



**Faculty of Manufacturing Engineering**

**STATIC COLDCURE VULCANIZATION ON  
EMBOSSSED RUBBER COTSHEETS USING CHAMBERS**

**Tony Fam Chee Hoe**

**Master of Manufacturing Engineering  
(Manufacturing System Engineering)**

**2019**

**STATIC COLDCURE VULCANIZATION ON  
EMBOSSSED RUBBER COTSHEETS USING CHAMBERS**

**TONY FAM CHEE HOE**

**A thesis submitted  
in fulfillment of the requirements for the degree of Master of  
Manufacturing Engineering (Manufacturing System Engineering)**

**Faculty of Manufacturing Engineering**

**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**2019**

## DECLARATION

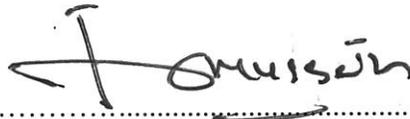
I declare that this thesis entitled "Static Coldcure Vulcanization on Embossed Rubber Cotshets Using Chambers" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....  
Name : Tony Fam Chee Hoe.  
Date : 29/8/19

## APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Manufacturing Engineering (Manufacturing System Engineering).

Signature



Supervisor Name

..... ASSOCIATE PROFESSOR, DR. NUR IZAN SYAHRIAH BINTI HUSSEIN.....  
DEPUTY DIRECTOR

Date

30/8/17

..... Life Long Learning Centre  
Universiti Teknikal Malaysia Melaka.....  
Hang Tuah Jaya  
76100 Durian Tunggal, Melaka

## **DEDICATION**

To my beloved mother, wife, son and daughter. Thank you for your support, understanding and encouragement for me to complete this thesis and master programme.

Thank you !

## ABSTRACT

Vulcanization is a technological process in rubber production in which raw rubber is converted into cure rubber. In the static coldcure process, vapor or fumed sulphur monochloride ( $S_2Cl_2$ ) is used to cure the embossed rubber cotsheet in a chamber. Since the embossed cotsheet is not agitated during the vulcanization process, therefore the end products have no folded marks on its surface after being cured. However, the top and bottom surface may be not uniformly cured if the vapor sulphur monochloride is not well controlled. Too high of temperature also can cause the bubbles over expand and become deformed after cooling down. These two factors result in collapsed bubbles on the cotsheet products. Condensation of the sulphur monochloride inside the chamber also leads to formation of sulphur stains which can contaminate the cotsheet. These two main defects result in high product rejection and heavy customers' complaints. Therefore various process parameters such as vulcanization time, inner temperature of chamber, pot surface temperature and amount of sulphur monochloride that cause these two issues need to be studied. Design of Experiment (DOE) was carried out using Response Surface Methodology (RSM). Data collected were analyzed in the Design-Expert 6.0.8 Portable software. The results show that internal heating piping temperature which contributes to the inner temperature of chamber has significant p value ( $<0.05$ ) to the response of collapsed bubbles and sulfur stains. The amount of ( $S_2Cl_2$ ) is significant to the collapsed bubbles only. Whereas, the other variables, pot surface temperature and vulcanization time are insignificant to the both responses. Optimization analysis shows that the optimum parameters to minimize both responses are internal heating pipe temperature  $0.6\text{kg/cm}^2$ , pot surface temperature  $4.0\text{ kg/cm}^2$ , vulcanization time 15 minutes and  $S_2Cl_2$  amount 450ml.

