CHAPTER 1

INTRODUCTION

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Amino resins are formed when an amine or amide (such as urea or melamine) reacts with an aldehyde (Diem and Matthias, 1986). When urea and formaldehyde react, an amino resin is formed which has many important industrial and commercial applications. Urea-formaldehyde resin is a mature product with little or no recent advances in the resin chemistry (Ebdon, Hunt and Al-Kinany, 1990). However, new applications such as the use of amino resins in soil binder applications are still found.

The polymerisation reaction proceeds with two distinct steps, addition and then condensation, to form either a white powder or viscous milky or clear concentrates, depending on the end use. Although only two reagents are used the reaction rate and end product are influenced by many parameters.

1.2 THE HISTORY OF UREA-FORMALDEHYDE RESINS

According to Meyer (1979) the history of UF-resins can be divided into six overlapping periods. These are:

- Discovery and synthesis of the raw materials
- The first reaction products were identified and reaction conditions were explored
- Discovery of the commercial potential of the resin
- Full-scale commercialisation
- Product maturing
- Renewed interest in basic resin chemistry, as a result of modern analytical techniques

G. Rouelle first identified urea in 1773, but only in 1824 did Wöhler manage to synthesise it (Meyer, 1979). This event shook the scientific world because it bridged the gap between organic and inorganic chemistry. Commercial production of urea was only possible after A. Basaroff's discovery in 1870 that the reaction intermediate, ammonium carbonate, can be obtained directly from the reacting gases, ammonia and carbon dioxide (Meyer, 1979). A.

Butlerov prepared formaldehyde in 1859 but it was only about 25 years later that the first investigation on urea and formaldehyde products was started.

Tollens in 1884 and C. Goldschmid in 1887 reported the first reaction product. Urea-Formaldehyde reactions remained poorly understood until well after 1901. Only by 1908 was a basic understanding of the chemistry and reaction products gained. The reason for this was that phenol-formaldehyde and cellophane were more economically important products at that time. Until 1925 the cost of urea-formaldehyde resins was twice that of phenol-formaldehyde resins.

The third period in the history of UF-resins commenced in 1918 when H. John filed the first important patent application. From this point onward the commercial value of UF-resins was recognised and both researchers and companies became interested in commercial applications. Besides that, various workers identified and studied the reaction products as well as the different reaction steps. Different reaction products were commercially applied and parameters influencing the properties of these products were investigated. Meyer (1979) provides a more detailed discussion on this period in the history of urea-formaldehyde resins.

The fourth period started after the Second World War when the housing industry boomed and the demand for plywood adhesives increased. At that time particleboard was introduced into the market and the resin became fully commercialised because of its use as a wood adhesive. The use of UF-resins in mouldings decreased slightly because of more competitive products, but universally the resin became more accepted in industry. The maturing period of UF-resins is difficult to separate from the period of full commercialisation, but from 1935 to about 1975 not much had changed concerning the chemistry of the resin. Although many new applications were found, not much further effort went into research.

The last period started when there was renewed interest in the resin chemistry. This came about with the introduction of new analytical technology such as Nuclear Magnetic Resonance spectroscopy (NMR) and Infrared (IR) and Raman spectroscopy. This made the *in situ* analysis of the reaction between urea and formaldehyde possible. This means that the reaction can be studied on a molecular level while it is taking place. Toward the end of the twentieth century lower production costs, environmental friendliness and occupational safety became important issues. To adapt an "old" product such as UF-resins to these conditions meant renewed research into formaldehyde emissions, water solubility, material safety, better reaction control and more effective reaction conditions. Because of its low production cost and inexpensive raw materials, UF-resin is a product that has many important modern applications and which will still be in use for a long time.

1.3 THE REAGENTS

The major raw materials used in the manufacture of amino resins are urea and formaldehyde. It is the relatively low cost of these raw materials that make amino resins so popular. Because the use of melamine and other sources of aldehydes such as furfural and glyoxal are not applicable to this specific study, they will not be discussed further, even though they are important subjects in amino resins.

Chemicals that are added in small amounts to cause slight, but often desirable, changes in either the chemical or physical properties of the resin are called modifiers. They include alcohols, amines and certain inert inorganic salts. These chemicals and the influences they have on various resin properties will be discussed in chapter 2.

1.3.1 FORMALDEHYDE

In the production of urea formaldehyde resins, the source of formaldehyde can either be solid paraformaldehyde, Formalin (which typically contains 37 % formaldehyde) or a urea-formaldehyde precondensate such as Inkunite® (Diem and Matthias, 1986). Formalin is the most frequently used source of formaldehyde. It is a clear liquid with a sharp odour and is completely miscible with water. Usually it contains 5 – 10 % methanol. In aqueous solutions formaldehyde is normally present as methylene glycol ($HO\text{-}CH_2\text{-}OH$). This is in equilibrium with its oligomers according to the following reaction:

$$n\ CH_2(OH)_2 = HO(CH_2O)_nH + (n-1)H_2O \qquad 1.$$

The pH of aqueous solutions of formaldehyde is 2,5 to 4,5 (Meyer, 1979). The acidity is due to the formation of formic acid, which is a consequence of the Cannizzaro reaction. It is a disproportiation reaction between two aldehydes to form an acid and an alcohol as described in the following reaction:

$$2CH_2O + H_2O = HCOOH + CH_3OH \tag{2.}$$

On long-term storage aqueous solutions of formaldehyde become hazy. This is caused by the paraformaldehyde that precipitates out of the solution. A stabiliser such as methanol can be added to slow down the precipitation process. It is thus clear that at any moment formaldehyde solution co-exists with many of its water derivatives in solution and that these solutions never contain pure formaldehyde.

There are various ways of synthesising formaldehyde. One of them is the catalytic oxidation of methanol according to Reaction 3:

$$2\ CH_3OH \dashrightarrow 2\ CH_2O + H_2O \tag{3.}$$

The reaction can be catalysed by the following (Reuss, 1986):

- Silver metal (the "silver crystal" process)
- A combination of metal oxides (the "mixed oxide" process)

In both processes methanol is vaporised by warming, mixed with air and possibly recycle gas, and introduced into a vessel containing a catalyst. The catalyst assists the oxidation of methanol into formaldehyde and is highly selective. After leaving the catalyst chamber, the hot gases containing the formaldehyde are passed through a heat exchanger to remove heat energy. The cooled gases then pass into absorption columns where the formaldehyde and small traces of unreacted methanol are absorbed into water to produce a high strength aqueous solution of formaldehyde. The source of the methanol, usually present in formaldehyde solutions, is thus the unreacted methanol from the synthesis process.

If necessary, the formaldehyde solution from the absorber is passed through a de-acidification tower to remove traces of formic acid. At various stages of the process, heat produced is recovered by generating steam. The "mixed oxide" process has a very high raw material conversion rate (over 90 %) and energy efficiency is high. Other environmental aspects of these modern plants are:

- There are no solid effluents
- No odour emanates from the plant
- Liquid waste is treated on site before discharge to sewer
- Gases exhausting to atmosphere are catalytically converted to carbon dioxide

1.3.2 UREA

Urea (otherwise known as carbamide or diamide) is usually supplied as a white, prilled material and is synthesised in a catalytic reaction involving gaseous ammonia and carbon dioxide. Urea is often used as a fertilizer, which is usually contaminated with ammonium salts, and because these salts act as hardeners during the resin reaction, care must be taken when using technical grade urea.

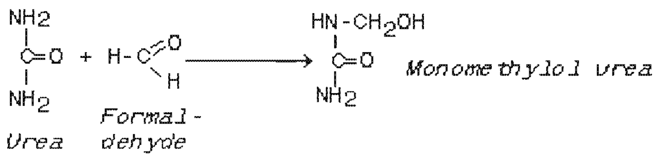
1.4 THE CHEMISTRY OF AMINO RESIN FORMATION

UF resins are produced industrially in a batch-wise process in vessels ranging up to 30 tonnes capacity. In the classical manufacturing method, the formaldehyde is charged to the reactor, at about 60 °C, the contents made alkaline and then urea is charged during which time the temperature falls to about 40 °C. The contents are then heated to about 95 °C, the pH adjusted to approximately 5,0 and the reaction is allowed to proceed until the desired degree of polymerisation has occurred. The reaction is quenched with alkali and the contents cooled. Water may be stripped off in a dehydration stage and some further urea charged to react with excess formaldehyde.

In the application of urea-formaldehyde resins as soil stabilisers, however, the resin is manufactured at room temperatures by mixing urea with Formalin, with the addition of an acid catalyst. Clearly the resin properties cannot be controlled as effectively as in the industrial process, but as a soil binder this is not as important. The necessary properties can be controlled with initial pH, urea to formaldehyde ratio and the use of modifiers and catalysts.

1.4.1 ADDITION REACTIONS

Addition reactions result in hydroxymethylation, the formaldehyde being added to urea. The four binding sites are associated with the hydrogens on the amine groups. Thus a maximum of four molecules of formaldehyde can react with urea. However, tetrahydroxymethylurea is very rarely found. Mono-, di- and trihydroxymethylurea are more common in urea-formaldehyde resins. If urea and formaldehyde are reacted in a slightly acidic (pH > 6) or basic medium a white precipitate can be observed after a few hours. This is a mixture of insoluble monohydroxymethylurea or monomethylolurea (MMU) and dihydroxymethylurea (DMU). The formation of MMU and DMU is shown in the next two Reaction schemes:



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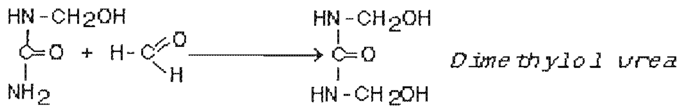
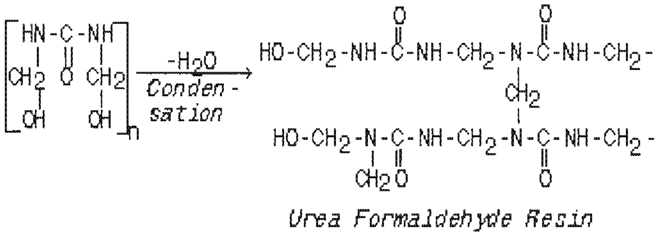


5.

Other reaction conditions such as excess water and a high formaldehyde to urea ratio also lead to the formation of other products such as acetals i.e. ether compounds. At high pH and low temperature methylene ethers are formed, but at higher temperatures they convert to methyl bridges (- N – CH_2 – N -). According to Meyer (1979) the most reactive formaldehyde to urea molar ratio is 1,5. The maximum molar ratio used commercially is 2,81 because, above that, no change in resin properties is observed (Duvenhage, 1992).

1.4.2 CONDENSATION REACTIONS

Condensation reactions only take place in acidic conditions. The reaction is illustrated in the Reaction scheme given below:



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The pH influences the reaction time as well as the texture and water permeability of the resin. Addition reactions occur in either alkaline or acidic conditions and proceed faster in alkaline conditions. When the reaction takes place in an acidic medium addition is directly followed by condensation reactions. This means that the time needed for the complete reaction to take place decreases as the pH decreases. This also implies that shorter chain polymers will form which will give the resin a more crystalline texture. Longer reaction times result in longer chains and the product has the texture of a hard gel.

It is difficult to derive equations for the reaction rate because of the large number of different species present. From the above equation it can be seen that the condensation reactions are responsible for chain growth and crosslinking. During the condensation reactions the viscosity increases slowly at first, and then, after a critical time, very steeply.

Urea-formaldehyde condensates having a formaldehyde to urea molar ratio of about 1 results in insoluble polymethylene-ureas that do not possess any adhesive properties, but if the molar ratio is decreased from a relatively high value (such as 4) during the course of the reaction (such as addition of more urea) adhesive properties can be obtained.

1.5 PHYSICAL AND CHEMICAL PROPERTIES

Table 1 summarises the chemical and physical properties of typical amino resins. It should be noted that actual values may differ, depending on the grade of the resin.

Table 1. *Typical chemical and physical properties of amino resins*

Relative Vapour Density (air = 1 at 20 °C)	1,07 *
Specific Gravity (20 °C)	1,2–1,4
% Volatile by Volume (water)	25–50
Solubility in Water (g/L @ 25 °C)	50
PH (25 °C):	4,5–8,2
Viscosity @ 25 °C (cP):	150–250
Solids content (%):	64–66

* for formaldehyde

Urea-formaldehyde resin is a colourless to milky viscous liquid, with a faint formaldehyde odour. It is soluble in water and alcohol. The free formaldehyde content of urea-formaldehyde resins is usually less than 5 per cent and typically less than 0,5 per cent depending on the specific grade (Duvenhage, 1992).

1.6 USES OF AMINO RESINS

Because of their unique properties, urea-formaldehyde resins have found widespread industrial and commercial use. The largest application of amino resins is their use in the woodworking industry. Adhesives based on formaldehyde are used as binders in the production of reconstituted wood panels such as particleboard, plywood, medium density fibreboard, laminated veneer lumber, finger joints and laminated beams. UF resins and other related formaldehyde resins are also used in resin impregnated decorative paper laminates, glass fibre insulation binders, foundry cores, pulp and papers processing aids, paper sizing, textile treatments, paints and enamels, and miscellaneous joinery applications. Another important use of amino resins is as a sand binder in moulds for metal casting (Ebdon *et al.*, 1990).

1.7 PROBLEM STATEMENT

Although literature on urea-formaldehyde resins is very extensive, especially the patent literature, it is mostly focused on how these parameters influence a product with a specific use, for example as an adhesive in particleboard. Because the use of urea-formaldehyde resin in soil binder systems is a more recent application, there is not much literature on this subject. The aim of this thesis is to determine the factors that influence the physical properties of a specific urea-formaldehyde resin and thus the effectiveness of the resin as a soil stabiliser. The factors that influence resin properties are reaction pH (amount of catalyst used), temperature, reactant molar ratio and the addition of bitumen emulsion. Additional factors that influence the soil stabilisation properties are the amount of resin and bitumen emulsion used, drying time, moisture, compaction and the addition of bitumen emulsion and conventional stabilisers such as lime and cement.

1.8 REFERENCES

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CHAPTER 2

FACTORS INFLUENCING RESIN PROPERTIES

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2.1 INTRODUCTION

Modification of the urea-formaldehyde resin is important because it can broaden its field of application. The resin-soil system itself is not waterproof, but with addition of bitumen the resin can be successfully applied in aqueous environments. By using ammonium salts as a hardening additive (Diem and Matthias, 1986) the resin strength can be increased, which allows it to be used in heavy load applications such as roads with a high traffic volume. By introducing fibres such as carbon fibre (Hollaway, 1990; Hollaway, 1993) it can be used as a cheap replacement for concrete in construction.

Adding modifiers is not the only way of changing resin properties. Properties such as elasticity and degree of crosslinking can be manipulated by choosing the correct reaction conditions. Other influences are temperature and amount of dilution. A product with specific characteristics, as required for a certain use, can thus be prepared.

Critical reaction parameters that affect physical properties of the resin are (Meyer, 1979):

- Stoichiometry i.e. the formaldehyde to urea ratio
- Type and concentration of catalyst used
- Temperature and pH, which affect the rate of reaction and therefore the required reaction time for a specified conversion
- The type and amount of modifier added to the reaction and the source of formaldehyde
- Reaction protocol i.e. the time spent on addition and condensation reactions, which can be controlled with pH.

The stoichiometry and the degree of conversion also affect the amount of free formaldehyde in the final resin that could be emitted during the end-use application.

The aim of this part of the investigation is to experimentally determine the influences of the above-mentioned parameters on the physical properties of urea-formaldehyde resins. The influences of pH, temperature, formaldehyde to urea molar ratio and the source of formaldehyde were investigated. This was done in a laboratory. Only the effects on the resin properties itself and not in a soil-resin binder system were determined.

2.2 EXPERIMENTAL PROGRAMME

For experimental purposes commercially available urea fertilizer was used (46 % nitrogen). Formalin (37 % formaldehyde / 7 % methanol) and Inkunite® (supplied by Resinkem (Pty) Ltd., Umbogintwini, Natal, 4120) were used as sources of formaldehyde. In all the experiments 0,6 g urea was added per g Formalin used (Resin A) and 0,7 g urea per g Inkunite® (Resin B). In both cases the resulting resin had a formaldehyde to urea molar ratio of 1,25:1. All the experiments were carried out at room temperature and an atmospheric pressure of about 85 kPa. After adding the reagents together a magnetic stirrer was used to ensure that all the urea has been properly dissolved before the experiment was continued. Citric acid was used as an acidic catalyst and sodium hydroxide (NaOH) used as an alkaline catalyst. When it was necessary to adjust pH, it was done with either the citric acid or the NaOH, depending on whether the pH had to be increased or decreased. It should be noted that formaldehyde to urea ratio refers to molar ratio and not mass ratio.

2.2.1 ANALYSIS OF REAGENTS AND PRODUCTS

The importance of Raman spectroscopy was mentioned earlier. In this study it was useful in comparing the differences on molecular level between the reaction products of urea with Formalin (Resin A) and urea with Inkunite® (Resin B). Peaks on the spectra obtained were identified with the aid of Table 2 (Philip and Aruldhas, 1990; Bleckmann and Thibud, 1990). The numbers above the table is the wave number in cm^{-1}.

Table 2. *Characteristic Raman absorption positions.*

4000 2500 2000 1800 1650 1550 650

O-H C-H	C≡C	Very	C=O	C=N	C-Cl
		Few			C-O
	C≡N	Peaks			C-N
N-H				C=C	C-C
	X=C=Y				
	(C,O,N,S)			N=O	

The Raman spectra of Formalin, Inkunite® and urea are shown in Appendix A. The Raman spectra of Resins A and B are also shown in Appendix A. These indicate the chemical differences between the reagents and products.

2.2.2 THE INFLUENCE OF PH ON RESIN PROPERTIES

The influence of pH on the resin properties such as texture and gel time was investigated. About 100 g of Resin A was prepared and the pH adjusted to a value of 7. For reactions at lower pH values, the pH was reduced incrementally by approximately 0,7 units with a 10 ml sample being taken at each stage. The pH values varied from 3 to about 9. The time needed for the solution to become milky (when the resin and the water phase separate), as well as the gel time was noted. The experiment was repeated using Resin B. The experiments were carried out in a water bath at 25 °C.

2.2.3 THE INFLUENCE OF TEMPERATURE ON RESIN PROPERTIES

In this experiment the influence of the temperature on the gel time of Resin A was investigated. Temperature varies according to changing seasons and atmospheric conditions. These air and soil temperature variations may affect the time available for application and the strength development of stabilised soils.

In this experiment 1,5 kg of Resin A was prepared. The pH was lowered to 4 by adding citric acid. Six water baths were prepared at constant temperatures of 13, 22, 24, 26, 29 and 34 °C spanning the temperature range expected in practice. Each of six 500 ml beakers were filled with 200 ml of the resin mixture and placed into these water baths and the gel time measured.

2.2.4 THE INFLUENCE OF THE FORMALDEHYDE TO UREA MOLAR RATIO ON RESIN PROPERTIES

In this experiment the influence of the urea-formaldehyde ratio at three different values of pH on the gel time of Resin A was investigated. Ratios between 2:1 and 1:1 were investigated because this is the range applicable to resins used as adhesives and mould binders (Duvenhage, 1992). The pH values of 4; 6,5 and 8,5 were investigated. These values were chosen to get an overview of the resin properties over a broad pH range.

The gel time (time needed for the resin to become a solid) was then noted for each of the samples at a specific pH and urea-formaldehyde ratio. The viscosity of a reaction mixture with a molar ratio of 2:1 was measured by using a Brookfield viscometer and the result compared to that of a resin with a molar ratio of 1,4:1 (formaldehyde to urea).

2.2.5 THE INFLUENCE OF FORMALDEHYDE SOURCE ON RESIN PROPERTIES

The source of formaldehyde can influence the resin properties in several ways. Critical factors that influence the final amino resin include:

- Amount of dilution
- The change in formaldehyde/urea ratio
- pH
- Reaction progress before addition of more urea

The experiments were conducted by adding Formalin and Inkunite® to urea in the same ratio as used in preparing Resin A. Three different mixtures were prepared and left to react and details are shown in Table 3.

Table 3. *Reacting mixtures used in Experiment 2.2.5.*

Formaldehyde source added to urea	End pH	F/U ratio in final product.
1. Inkunite®	5,45	1,37
2. Formalin	5,45	1,23
3. Formalin	3,85	1,23

The viscosities of all three mixtures were measured from the moment when all the urea was dissolved up to the gel point.

2.2.6 THE INFLUENCE OF BITUMEN EMULSION ADDITION ON RESIN PROPERTIES

Bitumen emulsion is added to the urea-formaldehyde mainly because of its waterproofing qualities. It was decided to investigate the effects of different types of bitumen emulsion (anionic and cationic) on the reaction time, viscosity, water resistance and product quality of

Resins A and B. Three different types of bitumen emulsion, supplied by Tosas (Pty) Ltd., Wadeville, Gauteng, 14159, were used (see Appendix B for their specification sheets):

- KRS60 – Cationic bitumen emulsion at pH 4-5.
- KMS60 – Cationic bitumen emulsion at pH 5-6.
- SS60 – Anionic bitumen emulsion at pH 11.

The influence of each of the different types of bitumen emulsions on Resins A and B were determined by measuring the viscosity of the reacting mixture at pH 4 and 5, drying the product and inspecting it. The dried product was then left underwater for 7 days and the resin inspected again. A Brookfield viscometer was used to measure the change in viscosity as the reactions proceeded.

2.3 RESULTS AND DISCUSSION

2.3.1 RAMAN SPECTRA

From the spectrum of Formalin the following peaks can be identified (Meyer, 1979):

- The methanol frequencies are C-O = 1033 cm^{-1}
- $C\text{-}H_{sym} = 2837\ cm^{-1}$
- $C\text{-}H_{asym} = 2942\ cm^{-1}$
- C-H bending = 1400 cm^{-1}
- O-H = 3683 cm^{-1}
- Methylol C-O-C = 910 cm^{-1}

From Appendix A it can be seen that the Raman spectrum of Inkunite® is a composite of the spectra of urea and Formalin. This is because although the hydroxymethylation and condensation reactions have only been partially taking place before it was inhibited by pH adjustment, it still contains free urea and formaldehyde.

There are a few differences and similarities in the spectra of the different products:

- The peak at 950 cm^{-1} is present in all the spectra, which means that the C-N bonds are present in all the products and were not broken during reaction

- In the product from Resin B the C-O-C peak is very strong, which suggests that methylene ether bridges are present because of the fast reaction rates and mechanism of product formation at low pH
- Resin B has a strong N-H peak, which suggests that less of the urea has reacted than is the case for Resin A. In Inkunite® the C-H and N-H peaks fall together, but in Resin B they are separate
- Both products contain the O-H peak, which means that there are still unreacted hydroxymethyl groups present. These can be formed by either the condensation reaction proceeded too fast and the molecules became trapped in the crosslinked molecular mass. Alternatively the reaction did not proceed to completion.

2.3.2 THE INFLUENCE OF pH ON THE AMINO RESIN

Figure 1 shows the influence of pH on the gel time of Resin A. Although there are 3 distinct products that are obtained at different pH (white solid, gel and precipitate), the curve is still continuous. It should also be noted that the graph of the time needed for the solution to become milky is not defined at pH higher than about 5,8 because only a precipitate is formed from the clear liquid.

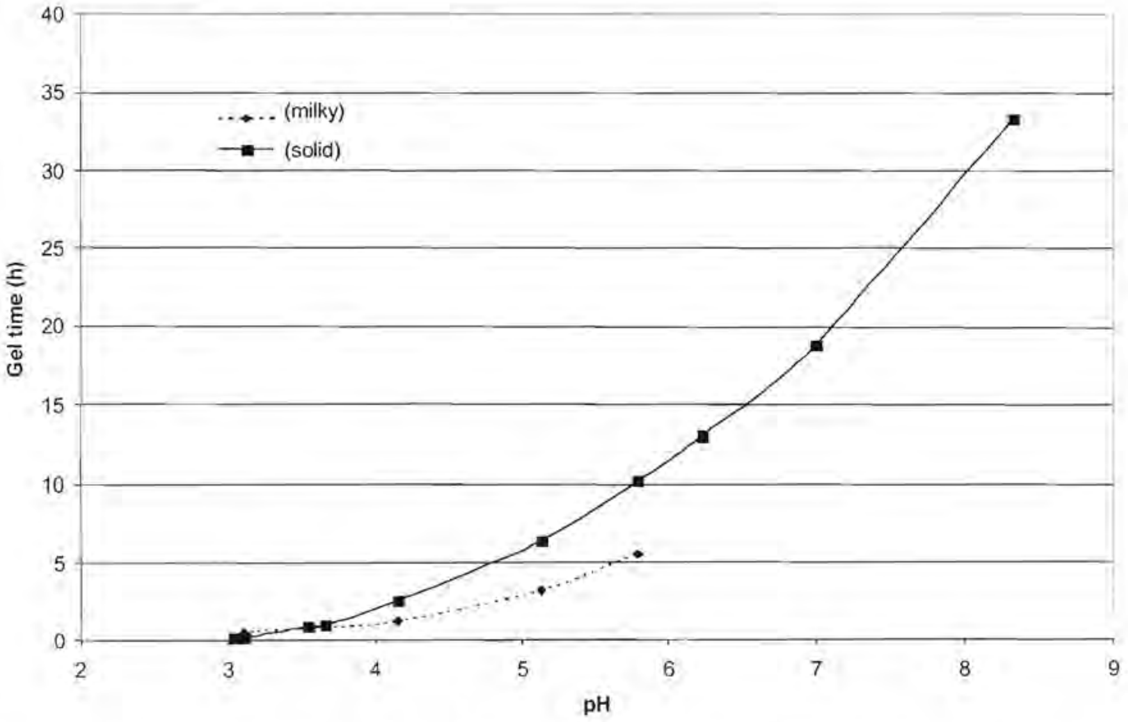

Figure 1. *Influence of pH on the gel time of Resin A (formaldehyde to urea molar ratio of 1,25:1).*

The gel time increases with an increase in pH, as expected. The reason for this is that both the hydroxymethylation and condensation reaction rates increase at a lower pH, but as the pH is increased the condensation reaction rate decreases until it stops at a pH of about 7,2 (Meyer, 1979). At higher pH the rate of hydroxymethylation reaction increases again to yield more soluble products.

Figure 2 shows the influence of pH on the gel times of Resins A and B. The gel times increase quite drastically with an increase in pH. The main reason for the differences is the fact that Resin B is closer to complete conversion that Resin A. In Resin B, the formaldehyde source is already substituted with urea in order to stabilise it.

