THE USE OF MODIFIED UREA-FORMALDEHYDE RESINS IN SOIL BINDER SYSTEMS

by

WILLEM ANDREAS GERMISHUIZEN

Presented in partial fulfilment of the requirements for the degree

Master in Engineering

Chemical Engineering

in the Faculty of Engineering

University of Pretoria

20 April 2000

ABSTRACT

THE USE OF MODIFIED UREA-FORMALDEHYDE RESINS IN SOIL BINDER SYSTEMS

by

Willem Andreas Germishuizen

Supervisor:
Professor W. W. Focke
Department of Chemical Engineering

Co-supervisor:
Professor A.T. Visser
Department of Civil Engineering

University of Pretoria

Amino resins are formed when an amide or an amine (such as urea or melamine) reacts with an aldehyde. When urea and formaldehyde react, an amino resin is formed that has many important industrial and commercial applications. Although urea-formaldehyde (UF) resin technology is mature, new applications, such as the use in soil binder applications, are still being found.

The aim of this study is to investigate the factors that influence the properties of specific UF resins and consequently their effectiveness as a soil binder. Important reaction parameters that affect physical and application properties of these resins are the reactant stoichiometry i.e. the formaldehyde to urea ratio, the type and concentration of catalyst used and the temperature and pH. These factors affect the reaction rate and therefore also the time required for achieving a specified conversion. In this study two modified urea-formaldehyde resins were

investigated The resins were obtained by reacting urea, either with a 37 % formaldehyde solution, or with a formaldehyde precondensate, i.e. Inkunite®.

Soil samples were compacted using the Marshall apparatus after appropriate treatment. Soil stabilisation efficiency was evaluated in terms of the indirect tensile strength (ITS). The soil used in this study was a brown shale that had an intrinsic indirect tensile strength of ca. 160 kPa. It was found that for best soil stabilisation performance, the soil moisture content, at the time of compaction, had to correspond to the optimum moisture content (OMC).

The optimum formaldehyde to urea molar ratio was found to be 2:1. It was also found that the ITS of the stabilised soil increased as the resin cure pH was decreased. The lowest usable value was pH = 4. Below this value the cure reaction proceeded so fast that insufficient time was available for effective application.

The ultimate dry strength of the soil was found to be independent of the two resin types used. The wet strength was poor, but could be improved dramatically, for at least one of the resins, by adding an anionic bitumen emulsion. A low resin dosage at a constant anionic bitumen emulsion content of 2 % caused a decrease in strength. Further increase in resin dosage improved strength until a plateau value was reached at about 2,5 % resin. Using the best UF resin and bitumen emulsion, both at 2 % dosage, resulted in a soil strength increase that exceeded 150 % that of the dry natural soil. This proves that urea-formaldehyde resin formulations are effective soil stabilisers for the brown shale. It was also found that the soil organic content plays a key role in the stabilisation efficiency of these resins.

Keywords: urea, formaldehyde, resin, soil, binder, stabiliser

OPSOMMING

THE USE OF MODIFIED UREA-FORMALDEHYDE RESINS IN SOIL BINDER SYSTEMS

deur

Willem Andreas Germishuizen

Promotor:
Professor W. W. Focke
Departement Chemiese Ingenieurswese

Mede-Promotor:
Professor A.T. Visser
Departement Siviele Ingenieurswese

Universiteit van Pretoria

Aminoharse word gevorm wanneer 'n amied of 'n amien (byvoorbeeld urea of melamien) met 'n aldehied reageer. As urea en formaldehied reageer word 'n aminohars gevorm met belangrike industriële toepassings. Alhoewel die tegnologie rakende urea-formaldehied harse reeds tot 'n groot mate ontwikkel is, word nuwe toepasings, soos die gebruik daarvan as grondstabiliseerders, steeds ontdek.