## ABSTRAK

Pemvulcanan ialah satu proses berteknologi untuk memasak getah mentah menjadi keras. Dalam proses pemasakan sejuk secara statik, asap atau wap sulfur monoklorida ( $S_2Cl_2$ ) digunakan untuk memasak getah dalam bilik ruangan yang terkurung. Oleh sebab produk yang digelar tika getah bertimbul, tidak bergerak dalam proses ini, maka tika yang terhasil tidak akan mempunyai kesan-kesan lipatan di atas permukaannya nanti. Walau bagaimanapun, permukaan atas dan bawah tika ini tidak dapat dimasak dengan rata jika wap sulfur monoklorida tidak dikawal dengan sempurna. Suhu yang terlalu tinggi juga akan menyebabkan timbulan getah berkembang keterlaluan. Ini sebaliknya akan menyebabkan timbulan-timbulan tika getah ini kempis. Kondensasi sulfur monoklorida dalam ruangan bilik terkurung juga boleh menghasilkan kotoran berwarna kuning yang boleh mencemarkan permukaan tika getah ini. Kedua-dua kecacatan ini menyebabkan pembuangan tinggi dan aduan pelanggan yang serius. Oleh yang demikian, pelbagai parameter pemprosesan seperti masa pemvulcanan, suhu dalaman bilik terkurung, suhu pot dan kuantiti sulfur monoklorida perlu dikaji. Design of Experiment (DOE) dijalankan dengan menggunakan Response Surface Methodology (RSM). Data yang dikumpul dianalisis dalam perisian Design-Expert 6.0.8 Portable. Akhirnya, takat optimum dan interaksi antara empat parameter ini boleh didapati. Oleh yang demikian, proses pemvulcanan dapat dikawal dengan sempurna. Ini meningkatkan kualiti produk pada akhirnya. Keputusan menunjukkan suhu pemanasan paip dalaman yang menyumbang kepada kepanasan dalam bilik ruangan mempunyai nilai kebarangkalian yang berkesan ( $<0.05$ ) terhadap kedua-dua tindak balas masalah timbulan kempis dan kotoran sulfur. Kuantiti  $S_2Cl_2$  pula hanya berkesan terhadap masalah timbulan kempis tika getah. Manakala pembolehubah yang lain iaitu suhu pada permukaan pot dan masa masakan tidak mempunyai kebarangkalian yang berkesan terhadap kedua-dua tindak balas tersebut. Analisis pengoptimuman menunjukkan parameter optimum yang dapat mengurangkan kedua-dua tindak balas ialah suhu pemanasan paip  $0.6\text{kg/cm}^2$ , suhu permukaan pot  $4.0\text{ kg/cm}^2$ , masa masakan 15 minit dan kuantiti  $S_2Cl_2$  450ml

## ACKNOWLEDGEMENTS

First and foremost, I would like to take this opportunity to express my sincere acknowledgement to my supervisor, Associate Professor Dr. Nur Izan Syahriah Binti Hussein from the Faculty of Manufacturing Engineering Universiti Teknikal Malaysia Melaka (UTeM) for her essential supervision, support and encouragement towards the completion of this thesis.

I would also like to express my greatest gratitude to Associate Professor Dr. Raja Izamshah Bin Raja Abdullah from Faculty of Manufacturing Engineering Universiti Teknikal Malaysia Melaka (UTeM) too for his guidance on analyzing the data using the Design-Expert 6.0.8 Portable software.

Special thanks to all my peers, colleagues and my entire family for their moral support in completing this degree. Lastly, thank you to everyone who had been to the crucial parts of realization of this project

## TABLE OF CONTENTS

	PAGE
DECLARATION	
APPROVAL	
DEDICATION	
ABSTRACT	i
ABSTRAK	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF APPENDICES	x
<b>CHAPTER</b>	
<b>1. INTRODUCTION</b>	<b>1</b>
1.1 Background	1
1.2 Problem Statement	2
1.3 Research Objectives	8
<b>2. LITERATURE REVIEW</b>	<b>9</b>
2.1 Rubbers	9
2.2 Natural Rubber	10
2.3 Rubber Vulcanization	12
2.4 Coldcure Process	14
2.5 Controlled Parameters in the Chamber	21
2.6 Safety Handling of Sulhur Monochloride	24
2.7 Response Surface Methodology	25
2.7.1 Box-Behnken Designs	28

