalic anhydride, which introduces more free carboxylic acid groups into the polymer system. Alkyd resin (7.1) was heated in a microwave for 4 minutes and poured into a 2 liter round-bottomed flask. Hexahydrophthalic anhydride was added to flask and the flask was equipped with heating mantle and a stainless steel 5-necked lid with mechanical propeller stirrer, PT100 temperature probe, nitrogen inlet, and Dimroth condenser. The amount of hexahydrophthalic anhydride was calculated using the following formula:

$$\text{Reagent (g)} = \frac{m * (AV_d - AV_m) * 154.16}{56100 - 154.16 * AV_d} \quad (3)$$

$m$  = amount of alkyd resin (g)

$AV_d$  = desired acid value (mg KOH/g resin)

$AV_m$  = measured acid value (mg KOH/g resin)

154.16 = molecular weight of hexahydrophthalic anhydride (g/mole)

56100 = molecular weight of potassium hydroxide (mg/mole)

The flask was kept under a nitrogen atmosphere for the duration of the reaction. The mixture was slowly heated to 160 °C and kept at this temperature for one hour. The acid value was measured twice, once with water added to the sample and once without water. When the acid values of these samples were equal this indicated complete conversion of the hexahydrophthalic anhydride. The heating mantle was removed and acetone was added in a drop wise manner, while the reaction mixture cooled down from 160 °C to about 55 °C, until the solid content of the mixture was 60-70 % (w/w). The mixture was filtered through a 240µm filter and stored in 1 liter cans.

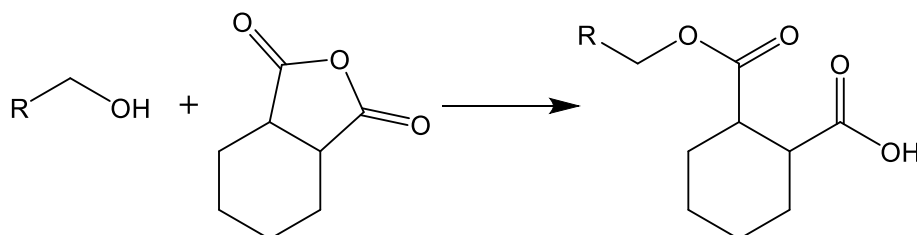


Figure 6 Reaction scheme of the post-modification with hexahydrophthalic anhydride. The "R" groups represent the alkyd resin backbone

### 7.3. Chain extension of alkyd resin with isophorone diisocyanate<sup>5</sup>

If alkyd resins with high molecular weights were synthesized by method 7.1, their viscosities may become too high to be able to modify and by method 7.2. To avoid this problem, the alkyd resins synthesized by method 7.1 had a relatively low molecular weight (3-10 kDa). To obtain higher molecular weights, these polymers can be chain extended by reaction the hydroxyl groups of the alkyd resin with diisocyanates.

(7.2) was added to a 2 liter round-bottomed flask equipped with a stainless steel 5-necked lid with mechanical propeller stirrer, PT100 temperature probe, heating mantle, nitrogen inlet, and Dimroth condenser. The flask was kept under a nitrogen atmosphere for the duration of the reaction. Isophorone diisocyanate was added to the mixture equal to 1.5 % (w/w) of the amount of solids present in the reaction mixture. Coscat® 83 catalyst was added to the reaction mixture equal to 0.1 % (w/w) of the amount of solids present in the mixture. The reaction mixture was heated to 58-60 °C. Conversion of the isocyanate groups was monitored by titration with a 798 MPT Titrimo by adding a known amount of a secondary amine, which was allowed to react with the isocyanate groups. Back titration with hydrochloric acid was performed to determine the amount of isocyanate groups. The reaction was stopped when the isocyanate content became less than 0.1 %. The reaction mixture was cooled, filtered through a 240 µm filter and stored in 1 liter cans.

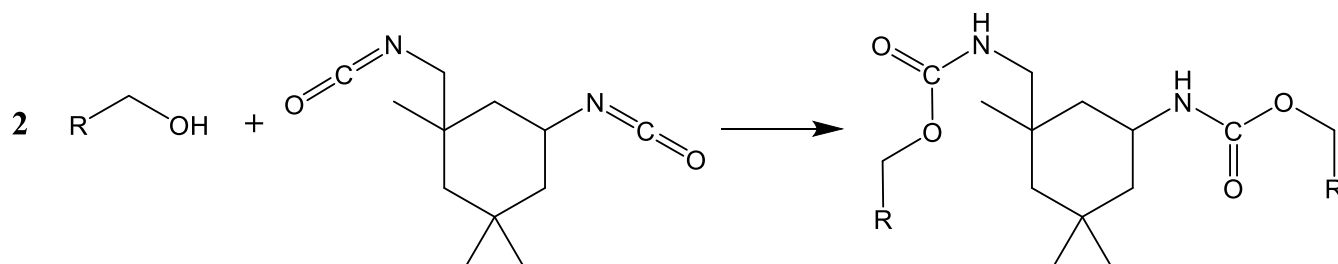


Figure 7 Reaction scheme of the chain extension reaction of alkyd resins with isophorone diisocyanate, the "R" groups represent the alkyd resin backbone

#### 7.4. Synthesis of a chain extended modified alkyd resin in one pot

The procedure described in chapter 7.1. was followed, with the modification of using amounts of reagents for a theoretical yield of 950 g in a 2 liter round-bottomed flask. After an alkyd resin with an acid value of 4-8 mg KOH/g resin was obtained, the reaction mixture was cooled to roughly 70 °C and a calculated amount of hexahydrophthalic anhydride was added to the flask. The mixture was slowly heated to 160 °C for one hour and the acid value was checked as described in chapter 7.2.

The alkyd resin was dissolved in acetone as described in chapter 7.2.

Method (7.3) was followed to complete the three-step synthesis in one pot.

#### 7.5. Emulsification of alkyd resin by the acetone process<sup>5,9</sup>

A cylindrical glass reactor with a glass 5-necked lid equipped with mechanical stirrer, PT100 temperature probe, and Dimroth condenser was charged with an alkyd resin in acetone solution with a solid content of 60-70 %. The following formula was used to calculate the amount of triethylamine, which was then added to the reactor:

$$TEA = \frac{m * \left(\frac{s}{100}\right) * AV * \left(\frac{N}{100}\right) * 101}{56100} \quad (4)$$

TEA = amount of triethylamine (g)

m = amount of alkyd resin solution (g)

s = solids content of the alkyd resin solution ( % )

AV = acid value of the alkyd resin (mg KOH/g resin)

N = desired degree of neutralization ( % )

The amount of water corresponding to 163 % of the mass of alkyd resin in the mixture was slowly added to the mixture. This resulted in a milky white opaque or semi-transparent liquid. The acetone was removed by distillation at reduced pressure at 40 °C until the solids content was 40 % (w/w). The emulsion was filtered through a 240 µm filter and stored in polyethylene jars at 7 °C. The emulsions were warmed to room temperature prior to application testing.

#### 7.6. Determination of the rate of hydrolysis of hexahydrophthalic acid from the alkyd resin backbone

A glass jar was charged with 20 g of alkyd resin solution in acetone. Triethylamine was added to neutralize 80 % of the carboxylic acid groups. 20 g water was slowly added to the mixture while stirring, after which acetone was added until a clear solution was obtained. The solids content of this solution was determined and the solution was divided over airtight vials. Half of these vials were stored at room temperature and half were stored at 50 °C. The acid value of the solution was measured at regular intervals and at the start of the experiment. The assumption was made that any increase in acid value is the result of carboxylic acid functional groups being introduced into the system via the hydrolysis of hexahydrophthalic acid from the polymer. The concentration of hexahydrophthalic acid

groups that were attached to the polymer as esters at the start of the experiment was known, so the concentration of these ester groups could be calculated at several points in time from the acid value measurements. By plotting the concentration of hexahydrophthalic acid groups on the polymer against the time the reaction rates at different temperatures could be calculated.

#### **7.7. Measurement of the film properties of alkyd resin emulsions**

To the emulsions, as prepared in (7.5), 2 % (s/s) Rheolate® 212 thickener and 1 % (s/s) Borchio® OXY-Coat 1101 drying catalyst was added. If a film was seen to develop craters, 1.25 % Byk 348 wetting agent was added to the emulsion and a new film was applied. The emulsions were diluted with demineralized water to a solids content of 38 %. A 100µm layer of an emulsion was applied to both a black scrub panel (uneven substrate) and a glass panel. After allowing the film to dry for 24 hours the black scrub panel was used for gloss measurement at 20° and 60° and the glass panel was used for König pendulum damping tests.

#### **7.8. Measuring the rheological properties of alkyd resin**

Alkyd resin, as prepared by (7.3) or (7.4), was placed on a MCR301 rheometer with P-PTD200 chamber at 120 °C until all the acetone in the sample evaporated. The chamber was placed on the sample with a gap of 0.5mm and the sample was allowed to anneal for 10 minutes at 23 °C. The viscosity of the sample was determined by steady state measurement at a shear stress of 5000Pa, wherein the viscosity at 5 minutes was taken as the true viscosity. Dynamic mechanical thermal analysis (DMTA) was performed with a frequency of 1Hz between -25 and 105 °C with a temperature change rate of 4 °C per minute.

#### **7.9. Particle size distribution analysis**

The particle size distribution of the emulsions as prepared by (7.5) were determined with a Polymer Laboratories PL-PSDA apparatus.

#### **7.10. Molecular weight distribution analysis**

The alkyd resins were analyzed by advanced polymer chromatography (APC) on a MIX-B column. Because this method does not yield exact values for  $\overline{M}_n$  and  $\overline{M}_w$ , the molecular weights of the polymers reported in chapter 8 cannot be compared to other polymers.



## 8. Results

Several alkyd resins were synthesized, modified with hexahydrophthalic anhydride, and chain extended with isophorone diisocyanate, either via the three-step synthesis method or in one pot. The products had an OH-value of 65-70, acid value of 32.2-32.8 mg KOH/g resin, and varying molecular weight and oil length as displayed in the table below.

Table 2 APC results and viscosity of the synthesized alkyd resins

Name:	Oil length (%)	$\overline{M}_n$	$\overline{M}_w$	Polydispersity index	Viscosity (Pa.s)
P_20K_OIL35_32.5	35	2745	48732	17.8	$4.31 \cdot 10^8$
P_5K_OIL38_32.5	38	2405	12466	5.2	$1.53 \cdot 10^7$
P_10K_OIL38_32.5	38	2617	24624	9.4	$9.16 \cdot 10^7$
P_21K_OIL38_32.5	38	2531	43417	17.2	$1.73 \cdot 10^8$
P_40K_OIL38_32.5	38	3339	98455	29.5	$2.10 \cdot 10^8$
P_70K_OIL38_32.5	38	Outlier	Outlier	Outlier	$1.52 \cdot 10^8$
P_42K_OIL40_32.5	40	Not determined	Not determined	Not determined	$2.24 \cdot 10^8$
P_20K_OIL42_32.5	42	2750	36299	13.2	$4.16 \cdot 10^7$
P_20K_OIL45_32.5	45	3132	33311	10.6	$8.80 \cdot 10^6$
P_5K_OIL50_32.5	50	2508	9963	4.0	$2.26 \cdot 10^5$
P_20K_OIL50_32.5	50	3273	24374	7.4	$3.21 \cdot 10^6$
P_40K_OIL50_32.5	50	3288	31111	9.5	$7.04 \cdot 10^6$

### 8.1. Influence of molecular weight on steady state viscosity

The viscosity of linear polyesters, polyamides and certain non-linear polymers can be accurately described by the following relationship<sup>2,3</sup>

$$\text{Log}(\eta) = A + C \overline{M}_w^{\frac{1}{2}} \quad (5)$$

Where  $\eta$  is the viscosity,  $\overline{M}_w$  is the weight average molecular weight, and A and C are constants dependent on temperature and oil length. A plot of  $\text{Log}(\eta)$  against  $\overline{M}_w^{1/2}$  for the alkyd resins with oil length 38 % and 50 % is displayed in figure 8.

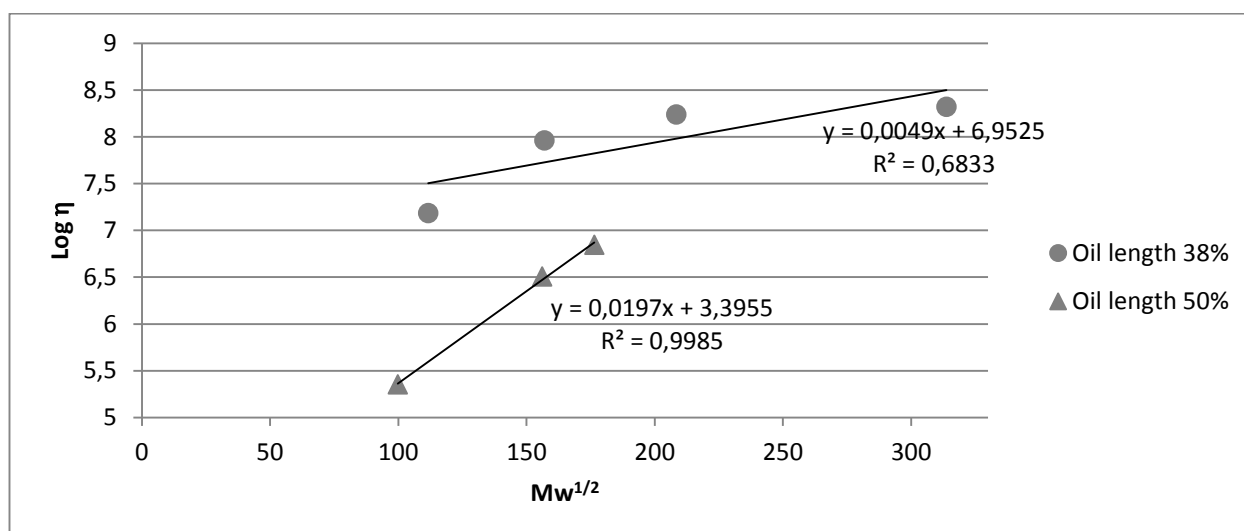


Figure 8 Plot of  $\log \eta$  versus  $\overline{M}_w^{1/2}$

The plot accurately describes the relationship of molecular weight and viscosity at an oil length of 50 %. At an oil length of 38 % the relationship provides a poorer fit. More research will be required to determine if  $\log(\eta)$  is a linear function of  $\overline{M}_w^{1/2}$  or if this relationship is not linear at an oil length of

38 %, which could be caused by the high polydispersity of the higher molecular weight polymers. A higher molecular weight alkyd resin with an oil length of 50 % would be beneficial to clarify this. Possibly the higher molecular weight polymers form highly entangled collections of molecules with rheological properties that differ from the relationship in equation 5.

