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FORMULATION DEVELOPMENT AND MICROSTRUCTURE ANALYSIS OF A POLYMER MODIFIED BITUMEN EMULSION ROAD SURFACING

A Thesis presented
in partial fulfilment of
the requirements for the Degree of
Master of Technology in Product Development
at Massey University, Palmerston North, New Zealand.

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ABSTRACT

The purpose of this research was to develop a formulation for a polymer modified bitumen emulsion road surfacing product called microsurfacing to a mid-scale prototype stage. A supplementary part of the development was to investigate the polymer-bitumen interactions and how they affected the products end properties using confocal microscopy.

The formulation development consisted of three stages: technical design specifications, initial design, detailed design. The technical specification was developed to define the product performance in quantitative measures, and set the initial formulation parameters to work within. The initial design development screened three polymers, four methods of adding polymer to the emulsion and two grades of bitumen. Experimental design techniques were used to determine the best polymer-bitumen combination and emulsion process method. Further experimental investigations consisted of screening three emulsifiers and assessing the effect of aggregate cleanliness on the surfacing abrasion and curing rate.

The detailed design used experimental factorial design to examine the effects of polymer concentration, emulsifier level, and emulsifier pH on the emulsion stability, microsurfacing wear resistance and cure rate.

The emulsion residue was observed using confocal microscopy with fluorescence light and the microsurfacing mixture using both fluorescent and reflected light.

The research showed that a emulsion using 100 penetration grade Safaniya bitumen with SBR latex polymer post added could provide microsurfacing abrasion resistance of less than 100 g/m^2; an improvement of 85% on the minimum specification. The vertical permanent deformation was less than the 10% and could not be attained without polymer addition. The use of aggregate with a high cleanliness and an alkyl amidoamine emulsifier resulted in surfacing cohesion development of 20 kg-cm within 90 minutes, which compares closely to the international specification.

Unexpected results not reported before were that the emulsion residue from biphase modified emulsions had a softening point up to 10°C higher than polymer modified hot bitumen with the same polymer concentration. The biphase emulsified binder residue also has a very different microstructure to hot modified bitumen and this structure has been proposed to help account for the improved resistance to high temperature and applied stress.

Modifications to the formulation are to improve the emulsion settlement and should focus on the density difference between the bitumen and polymer latex.

This research has shown that a microsurfacing roading product can be successfully formulated with New Zealand bitumen and aggregate sources to meet key specified performance requirements. By systematically investigating the effects of materials on the performance properties of the product, a formulation ready for a mid-scale experiment has been proposed.

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GLOSSARY

Aggregate	A hard inert mineral material, such as gravel, crushed rock, or sand.
Binder	Material which secures aggregate to road surface. Can comprise of bitumen, polymers, solvent or other solid material.
Biphase Emulsion	Polymer modified bitumen emulsion characterised by a dispersed phase made up of two types of droplets: bitumen and polymer.
Break	The destabilisation of an emulsion resulting in the separation of emulsified phases (demulsification).
Copolymer	A polymeric structure that is composed of at least two different monomers in alternating sections or a coupling group of low molecular weight.
Curing	The development of mechanical properties of the bitumen binder. This occurs after the emulsion has broken and the emulsion particles coalesce and bond to the aggregate.
Cut-back	Bitumen liquefied by blending with petroleum solvents.
Emulsifier	The chemical added to the water and bitumen that keeps the bitumen in stable suspension in the water.
Elastomer	Polymers that can easily undergo large elongation at relatively low stress levels and rapidly return to approximately its original size.
Latex	An aqueous, stable, colloidal emulsion of a polymer substance.
Microsurfacing	A mixture of polymer modified bitumen emulsion, crushed graded aggregate, mineral filler, additives, and water. Microsurfacing provides thin resurfacing of 10 to 20 mm to the pavement and returns traffic use in 1 to 1.5 hours under average conditions.
Monophase Emulsion	Polymer modified bitumen emulsion characterised by a dispersed phase composed of only polymer modified bitumen droplets.
Residue	The bitumen binder that remains after the emulsion has broken and cured.
Wetting	The reduction of interfacial tension.

1. INTRODUCTION

1.1 Background

The use of polymer modified bitumen emulsions for road sealing maintenance has the potential to be an important product area for New Zealand contractors. Unmodified bitumen softens under increased temperatures and this results in the pavement deforming (Whiteoak, 1990; Transit, 1993; Asphalt Institute, 1994). Common problems encountered are loss of stone chips and formation of wheel tracking ruts that cause an uneven surface. The loss of stone chips reduces tire traction. Wheel ruts in roads can cause vehicles to aquaplane due to water build-up and reduce braking effectiveness. These problems can be reduced by the addition of polymer modifiers to the bitumen to increase its strength and elasticity (Whiteoak, 1990; Transit, 1993; Bahia et al., 1998; Swanston & Remtulla, 1998).

But the only product alternatives in New Zealand to solve these problems are polymer modified hot-mix asphalt, or polymer modified hot *cut-back** bitumen as a sprayed layer covered with graded *aggregate* (Transit, 1993). Asphalt is expensive and must be laid in thick layers. Cutback bitumen contains petroleum solvent to reduce the temperature needed to lower the viscosity to a sprayable level. But, the spraying temperature is still around 160°C. Another drawback of solvent is that it also reduces the softening point of the bitumen, making it more susceptible to heat. The combination of high temperature and solvent present a safety risk for workers, high energy costs and environmental concerns over solvent evaporation (Asphalt Institute, 1994; Reed, 1996). Both of these options also require the whole section of road to be resurfaced even though in many cases it is only the wheel ruts that may be the problem.

In particular the *microsurfacing* product, which uses a polymer modified bitumen emulsion mixed with aggregate, has important benefits. The advantage of bitumen emulsions is that they are applied at ambient temperature, and generally require no solvent. In the USA and several countries in Europe the microsurfacing product is common and rapidly gaining acceptance (Asphalt Institute, 1994; Holleran, 1997).

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* Italicised words appear in the glossary.

Microsurfacing imparts protection to the underlying pavement and provides renewed surface friction. Wheel ruts of up to 40 millimetres can be easily filled using this product. Microsurfacing is quick setting, which allows traffic rapidly on the pavement. It can also be applied in the early evening or even at night-time.

1.2 Microsurfacing Product Design

The basic formulation aspects of a microsurfacing consists of:

1. Polymer modified bitumen emulsion
2. Graded aggregate
3. Setting additives
4. Extra water to wet the aggregate

The most challenging part of designing a microsurfacing is the emulsion formulation (Asphalt Institute, 1994; Holleran, 1997). The experimental work undertaken in this research focuses mainly on this part of the product. But, it is important to recognise the whole microsurfacing system and the experimental work also includes the emulsion-aggregate interactions in detail. The formulation development followed a common product design approach. The product design approach used in this experimental research consisted of the phases shown in Figure 1-1.

Figure 1-1. Product Design Stages to Develop the Microsurfacing Formulation

- Technical design specifications
- Initial design – material screening
- Detailed design
- Scale-up and validation
- Optimal design
- Production and launch

Phases covered in this research

1.3 Technical Specifications

Developing a set of technical specifications helps to define the product performance in quantitative measures, set the initial formulation parameters to work within and the process method to use. A set of preliminary specifications for the product was prepared to help guide the initial formulation development. This included suitable materials, process method and processing parameters. Performance criteria to compare the experimental products against were selected from technical literature. The technical specification developed is discussed in chapter 3.

1.4 Initial Laboratory Development

The scope of the product materials and their effect on the performance properties requires a screening process to adequately assess them. The polymer type and its method of addition to the emulsion can add different performance properties to the bitumen *binder*. The polymer can be added to an emulsion in four possible ways and it needed to be determined if there were significant performance differences. Bitumen can be supplied in different grades and this directly affects the durability of the microsurfacing and also the polymer processing method. The *emulsifier* type can affect the cure rate of the microsurfacing, which determines the time frame for allowing traffic on the surfacing. Aggregate type and quality are also suggested to be very important to the durability and *curing* aspects of the surfacing (Asphalt Institute, 1994). Hence, the experiments had to investigate these aspects to understand material interactions, in order to select the viable polymer(s), bitumen, emulsifier, aggregate, and emulsion process method.

1.5 Formulation Detailed Design

The detailed design experiment took the best polymer, emulsifier, bitumen type, aggregate type and emulsion processing method determined from the initial formulation material screening. The emulsion was further investigated in detail by examining the effects of the polymer, emulsifier and emulsifier solution pH. These aspects were selected as they could affect in some way the emulsion stability, the bitumen resistance to deformation and also the microsurfacing cure rate. The aim was to refine the material addition levels to produce an optimal set of microsurfacing performance characteristics.

To investigate the overall research questions a selection of experimental design trials were used to systematically examine the performance effects of materials and refine step by step the formulation to be ready for a mid-scale trial.

1.6. Confocal Microscopy Research

Polymer modified bitumen should ideally have a microstructure that consists of a fine dispersion of polymer throughout the bitumen (Piazza et al., 1980; Bouldin et al., 1990; Morgan & Mulder, 1995; PIARC, 1999). But the addition of polymer to bitumen can cause compatibility problems in the polymer-bitumen blend. The problem can manifest itself as phase separation whereby the polymer rises to the top of the bitumen. Or the polymer can coagulate into lumps at a microscopic level giving an uneven distribution. This incompatibility is strongly dependent on the bitumen source (Morgan & Mulder, 1995; Loeber et al, 1996). Incompatible binders can cause storage stability problems and also can result in early aggregate loss from a road surfacing.

Microscopy techniques have been used in several studies to examine the compatibility of polymers with bitumen (Piazza et al., 1980; Bouldin et al., 1990; Loeber et al., 1996; Rozeveld et al., 1997; Lu et al., 1999). But there has been no reported literature regarding the compatibility of polymers with New Zealand's source of bitumen at a microstructural level. Another gap in the research literature relates to the microstructure of polymer modified bitumen emulsion binder. The modified binder after evaporation of the water phase is supposed to result in the same properties of a hot sprayed modified bitumen (Asphalt Institute, 1994). The research investigates this effect, but also goes further and investigates the way that the polymer improves the properties of bitumen, and how they resist stress in the binder and microsurfacing. A technique called confocal microscopy was used to assess the binder and microsurfacing microstructure.

Chapter 2 will cover the technical aspects of bitumen emulsions, polymer modification, and microsurfacing technology to give an overview to understand the critical parameters involved.

The research has been partially funded by the Higgins Group of Companies and Technology New Zealand, and the formulations should be treated as confidential.

1.7 Research Aims and Objectives

1.7.1 Aim

The research aim is to investigate and develop a polymer-modified emulsion based road surfacing (microsurfacing) formulation to a mid-scale prototype stage. A supplementary part of the development was to investigate the polymer-bitumen interactions and how they affect the products end properties by using confocal microscopy.

1.7.2 Research Objectives

- Identify and measure the effects of polymers to meet the performance requirements of the microsurfacing.
- Determine the required effect of emulsifiers and aggregate quality to obtain a rapidly curing microsurfacing.
- Use a combination of qualitative (microscopy) and quantitative (physical testing) techniques to understand the performance enhancing properties of polymer-modified bitumen.
- Compare and relate the test results of the modified bitumen binder and microsurfacing to results from overseas studies.
- Measure and determine the effect of varying the method of adding the polymer to the emulsion.

1.7.3 Research Constraints

Product Constraints

- Bitumen sourced from Marsden Point refinery must be used.
- Meet relevant industry specifications for performance.

Process Constraints

- Prototype emulsions produced using the Higgins laboratory colloid mill.

2. REVIEW OF BITUMEN EMULSION SCIENCE, POLYMER MODIFICATION, AND MICROSURFACING TECHNOLOGY

2.1 INTRODUCTION

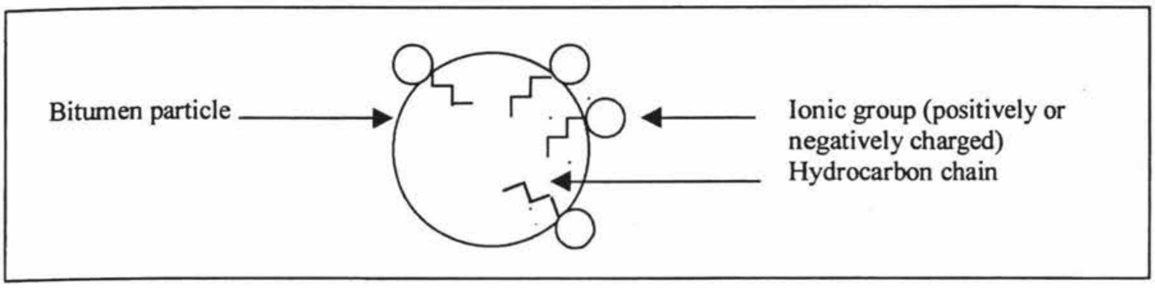
The review consists of three parts. Firstly a review of bitumen emulsion science and technology, raw materials, and production. Secondly, the modification of bitumen emulsion properties and performance by addition of a polymer. The third part gives an overview of the microsurfacing pavement system that the modified emulsions are used in, and covers the design, raw materials and application of the surfacing. The reviews form the basis for understanding the product and its design, and assists in developing the product specifications and initial formulation guidelines.

2.2 BITUMEN EMULSIFICATION

Bitumen and water are immiscible under normal circumstances, but they can be emulsified to produce a homogeneous blend. Suspending bitumen particles in water by means of emulsifying and stabilising agents forms the emulsion. The size of the particles is typically in the range of 1 to 10 μm. Common bitumen contents of an emulsion vary depending on the application, but is usually between 55-75% for road sealing (Asphalt Institute, 1994). Bitumen is normally referred to as the dispersed phase or discontinuous phase while the water phase is referred to as the aqueous, soap, or continuous phase (Lissant, 1974).

Emulsifying agents keep the bitumen droplets in stable suspension and controls the *breaking* time. The surfactant changes the surface tension at the bitumen/water interface; this permits the bitumen to remain in a suspended state. The particles, all having a similar electrical charge repel each other, which aids in their remaining in a suspended state (Asphalt Institute, 1994). Ionic emulsifying agents consist of a long hydrocarbon chain, which has an anionic or cationic functional group at one end. Figure 2-1 illustrates the orientation of the emulsifier on a bitumen droplet.

Figure 2-1 Emulsifier Behaviour on a Bitumen Particle



The object of bitumen emulsions for road surfacing is to make a dispersion of the bitumen in water, stable enough for pumping, prolonged storage, and mixing. Furthermore, the emulsion should break down quickly after contact with aggregate in a mixer, or after spraying on the roadbed. Upon curing, the residual bitumen retains all of the adhesion, durability, and water-resistance of the original bitumen (Asphalt Institute, 1994).

2.3 Advantages of Bitumen Emulsions

Bitumen emulsions have distinct advantages over heated bitumen and the use of solvent (cutback) bitumen (Asphalt Institute, 1994; Baker, 1996; Reed, 1996; Kala et al., 1999):

1. Safety/ Energy conservation/ pollution control
2. Versatility
3. Performance

Worker safety

Emulsions are water based. They have no flash point, and are not flammable or explosive. They do not pose a serious health risk to workers as hydrocarbon fumes are virtually eliminated, and they do not cause severe burns as they are generally applied cold or only heated to about 60°C, or 85°C for high residual spray grades of 68-80% bitumen (Transit, 1994).

Energy Conservation

For cutback bitumen, the solvent is only added to reduce the viscosity of the bitumen to a level where it can be sprayed at a lower temperature. The solvent is expected to evaporate into the atmosphere, and if it does not, the bitumen will retain a lower softening point long after being applied to the road. The use of emulsions can also generate a significant saving in fuel products such as kerosene, naphtha and diesel (Reed, 1996).

Pollution control

Because emulsions carry little if any solvents, hydrocarbon emissions, which lower air quality, are reduced.

Versatility

There are many different applications for emulsions such as spray chip sealing, slurry surfacing, microsurfacing, and other cold mixes. They can also be stored in drums for remote work. They can be used in all instances where hot bitumen is used.

Performance

- Improvement in adhesion to aggregates (better *wetting*, ability to mix well with wet aggregate, and binding is assisted by a physico-chemical process for cationic emulsions).
- Extension of the range of conditions for emulsion application (sealing in marginal conditions).
- Reduced energy costs.
- Reductions in safety related downtime.
- Reduced labour costs with heating.
- Reduced material costs, particularly solvents and adhesion agents.

2.4 Emulsion Classification

Bitumen emulsions are divided into three categories: Anionic, cationic, and non-ionic. These classifications refer to the type of electrical charge that is induced around the bitumen particle. The first two types are primarily used in road surfacing, with the cationic the more favoured option as it has a greater affinity for a variety of solid surfaces and generally break and cure faster (Nealyon & Gillespie, 1994). Further classification is based on how quickly the bitumen will coalesce (reform to basic bitumen). These are rapid set (RS), medium set (MS), and slow set (SS) types (Asphalt Institute, 1994). An RS emulsion has little or no ability to mix with an aggregate, an MS is expected to mix with coarse but not fine aggregate, and an SS to mix with fine or sandy aggregate.

The letter 'C' is used in front of the emulsion type to denote a cationic. Anionic can be denoted with an 'A' at the front of 'RS', but the ASTM specification is to denote the emulsion as anionic or non-ionic if the 'C' is absent. Also numbers are used to indicate the viscosity range of the emulsion i.e. 1 or 2. An 'h' follows certain grades to imply harder base bitumen such as 80/100 pen has been used. An 's' indicates that additional solvent has been added to the emulsion.

Example: cationic rapid set, of viscosity rating 1, and hard grade of bitumen (CRS-1h).

2.5 Raw Materials

Basic bitumen emulsions generally consist of five main materials; bitumen, emulsifier, water, acid or alkali, and additives.

2.5.1 Bitumen

Bitumen is a complex material, but can be defined as a black cementitious hydrocarbon material that is naturally occurring or refined from crude oil (Holleran, 1994). All bitumen show a visco-elastic behaviour, their resistance to deformation being dependent on both the temperature and time during which a force is applied. Only under extreme conditions does a bitumen behave as either a typical elastic solid (low temperature very short loading time) or as a viscous liquid (high temperature, long loading time). Under normal temperature conditions, both viscous and elastic behaviour occurs (Whiteoak, 1990). The common commercially available type of bitumen is petroleum bitumen. The bitumen consists of colloidal dispersed hydrocarbons in crude petroleum and is obtained by refining petroleum crudes. In New Zealand petroleum crude is refined at Marsden Point to produce the bitumen used for road sealing purposes. It is the residue from the vacuum distillation tower at the refinery (Transit, 1993).

Bitumen contains a combination of the following three arrangements by which the carbon atoms are linked with each other (Whiteoak, 1990):

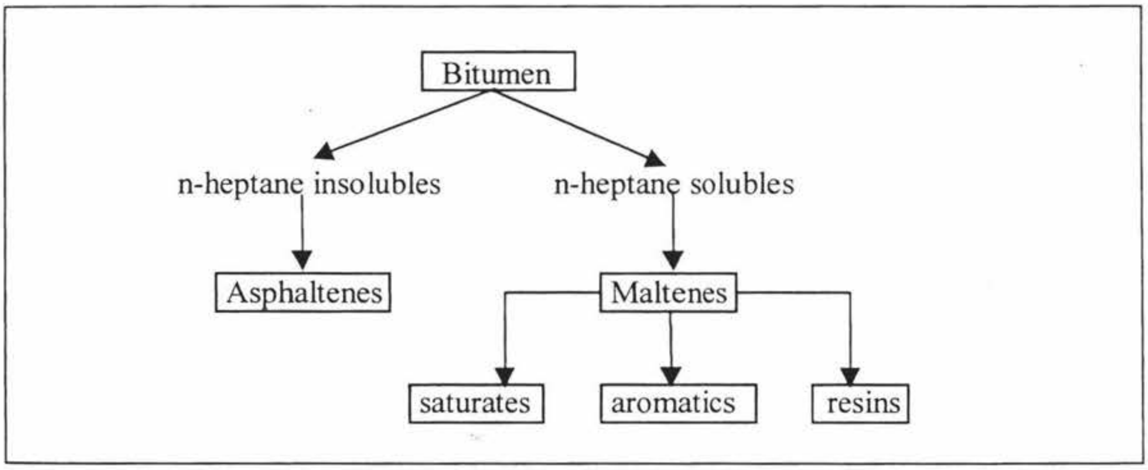
1. Straight or branched chains. Bitumen of this type are referred to as "aliphatic" or "paraffinic".

2. Simple or complex saturated rings. "Saturated" means the highest possible hydrogen/carbon ratio in the bitumen molecules. These bitumen are often referred to as "naphthenic" types.
3. One or more stable six-carbon condensed unsaturated ring structures (benzene, naphthalene). Normally referred to as "aromatic".

Naphthenic bitumen have higher acid values than paraffinic types (West, 1985). Middle Eastern bitumen used in New Zealand usually has a low acid value and high salt content, making emulsification in particular more difficult with the paraffinic nature of the bitumen. The precise composition of the bitumen varies depending on the crude source, the manufacturing process, and subsequent ageing in service (Holleran, 1994).

Bitumen can be separated into four chemical types called saturates, aromatics, resins and asphaltenes by the chemical n-heptane. A schematic is shown in Figure 2-2.

Figure 2-2 Main Chemical Constituents of Bitumen



2.5.1.1 Asphaltenes

Asphaltenes are high molecular weight fractions that are insoluble in n-heptane. They form highly condensed systems, are highly polar and interact strongly (Whiteoak, 1990). They are black or brown amorphous solids and constitute 5% to 25% of the bitumen. Molecular weights of asphaltenes tend to range from 1,000 to 100,000 (Whiteoak, 1990). But, this seems to be a large variation in molecular weight. The asphaltenes content has a large effect on the rheological characteristics of bitumen. Increasing the asphaltenes content produces a harder, higher viscosity bitumen with a lower penetration, and higher softening point (Whiteoak, 1990; Rozeveld et al., 1997).

2.5.1.2 Maltenes

Maltenes are n-heptane solubles. They are often categorised as resin and oil fractions (Whiteoak, 1990).

Resins

Are dark brown in colour, solid or semi-solid, and are very polar in nature. This makes them strongly adhesive. They react as dispersing agents or peptizers for the asphaltenes and the proportion of resins to asphaltenes determines to a degree the solution (Sol) or the gelatinous (Gel) characteristics of the bitumen (Roberts et al., 1991). The molecular weight varies from 500 to 50,000 (Whiteoak, 1990).

Oil Fraction

Further categorised as aromatics and saturates.

Aromatics

Aromatics are the lowest molecular weight naphthenic aromatic compounds. They are non-polar but can be polarised. Aromatics make up the major portion of the dispersion medium for the peptised asphaltenes. They constitute 40 to 65% of the total bitumen and are dark brown viscous liquids. Average molecular weight ranges between 300 to 2,000 (Whiteoak, 1990; Loeber et al., 1998).

Saturates

Are non-polar straight chain and branched paraffins, and alkyl naphthenes. They are viscous oils and straw or white in colour. The average molecular weight is 300 to 2,000, and compounds include waxy and non-waxy saturates. The fraction makes up about 5% to 20% of the bitumen, and contributes to the viscous nature of bitumen (Whiteoak, 1990; Rozeveld et al., 1997).

The constituents have a major effect on the suitability of the bitumen for road sealing, and for improved modification of the bitumen properties such as polymer additives or bitumen emulsification (Piazza et al., 1980; Whiteoak, 1990; Hesp & Woodhams, 1992; Loeber et al., 1998; Lu et al., 1999). In particular, asphaltene levels above 12% lead to emulsion and polymer modification problems (Bouldin et al., 1991; Brule, 1995; Holleran & Reed, 1999).

2.5.1.3 New Zealand's bitumen constitution

Safaniya Bitumen 180/200 pen (Herrington, 1999):

Asphaltenes	14.8%
Aromatics	11.2%
Resins	45.0%
Saturates	29.0%

The aromatic content of 11.2% is considerably less than the typical range proposed by Whiteoak (1990) and Lu et al.(1999). The saturates content of 29% is also considerably higher. The saturates fraction decreases the ability of the maltenes to disperse the asphaltenes and high saturates fractions can lead to increased agglomeration of the asphaltenes (Domke, et al., 1999).

Colloidal Index

Loeber et al. (1998) propose that the bitumen constituents can be expressed as the colloidal index (CI).

$$\mathrm{CI} = \frac{\text{dispersed constiuents}}{\text{Flocculated constituents}} = \frac{\text{aromatics} + \text{resins}}{\text{saturates} + \text{asphaltenes}} \qquad (1)$$

A higher colloidal index (greater than 2.5) means the asphaltenes are more peptised (dispersed) in the oil based medium. Loeber et al. (1998) concluded that a low colloidal bitumen has a connected network structure. Whereas, higher colloidal bitumen is made of individual domains of asphaltene particles which results in bitumen that is more stable when modified (Lu et al., 1999). The presence of resins appears necessary to obtain well-dispersed suspensions, whereas if absent, flocculation takes place and leads to less homogeneous bitumen. Increasing the asphaltene level leads to a more flocculated system and increasing bonds between particles. A network structure will be formed with more elastic behaviour and higher stiffness. Increasing the aromatic oil content leads to a more dispersed and viscous system. The addition of resins homogenise bitumen as they peptise the asphaltenes by forming smaller asphaltene micelles. This indicates that a higher colloidal index is preferable for emulsifying bitumen, as smaller asphaltene micelles will be present because they are better dispersed in the oil phase. The colloidal index of the Safaniya bitumen is 1.3, which is quite low and indicates that stability problems may occur with emulsification, as the asphaltenes will not be well dispersed by the oils.

Resins/Asphaltene Effects

The work by Salou et al. (1998) assessed the stability of bitumen emulsions using the Resins/Asphaltenes ratio (r/a ratio). They contend that a bitumen with a high r/a ratio (>3.0) will disperse better in acid water. A high resin content seems to facilitate the migration of the natural surfactants at the bitumen-water interface. They observed that high r/a ratios tended to give stable emulsions, whereas lower r/a ratios give unstable emulsions. The proposed reason for this is that the higher r/a ratio results in a different distribution of the bitumen polar species at the bitumen-acid water interface during emulsion manufacturing. The Safaniya bitumen that New Zealand uses has a r/a ratio of 3.0 and this indicates that relatively stable emulsions are possible with this bitumen. This result conflicts with that of the colloidal index which indicates that stable emulsions may be difficult. This indicates that there could be other factors having an effect, or that the relationships used are not very reliable and should be treated with caution.

2.5.1.4 Bitumen Manufacture and Grades

The sources of crude oil have different levels of the various constituents and a comparison of bitumen is held in Appendix 2-1. It highlights the great variation that is possible with different crude sources, even those from the same country, and how the bitumen properties vary accordingly. New Zealand's source of bitumen is from the Persian Gulf (Saudi Arabia – Safaniya Crude). Bitumen from different processing routes will also have a different final rheology (Herrington, 1993; Holleran, 1994). Bitumen produced at Marsden Point is by the straight run method and is hardened by propane/butane precipitation (Transit, 1993; Pidwerbesky, 1999).

Penetration Grade Bitumen

Bitumens are available as various types and grades. Bitumen is produced in New Zealand in two grades 44/55 pen and 180/200 pen. Typical paving grades used by civil engineering contractors are 80/100 and 180/200, with the 80/100 grade a blend of 44/55 and 180/200 penetration bitumen. Penetration grade bitumen are specified by penetration and softening point. Penetration is a measurement of the hardness of the bitumen grade. It is measured by a needle of specified dimensions allowed to penetrate into a sample of bitumen, under a known load (100 g), at 25°C, for 5 seconds. The distance the needle penetrates, in decimillimetres (dmm) is termed the penetration (Whiteoak, 1990). The greater the penetration the softer the bitumen. An 80/100 pen bitumen has a penetration of 90 ± 10 i.e. 80 - 100.

2.5.2 Emulsifiers

In bitumen emulsions, surface-active chemicals (emulsifiers), are water-soluble substances that profoundly change the properties of the solvent and the surfaces they contact. They are defined according to the manner in which they dissociate or ionise in water, and are characterised structurally by having a lipophilic, hydrocarbon "tail" and a polar hydrophilic "head" (Dybalski, 1985; Reed, 1996).

Surface active agents in bitumen emulsification owe their physico-chemical behaviour to their property of being absorbed at the interface between liquids and solids phases. They tend to concentrate in an oriented manner, at the interface, so that they turn a majority of their hydrophilic groups toward the more polar phase and most of their lipophilic groups away from the polar phase. The surface-active molecule acts as a bridge between two phases (Asphalt Institute, 1994).

Cationic emulsions possess a positive electro-chemical charge, which is imparted to the bitumen at the time of emulsification. Cationics are based on acid salts of amines prepared from fatty acids. Examples are fatty diamines, imidazolines, amidoamines, and quaternary ammonium compounds. Figure 2-3 shows a diagram of the structure of a cationic molecule where the hydrocarbon chain is about 16-19 carbon units long (Reed, 1996). The fatty amines are converted into a water-soluble salt form by reacting with an acid, most often hydrochloric (HCl), but H_2SO_4, HNO_3, Acetic acid, and sometimes

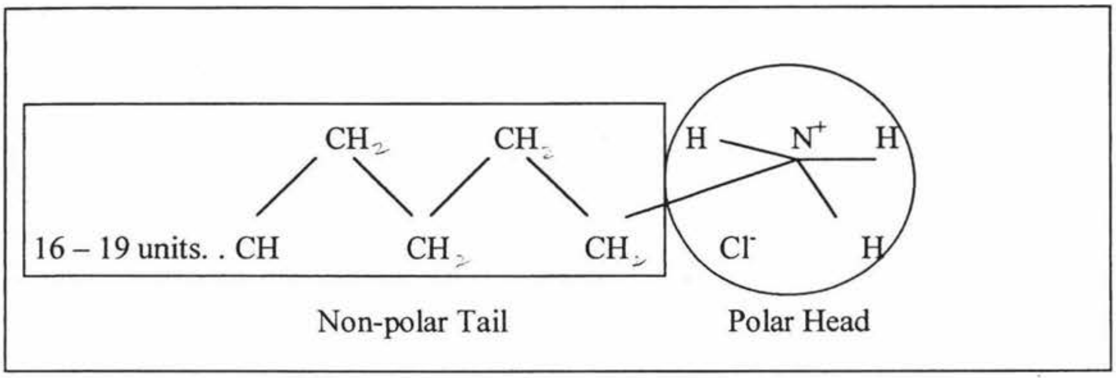
H_3PO_4 are used. The quaternaries are usually water-soluble as produced and do not require an acid (Reed, 1996).

The reaction to produce the amine salt is shown below:

$$R - NH_2 + HCl \longrightarrow R - NH_3^+ + Cl^-$$

Fatty amine + hydrochloric acid ⟶ Amine hydrochloride

Figure 2-3 Cationic Emulsifier



2.5.2.1 Cationic slow set (CSS) emulsifier characteristics

These emulsifiers are used for slurry surfacing mixes due to the slow setting nature of the emulsifier allowing sufficient mixing with fine aggregate before setting. Slow set emulsifiers usually contain cyclic hydrocarbon groups, such as lignin, and rosin derivatives. These "bulky" emulsifiers are unable to orient themselves in orderly close-packed molecular films around the emulsion droplets. They tend to stabilise the emulsion by clumping together as aggregates that act as barriers between the bitumen. The emulsifier concentrations required are generally above the critical micelle concentrations and serves to explain the usual ability of CSS emulsions to withstand high dilution with water together with good stability retention (Lissant, 1974).

2.5.2.2 Emulsifier concentration and solution pH

Low and medium setting emulsifiers tend to be 0.8 – 1.5% of the total emulsion and require a soap solution pH of normally 2.0 – 7.0 (Holleran & Reed, 1999). Emulsifier levels above 1.5% tend to result in free emulsifier in the water phase, which is not absorbed onto the bitumen. Instead the free emulsifier will be absorbed more quickly onto the surface of the aggregate than the bitumen, and this modifies the surface charge of the aggregate and reduces its reactivity to the bitumen droplets. The result is a slower rate of cohesion development in cold mix surfacings (Engman et al., 1998).

2.5.3 Water

Water wets, dissolves, adheres to other substances, and it moderates chemical reactions. These aspects are important to producing a good emulsion (Asphalt Institute, 1994). Water can adversely affect emulsion properties because of impurities, either in solution or colloidal suspension. The presence of ions is the main factor concerning water quality for emulsions (Dybalski, 1985). Calcium and magnesium ions assist in making a more stable cationic emulsion, whereas the presence of phosphate and carbonate ions form insoluble salts with amine hydrochlorides present in cationic emulsifiers (Clark, 1998). The water supply used for production purposes at Higgins is artesian bore water generally higher in magnesium ion concentrations, although there are no figures available.

2.5.4 Acids

Acids are used to ionise cationic heads of emulsifiers to allow dispersion in water. Hydrochloric acid is most commonly used in the industry (Whiteoak, 1990) but other acids such as phosphoric, and acetic acid are sometimes used. Acidity and pH can have a major impact on emulsion properties such as settlement and binder cohesion and is therefore a key factor to be controlled during production.

2.5.5 Additives

Various additives can be added to an emulsion to improve certain performance aspects, and are listed below (Whiteoak, 1990):

- Kerosene – small amounts can reduce the tendency of bitumen with high specific gravity to settle, but increases the emulsion viscosity and softens the bitumen.
- Salts - such as calcium chloride can be added in very small amounts to also reduce settlement by increasing the specific gravity of the aqueous phase. They also reduce the surface tension of the water. But, too much will destabilise the emulsion causing early breaking (Menon & Wason, 1988).

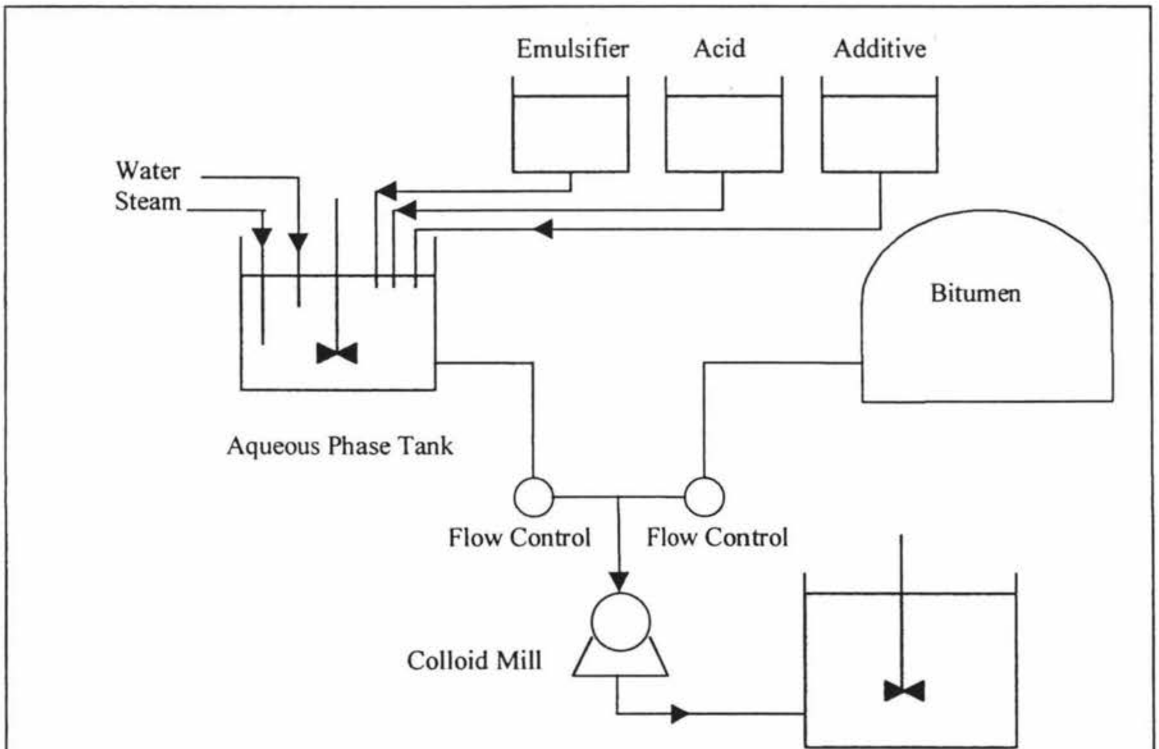
- Polymers – Addition of thermoplastic polymers reduce the bitumen temperature susceptibility allowing better performance at higher and lower temperatures, and increases the strength of the bitumen to help resist deformation.

2.6 Emulsion Production

The production of a bitumen emulsion involves the preparation of the emulsifier solution and the bitumen phase. The cationic emulsifier is generally mixed with a percentage of the total water that has acid added and is heated to aid dispersion of the emulsifier. Once the concentrate is thoroughly mixed the remaining water is added and the pH adjusted to the required level with further acid. Other additives such as a salt or *latex* polymer can also be added to the aqueous phase.

Bitumen makes up the dispersed phase and is known as the binder. The two streams are fed separately but simultaneously into a blender or mill device to form the emulsion. A schematic diagram of the production process is shown in Figure 2-4.

Figure 2-4 Schematic Diagram of an Emulsion Production Process



There are several devices available to produce an emulsion (Walstra, 1983). The key types of devices are listed as follows:

1. Stirring (high speed Silverson mixer)
2. Homogenizers
3. Colloid mill

2.6.1 Stirring

High-speed blenders such as Silverson mixers are more commonly used for forming emulsions in the food industry (McClements, 1999) but have been used to produce bitumen emulsions in several laboratory studies and patents (Sabbagh & Lesser, 1998; Al-Sabagh et al., 1997; European Patent 561472A1). But, there have been no references found that refer to any large industrial scale manufacture using high-speed mixers. The rapid rotation of the stirring blade generates a combination of longitudinal, rotational, and radial velocity gradients in the liquids which disrupts the interface between the oil and water, causing the liquids to become intermixed, and breaks down the larger droplets. The average droplet size typically produced in high-speed blenders is about 2 to 10 μm in diameter (McClements, 1999).

