

**STUDY THE EFFECT OF CHITOSAN AS AN EMULSIFIER  
AND AS AN ADDITIVE OVER CATIONIC BITUMEN  
EMULSION**

Dulanka Rangana Mallawarachchi



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
www.lib.mrt.ac.lk

Degree of Master of Science

Department of Chemical and Process Engineering

University of Moratuwa  
Sri Lanka

November 2014

## DECLARATION

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Also, I hereby grant to University of Moratuwa the non-exclusive right to reproduce and distribute my thesis, in whole or in part in print, electronic or other medium. I retain the right to use this content in whole or part in future works.

Signature:

Date:



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

The above candidate has carried out research for the Master's thesis under my supervision.

Signature of the supervisor:

Date

## ABSTRACT

Chitosan has amine and amino groups which have the ability to generate cationic type surfactants when combine with H<sup>+</sup> ions. Thus its action as a cationic emulsifier is suitable for negatively charged siliceous aggregates used for road paving in Sri Lanka. This study consisted of two parts. Firstly, water soluble Chitosan was tested for suitability of using as an emulsifier in the production of cationic bituminous emulsions and secondly Chitosan was used as an additive to mix with bitumen emulsion. In the first part, currently using amine emulsifier was replaced at 20% intervals and tested for emulsion properties; emulsion viscosity, storage stability, settlement test, sieve test and breaking of emulsion. In the second part, Chitosan was added to emulsion and viscosity, storage stability and break time were tested. Results of first part indicated that Chitosan replacement was only possible up to 10% replacement for cationic slow setting type of emulsions but rheological properties of rapid setting emulsions could be improved by replacing up to 60% of amine emulsifier with Chitosan. A significant increase in viscosity from 16 SSU (with 0% Chitosan) to 43 SSU (with 60% Chitosan) was observed for rapid setting emulsions. Storage Stability showed the optimum value of zero at 40% replacement and all the values up to 60% replacement were found to be within the ASTM specified level of  $\pm 1\%$ . Break time measurements suggested that for slow setting type emulsions Chitosan use as an emulsifier has increased the emulsion breaking rate. Further high viscous and stable rapid setting emulsion could be obtained without hindering the compliance to ASTM standard by replacing the amine emulsifier with Chitosan. Results of second part suggested that Chitosan acts as a viscosity modifier and increases the emulsion viscosity from 26SSU to 92SSU when added at 0.2% of emulsion weight. But this addition has increased the settling tendency of emulsion thus most suited to be mixed at the point of use. In both cases, at a critical amount of added Chitosan was observed. This maximum limit was found to be 0.2% (w/w).

**Key words:** Chitosan, Bitumen Emulsion, Viscosity Modifier



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

## **DEDICATION**

I dedicate this thesis to my father who could not see my achievements in his life and to my mother who has brought me thus far on her shoulders.



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

## ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis supervisors Dr. A D U S Amarasinghe and Dr. M A B Prashantha for their guidance, understanding, kind support, encouraging advices, criticism, and valuable discussions throughout my thesis.

I am greatly indebted to Mr. B.R.Perera, Chairman, Maga Neguma Emulsion Production Company (Pvt) Ltd for supporting and providing me every opportunity to use the instruments in the company laboratory.

Special thanks go to Mr. S. Nanayakkara, Additional General Manager, Neguma Emulsion Production Company (Pvt) Ltd for his technical support and especially the guidance provided for me like a father to me.

I wish to thank Miss. Lakmali Jayawardane, Mr. Amila Attanayeka and Mr. Hemal Wimalasuriya, who have always being right beside me and gave their fullest commitment to make this work successful.