### 8.2. Influence of oil length on viscosity

Several resins were synthesized with the same theoretical molecular weight, which was calculated from the ratio of reagents used in the synthesis. In practice, as can be seen from the APC measurements, these molecular weights varied and became lower as the oil length rose. However, since the effect of oil length on viscosity is much greater than the effect of molecular weight on viscosity, this difference was neglected and the oil length was directly plotted against  $\log(\eta)$ . The resulting relationship can be described with the following formula:

$$\text{Log}(\eta) = A + C * \text{OIL \%} \quad (6)$$

Where  $\eta$  is the viscosity, OIL % is the oil length, and A and C are constants dependent on temperature and molecular weight.

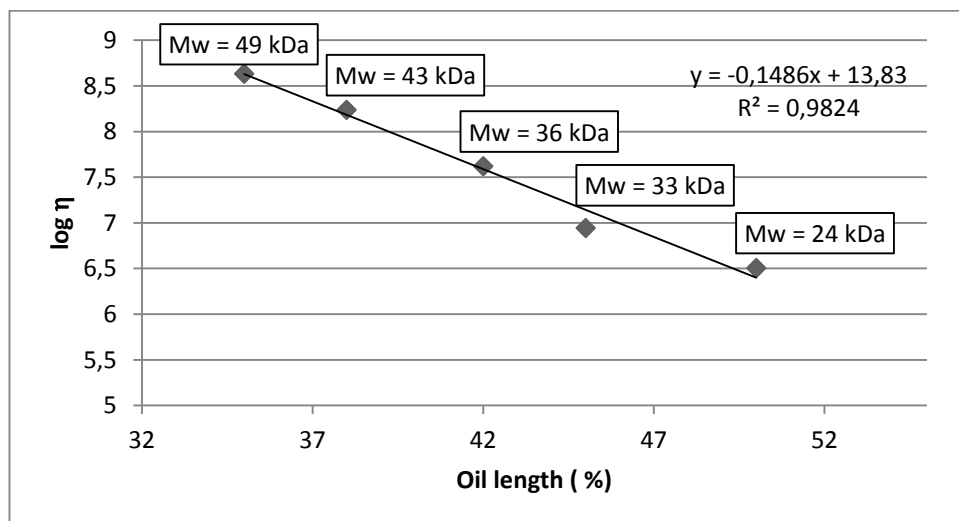


Figure 9 Plot of  $\log \eta$  versus oil length (%)

This relationship can be explained by the effect of oil length on the glass transition temperature of the alkyd resin. In DMTA tests the shift in temperature at a certain phase angle is an indication of the relative shift in glass transition temperature, which, when plotted against the oil length, shows a nearly identical relationship as the relationship of oil length and  $\log \eta$ .

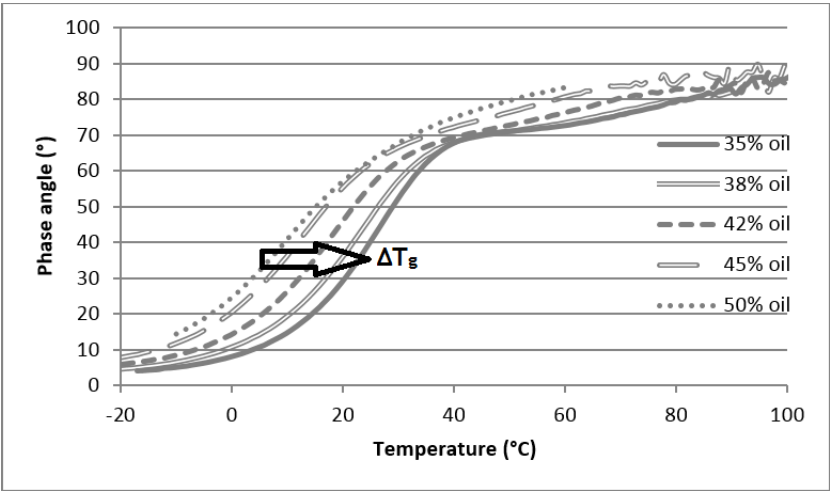


Figure 10 Phase angle versus temperature, DMTA measurement

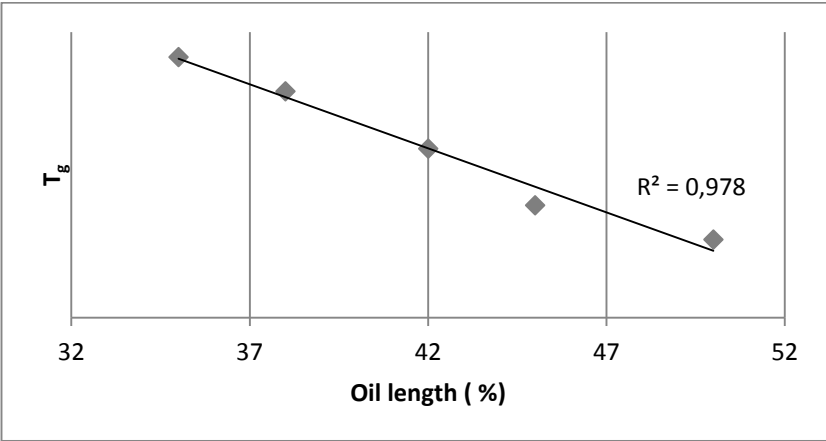


Figure 11 Plot of oil length (%) versus the glass transition temperature

The absolute shift in glass transition temperature is dependent on the phase angle at which the shift is observed. For this particular instance, a phase angle of  $36^\circ$  was chosen because the temperature shift at this phase angle is clearly visible.

### 8.3. Influence of viscosity and oil length on the coating properties<sup>8</sup>

The alkyd resin emulsions (7.5) were applied on black scrub panels (uneven substrate) and glass panels. After 24 hours of drying the coating properties were measured (7.7).

Table 3 Properties of alkyd resins and emulsions and their resulting coating properties

Name:	Oil length (%):	Neutralization (%):	Mean particle diameter (nm):	Viscosity of alkyd resin (Pa.s):	Gloss 20°:	König hardness (s):	Wetting agent added:
P_20K_OIL35_32.5	35	80	101	4.31*10 <sup>8</sup>	30	66	No
P_5K_OIL38_32.5	38	95	63	1.53*10 <sup>7</sup>	72	40	No
P_10K_OIL38_32.5	38	80	96	9.16*10 <sup>7</sup>	40	49	No
P_10K_OIL38_32.5	38	90	98	9.16*10 <sup>7</sup>	41	42	Yes
P_10K_OIL38_32.5	38	95	109	9.16*10 <sup>7</sup>	41	59	No
P_21K_OIL38_32.5	38	80	81	1.73*10 <sup>8</sup>	31	57	No
P_21K_OIL38_32.5	38	90	84	1.73*10 <sup>8</sup>	27	48	Yes
P_21K_OIL38_32.5	38	95	109	1.73*10 <sup>8</sup>	28	61	No
P_40K_OIL38_32.5	38	80	136	2.10*10 <sup>8</sup>	27	59	No
P_70K_OIL38_32.5	38	80	209	1.52*10 <sup>8</sup>	30	58	No
P_42K_OIL40_32.5	40	80	110	2.24*10 <sup>8</sup>	21	52	No
P_20K_OIL42_32.5	42	80	142	4.16*10 <sup>7</sup>	34	45	No
P_20K_OIL45_32.5	45	80	83	8.80*10 <sup>6</sup>	44	40	No
P_5K_OIL50_32.5	50	80	102	2.26*10 <sup>5</sup>	87	17	Yes
P_20K_OIL50_32.5	50	80	47	3.21*10 <sup>6</sup>	50	21	Yes
P_40K_OIL50_32.5	50	70	50	7.04*10 <sup>6</sup>	43	24	Yes

Given the leveling equation<sup>1</sup>, one would expect the gloss of a coating to be dependent on the viscosity of the alkyd resin only, as described in the following formula in which A and B are constants dependent on the coating thickness, surface tension and substrate unevenness.

$$\text{Gloss } 20^\circ = A * \text{Log}(\eta) + B \quad (7)$$

However, when the gloss of the coating with oil length 38 % and 50 % are plotted against the viscosity of the alkyd resins, it becomes evident that equation 7 is incomplete.

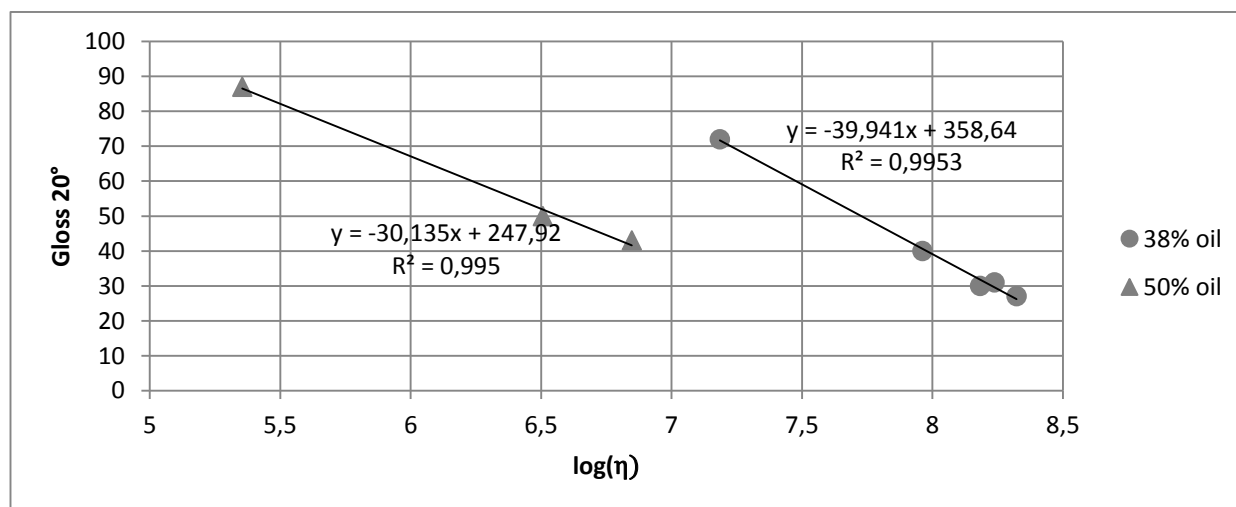


Figure 12 Log  $\eta$  versus gloss 20° for alkyd resins with oil length 38 % and 50 %

If equation 7 accurately described the relationship between gloss and viscosity, the constants A and B in the plots of figure 10 would be the same. Instead, there is a considerable difference in the constant B. Since the only varying property between the lines in figure 10 is the oil length, the difference in B must be attributed to the difference in oil length. A possible explanation is that a decrease in oil length decreases the rate of oxidative crosslinking in an alkyd resin, a reaction that takes place between the fatty acid chains described in chapter 6.3. The same effect is noticed when the gloss of alkyd resins with the same molecular weight and varying oil lengths are plotted against the viscosity.

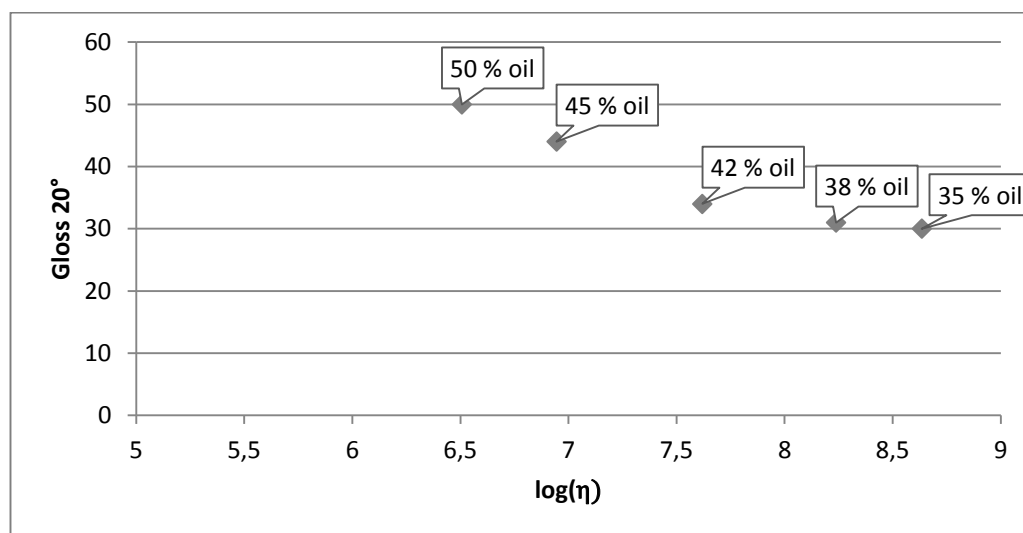


Figure 13 Plot of gloss 20° versus log η for alkyd resins with equal molecular weight and different oil lengths

Equation 7 suggests a linear relation expected between the gloss and log η. The alkyd resins with oil lengths of 38 % and 35 % however are too glossy for this linear relation to be true. After all, if lower oil length alkyd resins undergo slower oxidative crosslinking, the viscosities of these alkyd resins would increase more slowly and the film layers would undergo leveling for a longer time, increasing the gloss. Equation 7 was modified as follows to allow for this effect of changing oil length.

$$\text{Gloss } 20^\circ = A * \text{Log}(\eta) + B * \text{Oil \%} + C \quad (8)$$

In which A and C are constants dependent on surface tension, coating thickness and substrate unevenness, and B is a constant dependent on the type of fatty acids used in the synthesis of the alkyd resin. Constants A, B and C were determined by calculating the line of best fit, resulting in  $A = -34.93$ ,  $B = -3.75$ , and  $C = 461.93$  with a regression error of 4, calculated by regression analysis. When these values are inserted into equation 8 it can be rewritten as follows:

$$\text{Gloss } 20^\circ = -34.93 * \text{Log}(\eta) - 3.75 * \text{Oil \%} + 461.93 \pm 4 \quad (9)$$

The linear regression of  $\text{Gloss } 20^\circ - 3.75 * \text{Oil \%}$  versus  $\text{log}(\eta)$  of all emulsions is displayed in figure 14. Liyun Liang *et al.* reported a significant increase in the drying time and decrease in hardness of acrylate-modified alkyd resin coatings with neutralization grades of 90 % and higher when neutralized with triethylamine<sup>15</sup>. If this were to apply to the alkyd resin emulsions in table 3, of which several were neutralized to different extents, different gloss and König hardness would be expected compared to their counterparts with 80 % neutralization. However, the gloss stayed the same at different neutralization grades, and the König hardness increased at higher neutralization grades in emulsions where no wetting agent was added. In all emulsions where wetting agent had to be added in order to prevent cratering in the film the König hardness decreased significantly. This had no influence on the gloss, but it makes it impossible to find a relationship between viscosity, oil length and König hardness

for these emulsions since the emulsions with oil lengths of 50 % could not be applied without wetting agent.