<b>3. RESEARCH METHODOLOGY</b>	<b>29</b>
3.1 Design of Experiment	29
3.2 Data Analysis	32
3.3 Research Flow	34
<b>4. RESULTS AND DISCUSSION</b>	<b>36</b>
4.1 Results And Discussion	36
4.2 Collapsed Bubbles	37
4.2.1 Diagnostics on Collapsed Bubbles	37
4.2.2 Analysis on Variants (ANOVA) on Collapsed Bubbles	39
4.2.3 Interaction between the Variables for the Response of Collapsed Bubbles	42
4.3 Sulphur Stains	47
4.3.1 Diagnostics on Sulphur Stains	47
4.3.2 Analysis of Variance (ANOVA) on Sulphur Stains	49
4.3.3 Interaction between the Variables for the Response of Sulphur Stains	52
4.4 Process Optimization	56
<b>5. CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH</b>	<b>59</b>
5.1 Conclusion And Recommendations For Future Research	59
<b>REFERENCES</b>	<b>61</b>
<b>APPENDICES</b>	<b>66</b>

## LIST OF TABLES

TABLE	TITLE	PAGE
2.1	Physical and Chemical Properties of Sulphur Monochloride	17
2.2	Advantages and Disadvantages of Coldcure Process Compared to Moulding Process	19
2.3	Chamber Parameters and Importance of Their Controls	21
3.1	Variables of Chamber Vulcanization to be Analysed	29
4.1	Order of Significance Towards Collapsed Bubbles	40
4.2	Temperature Readings Inside the Chamber	46
4.3	Order of Significance Towards Sulphur Stains	50
4.4	Validation Test Based on 1st Solution	58

## LIST OF FIGURES

FIGURE	TITLE	PAGE
1.1	Placing a Cotsheet on a Tray and Loading into a Trolley.	3
1.2	An Engineering Drawing of a Chamber	3
1.3	A Front View of a Chamber	4
1.4	A Rear View of a Chamber	4
1.5	The Loaded Trolley Is Placed into a Chamber and Then Vulcanized.	5
1.6	Cotsheet with Collapsed Bubbles	6
1.7	Cotsheet with Good Bubbles	7
1.8	Cotsheet with Sulphur Stains	7
2.1	A Rubber Tree, <i>Hevea Brasiliensis</i>	10
2.2	Poly-cis-1.4-isoprene	11
2.3	Sulphur Vulcanization	14
2.4	Vulcanization Using $S_2Cl_2$ on Rubber	18
2.5	Stimulation Test Using an Infra-red Toaster Shows that Cotsheet Bubbles Start to Expand when the Temperature Reaches about 65 °C	23

2.6	An Operator Wears Personal Protective Equipment (PPE) to Handle $S_2Cl_2$	25
3.1	Design Summary	31
3.2	Design Matrix	31
3.3	Design Matrix (continued)	32
3.4	Research Flow	34
3.5	Research Flow (continued)	35
4.1	Experiment Results for Collapsed Bubbles and Sulphur Stains	36
4.2	Box-Cox Plot for Collapsed Bubbles	37
4.3	Normal Plot of Residuals for Collapsed Bubbles	38
4.4	Outlier T for Collapsed Bubbles	39
4.5	ANOVA for Collapsed Bubbles	40
4.6	Linear Mathematical Model to Predict Collapsed Bubbles	41
4.7	Linear Model Summary for Collapsed Bubbles	42
4.8	Response Surface Plot for the Variation in Collapsed Bubbles as a Function of Internal Pipe temperature and Vulcanization Time	43
4.9	Response Surface Plot for the Variation in Collapsed Bubbles as a Function of Vulcanization Time and Pot Surface Temperature	44
4.10	Response Surface Plot for the Variation in Collapsed Bubbles as a Function of Vulcanization Time and $S_2Cl_2$ Quantity	45
4.11	Box-Cox Plot for Sulphur Stains	47

4.12	Normal Plot of Residuals for Sulphur Stains	48
4.13	Outlier T for Sulphur Stains	48
4.14	ANOVA for Sulphur Stains	49
4.15	Fit Summary for Sulphur Stains	50
4.16	Linear Mathematical Model for Sulphur Stains	51
4.17	Model Summary of Linear Model for Sulphur Stains	52
4.18	Response Surface Plot of Sulphur Stain versus Internal Pipe Temperature and Vulcanization Time	53
4.19	Response Surface Plot of Sulphur Stain versus Pot Surface Temperature and Vulcanization Time	54
4.20	Response Surface Plot of Sulphur Stain versus S <sub>2</sub> Cl <sub>2</sub> Amount and Vulcanization Time	55
4.21	Suggested Solution for Process Optimization	57

## LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Examples of Collapsed Bubbles on Upper Layer of Cotsheet during the Experiments	66
B	Examples of Collapsed Bubbles on Lower Layer of Cotsheet during the Experiments	67
C	Examples of Sulphur Stains on the Lower Layers of Cotsheets during the Experiments	68
D	Gant Chart : Master Project Planning	69

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Unlike the traditional heat vulcanization technique using sulphur powder, the coldcure vulcanization process using vapor or fume sulphur monochloride ( $S_2Cl_2$ ) is very less popular due to its safety issues and corrosive effects on its surroundings. In addition, the sulphur monochloride solution has high toxicity and the vulcanizates have poor aging properties because the product is vulcanized on the external surface only. Therefore, finding the information to support the research is rather limited. So, down-to-earth approach and hands-on experience are important when handling this coldcure process. Nevertheless, if the process is well controlled after knowing the important factors, rejection of the products will be reduced and hence improve the company's revenue and customers' satisfaction.

The main advantage of coldcure using  $S_2Cl_2$  is that the wastes and scraps produced at the preceding processes of the vulcanization such as calendaring and embossing can be recycled. This is because rubber sheeting has not been cross-linked (vulcanized) yet up to these two stages. Therefore, processing cost can be minimized.

This type of external vulcanization is suitable to vulcanize the final shaped product. For cold coldcure products, most common forming process before vulcanization is the

formation of air bubble or known as embossing process to form various shape of bubbles that can be designed for various purposes. Embossed rubber cotsheet is one of them.

## 1.2 Problem Statement

Vulcanization is a technological process in rubber production in which raw rubber is converted into cure rubber. In the coldcure process, vapor sulphur monochloride is used to cure the rubber. The term “coldcure” is used as the process takes place at about ambient temperature up to 65°C, relatively lower than that of the common heat vulcanization using sulphur powder which can reach as high as 200°C.

In the static coldcure vulcanization process, the rubber product namely embossed or air- filled cotsheet, is placed on a net tray. The tray is then loaded into a trolley which can accommodate 24 units of trays as shown in Figure 1.1. The trolley is placed into a chamber in which vapor sulphur monochloride is pumped into. The engineering structure of a chamber is illustrated in the Figure 1.2. The chamber picture, front and rear view is shown in the Figure 1.3 and Figure 1.4 respectively. Figure 1.5 depicts the view of the chamber when a trolley is loaded in.