2.6.2 Homogenizers

In a homogenizer the liquid streams are brought under high pressure by a positive pump and are forced through a narrow adjustable valve slit; due to the pressure, the valve opens against a spring and the liquids obtain a high velocity. The combined liquids experience a combination of intense shear, cavitational, and turbulent flow conditions and cause the larger droplets to be broken down into smaller ones. The residence time of the emulsion in the homogenizer is less than 0.1ms and the method is more efficient at emulsifying liquids with a viscosity less than 1,000 centipoise (cP) (McClements, 1999). Homogenizers are more effective at reducing the size of pre-existing coarse emulsions prepared by blending than by creating an emulsion from two separate liquid phases. A minimum droplet size of 0.1μm can be produced with the method. High-pressure homogenizers are most commonly used in the food industry for producing fine emulsions and no literature has been found that indicates the use of the method for bitumen emulsions. Possible reasons are that the bitumen phase is usually of a viscosity of about

200 cP and makes the method less efficient than colloid mills (Walstra, 1983; McClements, 1999) and the residence time of the emulsion may be too quick to allow adequate coating of the bitumen droplets with emulsifier.

2.6.3 Colloid Mills

The general method of emulsification using a colloid mill involves concurrent streams of molten bitumen and soap solution directed by pumps into the intake of the colloid mill. The materials flow through a narrow gap between two disks: the rotor (a rotating disk) and the stator (a static disk). The rapid rotation of the rotor generates a shear stress in the gap, which causes the larger droplets to be broken down into smaller ones. The intensity of the shear stresses can be altered by varying the thickness of the gap between the rotor and stator (from about 50 to 1000 μm), and varying the rotation speed (from about 1,000 to 20,000 rpm) (Whiteoak, 1990; McClements, 1999). The individual droplets of bitumen are coated with the emulsifier, which gives the surface of the droplets an electrical charge, and the resulting electrostatic forces prevent the droplets from coalescing. Colloid mills are extensively used for producing bitumen emulsions for the roading industry and Higgins have a laboratory sized Charlotte G-3 colloid mill and a full size G-75 mill at the Napier production facility. A bitumen emulsion can be passed through a colloid mill a second time to produce a finer particle size; and has been performed by Holleran (1995) and Hermadi & Strirling (1998). But this process is not seen as economic in the industry.

The rest of the production and processing review aspects of bitumen emulsions relates to the colloid mill method of production.

2.6.4. Processing Variables

There are several processing variables that are important in the production of bitumen emulsions (Whiteoak, 1990; Durand, 1994):

1. Rotational speed of colloid mill
2. Gap between rotor and stator
3. Mill pressure
4. Temperature of both phases before emulsification

2.6.4.1 Rotational speed and mill gap

Both of these variables contribute to shear rate variation in the gap of the colloid mill. The higher the shear rate the smaller the particles created and a less polydisperse particle size distribution. This can influence product characteristics such as emulsion viscosity and storage stability. The gap setting is usually between 0.17 to 0.50 mm and this creates an emulsion with an average bitumen particle size between 1 to 10 μm (Asphalt Institute, 1994).

2.6.4.2 Mill pressure

Colloid mills typically operate at atmospheric pressure but they can be operated above atmospheric pressure by increasing pressure on the exit line. This can result in a decreased particle size and more stable emulsions (Durand, 1994). Also bitumen contents of greater than the theoretical limit of 74% can be achieved this way. Mills operated under pressure require a heat exchanger to cool the emulsions below 100°C to avoid evaporation and coalescence. The Higgins colloid mills both operate at atmospheric pressure.

2.6.4.3 Temperature of both phases before emulsification

The viscosity of the bitumen should not exceed 200 cP and the typical temperature required to achieve this is 100°C to 150°C. A higher bitumen temperature will produce a lower bitumen viscosity and a smaller particle size (Whiteoak, 1990).

The soap phase temperature is partially dependent on the temperature at which the emulsifier will disperse and the resulting emulsion exit temperature. Soap temperatures between 30°C to 60°C are typical.

The exit temperature is directly controlled by the two phases entering the mill. Exit temperatures above 92°C can lead to coalescence of the emulsion and typical exit temperatures for emulsions with 60% to 65% bitumen contents are 78°C to 85°C.

2.7 Emulsion Formulation Characteristics

The end use of the bitumen emulsion determines its main properties. But in general the emulsion should be mechanically stable to facilitate storage, handling and transport without significant deterioration in dispersion quality. The chemical stability of the emulsion varies depending on the type of aggregate it is to be mixed with, or how quickly it is required to break after application. Emulsion viscosity is critical as it determines the method and thickness of application to the substrate concerned. The key properties of the emulsion are summarised as (Hulshof, 1985; Whiteoak, 1990; Reed, 1996):

1. The stability of the emulsion;
2. The breaking process;
3. The adhesion of the emulsion;
4. The cohesion development;
5. The viscosity of the emulsion.

2.7.1 Emulsion Stability

The stability of the emulsion involves storage stability and in particular its settlement or sedimentation, flocculation, and coalescence (Whiteoak, 1990).

2.7.1.1 Storage stability

The storage stability of the emulsion is initially indicated by the settlement of the emulsion, resulting in a bitumen lean upper layer and a bitumen rich lower layer. Settlement occurs as a result of gravity acting upon the denser discontinuous bitumen droplets. The velocity of the downward movement of the droplets can be estimated by Stokes Law, which states the settlement velocity (V) as (Whiteoak, 1990):

$$V = \frac{2Gr^2(\rho_1 - \rho_2)}{9\eta} \qquad (2)$$

Where G = Gravitation acceleration (ms^{-2})

r = Particle radius (m)

η = Viscosity of continuous phase ($kg\ m^{-1}s^{-1}$)

ρ_1 = Density of dispersed phase (kgm^{-3})

ρ_2 = Density of continuous phase (kgm^{-3})

In addition to gravity, repulsive and attractive forces act upon the emulsion. Repulsive forces occur between the electrostatic double layers on the droplets created by the ionised emulsifier. The attractive force is associated with the mass of the droplets (Whiteoak, 1990). If the droplets are large, or if the distribution of particle sizes is wide, the attractive force becomes a repulsive force. The sedimentation of an emulsion determines how long it may be stored. This is particularly important if the emulsion is to be stored for any lengthy period of time.

2.7.1.2 Flocculation

After settlement bitumen droplets agglomerate into clumps creating a floc, this is referred to as flocculation (Whiteoak, 1990). At this stage the process is reversible and the flocks can be broken up by gentle agitation.

2.7.1.3 Coalescence

The coalescence of flocculated particles is a function of the surface charge and factors such as shearing and temperature. This stage is irreversible, in which the flocks fuse together to form larger globules. These globules are no longer able to be held in solution and settle out. When this occurs throughout the emulsion the emulsion is deemed broken, which is visually characterised by a colour change from brown to black.

2.7.2 Breaking process

The emulsion contains emulsifier molecules in both the water phase and on the surface of the bitumen droplets. The ions around the droplet are attracted to the negative ions on the aggregate surface, which weakens the charge on the surface of the droplets, which initiates the breaking process. A point is then reached where the charge on the droplets is so depleted that rapid coalescence takes place and the bitumen is liberated to adhere to the aggregate. The effects of pavement temperature, air temperature, humidity, emulsifier type, aggregate type, and wind also affect the breaking process (Asphalt Institute, 1994).

The cure of the emulsion film is the development of mechanical properties of the bitumen. A continuous film holds the aggregate in place with a strong adhesive bond. The cure rates are dependent on the water content, rate of evaporation and the diffusion of water through the curing binder (Holleran, 1999).

2.7.3 Emulsion Adhesion

Adhesion is the capacity to provide both the wetting of the aggregate surface by the binder and its bonding to the mineral surface and the base pavement (Chazel & Lozier, 1999). A prime requirement is that bitumen 'wets' the surface to create a maximum contact area. With dry substrates the 'critical surface tension of wetting' of the aggregate is usually high enough to ensure that the bitumen spreads easily over the surface. However, with damp aggregate, the 'wetting' can only occur if the balance of the interfacial energies favours wetting by the bitumen. Cationic emulsifiers provide immediate bonding between the aggregate and the binder due to their chemical affinity (Nealyon & Gillespie, 1994).

2.7.4 Cohesion

The cohesion of the binder is its capacity to withstand forces, which tend towards internal breaking of the binder (Chazel & Lozier, 1999). Cohesion should develop in a pavement mix after the emulsion has broken and the bitumen has formed an adhesive bond to the aggregate. Development of early cohesive strength is particularly important as it enables a pavement surfacing to be opened to traffic as soon as possible. The type and concentration of emulsifier have a major influence on the cohesion development.

Overall, the quality of the bond between the bitumen and aggregate depends on the following factors (Whiteoak, 1990; Asphalt Institute, 1994; Glet, 1999):

1. The type and amount of emulsifier;
2. The bitumen grade and constitution;
3. The pH of the emulsifier solution;
4. The particle size distribution of the emulsion;
5. The aggregate type and cleanliness.

2.7.5 Viscosity

The viscosity is important because the majority of emulsions are applied in the form of a spray, particularly for chip sealing in New Zealand (Transit, 1994). The distribution of an emulsion from a spray bar is a function of the viscosity of the emulsion. Additionally for slurry or Microsurfacing systems the viscosity must be high enough to prevent runoff from the aggregate and prevent settlement problems, but must not be too high or mixing problems can occur.

2.8 Characteristics of General Emulsion Stability

The following factors favour emulsion stability (Shaw, 1992; Salou et al., 1998; Holleran, 1999):

1. Low interfacial tension
2. Zeta Potential
3. Electrical double layer repulsion's
4. Narrow droplet size distribution
5. High viscosity

2.8.1 Low Interfacial Tension

The adsorption of surfactant at oil-water interfaces causes a lowering of interfacial energy, therefore facilitating the development and enhancing the stability of the large interfacial areas associated with emulsions. In emulsion manufacture, aromatics and resins have a lower interfacial tension (IFT) with water than asphaltenes and saturates. This is possibly due to the increased polarity of the aromatics and resins as they have an increased affinity with the polar aqueous phase, hence reducing IFT (Al-Sabagh et al,. 1997). This seems to indicate that increasing the aromatics and resins content of the bitumen results in an increased stability of its emulsion with water. Comparing the aromatic and resins content of the bitumen used by Al-Sabagh et al. (1997) and New Zealand's bitumen gives the following result:

Aromatic-Resin content (Al-Sabagh) = 82.3%
Aromatic –Resin content (New Zealand) = 56.2%

The difference is 26%, and possibly indicates that the bitumen used in New Zealand is not entirely suitable for producing emulsions that are stable to flocculation and coalescence effects without the aid of additives or increased emulsifier levels to help lower the interfacial tension. To a certain extent this phenomenon has been observed in emulsions that Higgins have produced and high settlement results are common.

2.8.2 Zeta Potential

Zeta Potential is the electrical potential between the surface of the bitumen particle and the bulk solution. The emulsifier adsorbed onto the surface of the bitumen determines zeta potential. The form of the double layer around the bitumen droplet depends on the concentration and ionic density of the emulsifier and the pH. A large zeta potential indicates a greater double layer, faster movement and greater repulsion between particles. Larger repulsion's produce stable emulsions (Reed, 1996). Zeta potential for cationics range from +128 millivolts (mv) to +18 millivolts (mv) (West, 1985).

2.8.3 Electrical Double Layer Repulsions

Inter-particle repulsion due to the overlap of similarly charged electric double-layers is an important stabilising mechanism in o/w emulsions (Shaw, 1992; Holleran, 1999). When ionic emulsifying agents are used, a lateral electric double layer repulsion can prevent the formation of a close packed film. This film-expanding effect can be reduced by using a mixed ionic plus non-ionic film and/or increasing the electrolyte concentration in the aqueous phase (Reed, 1996).

2.8.4 Narrow Droplet Size Distribution

Larger droplets are less unstable than smaller droplets due to their smaller area-to-volume ratio, and will tend to grow at the expense of the smaller droplets. If this continues, the emulsion eventually breaks. Emulsions with uniform droplet sizes are less prone to this effect.

2.8.5 High Viscosity

A high Newtonian viscosity retards the rates of creaming, settlement, and coalescence. However, the overall rheological properties of a viscous emulsion may not be acceptable, such as causing difficulty in mixing. The end product use of the emulsion must be considered in the formulation.

2.9 Modification of Bitumen Emulsion Properties

The basic properties of an emulsion such as viscosity, storage stability, breaking rate and particle size distribution can be modified by (Whiteoak, 1990):

- Changing the grade, concentration or origin of the bitumen;
- Changing the emulsion formulation;
- Changing the type of emulsifier and/or its concentration.

2.9.1 Increasing the Viscosity of the Emulsion

Increasing the bitumen content, modifying the aqueous phase, increasing the mill flow rate, and decreasing the bitumen viscosity can increase the viscosity of an emulsion.

Increasing the bitumen content

Bitumen concentrations over 65% induce a rapid increase in viscosity which can help minimise settlement of the emulsions, and prevent run-off on application to the road surface. But a higher viscosity can severely reduce spraying performance. But this is not applicable for slurry or microsurfacing systems, as the bitumen content is limited to 60% to 65%.

Modification of the aqueous phase

Decreasing the acid content, or increasing the emulsifier content can increase the viscosity.

Increasing the flow rate through the colloid mill

At bitumen contents below 65% the viscosity is virtually independent of flow rate (Whiteoak, 1990). But at higher levels the bitumen droplets are packed more closely, inducing a change in the particle size distribution and increasing the viscosity.

Decreasing the viscosity of the bitumen

Lowering the bitumen viscosity before it enters the mill reduces the particle size of the emulsion and tends to increase the viscosity of the emulsion.

2.9.2 Decreasing the Viscosity of the Emulsion

To reduce the viscosity the following changes can be made (Whiteoak, 1990):

- Reduce the bitumen content. But this results in the need to apply a greater amount of emulsion (which increases costs) to achieve the same residual bitumen coverage as cutback bitumen.
- Decrease the flow rate through the colloid mill.
- Modify the emulsification formula. By increasing the acid content, or decrease the amine content. But must keep in mind that the aqueous phase properties have a large effect on the other emulsion properties.

2.9.3 Changing the Emulsion Breaking Rate

The breaking rate is strongly dependent on the aggregate type and size distribution; but other modifications are (Dybalski, 1985; Whiteoak, 1990):

Modify the aqueous phase composition

The breaking rate of the emulsion can be increased by reducing the acid content, increasing the emulsifier content or by decreasing the ratio between the acid and emulsifier contents.

Increasing the bitumen content

An increase in the bitumen content increases the breaking rate of the emulsion; the rate of increase is dependent on the aqueous phase composition.

Other parameters

Additional influences on the breaking rate are:

- Type of emulsifier used;
- Particle size distribution, the finer the particle size the smaller the dispersion the slower the breaking rate;
- Temperature, the higher the ambient temperature the faster the breaking rate of the emulsion (faster evaporation of water from the emulsion).

2.9.4 Storage Stability

A deficiency in the storage stability of an emulsion usually appears in the form of settlement for which there are several causes (Whiteoak, 1990; Holleran, 1999):

Bitumen Specific Gravity

Bitumen with high specific gravity will tend to settle when emulsified. The problem can be reduced by:

- Adding kerosene to the bitumen before emulsification to reduce the specific gravity, this will however result in an increased emulsion viscosity and a reduced viscosity of the binder on the substrate.
- By increasing the specific gravity of the aqueous phase by the addition of a salt such as calcium chloride.

Emulsion Viscosity

Low viscosity emulsions are more prone to settlement than high viscosity emulsions because the particles have more freedom to move. But if the viscosity is increased too much the emulsion will not spray evenly for chip sealing operations. But a higher viscosity is not too critical for applications such as slurry sealing or microsurfacing.

Electrolyte content

The presence of electrolytes in the bitumen can reduce the storage stability of an emulsion. In cationic emulsions a high sodium concentration can induce premature breaking during storage (Dybalski, 1985). This can be counteracted by the addition of a salt to the aqueous phase.

Particle Size Distribution

The size distribution of the emulsion droplet is dependent on the interfacial tension between the bitumen and aqueous phase (a lower interfacial tension results in the bitumen dispersing easier) and on the energy used in dispersing the bitumen. For a given mechanical input, harder bitumen (80/100 pen or less) will produce coarser emulsions, and high penetration (180/200) or cutback bitumen finer emulsions. Bitumen emulsions with a broad spectrum of particle sizes are more prone to settlement than those with a narrow size distribution (Tausk & Wilson, (1981); Holleran, 1999). This is due to large particles settling more quickly because of the repulsion forces between the particles. Hence, emulsions with a relatively narrow particle size distribution are more storage stable.

2.10 POLYMER MODIFIED BITUMEN AND EMULSIONS

2.10.1 Polymer Modified Bitumen

The limits of mechanical stability of road surfacing are often exceeded and this results in damage such as cracking and deformation. To control these problems, road surfacing requires:

- Better resistance to fatigue,
- Increased resistance to permanent deformation,
- Greater flexibility at low temperatures,
- Higher resistance to stone loss and abrasion,
- Adequate resistance to ageing.

To obtain these performance characteristics, modification of the bitumen's basic properties is needed. Polymers are ideal bitumen modifiers because (Exxon, 1996):

- Polymers and bitumen are basically compatible, as they are both largely polar materials.
- Polymers can be engineered to provide specific characteristics.
- Polymers added to bitumen result in a material with hybrid characteristics - a bitumen composite.

Improvements made by using polymers to modify bitumen include (Exxon, 1996; Morgan & Mulder, 1995):

- Increasing the viscosity of the binder in service,
- Reducing the thermal susceptibility of the binder,
- Widening the range of plasticity,
- Increasing the cohesion of the bitumen,
- Increasing the resistance to permanent deformation,
- Improving the resistance to fatigue at low temperatures,
- Improving binder-aggregate adhesion,
- Slowing down the ageing process of bitumen.

2.11 Types of Polymers Used

There are two types of polymers used to modify the properties of bitumen:

1. Plastomers - normally based on ethylene *copolymers*. Examples are Ethylene Vinyl Acetate (EVA), Ethylene Methyl Acrylate (EMA).
2. Elastomers - normally consisting of styrene-block copolymers. Key examples are Styrene Butadiene Rubber (SBR), Styrene Butadiene Styrene (SBS), Neoprene, and Natural Rubber

2.11.1 Plastomers

Are based on random copolymers of ethylene. They are rigid polymers due to their hydrocarbon backbone and provide stiffness to the bitumen. Plastomers are generally referred to as semi-crystalline polymers. This means that there is a degree of regularity in the molecular structure. Plastomers can be classed by their melt transition temperatures (T_m), which means the temperature at which crystalline elements such as ethylene go from a solid to a liquid state (PIARC, 1999). Plastomers provide good low temperature resistance to cracking.

2.11.2 Elastomers

Elastomers can be stretched to many times their original length and return back to their original shape without permanent deformation. They are amorphous polymers, meaning that they do not exhibit any structural order. Their arrangement of molecules tangle around each other in a jumbled mess. Elastomers have glass transition temperatures (T_g) below room temperature. Glass transition temperature is the temperature below which chain motion in the polymer is frozen in. It effectively means that above its T_g the elastomer is soft and pliable, and below it becomes hard and glassy (Herman, 1996). Neoprene, natural rubber, and SBR are referred to as thermoplastic rubbers. But SBS, SIS are referred to as rigid thermoplastic elastomers as they are block copolymers. This means both ends to a rigid material such as styrene chemically bond the elastomer segment, which is hard at room temperature. Elastomers provide greater high temperature resistance to pavement deformation.

A network formed by the polymer with the bitumen achieves improved binder properties. This network is composed of flexible branches linked together by thermo-reversible bonds. The primary factors affecting the formation of a polymer network, and to give the improvement in binder performance are (Brule, 1995; Morgan & Mulder, 1995; Exxon, 1996):

- Bitumen composition, in particular asphaltene content.
- Compatibility between the bitumen oils and resins fractions and the flexible polymer branches.

The choice of polymer to use depends on the environmental conditions, topography, and traffic loading the road surface is subject to. Exxon (1996) state that plastomeric polymers have been found to be compatible with paraffinic, naphthenic and some aromatic bitumen, while elastomeric polymers have been found to be compatible with aromatic bitumen. But, the reasons why this is so are not documented.

2.12 Interactions During Manufacture

When the polymer is added to hot bitumen, the maltene components immediately start to penetrate into the polymer particles, causing (in the instance of SBS polymer) the styrene and butadiene domains of the polymer to become solvated and swollen (Mulder & Morgan, 1995). The physical form of the polymer at this stage is important, as the dissolution of it is largely dependent on its surface area. The greater the surface area, the faster the dissolution process will proceed. Dissolution is easy to achieve with finely divided polymer forms such as powder in a low shear mixer. If the polymer is in the form of 3 mm pellets, it is necessary to reduce the particle size as quickly as possible, this can be achieved by using a high shear disintegrator.

The uptake of the maltenes by the polymer generally amounts to 6 to 9 times the mass of the polymer (polymer rich phase). Blends of bitumen and polymer are not necessarily always homogeneous and single phase, and on cooling a two-phase system can become apparent. The second phase is made up of asphaltenes and the balance of the maltenes (Mulder & Morgan, 1995; Rozeveld, et al., 1997).

The key parameters influencing the mixing process include:

- grade of polymer,
- physical form of polymer,
- nature and grade of bitumen,
- type of equipment (low shear or high shear).

2.12.1 Grade of polymer

The molecular weight of the polymers is an important consideration, as very high values will generally cause more viscous and unworkable blends. For SBS there are linear and radial polymer types, with the radial having a much higher molecular weight and is more difficult to process.

2.12.2 Physical form of polymer

Polymers can be in powdered, pellet, or liquid form depending on the polymer type and grade. Powdered and liquid forms are easy to disperse with low shear equipment. But pellets require physical size reduction (Exxon, 1996).

2.12.3 Nature and grade of bitumen

A high maltenes content and high aromatics content in bitumen will facilitate swelling of the polymer to a greater extent than those with high asphaltene content. This is viewed as beneficial for low shear mixing with powdered polymers (Mulder & Morgan, 1995). Low viscosity bitumen aids pre-dispersion of the polymer in the bitumen and speeds the penetration and swelling of the polymer particles. The temperature of the bitumen is usually $170^{O}C$-$190^{O}C$ when adding the polymer, any higher can lead to viscosity increases and degradation of the polymer.

2.12.4 Mixing equipment

Low shear – facilitates swelling and dissolving of the polymer by the bitumen.

High shear – physically reduces the polymer particles, leads to faster dispersion and solution.

Higgins Contractors has only low shear blending equipment so the range of polymers available is restricted to powdered, or easily dispersed pellet forms, or latex's.

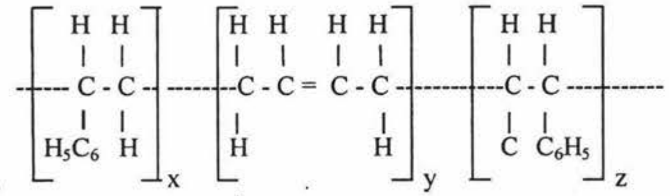
2.13 Elastomeric Polymers

2.13.1 Styrene Butadiene Styrene (SBS)

Structure: Tri-block copolymer.

- SSSSSSSSSS - BBBBBBBB - SSSSSSS -

styrene butadiene styrene



$$-\left[\overset{H}{\underset{H_5C_6}{C}} - \overset{H}{\underset{H}{C}} \right]_x - \left[\overset{H}{\underset{H}{C}} - \overset{H}{C} = \overset{H}{C} - \overset{H}{\underset{H}{C}} \right]_y - \left[\overset{H}{\underset{C}{C}} - \overset{H}{\underset{C_6H_5}{C}} \right]_z -$$

An amorphous thermoplastic, it has an atactic structure as butadiene lacks the ability to crystallise. The copolymer is produced by a sequential operation of successive polymerisation of styrene and butadiene (Brydson, 1989).

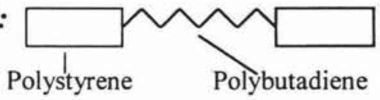
The glass transition temperature (T_g) of styrene = 100°C, and for butadiene = -90°C.

T_g of copolymer = -55°C.

The polymer is available in powdered form for low-shear blending equipment.

There are two key types used for bitumen modification - linear, and radial.

Linear SBS:

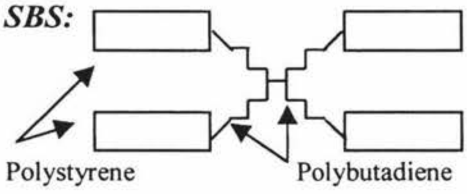


Its number molecular weight (M_n) is approximately 104,000 (A dimensionless quantity)

Styrene content typically 29%

Butadiene content typically 71%

Radial SBS:



Molecular weight approximately 204,000

Styrene content typically 30%

Butadiene content typically 70%

SBS obtains its strength and elasticity from a physical rather than chemical cross-linking of the molecules into a 3-dimensional network. The physical cross-links result from the inherent incompatibility between mid-blocks and the styrene end blocks. The different blocks tend to separate into discrete phases, but are chemically linked. Polystyrene end blocks impart strength, and the butadiene mid-blocks provide elasticity (Morgan & Mulder, 1995).

The main differences between linear and radial SBS is that radial grades have a much higher molecular weight and subsequently are much more viscous. This makes them more difficult to incorporate into the bitumen and maintain an acceptable stability; also they can be too viscous to effectively emulsify the bitumen.

SBS improves:

- Ductility of pavements (more flexible and crack resistant at low temperature)
- Elasticity of the binder at high temperatures, reduced rutting
- Aggregate retention
- Binder softening point to reduce flushing

Network effects of SBS

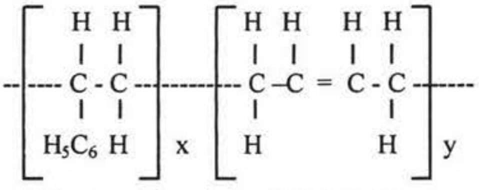
On addition of SBS to bitumen, oily maltenes are absorbed by the polymer, which results in swelling and extension of the polymer, which swells to 6 - 9 times its initial volume. In a 2-phase system this is referred to as the polymer rich phase, and if this phase is sufficiently extended will become macroscopically continuous throughout the total blend. This happens at about 3 - 8% concentration of the polymer into the bitumen. Formation of the continuous network is usually evidenced by the S-shaped softening point vs polymer concentration curve (Morgan & Mulder, 1995).

Elastic networks form upon cooling i.e. <70°C if sufficient polymer is available, usually at over 3%, and [illegible] that the bitumen is compatible. Then the styrene blocks tend to associate into domains throughout the bitumen and link together.

2.13.2 Styrene Butadiene Rubber (SBR)

Structure: Linear random copolymer

- - - SSBBSBBSBSSSBBSBBB - - -



$$\left[-\mathrm{CH}(\mathrm{C_6H_5})-\mathrm{CH_2}-\right]_x-\left[-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\right]_y$$

Polystyrene Polybutadiene

SBR has an amorphous structure; it lacks the ability to crystallise, as the chain mobility is not limited.

Glass Transition temperature (T_g) = - 45°C.

Manufactured by emulsion polymerisation (latex) so is available in an aqueous form (Feldman & Barbalata, 1996).

SBR is a high molecular weight copolymer, approximately 175,000.

Typical styrene content	: 24%
Typical butadiene content	: 76%

SBR improves:

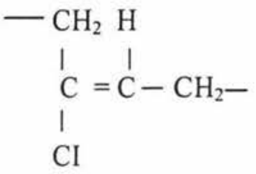
- Ductility of pavements (more flexible and low temperature crack resistant)
- Elasticity of the binder at high temperatures, reduced permanent deformation
- Aggregate retention
- Binder softening point to reduce flushing

SBR network effects

At a concentration of 1%, SBR acts like a dispersed polymer. The concentration is small enough that it does not significantly affect the rheological properties. At 2% to 3% SBR begins to form a localised network structure (Lee et al., 1997). At contents greater than 3% the local networks begin to interact forming a continuous network throughout the bitumen. This network acts as a support structure for the bitumen, resisting deformation. The modified bitumen viscosity increases at higher polymer contents due to the increasing density of the global network.

2.13.3 Neoprene (Polychloroprene)

Structure: Polymer



$$-CH_2-C(Cl)=C(H)-CH_2-$$

Trans – 1,4 polychloroprene (the most common produced).

Produced by emulsion polymerisation.

Molecular weight is approximately 100,000 for fluid grades of the material.

$T_g = -43°C$ $T_m = 45°C$

It is available in latex form for low-shear blending. Neoprene is the common name used and in bitumen the polymer improves:

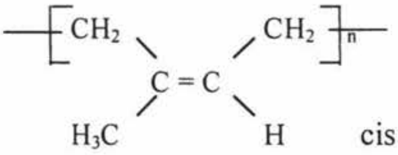
- Aggregate retention
- Resistance to cracking
- Permanent deformation

At usual ambient temperature the rubber exhibits a measure of crystallinity. Hence, both the raw and cured polychloroprene have higher tensile strength due to stress-induced crystallisation (Feldman & Barbalata, 1996).

The polymer has excellent resistance to solvents, weathering and oxidation, and to ozone attack compared to natural rubber. But has poor low temperature properties due to crystallisation. The density of polychloroprene is high (1230 kgm^{-3}) and this can increase the price of the elastomer on a volume basis (Feldman & Barbalata, 1996).

2.13.4 Natural Rubber (Polyisoprene)

Natural rubber is a diene polymer, meaning that it has a carbon-carbon backbone.



cis – 1,4 Polyisoprene

The polymer can be harvested from the sap of the Hevea Tree or synthesised by Ziegla-Natta polymerisation. Natural rubber is highly amorphous, with a molecular weight of 200,000 to 500,000. It's T_g is around $-70^{\circ}C$, so it has good low temperature properties (Brydson, 1989).

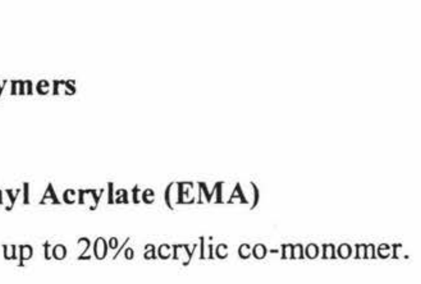
The polymer has high elastic properties so it can resist stone loss in road surfacing. But, it imparts small stiffness properties compared to SBS, SBR or plastomer polymers. The high molecular weight of natural rubber gives rise to very high viscosity when added to hot bitumen and should not exceed about 1% (Whiteoak,1990; Transit,1993).

2.14 Plastomeric Polymers

2.14.1 Ethylene Methyl Acrylate (EMA)

Copolymer containing up to 20% acrylic co-monomer.

Structure:



$$-\left[\begin{matrix} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C} - & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{H} \end{matrix}\right]_x - \left[\begin{matrix} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C} - & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{COOR} \end{matrix}\right]_y -$$

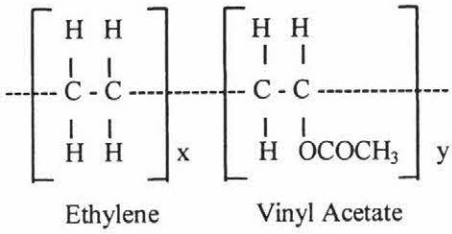
$R = CH_3$ or C_2H_5

Prepared by free radical, high-pressure polymerisation technique.

Ethylene is crystalline but the copolymerisation processes will likely cause irregularity of the overall molecule, so EMA is probably semi-crystalline. EMA has better thermal and abrasion resistance than ethylene vinyl acetate but lower toughness (Feldman & Barbalata, 1996). It improves bitumen performance at low and high temperatures due to its stiffness, but provides less improvement at higher temperatures than for SBS/SBR except in asphalt where it has good rut resistance. The copolymer causes a linear increase in softening point as there is no network structure as in the elastomeric polymers, and gives a higher viscosity than for SBS at the same percentage content (PIARC, 1999).

2.14.2 Ethylene vinyl acetate (EVA)

Structure: A random copolymer.



$$-\left[\begin{array}{cc} H & H \\ | & | \\ C\,- & C \\ | & | \\ H & H \end{array}\right]_x - \left[\begin{array}{cc} H & H \\ | & | \\ C\,- & C \\ | & | \\ H & OCOCH_3 \end{array}\right]_y -$$

Vinyl acetate content varies between 5-50% and controls crystallinity and the flexibility of the material (Feldman & Barbalata, 1996). The polymer has both crystalline and amorphous characteristics.

__Molecular weight__

Standard practice for EVA's is to measure melt flow index (MFI) in g/10 minutes, a viscosity test that is inversely related to molecular weight. The higher the melt, the lower the molecular weight (Morgan & Mulder, 1995).

__Vinyl acetate content__

Regular polyethylene segments pack together (crystalline region) and the bulky vinyl acetate groups disrupt this arrangement to give amorphous rubbery regions. The more vinyl acetate the more rubbery regions and less stiffness of the material.

There are a range EVA's based on MFI and vinyl acetate content, for example: An EVA with a MFI of 150 and VA of 19% is a 150/19 grade.

Exxon Chemicals have EVA grades as follows under the Polybilt brand (Exxon, 1996):

Type :	101	102	103	106
MFI/VA:	2020/14	150/19	45/33	1.8/24

EVA copolymers are generally more easily dispersed in and have relatively good compatibility with bitumen, particularly the lower molecular weight types such as Exxon's Polibilt 101. It also tends to improve bitumen mix workability because of its susceptibility to shear (Exxon, 1996). EVA provides stress cracking resistance, and low temperature flexibility. But provides very good rut resistance in asphalt. But is not often used in spray seals but has been used in Microsurfacing and Hot Mix Asphalt. It also gives a linear increase in bitumen softening point, as there is no network structure present. Hence, the softening point achieved is less than that for elastomers but will depend on EVA grade and concentration.

2.15 Bitumen/Polymer Compatibility

Bitumen/polymer compatibility is a key aspect that has caused manufacturers problems since the blends were first produced. There have been several attempts to describe the compatibility of particular bitumen for polymer modification. But the issue is very complex and is dependent upon many variables (Morgan & Mulder, 1995; Bearsley, 1999):

- Composition of the bitumen
- Average molecular weight of the individual bitumen fraction
- Type of polymer
- Average molecular weight of the polymer
- Structure of the polymer
- Polymer content of the final blend
- Blending temperature and duration
- Shear experienced during blending

The successful manufacture of polymer modified bitumen is dependent upon the chemistry of the two phases as well as the resulting morphology. The morphology can be controlled through a combination of chemistry, initial polymer physical form, and blending parameters. Definitions of compatibility vary but generally can mean (Bearsley, 1999):

- The polymer is easy to disperse in the bitumen
- The blended polymer modified bitumen has the desirable mechanical properties
- The blended polymer modified bitumen keeps these desirable properties after ageing
- The blended polymer modified bitumen does not undergo phase separation if stored at high temperatures

Brule (1995) states that three results are obtained when bitumen and a given thermoplastic polymer are mixed hot:

1. The mix is heterogeneous: the polymer and bitumen are incompatible. The components separate and the mix has poor characteristics.
2. The mix is totally homogeneous, including at the molecular level. The oils in the bitumen solvate the polymer perfectly and destroy any inter-macromolecular interactions. The resulting binder is extremely stable, but only very slight modification compared to the base bitumen is achieved. Only its viscosity increases.
3. The mix is mirco-heterogeneous, and is comprised of two distinct finely interlocked phases. This is the desired result, as the compatible polymer "swells" by absorbing some of the oily fractions of the bitumen to form a polymer phase distinct from the residual bitumen phase.

Bitumen can be characterised by its colloidal instability index (Serfass et al., 1992). This is defined as the ratio of dispersed phase/dispersing phase as follows:

$$Ic = \frac{A + S}{R + Ar} \qquad (3)$$

A = Asphaltenes
R = Resins
Ar = Aromatics
S = Saturates

The Colloidal Instability index is actually the inverse of the Colloidal Index (equation 1, pp 15). The Colloidal Instability Index approach has been tested using SBS polymers and may not be applicable to other polymers. There is no precise borderline between "compatible" and "incompatible" bitumen. Bitumen with an Ic higher than 0.25 are definitely incompatible, those with an Ic of less than 0.15 are generally compatible (Serfass et al., 1992). The Ic of the Safaniya (Saudi Arabian) bitumen that New Zealand uses is 0.80 which suggests that it is very incompatible for modification with SBS and may require stabilising with additives. Incompatibility with Safaniya bitumen has been noted by Transit, (1993). Chemical cross-linking of the polymer and bitumen can effectively force the two materials to be compatible by a stabilisation mechanism. The use of sulphur (Lesueur et al., 1998), peroxides (PIARC, 1999) and maliec anhydride (Engel et al., 1991) has been successful in this respect.

The introduction of any polymer with a high molecular weight disturbs the dynamic equilibrium and reduces the homogeneity of the bitumen system (Lu et al., 1999). The polymer competes for the light fractions of the bitumen, resulting in association of asphaltene micelles which often leads to phase separation of the PMB blends. Lu et al. (1999) conclude that for Styrene Butadiene Styrene (SBS), bitumen with a higher aromatic content of 60% to 65% exhibit lower phase separation. An increase in asphaltenes can also increase the phase separation of the PMB blends. The aromatic content of New Zealand's bitumen is only 11.2% which suggests that the addition of polymer (particularly SBS) will result in phase separation due to the decreased solvating power of the aromatics and resins content available.

2.16 Microscopic Investigations of Bitumen/Polymer Blends

Microscopic observation techniques can be used to assess the dispersion of the polymer phase in the bitumen or emulsion and to characterise the microstructural interactions. Fluorescence microscopy is the most frequently used technique for assessing the state of dispersion of the polymer and bitumen phases (PIARC, 1999). It is based on the principle that the polymers, swollen by some of the constituents of the bitumen to which they have been added, fluoresce in ultraviolet light. They emit yellow-orange light while the bitumen phase remains black. The method uses mercury or xenon arc lamps to provide the light source.

But, while acceptable images are obtained using fluorescence microscopy, the level of resolution is not as good to that produced if a laser is used as the light source, such as in confocal laser scanning microscopy (CLSM) (Rost, 1992; PIARC, 1999). Both fluorescence and reflection methods can be used with CLSM and the technique requires no special sample preparation (Rozeveld et al., 1997). The CLSM technique has been used by several studies to assess the polymer distribution, network formation and compatibility for polymer modified bitumen (Lee et al., 1997; Rozeveld et al., 1997; PIARC, 1999) but not emulsion binder *residue* or cold mix surfacing.