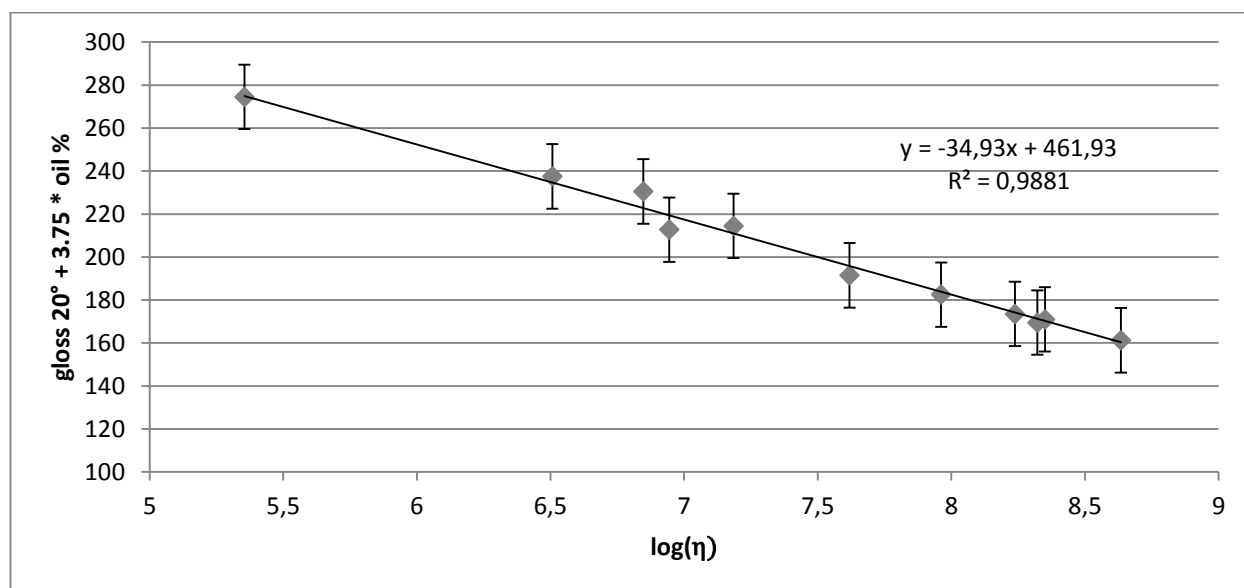


Figure 14 Plot of gloss 20° - 3.75 \* Oil % versus log η

#### 8.4. Stability of emulsions at different temperatures

Several emulsions with alkyd resins of varying oil lengths and molecular weights were stored in airtight vials at room temperature and at 40 °C. At room temperature the emulsions remained stable for several weeks, with some emulsions with smaller particle sizes remaining stable for several months. However, at 40 °C emulsions with larger particle sizes were seen to become unstable in less than 24 hours. No emulsions remained stable after 7 days at 40 °C.

Two explanations can be given for this, either the increased temperature dramatically increased the rate of particle coalescence and sedimentation, resulting in emulsion instability after short amounts of time, or some of the ester bonds in the alkyd resin undergo hydrolysis at significantly higher rates at increased temperatures. Phthalic anhydride, pentaerythritol, benzoic acid and soybean fatty acids have been proven to be suitable reagents for alkyd resins in the waterborne paint industry. Emulsions with alkyd resin composed of these reagents are known to be stable at 40 °C for at least four weeks. Polyurethane-alkyd resins synthesized with isophorone diisocyanate are also known to form stable emulsions. This leaves the ester bonds synthesized from hexahydrophthalic anhydride as the only bonds of the alkyd resin that possibly have a high susceptibility towards hydrolysis. To verify this, the rate of hydrolysis was determined as described in method (7.6). Since the solutions prepared in this method are acidic, the hydrolysis is assumed to only take place via the acid catalyzed hydrolysis mechanism, of which the reaction scheme is displayed in figure 15. In this reaction scheme the R groups represent the polymer backbone of the alkyd resin.

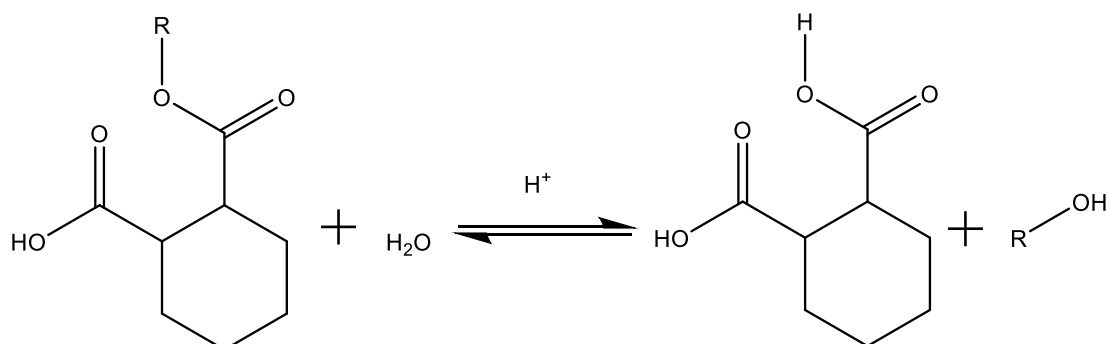
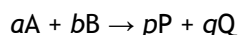


Figure 15 Reaction scheme of the acid catalyzed hydrolysis of hexahydrophthalic acid

Because an excess of water is used and because the esterification of the diacid with alkyd resin does not take place at a noticeable rate at 50 °C, the reaction is assumed to go to completion and the reaction rate is first order with respect to the ester. It should be noted that for every ester bond that hydrolyzes, another carboxylic acid group is formed. This increases the concentration of the catalyst and reaction rate. Thus, the higher the conversion becomes, the further the reaction rate will differ from the first order reaction which was observed at the start of the reaction. This was neglected in order to calculate the reaction rate as a first order reaction.

The reaction described in figure 15 could also be described as follows:



In this reaction the lowercase letters represent the stoichiometric parameters. The reaction rate for this reaction is defined as presented in equation 10.

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt} \quad (10)$$

When applied to the reaction in figure 13 the following equation is obtained, in which  $k$  is the reaction rate constant.

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k * [A] \quad (11)$$

Rearranging equation 11 and integrating results in:

$$\ln[A] = -k * t + \text{constant} \quad (12)$$

With the concentration of A at the start of the reaction given as  $[A]_0$  and the concentration of A at any given time as  $[A]_t$ , the constant in equation 12 is found to be  $\ln[A]_0$  and the equation can be rewritten as follows:

$$\ln[A]_t = -kt + \ln[A]_0 \quad (13)$$

If  $\ln[A]$  is plotted versus the reaction time with intercept  $\ln[A]_0$ , the resulting slope is equal to  $-k$ .

Because the solids content of the solution and the amount of hexahydrophthalic anhydride in the synthesis of the alkyd are known, the concentration of remaining hexahydrophthalic acid esters could be directly calculated from the measured acid values of the solutions with equation 14.

$$[HHPA\ ester]_t = [HHPA\ ester]_0 - \frac{(AV_t - AV_0) * SC}{56.1} \quad (14)$$

In which  $[HHPA\ ester]_t$  is the concentration of hexahydrophthalic acid esters in mmol/gram alkyd resin,  
 $[HHPA\ ester]_0$  is the concentration of hexahydrophthalic acid esters at the start of the reaction in mmol/gram alkyd resin,  
 $AV_t$  is the measured acid value of the solution in mg KOH/g solution,  
 $AV_0$  is the measured acid value at the start of the reaction in mg KOH/g solution,  
 $SC$  is the solids content of the solution in %(m/m).

Table 4 Concentration of hexahydrophthalic acid esters at several points in time, in mmol HHPA esters/g resin

Time (days)	50 °C	23 °C
0	0.428	0.428
4	0.288	0.404
8	0.232	0.401
12	0.173	0.394

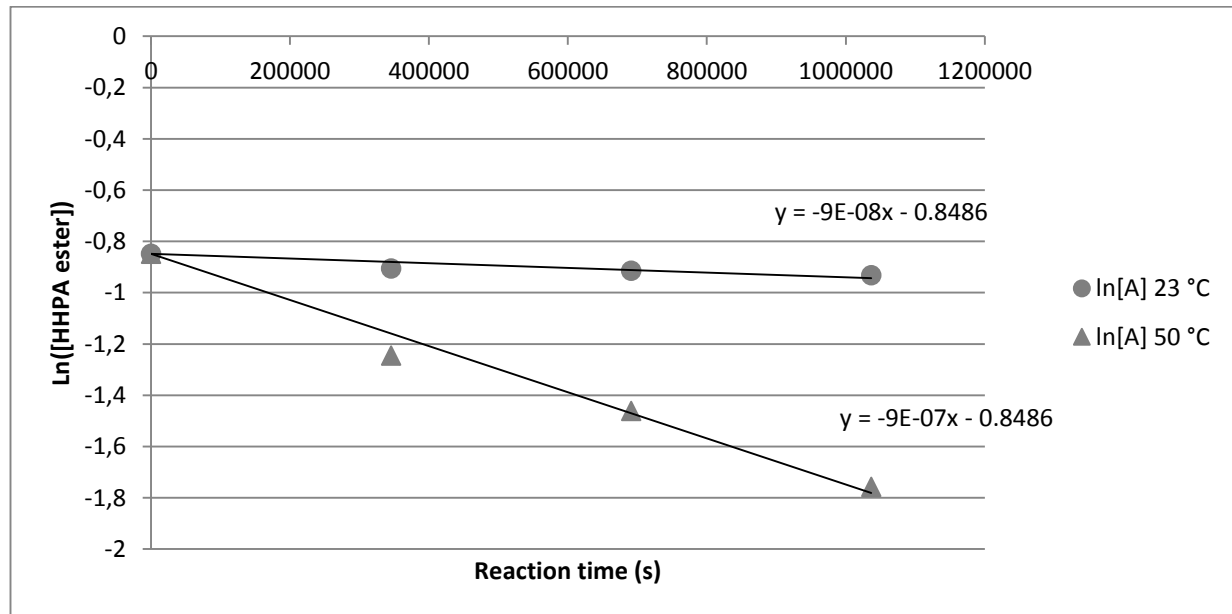


Figure 16 Plot of  $\ln[HHPA\ ester]$  versus reaction time at 23 and 50 °C

The slope of the regression equals  $-k$ , so the reaction speed coefficients are  $9 \cdot 10^{-8}$  at 23 °C and  $9 \cdot 10^{-7}$  at 50 °C. From these values the activation energy for the hydrolysis reaction was calculated using the Arrhenius equation given below.

$$k = A * e^{-\frac{E_a}{R * T}} \quad (15)$$

In which  $k$  is the reaction rate coefficient,  
 $A$  is the Arrhenius constant,  
 $E_a$  is the activation energy in J/mole,  
 $R$  is the universal gas constant,  
 $T$  is the temperature in degrees Kelvin.



Assuming the Arrhenius constant remains the same at different temperatures, equation 15 can be rewritten as follows, in which  $k_1$ ,  $k_2$ ,  $T_1$  and  $T_2$  are different reaction rate coefficients and their corresponding temperatures.

$$\frac{k_1}{k_2} = \frac{A}{A} * \frac{e^{-\frac{E_a}{R*T_1}}}{e^{-\frac{E_a}{R*T_2}}} \quad (16)$$

Which simplifies into the following equation which was used to calculate the activation energy of the hydrolysis reaction.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R * T_2} - \frac{E_a}{R * T_1} \quad (17)$$

The resulting activation energy was 67854 J/mole, or 67.85 kJ/mole. Decreasing the temperature from 23 °C to 7 °C, the temperature of a typical refrigerator, will result in a decrease in reaction rate of a factor 4.8.

### 8.5. Particle size of alkyd resin emulsions

There was no clear regression between the particle sizes of the emulsions when the molecular weight, oil length or neutralization grade were varied. The neutralization grade could however be raised upwards to 95 % to obtain better emulsion stability. For the alkyd resin named P\_5K\_OIL38\_32.5 stable emulsions could not be acquired with neutralization grades less than 95 %. When the alkyd resin named P\_40K\_OIL50\_32.5 was emulsified with a neutralization grade of 80 %, the viscosity of the emulsion became too high for application as a coating. When the neutralization grade was lowered to 70 % the viscosity became sufficiently low. Furthermore, the particle sizes appear to be at a minimum at a molecular weight of 30-40 kDa. The particle sizes generally decreased as the oil length increased, except for emulsion P\_20K\_OIL42\_32.5, which has an extraordinarily high mean particle size. The particle sizes were not significantly influenced when the neutralization grade was increased from 80 % to 90 %, but the particle sizes did increase when the neutralization grade was increased from 90 % to 95 %.

## 9. Discussion and conclusions

A series of alkyd resins with different molecular weights and oil lengths were successfully synthesized and post-modified with hexahydrophthalic anhydride to increase the acid value. These alkyd resins were dissolved in acetone and further increased in molecular weight by chain extension with isophorone diisocyanate. The expected relationship between viscosity and molecular weight,<sup>2,3</sup>

$\text{Log}(\eta) = A + C\overline{M}_w^{\frac{1}{2}}$ , could accurately be applied to the series of alkyd resins with an oil length of 50 %. For the alkyd resins with an oil length of 38 %, this equation did not provide an accurate fit. More alkyd resins would have to be synthesized at lower oil lengths and higher molecular weights to conclude when this equation can be applied to describe the relationship between alkyd resin viscosity and molecular weight. A similar relationship was found between the viscosity and oil length,  $\text{Log}(\eta) = A + C * \text{OIL} \%$ , a relationship identical to the relationship between the glass transition temperature and oil length, as was concluded from the DMTA measurements.

