

A STUDY OF  
SOME ACCELERATOR COMBINATIONS IN  
THE VULCANIZATION OF RUBBER

BY

K. C. RASARATNAM

SUPERVISORS: Dr. H. K. TOH  
Dr. D. B. V. PARKER

A THESIS SUBMITTED TO THE UNIVERSITY OF  
SCIENCE OF MALAYSIA, FOR THE DEGREE OF  
MASTER OF SCIENCE

October 1975

CONTENTS

Acknowledgements	(III)-(IV)
Key to symbols and abbreviations	( V )-(VI)
Key to codes of rubber compound formulations	(VII)-(VIII)
Abstrak (Malay translation of abstract)	( IX)-(XI)
Abstract	(XII)-(XIV)

Chapter I : Introduction

1.1 Sulphur vulcanization of rubber	1 - 2
1.2 Developments of modifications of sulphur vulcanization.	2 - 3
1.3 Accelerator combinations in sulphur vulcanization of rubber.	3 - 4
1.4 The present study	4 - 9

Chapter II : Theoretical

2.1 Brief historical account of the prevulcanization days of rubber.	10 - 12
2.2 The problems encountered in using rubber goods in the unvulcanized form.	13
2.3 What is vulcanization	14 - 15
2.4 Discovery of vulcanization	15 - 21
2.5 Vulcanizing agent	22
2.6 Other compounding ingredients	23 - 27
2.7 Preparation of rubber for vulcanization	27 - 29
2.8 Vulcanizing techniques	29 - 31

Acknowledgements

The author wishes to express his grateful acknowledgements to, the Vice Chancellor and the Universiti Sains Malaysia for giving him a place in this University to carry out this work; Prof. P.D. Ritchie, the Dean of the School of Applied Sciences, for providing all laboratory facilities and for his kind advice during difficulties and support in obtaining some financial assistance; Dr. H.K. Toh for supervising this work and for his constant encouragement, valuable guidance and help in many other ways throughout this work; Dr. D.B.V. Parker for supervising this work during the absence of Dr. Toh; the Lee Foundation of Malaysia for their kind financial assistance; Dr. Sekaran Nair, Mr. Sin Siew Weng and his colleagues of the Specifications and Technology Division of the Rubber Research Institute of Malaysia for supplying most of the materials required for this work, including some references; Mr. Oon Choo Hin of Bayer (Malaysia) for supplying most of the accelerators and some references; all members of the staff of the School of Applied Sciences of this university for their encouragement; the Dean and technical staff

of the School of Physics and the laboratory staff of the School of Applied Sciences for their technical assistance; Mrs. Chin (Bayer Malaysia) and Miss Goon of this university for their dedication shown in obtaining good quality typescripts used in this thesis, and Mrs. Wilvamalar Rasaratnam for typing the first draft and helping in proof reading and compiling this work, and Mr. C. Ganesalingam, Principal Malayan Teachers College, Penang for his encouragement and help in many ways.

Key to Abbreviations and Symbols

A	- temperature coefficient of vulcanization.
CBS ) CHBS ) CHBTS)	- Cyclohexyl benzothiazyl sulphenamide.
DEBTS	- Diethyl benzothiazyl sulphenamide.
DPG	- Diphenyl guanidine.
DPPH	- Diphenyl picryl hydrazyl.
GRS	- Government rubber styrene.
HMT	- Hexamethylene tetramine.
H <sub>2</sub> S	- Hydrogen sulphide.
ICI	- Imperial Chemical Industries.
K.Cals/mole-	Kilo calories per mole.
Kgs/cm <sup>2</sup>	- Kilograms per square centimeter.
MBT	- Mercapto benz thiazole.
MBTS	- Dibenzo thiazyl disulphide.
NR	- Natural rubber.
ph <sub>r</sub>	- parts per hundred parts of rubber.
psi	- pounds per square inch.
rpm	- revolutions per minute.
RAPRA	- Rubber and Plastics Research Association.
SBR	- Styrene butadiene rubber.
SMR	- Standard Malaysian rubber

(VI)

- TMTD - Tetra methyl thiuram disulphide.
- TMTM - Tetra methyl thiuram monosulphide.
- TBBS - N-tertiary butyl benz thiazole-2-sulphenamide.
- ZDDC - Zinc diethyl dithiocarbamate.
- ZDMC - Zinc dimethyl dithiocarbamate.
- Zn - Zinc
- ZMBT - Zinc salt of mercapto benz thiazole.