Die doel van die studie was om die faktore wat die fisiese eienskappe van die hars beïnvloed te ondersoek en daarvolgens dan die effektiwiteit van die hars as 'n grondstabiliseerder te bepaal. Belangrike reaksieparameters wat die fisiese sowel as die gebruikseienskappe van die hars beïnvloed, is die stoichiometrie, dit wil sê die formaldehied tot urea verhouding, die tipe en konsentrasie van die katalis wat gebruik word en die temperatuur en pH. Hierdie faktore beïnvloed die reaksietempo en gevolglik ook die tyd benodig om 'n sekere omsetting te bereik. Twee verskillende urea-formaldehied harse was in hierdie ondersoek gebruik. Die

harse was berei deur die reaksie van urea met óf 'n 37 % formaldehiedoplossing óf 'n formaldehied voorkondensaat (Inkunite®).

Die grondmonsters was gekompakteer met 'n Marshall apparaat na die toepaslike behandeling van die grond. Die indirekte treksterkte (ITS) van die monsters was gebruik om die effektiwiteit van die stabilisasie te evalueer. 'n Bruin skalie met 'n natuurlike treksterkte van ongeveer 160 kPa was in die studie gebruik. Daar was gevind dat, vir die beste stabilisasie, die grond tydens kompaksie by die optimum voginhoud moes wees.

Die optimum formaldehied tot urea molêre verhouding was 2:1. Daar was ook gevind dat die indirekte treksterkte van die gestabiliseerde grond toeneem as die pH van die reaksiemengsel afneem. Die laagste praktiese pH het 'n waarde van 4 gehad. Onder hierdie waarde het die reaksie te vinnig plaasgevind om die hars maklik aanwendbaar te maak.

Die finale droë sterkte van die grond was onafhanklik van die twee tipes harse wat gebruik is. Alhoewel die natsterkte baie laag was, was dit moontlik om dit vir ten minste een van die harse te verbeter deur die byvoeging van anioniese bitumen emulsie. 'n Lae hars dosering, tesame met 'n konstante bitumen emulsie konsentrasie van 2 %, het gelei tot 'n afname in sterkte. As die dosering van die hars verhoog word, neem die sterkte toe tot 'n konstante limietwaarde bereik word by 'n dosis van 2,5 %. Deur die beste dosering vir beide die hars en die bitumen emulsie te gebruik (2 % vir albei) het die natuurlike droë grondsterkte met meer as 150 % toegeneem. Dit bewys dat die urea-formaldehied harse effektief was as grondstabiliseerders van die bruin skalie. Dit was verder gevind dat die organiese inhoud van die grond 'n sleutelrol speel in die effektiwiteit van die harse.

Sleutelwoorde: urea, formaldehied, hars, stabiliseerder, bindmiddel

ACKNOWLEDGEMENTS

I would like to thank the following people for their valuable contributions and support:

- Professor W. W. Focke, Department of Chemical Engineering, Pretoria University
- Professor A. T. Visser, Department of Civil Engineering, Pretoria University
- Soillab (Pty) Ltd, Pretoria
- Mr. H de Bruyn, Techneco (Pty) Ltd, Pretoria
- G &W Base and Industrial Minerals (Pty) Ltd., Wadeville
- Ms. R. Bornman, University of Cambridge, United Kingdom