When the microstructure is very fine, less than one micron, the use of electron microscopy becomes necessary. Scanning electron microscopy (SEM), and environmental scanning microscopy (ESEM) are two methods, but they require preliminary treatment of the sample to remove oily fractions that can create artefacts in the images (Rozeveld et al., 1997; Michon et al., 1998). An additional technique is that of Atomic force microscopy which enables the study of bitumen and polymer modified bitumen binder network structures (Loeber et al., 1996; Loeber et al., 1998). The technique can resolve particles of less than one micron like the ESEM and SEM techniques.

Microscopy techniques have often been used to characterise the microstructure interactions between bitumen and polymers for modified binders and for asphalt concrete (Piazza et al., 1981; Loeber et al., 1996; Rozeveld et al., 1997; Michon et al., 1998). But there has been little publication regarding the microstructure and curing aspects of polymer modified bitumen emulsion binders for cold mix applications using any microscopy method. Normally physical testing methods are employed to characterise the degree of modification of the binder, but direct observations can help improve the understanding of the interaction between the emulsified bitumen-polymer after curing by water evaporation and the addition of aggregate.

2.17 Polymer Modified Emulsions

Polymer Modified Bitumen (PMB) while having considerable in-service performance advantages over unmodified or cutback bitumen, does have its own shortcomings as follows:

- Application period is usually quite short and needs to be strictly enforced. The road surface prior to spraying must be dry and not too cold (typically a minimum of 20°C)
- The aggregates must also be completely dry
- Often chip, pre-coated with bitumen has to be used, introducing another process step
- The binder is still applied at a very high temperature (approximately 180°C)
- PMB binders still require adhesion agents to maintain a bitumen-aggregate bond
- Binder bond is susceptible to rain for several hours after application

- The use of solvents is often recommended which can cause problems for overlay sealing due to the bitumen bleeding and also the environmental/safety risks associated.

Polymer modified emulsion (PME) can overcome all of the above drawbacks of PMB's except for initial susceptibility of rain to the binder-aggregate bond. A PME has the same basic advantages of a normal bitumen emulsion as outlined in Section 2.2 Bitumen Emulsification, but has the added performance properties of the polymer.

2.18 Modified Emulsion Definitions

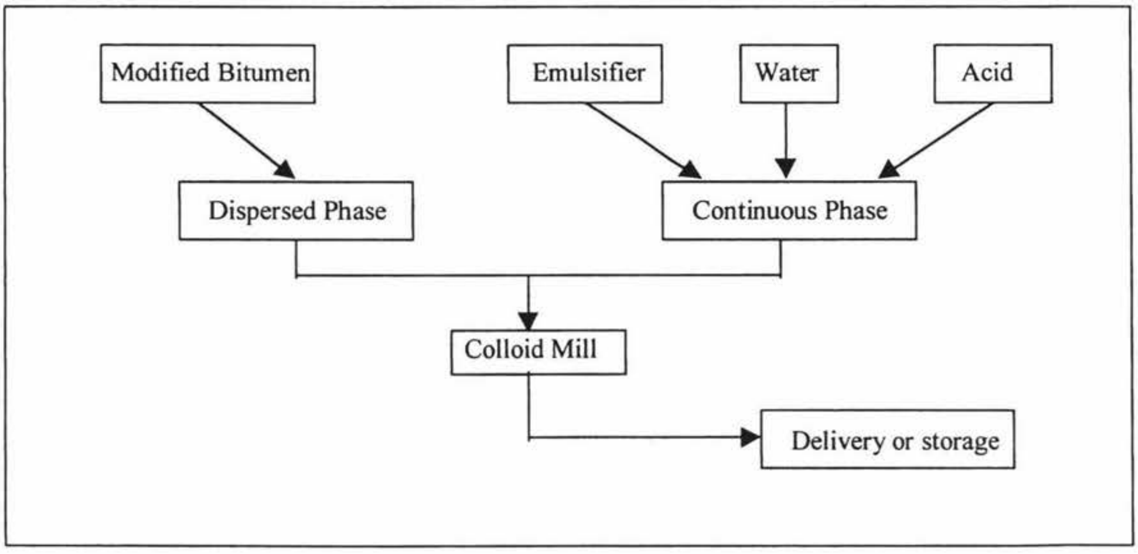
There are two types of polymer modified emulsions: *monophase* modified emulsions and *biphase* modified emulsions. The former are characterised by a dispersed phase composed of only modified bitumen droplets (a polymer bitumen). Biphase modified emulsions have a dispersed phase made up of two droplet types: bitumen and polymer (PIARC, 1999).

2.19 Manufacturing Processes

Polymer modified emulsions are manufactured with the same basic colloid mill process as conventional emulsions as outlined in Section 2.6.4 except for the addition of the polymer.

Monophase emulsions are manufactured from a polymer modified bitumen (Figure 2-5).

Figure 2-5 Manufacturing Process of Monophase Modified Bitumen Emulsion



The addition of polymer to the bitumen phase increases the viscosity. This results in the need to increase the bitumen phase temperature in order to obtain the required viscosity of around 200 centipoise entering the mill. An increase in the bitumen phase temperature will require a reduction in the soap/water phase temperature in order to maintain an emulsion exit temperature of less than 90°C. Bitumen phase temperatures over 160°C are unlikely to be counteracted enough by the soap phase, as the soap phase temperature is strongly dependent on the solubility of the emulsifier. This places a restriction on the amount of polymer that can be added with this method in a conventional colloid mill set up. The use of higher bitumen phase temperatures requires the use of pressurised mill conditions and a suitable heat exchanger to provide the desired exit temperature.

Currently the experience with polymers investigated for bitumen modification show higher than desired viscosities. The values typically obtained using 180/200 pen bitumen (Bearsley, 1998; Clark, 1999) are shown in Table 2-1.

Table 2-1. Comparison of Viscosities for Polymer Modified Bitumen

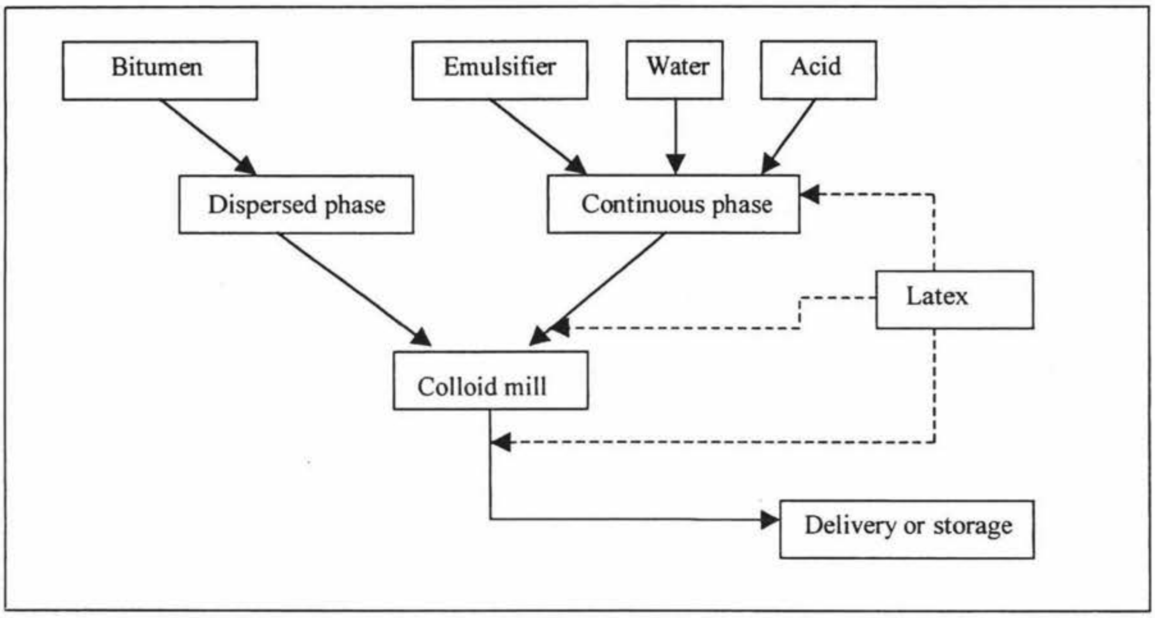
	SBS (3%)	**SBR (3%)**	**EMA (3%)**	**Neoprene (3%)**
Viscosity (135°C, 50rpm, cP)	475	625	615	788
Viscosity (165°C, 50rpm, cP)	210	220	200	225

Indications are that SBR and Neoprene would be the more difficult to emulsify adequately due to its higher viscosity, while SBS and EMA may be the best possibility given the current mill equipment available. There are no viscosity values available for EVA. The realistic polymer content available is probably 3% to add based on viscosity effects on the emulsion exit temperature. Both SBS and SBR provide better high temperature performance than EMA does on road application.

In biphase modified emulsions, the polymer is added as an emulsion (a latex). The addition of latex can be performed by several methods: dispersion in the soap phase, co-milling by direct injection into the soap line before the mill, or dispersion in the emulsion when it has been manufactured as shown in Figure 2-6.

Dispersion in the soap phase allows regulation of the soap solution pH and achieves good homogeneity in the dispersion. But the latex does have a tendency to have blockage problems in the soap line filter. The method is usually restricted to a 3% latex addition level. Co-milling can cause gas formation and mill malfunctioning but levels of 12% latex can be added this way. Post addition of the latex can result in storage stability problems due to the mixture of two different emulsions with different properties and requires mixing before use. Up to 20% latex can be added this way (Holleran, 1997).

Figure 2-6 Manufacturing Process of a Biphase Modified Bitumen Emulsion



2.20 Polymer Modified Emulsion Properties

2.20.1 Storage Stability

The performance of monophase modified emulsions is similar to that of conventional bitumen emulsions (PIARC, 1999). But modified emulsions normally contain a wider droplet size distribution that has a lower median particle diameter than non-modified bitumen emulsions. This leads to a lower viscosity and greater tendency to settle (Rabiot & Jariel, 1993).

Biphase emulsions are more prone to stability problems due to the two distinct types of droplets present with different physico-chemical properties. In emulsions with medium concentrations of bitumen it is common to encounter creaming of the latex phase in that the polymer–bitumen interaction is greater in the upper part of the storage tank than in the bottom.

The tendency to settle of these emulsions can be counteracted by modifying the particle size distribution, which can be achieved in several ways (refer to Section 2.9.4-Storage Stability). An additional method is to use bitumen additives such as an amine derivative or napthenic acid. These both decrease the mean particle size in the emulsion by lowering the interfacial tension between the bitumen and soap phases, which helps to increase viscosity and decrease settlement.

2.20.2 Breaking Process

The breaking rate of the bitumen emulsion can be increased by (Rabiot & Jariel, 1993):

- Decreasing the amount of emulsifier in the formulation.
- Using a bitumen-polymer combination that will provide interfacial properties that can enable the rapid breaking of the emulsion and have good adhesive properties between the residual bitumen and the aggregate.

2.20.3 Choice of bitumen

Rabiot & Jariel (1993) indicate that naphthenic bitumen has a very rapid breaking rate, which can be undesirable. This then requires higher levels of emulsifier to stabilise the emulsion. Paraffinic bitumen tends to give less rapid break properties. The bitumen used must be Safaniya bitumen, which is classed as paraffinic. Although Holleran (1997) and West (1985) suggest that bitumens with high paraffinic levels are more difficult to emulsify and often cure slower. To overcome this problem aromatic oils, or aromatic polar materials such as naphthenic acids are suggested to add to the bitumen (Holleran, 1999).

Safaniya bitumen generally produces acceptable emulsions for New Zealand emulsion standards, but the viscosity can be slightly low and the emulsions affected by some sedimentation (Transit, 1994).

2.21 MICROSURFACING TECHNOLOGY

2.22 Introduction

Microsurfacing is a mixture of polymer modified bitumen emulsion, mineral aggregate, mineral filler, water, and other additives, properly proportioned, mixed and spread on a paved surface using a compartmented, self-powered truck. Microsurfacing differs from slurry surfacing by the addition of polymer and the increased thickness of the surface layer applied. As a surface treatment, microsurfacing adds protection to the underlying pavement and provides renewed surface friction values. Quick set emulsifiers allow the return of traffic to the surface under average conditions between one to one and half-hours. Microsurfacing features and benefits are (Asphalt Institute, 1994; ISSA, 1995):

- Quick set, quick traffic feature.
- A chemical break allows night time application.
- Suitable for use on high traffic volume roads and on airfields.
- Single pass applications can yield microsurfacing depths from 9 to 16 mm.
- Wheel ruts up to 40 mm can be filled with one pass.
- Excellent surface texture and friction resistance.
- Has a greater noise reduction than chip seals.

2.23 History and Relevance of Microsurfacing to New Zealand

Microsurfacing was pioneered in Germany in the late 1960's and early 1970's. Conventional slurry was modified with polymer and specially graded aggregates to allow thicker applications to be applied. The technique was introduced in the United States in 1980 and is now one of the leading cost effective preventative maintenance treatments for roads. Microsurfacing is now also used in Europe and Australia (Reed, 1996).

Microsurfacing has not been introduced into New Zealand as yet mainly due to the technical difficulties involved in producing a quality product. The cost of a slurry seal varies upon the thickness but is typically \$4.50 - \$9.00/m^2. The cost of microsurfacing is expected to be approximately \$7.00 - \$11.00/m^2 due to the increased thickness and added polymer. Higgins produce slurry surfacing as do several competitors such as Fulton

Hogan, Technic, and Bitumix, but none of these as yet have any micro-surfacing products. The slurry sealing market has recently experienced a lack of confidence with the products due to some performance failures by contractors, and hence the market potential has suffered. Microsurfacing presents a useful market if reliable products can be produced that give a durable well performing surface. Microsurfacing provides benefits for applications such as rut filling and re-profiling and can become a very useful technique for maintenance contracts, which are an important source of revenue for Higgins.

2.24 Manufacture of Microsurfacing

Microsurfacing and slurry surfacing are made and applied to existing pavements by a specialised machine, which carries all components, mixes them on site, and spreads the mixture onto the road surface. A schematic view of the process is shown in Figure 2-7.

The mixing chamber is a double shafted, multi-bladed pugmill that quickly combines and thoroughly mixes the materials. The semi-fluid microsurfacing mixture falls into an augured spreader box and is deposited on the pavement across a full lane width as the truck moves forward on the road.

All areas of the pavement before application of the microsurfacing must be cleaned of all loose material, oil spots, vegetation and any other foreign matter. Cracks in the surface are normally repaired with a crack sealant. Hand squeegees are used to improve joints, correct minor imperfections and place the microsurfacing in areas inaccessible to the machine (Asphalt Institute, 1994; ISSA, 1995).

Figure 2-7. Microsurfacing Process

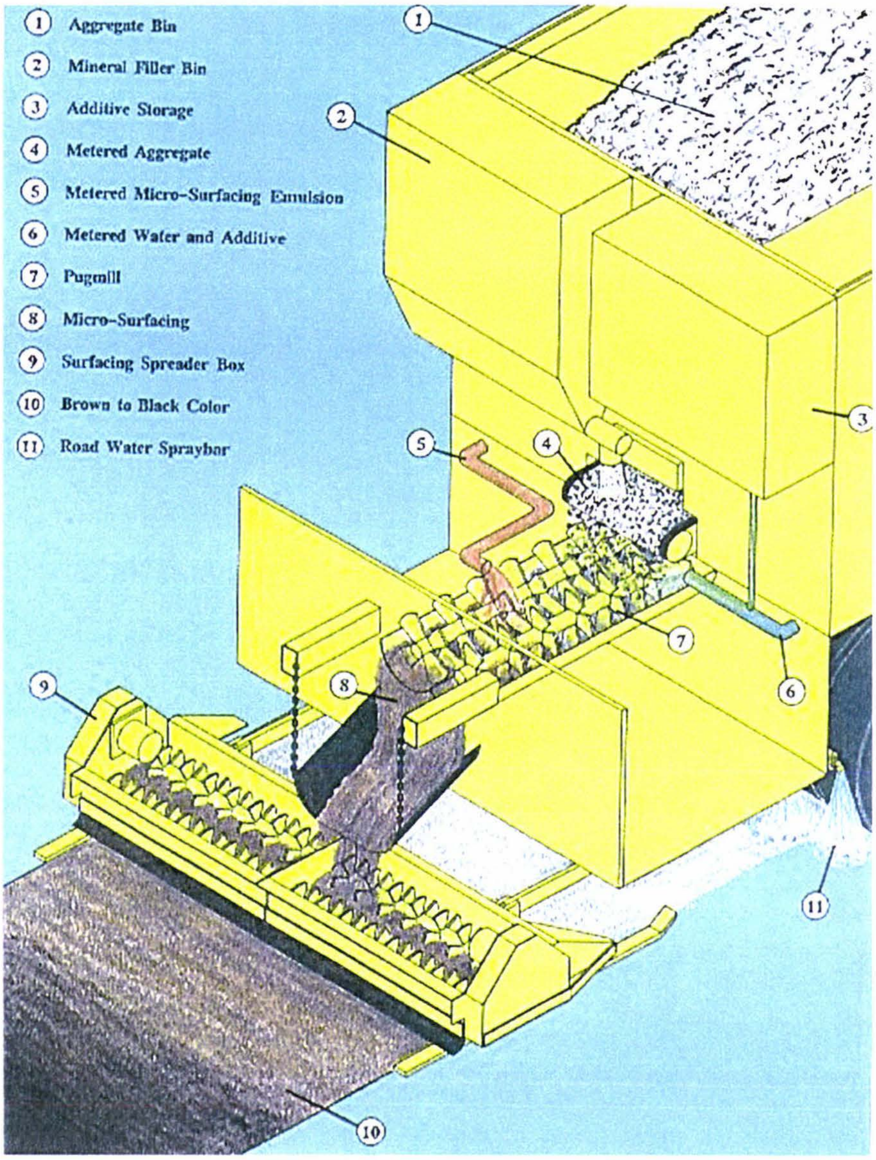


Image from ISSA, (1995).

2.25 Materials

The materials within the microsurfacing are very important to the overall performance and quality of the surfacing. The International Slurry Surfacing Association (ISSA) provides recommended general specifications (ISSA, 1996) for the materials within microsurfacing. The materials used are emulsified bitumen, aggregate, mineral filler, water and additives.

2.25.1 Polymer Modified Emulsion

The emulsion used for microsurfacing is normally a cationic slow set (CSS) type with polymer modifier added. The addition of the polymer greatly improves the mechanical properties of the mix by improving abrasion resistance and plastic deformation (rutting) as outlined in Section 2.11. Latex polymers contain their own emulsifier system, which are usually of a very slow set nature. This has to be compensated for in the emulsion design as it can lead to longer mix times and slower setting (Holleran, 1997). The key guidelines for the emulsion specification and performance are (ISSA, 1996):

- Bitumen content of 60 to 65% with a typical value of 62%.
- A 3% polymer solids content based on bitumen weight is considered the minimum.
- Softening point of the binder is specified at 57°C minimum.
- A harder grade of bitumen is normally used.

2.25.2 Aggregate

The aggregate is specified to consist of manufactured crushed stone such as granite, limestone, greywacke, or a suitable high quality aggregate (Asphalt Institute, 1994). It is important that the aggregate is clean and relatively free from dust, clay or dirt. The dust tends to produce a film that prevents the bitumen from adhering to the aggregate surface. This can lead to poor cohesion development and results in a pavement mixture that will cure slower and be susceptible to early traffic damage. The Sand Equivalence determines the cleanliness of the aggregate. Sand Equivalence is the ratio of sedimented sand and suspended clay particles in a solution prepared in a graduated cylinder. The ratio is represented as a percentage and is shown below.

$$\text{Sand Equivalent} = \frac{\text{Sand reading}}{\text{Clay reading}} \times 100 \qquad (4)$$

The ISSA specification recommends a sand equivalent value of the aggregate of 60% minimum. A higher sand equivalence value indicates a cleaner aggregate.

Grading

There are two specified types of aggregate gradations for microsurfacing: Type 2 and Type 3, and are shown in Table 2-2. Type 2 aggregate is used for general resurfacing of streets and medium volume roads. Type 3 aggregate is used for heavy traffic resurfacing, minor re-profiling, rut filling and areas that require high friction values.

Table 2-2 Aggregate Gradings for Microsurfacing

Sieve Size	Type II Percent Passing	Type III Percent Passing
9.5 mm	100	100
4.75 mm	90-100	70-90
2.36 mm	65-90	45-70
1.18 mm	45-70	28-50
600 μm	30-50	19-34
300 μm	18-30	12-25
150 μm	10-21	7-18
75 μm	5-15	5-15

2.25.3 Mineral Filler

Mineral filler is used in a microsurfacing system to produce better control of mix consistency and set times. The filler act as an accelerator by increasing pH and destabilising the cationic emulsion which, initiates breaking of the emulsion. The fillers normally recommended are portland cement or hydrated lime. If the emulsion properties are correct and aggregate quality good then it is likely that the fillers will not be required which simplifies the mix design and application process for the roading crew.

2.25.4 Water

Extra water is added to the microsurfacing mix to wet the aggregate to enable the emulsion to better deposit the modified bitumen onto the aggregate surface. It can also help produce the desired mix consistency. The amount added must be minimised (<12%) or the mix consistency will be too runny, leading to aggregate segregation and will retard cohesion development leading to increased traffic times (Glet, 1999). The water should be free from soluble salts or reactive chemicals and any other contaminants.

2.25.5 Additives

Additives are added to the mixture to control the quick traffic properties of the microsurfacing. This is necessary due to changing weather situations and other environmental aspects than can affect the traffic times. Control agents such as a dilute solution of slow set emulsifier or aluminium sulphate can be used (Holleran, 1997). These additives can also retard the slurry mix time if required. The use of a dilute emulsifier can reduce the amount of pre-wet water as it aids 'wetting' of the aggregate. But they can be expensive and promote foaming of the mix. Aluminium sulphate can be used in smaller volumes than the emulsifier and requires less water to be effective in providing a better mix consistency.

2.26 Mix Design

The microsurfacing mix design is dependent on the emulsion properties and the quality and cleanliness of the aggregate the properties of these two materials determine the amounts of pre-wet water, fillers, and additives to add. Hence, there is no exact formulation but guidelines are provided by the ISSA Recommended Performance Guidelines for Microsurfacing A143. These guidelines are shown in Table 2-3 but the exact design must be trialed and tested in the laboratory for consistency of mix and performance properties.

Tests used include:

- Wet track abrasion for resistance to aggregate stripping.
- Loaded wheel test to measure rutting performance.
- Slurry cohesion to determine the earliest traffic time.
- Mix time to predict how long the material can be mixed in the machine and deposited to the road before it begins to break.

Table 2-3 Microsurfacing Mix Design Guidelines

Material	Concentration
Residual Bitumen	5.5% to 10.5% by dry weight of aggregate
Mineral Filler	0% to 3% by dry weight of aggregate
Polymer	3% minimum solids based on bitumen weight content
Additive	As needed
Water	As required to produce proper mix consistency
Aggregate	To 100%

2.27 Rate of Application

The average application rate using type II aggregate for urban and residential streets, and airport runways is recommended as 5.4 – 18.6 kg/m^2. For heavy traffic roads and highways the application rate using Type III aggregate is recommended as 8.1 – 16.2 kg/m^2 (ISSA, 1996).

2.28 Weather Limitations

Like all bitumen based surface treatments the microsurfacing should not be applied in the rain or when rain is immediately imminent. The pavement or air temperature must be at least 7°C and rising and should not be applied if there is the possibility that the surfacing will be exposed to a frost within 24 hours as this will result in susceptibility to aggregate loss.

2.29 Chapter Conclusions

The key to a good quality microsurfacing involves considering the whole system of modified emulsion binder, aggregate, and additives, not just the binder. Although the binder is extremely important, the quality and selection of other materials could mean the difference between good surfacing and an acceptable one. The most important material is bitumen and its relative proportions of asphaltenes, resins, saturates and aromatics. This has a major influence on the emulsion properties and binder properties after polymer modification. The Safaniya bitumen that New Zealand uses has been prone to settlement problems in the past and incompatibility with polymer addition. But, there are additives that can be used to solve or reduce these problems. The addition of polymer to emulsions has been studied little at Higgins and there is plenty of further scope for studying the effects.

Higgins has experience in slurry surfacing and this can help narrow the basic emulsion and mix design parameters. The key aspects of the microsurfacing to achieve are:

- Suitable emulsion stability
- A high binder softening point
- A mix time that is sufficiently long enough to allow spreading
- Rapid cohesion development
- Resistance to deformation of the surfacing

These properties are a function of all the materials and the tests carried out should measure these properties.

Other key points discovered are that the interactions among the materials are very important particularly the bitumen-polymer binder. The physical and microstructural effects on the emulsion binder by adding polymer are a key area as well as the polymer compatibility.

Overall the literature review has provided the background and understanding of the emulsion and mixture design properties, and the means to develop a technical specification and product formulation, which is covered in Chapter 3.

3. PRODUCT TECHNICAL SPECIFICATIONS AND REQUIREMENTS

3.1 Introduction

A set of preliminary product technical specifications helps to focus what the formulation design phase is expected to achieve. It consists of the possible materials, processing method(s), and broad processing parameters in which to begin a formulation design investigation.

3.2 Suitability and Addition Levels of Polymers for Emulsification

Production of monophase polymer modified emulsions at Higgins requires the polymer to be easily dispersed in the bitumen by being either in a latex, powder, or easily melted pellet form. Production of biphase polymer modified emulsions requires latex polymers. The polymers suitable for polymer modified emulsions at Higgins are shown below:

Elastomers

- Styrene butadiene styrene (SBS)
- Styrene butadiene rubber (SBR)
- Neoprene
- Natural Rubber Latex

Plastomers

- Ethylene methyl acrylate (EMA)
- Ethylene vinyl acetate (EVA)

The performance issues for microsurfacing are related to the thickness of the surface layer(s) applied and are:

- Adhesion and cohesion
- Abrasion resistance
- Bleeding resistance
- Durability
- Deformation resistance (rutting)

All of the polymers are suitable for use in microsurfacing as they all provide resistance to abrasion, surface bleeding, cracking, and deformation. SBR will generally provide the greatest improvement when the polymers are added at 3%. EVA and EMA provide the best resistance to rutting of the polymers due to their stiffness properties. Table 3-1 shows the potential addition methods of the polymers to the bitumen emulsion and the typical concentrations available. The concentration limits are based on the restrictions of the colloid mill used and the likely effects on emulsion stability. An additional aspect that needs to be kept in mind is the expense of the polymer level added, versus the degree of performance improvement to the microsurfacing.

Table 3-1. Polymer Addition Methods and Concentrations Suitable

Polymer Type	**Bitumen Phase**	**Co-milled**	**Soap Phase**	**Post Addition**
Styrene Butadiene Styrene	3.0%	-	-	-
Styrene Butadiene Rubber	3.0%	3.0 – 6.0%	3.0%	3.0 – 7.0%
Neoprene Latex	3.0%	3.0 – 6.0%	3.0%	3.0 – 7.0%
Natural Rubber Latex	-	3.0 – 6.0%	3.0%	3.0 – 7.0%
Ethylene Methyl Acrylate	3.0%	-	-	-
Ethylene Vinyl Acetate	3.0%	-	-	-

3.3 Product Attributes

The key microsurfacing product attributes and the materials expected to have the major influence on them are shown in Table 3-2.

Table 3-2. Product Attributes and Material Solutions for Microsurfacing

Product Attribute	**Material**
Resistance to permanent deformation	Bitumen grade, polymer
Abrasion resistance	Bitumen, polymer, aggregate
Improved high & low temperature properties	Polymer
Quick curing slurry	Emulsifier, aggregate quality
Consistent emulsion break rate	Emulsifier

3.4 Preliminary Technical Specification for Microsurfacing

3.4.1 Scope

The initial technical specification provides details of the requirements for manufacturing a high quality Micro-surfacing product. It describes the formulation, possible raw materials, handling, potential means of processing, and testing requirements for the product. The specification is a concise guide to producing a starting formulation and manufacturing process, and was developed from the literature search of modified emulsions, microsurfacing, and experience with slurry formulations at Higgins. The specification draws additional product requirements from industry specifications ISSA 143A Recommended Performance Guidelines for Microsurfacing, ASTM D2397 – 94 Standard Specification for Cationic Emulsified Asphalt, TRANSIT (1996) M/1 Specification for Roading Bitumen, and ASTM D244 Standard test Methods for Emulsified Asphalts.

3.4.2 Description

Micro-surfacing is a mixture of polymer-modified bitumen emulsion, mineral aggregate, mineral filler, water, and other additives, mixed and spread by a self-contained paving machine. Microsurfacing imparts protection to the underlying pavement and provides renewed surface friction values. A single pass application can yield a surface up to 16 mm in depth. Minor re-profiling can be performed with multiple application, and the filling of wheel ruts up to 40 mm deep can be achieved. The product allows the return of straight running traffic to the surface in ideally less than one hour. Microsurfacing provides a preventative and a corrective maintenance technique suitable for urban and residential streets, and carparks.

3.4.3 Materials

Bitumen

The bitumen is supplied by Marsden Point Refinery and is produced using Safaniya Crude from Saudi Arabia. The base bitumen used shall preferably be 80/100 or 180/200 grade and conform to the requirements of TNZ M/1 specification.

Polymer

The polymer shall be either an elastomer selected from either Styrene Butadiene Rubber (SBR) latex, Styrene Butadiene Styrene (SBS), Polychloroprene (Neoprene) latex, and Natural Rubber latex, or a plastomer selected from either Ethylene Vinyl Acetate (EVA), Ethylene Methyl Acrylate (EMA). The polymer can be milled or blended into the bitumen or emulsifier solution prior to the emulsification, or post added to the manufactured bitumen emulsion. The residual polymer content should be 3% to 5% based on the total binder content. Suitable, available polymers are shown in Table 3-3.

Table 3-3. Possible Polymers for Microsurfacing

Polymer Type	Trade Name	Supplier	Physical Form
SBR Latex	Confidential	BASF	Aqueous
SBS	Confidential	Exxon	Powder
	Confidential	Shell	Powder
Natural Rubber latex	Confidential	Alchemy	Aqueous
Polychloroprene latex	Neoprene	Du Pont	Aqueous
EVA	Confidential	Exxon	Pellet
	Confidential	Exxon	Pellet
EMA	Confidential	Exxon	Pellet

Emulsifiers

The emulsifiers used must be primarily cationic, and of quick set traffic type, and be stable to an aggregate mixing time of around 2 minutes. The emulsifier must be made up in the soap phase with Hydrochloric Acid (HCl) and water. The possible emulsifier options are outlined in Table 3-4.

Table 3-4. Possible Quick Setting Emulsifiers

Emulsifier	Type	Concentration Range
Emulsifier B	Alkyl amidoamine	1.0 - 2.0%
Emulsifier A	Quaternary ammonium	1.0 – 2.0%
Emulsifier C	Imidazoline	1.0 – 1.5%
Emulsifier D	Tall oil fatty acid polyamine	1.2 – 1.5%

Aggregate

The mineral aggregate shall be a Type II or type III, or proprietary graded high quality manufactured crushed stone of igneous (granite, basalt) or sedimentary rock (limestone, greywacke) origin. The aggregate must conform to the requirements outlined in Table 3-5 and 3-6. The aggregate sand equivalence value should be at a level that does not adversely effect the microsurfacing cure or abrasion properties. The recommended value from ISSA (1996) was 60% minimum. But further testing was required to determine the effect of varying aggregate cleanliness.

Table 3-5. Grading of Type II Aggregate

Sieve Size		Percent Passing	
	Minimum	Maximum	Typical
9.5 mm	100	100	100
4.75 mm	90	100	95
2.36 mm	65	90	77
1.18 mm	45	70	57
600 μm	30	50	40
300 μm	18	30	24
150 μm	10	21	15
75 μm	5	15	10

Table 3-6. Grading of Type III Aggregate

Sieve Size		Percent Passing	
	Minimum	Maximum	Typical
9.5 mm	100	100	100
4.75 mm	70	90	80
2.36 mm	45	70	57
1.18 mm	28	50	39
600 μm	19	34	27
300 μm	12	25	19
150 μm	7	18	13
75 μm	5	15	10

Mineral Filler

To obtain the desired set times or product consistency mineral filler can be used. If required, it shall be any recognised brand of non-airentrained Portland Cement or Hydrated Lime that is free from lumps. It shall be considered part of the aggregate gradation and the quantity shall be 0% to 3% by dry weight of aggregate, with typical addition levels of 0.5% to 1.0%.

Water

The water should have a low total dissolved solids content, and must be free from harmful soluble salts or reactive chemicals, and any other contaminants.

Additives

Additives may be added to the emulsion mix or any of the component materials to provide the control of the quick-traffic properties. They must be included as part of the mix design and be compatible with the other components of the mix. Possibilities are retarder A, or extra emulsifier solution.

3.4.4 Manufacturing Requirements

Emulsion Production

The polymer can be added to the soap phase or the bitumen phase prior to emulsification depending on its physical form. SBR latex, Polychloroprene latex, and Natural rubber latex can be added to the soap phase, but only the first two can be added also to the bitumen phase, while SBS, EMA, and EVA must be added to the bitumen phase only, due to their solid form. SBS, SBR (if added to the bitumen phase), EVA, and EMA, are blended into the bitumen at 180°C and mixed for 1-2 hours to fully disperse the polymer.

Latex addition will increase the emulsifier level and will need to be compensated for by a reduction in the primary emulsifier in the formulation.

The addition of polymer to the bitumen phase results in a sharp increase in viscosity, and will require a higher temperature to maintain a viscosity of around 200 cP. This requires a lower soap temperature to keep the emulsion exit temperature to below 90°C.

The emulsion shall be a Cationic Quick Set (CQS-1h) type with residual bitumen of 60% to 65%. The pH shall be between 2 – 7, and the emulsion must show stability to the desired level of mixing with aggregate/filler/additives and have a controlled break time. Typical laboratory colloid mill parameters are outlined in Table 3-7.

Table 3-7. Potential Production Characteristics

Mill Characteristics	Criteria
Bitumen Temperature	140-165°C
Soap Temperature	30-50°C
Exit Temperature	80-90°C
Bitumen Flow Rate	860 cc/min
Soap Flow Rate	500 cc/min
Gap Between Rotor and Stator	0.170 mm
Rotor Speed	2840 rpm

3.4.5 Mix Design

The Micro-surfacing mix design must be prepared and tested in the laboratory to verify the quantities of the various mix components. For full-scale production, the quantities of the materials would be proportioned by a metering system and mixed in a pugmill positioned on the Higgins Macropaver Slurry Machine. The application temperature for the mix should be 20°C – 70°C. A typical range of percentages for the materials are shown in Table 3-8.

Table 3-8. Approximate Mix Design Components

Material	Concentrations
Residual Bitumen	15%
Polymer Modifier	3% minimum solids
Mineral Filler	0.0% - 3.0%
Additive	1.5 – 2.0%
Water	7.0 – 8.0%

Note: Mix design based on dry weight of aggregate.

3.4.6 Test Requirements

Tables 3-9, and 3-10 outline the test criteria for the emulsion and completed mix.

Table 3-9. Acceptance Criteria for Microsurfacing Emulsion and Binder

Test	Criteria	Typical Value
pH @ 25°C	2.0 – 7.0	3.0
Viscosity (25°C, 5 rpm)	40 – 300 cP	160 cP
Residue by Evaporation (135°C)	60 - 65%	62%
Bitumen Content	60 – 65%	62%
Polymer Content	3 – 5%	3%
Settlement (After 5 days @ 21°C)	<5%	<5%
Particle Size (150µm)	<0.10%	<0.10%
Softening Point	57 – 90°C	-

Table 3-10. Acceptance Criteria for Microsurfacing Slurry

Test	Criteria
Wet Cohesion @ 30 minutes (set)	>12 kg-cm
@ 60 minutes (traffic)	>20 kg-cm
Wet Track Abrasion Loss (1 hour)	< 800 g/m^2
Lateral Displacement	<5%
Height Displacement	<10%
Mix Time @ 21°C	120 sec .min

Additional Testing

Confocal laser scanning microscopy to assess the degree of polymer dispersion, and possible networking between bitumen/polymer and aggregate.

4. MATERIALS AND METHODS

4.1 MATERIALS

Bitumen

Safaniya bitumen supplied in hard 80/100-penetration grade and soft 180/200-penetration grade was used. These are the standard commercial roading grades produced by Marsden Point refinery from the Safaniya crude oil. Two trials were performed with 130/150-penetration bitumen, which is a blend of 25% 80/100 and 75% 180/200 bitumen.

Polymer

The polymers used were Styrene Butadiene Rubber (SBR) supplied by BASF, Styrene Butadiene Styrene (SBS) supplied by Shell, and Ethylene Methyl Acrylate (EMA) supplied by Exxon. The polymer grades could not be disclosed due to commercial sensitivity.

Bitumen Additives

Amine Derivative A

To facilitate the production of monophase modified emulsions amine A (supplier confidential) was added to two monophase emulsions with SBR added to the bitumen phase. Amine A is a fatty amine derivative, which is used as a peptiser to enhance bitumen compatibility. The additive is meant to improve the emulsifibility by producing a smaller average droplet size and a narrower particle size distribution. The recommended dosage is 0.2 - 1.0%.

Aromatic Oil A

Aromatic oil A is an extender oil for polymer modified bitumen. It is a bitumen extract that is high in aromatics (88.8%) and extremely low in asphaltenes (0.1%). Aromatics help in dispersing the asphaltenes, which increases emulsion stability. The recommended dosage is normally 5.0%. It was added to two monophase emulsions produced with SBR added to hot bitumen.

Cross-linking agent

Cross-linker A is a well known cross-linking agent and is used to stabilise hot polymer modified bitumen and prevent phase separation. The product supplier cannot be named due to commercial sensitivity.

Emulsifiers

Microsurfacing emulsions require emulsifiers that will be stable to mixing with fine aggregate but cure quickly soon after breaking. The suitable emulsifiers readily available are shown in Table 4-1:

Table 4-1. Microsurfacing Emulsifiers

Emulsifier	Type	Supplier
Emulsifier A	Quaternary ammonium	Akzo Nobel
Emulsifier B	Alkyl amidoamine	Akzo Nobel
Emulsifier C	Imidazoline	Valley Slurry Seal

Acid

Industrial strength hydrochloric acid (32.5% w/w) was used to regulate the emulsifier solution pH.