## Key to "Codes" of rubber compound formulations

CODE	SMR5	Polyisoprene	Zinc oxide	Stearic acid	Sulphur	MBT	MBTS	TMTD	HMT	ZDDC	DPG	Hydroquinone
101	100	-	5	2.5	2.4	1.2						
102	100	-	5	2.5	2.4		1.2					
103	100	-	5	2.5	2.4						1.2	
107	100	-	5	2.5	2.4			1.2				
108	100	-	5	2.5	2.4					1.2		
109	100	-	5	2.5	2.4				1.2			
* 101073	100	-	5	2.5	2.4	0.84		0.36				
* 101025	100	-	5	2.5	2.4		0.6				0.6	
101-MT 10107CA	100	-	-	-	2.4	0.876		0.324				
101-11	100	-	-	-	2.4	1.2						
101-12	100	-	-	-	2.4			1.2				
101-13	-	100	-	-	2.4	0.876		0.324				
101-16	-	100	1	1	2.4	0.876		0.324				
101-19	100	-	5	2.5	2.4	0.876		0.324				
101-20	100	-	5	2.5	2.4	0.876		0.324				0.4
101-21	100	-	5	2.5	2.4	0.876		0.324				0.8
101-22	100	-	5	2.5	2.4	0.876		0.324				2.4
101-26	-	100	-	-	2.4			1.2				
101-31	-	100	5	2	2.4			1.2				
10107C	100	-	5	2.5	2.4	0.876		0.324				

1. Tables 2-21 contain all the codes referring to the different ratios of the four combinations studied. Considering combination A (MBT-TMTD) as an example, the code for the compound formulation containing 30% of TMTD and 70% of MBT is 101073. Codes for all other accelerator combinations are given on the same basis.
  
2. 101-MT and 10107CA refer to the same formulation. 10107C refers to the formulation containing the critical ratio of MBT and TMTD. Similarly 10109C, 10108C and 10203C refer to the formulations containing the critical ratios of the combinations B, C and D. The letter "A" refers to the absence of zinc oxide and stearic acid. 10107CA is 10107C with no zinc oxide and no stearic acid.
  
3. The letters HQ refer to the presence of Hydroquinone.  
(usually 1.0 phr)
  
4. The letters DPPH refer to the presence of DPPH.  
(usually 0.35 phr)
  
5. The letters Resor refer to the presence of Resorcinol.  
(usually 1.0 phr)



ABSTRAK

Penyelidikan dan perkembangan yang berterusan terhadap pembaikan vulkanisasi belerang sejak terciptanya pada tahun 1839 telah mengakibatkan penukaran yang berfaedah seperti penggunaan aselerator tunggal dan aktivator-aktivator dalam sistem belerang biasa sistem E.V. (efficient vulcanization) dan applikasi kombinasi aselerator-aselerator. Penggunaan aselerator-aselerator organik dimulakan pada awal tahun 1930. Ada beberapa aselerator organik bila digunakan secara kombinasi menunjukkan kesan yang aktif atau kesan sinergistik dalam kadar vulkanisasi dan sifat fizikal getah vulkanisa. Cara dan mekanisme pergerakan aselerator-aselerator sehingga sekarang belum dapat dijelaskan dengan memuaskan, kerana itu tidak ada teori asas yang boleh menyatakan kadar yang tepat untuk kombinasi-kombinasi aselerator yang boleh menghasilkan kesan sinergistik maksima.

Pendapat-pendapat awal mengenai tajuk ini ialah kombinasi-kombinasi menambahkan aktiviti (atau kesan aktif) adalah kerana pembentukan sebatian kompleks molikul seperti garam daripada kedua-dua aselerator dan kompleks ini lebih larut didalam getah dengan itu

memperlihatkan aktiviti yang bertambah itu.

Keterangan lain mengenai pergerakan ini seperti yang diberi oleh "Dogadkin" adalah berasakan makenisma radikal bebas. Beliau menyatakan vulkanisasi belerang dengan aselerator berlaku melalui makenisma radikal bebas dan radikal-radikal bebas itu dibentuk pada keseluruhannya oleh ceraian thermal. Bagi kombinasi-kombanasi aselerator radikal-radikal bebas dibentuk oleh tiadakbalas kimia diantara aselerator-aselerator (rujuk bahagian 2.16) yang mungkin berlaku dengan tenaga yang kurang daripada tenaga ceraian thermal, dan oleh sebab itulah lebih banyak radikal-radikal bebas dapat dipusatkan dan dengan itu menambahkan aktiviti.

Makenisma radikal bebas tidak dapat diterima seperti yang dibincangkan dan dijelaskan dalam bahagian 4.2.1. Makenisma polar mungkin digunakan untuk menerangkan keputusan dan penghasilan pengajian ini.