The substitution reaction of urea with formaldehyde is highly pH dependent (Diem and Matthias, 1986). Thus, the H^+ ion plays a role in chain formation (condensation reactions) and formaldehyde addition to urea (hydroxymethylation reaction) and that is why different products can form at different pH when formaldehyde and urea is reacted.

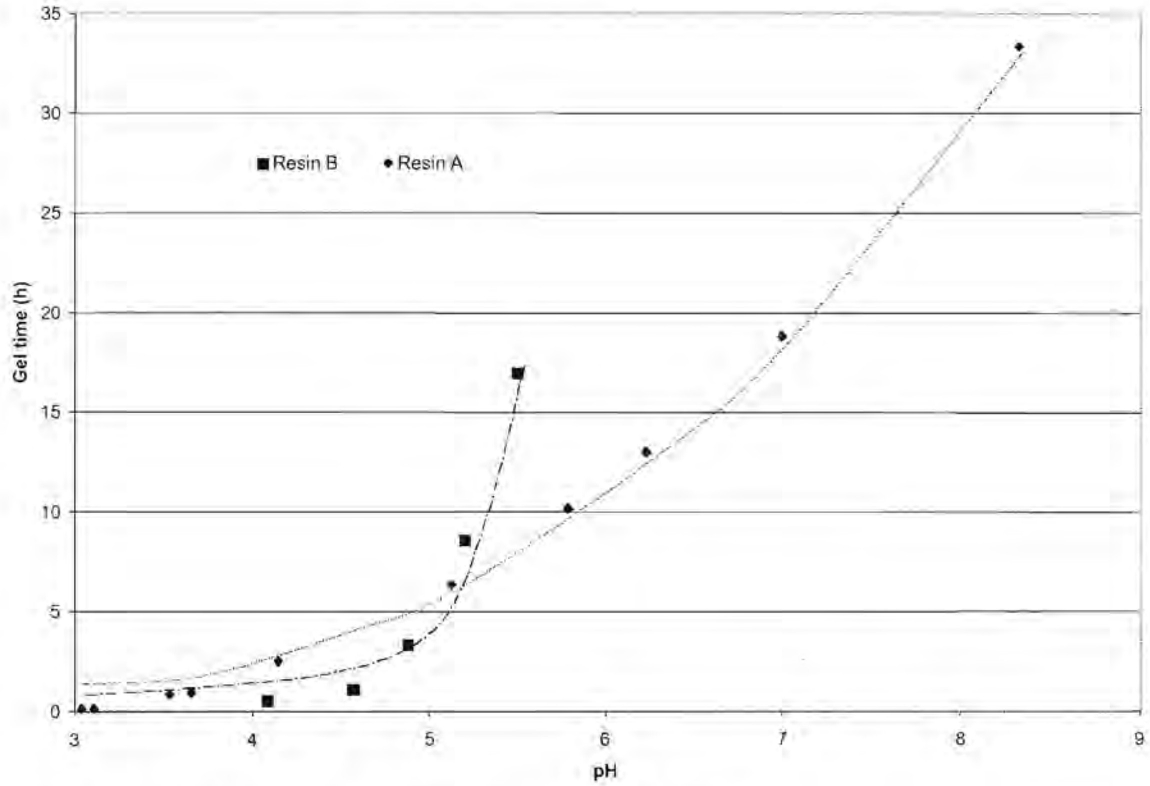

Figure 2. *Influence of pH on the gel times of Resins A and B*

When Inkunite® is used, the urea is already substituted and so the H^- ion is only involved in catalysing chain growth. That is why only the gel time changes, but not the product properties. This means that similar final products can be obtained using different reaction protocols. All the reaction products were hard, homogeneous, strong and had excellent water resistance.

2.3.3 THE INFLUENCE OF TEMPERATURE ON RESIN PROPERTIES

The influence of temperature on the reaction time of urea-formaldehyde can be seen in Figure 3. From the figure it is clear that the reaction rate increases and gel time decreases as the temperature increases. These results correlate well with the literature (Duvenhage, 1992; Diem and Matthias, 1986; Meyer, 1979).

The kinetic rate equation for a curing reaction can be generalised as follows:

$$\frac{dx}{dt} = f(x).g(T) \qquad 7.$$

where g(T) = $k_0 e^{-E/RT}$ is the Arrhenius temperature dependence of the rate constant with k_0 a constant, E the activation energy, R the gas constant and T the temperature in K. For isothermal reactions:

$$\int_0^{x_{gel}} \frac{dx}{f(x)} = \text{constant} \qquad 8.$$

So that the temperature dependence of the gel time can be written as:

$$\ln t_{gel} = \frac{E}{RT} + \text{constant} \qquad 9.$$

From the graph the activation energy can be obtained as 47,64 kJ/mol and the constant is $2{,}89 \times 10^{-5}$ when t_{gel} is measured in seconds.

Temperature has a large effect on the reaction rate, but does not influence the product properties (Duvenhage, 1992). The temperature range in which the experiments were conducted, conforms to that found in practice. At lower temperatures dimethylolurea is formed as intermediate, rather than the carbonyl diurea derivative (as with high pH). This means that the urea becomes substituted. However, the final chain growth is independent of temperature.

At higher temperatures the chains grow faster because the formation of diurea derivatives are favoured above the formation of the substituted urea. This also means that crosslinking at higher temperatures is not that effective since a complex crosslinked structure depends on the substitution of urea in order to form more nodes for chain formation and connections.

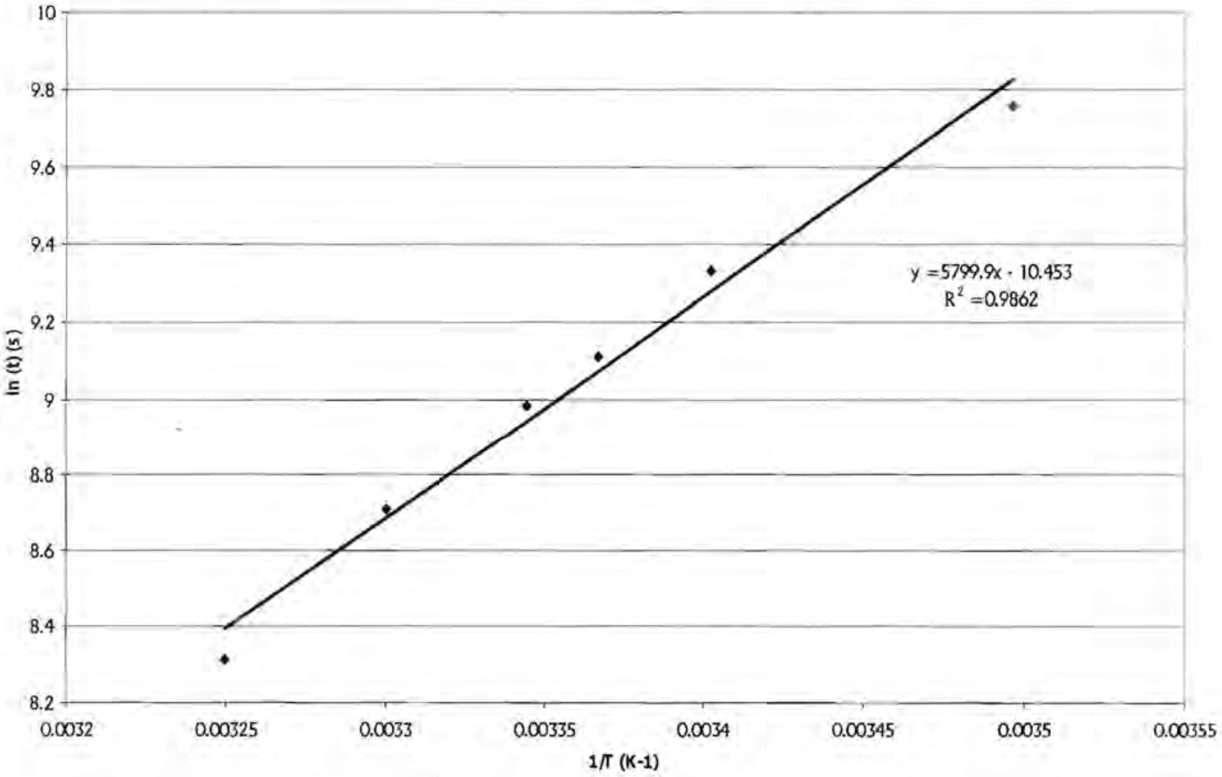

Figure 3. *Influence of the temperature dependency on the isothermal reaction of Resin A*

At low temperatures the time required for the resin to cure after it became milky is nearly constant. At higher temperature this is not true since there are fewer substituted urea products and thus less condensation reactions. The products formed at lower temperatures were stronger and more homogeneous than the products formed at high temperature.

It should be noted that at very high temperatures (above 45 °C) urea could react with water in the weak acid medium to yield CO_2 and NH_3. This leads to the decrease of substituted urea compounds and thus fewer building blocks to increase chain length and crosslinking.

2.3.4 The Formaldehyde to Urea Molar Ratio

In Figure 4 the influence of the formaldehyde to urea molar ratio on the gel time of Resin A at a pH of 3,9 is shown. From the figure it can be seen that the time needed for the solution to become milky decreases with a higher formaldehyde to urea ratio. The reason for this is because of the higher molar ratio the reactions (hydroxymethylation and condensation) can take place faster as a result of more formaldehyde being available. The polymer chains gain length and crosslinking takes place faster because of the higher concentration of formaldehyde and that is why it becomes milky at an earlier stage. On average it takes about 10 minutes for the resin to harden once it has become milky, i.e. for the resin and the water to phase separate. This time also decreases as the molar ratio increases.

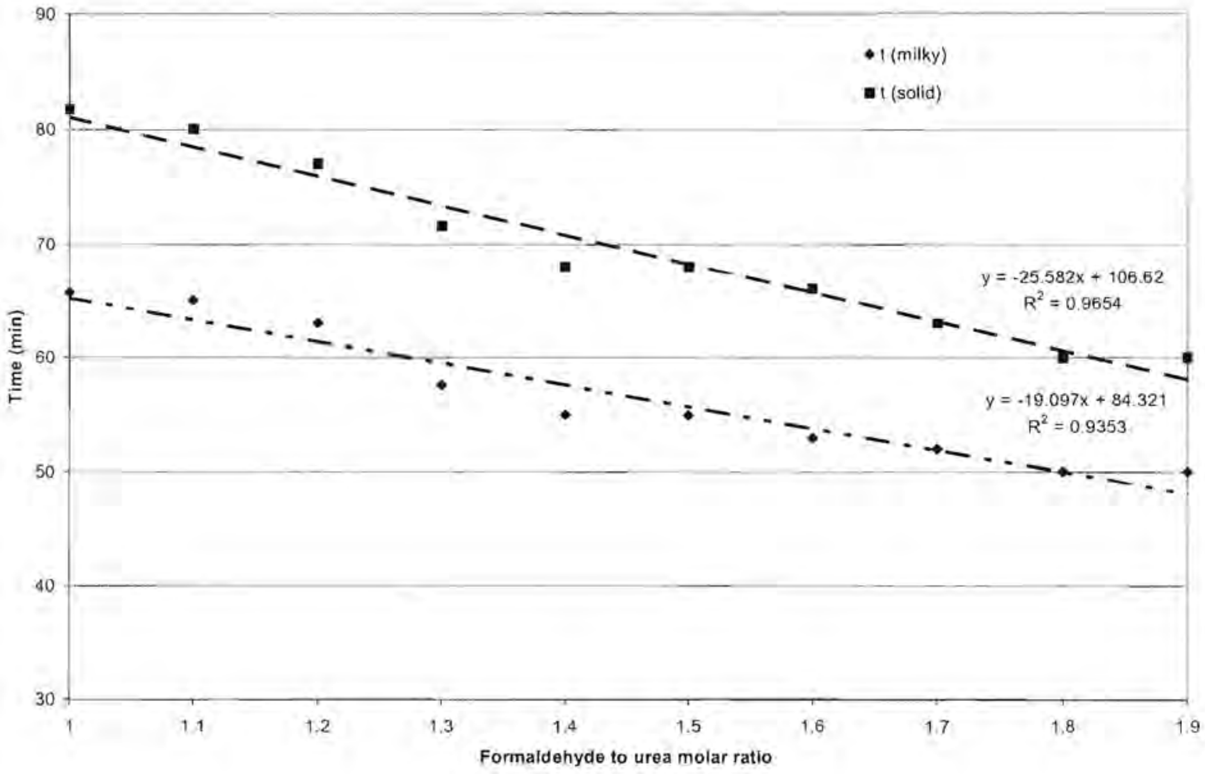

Figure 4. *Influence of urea/formaldehyde ratio on the gel time of Resin A at a pH of 3,9*

The influence of molar ratio on gel time of Resin A at a pH of 6,6 and 8,5 is shown in Figure 5. From the figure it can again be seen that the time needed for a precipitate to form (because of the high pH the product is a white precipitate) decreases with a higher molar ratio. It should be noted that the time needed for a solid product to form increases with an increase in pH.

Figure 6 shows the fraction of the total weight of Resin A that has precipitated after 120 hours as a function of molar ratio at a pH of 6,6 and 8,5. From the graph it is clear that the amount precipitated increases at higher molar ratios. As the pH is increased, fewer solids are precipitated because less insoluble products are formed.

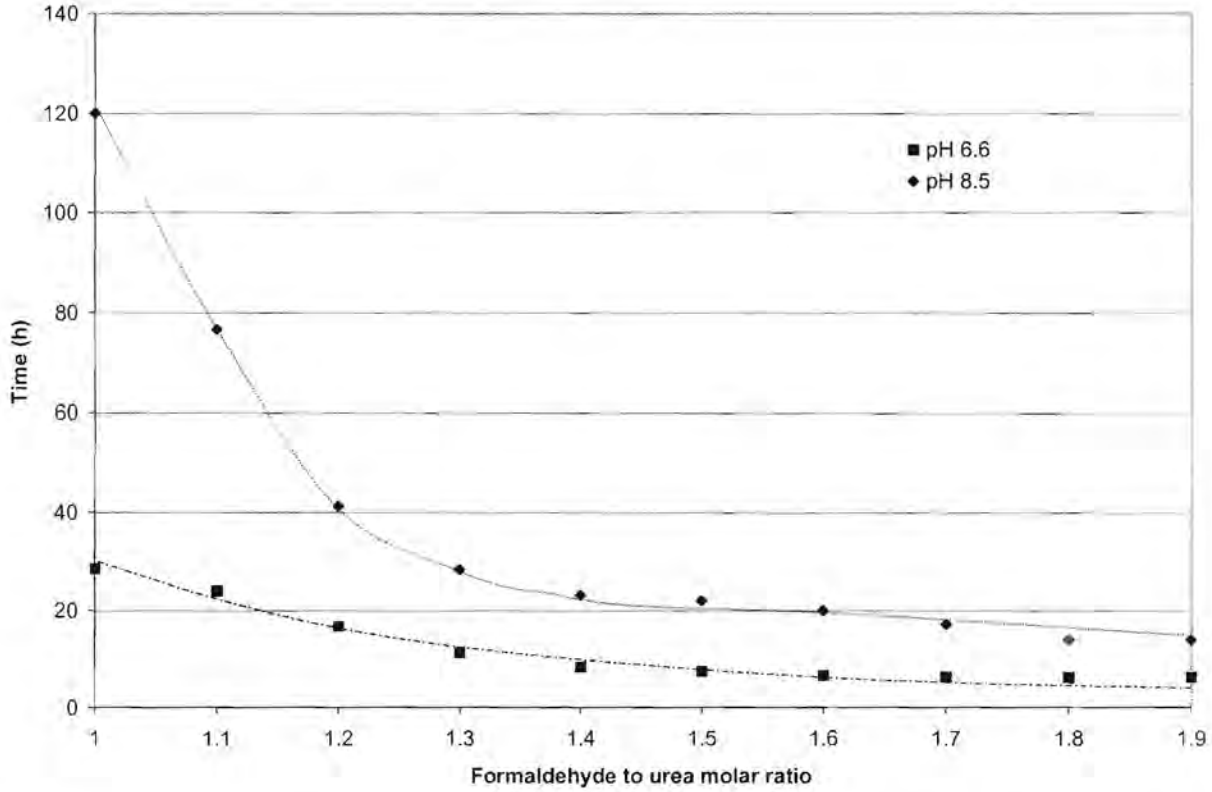

Figure 5. *Influence of the formaldehyde to urea ratio on the time needed for a precipitate of Resin A to form at pH 6.6 and 8.5*

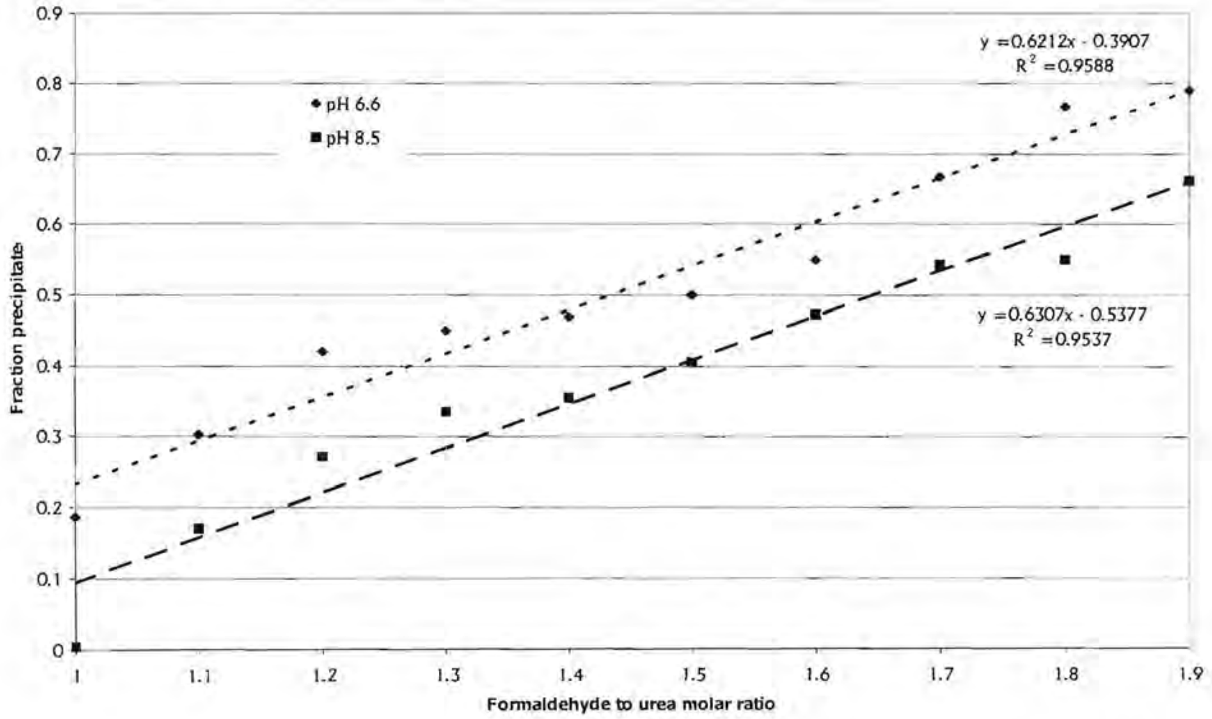

Figure 6. *Influence of formaldehyde to urea ratio on the amount of precipitate formed after reaction of Resin A for 120 hours at a pH of 6.6 and 8.5*

The viscosity is an important property when it comes to comparing two reactions because it affects processability. Figure 7 shows the difference in viscosity of the two different resins. It was found that Resin A at a molar ratio of 2:1 gelled rapidly, but took three days to solidify completely. With the addition of more urea (formaldehyde to urea molar ratio of 1,4:1) the solidification reaction proceeded faster. In this case there are more nodes to effect crosslinking of the substituted urea compounds. Crosslinking happens relatively quickly because there are enough links between the substituted urea nodes.

In the case of the higher ratio (2:1) there is less free urea to react with the formaldehyde and other substituted urea molecules. Chain growth proceeds quickly because most of the urea present is already substituted (and results in much quicker insoluble product), but the crosslinking takes much longer because there are fewer nodes for chains to connect and branch. Resin A, with the molar ratio of 2:1, initially reacted faster because the free urea first reacts with the formaldehyde (hydroxymethylation) before chain growth started.

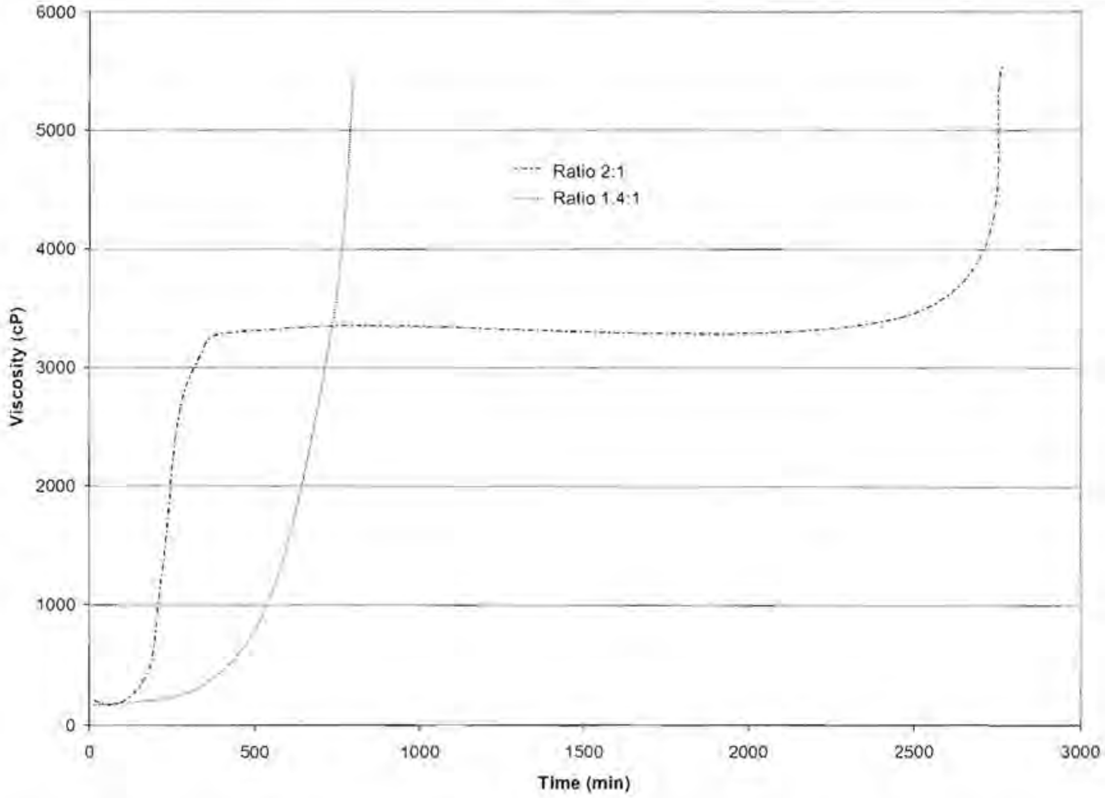

Figure 7. *Influence of molar ratio on the viscosity change of Resin A with formaldehyde to urea ratio of 2:1 and 1,4:1 during the curing stage.*

The product derived from the 2:1 molar ratio was smooth, hard and crack free. The other product (with the ratio of 1,4:1) was more brittle and had small cracks caused by the water trapped inside the crosslinked matrix. Both these products become soft when placed in water for a while, but when they were dried thereafter, they became hard again. No swelling was observed when the resinous products were placed in water.

Although it took about three days for Resin A to become completely solid, the final product had much better water resistance. Another advantage is the fact that much less (40 %) urea is needed to produce the resin, which implies a decrease in production cost.

2.3.5 THE USE OF FORMALIN AND INKUNITE® AS A SOURCE OF FORMALDEHYDE

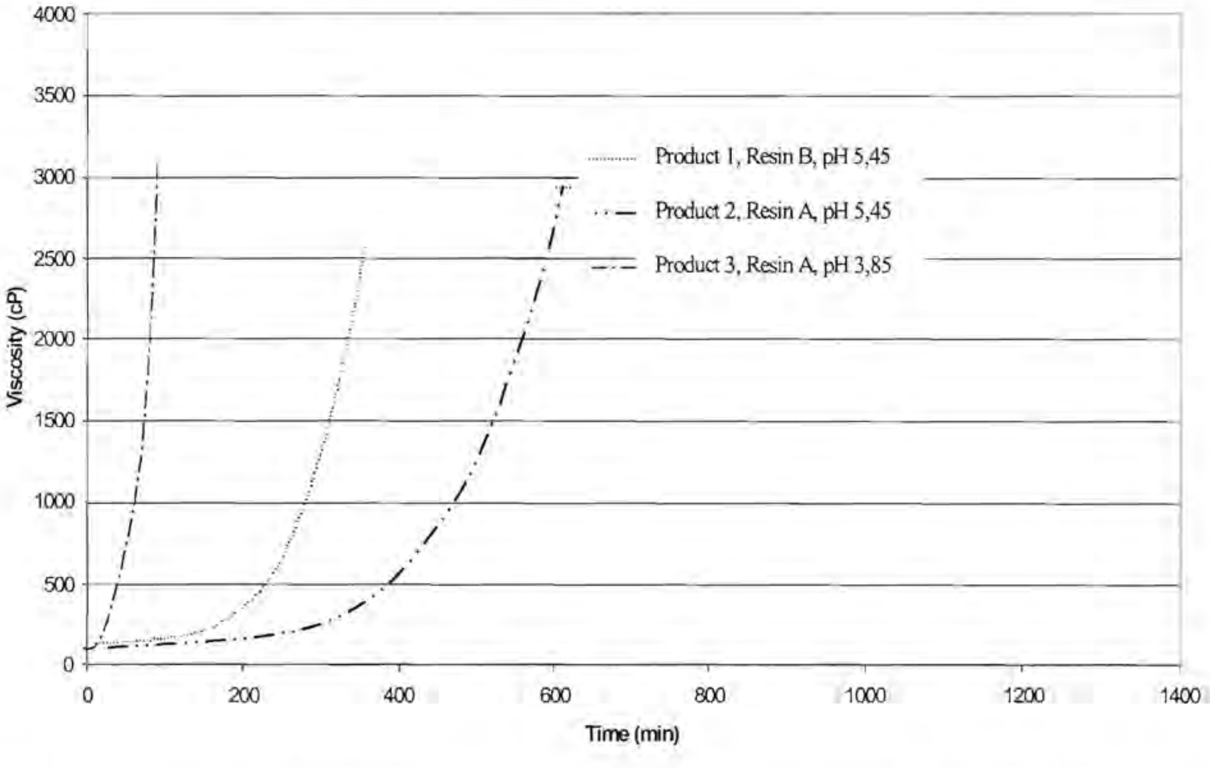

Figure 8. *Influence of pH and molar ratio on the gel time and viscosity of 3 different resinous products (detail given in Table 3).*

Table 4 shows the gel times of the different products obtained for the mixtures described in Table 3. The influence of the molar ratio cannot be clearly seen, but the pH has a large effect. Product 3 has a shorter gel time, as expected for the lower reaction pH. Although products 1 and 2 reacted at the same pH, product 1 reacted much faster because the urea-formaldehyde precondensate used contains urea and formaldehyde that was already partially reacted. At the gel time the slope of the viscosity curve is almost infinite, as seen from Figure 8.