The alkyd resins were successfully emulsified via the acetone process, in which the carboxylic acid groups of the alkyd resin were partially (70-95 %) neutralized with trimethylamine to provide the ionic stabilization required to form stable emulsions. The particle sizes of these emulsions were seen to decrease as the molecular weight, oil length or neutralization grade of the alkyd resins increased. The emulsions were applied to black scrub panels (uneven substrate) to measure the resulting gloss, and to glass panels to measure the König hardness. The gloss was found to be dependent on both the viscosity and the oil length of the alkyd resin in accordance to the following equation, which was found by calculating the line of best fit:

$$\text{Gloss } 20^\circ = -34.93 * \text{Log}(\eta) - 3.75 * \text{Oil } \% + 461.93 \pm 4$$

The constants in this equation are dependent on the surface tension, coating thickness, substrate unevenness and type of fatty acids used in the synthesis of the alkyd resin.

The influence of the extent of neutralization and the addition of a wetting agent on the gloss and König hardness was explored by varying the neutralization grade of several emulsions and adding wetting agent to the emulsions that cratered when applied as a film. The gloss was unaffected by both neutralization grade and the addition of wetting agent, but the König hardness decreased significantly when wetting agent was added. The König hardness increased by 7-25 % upon increasing the neutralization grade from 80 to 95 %.

The emulsions were found to remain stable at room temperature for at least 3 weeks, with some emulsions remaining stable for over two months. At 50 °C however, the emulsions became unstable after 24 hours to 7 days depending on the particle size of the emulsion. The emulsions with larger particle sizes were found to become unstable the fastest. The cause for this is the hydrolysis of the ester bonds of hexahydrophthalic acid on the backbone of the alkyd resin, which decreases the ionic stabilization of the dispersed phase (alkyd resin) and increases the electrolyte concentration of the continuous phase (water).

The rate constants of this hydrolysis reaction at 23 and 50 °C were determined in a solution of alkyd resin, triethylamine, acetone and water. From these reaction rate constants an activation energy of 67.85 kJ/mole was calculated. The reaction rate at 50 °C was found to be ten times as high as the reaction rate at 23 °C. Decreasing the temperature from 23 to 7 °C, by storing the emulsions in a fridge, would in theory decrease the reaction rate by a factor 4.8, thus increasing the shelf life of the emulsions significantly.

## 10. References

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## 11. Appendix

### 11.1. Steady state measurements

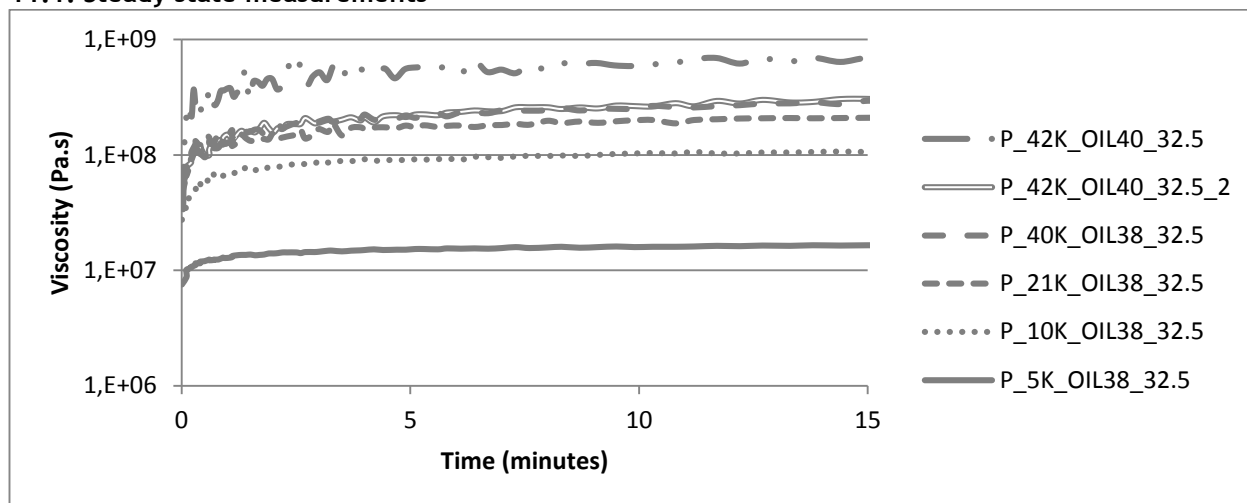


Figure 17 Steady state measurements; Alkyd resins with oil lengths of 38 and 40 %

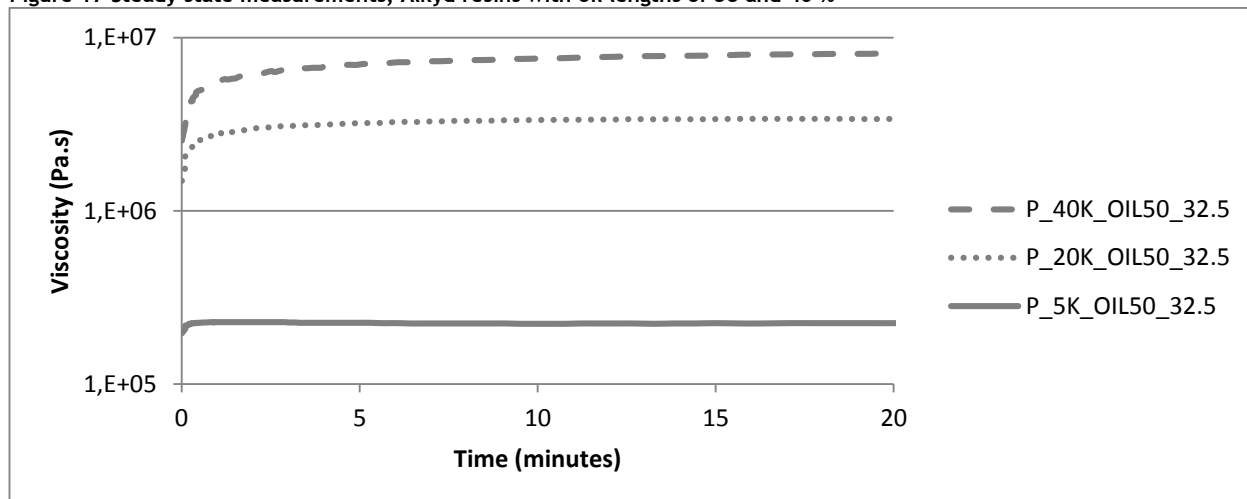


Figure 18 Steady state measurements; Alkyd resins with an oil length of 50 %

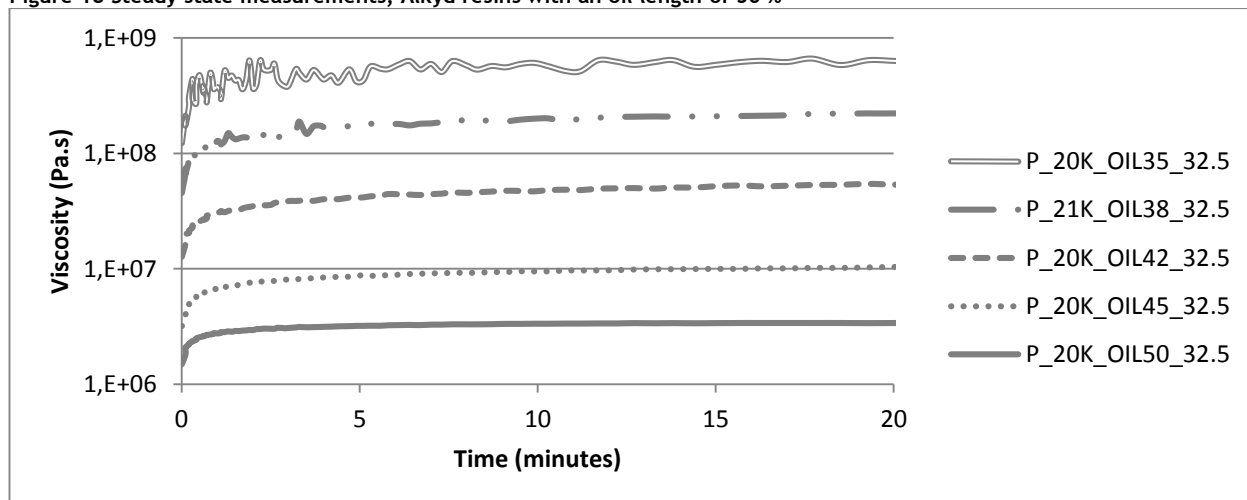


Figure 19 Steady state measurements; Alkyd resins with varying oil lengths

## 11.2. Dynamic mechanical thermal analysis measurements

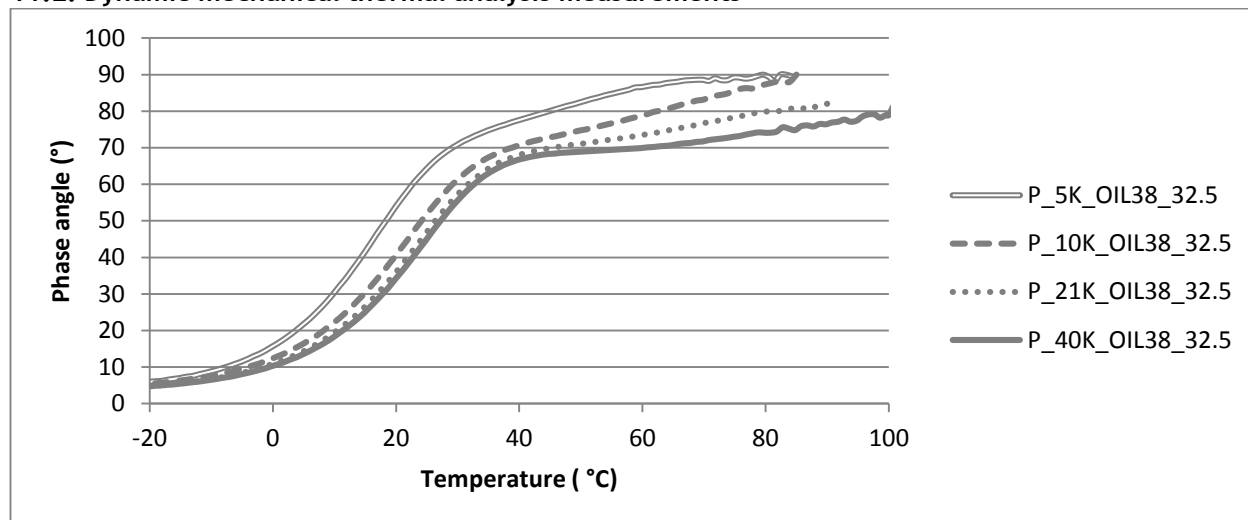


Figure 20 Dynamic mechanical thermal analysis; Alkyd resins with an oil length of 38 %

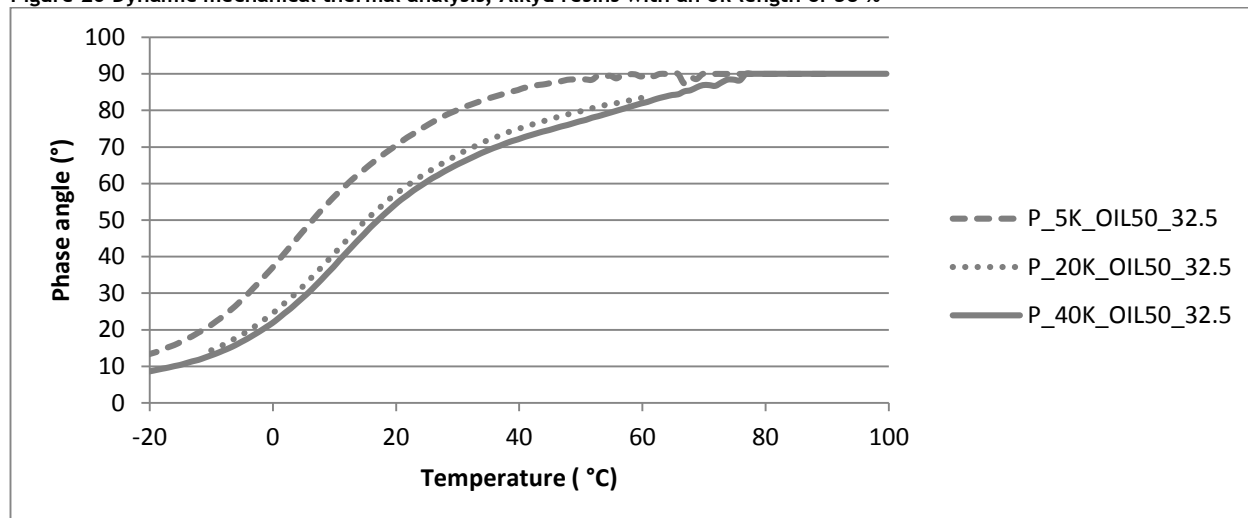


Figure 21 Dynamic mechanical thermal analysis; Alkyd resins with an oil length of 50 %

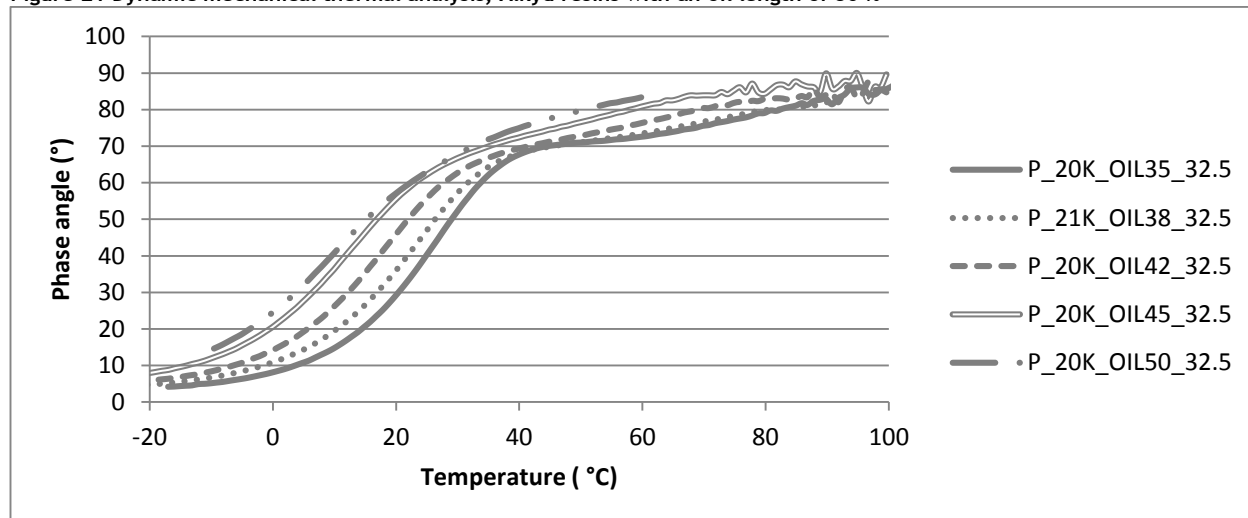


Figure 22 Dynamic mechanical thermal analysis; Alkyd resins with varying oil lengths