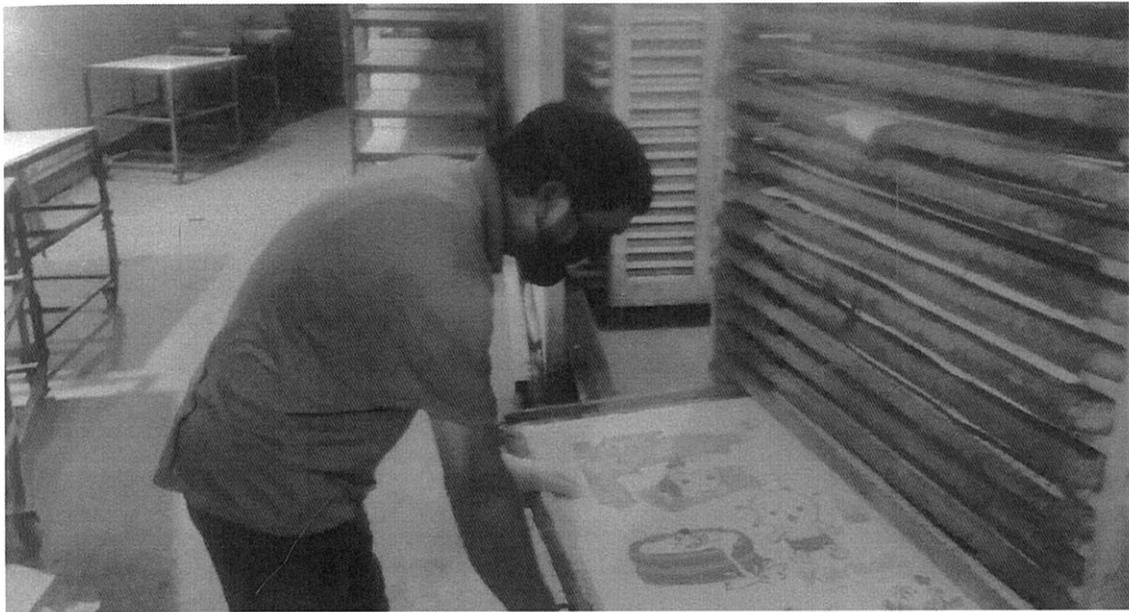


Figure 1.1 : Placing Cotsheet on a Tray and Loading into a Trolley

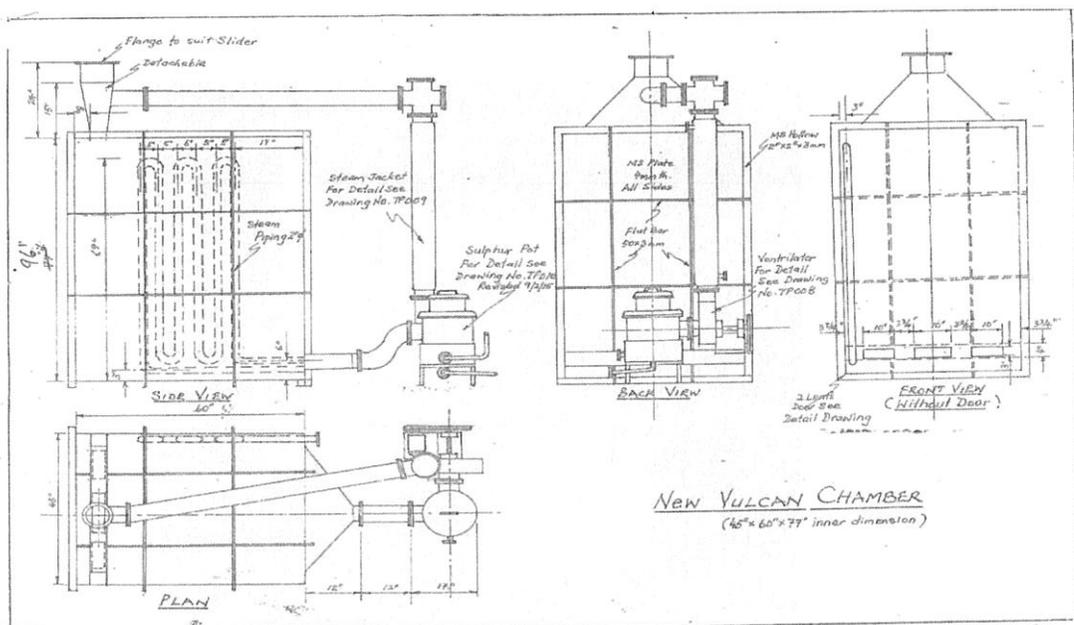


Figure 1.2 : An Engineering Drawing of a Chamber

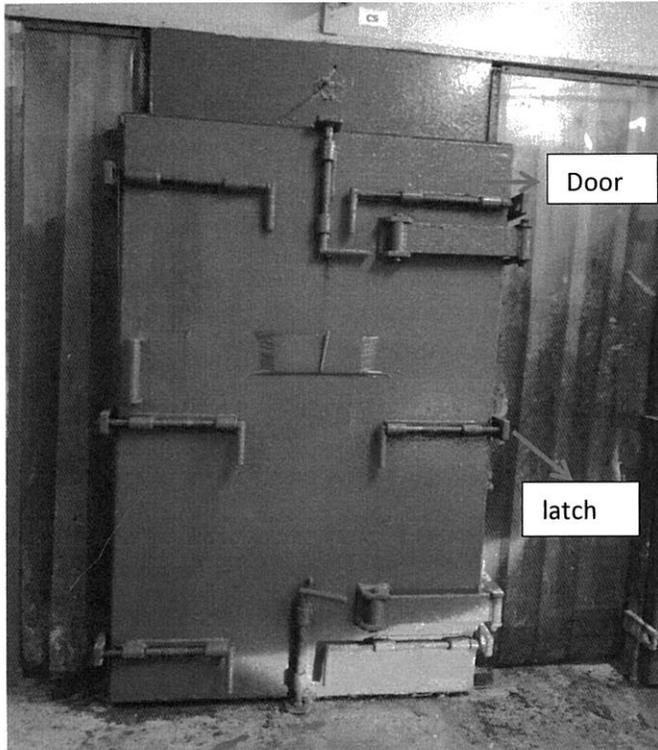


Figure 1.3 : A Front View of a Chamber

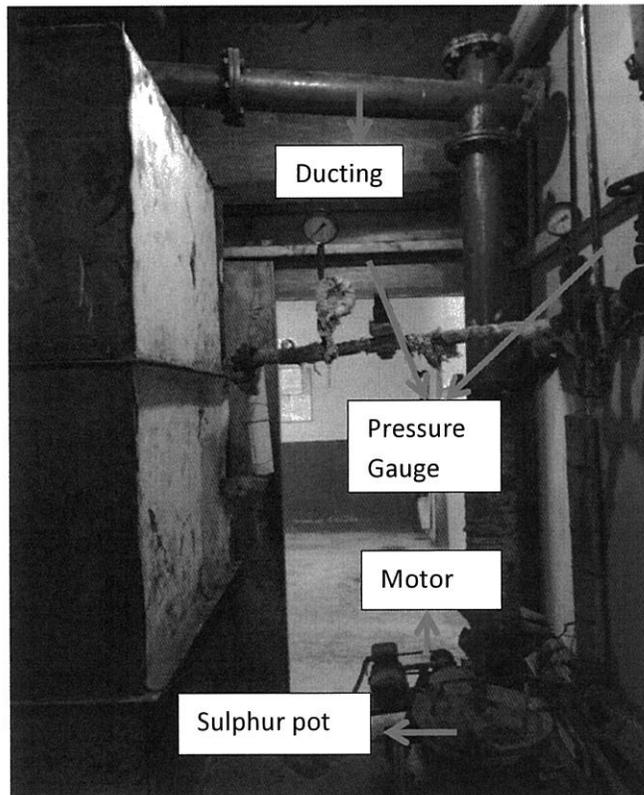


Figure 1.4 : A Rear View of a Chamber



Figure 1.5 : The Loaded Trolley Is Placed into a Chamber and Then Vulcanized

Since the embossed cotsheet “sits statically” on the tray and is not agitated during the vulcanization process, therefore it is not crumpled, so the end product has no folded marks on its surface after being cured. As a result, the cured cotsheet has better bubble appearance compared to the agitated method using rotating drums.

However, since the cotsheet is not agitated, its top and bottom surface may be not uniformly cured if the vapor sulphur monochloride is not well controlled. The cotsheet surface which is less cured will have collapsed bubble appearance. In addition, if the internal temperature of a chamber is too high during vulcanization, the bubbles will over expand and subsequently become deformed and hence collapsed after cooling down. The

poor bubble appearance on the cotsheets causes product rejection and customer complaints. Please refer Figure 1.6 and Figure 1.7. Replacement on the rejected quantity incurs additional costs to the production and causes delays in the shipments whereas the customer complaints tarnish the image of the company.

Poor control of this coldcure process will also cause the tendency of the vapor sulphur monochloride inside the chamber to condensate on its surrounding, causing contamination in the form of sulphur stains on the cotsheet surface. Minor stains may be removed using water, but not the major stains which remain permanently on the product surface. The later causes the rubber products to be rejected too. Please refer Figure 1.8

