

**SYNTHESIS, CHARACTERIZATION AND EVALUATION OF
MACROMONOMERS USED TO PREPARE RHEOLOGY
MODIFIERS FOR POSSIBLE IMPROVEMENT OF THE
PIGMENTATION OF DECORATIVE COATINGS.**

BY

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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not in its entirety, or in part, been submitted at any university as a degree.

ABSTRACT

There is a decrease in viscosity when universal colorants are added to the latex coating system. Two different routes were taken to investigate this problem. The first was to investigate the thickening mechanism of the coating system. For this purpose six different hydrophobically modified alkali-soluble (HASE) thickeners were synthesized. The second was to compile new color concentrate formulations.

The HASE thickeners consist of acrylic acid and a second associative monomer. The associative monomer (macromonomer) contained a long chain hydrophilic segment, terminated with a hydrophobic group. The hydrophilic segment consists of polyethoxylation, situated between the ethylenic unsaturation at one end of the molecule and the terminal hydrophobe at the other end. Three different macromonomers were prepared by coupling the hydroxyl end groups of three commercially available nonionic surfactants with either acrylic acid or acryloyl chloride. A much higher yield of macromonomer was obtained when the nonionic surfactants were reacted with the acryloyl chloride.

Six HASE thickeners were synthesized by means of free radical addition polymerization. The first three HASE thickeners had the same backbone length and each thickener containing one type of hydrophobic macromonomer. The hydrophobic macromonomers differed in the length of their repeating oxyethylene units. They contained either 20, 50 or 100 oxyethylene units. The next three HASE thickeners were very similar to the first three except that 5% of the acrylic acid in the backbone was substituted with a second, phosphated, macromonomer, meaning that these thickeners each contained two types of macromonomers.

These thickeners were then introduced into a standard latex coating formulation. By comparing the rheology profiles of the different coatings it was possible to determine the thickening efficiencies of the different thickeners. These coatings were also evaluated for their viscosity stability when tinted with a universal colorant. The HASE thickeners containing the second phosphated macromonomer showed superior thickening efficiency. All six coatings showed excellent stability on tinting with a universal colorant.

Following the second route of investigation, eight universal colorant formulations consisting of only one polymeric dispersant in each of the formulations as sole wetting

and dispersing additive were made up. A commercially available universal colorant was used as standard against which the new formulations were tested. The colorants were tested for color strength, their compatibility with the different coating groups, and the rheology profiles of the tinted vs. untinted coating systems. The two colorant formulations that contained EFKA 4550 as the polymeric dispersant performed very well in all the coating groups.

OPSOMMING

Daar is 'n afname in viskositeit wanneer universele kleurstowwe by die lateks-bedekkingsstelsel gevoeg word. Twee verskillende roetes is gevolg om die probleem te ondersoek. Die eerste was om die verdikkingsmeganisme van die bedekkingsstelsel te ondersoek. Vir die doel is ses verskillende hidrofobiese gemodifiseerde alkali-oplosbare (HASE)-verdikkingsmiddels gesintetiseer. Die tweede was om nuwe kleurkonsentraatformulerings saam te stel.

Die HASE-verdikkingsmiddels bestaan uit akrielsuur en 'n tweede assosiatiewe monomeer. Die assosiatiewe monomeer (makromonomeer) bevat 'n langketting-hidrofiliese segment, met 'n hidrofobiese endgroep. Die hidrofiliese segment bestaan uit herhalende oksietileen eenhede, tussen die etiliese onversadigde aan die een punt van die molekule en die hidrofobiese endgroep aan die ander punt. Drie verskillende makromonomere is voorberei deur die koppeling van die hidroksiel-endgroepe van drie kommersieel beskikbare anioniese sepe met akrielsuur of akriëelchloried. 'n Baie hoër opbrengs van makromonomere is verkry toe die anioniese sepe met die akriëelchloried gereageer is.

Ses HASE-verdikkingsmiddels is gesintetiseer deur middel van vrye radikaal addisie polimerisasie. Die eerste drie HASE-verdikkingsmiddels het dieselfde ruggraatlengte en elke verdikker bevat een tipe hidrofobiese makromonomeer. Die hidrofobiese makromonomere verskil in die lengte van hul herhalende oksietileen eenhede. Die hidrofobiese makromonomere bevat of 20, 50 of 100 oksietileen eenhede. Die volgende drie HASE-verdikkingsmiddels stem baie ooreen met die eerste drie behalwe dat 5% van die akrielsuur in die ruggraat vervang is deur 'n tweede, fosfaatbevattende makromonomeer, wat beteken dat hierdie verdikkingsmiddels elk twee tipes makromonomere bevat.

Hierdie verdikkingsmiddels is in 'n standaard lateks bedekking formulering gevoeg. Deur die vergelyking van die reologie profiele van die verskillende bedekkings was dit moontlik om die verdikkings effektiwiteit van die verskillende verdikkingsmiddels te bepaal. Hierdie bedekkings is ook geëvalueer vir hulle viskositeits stabiliteit as dit met 'n universele kleurstof gekleur word. Die HASE-verdikkingsmiddels wat die tweede fosfaatbevattende makromonomeer bevat, het uitstekende verdikkings effektiwiteit getoon. Al ses bedekkings het uitstekende stabiliteit getoon tydens kleuring met 'n universele kleurstof.

Deur die tweede roete van ondersoek te volg, is agt universele kleurstof formuleringe wat bestaan uit slegs een polimeriese disperseermiddel opgemaak. 'n Kommersieel beskikbare universele kleurstof is gebruik as standaard waarteenoor die nuwe formuleringe getoets is. Die kleurstowwe is getoets vir kleursterkte, hul verenigbaarheid met die verskillende bedekkingsgroepe, en die reologie profiele van die gekleurde teenoor die ongekleurde bedekkingsisteme. Die twee kleurstof formuleringe wat EFKA 4550 as die polimeriese disperseer middel bevat, het baie goed gevaar in al die bedekkingsgroepe.

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CHAPTER 1

GENERAL INTRODUCTION AND OBJECTIVES

1.1 INTRODUCTION

Today the paint manufacturer can provide the homeowner with a large selection of paint shades (many offer about 1500 different shades) by having in their inventory only 12 universal color concentrates or tinting colors and only three tint bases within each chemical coating group. However prior to the end of World War II, however, there were very few color pigments and binder systems available to the paint manufacturer, but from the late 1940's up to the mid to late 1950's many technical improvements and discoveries came about in raw materials as well as in manufacturing and processing equipment [1]. These new and exciting developments gave the paint manufacturer a variety of opportunities to provide the customer with specific, long-lasting coatings for every specific application. All these advantages soon mushroomed into a monumental problem for the paint manufacturer. There were so many new colors and paint systems, how were they going to keep up with all this? It was during this time that paint chemists began to realise that many colour pigments had to be ground up separately into color concentrates. Universal colorants were then designed for tinting of both latex (water based) and alkyd (solvent based) systems.

Both the paint and colorant system are very complex and are made up from a number of different components. As individual systems they may be stable, but this stability must be upheld when the colorant is added to the paint system. This means that good compatibility must be maintained between the two systems. In practice this is not so easy, because of the wide variety of color concentrates and chemical coatings.

In spite of all the raw materials available today, one of the major problems that still occurs when colorants are added to a coating system is the drop in viscosity of the coating. This may indicate that the colorants disrupt the thickening mechanism of the coating system. To investigate the above mentioned problem, there are two different routes one could take. The first is to investigate the thickening mechanism of the coating system and the second is to investigate the colorant concentrate formulations.

In this thesis the first route of investigation was into hydrophobically modified alkali-soluble (HASE) thickeners in latex coatings. This group of thickeners was selected because they work by means of a dual thickening mechanism [2-7].

The second route of investigation was into compiling new color concentrate formulations. The composition of universal colorants is based primarily on pigments, ethylene glycol, water and surface-active agents selected to provide compatibility of the colorants in both organic- and water-based coating formulations [8]. The new color concentrate formulations are based on substituting the surface-active agents with a single, commercially available polymeric dispersant.

1.2 OBJECTIVES

Throughout the research, the author ultimately aim to create a better understanding of the viscosity problem (drop in viscosity) that arises when coating systems are tinted with universal colorants and to provide certain solutions.

The first main objective of this thesis was to synthesise different HASE thickeners that would provide stable thickening of a latex coating system. The viscosity of these coatings should also be stable when tinted with universal colorants.

The second main objective was to formulate color concentrates which contains only one polymeric dispersant as sole wetting and dispersing additive.

Towards achieving these main objectives there were certain secondary objectives. These included:

1. To synthesize macromonomers from commercially available nonionic surfactants with varying degrees of ethoxylation.
2. In synthesizing the macromonomers, a monomer containing polymerizable ethylenic unsaturation is coupled to the nonionic surfactant by means of a esterification reaction. Two different esterification reactions are to be used and compared to one another.
3. To characterize the macromonomers by means of Proton Nuclear Magnetic Resonance spectrometry ($^1\text{H-NMR}$) and Fourier Transform Infrared spectrometry (FTIR).
4. To synthesize HASE thickeners by means of free radical addition polymerization.
5. To characterize the HASE thickeners by means of solid state carbon 13 nuclear magnetic resonance spectrometry ($^{13}\text{C NMR}$).
6. To test the thickening efficiency of the HASE thickeners by introducing them into a latex coating system and then to draw up a rheology profile of each of the coatings.
7. To test the thickening stability of the coatings by tinting them with a commercially available universal colorant.
8. To test the colour concentrates to be formulated in three different chemical coating systems. The colorant concentrates are to be evaluated according to their compatibility, colour strength and their influence on the rheology profile of the different coatings.

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CHAPTER 2

HISTORICAL BACKGROUND

ASSOCIATIVE THICKENERS AND COLORANTS

2.1 ASSOCIATIVE THICKENERS

2.1.1 WHY THICKENERS ARE NEEDED IN LATEX PAINTS.

Coating formulations based on aqueous polymer latices usually require adjustment of viscosity or, more precisely, their rheology profile. A rheology profile describes the shear rate and time-dependent paint viscosity that affects such properties as pigment settling, brush and roller pickup, film build, leveling and the sagging of the film on vertical surfaces. The relationship between fundamental rheology parameters and several of these practical paint flow properties have been discussed by Glass [1,2] and Patton [3]. Although viscosity can be adjusted by varying the concentration of the latex and other solids dispersed in the formulation, this option offers limited control. The viscosity of a latex or other dispersions is essentially dictated by the volume solids concentration of the dispersion. Although the effective solids volume can be controlled to some extent by manipulating particle size distribution and absorbed or grafted materials such as surfactants or low molecular weight water-soluble polymers, this nonetheless falls short of what the paint formulator needs, and almost inevitably involves compromise of other performance properties. In addition, increases in solids volume have relatively little effect on viscosity until a crowded particle condition is reached, and then viscosity increases rapidly as close packing is approached. This allows little margin for error: Slightly lower solids volume results in viscosity too low for desired performance, whereas slightly high solids volume may lead to excessive viscosity, dilatency, or even gelation. Finally, increasing the solids volume is the most expensive way to increase viscosity, particularly in latex-rich formulations.

Water-soluble polymers afford a much more efficient and controllable means of adjusting viscosity. In this case viscosity and rheology are a function not only of the concentration of polymer but also of its molecular weight, the flexibility of its backbone and, for ionic polymers, the charge concentration along the backbone and the ionic strength. Of course, specific as well as nonspecific interactions of these water-soluble polymers with the latex particles and other dispersed-phase particles, such as by adsorption, can also profoundly affect overall coating rheology.

The efficiency of water-soluble polymers in increasing viscosity is a major practical consideration. Thickening efficiency may be expressed in terms of the viscosity provided at a given concentration of the water-soluble polymer (as it often is in the product literature of thickener manufacturers), but in the coatings industry it is usually expressed in terms of the amount of thickener required to obtain a target viscosity in a latex formulation. Cost is only one reason why thickening efficiency is of concern to coatings manufacturers. Because a key property of most water-based coatings formulations is their ability to resist water once a film is formed, and water-soluble polymeric thickeners will inevitably compromise this performance to some extent, it is important to use only as much thickener as is necessary to achieve the desired rheology. Unfortunately, the most efficient thickeners are not always the best in providing the overall rheology profile necessary for a given application and the formulator is often faced with difficult choices.

2.1.2 CLASSIFICATION OF THICKENERS

Paint thickeners can be classified in several ways, according to whether they are organic or inorganic, naturally derived or completely synthetic, nonionic or anionic (alkali-swellable), soluble or swellable, and, of main interest here, whether they are "associative" or nonassociative. We define associative thickeners (ASTs) as water-soluble or water swellable polymers that have chemically attached hydrophobic groups that are capable of non-specific hydrophobic association similar to those of conventional surfactants. As Table 2.1 suggests, associative thickener analogs exist for many of the important nonassociative water-soluble polymers [4], including those that have been used extensively as paint thickeners.

Table 2.1

 Classification of thickener type.

ORGANIC THICKENERS**Nonassociative****Naturally derived**

Nonionic cellulosics, e.g., hydroxyethyl cellulose, methyl cellulose, ethyl hydroxyethyl cellulose, hydroxypropyl cellulose

Anionic cellulosics, e.g., carboxymethyl cellulose

Other polysaccharides, e.g., dextran, alginates

Other, e.g., caseinates

Synthetic

Nonionic, e.g., poly (ethylene oxide), poly (vinyl alcohol), polyacrylamide, ethylene-oxide based polyurethanes

Alkali-soluble, e.g., acrylics, styrene/maleic

Alkali swellable, e.g., cross-linked acrylic acid emulsions

Associative**Naturally derived**

Nonionic

Hydrophobically modified hydroxyethyl cellulose (HMHEC)

Synthetic

Nonionic

Hydrophobically modified ethylene oxide urethane (HEUR)

Hydrophobically modified polyacrylamide (HPAM)

Anionic

Hydrophobically modified alkali soluble (or swellable) emulsion (HASE)

INORGANIC THICKENERS

Clays, e.g., attapulgite, bentonite

Titanium chelates

2.1.3 CELLULOSE THICKENERS

Cellulose derivatives, especially cellulose ethers, are by far the most important nonassociative thickeners in the paint industry [5-7]. Cellulose itself is a naturally occurring polysaccharide consisting of repeating anhydroglucose units, which provide a relatively straight and stiff polymeric backbone. A greater volume is occupied in solution by the stiff, extended conformation thickeners, derived from cellulose, than other water-soluble polymers of similar molecular weight, such as poly (ethylene oxide) and polyacrylamide, hence cellulose is very effective in increasing the viscosity of water. The most widely used cellulose ethers are hydroxyethyl cellulose (HEC) (Figure 2.1). Other cellulose ethers that find some use in paints are methyl cellulose, hydroxypropylmethyl cellulose, and ethylhydroxyethyl cellulose.

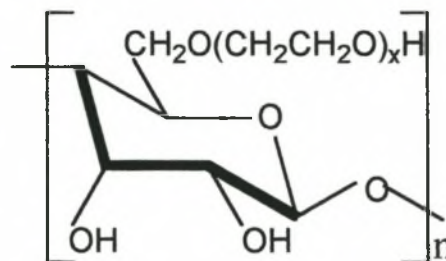


Figure 2.1

The structure of hydroxyethyl cellulose

For over 35 years cellulose ethers have been the standard thickeners of the latex paint industry, but they have been unable to provide latex paints with the application and appearance properties of solvent-based alkyd paints. At low shear rates the high viscosity impedes the leveling of brush marks and at high shear rates the low viscosity limits film build up, which is important for both hiding and protection of the substrate. Conventional cellulosic thickeners have the tendency to flocculate latex formulations and thereby hinder gloss development. In cases where small particle size latices are used, these limitations are especially severe and since small particle size latices are usually best for pigment binding and adhesion, providing the best properties in the dry paint film, this represents a significant limitation to latex paint technology. The high molecular weight cellulose ether thickener also causes paints to spatter excessively, specially when applied by roller. Like other naturally derived thickeners, they are also prone to

enzymatic degradation and therefore a decrease in viscosity of the paint during storage [8-9]. This problem was partially overcome when a hydroxyethyl cellulose (Natrasol 250 HBR) of improved biostability was developed. This product has a significantly lower unsubstituted glucose content than normal, which makes it resistant to attack by microorganisms. When it is used as a thickener in latex paints it extends the time the paint will be viscosity-stable if contamination should occur [10-11].

Cellulosic thickeners can also be hydrophobically modified and this modification gives them the same thickening efficiency than much higher molecular weight grades of normal HEC thickeners. A schematic presentation of a hydrophobically modified hydroxyethyl cellulose (HMHEC) molecule is shown in Figure 2.2. HMHEC appears to associate very little with latex particles themselves, interacting more strongly with pigments and extenders and with the dispersants and surfactants used to stabilize them [12-13].

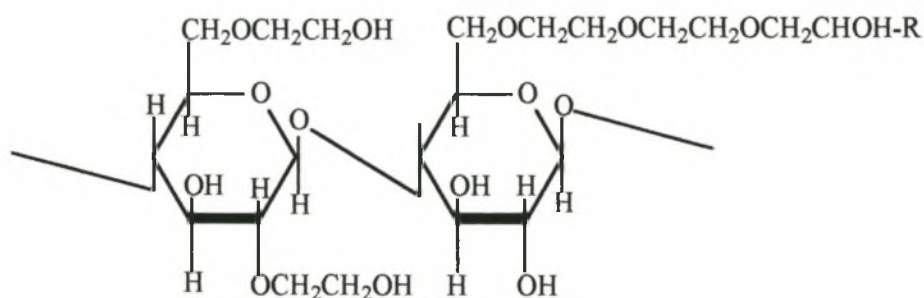


Figure 2.2

Schematic representation of HMHEC molecule. R represents a hydrophobic alkyl group.

2.1.4 HYDROPHOBICALLY MODIFIED ETHYLENE OXIDE URETHANE (HEUR) THICKENERS

HEUR thickeners consist typically of hydrophilic polyethylene oxide polyethers and hydrophobic aliphatic groups which are bound together with poly(isocyanates) via urethane groups. Figure 2.3 gives a schematic representation of possible HEUR thickener molecules. The wide variety in the structure of the individual components allows the synthesis of HEUR thickeners with very

different compositions and thus a differing degree of effectiveness. For example, the performance in latex formulations can be fine-tuned by adjusting the hydrophobic blocks in the polymer chain by varying the hydrophobe carbon content, using diisocyanates of varying hydrophobicities. The use of polyisocyanates and polyols can produce branched or star shaped structures. All of these can produce major or subtle variations in thickening efficiency, shear rate dependence of viscosity, and dependence of these properties on other components in a formulated aqueous system such as cosolvents, surfactants, type of latex, and pigment dispersion [14-20]. Since the HEUR thickeners are all highly associative, and all have surfactant-like character, their performances are highly formulation-dependent.

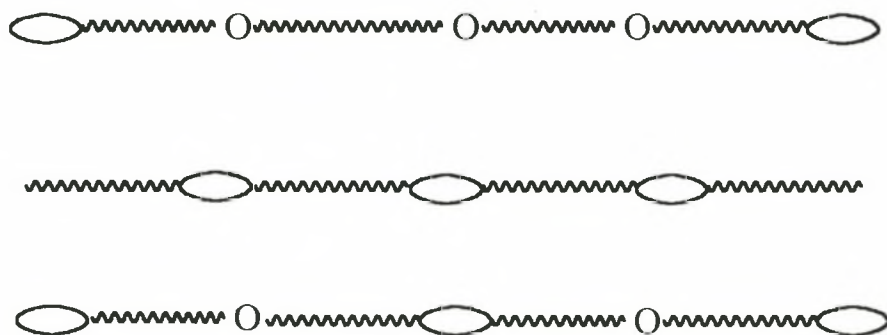


Figure 2.3

Schematic representation of possible HEUR thickener molecules. Wavy lines represent poly(ethylene glycol) hydrophilic blocks, while oblongs and circles represent hydrophobic blocks of various sizes.

2.1.5 ALKALI-SWELLABLE AND ALKALI-SOLUBLE THICKENERS (AST)

2.1.5.1 INTRODUCTION

We define these thickeners as carboxyl-group functionalized copolymers produced by the free radical polymerization of ethylenically unsaturated monomers. At low pH values the copolymers are substantially insoluble in water, but at higher degrees of ionization they exhibit thickening on swelling or dissolution in aqueous media. In their ionic form (partially or fully neutralized), ASTs generally belong to the broad classes of aqueous polymers known as WSPs (water-swella-

water-soluble polymers) and HWSPs (hydrophobically modified, water-swellaable or water-soluble polymers).

The carboxyl functionality of ASTs give them their anionic character. This anionic character allows a variety of synthetic techniques to be used for their preparation, including solution polymerization in organic solvent, precipitation polymerization in organic diluent, aqueous suspension polymerization or, more commonly and most advantageously, aqueous emulsion polymerization. Because of their performance characteristics and convenient handling (particularly the emulsions), ASTs find wide industrial application in latex paints, carpet backing, adhesives, paper coatings, print pastes, agrochemical products, personal care products, household and industrial cleaners, and in oil field drilling-recovery operations.

2.1.5.2 CLASSIFICATION BY CHEMICAL COMPOSITION

“Conventional” (those lacking associative functionality) or “associative” are the two main structural groups into which ASTs are generally classified. The structural distinction is usually supported by the contrast in the rheology properties observed. A wide variety of ethylenically unsaturated monomers have been copolymerized to prepare conventional and associative ASTs. The only substantial limitation for both types of thickeners is that at least one of the monomer components have a carboxyl functional group and be present in sufficient concentration to render the polymer water-swellaable or water-soluble on partial or complete neutralization with an appropriate base.

Acrylic, methacrylic, itaconic, citraconic, maleic, fumaric, crotonic acids, and maleic anhydride, and citraconic anhydride are among the carboxylic acid and anhydride functional monomers that have been employed in the synthesis of these polymeric thickeners. Carboxylic homopolymers, where they can be formed, might be considered the simplest examples of ASTs were it not for the fact that they are not copolymers as defined, and so are water soluble in their unionized state. The un-ionized free-radical-polymerized atactic forms of polyacrylic acid [21] and polymethacrylic acid [22], which are both readily soluble in water, are examples of carboxylic homopolymers.

Most conventional ASTs are copolymers consisting of just two monomers, and these thickeners are presumed to lack associative properties except for a few possible exceptions, which will be

mentioned later. In addition to the more hydrophilic carboxyl containing acid monomers previously mentioned, conventional ASTs must contain one or more hydrophobic comonomers to obtain water-insolubility at low pH. To provide a proper hydrophilic-hydrophobic balance and to render the copolymer water-insoluble prior to neutralization, but allow swelling or solubility in aqueous media at some higher pH, the hydrophobic monomers must also be present in appropriate concentrations. This behaviour is summarized in Figures 2.3 and 2.4 [23]. The carboxylic and hydrophobic monomers are mutually dependent in that respect. The alkyl acrylates, alkyl methacrylates, styrene, vinyl acetate, ethylene, butadiene, and acrylonitrile are typical hydrophobic monomers that have been used in the preparation of conventional ASTs. Ethyl acrylate is most frequently cited.

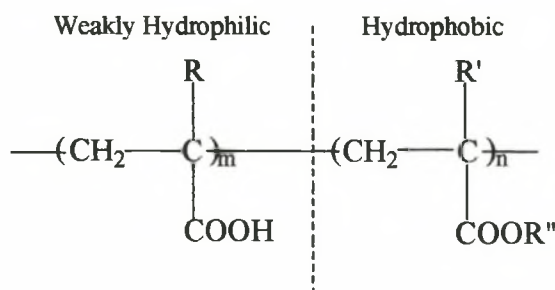


Figure 2.4

**Carboxylated emulsion polymer
in free acid form, pH below 6.**

The product is water insoluble.

**R and R' are H or CH₃. R'' is alkyl
(e.g. CH₃, C₄H₉).**

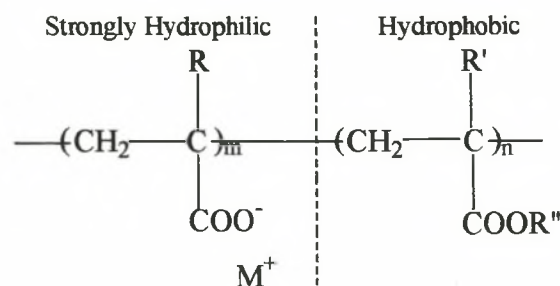


Figure 2.5

**Carboxylated emulsion polymer
in neutralized form, pH above 7.**

The product is water soluble.

R, R' and R'' as in Figure 2.4.

More recently, conventional ASTs have been modified with monomers (macromonomers) containing ethoxylate and terminal hydrophobe functionality to produce associative ASTs. There is overwhelming agreement that these and the more common nonionic associative polymers (e.g., HEUR, or hydrophobically modified ethoxylated urethane) represent a significant advance in thickener technology, by conferring higher degrees of thickening or unique rheology to aqueous solutions and aqueous media containing dispersed-phase components. The

advantages and disadvantages of the use of associative thickeners in general [24] and their influence on coating performances have been assessed [25-29].

From a theoretical point of view, any WSP can be suitably modified to construct an associative thickener. Associative ASTs, however, are usually terpolymers consisting of a carboxylic acid monomer, hydrophobic monomer, and a third monomer that is associative. These thickeners are prepared by using many of the same polymerization procedures used for conventional ASTs, and many of the same carboxylic acid monomers and hydrophobic monomers are employed. The presence of carboxylic acid or anhydride monomer is, of course, mandatory, but the hydrophobic monomer can be omitted if the associative monomer is able to impart the proper hydrophilic-hydrophobic balance for the necessary pH-dependant solubility. In Figure 2.6, the schematic structure of an associative AST is compared with that of a conventional AST [30]. Also depicted are other associative moieties, including a nonionic surfactant, an ethoxylated anionic surfactant, and a typical nonionic associative thickener structure.

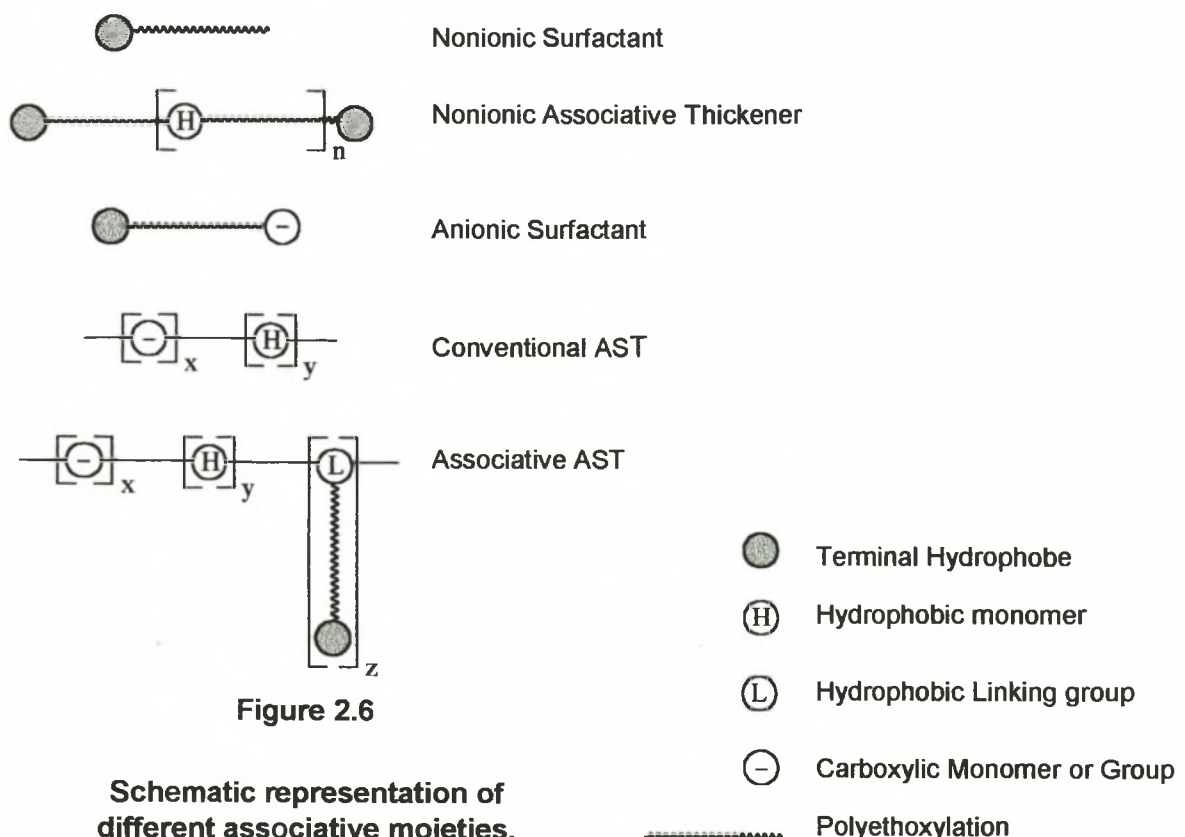


Figure 2.6

Schematic representation of different associative moieties.

The associative monomers used to prepare associative ASTs most frequently contain a long-chain hydrophilic segment terminated with a hydrophobic group. The hydrophilic segment usually consists of polyethoxylation or poly (ethoxylation-propoxylation) situated between the ethylenic unsaturation at one end of the molecule and the terminal hydrophobe at the other end. In one common method of synthesis, the associative macromonomers are conveniently prepared by coupling the hydroxyl end group of a conventional nonionic surfactant with a monomer containing polymerizable ethylenic unsaturation. Variability within the macromonomer structure is obtained by altering the type of terminal hydrophobe, type of ethylenic unsaturation, and ratio and degree of poly (ethoxylation-propoxylation). As an option in both associative and conventional ASTs, some minor amounts of other water-soluble or water-insoluble monomers may be included, as well as minor amounts of polyethylenically unsaturated monomers, to provide a low degree of cross-linking.

2.1.5.3 AST THICKENING MECHANISMS

The increase in viscosity that occurs on neutralization of certain types of carboxylated copolymers in aqueous medium is a well known phenomenon, and the earliest theoretical description of the process is still substantially accepted [31-33]. In the generalized case for linear polymers forming true solutions, as pH is raised and carboxyl groups are neutralized, the polymer becomes hydrated, and their molecular coils expand because of electrostatic repulsion of the carboxyl anion charge centers. This coil expansion results in dissolution and an increase in the polymer's hydrodynamic dimensions, which in turn increases intermolecular entanglement and resistance to flow. The increase in solution viscosity that occurs in this process is referred to as "hydrodynamic thickening" (Figure 2.7) [34].

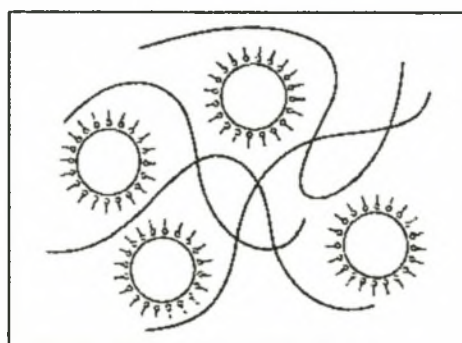


Figure 2.7

Schematic of hydrodynamic thickening mechanism.

The thickening mechanisms of linear carboxyl-containing emulsion polymers have been studied in considerable detail. The polymer molecules of AST emulsions are initially in a coiled configuration within individual latex particles of submicrometer size, and the viscosity of the diluted latex emulsion is similar to that of water prior to neutralization. On the addition of base, the carboxyl groups are ionized, and hydrophilic polymer is formed within the particles. Depending on various factors, which are set out in Table 2.2, the particles may only swell or dissolve completely, or the surface polymer may dissolve and leave swollen cores.

Table 2.2

Factors known to affect the thickening, swelling, or dissolution behavior of conventional AST emulsion polymers (ASE thickeners)

Type of carboxylic monomer

Level of carboxylic monomer

Hydrophilicity of the hydrophobic comonomer

Glass transition temperature of the hydrophobic comonomer

Polymer chain configuration

Degree of polymerization

Degree of cross-linking

Degree of neutralization

Swelling and dissolution temperature

Monomer polarity

Monomer sequence distribution

Polymerization procedure

Emulsion particle size

Verbrugge [35] concluded that a single mechanism explains the thickening process during neutralization of all (conventional) acid -containing latices; there are varying degrees of particle swelling followed by dissolution of the more hydrophilic copolymers. The particles commonly exhibit a highly swollen state with maximum viscosity at some lower degree of neutralization. At some higher pH, the polymers are solubilized if they are sufficiently hydrophilic, and the viscosity drops. However, the solution viscosity at the higher pH is still much greater than that of the unneutralized latex. Muroi [36] reported coagulation on reacidification of what appeared to be solubilized ASE polymer, a result suggesting that the particles had been mostly dissolved and could not be reconstituted to their original particulate form.

In the presence of colloidal particles e.g. pigment and latex particles, thickening and rheology is further impacted by an additional mechanism which is descriptively referred to as "volume restriction" or "depletion" flocculation (Figure 2.8) [37]. The volume restriction mechanism has been examined in both experimental [38-40] and theoretical treatments [41-42]. Flocculation rheology has been modeled by computer simulation [43]. According to theoretical models, the flocculation mechanism is caused by an osmotic pressure difference between the disperse phase colloidal particles and the surrounding solution on exclusion of the water-soluble thickener polymer from the particle interstices. This results in an interactive force between the particles causing them to phase separate or aggregate into latex/pigment rich and thickener rich domains. The resulting flocculation structure is readily observable on microscopic examination.

Among the negative manifestations of depletion flocculation is extremely shear thinning behavior. Occasionally these coatings also show time dependant behavior (thixotropy) with prominent hysteresis in rheograms. The shear thinning behavior is characterized by high low-shear viscosity resulting in poor flow and leveling, and low high shear viscosity resulting in overspreading due to low film build.

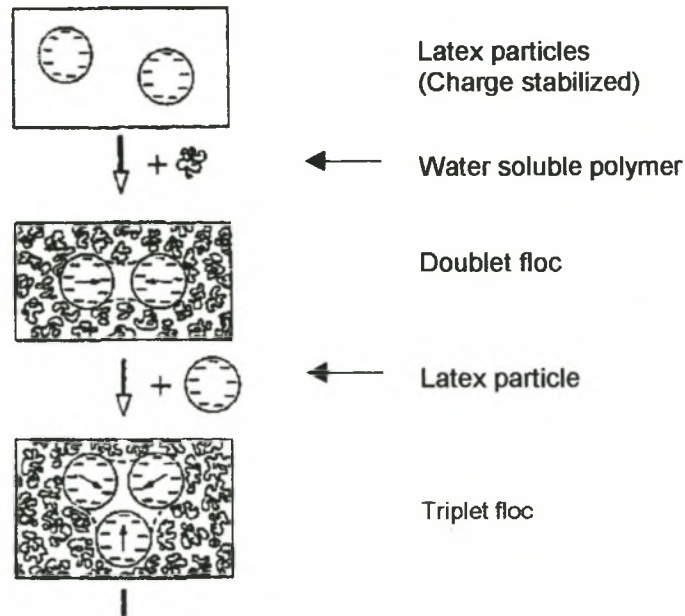


Figure 2.8

The mechanism for volume restriction flocculation [20].

2.1.5.4 THE THICKENING MECHANISM OF ASSOCIATIVE ASTs

Nonionic and anionic associative thickeners are very important in many different industrial applications. The anionic associative thickeners are a subclass of hydrophobically modified, water-soluble polymers (HWSPs), and are predominantly represented by hydrophobically modified ASTs (HASE), the chemical structures of which were described in section 2.1.5.2. Because these polymers are very similar to conventional ASTs in molecular weight and carboxyl content, thickening is by a dual mechanism: hydrodynamically and associatively (because of hydrophobic interaction). This dual mechanism is illustrated in Figure 2.9. Because the hydrodynamic component of thickening is present for both conventional and associative ASTs, it is the associative mechanism that is responsible for the enhanced thickening and unique rheology frequently observed in aqueous solutions and dispersed-phase systems containing these thickeners.

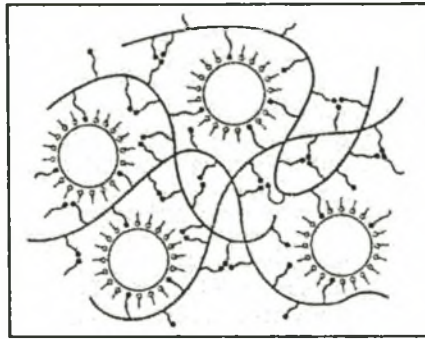


Figure 2.9

Schematic representation of dual thickening mechanism.

The associative mechanism of thickening has been variously described, but is generally thought to result from nonspecific hydrophobic association of water-insoluble groups in water-soluble polymers [37, 44]. For associative ASTs, the terminal hydrophobes of the ethoxylated side chains are considered to be the primary interactive components. These hydrophobes can interact with each other via intermolecular association, and can also interact with hydrophobic particle surfaces when present. The specific interaction with dispersed-phase components such as latex particles has been shown to be one of surface adsorption [45]. In essence, the associative component of thickening in dispersed-phase systems also has dual character resulting from the building of structure within the aqueous phase and interaction with particle surfaces.