## 11.3. APC chromatograms

DSM Resins bv

Analytical Department

## OVERLAY\_OPENSHOP

Project Name GPC\MIX\_B\_WW

Current Date 5/6/2015

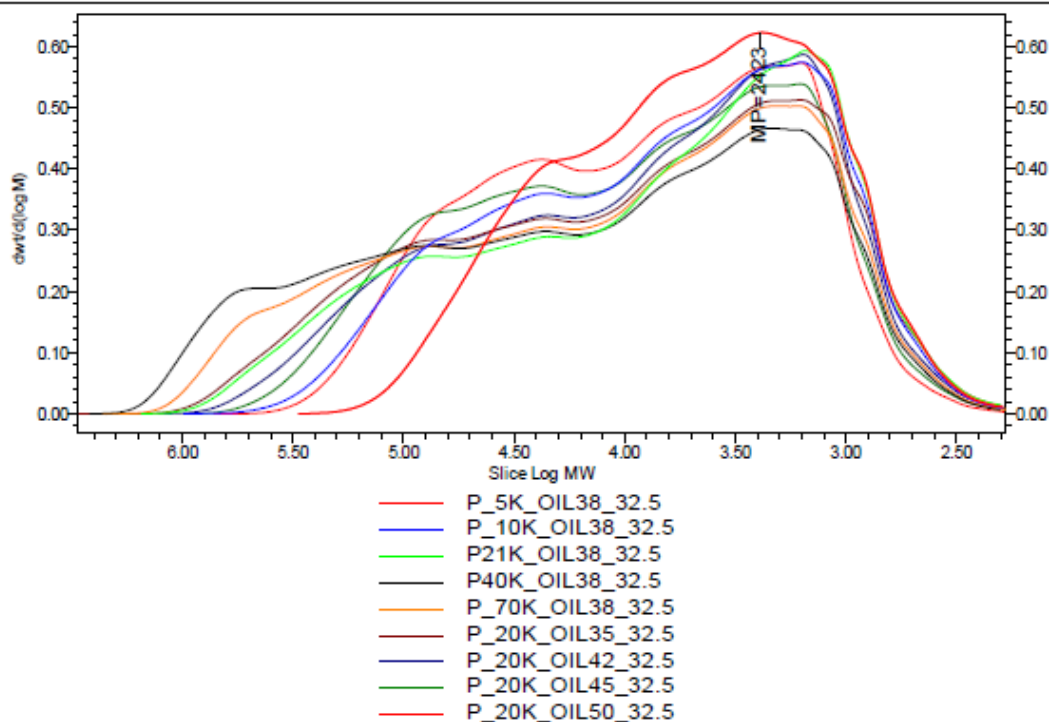
Requested by: J v/d Hoek

Processing Method MIXB\_WW

The molecular weights are calculated with respect to polystyrene by SAM-5019 (60 cm columns from 02-06-2001)  
 These values are no absolute values and need to be round off as follow: <10.000 to 10 (9210)

10.000 - 100.000 to 100 (10.800)

&gt;100.000 to 1000 (191.000)



## GPC Results

	SampleName	Mn	Mw	Mp	D.
1	P_5K_OIL38_32.5	2405	12466	2423	5.2
2	P_10K_OIL38_32.5	2617	24624	1600	9.4
3	P21K_OIL38_32.5	2531	43417	1535	17.2
4	P40K_OIL38_32.5	3339	98455	2240	29.5
5	P_70K_OIL38_32.5	3097	70313	2181	22.7
6	P_20K_OIL35_32.5	2745	48732	2097	17.8
7	P_20K_OIL42_32.5	2750	36299	1578	13.2
8	P_20K_OIL45_32.5	3132	33311	2262	10.6
9	P_20K_OIL50_32.5	3273	24374	1614	7.4

Figure 23 APC chromatogram; Alkyd resins with various oil lengths and molecular weights

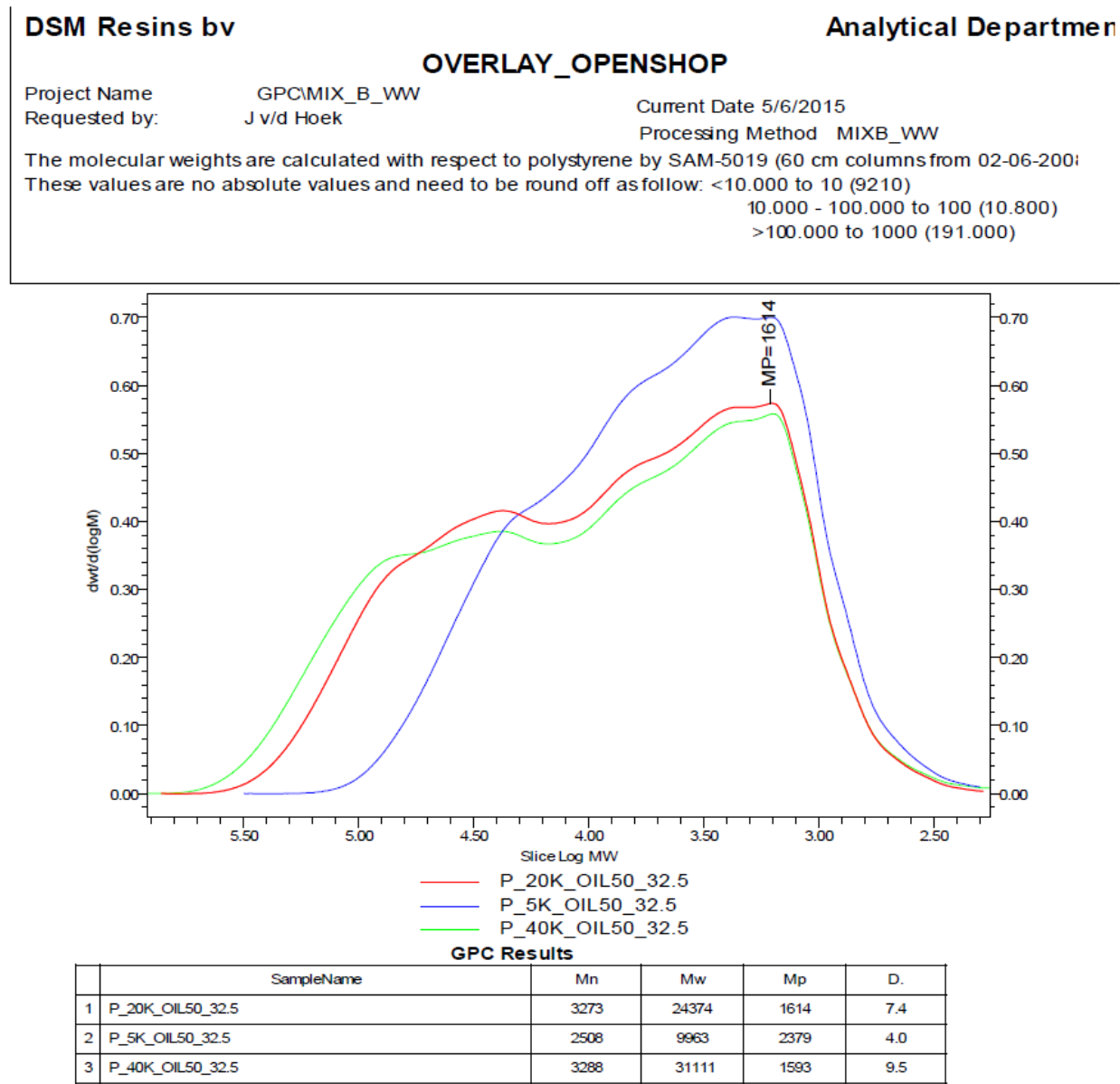


Figure 24 APC chromatogram; Alkyd reins with an oil length of 50 %

11.4. Particle size distribution analysis

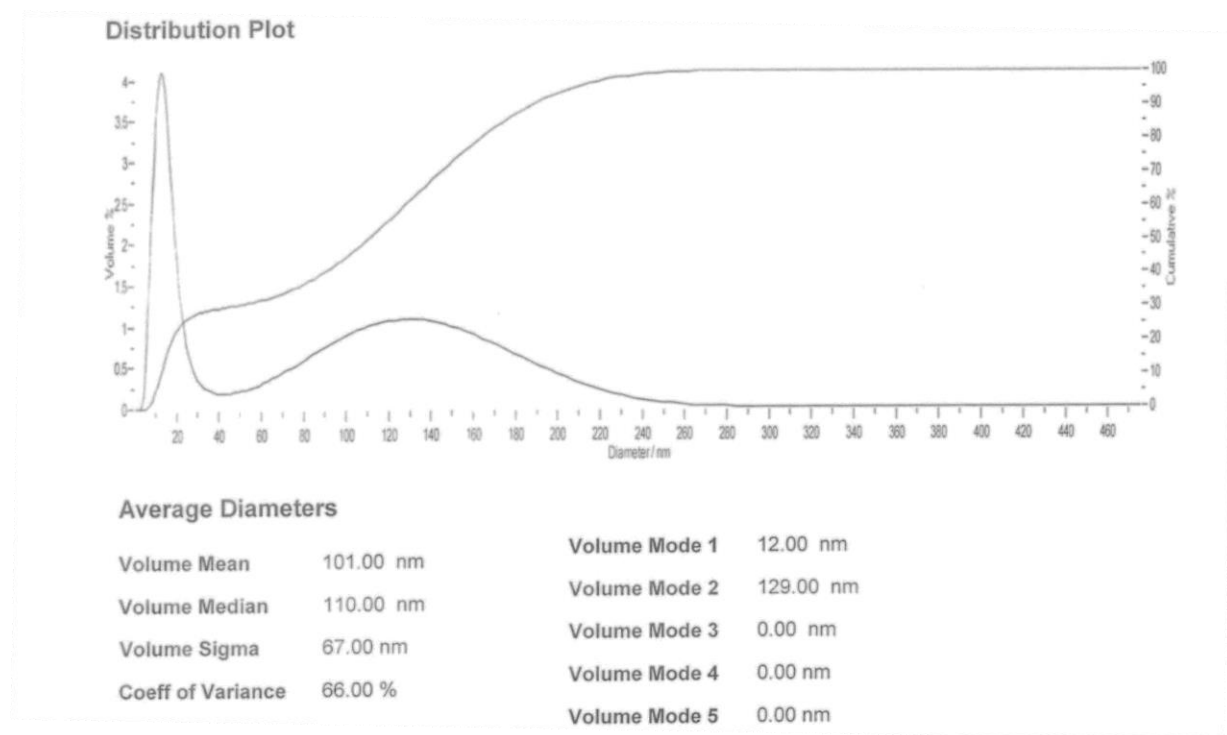


Figure 25 Particle size distribution analysis; P\_20K\_OIL38\_32.5, neutralization grade 80 %

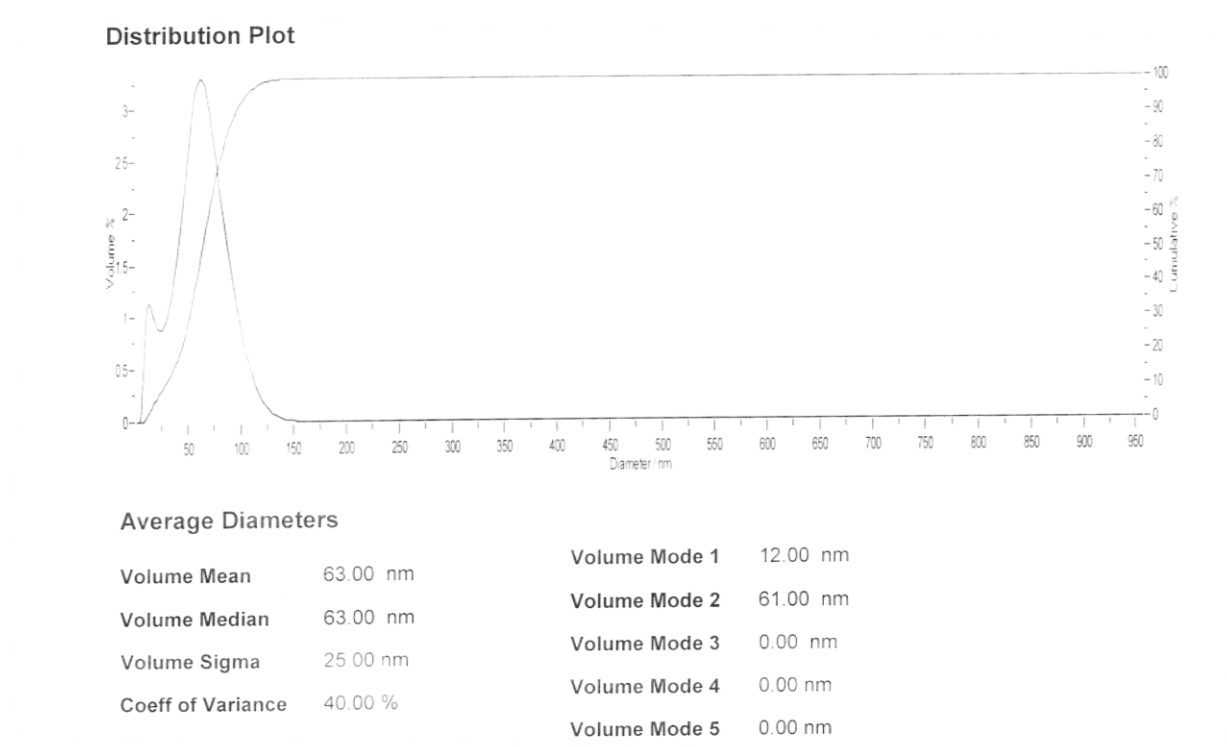


Figure 26 Particle size distribution analysis; P\_5K\_OIL38\_32.5, neutralization grade 95 %