Table 4. *The gel times of the various reaction products*

Formaldehyde source	End pH	F/U molar ratio in final product	Gel time (min)
Inkunite® (product 1)	5,45	1,37:1	310
Formalin (product 2)	5,45	1,23:1	600
Formalin (product 3)	3,85	1,23:1	65

2.3.6 THE INFLUENCE OF BITUMEN EMULSION ADDITION

Figure 9 shows the influence of bitumen emulsion (KRS60) on the viscosity of Resin A at pH 4 and 5. The viscosity (which is related to the rate of the reaction) increases faster for the reaction at low pH than for the one at higher pH, as is expected. The influence of the different bitumen emulsions on the curing of Resins A and B at pH 4 and 5 are presented in Appendix C. The trends are similar to the ones observed in Figure 9. The viscosity changes with any specific bitumen emulsion were slight except for Resin B in combination with KMS60, where the viscosity increased more linearly, and for SS60 where the reaction rates were slightly faster. This means that in all cases the bitumen emulsion did not significantly influence the cure reactions.

However, the way in which the bitumen emulsions were incorporated into the crosslinked resin, did differ. The properties of the different products can be seen in Table 5. Most of the different bitumen emulsions caused the Resin A product to become softer. At low pH the product tends to be granular and brittle, but some improvement can be observed with an increase in pH. SS60 produces a smooth, hard and brittle product at all pH values. When SS60 is used with Resin B the product was again smooth and hard, but became ductile and homogeneous at pH 4 and 5. The other bitumen emulsions resulted in better properties at higher pH when used with Resin B in comparison to Resin A.

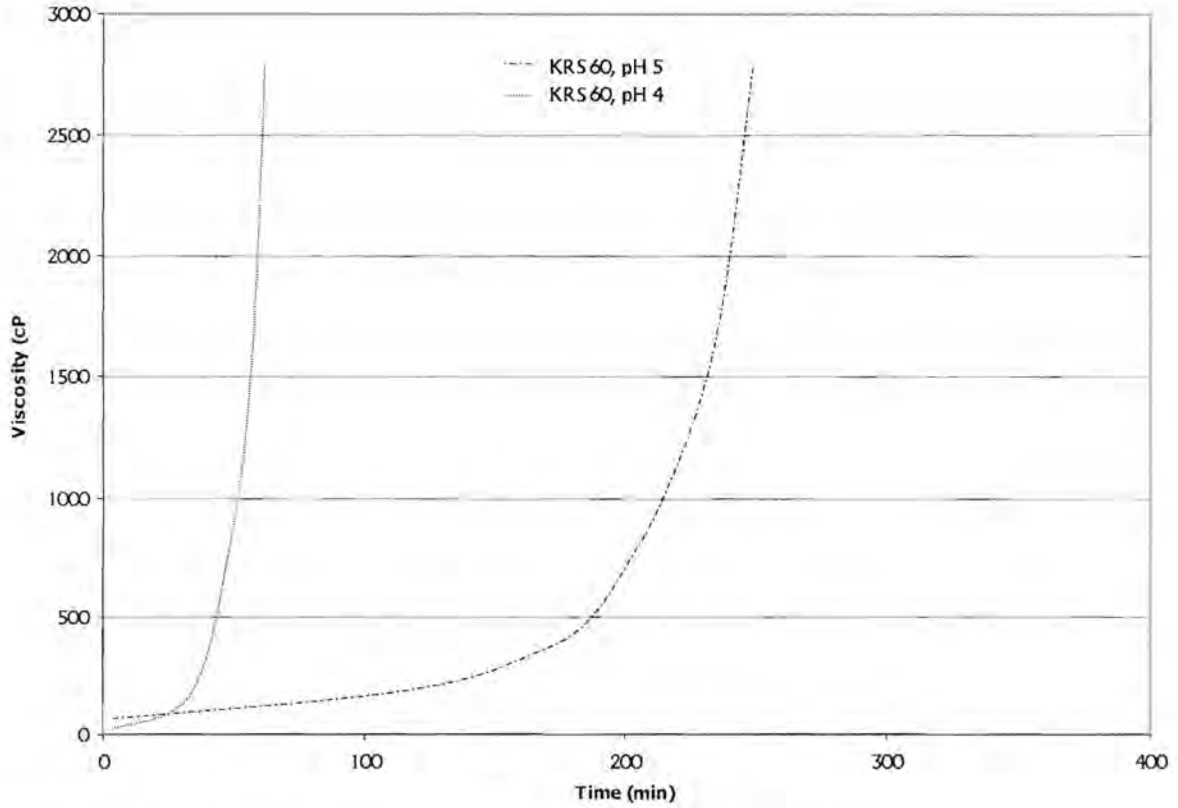

Figure 9. *Influence of KRS60 on the viscosity of Resin A at pH 4 and 5*

Table 5. *The different urea-formaldehyde bitumen products*

Source of formaldehyde	Bitumen	Reaction pH	Texture
Resin A	KRS60	4	Brittle, soft, granular
		5	Soft, brittle, smooth
	KMS60	4	Brittle, soft, granular
		5	Soft, brittle, smooth
	SS60	4	Brittle, hard, smooth
		5	Brittle, hard, smooth
Resin B	KRS60	4	Brittle, hard, granular
		5	Ductile, hard, smooth
	KMS60	4	Brittle, hard, granular
		5	Ductile, hard, smooth
	SS60	4	Ductile, hard, smooth
		5	Ductile, hard, smooth

The reason for the differences in the products can be attributed to the emulsifying agent used in the different emulsions. At higher pH the anionic surfactant is stable in the SS60 and allows the bitumen emulsion to be evenly distributed throughout the resin matrix. At lower pH the anionic bitumen emulsion becomes unstable and poor distribution results, leading to droplet formation. This is the result of the neutralisation of the emulsifying agent. In the case of Resin A where the reactions (hydroxymethylation and condensation) have to proceed from the beginning, the polarity of the bitumen emulsion can cause slight differences in the rate of reaction (especially the addition of the methylol to the urea), but in the case of Resin B the hydroxymethylation is already carried out and is not appreciably influenced by the presence of the bitumen. As a rule the bitumen emulsions cause the final products to take a longer time to dry out. At pH values above 7, the cationic resin-bitumen mixtures were very slow to react to completion. Instead a high viscosity liquid was formed that did not solidify, even after 48 hours.

From Figure 10 it can be seen that at the same pH the reactions of Resins A and B proceeded in the same way (the other combinations are shown in Appendix C). However, at higher pH values the cure reaction of Resin A took longer than the reaction of Resin B.

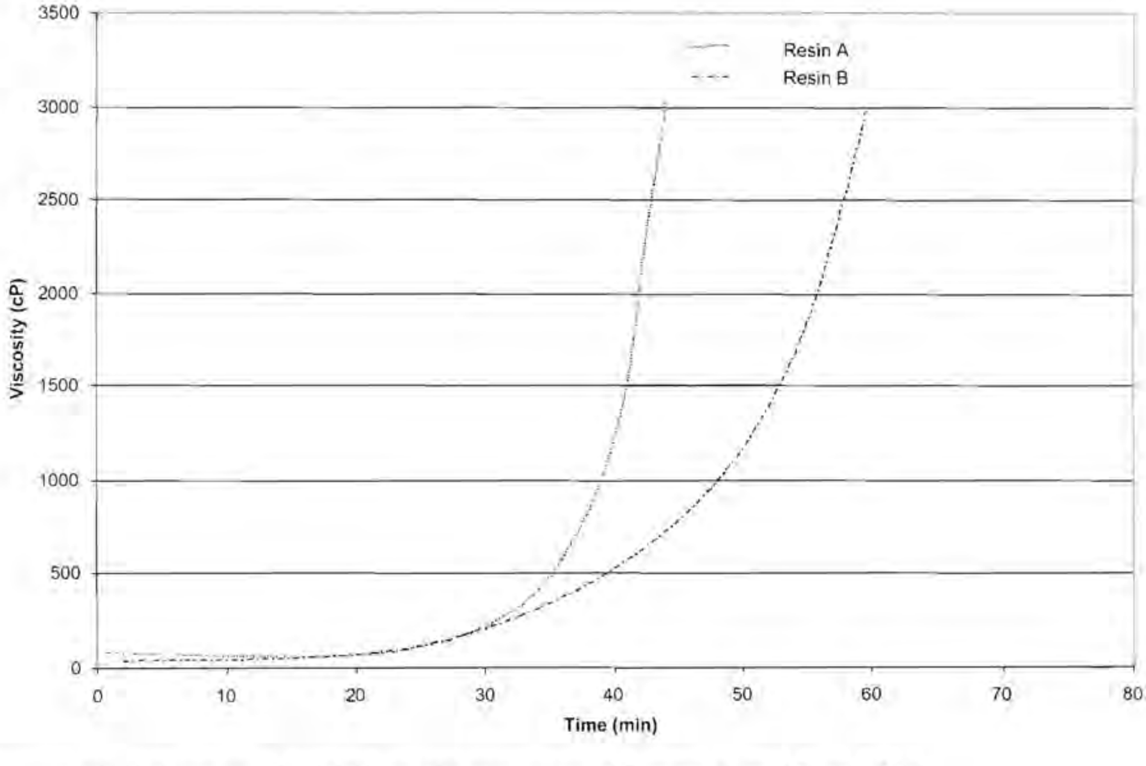

Figure 10. *Influence of KRS60 on the viscosity of Resins A and B at pH 4*

The SS60 addition generally resulted in better products. At high pH and with Inkunite® as a source of formaldehyde KMS60 and KRS60 also resulted in good products, but at lower pH the products were brittle and not very useful. After 7 days under water only the cationic emulsions with Resin A softened, while the others were unaffected.

2.4 CONCLUSIONS AND RECOMMENDATIONS

From the Raman spectra it can be seen that the resinous products (Resins A and B) are essentially the same product albeit with some minor variation in the functional groups. The spectra of both Resins are combinations of the spectra of urea and Formalin or urea and Inkunite®.

Three different amino resin products can be identified, depending on the pH: a strong, brittle solid at pH below 5,2; a slow-hardening gel between 5,2 and 6,4 and a powdery precipitate in a clear liquid above pH 6,4. The solubility of these precipitates decreases at higher molar ratio and lower pH. Gel time decreased with lowering of the pH and increased with the molar ratio of formaldehyde to urea.

The resin synthesised with Formalin at a pH of 5,4 had a much longer gel time than the resin made from Inkunite®. From the viscosity data it is clear that the hydroxymethylation takes place first and is then followed by condensation. At low pH these reactions cannot be differentiated because of the short gel time. Longer reaction times resulted in longer chains with subsequent improved crosslinking behaviour.

Although the gel time of Resin B increased quite drastically with an increasing pH, it approached a limit. The final product properties for both resins were similar. This means that the same product can be obtained in different times. Under appropriate reaction conditions, all the products were homogeneous, hard and strong with excellent water resistance. It is recommended that the microstructure of the different products be compared to see if there are any microscopic differences.

The curing rate of Resin A was measured and found to increase with temperature as expected. Although the temperature affected the reaction rate, it did not significantly influence final product properties. Nevertheless, the products formed at lower temperatures were slightly stronger and slightly more homogeneous than the products formed at high temperature. It is suggested that the influence of temperature on the cure reaction of Resin B also be investigated.

Resin A with a formaldehyde to urea molar ratio of 2:1 gelled rapidly but took three days to solidify. With a molar ratio of 1,4:1 the reaction was slower at first, but solidification occurred earlier. The product obtained at a 2:1 molar ratio was very smooth, hard and crack free. The other product was brittle and had small cracks caused by the water that was trapped inside the crosslinked matrix.

SS60 addition generally resulted in a better product, independent of the reaction conditions used, including pH. At high pH and with Inkunite® as a source of formaldehyde KMS60 and KRS60 also resulted in good products, but at lower pH the products were brittle and not very useful. After 7 days of water immersion, only Resin A with cationic emulsions (KMS60 and KRS60) softened, while the others were unaffected. It is therefore concluded that the addition of bitumen emulsions did not materially affect the result of the cure reactions, except for slowing them down at higher pH.

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CHAPTER 3

THE SOIL STABILISING PROPERTIES OF UREA-FORMALDEHYDE RESINS

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THE SOIL STABILISING PROPERTIES OF UREA-FORMALDEHYDE RESINS

3.1 INTRODUCTION

Soil stabilisation is the treatment of road building materials such as soils to improve their engineering properties. Increased durability, workability, strength and a decrease in water permeability and shrinkage are the desired effects of soil stabilisation. All these contribute to sustained resistance of the stabilised material to deformation under repeated loads in wet and dry conditions (Ballantine and Rossouw, 1989). The substances most often used for soil stabilisation include cement, lime, bitumen and tar. Extensive testing has been done on these materials and their proven effectiveness as soil stabilisers has lead to their widespread use.

Polymers are used in civil engineering mostly in the form of geotextiles (Koerner, 1998). The use of polymeric stabilisers, however, is a relatively new application and much work still needs to be done to prove their effectiveness as soil stabilisers. Some polymers could be viable alternatives to traditional stabilising materials such as cement and lime. In many cases the difficulty of properly mixing the stabilising agent with soil poses problems. In others, their environmental impact prevents them from being used as soil stabilisers.

Effective polymers should be able to bind the soil particles together to withstand applied forces and to eliminate the destabilising effects of water. According to Van Heerden and Goddard (1997), the ideal polymer for road stabilisation must have the following characteristics:

- The polymer used in soil stabilisation must be stable at application temperatures.
- In the final state the polymer must not be too elastic, since this can lead to large deformations. A too rigid polymer, on the other hand, will fracture under applied stress.
- There should be a strong bond between the polymer and the soil particles in order to be able to withstand large loads.
- The polymer should not leach from the soil.

There are many factors that influence the effectiveness of a soil stabiliser and these include the following:

- The amount of stabiliser added to the soil
- The moisture content of the soil and the stability of the stabilising agent in the presence of moisture
- **The type of soil**. The amount of clay, sand and silt will determine its plasticity index and its natural strength and thus the type and amount of stabiliser that needs to be used
- **The application method**. Proper mixing of the agent into the soil and the degree of compaction can largely influence the effectiveness of the soil stabiliser
- In the case of cement and lime and other agents the time after application plays an important role
- **Modifying agents**. These include pH modifiers, hardeners and additives such as bitumen for reduced water permeability

The aim of this part of the study is to evaluate the suitability of modified urea-formaldehyde resins as soil stabilisers, taking into account the results of the previous section. Various tests were conducted to determine the influence of the above-mentioned factors on the effectiveness of the resin as a soil stabiliser. Variables that were investigated included the formaldehyde to urea molar ratio, the amount of bitumen emulsion added and the type of resin (Resin A and Resin B, which differ with respect to the source of formaldehyde used).

The indirect tensile strength (ITS) was used as a measure of the soil stabilisation properties of the resin since it is easy to determine and small amounts of material are used. The tests were conducted in a soil laboratory, using the applicable standard testing methods.

3.2 TERMINOLOGY

The following are some of the basic terminology used in civil engineering and soil stabilisation and is included to clarify some of the terms used in this chapter:

Atterberg limits. These are the soil properties used to characterise a soil in terms of its water retentivity and plasticity. They are the liquid limit (LL), Plastic limit (PL) and the Plasticity index (PI). It is conventional to use only that fraction of the soil with a particle size less than 0,425 mm. They are described in further detail below.

California bearing ratio. This is a test for the load-carrying capacity of a soil, expressed as a percentage of a standard value.

Cohesive soil. A soil, usually containing at least 15 % clay, whose particles strongly adhere together.

Compaction. A process where the density of the soil is increased by packing the soil particles more closely together, using mechanical means such as rolling,.

Gravel. Soil particles larger than 2,0 mm in size.

Liquid limit. The moisture content at which the soil passes from the plastic to the liquid state.

Modified AASHTO density. The highest dry density obtained when using a modified hammer as the compactive effort. AASHTO is the abbreviation for Standard American Association of State Highway and Transport Officials.

Moisture content. The loss in mass (expressed as a percentage of the dry material) when a soil is dried to constant mass at 105 °C.

Optimum moisture content (OMC). That moisture content at which a specified amount of compaction will lead to the maximum dry density.

Plasticity index (PI). The numerical difference between the liquid limit and the plastic limit of a soil.

Plastic limit (PL). The moisture content at which the material passes from the semi-solid state to the plastic state under specified test conditions.

Soil. Usually consists of naturally occurring rock decomposition products containing all particle sizes below 75 mm.

Standard AASHTO density (Proctor density). The maximum dry density obtained when using the Proctor hammer as the compactive effort.

3.3 SOIL STABILISATION

Soil properties can be modified in various ways, for example chemical, mechanical, thermal and others (Ingles and Metcalf, 1972). It is generally accepted that none of these methods can treat all the available soils and that some stabilising methods are used specifically with certain types of soil. The important soil properties are its volume stability, strength, permeability and durability (Ingles and Metcalf, 1972). An effective soil stabiliser should be able to upgrade most or all of these properties simultaneously.

Because of the low cost of soil and its availability, it is an ideal engineering material. Often, however, it is not suited for a specific use in construction because of its water permeability, swelling or low wet strength. Either this material can be used with its poor properties taken into account during design, or it can be removed and replaced with a different material. Another alternative is to modify the existing soil properties to such an extent that it becomes useful. This process is called soil stabilisation.

Stabilisation can be divided into two categories, namely modification and cementation. Modification is used to change the effect of clay soils, and this is done by addition of lime to the soil. This is a fast process and a notable increase in workability and strength and a decrease in the plasticity index results. Cementation is a long-term process where the soil particles are bound together to increase the soil strength (Ballantine and Rossouw, 1989; Visser, 1994).

The characteristic of a soil to withstand any swell or shrinkage due to a change in its moisture content is called its volume stability. It is known that many clay soils shrink or swell with changes in their moisture content and this can cause disruption of road surfaces and cracking of buildings. This characteristic of certain soils can thus lead to great economic loss. There are two ways of preventing shrinkage or swelling: the first is to convert the soil to a granular mass by chemical or thermal treatment and the second is to block the pores by means of a sealing process, e.g. with bitumen or by using impermeable membranes.

The ability of a soil to withstand deformation when it is subjected to loading is a measure of its strength (Ingles and Metcalf, 1972). There are a variety of factors that can influence the strength of a soil, and these include its moisture content and the type of soil. With few exceptions, an increase in density translates into increase soil strength. The density can be increased by mechanical stabilisation, e.g. compaction. The conversion of a material to a granular mass also increases strength. It is also important to realise that the exclusion of water can maintain soil strength.

Permeability is the measure of how easily water can move through the soil. Bulk flow of water can occur when large pores are present in the soil and capillary action takes place in micropores as found in clays. Permeability can lead to many problems in the construction of roads, dams etc. because of drainage problems and reduced strength of the soil. Inadequate pore pressure dissipation can lead to slip failures and high seepage flow can lead to tunnelling and breaching failures. High permeabilities can be reduced by compaction or by introducing sealants. The sealants do not completely block the fine pores and only serve to reduce the rate of water flow. Other additives can make the soil partly hydrophobic.

The resistance to weathering or erosion of soils is called its durability. Poor durability leads to loss of integrity of roads and other constructions and results in high maintenance cost (Ingles and Metcalf, 1972). In natural soils poor durability can be caused by factors such as insufficient clay content and in stabilised soils this can be attributed to an incorrect choice of stabiliser or an insufficient dosage. In general the durability of stabilised soils greatly exceeds that of natural soils due to the increased resistance to chemicals and water.

3.4 CONVENTIONAL STABILISING AGENTS

3.4.1 LIME

Most of the lime used for road stabilisation is hydrated or slaked lime (calcium and/or calcium-magnesium hydroxide), although quicklime (calcium and/or calcium-magnesium oxide) is also used (Ballantine and Rossouw, 1989). Lime has no ingredient that causes hardening when water is added. Any increase in strength is caused by the interaction of the lime with clays or pozzolans. This means that lime only increases soil strength when clayey soils are used.

In lime stabilisation both modification and cementation takes place. The modification reaction results in the reduction of the PI, the liquid limit as well as the shrinkage and an increase in bearing strength and compaction. The lime reacts with the clay particles both physically and chemically. Ion exchange between the lime and clay particles takes place immediately, which replaces the intercalated ions, e.g. sodium ions, in the clay with calcium ions from the lime. This dramatically reduces the swelling ability of the clay, as the sodium cation can hold 79 molecules of water, whereas calcium can only hold 2. This means that the soil changed from a hydrophilic to a hydrophobic condition. Bound water is released and the plastic limit of the soil is raised above the optimum moisture content (Ballantine and Rossouw, 1989). Another physical reaction that takes place is the concentration of calcium ions on the lime surface, which changes its surface charge to a positively charged one. Interaction with the negatively charged clay particles causes flocculation of the soil.

Cementation of the soil in the presence of added lime is a long-term effect. The free lime (which did not interact with the clay in the modification reaction) reacts chemically with the clay minerals. In the process the clay minerals are destroyed and finely divided, crystalline gels result, similar to the gels formed in the hydration of Portland cement. The reaction is irreversible and consequently little or no lime leaches out of the stabilised material over time.

Carbonation is the process where lime is converted into calcium carbonate when its reacts with carbon dioxide from the atmosphere. The formation of calcium carbonate prevents stabilisation because the active component, calcium or calcium-magnesium hydroxide, is converted into an inactive species that has no stabilising properties. In order to prevent carbonation the layer of lime and soil should be sealed as soon as possible after mixing (Ballantine and Rossouw, 1989). Carbonation can also take place with cement stabilisation.

3.4.2 PORTLAND CEMENT

Portland cement is the cement used most frequently in soil stabilisation, although others such as sulphate resisting cement and masonry cement are also used. Cement is formed when limestone and shale is fired at a high temperature to form a clinker, to which a small quantity of gypsum is added. The mixture is then ground to a fine powder. Cement contains tri-calcium and di-calcium silicates, which form needle-like calcium silicate hydrates when water is added. These needles lock into each other and around soil particles to increase the strength of the stabilised material (Ballantine and Rossouw, 1989).

The cement is self-hardening when water is added and can consequently be used for stabilisation of sand and gravel (Ingles and Metcalf, 1972). The hardening is the result of the hydration process, which takes place and will continue as long as water is present. Although the strength increases continuously over a long period of time, much of the increase in strength occurs during the first 28 days.

Another reaction also takes place when cement is added to soil in the presence of water. During the hydration of the calcium silicates calcium hydroxide is formed, which in turn can contribute to the ion exchange occurring on the clay surface. This results in modification of the soil and thus a reduction in plasticity (Ballantine and Rossouw, 1989), but has a limited effect on the increase of soil strength.

3.5 STABILISATION WITH POLYMERS

Many polymers have been proposed as soil stabilisers because of their properties and mechanism of stabilisation. Although many of them can be potential soil stabilisers, they are not used simply because of economical constraints. Other factors that influence their applicability are the ease of mixing and environmental stability (resistivity to chemical and ultra-violet degradation). Much work on materials for soil stabilisation was conducted by the United States Army and the effectiveness of many agents, including polymers, were reported (Oldham, Eaves and White, 1977). Since it falls outside the scope of the report to list them all, only the basic types will be discussed.

3.5.1 CATIONIC POLYMERS

Cationic polymers carry positively charged substituent groups and can form ionic bonds with negatively charged clay and silica. This causes flocculation of the soil (Ingles and Metcalf, 1972) and results in increased resistance to shear forces. On the other hand, this can lead to resistance to compaction and thus a lower density of the compacted soil. This also results in greater water permeability. Cationic soil stabilisers that have been proposed include polyacrylamides (PAA) and quaternary compounds such as cetyl trimethyl ammonium bromide (CTAB).

3.5.2 ANIONIC POLYMERS

Sulphonates and lignosulphonates are typical anionic stabilisers. The electrical charge of the polymer is the same as that of the clay surface and this reduces shear strength and enhances compactibility. These additives can thus be described as compaction aids (Ingles and Metcalf, 1972).

3.5.3 NON-IONIC POLYMERS

Non-ionic stabilisers include polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC). These types of polymers are also effective when used with clays. The hydroxyl on the polymer reacts to form strong bonds with the surface oxygen of the clay minerals (Ingles and Metcalf, 1972). The polymeric stabilisers also cause coagulation and flocculation of the clayey material and can thus result in lower densities of the compacted material.

3.5.4 RESINS

Resins form a three-dimensionally crosslinked network and this can be advantageous because the resin is distributed throughout the voids in the soil system and traps the soil particles, either physically or chemically. It also provided a means of dissipating impact energy. In the past resins were only used as waterproofing agents with little or no increase in strength. Another factor that affected their use was the acidity of the soil; only acid soils responded to treatment. Furthermore, natural resins are susceptible to biodegradation. A possible advantage can be the incorporation of fibers into the resin network, which can greatly improve the mechanical properties of the soil. Synthetics include melamine- and urea-formaldehyde resins, but their uses are limited owing to the environmental impact of associated toxic emissions.

3.6 BITUMEN EMULSIONS

A basic understanding of bitumen emulsions is necessary to explain their effects on urea-formaldehyde resin properties, as well as to predict and solve problems arising from their use in resin-soil systems.

Bitumen emulsion is traditionally used in road construction and maintenance as a binding and waterproofing agent (CSIR, 1982). This makes it a potential amino resin additive. Waterproofing the resin-soil mixture is important because it prevents the loss of binder integrity, which can easily occur through erosion of the soil particles that are not tightly bound. Since only about 2 to 3 % of the soil-resin system consists of the resin itself and loose soil particles do occur, it is also advantageous to have bitumen that acts as an extra binder.