Aggregate

Crushed Greywacke aggregate from Bulls was supplied by Higgins and conformed to a grade II type microsurfacing grading. It is a sedimentary class rock and is formed by natural cementing together of individual particles by processes such as erosion. Crushed Andesite aggregate from New Plymouth was supplied by New Plymouth Quarries, it also was a type II microsurfacing grading. It is an igneous class of rock produced by volcanic formation. The actual grading of the aggregates used in the experiments is shown in Table 4-2. All of the aggregate gradings used conformed to the Type II microsurfacing specification.

Table 4-2. Grading of Aggregates used for Investigations

	Aggregate Source			
	Bulls	Bulls	Bulls	New Plymouth
Sand Equivalent (%)	49	54	70	82
Grading				
% Passing 9.5mm	100	100	100	100
% Passing 4.75mm	97	97	100	92
% Passing 2.36mm	71	69	75	69
% Passing 1.18mm	50	47	54	48
% Passing 0.600mm	36	33	38	33
% Passing 0.300mm	26	22	27	21
% Passing 0.150mm	19	15	18	13
% Passing 0.075mm	13.0	8.3	11.8	8.2

Mineral Filler

Portland cement supplied by Golden Bay Ltd was used to control the mix times and slurry consistency.

Microsurfacing Additives

The control of the quick traffic properties was aided by using either a 10% solution of emulsifier B or a 10% solution of retarder A. The supplier of retarder A could not be disclosed.

4.2 PROCESSING VARIABLES

4.2.1 Colloid Mill

A Charlotte G-3 colloid mill was used for the laboratory emulsions and operates under atmospheric pressure.

Mill gap and mill speed

The mill has a smallest gap setting of 0.17 mm, which creates a finer emulsion, and this setting is normally used for all slurry emulsions. The mill speed is fixed at 2840 rpm

4.2.2 Bitumen phase temperature

The bitumen phase temperature for biphase modified emulsions using 180/200 bitumen was set at 140°C and for 80/100 bitumen at 150°C due to the higher viscosity of the harder bitumen. For monophase emulsions using hot polymer modified 130/150 bitumen and 180/200 bitumen the modified bitumen was heated to 160-165°C to lower the viscosity to approximately 200 centipoise entering the mill.

4.2.3 Soap phase temperature

The soap phase temperature was set to allow an emulsion exit temperature of 80 – 85°C. For the biphase emulsions using 180/200 bitumen a soap temperature of 50 – 51°C was used. Monophase modified emulsions using 180/200 or 130/150 bitumen required a soap phase temperature of 31 – 33°C. The biphase modified emulsions produced with 80/100 bitumen had a soap temperature of 40 – 42°C. The preparation of the emulsifier concentrates was performed at 47 – 52°C to aid dispersion of the emulsifiers in the acid water.

4.2.4 Flow rates

The bitumen flow rate into the mill was consistent at 860 – 865 cc/min while the soap phase was set at 500 cc/min. These flow rates result in a binder content of 61 – 62%. The co-milling of polymer latex when required used a flow rate of 40 cc/min in order to add 3% polymer by weight of bitumen.

4.3 PREPARATION OF MONOPHASE MODIFIED EMULSIONS

SBR modified bitumen

The desired quantity of the additives aromatic oil A and amine A were added to bitumen heated to 180°C while stirring with a Heidolph RZR 2020 mixer at 800 rpm. The SBR latex was slowly added to the bitumen and stirred for one hour.

EMA modified bitumen

Cross-linker A was slowly added to 180/200 bitumen heated to 180°C while stirring at 600 rpm. The EMA polymer was slowly added into the bitumen and mixed for one hour.

The same method was also used for the addition of SBS polymer.

The second trial used 130/150 bitumen heated to 180°C and stirred at 600 rpm but with only the EMA polymer added. Mixing was continued for one hour.

4.4 PREPARATION OF BIPHASE MODIFIED EMULSIONS

The production of the biphase emulsions involved the addition of SBR polymer latex in three methods:

1. Co-milling the latex
2. Pre-blending the latex into the soap phase
3. Post adding the latex to manufactured emulsions

Co-milling

The polymer latex was metered into the soap line just before entering the mill.

Pre-blending in the soap phase

The emulsifier solution was adjusted to its required pH and the latex then added into the solution and stirred to uniformly mix.

Post addition

The required quantity of latex was slowly stirred into the unmodified bitumen emulsion using a Heidolph RZR 2020 stirrer at 250 rpm until completely added.

4.5 TEST METHODS

The tests adopted for the investigations follow specifications where possible as outlined in ASTM D 2397 – 94 Specification for Cationic Emulsified Asphalt, and ISSA Recommended Performance Guidelines for Microsurfacing A143 – 1996. The tests can be classified into testing emulsion properties, binder properties, and slurry properties.

Emulsion properties

- pH of final emulsion
- Viscosity
- Binder residue
- Settlement
- Sieve residue

Binder properties

- Softening Point
- Microscopy analysis

Slurry properties

- Wet track abrasion
- Loaded wheel test
- Slurry cohesion
- Microscopy analysis
- Mix time

Emulsion pH and binder residue were tested as production checks and not for formulation optimisation. The other remaining tests summarise the main response variables to be investigated during the experimental trials.

4.5.1 Emulsion pH

A sample of the emulsion was stored for 12 hours at 25°C and the pH measured with an Orion Model 210A pH Meter coupled with a Mettler Toledo ATC Probe.

4.5.2 Viscosity

Viscosity of the emulsion was measured using the Brookfield RVT Synchro-Lectric Dial Viscometer. The following sampling conditions were used:

- Emulsion Temperature 25°C
- Spindle # 1 for low viscosity measurement
- Spindle Speeds of 5, 10, 20, and 50 rpm.
- The spindle was allowed to spin for 30 seconds before taking the reading.

4.5.3 Binder Residue

Residual binder was tested to monitor that all emulsions had a binder level between 60 – 63%. The residual binder was measured using a Mettler LP16 Infra-red moisture meter. A 10 g sample of emulsion was exposed to 135°C heat until all water had evaporated and the weight remained constant for a 30 second period.

4.5.4 Emulsion Settlement

This test was used to indicate the storage stability of the emulsions in accordance with ASTM D244-95. A 500 ml sample of emulsion was left to settle in a glass cylinder for five days and the difference between the residual binder of the top 50 mls and the bottom 50 mls determined.

4.5.5 Sieve residue

The sieve residue test was used to indicate the effects of formulation changes on the width of the emulsion particle size distribution and to identify early coalescence problems. A 50 ml sample of the emulsion was passed through a 150 μm sieve according to ASTM D244-95. Coalesced binder globules are retained on the sieve and the weight of the retained globules was calculated as a percentage.

4.5.6 Softening point

The Ring and Ball method (ASTM D36-95) is used to measure the softening point of the binder. This determines the modified bitumen resistance to high temperature exposure and is a determination of the effect of polymer addition. Two horizontal disks of binder, cast in shouldered brass rings are heated at a controlled rate in a liquid bath while each supports a steel ball. The softening point is reported as a mean of the temperatures at which the two disks soften to allow each ball enveloped in binder to fall a distance of 25 mm. A sample of the emulsion was cured at 60°C for 24 hours to evaporate the water and the residual binder was then applied into the brass rings.

4.5.7 Laser scanning confocal microscopy (CLSM)

The distribution and microstructure of the bitumen-polymer was viewed to investigate the interactions within the binder and between the binder and aggregate. A Leica DM-RBE confocal microscope with a TCS 40 laser-scanning head was used to examine the polymer modified emulsion residues and the microsurfacing. Images were recorded in fluorescent mode for the binder images and in both reflected and fluorescent modes for the binder aggregate sample using an argon-krypton laser with a wavelength of 488 nm (blue light). A long pass filter LP515 allowed the fluorescent light to reach the detector (Rozeveld et al., 1997). A single line scan method was used to view the binder samples. The binder-aggregate images were taken using the depth scan mode whereby 25 sections were scanned to a depth of 139 μm and overlaid to produce a 3-dimensional image. All images were recorded in a 512 pixels X 512 pixels TIFF format.

The emulsion residue was obtained by placing a drop of emulsion on a concave microscope slide and drying at 60°C for 6 hours to evaporate the water phase. This is similar to the pavement temperature expected in the peak of summer to simulate the drying effects for the road surfacing. Samples of hot polymer modified bitumen were obtained by placing a drop directly onto a slide.

4.5.8 Wet track abrasion

The wet track abrasion test determines the resistance of the microsurfacing to stone stripping and determines the minimum emulsion content. The test method in accordance with ISSA A143-96 involves a slurry mixture of fine graded aggregate, emulsion and water prepared to a homogeneous flowing consistency. The mixture was then cast into a circular mould laid on roofing felt. The cast mould was cured for 24 hours at 60°C to obtain a constant weight. The cured slurry was then immersed in a 25°C water bath for 1 hour, then mechanically abraded under a water layer with a rubber hose for 5 minutes. The total weight lost being expressed as grams lost per area. The AUSTROADS (1998) specification for microsurfacing is less than 800 g/m^2 surfacing loss.

4.5.9 Loaded wheel test

This test enables the plastic deformation (rutting resistance) of the microsurfacing to be measured as outlined in ISSA A143-96. A sample specimen of slurry (200 g) is cast in a mould and dried for 24 hours at 60°C, then cooled to room temperature. The specimen was measured using a Mitutoyo Dial Caliper/Depth Gage at specified points. The mould was mounted on a loaded wheel machine and 1000 cycles at a specified load were completed. The specimen was re-measured at the specified locations and the change in width and height was presented as a percentage change.

4.5.10 Microsurfacing Cohesion

This determines the set and cure characteristics of the slurry mix. Samples of fresh slurry are cast in moulds and placed in a 25°C oven until the measurements are required. The specimen is placed under a rubber-padded foot, which is connected to a torque meter. The instrument air pressure is set at 200 kPa. Torque measurements can be made at 30, 60, 90, 120, 150, 180, and 210 minutes. The torque required to move the torque wrench through 90° is determined and is related to the slurry cure characteristics. The time to allowing early rolling traffic on a surfacing occurs at 20 kg-cm. A quick set microsurfacing system should reach this value within 60 minutes.

4.5.11 Mix time

This measures the amount of time the slurry remains workable for before stiffening when applied in the field. 100 g of slurry is mixed, and the mix time is determined when the mixture stiffens and breaks.

4.6 PROCESS CAPABILITY AND TEST REPEATABILITY

Knowledge of the variance involved in the process and the testing assists in the understanding of experimental error and provides an indication of the level of confidence in the test results (Montgomery, 1991; Barnes, 1997). Knowing the variance in the testing can help establish if changes in product properties are from deliberate changes to inputs, random process variation or variation in the testing methods.

The process capability was tested using three identical formulations to determine the ability of the process to reproduce samples. Test repeatability was assessed using a single emulsion, with the various tests repeated 5 times. 95% confidence intervals were calculated on the averages of the test repeatability data to provide an indication of the variation. Table 4-3 shows the percentage variation calculated from the study.

Overall the test variation was less than the process variation. All the emulsion and binder tests had lower variation than the process. But the microsurfacing cohesion results gave similar results for both the test and process variation. In particular, the Loaded Wheel Test for permanent deformation had very high variation as does the microsurfacing mix time. The high variation in the microsurfacing results are likely due to the effects of the aggregate and its adhesion and cohesion with the binder. Subsequent experimental trials (see Chapter 5) confirmed that the quality of the aggregate has a major influence on the variation in the microsurfacing tests.

Table 4-3. Variation in Laboratory Production Process and Testing Methods

Test	Process Error ± %	Test Error ± %
pH	25.63	1.16
Viscosity 5 rpm	5.89	0.00
10 rpm	8.61	0.00
20 rpm	8.53	3.01
50 rpm	10.35	0.00
Binder Residue	2.77	0.30
Settlement	42.26	8.78
Sieve Residue	33.10	7.75
Softening Point	3.27	2.90
Wet Track Abrasion	21.07	15.30
Permanent Deformation (Height)	45.31	24.29
(Width)	84.57	65.04
Slurry Cohesion 60 min	17.56	17.35
120 min	14.21	12.43
150 min	9.16	15.52
180 min	20.19	6.03
210 min	19.09	18.25
Mix Time	39.91	30.77

The high variation in the microsurfacing slurry tests indicates that these tests were likely to have a reduced ability to detect small changes in the output properties from deliberate changes in the formulation. Factors that had a large effect on the properties could probably be detected despite the large variation. Past experience and comments from other studies (Lu & Issacson, 1995; Holleran, 1996; Reed et al., 1997) tend to confirm that most of the slurry tests are only good as indicators of trends rather than accurate assessment methods as the tests are mainly for production and process control.

4.7 DEVELOPMENT METHODOLOGY

Three experimental phases were undertaken during the laboratory development:

1. Initial Design investigation

- Using an experimental design to investigate different polymer addition methods to the emulsion, and different bitumen grades.
- Investigate potential to emulsify different polymers.

2. Emulsifier Investigation

- Comparing properties of other emulsifiers.
- Comparing different aggregate sources and quality

3. Detailed Design Investigation

- Exploring specific formulation parameters using experimental design.

4.7.1 Initial Design

There are four potential avenues for adding the polymer to the emulsion:

- Pre-blend polymer into the bitumen phase;
- Pre-blend the polymer into the soap phase;
- Co-mill the polymer by metering it into the mill just before the soap line;
- Post adding the polymer to the manufactured emulsion.

Each of these methods required assessing to determine which one would disperse the polymer the best, and if the methods used had a major effect on emulsion and slurry performance. All the addition methods were to be assessed with each polymer where the process allowed, and two bitumen grades – 80/100 and 180/200 to assess resistance to permanent deformation. The polymer concentration was fixed at 3%. An experimental design method was used for the addition methods of co-milling, post adding, and pre-blending in the soap solution for SBR latex.

A separate trial incorporated SBS, and EMA as these polymers can only be added to the bitumen phase. SBR latex can also be added to the bitumen phase and was used in this trial as well. This trial investigated monophase modified emulsions.

A standard slurry formulation and mix design was used in all of the initial polymer investigation trials as shown in Tables 4-4 and 4-5 to help develop familiarity with the product and improve the formulation as increased data was collected. Unmodified emulsions using both bitumen types were used as controls to compare the polymer modified emulsions performance against.

Table 4-4. Initial Emulsion Formulation

Materials and conditions	**Criteria**
Bitumen	62%
Polymer	3%
Emulsifier A	1.5%
pH	3.0

Table 4-5. Initial Microsurfacing Mixture Design

Material	**Proportion**
Type II Bulls Aggregate	100%
Emulsion	15%
Cement	0.0 – 0.5%
Control Additive (emulsifier A) 10%	1.5 – 2.0%
Water	7.0 – 8.0%

Note: Mix design based on dry weight of aggregate

The experimental design consisted of qualitative variables bitumen grade and polymer addition method. The design consisted of two bitumen levels and three polymer latex addition methods. To enable the experimental design to be analysed with statistical software a coding system was used to identify the variables. Bitumen was coded 100 and 200 for the respective grades. While the latex polymer addition methods were coded 1, 2, 3 for co-milling, soap addition, and post addition as shown in Table 4-6.

Table 4-6. Experimental Design Matrix for SBR latex Biphase Emulsions

Run	Random	Bitumen	Polymer Addition
1	3	100	3 (Post Add)
2	1	100	1 (Co-mill)
3	4	200	1 (Co-mill)
4	5	200	2 (Soap Phase)
5	2	100	2 (Soap Phase)
6	6	200	3 (Post Add)
7*	7	200	2 (Soap Phase)

* Replicate run

4.7.1.1 Monophase Emulsion Investigations

An initial emulsion was produced with SBS polymer added to the higher viscosity 80/100 bitumen to determine if monophase modified emulsions could be produced in the colloid mill. The reason being to test if the polymer-bitumen phase could be heated enough to allow it to be milled adequately. SBS produces a lower viscosity when mixed with hot bitumen than either of EMA or SBR so it would be the most likely combination to work. The result of this experiment led to the abandonment of pre-blending polymer with hot 80/100 bitumen before the emulsion process. Instead the trials used the lower viscosity 180/200 bitumen and are shown in Table 4-7. Previous development work by Higgins has determined that cross-linker A successfully stabilises SBS and EMA against phase separation. The additives aromatic oil A and amine A were recommended by suppliers as a possible means to help the emulsification of SBR.

Table 4-7. Initial Trial Runs for Producing Monophase Polymer Modified Emulsions

Trial	Polymer	Bitumen	Polymer Content	Additives	Additive Content
1	SBS	80/100	3%	Cross-linker A	0.05%
2	SBS	180/200	3%	-	-
3	EMA	180/200	3%	Cross-linker A	0.05%
4	SBR	180/200	3%	Aromatic oil A Amine A	5.0% 0.5%

Table 4-8. Formulations for Monophase Polymer Modified Emulsions using 130/150 Bitumen

Trial	Polymer	Bitumen	Polymer (%)	Additive	Additive Content
1	EMA	130/150	3	-	-
2	SBR	130/150	3	Aromatic oil A	2.0%
				Amine A	0.5%

Two further trials were conducted using EMA and SBR polymer. The EMA trial used 130/150 bitumen and without cross-linker A added. This was to assess the emulsion stability without cross-linker A, and the slurry performance improvement by using bitumen with a higher stiffness than 180/200 bitumen, but lower viscosity than 80/100 bitumen. The SBR trial also used 130/150 bitumen, but with a lower aromatic oil A content. The two trial formulations are shown in Table 4-8. The results were analysed by comparing with an unmodified emulsion, and with the results of the biphase emulsion experiments. The polymer addition method, bitumen type, and polymer that displayed the optimum properties for the emulsion and slurry were to be used for the remainder of the investigation.

4.7.2 Emulsifier Investigation

This brief investigation aimed to identify if increased cohesion development times, and increased emulsion stability resulted from two alternative microsurfacing emulsifiers. Additionally a comparison between aggregate sourced from New Plymouth and the Bulls aggregate was investigated due to the previous poor results.

The experimental work from sections 4.7.1 determined that 80/100 bitumen and post addition of SBR latex polymer to the emulsion provided the best mix of performance properties. These aspects were included in the formulation design for this experiment. Table 4-9 shows the formulation design for the trials. The emulsifier quantities and associated pH levels were determined from supplier literature. The loaded wheel test for permanent deformation was not included due to equipment breakdown. The results from the investigation were compared with those from the post addition trial run with 80/100 bitumen in the latex addition trial.

Table 4-9. Formulations for Emulsifier Experiment

	Trial 1	Trial 2
Emulsifier	Emulsifier C	Emulsifier B
Emulsifier Content	1.2%	1.2%
pH	2.0	2.0
Polymer	SBR latex	SBR latex
Polymer Content	3%	3%

4.7.3. Aggregate Assessment

Time constraints meant a brief aggregate assessment could only be made. This investigation examined the aggregate source, cleanliness, and cement content on the performance of the microsurfacing. Two aggregate sources were used, Bulls aggregate (Greywacke) and New Plymouth (Andesite). Two sand equivalent values were tried with Bulls aggregate, 54% and 70%. The New Plymouth aggregate had a sand equivalence of 82%. The cement was set at 0% and 0.5%. The emulsion used for the trial was identical to the 100-pen bitumen and post added SBR latex run from the biphase emulsion trial. The investigation runs are shown in Table 4.10. The mix design was unchanged except for the cement level variation.

Table 4-10. Experimental Plan for Aggregate Assessment

Run	Source	Sand Equivalent (%)	Cement (%)
1	Bulls	54	0.0
2	Bulls	54	0.5
3	Bulls	70	0.0
4	Bulls	70	0.5
5	New Plymouth	82	0.0
6	New Plymouth	82	0.5

The microsurfacing samples were tested for abrasion and cohesion development to assess the performance effects.

4.7.4 Formulation Detailed Design

The initial formulation design phase and emulsifier experiment provided sufficient information to allow selection of the emulsion and microsurfacing materials, and refine the emulsion processing method. This provided the base from which to perform a more detailed formulation design and analysis.

4.7.4.1 Design of experiment

A full factorial two level experimental design was used to refine the emulsion properties. Time constraints only allowed three factors to be studied. The key parameters identified from the previous experimental trials and from emulsion literature for modified emulsions were:

- SBR Polymer content
- Emulsifier B content
- Soap solution pH

The polymer content has a direct influence on the binder properties and the resistance to permanent deformation of the microsurfacing. The emulsifier content and pH are important factors for emulsion stability, while the emulsifier is a determinant of how quickly slurry cohesion development can be attained. The levels of the factors to be studied are shown in Table 4-11 and are also derived from a combination of the experimental work performed so far, and technical literature.

Table 4-11. Factors and Levels for Experimental Detailed Design

Code	Factor	High Level	Low Level
a	Polymer Content	5.0	3.0
b	Emulsifier Content	1.4	1.0
c	pH	2.4	1.6

The experimental design includes three centre point runs to allow an estimation of the experimental error and determine the significance of the results. The design matrix is seen in Table 4-12 with the high factor levels denoted with a '+' and low levels with a '-', the centre points are indicated by a'0'. The treatment table for the design, which includes the specified component levels and the randomised order, is shown in Table 4-13. A Yates coding system was used to identify the runs. The results were analysed with the Minitab statistical software program to investigate interactions between factors and effects of the factors on response variables.

Table 4-12. Full Factorial Experimental Design Matrix for Three Factors at Two Levels

Run	Code	Polymer	Emulsifier	pH
1	1	-	-	-
2	a	+	-	-
3	b	-	+	-
4	ab	+	+	-
5	c	-	-	+
6	ac	+	-	+
7	bc	-	+	+
8	abc	+	+	+
9	Centre_1	0	0	0
10	Centre_2	0	0	0
11	Centre_3	0	0	0

Table 4-13. Experimental Design Treatment Combinations for Three Factors and Two Levels

Run	Random	Polymer	Emulsifier	pH
1	11	3.0%	1.0%	1.6
2	1	5.0%	1.0%	1.6
3	8	3.0%	1.4%	1.6
4	3	5.0%	1.4%	1.6
5	6	3.0%	1.0%	2.4
6	9	5.0%	1.0%	2.4
7	10	3.0%	1.4%	2.4
8	7	5.0%	1.4%	2.4
9	2	4.0%	1.2%	2.0
10	4	4.0%	1.2%	2.0
11	5	4.0%	1.2%	2.0

The processing variables and characteristics used are shown in Table 4-14. The slurry mixture design is shown in Table 4-15 and outlines the materials and proportions expected to be used. The control additive used was retarder A, instead of emulsifier A as an assessment determined that both additives produced the same effect but, retarder A was cheaper (S, Bearsley, 5 January 2000, personal communication).

Table 4-14. Emulsion Formulation and Processing Conditions for Detailed Design

Processing Characteristics	Criteria
Bitumen	80/100 penetration
Polymer	SBR latex
Emulsifier	Emulsifier B
Acid	HCl
Polymer addition method	Post Addition
Bitumen temperature	150°C
Soap temperature	40°C
Bitumen flow rate	862-865 cc/min
Soap flow rate	500 cc/min

Table 4-15. Microsurfacing Mixture Design for Detailed Design Formulation

Material	Proportion
Type II Bulls aggregate	100%
Emulsion	15%
Retarder A 10% solution	0.5 %
Water	7.0 %
Aggregate sand equivalence	70%

Note: Mix design based on dry weight of aggregate

The assessment of permanent deformation was performed on samples of 0, 3, 4 and 5% polymer addition and not the entire design due to equipment failure.

5. LABORATORY DEVELOPMENT RESULTS

5.1 Introduction

The methodology of the experimental work was broken down into three phases as outlined in Chapter 4: initial design, emulsifier/aggregate investigation, and detailed design. The initial design phase explored the ability of three different polymers to be emulsified using different bitumen grades. The latex polymer SBR added another dimension to the potential emulsion production process in that it can be added to an emulsion in four methods. This degree of flexibility allows for increased polymer concentrations and a simplified production process. The emulsifier experiment compared the effects of other emulsifiers on emulsion properties and the effects of aggregate quality on the cure rate of the microsurfacing. The detailed design experiment was based around the data collected from the previous investigations and allowed a more detailed exploration of the emulsion formulation to identify a likely starting prototype microsurfacing. This chapter describes the results of these design phases on the formulation development of the microsurfacing. Chapter 6 describes in detail the confocal microscopy imaging results of the binders and microsurfacing.

Part of the result analysis for the experimental design used 'Minitab' statistical software (version 12.23, produced by Minitab Inc, USA). The significance of individual factors and interactions between them were assessed for statistical significance at a 95% confidence level. The significance of factors is represented by the p-value, which represents the significance of the effects. A value of less than 0.05 (or 5%) means the probability of an observed change in a property, which did not result from a deliberate change in the factor levels, would be less than 5% or significant to a 95% confidence level.

5.2 INITIAL DESIGN INVESTIGATION

5.2.1 SBR Latex Modified Biphase Emulsion Results

Seven biphase emulsions were produced using SBR polymer latex. The polymer was added to the emulsion in three methods: co-milling, soap phase addition and post addition as described in section 4.7.1. The other factor varied was the bitumen grade used, which consisted of stiffer 80/100 penetration bitumen and softer 180/200 penetration bitumen. A summary of the experimental run results is shown in Table 5-1. The full results are held in Appendix 5-1.

The significance of the variance of the factors on the response variables is shown in Table 5-2 where the statistical p-values are recorded for each emulsion property. The qualitative nature of the factors meant in-depth effect analysis could not be done.

5.2.1.1 Emulsion Production Control Properties

Final Emulsion pH

The soap solution pH and the polymer latex pH determined the final emulsion pH. When compared to an unmodified emulsion the effect of adding latex is to increase the emulsion pH. The final pH was recorded as a check of production quality. For stability purposes the pH must be less than 7.0.

Binder Residue

The residual binder residue was required by specification to be within 60 – 65% with a target of 62% and is recorded as a production check. The emulsions were produced between 60.53 – 63.15% with a mean of 61.90% and standard deviation of 0.91%.

Table 5-1. Summary of Test Results from SBR Latex Biphase Emulsion Investigation

	Emulsion Sample								
	Unmodified 200-pen ^{X}	Unmodified 100-pen ^{X}	Post Added 200-pen	Soap Phase 200-pen	Soap Phase 200-pen #	Co-mill 200-pen	Post Add 100-pen	Soap Phase 100-pen	Co-mill 100-pen
pH (Units)	3.59	4.07	5.23	4.87	4.86	4.72	4.86	4.76	4.63
Binder Residue (%)	60.53	61.27	61.19	63.15	63.05	61.78	60.90	62.44	61.36
Viscosity*(cP)	120	120	130	130	120	80	120	100	90
Settlement (%)	16.65	16.43	14.65	14.90	18.86	50.72	21.27	36.23	39.99
Sieve Residue (%)	0.62	0.35	0.47	0.69	0.62	1.00	0.39	0.41	0.56
Softening Point (°C)	41.9	51.0	49.1	50.9	52.2	49.4	60.3	63.8	63.3
Abrasion (g/m^2)	1658	1921	1550	1474	1573	1330	1905	1457	1935
Deformation (%) Height	37.8	36	29	26	32	42	14	14	24
Width	52.8	30	25	13	22	32	0	3	7
Slurry Cohesion (kg-cm)									
60 minutes	9.6	9.0	12.0	11.0	10.0	9.0	9.0	9.0	9.0
120 minutes	13.4	13.0	17.0	14.0	13.0	13.0	14.0	13.0	16.0
Slurry Mix Time (sec)	184	170	450	150	120	30	360	120	120

* Viscosity at 5 rpm.

Replicate Run

^{X} Unmodified Control Emulsions

Table 5-2. Significance of Variables from SBR Latex Biphase Emulsion Investigation

	Response Variables								
	Viscosity*	**Settlement**	**Seive Residue**	**Softening Pt**	**WTA**	**LWT**	**Cohesion(60)**	**Cohesion(120)**	**Mix Time**
Factor	**P-value**	**P-value**	**P-value**	**P-value**	**P-value**	**P-value**	**P-value**	**P-value**	**p-value**
Bitumen	0.373	0.259	0.096	0.037	0.116	0.130	0.225	0.282	0.814
Polymer Addition Mode	0.170	0.099	0.136	0.278	0.262	0.298	0.426	0.245	0.040
Bitumen* Polymer Mode	0.354	0.172	0.265	0.559	0.187	0.923	0.426	0.398	0.228

*Viscosity at 5 rpm

Key: ☐ Most Significant variable

5.2.1.2 Emulsion Viscosity

There was a slight decrease in viscosity between the modified emulsions with 200 pen bitumen and 100 pen bitumen. The modified runs with 200 pen bitumen ranged from 80 – 130 cP, while for 100 pen the range was 90 – 120 cP. The emulsion viscosity varied little between the soap solution addition method and post addition of the polymer. Co-milling the latex saw a drop in viscosity of 30 – 40 cP at 5 rpm. The shear rate of 5 rpm was chosen as it is normally referred to by industry specifications. Harder bitumen emulsions such as 100 pen should have lower a viscosity and this trend was observed.

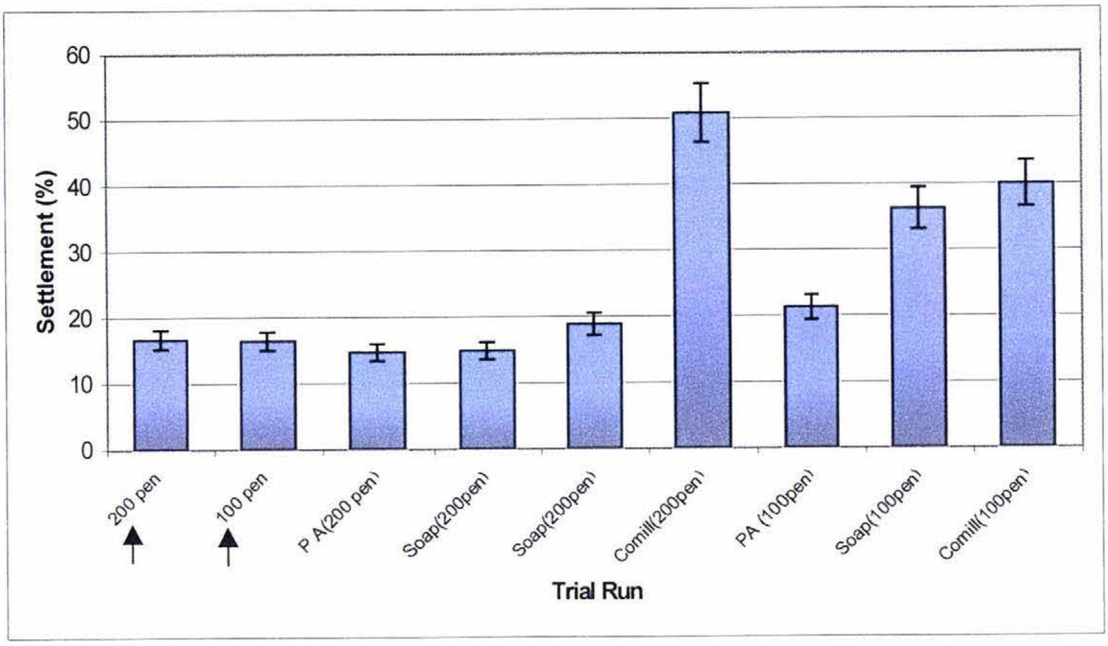
In theory (Rabiot & Jariel, 1993) the polymer should reduce the viscosity as the emulsion would have a wider particle size distribution, but this effect is not consistently apparent except for the co-mill runs. The most significant effect on the viscosity was method of latex addition though it only had a significance of 0.17.

5.2.1.3 Emulsion Settlement

The emulsion settlement specification for five days storage is less than 5%. This means the binder solids content between the top portion and bottom portion of the emulsion should not be different by more than 5%. The co-mill runs both had very high settlement results of 39.99% with 100 pen bitumen and 50.72% with 200 pen bitumen indicating a lack of stability. All of the modified emulsions experienced creaming of the latex to the top of the sample. Emulsions produced with harder grade penetration bitumen do tend to have higher settlements than those with softer 200 pen bitumen and this trend is observed in the settlement results as shown in Figure 5-1. Post adding the polymer latex to the emulsion provides the lowest settlement of the 100 pen bitumen emulsions. The polymer addition mode to the emulsion was the most significant factor with a p-value of 0.099, which indicates that it was significant to a 90% confidence level.

The co-mill runs and the soap addition run with 100 pen bitumen have the lowest viscosities. This often leads to higher sedimentation as the particles are freer to move, and the settlement results reflect this. The density difference between the bitumen and latex causes the creaming of the latex. The density difference is slightly higher with 100 pen bitumen than softer 200 pen bitumen. This was the prime cause of the higher settlement values compared to unmodified emulsions.

Figure 5-1. Five Day Emulsion Settlement for SBR Biphase Emulsion Investigation



Key: → Unmodified control emulsions

5.2.1.4 Emulsion Sieve Residue

The modified emulsions with 100 pen bitumen had a lower sieve residue than those with 200 pen bitumen. The same effect occurs with the unmodified control emulsions. The co-mill runs had high levels of retained particles, 1.00% with 200 pen bitumen and 0.56% for 100 pen. There were no factors significant to a 95% confidence level, though bitumen grade was to a 90% level.

Harder grade bitumen does tend to give a particle size distribution that has a higher mean particle diameter and a broader distribution. But the sieve results indicate that the distribution width may be narrower than the 200 pen runs. It is expected that if the settlement is low the particles retained on the 150 μm sieve would be low as the particle size distribution would be narrower (Whiteoak, 1990). But while the high settlement results from the co-milled runs are also paired with high sieve residue, so are the two 200 pen bitumen runs with polymer soap added which have low settlement values as seen in Table 5-1. The high sieve residue could be an indication of early coalescence within the emulsions.

5.2.1.5 Binder Properties

The SBR polymer as expected increased the softening point of the binder as seen in Table 5-1. The addition of 3% SBR generally provided a 10°C increase in the softening point over an unmodified emulsion but, interestingly about 4°C - 5°C higher than hot polymer modified bitumen with the same polymer.

This result is important as literature studies (Coyne, 1987; Anderson, 1992; PIARC, 1999) show the softening point of modified emulsions as being very similar to hot polymer bitumen. A higher softening point is desirable as it helps the bitumen resist thermal stress. There was no significant effect with polymer addition mode, but the grade of bitumen is significant which is expected as 100 pen bitumen is stiffer and has a higher softening point than 200 pen bitumen.

The microstructure of the modified samples shows how the polymer improves the bitumen properties and is covered in detail in Chapter 6.

5.2.1.6 Microsurfacing Abrasion Resistance

The best result was 1330 g/m^2 for the co-mill run with 200 pen bitumen and the other co-mill run the highest at 1935 g/m^2. The results as seen in Table 5-1 show considerable variation and at times the trials with harder 100 pen bitumen with polymer modification had worse results than the unmodified 200 pen bitumen slurry. Bitumen grade was not significant with a p-value of 0.116, though it was expected that it would be.

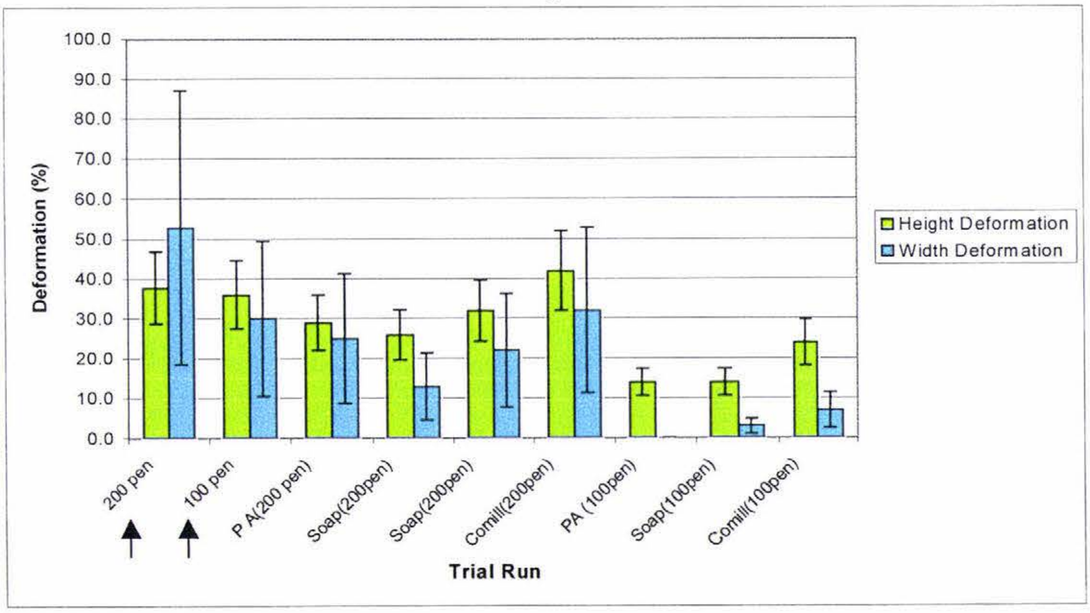
The specification for Wet Track Abrasion is less than 800 g/m^2. The results indicated that there was an inherent problem with the test itself, or that the aggregate/binder adhesion and cohesion was poor and the aggregate was not sufficiently bound by the binder. The cause was suspected as being the cleanliness of the aggregate, which can reduce the ability of the emulsion to adequately coat the aggregate. Another possibility was emulsifier type and concentration in particular as higher levels can retard the cohesion due to too much free emulsifier in the water phase of the emulsion.

5.2.1.7 Microsurfacing Permanent Deformation

The Loaded Wheel Test results in Figure 5-2 shows an improvement in the performance when the harder 100 pen bitumen is used with SBR latex. The height deformation target was less than 10%, which was not quite achieved in the results. The bitumen grade had a significance of only 0.116 and was not significant.

Bitumen grade would be expected to be significant but the high p-value reflects the variation observed in the results. The error in the test was very high but the degree of improvement obtained by using 100 pen bitumen is still clear. Variable binder cohesion with the aggregate was suspected as being the main cause of the variation in much the same way as the abrasion test.