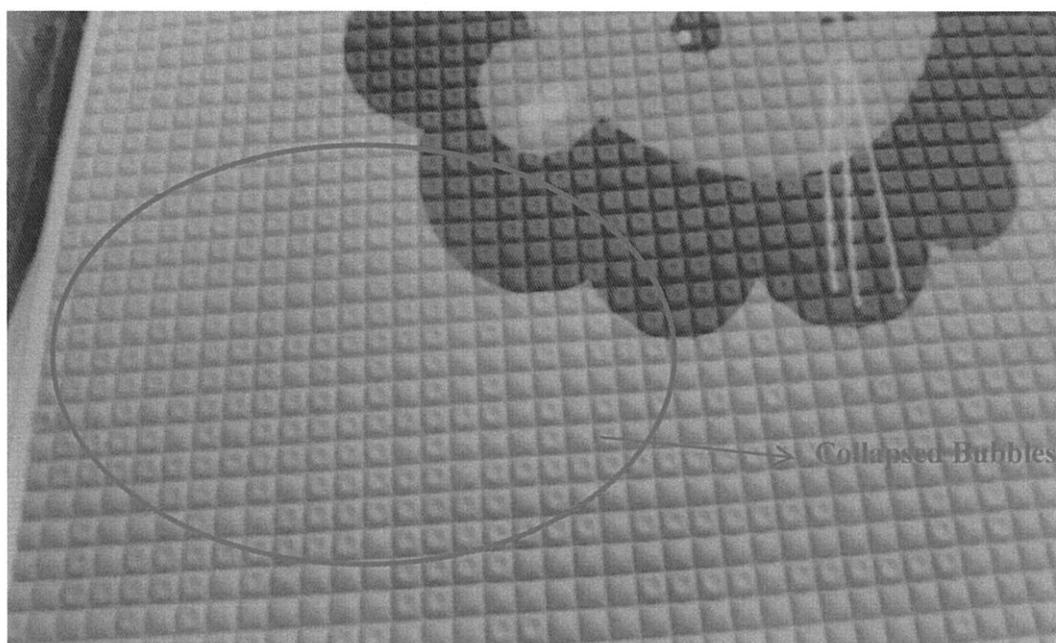


Figure 1.6 : Cotsheet with Collapsed Bubbles

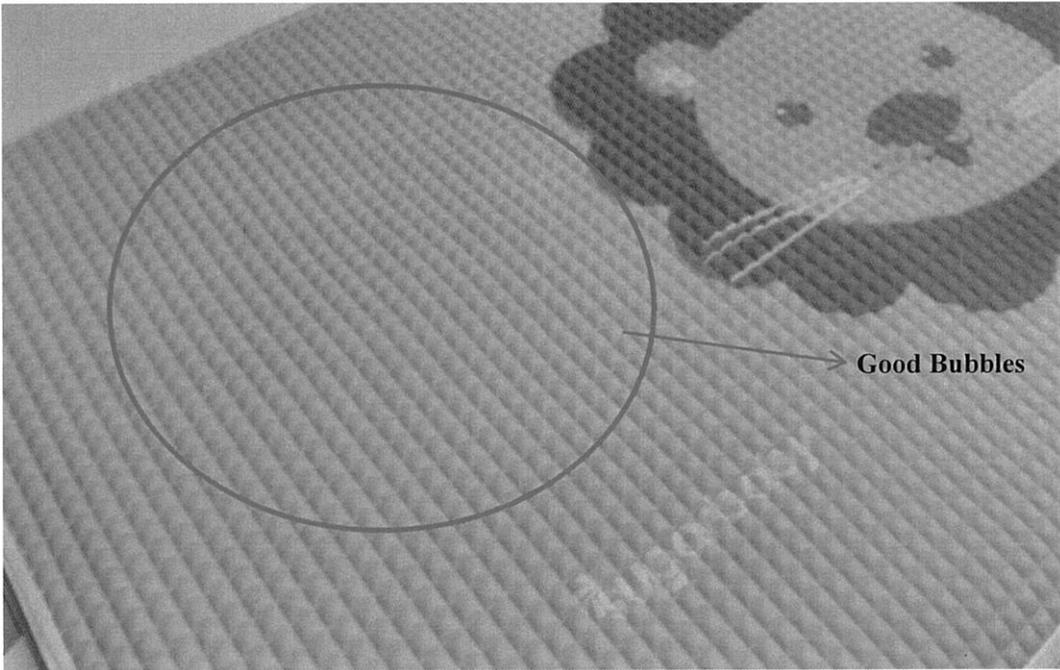


Figure 1.7 : Cotsheet with Good Bubbles

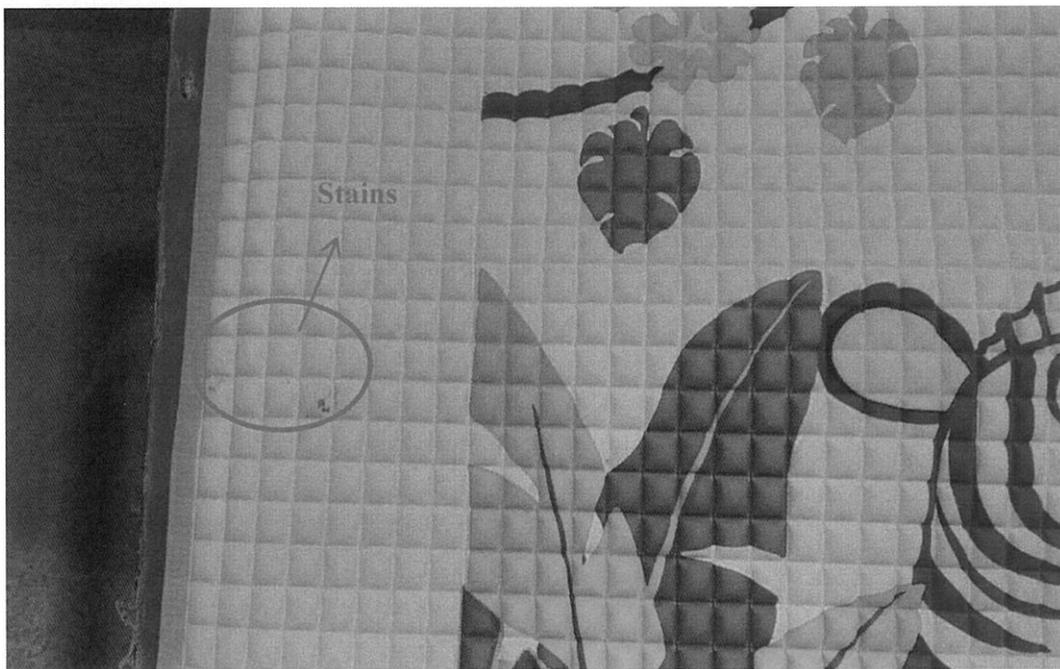


Figure1.8 : Cotsheet with Sulphur Stains

In order to reduce the rejection rate and improve customer satisfactions, these defects need to be eliminated. Various factors that can cause bubble collapse and sulphur stain issues need to be studied such as time of vulcanization, internal chamber temperature, pot temperature and amount of sulphur monochloride. Response surface methodology (RSM) is a useful multivariate statistical tool to serve this purpose. After getting optimum levels of these process parameters, only then the process can be well controlled to reduce and minimize the collapsed bubble and sulphur stain issues.

### **1.3 Research Objectives**

The objectives of this study are:-

- i. To investigate the effects of the vulcanization time, internal chamber temperature, pot temperature and amount of sulphur monochloride towards the percentage of collapsed bubbles and sulphur stains of the rubber embossed cotsheets.
- ii. To propose the optimum combination of these process parameters that yield good quality of cotsheets with minimum collapsed bubbles and sulphur stains.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Rubbers

Metador (2007) cited that rubbers are elastomers. They are polymer materials which are characterized by ability of reversible deformation under influence of external deformation forces. This property, marked as elastic, has entropy character. It rests in ability of the rubber macromolecules to occupy more ordered forms under stress, and on removal of stress to return to their ideal statistically random conformation, under ideal conditions without deformation of chemical bond distances or their angles.

The rubbers have usually long and regular macromolecule chains without large substituents, with spatially oriented structural units. Thus their segments are movable and also at low temperatures they can freely rotate around simple chemical bonds.

Presently, a lot of rubber types are on the market that can be divided into more groups in accordance with different criteria, e.g. saturated an unsaturated, natural and synthetic, polar and non-polar, crystallizing and non-crystallizing, etc. In view of their usage and basic properties, they also can be divided into:

- i) Rubbers for general use – they have properties complying with requirements of more products, often also with different properties, they are relatively cheap, produced and consumed in big volume.