3.6.1 THE MANUFACTURE OF BITUMEN EMULSIONS

Bitumen is a complex mixture, consisting mainly of asphaltenes, naphtene aromatics, polar aromatics and saturates such as paraffin. The primary source of bitumen is the refinery distillation of crude oil (Corbett and Urban, 1986). Distillation is necessary to separate the bitumen-containing residual fraction from the more volatile fractions such as heavy and light gas oils, kerosine and gasoline. The bitumen-containing residue is treated further with solvents to recover the small quantities of volatile products still present and to produce pure bitumen.

Some crude oils are more suitable for bitumen manufacture than others (Corbett and Urban, 1986). The lower API gravity crude oils, or heavy crudes, have the highest bitumen content and the lowest percentage of volatile fractions.

Bitumen emulsions have been manufactured locally from the 1920's (CSIR, 1982). These emulsions are prepared by mechanically distributing warm liquid bitumen in water containing an emulsifying agent in a colloid mill. Thus, bitumen emulsions consist of two phases: the continuous phase, which is water, and the distributed phase, which is bitumen. The emulsifying agent ensures that the bitumen drops are suspended in the water.

The emulsifier is absorbed onto the small, distributed bitumen drops, which is then stabilised mostly with electrical charges. The emulsifier causes a specific charge on the surface of the bitumen droplet and because identical charges repel each other the droplets are prevented to combine. Mainly two types of emulsifiers are used. They are:

- Anionic emulsifiers
- Cationic emulsifiers

3.6.2 PROPERTIES OF BITUMEN EMULSIONS

The following are important characteristics of a bitumen emulsion:

- Type of emulsifying agent
- The grade of the bitumen used
- The amount of bitumen in the emulsion and its viscosity

Sodium and potassium salts of fatty acids are usually used as anionic emulsifiers. These emulsifiers induce a negative charge on the surface of the bitumen droplet and have an alkaline reaction. Cationic emulsifiers have an acidic reaction because of their positive charge. These are usually hydrogen chloride solutions of amines (CSIR, 1982). Cationic emulsions also contain a small amount of an anti-stripping agent, which prevents water from causing the soil particles to detach from the bitumen (Green, 1991).

Bitumen grades are usually differentiated in terms of their penetration value. A weighted needle is allowed to bear on the surface of bitumen for a specified length of time at a standard temperature, usually 25 °C. The depth of penetration of the needle into the bitumen is termed the penetration of the bitumen and is measured in 0,1 mm units. The needle penetrates more into soft bitumen and less into harder grades. The penetration of bitumen is therefore an indication of its softness. The type or grade of bitumen used in a bitumen emulsion depends on the required penetration of the emulsion. The penetration is specified by taking into account the climate of the area where it is used, the weather conditions at the time of application and the traffic volume of the road that is being built (CSIR, 1982; Green, 1991).

The viscosity of the bitumen emulsion is a property of the emulsion itself and does not depend on the viscosity of the bitumen. The viscosity is influenced mainly by the amount of bitumen in the emulsion and the size of the bitumen droplets. The bitumen content per mass of emulsion is usually between 60 to 67 %, depending on the method of application of the emulsion.

3.6.3 THE CHEMICAL REACTIONS OF BITUMEN EMULSIONS

It is important to keep in mind that bitumen and bitumen emulsions react with the environment and that this determines its suitability for a specific application. When bitumen emulsion is used as a modifier in urea formaldehyde resins it is necessary to realise the influence of water, acids and bases and other chemicals on the stability of the emulsion, as well as its hardening and binding properties.

Bitumen emulsions are usually resistant to mild chemicals (Corbett and Urban, 1986). Strong acids react with bitumen to give substitution products. Weak acids can cause the bitumen to harden slowly. Any disturbance of the pH as a result of acid or base addition to an anionic or cationic emulsion can cause the emulsifying agent to react and destabilise the droplets (refer to the results presented in Chapter 2).

Under ambient conditions bitumen emulsions oxidise slowly when exposed to air and sunlight. This causes the viscosity of the bitumen to increase. In road building this effect is minimised by compacting the aggregate mixtures to decrease the exposed fraction of bitumen. In waterproofing applications the bitumen is applied in thick layers and here the weathering of the top layers protects the inner layers.

A bitumen emulsion is used mainly for easier application of the bitumen to the soil because of a lower viscosity. When the emulsion is applied the water must first evaporate before the bitumen droplets can combine to cover the surface of the aggregate.

3.6.4 THE CHOICE OF BITUMEN EMULSION

The behaviour of anionic emulsion differs significantly from that of cationic emulsions when they are applied in practice (CSIR, 1982). It is logical to assume that anionic emulsions will give the best results when it is applied to basic aggregate such as dolerite and dolomite. When applied to acidic aggregates such as quartzite and granite the anionic emulsions give varying results.

Cationic emulsions have a great affinity for basically any type of aggregate, whether it is acidic or basic. This can be attributed to the type of emulsifier used in their manufacture.

These emulsions also have better wetting characteristics and binding properties and can easily displace any water present on the aggregate surface (Green, 1991).

When bitumen emulsions are applied to an aggregate the soil moisture content and the atmospheric conditions play an important role in the effectiveness of the bitumen to cover and bind the soil particles. This study is only concerned with the use of bitumen emulsions as an additive to amino resins in a soil binder system. It will therefore be highly dispersed in the soil and only a small portion will be exposed to the atmosphere. Atmospheric factors will not be discussed in further detail. The bitumen is used as an additive primarily for its hydrophobic characteristics and not as a soil binder. Its effectiveness as a soil binder and the influences of atmospheric and soil conditions on that are therefore not important, and since these factors do not influence its water permeability they are not considered.

The choice of bitumen emulsion as an additive depends primarily on the way it influences the pH and the water resistance properties, and consequently other properties such as reaction time, resin elasticity and strength. It should be noted that the optimum reaction pH is about 4,9 to 5,2 and that it is possible to achieve this pH without addition of catalyst when a cationic bitumen emulsion is used. On the other hand, when an anionic emulsion is used, more acid catalyst must be added to reach a pH of about 5. This can also cause destabilisation of the emulsion.

3.6.5 THE HANDLING OF BITUMEN EMULSIONS

The following are important when handling bitumen emulsions (CSIR, 1982):

- Bitumen emulsions are generally not stored for longer than three months. When bitumen emulsion was stored for a long time, the drums or containers must be rolled a few times to ensure that the emulsion is homogeneous. This also increases the life of the pump that is used because it lowers the wear caused by viscous emulsions.
- Cationic and anionic bitumen emulsions should never be mixed. Mixing will cause coalescence and consequently phase separation. The high viscosity of bitumen cause damage to pumps, pipelines and equipment and is difficult to clean.
- Containers must be stored at room temperature. Low temperatures can cause the emulsion to become highly viscous and difficult to handle.

- When water is added to dilute the bitumen emulsion, care must be taken that the water does not contain a high concentration of dissolved minerals and salts. This can also lead to destabilisation of the emulsion.

3.6.6 ENVIRONMENTAL AND SAFETY ASPECTS

Bitumen and bitumen emulsions are essentially safe products (Green, 1991). Numerous studies have indicated that bitumen does not present an occupational health risk to people exposed to it, nor does it pose an environmental threat when normal care is taken and good working practice are adhered to.

Health hazards are only likely to arise in circumstances where there is prolonged skin contact or inhalation of vapours and fumes. Bitumen is usually applied at high temperatures and there is a risk of burns, but in the case of bitumen emulsions there is no such risk since it is used at room temperature. Inhalation can be limited when the worker is working upwind of the bitumen source or when there is adequate ventilation when working indoors. Skin contact can be minimised by wearing protective clothing. Usually normal working clothes with long sleeves and trousers is adequate.

3.7 THE TYPES OF SOIL

The type of soil is important in determining the effectivity of a soil stabiliser. The type of soil determines its characteristics and thus its strength, durability and permeability and the amount and type of stabiliser that needs to be used. The different soil fractions, e.g. sand and clay etc., are classified in terms of particle size rather than chemical composition (Das, 1990). Soil particles between 2,0 and 75,0 mm are termed gravel, and all the particles smaller than that are visible to the naked eye are termed sand. It mostly consists of quartz and feldspar. Silt and clay particles are too small to be seen by the naked eye. Silt refers to the particles between 0,075 and 0,002 mm. All particles smaller than 0,002 mm are usually flake-shaped and represent the clay fraction of the soil.

Clay minerals are complex aluminium silicates (Das, 1990) and have a negative electric charge at the surface, normally resulting in a basic soil pH. Clay minerals groups include kaolinite, illite and montmorillonite. The chemical composition of the clay minerals and the rest of the constituents of soil are beyond the scope of this thesis, but Das (1990) and CSIRO

(1964) provide further detail. The above-mentioned types of material are mostly found together, in different proportions, to make up a soil. Table 6 summarises the composition and resulting properties of some soils.

Table 6. *Soil composition and its resulting properties (Ingles and Metcalf, 1972)*

Sandy soils	Good engineering properties but will need stabilisation if they do not have a good grading.
Silty soils (high silt content, some clay)	Good properties when dry, but lose all strength when wet.
Silty soils (high silt content, no clay)	Dusty and with poor cohesion when dry and no strength when wet.
Clayey soils (high clay content)	Large volume changes owing to moisture content variations. Basic pH. Poor load-bearing capabilities when wet.
Clayey soils (open-textured)	Good, useful properties when well-compacted

3.8 TEST METHODS

Standard methods exist for the testing of materials as soil stabilisers. Only a brief description of the tests procedures used in this investigation is given. Full descriptions of the test procedures are given in TMH1 (CSRA, 1990).

- **The wet preparation and sieve analysis of gravel, sand and soil samples (Method A1(a)).** The preparation of the soil sample involves the qualitative separation of the fines portion of the soil (the material passing the 0,425 mm sieve) from the coarse portion as well as the sieve analysis of the coarse material. The fines are required for the determination of the Atterberg constants and the mechanical analysis.

- **The dry preparation and sieve analysis of gravel, sand and soil samples (Method A1(b)).** In this method the fines portion of a soil is separated from the coarse material by dry sieving where heating of the fines may influence the test results. The sieve analysis is done by washing the material through certain sieves and includes the determination of the fraction passing the 0,075 mm sieve, as described in TMH 1 Method A5 (CSRA, 1990).

- **The determination of the maximum dry density and the optimum moisture content (Method A7).** The maximum dry density and optimum moisture content are determined by compacting the soil at different moisture contents with the Modified AASHTO compaction effort to obtain the moisture-density relationship of the material. The maximum density of a material for a specific compaction effort is the maximum density obtainable if the compaction is carried out at different moisture contents. The optimum moisture content for a specific material and compactive effort is the moisture content at which the maximum density is obtained.

- **The determination of the unconfined compressive strength (UCS) of a soil (Method A14).** The UCS of a material (stabilised or natural) is the load in kPa required to crush a cylindrical specimen (127 mm high and 152,4 mm in diameter) to total failure at a rate of application of load of 140 kPa/s.

- **The determination of the indirect tensile strength (ITS) of stabilised materials (Method A16T).** The indirect tensile strength of stabilised soil, gravel or crushed stone is determined by measuring the resistance to failure of a cylindrical prepared specimen when a constantly increasing load is axially applied to the curved sides of the specimen.

3.9 EXPERIMENTAL PROGRAMME

3.9.1 EXPERIMENTAL TEST PROCEDURE

The effectiveness of cold-setting modified urea-formaldehyde resin as a soil stabilising agent was determined by mixing the liquid resin with the soil, compacting the mixture and after some time subjecting it to the indirect tensile strength test. The ITS was used as a measure of the effectiveness of the resin as a soil stabiliser because of the limited amount of soil and resin available. In all the cases the same soil was used (a brown shale, with properties as outlined in Appendix D).

All the stabilised soil samples subjected to ITS determination were prepared using the Marshall apparatus used in testing the resistance to flow of a cylindrical briquette of a bituminous mixture (TMH1, Method C2). The method used for compacting the soil samples differed from Method C2 in the sense that instead of compacting the sample with 75 blows on each side, as for bituminous mixtures, only 50 blows on each side were used. All the samples were prepared in standard moulds, which had an inside diameter of 101,6 mm. The height of the sample is a function of the compaction and was approximately 60 mm. The actual indirect tensile strength of the sample is calculated from the following formula:

$$ITS = \frac{2 \times Gauge\,Value \times 0.0225}{\pi \times D \times h} \qquad 10.$$

where D is the diameter of the mould (101,6 mm), h is the height of the sample in mm and Gauge Value is the value obtained from the instrument used for determining the ITS in kPa.

Due to a lack of specific tests for polymer-stabilised materials, the standard tests were used as a basis for preparing and treating the samples, but because of the different mechanisms of stabilisation of the resin and conventional agents, different preparation methods had to be used. The resin was prepared and additional water was added to bring the amount of liquid stabiliser to the value needed to obtain the optimum moisture content when introduced into the soil. The soil had an optimum moisture content of 9,6 % and a hygroscopic moisture content of 2,6 %. This means that a total of 70 g liquid had to be added to bring 1 kg of the soil to its optimum moisture content (OMC). In most of the cases 2 % (by mass of the dry soil) resin was added and 2 % bitumen emulsion (unless otherwise noted). This means that 30 g water had to be added. Because the bitumen emulsion contains 60 % bitumen and 40 % water and the resin also consists of about 40 % solids, an additional 20 g of water had to be added to compensate for the mass of solids in the mixture. So 50 g of water was added in most cases to bring the soil to its optimum moisture content, which is beneficial in compaction. If no bitumen was used 60 g of water was added to the resin. The moisture content of the soil was kept constant for all the experiments by keeping it in an air-tight container to prevent it from taking up moisture from the atmosphere, or drying out.

In the experiments urea-formaldehyde resin was used as a soil stabilising agent. Resin A is a resin prepared from 1,67 gram Formalin per gram urea, while Resin B is a resin prepared from 1,67 gram Inkunite® per gram urea. For experimental purposes commercially available urea fertilizer was used (46 % nitrogen). Formalin (37 % formaldehyde / 7 % methanol) was used as a source of formaldehyde for Resin A. When 20 g of the resin had to be added, it meant that 7,5 g urea and 12,5 g of the formaldehyde source were used.

Bitumen emulsion is used in non-cohesive soils to add cohesive strength and in cohesive materials as a waterproofing agent. It forms a thin film on the surfaces of sandy particles and blocks pores in clayey soils (Ingles and Metcalf, 1972). Bitumen emulsion (anionic SS60, unless otherwise stated) was used to achieve better stabilisation, based on the earlier tests reported in Chapter 2.

The liquid resin was prepared by dissolving the urea into the required amount of water. The source of formaldehyde was then added followed by the bitumen emulsion (where necessary). Citric acid was used as the acid catalyst: the pH of the whole mixture was adjusted to 4,5. The required quantity of the mixture was then added to 1 kg of dry soil and thoroughly mixed to ensure a good distribution of the reagents throughout the soil phase. The sample was compacted by using the Marshall apparatus (as described above) and left to air-dry for a pre-determined time. For the wet strength tests the samples were soaked in water for 24 hours, unless otherwise stated.

All the experiments were carried out at constant temperature of 23 °C and an atmospheric pressure of about 85 kPa. In each experiment the temperature, pH, mass and height of the sample were noted. Most experiments were conducted in triplicate in order to determine the variability of the results (see Appendix E).

3.9.2 INVESTIGATION OF THE FACTORS INFLUENCING SOIL STABILISATION

3.9.2.1 DRYING TIME

In this experiment the increase in strength of samples stabilised with Resin A and Resin B was determined as a function of the air-drying time of the stabilised soil. For Resin A the strength of soil and resin with and without bitumen emulsion as a function of drying time was determined in wet and dry conditions.

Another test was conducted by covering the Resin A samples (with and without bitumen emulsion) in a plastic bag to simulate conditions where the loss of moisture from the stabilised material is appreciably slower. Again the strength development as a function of time was determined. For Resin B the strength of the resin without bitumen emulsion and the wet strength of the resin with bitumen emulsion was determined as a function of time. Table 7 describes the experimental design (in all cases 2 % resin and 2 % bitumen emulsion was used, where applicable). The strength was determined after 6 hours and 1, 2, 3, 4, 6, 8, 17, 24 and 60 days. The wet tests with Resin B without bitumen was not conducted because the tests done with Resin A it was clear that bitumen emulsion was necessary in order to provide water resistance. In another experiment samples stabilised with 2 % Resin A and 2 % bitumen emulsion were soaked in water and their strength as a function of the soak time was determined. These samples were dried for 21 days prior to soaking them in water.

Table 7. *The experimental setup for determining the time-strength relationship of the stabilised material*

Resin used	Dry test		Wet test	
	Bitumen emulsion added	Covered	Bitumen emulsion added	Covered
Resin A	No	No	No	No
Resin A	Yes	No	Yes	No
Resin A	No	Yes		
Resin A	Yes	Yes		
Resin B	No	No		
Resin B			Yes	No

3.9.2.2 INITIAL MOISTURE CONTENT

The amount of water added to the pure urea-formaldehyde resin (Resin A and Resin B) is an important factor in formulating the soil stabiliser for optimum effectiveness. The amount of water added will determine the moisture content of the soil when the sample is compacted. Too little or too much water will result in ineffective compaction. Compaction will be optimal if the sample is at its OMC (for a specific compactive effort). Water, on the other hand, is a diluent and is necessary for good mixing and distribution of the resin throughout the soil phase. In one experiment samples were prepared by using 20 g (2 %) Resin A and 40, 50, 60, 70, 80, 90 and 100 g of water respectively. The resin/water mixture was then mixed thoroughly with the soil (1 kg soil in each case) and compacted. It was decided to allow 7 days for the samples to air-dry. At this point the soil strength was above that of its natural value (210 kPa) and the strength values of the soil stabilised Resin A and Resin A with bitumen emulsion were still approximately the same. This means that the influence of factors such as compaction and moisture content can be readily compared.

The same experiment was repeated to determine the contribution of the bitumen emulsion towards the moisture content. This was done by adding 20 g Resin A and 20 g bitumen emulsion, mixed with 30, 40, 50, 60, 70, 80 and 90 g of water to 1 kg soil respectively. The amounts of water used as a diluting agent is in each case 10 g less than in the experiment without bitumen emulsion because the emulsion contributes about 10 g of water when added to the mixture. It is important to note the density of the sample since it is an indication of the OMC of the soil with the compactive effort used in the Marshall apparatus. This compactive effort is different from the one used to determine the OMC value reported in Appendix D.

When the samples were air-dried for only 7 days, it was observed that not all the surface moisture had evaporated from the samples, especially if the initial moisture content was high or when bitumen emulsion was added. The remaining moisture can influence the strength of the sample, and in order to exclude this from the investigation, it was decided to repeat certain tests, but this time allowing 21 days for drying. Samples were prepared by adding 2 % Resin A and 2 % bitumen emulsion and 30, 50, and 70 g of water to 1 kg soil, respectively. Both wet and dry tests were conducted. The experiment was repeated, but Resin B was used in place of Resin A.

3.9.2.3 COMPACTION

Compaction of the stabilised soil is an important parameter because the compaction will influence the density of the sample, which is critical when water permeability is considered. The densification resulting from compaction also leads to the interlocking of soil particles (depending on the type of soil) and thus a stronger end product. The particles become more closely packed and, in the case of resin stabilisation, bonding of the particles is improved since they are closely orientated in the resin network. Coating of the particles can also be improved because less resin is used to fill the voids resulting from the shape and packing of the soil particles.

In this experiment the effect of compaction on the strength of the stabilised material was determined by compacting samples stabilised with 2 % Resin A and 2 % bitumen emulsion (with the addition of 60 g of water) with 10, 20, 30, 40, 50, 60, 70, 80 and 90 blows per side respectively. The samples were dried for 7 days at ambient conditions after which their ITS were determined.

3.9.2.4 THE UREA-FORMALDEHYDE DOSAGE

The amount of resin added is important because it is the active reagent in the stabiliser mixture and will determine the surface coating performance of the resin and to a lesser extent the water permeability. Increasing the Resin A applied to the soil will increase the particle surfaces which will be coated and can thus increase the bond strength between the particles and the resin network. The effect of dosage on the stabilisation efficiency was determined by adding 0; 0,5; 1; 1,5; 2; 2,5 and 3 % Resin A with 2 % bitumen emulsion to 1 kg of dry soil. The influence of the resin dosage on the wet strength was also determined by repeating the above experiment, but this time soaking all the samples for 24 hours before determining their ITS. All the samples were weighed to determine whether the amount of Resin A had an influence on the water uptake and evaporation rate (these are reported in Appendix F). Again all the samples were air-dried for 7 days.

An experiment was conducted to determine the influence of the Resin A and Resin B dosage on the wet and dry strength of the soil after the stabilised samples were dried for 21 days. 1, 2 and 4 % Resin A and 2 % bitumen emulsion was used to stabilise the samples respectively. Both wet and dry strengths were determined. The experiment was repeated by using Resin B in place of the Resin A.

3.9.2.5 THE BITUMEN EMULSION DOSAGE

In this experiment 2 % Resin A for all the samples was used with differing amounts of bitumen emulsion. The influence of bitumen emulsion dosage on the dry strength of the stabilised soil, as well as the wet strength, after being soaked for 24 and 48 hours respectively, was determined. The bitumen emulsion dosage was varied from 1 % to 5 %. All the samples were dried for 7 days before testing.

Another experiment was conducted to determine the influence of the bitumen emulsion dosage on the wet and dry strengths of the soil after the Resin A and Resin B stabilised samples were dried for 21 days. 2 % Resin A and 2, 3 and 5 % bitumen emulsion was used to stabilise the samples respectively. Both wet and dry strengths were determined. The experiment was repeated by using 2 % Resin B in place of the Resin A.

3.9.2.6 REACTION PH

In this experiment the effect of the pH of the stabilising properties of Resin A was investigated. The urea, formaldehyde source, the water and the bitumen emulsion were added together and the mixture pH adjusted to about 7, 6, 5 and 4 respectively. This mixture was then added to the soil and mixed properly. 2 % Resin A and 2 % bitumen emulsion was used. The experiments were conducted in both dry and wet conditions. The above procedure was repeated, excluding the bitumen emulsion.

To eliminate the influence of moisture content on the strength of the stabilised material, soil was stabilised with 2 % Resin A and 2 % bitumen emulsion at a pH of 6,2; 4,55 and 3,9 respectively and the samples dried for 21 days. Both wet and dry strengths were determined. The experiment was repeated by using Resin B in place of the Resin A.

3.9.2.7 THE FORMALDEHYDE TO UREA MOLAR RATIO

In this experiment the effect of the reactant molar ratio on the wet and dry strength was determined. The resin mixtures were prepared by adding 2 % Resin A, 2 % bitumen emulsion and 6 % water. Table 8 outlines the composition of the resin mixtures. The samples were dried for 7 days before testing. The wet strengths were determined after a 24 hours soak in water.

Table 8. *The formulation of resin mixtures with different formaldehyde to urea molar ratios*

Molar ratio	Formalin (g)	Urea (g)	Bitumen emulsion (g)	Water (g)
1:1	11,5	8,5	20	60
1,5:1	13,4	6,6	20	60
2:1	14,6	5,4	20	60
3:1	16,1	3,9	20	60
4:1	16,9	3,1	20	60

The above experiment was repeated using formaldehyde and urea in molar ratios of 1:1, 2:1 and 4:1 respectively. Both wet and dry strengths were determined after the samples were air-dried for 21 days. In a further repeat, Resin B was used in the place of Resin A. Molar ratios of 1,4:1, 2:1 and 3:1 was used.

3.9.2.8 TYPE OF BITUMEN EMULSION

In this experiment the influence of different types of bitumen emulsion on the effectiveness of Resin A and Resin B was determined. SS 60 was used as an example of an anionic bitumen emulsion, while KMS 60 and KRS 60 were used as examples of cationic bitumen emulsions. KRS 60 has a pH of 4 to 5, while KMS 60 has a pH of 5 to 6. Table 9 outlines the different tests that were conducted. In all the cases the wet and dry strength of the stabilised soil was determined. The samples were air-dried for 21 days prior to determining their dry and wet ITS.

Table 9. *The resin and bitumen emulsion used to determine the influence of the type of bitumen emulsion on the wet and dry strength of soils stabilised with Resin A and Resin B*

Resin used	Bitumen emulsion
2 % Resin A	2 % SS 60
	2 % KMS 60
	2 % KRS 60
2 % Resin B	2 % SS 60
	2 % KMS 60
	2 % KRS 60

3.9.2.9 ADDITION OF PORTLAND CEMENT

In this experiment the influence of Portland cement on the effectiveness of Resin A as a soil stabiliser was determined. Alpha Portland Cement type CEM 142,5 was used in all the cases. As control, the effect of cement addition on its own to soil was determined at dosage levels of 2, 4 and 6 %. After thorough mixing, 70 g of water was added to bring the moisture content to the OMC. After the samples were left for 4 hours, they were compacted and placed in a humidity chamber. After 7 days the samples were taken out and left to dry for 24 hours to determine their dry strength. The experiment was repeated, but after 7 days in the humidity chamber the samples were placed in water for 24 hours before measuring their ITS. This was done to measure the wet strength of the samples. This method corresponds to the standard method for determining the strength of a material stabilised with cement (TMH1, Method A13 T).

An experiment was conducted by using the same method as outlined above, but by using 2 % Resin A with 2, 4 and 6 % cement respectively. Again both the wet and dry strengths were determined. In this case 60 g of water was added to each of the samples to increase the moisture content to the OMC.

Another experiment was conducted by using 2 % Resin A with 2, 4 and 6 % cement respectively, but this time the samples were compacted immediately after the cement, Resin A and water was added. The samples were then left to dry for 7 days at room temperature before measuring their wet and dry ITS.

3.9.2.10 ADDITION OF LIME

In this experiment the influence of lime on the effectiveness of Resin A as a soil stabiliser was determined. The effect of lime addition to soil without Resin A was determined to act as a control. 2, 4 and 6 % lime was added to soil samples (1 kg each) and mixed properly. 70 g of water was then added and mixed properly with each of the samples to bring it to OMC. After the samples were left for 4 hours, as in the case of the experiments conducted with cement, they were compacted and placed in a room with a very high humidity. After 11 days the samples were taken out and left to dry for a day to determine their dry strength. The experiment was repeated, but after 11 days in the high humidity chamber the samples were placed in water for 1 day before measuring their ITS. This was done to measure the wet strength of the samples. This method corresponds to the standard method for determining the strength of a material stabilised with lime (TMH1, Method A13 T).

The experiment as outlined above was repeated, but 2 % Resin A was added to the 2, 4 and 6 % lime respectively. Both the wet and dry strength tests were conducted.