Figure 5-2. Microsurfacing Permanent Deformation for SBR Biphase Emulsion Investigation



Key: → Unmodified control microsurfacings

5.2.1.8 Microsurfacing Cohesion

After 60 minutes all of the trial run combinations have cohesion values between 9 – 12 kg-cm as shown in Table 5-1. There was no significant effect with the factors. The emulsifier A system used for this stage of the laboratory trials did not meet the target cohesion until 180 – 210 minutes.

The target slurry cohesion strength for a microsurfacing system is 20 kg-cm after 60 minutes to allow traffic quickly back onto the pavement. The type and level of emulsifier and aggregate were important aspects to further investigate for cohesion development.

5.1.2.9 Mix Time

The mix times of the microsurfacing slurry were affected by the method of adding the polymer to the emulsion as shown by the times in Table 5-1. Polymer addition method had a p-value of 0.040, which is significant. The co-mill emulsion run with 200 pen bitumen broke in 30 seconds, which was too quick, indicating the emulsion was not stable. The others were between 120 to 150 seconds breaking time. The desirable minimum mix time was 180 seconds, which post addition easily achieved. The post addition run with 200 pen bitumen had a break time of 450 seconds that was slightly too long, while the run with 100 pen bitumen was 360 seconds which was acceptable. The full mix design and mix time results are held in Appendix 5-2.

A longer mix time enables more time for the mixture to be laid and areas to be hand worked where necessary. The emulsifier in the polymer latex system is a very slow setting type and this can retard the break time of the overall emulsion.

5.2.2 Monophase Polymer modified Emulsion Results

Three different polymers were investigated where each was dispersed into hot bitumen and mixed for one hour before being emulsified as described in Section 4.3. The polymers SBS and EMA are only dispersible in hot bitumen while SBR latex can be dispersed in all methods and was included in this investigation of monophase emulsions.

To maintain compatibility with the hot bitumen and prevent phase separation of the polymer, various additives were added to the bitumen depending on the polymer characteristics as described in Sections 4.1 and 4.7.1. The effects on emulsion stability, binder performance, and microsurfacing properties were compared. The overall properties of the monophase emulsions were then compared with the biphase emulsions to determine the best polymer and addition method.

5.2.2.1 Emulsification of 100-penetration Bitumen and SBS

An attempt to emulsify 3% SBS with 80/100 penetration bitumen failed. The bitumen-polymer blend temperature was 160°C and the soap temperature 34°C. The mill rotor clearance was set at the lowest setting of 0.17 mm but significant backpressure was encountered with no product produced. The mill gap was increased to 0.212 mm but only bitumen-polymer sludge was produced and there was still backpressure occurring.

It appeared that the mill was unable to shear the bitumen blend and this could be due to several factors:

1. The bitumen-polymer blend viscosity was too high.
2. The addition of cross-linker A to cross-link the polymer to the bitumen may make it difficult to shear the bitumen, as the styrene ends are not disassociating under stress and heat.
3. The elastic properties of elastomer polymers are normally meant to prevent the susceptibility of bitumen to shearing forces encountered on roads. Hence the cross-linked polymer may have prevented the bitumen being sheared into droplets.

It is noted that all of the literature studies encountered on emulsifying Linear SBS through a colloid mill have used softer 180 – 220 penetration grade of bitumen and not the harder 80/100 grade (Coyne, 1987; Anderson, 1992; Serfass et al., 1992; Rabiot & Jariel, 1993). This could be due to the difficulty in emulsifying hard penetration bitumen modified with SBS.

5.2.2.2 Emulsification of 200-penetration bitumen and SBS

A second attempt to emulsify SBS was tried but using 180/200 pen bitumen without cross-linker A addition. The mill temperature was 160°C and soap temperature 32°C. The lowest mill gap of 0.170 mm was used. The blend was emulsified satisfactorily but the exit temperature was 90 - 91°C, which was about the upper limit desirable for an emulsion. After discharge a thin amount of stringy residue was observed floating on the top of the emulsion. Approximately one hour after production the bitumen-polymer droplets were rapidly coalescing and forming stringy residue around the sides of the can indicating poor stability.

The probable cause for the poor stability of the modified emulsion is that the SBS polymer is not stable by itself in the Safaniya bitumen supplied to New Zealand (Transit, 1993). This will require further investigation into methods of compatibilising the polymer-bitumen blend. Due to time constraints further investigations were outside the scope of this study.

The planned emulsification of EMA and SBR pre-blended with 80/100 bitumen was abandoned as the blends have a viscosity similar or greater than SBS modified bitumen. It was extremely unlikely that a suitably high enough temperature to reduce the blend viscosity to around 200 cP entering the mill would be achievable. Also the temperature of the soap phase would not be low enough to prevent excessive exit temperatures from the mill.

5.2.2.3 Emulsification of SBR Modified Bitumen and EMA Modified Bitumen

The emulsification of modified blends of EMA and SBR with 200 pen bitumen and 150 pen bitumen was successful. Problems encountered were that cross-linker A reacted with hydrochloric acid from the emulsifier phase to produce undesirable toxic fumes. Hence, the trial run with EMA and 150 pen bitumen was processed without cross-linker A to determine if it was necessary for emulsion stability. The SBR trial with 150 pen bitumen had some polymer residue retained in the bitumen tank filter and indicated that less than 3% polymer was actually added into the emulsion. A summary of the experimental run results is shown in Table 5-3. The full experimental results are held in Appendix 5-3.

5.2.2.3.1 Final Emulsion pH and Binder Residue

The final emulsion pH for the runs with SBR polymer were very closes a neutral value of 7.0. This was due to the addition of amine A which is an amine derivative with a high pH. The binder residue varied between 60.91% – 61.48% for the four trials, which was within specification.

5.2.2.3.2 Emulsion Viscosity

The emulsions with EMA maintained a higher viscosity with each bitumen type used. The values at 5 rpm were 120 cP (EMA 200 pen) and 105 cP (EMA 150 pen). Only the run with SBR and 150 pen bitumen had a significantly lower viscosity value of 90 cP.

Emulsifying harder bitumen results in larger particles which lowers the viscosity and this effect was consistent with the results.

Table 5-3. Summary of Test Results from Monophase Emulsion Investigation

	Emulsion Sample				
	Unmodified 200 pen	**A**	**B**	**C**	**D**
pH (Units)	3.59	3.56	6.56	4.03	6.45
Binder Residue (%)	60.53	60.91	61.48	61.45	61.27
Viscosity*(cP)	120	120	110	105	90
Settlement (%)	16.65	10.90	16.39	15.13	22.20
Sieve Residue (%)	0.62	0.40	0.12	0.41	0.18
Softening Point (°C)	41.9	48.7	45.3	52.3	49.3
Abrasion (g/m^2)	1658	2320	1757	2043	2273
Deformation (%) Height	37.8	42	56	38	47
Width	52.8	42	60	33	40
Slurry Cohesion (kg-cm)					
60 minutes	9.6	9.0	10.0	10.0	10.0
120 minutes	13.4	13.0	11.0	13.0	12.0
Slurry Mix Time (sec)	184	100	60	300	180

* Viscosity at 5 rpm

Key: A = EMA with 200-pen bitumen, 0.03% cross-linker A
B = SBR with 200-pen bitumen, 5% aromatic oil A, 0.5% amine A
C = EMA with 150-pen bitumen
D = SBR with 150-pen bitumen, 2% aromatic oil A, 0.5% amine A

5.2.2.3.3 Emulsion Settlement

The monophase modified emulsions are more storage stable than biphase emulsion and are not affected by creaming of the polymer. The EMA modified emulsions were the most stable to settlement with a value of 10.9% with 200 pen bitumen and 15.1% with 150 pen bitumen. SBR had slightly higher results of 16.4% with 200 pen bitumen and 22.2% with 150 pen bitumen but, these emulsions have far better settlement than the biphase emulsions in Section 5.2.1.3. The subsequent drop in viscosity with the SBR/150 pen bitumen emulsion is reflected in the increased settlement result.

The moderate 5% increases in the settlement results are probably attributable to the harder penetration bitumen used, rather than through any significant instability. The settlement results were also helped by not experiencing any creaming of the polymer as observed in the biphase emulsions due to the latex portion of SBR flashing off in the hot bitumen. The elimination of the cross-linker A from the 150 pen trial with EMA polymer appeared to have not affected the settlement of the emulsion, as the small increase in settlement was more likely due to the harder bitumen used.

5.2.2.3.4 Sieve Residue

The sieve residue results between each polymer were very similar despite using two different penetration grade bitumen. EMA had residues of 0.40% and 0.41% with 200 pen and 150 pen bitumen respectively. The SBR modified emulsion had residues of 0.12% and 0.18% respectively.

The higher results for the EMA possibly suggest a larger spread of particle sizes but the trials had better settlement than the SBR. This could be due to the better compatibility of EMA or that the EMA emulsions have a lower median particle diameter. The almost identical results for the EMA trials also suggest that cross-linker A has little effect on the emulsion stability.

5.2.2.3.5 Binder Properties

The softening point of EMA modified 200 pen bitumen emulsion residue was 48.7°C but a higher softening point was required for microsurfacing. The change to 130/150 bitumen increased the softening point for EMA to 52.3°C still below the desired specification of 57°C minimum.

As a comparison, EMA added to hot 200 pen bitumen before emulsification has a softening point of 48°C to 50°C (Bearsley, 1998), which is the same as the emulsion residue. This result is important because as already seen the biphase emulsion residue has a far higher softening point than expected.

The SBR modified binder with 200 pen bitumen had a softening point of 45.3°C. The biphase emulsions with the same bitumen had values of 49°C to 52°C. The addition of

Aromatic oil A appears to have lowered the softening point of the SBR binder by 4°C – 5°C. The aromatic oil content was reduced to 2% for the emulsification with 150 pen bitumen to reduce this effect. At 2% addition the aromatic oil was expected to lower the softening point by approximately 1°C. But the result of 49.3°C was around 4°C - 5°C lower than expected.

Aromatic oil is known to decrease the softening point as it contains mostly aromatic oil, which have molecular weights between 300-2,000. But, asphaltenes have molecular weights between 1,000-100,000 (Whiteoak, 1990) and the asphaltene content in the bitumen is lowered by addition of the oil. The low result for the 150 pen bitumen run could be caused by having less than 3% SBR in the binder, and the polymer residue retained in the filter of the colloid mill bitumen tank tends to suggest this was the case.

5.2.2.3.6 Microsurfacing Abrasion

The wet track abrasion results were very high with all of the sample values over two times higher than the specification of 800 g/m^2. There was some improvement using the harder bitumen with EMA but still provided a poor value of 2043 g/m^2, while the SBR/150 pen bitumen combination actually provided a worse result of 2273 g/m^2.

The poor results with SBR polymer and 200 pen bitumen could be due to the softening effects of aromatic oil A, and with the 150 pen bitumen run the proposed reduction in actual polymer added. As with the abrasion results obtained in the biphase emulsion investigation the cause of the poor abrasion is attributed to two areas:

1. Poor quality and/or source of aggregate which, can interfere with binder adhesion and subsequently binder cohesion (Asphalt Institute, 1994).
2. Excess free emulsifier in the water phase, which retards cohesion development (Engman et al, 1998).

5.2.2.3.7 Microsurfacing Permanent Deformation

The permanent deformation of the slurry using 200 pen bitumen was very high for both EMA (42% height and 42% width) and SBR (56% height and 60% width). The SBR result was worse than that of unmodified sample as seen in Table 5-3. The resistance improved with the use of 130/150 bitumen for EMA (38% height and 33% width deformation) and for SBR (47% height and 40% width), but the rutting was still too high. The probable loss of polymer during emulsification of the SBR/150 pen bitumen would have contributed to the high result. Interestingly EMA is a plastomer and has high stiffness properties. It was expected that it would have performed better than it did in the test with 150 pen bitumen. The loaded wheel test has a high test error, which is due to the test result being a function of the emulsion and aggregate properties. Poor adhesion and subsequent cohesion development between the binder and aggregate because of excessive dirt particles would reduce the effectiveness of the surfacing to resist deformation.

The Bulls aggregate used is the standard product produced at the plant. But the sand equivalence of the Bulls aggregate was 49%, and is actually well under the ISSA (1996) A143 specification of 60%. Normal slurry surfacing requires a minimum aggregate cleanliness of 45% but this did not appear good enough for resisting deformation in a microsurfacing.

5.2.2.3.8 Microsurfacing Cohesion

The slurry cohesion was slow to develop and the maximum any of the four trials attained after two hours was 13 kg-cm, which was well below the target specification of 20 kg-cm.

Like the biphase cohesion results the main cause could be too much free emulsifier in the water phase of the emulsion as the bitumen droplets are saturated with emulsifier. Or alternatively, the emulsifier is not effective in adequately penetrating the bitumen droplets as suggested by Engman et al. (1998). The level of emulsifier in the emulsions has been consistently 1.5% to maintain stability but this may be at the expense of cohesion development. Emulsifier A is not a quick setting type and a different emulsifier could also improve the cohesion development.

5.2.2.3.9 Mix Times

The SBR microsurfacing slurry with 200 pen bitumen had a mix time of 60 seconds even with the emulsifier additive to retard the break time at the high level of 2.0%. This doesn't allow enough time for adequate hand working of areas by the slurry crew. The

EMA slurry with 200 pen bitumen produced a mix time of 100 seconds which is still slightly too quick. Both of the polymers with 150 pen bitumen had acceptable mix times mainly by changing to a harder bitumen, as the mix design was kept the same except for 0.5% more pre-wet water added. The mix design results are shown in Table 5-4.

Table 5-4. Slurry Mix Design Results for Monophase Emulsion Investigations

	Sample			
	A	B	C	D
Mix Design				
Aggregate (%)	100	100	100	100
Emulsion (%)	15	15	15.1	15
Emulsifier A 10% solution (%)	2.0	2.0	2.0	2.0
Cement (%)	0.5	0.5	0.5	0.5
Water (%)	7.0	7.0	7.5	7.5
Mix Time (sec)	100	60	300	180
Sand Equivalent (%)	49	49	49	49

Note: Mix design based on dry weight of aggregate.

Key:
A = EMA with 200-pen bitumen, 0.03% cross-linker A
B = SBR with 200-pen bitumen, 5% aromatic oil A, 0.5% amine A
C = EMA with 150-pen bitumen
D = SBR with 150-pen bitumen, 2% aromatic oil A, 0.5% amine A

5.2.3 Conclusions

Overall, it is apparent from these results that the hard 80/100 penetration grade bitumen must be used as the 150 pen and 200 pen grades are too soft. SBR latex was the most suitable polymer to provide the necessary resistance to deformation of the microsurfacing pavement. It was also the only polymer capable of being added to 100 pen bitumen. SBS was unsuitable for emulsification, while EMA was stable but not suitable with 100 pen bitumen. The softening point of the SBR modified binder using 100-pen bitumen was 60°C to 63°C, which exceeded the minimum specification required.

Biphase emulsions produced with SBR latex were the only way of modifying 100 pen bitumen to give stable emulsions and the required microsurfacing properties. The post addition method of addition provided the best combination of emulsion stability properties. This method was selected for further investigations. The addition method appeared to have no significant effect on the slurry properties except that post addition resulted in a longer slurry mix time.

Monophase modified emulsions could only be produced adequately with EMA using two bitumen grades, 150 pen and 200 pen. SBR could only be produced using 200 pen bitumen. The binder performance was not sufficient for a microsurfacing, but the EMA emulsion could have use as a spray chip-sealing product. Both SBR and SBS require further investigation into compatibilising additives that will be stable when emulsified with Safaniya bitumen.

The microsurfacing abrasion resistance was poor for all of the polymer modified runs and suffered wide variation. The main cause for this could be that the aggregate contained too many fines less than 75 μm, resulting in the low sand equivalence value. This could also be the problem with the variable permanent deformation results. The slurry cohesion was also slow to develop and possible causes were again the aggregate fines and/or too much free emulsifier in the water phase of the emulsion. The quality of aggregate is an aspect to further investigate.

An unexpected result was that emulsifying the modified bitumen improves the binder softening point by 4°C to 5°C over a hot modified bitumen typically used for spray chip sealing. This result has not been reported in literature and indicates that emulsifying not only has environmental and safety advantages but it may improve the binder performance as well. There could be two reasons:

1. The intense shearing action associated with the emulsifying process that causes hardening of the bitumen.
2. The emulsifier added to the binder improves the resistance to temperature deformation.

5.3 EMULSIFIER INVESTIGATION RESULTS

The performance of two microsurfacing emulsifiers emulsifier C and emulsifier B were compared with the slow set emulsifier A used in the previous work. The SBR polymer latex was post added to the emulsions and 100 pen bitumen was used. The formulation and method details are outlined in Section 4.7.2. The effects on the emulsion properties, abrasion resistance and cohesion development were used to determine the preferred emulsifier. Table 5-5 summarises the results.

Table 5-5. Summary of Test Results from Emulsifier Investigation

	Emulsion Sample			
	Emulsifier A No Polymer	**Emulsifier A**	**Emulsifier C**	**Emulsifier B**
Final pH (Units)	4.07	4.86	2.24	2.41
Binder Residue (%)	61.27	60.90	61.95	61.88
Viscosity *(cP)	120	120	180	260
Settlement (%)	16.43	21.27	41.68	54.70
Sieve Residue (%)	0.35	0.39	0.75	0.17
Softening Point (°C)	51.0	60.3	67.5	67.5
Abrasion (g/m^2)	1921	1905	520	536
Cohesion (kg-cm)				
60 min	9.0	9.0	8.0	8.0
120 min	13.0	14.0	16.0	15.0
150 min	16.0	16.0	18.0	17.0
Slurry Mix Time (sec)	170	360	300	300

* Viscosity at 5 rpm

5.3.1 Emulsion Viscosity

The change to the microsurfacing emulsifiers had a dramatic increase on viscosity. Emulsifier C had a viscosity of 180 cP and emulsifier B 260 cP, compared to emulsifier A which produced a viscosity of 120 cP.

The increase in viscosity is due to the higher density of the emulsifiers compared to emulsifier A. Emulsifier C has a density of 950 kg/m^3, emulsifier B 900 kg/m^3 and emulsifier A 1070 kg/m^3. An emulsion with higher viscosity should result in lower settlement.

5.3.2 Emulsion Settlement

Emulsifier C had a settlement of 41.68% while emulsifier B had 54.70%. Both the runs were much higher than emulsifier A, which had a value of 21.27%. Despite the higher settlement the particles within the emulsions had only flocculated and could be easily dispersed by gentle stirring.

The high settlement was an unusual result, as it would be expected that the settlement would be improved by having an increased viscosity. It was unknown what the cause was for this effect. One possibility was that the concentrations of the two emulsifiers were lower at 1.2% compared to 1.5% for emulsifier A but this was necessary due to supplier recommendations regarding suitable ranges for each. Increasing the emulsifier content should result in a lower settlement but 1.5% is regarded as the upper limit for emulsifier C and emulsifier B.

5.3.3 Emulsion Sieve Residue

The use of emulsifier B resulted in only 0.17% retained particles on the 150 μm sieve compared to 0.75% with emulsifier C. Emulsifier A had a mid-range value of 0.39%.

A lower value can indicate that the width of the particle size distribution is narrower which should result in lower settlement due to fewer larger particles (Whiteoak, 1990). But the high settlement values tend to disagree with this unless some other effect has occurred to increase the settlement. High amounts of retained sieve particles can also indicate early signs of coalescence and instability in the emulsions.

5.3.4 Binder Properties

Both the runs with emulsifier C and emulsifier B had a softening point of 67.5°C. This was an increase of 7°C over the emulsion that used emulsifier A, keeping in mind that all the runs had 3% SBR latex post added. Replicate test measurements of the softening points confirmed the results and eliminated test error as the cause. An unmodified emulsion using emulsifier B had a softening point of 54.7°C while the emulsifier A emulsion was 51°C. This also suggests that some of the increase may occur because of an interaction between polymer and emulsifier.

The results suggest that the type of emulsifier can influence the softening point of the binder. It was unknown if the increase in softening point results from an interaction between the emulsifier and bitumen or the polymer and emulsifier.

5.3.5 Microsurfacing Abrasion Resistance

The abrasion resistance of the surfacing improved dramatically by changing the emulsifier. The sample with emulsifier B had an abrasion loss of 536 g/m^2 while emulsifier C had a similar result of 520 g/m^2. Both of the results easily meet the target specification of <800 g/m^2 abrasion. These results can be compared with the emulsifier A sample that lost 1905 g/m^2.

The aggregate sand equivalence was consistent at 49% for all the samples and the mix design kept the same. The change in emulsifier was the only change in formulation. Jones (1989) reported that an emulsion that used a quaternary emulsifier of which 611 is a type, performed worse than samples of other emulsifiers in the test. But neglected to state what other type(s) of emulsifiers were used. The result observed in this investigation was consistent with that by Jones (1989). It appears that the emulsifier type had a significant impact on the adhesion and cohesion of the binder to the aggregate to resist the abrasion forces.

5.3.6 Microsurfacing Cohesion

The cohesion values for all three emulsifiers were similar as seen in Table 5-5. None of the samples reached the target cohesion of 20 kg-cm after 60 minutes; the range was only 8.0 to 9.0 kg-cm. After 150 minutes the samples had reached a range of 16 to 18 kg-cm.

The level of emulsifier used could be a reason for the slow cohesion or alternatively the cleanliness of the aggregate could result in too many fines in the aggregate and result in less binder adhesion to the larger stones. Holleran (1997) reports that the addition of 3% SBR latex can lead to an increase in cohesion development of up to 25% after 60 minutes but this effect has not been noticed in comparing unmodified samples with modified ones so far.

5.3.7 Mix Time

Both emulsifier C and emulsifier B had mix times of 300 seconds, which was a decrease by 60 seconds over emulsifier A. All the times allow plenty of workability of the mix and do not indicate any stability problems such as rapid breaking of the emulsion.

Both emulsifier C and emulsifier B were added in 1.2% quantities to the emulsion which tends to explain the slightly quicker mix times as higher emulsifier levels result in a more stable emulsion.

The control additive selected for the detailed design was retarder A instead of emulsifier A, as an assessment determined that both additives produced the same effect but, retarder A was cheaper (S, Bearsley, 5 January 2000, personal communication).

5.4 AGGREGATE INVESTIGATION RESULTS

This investigation describes the effects of aggregate source, cleanliness, and cement addition on the performance of the microsurfacing abrasion and cohesion development. The details of the method are covered in Section 4.7.3. The aim was to determine if a particular set of aggregate characteristics could further improve the microsurfacing. Table 5-6 shows the results of the investigation.

Table 5-6. Test Results from Aggregate Investigation

Run	Source	SE* (%)	Cement (%)	Abrasion (g/m^2)	Cohesion (kg-cm) 60 min	90 min	120min	150min
1	Bulls	54	0.0	954	15	19	17	19
2	Bulls	54	0.5	1270	7	8	9	11
3	Bulls	70	0.0	332	7	7	7	8
4	Bulls	70	0.5	1826	8	7	9	12
5	New Plymouth	82	0.0	438	6	6	7	8
6	New Plymouth	82	0.5	1336	8	7	8	8

* Sand Equivalence

5.4.1 Microsurfacing Abrasion Resistance

For the Bulls aggregate an increase in sand equivalence from 54% to 70% saw the abrasion drop from 954 g/m^2 to 332 g/m^2 as seen in Table 5-6. The abrasion loss using New Plymouth aggregate was 438 g/m^2.

The addition of cement to the mixture dramatically increased the abrasion loss to over 1250 g/m^2 in all the samples.

The results indicate that a cleaner aggregate will improve the abrasion resistance of the microsurfacing and addition of cement will considerably increase the abrasion loss. The possible reason for the effect of cement is that addition of it increases the fine particle content of the aggregate and may lead to excessive build-up of binder with the fines and not with the larger aggregate. A similar effect could be behind the improved abrasion results of having higher sand equivalence in the aggregate. Cement is normally used to obtain desired mix consistencies or to accelerate the break of the mixture (Asphalt Institute, 1994) but there has been no literature regarding possible adverse effects on abrasion resistance. New Plymouth aggregate is of andesite origin and is more brittle than greywacke which may account for the higher abrasion loss observed even though the aggregate was cleaner. This suggests that the geology of the aggregate also has an effect on the abrasion resistance. Time constraints meant it was not possible to determine if higher sand equivalence than 70% with greywacke further improved abrasion resistance.

5.4.2 Microsurfacing Cohesion

The addition of cement appeared to make little difference to the cohesion values, which ranged from 7.0 to 8.0 kg-cm at 60 minutes and 90 minutes, while at 120 minutes the values were 8.0 to 9.0 kg-cm. The cohesion values with cleaner aggregate and no cement were almost identical except the run with Bulls at a sand equivalence of 54% which had values of 15.0 kg-cm, 19.0 kg-cm and 17.0 kg-cm at 60, 90 and 120 minutes respectively.

The results indicate that cement is not a significant factor in cohesion rate. But it is not clear if aggregate cleanliness is important, as the high cohesion values with the Bulls aggregate at a cleanliness of 54% are possibly an unusual result. The other possible determinant for cohesion development is likely to be the level of emulsifier in the emulsion (Engman et al,. 1998).

5.4.3 Conclusions

The main advantage of emulsifier C and emulsifier B are that they both considerably improve the abrasion resistance of the microsurfacing compared to emulsifier A. It appears the chemical constitution of the emulsifier can significantly increase the adhesion and cohesion strength of the binder-aggregate bond. Additionally the emulsifiers both lead to a 7°C increase in softening point over emulsifier A.

Emulsifier A provides much lower settlement but mixing could easily disperse the flocculated particles of the other emulsifier runs. The slurry mix times indicated that no stability problems were apparent and the mixtures provided good workability.

Both emulsifier C and emulsifier B provide similar performance and have improved benefits for the microsurfacing properties. Emulsifier B only was chosen for continued work as time allowed for detailed investigation of one emulsifier only.

Bulls aggregate with a sand equivalent of 70% produced dramatic abrasion loss improvement and the addition of cement to control the mix times significantly increased the abrasion loss. It also appeared that greywacke type aggregate improved the abrasion loss more than andesite aggregate as it was not as brittle.

Bulls aggregate with a sand equivalent of 70% was recommended to use while cement was removed from the mix design and only dilute emulsifier or dilute retarder A was used to control set times.

5.5 DETAILED DESIGN INVESTIGATION RESULTS

The levels of polymer, emulsifier and pH were identified as key variables to be investigated in the experimental design outlined in Section 4.7.4. All of the variables can affect the emulsion stability and the polymer the microsurfacing's permanent deformation resistance. The level of emulsifier could affect the speed of cohesion development of the microsurfacing. Table 5-7 summarises the test results from the experimental runs and compares them with two unmodified trials. Full results are held in Appendix 5.4. The results of the experimental design were analysed with 'Minitab' statistical software (version 12.23). The effects of varying single factors from low to high levels were determined as well as interactions between two and three factors.

The results of the experimental design were analysed by a factorial fit analysis with the Minitab program. The outputs of the analysis included determining the effect and significance of varying the three factors over the experimental runs. The effects values described the size and direction of changes in the emulsion and microsurfacing properties, which resulted in changes to the independent variables. The p-value represents the significance of the effects, and a value of less than 0.05 (or 5%) means the probability of an observed change in a property which did not result from a deliberate change in the factor levels would be less than 5%. A p-value less than 0.05 is significant to a 95% confidence level. The effects and significance values are shown in Table 5-8 with the significant variables highlighted.

5.5.1 Final Emulsion pH and Binder Residue

The final emulsion pH and binder residue was not analysed as part of the experimental design as they are to help determine production control only. The final emulsion pH varied between 1.64 to 2.85 and was very dependent on the soap solution pH the low final pH values corresponded to the low soap solution pH level and vice versa.

The binder residue ranged from 61.65% to 62.33% with mean of 62.02% and a standard deviation of 0.20% indicating good process control.

Table 5-7. Summary of Test Results for Emulsion Detailed Design

	Sample Code												
	No [X] Polymer	No [XX] Polymer	1	a	b	ab	c	ac	bc	abc	CP1	CP2	CP3
pH (Units)	4.07	2.04	1.71	1.98	1.64	1.66	2.58	2.63	2.85	2.81	2.09	2.28	2.33
Residue (%)	61.27	62.01	62.02	61.67	62.00	62.33	62.20	62.02	62.16	62.11	61.65	62.02	62.01
Viscosity* (cP)	120	230	180	160	280	290	190	180	280	240	200	200	220
Settlement (%)	16.43	35.12	42.99	43.97	55.32	56.68	43.22	46.78	54.18	62.09	51.64	49.27	51.46
Sieve Residue (%)	0.35	0.15	0.08	0.10	0.10	0.08	0.14	0.12	0.17	0.14	0.15	0.13	0.15
Softening Point (°C)	51.0	54.7	68.0	81.3	67.4	80.0	67.3	79.0	66.2	80.5	70.7	72.5	72.0
Abrasion (g/m²)	1921	305	270	112	59	72	89	125	174	171	171	49	63
Cohesion (kg-cm)													
60 min	9.0	9.0	16	16	9.0	10.0	18.0	14.0	9.0	9.0	11.0	11.0	10.0
90 min	-	13.0	20	20	14.0	13.0	22.0	20.0	9.0	12.0	15.0	16.0	17.0
120 min	13.0	16.0	21	22	18.0	20.0	23.0	22.0	11.0	10.0	18.0	18.0	15.0
Mix Time (sec)	170	180	100	280	240	280	80	250	300	300	300	300	300

* Viscosity at 5 rpm

[X] Unmodified Emulsion using Emulsifier A

[XX] Unmodified Emulsion using Emulsifier B

Key: a: Polymer b: Emulsifier c: pH

Table 5-8. Significance and Effects of Variables Controlling the Emulsion and Microsurfacing Properties

	Viscosity*		Settlement		Sieve Residue		Softening Point		Abrasion	
Code	**Effect**	**P**	**Effect**	**P**	**Effect**	**P**	**Effect**	**P**	**Effect**	**P**
a	-15	0.208	3.45	0.066	-0.013	0.265	12.98	0.003	- 28	0.613
b	95	0.007	12.83	0.005	0.013	0.265	- 0.38	0.626	- 30	0.590
ab	0	1.000	1.18	0.333	-0.013	0.265	0.48	0.545	33	0.557
c	-5	0.603	1.83	0.189	0.053	0.023	- 0.93	0.294	12	0.830
ac	-10	0.345	2.28	0.134	-0.013	0.265	0.03	0.973	46	0.445
bc	-20	0.110	0.31	0.773	0.013	0.265	- 0.58	0.336	96	0.180
abc	-15	0.208	0.99	0.399	0.008	0.455	0.83	0.336	- 53	0.473

	Cohesion (60)		Cohesion (90)		Cohesion((120)		Mix Time	
Code	**Effect**	**P**	**Effect**	**P**	**Effect**	**P**	**Effect**	**P**
a	- 0.8	0.208	0.00	1.000	0.3	0.857	98	0.000
b	- 6.8	0.004	- 12.02	0.007	- 7.3	0.027	103	0.000
ab	1.3	0.092	- 1.41	0.293	0.3	0.857	- 78	0.000
c	- 0.3	0.603	1.41	0.293	- 3.8	0.092	8	0.182
ac	- 1.3	0.092	0.71	0.553	- 1.3	0.415	- 13	0.063
bc	- 0.3	0.603	- 2.83	0.106	- 4.8	0.061	33	0.005
abc	0.8	0.208	2.12	0.168	- 0.3	0.857	- 8	0.851

* Viscosity at 5 rpm

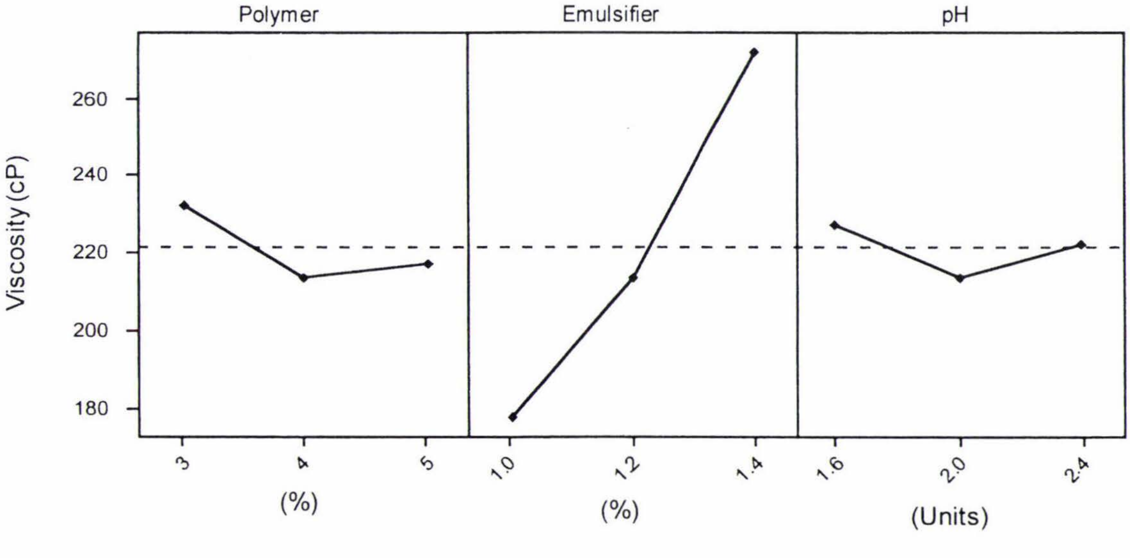
Key: a: Polymer b: Emulsifier c: pH

☐ Significant variable

5.5.2 Emulsion Viscosity

The emulsifier level controlled the viscosity of the emulsion and was highly significant with a p-value of 0.007. The effect can be seen in the main effects plot, Figure 5-3. The middle point between the high and low factor levels is the mean value of centre point runs. This shows the effect on the response variable by holding the factors at half way between the high and low levels. From Figure 5-3, it can be seen that emulsifier level has the greatest effect due to the steep slope between the high and low levels. A high level of emulsifier led to a viscosity range of 240 cP to 290 cP while the low level was 160 cP to 190 cP. The effect of the high emulsifier level was to increase the viscosity by 95 cP as seen in Table 5-8. There were no higher order interactions of significance.

Figure 5-3. Main Effects Plot for Emulsion Viscosity



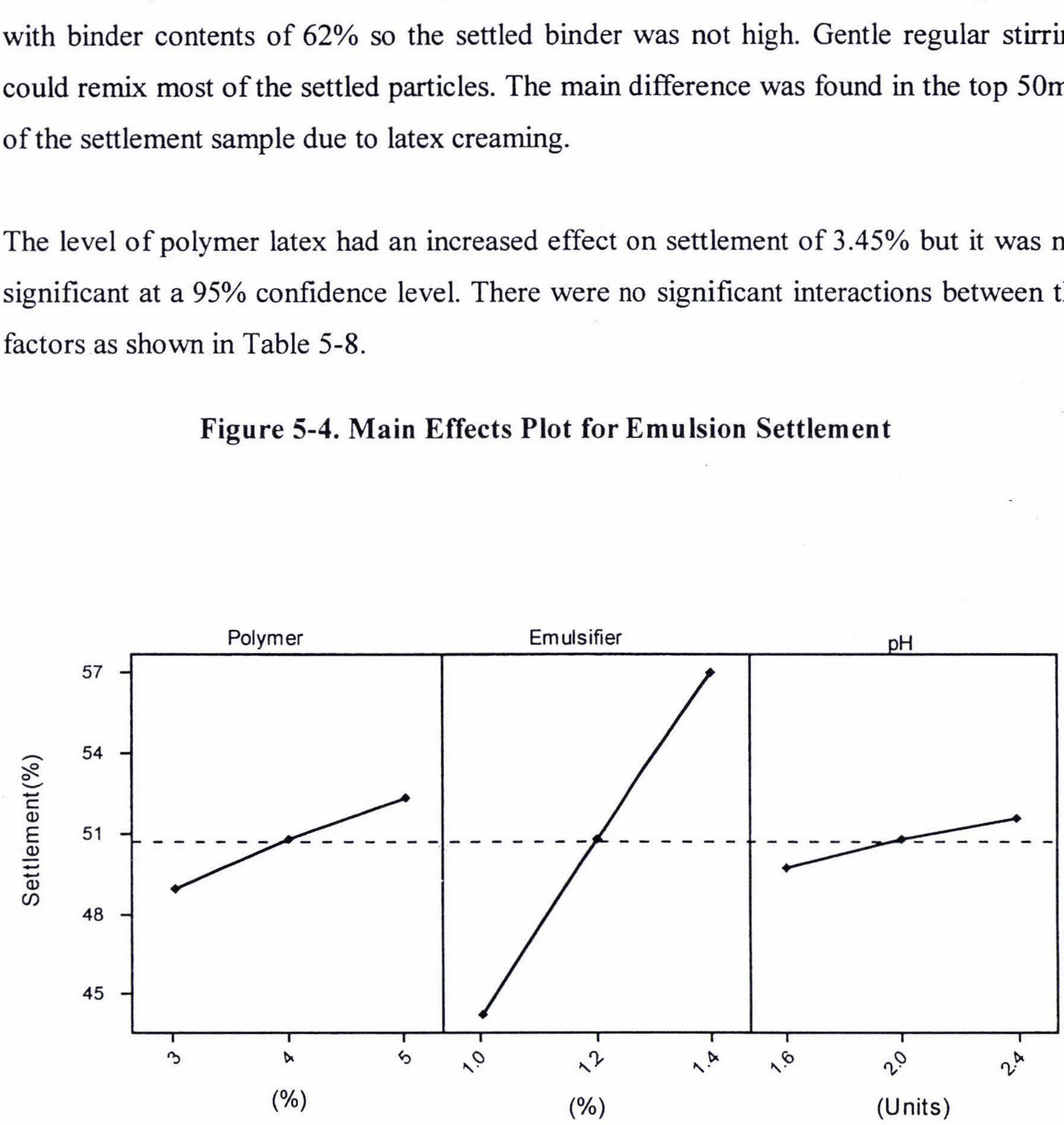
The effect is consistent with that proposed by Whiteoak (1990) for modifying the viscosity of an emulsion. A higher viscosity should result in lower particle settlement, as the particles are less free to move.