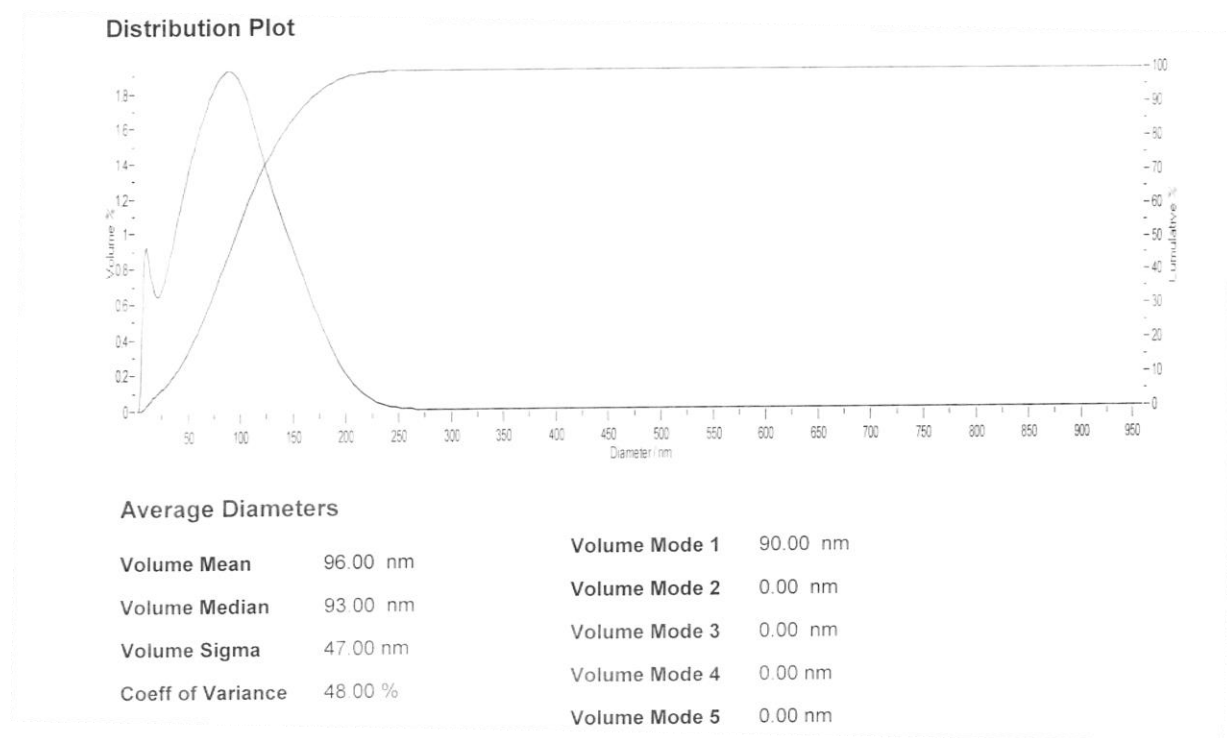


Figure 27 Particle size distribution analysis; P\_10K\_OIL38\_32.5, neutralization grade 80 %

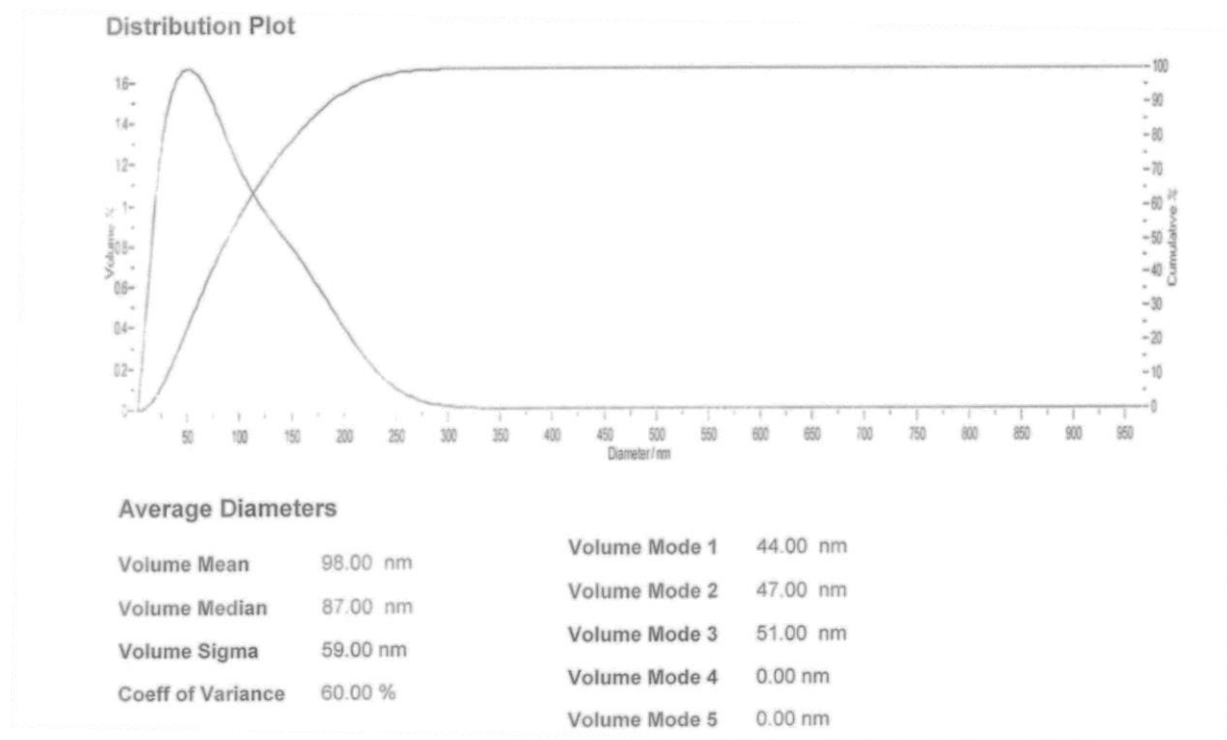


Figure 28 Particle size distribution analysis, P\_10K\_OIL38\_32.5, neutralization grade 90 %

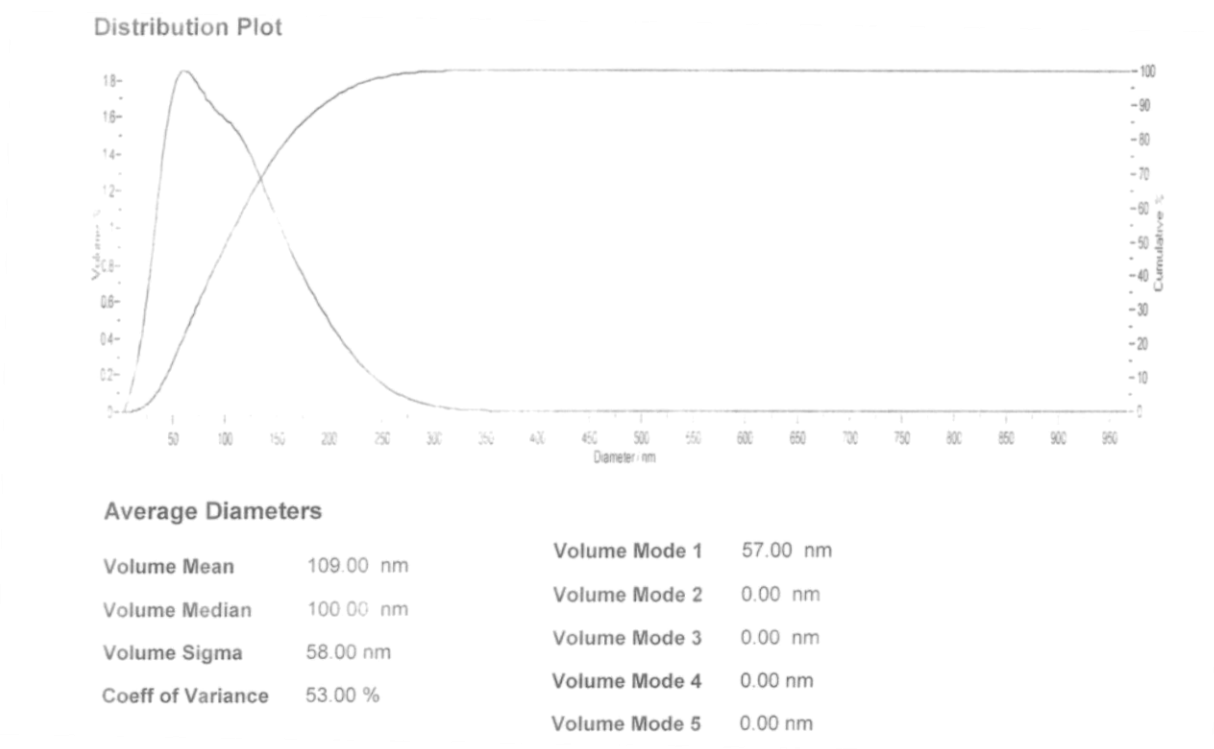


Figure 29 Particle size distribution analysis; P\_10K\_OIL38\_32.5, neutralization grade 95 %

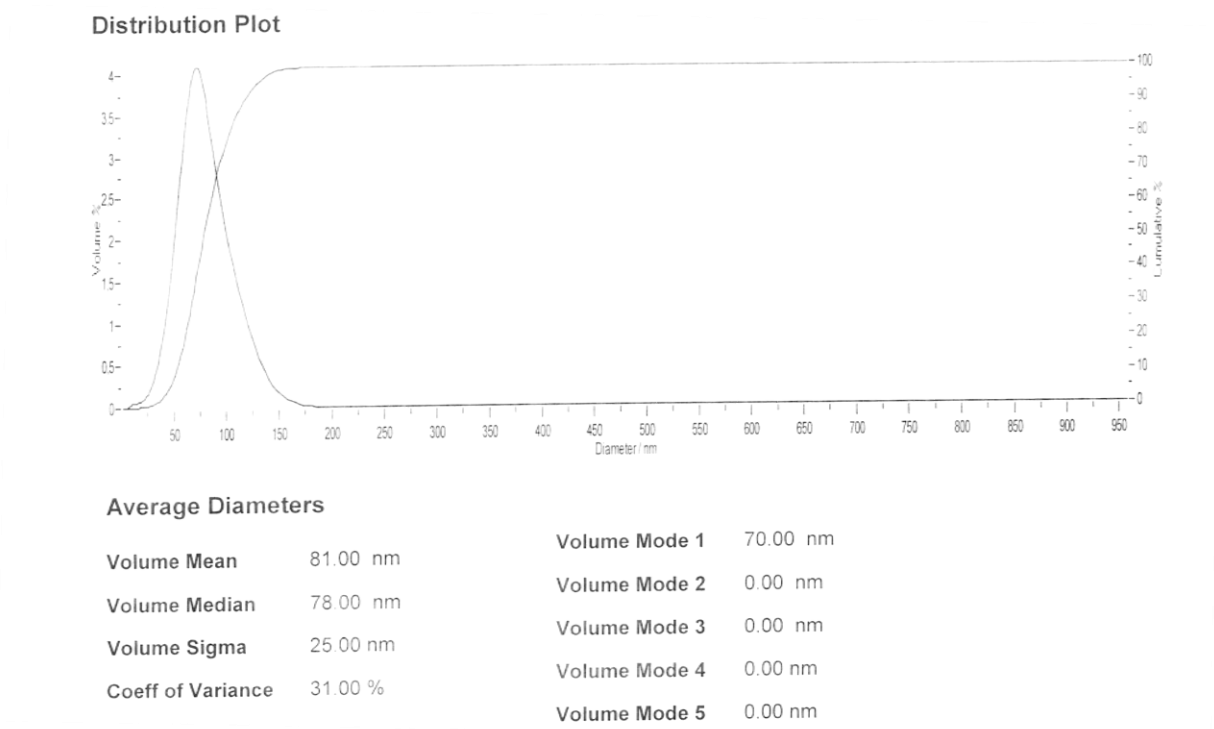


Figure 30 Particle size distribution analysis; P\_21K\_OIL38\_32.5, neutralization grade 80 %

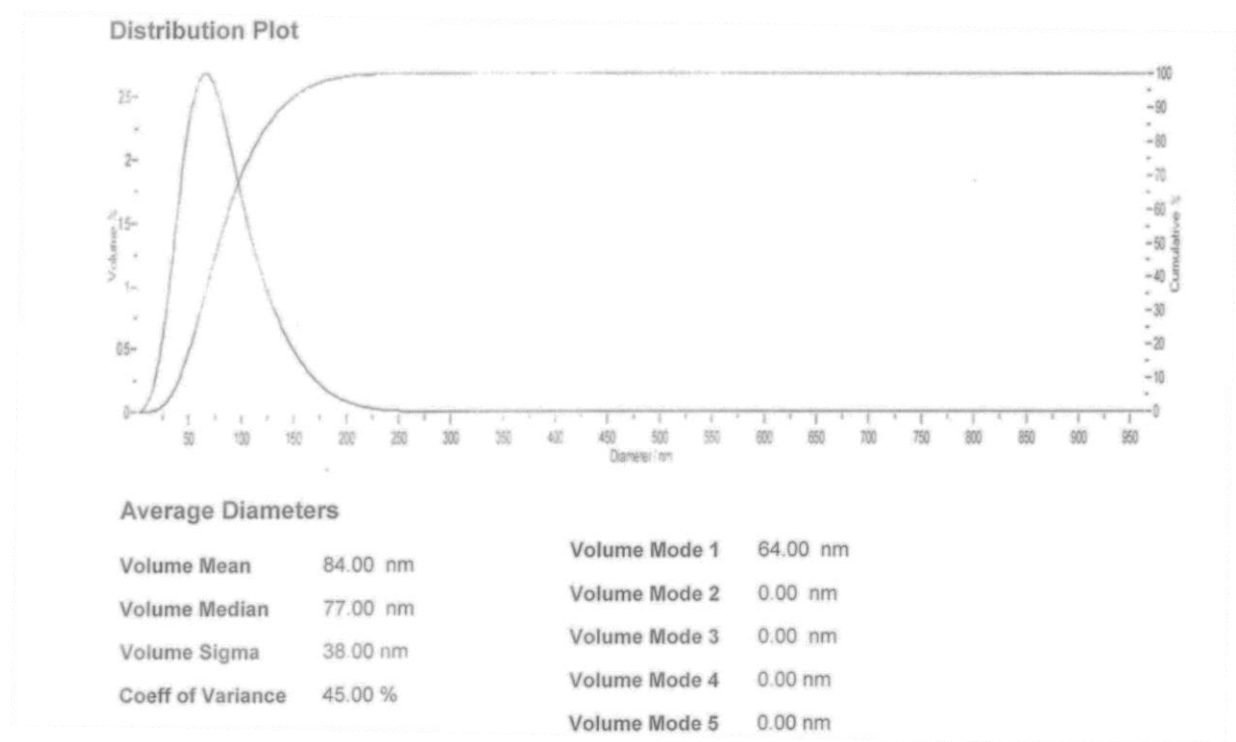


Figure 31 Particle size distribution analysis; P\_21K\_OIL38\_32.5, neutralization grade 90 %