The intermolecular association of the terminal hydrophobes of associative ASTs in aqueous solution is analogous to the association of surfactant hydrophobes to form micelles. But, unlike conventional surfactants that have hydrophilic-hydrophobic (head-tail) polarity, the associative ASTs, if relatively uniform in composition, would be expected to have an overall hydrophilic-hydrophobic symmetry, resulting in a tendency to micellize in continuous associative networks. However, because of the functional similarities to surfactants, these polymers are sometimes referred to as "polymeric surfactants" or "polysoaps". Chu and Thomas [46] reported that under appropriate conditions, polyelectrolytes with hydrophobic side chains forms microdomains in solution, exhibiting behavior similar to that of polar surfactants micelles.

Structurally, the backbone of an associative AST copolymer is predominantly hydrophilic because it contains sufficient carboxyl anion to render it water soluble at elevated pH. The

ethoxylated side chains attached to the backbone are also hydrophilic, and thus, the interior of the molecule would be expected to be highly hydrated. The terminal hydrophobes at the ends of the ethoxylated side chains would, hypothetically, be repelled from this environment and at the same time attracted to other terminal hydrophobes or hydrophobic surfaces if present. Like surfactants, the driving force for association is a result of the entropy gained by loss of water structuring around the hydrophobes and a minimization of the water-hydrophobe contact [47].

Because the hydrodynamic thickening mechanism of conventional ASTs is also present in the associative ASTs, common factors affecting the thickening behavior of both types of thickeners would be expected, and are indeed observed. The factors that effect the thickening efficiency of conventional ASTs mentioned in Table 2.2 are also applicable to associative ASTs. Table 2.3 contains a list of additional factors that affect the thickening efficiency or rheology of AST emulsions (HASE thickeners).

Table 2.3

Factors known to affect the thickening efficiency or rheology of associative AST emulsions (HASE thickeners)

Type of terminal hydrophobe*
Length of terminal hydrophobe*
Degree of ethoxylation*
Type of linking functionality*
Type of polymerizable unsaturation*
Level of associative monomer
Presence of water soluble solvents, salt, and surfactants
Presence of dispersed hydrophobic particles

* In the associative monomer.

Since associative ASTs provide viscosity by intermolecular association with disperse phase components, their molecular weights can be, and frequently are, much lower than those of conventional thickeners. Consequently, under ideal conditions, coatings containing associative thickeners are highly dispersed and show little evidence of depletion flocculation. This not only improves the coating rheology but also may impart improved hiding and gloss.

Unlike associative thickeners, conventional thickeners exhibit a strong tendency to produce "spatter" on roll application. Although Glass [48] recognized the importance of high shear viscosity (HSV) and elasticity, the only parameter that gave good correlation with roll spatter was dynamic uniaxial extensional viscosity (DUEV); decreased spatter was obtained with lower DUEV. It is now fairly well documented that, as a class, associative thickeners tend to have low DUEVs (a manifestation of the thickening mechanism and the low molecular weight), while most conventional thickeners have high DUEVs. Following on from this, Masouda [49] combined the physics of spatter formation with shear rheology to calculate filament axial stress resulting from the combined effects of extensional and viscoelastic flows. Good correlation was obtained; lower axial tension resulted in less spatter due to destabilization of the filaments thereby allowing them to break earlier.

In theory, thickeners which produce high extensional viscosity generate more filaments of longer length behind the roller nip on application. When these filaments break, droplets form and are ejected resulting in spatter. The situation is exacerbated with conventional thickeners since the long filaments generated also result in a nonuniform pattern behind the roller. This pattern is sometimes referred to as "chicken-tracking" or "stippling". Because these thickeners also have high low-shear viscosity (LSV), the pattern that forms does not flow out. In essence, a problem is created primarily due to high DUEV and cannot be corrected because of high LSV. In contrast, associative thickeners form fewer filaments of shorter length, resulting in a reduction of both spatter and pattern formation. Because associative thickeners tend to have low LSV, the minimal amount of pattern formed flows out to provide a smooth finish.

2.2 COLORANTS

2.2.1 INTRODUCTION

Prior to World War II, the choice of colored pigments was limited to a very small number of primarily naturally occurring inorganic pigments, such as ochres, siennas, umbers, and iron oxides (and their derivatives), along with some other metallic complex pigments, such as those we know today as ultramarine blue, iron, miori or Prussian blue, and even some of the chromium, lead, and other oxides.

At this time, there were also very few binder systems available to the paint manufacturer. The main one was linseed, which, along with rosin, gum arabic, shellac, and a few other vegetable extracts, made up the binders of the coating systems. During the next decade, and up to the mid to late 1950s, many new raw materials were discovered and technical improvements made in manufacturing and processing equipment. Titanium dioxide, phthalo pigments, quinacridones, perylenes, and many other pigments emerged, and along with them came a new breed of paint binder or vehicle system, nl. alkyds. Water-based latex systems, poly(vinyl alcohol), poly(vinyl chloride), and even some acrylics started to evolve. New types of grinding (dispersion) equipment such as pearl mills, pebble mills, roller mills, sand mills, and even high speed mixing equipment started to make their way into paint manufacturing [50].

These new developments in pigments, as well as the availability of a variety of new coating resin systems (alkyds, epoxies, acrylics, nitrocellulose lacquers, and latex emulsions) were exciting developments, leading to a variety of opportunities for paint manufacturers to provide customers with a specific, long-lasting coating for every specific application. But these advantages soon presented the paint manufacturers with huge problems. There were now so many new colors and paint systems, how were they going to keep up with all this?

At this time, paint chemists began to realize that many pigments had to be ground separately into color concentrates, master batches, or what we today call tint aids, tinting colors, or shading pastes.

Universal colorants were introduced when latex paints started to gain popularity. These colorants were designed for tinting both latex (water-based) and alkyd and linseed oil/alkyd (solvent based) systems. Their composition was based primarily on pigments, ethylene glycol,

water and surface-active agents selected to provide compatibility of the colorants in both organic- and water- based coating formulations with minimal adverse effects.

These “universal” colorants make up a large percentage of the colorants used by trade sales paint companies today. It is these universal color formulations that are used for “in-store” tinting systems, allowing a paint company to make available to the homeowner a large selection of paint shades (many offer about 1500 different shades) by having in their inventory only 12 color concentrates or tinting colors and only three tint bases within each chemical coating group.

2.2.2 IMPORTANT PROPERTIES OF PIGMENT CONCENTRATES

Each component of a tinting colorant should be carefully considered and then evaluated in terms of the specific need. Some considerations are discussed in the following paragraphs.

2.2.2.1 Pigment

The highest possible pigment content needs to be obtained and other ingredients should be kept to a minimum in order to bring mainly the pigment and not so many extraneous materials (unwanted resins, solvents) into the final paint system.

Color: Naturally, this seems like it should be the first requirement. However, depending on the requirements of the actual application, one might find that what one wanted in terms of color is not available in combination with the desired quality.

Lightfastness: The application will determine the degree of lightfastness. This property will therefore narrow the color selection.

Bleed resistance: Again, this property may take priority over color, depending on the application.

Bake resistance: Most pigments used by the coatings industry are sensitive not only to certain temperature levels, but also to the amount of time to which they are subjected to that temperature.

Opacity and/or Transparency: There are many coatings where the pigment is chosen only for its ability to opacify, and others where total clarity or transparency is required. In some cases, however, although the coating system may be opaque, some of the pigments should be

transparent in order to achieve the desired effect, an example being metallic coatings. Opacity is generally obtained from the metallic flake. The color pigment used should however have excellent transparency in order to allow the aluminum particle to reflect through the colored film.

Chemical composition: Depending on the specific application, certain metallic compounds or organic complexes may have to be avoided because of reactivity with the expected end-use system or because of certain regulations, such as “Lead in Paint” or FDA regulations.

2.2.2.2 Vehicle, Binder, Dispersing Agent, and/or Wetting Agents Used

The pigment concentrates should have no adverse effects on the paint performance (mechanical and chemical durability). This is controlled mainly by the grinding resin and the solvents/additives used. Only a suitable pigment wetting and dispersing additive can reduce the paste viscosity so that the pigment content can be drastically increased. Pigment loading with and without the additive can differ greatly. Additionally, the pigments become deflocculated (which is necessary for high gloss and color stable topcoats). Stabilization of the pigment grind by additives also prevents shock during the let down and mixing of the concentrates. To avoid flooding and floating as much as possible, pigments should not only be deflocculated, but the mobility and the electrical charges of the pigments should also be equalized.

2.2.2.3 Important Dispersion Attributes

Along with the composition of the tinting colorants, their physical properties may be key properties to consider and must be matched to the requirements and application of the actual coating or system in which they are going to be used. Some of these key physical attributes are as follows.

Fineness of Grind: The fineness of grind or particle size has an effect on a number of coating characteristics, including gloss, transparency, opacity, rate of settling, color development, and cleanliness of hue. In some cases, some of these properties are dependent on film thickness. Hence, what is beneficial in one area may be somewhat of a detriment in another.

Viscosity and Rheology: Tinting colors vary in their viscosity as well as their rheology, not only because of the specific manufacturer’s technique but also because of the specific vehicle system, pigment type used, and intended use. The viscosity and rheology of a tinting color will affect its performance, ease of handling and use, storage stability, and the overall economics.

Specific Gravity: Although this property is generally a function of the particular pigment used in the given tinting color and thus irrelevant to its selection, there are systems that use tinting colorants solely on a volumetric basis such as in dispensing machine tinting. The specific gravity of the colorant is an important characteristic, as it will determine the volumetric tint strength of that given colorant and thus its actual economics.

Stability: Good pigment grind stabilization is a very important property of a tinting colorant, because it prevents certain negative effects, such as settling, syneresis, and drying out of the pigment concentrate.

Compatibility: The tinting colorant should be easy to incorporate into the paint resin. Good compatibility between the tinting colorant and the base paint prevents shock of one on the other, which would result in nonuniform color distribution.

2.2.3 TYPICAL COMPOSITION OF PIGMENT CONCENTRATES

In the following section, the typical composition of three different types of pigment concentrates designed for the following three areas: solvent-based industrial and architectural coatings, aqueous systems, and solvent based and architectural paints in which universal glycol pastes are used, will be discussed [51].

Table 2.4: Pigment concentrates for solvent-based industrial and architectural coatings.

Pigment	
Grinding resin	Good compatibility to the binder systems used
Solvents	Mixture of MPA and aromatic solvent like Solvesso 100; other ester solvents may replace MPA.
Wetting and dispersing additive	Good compatibility to the grinding resin and binder system, excellent pigment stabilization.
Anti-settling agent	Bentonites or pyrogenic silicas to avoid settling of (heavy) inorganic pigments.

Table 2.5: Pigment concentrates for aqueous systems

Pigment	
Water soluble grinding resin.	Not always necessary; resin free concentrates are possible.
Water	
Co-solvent	Used to avoid drying out of the concentrate (butyl glycol)
Wetting and dispersing additive	
Silicone defoamer	To prevent foam formation during pigment grind; selection depends on the final paint requirements.
Anti-settling agent	Bentonite or pyrogenic silicas to avoid settling of (heavy) inorganic pigments.
pH value should be adjusted to 7.5 - 9	

Table 2.6: Glycol (universal) pastes; only as shading pastes for architectural coatings

Pigment	
Co-solvent	For freeze-thaw stability and to avoid drying out of the concentrate (mono ethylene glycol or propylene glycol).
Water	
Wetting and dispersing additive	Good pigment stabilization
Anti-settling agent	To prevent settling of pigments(Rheolate 2001)
Biocide	
Defoamer	Selection of the defoamer depends on the requirements of the final paints.

2.2.3.1 Pigments:

The most important component of a concentrate is the pigment. The pigment content should be as high as possible, because it is the intention to transport via the paste as much pigment as possible into the final paint. If the pigment content is too high, flocculation and shock may occur during mixing. The pigmentation level for inorganic pigments is in the range of 50 – 70 %; for organic pigments, 20 – 35 %; and for carbon blacks, 10 – 25 %.

2.2.3.2 Grinding resin:

The second most important component is the grinding resin. It is selected mainly upon the basis of (1) its compatibility with the paint binder, (2) possible influences on paint performance (durability) and (3) rheological performance. The amount of grinding resin in the concentrate should be fairly low; available starting formulations for many pigments can be used as a guideline. It is also possible to produce pigment concentrates without grinding resin: they will exhibit no compatibility problems with letdown resin and no negative influence on paint performance (durability). However, these concentrates are often not stable; they dry easily and are difficult to incorporate (shock phenomena). Concentrates with grinding resin are therefore preferable, at least for solvent-based coatings. In aqueous systems, binder-free pigment concentrates can work satisfactory if they are formulated with the proper wetting and dispersing additive.

2.2.3.3 Solvents:

In addition to solvents coming into the system via the grinding resin, solvents are also necessary for the processing of the concentrates. The selection of the correct solvents is important since it can also influence concentrate storage stability and may enable the formulator to use less solvent (and therefore more easily fulfil VOC requirements). Naturally, the solvents must demonstrate good solvation power for the grinding resin and the wetting and dispersing additive.

2.2.3.4 Additives:

Another important part of the pigment concentrate is the additive component. A deflocculating pigment wetting and dispersing additive is used to reduce paste viscosity and to achieve the highest possible pigment load.

The selection of the additive depends on its binder system compatibility. Besides viscosity reduction, the additive also avoids pigment separation after mixing (flooding and floating), avoids flocculation, improves incorporation of the concentrate, avoids syneresis and settling, and ensures reproducible production.

High molecular weight polymeric additives have proven their effectivity in many paint formulations over the last few years and can also be used successfully in concentrates [52-53]. They provide excellent stabilization and deflocculation (important for a defined and stable color), strong viscosity reduction and better durability than conventional wetting and dispersing additives. Polymeric dispersants will be addressed at length later in section 2.2.4.

The usage level of wetting and dispersing additives required for optimum efficiency depends on the pigment particle size. The necessary additive amount can be roughly calculated from the oil absorption number or the BET surface area of the pigments. However, the surface treatment of the pigments often makes this calculation unreliable. Starting point formulations, which are available for many pigments, are a better guideline.

Classical wetting and dispersing additives based upon low molecular weight polymers should be utilized in quantities of 0.5 – 2.0 % with inorganic pigments and in quantities of 1.0 – 5.0 % with organic pigments (additive delivery form based upon pigment weight). Considerably higher usage levels of the high molecular weight additives are necessary, especially with small particle size organic pigments. Such levels are no cause for concern though, since the resinlike properties of the polymeric additives do not negatively influence coating durability.

2.2.4 POLYMERIC DISPERSANTS

2.2.4.1 The mechanism of action of polymeric dispersants.

Polymeric dispersants stabilize colloidal systems via a mechanism commonly known as steric stabilization. An understanding of this mechanism requires at least a simplified explanation of the behavior of polymer solutions, as developed by Flory [54].

The polymer molecules in an ideal solution will show no tendency to associate with each other, and the polymer will have zero volume. In practice, the first criterion is rather unlikely and the second criterion is impossible. However, in terms of the real overall thermodynamic behavior, the effect of the association between the polymer molecules is opposite to that of the finite

volume of the polymer molecules. The result is that under certain conditions of temperature and solvency these effects are in balance, even at quite high polymer concentrations. These conditions, commonly known as *theta* conditions, give a nonideal polymer solution system that behaves thermodynamically like an ideal system. A *theta* solvent is therefore a slightly poor solvent system for a polymer in that there will be a degree of association between the dissolved polymer molecules. A comprehensive review of polymer–stabilized colloidal systems [55] has demonstrated that stability is obtainable only when the solvent is a “better than *theta*” solvent for the polymer (or for one of the polymer chains in a block polymer). A major consequence of this behavior is that since a polymeric dispersant can be effective only in “better than *theta*” solvent system, it will not be possible to devise a universally effective dispersant. The efficiency of any polymeric dispersant will always be specific to a limited range of solvent systems.

2.2.4.2 The fundamental design of polymeric dispersants.

The concept behind polymeric dispersants is very simple. A layer of polymeric material must be adsorbed onto the surfaces of particles in a colloidal system, and then, for the thermodynamic reasons described previously, the particles can be kept apart. The polymeric dispersant must therefore have a structure that meets two very different requirements: (1) The molecule must contain polymeric chains that give steric stabilization in the required solvent or resin solution system, and (2) it must be capable of being strongly adsorbed onto the particle surface.

Clearly, homopolymers are not going to meet these two different, often conflicting, requirements. Obviously, some form of functionalized polymer or copolymer offers the best opportunity. There are many copolymer/functional polymer configurations that might be expected to give effective polymeric dispersants, and six possible arrangements are illustrated in Figure 2.10. These anchor onto the particle surface either through functional groups (b and c) or through polymeric blocks (a and d-f). The steric stabilization polymer chain is either anchored to the particle surface at one end (b, d, and f) or at both ends (a, c and e). A systematic study of the relative merits of steric stabilization chains anchored at one end or at both ends is reported by Jakubauskas [56]. This study concludes that steric stabilization chains anchored at only one end are most efficient.

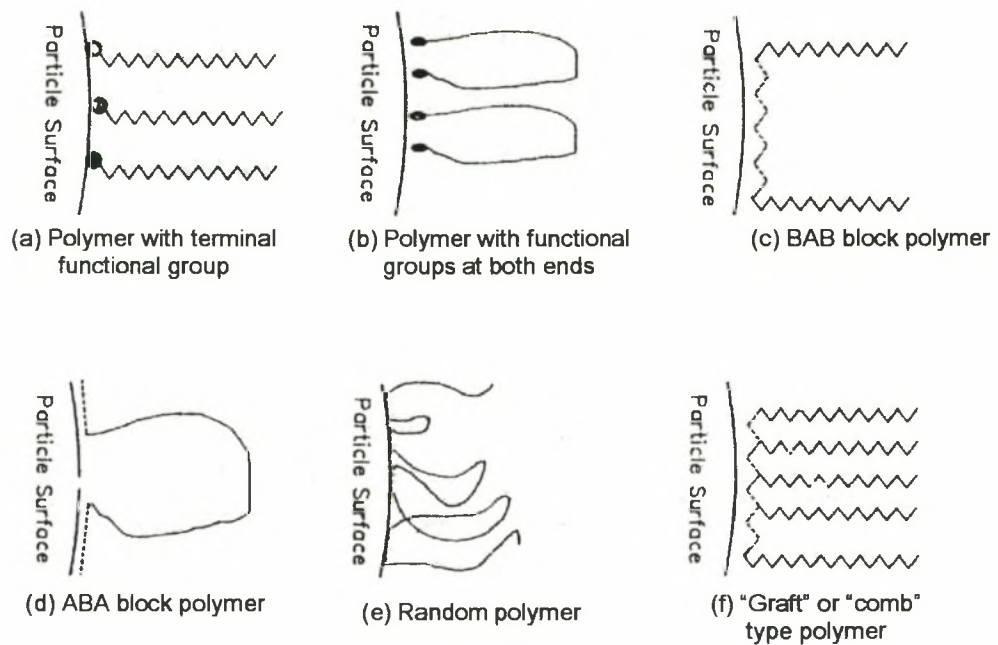


Figure 2.10:

Possible polymeric dispersant arrangements.

2.2.5 THE DISPERSION PROCESS

By regarding color development as a function of time, the quality of the dispersion process is measurable. The dispersion process may be viewed as pursuing three different objectives simultaneously [57].

2.2.5.1 Wetting of pigment particle surfaces

During wetting, air is displaced from the pigment through the liquid of the grinding mixture. The ease with which an agglomerate is wetted is favored by a high surface tension and low contact angle at the solid liquid interface whilst the viscosity of the medium should be as low as possible. Especially when pigments or extenders and/or fillers have nonpolar surfaces in waterborne systems, a wetting agent must be used.

2.2.5.2 Mechanical deagglomeration of pigment particles

The second stage of the dispersion process, separation of the fundamental pigment particles, is usually achieved by mechanical action by either shear or impacts, such as in cavitation (high speed) mixing, ball milling, sand or bead milling. Most agglomerates can be reduced in size into a distribution matrix, similar to a bell shaped curve. As the average particle size is reduced, the desirable properties of the dispersion such as tinctorial strength and gloss are enhanced. Additives have relatively little influence during the deagglomeration process, which is more dependent on the amount of energy input and time duration. It can be noted that a complete separation of every primary particle and aggregate is very rarely achieved in practice.

2.2.5.3 Modes of stabilization

The aim of stabilization is to keep the pigment particles separated as achieved in the last step, and to control that level of separation through the letdown and filling phase, storage and application, so it is a somewhat complex matter. Stabilization is achieved through adsorbing of the polymer on the pigment surface, so that repulsive forces prevent other particles from approaching close enough for the attractive van der Waals forces to cause agglomeration.

Electrostatic stabilization occurs whereby equally charged local sites on the pigment surfaces come into contact with one another (Figure 2.11). Two particles having the same charges give a repelling effect. The resulting Coulomb-repulsion of the charged particles allows the system to remain stable. In aqueous systems where the liquid medium has a high dielectric constant, this stabilization mechanism works well. However in media with low dielectric constants (or polarities), such as hydrocarbons, the effectivity of the charge stabilization mechanism is very much less than that of steric stabilization which relies on the spatial arrangement of the adsorbed polymers.

A pigment is sterically stabilized when the surfaces of the solid particles are completely covered by polymers, making particle-to-particle contact impossible (Figure 2.12). Strong interaction between polymers and solvents (organic solvent or water) prevent the polymers from coming too close into contact with one another and therefore prevents flocculation.

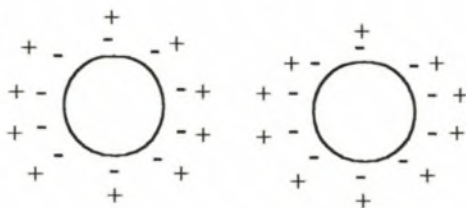


Figure 2.11

Electrostatic stabilization

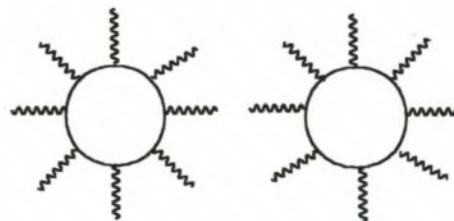


Figure 2.12

Steric stabilization

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CHAPTER 3

THE SYNTHESIS OF ASSOCIATIVE MONOMERS (MACROMONOMERS)

3.1 INTRODUCTION

Conventional ASTs have been modified with monomers (macromonomers) containing ethoxylation and terminal hydrophobe functionality to produce associative ASTs. There is overwhelming agreement that these and nonionic associative polymers (e.g., HEUR) represent a significant advance in thickener technology by conferring higher degrees of thickening or unique rheology to aqueous solutions and aqueous media containing dispersed-phase components (1-6). From a theoretical point of view, any WSP can potentially be suitably modified to create an associative thickener.

The associative monomers most frequently used to prepare associative ASTs contain a long-chain hydrophilic segment terminated with a hydrophobic group. The hydrophilic segment usually consists of polyethoxylation or poly(ethoxylation-propoxylation) situated between the ethylenic unsaturation at one end of the molecule and the terminal hydrophobe at the other end. In one common mode of synthesis, the associative macromonomers are prepared by coupling the hydroxyl end group of a conventional nonionic surfactant with a monomer containing polymerizable ethylenic unsaturation. Variability within the macromonomer structure is obtained by altering the type of terminal hydrophobe, type of ethylenic unsaturation, ratio and degree of poly(ethoxylation-propoxylation), and component-linking groups (7-10).

3.2 OBJECTIVES

The main objective in this chapter was to synthesize macromonomers from commercially available nonionic surfactants with varying degrees of ethoxylation. Two different esterification reaction methods will be compared and used to couple the terminal hydroxy group of the nonionic surfactant with a monomer containing polymerizable ethylenic unsaturation.

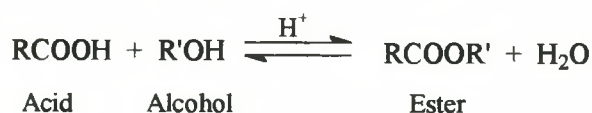
- In method one the surfactants are reacted with acrylic acid.
- In method two the surfactants are reacted with acryloyl chloride, the more reactive derivative of acrylic acid.

The different macromonomers are to be characterized by means of nuclear magnetic resonance spectrometry and infrared spectrometry.

3.3 BACKGROUND ON ESTERIFICATION REACTIONS

3.3.1 General

A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of a mineral acid, usually concentrated sulfuric acid or dry hydrogen chloride. This reaction is reversible, and generally reaches equilibrium when there are appreciable quantities of both reactants and products present. This reversibility is a disadvantage in the preparation of an ester directly from an acid.

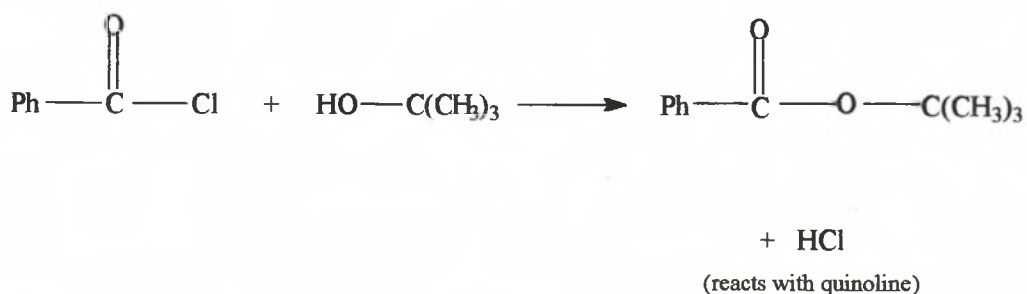
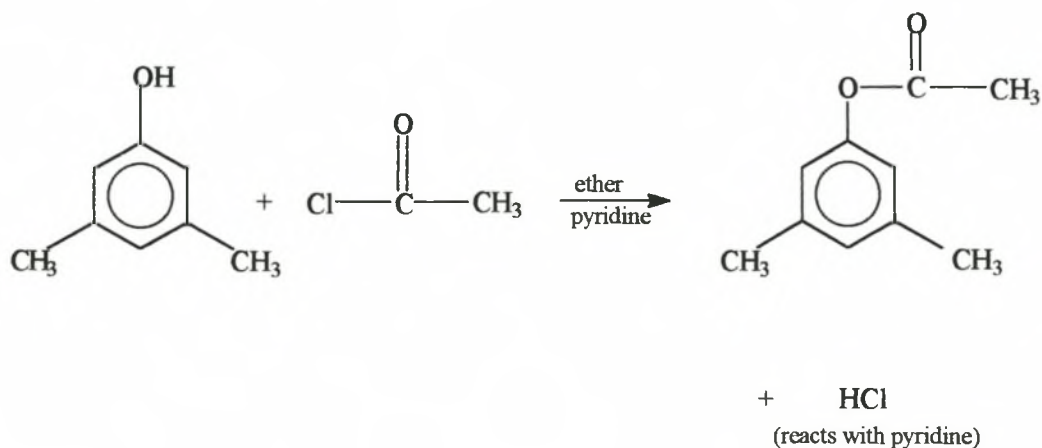


As an alternate route, acids are frequently converted into their esters via the acid chlorides:



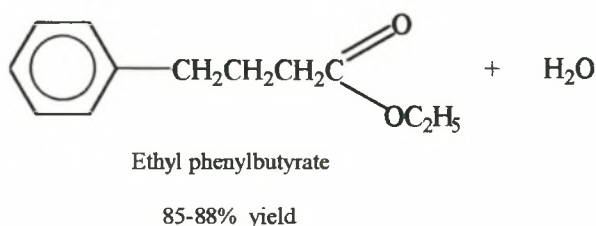
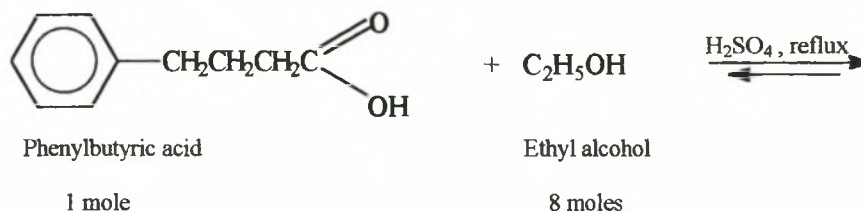
Esters are formed rapidly when acid chlorides react with alcohols and phenols. The strong preference for using the acid chloride route is because both the preparation steps: formation of acid chloride from acid, and preparation of ester from acid chloride are essentially irreversible and react to completion. Aromatic acid chlorides (ArOCl) are considerably less reactive than the aliphatic acid chlorides. With cold water, for example acetyl chloride reacts almost explosively whereas benzoyl chloride reacts only very slowly.

In principle, the HCl liberated in the reaction need not be neutralized, since alcohols and phenols are not basic enough to be extensively protonated by the acid. However, some esters (such as t-butyl esters) and alcohols (such as tertiary alcohols) are sensitive to acid. In practice, a tertiary amine like pyridine is normally added to the reaction mixture or is even used as solvent to neutralize the HCl (11).

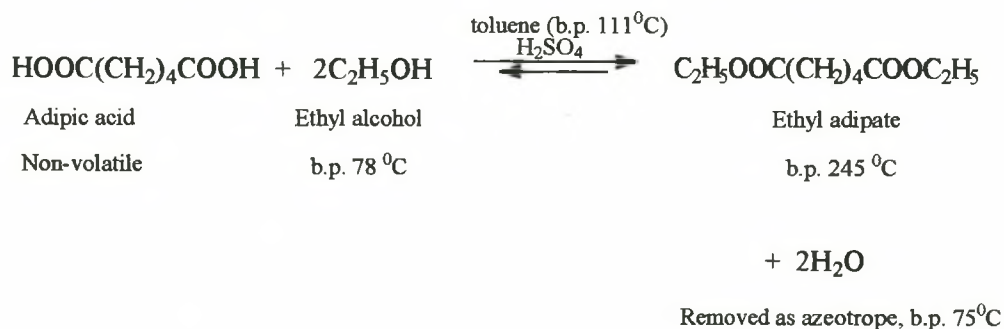


Direct esterification, however, has the advantage of being a single-step synthesis; it can often be made useful by application of our knowledge of equilibria. If either the alcohol or acid is cheap

and readily available, it can be used in large excess to shift the equilibrium towards the end products and thus increases the yield of ester. For example, it is worthwhile to use eight moles of inexpensive ethyl alcohol to convert one mole of valuable phenylbutyric acid more completely into the ester:



Sometimes the equilibrium is shifted by removing one of the products. This is illustrated in the preparation of ethyl adipate. The dicarboxylic acid adipic acid, an excess of ethyl alcohol, and toluene, are heated with a little sulfuric acid using a distillation column. The lowest boiling component (b.p. 75°C) of the reaction mixture is an azeotrope of water, ethyl alcohol, and toluene. Consequently, as fast as water is formed it is removed as the azeotrope by distillation. In this way a 95- 97 % yield of ester is obtained:



The equilibrium is particularly unfavourable when phenols (ArOH) are used instead of alcohols, yet if water is removed during the reaction then phenolic esters (RCOOAr) are obtained in high yield.

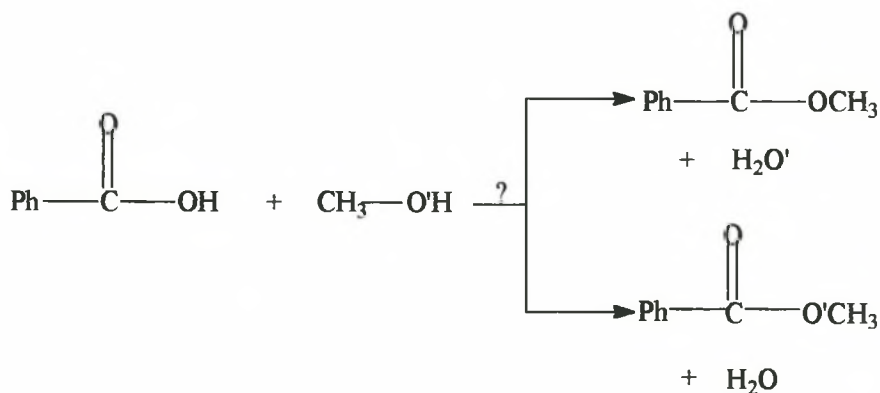
The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slow down esterification. This steric hindrance can be so marked that special methods are required to prepare esters of tertiary alcohols or esters like 2,4,6-trimethylbenzoic acid (mesitoic acid).

Reactivity in esterification: $\text{CH}_3\text{OH} > 1^\circ > 2^\circ (> 3^\circ)$



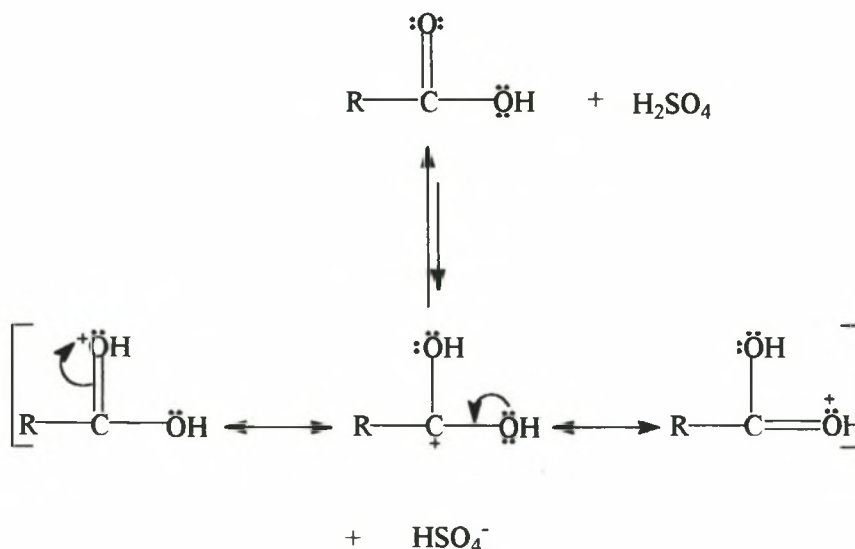
3.3.2 The reaction mechanism for acid-catalyzed esterification.

To be able to write a mechanism for acid-catalyzed esterification, it is essential that we know whether the oxygen of the water liberated in the reaction comes from the alcohol or from the acid (12-14).

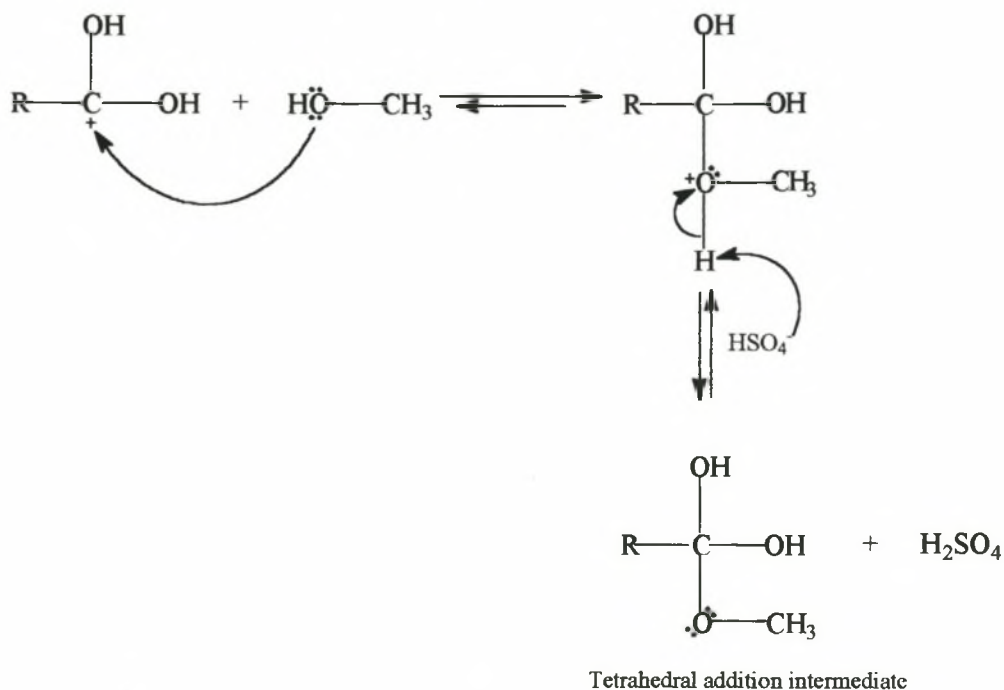


This question was answered in 1938, after using the ^{18}O isotope to label the alcohol oxygen; The water produced comes exclusively from the carboxylic acid. Acid-catalyzed esterification is therefore a substitution of $-\text{OH}$ (as water) at the carbonyl group of the acid by the alcohol.