5.5.3 Emulsion Settlement

The level of emulsifier was a significant effect on the settlement as seen in the main effects plot in Figure 5-4. Increasing the emulsifier level by 0.4% led to an effect of increasing the settlement by 12.83%, this had a p-value of 0.005. The lowest levels of settlement were around 42% to 43% and are still high compared to the target specification of <5%. A key point of note is that the bottom 50ml sample residue of the settlement cylinders was consistently around 67% to 69%. The emulsions were produced with binder contents of 62% so the settled binder was not high. Gentle regular stirring could remix most of the settled particles. The main difference was found in the top 50mls of the settlement sample due to latex creaming.

The level of polymer latex had an increased effect on settlement of 3.45% but it was not significant at a 95% confidence level. There were no significant interactions between the factors as shown in Table 5-8.

Figure 5-4. Main Effects Plot for Emulsion Settlement



Increasing the emulsifier should decrease the settlement rate (Whiteoak, 1990), but this effect has not been observed. The possible reason is that emulsifier B increases the density of the bitumen so the density difference between the dispersed and continuous phase is increased. Increasing the emulsifier content increases the density difference further leading to higher settlement. As a comparison, Table 5-7 includes two unmodified emulsion runs, one with emulsifier B at 1.2% the other with emulsifier A at 1.5% from the initial trials with emulsifier A having a much lower settlement. A solution to overcome this problem is to increase the density of the aqueous phase by the addition of calcium chloride in a very small concentration.

The factorial analysis indicates that polymer level has a small effect on settlement but, a comparison with the unmodified sample in Table 5-7 indicates otherwise. The settlement was 35% and the formulation was identical to the centre point runs except they have 4% polymer added. There is generally an increase in settlement of 8% to 12% by adding the latex, which is to be expected as the latex creams to the top of the samples.

5.5.4 Emulsion Sieve Residue

The amount of particles retained on the 15 μm sieve was affected by the soap solution pH, which was significant with a p-value of 0.023. The effect was to increase the particle size by 0.053% by decreasing the pH level. This indicates that the particle size distribution became narrower as the acid was increased which agrees with the effect proposed by Whiteoak (1990). But, this effect did not appear to improve the settlement to any degree as seen in the settlement results. There were no other main effects for sieve residue as shown in Table 5-8 and the main effects plot in Figure 5-5.

5.5.5 Binder Softening Point

The softening point rapidly increased when 5% SBR latex was added providing values between 79.0 to 81.3°C. An unmodified emulsion residue had a softening point of 54.7°C, which compared with the modified results show the benefit of polymer modification. As expected the polymer was the only significant factor and had an effect of increasing the softening point by 12.98°C at 5% addition.

Figure 5-5. Main Effects Plot for Emulsion Sieve Residue

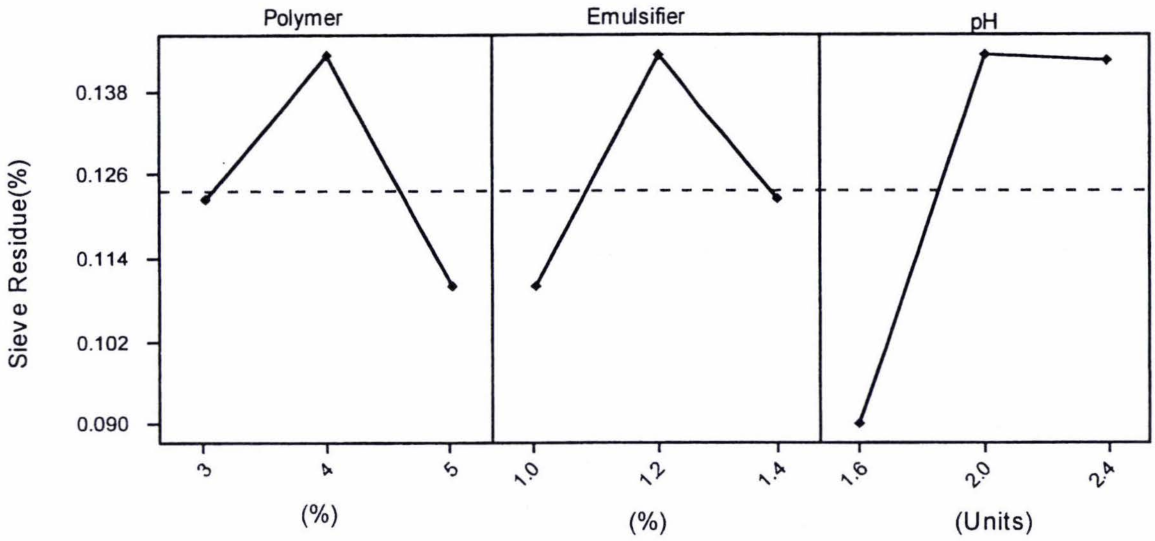
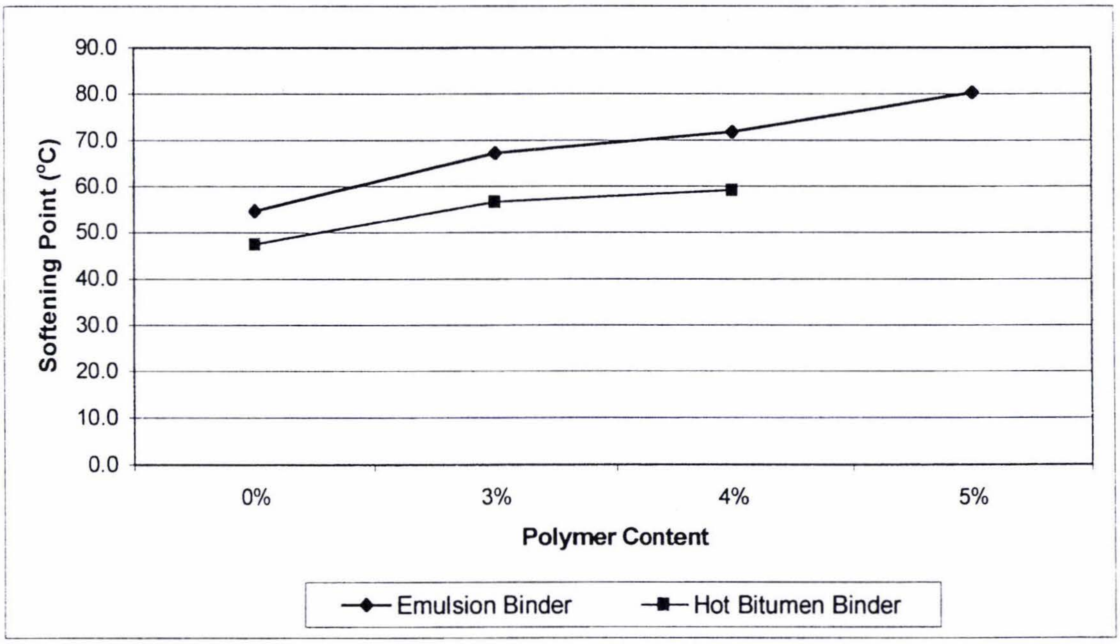


Figure 5-6. Softening Point Comparison between SBR Polymer Modified Emulsion Binder and Hot SBR Polymer Modified Bitumen.



The degree of increase in the softening points obtained with polymer modified emulsions is an important new result, first identified in Section 5.2.1. The binder residue obtained from emulsions by evaporating the water phase, was expected to yield very similar softening point results to those of hot polymer modified bitumen binders used for spray chip sealing and hot asphalt applications (Coyne, 1987; Anderson, 1992; PIARC, 1999). But emulsion binders provide higher softening points as shown in Figure 5-6 with or without polymer added to 80/100 pen bitumen. At 3% polymer modification the difference is about 10°C using emulsifier B.

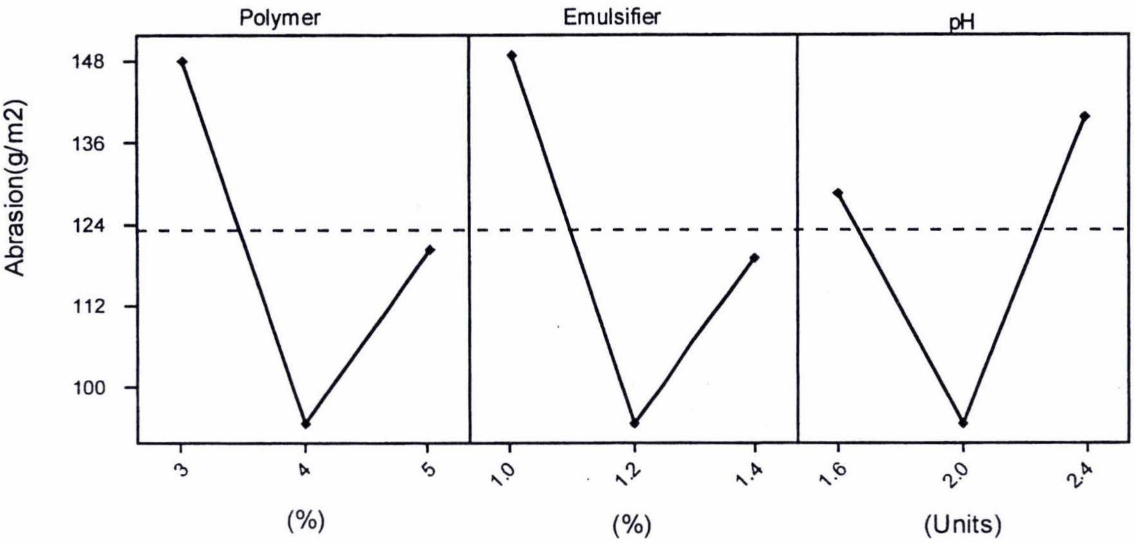
An interaction between the emulsifier and polymer was not significant, so the other possibility is that the emulsifier has an effect of modifying the bitumen properties and helping it resist thermal susceptibility.

The way the emulsion sample is prepared for the softening point test can also possibly have an impact on the results. The method used to obtain the binder residue from the emulsion in this study involved heating a small sample of emulsion at 60°C to evaporate the water phase. This temperature was selected as the binder in microsurfacing is generally not exposed to pavement temperatures higher than 60°C. There is a danger of thermally degrading the polymer if the binder is heated at high temperatures such as over 130°C for any prolonged time (Holleran, 1997; Wloczysiak et al., 1997). This temperature is often used to quickly determine binder content in emulsions, but if it was used to prepare samples for softening point tests then the results may be understated due to polymer degradation.

5.5.6 Microsurfacing Abrasion Resistance

All of the abrasion test results were well under the target specification of <800 g/m^2 with a range from 49 g/m^2 to 270 g/m^2. There were no significant factors contributing to the wet track abrasion resistance of the microsurfacing as shown in Figure 5-7. This is a realistic result as the aggregate quality and bitumen grade has a very large influence on the abrasion resistance. It appears clear from the plot that the centre point levels of the factors result in lower abrasion loss. The two-way interaction between the emulsifier and soap pH was the most significant at 0.180 (significant at 82% confidence level), with an effect of increasing the abrasion by 96 g/m^2 as shown in Table 5-8.

Figure 5-7. Main Effects Plot for Abrasion Resistance



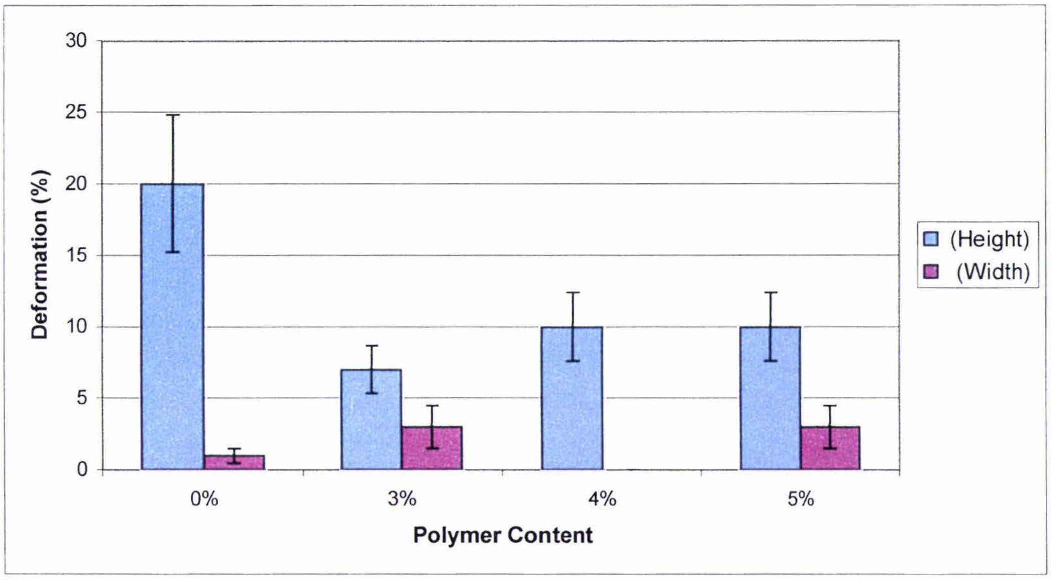
A contour plot of the effects of emulsifier and pH can be seen in Appendix 5-5. It shows that a high emulsifier level and low pH would lead to abrasion losses of less than 90 g/m^2. But the plot also suggests that a 1.1% emulsifier and 2.0 pH combination would give a result around 100 g/m^2. A contour plot of polymer and pH showed that 4% polymer with a pH range of 1.6 to 2.3 would result in abrasion loss of less than 110 g/m^2. The contour plot is held in Appendix 5-6, but care must be taken with the interpretation of the interaction, as the p-value was only 0.445. An increase in SBR polymer content was observed by Holleran (1997) to improve the abrasion resistance but the effect is not significant in these results. A comparison with an unmodified sample as seen in Table 5-7 had 305 g/m^2 abrasion, and shows that 3% polymer addition improves the abrasion resistance.

The abrasion test has inherent variation as seen in the initial polymer trial investigations and the process capability results. The use of aggregate with a cleanness value of 70% does appear to have improved the variation in the test as the standard error was 17% compared to the process capability test error from Section 4.6 of 21%. The experimental errors for the detailed design are held in Appendix 5-7.

5.5.7 Microsurfacing Permanent Deformation

Permanent deformation of the microsurfacing improved with the addition of SBR polymer at 3% which agrees with the result by Holleran (1997), but there was little difference in the results between 3% to 5% as shown in Figure 5-8. The target specification for width deformation was less than 5%, which was achieved even without polymer added. But to meet the specification of less than 10% height deformation required polymer addition.

Figure 5-8. Changes in Microsurfacing Permanent Deformation by Increased Polymer Addition



The addition of higher levels of polymer was expected to further improve the permanent deformation, but this was not observed as the addition of 3% produced a better result than 4% or 5% polymer. Why this result occurred is unknown. But the high error in the test requires some caution in interpreting the results. The test error was originally determined using poor quality aggregate, and the subsequent significant improvement in the abrasion and cohesion results and their standard errors (held in Appendix 5-7) indicate that some of the variation can be controlled.

5.5.8 Microsurfacing Cohesion

The cohesion development of the microsurfacing was measured at intervals of 60, 90, 120, 150, and 180 minutes. The aim was to achieve cohesion of 20 kg-cm within 60 minutes so only the results up to 120 minutes are analysed in detail. The full results are held in Appendix 5-4. The experimental errors in the cohesion results were less than 8% a significant improvement on the process capability errors of 9% to 17% in Section 4.6

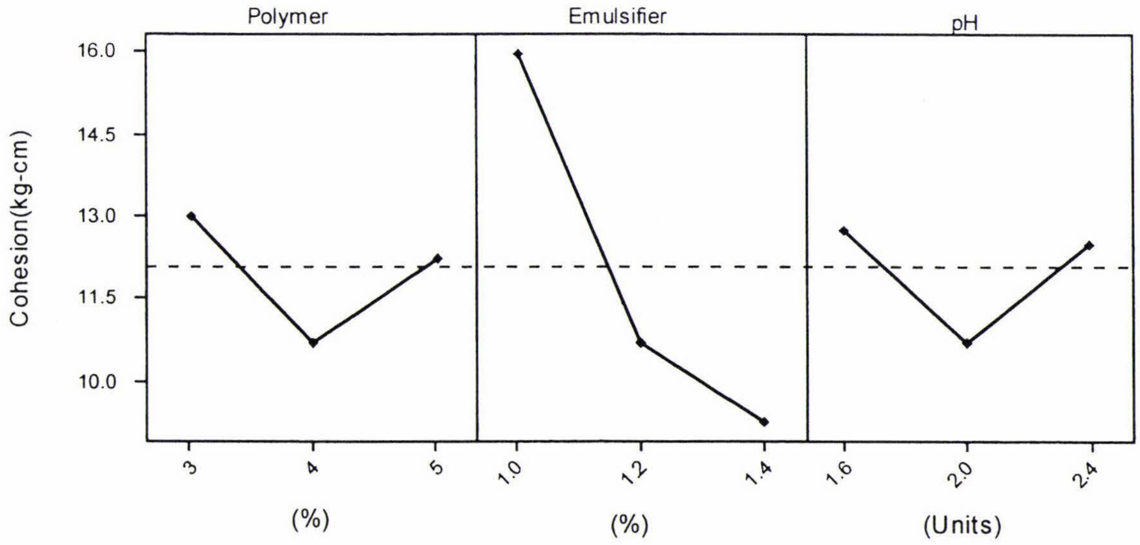
Cohesion 60 minutes

The level of emulsifier was the most significant effect for cohesion as shown by the main effects plot in Figure 5-9. Emulsifier level had an effect of – 6.8 kg-cm and a significant p-value of 0.004. When the emulsifier level was at 1.0% the cohesion values ranged from 14.0 to 18.0 kg-cm. When the emulsifier was set at 1.4% the cohesion was 9.0 to 10.0 kg-cm.

Cohesion 90 minutes

Again the level of emulsifier was the significant factor with an effect of –12.02 kg-cm and a p-value of 0.007. The range of cohesion values with 1.0% emulsifier were 20.0 to 22.0 kg-cm which indicates that the microsurfacing could be opened to traffic at 90 minutes based on the test conditions. The large effect indicates that there was a more rapid increase in the overall cohesion between 60 and 90 minutes. At 1.4% emulsifier the cohesion range was still only 9.0 to 14.0 kg-cm.

Figure 5-9. Main Effects Plot for Microsurfacing Cohesion after 60 minutes



Cohesion 120 minutes

The emulsifier level was the only significant factor ($p = 0.027$), indicating a 7.3 kg-cm decrease in cohesion if the emulsifier was at 1.4%. The range of values for this emulsifier level were 10.0 to 20.0 kg-cm. Table 5-8 shows an interaction between emulsifier and soap pH that is significant at a 90% level of confidence ($p = 0.061$). But has an effect of – 4.8 kg-cm, which is reflected in the two low results for the trials with high emulsifier and high soap pH. This indicates that having both factors at high level results in the worst cohesion rate.

The centre point runs with emulsifier at 1.2% reached the target cohesion at 150 minutes and tended to provide values midway between the runs at 1.0 and 1.4%. Figure 5-10 shows a quadratic relationship between emulsifier and cohesion up to 60 minutes. This shows that the water is rapidly forced out of the surfacing and the emulsifier draws the bitumen to the aggregate very quickly. But, a linear relationship in the effect on cohesion between 60 to 90 minutes is shown in Figure 5-11. The R^2 value for cohesion at 120 minutes was only 53% and indicated a poor fit.

Figure 5-10. Regression Plot for Microsurfacing Cohesion after 60 minutes

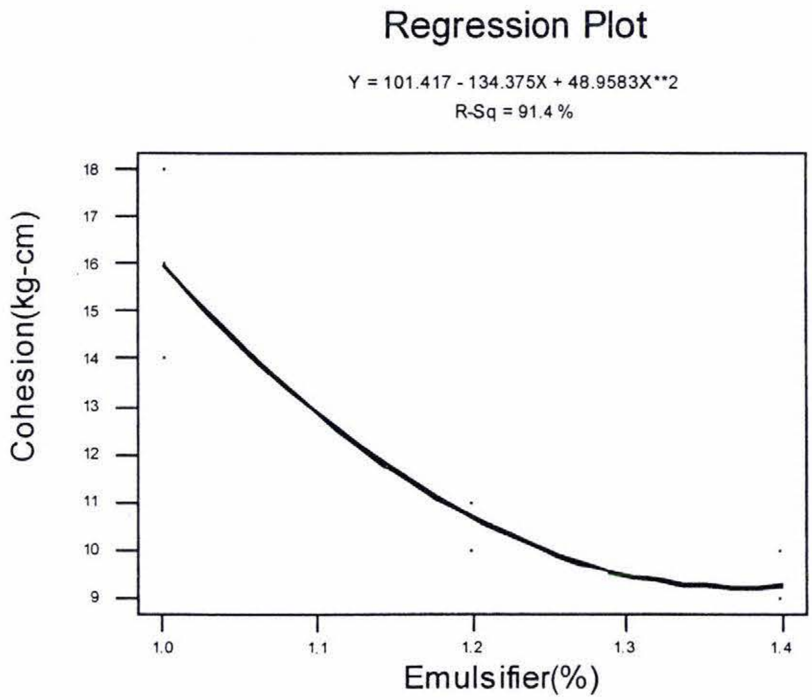
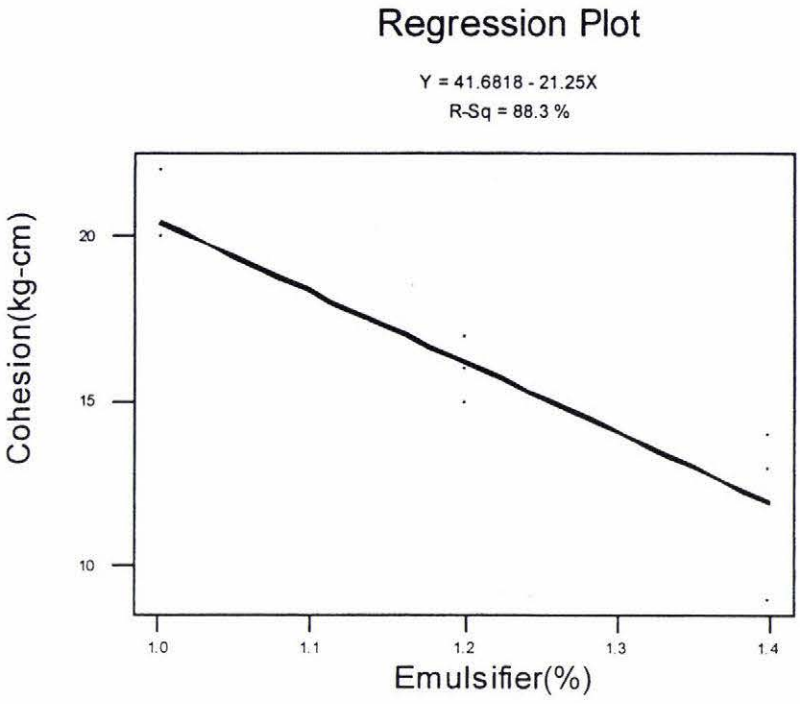


Figure 5-11. Regression Plot for Microsurfacing Cohesion after 90 minutes



The results are consistent with the hypotheses that there was too much free emulsifier in the water phase of the emulsions in the first two experimental investigations and with the observations by Boussad & Martin (1996) and Engman et al (1998). The free emulsifier can be absorbed more quickly onto the aggregate surface than the droplets of bitumen and the absorbed emulsifier modifies the surface charge of the aggregate and reduces its reactivity to the bitumen droplets. The less emulsifier in the water phase, the more rapid the reaction with aggregates which results in rapid adhesion and subsequently rapid cohesion.

The cohesion test was performed under conditions of 25°C and could not take effect of warmer air temperatures or wind, which can speed up the evaporation of water in the mixture. This effect was apparent when samples were placed outside on the pavement. Alternatively cooler conditions would slow the cohesion rate down as well.

5.5.9 Microsurfacing Mix Time

The main factors of polymer and emulsifier had highly significant p-values of 0.000 as seen in Table 5-8. The main effects plot in Figure 5-12 shows both factors have steep slopes and the greatest effect on mix time. The effect of increasing the polymer was to increase the mix time by 98 seconds and an increase in emulsifier from 1.0 to 1.4% increased the mix time by 103 seconds. The plot also indicates that a pH of 2.0 can increase the mix time more than 1.6 or 2.4 indicating some curvature.

There were two other significant interactions consisting of polymer and emulsifier with an effect of –78 seconds, the other being emulsifier and soap pH with an effect of 33 seconds. The interaction plot in Figure 5-13 shows that decreasing the polymer and emulsifier will drop the mix time to 100 seconds but, increasing the polymer to 5% and maintaining the emulsifier at 1.0% increased the mix time to nearly 300 seconds. The level of polymer makes little difference to the mix time if the emulsifier is 1.4%. The interaction plot between emulsifier and soap pH in Figure 5-14 shows that maintaining a low pH and high emulsifier level will increase the mix time but, a high pH and high emulsifier will also increase the mix time even further. A high pH and low emulsifier level will slightly decrease the mix time.

Figure 5-12. Main Effects Plot for Microsurfacing Mix Time

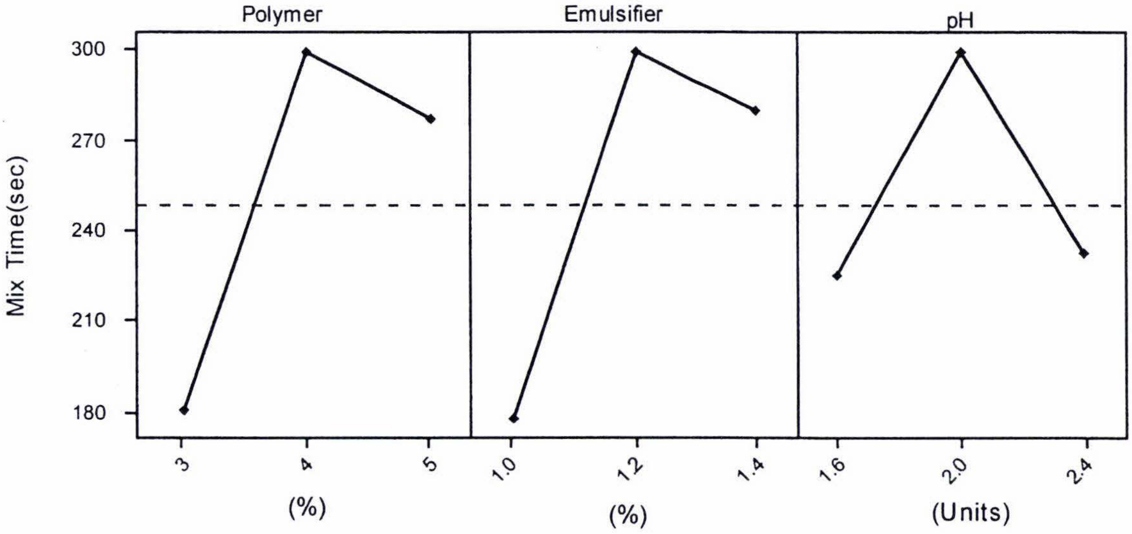


Figure 5-13. Interaction Plot for Mix Time of Polymer and Emulsifier

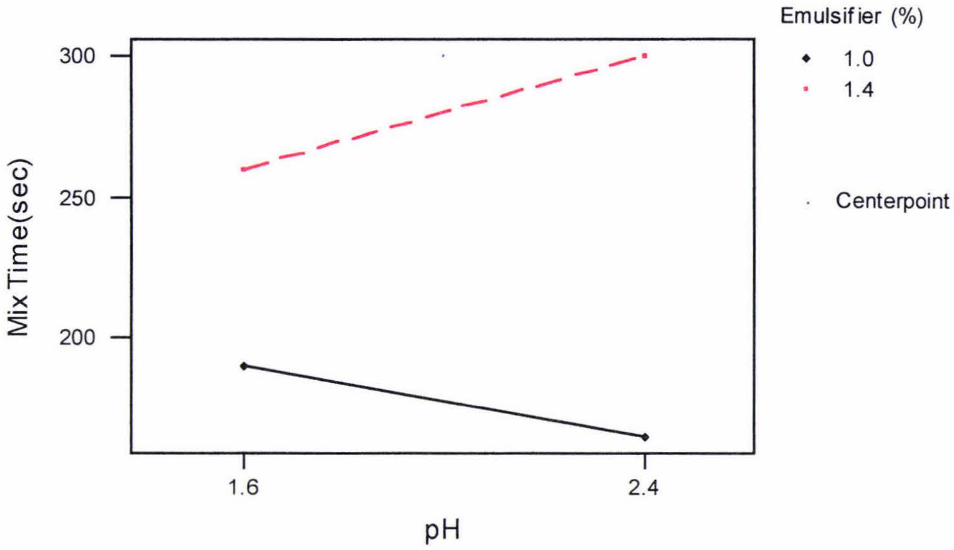
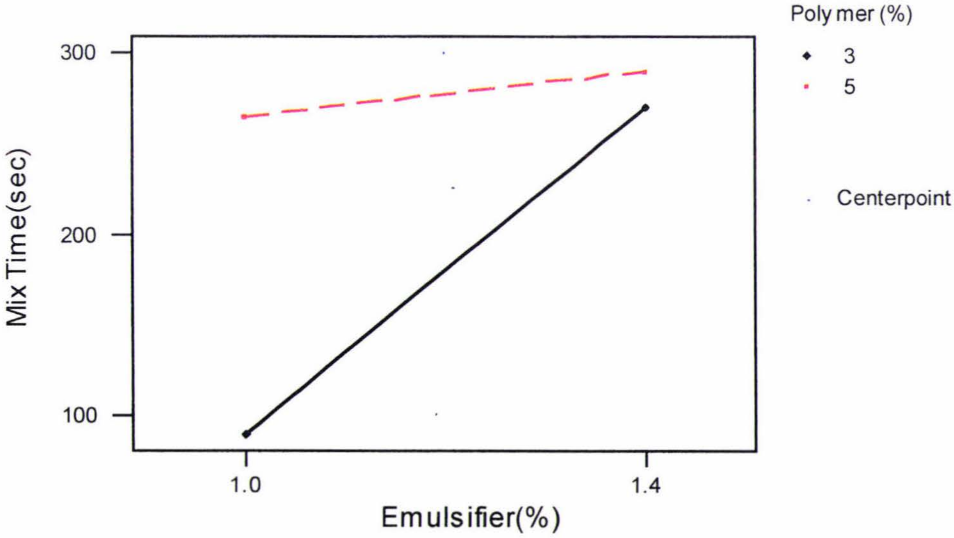


Figure 5-14. Interaction Plot for Mix Time of Emulsifier and Soap pH



A contour plot of emulsifier and polymer level is shown in Figure 5-15 and shows that achieving a mix time of at least 200 seconds with the emulsifier set at 1.0% requires the polymer to be about 3.8%. Alternatively if the polymer was maintained at 3% then the emulsifier needs to be about 1.20% to 1.25%.

When the pH is set at 1.6 the emulsifier should be about 1.05% to maintain a mix time of at least 200 seconds as shown by the contour plot in Figure 5-16. If the emulsifier is set at 1.0% the pH can vary between 1.7 to 2.1 and maintain a mix time of 200 seconds. The plot indicates that an emulsifier level above 1.2% with a pH between 1.85 to 2.2 will quickly increase the mix time to over 300 seconds. Laboratory trials would need to be performed to determine if these results would occur.

The ramifications for formulation design are that a low emulsifier level and low polymer level will result in a rapid break time of less than 100 seconds, which is too quick. Increasing the emulsifier content to 1.2% will give a good mix time but will decrease the cohesion rate and slow the cure time. Increasing the polymer to 4% and maintaining the emulsifier at 1.0% will give a suitable mix time and will not affect the slurry cohesion rate. The emulsifier as already shown has a key influence on the cohesion development in the microsurfacing and increases above 1.1% are likely to adversely affect cohesion. Polymer content has no apparent effect. The cost implications of increasing the polymer must be compared against the emulsifier cost but more importantly the effect on microsurfacing cohesion performance should be considered.

Figure 5-15. Contour Plot for Mix Time of Polymer and Emulsifier Level

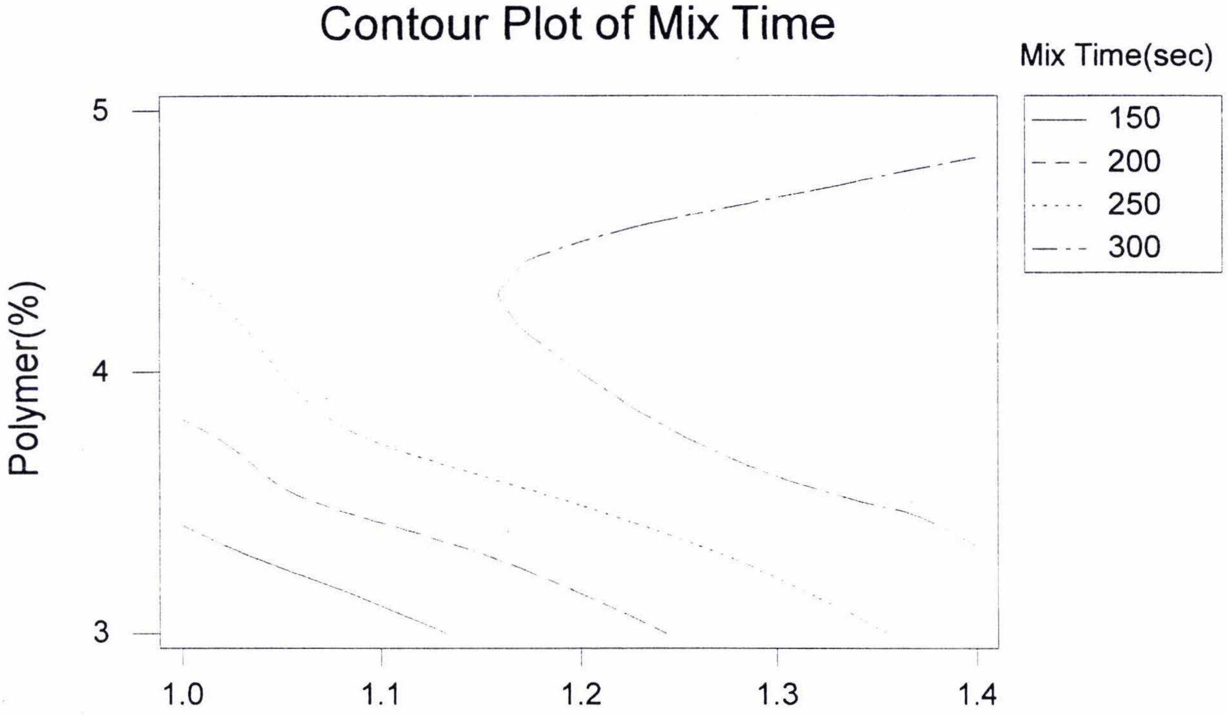
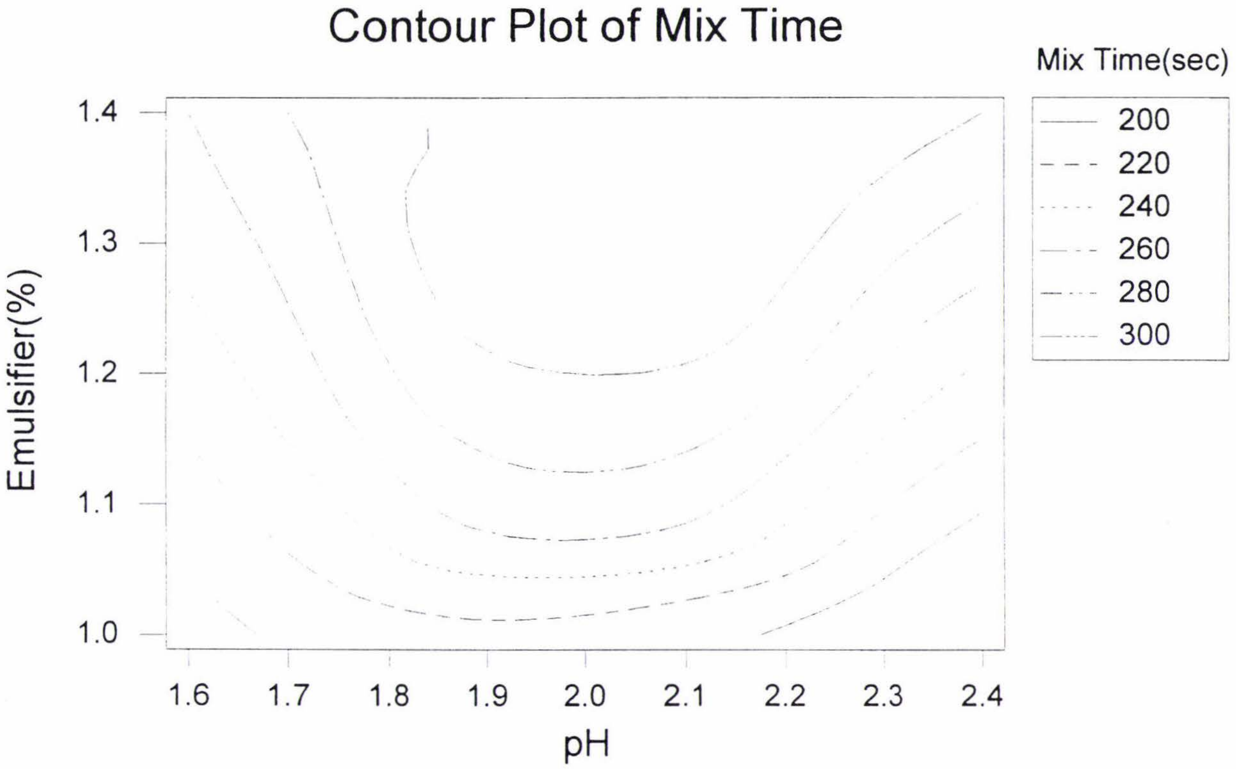


Figure 5-16. Contour Plot for Mix Time of Emulsifier and pH Level



5.6 Determining an Optimum Formulation Range

The significant effects controlling each of the emulsion and microsurfacing properties are summarised in Table 5-9. This information has been used to identify the key factors that control the performance and produce an optimal range of values to investigate by a mid-scale trial. Permanent deformation was not included as a response in the experimental design but polymer addition of at least 3% was shown to be necessary to meet performance specification.