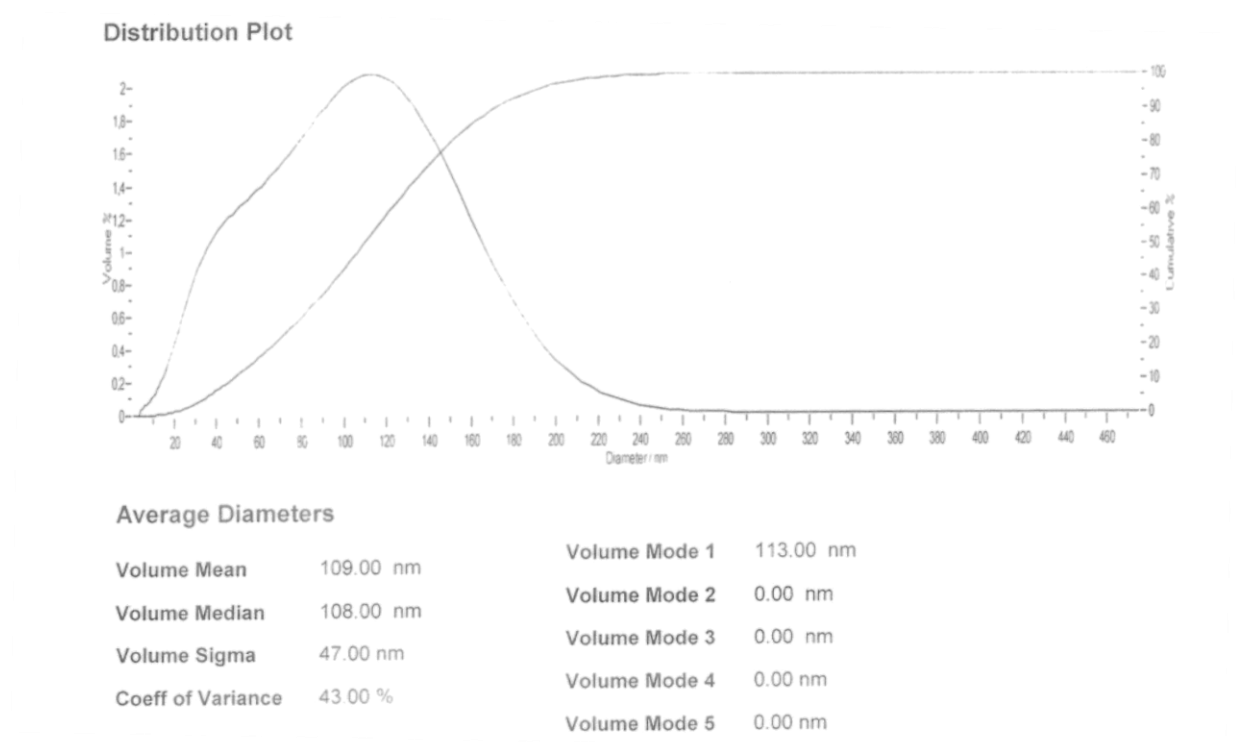


Figure 32 Particle size distribution analysis; P\_21K\_OIL38\_32.5, neutralization grade 95 %

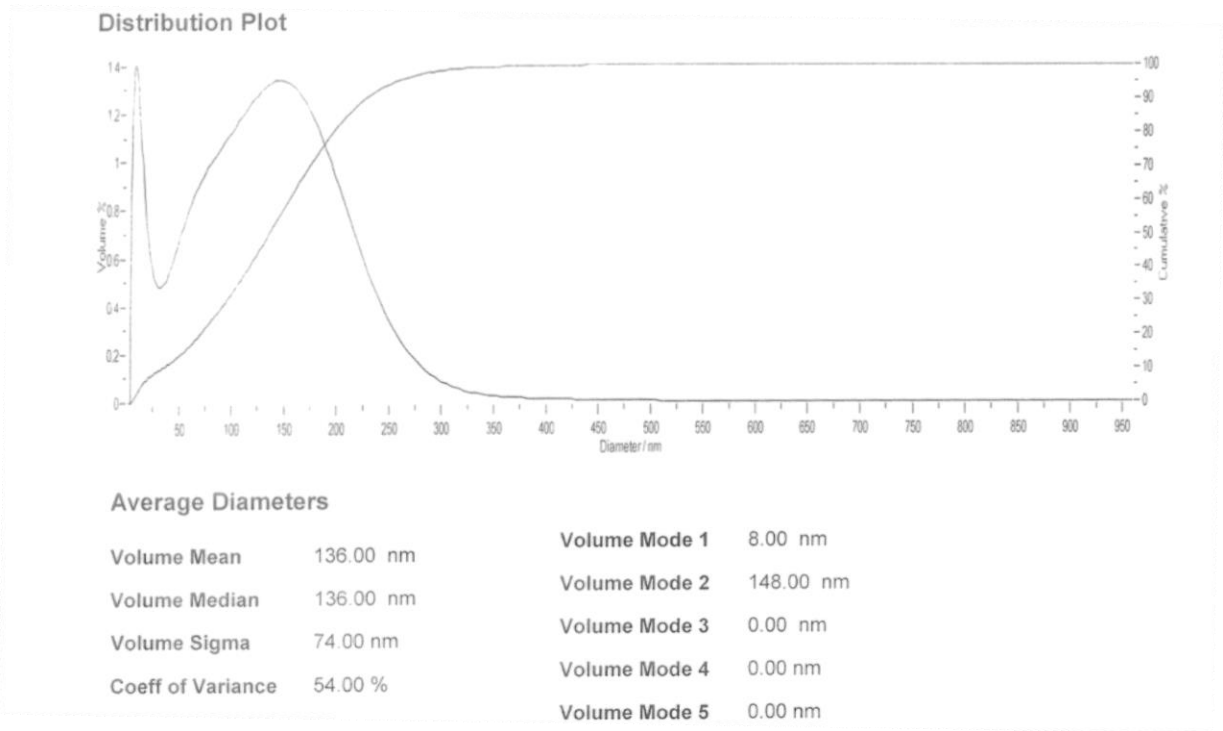


Figure 33 Particle size distribution analysis; P\_40K\_OIL38\_32.5, neutralization grade 80 %

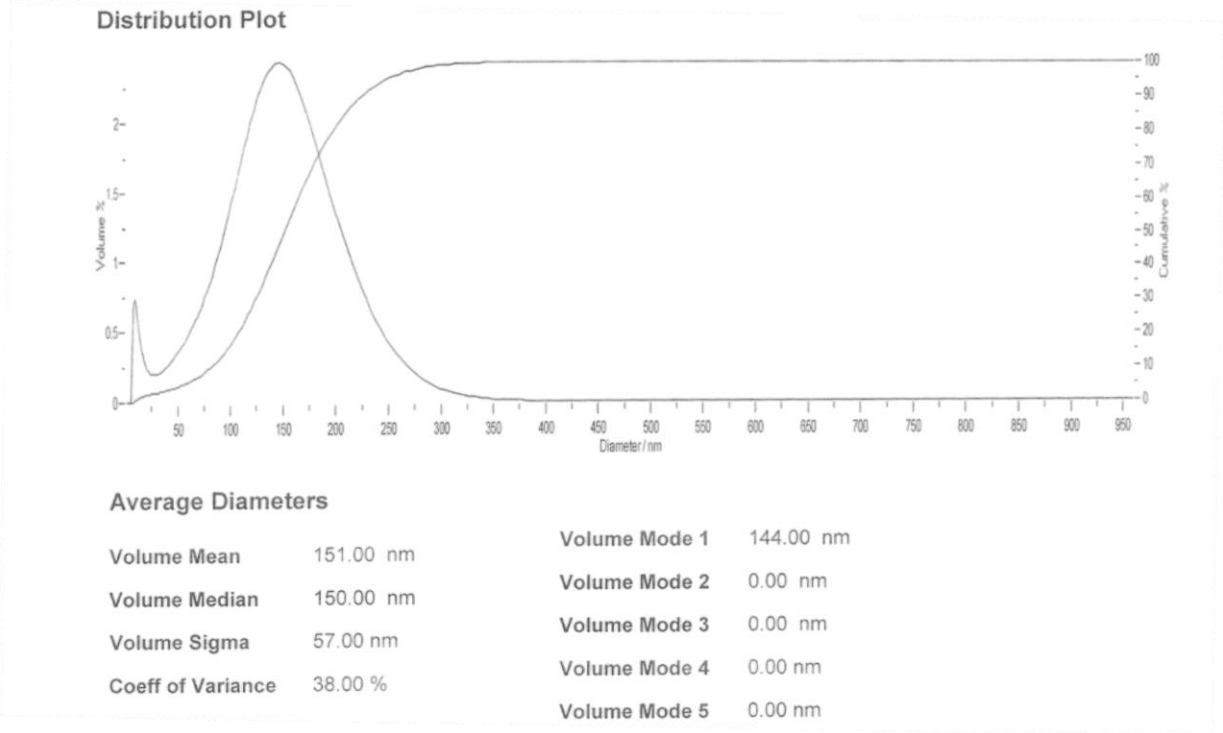


Figure 34 Particle size distribution analysis; P\_70K\_OIL38\_32.5, neutralization grade 80 %

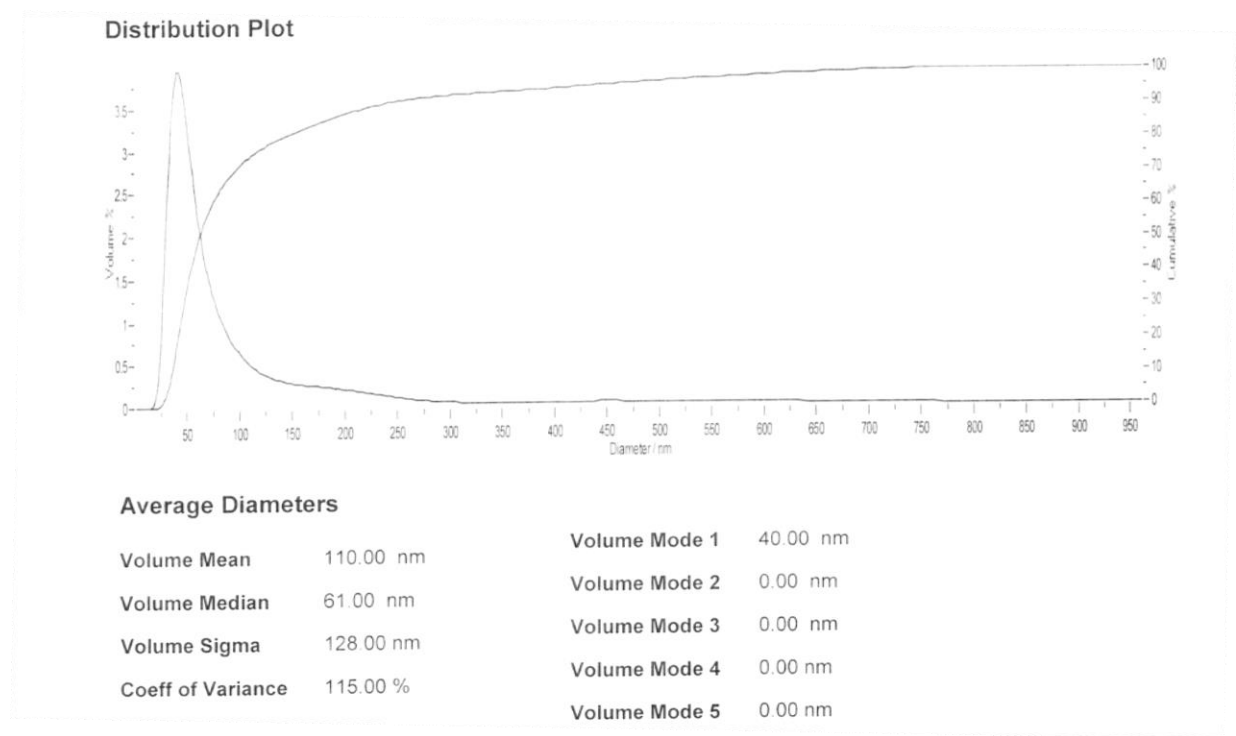


Figure 35 Particle size distribution analysis; P\_42K\_OIL40\_32.5, neutralization grade 80 %