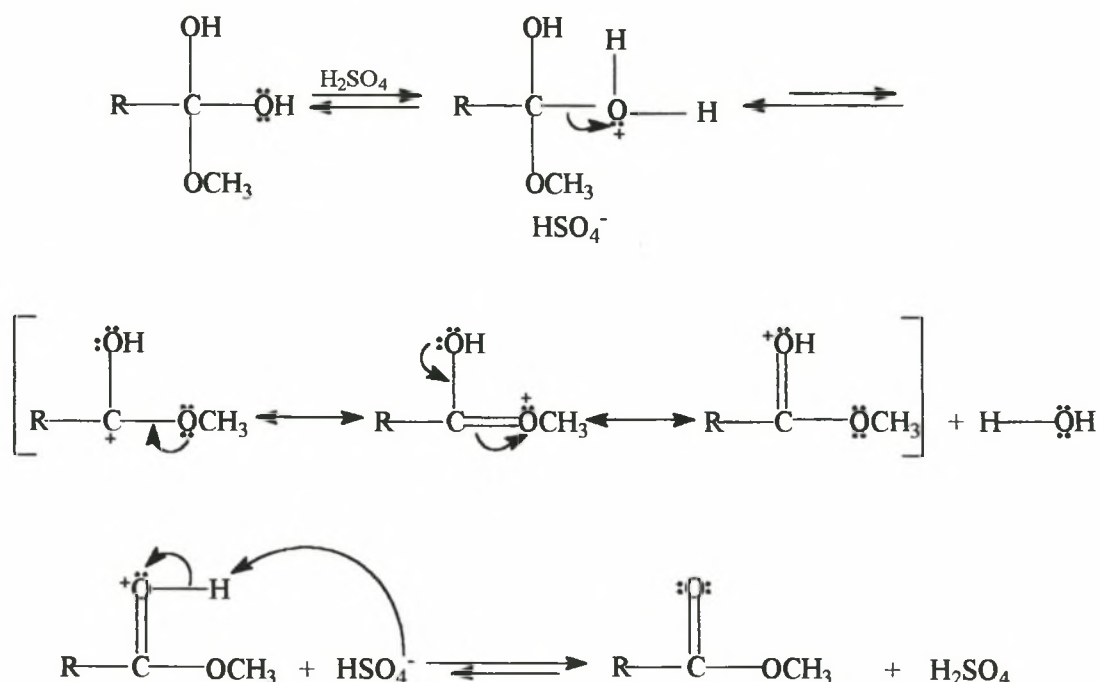
In this mechanism, the carboxylic acid is first protonated.



As the resonance structure shows, the protonated intermediate has carbocation character. Alcohol attacks this "carbocation" to form, after loss of a proton, a tetrahedral addition intermediate.

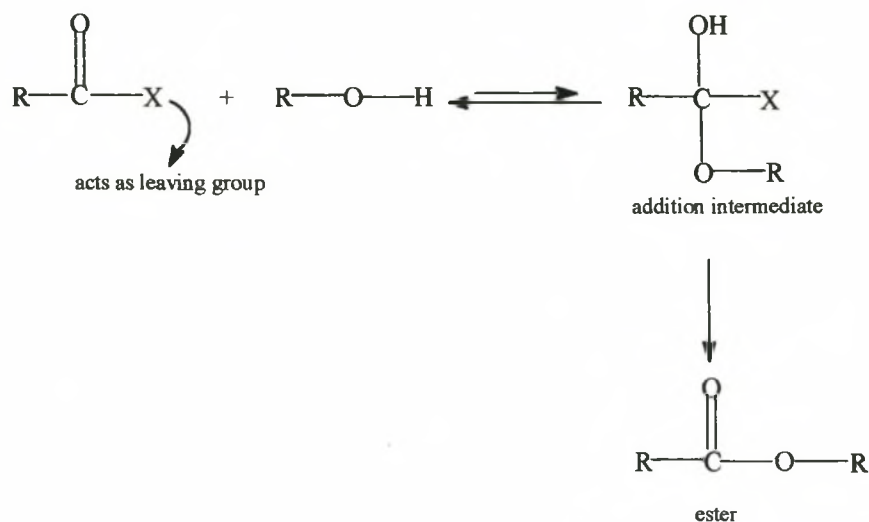


The tetrahedral addition intermediate reacts further by protonation, loss of water, and deprotonation to give the ester product.



3.3.3 Reaction mechanism for the preparation of carboxylic acid derivatives

In the case of carboxylic acid derivatives, such as acid chlorides, the reaction mechanisms also involve the formation of tetrahedral addition intermediates. The mechanisms of these reactions are extensions of the mechanisms of carbonyl addition. In a carbonyl-substitution reaction, a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative in exactly the same way that it attacks an aldehyde or ketone, and an addition compound is formed. Subsequently, a group $-\text{X}$ from the original acid derivative ($-\text{X} = -\text{OH}$ in a carboxylic acid itself) is expelled as a leaving group from the addition intermediate to give a new carboxylic derivative. In this chapter, these new carboxylic derivatives are represented by the esters formed, by reacting an acid chloride with a primary alcohol.



In other words, substitution at a carbonyl group is really a sequence of two processes: addition to the carbonyl group followed by elimination to regenerate the carbonyl group.

3.4 EXPERIMENTAL

3.4.1 Reaction method 1 – The esterification reactions between acrylic acid and three nonionic surfactants (7).

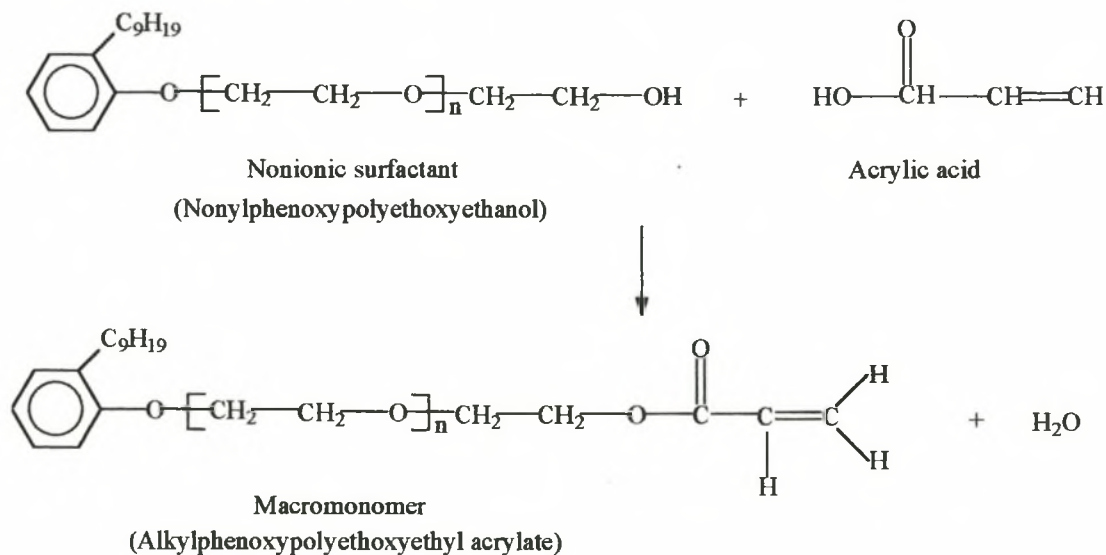


Figure 3.1:

The esterification reaction of a nonionic surfactant with acrylic acid.

3.4.1.1 Materials

- The acrylic acid was obtained from Sigma Aldrich – 95 % purity.
- Three different grades of nonylphenoxypolyethoxyethanol were used, containing 100, 50, and 20 oxyethylene units. The grade containing 100 oxyethylene units (IGEPAL CO-990) was obtained from Sigma Aldrich. The other two grades containing 50 (Berol 291) and 20 (Berol 292) oxyethylene units were obtained from Akzo Nobel Surface Chemistry AB.
- Sigma Aldrich also supplied the *p*-toluenesulfonic acid (acid catalyst), *p*-methoxyphenol (inhibitor).

3.4.1.2 The reaction procedure

The alcohol and the acid were reacted under anhydrous or substantially anhydrous conditions to effect the esterification of the alcohol through reaction between the acid groups and the terminal hydroxy groups of the alcohol.

A 500-ml reaction flask equipped with overhead stirrer was charged with 0.05 mole of a specific nonionic surfactant. The reaction flask was placed in oil bath and heated to a temperature of 40 to 80°C, sufficient to melt the alcohol, and then 0.1 mole of acrylic acid was added. The reaction was carried out in the presence of an acid catalyst, *p*-toluenesulfonic acid, and also in the presence of a small but inhibiting amount of paramethoxy phenol. The inhibiting agent was employed to prevent or inhibit the copolymerizing of the unsaturated acid employed in the acid alcohol reaction.

The mixture was stirred, heated to 120°C and held at this temperature for two hours to drive off the water formed during the esterification reaction and to form a monomeric ester product. The esterification reaction was carried out in contact with air, to further inhibit polymerization of the acrylic acid.

Table 3.1 contains the quantities of the different components used in each of the three reactions, that followed reaction method one.

Table 3.1:

Quantities of the different components used in each of the three reactions, that followed reaction method one.

	Number of oxyethylene units in the surfactant	Surfactant (grams)	Acrylic acid (grams)	p-Toluene sulfonic acid (grams)	p-Methoxy phenol (grams)
Reaction 1	100	231.25	7.2	2.38	0.05
Reaction 2	50	121.15	7.2	1.29	0.025
Reaction 3	20	55.05	7.2	0.62	0.015

3.4.2 Reaction method 2 – The esterification reaction between acryloyl chloride and three nonionic surfactants.

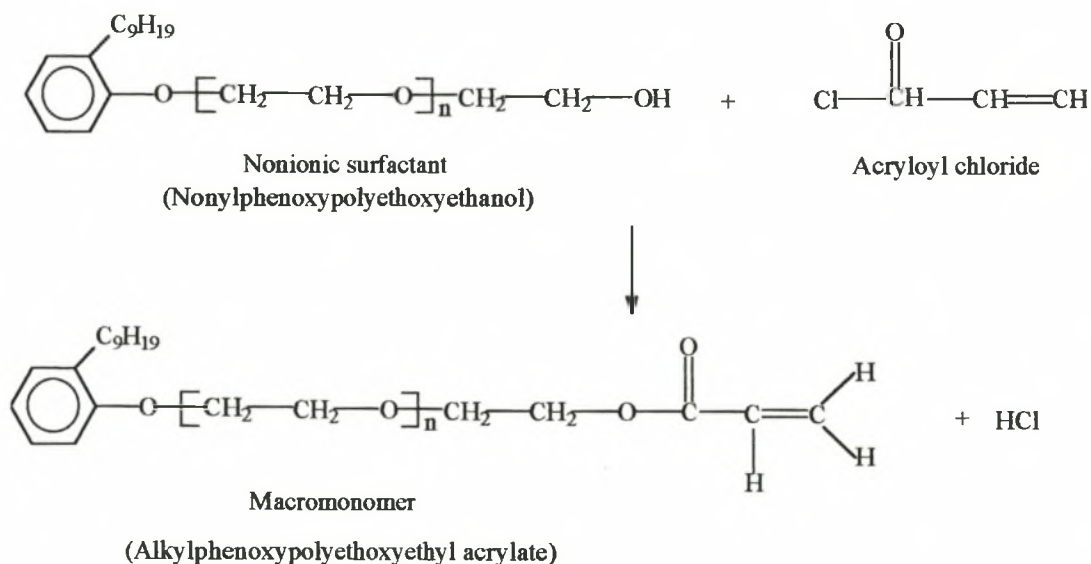


Figure 3.2:

The esterification reaction of a nonionic surfactant with acryloyl chloride.

3.4.2.1 Materials

- Acryloyl chloride of 95 % purity was obtained from Sigma Aldrich.
- The same three nonionic surfactants as in reaction method 1 were used (section 3.4.1.1).
- Tetrahydrofuran - 95 % purity
- Magnesium turnings

3.4.2.2 Removing water from the reaction solvents and nonionic surfactants.

The tetrahydrofuran was boiled under reflux, over magnesium turnings, for two hours to remove any water present in the solvent. Limiting the amount of water present in the reaction system is of great importance, because of the high reactivity of acryloyl chloride with water. A completely water free reaction system is unfortunately not possible, because of the introduction of water by the nonylphenoxypolyethoxyethanols used in the esterification reactions. The water molecules are tightly bound to the oxyethylene units by means of hydrogen bonding forming a water sheath around the oxyethylene units, which is not easily removed. This problem is overcome by reacting the alcohols with a tenfold excess of the acryloyl chloride. So what in actual fact happens is that the first molecules of acryloyl chloride introduced into the system react and remove any water molecules present in the reaction system. Once the water is removed from the system the acryloyl chloride then reacts with the hydroxyl group of the surfactant.

3.4.2.3 The reaction procedure

A 500-ml reaction flask was charged with 250 ml of tetrahydrofuran (reaction solvent) and the nonionic surfactant was dissolved into this reaction solvent. The reaction flask was equipped with a dropping funnel and an immersion thermometer. Agitation of the reaction system was done by means of a magnetic stirrer.

The reaction flask was placed in an ice bath so that the reaction could be carried out at 0°C, because of the high reactivity of the acryloyl chloride. The dropping funnel was charged with acryloyl chloride and the dropwise addition of the acryloyl chloride, scheduled to last for one hour, was begun. Once the reaction was completed the reaction solvent and excess acryloyl chloride were removed by evaporation on a rotary evaporator at 60 °C. Table 3.2 contains the

quantities of the different components used in each of the three reactions, that followed reaction method two.

Table 3.2:

Quantities of the different components used in each of the three reactions, that followed reaction method two.

	Number of oxyethylene units in the surfactant	Surfactant (grams)	Acryloyl chloride (grams)
Reaction 1	100	51.68	10
Reaction 2	50	27.35	10
Reaction 3	20	12.75	10

3.5 CHARACTERIZATION

3.5.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

3.5.1.1 Experimental

The unreacted surfactants and synthesized associative macromonomers were characterized by ^1H -NMR spectroscopy. The ^1H -NMR spectra were recorded at 30 °C using a Varian VXR 300 spectrometer operating at 300 MHz. The macromonomer samples for the NMR analysis was prepared by dissolving 65 milligrams of the macromonomer in 0.65 ml of deuterium trichloride (CDCl_3) as solvent. All spectra obtained in CDCl_3 were calibrated using 0.05 % TMS as the internal standard.

3.5.1.2 Results and Discussion

In the following discussion the surfactant and macromonomers containing an average of 20 oxyethylene units will be used as an example. The ^1H – NMR spectra of the surfactants and

macromonomers containing an average of 50 and 100 oxyethylene units are given and discussed in Appendix A.

3.5.1.3. The nonionic surfactant molecule

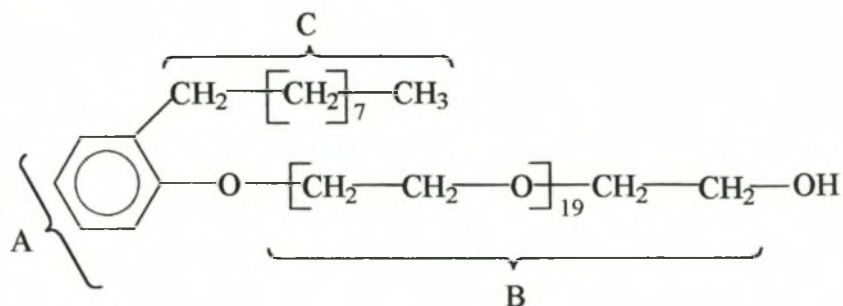


Figure 3.3:

Nonionic surfactant containing an average of 20 oxyethylene units.

The surfactant molecule has been divided into three groups, the aromatic ring, the repeating oxyethylene units and the aliphatic side chain. The complete ^1H -NMR spectrum of the nonionic surfactant are presented in Figure 3.4. Specific sections of the ^1H -NMR spectrum have been enlarged and are presented in Figures 3.5 – 3.7.

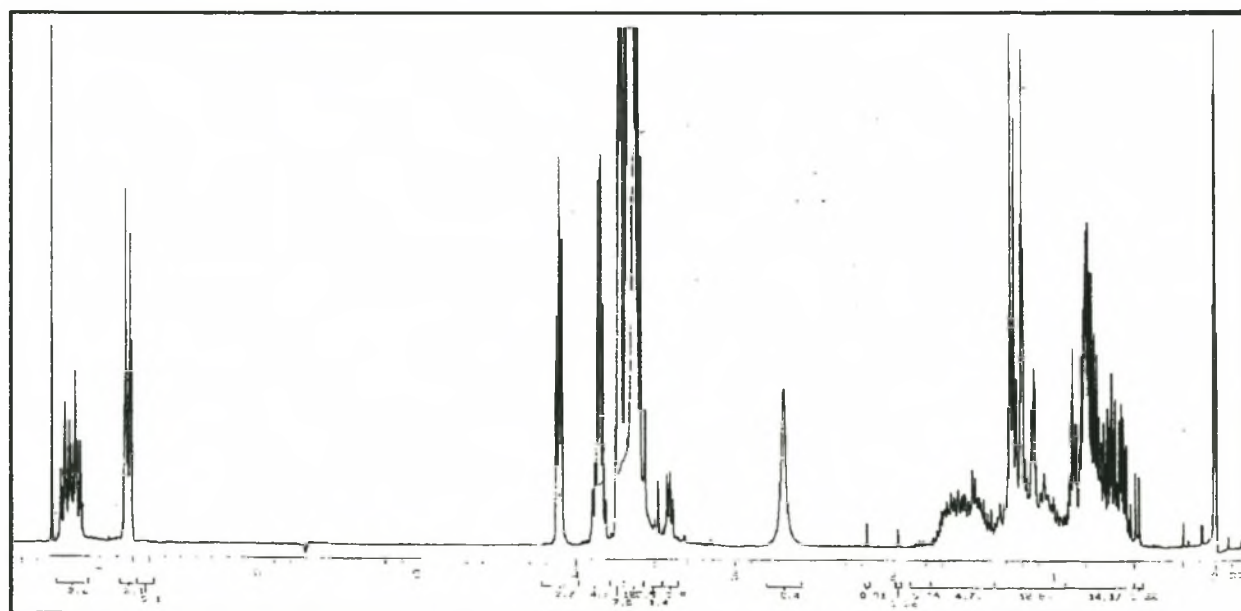
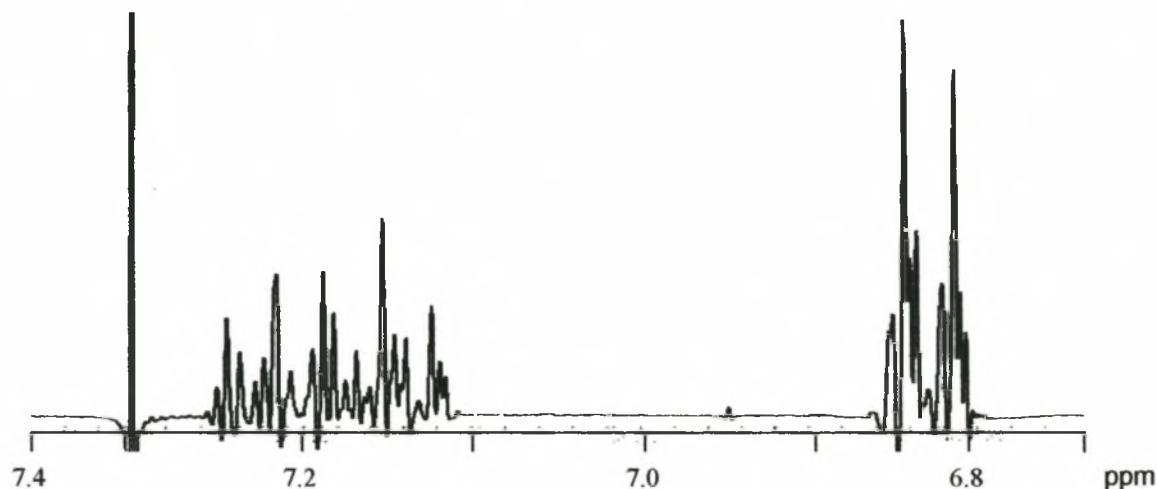
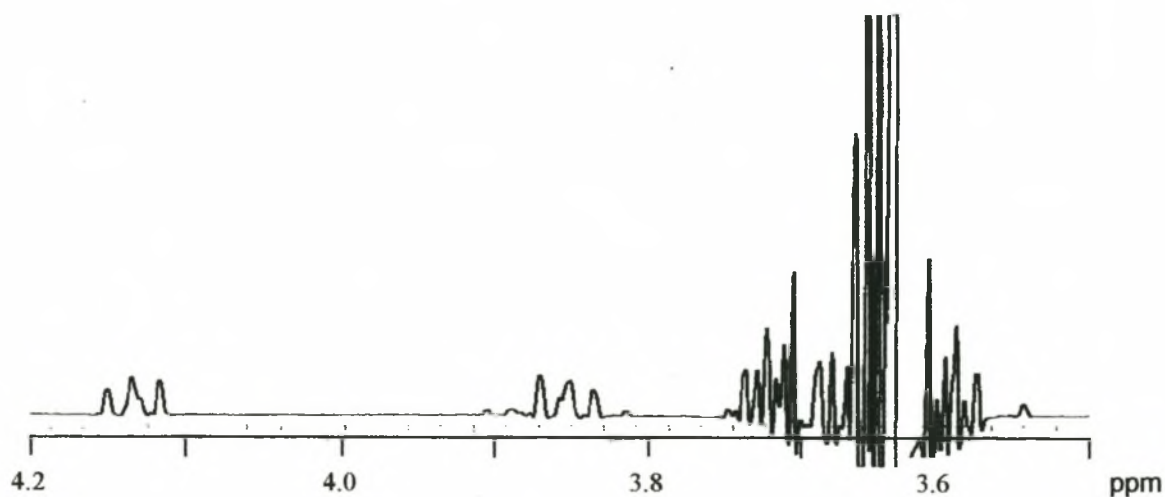


Figure 3.4:

^1H – NMR spectrum of the nonionic surfactant alcohol containing an average of 20 oxyethylene units (300 MHz).

Group A – The aromatic ring.**Figure 3.5:****The splitting pattern of the four H-atoms in the aromatic ring.**

At a chemical shift of 7.10 – 7.26 ppm and at 6.80 – 6.86 ppm two multiplets are seen. These two multiplets represent the four H-atoms in the para-substituted aromatic ring and each one of these multiplets integrates for two H-atoms.

Group B – The repeating oxyethylene units.**Figure 3.6:****The splitting pattern of the H-atoms in the oxyethylene repeating units.**

Each of the oxyethylene units contains two CH₂ groups and the H-atoms of each group will be represented by a triplet of peaks. At a chemical shift of 4.11 and 3.84 ppm two sets of triplet peaks can be seen and they represent the H-atoms of the oxyethylene unit closest to the aromatic ring. It is the interaction of the aromatic ring with the H-atoms of these oxyethylene units that causes these two sets of triplets to be shifted up higher in the field. At a chemical shift of 3.64 – 3.74 ppm a multiplet can be seen which integrates for 76 H-atoms and represents the rest of the H-atoms in the repeating oxyethylene units, except the two H-atoms of the last CH₂ group that is adjacent to the hydroxy group. These two H-atoms are represented by a triplet at a chemical shift of 3.61 ppm. This triplet of peaks are very important when the spectra of the surfactant and macromonomer molecules are compared later in this chapter (section 3.5.1.4).

Group C – The aliphatic side chain.

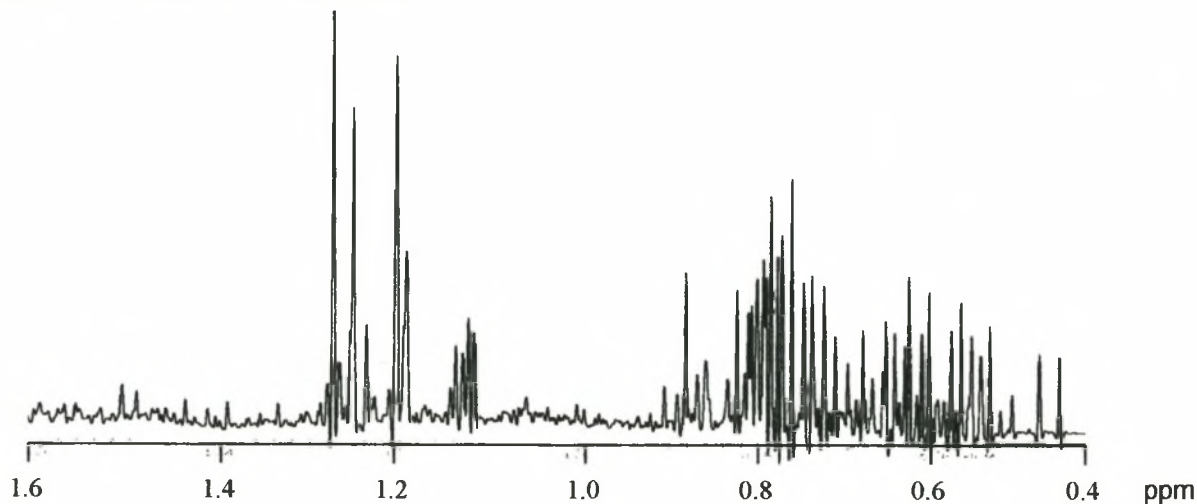


Figure 3.7:

The splitting pattern of the H-atoms in the aliphatic side chain.

At a chemical shift of 0.50 – 1.77 a broad multiplet is present that integrates for 19 H-atoms and represents the 19 H-atoms in the aliphatic side chain.

3.5.1.4 The macromonomer molecule.

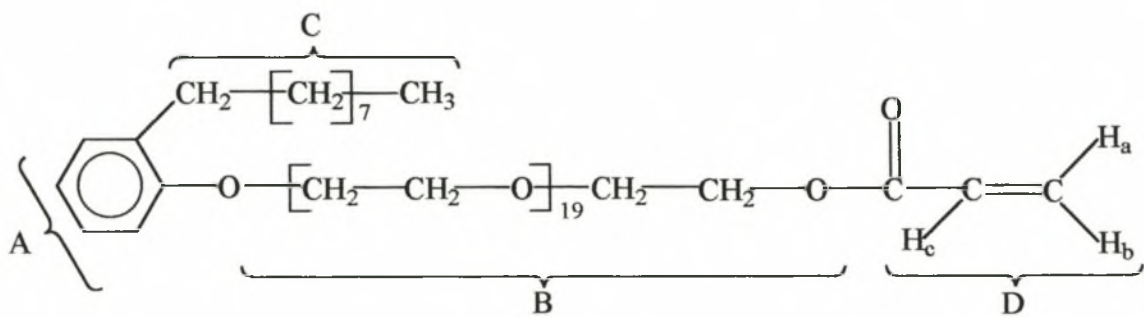


Figure 3.8:

The macromonomer containing an average of 20 oxyethylene units.

The macromonomer molecule has been divided into four groups, the aromatic ring, the repeating oxyethylene units, the aliphatic side chain and the ethylenic unsaturation. Figure 3.9 contains the complete $^1\text{H-NMR}$ spectrum of the macromonomer synthesized by reaction method two. Specific sections of the $^1\text{H-NMR}$ spectrum in Figure 3.9 have been enlarged and are presented in Figures 3.10 – 3.13.

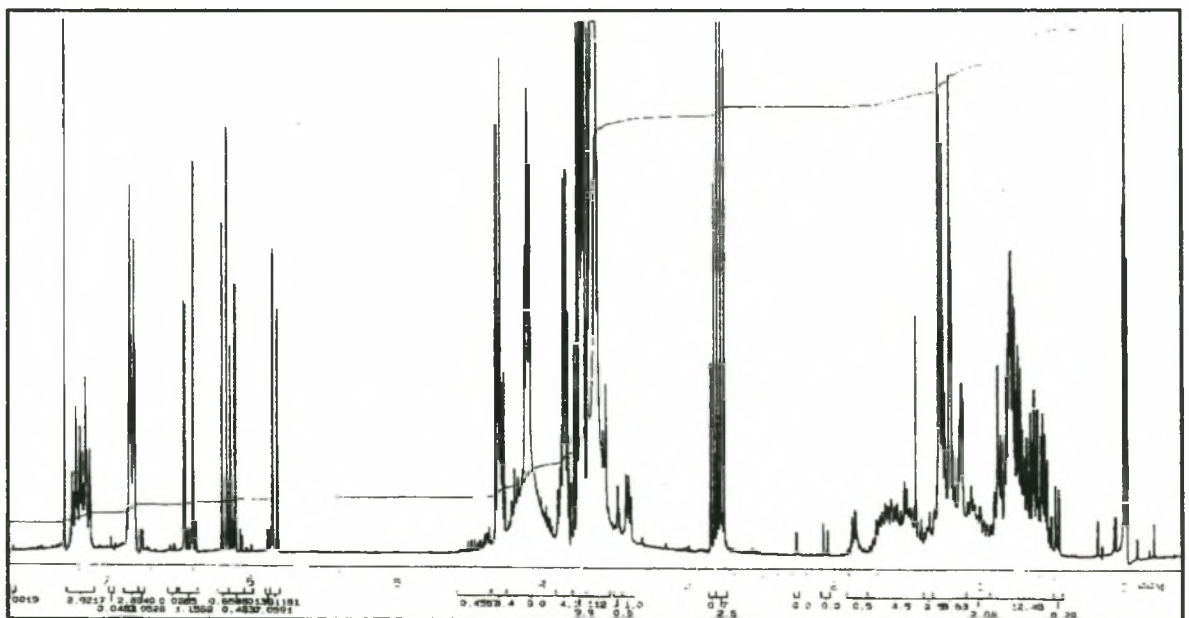
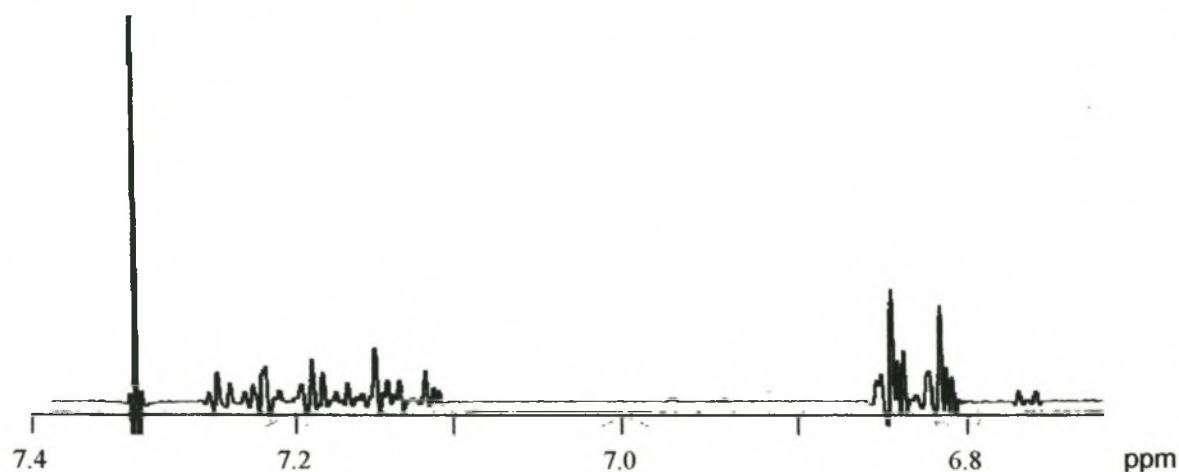


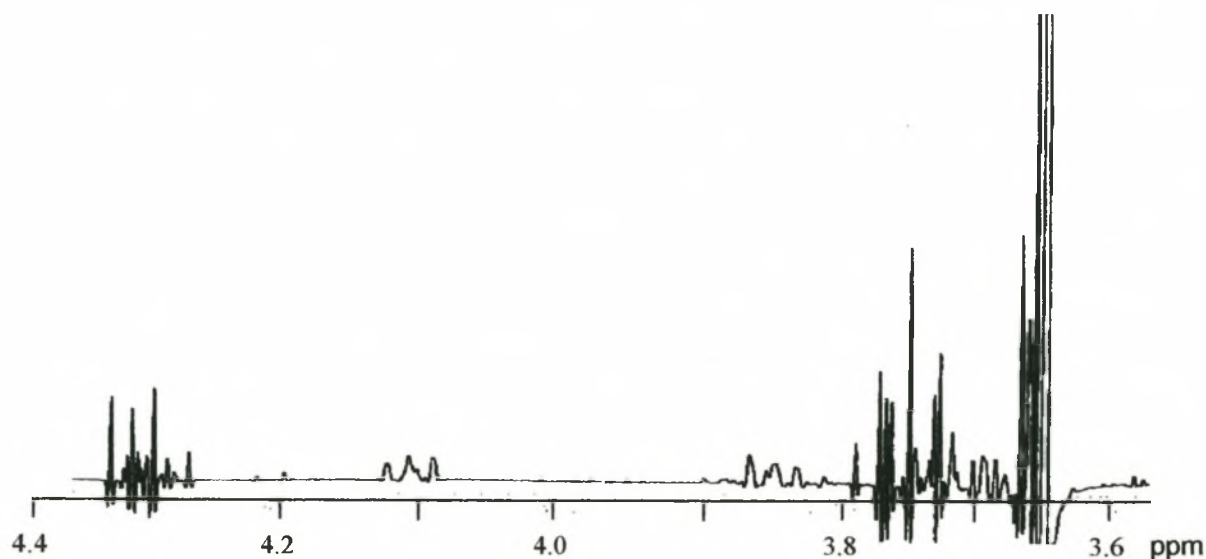
Figure 3.9:

^1H – NMR spectrum of the macromonomer containing an average of 20 oxyethylene units synthesized by reaction method two (300 MHz).

Group A – The aromatic ring.**Figure 3.10:**

The splitting pattern of the H-atoms in the aromatic ring.

At a chemical of 7.12 – 7.25 ppm and at 6.81 – 6.85 ppm two multiplets can be seen. These two multiplets represent the four H-atoms in the para-substituted aromatic ring and each one of these multiplets integrates for two H-atoms.

Group B – The repeating oxyethylene units.**Figure 3.11:**

The splitting pattern of the H-atoms in the oxyethylene repeating units.

The two triplets of peaks at δ 4.11 and 3.85 ppm represent the H-atoms in the oxyethylene unit next to the aromatic ring. Each of these triplets integrates for two H-atoms. The multiplet of peaks that can be seen at δ 3.64 – 3.79 ppm integrates for 76 H-atoms and represent the H-atoms in the rest of the oxyethylene units, except for the two H-atoms in the last CH₂ group next to the ester group. In the surfactant molecule the triplet of peaks representing these two H-atoms were present at δ 3.61 ppm. In the spectrum of the macromonomer from reaction method two there is no triplet present at δ 3.61 ppm, but a new triplet can be seen at δ 4.32 ppm. The complete shift of the triplet of peaks from δ 3.61 ppm to δ 4.32 ppm indicates that the reaction went to completion. This underlines the fact that reaction method two follows an irreversible reaction mechanism.

Group C – The aliphatic side chain.