3.9.2.11 THE INFLUENCE OF ADDITIVES AND RESIN PREPARATION ON STABILISATION

For the purposes of these experiments the acid catalyst was modified by adding 33,3 g sugar to 66,6 g citric acid and then diluting it with 110 g water. The additives that were used in each test are described in Table 10. 2 % of Resin A was used with the required amount of water. After mixing the resin and compaction the samples were dried for 7 days.

Table 10. *The experimental outline describing the additives used to determine their influence on the effectiveness of Resin A as a soil stabiliser*

Acid	Additive
Citric acid and sugar	None
Citric acid and sugar	20 g Bitumen emulsion
Citric acid and sugar	Colourant
Citric acid and sugar	5 g $(NH_4)_2SO_4$
Citric acid	None

In another experiment the difference in ITS values for different sequences of adding the reagents were investigated. Firstly urea, Formalin and citric acid added and then the bitumen emulsion, while in the next run urea and the Formalin was added and then the bitumen emulsion, followed by adjusting the pH to 4,5 with citric acid. The case where urea and bitumen emulsion were added first, then Formalin and finally the citric acid, in order to increase working time on the resin, was also investigated.

3.10 RESULTS AND DISCUSSION

3.10.1 THE INFLUENCE OF DRYING TIME ON THE STRENGTH OF THE STABILISED SOIL

The influence of bitumen addition to the Resin A stabilised soil strength as a function of time can be seen in Figure 11. Although both systems showed the same initial strength increase, the Resin A bitumen emulsion combination, resulting in higher ultimate strength of the stabilised material. The raw experimental data is given in Appendix F.

Although the resin solidified after about 3 hours, the strength continued to increase for between 17 to 24 days before it remained constant. This can be attributed to the presence of moisture in the prepared sample. The strength increased as the water evaporated out of the sample (as seen in Figure 12). Evaporation takes place until all the free water is removed. Water evaporated faster from samples that were not treated with bitumen emulsion, so initially those had higher dry strengths. But this also means that water ingress will be retarded by the bitumen emulsion and those samples treated with bitumen emulsion normally have higher wet strength values (see Appendix F).

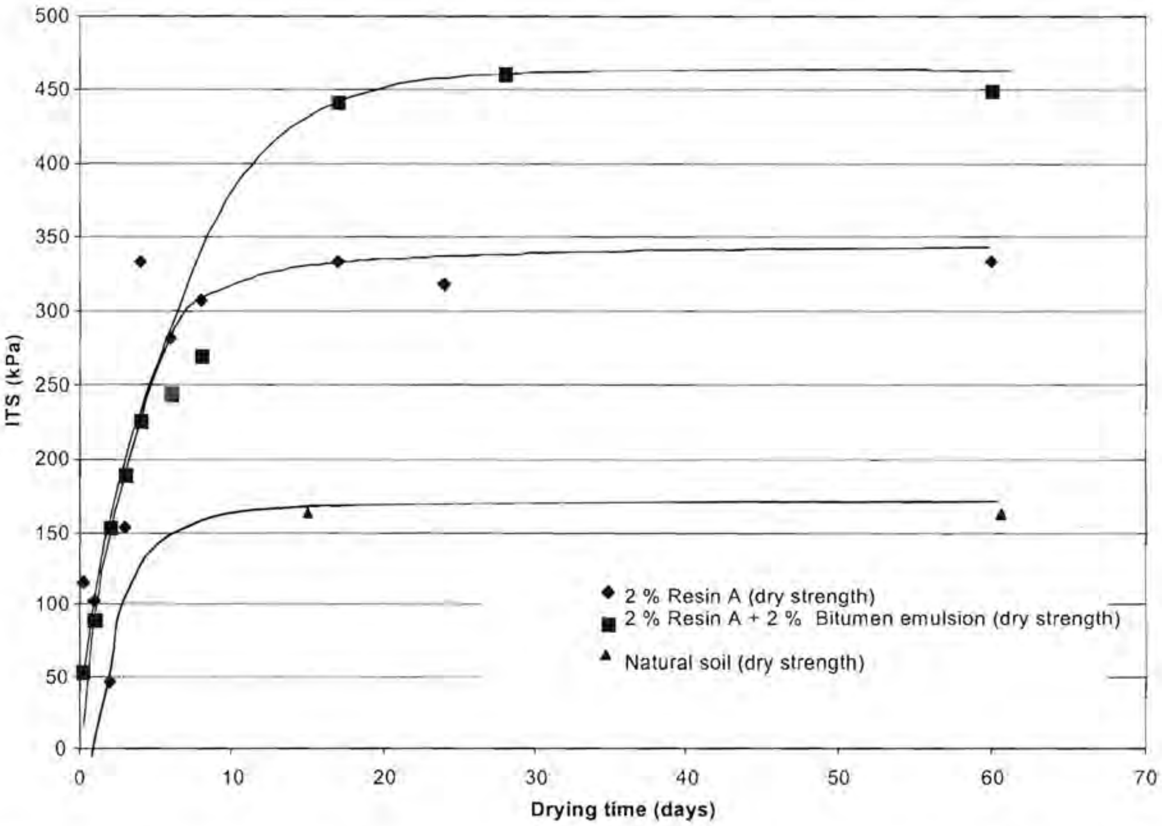

Figure 11. *The influence of bitumen emulsion addition on the time-strength dependence of the soil stabilised with Resin A*

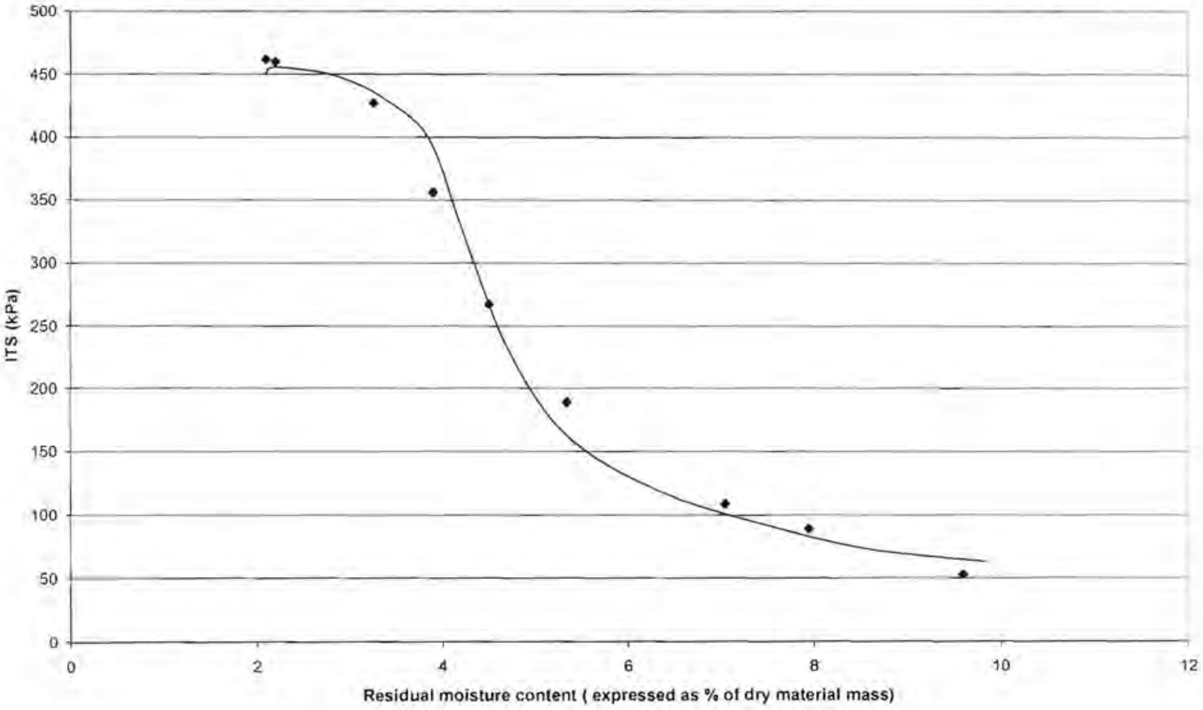

Figure 12. *The relationship between the percentage residual moisture in the sample and the dry strength increase of the soil stabilised with 2 % Resin A and 2 % bitumen emulsion*

The dependence of the strength on the moisture content of the samples can also be seen in Figure 13. In the case where the samples were covered with bags relatively little strength gain can be noted. From Figure 13 it is clear that in order to obtain any notable increase in soil strength, the moisture in the stabilised soil must be allowed to evaporate. The addition of bitumen emulsion did not have any effect on the strength increase when the samples were covered because there was no noticeable difference between the strength values of the samples treated with Resin A and those treated with Resin A and bitumen emulsion.

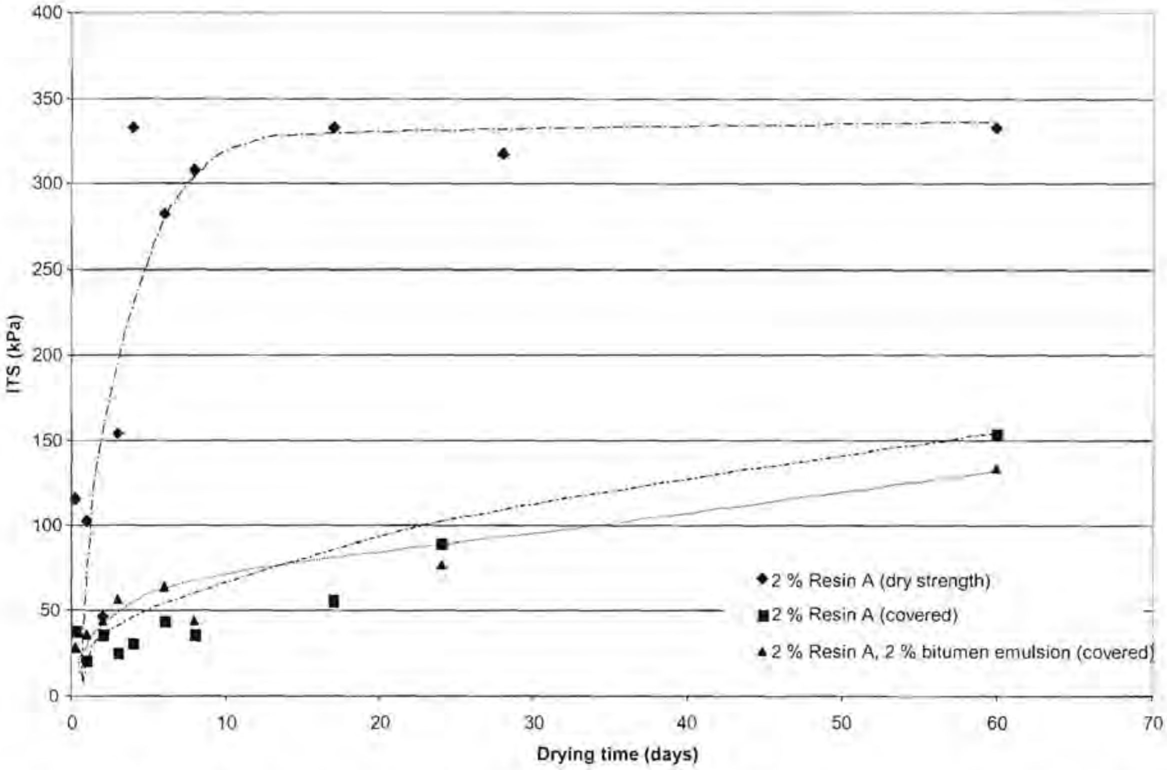

Figure 13. *The influence of restricted moisture loss on the strength of both Resin A and Resin A and bitumen emulsion stabilised soil*

In Figure 14 the influence of water ingress on the stabilised soil strength can be seen. After the samples were dried for the specific length of time, they were soaked in water for 1 hour. The samples that were not treated with bitumen emulsion failed. The untreated soil sample disintegrated in water after about 5 minutes and the soil sample treated with only 2 % bitumen and no Resin A had an ITS value of 120 kPa after being dried for 7 days and soaked for 1 hour. These can be used as control values for the other tests. It is also clear that the resin and bitumen emulsion mixture have a synergistic effect on the wet strength on the soil, and after an hour the water had not penetrated through the samples and this had a negligible effect on the strength of the samples. Only the outer layer of 3 mm thickness of the samples was wetted. From this it was decided to soak the samples for 24 hours when determining the wet strength for all the following experiments, since 1 hour was an insufficient time for the sample to become completely soaked.

As the sample, after it had dried out, took up moisture the strength decreased again. Figure 15 shows the decline in strength as the samples took up moisture while being soaked for a specific time. Since the moisture uptake is a function of time the strength decreased over time.

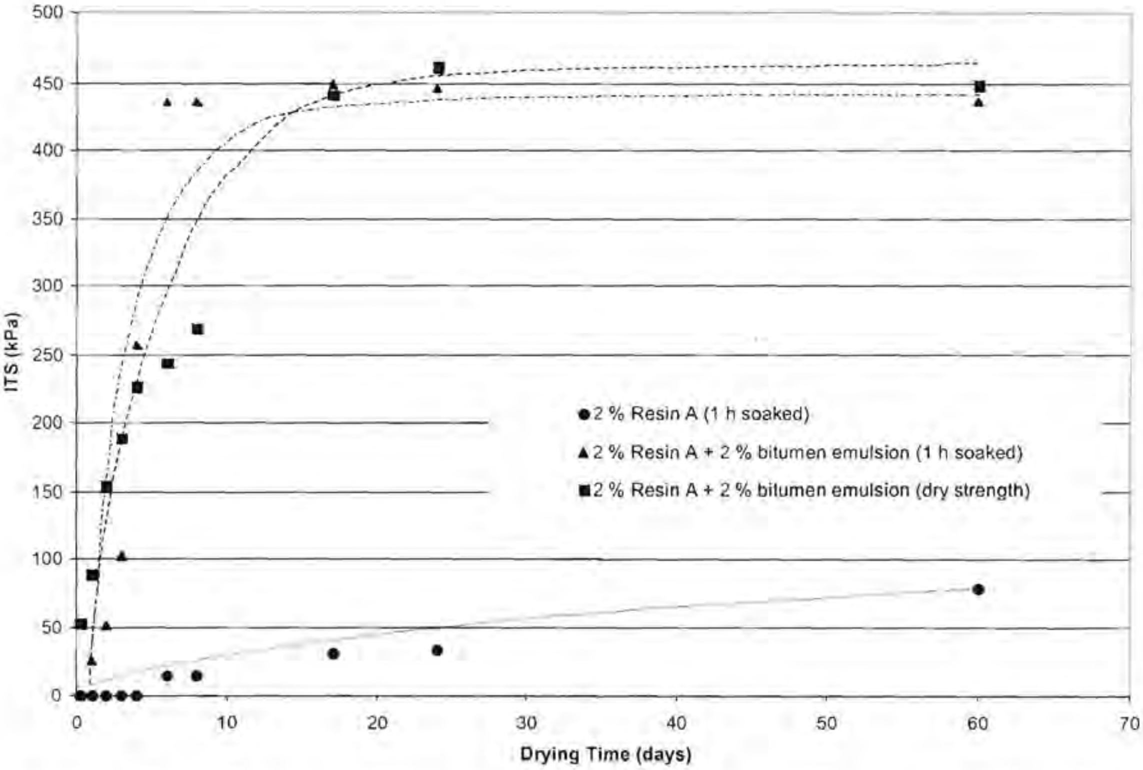

Figure 14. *The influence of bitumen emulsion addition on the wet strength of the soil stabilised with Resin A*

Resin B-stabilised soil initially had a lower strength than that stabilised with Resin A. However, with time the strengths increased to values exceeding those obtained with Resin A. Resin B with bitumen emulsion resulted in lower wet strength than the same samples treated with Resin A and bitumen emulsion. It is speculated that the reason for this can be found in the mechanism by which the stabilisation takes place. Resin B has superior adhesive properties than Resin A, and this can result in higher bonding strength. However, it is also more viscous than Resin A, and therefore has a lower surface wetting capability. The latter can lead to incomplete coating in places, making the system vulnerable to attack by water. Presumably the bitumen film provides only partial protection. Figure 16 shows these effects.

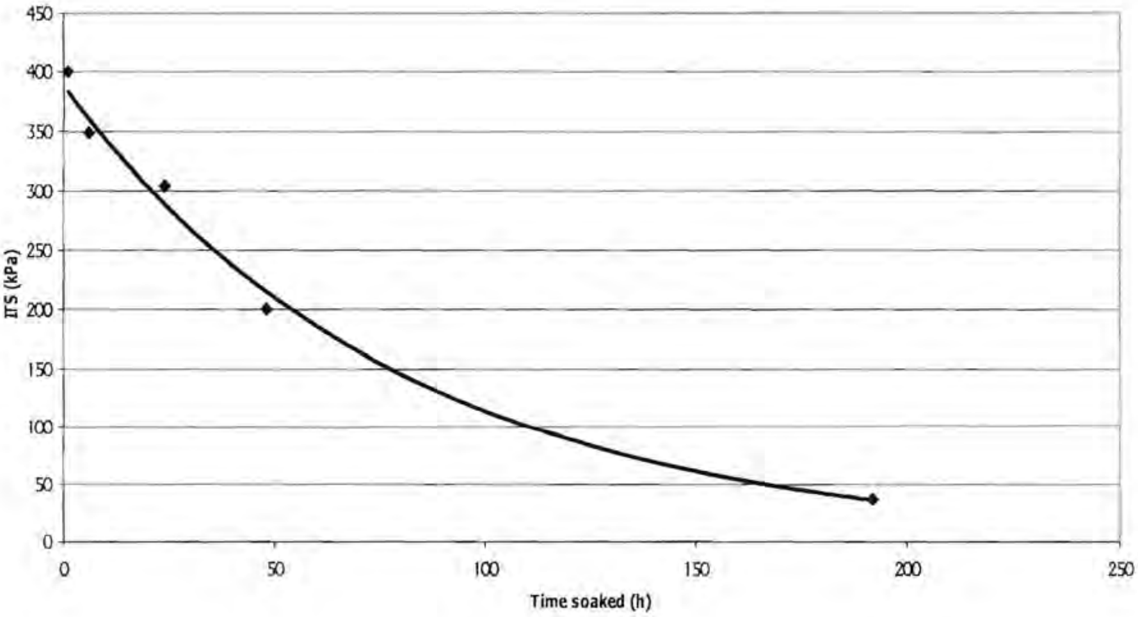

Figure 15. *The decrease of strength of soils stabilised with 2 % Resin A and 2 % bitumen as a function of time soaked. The samples were dried for 21 days before soaking.*

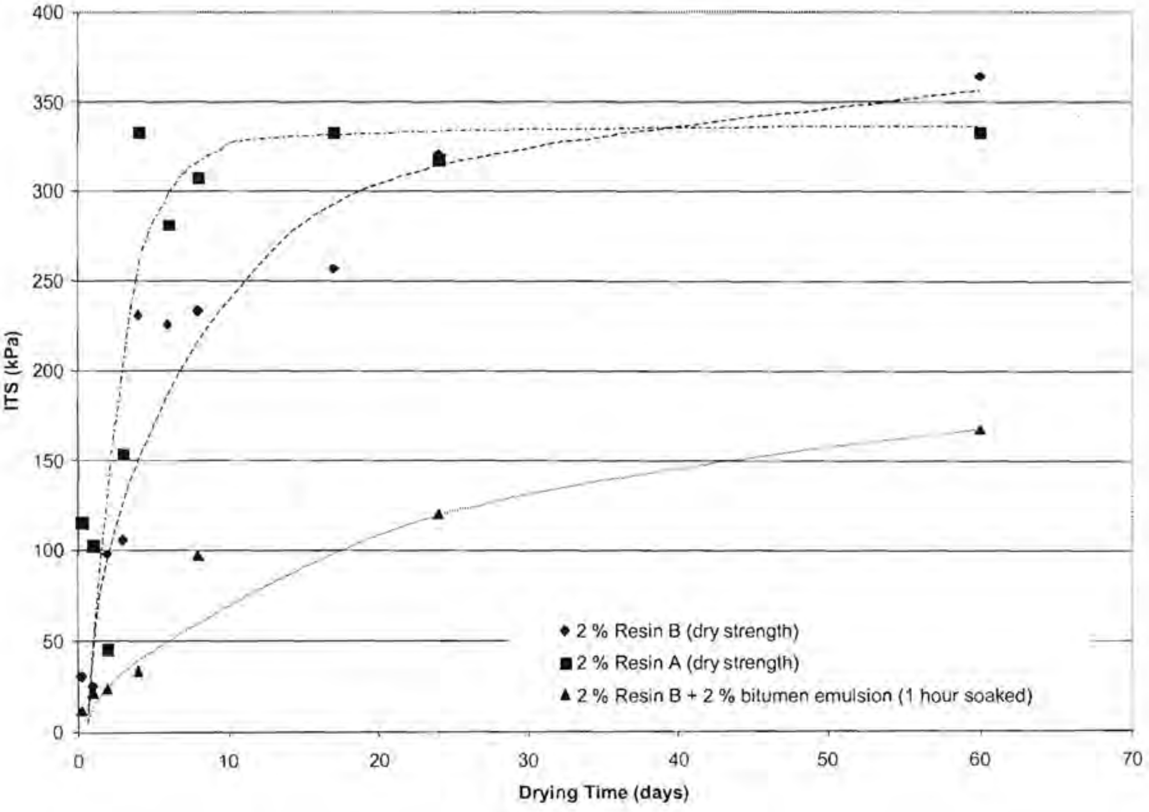

Figure 16. *The difference between soils stabilised with Resin A and Resin B as a function of time and wet strength.*

There are several advantages in using Resin B as a soil stabiliser instead of Resin A. Resin B is more environmentally friendly than Resin A. The formaldehyde in solution is stabilised by urea, with which it is partially reacted. Reduced emission of formaldehyde fumes also contributes to safer and easier handling and application.

3.10.2 THE INFLUENCE OF THE INITIAL MOISTURE CONTENT ON THE STABILISED MATERIAL

Figure 17 shows the effect of initial moisture content on the stabilised material strength. The influence of water added on the strength of the soil when stabilised with Resin A and bitumen emulsion is also shown. The values for the soil stabilised with Resin A in the presence and absence of bitumen emulsion are similar. This implies that bitumen addition does not affect the interfacial bonding characteristics of the Resin. From the statistical analysis (Appendix E) it can be concluded that the variability of the data is low (standard deviation equals 18 kPa) and that the strength generally decreases with water addition.

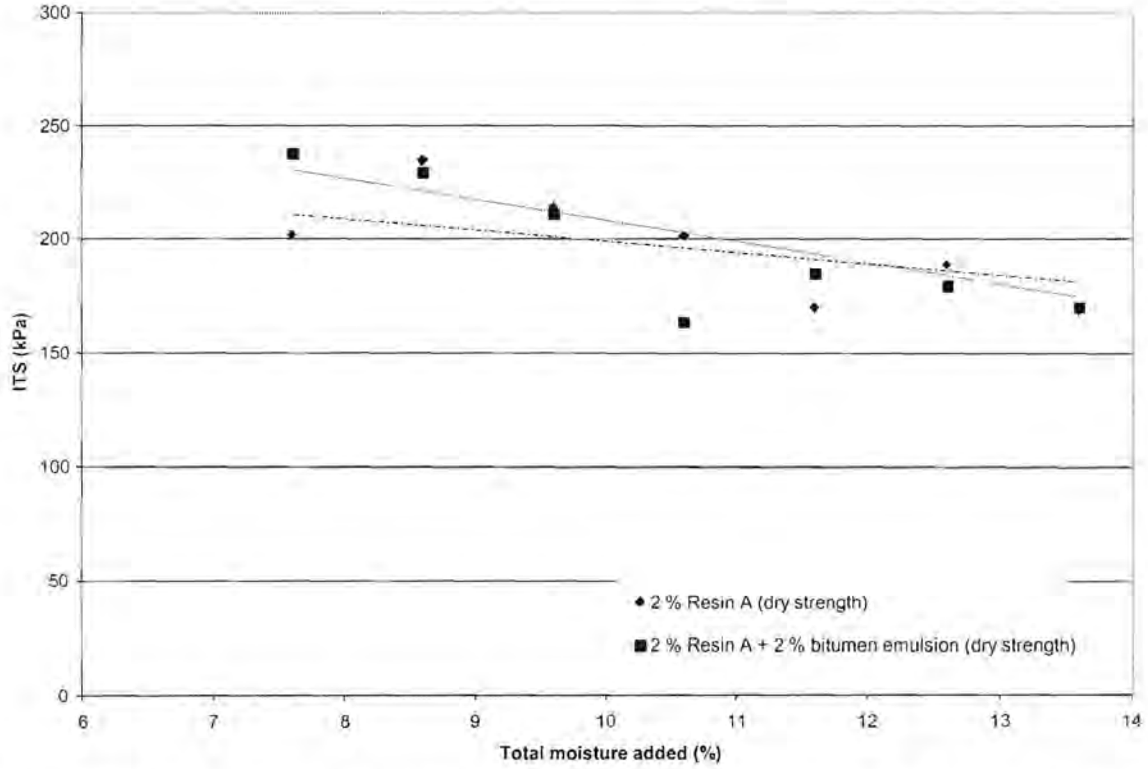

Figure 17. *Influence of the initial water content of the samples on the dry strength of the stabilised soil after 7 days of air- drying*

The strength generally declines as more water is added, although the highest density, and thus the OMC, is reached when the total moisture content is about 9 % (from Figure 18). The reason for this could be that although better compaction is reached at higher moisture levels, the moisture in the sample causes a weaker bond between the resin and the particle surfaces and after longer drying times the strength of the samples will more closely correlate with the density of the sample. It should also be noted that the California Bearing Ratio (CBR) is higher below the OMC and this could also contribute to the higher strength values at lower moisture content. From Figure 18 the trend can be observed that more moisture is lost from the sample at higher moisture levels since a higher driving force for evaporation from the sample exists.