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

## TABLE OF CONTENT

DECLARATION	i
DEDICATION	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
TABLE OF CONTENT	v
LIST OF FIGURES	viii
LIST OF TABLES	x
LIST OF ABBREVIATIONS	xi
LIST OF APPENDICES	xii
CHAPTER	
1.0 Introduction	1
1.1 Bitumen Emulsion	1
1.2 Chitosan	2
1.3 Aim and Scope	3
1.4 Thesis Outline	3
2.0 Literature Review	4
2.1 Bitumen Emulsion	4
2.1.1 Bitumen Emulsion Applications	6
2.1.2 Emulsification Process	6
2.1.3 Raw materials used	7
2.1.3.1 Bitumen	7
2.1.3.2 Water	9
2.1.3.3 Emulsifier	10
2.1.3.4 Acid	11
2.1.3.5 Calcium chloride	12
2.1.4 Emulsification Equipment	12
2.1.5 Emulsion Breaking and setting process	12
2.1.5.1 Electrostatic Theory	13
2.1.5.2 Chemical Bonding Theory	16
2.1.5.3 Mechanical Theory	16
2.1.5.4 Thermodynamic Theory	16
2.2 Chitosan	17
2.2.1 Chemical Properties of Chitosan	18
2.2.2 Applications of Chitosan	19



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

2.2.2.1	Water Treatment	19
2.2.2.2	Food Industry	19
2.2.2.3	Agricultural Industry	20
2.2.2.4	Cosmetics	20
2.2.3	Emulsification potential of Chitosan	20
3.0	Methodology	22
3.1	Introduction	22
3.2	Experiment of using Chitosan as an emulsifier in the production of bitumen emulsion	22
3.2.1	Materials	22
3.2.1.1	Bitumen	22
3.2.1.2	Acid	23
3.2.1.3	Chitosan	23
3.2.1.4	Water	23
3.2.1.5	Kerosene	23
3.2.1.6	Emulsifier	23
3.2.1.7	Stabilizer	23
3.2.2	Equipment	24
3.2.3	Bitumen Phase Preparation	25
3.2.4	Soap Phase preparation	25
3.2.5	Emulsion Production	26
3.2.6	Sample Storing	28
3.2.7	Sample testing	28
3.2.7.1	Viscosity	28
3.2.7.2	Storage Stability and Settlement test	29
3.2.7.3	Testing for breaking and setting behavior	29
3.2.7.4	Sieve Test	30
3.3	Experimenting Chitosan as an additive to bitumen emulsion	30
3.3.1	Bitumen Emulsion	31
3.3.2	Chitosan	31
3.3.3	Equipment	31
3.3.4	Methodology	31
3.3.5	Sample Storage	32
3.3.6	Sample testing	32
4.0	Results and Discussion	33
4.1	Chitosan as an emulsifier	33
4.1.1	Compatibility for Cationic Slow Setting (CSS) type of emulsion	33
4.1.2	Compatibility for Cationic Rapid Setting 1(CRS 1) type of emulsion	33
4.1.3	Optimization of properties	33
4.1.3.1	Emulsion Viscosity	34
4.1.3.2	Storage Stability	36
4.1.3.3	Settlement Test	37
4.1.3.4	Sieve Test	39
4.1.4	Proposed model for explanation of results	39

4.1.5 Breaking and setting of Emulsion	42
4.1.5.1 Explanation using Electrostatic theory	44
4.1.5.2 Explanation using Chemical Bonding Theory	44
4.1.5.3 Explanation using Mechanical Theory	44
4.1.5.4 Explanation using Thermodynamic Theory	44
4.2 Use of Chitosan as an additive to bitumen emulsion	45
4.2.1 Variation of Viscosity	46
4.2.2 Storage Stability	47
4.2.3 Storage Stability in the long run	47
5.0 Conclusion and Future Work	50
5.1 Conclusion	50
5.2 Future Work	51
6.0 References	52
Appendix A: Specifications of Chitosan	56
Appendix B: Drinking Water Standards	57
Appendix C: Calculation of Chitosan : Bitumen Ratio	58
Appendix D: Specifications for industrial Kerosene	59



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)