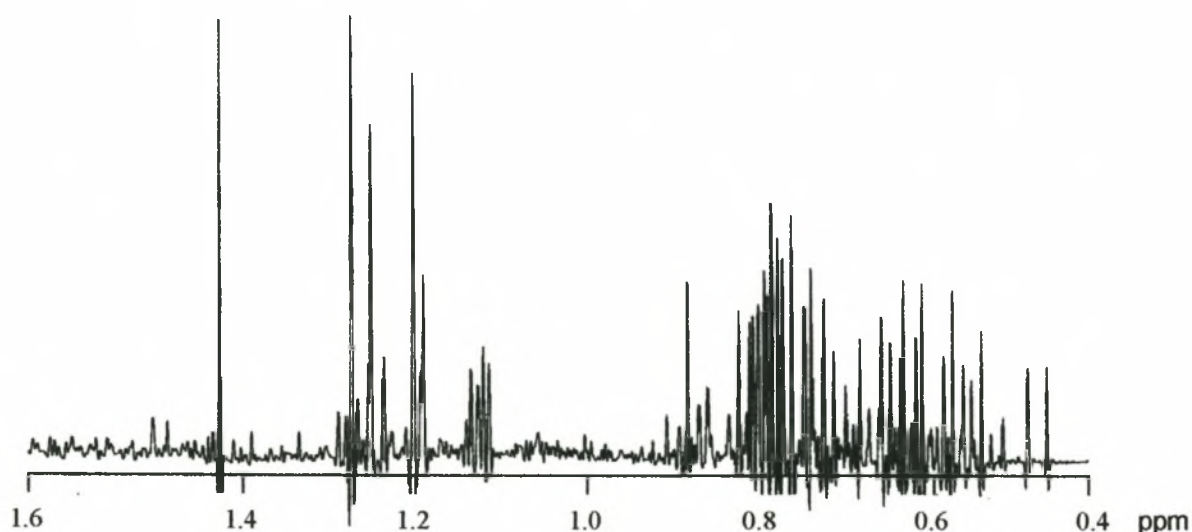
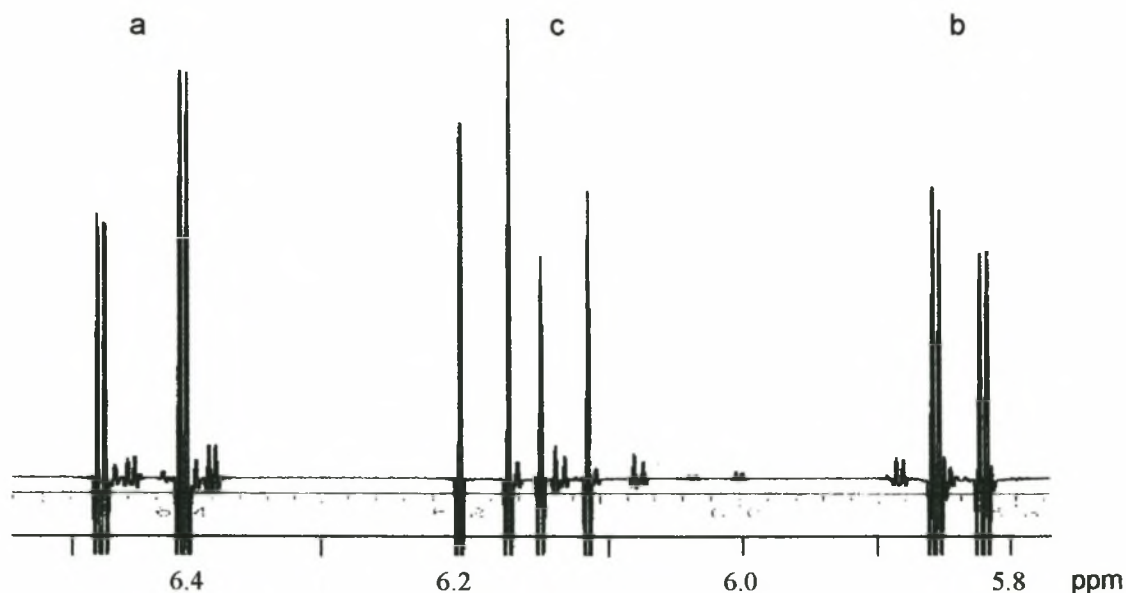


Figure 3.12:

The splitting pattern of the H-atoms in the aliphatic side chain.

The H-atoms in the aliphatic side are represented by a multiplet of peaks at δ 0.5 – 1.70 ppm and the multiplet integrates for 19 H-atoms.

Group D – The ethylenic unsaturation.**Figure 3.13:**

The splitting pattern of the H-atoms in the ethylenic unsaturation.

The three vinylic protons in the macromonomer molecule form a ABC coupling system, which gives a unique splitting pattern in the $^1\text{H-NMR}$ spectrum. There are three different types of splitting between the vinylic protons, ie. trans splitting between protons a and c, cis splitting between protons b and c, and geminal splitting between protons a and b. Figure 3.14 contains the splitting diagram for the $^1\text{H-NMR}$ spectrum of the vinylic protons in the macromonomer.

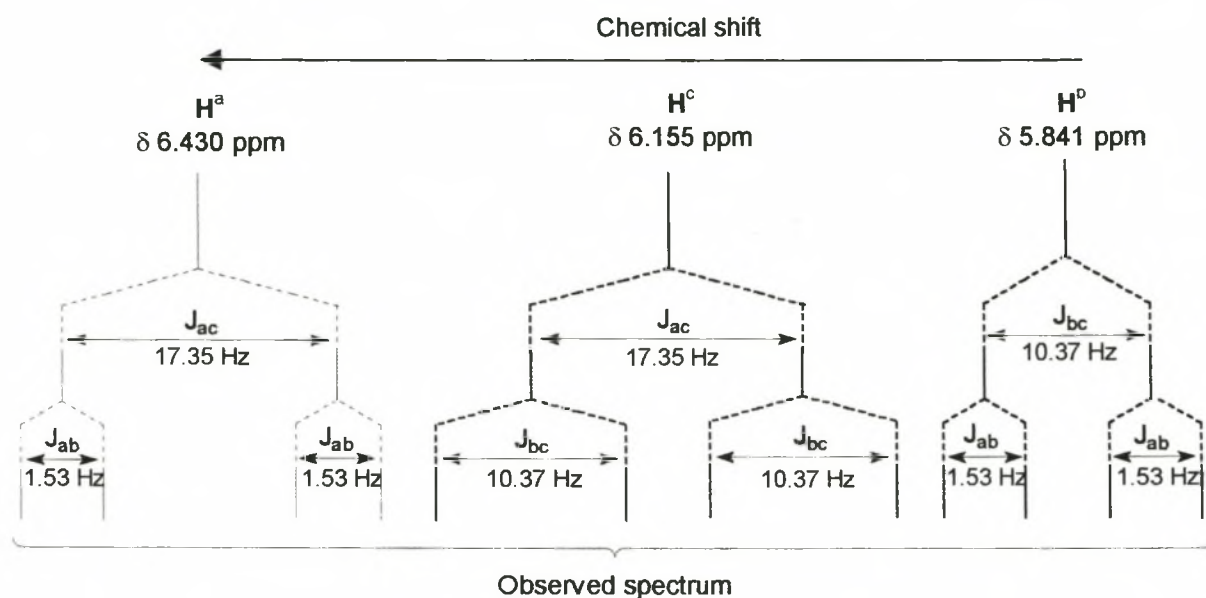


Figure 3.14:

Splitting diagram for the ^1H -NMR spectrum of the vinyl protons in the macromonomer.

The complete ^1H -NMR spectrum of the macromonomer synthesized by reaction method one can be seen in Figure 3.15 and the NMR data which is very similar to that of the macromonomer synthesized by reaction method two is summarized in Table 3.3.

If one compares the ^1H -NMR spectra of the macromonomers synthesized by the two different methods then two main differences emerge. The first is the peak intensities of the vinyl protons and the two sets of triplets that account for the same CH_2 group in the case of the macromonomer synthesized by reaction method one. This is a clear indication that not all the surfactant has reacted with the acrylic acid.

Table 3.3

The $^1\text{H-NMR}$ data of the macromonomer synthesized by reaction method one.

	Type of splitting pattern	Number of H-atoms	Chemical shift(δ) (ppm)	Coupling constants (when calculated)
GROUP A				
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.850 2: 7.119 – 7.251	- -
GROUP B				
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.110	- -
19 Oxyethylene units	Multiplet	78	3.601 – 3.807	-
Last CH₂ group next to the ester group	Triplet	2	1: 3.612 2: 4.314	- -
GROUP C				
The aliphatic side chain	Multiplet	19	0.465 – 1.753	-
GROUP D				
Ethylenic unsaturation (ABC coupling system)	Six doublets	Each H-atom is represented by two doublets	H ^a : 6.427 H ^b : 6.108 H ^c : 5.837	J _{ab} = 17.34 Hz J _{ac} = 1.55 Hz J _{bc} = 10.40 Hz

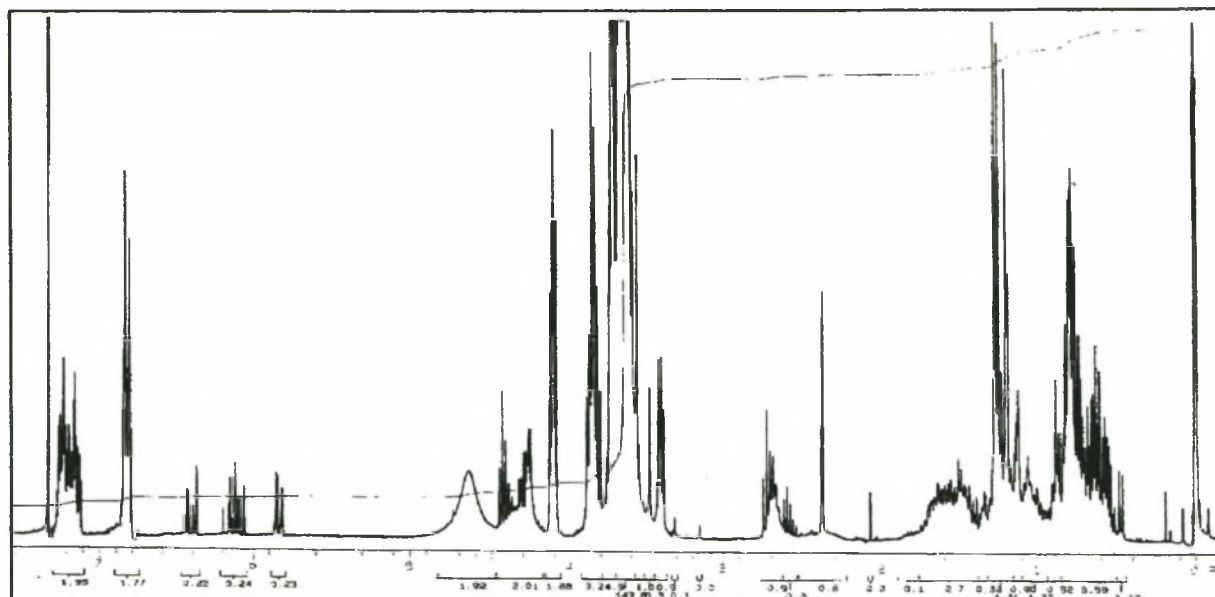


Figure 3.15:

¹H – NMR spectrum of the macromonomer containing an average of 20 oxyethylene units synthesized by reaction method one (300 MHz).

3.5.1.5 The conversion percentages of the different reactions.

It has already been shown in Section 3.5.1.3 that reaction method two goes to completion since the triplet that represents the CH₂ group next to the hydroxy group in the surfactant undergoes a complete chemical shift from 3.61 ppm to 4.32 ppm. The macromonomers synthesized by reaction method one show triplet peaks at both these chemical shifts, which indicates that not all the hydroxy groups in the surfactant have reacted.

To calculate the percentage conversion of the different reactions one first needs to identify a reference group, whose environment does not undergo change during the reaction and secondly a reactive group whose environment does undergo change. The aromatic group is a good reference and is represented by two multiplets in the NMR spectra. We know that each of the multiplets represents two protons and the integration value for each of the multiplets are given in the ¹H-NMR spectrum.

In each of the macromonomer spectra the first multiplet at δ 7.119-7.251 ppm is used as reference. In the case of the macromonomers synthesized by reaction method two the CH₂ group next to the ester bond is chosen as the reactive group and is represented by a triplet in the ¹H-NMR spectrum. The percentage conversion is calculated by equation 3.1 and conversion percentages of macromonomers synthesised by reaction method two presented in Table 3.4.

$$\% \text{ Conversion} = [(\text{Integral of CH}_2 \text{ triplet}) / (\text{Integral of aromatic multiplet})] * 100 \quad (3.1)$$

Table 3.4:

The conversion percentages of the macromonomers synthesized by reaction method two.

Number of oxyethylene units in macromonomer	Integral of aromatic multiplet	Integral of CH ₂ triplet	% Conversion
20	2.922	3.400	116.36
50	1.553	1.654	106.50
100	0.838	0.804	95.94

When one compares the integrals of different groups within the same molecule there is a 10 % deviation that occurs (15). This is one of the reasons why the above obtained conversions do not work out on a 100% conversion, as one would expect, although we know that all the hydroxy groups in the surfactants have been reacted. The second reason is that the commercial anionic surfactants used are not 100% pure and this lead to further deviations in the percentage conversion. In Section 3.5.2. this is proved by HPLC analysis.

In the case of the macromonomers synthesized by means of reaction method one the CH₂ group next to the ester bond cannot be used as a reactive group, because there is too much overlapping of peaks in that specific area. We know that full conversion was not obtained as explained in Section 3.5.1.3. The double bond at the end of each macromonomer is to be used

as the reaction response and the aromatic ring will still be used as the reference group. Each one of the protons in the double bond is represented by a set of doublets in the $^1\text{H-NMR}$ spectrum. The integral of the first doublet at a δ 6.40 ppm is used to calculate the conversion percentages. The percentage conversion is calculated by equation 3.2 and the conversion percentages of the macromonomers synthesized by reaction method one is presented in Table 3.5.

$$\% \text{ Conversion} = [(\text{Integral of the doublet}) * 2 / (\text{Integral of aromatic multiplet})] * 100 \quad (3.2)$$

Table 3.5:

The conversion percentages of the macromonomers synthesized by reaction method one.

Number of oxyethylene units in macromonomer	Integral of aromatic multiplet	Integral of the doublet	% Conversion
20	1.950	0.22	22.56
50	3.230	0.39	24.15
100	1.177	0.288	48.94

The same factors that influenced the conversion percentages of the macromonomers synthesized by reaction method two are also applicable to the macromonomers synthesized by reaction method one. There is in fact an additional factor that comes into play when you use the double bond functionality as your reactive group. Any unreacted acrylic acid will also be detected in the $^1\text{H-NMR}$ spectrum and will increase the integral of the doublet, which will then increase the percentage conversion calculated.

Although the percentages calculated for the two different reaction methods are not 100 % accurate, it is clear that reaction method two gives much higher conversions than reaction method one.

3.5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The unreacted surfactants and the macromonomers synthesized by the two different reaction methods were analyzed by FTIR spectroscopy to confirm certain results obtained from the ^1H -NMR analysis.

3.5.2.1 Experimental

The FTIR spectra were recorded by a Paragon 1000 Fourier Transform Infrared Spectrometer. The samples were prepared by heating the surfactants and macromonomers sufficiently to liquefy them, and then casting films onto sodium chloride disks.

3.5.2.2 Results and Discussion

Surfactant and macromonomers containing an average of 100 oxyethylene units will be used as examples in the following discussion. The FTIR spectra of the surfactants and macromonomers containing an average of 20 and 50 oxyethylene units are discussed in appendix A. The nonionic surfactants and macromonomers have been well characterized by NMR analysis and therefore the FTIR analysis are used to indicate if certain functional groups are present in the surfactants and macromonomers, which would verify that the reactions did indeed take place and if possible to what extent.

Figures 3.16–3.18 contain the FTIR spectra of the nonionic surfactant and the macromonomers synthesized by the two reaction methods. There are three main functional groups that are of importance, i.e. the -OH-group in the surfactant molecule, the C=O and -CH=CH₂ group in the macromonomer molecules. Table 3.6 contains the FTIR data of the above mentioned functional groups.

In the FTIR spectrum of the surfactant molecule only the absorption band for the OH functional group is present as one would expect. The FTIR spectrum of the macromonomer synthesized by means of reaction method one contains absorption bands for all three of the functional groups. In comparison to this the FTIR spectrum of the macromonomer synthesized by means of reaction method two only contains absorption bands for the C=O and C=C groups. This leads one to conclude that reaction method one does not reach full conversion as is the case with

reaction method two. In other words, in the case of reaction method two all the hydroxy groups of the surfactant have reacted with the acryloyl chloride.

Table 3.6:

FTIR data of the surfactant and macromonomers containing an average of 100 oxyethylene units.

	Functional group	Absorption band frequency (cm ⁻¹)
Surfactant	-OH	3481.28
Macromonomer (reaction method one)	-OH	3489.75
	C=O	1720.98
	-CH=CH ₂	1643.11
Macromonomer (reaction method two)	C=O	1724.59
	-CH=CH ₂	1633.35

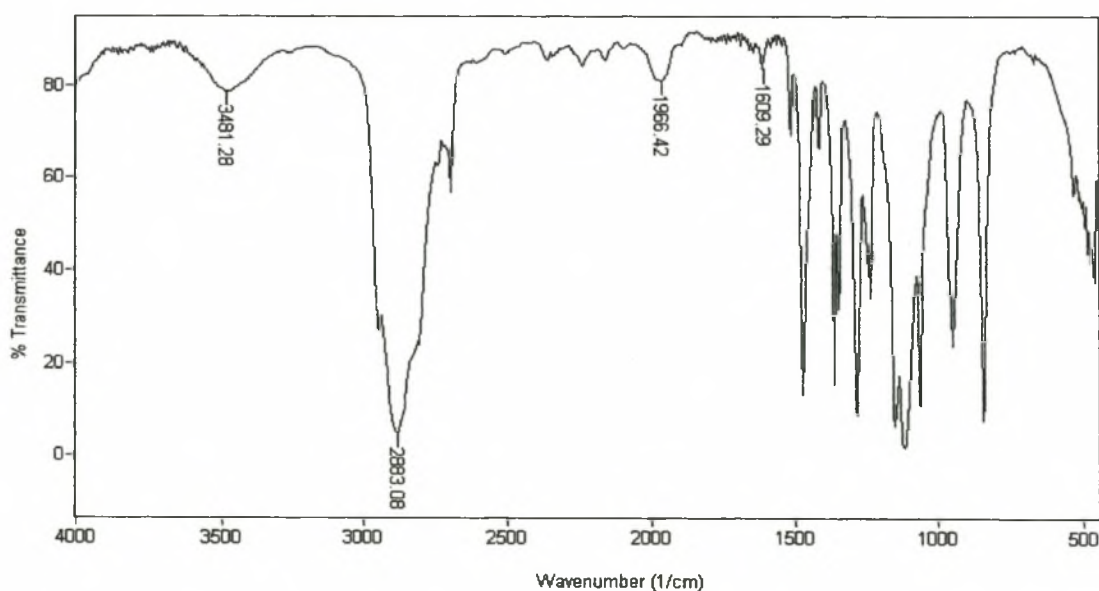


Figure 3.16:

FTIR spectrum of the nonionic surfactant containing an average of

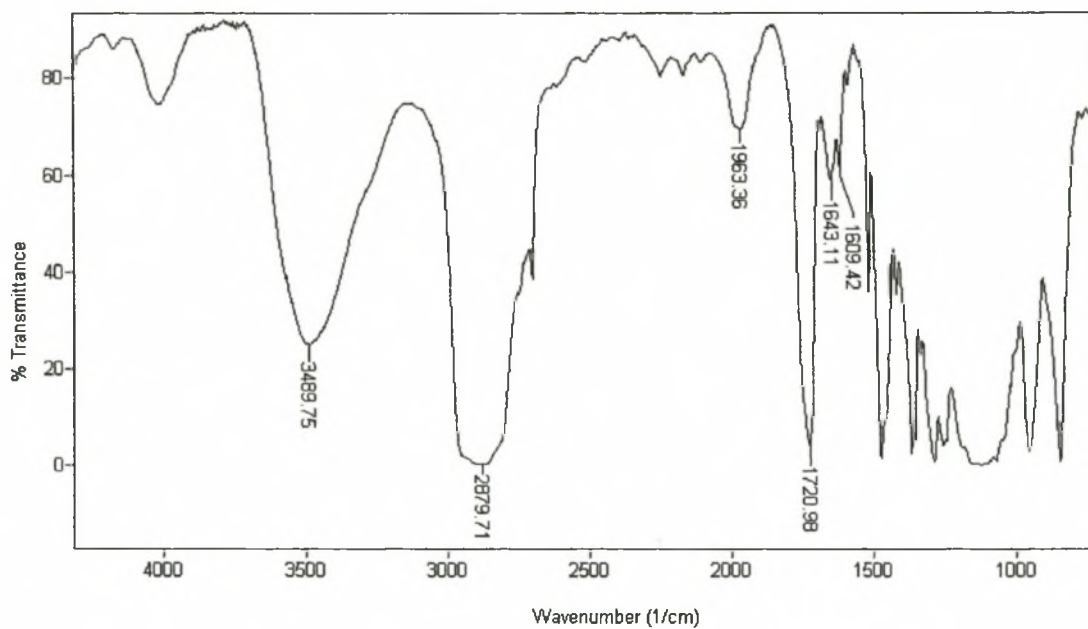


Figure 3.17:

FTIR spectrum of the macromonomer containing an average of 100 oxyethylene units synthesized by reaction method one.

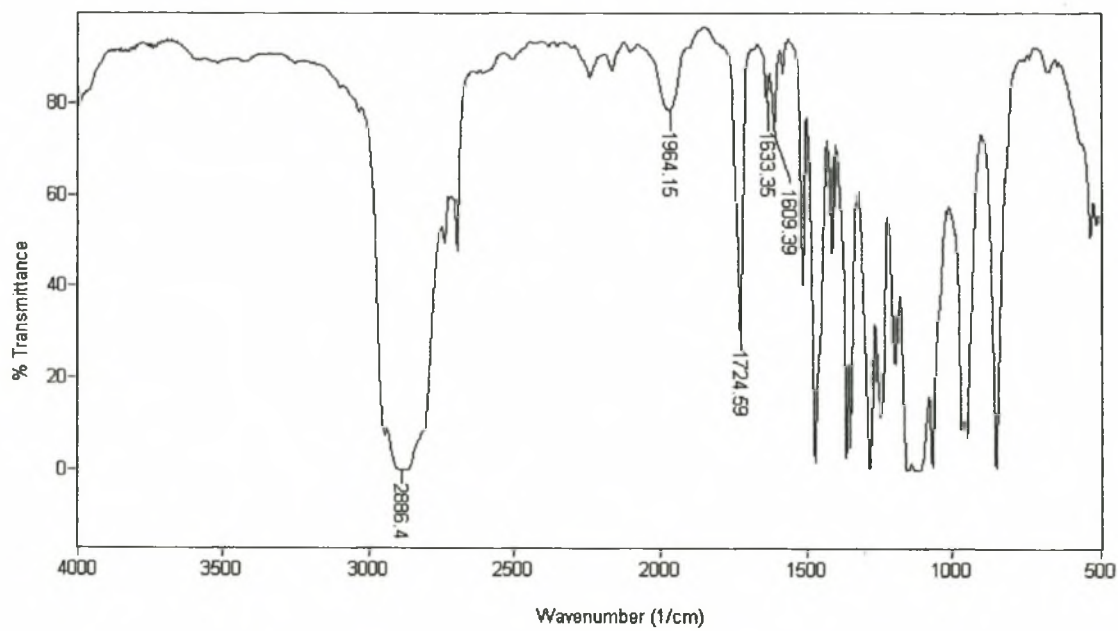


Figure 3.18:

FTIR spectrum of the macromonomer containing an average of 100 oxyethylene units synthesized by reaction method two.

3.5.3 Normal phase high-performance liquid chromatography(HPLC) analysis

The HPLC analysis of the three nonionic surfactants was done to determine whether any impurities were present in the anionic surfactants that would influence the amount of conversion obtained. This experimental work was done by Mr. Abrie Mayburg at Somchem laboratories.

3.5.3.1 Chromatography equipment, columns and solvents used

- HP 1100 gradient HPLC system was used.
- Detector : HP1100 DAD @ 220 nm.
- The column oven temperature was at 30 °C.
- The flow rate of the solvent was 1 ml/min.
- Injection volume was 20 μ l.
- Columns – Spherisorb C₁₈ colom and a C₁₈ pre-colom.
- 36 % concentrations of the samples were made up by dissolving the surfactants in a 80:20 MeOH:H₂O solution.
- The gradient system used was 80:20 MeOH:H₂O $\xrightarrow{20 \text{ min}}$ 60:40 MeOH:H₂O
- Samples:

Berol 292 – Surfactant containing an average of 20 oxyethylene units.

Berol 291 - Surfactant containing an average of 50 oxyethylene units.

Igepal CO-990 - Surfactant containing an average of 100 oxyethylene units.

3.5.3.2 Results and discussion

Figure 3.19 contains the the HPLC graphs of the three nonionic surfactants.

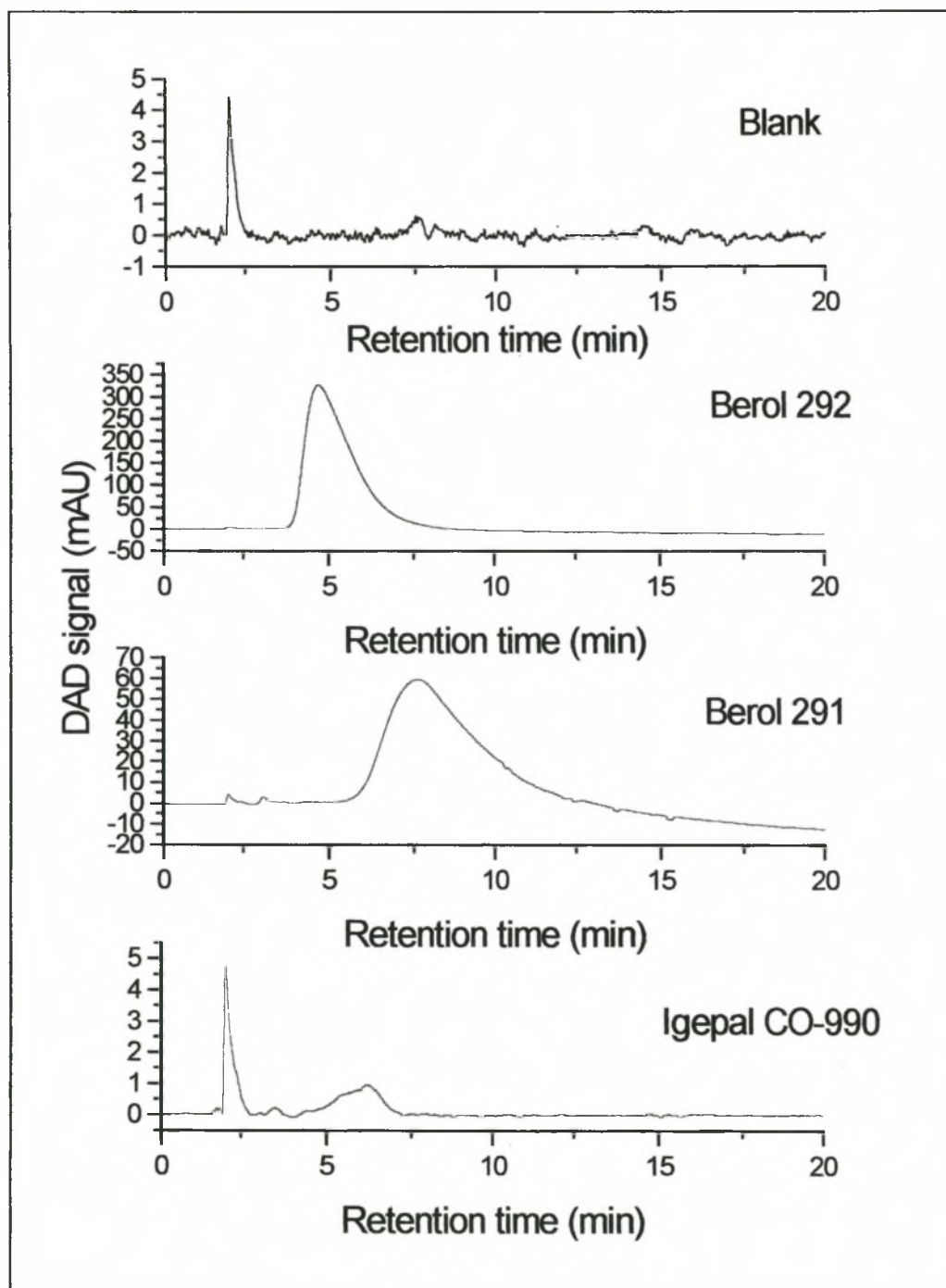


Figure 3.19

Gradient HPLC analysis of the three surfactants and a blank solvent run.

The blank run which is the first graph in Figure 3.19 shows a single peak at a retention time of 2.05 min and this peak is also present in every one of the graphs of the surfactants. This is due to an inherent property of the methanol and water which was used as both solvent and eluent. Except for the solvent peak there are two additional peaks in each of the graphs of the surfactants. The retention times for the peaks are given in Table 3.7. The second peak in the graphs show the presence of impurities in the surfactants. The large peaks with the highest retention times represent the pure surfactant molecules. In Figure 3.20 a section of the graph of Berol 292 has been enlarged to show the impurity peak at 3.14 min.

Table 3.7:

The retention times of the peaks in the graphs of the HPLC analysis.

	Blank (peak 1) (min)	Impurity (peak 2) (min)	Surfactant (peak 3) (min)
Berol 292	2.05	3.12	4.75
Berol 291	2.05	3.14	7.62
Igepal CO-990	2.05	3.12	6.20

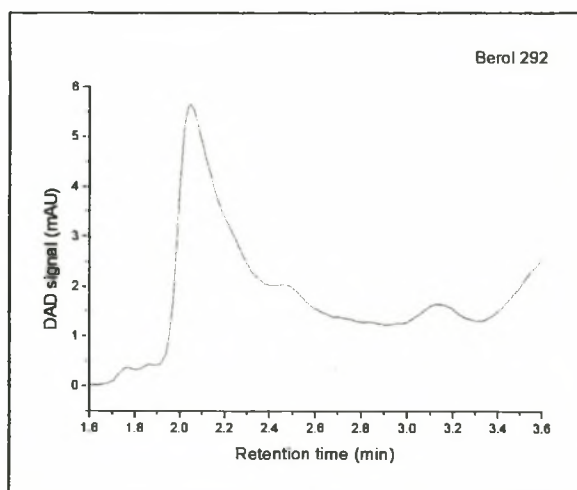


Figure 3.20

Enlarged section of gradient HPLC analysis of Berol 292

3.6 CONCLUSIONS

- The main objective, to synthesize macromonomers from commercially available nonionic surfactants with varying degrees of ethoxylation, was carried out successfully.
- Three macromonomers, containing either 20, 50 or 100 oxyethylene units, were synthesized by each of the two esterification reaction methods used.
- All six of the macromonomers and the three nonionic surfactants were characterized by means of $^1\text{H-NMR}$ spectrometry and FTIR spectrometry.
- A much higher conversion from surfactant to macromonomer was obtained with reaction method two where the surfactants were reacted with acryloyl chloride, than with reaction method one where acrylic acid was used.
- In reaction method two all the terminal hydroxy groups of the surfactants underwent complete conversion to ester groups. This confirmed that reaction method two follows an irreversible mechanism and therefore the reaction goes to completion. In contrast to this reaction method one follows a reversible mechanism which reaches equilibrium and therefore lower conversions are obtained.

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15. Mr. H.S.C. Spies, NMR laboratories, Department of Chemistry, University of Stellenbosch.

CHAPTER 4

THE SYNTHESIS OF HYDROPHOBICALLY-MODIFIED ALKALI-SOLUBLE (HASE) THICKENERS BY MEANS OF FREE RADICAL ADDITION POLYMERIZATION

4.1 INTRODUCTION

In coating formulations based on aqueous polymer latexes, an adjustment of the rheology profile is usually required (1,2). A rheology profile describes the shear rate and time dependent paint viscosity that effects such properties as pigment settling, brush and roller pickup, film build, leveling and the sagging of the film on vertical surfaces. Water-soluble polymers provide very efficient and controllable means of adjusting viscosity (3-7). The viscosity and rheology in this case are a function not only of the concentration of polymer but also of its molecular weight, the flexibility of its backbone and, for ionic polymers, the charge concentration along the backbone and the ionic strength. The efficiency of water-soluble polymers in increasing viscosity is a major practical consideration and in the coatings industry it is usually expressed in terms of the amount of thickener required to obtain a target viscosity in a latex formulation (8).

OBJECTIVES

- The first major objective here was to synthesize six different HASE thickeners, using acrylic acid as the backbone monomer and inserting the different macromonomers synthesized in Chapter 3 to give the HASE thickeners their hydrophobic character.

The first three HASE thickeners have the same length backbone, with each thickener containing one type of hydrophobic macromonomer. The hydrophobic macromonomers differ in the length of their repeating oxyethylene units. They contain either 20, 50 or 100 oxyethylene units. The next three HASE thickeners are very similar to the first three except that 5% of the acrylic acid in the backbone is substituted with a second, phosphated, macromonomer, which would mean that these thickeners will each contain two types of macromonomers.

- The HASE thickeners are to be characterized by means of C^{13} -NMR spectrometry.
- The thickeners are to be used in a standard latex coating formulation. The rheology profiles of the different coatings will be compared and from that one should be able to determine the thickening efficiencies of the different thickeners.
- The above mentioned six coatings will also be evaluated for their viscosity stability when tinted with universal colorants.

4.2 THEORETICAL BACKGROUND

4.3.1 General

Addition polymerization, vinyl polymerization, or chain growth polymerization are the name given to the process whereby the double bond of a monomer is rearranged to form an active chain carrier which permits the monomer units to grow to macromolecular proportions. The products of addition polymerization are known as addition polymers (9-10). Addition polymerization has two distinct characteristics:

1. No molecule or segment is split out; hence, the repeating unit has the same chemical formula as the monomer.
2. The polymerization reaction involves the opening of a double bond.

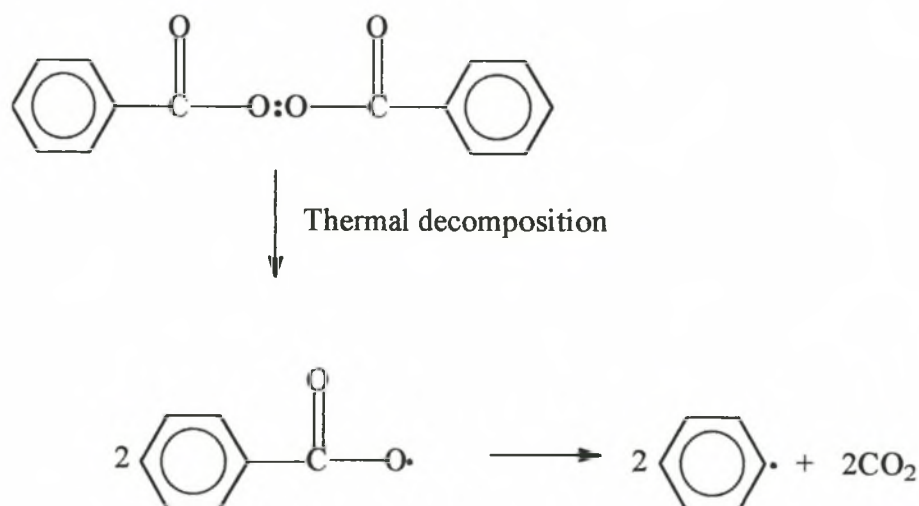
One of the most important types of addition polymerization is initiated by the action of free radicals, electrically neutral species with an unshared electron. In the text which follow, a dot (·) will represent a single electron. The single bond, a pair of shared electrons, will be denoted by a double dot (:) or, where it is not necessary to indicate

electronic configuration, by the usual sign (-). A double bond, two shared electron pairs, is indicated by $::$ or $=$.

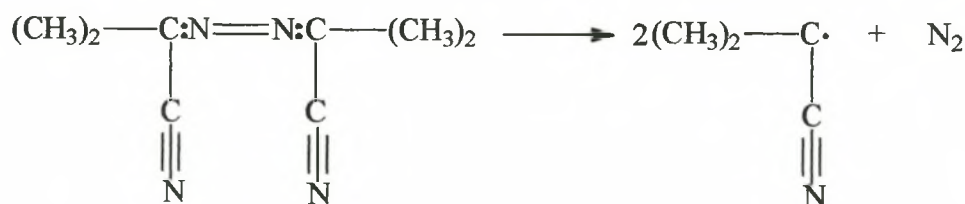
Free radicals for the initiation of addition polymerization are usually generated by the thermal decomposition of organic peroxides or azo compounds. Thermal initiation using persulphates is also very popular, especially in emulsion polymerization. Ammonium, sodium and potassium persulphates cleave at elevated temperatures (75-85 °C) to form free radicals capable of reacting with the vinyl unsaturation of monomers. In water, this cleavage reaction is a first order reaction dependent solely on temperature, but in the presence of monomer, the rate is more complex.

Examples of free radical generation are given:

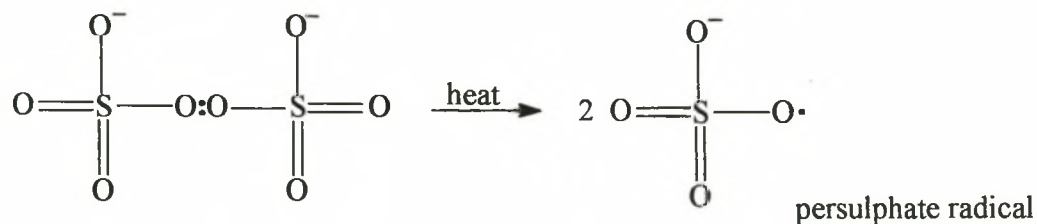
Benzoyl Peroxide



Azobisisobutyronitrile



Persulphate radical



4.3.2 Mechanism of polymerization

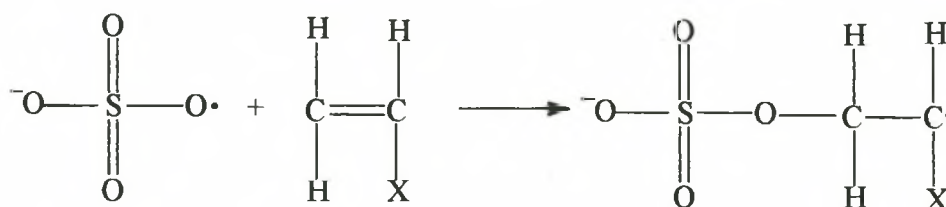
The growth of addition polymers takes place via a chain mechanism and can be described by the following chain reaction steps: Decomposition, Addition, Propagation, and Termination.