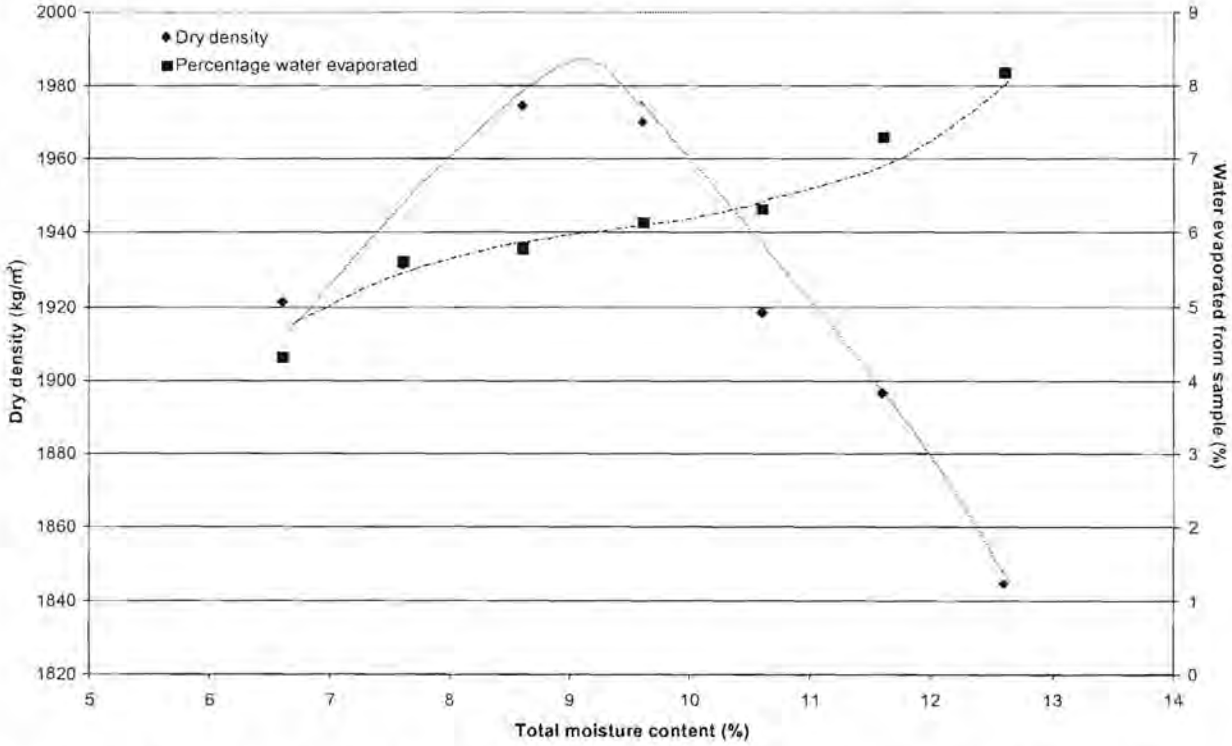

Figure 18. *Influence of the initial water content on the density of the compacted material and the amount of water evaporated after 7 days. 2 % Resin A was added.*

In Figure 19 it can be seen that the strength of most of the samples increased with drying time. The effect that any remaining moisture might have had on the soil samples was compensated for by drying them for 21 days. These results therefore give a more reliable indication of the influence of initial moisture content on the stabilised material. The wet and dry strength of the soil samples dried for 21 days had a maximum value at a total moisture content of 9 %. This is the amount of water needed to bring the sample to its optimum moisture content. At this moisture content the maximum compaction is obtained, as described previously and shown in Figure 18. Since the trend in strength correlates with the trend in density (Figure 20), it is concluded that the initial moisture content only acts as a compaction aid.

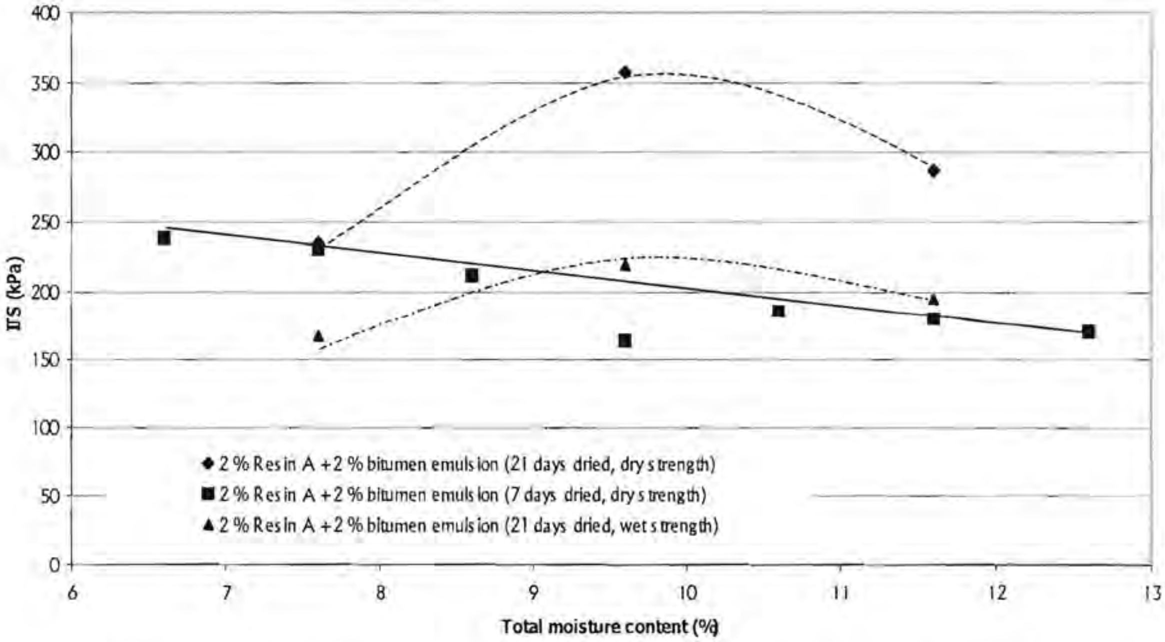

Figure 19. *Influence of the initial water content on wet and dry strength of soil stabilised with 2 % Resin A and 2 % bitumen emulsion after 7 and 21 days of drying, respectively*

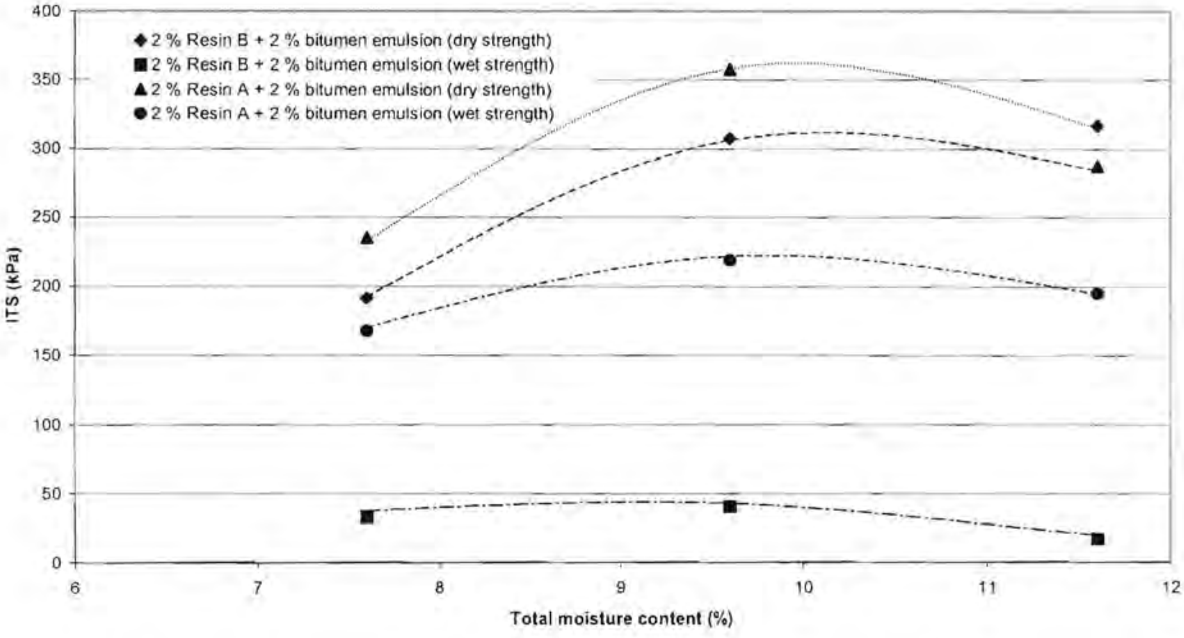

Figure 20. *Influence of the initial water content on wet and dry strength of soil stabilised with Resin A and Resin B after 21 days of drying*

From Figure 20 it can be seen that the influence of initial moisture content was approximately the same for both Resin A and Resin B stabilised soil. All the results indicate that the optimum strengths of the samples were obtained when the OMC was reached. Samples stabilised with Resin A and Resin B had about the same dry strength values, but when soaked in water for 24 hours the samples treated with Resin B had a much lower wet strength. While Resin B is marginally effective as a soil stabiliser in wet conditions, Resin A provides much higher wet strength values.

3.10.3 THE EFFECT OF COMPACTION ON THE STRENGTH OF THE STABILISED SOIL

The strength of the stabilised material increased as the amount of compaction increased and follows the trend observed for the change in density (Figure 21). The density increased as the compaction increased, but approached an asymptotic value.

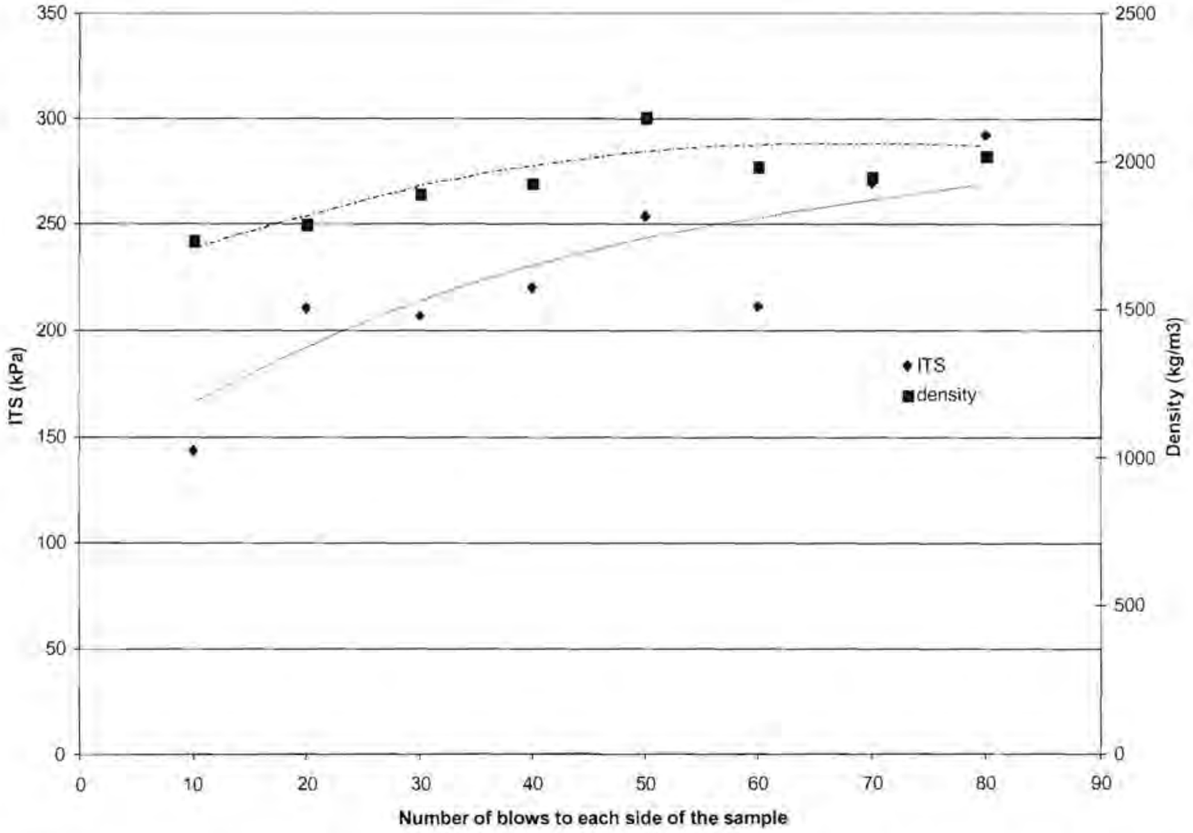

Figure 21. *The influence of compaction on the density and strength of the stabilised soil after 7 days of drying. 2 % Resin A and 2 % bitumen emulsion were added.*

Better packing of the soil particles probably resulted in the increased strength. Since the particles were more closely spaced the resin bridges between them were shorter and thus stronger. Coating of the particles was improved because the voids were smaller and less resin was required to fill them. The resin and soil were more intimately bound together and this means that the wet strength of the stabilised material could also be improved since water penetration to the interface between the resin and the soil particle surfaces was greatly reduced at higher compaction.

3.10.4 THE EFFECT OF RESIN DOSAGE ON STABILISATION

Figure 22 shows that bitumen emulsion, on its own, also had a stabilising effect on the soil samples. However, addition of a small amount of resin had a destabilising effect and the strength decreased. At higher dosage levels, both the wet and dry strength of the samples increased as the amount of Resin A was increased (Figure 22), up to an upper limit. The relatively low dosage level at which the limit was reached is typical for surface-active agents.

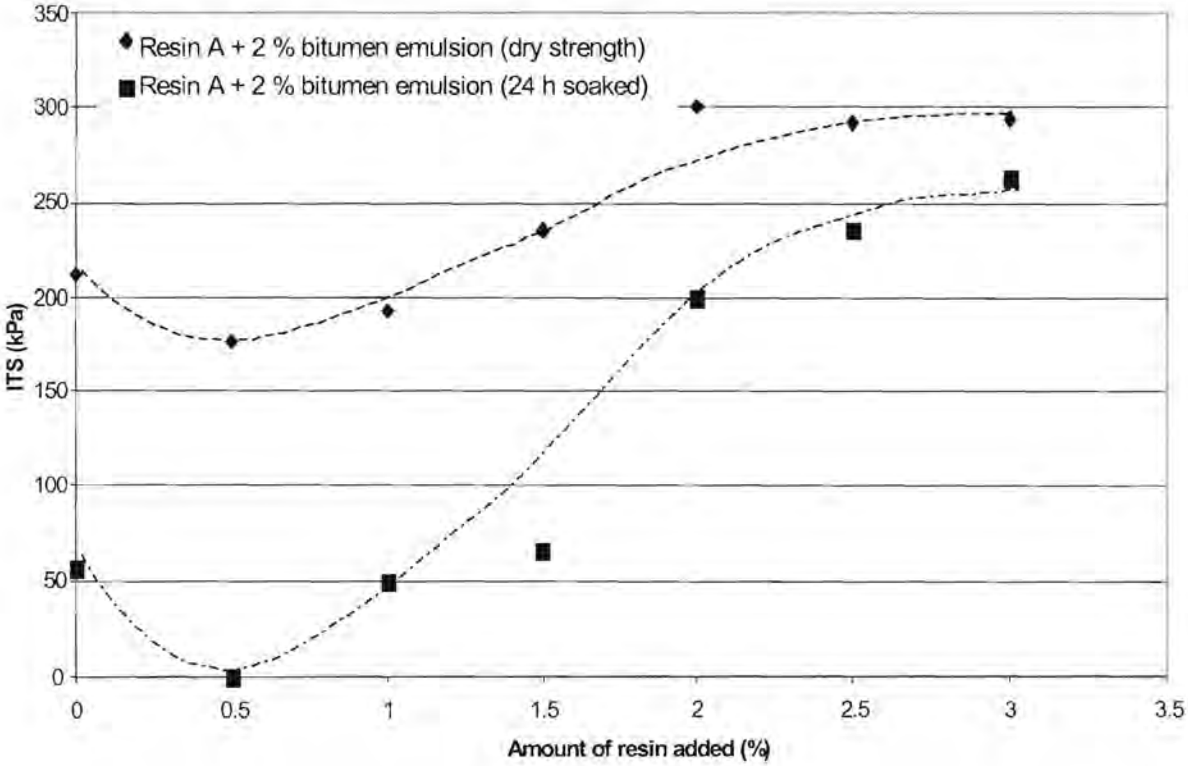

Figure 22. *The effect of increasing resin dosage on the stabilised soil strength after 7 days of drying*

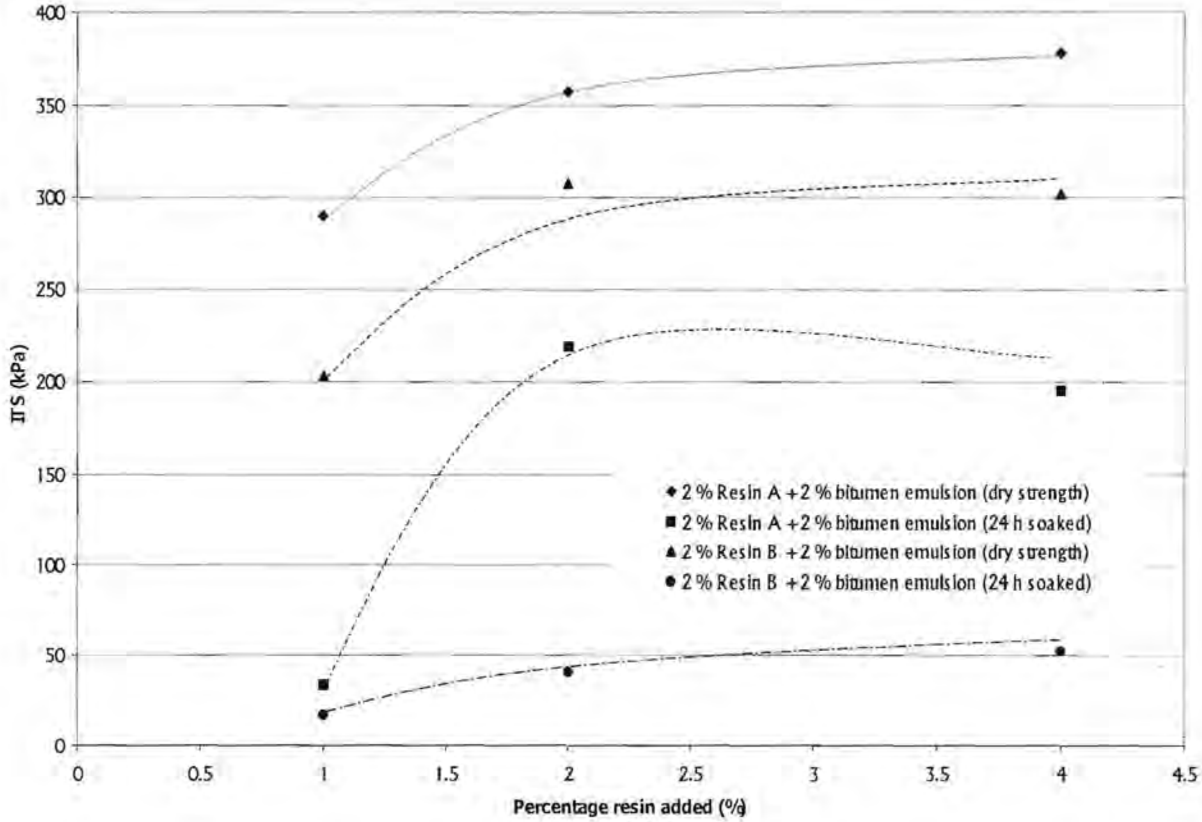

Figure 23. *The effect of increasing Resin A and Resin B dosage on the stabilised soil strength after 21 days of drying*

From Figure 23 it can be seen that both the wet and dry strength of the stabilised soil increased with resin dosage. Resin B resulted in lower dry strength values as compared to samples treated with Resin A, with very low wet strengths. The strengths of the samples treated with Resin A and dried for 21 days were generally higher than those dried for only 7 days, but in both cases it is clear that the strength increase reached an asymptote as more resin was added.

3.10.5 THE INFLUENCE OF THE BITUMEN DOSAGE ON STABILISATION

From Figure 24 it can be seen that the dry strength of the soil stabilised with 2 % of Resin A was not noticeably influenced by an increase in bitumen emulsion dosage. However, higher bitumen emulsion dosages resulted in better retention of strength following soaking. The resin network is protected from water ingress and this is verified by noting the decrease in water uptake of the soaked samples at higher bitumen dosages (see Appendix F). At 5 % bitumen emulsion dosage the sample was particularly stable in water. Note, however, that the lower moisture permeability of the samples at higher bitumen emulsion dosages, will affect the required drying times accordingly.

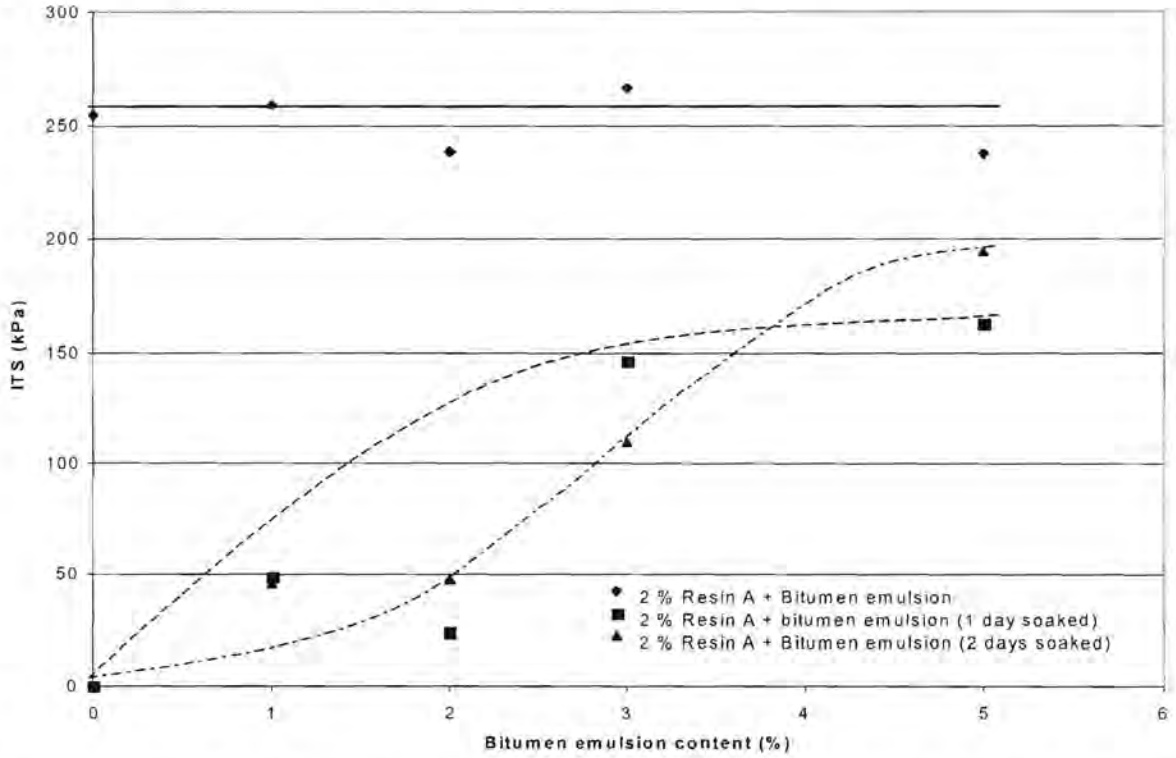

Figure 24. *The effect of bitumen emulsion dosage on soil stabilised with Resin A. Samples were dried for 7 days before testing.*

Figure 25 shows the increase in wet strength for samples treated with Resin A and Resin B as the bitumen emulsion dosage increased. Again, as in Figure 24, the bitumen dosage did not have a noticeable influence on the dry strength of both Resin A and Resin B stabilised samples.. The longer drying time required at a high bitumen content can explain the dramatic increase in wet strength of the samples after 7 days of drying, as compared to the lower increase in wet strength observed after 21 days of drying. Again the use of Resin B resulted in lower wet strength values when compared to Resin A. It should also be kept in mind that these trends are valid for the specific soil investigated. There might be differences in other types of soil. In addition the compression strength may be affected differently than the tensile strength.

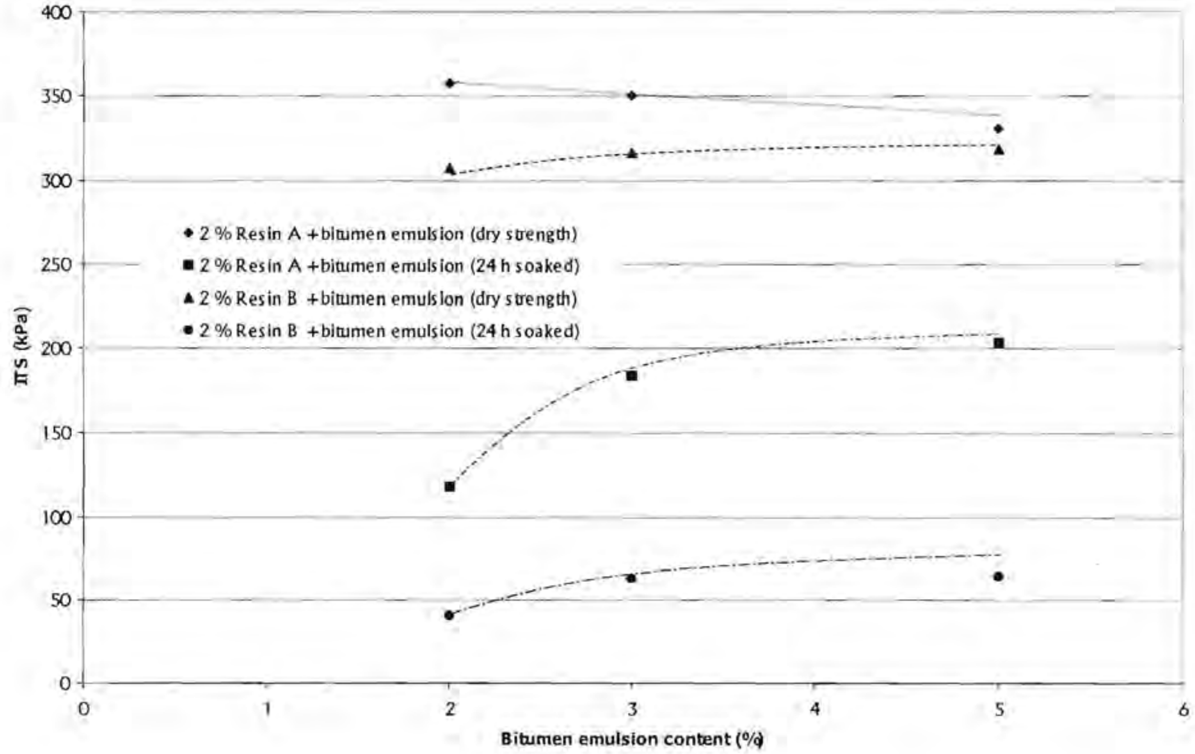

Figure 25. *The effect of bitumen emulsion dosage on the Resin A and Resin B stabilised soil strength. Samples were dried for 21 days before testing.*

3.10.6 THE INFLUENCE OF PH ON STABILISATION

The strength of the stabilised soil increased as the reaction pH was lowered from 7 to about 4 and this increase was enhanced by the addition of bitumen emulsion. At higher pH the strength decrease reached a limit, which was the strength of the soil stabilised with bitumen.