Kadar vulkanisasi sistem-sistem yang mengandungi getah asli, belerang, oksid zinkam dan asid stearik yang tetap dan kadar molar yang berubah (tetapi jumlah berat adalah sama) bagi empat kombinasi-

kombinasi aselerator pilihan diukur pada lima suhu yang berlainan dengan menggunakan reometer Monsanto 100.

Keputusan-keputusan dari kajian ini dapat menunjukkan kesan sinergistik maksima dalam vulkanisasi, tenaga aktivasi, masa "scorch" dan tinggi kesan reometer pada suatu kadar "critical" (berat) komponen aselerator-aselerator dalam tiap-tiap kombinasi yang dikaji, menunjukkan kadar "critical" untuk tiap-tiap kombinasi yang menunjukkan keadaan yang mungkin pada struktur struktur aselerator bagi kompleks zing - ion, yang terlibat dalam sistem ini sebagaimana yang diterangkan dalam bahagian 4.2.2. Pendapat ini telah membuka jalan untuk memilih pertimbangan yang tepat bagi kadar berat komponen aselerator untuk menghasilkan faedah maksima dari kombinasi aselerator dengan kesan sinergistik untuk vulkanisasi belerang getah.

Daripada keputusan-keputusan dan penghasilan-penghasilan ini mungkin dapat menimbulkan minat yang lebih aktif untuk penyelidikan yang lebih dalam pada masa hadapan mengenai perkara ini yang penting dalam teknologi getah.

ABSTRACT

Continuous research and development towards the improvement of sulphur vulcanization since its discovery in 1839, has resulted in useful modifications such as the use of single accelerator and activators in the conventional sulphur systems, the E.V. (efficient vulcanization) systems, and the applications of accelerator combinations. The use of combinations of organic accelerators started as early as 1930s. Certain organic accelerators when used in combinations were found to give boosted effects or synergistic effects in the rate of cure and physical properties of the vulcanized rubber. The mode of their action and mechanisms have not been satisfactorily explained hitherto, and thus there is no theoretical basis available to predict the favourable ratio (of the components of any accelerator combination), which could give the maximum synergistic effects.

Early opinion of this subject was that the combinations of accelerators gave increased activity (or boosting effect) due to the formation of a salt like molecular complex compound by the two accelerators, and this complex was more soluble in rubber thus

showing the increased activity.<sup>98-100</sup> Another explanation of this synergistic action, is based on a free radical mechanism by Dogadkin<sup>101</sup>. He has stated that the accelerated sulphur vulcanization reactions proceed through a free radical mechanism and these free radicals are formed generally by thermal dissociation. In the case of accelerator combinations the free radicals are formed by chemical action between accelerators (refer section 2.16) which probably occurs with less energy than that by thermal dissociation and thus provides a larger concentration of free radicals leading to increased activity.

A free radical mechanism does not prove to be acceptable as reasoned and elaborated in section 4.2.1. A polar mechanism appears to be more feasible in explaining the results and observations of this study.

The rates of cure of systems containing fixed amount of natural rubber, sulphur, zinc oxide and stearic acid and variable molar ratios (but the same total weight) of four selected accelerator combinations were measured at five different temperatures using a Monsanto rheometer 100.

The results of this study, showing maximum synergistic effects in the rate of cure, activation energy, scorch time, and the height of the rheometer curve, around a critical (weight) ratio of the component accelerators in each of the combinations studied, point to a critical molar ratio giving the highest activity thus throwing some light on the nature of the probable structures of the accelerator-zinc ion-complexes, involved in these systems, as explained in section 4.2.2. This idea, opens a path for one to select, on a rational basis the favourable weight ratios of the component accelerators, to obtain the maximum benefits, from an accelerator combination exhibiting synergistic effects, for sulphur vulcanization of rubber.

It is envisaged that these results and observations may arouse more active interest in deeper research in the future, on this important subject in rubber technology.

## Chapter I

### Introduction

#### 1.1 Sulphur vulcanization of rubber

The success of the rubber industry was in great doubt in the 1830s due to the undesirable properties of unvulcanized natural rubber (NR) becoming soft and sticky in hot summer time and hard and brittle in cold winter weather (refer section 2.2). Sulphur vulcanization which was discovered in 1839 emerged as an apt and timely answer to this problem, giving a new long lease of life to the NR industry. Sulphur, the oldest vulcanizing agent which awakened an active interest in the great industrial potential of rubber is still the most popular vulcanizing agent in use. Many other vulcanizing agents have been discovered during the past 136 years. But the rubber compounds used in the Concordes' tyres are still vulcanized with sulphur, because of the intrinsic excellence of sulphur in conferring the overall balance of desirable technological and physical properties to rubber. This is why sulphur vulcanization of NR has