The initiator molecule, represented by I, undergoes a first-order decomposition with a rate constant k_d to give two free radicals, R^\cdot :

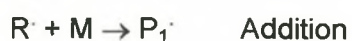


The radical then adds a monomer by pairing with an electron from the electron rich double bond, forming a single bond with the monomer, but leaving an unshared electron at the other end:

Example:

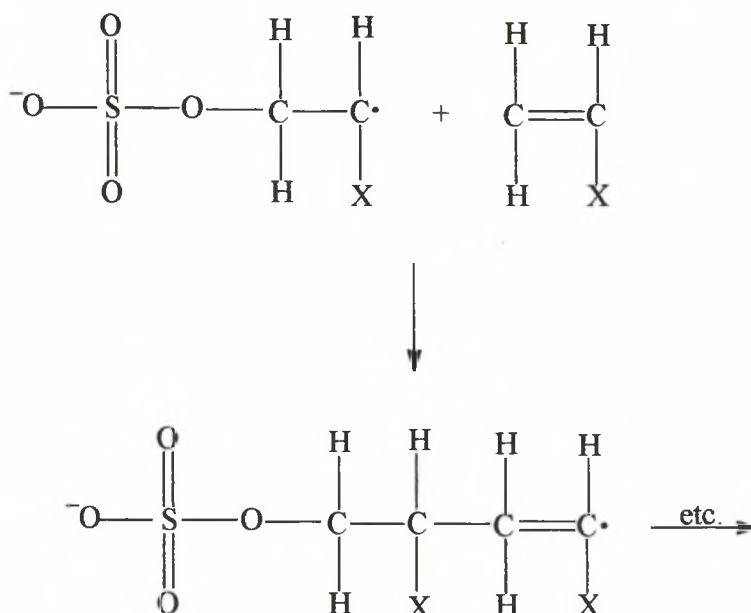


This may be abbreviated by



where P_1 represents a growing polymer chain with 1 repeating unit. Note that the product of the addition reaction is still a free radical; it proceeds to propagate the chain by adding another monomer unit:

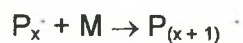
Example



again maintaining the unshared electron at the chain end, which adds another monomer unit:



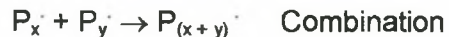
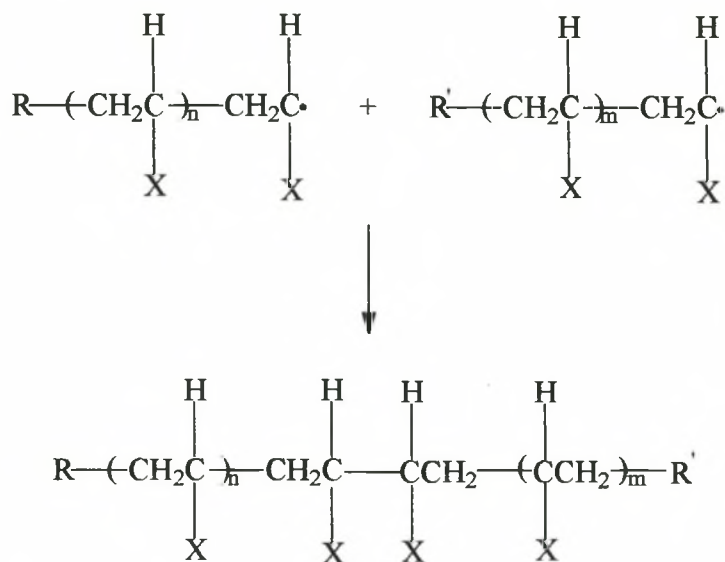
and so on. In general the propagation reaction is written as



We have assumed that reactivity is independent of chain length by using the same k_p for each propagation step.

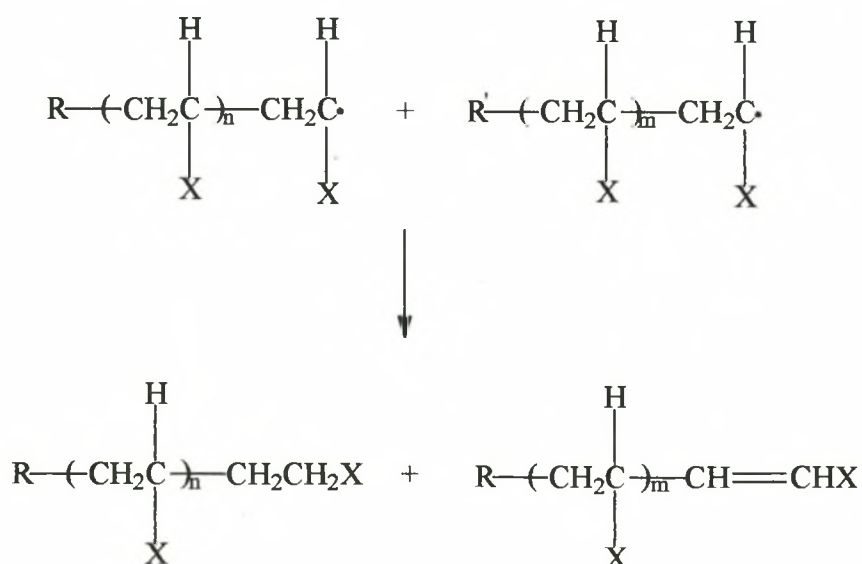
Termination of growing chains can occur by several mechanisms. Two can collide and react, their unshared electrons combining to form a single bond between them (combination).

Example



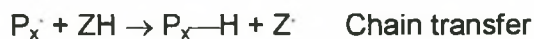
where $P_{(x+y)}$ is a dead polymer chain of $(x + y)$ repeating units. Or, one can abstract a proton from the penultimate carbon of the other (disproportionation):

Example:





The third possibility is by chain transfer, in which normally a hydrogen atom is abstracted from the reagents, products, initiator, impurity or agent added specifically for this purpose. ZH represents such a substrate or chain transfer agent.



4.4 EXPERIMENTAL

4.4.1 SYNTHESIS OF HASE THICKENERS

4.4.1.1 Materials

- The acrylic acid was obtained from Sigma Aldrich – 95 % purity.
- The associative macromonomers were synthesized as described in Chapter 3.
- Ethylene glycol methacrylate phosphate – Sigma Aldrich
- Sigma Aldrich also supplied the sodium persulphate and sodium metabisulphate.

4.4.1.2 The reaction procedure

The reaction was carried out in a one-liter reaction flask, which was equipped with stirrer, immersion thermometer, three dropping funnels and areflux condenser. The reflux condenser was placed on the reaction flask to avoid any loss of monomer or water. The reaction was carried out at 75 °C and therefor the reaction flask was placed in a oil bath in order to elevate the temperature. A solution of 0.5 gram of sodium persulphate in 50 grams of deionized water was added to one of the dropping funnels, and a solution of 0,5 gram of sodium metabisulphate in 50 grams of deionized water was added to a second dropping funnel. The associative monomer (0.0017 mole) was dissolved in 75 grams (1.0408 mole) of acrylic acid. This mixture of acrylic acid and macromonomer was placed in the third dropping funnel. The reaction flask was then charged with 375 grams of deionized water and heated up to 75 °C. Once the temperature reached 75 °C the dropwise addition of the solutions and the monomers

was begun and scheduled to last for one hour. After one hour the external heat source was removed and the batch was allowed to cool to room temperature while stirring for another hour.

The only variable between the first three reactions was the number of oxyethylene units in the associative macromonomer used. In reactions four, five and six 5% (mass) of the acrylic acid was substituted by a second phosphated macromonomer (ethylene glycol methacrylate phosphate).

Table 4.1:
The quantities of each of the components used in the six polymerization reactions.

	Number of oxyethylene units in the macromonomer	Macromonomer (grams)	Acrylic acid (grams)	Phosphated macromonomer (grams)
Reaction 1 (EO-100)	100	8.00	75.00	-
Reaction 2 (EO-50)	50	4.20	75.00	-
Reaction 3 (EO-20)	20	1.96	75.00	-
Reaction 4 (EO-100P)	100	8.00	71.25	10.94
Reaction 5 (EO-50P)	50	4.20	71.25	10.94
Reaction 6 (EO-20P)	20	1.96	71.25	10.94

The volume solids of the HASE thickeners \cong 15 %.

4.4.2 The latex coating formulations

The six latex coatings, each containing a different HASE thickener were prepared on a Siemens micromaster mixer. First a pastel tint millbase was prepared from which a 47% PVC pastel tint base was made up. An acrylo-styrene emulsion was used in the pastel tint base. Table 4.2 lists which HASE thickener each of the six coatings contained. All materials were obtained from Plascon Research Centre.

Table 4.2:
The HASE thickener in each of the six coating formulations.

Coating number	HASE thickener
1	EO-100
2	EO-50
3	EO-20
4	EO-100P
5	EO-50P
6	EO-20P

Table 4.3:
The pastel tint millbase formulation.

	Components	%	Actual Values (g)
	Water	22.081	902.50
pH Buffer agent	AMP 95	0.209	8.55
Wetting agent	Calgon "PT"	0.139	5.70
Dispersing agent	Orotan 731	1.162	47.50
Humectant	Propylene Glycol	4.653	190.20
Tinting compatibility agent	Triton X-100	0.407	16.63
Anti-foaming agent	Foamaster "VL"	0.418	17.10
Cellulose thickener	QP 4400	0.210	8.55
Rutile titanium dioxide	RCR 40	34.864	1425.00
Calcium China clay – Filler	ECC Speswhite	5.811	237.50
CaCO ₃ - Filler	Kulu 2	29.053	1187.50
	Water	0.446	18.20
Flow control agent	Rheolate 2001	0.430	17.58
Biocide	Acticide HF	0.117	4.80
	Total	100	4087.31

Table 4.4:
The 47% PVC pastel tint base formulation.

	Components	%	Actual values (g)
	Millbase	43.020	430.20
	Water	3.000	30.00
PH Buffer agent	AMP 95	0.060	0.60
Emulsion	Lipaton X-5025	22.622	226.22
	Water	4.000	40.00
Coalescent	UCAR IBT	1.000	10.00
Anti-foaming agent	Foamaster "VL"	0.050	0.50
Cellulose thickener	3.3% HEC (QP 4400)	10.000	100.00
	Water	6.000	60.00
	HASE Thickener	1.500	15.00
	Water	5.000	50.00
Anti-foaming agent	Foamaster "VL"	0.050	0.50
	Water	3.578	35.78
Biocide	Acticide "HF"	0.120	1.20
	Total	100.00	1000.00

4.5 CHARACTERIZATION OF HASE THICKENERS.

4.5.1 Experimental

The HASE thickeners were characterized by solid state ^{13}C -NMR spectroscopy. The ^{13}C -NMR spectra were recorded at $30\text{ }^{\circ}\text{C}$ using a Varian VXR 300 spectrometer operating at 127 MHz.

In preparing the NMR samples the water first had to be removed. This was done by placing the HASE thickener, which was in solution, in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 12 hours. The samples were then washed with methanol and dried in the vacuum oven at $60\text{ }^{\circ}\text{C}$.

4.5.2 ^{13}C -NMR SPECTRA

The solid state ^{13}C -NMR spectra of all six HASE thickeners are very similar and therefore the HASE thickener with the macromonomer containing an average of 20 oxyethylene units will be used as an example here, while the ^{13}C -NMR spectra of the other five HASE thickeners are discussed in Appendix B. Figure 4.1 shows a schematic of the chemical structure of the HASE thickeners. Figure 4.2 contains the ^{13}C -NMR spectrum and Table 4.5 the ^{13}C -NMR data of HASE thickener EO-20.

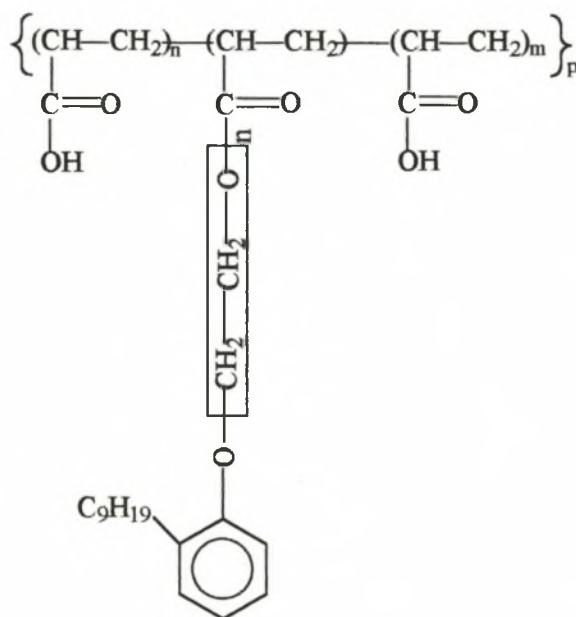


Figure 4.1:

Schematic representation of the chemical structure of the HASE thickeners.

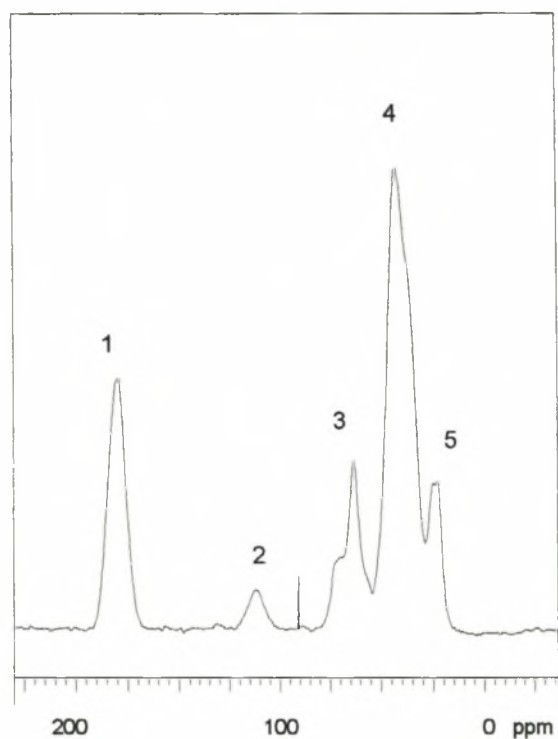


Figure 4.2:

¹³C-NMR spectrum of HASE thickener EO-20.

Table 4.5:

¹³C-NMR data of HASE thickener EO-20.

Peak Number	Chemical Shift (ppm)	Group
1	179.42	C=O
2	112.03	Aromatic ring
3	63.03	Ethylene oxide side chain
4	42.29	CH - groups in backbone
5	23.71	CH ₂ - groups in backbone

4.6 RESULTS AND DISCUSSION

4.6.1 KREBS STORMER VISCOSITIES

The Krebb Stormer viscosities of the coatings were measured by a Sheen 407A viscometer. The test samples were conditioned for 24 hours at 25 °C before viscosity readings were measured. The viscosity readings of the six coatings are presented in Figure 4.3. It is clear from the viscosity graphs that as the number of oxyethylene units in the macromonomers of the HASE thickeners decrease, there is also a decrease in the viscosity of the coatings. Coatings four, five and six, also containing the second, phosphated macromonomer in the HASE thickener, show an overall increase in viscosity over coatings one, two and three containing only the one type of macromonomer in the HASE thickener.

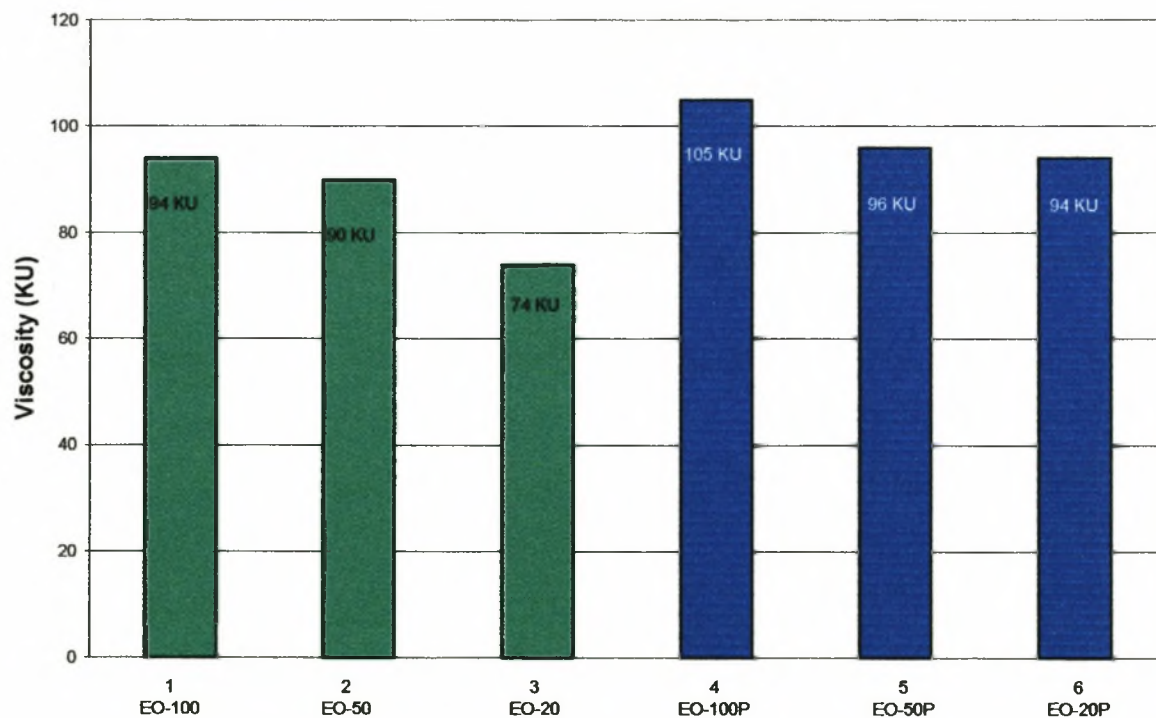


Figure 4.3:

The Krebs Stormer Viscosities of the six coatings, each containing a different HASE thickener.

4.6.2 RHEOLOGY ANALYSES

The rheology analyses of the various paint samples were done with a Haake Rheostress RS 150 rheometer and controlled rate (CR) was used as measuring mode. Flow curves (shear rate vs. shear stress) were recorded for each sample, using the following parameter settings:

1 – Time curve – samples were pre-sheared for 30 s at a shear rate of 1000 s^{-1} .

2 – Up flow curve – 0.50 to 6668 s^{-1} over 120 s.

The rheometer software then convert the data to give a rheology profile of viscosity vs. shear rate.

Figures 4.4 and 4.5 contain the rheology profiles of the six coatings.

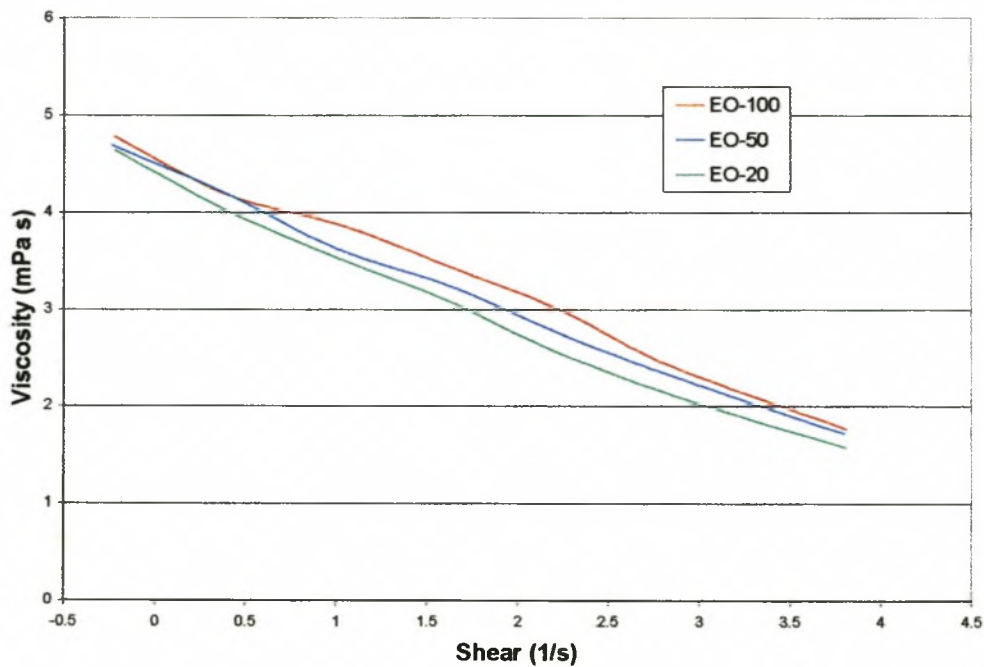


Figure 4.4:

Rheology profiles of coatings one (EO-100), two (EO-50) and three (EO-20)

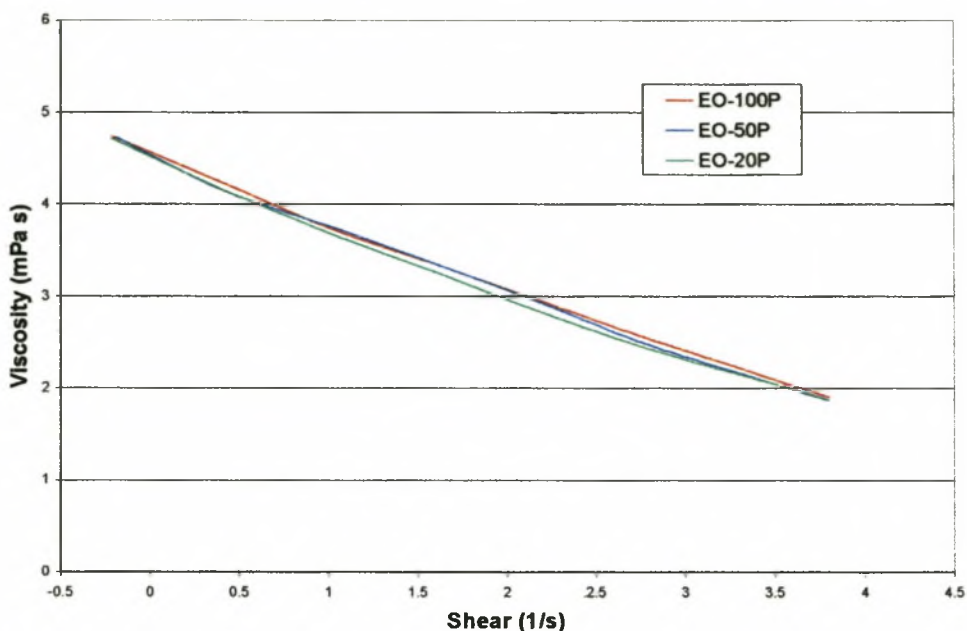


Figure 4.5:

Rheology profiles of coatings four (EO-100P), five (EO-50P) and six (EO-20P).

In Figure 4.4 the coatings thickened by the HASE thickeners containing only one type of macromonomer show significant differences in their rheology profiles. The only difference between the HASE thickeners are the number of oxyethylene units in the macromonomer. This correlates with the Krebb Stormer viscosities in section 4.6.1 where the higher number of oxyethylene units gave the higher viscosity. In Figure 4.5 the rheology profiles of the coatings are much closer and similar to one another. This means that when the second phosphated macromonomer is added into the HASE thickeners the effect of the difference in the number of oxyethylene units is not as significant any more.

In Figures 4.6, 4.7 and 4.8 direct comparisons are made between the HASE thickeners that contain the second, phosphated macromonomer and those that do not. In Figure 4.5 the rheology profile of coating six shows an increase in viscosity over coating three, over the entire shear range. A similar result can be seen in Figure 4.6 where the rheology profiles of coatings two and five are compared, but in this case the viscosity increase is not as big. In Figure 4.8 the rheology profiles of coatings one and four lie on top of one another. The effect of the second phosphated macromonomer is therefore much bigger when it is combined with the macromonomers containing a smaller number of oxyethylene units.

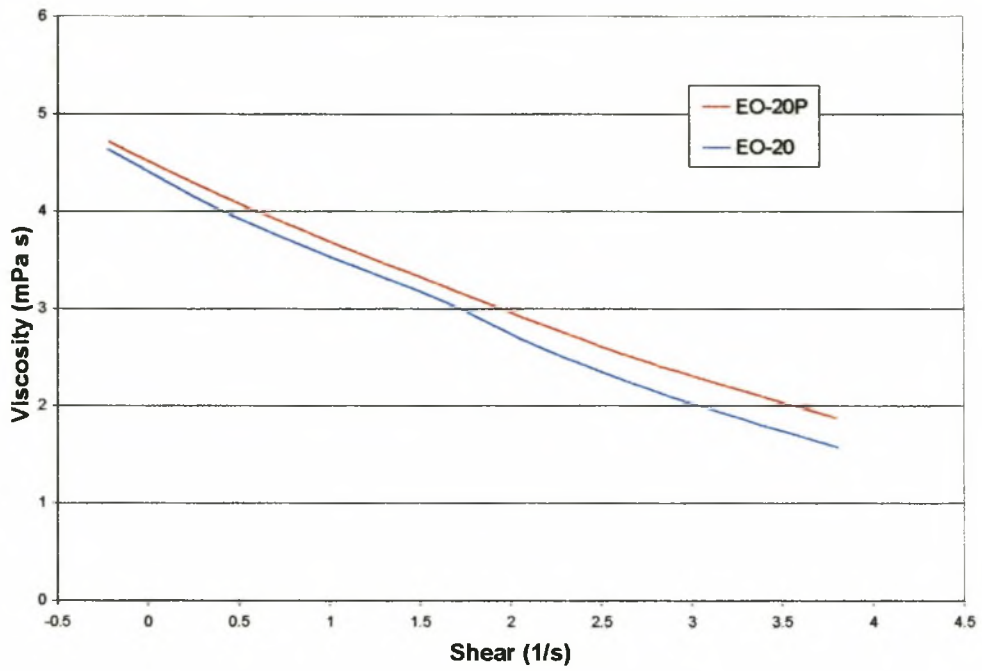


Figure 4.6:

The rheology profiles of coatings three (EO-20) and six (EO-20P).

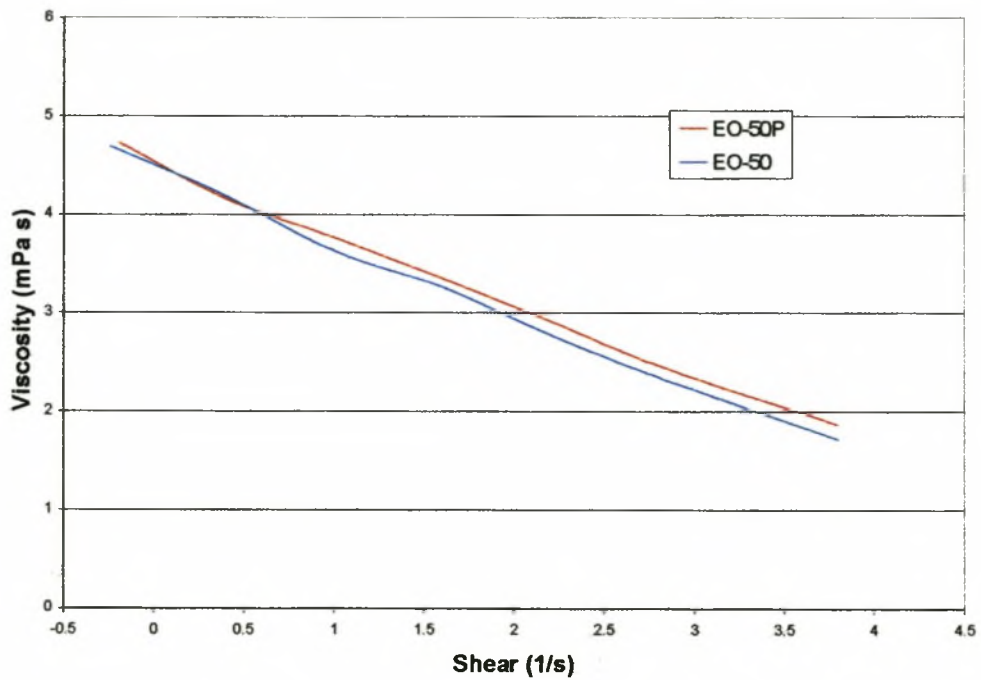


Figure 4.7:

The rheology profiles of coatings two (EO-50) and five (EO-50P).

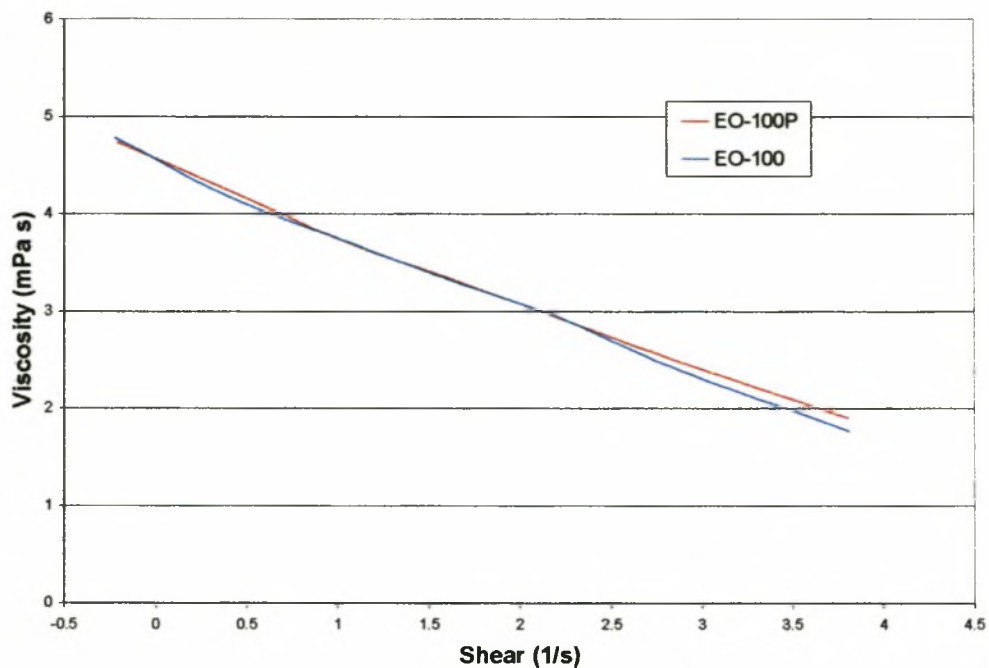


Figure 4.8:

The rheology profiles of coatings one (EO-100) and four (EO-100P).

4.6.3 VISCOSITY STABILITY ON TINTING WITH UNIVERSAL COLORANTS

In this section an universal colorant is added to the latex paint and then rheology profiles were drawn up to determine what the influence of the colorants were on the latex coating. A commercially available universal colorant from ICC containing the organic pigment phalocyanine blue was used.

The samples were prepared according to a Plascon test method.

Amount of pastel base paint = (S.G. × 396)g

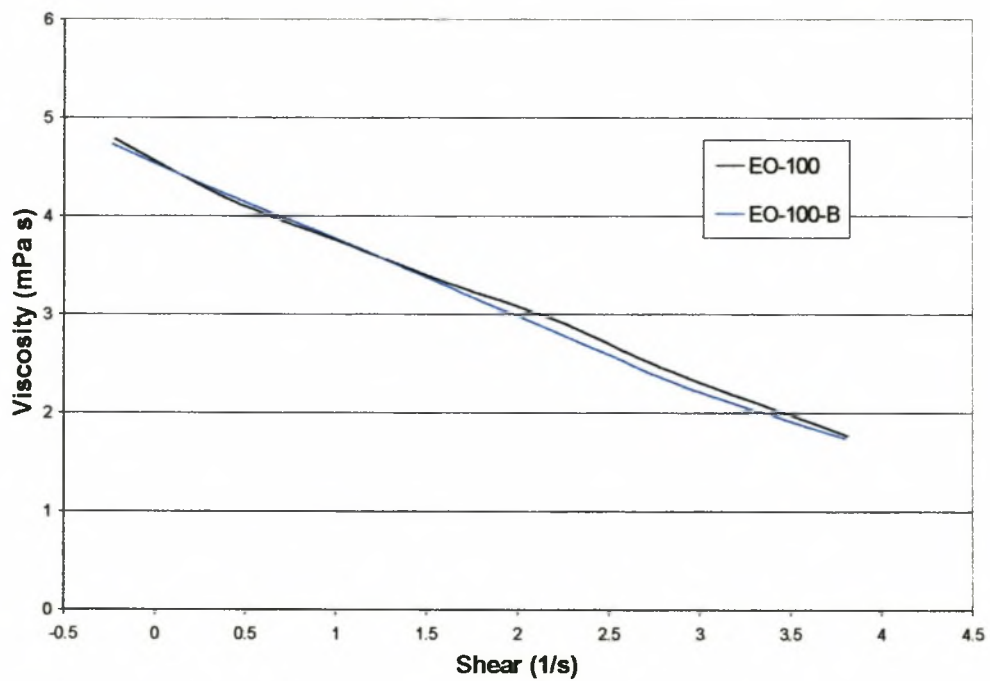
Amount of colorant = (S.G. × 12.48)g The S.G. of the colorant is 1.498 g/cm³

The colorant was added to the base paint and then shaken for 5 min. on a rotaspin (model LO-5), after which rheology analysis was done.

The rheology profiles of the tinted vs. untinted coatings are given in Figures 4.9 – 4.14.

Table 4.6:**The specific gravity and pH of the six latex coatings.**

Coating number	Specific Gravity (g/cm ³)	pH
1	1.266	8.54
2	1.266	8.50
3	1.273	8.43
4	1.270	8.13
5	1.073	8.08
6	1.268	8.21

**Figure 4.9:****The rheology profiles of untinted vs. tinted (B) coating one.**

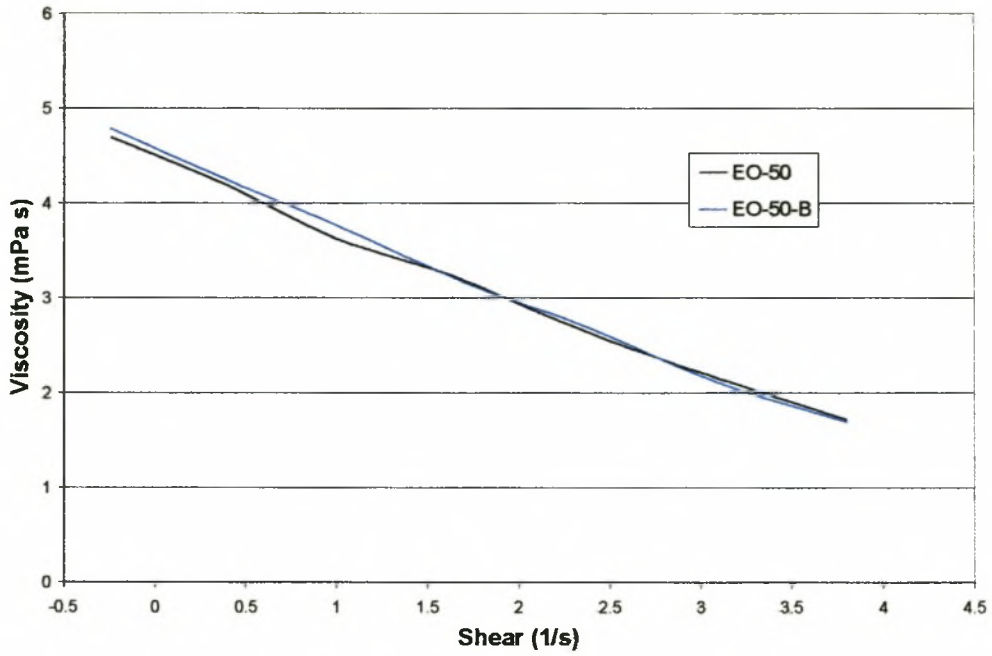


Figure 4.10:

The rheology profiles of untinted vs. tinted (B) coating two.