## LIST OF FIGURES

		Page
Figure 1.1	Application of Bitumen emulsion.....	1
Figure 2.1	Oil in Water emulsion.....	5
Figure 2.2	Water in oil emulsion.....	5
Figure 2.3	Multiple W/O/W emulsion.....	5
Figure 2.4	Colloidal mill.....	7
Figure 2.5	Flow Chart of Emulsion manufacturing process.....	8
Figure 2.6	Asphaltene dispersed in Maltene.....	10
Figure 2.7	Polyammonium Salts .....	12
Figure 2.8	Diamines.....	12
Figure 2.9	Possible stages in the setting of cationic emulsion.....	14
Figure 2.10	Electrical Double layer around a particle.....	15
Figure 2.11	Chitin and Chitosan Structure.....	19
Figure 2.12	Chitosan Structure.....	19
Figure 2.13	Cationic form of Chitosan .....	20
Figure 3.1	Laboratory Mill for emulsion manufacturing .....	25
Figure 3.2	Bitumen Heating.....	26
Figure 3.3	Soap Solution Preparation.....	27
Figure 3.4	Saybolt Viscometer to measure emulsion viscosity.....	29
Figure 3.5	Sketch of mixing arrangement.....	32
Figure 4.1	Viscosity of CRS1 type of emulsion .....	36

Figure 4.2	Viscosity of CSS1 type of emulsion.....	37
Figure 4.3	Storage Stability (24 hour) of CRS 1 type of emulsion.....	38
Figure 4.4	Settlement (5 day) of the CRS1 type of emulsion.....	39
Figure 4.5	Settlement difference between 5 day and 1 day.....	40
Figure 4.6	Colloid particles of bitumen emulsion being stable by repelling each other.....	41
Figure 4.7	Bound particles and unbound particles.....	41
Figure 4.8	All particles bound to Chitosan molecules.....	42
Figure 4.9	Interpolymeric Complex.....	42
Figure 4.10	(a) CSS1 Emulsion produced using Chitosan as 10% of emulsifier is applied on aggregate looked brownish color just after applied.....	43
Figure 4.10	(b) Emulsion color has turned in to black after 15 minutes.....	43
Figure 4.11	(a) CSS1 Emulsion produced without using Chitosan is applied on aggregate looked brownish color just after applied.....	44
	(b) Emulsion color has turned in to black after 21 minute.....	44
Figure 4.12	CRS1 Emulsion produced with using Chitosan when applied on sand (a). .....	44
	CRS1 Emulsion produced without using Chitosan when applied on sand (b).....	44
Figure 4.13	Air bubbles trapped at the top of the emulsion sample.....	47
Figure 4.14	Viscosity of Chitosan modified emulsion.....	47
Figure 4.15	Storage Stability of Chitosan modified emulsion.....	48
Figure 4.16 (a)	Layer Separation when stored.....	50
Figure 4.16 (b)	Homogeneous emulsion when mixed.....	50



## LIST OF TABLES

		Page
Table 1.1	Emulsifier volume and cost elements in percentages	2
Table 2.1	Elemental composition of bitumen	9
Table 3.1	Formulation of CRS1 type emulsion	28
Table 3.2	Formulation of CSS1 type emulsion	28
Table 3.3	Formulation of cold mix design	31
Table 4.1	Properties of CSS1 emulsion	35
Table 4.2	Properties of CRS1 emulsion	35
Table 4.3	Properties of Chitosan modified emulsion (CRS1 type)	46



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

## LIST OF ABBREVIATIONS

Abbreviation	Description
ASTM	American Society of Testing and Materials
CPC	Ceylon Petroleum Corporation
CRS	Cationic Rapid Setting
CSS	Cationic Slow Setting
DD	Degree of Deacetylation



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)

## LIST OF APPENDICES

Appendix	Description	Page
Appendix A	Specifications of Chitosan	56
Appendix B	Drinking Water Standards	57
Appendix C	Calculation of Chitosan: Bitumen ratio	58
Appendix D	Specifications for Industrial Kerosene	59



University of Moratuwa, Sri Lanka.  
Electronic Theses & Dissertations  
[www.lib.mrt.ac.lk](http://www.lib.mrt.ac.lk)