been continuously developed inspite of the discovery of other vulcanizing agents, and today there are certain developments of new modifications of sulphur vulcanization such as the E.V. systems available (refer section 1.2 below) which are useful to some extent, in promoting the continued use of NR in various applications, at a time when NR is faced with a strong challenge from the synthetic rubbers. Further developments, aimed at better technological and superior physical properties for NR, may perhaps result from more extensive research towards a clearer understanding of various aspects of accelerated sulphur vulcanization of rubber. Much work has been done in this field, but there are some important aspects, like the action of synergistic accelerator combinations, in sulphur vulcanization, which are not clearly unravelled or satisfactorily explained yet.

### 1.2 Developments of modifications of sulphur vulcanization

Many modifications have been introduced in the sulphur vulcanization of rubber, over a century of continuous research and development, towards its



improvement. Use of organic accelerators evolved the first major modification of sulphur vulcanization followed by the introduction of activators which gave further advantages, such as directing the accelerators to be more specific in efficiently utilizing the sulphur for crosslinking. Recent developments on this subject were centered around the more efficient use of this sulphur. Results of some extensive research work at the Malaysian Rubber Producers Research Association (MRPRA) at U.K. have aided to formulate some efficient vulcanization systems (E.V. systems) based on very low dosage of sulphur and higher dosage of accelerators<sup>133</sup>.

### 1.3 Accelerator combinations in sulphur vulcanization of rubber

Another technologically relevant modification of the sulphur vulcanization of rubber is the use of combinations of accelerators instead of single accelerator. No complete study has yet been published on this subject. Of the papers available, (see section 2.16.1), most are of commercial orientation and give very little informations regarding the

mechanism of the reaction. But the application of accelerator combinations in rubber industries has been in use for quite some time. Some suppliers of accelerators are marketing such combinations, as new products (see section 2.16). The consumer, manufacturer and the accelerator supplier, all three sectors accrue benefits through the applications of accelerator combinations. By replacing a single accelerator with the same weight part or even less of an accelerator combination, the consumer is able to get better end properties and thus improved performances. The manufacturer is able to get much faster cure rate and sometimes even longer scorch time plus faster cure. The supplier naturally can get better profits and greater demands for the accelerator combinations by marketing them as new products.

#### 1.4 The present study

The present study, on the action of accelerator combinations in the sulphur vulcanization of rubber, has been undertaken by the author to investigate some of the gaps that exist on the accumulated knowledge already available on this technologically

important subject. The author has worked for eight years, in the compound development and quality control divisions of the tyre industry, which has helped him to gain considerable experience in the handling of accelerators. In the writing of this thesis, a great deal of knowledge has been drawn from this practical experience, which together with the valuable guidance of his supervisor at the Universiti Sains Malaysia, is hoped will make a small positive contribution towards this important but hitherto not fully understood area of the accelerated sulphur vulcanization of rubber.

As stated in section 2.16, the earlier work done on this subject of accelerator combinations by Minotaya, Kojima and Nagai<sup>98,99</sup> has expressed the views that the increased activity of the combination is due to the formation of a salt like complex. Another group of authors<sup>101</sup> have classified the combinations into three classes viz. (1) systems with mutual activation, (2) systems with activation of one of the accelerators, and (3) systems with additive action. These authors in attempting to explain the action of these binary accelerator

systems, by a free radical mechanism, have stated that the free radical formation by chemical action between accelerators probably occurs with less energy than that by thermal dissociation and thus provides a larger concentration of free radicals. But the mode of this chemical action is not made clear by them. Considering a combination of MBTS and DPG, they assumed that a molecular complex compound is formed between the two accelerators, and that this complex dissociates into free radicals thus initiating the crosslinking reaction.



If this is true then free radical inhibitors should reduce the rate of vulcanization. Dogadkin et al<sup>101</sup> also stated that the greatest activity of this accelerator combination is obtained at a ratio of accelerators, which provides the maximum formation of MBT. This ratio which gives the greatest activity may provide some clues regarding the nature of the structural configuration of the zinc-accelerator complex formed in such combinations.

Hence in this study it is intended to:

- (1) Measure the rates of vulcanization effected by a few accelerator combinations in natural rubber-sulphur systems in the presence of zinc oxide and stearic acid, at various ratios of the relevant accelerators involved in each combination and to find out the critical ratio at which the maximum rate of vulcanization (i.e. maximum activity) occurs for each combination.
- (2) Measure the rates of vulcanization of the different ratios of each combinations of accelerators at different temperatures and to find out how the activation energy values change with the different ratios for each combination of accelerators, and,
- (3) to find out whether there is any experimental evidence for a free radical mechanism in the sulphur vulcanization systems, using combinations of accelerators.