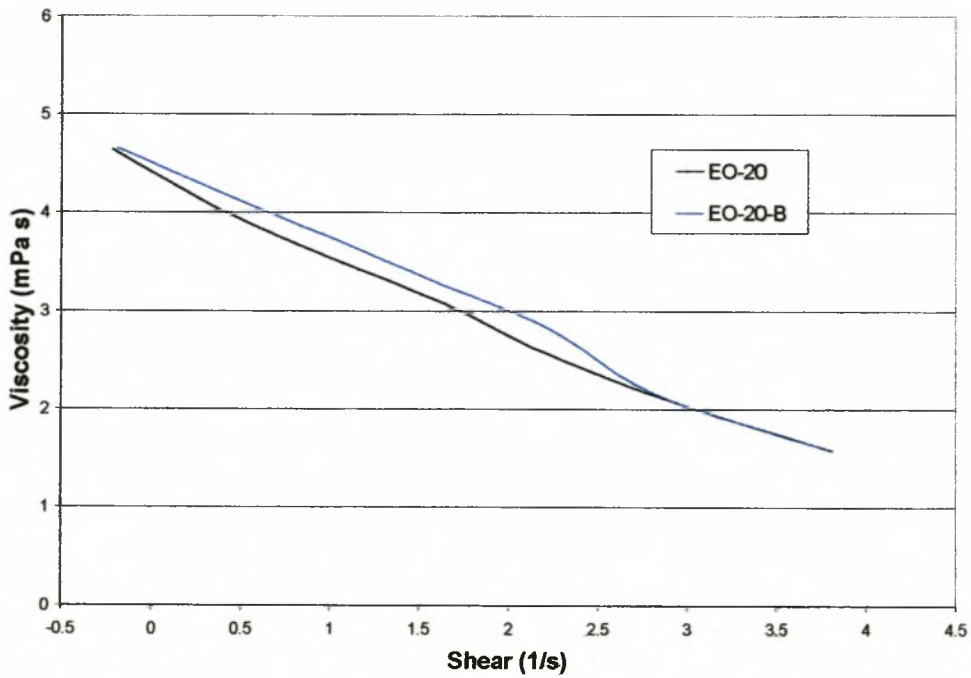


Figure 4.11:

The rheology profiles of untinted vs. tinted (B) coating three.

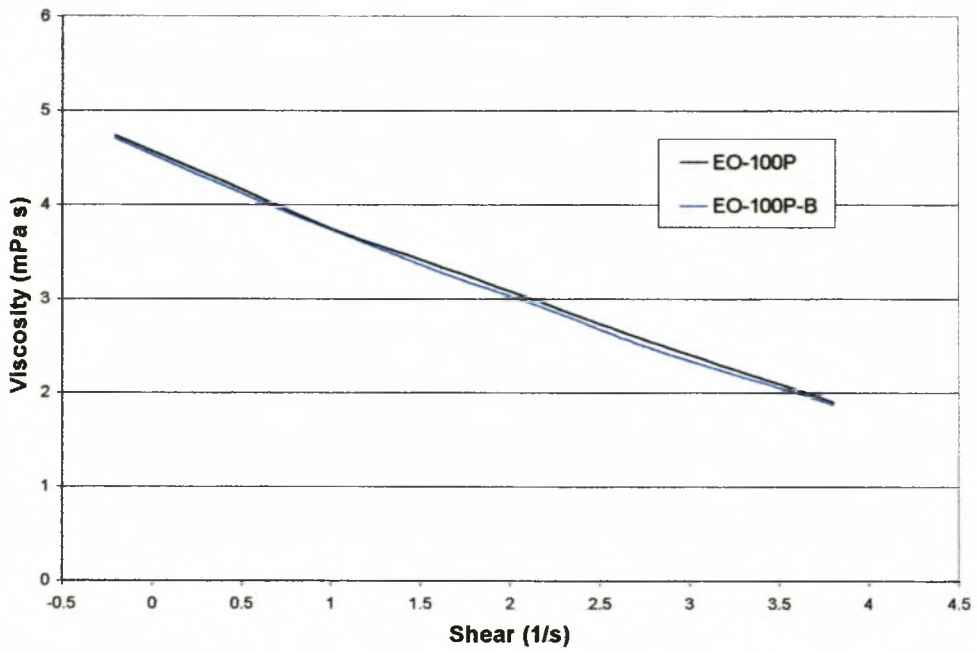


Figure 4.12:

The rheology profiles of untinted vs. tinted (B) coating four.

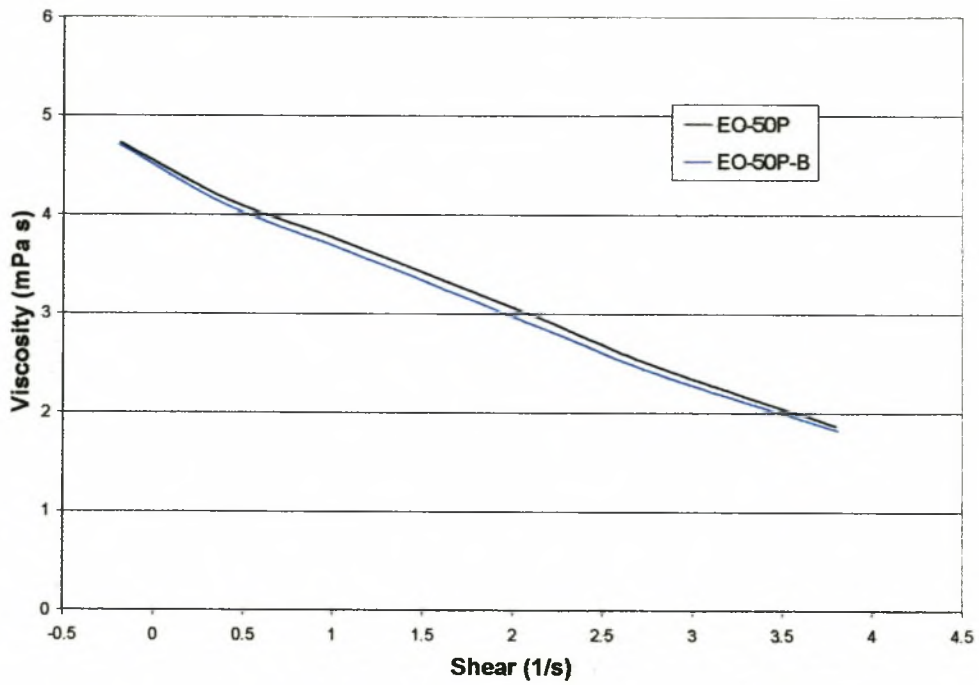


Figure 4.13:

The rheology profiles of untinted vs. tinted (B) coating five.

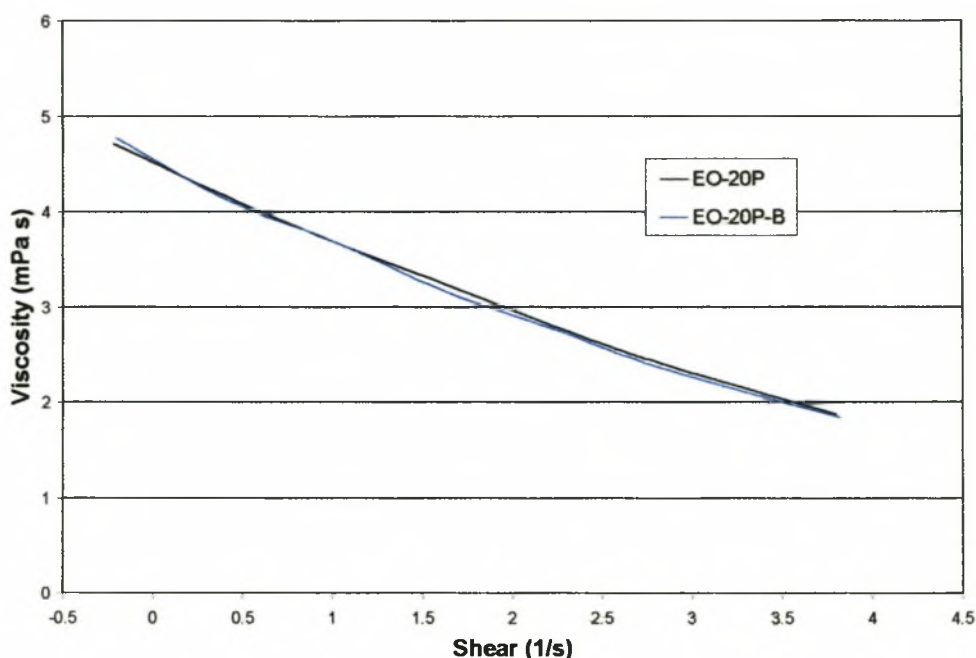


Figure 4.14:

The rheology profiles of untinted vs. tinted (B) coating six.

There was no significant drop in viscosity of any of the six coatings once they were tinted with the colorant. The only deviation detected was in the case of coating three in Figure 4.10 where addition of the colorant increased the viscosity. This was attributed to the low viscosity of coating three before tinting. The low viscosity of coating three relates to the weak thickening efficiency of HASE thickener EO-20.

4.7 CONCLUSIONS

The six HASE thickeners were successfully synthesized by free radical addition polymerization and characterized by ^{13}C -NMR spectrometry. The different thickening efficiencies of the various HASE thickeners were determined. The thickening efficiencies of the HASE thickeners showed a direct correlation with the number of oxyethylene units in the macromonomers. The longer the oxyethylene chain lengths of the HASE thickeners, the higher the viscosities of the specific

coatings. This effect was slightly suppressed once the second phosphated macromonomer was added to the HASE thickener. The second phosphated macromonomer also enhanced the thickening efficiencies of the HASE thickeners they were incorporated in and this effect was more pronounced when combined with macromonomers of shorter oxyethylene chain lengths. Excellent viscosity stability was shown by all six of the coatings, since none of the coatings showed any significant drop in viscosity once they were tinted with a universal colorant.

4.8 BIBLIOGRAPHY

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CHAPTER 5

UNIVERSAL COLORANTS

5.1 INTRODUCTION

It was only once latex paints started to gain popularity that universal colorants were introduced. At that time, however alkyd paints were still in high demand for interiors, as were linseed oil/alkyd combinations for exteriors. These colorants were designed for tinting both latex (water-based) and alkyd and linseed oil/alkyd (solvent based) systems. They mainly consist of pigments, ethylene glycol, water, and surface-active agents selected to provide compatibility of the colorants in both organic- and water- based coating formulations with minimal adverse effects[1]. In chapter two Table 2.6 shows the typical composition of an universal pigment concentrate [2].

These “universal” colorants make up a large percentage of the colorants used by paint companies today. It is these universal color formulations that are used for “in-store” tinting systems, allowing a paint company to make available to the homeowner a large selection of paint shades (many offer about 1500 different shades) by having in their inventory only 12 color concentrates or tinting colors and, only three tint bases within each chemical coating group.

In this chapter commercially available high molecular weight polymeric additives will be used to formulate color concentrates. They provide excellent stabilisation and deflocculation (important for a defined and stable color), strong viscosity reduction of the color concentrate and better durability than conventional wetting and dispersing additives [3-4].

5.2 OBJECTIVES

- To compile new colorant formulations with only one polymeric dispersant in each of the formulations as sole wetting and dispersing additive.

- To make up these formulations and test them in three different chemical coating groups. A commercially available universal colorant from ICC will be used as standard. This colorant formulation contains five different wetting and dispersing additives.
- The colorants will be tested for color strength, their compatibility with the different coating groups and the rheology profiles of the tinted vs. the untinted coating systems.

5.3 EXPERIMENTAL

Eight colorant formulations were made up. The phthalocyanine blue pigment particles were ground down to under 15 μm by a Hockmeyer basket mill. Two different grinding gauges were used to measure the finest of grind of the pigment particles: A 0 – 15 μm grind gauge from Erichsen and a 0 – 25 μm grind gauge from Sheen Instruments. The color concentrates were tested in six base paints, which were supplied by Plascon. The statistical analysis of these experiments are presented in Appendix C.

5.3.1 Materials

A. Plascon base paints

Water based: (1) Polvin – TAP 1000 (pastel)

TAP 3000 (transparent)

(2) Wall & All – TWA 1000 (pastel)

TWA 3000 (transparent)

Solvent based: (1) Enamel – TSE 1000 (pastel)

TSE 3000 (transparent)

The following components were used to make up the eight color paste formulations:

1. Commercially available polymeric dispersants

- a) HYDROPALAT 1080
- b) HYDROPALAT 3275
- c) EFKA 4550
- d) EFKA 1501 / EFKA 4550 in combination

2. Co-solvent

- a) Mono ethylene glycol
- b) Propylene glycol

3. Water

4. Defoamer

- a) Bevaloid 513

5. Pigment

- a) Phthalocyanine blue BSNF

6. Filler

- a) Pyrofil
- b) Pyrofil (75%) / Blanc Fix (25%)

7. Anti-settling agent

- a) Bentone ew
- b) Rheolate 2001

8. Biocide

2. Rheology

Instrument: Haake Rheostress RS 150

Measuring mode: Controlled rate (CR)

Three shear rates were chosen to measure the rheology trend.

1. Low shear rate at 0.800 s^{-1}
2. Medium shear rate at 100 s^{-1}
3. High shear rate at 5000 s^{-1}

The viscosity was measured in [mPa s]

These parameter settings were selected to predict application behavior. Properties such as in-can stability, sagging and spattering can be compared using these settings. Viscosity graphs are then plotted and used for comparative studies.

4. Krebb Stormer viscosity

The Krebb Stormer viscosities were measured by a sheen 407 A viscometer and the test samples were conditioned for 24 hours at $25 \text{ }^{\circ}\text{C}$ before viscosity readings were measured. This method was used to measure the viscosity of the color concentrates.

5. Color Strength

The determination of color strength was done at Plascon Cape Town with a CS-5 Chroma Sensor spectrophotometer. The samples were drawn down onto sealed white cardboard at $200 \text{ }\mu\text{m}$ wet film thickness. The commercially available blue pigment paste supplied by ICC was used as standard. Only the Polvin pastel tint base was used for color strength measurements.

6. Compatibility

Samples were drawn down onto sealed white cardboard at $200 \text{ }\mu\text{m}$ wet film thickness. Immediately afterwards a small area of the wet paint was rubbed with a finger until the paint film become slightly tacky. Care was taken not to expose the substrate. The paint film was then

allowed to dry and the two areas (rubbed vs. not rubbed) were compared for signs of color variation. Only the three pastel tint bases were used for compatibility measurements.

5.3.3 Formulations

The compositions of the eight color concentrate formulations are given in Tables 5.2 – 5.9.

Table 5.2:**Formulation 1**

<u>FORMULATION 1</u>	%
WATER	19.83
BENTONE EW	0.25
HYDROPALAT 1080	10.00
BEVALOID 513	0.30
PROPYLENE GLYCOL	15.41
METATIN GT	0.10
TRG. BLUE BSNF	5.40
PYROFIL	31.52
<u>LET DOWN</u>	
WATER	2.88
HYDROPALAT 1080	2.00
BEVALOID 513	0.10
PROPYLENE GLYCOL	4.59
PYROFIL	7.62
TOTAL	100

Table 5.3:**Formulation 2**

<u>FORMULATION 2</u>	%
WATER	6.72
HYDROPALAT 3275	22.07
BEVALOID 513	0.36
PROPYLENE GLYCOL	13.79
METATIN GT	0.10
IRG. BLUE BSNF	5.40
PYROFIL	25.81
BLANC FIX	10.52
RHEOLATE 2001	0.20
<u>LET DOWN</u>	
WATER	1.11
HYDROPALAT 3275	1.93
BEVALOID 513	0.04
PROPYLENE GLYCOL	6.21
PYROFIL	5.74
TOTAL	100

Table 5.4:
Formulation 3

<u>FORMULATION 3</u>	%
WATER	7.84
BENTONE EW	0.20
HYDROPALAT 3275	20.00
BEVALOID 513	0.30
ETHYLENE GLYCOL	14.96
METATIN GT	0.10
IRG. BLUE BSNF	5.40
PYROFIL	28.63
<u>LET DOWN</u>	
WATER	1.97
HYDROPALAT 3275	4.00
BEVALOID 513	0.10
ETHYLENE GLYCOL	6.00
PYROFIL	10.50
TOTAL	100

Table 5.5:
Formulation 4

<u>FORMULATION 4</u>	%
WATER	16.51
HYDROPALAT 1080	10.00
BEVALOID 513	0.30
ETHYLENE GLYCOL	11.00
METATIN GT	0.10
IRG, BLUE BSNF	5.40
PYROFIL	21.00
BLANC FIX	10.52
RHEOLATE 2001	0.20
<u>LET DOWN</u>	
WATER	3.37
HYDROPALAT 1080	2.00
BEVALOID 513	0.10
ETYLENE GLYCOL	9.00
PYROFIL	10.50
TOTAL	100

Table 5.6:
Formulation 5

<u>FORMULATION 5</u>	%
WATER	10.00
EFKA 4550	16.00
BEVALOID 513	0.30
PROPYLENE GLYCOL	12.00
METATIN GT	0.10
IRG. BLUE BSNF	5.40
PYROFIL	34.40
RHEOLATE 2001	0.20
<u>LET DOWN</u>	
WATER	2.88
EFKA 4550	3.00
BEVALOID 513	0.10
PROPYLENE GLYCOL	8.00
PYROFIL	7.62
TOTAL	100

Table 5.7:
Formulation 6

<u>FORMULATION 6</u>	%
WATER	16.53
BENTONE EW	0.12
EFKA 1501	8.18
EFKA 4550	3.93
BEVALOID 513	0.18
PROPYLENE GLYCOL	9.07
METATIN GT	0.06
IRG. BLUE BSNF	5.40
BLANC FIX	10.52
PYROFIL	21.00
<u>LET DOWN</u>	
WATER	5.51
EFKA 1501	2.73
EFKA 4550	1.31
BEVALOID 513	0.06
PROPYLENE GLYCOL	4.90
PYROFIL	10.50
TOTAL	100

Table 5.8:
Formulation 7

<u>FORMULATION 7</u>	%
WATER	18.46
EFKA 1501	8.20
EFKA 4550	4.20
BEVALOID 513	0.18
ETHYLENE GLYCOL	11.92
METATIN GT	0.10
IRG. BLUE BSNF	5.40
PYROFIL	31.52
RHEOLATE 2001	0.16
<u>LET DOWN</u>	
WATER	1.62
EFKA 1501	2.80
EFKA 4550	1.80
BEVALOID 513	0.06
ETHYLENE GLYCOL	3.08
PYROFIL	10.50
TOTAL	100

Table 5.9:
Formulation 8

<u>FORMULATION 8</u>	%
WATER	10.00
BENTONE EW	0.20
EFKA 4550	16.00
BEVALOID 513	0.30
ETHYLENE GLYCOL	11.00
METATIN GT	0.10
IRG. BLUE BSNF	5.40
BLANC FIX	10.52
PYROFIL	21.00
<u>LET DOWN</u>	
WATER	2.88
EFKA 4550	3.00
BEVALOID 513	0.10
ETHYLENE GLYCOL	9.00
PYROFIL	10.50
TOTAL	100

5.4 RESULTS AND DISCUSSION

5.4.1 Krebb Stormer Viscosity, Specific Gravity and Finest of Grind Measurements of the color concentrates

Table 5.10 contains the results of the Krebb Stormer, Specific Gravity and Finest of Grind measurements of the color concentrates.

Table 5.10:

Results of the Krebb Stormer, Specific Gravity and Finest of Grind measurements of the color concentrates.

FORMULATION	Viscosity (KU)	S.G. (g/cm ³)	F.O.G. (μm)
1	112	1.3259	12
2	108	1.4617	13
3	118	1.2747	12
4	83	1.4607	13
5	109	1.4399	13
6	93	1.4500	12
7	101	1.3928	14
8	107	1.4995	12

5.4.2 Compatibility

The test showed that only formulations two and three were not completely compatible in all three chemical coating groups. In both these formulations HYDROPALAT 3275 was used as polymeric dispersant, hence it could not be used in a universal colorant. The compatibility results are given in Table 5.11.

Table 5.11:**The compatibility results of the color concentrates.**

FORMULATION	POLVIN (TAP 1000)	WALL & ALL (TWA 1000)	ENAMEL (TSE 1000)
1	YES	YES	YES
2	YES	YES	NO
3	YES	YES	NO
4	YES	YES	YES
5	YES	YES	YES
6	YES	YES	YES
7	YES	YES	YES
8	YES	YES	YES

5.4.3 Color strength measurements

The Polvin pastel tint base tinted with the ICC standard was used as reference. The spectrophotometer measures the whiteness of the samples in comparison to that of the reference. The spectrophotometer then gives a percentage of how much stronger or weaker the whiteness of the sample is. If the sample is weaker in whiteness than that of the reference it indicates an increase in color strength and if it is stronger in whiteness then the sample has a lower color strength.

It is only formulations one and four that show superior color strength to that of the ICC standard and in both the formulations HYDROPALAT 1080 was used as the polymeric dispersant. Formulations five and eight in which EFKA 4550 was used as polymeric dispersant are only slightly weaker in color strength than that of the ICC standard. Formulations two, three, six and

seven show a major drop in color strength compared to that of the ICC standard. This shows that HYDROPALAT 3275 and EFKA 1501 do not develop good color strength.

Table 5.12:
The results from the color strength measurements.

FORMULATION	% STRONGER/WEAKER	FORMULATION	% STRONGER/WEAKER
1	1.28 - weaker	5	5.25 – stronger
2	20.46 – stronger	6	28.22 – stronger
3	27.81 – stronger	7	40.38 – stronger
4	8.12 - weaker	8	3.53 - stronger

5.4.4 Rheology

Formulations two and three failed the compatibility test and formulations six and seven showed very poor color strength. Although all the rheology results are given in Figures 5.1 – 5.6 the discussion will focus on formulations one, four, five and eight. In formulations one and four and in formulations five and eight HYDROPALAT 1080 and EFKA 4550 was the polymeric dispersants, respectively.

Polvin (TAP) – Formulations five and eight showed no drop in viscosity over the entire shear range in the pastel or transparent tint bases. In the transparent tint base an increase in viscosity could be seen. The opposite was observed for formulation one, four and the ICC standard, were a drop in viscosity was observed on tinting in both the pastel and transparent tint bases.

Figure 5.2:

Rheology profiles of the tinted vs. untinted polvin transparent tint base (TAP 3000).

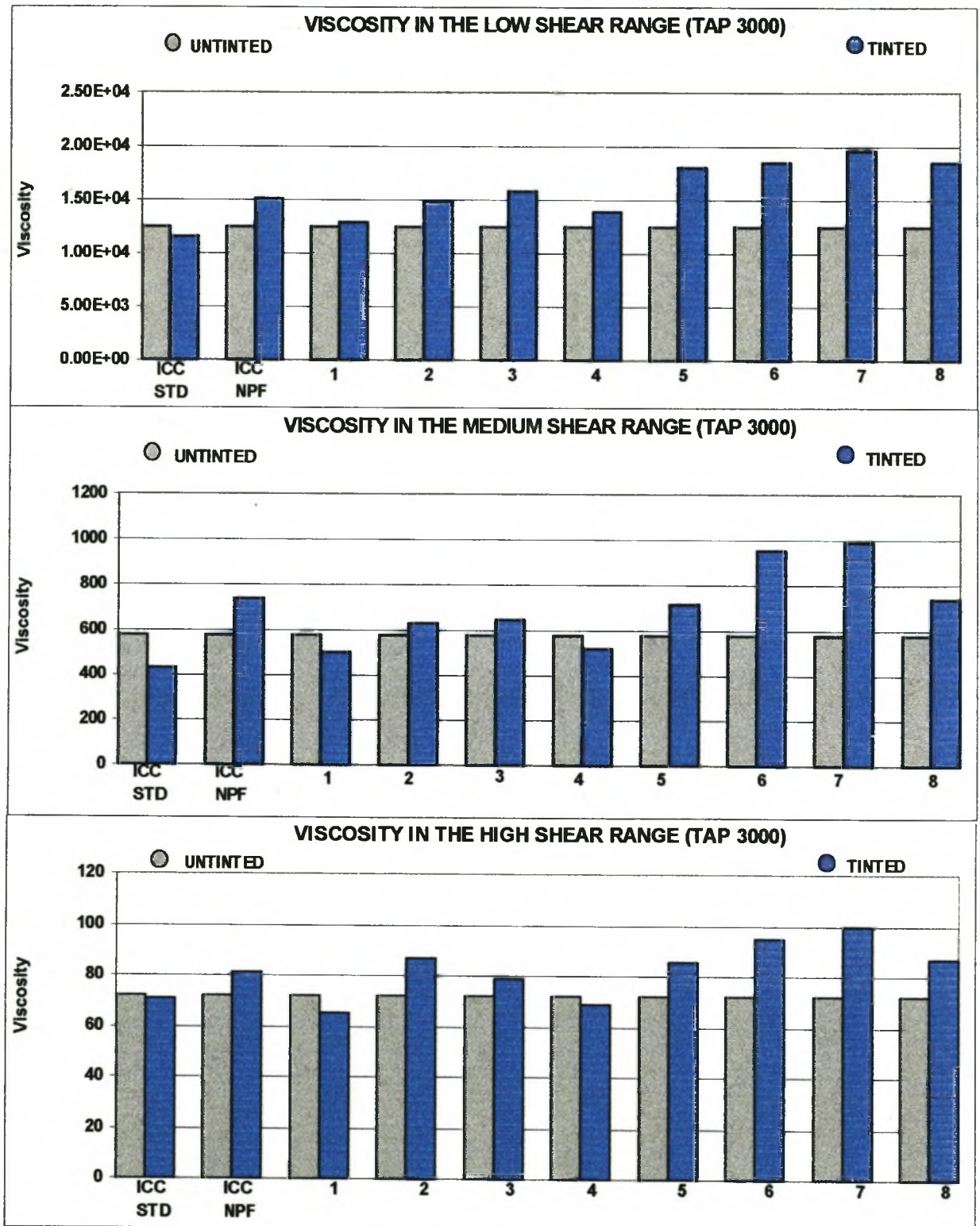


Figure 5.3:

Rheology profiles of the tinted vs. untinted Wall & All pastel tint base (TWA 1000).

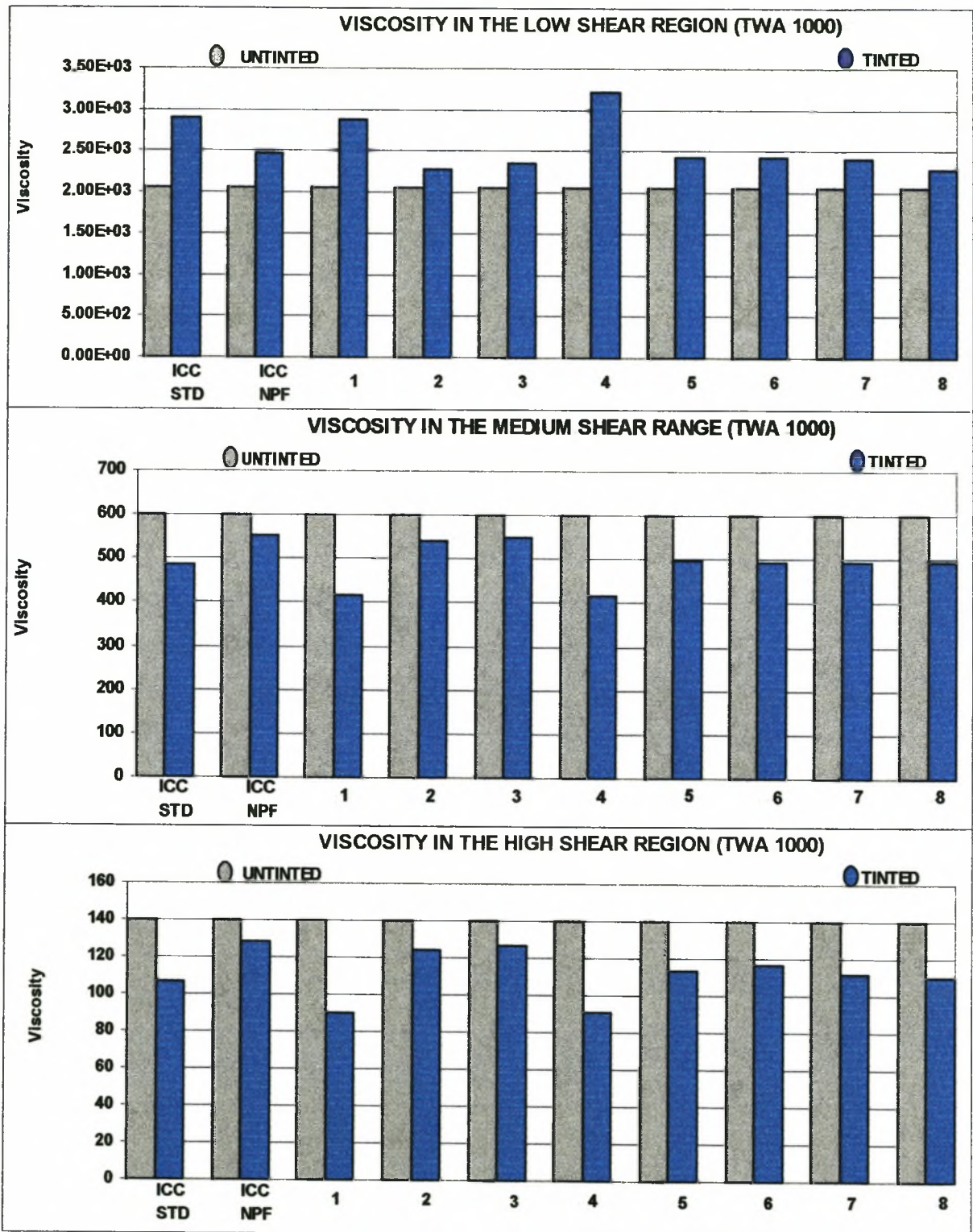


Figure 5.4:

Rheology profiles of the tinted vs. untinted Wall & All transparent tint base (TWA 3000).

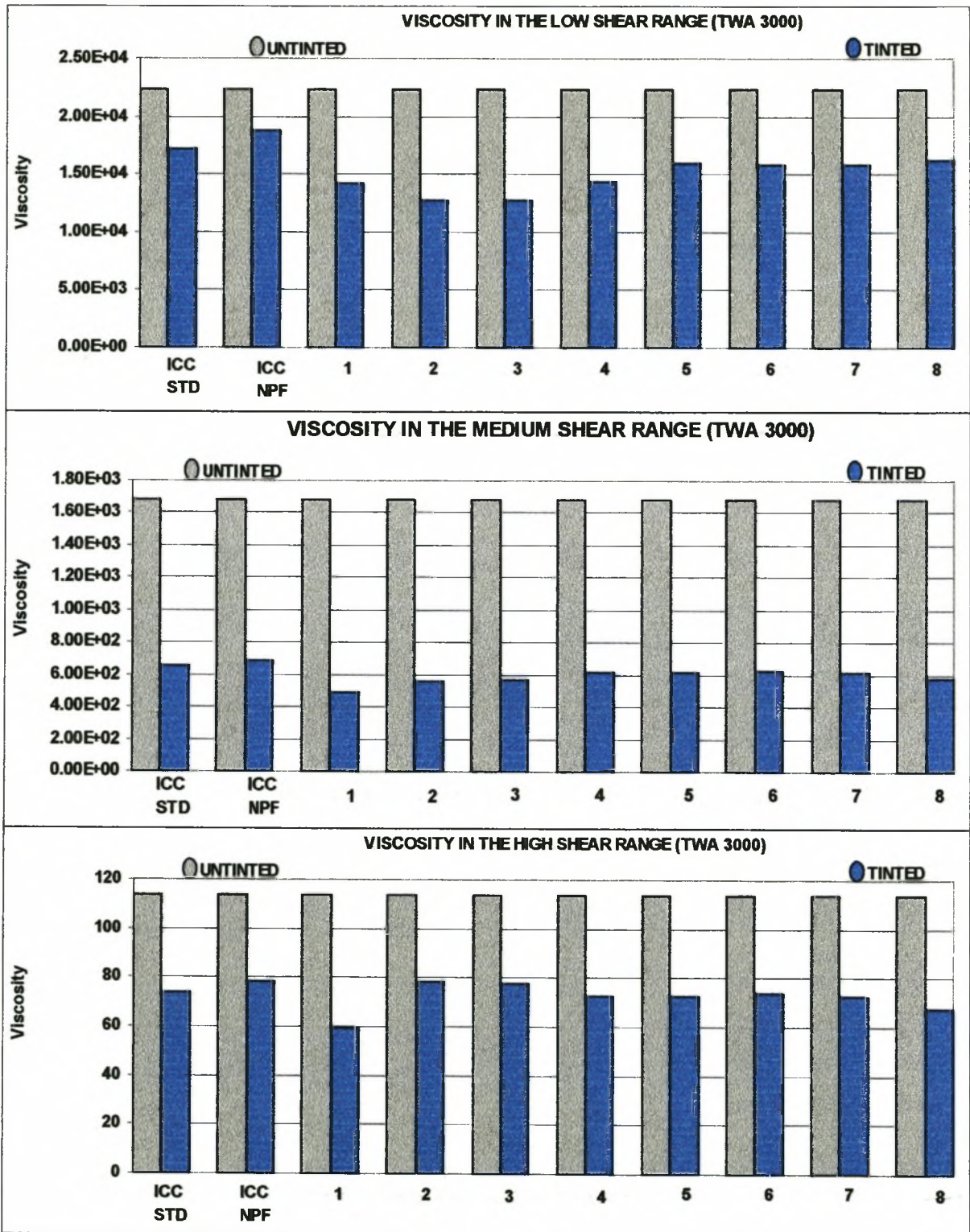


Figure 5.5:

Rheology profiles of the tinted vs. untinted Enamel pastel tint base (TSE 1000).