TABLE OF CONTENTS

Chapter 1 ..... **2**

Introduction **2**

1.1 Introduction 2

1.2 The History of Urea-Formaldehyde Resins 2

1.3 The Reagents 4

1.3.1 Formaldehyde 4

1.3.2 Urea 6

1.4 The Chemistry of Amino resin Formation 6

1.4.1 Addition Reactions 6

1.4.2 Condensation Reactions 7

1.5 Physical and Chemical Properties 8

1.6 Uses of Amino resins 9

1.7 Problem Statement 9

1.8 References 9

Chapter 2 ..... **12**

Factors Influencing Resin Properties **12**

2.1 Introduction 12

2.2 Experimental Programme 13

2.2.1 Analysis of Reagents and Products 13

2.2.2 The Influence of pH on Resin Properties 14

2.2.3 The Influence of Temperature on Resin Properties 14

2.2.4 The Influence of the Formaldehyde to Urea Molar Ratio on Resin Properties 14

2.2.5 The Influence of Formaldehyde Source on Resin Properties 15

2.2.6 The Influence of Bitumen Emulsion Addition on Resin Properties 15

2.3 Results and Discussion 16

2.3.1 Raman Spectra 16

2.3.2 The Influence of pH on the Amino resin 17

2.3.3 The Influence of Temperature on Resin Properties 19

2.3.4 The Formaldehyde to Urea Molar Ratio 20
2.3.5 The Use of Formalin and Inkunite® as a Source of Formaldehyde....24
2.3.6 The Influence of Bitumen Emulsion Addition....25
2.4 Conclusions and Recommendations....28
2.5 References....29

Chapter 3....32

The Soil Stabilising Properties of Urea-Formaldehyde Resins....32

3.1 Introduction....32
3.2 Terminology....33
3.3 Soil Stabilisation....35
3.4 Conventional Stabilising Agents....36
3.4.1 Lime....36
3.4.2 Portland Cement....37
3.5 Stabilisation with Polymers....38
3.5.1 Cationic Polymers....38
3.5.2 Anionic Polymers....39
3.5.3 Non-Ionic Polymers....39
3.5.4 Resins....39
3.6 Bitumen Emulsions....40
3.6.1 The Manufacture of Bitumen Emulsions....40
3.6.2 Properties of Bitumen Emulsions....41
3.6.3 The Chemical Reactions of Bitumen Emulsions....42
3.6.4 The Choice of Bitumen Emulsion....42
3.6.5 The Handling of Bitumen Emulsions....43
3.6.6 Environmental and Safety Aspects....44
3.7 The Types of Soil....44
3.8 Test Methods....45
3.9 Experimental Programme....46
3.9.1 Experimental Test Procedure....46
3.9.2 Investigation of the Factors Influencing Soil Stabilisation....48
3.9.2.1 Drying Time....48

3.9.2.2 Initial Moisture Content 49
3.9.2.3 Compaction 50
3.9.2.4 The Urea-Formaldehyde Dosage 51
3.9.2.5 The Bitumen Emulsion Dosage 51
3.9.2.6 Reaction pH 52
3.9.2.7 The Formaldehyde to Urea Molar Ratio 52
3.9.2.8 Type of Bitumen Emulsion 53
3.9.2.9 Addition of Portland Cement 53
3.9.2.10 Addition of Lime 54
3.9.2.11 The Influence of Additives and Resin Preparation on Stabilisation 54
3.10 Results and Discussion 55
3.10.1 The Influence of Drying Time on the Strength of the Stabilised Soil 55
3.10.2 The Influence of the Initial Moisture Content on the Stabilised Material 60
3.10.3 The Effect of Compaction on the Strength of the Stabilised Soil 63
3.10.4 The Effect of Resin Dosage on Stabilisation 64
3.10.5 The Influence of the Bitumen Dosage on Stabilisation 65
3.10.6 The Influence of pH on Stabilisation 67
3.10.7 The Influence of Reagent Ratio on Stabilisation 69
3.10.8 The Effect of the Type of Bitumen Emulsion 71
3.10.9 The Effect of Portland Cement Addition on Stabilisation 71
3.10.10 The Effect of Lime Addition on Stabilisation 73
3.10.11 The Influence of Additives and Resin Preparation on Stabilisation 74
3.11 Conclusions and Recommendations 75
3.12 References 77

Chapter 4 80

The Soil Organic Content 80

4.1 Introduction 80
4.2 The Soil Organic Content 80
4.3 Experimental 82
4.4 Results and Discussion 83
4.5 Conclusions and Recommendations 85

4.6 References 86

Chapter 5 ..... **88**

Conclusions **88**

Appendix A: Raman Spectra **92**

Appendix B: Bitumen Emulsion Specification Sheets **103**

Appendix C: Influence of Bitumen Emulsion on Resins A and B **107**

Appendix D: Soil Properties **111**

Appendix E: Statistical Analysis **113**

Appendix F: Experimental Data **115**