The level of polymer had effects on the emulsion settlement, the binder softening point, and the microsurfacing mix time. A 5% level of SBR latex increased the settlement slightly due to increased creaming but the latex could be easily re-mixed back through the emulsion. Increasing the polymer rapidly raises the binder softening point, which was desirable. Increasing the polymer latex also extended the mix time. But a 3% latex level with a 1.0% emulsifier level decreased the mix time considerably. There was not a dramatic improvement in abrasion or permanent deformation resistance using 5% polymer so an optimum would appear to be 3.0% to 4.0%.

Table 5-9. Summary of Significant Effects Controlling the Microsurfacing Properties

Response Variable	Significant Effects	Effect	p-Value
Viscosity	Emulsifier	95 cP	0.007
Settlement	Polymer	3.45%	0.066
	Emulsifier	12.83%	0.005
Sieve Residue	Soap pH	0.053%	0.023
Softening Point	Polymer	12.83°C	0.003
Abrasion	Emulsifier/Soap pH	96 g/m^2	0.180
Cohesion 60 minutes	Emulsifier	- 6.8 kg-cm	0.004
Cohesion 90 minutes	Emulsifier	- 8.5 kg-cm	0.007
Cohesion120 minutes	Emulsifier	- 7.3 kg-cm	0.027
Mix Time	Polymer	98 sec	0.000
	Emulsifier	103 sec	0.000
	Polymer/Emulsifier	- 78 sec	0.000

Emulsifier level had the most wide spread impact on the formulation. It affected every response variable except sieve residue and binder softening point. Having a low emulsifier level of 1.0% results in an acceptable viscosity of 160 to 190 cP and a lower settlement. The major impacts of emulsifier level are on the cohesion development and mix time. A 1.0% emulsifier level results in the microsurfacing meeting the cohesion specification at 90 minutes while the high level of 1.4% extends the time to approximately 150 minutes. The mix time decreases far too much at a 1.0% emulsifier and 3% polymer latex level. A high level of polymer latex of 5% with a 1.0% emulsifier level result in good mix times. The only formulation aspect that a low emulsifier level adversely affected was the mix time.

The soap pH significantly affected the emulsion sieve residue, mix time and possibly the abrasion loss. A pH of 1.6 resulted in less retained particles on the sieve possibly indicating a narrower particle size distribution and less susceptibility to early emulsion coalescence. There was a small increase in mix time by setting the pH at 1.6. An interaction between the pH at a high level of 2.4 and emulsifier at high 1.4% level would increase the abrasion loss but the significance p-value was only 0.180.

The key factor in the detailed design experiment was the emulsifier level. To obtain the quickest traffic times onto the microsurfacing requires a level of 1.0% as even a slight increase will rapidly slow the cohesion rate. The emulsion was stable at 1.0% emulsifier level and gave improved settlement. The addition of 4% polymer latex while keeping the emulsifier at 1.0% should enable suitable mix times over 200 seconds to be achieved. The increased polymer also improves the binder performance properties. An additional possibility to control the speed of the mix time is to increase the proportion of setting retarder additive in the mix design.

The proposed refined formulation to be tested by a mid-scale trial is shown in Table 5-10. But it would need to be tested with a laboratory sized trial first to assess if the performance properties match the predicted results.

Table 5-10. Refined Emulsion Formulation for a Mid-Scale Trial

Formulation Components	Criteria
Bitumen 80/100	62%
SBR Latex*	4%
Emulsifier B	1.0%
Soap pH	1.6
Water	to 100%
Bitumen Temperature	150°C
Soap Temperature	40°C
Mill gap	0.170 mm

* Latex post added to manufactured emulsion.

The microsurfacing mixture design was unchanged throughout the detailed design experiment and requires no modification at this stage. The design to be used for a mid-scale trial is shown in Table 5-11.

Table 5-11. Microsurfacing Mixture Design for Mid Scale Trial

Materials	Criteria
Type II Bulls Aggregate	100%
Emulsion	15%
Retarder A (10%) Solution	0.5%
Water	7.0%
Aggregate Sand Equivalent	70%

Note: Mix design based on dry weight of aggregate

The one aspect still to be improved upon is the emulsion settlement. While the settlement is high the flocculated particles can be easily dispersed by gentle agitation. The addition of a small amount of calcium chloride such as 0.02% to 0.03% to the aqueous phase of the emulsion or to the latex before addition to the emulsion is a possible solution to further investigate.

6. CONFOCAL MICROSCOPY INVESTIGATIONS

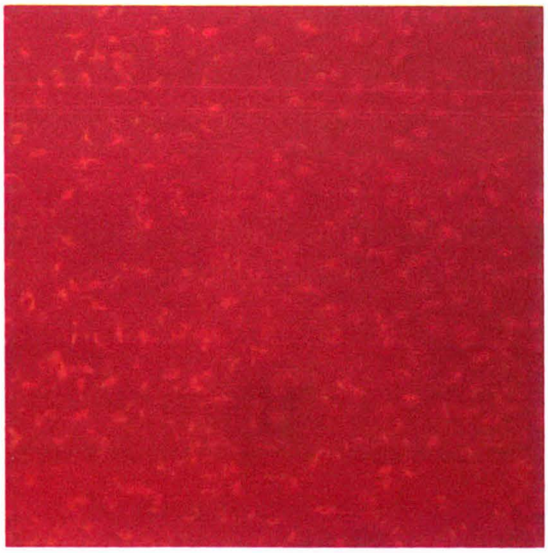
6.1 Introduction

Unmodified and polymer modified bitumen binders were viewed with Confocal Laser Scanning Microscopy (CLSM) using fluorescent and reflected light. The samples for hot bitumen binder; emulsion binder and microsurfacing were prepared for viewing as described in the Materials and Methods chapter 4.5.7. The binder films were viewed to assess the polymer distribution and the relative microstructures of hot modified bitumen and modified bitumen emulsion binder. The physical performances of the binders as determined in Chapter 5 were compared with the microscopy results. The results of the comparison were used to understand the interactions between bitumen and the polymer and how this affects binder performance in road surfacing.

6.2 Unmodified Bitumen

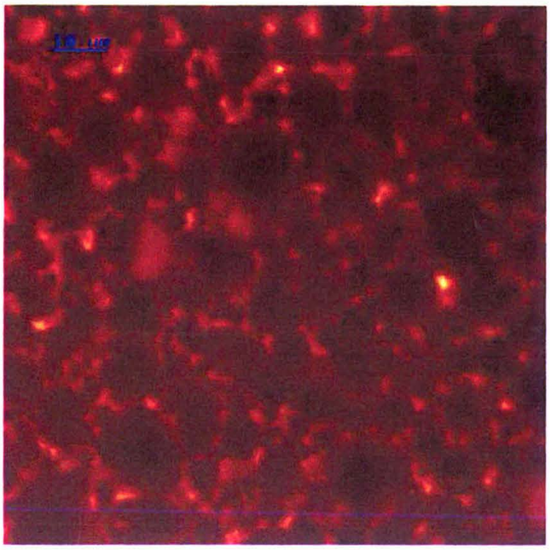
The irradiation of bitumen with UV or blue light should result in little if any fluorescence due to the asphaltenes phase. The image in Figure 6-1 is a sample of unmodified bitumen and shows a smooth blend of the constituents. The image shows no fluorescence as expected to confirm the methods validity.

Figure 6-1. CLSM Fluorescence Image of Unmodified Bitumen (1000x Magnification)



A sample of unmodified emulsion residue has a completely different structure and is shown in Figure 6-2. The binder has a droplet type structure resembling a matrix that is formed of dark asphaltene particles surrounded by what is probably the oil phase of the bitumen. This observation appears consistent with Bouldin et al (1990) who reported that asphaltenes, saturates were dark and polar aromatics emitted slight fluorescence.

Figure 6-2. CLSM Fluorescence Image of Unmodified Bitumen Emulsion Residue (1000x Magnification)



This binder structure has not been mentioned in any literature reviewed. The expectation was that the binder would be very similar if not identical to that in Figure 6-1. Emulsified binders are supposed to retain the same properties of hot bitumen binders when applied to a surface (Asphalt Institute 1994) but the different microstructure indicates that there is major difference.

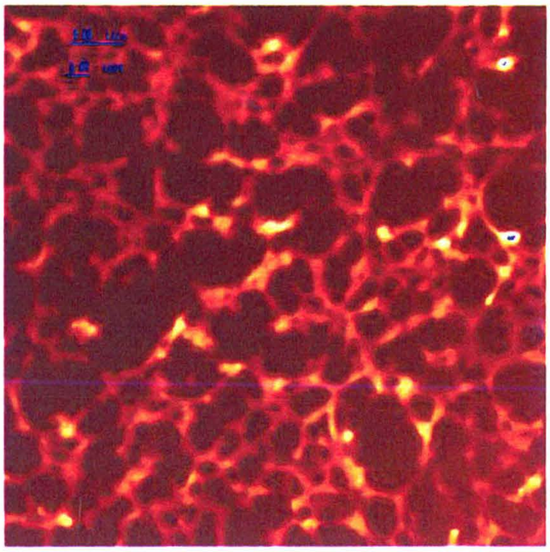
6.3 Hot Polymer Modified Bitumen and Resulting Emulsion Binders

6.3.1 SBS Modified Binder

The addition of styrene butadiene styrene (SBS) polymer to bitumen results in a three-dimensional polymer network as shown by the fluorescence mode image in Figure 6-3. The polymer has linked together throughout the bitumen to provide a support mechanism to resist deformation. Also, the polymer phase has swollen with part of the maltenes phase of the bitumen.

SBS forms a physical 3-D network due to the styrene ends of the tri-block copolymer linking together. The physical network observed agrees with the explanations by Morgan & Mulder (1995) and PIARC (1999) as to how SBS improves the high temperature properties and elasticity of bitumen. A comparison to emulsified SBS modified bitumen was not possible due to the inability to produce a stable emulsion as outlined in Section 5.2.2.

Figure 6-3. CLSM Fluorescence Image of Bitumen Modified with 3% SBS Polymer (400x Magnification)



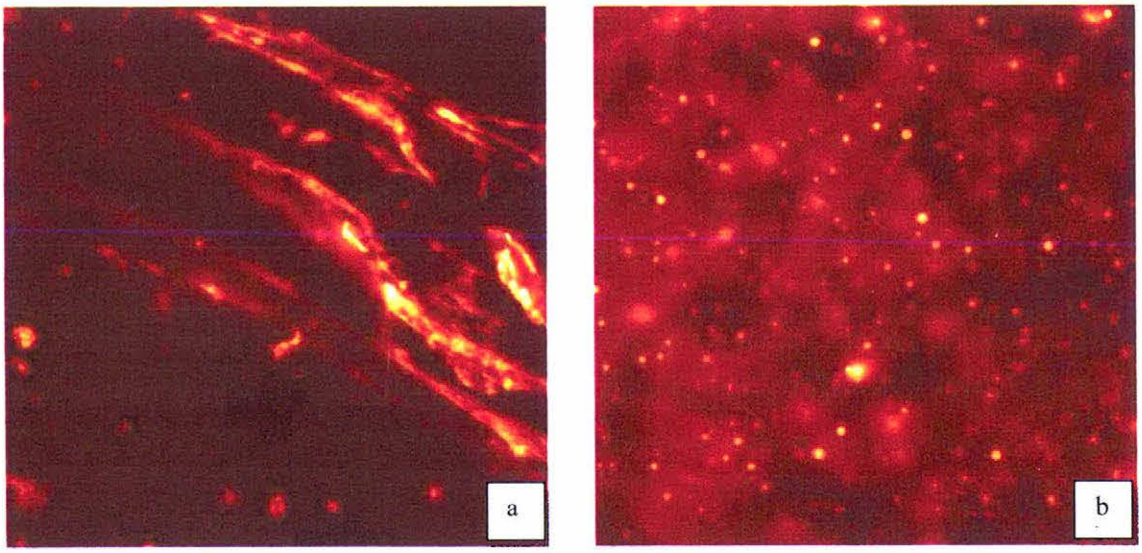
6.3.2 SBR Modified Binder

Blending 3% styrene butadiene rubber (SBR) into hot bitumen is shown in Figure 6-4 (a). The image shows the polymer swollen with maltenes from the bitumen but dispersed in areas of large coalesced droplets. The bright yellow areas are the styrene sections of the polymer. While the light yellow/orange areas are the butadiene elastomer swollen with maltenes. SBR is a random copolymer and does not form a physical network like SBS as there are no connecting styrene blocks.

The same binder after emulsifying (a monophase emulsion) and evaporation of the water phase is shown in Figure 6-4 (b). The microstructure consists of dark areas of asphaltene aggregations and fluorescent styrene particles which, are surrounded by a swollen butadiene-maltenes phase. The binder film is far more homogeneous than the binder before emulsification and has better polymer distribution.

The microstructure of a compatible copolymer should be composed of fine evenly distributed particles (Morgan & Mulder 1995; PIARC 1999) but the coalesced polymer shows the evolution of two different phases. This indicates that the polymer-bitumen blend was still incompatible despite the addition of the additives aromatic oil A and amine A. PIARC (1999) also reported that a coarse structure results if the polymer was not readily soluble in the bitumen. The image in Figure 6-4(a) seems to confirm this.

Figure 6-4. CLSM Fluorescence Images of 3% SBR Latex Pre-blended into Hot Bitumen a). The Pre-blended SBR-Bitumen Residue after Emulsifying b). (1000x Magnification)



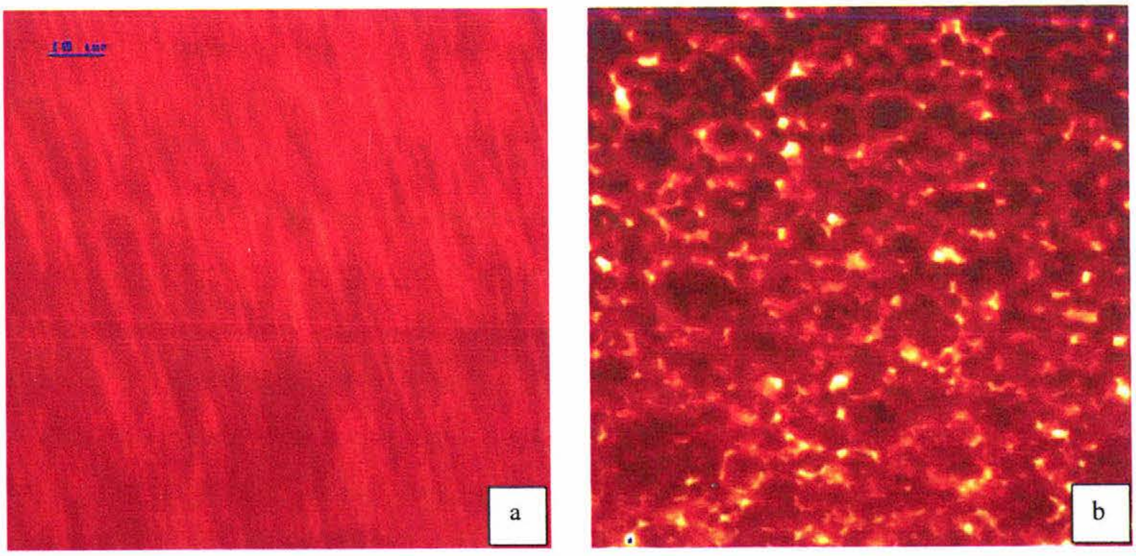
Asphaltenes and polymer compete for the solvency power of the low molecular weight maltenes to remain in solution (Piazza et al 1980; Bouldin 1990; Whiteoak, 1990; Lu et al, 1999; PIARC 1999). But if the asphaltene content is high or the polymer is of a very high molecular weight then it becomes more difficult to obtain solubility. Safaniya bitumen has as high asphaltene content and SBR a high molecular weight so this further indicates the blend was incompatible.

Though the SBR monophase modified emulsion performed poorly compared to the biphase emulsion binder in chapter 5 the polymer dispersion is a useful improvement. This is because improved polymer distribution in the film should lead to more consistent binder properties in terms of cohesion development and stone retention. This has definite advantages for the spray chip sealing method where stone retention is very important and difficult to attain consistently with hot modified bitumen.

6.3.3 EMA Modified Binder

The effect of adding cross-linker A to the ethylene methyl acrylate (EMA) and bitumen blend resulted in a microstructure of very fine polymer particles as seen in Figure 6-5(a). The same modified binder residue after emulsifying is shown in Figure 6-5(b) and shows dark aggregations of asphaltene particles surrounded by a swollen polymer-maltenes phase. This indicates a network type structure formed within the binder film. Again it is apparent that a different microstructure results when the modified binder is emulsified. But the similar softening points determined in Section 5.2.2 indicate that the actual binder performance was similar in each.

Figure 6-5. CLSM Fluorescence Images of 3% EMA Modified Bitumen a). EMA-Bitumen Binder Residue after Emulsifying b). (1000x Magnification)



The addition of cross-linker A to EMA produces a chemical bonding of the polymer to bitumen rather than a physical bonding such as with SBS. This chemical bonding has been reported by Lesueur et al (1998) and PIARC (1999) to produce a fine structure. The image in Figure 6-5(a) indicates this effect. Modification of hot bitumen by EMA normally requires a cross-linking agent to prevent phase separation, if the binder is to be used for spray sealing or asphalt. The good stability of the EMA modified emulsions both with and without cross-linker A indicated that its addition was not necessary to produce stable emulsions. This was important due to the formation of toxic fumes by the reaction of cross-linker A and acid. Unfortunately time constraints did not allow an image of the hot binder without cross-linker A to be obtained.

6.4 Observations of Biphase Emulsions Containing SBR Latex

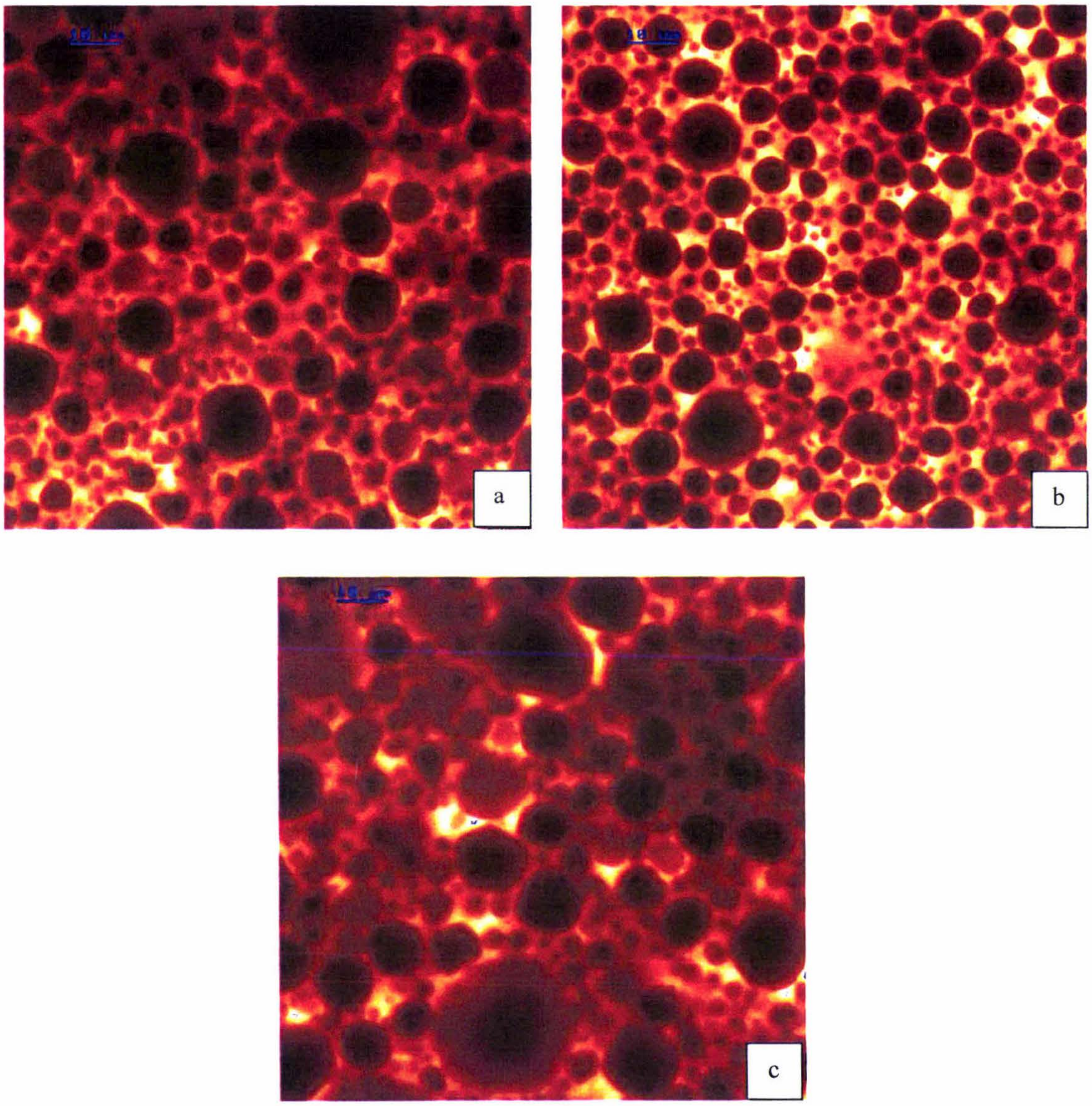
The addition of SBR latex by either of post adding, dispersion in the soap phase or co-milling results in a much different binder microstructure as shown in Figure 6-6. The fluorescent mode images show a polymer network structure formed after evaporation of the water phase. The butadiene has swollen with absorbed maltenes and linking networks of styrene surrounds the dark asphaltene particles, which do not fluoresce. The asphaltene particles vary from about 3 – 17μm in diameter. The processing of latex through the emulsion soap phase and by co-milling appears to provide a slightly more even distribution of polymer in the binder.

The polymer network appears to be formed around the asphaltenes rather than in the image of the block copolymer SBS (Figure 6-3) which shows 3-D linkages through the bitumen.

The high molecular weights of the polymer and of the asphaltenes helps to reduce flow of the bitumen at higher temperatures. The asphaltenes provides the strength and stiffness to bitumen and the polymer network surrounding the asphaltenes adds strength and also elasticity, so thereby improving the overall binder properties. This network structure provides one reason why the biphase emulsion binders produce higher softening points compared to polymer modified bitumen binders as described in chapter 5.

The cause of the different binder structures obtained by adding the polymer to the bitumen before emulsification compared to adding it during or after emulsification is due to the polymer being dispersed throughout the bitumen. This method of addition produces the monophase emulsion – a single phase of polymer modified bitumen droplets. Whereas the other methods of latex addition produce the biphase emulsions, which are a combination of two phases – bitumen droplets and polymer droplets. The interaction between the bitumen and polymer does not take place until the emulsion breaks, as seen by the binder images in Figure 6-6.

Figure 6-6. CLSM Fluorescence Images of 3% SBR Latex Modified Biphase Emulsion Binders (1000x Magnification)



Key: a: Post Additon of Latex

b: Soap phase addition of Latex

c: Co-milling of Latex

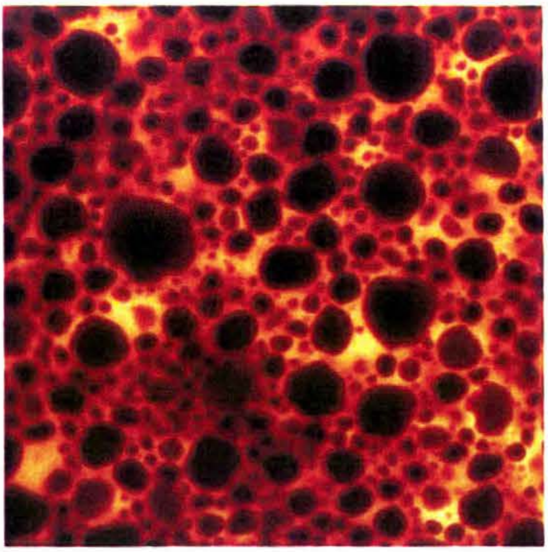
6.4.1 Resistance of the Microstructure to Higher Temperatures

The emulsion residue was obtained by drying the emulsion sample at 60°C in order to simulate the higher temperatures expected during application of the microsurfacing. But the effect of increasing the temperature was performed to compare the microstructure.

The resistance to higher temperatures of the modified biphase emulsion residue is shown in Figure 6-7. This shows the binder from Figure 6-6(b) but after drying at 109°C for two hours. The polymer has prevented the asphaltenes from significantly flowing under the higher temperature and the network support microstructure remains. The glass transition temperature of styrene is 100°C so only at temperatures above this will it start to progressively soften and flow. In biphase emulsions the SBR polymer is not exposed to temperatures above 85°C. But in monophase emulsions the temperature is usually up to 180°C, well above the glass transition temperature of styrene. Hence, polymer degradation is likely to occur. This presents a major advantage with biphase emulsions.

This result shows how the polymer helps the bitumen resist much higher temperatures and why it is required for roads in hot climatic areas. This modification prevents the bitumen binder adhering to vehicle tires in very hot summer weather. It also stops the pavement softening under load to limit permanent deformation (rutting).

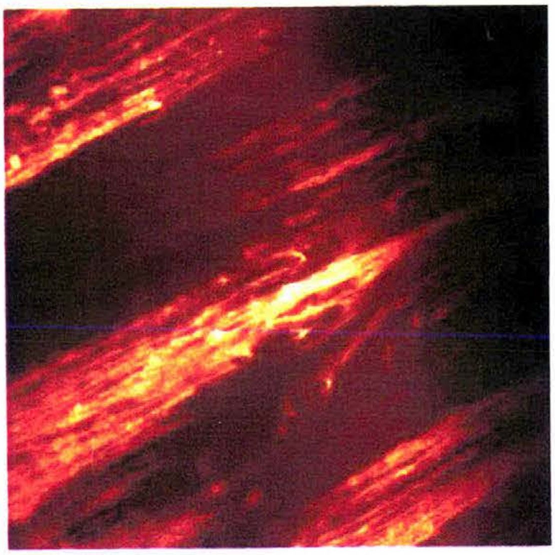
Figure 6-7. CLSM Fluorescence Image of Biphase Emulsion Residue after Heating at 109°C (1000x Magnification)



6.4.2 Binder Resistance to Applied Stress

The CLSM fluorescence image in Figure 6-8 shows the resistance of the polymer to shear stress within the binder. As stress is applied the polymer elongates from the round forms seen in Figure 6-6 due to its elastic properties and resists deformation. The butadiene part of the polymer helps the system recover from a given loading.

Figure 6-8. CLSM Fluorescence Image of Biphase Emulsion binder under Shear Strain (1000x Magnification)

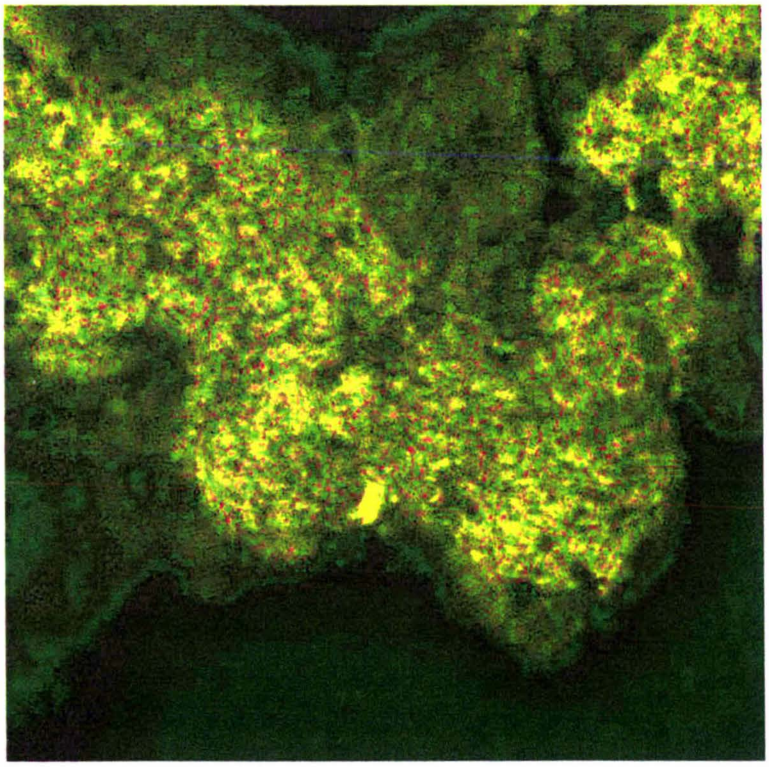


This effect provides a demonstration to the proposed dynamic interaction between bitumen and polymer suggested by Loeber et al., (1996). The deformation resistance properties imparted by addition of polymer shown in Figure 6-8 are important for any type of road surfacing. Chip retention as already mentioned is particularly important and the elastic properties of the polymer help bind the stone to the surface. Unmodified bitumen has no elastic properties and minor flexibility so the effects of turning traffic in particular more easily remove stones. The strength and elasticity of the polymer also provides rutting resistance and reduced lateral displacement in the pavement which, was observed by the results in chapter 5. The effect has been demonstrated in physical pavement tests in other studies (Asphalt Institute, 1994; Holleran, 1997; Lee et al., 1997; Takamura & Heckmann, 1999) but the mechanism is also shown visually in this research.

6.5 Observations of Microsurfacing

Confocal microscopy in both fluorescence and reflected modes can be very useful for visualising the interaction between the polymer-modified binder and aggregate in the microsurfacing pavement. Separate images of the microsurfacing using both modes can be seen in Figure 6-9 and 6-10. The depth scan fluorescence image shown in Figure 6-9 shows distribution of the binder in the aggregate sample at 100x magnification. The bright yellow areas are the pure polymer and the lighter areas the swollen polymer-maltenes phase. The polymer still retains a network arrangement around the asphaltenes within the bitumen and this network helps the aggregate stay bound together under stress from loading and the surfacing softening at higher temperatures.

Figure 6-9. CLSM Depth Scan Image of Microsurfacing under Fluorescence Light (100x Magnification)



The aggregate within the sample can be seen in the depth scan reflected image in Figure 6-10 at 100x magnification. Here the light reflects from dense particles and only the aggregate and areas of asphaltenes in the bitumen along with dense binder are shown around some of the particles. The bright areas are the aggregate at the top of the sample.

The two images can be overlaid as seen in Figure 6-11 where the polymer is shown in red and the aggregate in green showing the polymer-bitumen networks binding the aggregate.

Figure 6-10. CLSM Depth Scan Image of Microsurfacing under Reflected Light (100x Magnification)

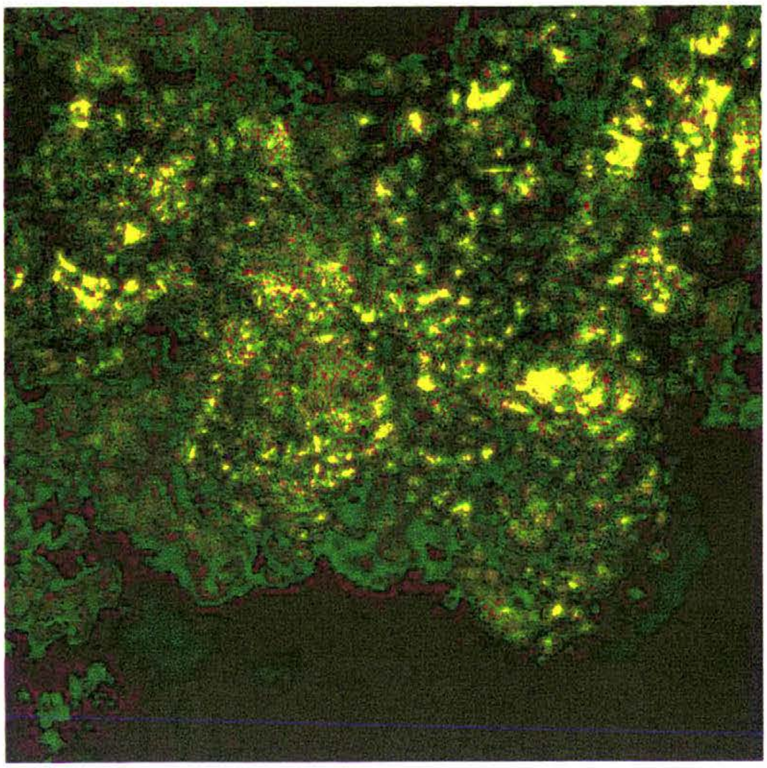
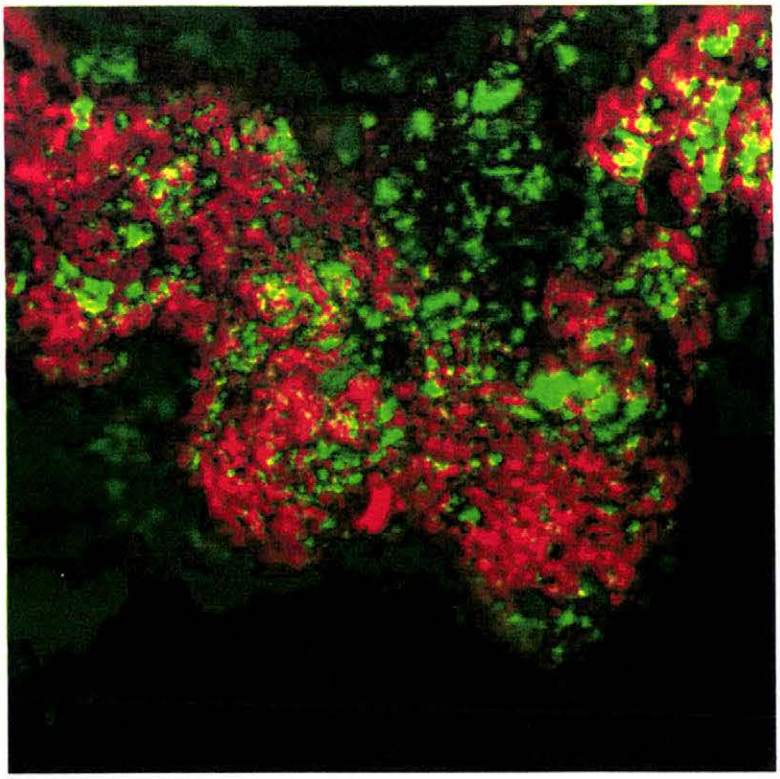


Figure 6-11. CLSM Composite Depth Scan Image of Microsurfacing with Combined Fluorescence/Reflected Light (100x Magnification)



The deposition of the polymer network around the asphaltenes provides the added strength to a microsurfacing system as demonstrated in Figure 6-11. This support network shows how the polymer improves the rutting and abrasion resistance of microsurfacing and why it can be applied in thicker layers to the pavement. The fine aggregate particles less than 300μm diameter appear to be well coated with binder but it is not clear if larger aggregates up to several millimetres in diameter are also coated.

The identification of polymer networks within the microsurfacing agrees with the findings of Takamura & Heckmann (1999). They reported honeycomb structures of polymer around the asphaltene particles within a microsurfacing sample but they used the scanning electron microscopy (SEM) technique. The depth scan technique for CLSM provides the means to observe 3-dimensional effects of the binder-aggregate mixture where it is difficult to obtain a flat sample whereas single line scanning only provides a partial view of how the modified binder and aggregate interact.

7. DISCUSSION AND CONCLUSIONS

7.1 Introduction

This projects aim was to investigate and develop a polymer modified emulsion based surfacing (microsurfacing) formulation to a mid-scale prototype stage. Additionally, the analysis of polymer-bitumen interactions and how they affect the products end properties by using microscopy was an important part. The scope of the project meant that a large-scale trial under normal processing conditions on a road surface could not be achieved. But the formulation was sufficiently developed so that this would be the next step.

This discussion looks at how successful the investigations were to develop the formulation to the mid-scale stage and areas for further investigation. The process followed for the development looked at investigating the effects of several key materials and the emulsion process method. The material aspects included polymers, bitumen, emulsifiers, and aggregate. While the process aspect included the method of polymer modification of the bitumen emulsion. The overall process followed aimed to produce the right mix of materials and method to develop a microsurfacing that would meet performance specifications.

7.2 Initial Product Specification

The development of a preliminary technical specification to guide the initial formulation direction had to consider the limitations of the colloid mill and industry performance criteria. It was found that polymers in powdered, easily dispersible pellet, and aqueous latex forms could only be used to modify the emulsion in this study. This has now defined a range of suitable polymers available. These are SBS, SBR, EMA, EVA, Neoprene, and Natural Rubber. SBR, neoprene, and natural rubber can be added in greater quantities to a bitumen emulsion because they are latex polymers.

The ability to analyse modified bitumen with microscopy techniques was a useful finding to incorporate into the testing methodology. There has been little if any analysis of this nature published within New Zealand or comparisons using Safaniya bitumen. Additionally, analysis of emulsion residue is scarce and presented a new dimension to support the quantitative tests.

7.3 Initial Design

7.3.1 SBR Latex Biphase Emulsion Investigation

SBR latex polymer was added to the emulsion by three methods for this investigation: co-milling, addition through soap phase and post adding. These methods all produce a biphase emulsion consisting of bitumen droplets and polymer droplets. The emulsion settlements were affected by creaming of the polymer latex. The density difference between the bitumen and latex causes this problem. The density difference is slightly higher with 100 pen bitumen than softer 200 pen bitumen. This was the prime cause of the higher settlement values in the modified emulsions compared to the unmodified control emulsions.

The addition method produced interesting emulsion stability results. Claims by Holleran (1997) and PIARC (1999) state that post addition of the polymer latex results in viscosity decreases and high settlement compared to the other two methods. But the results in this investigation actually indicate the opposite. Takamura & Heckmann (1999) post added SBR and reported acceptable stability characteristics. A possible reason for the discrepancy could be the type of SBR latex used. SBR is available in several grades and each can impart different characteristics to the emulsion stability.

Co-milling the latex was reported by Holleran (1997) to result in higher viscosity due to alteration of the particle packing by shear forces. But the stability results with both bitumen grades showed high settlement, and low viscosity, indicating early instability and coalescence. The reason for this effect was unclear.

The polymer addition method appeared to have little effect on the microsurfacing properties apart from post addition which gave longer mix times, allowing better mixture workability before setting.