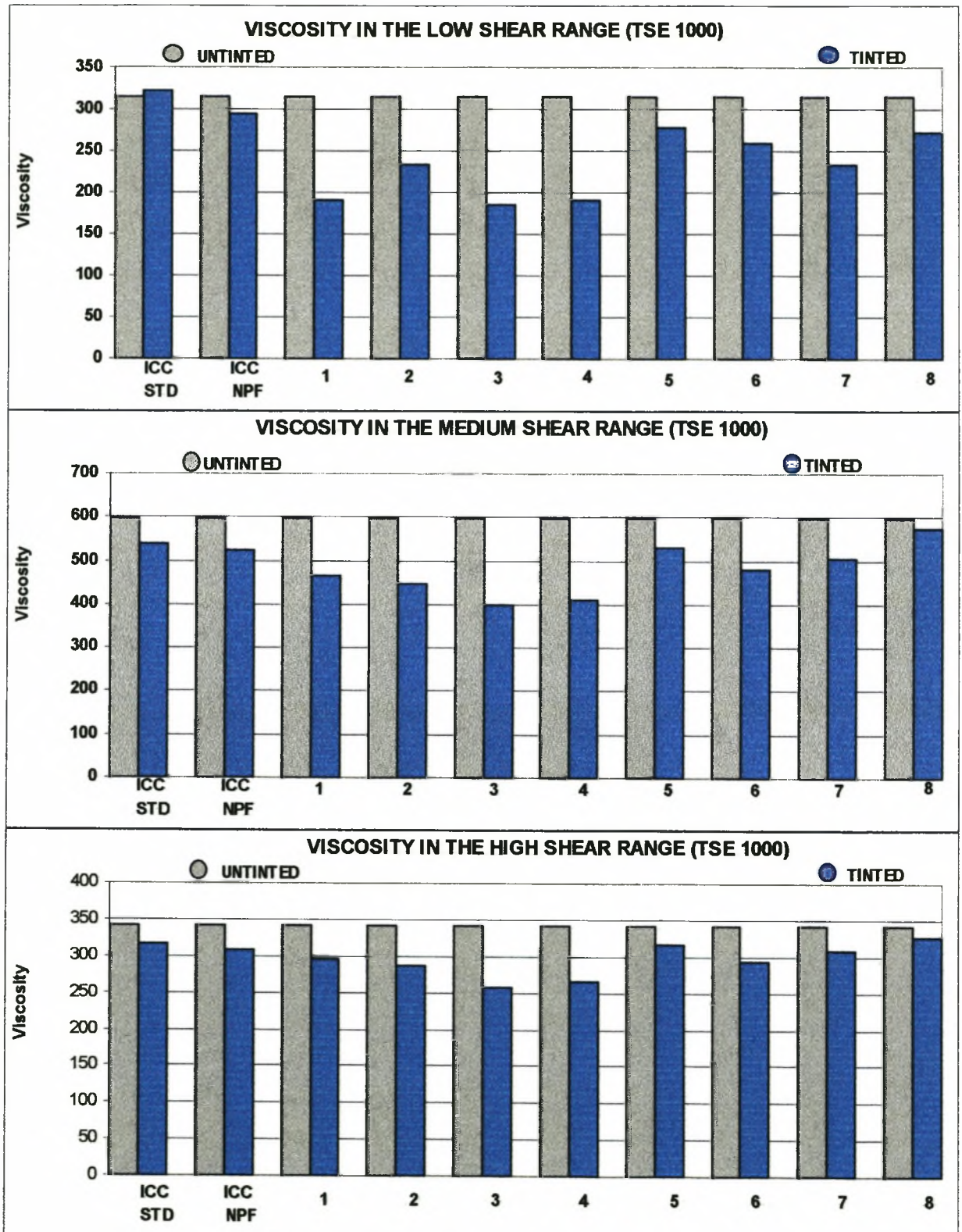
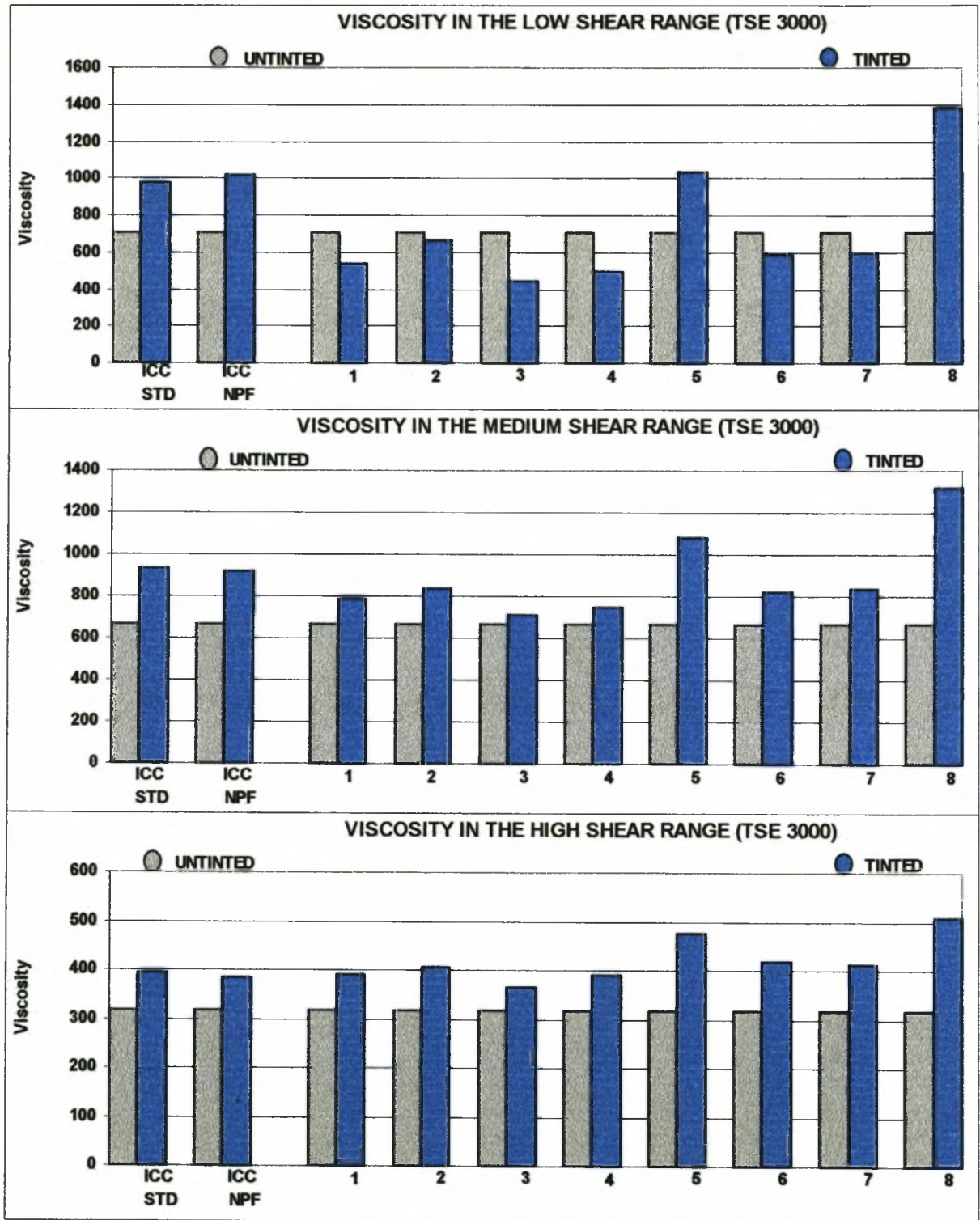


Figure 5.6:

Rheology profiles of the tinted vs. untinted Enamel transparent tint base (TSE 3000).



Wall & All (TWA) – All the formulations showed a drop in viscosity in the rheology profile of the pastel tint base. A major drop in viscosity could be seen for all the formulations in the transparent tint base over the entire shear range.

The two water based coatings used for testing the color concentrate formulations showed major differences in their rheology trends. Wall & All showed a major drop in viscosity on tinting, indicating a big disruption of the coating system. We know that one of the major differences between the base paints are their thickening systems. It looks like the HEUR thickening system of Wall & All is more prone to disruption on tinting, than that of the HASE thickening system used in Polvin.

Enamel (TSE) – Formulations five, eight and the ICC standard performed very similarly in both the pastel and transparent tint bases. In the pastel tint base they all showed a drop in viscosity, but in the transparent base an increase in viscosity was observed. Formulations one and four showed a greater loss in viscosity in the pastel tint base, and in the transparent tint base the viscosity increase was lower than that of formulations five and eight.

5.5 CONCLUSIONS

Of the eight formulations made up and tested, five and eight performed the best throughout the entire range of tests. In both formulations EFKA 4550 was used as the dispersant. These two formulations showed better rheology profiles than that of the ICC standard in all the chemical coating groups and their color strength was not far off from that of standard.

Formulations one and four showed extremely good color strength, which would indicate good dispersion of the pigment particles. Unfortunately their rheology performances were not very good in comparison to those of formulations five and eight.

The fact that formulations two and three are incompatible in solvent base coatings makes them unsuitable for universal colorants. These two formulations together with formulations six and seven also gave weak color strength and rheology profiles.

5.6 BIBLIOGRAPHY

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CHAPTER 6

CONCLUSIONS

The conclusions of this research endeavor into the synthetic and rheological studies of the pigmentation of decorative coating systems are as follow:

1. Three commercially available nonionic surfactants (Berol 292, Berol 291 and IGEPAL C-990) containing an average of 20, 50 or 100 oxyethylene units were successfully used to synthesise three different macromonomers.
2. In both the esterification reaction methods used in (1) a monomer containing ethylenic unsaturation was successfully coupled to the three different nonionic surfactants. In reaction method one the monomer was acrylic acid and in reaction method two it was the acid derivative of acrylic acid, acryloyl chloride. Reaction method one gave a much lower percentage conversion of surfactant to macromonomer than that of reaction method two. The reason for this is that reaction method one (a one step reaction method) is reversible and therefore reaches equilibrium when there are appreciable quantities of both reactants and products present. In reaction method two (a two step reaction method) both steps are essentially irreversible and therefore goes to completion, which leads to higher conversions.
3. All the surfactants and macromonomers were characterised in full by Proton Nuclear Magnetic Resonance spectrometry. All the relevant functional groups of the surfactants and macromonomers involved in the esterification reactions were characterised by Fourier Transform Infrared spectrometry.
4. Acrylic acid and the macromonomers were then used to synthesise the HASE thickeners by means of free radical addition polymerisation.

5. All the relevant components of the six HASE thickeners were successfully characterised by solid state carbon 13 nuclear magnetic resonance spectrometry.
6. The three unique HASE thickeners containing the additional phosphated macromonomer showed increased viscosity in the latex coatings over the three HASE thickeners that only contained the single macromonomer. The higher the number of oxyethylene units in the macromonomers of the HASE thickeners the higher was the viscosity of the latex coating. This effect was much more pronounced in the three HASE thickeners containing only the one type of macromonomer than in the three that contain the additional phosphated macromonomer.
7. The thickening stability of all six the latex coatings, containing the different HASE thickeners, were excellent. Not one of them show any significant decrease in viscosity over their entire rheology profile once they were tinted with an universal colorant.
8. The two color concentrates containing EFKA 4550 as the polymeric dispersant showed the best performances of all eight color concentrates that were made up. These two color concentrates showed good compatibility and color strength in the different chemical coating groups when compared to a commercially available color concentrate from ICC. These two formulations showed improved rheology profiles in almost all the different coatings used to test them in.

The results of this research project offer the paint industry possible solutions to the drop in viscosity that occurs when colorants are added to a coating system.

Appendix **A****A.1 ¹H-NMR ANALYSIS OF THE SURFACTANTS AND MACROMONOMERS**

Table A.1

The ¹H-NMR data of the surfactant containing an average of 50 oxyethylene units

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)
GROUP A			
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.851 2: 7.119 – 7.252
GROUP B			
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.111
49 Oxyethylene units	Multiplet	196	3.599 – 3.800
Last CH₂ group next to the OH group	Triplet	2	3.610
GROUP C			
The aliphatic side chain	Multiplet	19	0.466 – 1.704

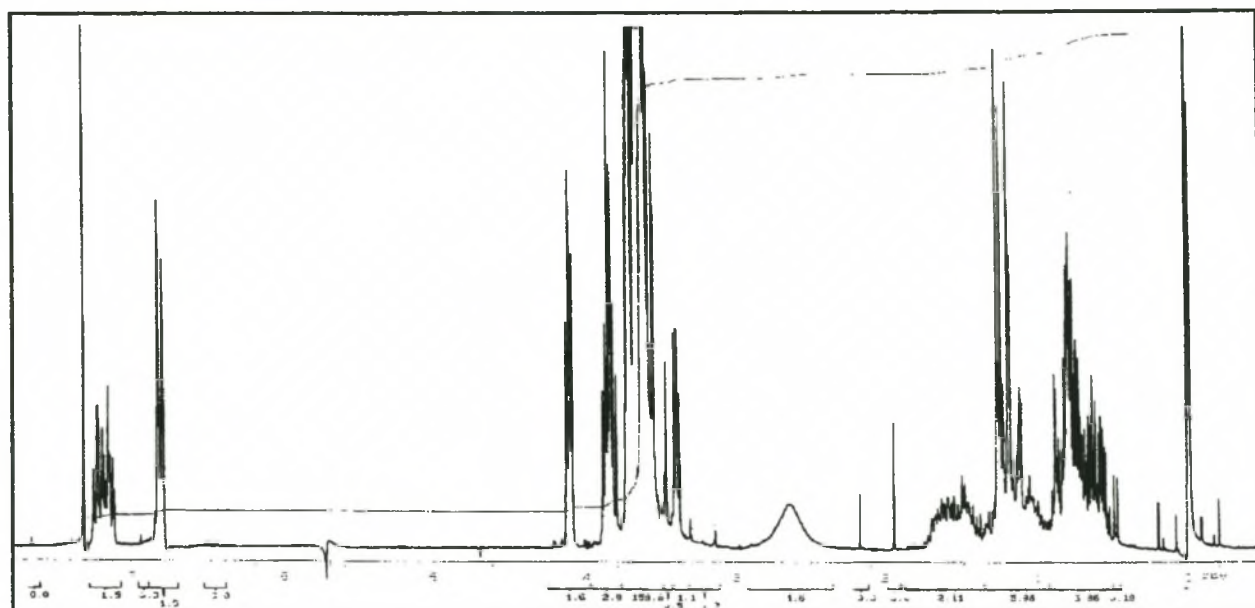


Figure A.1

^1H – NMR spectrum of the nonionic surfactant alcohol containing an average of 50 oxyethylene units (300 MHz).

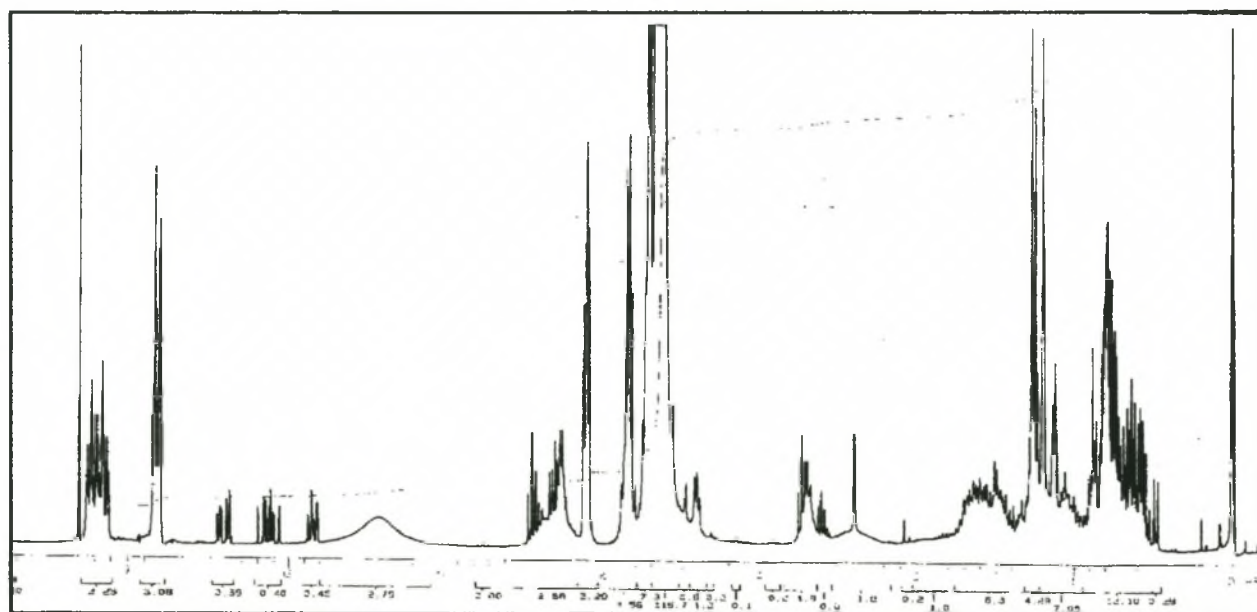


Figure A.2

^1H – NMR spectrum of the macromonomer containing an average of 50 oxyethylene units, synthesized by reaction method one (300 MHz).

Table A.2

The $^1\text{H-NMR}$ data of the macromonomer containing an average of 50 oxyethylene units, synthesized by reaction method one.

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)	Coupling constants (when calculated)
GROUP A				
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.851 2: 7.119 – 7.246	- -
GROUP B				
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.110	- -
49 Oxyethylene units	Multiplet	196	3.601 – 3.807	-
Last CH_2 group next to the ester group	Triplet	2	1: 3.610 2: 4.315	- -
GROUP C				
The aliphatic side chain	Multiplet	19	0.466 – 1.753	-
GROUP D				
Ethylenic unsaturation (ABC coupling system)	Six doublets	Each H-atom is represented by two doublets	H^{a} : 6.428 H^{b} : 6.154 H^{c} : 5.860	$J_{\text{ab}} = 17.34 \text{ Hz}$ $J_{\text{ac}} = 1.55 \text{ Hz}$ $J_{\text{bc}} = 10.38 \text{ Hz}$

Table A.3

The $^1\text{H-NMR}$ data of the macromonomer containing an average of 50 oxyethylene units synthesized by reaction method two.

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)	Coupling constants (when calculated)
GROUP A				
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.975 2: 7.116 – 7.256	- -
GROUP B				
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.110	- -
49 Oxyethylene units	Multiplet	196	3.645 – 3.785	-
Last CH_2 group next to the ester group	Triplet	2	4.315	-
GROUP C				
The aliphatic side chain	Multiplet	19	0.465 – 1.752	-
GROUP D				
Ethylenic unsaturation (ABC coupling system)	Six doublets	Each H-atom is represented by two doublets	H^a : 6.427 H^b : 6.154 H^c : 5.839	$J_{ab} = 17.30 \text{ Hz}$ $J_{ac} = 1.50 \text{ Hz}$ $J_{bc} = 10.38 \text{ Hz}$

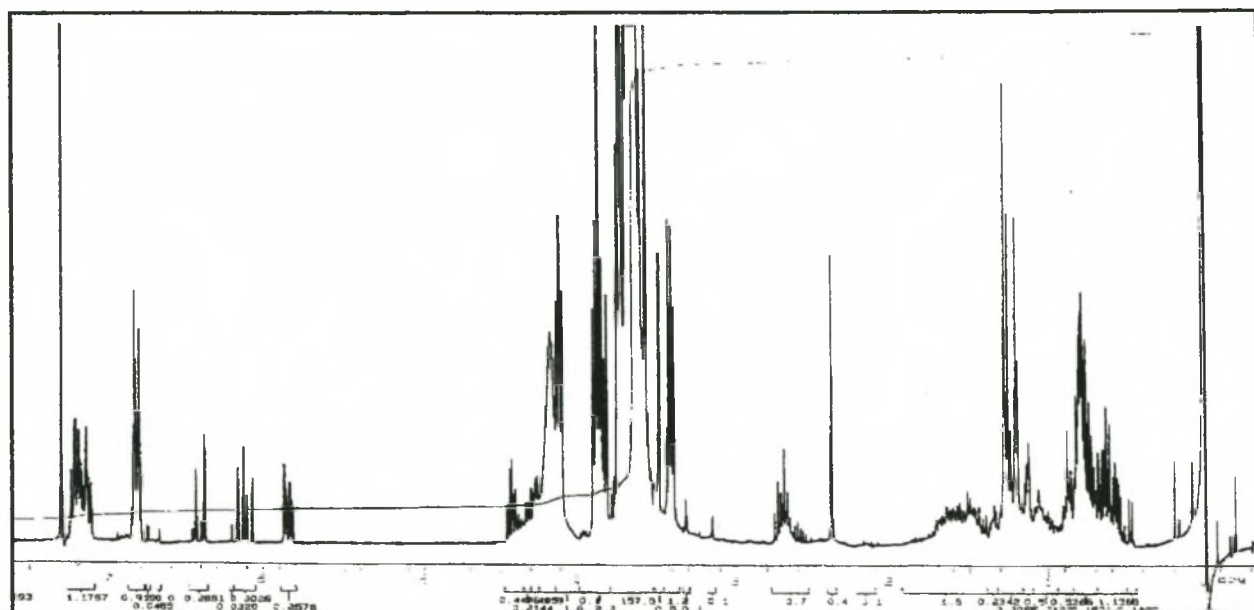


Figure A.5

¹H – NMR spectrum of the macromonomer containing an average of 100 oxyethylene units, synthesized by reaction method one (300 MHz).

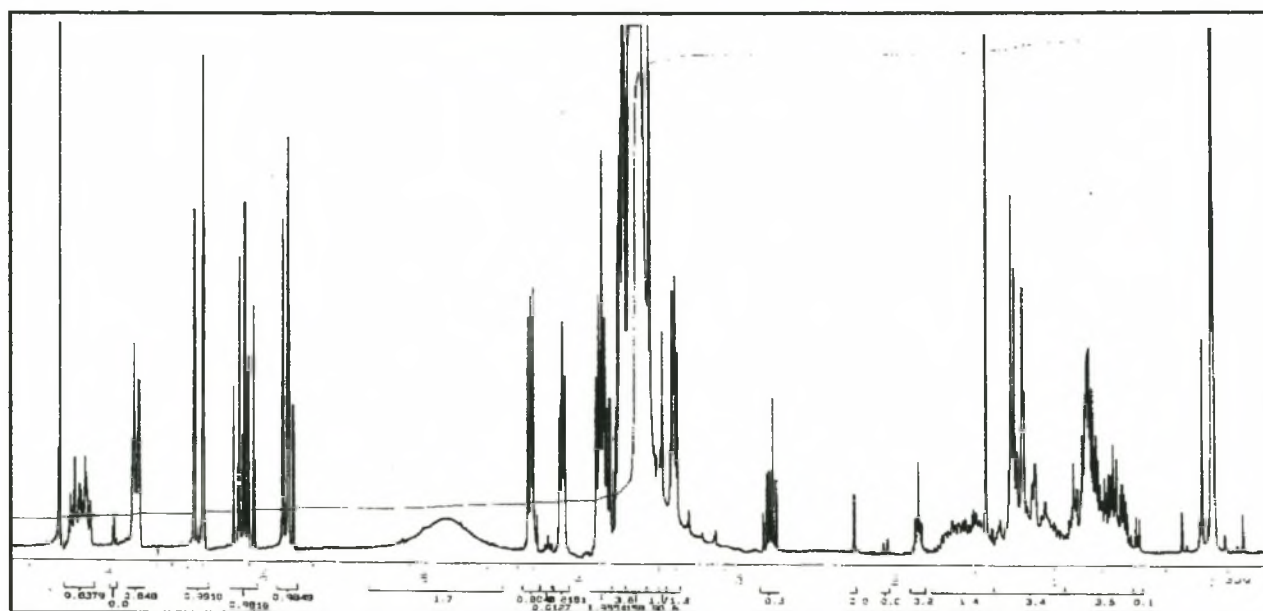


Figure A.6

¹H – NMR spectrum of the macromonomer containing an average of 100 oxyethylene units, synthesized by reaction method two (300 MHz).

Table A.4

The $^1\text{H-NMR}$ data of the surfactant containing an average of 100 oxyethylene units

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)
GROUP A			
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.850 2: 7.123 – 7.246
GROUP B			
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.843 2: 4.110
99 Oxyethylene units	Multiplet	332	3.600 – 3.814
Last CH₂ group next to the OH group	Triplet	2	3.613
GROUP C			
The aliphatic side chain	Multiplet	19	0.552 – 1.704

Table A.5

The ^1H -NMR data of the macromonomer containing an average of 100 oxyethylene units, synthesized by reaction method one.

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)	Coupling constants (when calculated)
GROUP A				
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.814 – 6.850 2: 7.115 – 7.256	- -
GROUP B				
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.110	- -
99 Oxyethylene units	Multiplet	332	3.601 – 3.807	-
Last CH_2 group next to the ester group	Triplet	2	1: 3.612 2: 4.315	- -
GROUP C				
The aliphatic side chain	Multiplet	19	0.465 – 1.753	-
GROUP D				
Ethylenic unsaturation (ABC coupling system)	Six doublets	Each H-atom is represented by two doublets	H^a : 6.428 H^b : 6.154 H^c : 5.838	$J_{ab} = 17.34$ Hz $J_{ac} = 1.55$ Hz $J_{bc} = 10.39$ Hz

Table A.6

The $^1\text{H-NMR}$ data of the macromonomer containing an average of 100 oxyethylene units synthesized by reaction method two.

	Type of splitting pattern	Number of H-atoms the signal integrates for.	Chemical shift (δ) (ppm)	Coupling constants (when calculated)
GROUP A				
Aromatic ring	Two sets of multiplets	Two H-atoms per multiplet	1: 6.807 – 6.974 2: 7.123 – 7.245	- -
GROUP B				
Oxyethylene unit next to aromatic ring	Two sets of triplets	Two H-atoms per triplet	1: 3.844 2: 4.110	- -
99 Oxyethylene units	Multiplet	332	3.645 – 3.788	-
Last CH_2 group next to the ester group	Triplet	2	4.315	-
GROUP C				
The aliphatic side chain	Multiplet	19	0.465 – 1.703	-
GROUP D				
Ethylenic unsaturation (ABC coupling system)	Six doublets	Each H-atom is represented by two doublets	H^{a} : 6.423 H^{b} : 6.154 H^{c} : 5.869	$J_{\text{ab}} = 17.30 \text{ Hz}$ $J_{\text{ac}} = 1.55 \text{ Hz}$ $J_{\text{bc}} = 10.37 \text{ Hz}$

A.2 FTIR ANALYSIS OF THE SURFACTANTS AND MACROMONOMERS

Table A.7:

FTIR data of the surfactant and macromonomers containing an average of 50 oxyethylene units.

	Functional group	Absorption band frequency (cm ⁻¹)
Surfactant	-OH	3476.22
Macromonomer (reaction method one)	-OH	3481.69
	C=O	1734.65
	-CH=CH ₂	1636.50
Macromonomer (reaction method two)	C=O	1724.12
	-CH=CH ₂	1633.45

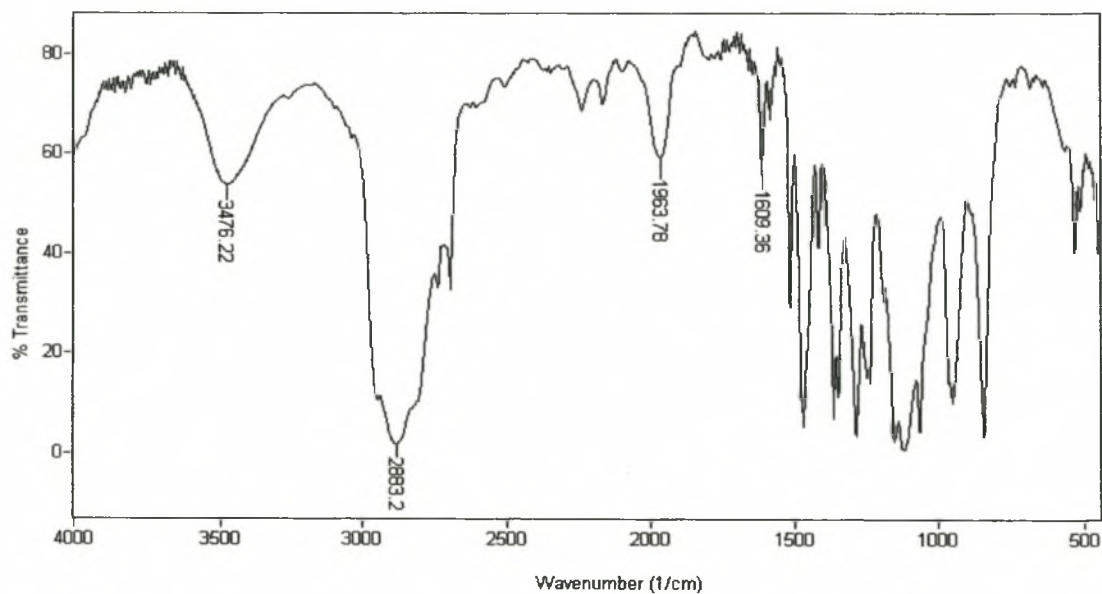


Figure A.7:

FTIR spectrum of the nonionic surfactant containing an average of 50 oxyethylene units.

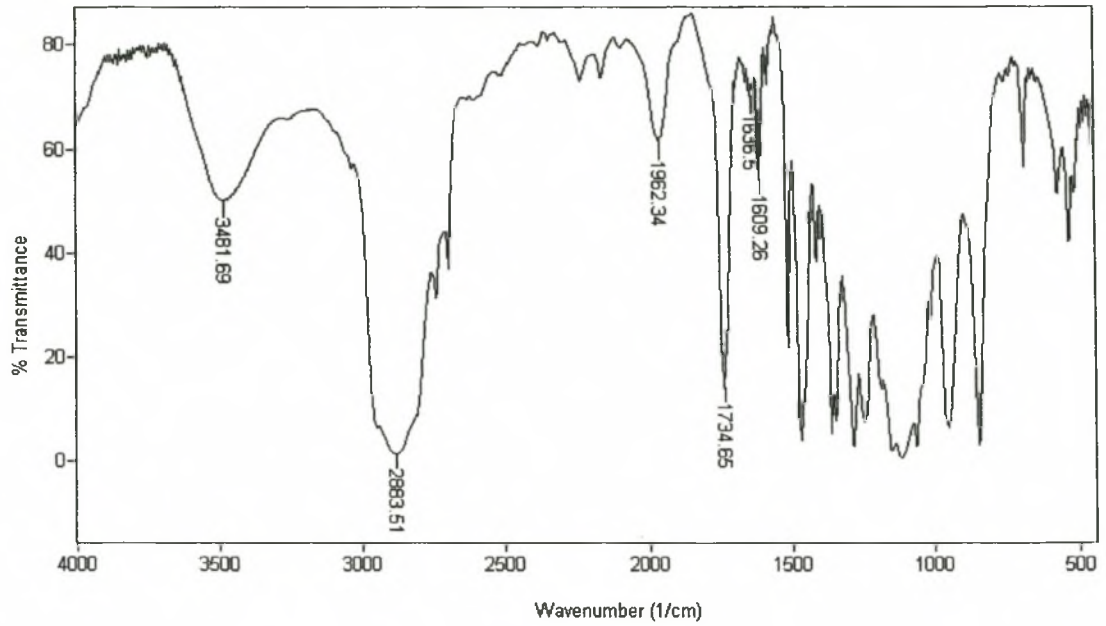


Figure A.8:

FTIR spectrum of the macromonomer containing an average of 50 oxyethylene units synthesized by reaction method one.

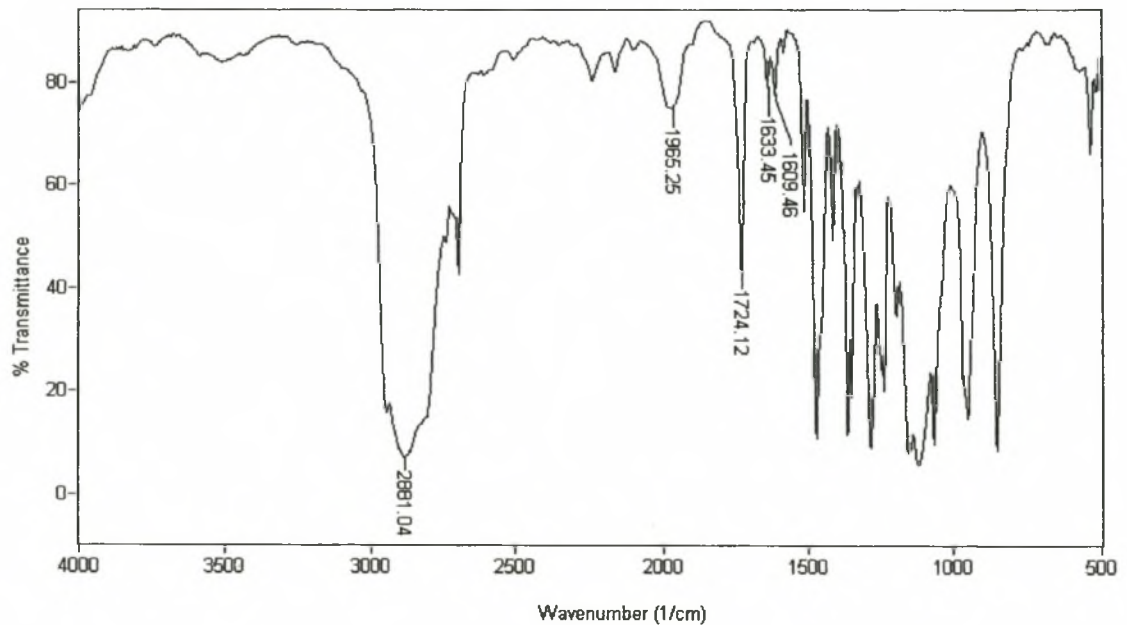


Figure A.9:

FTIR spectrum of the macromonomer containing an average of 50 oxyethylene units synthesized by reaction method two.

Table A.8:

FTIR data of the surfactant and macromonomers containing an average of 20 oxyethylene units.

	Functional group	Absorption band frequency (cm ⁻¹)
Surfactant	-OH	3462.76
Macromonomer (reaction method one)	-OH	3568.69
	C=O	1724.81
	-CH=CH ₂	1636.83
Macromonomer (reaction method two)	C=O	1737.5
	-CH=CH ₂	1633.51

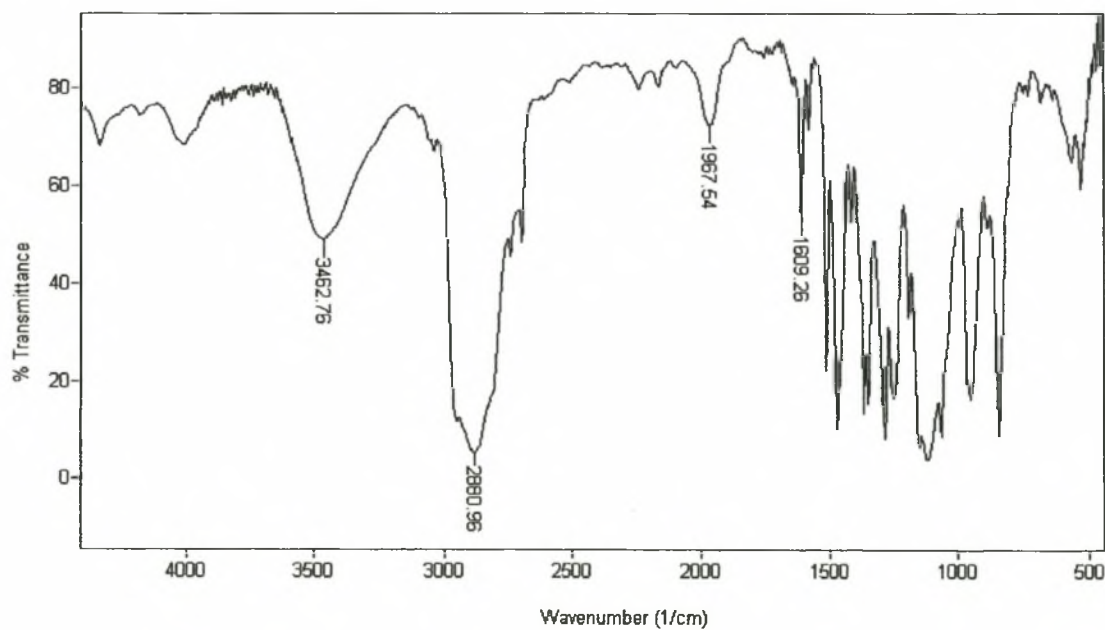


Figure A.10:

FTIR spectrum of the nonionic surfactant containing an average of 20 oxyethylene units.

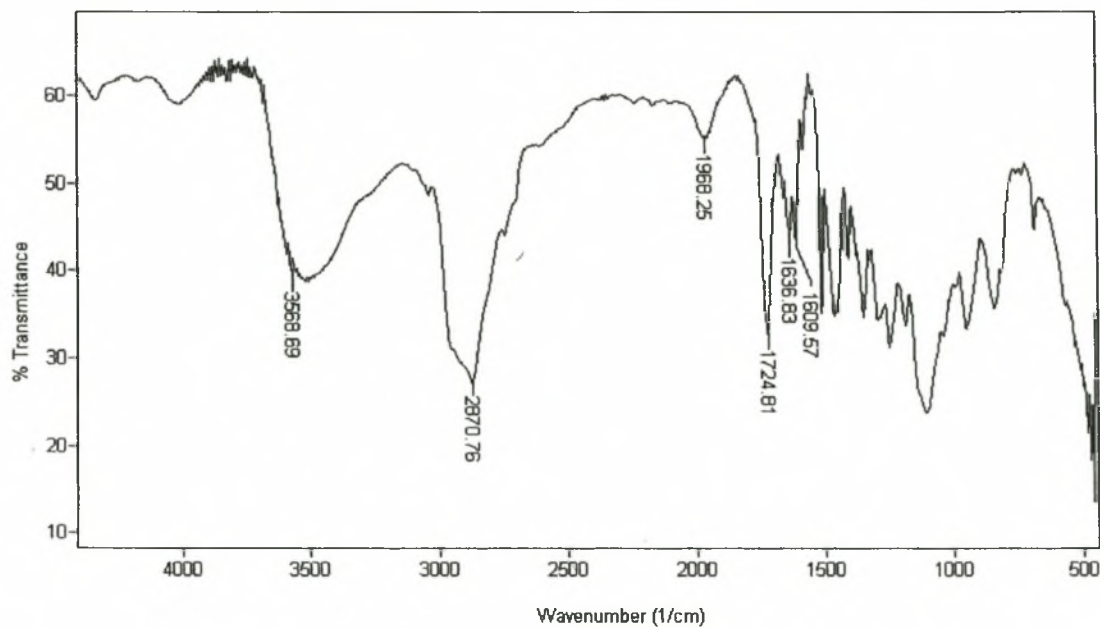


Figure A.11:

FTIR spectrum of the macromonomer containing an average of 20 oxyethylene units synthesized by reaction method one.