The measured mass loss of the soil sample following complete drying showed that the resin did cure. Curing at high pH results in products that are brittle and weak, with large pores, explaining the poor soil strength obtained.

At lower pH longer chain, crosslinked products form, which are more effective in binding the soil particles together. At pH less than 3.5 the condensation reaction proceeded too fast and caused the resin to set even before it could be applied to the soil.

The synergy between Resin A and the bitumen emulsion can be as a result of hydrogen or ionic bonds between the resin and the bitumen, which is facilitated at lower pH. It can also be seen from Figure 26 that the reaction pH and thus the composition and properties of the resin network did not influence the wet strength since all the wet strength values were proportional to the dry strength values.

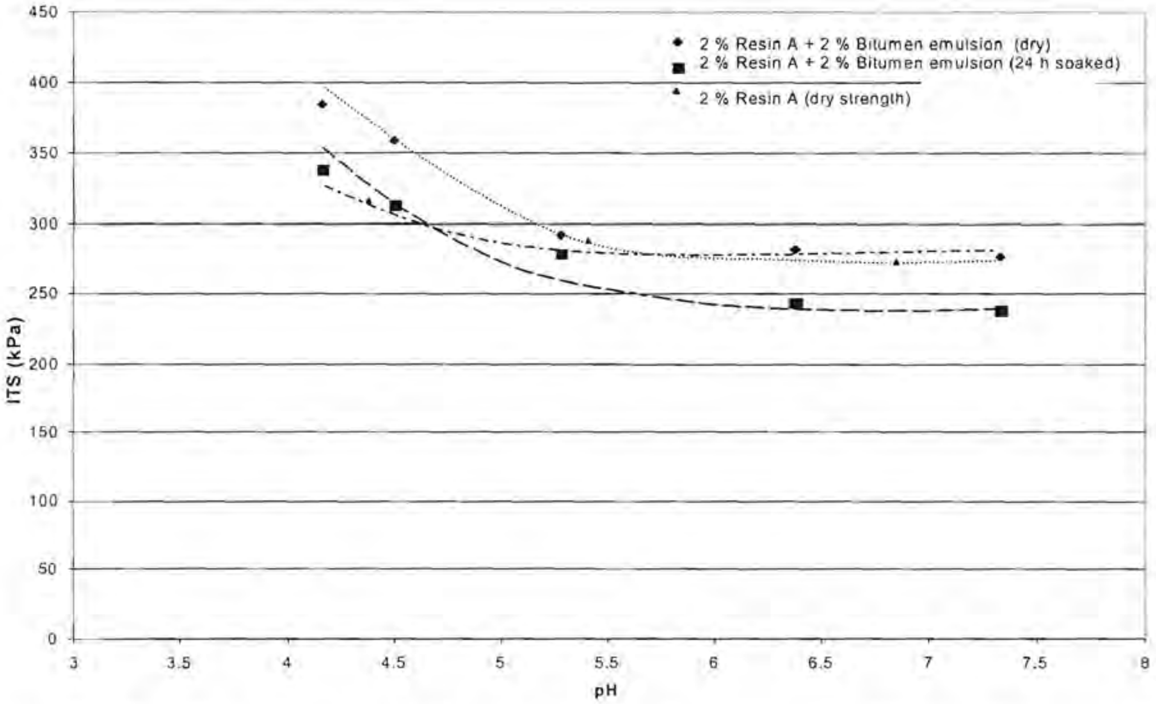

Figure 26. *The effect of reaction pH on the stabilised soil strength. The samples were dried for 7 days before testing.*

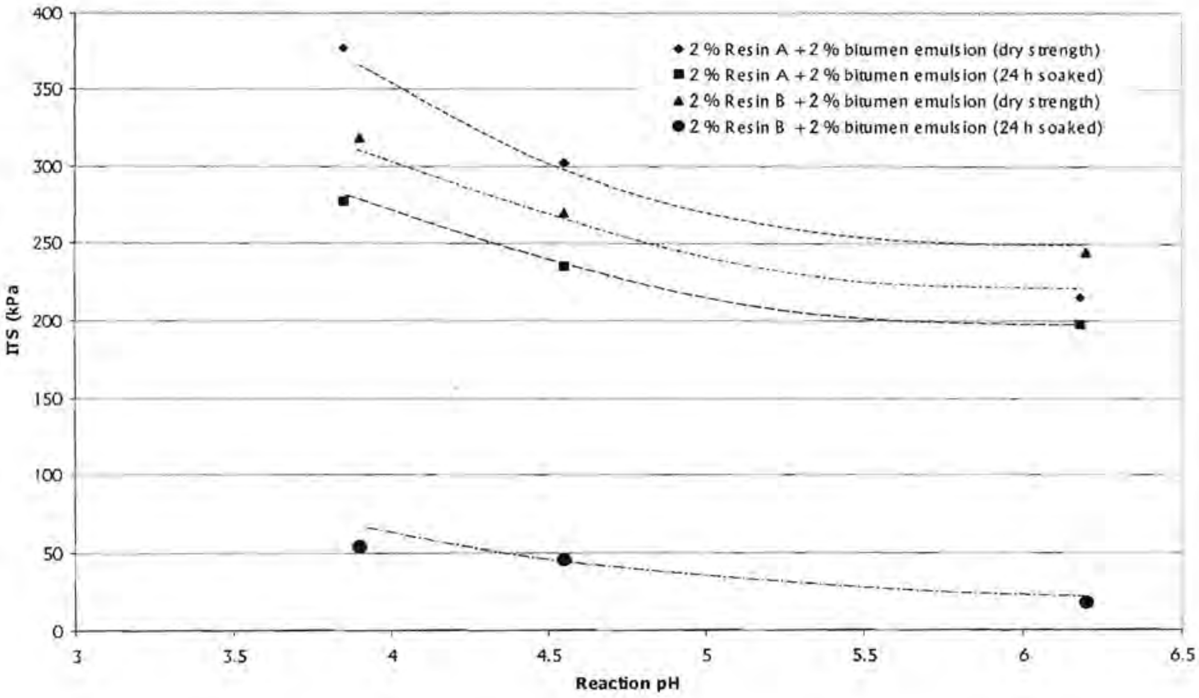

Figure 27. *The effect of reaction pH on the strength of soil stabilised with Resin A and Resin B. The samples were dried for 21days before testing.*

The same trend observed in Figure 26 is evident in Figure 27, when the samples were dried for 21 days. The wet en dry strength of the samples increased as the pH was lowered. The wet strength of samples treated with Resin A was proportional to the dry strength and from this it is concluded that only the water ingress played a role in the wet strength of the sample. The strengths for drying times of 7 and 21 days, were similar. This can be attributed to the fact that in both cases about the same amount of water was evaporated, implying similar moisture contents (see Appendix F). The Resin B dry strength values were again slightly lower than those for Resin A, but the soil strength dramatically reduced when soaked in water.

3.10.7 THE INFLUENCE OF REAGENT RATIO ON STABILISATION

At lower formaldehyde to urea ratios the formation of high molecular weight products is increased under acidic conditions. At very low ratios there is insufficient formaldehyde to complete the condensation reactions and this results in a network with weak interbond strength and little crosslinking. At very high ratios the solid content decreases and a liquid resin results. From Figure 28 it can be seen that there was an optimum value for the formaldehyde to urea ratio at which a high molecular weight, crosslinked resin network was formed. Since the strength of the wet samples was proportional to the strength of the dry samples, it can be concluded that the molar ratio did not have a significant effect on the water resistance of the resin.

At a molar ratio of 2:1 the strength of the stabilised soil was higher than that of the natural soil (about 200 kPa), but at lower and higher values the resulting resin proved ineffective as a soil stabiliser.

Figure 29 confirms the trends observed in Figure 28. In all the cases the strength (both wet and dry strength) of the samples reached an optimum value at formaldehyde to urea molar ratio of 2:1. The average strength in Figure 29 is higher than in Figure 28, as expected, as a result of the strength increase as more water evaporated from the samples. Samples treated with Resin A and Resin B gave generally the same dry strength values, but the wet strength of Resin B was higher.

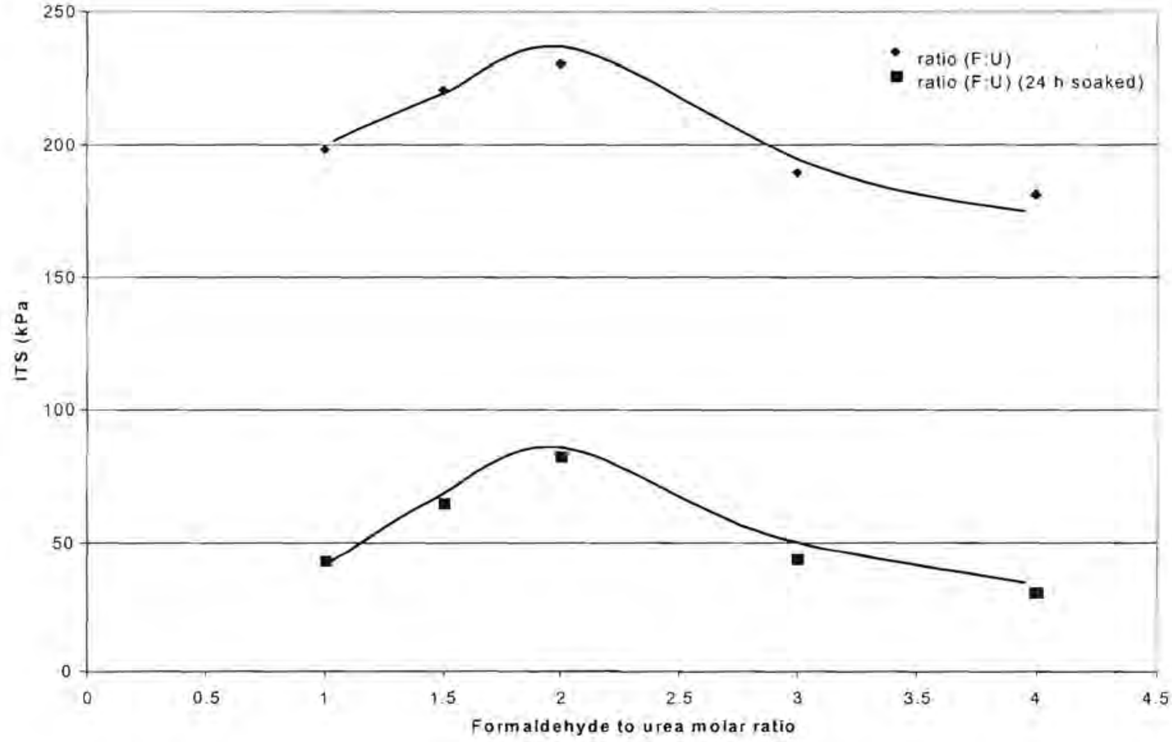

Figure 28. *The effect of formaldehyde to urea molar ratio of Resin A on the stabilised soil strength. The samples were dried for 7 days.*

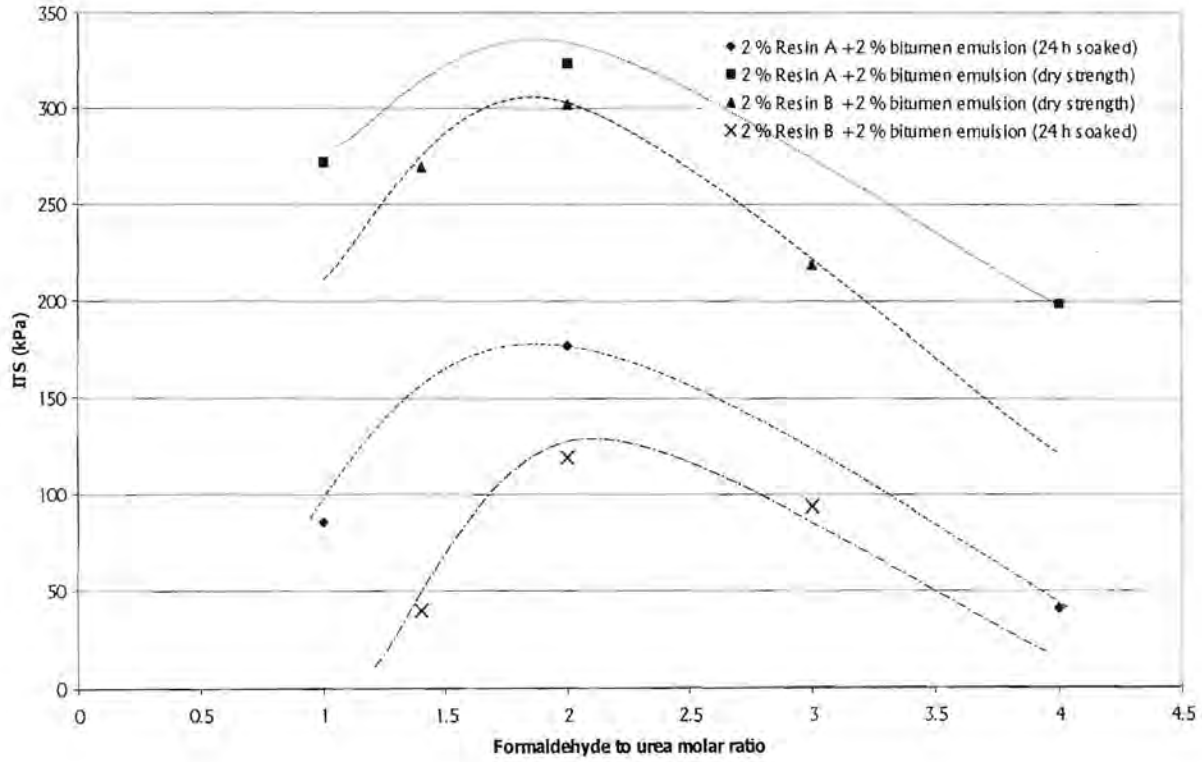

Figure 29. *The effect of formaldehyde to urea molar ratio of Resin A and Resin B on the stabilised soil strength. The samples were dried for 21 days*

3.10.8 THE EFFECT OF THE TYPE OF BITUMEN EMULSION

Table 11 shows a summary of the results obtained to indicate the effect of different types of bitumen emulsion on the effectiveness of Resin A and Resin B as soil stabilisers. From the Table it can be seen that the type of bitumen emulsion did not significantly affect the dry strength. However, the type of bitumen emulsion influenced the wet strength, with only the anionic bitumen emulsion, SS 60, proving effective. Both types of the cationic bitumen emulsion lead to failure of the samples when soaked in water. This can be attributed to the pH of the soil used. Anionic bitumen emulsion will associate more closely with positively charged soil particles, while cationic bitumen emulsion will be attracted by negatively charged soil particles. This specific soil had a pH of 6,52, which means that it was a slightly positively charged soil and this could explain why anionic bitumen emulsion had a better stabilising effect on the soil. It must be kept in mind that the tests were conducted only with one type of soil, and that different results may be obtained when a different soil is used.

Table 11. *The effect of different types of bitumen emulsion on the strength of soil treated with Resin A and Resin B. 21 days were allowed for drying of the samples.*

Resin used	Bitumen emulsion	Dry strength (kPa)	Wet strength (kPa)
2 % Resin A	2 % SS 60	357,68	219,14
	2 % KMS 60	269,74	9,90
	2 % KRS 60	316,76	0,00
2 % Resin B	2 % SS 60	236,77	39,59
	2 % KMS 60	282,11	0,00
	2 % KRS 60	252,41	0,00

3.10.9 THE EFFECT OF PORTLAND CEMENT ADDITION ON STABILISATION

Figure 30 shows the dramatic effect that Resin A has on the strength of soil stabilised with cement. Even though the stabilised samples were in the humidity chamber for 7 days, they still had high wet and dry strength values (as compared to the low values when only Resin A was used). There existed a synergistic relationship between Resin A and cement. The soil treated with Resin A needs to be dried before it reaches its ultimate strength, while water needs to be added to soil stabilised with cement. Separately the Resin A in moist conditions and the cement with that specific soil are not effective as soil stabilisers, but together they significantly improve the wet and dry strength of the soil.

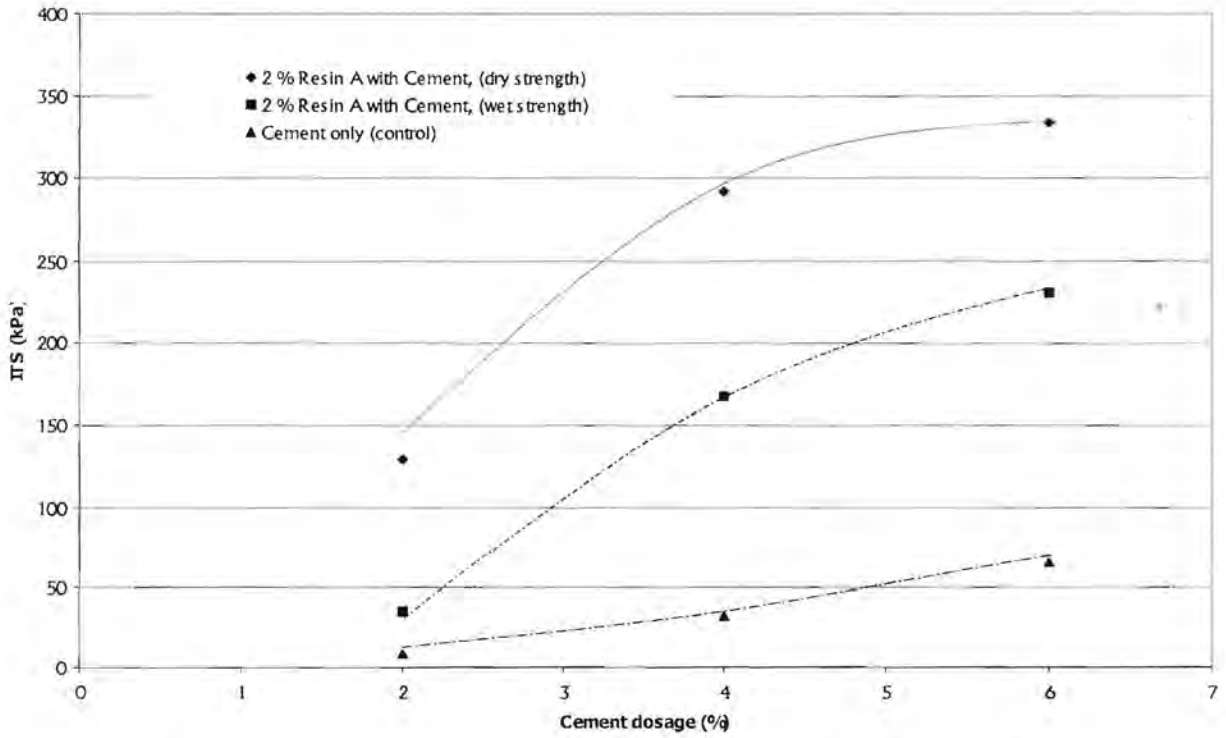

Figure 30. *The effect of Resin A addition to cement stabilisation of soils. The samples were prepared as prescribed in TMH1, Method A13T and placed in humidity chamber for 7 days.*

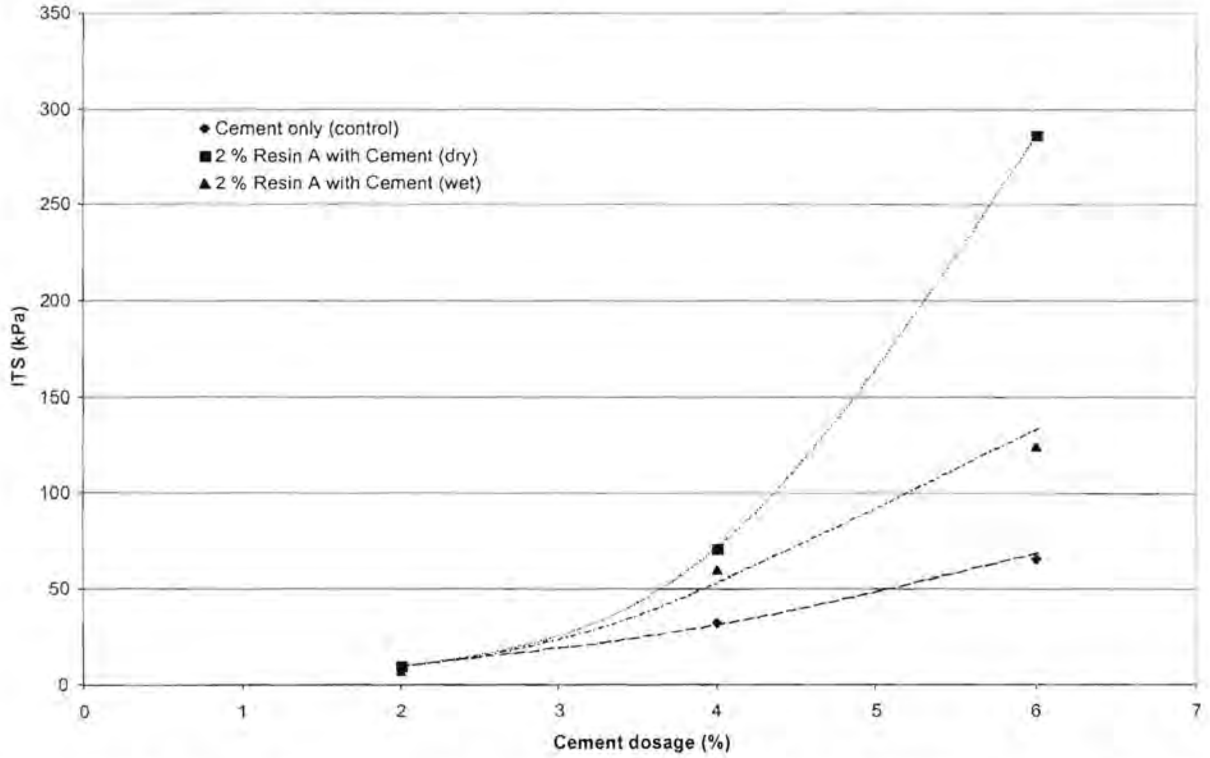

Figure 31. *The effect of cement on the wet and dry strength of soil treated with 2 % Resin A. The samples were dried for 7 days.*

The wet and dry strength of the soil increased as the cement dosage increased. When cement was added to soil stabilised with Resin A, it lead to high initial wet and dry strength. This may be due to the fact that cement used the water added to the sample, while for the Resin A to be effective the moisture needed to be removed. So cement can be added to Resin A treated samples where high initial strength is required, or when the Resin A treated soil is prevented from drying. At higher dosages there might exist an antagonistic effect when the resin and cement start to oppose each other. Figure 31 shows the effect of cement on the samples prepared normally. It shows that the strengths are generally higher, as can be expected.

It should again be noted that these results apply to the soil tested. Different results are possible if other soils are tested, especially more sandy soils. The results may also be different when the compression strength, rather than the tensile strength, is measured. Also, bitumen emulsions were not used in any of these experiments. When bitumen emulsion is used in the presence of cement, it will break sooner.

3.10.10 THE EFFECT OF LIME ADDITION ON STABILISATION

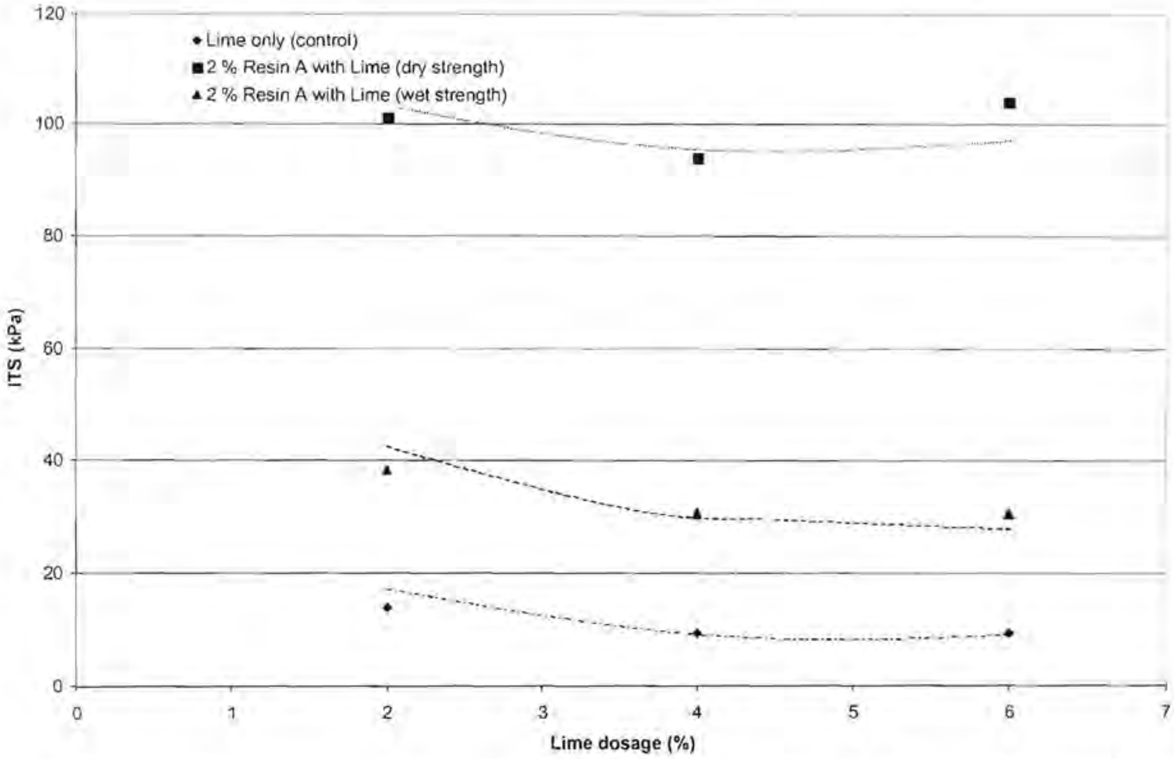

Figure 32. *The effect of lime on the wet and dry strength of soil treated with 2 % Resin A. The samples were dried for 7 days.*

Figure 32 shows that addition of lime had no obvious beneficial effect on the strength of the soil treated with Resin A. Addition of lime to Resin A resulted in higher strength values compared to lime alone. However, they were lower than those for Resin A on its own. Thus, lime lowered the wet and dry strength of the treated soil. Again this was specific to the particular soil used. In more clayey soils, the addition of lime might lead to improved results.