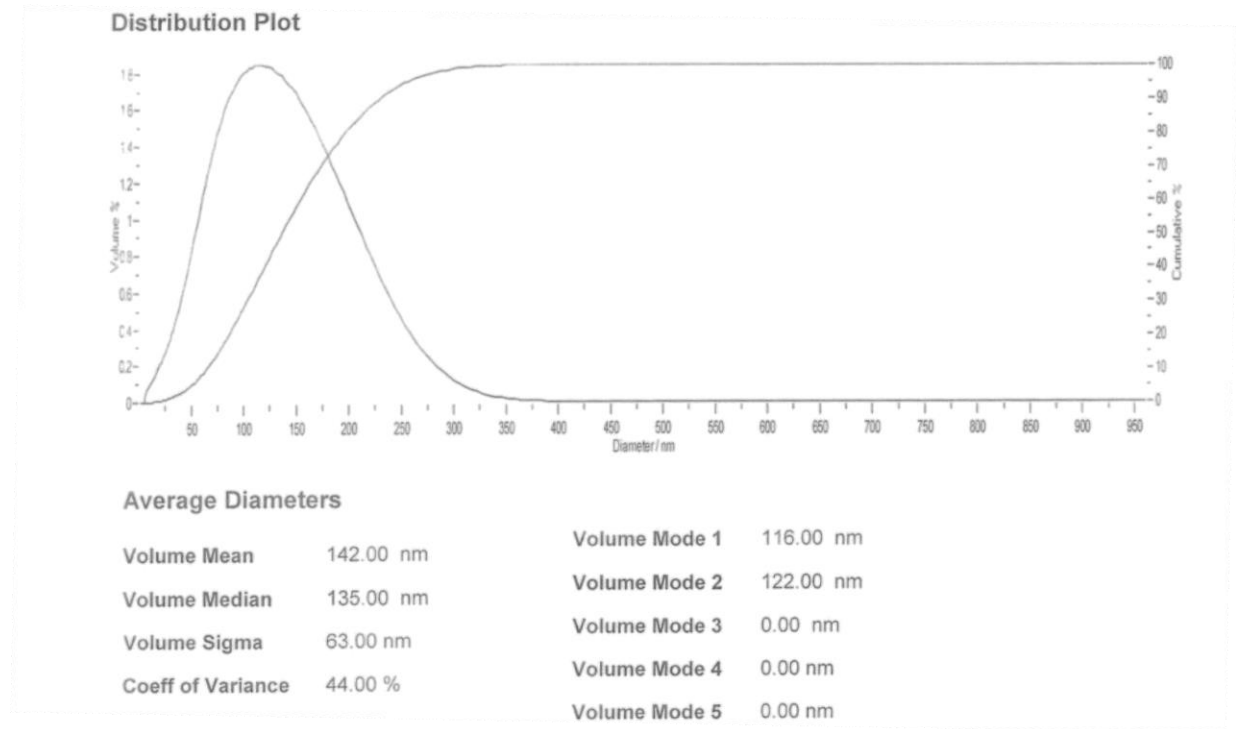


Figure 36 Particle size distribution analysis; P\_20K\_OIL42\_32.5, neutralization grade 80 %

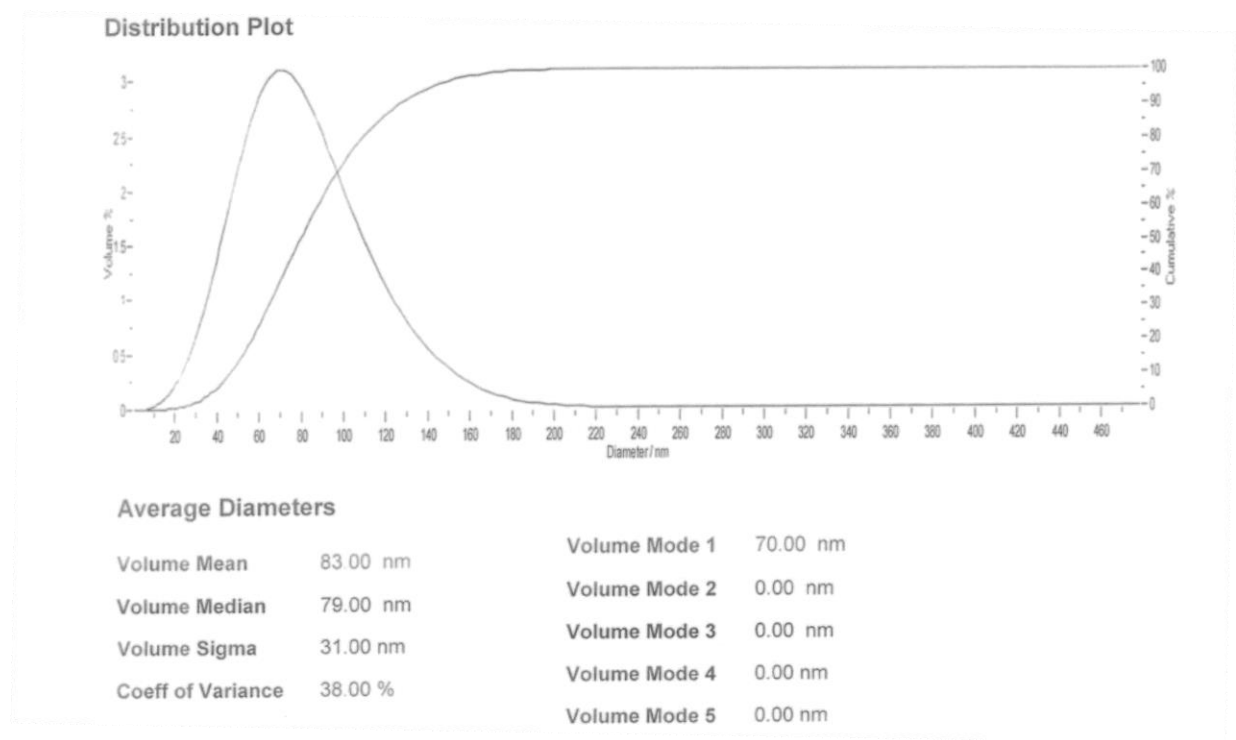


Figure 37 Particle size distribution analysis; P\_20K\_OIL45\_32.5, neutralization grade 80 %

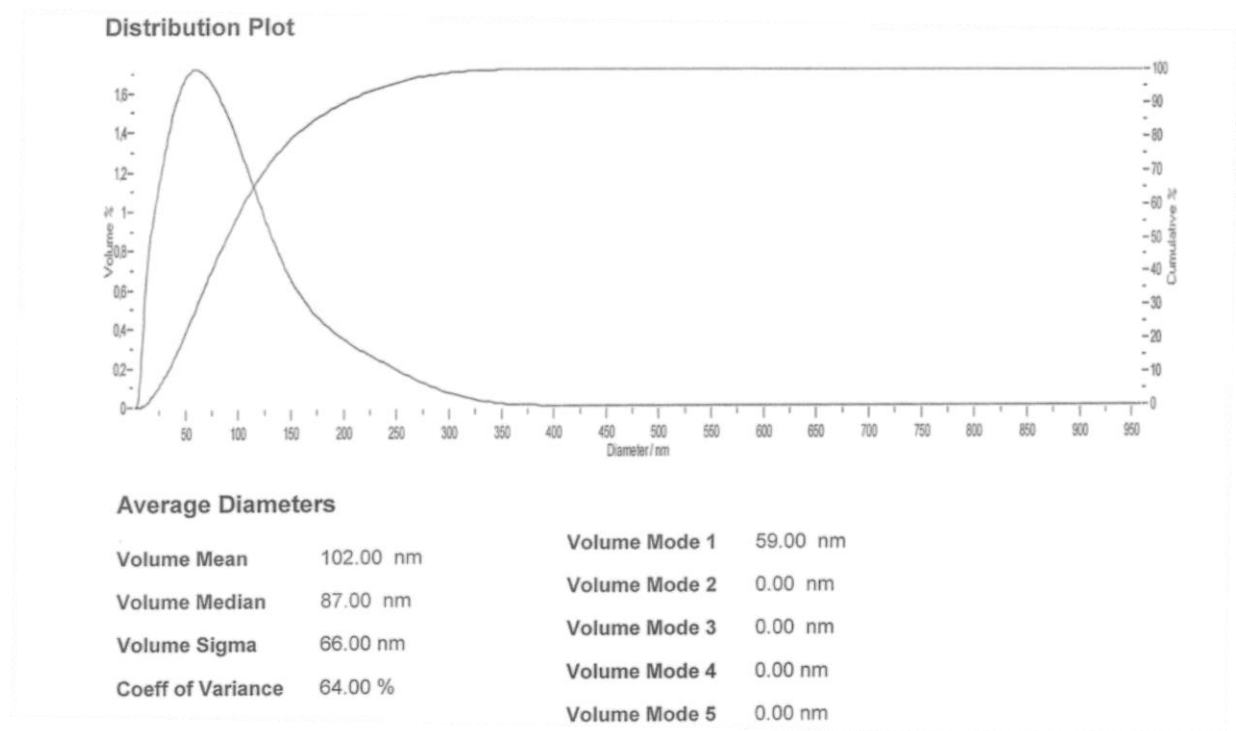


Figure 38 Particle size distribution analysis; P\_5K\_OIL50\_32.5, neutralization grade 80 %

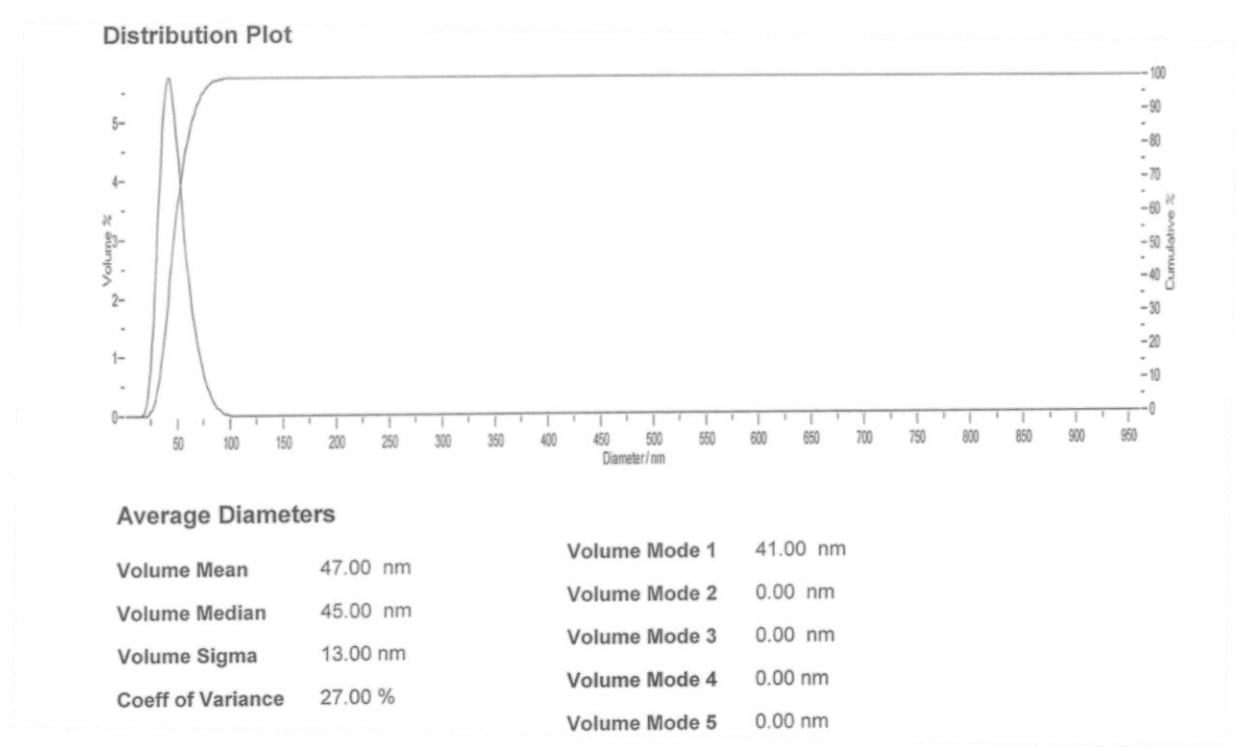


Figure 39 Particle size distribution analysis; P\_20K\_OIL50\_32.5, neutralization grade 80 %

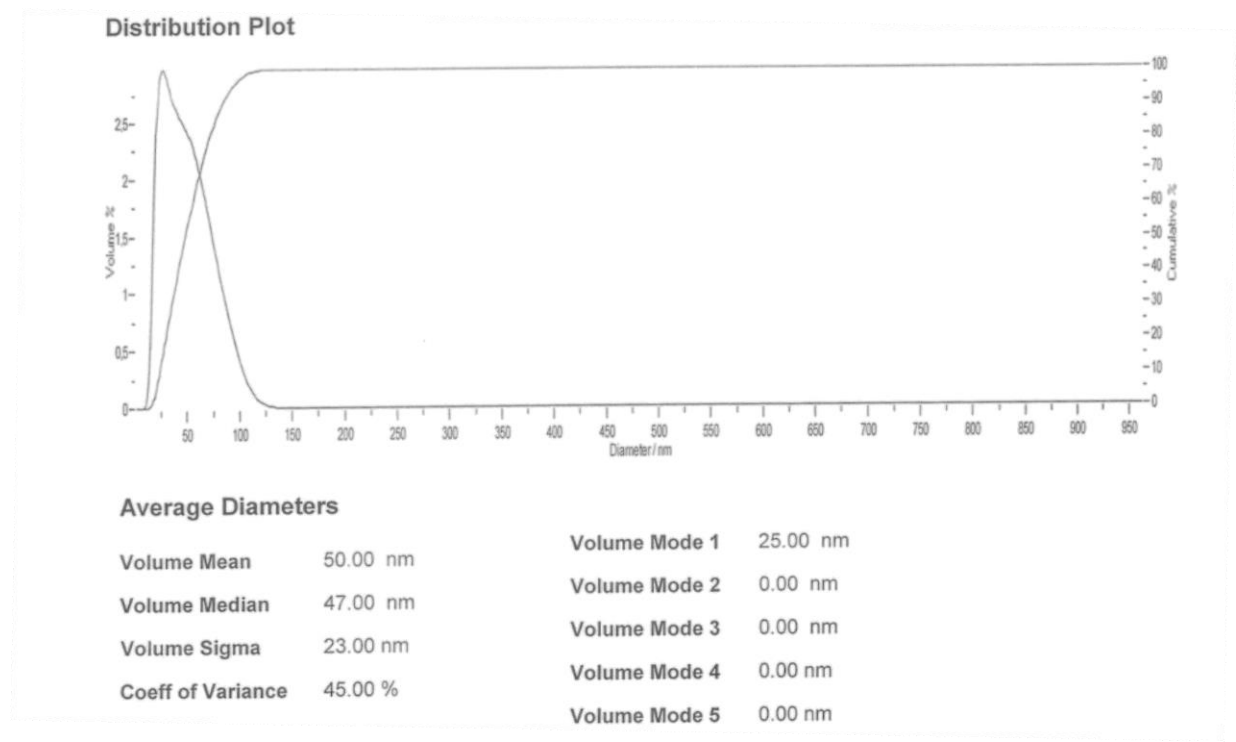


Figure 40 Particle size distribution analysis; P\_40K\_OIL50\_32.5, neutralization grade 70 %