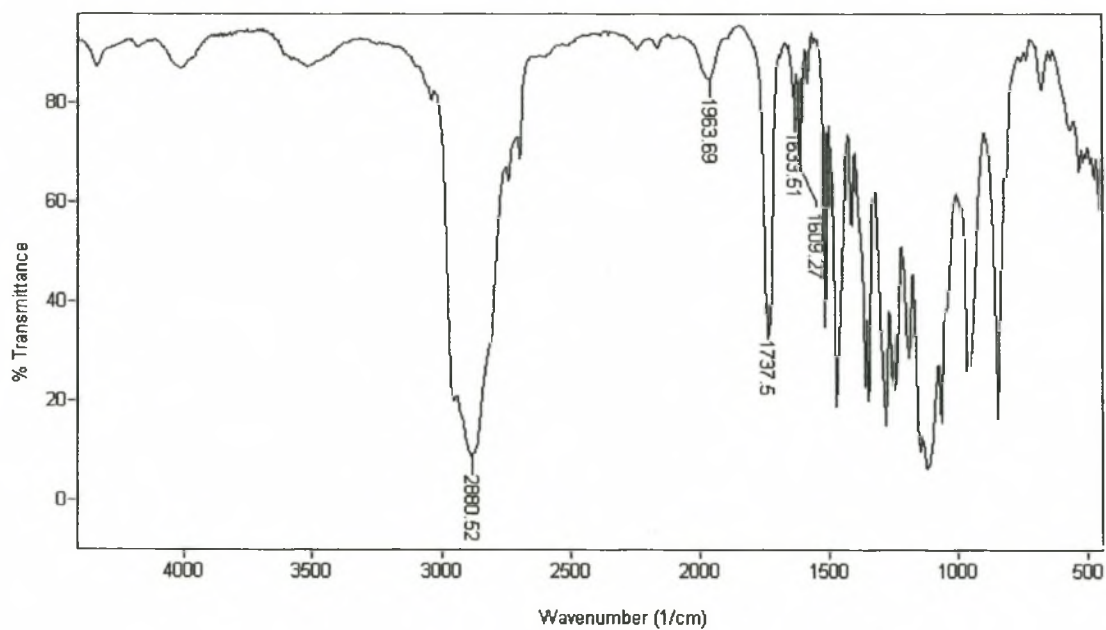


Figure A.12:

FTIR spectrum of the macromonomer containing an average of 20 oxyethylene units synthesized by reaction method two.

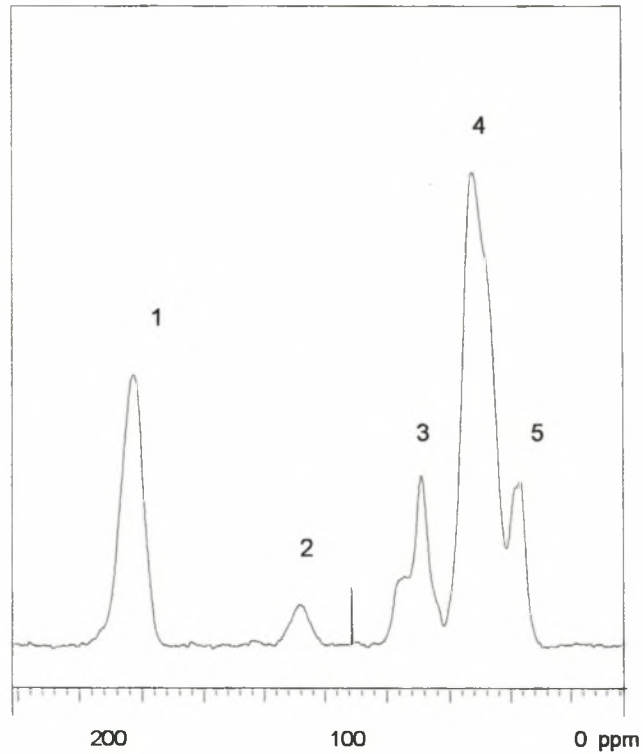
B.1 SOLID STATE ^{13}C -NMR ANALYSIS OF HASE THICKENERS**Figure B.1:** **^{13}C -NMR spectrum of HASE thickener EO-50.**

Table B.1: **^{13}C -NMR data of HASE thickener EO-50.**

Peak Number	Chemical Shift (ppm)	Group
1	178.40	C=O
2	110.27	Aromatic ring
3	61.16	Ethylene oxide side chain
4	40.02	CH - groups in backbone
5	21.83	CH ₂ - groups in backbone

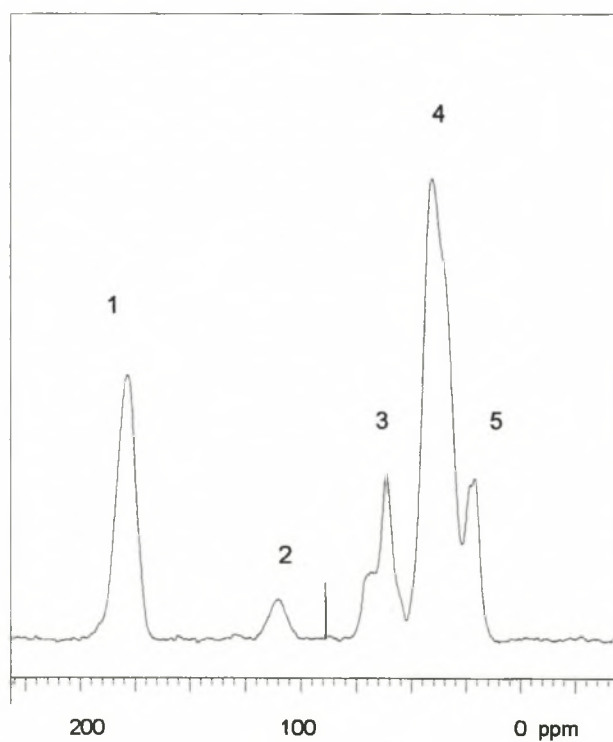
**Figure B.2:** **^{13}C -NMR spectrum of HASE thickener EO-100.**

Table B.2:
 ^{13}C -NMR data of HASE thickener EO-100.

Peak Number	Chemical Shift (ppm)	Group
1	179.82	C=O
2	111.17	Aromatic ring
3	61.40	Ethylene oxide side chain
4	41.54	CH - groups in backbone
5	21.30	CH ₂ - groups in backbone

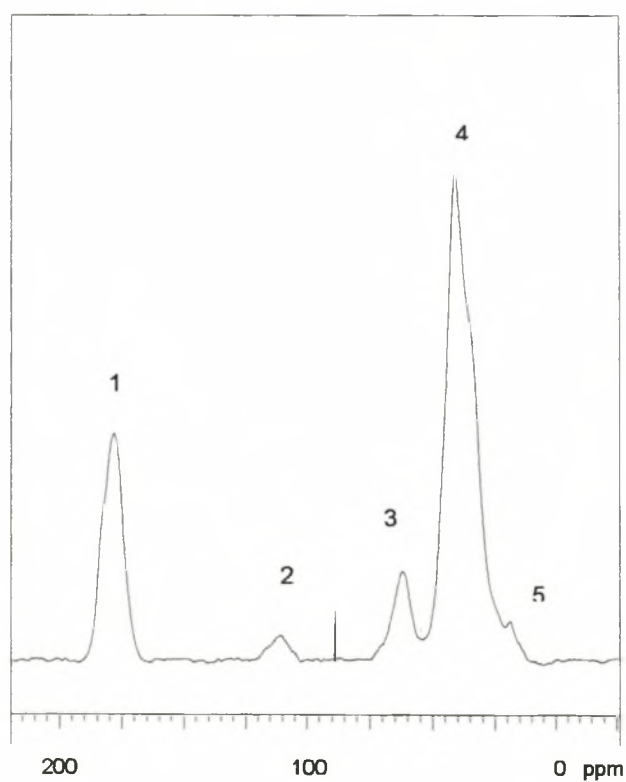


Figure B.3:
 ^{13}C -NMR spectrum of HASE thickener EO-20P.

Table B.3:

¹³C-NMR data of HASE thickener EO-20P.

Peak Number	Chemical Shift (ppm)	Group
1	178.16	C=O
2	110.55	Aromatic ring
3	62.03	Ethylene oxide side chain
4	40.91	CH - groups in backbone
5	18.73	CH ₂ - groups in backbone

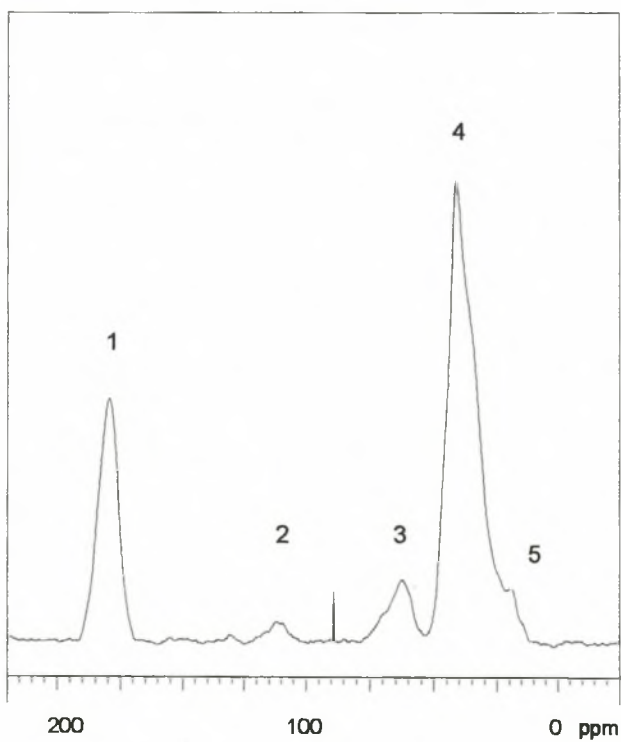


Figure B.4:

¹³C-NMR spectrum of HASE thickener EO-50P.

Table B.4:
¹³C-NMR data of HASE thickener EO-50P.

Peak Number	Chemical Shift (ppm)	Group
1	178.16	C=O
2	110.55	Aromatic ring
3	62.03	Ethylene oxide side chain
4	40.91	CH - groups in backbone
5	18.73	CH ₂ - groups in backbone

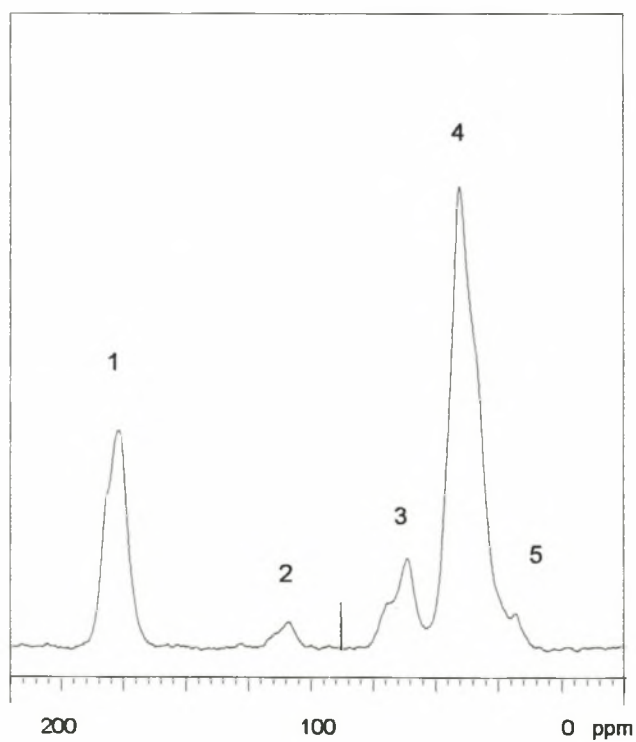


Figure B.5:
¹³C-NMR spectrum of HASE thickener EO-100P.

Table B.5:
¹³C-NMR data of HASE thickener EO-100P.

Peak Number	Chemical Shift (ppm)	Group
1	178.16	C=O
2	110.55	Aromatic ring
3	62.03	Ethylene oxide side chain
4	40.91	CH - groups in backbone
5	18.73	CH ₂ - groups in backbone

THE STATISTICAL ANALYSIS OF THE UNIVERSAL COLORANT EXPERIMENTS (CHAPTER 5)

C.1 Experimental

A Stoneman[1] $2^3 \times 4^1$ factorial design was used to plan and analyse the experimental runs. Four factors were chosen and are coded below. Table C.1 contains the factor levels for the different runs. Dr. Nico Laubcher did the statistical analyses of the experimental runs.

Factor 1: Filler

X1 = -1 → Pyrofil : Blanc Fix = 100 : 0 %

X2 = 1 → Pyrofil : Blanc Fix = 75 :25 %

Factor 2: Anti-settling agent

X2 = -1 → Bentone EW

X2 = 1 → Rheolate

Factor 3: Co-solvent

X3 = -1 → Propylene glycol

X3 = 1 → Mono-ethylene glycol

Factor 4: Dispersing agent

X4 = -2 → EFKA 4550/1501

X4 = -1 → HYDROPALAT 3275

X4 = 1 → HYDROPALAT 1080

X4 = 2 → EFKA 4550

Table C.1:

The factor levels for a 8 run fractional factorial design

Run	X1	X2	X3	X4
1	-1	-1	-1	1
2	1	1	-1	-1
3	-1	-1	1	-1
4	1	1	1	1
5	-1	1	-1	2
6	1	-1	-1	-2
7	-1	1	1	-2
8	1	-1	1	2

The two responses that were measured for the experimental runs are color strength and rheology. The color strength measurements have been explained in chapter 5, section 5.4.3. The rheology response for the color concentrates was measured in four different coatings (Polvin pastel and transparent base and Wall & All pastel and transparent base). The rheology profile of the tinted coating was compared to that of the untinted coating by calculating the area difference between the two-rheology profiles and so a single response was obtained for a specific experimental run.

C.2 Results and discussion

Table C.2 contains a summary of all the responses of all the variables that were investigated.

Table C.2:**The responses measured for the 8-run fractional factorial design.**

Run	X1	X2	X3	X4	Rheology TAP 1000	Rheology TAP 3000	Rheology TWA 1000	Rheology TWA 3000	Color strength
1	-1	-1	-1	1	-15996	-0.18282	-0.38108	-1.53105	-1.28
2	1	1	-1	-1	0.181433	0.091275	-0.09539	-1.37102	20.46
3	-1	-1	1	-1	0.227443	0.110954	-0.06191	-1.34734	27.81
4	1	1	1	1	-0.08583	-0.01093	-0.34783	-1.61053	-8.12
5	-1	1	-1	2	0.356992	0.251917	-0.19521	-1.23146	5.25
6	1	-1	-1	-2	0.65248	0.319421	-0.1756	-1.18894	28.22
7	-1	1	1	-2	0.735685	-0.36206	-0.1846	-1.19645	40.38
8	1	-1	1	2	0.41576	0.264503	-0.22316	-1.29388	3.53

The results of the experiment may be represented graphically by series of trellis graphs where X1 provides the horizontal categorization, X2 the vertical categorization. The X-variable is taken to be X4 and the color strength or rheology area as the response variable. A separate coding symbol is used for each value of co-solvent X3. The dispersing codes are as follows:

A = EFKA 4550/1501

B = HYDROPALAT 3275

C = HYDROPALAT 1080

D = EFKA 4550

The trellis graphs are shown in Figure C.1 – C.5.

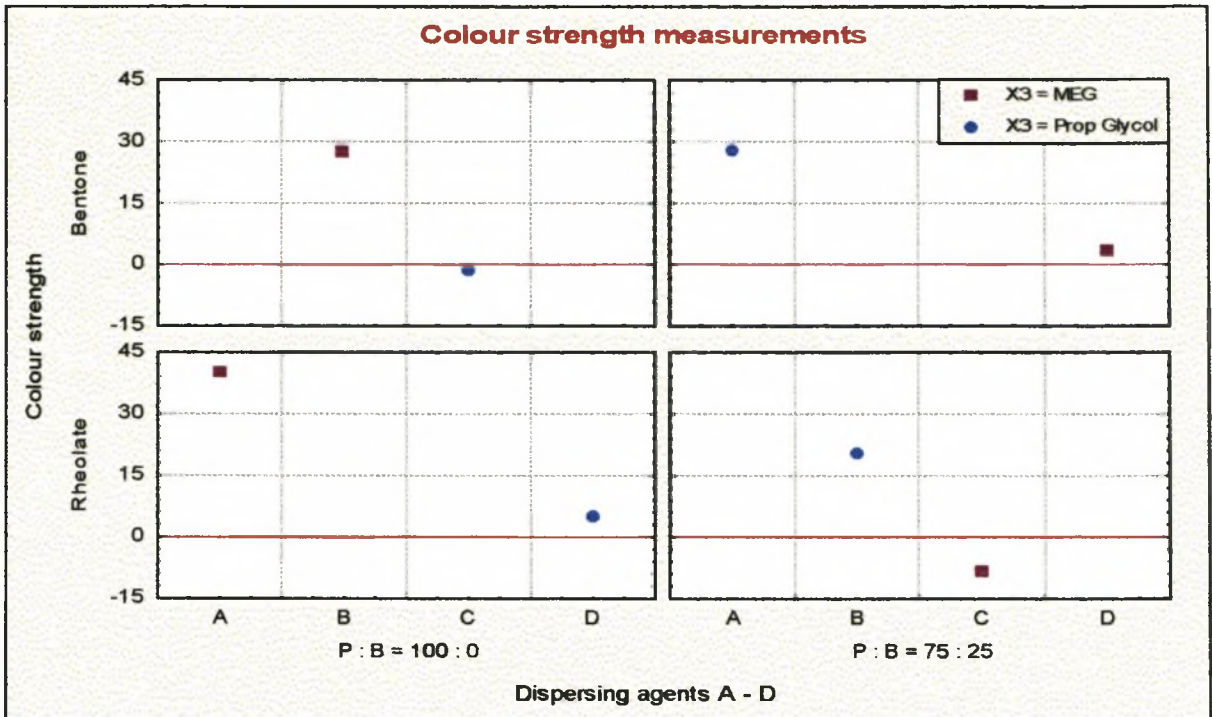


Figure C.1:
Trellis graphs of the color strength measurements

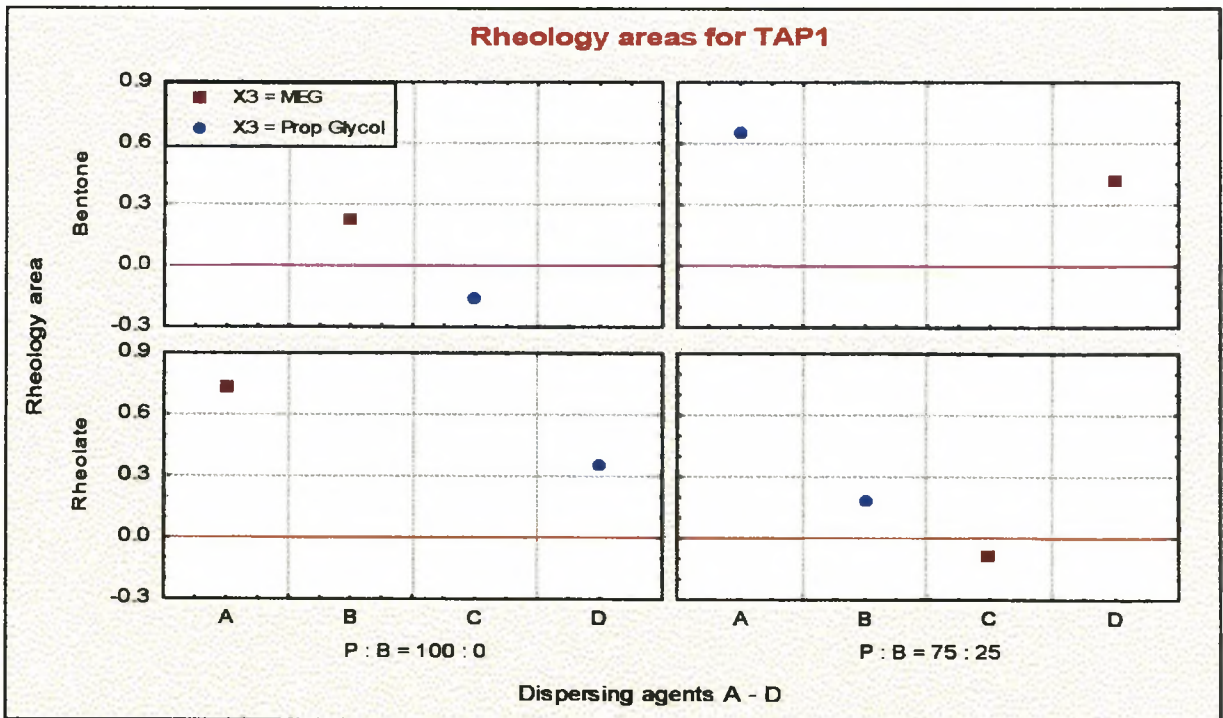


Figure C.2:
Trellis graphs of the rheology areas for TAP 1000

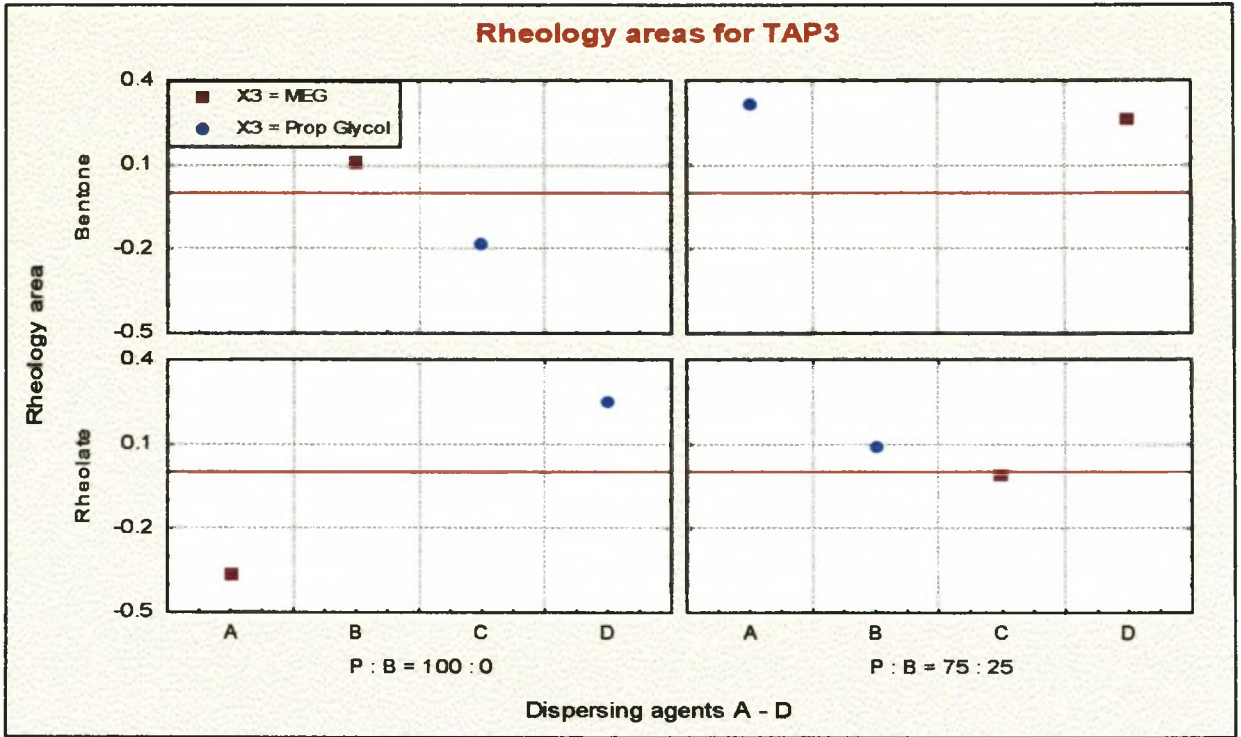


Figure C.3:
Trellis graphs of the rheology areas for TAP 3000

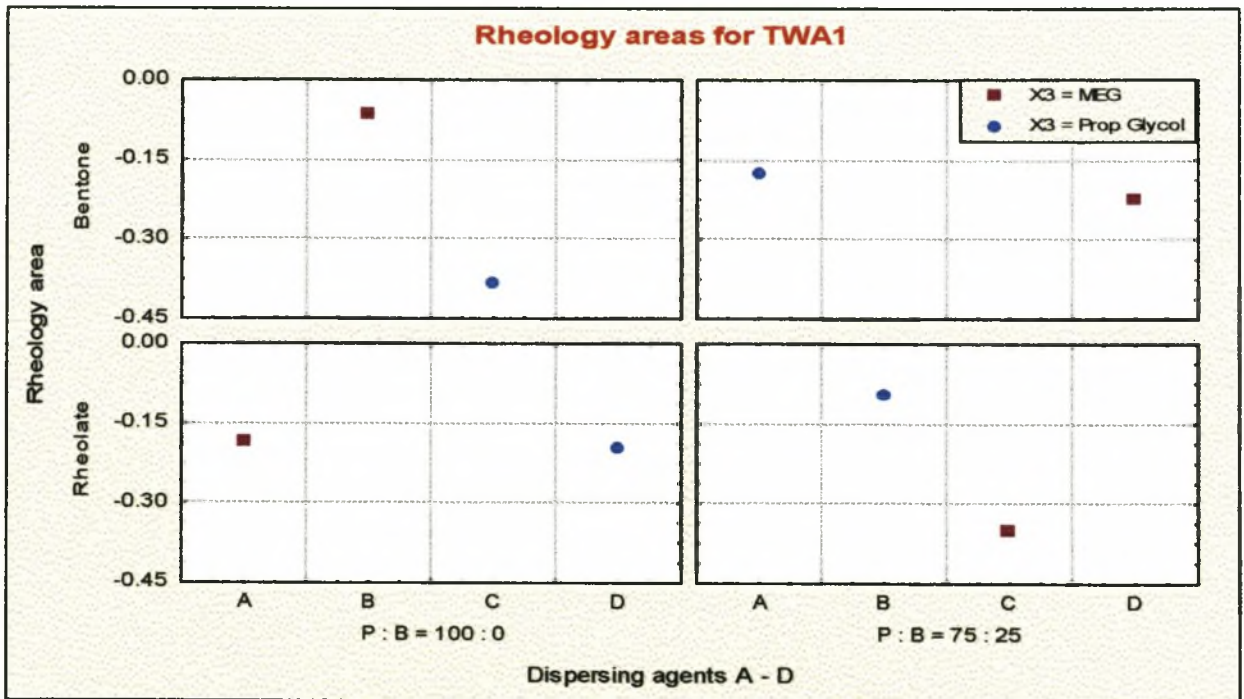


Figure C.4:
Trellis graphs of the rheology areas for TWA 1000

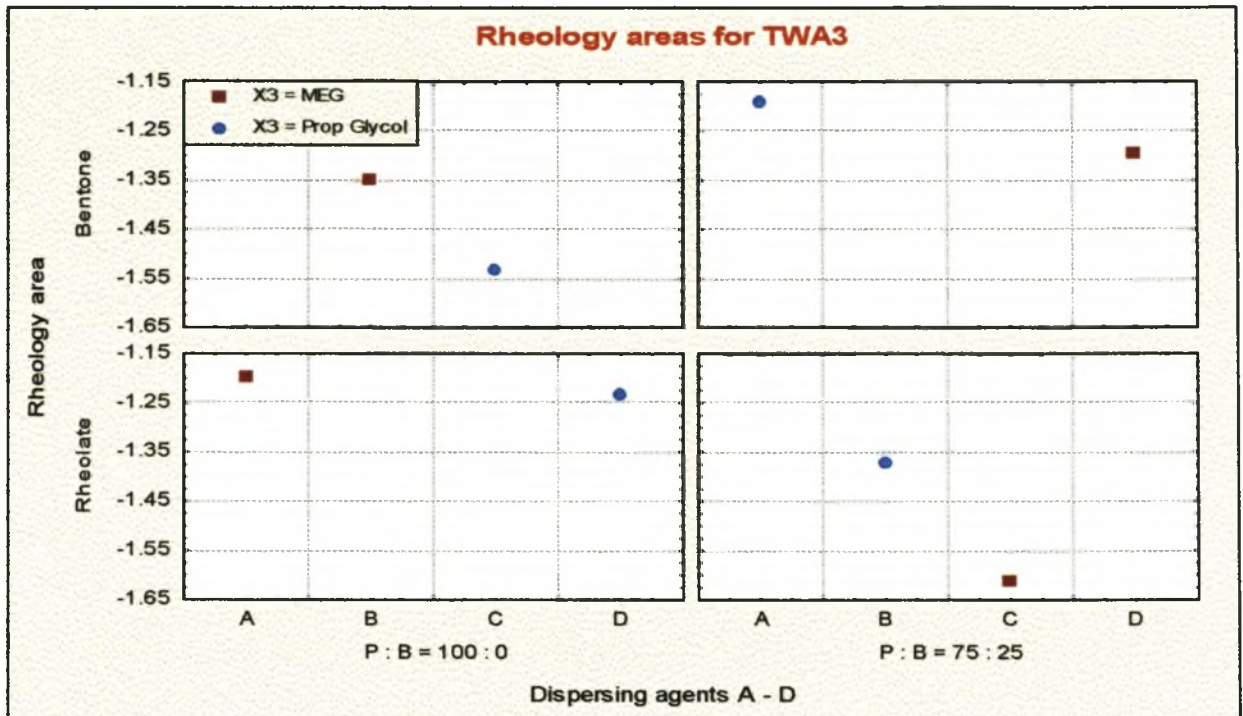


Figure C.5:
Trellis graphs of the rheology areas for TWA 3000

In order to test if any of the factors are "active" (i.e. the responses at the different levels are significant say at the 5% level of significance) a simple regression model in the qualitative factors will be applied. The regression coefficient will be tested under hypothesis that its value is zero. If this hypothesis is upheld it is deduced that the factor is inert (i.e. no significant difference between the responses at its levels).

The fact that factor X4 has more than two levels require recoding the regression as described in Chapter 11 of the following reference. Specifically pp. 464 – 466

Reference: Neter, J., Kutner, M.H., Nachtsheim, C.J., & Wasserman, W., (1996), "Applied linear statistical models", (4th ed.), Irwin: Chicago.

The role of the three dummy variables is to replace X4. These are identified by X4A, X4B and X4C, which are coded according to the value of X4 as follows:

$X_{4A} = 1$ if $X_4 = -2$ and zero otherwise,

$X_{4B} = 1$ if $X_4 = -1$ and zero otherwise

$X_{4C} = 1$ if $X_4 = 1$ and zero otherwise,

From this the following matrix of values of X_4 and the equivalent rows of values of the dummy variables may be written down.

X_4	X_{4A}	X_{4B}	X_{4C}
-2	1	0	0
-1	0	1	0
1	0	0	1
2	0	0	0

The full regression model is: $E[Y] = \beta + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{4A} X_{4A} + \beta_{4B} X_{4B} + \beta_{4C} X_{4C}$

The "effect" of factor X_1 (for example) is the difference between the expected values as X_1 changes from $X_1 = -1$ to $X_1 = +1$. This difference is precisely $2b$ and hence the regression coefficient is half of the effect. Similarly for X_2 and X_3 . Thus a statistical test for the significance of the regression coefficients is equivalent to a test for whether or not the corresponding factor is active.

If the estimated regression equation is denoted by:

$$Y = b + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{4A} X_{4A} + b_{4B} X_{4B} + b_{4C} X_{4C} + \text{error},$$

then the estimated regression coefficients are used to test the significance of the effects. Thus the standard t-test for regression coefficients (5% level of significance) is used to test whether or not the corresponding factor is active.

Now, to test if there is an effect as X_4 is changed from $X_4 = -2$ to $X_4 = +2$, for example, we compute the expected values at these two levels (keeping the other factors fixed)

Thus at $X_4 = -2$ the expected value is

$$E[Y] = \beta + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{4A}$$

and at $X_4 = +2$ the expected value is

$$E[Y] = \beta + \beta_1X_1 + \beta_2X_2 + \beta_3X_3$$

The "effect" of X_4 is the difference in expected values as X_4 is changed from $X_4 = -2$ to $X_4 = +2$ and this can be seen to be estimated by the regression coefficient b_{4A}

Thus a statistical test for the significance of the regression coefficient b_{4A} provides a test for the effect of factor X_4 (comparing $X_4 = -2$ to $X_4 = +2$).

Similarly the t-test for significance of b_{4B} provides a test for the differential effect of $X_4 = -1$ over $X_4 = +2$ and the t-test for b_{4C} is a test for the differential effect of $X_4 = -2$ over $X_4 = +2$.

If it is desired to contrast other combinations of these factors (e.g. X_4 at -1 versus X_4 at $+1$) a regression has to be done on a different parameterization of X_4 .

Of course, we have to note that data are very scarce and the model is only a simple linear model without any interactions. The assumptions of normality on which the t-test rests, may also be queried. These tests are designed to provide only a broad indication of any trends that may be present.

C.2.1 Regression values

Color strength

Regression Summary for Dependent Variable: Color strength

R= .99697036 R²= .99394990 Adjusted R²= .95764933

F(6,1)=27.381 p<.14525 Std.Error of estimate: 3.5108

	Regression		St. Err.		
	Coefft (B)	Value	of B	t(1)	p-value
Intercept	b	4.3900	2.4825	1.77	0.3276
X1	b ₁	-3.5088	1.2413	-2.83	0.2165
X2	b ₂	-0.0388	1.2413	-0.03	0.9801
X3	b ₃	1.3688	1.2413	1.10	0.4689
X4A	b _{4A}	29.9100	3.5108	8.52	0.0744
X4B	b _{4B}	19.7450	3.5108	5.62	0.1120
X4C	b _{4C}	-9.0900	3.5108	-2.59	0.2346

The P-values of the t-test show that there is some indication of significance for b_{4A} (with P = 0.07). This means that X4 is the only somewhat active factor and that there is some indication that X4 at -2 is significantly different from X4 at +2. The other comparisons are not significant.

Rheology

TAP 1000

Regr. Coefficients; Var.:TAP1; R-sqr=.99992; Adj:.99941

6 factors at two levels; MS Residual=.0000596

DV: TAP1:

	Regression				
	Coefft (B)	Value	Std.Err.	t(1)	
Intercept	b	0.3864	0.0055	70.77	0.0090
(1)X1	b ₁	0.0005	0.0027	0.17	0.8938
(2)X2	b ₂	0.0066	0.0027	2.41	0.2507
(3)X3	b ₃	0.0328	0.0027	12.00	0.0529
(4)X4A	b _{4A}	0.3077	0.0077	39.85	0.0160
(5)X4B	b _{4B}	-0.1819	0.0077	-23.56	0.0270
(6)X4C	b _{4C}	-0.5093	0.0077	-65.96	0.0097

The last three effects are significant at the 5% level (X4C at the 1% level)

TAP 3000

Regr. Coefficients; Var.:TAP3; R-sqr=.7637; Adj:0.

6 factors at two levels; MS Residual=.0925488

DV: TAP3

	Regression				
	Coefft (B)	Value	Std.Err.	t(1)	p
Intercept	b	0.2582	0.2151	1.20	0.4422
(1)X1	b ₁	0.1058	0.1076	0.98	0.5053
(2)X2	b ₂	-0.0677	0.1076	-0.63	0.6422

(3)X3	b ₃	-0.0597	0.1076	-0.55	0.6776
(4)X4A	b _{4A}	-0.2795	0.3042	-0.92	0.5269
(5)X4B	b _{4B}	-0.1571	0.3042	-0.52	0.6965
(6)X4C	b _{4C}	-0.3551	0.3042	-1.17	0.4510

There are NO significant effects

TWA 1000

Regr. Coefficients; Var.:TWA1; R-sqr=.98429; Adj:.89

6 factors at two levels; MS Residual=.0013439

DV: TWA1

		Regression			
	Coefft (B)	Value	Std.Err.	t(1)	p
Intercept	b	-0.20918	0.025922	-8.06975	0.07849
(1)X1	b ₁	-0.0024	0.012961	-0.18505	0.883513
(2)X2	b ₂	0.002341	0.012961	0.180622	0.886239
(3)X3	b ₃	0.003724	0.012961	0.287318	0.821885
(4)X4A	b _{4A}	0.029085	0.036659	0.793384	0.573023
(5)X4B	b _{4B}	0.130532	0.036659	3.560708	0.1743
(6)X4C	b _{4C}	-0.15527	0.036659	-4.23557	0.147601

There are NO significant effects

TWA 3000

Regr. Coefficients; Var.:TWA3; R-sqr=.99985; Adj:.99896

6 factors at two levels; MS Residual=.000025

DV: TWA3

	Regression				
	Coefft (B)	Value	Std.Err.	t(1)	p
Intercept	b	-1.26267	0.003533	-357.437	0.001781
(1)X1	b ₁	-0.01976	0.001766	-11.1863	0.05676
(2)X2	b ₂	-0.00603	0.001766	-3.41512	0.181343
(3)X3	b ₃	-0.01572	0.001766	-8.89774	0.07125
(4)X4A	b _{4A}	0.069973	0.004996	14.00637	0.045375
(5)X4B	b _{4B}	-0.09651	0.004996	-19.3176	0.032926
(6)X4C	b _{4C}	-0.30812	0.004996	-61.6762	0.010321

The X1 and X3 main effects are significant only at the 10% level

The last three effects are significant at the 5% level

C.3 CONCLUSIONS

Although no clear trend can be observed from the regression values, X4 is the only factor that shows a significant influence on the color concentrate formulations. X4 is the specific factor for all the dispersants, the individual dispersants could not be significantly separated. This highlights the importance of the dispersing agent in a universal colorant formulation.