3.10.11 THE INFLUENCE OF ADDITIVES AND RESIN PREPARATION ON STABILISATION

The effectiveness of Resin A as a soil binder is highly dependent on the pH during reaction and thus the amount and composition of the acid catalyst. Catalyst modifiers can include sugar, which can form both hemiacetals and more stable methylene ethers. These products are water-resistant, but it should be noted that up to 5 moles of formaldehyde could be absorbed by each mole of sugar. Table 12 summarises the results obtained from the initial experiments.

Table 12. *The effect of modifiers and colourants on the performance of 2 % Resin A (after 7 days drying time)*

Acid	Additive	ITS (kPa)
Citric acid and sugar	None	274
Citric acid and sugar	Colourant (3 drops)	257
Citric acid and sugar	Bitumen	403
Citric acid and sugar	5 g $(NH_4)_2SO_4$	267
Citric acid	None	276

It can be seen that adding sugar to the citric acid did not significantly influence the acid catalyst, while adding colourant and $(NH_4)_2SO_4$ slightly lowered the indirect tensile strength of the stabilised material. The difference in values could be due to experimental variation and do not necessarily reflect a direct influence of the modifier.

Typical strengths obtained with bitumen emulsion and citric acid were of the order of 360 kPa (see Figures 19, 20, 23 and 25). The strength was significantly increased (from 360 to 403 kPa) when adding sugar to the acid catalyst as shown in Table 12. This may be the result of the sugar reacting with the resin.

3.11 CONCLUSIONS AND RECOMMENDATIONS

Soils stabilised with Resin with or without bitumen emulsion had the same initial increase in strength, but the addition of bitumen resulted in a higher maximum strength of the stabilised material. The maximum strength was reached after most of the water had evaporated from the sample (about 17 to 24 days), after which it remained constant. The strength of the stabilised material increased as the water evaporated out of the sample. In order to obtain any notable increase in soil strength, the moisture in the stabilised soil must be allowed to escape.

The stabilised samples that were not treated with bitumen emulsion inevitably failed in water. Combinations of resin and bitumen showed a synergistic effect with respect to the wet strength of the soil. However, the strength of the stabilised material decreased as water was taken up during soaking.

Resin B stabilised soil initially had a lower strength than that stabilised with Resin A. However, ultimate values were higher than those obtained with Resin A. Addition of bitumen emulsion was more effective in Resin A for strength retention during soaking.

Maximum strengths of the treated soils were attained when the required amount of water was added to bring the soil to its OMC. This was also true when bitumen emulsion was added to the resins.

The strength of the stabilised material increased with the amount of compaction up to a limit. It correlated well with the change in soil density. The strength increase is attributed to the more efficient packing of the soil particles. The resin and soil are more intimately bound together and this means that the wet strength of the stabilised material was also improved. Water penetration is significantly reduced at higher compaction levels.

Both the wet and dry strength of the stabilised material increased up to a plateau level as the resin dosage was increased. Adding increasing amounts of resin to soil containing 2 % bitumen showed a more complex behaviour. When just a small amount of resin was added, a lower strength was observed. However, at higher resin dosage levels the strength recovered. In general, Resins A and B resulted in the same dry strengths. On the other hand, Resin B bitumen formulations showed very poor wet strength values in contrast with the results for Resin A.

The strength of the stabilised soil was increased as the reaction pH was lowered from 7 to about 4 and this increase was enhanced by the addition of bitumen emulsion. At higher pH the strength decrease reached a limit, which was about the strength of the soil stabilised with bitumen alone. Again both Resin A and Resin B resulted in the same dry strength values, but when soaked the samples treated with Resin B retained very little strength.

The dry strength of the stabilised material was not influenced by an increase in bitumen emulsion dosage, although there was a dramatic increase in the wet strength of Resin A treated soils. This might be the result of a pore blocking mechanism for the protection of the resin network against water. Resin B treated soils were not appreciably influenced by bitumen addition and had very low wet strength values.

At a molar ratio of 2:1 the dry strength of the Resin A and Resin B stabilised soil reached a maximum value. At higher molar ratios the wet strength of soil treated with Resin B was improved. This could indicate that Resin B did not work effectively in wet conditions in any of the experiments because the desired degree of polymerisation was not achieved, owing to an insufficient amount of formaldehyde available for bridging the addition products.

All the bitumen emulsions resulted in adequate dry strength but most failed when soaked in water. Only the anionic bitumen emulsion (SS60) gave satisfactory wet strengths.

The addition of cement to Resin A treated soil resulted in higher initial wet and dry strengths. Resin A also increased the strength gained from cement stabilisation of the soil. When Resin A has to be applied in wet conditions the addition of cement can thus be beneficial.

The strength of the resin with bitumen was significantly increased by adding sugar to the citric acid, but none of the other additives tested had a positive effect on the effectiveness of Resin A as a soil binder. Resin A increased the strength obtained from lime stabilisation, but the addition of lime lead to lowering of the Resin A strength.

Resin B is an effective replacement for Resin A only when the dry strength is considered. It is recommended that creep, erodibility, as well as compression strength tests, be carried out to augment the results obtained here.

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CHAPTER 4

THE SOIL ORGANIC CONTENT

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4.1 INTRODUCTION

Humic substances are the most abundant of the naturally occurring organic macromolecules and are major components of the organic matter in humified soils (Wilson, Gray, *et al.*, 1991). They are also among the least understood materials (Davies, Ghabbour and Khairy, 1998). Because of the wide variety of precursors in a broad spectrum of biological and chemical processes in soil and because of the heterogeneity of the substrates, the formation and composition of humic substances are very complex.

Not only do soils differ in terms of their origin and physical characteristics e.g. their particle size distribution, but also in terms of their organic content. Soils from different locations have different constituent proportions of organic content, resulting from different sources and reaction conditions (Davies, Ghabbour and Khairy, 1998). These organic macromolecules dominate soil properties even at low concentrations (Davies, Ghabbour and Khairy, 1998).

The aim of this part of the study is to make a preliminary experimental determination as to whether the organic content of the soil affects soil stabilisation. The influence of organic matter on urea-formaldehyde stabilised soil was investigated by using two different materials (a washed sand and the brown shale described in Appendix D). The organic content of the soil was artificially controlled by adding either a lignosulphonate or formaldehyde derived formose. The effect of removing the organic part of the soil studied in this investigation was also considered.

4.2 THE SOIL ORGANIC CONTENT

Soil organic matter (SOM) refers to the non-living components of the organic material found in soils and sediments. The SOM is a heterogeneous mixture of unaltered materials such as fresh debris and untransformed older material, and transformed products, or humic substances (Davies, Ghabbour and Khairy, 1998; Kumada, 1987).

Humic substances are classified by their pH dependent aqueous solubility, which depends on the molecular mass, chemical composition and physical state (Davies, Ghabbour and Khairy, 1998). They are classified into 3 major groups:

- **Fulvic acids**. Fulvic acids are the smallest constituents of humic substances with $M_w <$ 5000 Daltons. They are part of the dissolved organic matter and are soluble at all pH values.
- **Humic acids**. These are highly functionalised biopolymers that can stabilise soils. Their adsorption on clays and minerals decreases their solubility at a specific pH.
- **Humins**. Humins are insoluble at all pH values. They are "coal-like" materials that have an aromatic character. They are weaker metal binders and water retainers than fulvic or humic acids.

Organic substances that can contribute to the humic substances in soils are the following:

- Fats and similar substances
- Carbohydrates and related substances (mono- and disaccharides, pentoses and hexoses, cellulose, hemicellulose and pectins etc.)
- Proteins and their derivates, amines and amino-acids
- Lignins and their derivates
- Tannic substances in simple and condensed form
- Resins and terpenes

The amount of humic substances in soils is determined by the amount of organic material present and its rate of decomposition, the soil texture and climatic conditions (Beck, Jones *et al.*, 1993). For any given soil type and land use the concentration of humic substances tends to an equilibrium value.

The major effects of humic substances on soils are the following (Beck, Jones *et al.*, 1993):

- Formation and stabilisation of soil aggregate structures
- Retention of plant nutrients by ion-exchange processes
- Enhancement of the buffering capacity of soils
- Improvement of water retention by soils

4.3 EXPERIMENTAL PROGRAMME

For the experiments an 18 % formose solution was used to act as an artificial soil organic compound. The formose solution was prepared by condensing a formaldehyde solution in an alkaline medium (Weiss, *et al.,* 1980). 100 g water was added to 100 g of a 37 % formaldehyde solution and heated to boiling point. 1 g of $Ca(OH)_2$ was added to the boiling mixture every 15 to 20 minutes until a total of 9 g was added. The reaction mixture turned dark brown after 2,5 hours. After 6 hours the mixture was allowed to cool to room temperature. Lignosulphonate, supplied by Lignotech S.A., P. O. Box 743, Umkomaas, 4170, was also used to augment the results obtained with the formose.

In the experiments urea-formaldehyde resin was used as a soil stabilising agent. Resin A was prepared from 1,67 gram Formalin per gram urea. The liquid resin was prepared by adding the urea and required water and the mixture was shaken to ensure that the urea was properly dissolved before the experiment was continued. The source of formaldehyde was then added. After that the organic additive followed, as well as an adequate amount of water to bring the total moisture content to that of the OMC of the soil (see Chapter 3). Citric acid was used as the acid catalyst to reduce the pH of the whole mixture to 4,5. The mixture was then added to 1 kg soil in the required amount and mixed thoroughly to ensure a good distribution of the reagents throughout the soil phase. The sample was then compacted by using the Marshall apparatus (as described in Chapter 3) and left to air-dry. In all cases only the dry strength was determined.

The same brown shale was used as in the previous experiments (with properties as outlined in Appendix D), as well as a well graded, washed sand. All the experiments were carried out at constant temperature of 23 °C and an atmospheric pressure of about 85 kPa. In each experiment the temperature, pH, mass and height of the sample were noted, since these are important factors in the investigation.

In the first experiment the plain soil (already containing naturally occurring humic substances) was used. 1, 3 and 5 % (by weight of the dry soil) of the formose solution was added to the soil together with enough water to bring the total moisture content to the OMC. The samples were compacted and air-dried for 7 days before the ITS was measured. This experiment provided a control to determine whether the artificial humic substance had any stabilising effects of its own. The experiment was repeated by added 2 % of Resin A to the 1, 3 and 5 % organic substance. In the next experiment 5 % lignosulphonate was used instead of the formose solution with and without 2 % of Resin A.

In the third experiment the natural humic substance content of the soil was removed by heating it at 500 °C for 30 minutes before washing it thoroughly with water. Again 1, 3 and 5 % (by mass of the dry soil) of the formose solution was added to the washed soil as well as enough water to bring the total moisture content to OMC. The samples were compacted and air-dried for 7 days before the ITS was measured. The experiment was repeated by adding 2 % of Resin A to the 1, 3 and 5 % organic substance. In another experiment 5 % lignosulphonate was used instead of the formose solution with and without 2 % of Resin A.

Thirdly washed sand was used. 1, 3 and 5 % of the formose solution was added to the sand with and without 2 % of Resin A. The samples were air-dried for 7 days before their ITS were determined.

4.4 RESULTS AND DISCUSSION

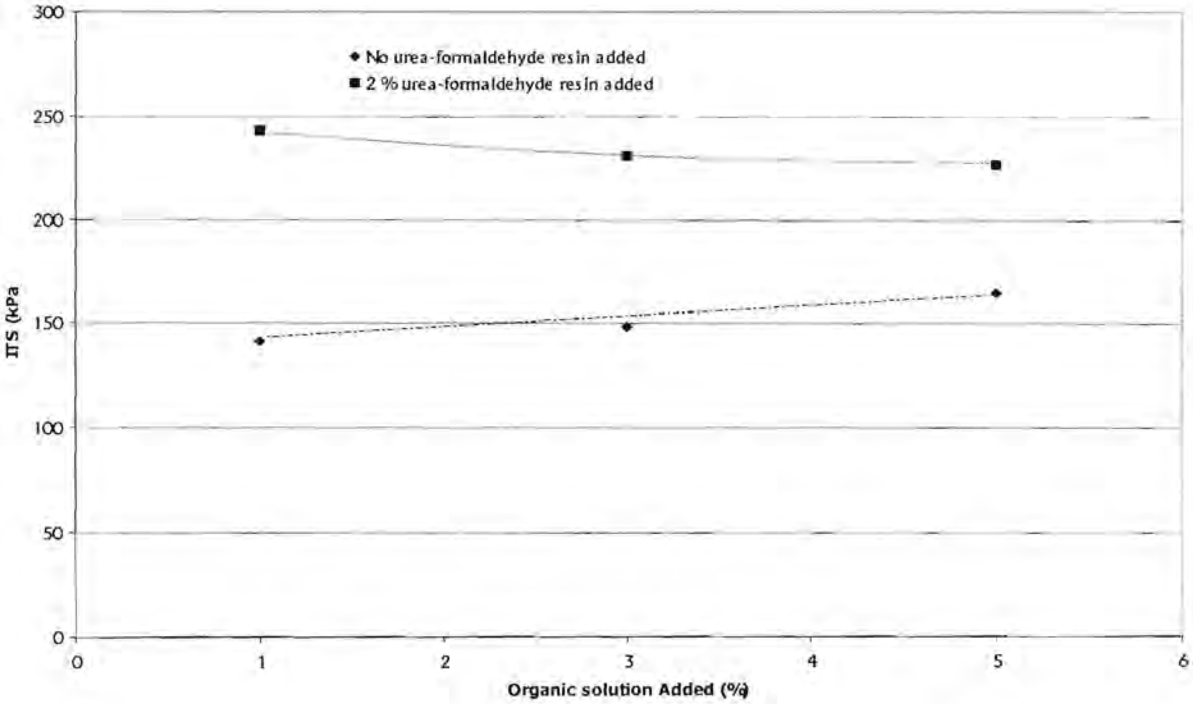

Figure 33. *The effect of adding a formose solution on the dry strength of the brown shale treated with 2 % Resin A. The samples were dried for 7 days.*

The addition of extra humic substances had no significant effect on the strength of the soil stabilised with Resin A alone when the naturally occurring organic substances were present. Figure 33 shows that increasing the artificial humic substance concentration had no effect on the soil strength or the effectiveness of Resin A as a soil stabiliser. The value of 150 kPa is approximately the same value as for natural soil. Adding 5 % lignosulphonates raised the ITS to 165 kPa. In the presence of 2 % of Resin A, this value increased to 182 kPa.

Figure 34 shows the effect of adding artificial organic substances to washed soil stabilised with Resin A. When the soil was stripped of its organic content it lost its natural cohesion and had virtually no natural strength left. Urea-formaldehyde resin without added organic content had no stabilising effect on the clean soil, but when formose was added the stabilising efficiency of the resin improved dramatically. The organic substance itself had some stabilising qualities, but only at higher concentrations. Addition of 5 % lignosulphonate resulted in an ITS of 32 kPa, but in the presence of 2 % of Resin A the value increased to 152 kPa. This represents a dramatic improvement in soil strength.

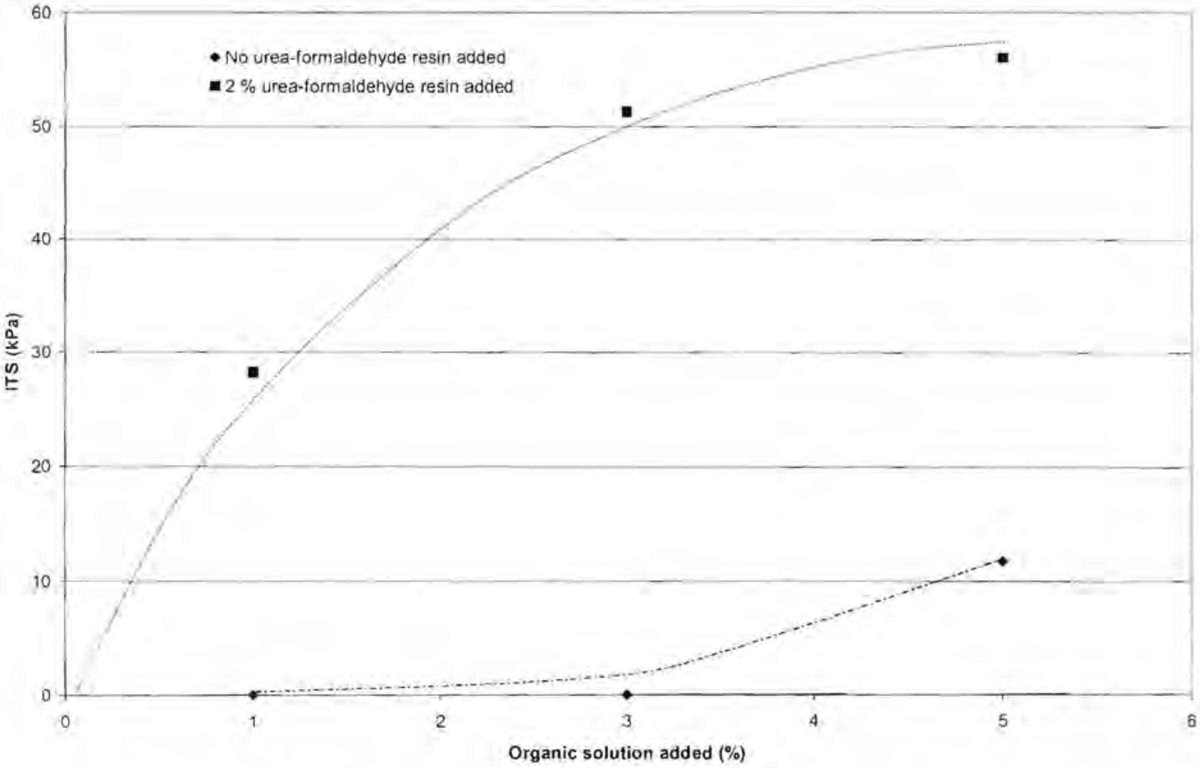

Figure 34. *The effect of organic compound addition on the dry strength of washed soil treated with 2 % Resin A. The samples were dried for 7 days.*

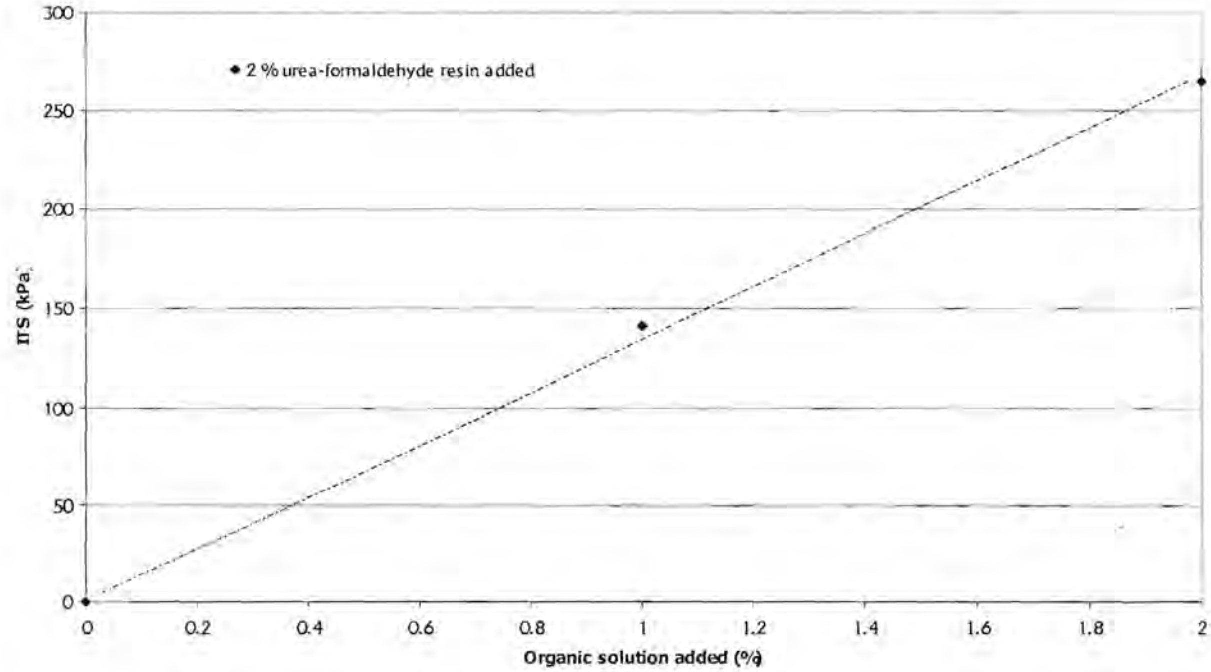

Figure 35. *The effect of formose solution dry strength of sand treated with 2 % Resin A. The samples were dried for 7 days.*

Figure 35 shows the effect of added formose on the stabilising effect of Resin A with sand. It must be kept in mind that adding urea-formaldehyde resin to washed sand had no stabilising effect on the soil. By adding humic substances alone resulted in a slight increase in strength, but the stabilised sand was very brittle and had no impact strength. The combination of urea-formaldehyde resin with 2 % formose solution resulted in adequate strength.

4.5 CONCLUSIONS AND RECOMMENDATIONS

Addition of synthetic organic substances (formose and lignosulphonates) to the unstabilised and Resin A stabilised soils had no effect on strength. This is attributed to the naturally occurring humic substances being present in sufficient quantities.

When the soil was stripped of its naturally occurring organic content, it lost all its strength. In the absence of this organic part, the stabilising effect of Resin A was lost as well. The natural stability of the soil and the stabilisation properties of the resin were recovered when the organic part was replenished by adding formose or lignosulphonates. Even washed sand could be stabilised by such additions. It is therefore concluded that the presence of appropriate organic matter is critical for effective soil stabilisation with urea-formaldehyde resins.

4.6 REFERENCES

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CHAPTER 5

CONCLUSIONS

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The utility of two different urea-formaldehyde resins as soil stabilisers was evaluated. Resin A and B were prepared by reacting respectively Formalin or Inkunite® with urea in a 5:3 mass ratio. Raman spectra showed that the final resin products (Resins A and B) are chemically similar although there are small differences in the functional groups. At a pH of 5,4 Resin A had a much longer gel time than Resin B; this translates into a longer application time. The final product properties for both resins were similar. This means that the same product properties can be obtained with different reaction times. Under appropriate reaction conditions, all the products were homogeneous, hard and strong with excellent water resistance.

Three different amino resin products can be identified, depending on the cure pH: a strong, brittle solid is obtained below pH = 5,2. Above pH = 6,4 the reaction results in a powdery precipitate in a clear liquid. At intermediate pH values a slow-hardening gel is obtained. The solubility of these precipitates decreases at higher formaldehyde to urea molar ratios and lower pH. Gel time decreased with pH and increased with the molar ratio.

The curing rate of Resin A was found to increase with temperature as expected. Although the temperature affected the reaction rate, it did not significantly influence final product properties. Nevertheless, the products formed at lower temperatures were slightly stronger and more homogeneous than those formed at higher temperatures.

Changing the formaldehyde to urea molar ratio of Resin A to 2:1 resulted in rapid gelling but it took three days for the resin to solidify completely. With a molar ratio of 1,4:1 the reaction was slower at first, but solidification occurred in a shorter time. The product obtained with a 2:1 molar ratio was smooth, hard and crack-free. The other product was brittle and had small cracks.

Addition of an anionic bitumen emulsion (SS60) to Resin A generally resulted in a better product, independent of the reaction conditions used, including pH. At high pH, cationic bitumen emulsions (KMS60 and KRS60) also resulted in good products when used in combination with Resin B, but at lower pH the products were brittle. After 7 days of water immersion, the Resin A-cationic emulsion combinations softened, while the others were unaffected. It is therefore concluded that the addition of bitumen emulsions did not materially affect the result of the cure reactions, except for slowing them down at higher pH.

Most of the soil stabilisation tests were conducted using a brown shale. The ultimate wet and dry strengths of Resin A and Resin B (with or without bitumen emulsion) treated soils reached an optimum value when enough water was added to bring the soil to its OMC during the sample preparation stage.

Soil stabilised with Resin A with and without bitumen emulsion had the same initial increase in strength, but the addition of bitumen resulted in higher maximum strengths of the stabilised material. Full stabilisation of the soil with these resins requires complete removal of moisture A maximum ITS of 460 kPa was reached when all the moisture was evaporated (after about 17 to 24 days air-drying). The natural soil strength also increases to a maximum value of ca. 160 kPa as the moisture content is reduced.

However, the strength of the stabilised material decreases as water is taken up during soaking. The addition of bitumen emulsion, especially in the case of Resin B, improved the water resistance significantly.

Resin B-stabilised soil initially had a lower dry strength than Resin A stabilised soil. Ultimate values were, however, higher for Resin B. Resin B-bitumen emulsion combinations featured much lower wet strengths than corresponding Resin A and bitumen emulsion samples.

The strength of the stabilised material increased as the amount of compaction (and thus density) increased and reached a plateau value of 290 kPa where the material density cannot be increased.

Both the wet and dry strength of the stabilised material increased as the Resin A and Resin B dosage was increased but in the case of the dry strength an upper limit of 380 and 300 kPa, respectively, was reached.

The strength of the stabilised soil reached 380 kPa as the reaction pH was lowered from 7 to about 4 and this increase was enhanced by the addition of bitumen emulsion. Again both Resin A and Resin B resulted in the same dry strength values, but when soaked the samples treated with Resin B had very little wet strength. At a molar ratio of 2:1 the dry strength of the Resin A and Resin B stabilised soil reached an optimum value.

Anionic bitumen emulsion (SS60) was the only bitumen emulsion that gave satisfactory wet strengths with both Resin A and Resin B. Although all the different bitumen emulsions used provided adequate dry strength, only samples treated with SS60 did not fail when soaked in water.

The addition of cement to Resin A treated soil resulted in higher initial wet and dry strength of the particular soil. Resin A also increased the strength gained from cement stabilisation of the soil (from 60 to 290 kPa). Resin A increased the strength obtained from lime stabilisation, but this lead to lower strengths than when Resin A was used on its own. The strength of the resin with bitumen was significantly increased by adding sugar to the citric acid, but none of the other additives had a positive effect on the effectiveness of Resin A as a soil binder.

The addition of Resin A did not have a stabilising effect on the soil when stripped of its naturally occurring organic content. Only with the addition of organic substances did the strength of the stabilised soil increase. The same is true for the washed sand. It can be concluded that for the sand and soil tested, the resin is only effective when organic substances are present.

This shows that the use of modified urea-formaldehyde resins can significantly improve the properties of the material evaluated.