The harder 100 pen bitumen resulted in significant improvement in the microsurfacing permanent deformation resistance compared to 200 pen bitumen. Harder bitumen grades are recommended in the microsurfacing specifications (ISSA 1996) and the results here confirmed that 200 pen bitumen was too soft. 100 pen bitumen must be used for microsurfacing, as it is stiffer and has a higher softening point than 200 pen bitumen and produced a much more durable surface. The permanent deformation test had a high test error and suffered from variation. The possible cause was attributed to the aggregate quality.

An unexpected finding was that the softening points of the biphase emulsion binder were 4.0 - 5.0°C higher than hot SBR modified bitumen binders. This showed that emulsified binders have improved resistance to high temperature. Coyne (1987), Anderson, (1992), PIARC (1999) all report softening points values for emulsion residue being very similar to hot modified binders. A possible reason is that the studies mentioned might have prepared the binders by evaporating the water phase at high temperatures such as 135°C. This temperature is commonly used for bitumen emulsions to determine the residual binder content. It has been stated by several authors (Bouldin et al 1990; Morgan & Mulder, 1995; Holleran, 1997; PIRAC, 1999) that exposure to temperatures above 100°C will gradually degrade polymers. The samples in this study were prepared by evaporating the water at 60°C in a forced air oven. Microsurfacing mixtures are generally not exposed to temperatures much more than 60°C. So, it may be possible that the other studies were actually understating the softening point values due to polymer degradation.

The specification for Wet Track Abrasion is less than 800 g/m^2 material loss. But the best of the trial runs in this experiment produced 1330 g/m^2 abrasion loss. The results indicated that there was an inherent problem with the test itself, or that the aggregate/binder adhesion and cohesion was poor and the aggregate was not sufficiently bound by the binder. The cause was suspected as being the cleanliness of the aggregate, which can reduce the ability of the emulsion to adequately coat the aggregate. Another possibility was emulsifier type and the concentration, as higher levels could retard the cohesion due to too much free emulsifier in the water phase of the emulsion.

The time taken to meet the microsurfacing cohesion specification of 20 kg-cm was over 3 hours. The type and level of emulsifier, and aggregate quality were possible reasons for the slow cohesion development.

7.3.2 Monophase Polymer Modified Emulsion Investigation

Emulsifying polymer modified 100pen bitumen was not possible with the conventional colloid mill used. Blending polymer into this grade of bitumen results in significant viscosity increases (well over 200 centipoise) due to the polymer molecular weight. Emulsifying SBS modified 100 pen bitumen was tried but only sludge was formed. It is noted that all of the literature studies encountered on emulsifying Linear SBS through a colloid mill operated at atmospheric pressure, have used softer 180 – 220 penetration grade of bitumen and not the harder 100 grade (Coyne, 1987; Anderson, 1992; Serfass et al., 1992; Rabiot & Jariel, 1993). This could be due to the difficulty in emulsifying hard penetration bitumen modified with SBS or the other polymers.

EMA modified 200 pen bitumen and SBR Polymer modified 200 pen bitumen has a low enough viscosity to be emulsified (approximately 200 centipoise). But only EMA can be successfully emulsified with 130/150 pen bitumen. A limit of 3% polymer addition was a restriction with the monophase emulsions due to viscosity increases. Adding kerosene could lower the viscosity, but this would soften the binder, and is an environmental concern.

The compatibility of the polymer and bitumen was another key factor encountered. SBS, SBR, and EMA all have phase separation problems when added to hot Safaniya bitumen. This compatibility problem is common around the world and depends on the relative proportions of asphaltenes, saturates, resins and aromatics in the bitumen. Safaniya bitumen has a high asphaltene and low aromatic content. This results in less maltenes available to solvate the polymer, resulting in compatibility problems. The phase separation effect has been solved by the use of a cross-linking agent in previous work. But it was discovered that the cross-linking agent A and hydrochloric acid from the emulsion aqueous phase produced toxic fumes. The trials with SBR used aromatic oil and an amine derivative to compatibilise the bitumen but, microstructure analysis of the binder still showed incompatibility.

A promising result was that EMA modified bitumen was stable by itself when emulsified indicating that a cross-linking agent is unnecessary. This could be a result of ethylene based copolymers being more compatible with bitumen as proposed by Whiteoak (1990).

There are two avenues to investigate for compatibilising the polymer in bitumen for monophase emulsions: cross-linking agents or aromatic oils. The cross-linking agents must not react with any of the emulsion components like cross-linking agent A did. Likewise, the type and level of aromatic oil(s) needs to consider the effect on softening point of the binder.

The softening points of the monophase emulsion binders were much lower than those obtained from the biphase emulsions. The result of 48.7°C obtained from EMA with 200 pen bitumen closely matches the result from the modified bitumen before emulsification. This agrees with PIARC (1999) who propose that modified monophase emulsions should have nearly identical properties to the modified bitumen. The result may again indicate that heating of the polymer to high temperatures from 160°C to 180°C to blend and then emulsify it with bitumen leads to polymer degradation.

The addition of aromatic oil to the SBR modified 200 pen bitumen resulted in a significant drop in softening point of 4.0 – 5.0°C. Aromatic oil 'A' is likely to decrease the softening point as it contains mostly aromatic oil, which have molecular weights between 300-2,000. But, the asphaltenes have molecular weights between 1,000-100,000 (Whiteoak, 1990), and the asphaltene content in the bitumen is lowered by addition of aromatic oil A. The low softening point for the 150 pen bitumen run could have been caused by having less than 3% SBR in the binder; and the polymer residue retained in the filter of the colloid mill bitumen tank tends to suggest this was the case.

The cohesion development in the microsurfacing samples was slow and required over 3 hours to reach. The causes could have been too much free emulsifier in the water phase of the emulsion as the bitumen droplets are saturated with emulsifier. Or alternatively, the emulsifier may not have been effective in adequately penetrating the bitumen droplets as suggested by Engman et al., (1998). The level of emulsifier in the emulsions was consistently 1.5% to maintain stability but this may have been at the expense of cohesion development. Emulsifier A was not a quick setting type and a different emulsifier could also improve the cohesion development. The other aspect that had to be considered was the aggregate quality.

The monophase modified emulsions had better settlement results than the biphase emulsions and generally a narrower particle size distribution indicating good stability. But, being unable to use 100 pen bitumen meant that the permanent deformation performance of the microsurfacing was poor. The monophase modified emulsion method is not suitable for producing microsurfacing emulsions.

7.3.3 Emulsifier Investigation

A key performance aspect of microsurfacing is the need to develop cohesion of 20 kg-cm within the mixture to enable traffic onto the surface within 60 to 90 minutes. The emulsifier is a major component to achieving this specification. Three emulsifiers were studied, Emulsifier A (a quaternary ammonium), Emulsifier B (alkyl amidoamine) and Emulsifier C (imidazoline). The cohesion development results from all three emulsifiers in this section were low with the cohesion target taking over 150 minutes to reach. There were several reasons considered for this effect. If the emulsifier level were too high within the emulsion then excess free emulsifier would be present in the aqueous phase. The excess can be absorbed onto the aggregates and modify the surface charge as suggested by Boussard & Martin (1996) and Engman et al (1998). Additionally cohesion can be slow if the aggregate is dirty or dusty, which results in a lower sand equivalence value. The dust particles present a large surface area and can absorb the binder and result in less binder adhering to the larger aggregate.

Emulsifiers B and C significantly increased the viscosity of the emulsion but strangely also increased the settlement. Theoretically an increase in viscosity should lower the settlement due to less particle movement (Whiteoak 1990). While the settlement was high the particles had only flocculated and could be re-mixed with gentle agitation. There appeared to be no stability problems as the emulsions did not break too quickly when mixed with aggregate. The polymer latex had creamed to the top of the emulsion but this was not the sole factor. A possible reason for the high settlement is that the emulsifiers both have a high density, and when absorbed onto the bitumen also of a high density the stabilised droplets then settle due to an increased density difference with water. If this has occurred then a solution is to increase the density of the water phase by adding a small amount of a salt such as calcium chloride. It must be kept in mind that too much salt will break the emulsion.

The emulsion produced with emulsifier B had a much lower sieve residue than that with emulsifier C. A lower value can indicate that the width of the particle size distribution is narrower which should result in lower settlement due to fewer larger particles (Whiteoak, 1990). But the high settlement values for both emulsions tend to disagree with this. This indicated some other effect occurred to increase the settlement as discussed in the previous paragraph.

The softening points of the emulsion binders using emulsifier B and emulsifier C had values of 67.5°C. This was an increase of up to 7°C over the post-added latex run with emulsifier A. This was very unexpected and a new result not previously reported with biphase emulsion binders. The only difference between the trial runs was the emulsifier used. It appears that the emulsifier type and chemistry has an effect of increasing the bitumen softening point. An unmodified emulsion binder using emulsifier B had a softening point of 54.7°C while the emulsion binder with emulsifier A was 51°C. This also suggests that some of the increase may occur because of an interaction between polymer and emulsifier.

The emulsifiers B and C had an effect of significantly decreasing abrasion loss in the microsurfacing to 535 g/m^2 and 520 g/m^2 respectively. The specification was for less than 800 g/m^2 abrasion loss. But none of the trials from the first two investigations of biphase and monophase emulsions came close to it. The aggregate used was identical between trials. This showed that emulsifier type has an effect on the adhesion and long term cohesion within the microsurfacing. Emulsifier A is a quaternary emulsifier and it was also found by Jones (1989) that this type resulted in higher abrasion loss.

Limitations with the testing of the emulsions were that the important properties of particle size distribution and interfacial tension measurement could not be performed due to the scope and workload of this study. Roading industry testing also does not cover these fundamental properties. But interfacial testing of bitumen emulsions is under research overseas to determine the most suitable method and to obtain consistently accurate results

(Lendresse et al 1996; Durand & Poirier 1999; Seive et al 1999). A problem with trying to determine particle size distributions with bitumen emulsions is that most institutions do not like bitumen near their equipment.

7.3.4 Aggregate Investigation

This investigation used 100 pen bitumen, SBR latex post added to the emulsion, and used emulsifier A. The cleanliness of the aggregate used for the microsurfacing was an important factor as was the addition of cement. The original investigations used Bulls aggregate with a sand equivalent of 49% as this is normally produced at the aggregate plant. Increasing the sand equivalence to 70% resulted in over 1250 g/m^2 abrasion loss, an improvement from 1905 g/m^2 lost with aggregate cleanliness of 49%. But when cement was removed from the mixture design the result was 332 g/m^2. The addition of cement increases the amount of fines in the aggregate grading and may have resulted in a build up of binder within these small particles rather than with large aggregate. Cement is used to regulate mixture consistency and accelerate break times (Asphalt Institute, 1994; ISSA, (1996). But there has been no literature indicating that it can increase the abrasion. The international microsurfacing specification recommends an aggregate cleanliness of 60% minimum and the results here agree that a higher cleanliness must be used. A sand equivalence of 70% was determined as being the optimum to use for the microsurfacing in this research.

Cement was also not necessary for the mix consistency and could be removed from the mixture design. The addition of dilute emulsifier or dilute retarder A solution controlled the setting time adequately. Cement also had no effect on the short-term speed of microsurfacing cohesion development.

A comparison of Bulls aggregate which is of greywacke origin and New Plymouth aggregate of andesite origin, showed that greywacke resists abrasion more. Andesite is volcanic and is more brittle than greywacke (Transit 1993) so the aggregate chips tended to wear under abrasion forces quicker.

The cleanliness of the aggregate had little effect on the early cohesion development. But does on the cohesion within the microsurfacing for the abrasion test. The likely reason for this apparent conflict is that the abrasion specimens are cured for 24 hours before testing to assess the surface wear on a fully cured sample. The cohesion samples were cured for short times, as this test is an indication of how quickly the surfacing reaches 20 kg-cm cohesion to allow traffic on it. So it can be possible that the cleanliness has a long-term positive effect on the cohesion but not at short times of less than 3 hours. This result suggested that some other effect was retarding early cohesion development. The factor suspected was emulsifier level.

7.4 Detailed Design Investigation

Three factors were investigated in detail within this investigation: polymer content, emulsifier content, and pH level. The emulsions produced were all stable indicating that the range of emulsifier level investigated was satisfactory. The settlement was over 50% using the high 1.4% emulsifier level. The unusual result encountered was that decreasing the emulsifier level actually improved the settlement to 43%. The viscosity dropped as was expected but the settlement dropped as well. It was observed that the bottom 50ml sample residue of the settlement cylinders was consistently around 67% to 69%. But, the top 50 mls had considerable creaming. The emulsions were produced with binder contents of 62% so the settled binder was actually not very high. A possible explanation for this effect is again the high density of the emulsifier and its possible effect of increasing the bitumen droplet density; and the creaming of the latex. Thus, increasing the density difference between the bitumen and water phases as proposed in Sections 5.5.3 and 7.3.1 could solve this. The settlement was still outside the desired specification of less than 5%, but so long as the emulsion is regularly stirred there would be minimal problems expected. The main concern would be potential blocking of the application device filters.

Lowering the emulsifier solution pH resulted in a significant reduction in the retained particles on the 150 μm sieve. This indicates that the particle size distribution became narrower as the acid was increased which agrees with the effect proposed by Whiteoak (1990). But, this effect did not appear to improve the settlement to any degree.

The softening points of the binders rapidly increased when 5% polymer was added. This indicated that the polymer was beginning to form more extensive networks within the bitumen to strengthen the binder, and agrees with the findings of Bouldin et al., (1990) and Lee et al., (1997) in their work with SBR modified bitumen. An interaction between the emulsifier and polymer was not significant, so the other possibility is that the emulsifier has an effect of modifying the bitumen properties and helping it resist thermal susceptibility.

The greatest changes in results were observed with the microsurfacing properties. The abrasion loss further improved from the results of the previous investigations. The results were similar to those observed by Jones (1989) which showed abrasion values less than $100g/m^2$. Emulsifier B appeared to help the long-term cohesion within the microsurfacing as the abrasion loss decreased considerably from the aggregate investigation values. It seems that the type of emulsifier used can improve the adhesion and subsequent cohesion of the binder with the aggregate as indicated by the results of Jones (1989). This indicates that emulsifier selection is crucial for emulsion stability but also for the degree of bonding with the aggregate. An unusual effect was that higher polymer addition did not result in significant abrasion resistance as proposed by Holleran (1997); why this occurred was unknown.

The addition of higher levels of polymer was expected to further improve the permanent deformation, but this was not observed as the addition of 3% produced a better result than 4% or 5% polymer. Why this result occurred is unknown. But the high error in the test requires some caution in interpreting the results. The test error was originally determined using poor quality aggregate and the subsequent significant improvement in the abrasion, and cohesion results and their standard errors indicate that some of the variation can be controlled.

The effect of emulsifier on the microsurfacing cohesion was dramatic. It was suspected that decreasing the level would increase the cohesion development. A low 1.0% level of emulsifier resulted in cohesion values of 20 kg-cm to be attained in 90 minutes. With high 1.4% levels the time increased to typically 150 minutes. The results seem to confirm that there has been too much excess free emulsifier in the water phase and this has been the major cause of the slow cohesion development as indicated by Boussard & Martin (1996); Engman et al (1998). The draw back of having the low level of emulsifier is that the mix time with aggregate was too short. But, increasing the polymer to 4% offset this by increasing the stability of the emulsion. The target cohesion specification of 60 minutes is difficult to attain. Comments from technical personnel indicate that this time is achievable under hot climatic conditions. But 90 minutes is more realistic under average New Zealand conditions. The cohesion test was performed under conditions of 25°C and could not take effect of warmer air temperatures or wind which, can speed up the evaporation of water in the mixture. This effect was apparent when samples were placed outside on the pavement. Alternatively cooler conditions would slow the cohesion rate down as well.

The microsurfacing results in this investigation were far more consistent than in previous investigations. This is particularly so when comparing the test variation error from the process capability trial and to the error values from the detailed design investigation. The suggested reason for this improvement is the quality of the aggregate. This highlights that the whole system of emulsion and aggregate must be considered carefully in formulating a microsurfacing product.

The key factor in the detailed design experiment was the emulsifier level. To obtain the quickest traffic times onto the microsurfacing requires a level of 1.0% as even a slight increase will rapidly slow the cohesion rate. The emulsion was stable at 1.0% emulsifier level and gave improved settlement. The addition of 4% polymer latex while keeping the emulsifier at 1.0% should enable suitable mix times over 200 seconds to be achieved. The increased polymer also improves the binder performance properties. The cost implications of increasing the polymer must be compared against the emulsifier cost but more importantly the effect on microsurfacing cohesion performance should be considered. An additional possibility to control the speed of the mix time is to increase the proportion of setting additive in the mix design.

The overall good results of the detailed design investigation have enabled the formulation values for a mid-scale trial to be determined. The first step is to determine if the formulation from Section 5.6 will achieve the predicted performance in a laboratory trial. If so, then the mid- scale trial could proceed, and the results compared.

7.5 Confocal Microscopy

The investigation of emulsion binder residue by microscopy methods has been scarce. This research showed that emulsifying bitumen and polymer modified bitumen results in a completely different structure to that of hot bitumen binders. This result had not been reported before and was unexpected as the Asphalt Institute (1994) and PIARC (1999) state that emulsified binders should retain the same properties of hot bitumen binders. The result questions the literature that claims emulsion binder when it has broken, should be the same as hot bitumen binder.

The most clear example of this difference was between SBR modified monophase emulsion residue and biphase emulsion residue. It appears that biphase emulsions produce a stronger structural support network with polymer and this effect helps raise the softening point of the binder compared to monophase emulsions. The biphase residue consisted of a network of polymer surrounding the asphaltene particles. While, the monophase emulsion residue appears more like what a hot compatible copolymer bitumen blend should look like. The residue has an even dispersion of polymer throughout the bitumen. The difference in structure is suggested to be one of the reasons why much higher softening points were recorded in the biphase binders compared to hot polymer modified bitumen.

The key difference between biphase and monophase binders is that the polymer modification of the bitumen does not take place until the emulsion breaks and the water evaporates. Hence, as the water is removed from the bitumen droplets the polymer then surrounds the asphaltenes by absorbing the some of the maltenes phase. This polymer addition method to the emulsion appears to effectively remove the compatibility issue with SBR. The network structure remains even when the binder was heated to 109°C showing how the binder resists softening at high temperatures.

The softening points of SBR polymer and EMA modified monophase emulsions were nearly identical to their hot modified bitumen counterparts (chapter 5). But biphase emulsions using SBR had much higher values. A hypothesis is that high the temperature that polymers are exposed to in producing monophase emulsions results in degradation of the polymer.

Images of the microsurfacing showed that the modified binder maintains a network within the aggregate mixture to bind the particles together and how the surfacing resists deformation by heavy loading. The identification of polymer networks within the microsurfacing agrees with the findings of Takamura & Heckmann (1999). They reported honeycomb structures of polymer around the asphaltene particles within a microsurfacing sample - but they used the scanning electron microscopy (SEM) technique.

7.6 Recommendations and Further Work

Recommendations for the microsurfacing product are covered as follows:

- Test the recommended formulation on a laboratory scale first.
- If the laboratory scale result meets performance specification, then perform the mid-scale trial and compare to laboratory results.
- Try to improve the settlement of the modified emulsion by adding a small concentration of calcium chloride to increase the density of the water phase. A small experimental design could be used to assess effects and interactions.
- Develop a testing methodology that can assess the microsurfacing cohesion development at a range of temperatures and also simulate wind effects. This could provide a guide to modifying the mix design to suit various environmental conditions on a given day to obtain the optimum cure rate.
- Investigate substituting neoprene or natural rubber latex into the emulsion and assessing the effects. This could enable a back-up polymer to be available if supply problems occurred.
- Further assess the sand equivalent values, and effect of fines content of the aggregate on the abrasion, and cohesion.
- Investigate why the high 5% polymer level did not significantly improve the permanent deformation.

Other investigations relating to the emulsions are:

- Further investigate emulsifier C, as initial work indicated that it performed similar to emulsifier B, and it also had slightly better settlement.
- Further develop the EMA modified emulsion as it has good stability attributes without cross-linking. It could be used as a spray chip seal emulsion in the future.
- Investigate suitable emulsion particle size distribution techniques.
- Further investigate developing a technique for determining the interfacial tension of the emulsions. This could help speed up assessment of future emulsifiers. It can also determine the required amount to stabilise the emulsion and avoid excess free emulsifier in the aqueous phase.

Investigations relating to polymer modified bitumen are:

- Research the effects of emulsifier addition to hot unmodified and polymer modified bitumen to determine if this increases the softening point of the binders.
- Research the effects of varying the cure temperature of the emulsions for the softening point test to determine if the increased temperature does result in polymer degradation. Confocal microscopy could be useful to assist as well.
- Further investigate methods of cross-linking or stabilising SBS and SBR in monophase emulsions. Or use a different acid instead of hydrochloric acid.
- Continue to utilise the confocal microscopy facility at Massey University for future research where applicable.

Additional areas to investigate are:

- Try to determine why cement has an adverse effect on the abrasion resistance of the microsurfacing. This is important, as the result has not been reported elsewhere. It maybe possible the effect is unique to New Zealand due to material interactions.
- Assess the degree of binder coating the larger stones within the microsurfacing by confocal microscopy.

7.7 Conclusions

This research has shown that a microsurfacing roading product can be successfully formulated with New Zealand bitumen and aggregate sources to meet key specified performance requirements. By systematically investigating the effects of materials on the performance properties of the product a formulation ready for a mid-scale experiment has been proposed.

There have been several materials that have been identified as having a key influence on the performance properties. Of these the aggregate quality, and the type and concentration of emulsifier used are very important. This is particularly so for abrasion wear, adhesion and cohesion development within the microsurfacing mixture. The main performance attributes of microsurfacing required a rapid traffic time, specified rutting resistance, and minimum abrasion wear. To meet these required the right mix of polymer concentration, bitumen grade, emulsifier level and aggregate quality. All of these performance aspects were met with the proposed formulation under a laboratory environment.

It has been shown that emulsified bitumen binders have a greater resistance to high temperatures than hot modified bitumen does. Also shown was that emulsified binder have a different microstructure that may account for the improved properties. Both of these aspects have not been reported before in literature reviewed. Biphase modified emulsions using SBR latex are easier to produce, have acceptable stability and have improved binder properties over monophase modified emulsions. Monophase emulsions can only be produced with softer grades of bitumen and have polymer-bitumen compatibility problems that make them unsuitable for microsurfacing.

Reduction in the emulsion settlement remains an issue to further investigate. While the settlement was high and not ideal, the particles had only flocculated and could be easily re-mixed. But a lower settlement would reduce the possibility of blocking filters in the application equipment. The mid-scale experiment of the proposed formulation will determine the scale-up effects and correlation to the laboratory sized batches and is the next development step.

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APPENDIX 2-1. COMPARISON OF CHEMICAL FRACTIONS WITHIN BITUMEN SOURCES

Source	**Grade**	**Asphaltenes** (%)	**Aromatics** (%)	**Resins** (%)	**Saturates** (%)	**CI***	**R/A****	**Reference**
Safaniya NZ	180/200	14.8	11.2	45.0	29.0	1.3	3.0	Herrington 1999
Venezuela	180/200	13.3	56.4	17.3	13.0	2.8	1.3	Lu et al 1999
Venezuela	70/100	22.0	45.1	19.7	13.2	1.8	0.9	Loeber et al 1998
Mexican	180/200	11.7	63.8	13.1	10.4	3.5	1.1	Lu et al 1999
Arabian	180/200	10.7	63.6	14.8	10.9	3.6	1.4	Lu et al 1999
Persian Gulf	180/200	19.8	57.6	15.1	7.5	2.7	0.8	Loeber et al 1998
Persian Gulf	150/200	10.3	36.2	46.1	7.2	4.7	4.5	Al-Sabagh et al 1997
Middle East	100/130	7.5	62.0	23.0	7.5	5.7	3.1	Wloczysiak et al 1997
Russian	180/200	13.7	51.1	18.3	16.9	2.3	1.3	Lu et al 1999
Italian	180/200	19.0	31.6	34.6	14.8	2.0	1.8	Piazza et al 1980
French	180/200	15.1	46.3	27.9	10.7	2.9	1.8	Engel et al 1991
French	?	7.5	68.7	19.9	3.9	7.8	2.7	Serfass et al 1992
North Sea	180/200	15.2	56.7	22.8	5.3	3.9	1.5	Loeber et al 1998
USA	180/200	12.0	39.7	31.4	16.9	2.5	2.6	Bouldin et al 1990

* Colloidal Index

** Resins/Asphaltenes Ratio

APPENDIX 5-1. EMULSION AND MICROSURFACING RESULTS FROM SBR LATEX BIPHASE EMULSION INVESTIGATION

	Emulsion Sample								
	Unmodified 200-pen [X]	Unmodified 100-pen [X]	Post Added 200-pen	Soap Phase 200-pen	Soap Phase 200-pen #	Co-mill 200-pen	Post Add 100-pen	Soap Phase 100-pen	Co-mill 100-pen
pH (Units)	3.59	4.07	5.23	4.87	4.86	4.72	4.86	4.76	4.63
Binder Residue (%)	60.53	61.27	61.19	63.15	63.05	61.78	60.90	62.44	61.36
Viscosity 5 rpm (cP)	120	120	130	130	120	80	120	100	90
Viscosity 10 rpm	80	85	85	90	85	55	80	70	60
Viscosity 20 rpm	57	63	60	65	60	43	58	50	45
Viscosity 50 rpm	46	53	47	50	49	41	49	45	42
Settlement (%)	16.65	16.43	14.65	14.90	18.86	50.72	21.27	36.23	39.99
Sieve Residue (%)	0.62	0.35	0.47	0.69	0.62	1.00	0.39	0.41	0.56
Softening Point (°C)	41.9	51.0	49.1	50.9	52.2	49.4	60.3	63.8	63.3
Abrasion (g/m^2)	1658	1921	1550	1474	1573	1330	1905	1457	1935
Deformation (%) Height	37.8	36	29	26	32	42	14	14	24
Width	52.8	30	25	13	22	32	0	3	7
Slurry Cohesion (kg-cm)									
60 minutes	9.6	9.0	12.0	11.0	10.0	9.0	9.0	9.0	9.0
120 minutes	13.4	13.0	17.0	14.0	13.0	13.0	14.0	13.0	16.0
150 minutes	16.0	16.0	16.0	18.0	19.0	16.0	16.0	18.0	17.0
180 minutes	18.4	18.0	18.0	19.0	18.0	21.0	18.0	19.0	21.0
210 minutes	19.6	20.0	21.0	18.0	21.0	20.0	19.0	20.0	25.0
Slurry Mix Time (sec)	184	170	450	150	120	30	360	120	120

Replicate Run

[X] Unmodified Control Emulsions

APPENDIX 5-2. MICROSURFACING MIX DESIGN RESULTS FOR SBR LATEX BIPHASE EMULSION INVESTIGATION

	Sample								
Polymer Addition Method	None	None	Post Add	Soap	Soap*	Co-mill	Post Add	Soap	Co-mill
Bitumen	200 pen	100 pen	200 pen	200 pen	200 pen	200 pen	100 pen	100 pen	100 pen
Mix Design									
Aggregate (%)	100	100	100	100	100	100	100	100	100
Emulsion (%)	15	15	15	15	15	15	15	15	15
Additive (%)	1.5	1.6	2.0	1.5	1.5	2.0	1.8	1.6	2.0
Cement (%)	0.5	1.0	1.0	0.3	0.3	0.5	1.0	0.5	0.5
Water (%)	7.0	7.9	7.0	7.7	7.7	7	7.9	7.8	7
Mix Time (sec)	184	170	450	150	120	30	360	120	120
Sand equivalent (%)	49	49	49	49	49	49	49	49	49

* Replicate Run

APPENDIX 5-3. EMULSION AND MICROSURFACING PROPERTIES FROM MONOPHASE MODIFIED EMULSION INVESTIGATION

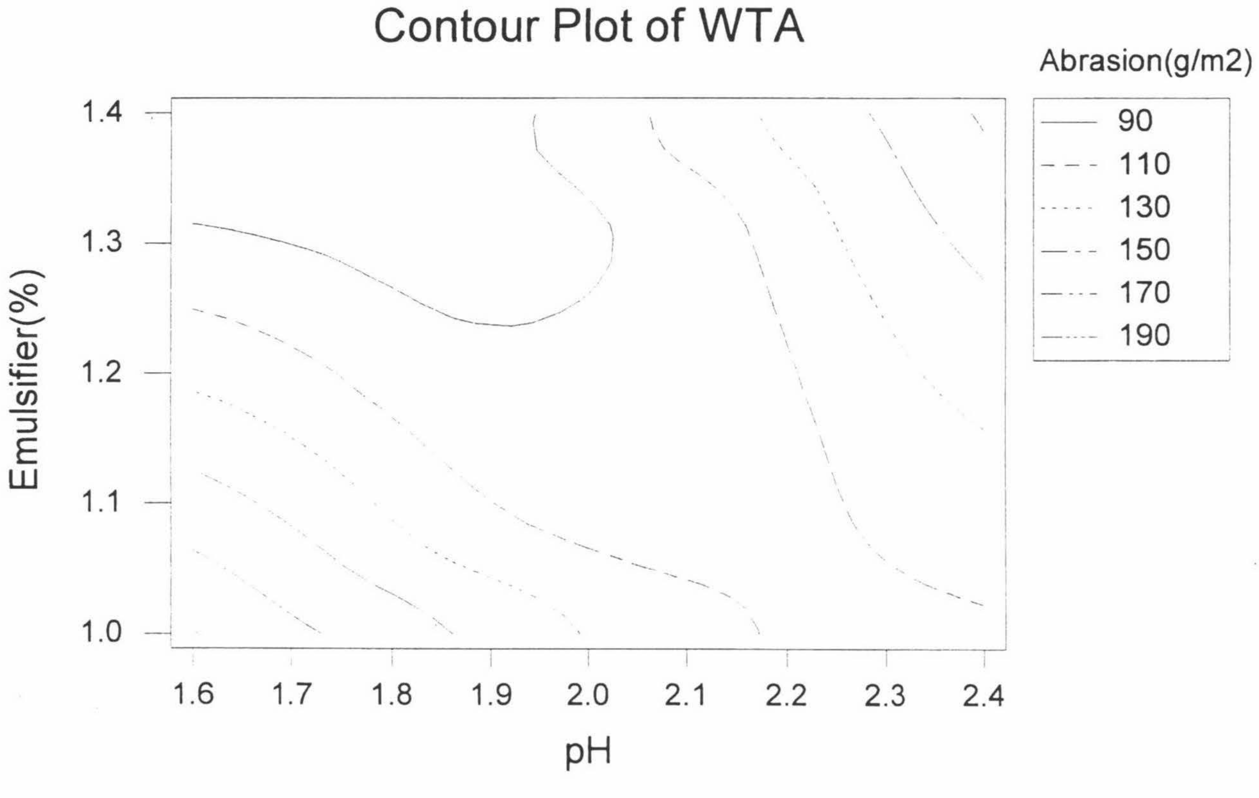
	SAMPLE			
	EMA (200-pen bitumen)	**SBR** (200-pen bitumen)	**EMA** (150-pen bitumen)	**SBR** (150-pen bitumen)
pH (Units)	3.56	6.56	4.03	6.45
Binder Residue (%)	60.91	61.48	61.45	61.27
Viscosity 5rpm (cP)	120	110	105	90
Viscosity 10rpm	80	75	73	65
Viscosity 20rpm	58	55	53	50
Viscosity 50rpm	46	50	45	47
Settlement (%)	10.90	16.39	15.13	22.20
Sieve Residue (%)	0.40	0.12	0.41	0.18
Softening Point (°C)	48.7	45.3	52.3	49.3
Abrasion (g/m^2)	2320	1757	2043	2273
Permanent Deformation (%) Height	42	56	38	47
Width	42	60	33	40
Cohesion (kg-cm) 60 minutes	9	10	10	10
120 minutes	13	11	13	12
150 minutes	15	14	15	15
180 minutes	18	15	17	16
210 minutes	23	15	19	16
Microsurfacing Mix Time (sec)	100	60	300	180

APPENDIX 5-4. EMULSION AND MICROSURFACING PROPERTIES FROM DETAILED DESIGN EXPERIMENT

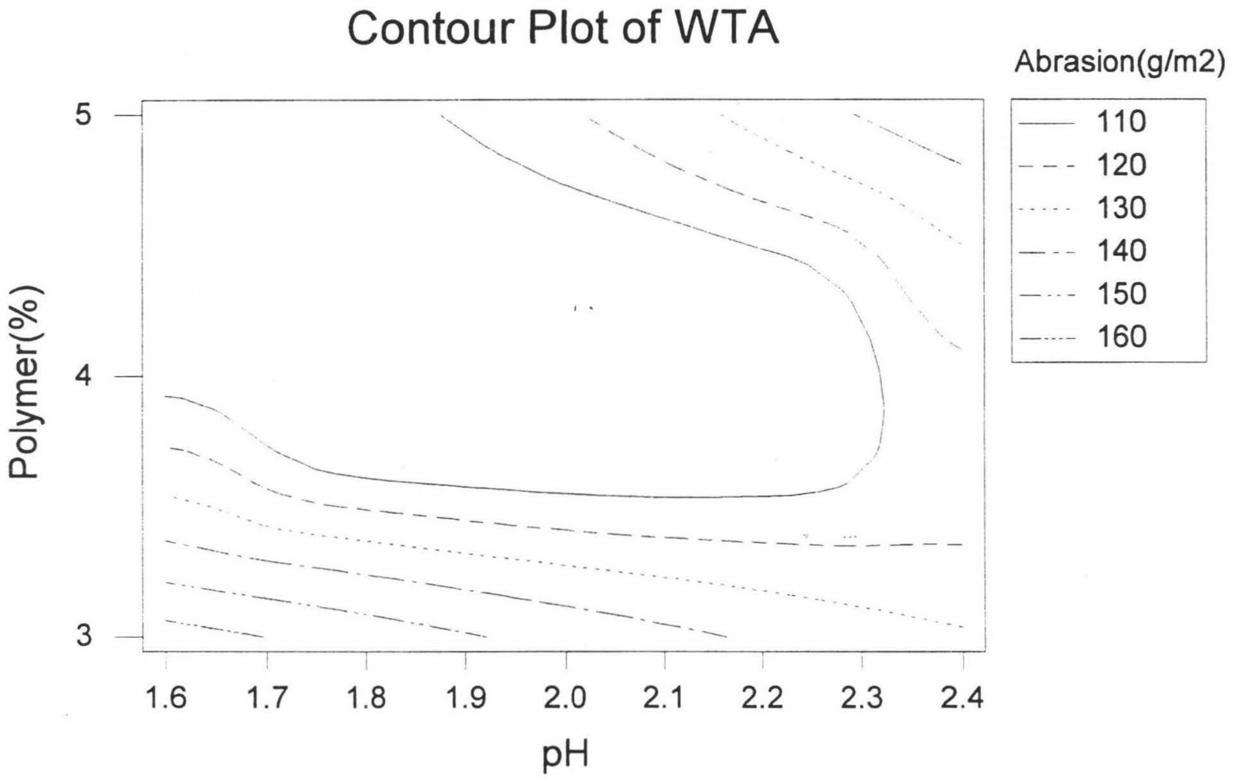
	Sample Code										
	1	**a**	**b**	**ab**	**c**	**ac**	**bc**	**abc**	**CP1**	**CP2**	**CP3**
pH (Units)	1.71	1.98	1.64	1.66	2.58	2.63	2.85	2.81	2.09	2.28	2.33
Residue (%)	62.02	61.67	62.00	62.33	62.20	62.02	62.16	62.11	61.65	62.02	62.01
Viscosity 5rpm (cP)	180	160	280	290	190	180	280	240	200	200	220
Viscosity 10rpm	120	105	180	180	125	120	175	155	130	140	140
Viscosity 20rpm	83	73	118	115	85	80	115	100	88	95	95
Viscosity 50rpm	60	54	74	73	61	59	75	68	62	65	66
Settlement (%)	42.99	43.97	55.32	56.68	43.22	46.78	54.18	62.09	51.64	49.27	51.46
Sieve Residue (%)	0.08	0.10	0.10	0.08	0.14	0.12	0.17	0.14	0.15	0.13	0.15
Softening Point (°C)	68.0	81.3	67.4	80.0	67.3	79.0	66.2	80.5	70.7	72.5	72.0
Abrasion (g/m^2)	270	112	59	72	89	125	174	171	171	49	63
Deformation (%) Height	7	10	-	-	-	-	-	-	-	10	-
Width	3	3	-	-	-	-	-	-	-	0	-
Cohesion (kg-cm)											
60 min	16	16	9	10	18	14	9	9	11	11	10
90 min	20	20	14	13	22	20	9	12	15	16	17
120 min	21	22	18	20	23	22	11	10	18	18	15
150 min	24	22	18	19	24	22	14	16	19	18	20
180 min	21	22	20	20	23	25	18	18	21	22	20
Mix Time (sec)	100	280	240	280	80	250	300	300	300	300	300

Key: a: Polymer b: Emulsifier c: pH

APPENDIX 5-5. CONTOUR PLOT FROM DETAILED DESIGN OF ABRASION LOSS FOR EMULSIFIER AND SOAP pH LEVEL



APPENDIX 5-6. CONTOUR PLOT FROM DETAILED DESIGN OF ABRASION LOSS FOR POLYMER AND SOAP pH LEVEL.



APPENDIX 5-7. EXPERIMENTAL ERROR RESULTS FROM DETAILED DESIGN EXPERIMENT

Response Variable	Mean	St Dev	SE Mean	Error (%)
Viscosity (cP)	221.8	45.3	13.7	6.2
Settlement (%)	50.69	6.15	1.85	3.6
Sieve Residue (%)	0.12	0.03	0.009	7.3
Softening Point (°C)	73.17	5.93	1.79	2.5
Abrasion (g/m^2)	123.2	67.7	20.4	16.6
Cohesion 60 minutes (kg-cm)	12.09	3.30	0.995	8.2
Cohesion 90 minutes	16.18	4.05	1.22	7.5
Cohesion 120 minutes	18.0	4.38	1.32	7.8
Cohesion 150 minutes	19.6	3.17	0.96	4.9
Mix Time (sec)	248.2	81.1	24.5	9.9