Extensive work on the chemical kinetics of sulphur vulcanization of rubber, has provided abundant literature and data, but the results are not consistent as may be seen from the work of Craig<sup>30</sup>,

Juve<sup>29</sup>, Lorenz et al<sup>38a</sup>, and Scheele et al<sup>38c</sup> in their attempts to determine the order of vulcanization reaction. The kinetics of sulphur vulcanization of rubber is as tangled as the polymer chains themselves, owing to the experimental difficulties involved in the correct estimation of the actual amount of crosslinks formed. Because crosslinking reaction is a complex one, with the added complications of the simultaneous occurrence of crosslink degradations and modifications. The effects of non-rubber constituents in the case of NR and added ingredients like zinc oxide and stearic acid also increase the complex nature of the kinetics of vulcanization. Nevertheless, kinetic studies with comparable systems, aimed at feasible objectives, do yield useful informations as may be seen from the present study.

The rates of cure of systems containing fixed amounts of natural rubber, sulphur, zinc oxide and stearic acid, and variable molar ratios (but the same total weight) of four selected accelerator combinations were measured at five different temperatures (145°C - 165°C) using a Monsanto

rheometer 100. Activation energy values of these systems have been calculated from the cure rate values using the Arrhenius equation given below as explained in section 2.13.4.

$$K = S e^{-E/RT}$$

The other parameters used in this study are the maximum rheometer torque values and the scorch time values, both of which have been obtained from the rheometer curves. Synergistic curves based on these parameters have been plotted, and the critical molar ratios (of all four accelerator combinations) which give the maximum activity have been calculated from these curves. These results and observations have been discussed in terms of certain proposed structures and mechanisms which are contained in later chapters.

Chapter IITHEORETICAL2.1 Brief historical account of the prevulcanization days of rubber

No account on vulcanization of rubber would be complete without a brief mention of the prevulcanization days.

Natural rubber has been known to the natives of the Amazon Basin of South America for several centuries before the discovery of vulcanization and has been used by them to make play balls, waterproof clothing and footwear. Columbus in 1496 was the first European<sup>1</sup> to see rubber in the form of play balls used by the natives of Haiti. It is believed that rubber has been used to make rubber goods such as play balls and footwear very much earlier. In fact the oldest known samples of rubber were discovered in 1924 in the Eocene lignite deposits of Germany, the age of which had been estimated as up to 55,000,000 years<sup>1</sup>. These samples were found to contain 2% combined sulphur probably absorbed by them from adjacent materials thus showing their affinity to sulphur.



Even though the news about rubber was carried by Columbus and his colleagues to Europe around 1496, about 344 years were to pass before the rubber became practically serviceable to human population through the discovery of vulcanization.

Probably around the beginning of the 17th century, some of the Portugese and Spanish sailors<sup>2</sup>, who saw the uses of rubber in the Amazon Basin, coated their caps with latex to make them waterproof. But this method of rubberising the fabrics was unsatisfactory. In 1760's some French Scientists<sup>2</sup> evaluated the use of turpentine as a solvent for crude rubber and this improved the method of application of rubber to fabric.

"Coutchouc" was the original name for rubber used by the natives of South America. The English Scientist Joseph Priestly gave the name "rubber" to this coutchouc, in 1770, when it was used in Europe to rub pencil marks.

But until around 1820, there were not enough practical demonstrations of the crude rubber goods made in Amazon Basin in the more developed countries like America and England to convince and make the people in those areas to realise the great industrial potential of this rubber.

A few pairs of crude rubber shoes made by the natives of Para were brought to Boston in 1820 and subsequently over 500 pairs were sold in America at US \$5.00 per pair<sup>3</sup>. This shows that rubber's property of keeping feet from dampness was recognised during these early days that these crude heavy and uncomfortable shoes could demand such a price indicating the great potential of rubber industry.

Around 1825 the Europeans and Americans also had started using the unvulcanized raw rubber for manufacturing rubber goods like footwear, mailbags, and raincoats and to market these goods in the unvulcanized crude form. Charles Mackintosh<sup>2</sup> was one of the outstanding manufacturers of rubber goods in England during this period. Use of coal tar naphtha as solvent for rubber had apparently given him a rubber film on fabrics less sticky during summer days than the films obtained from other solvents. He took a patent for this process in 1823 and Thomas Hancock was one of the first to apply for licence to use this patent.

## 2.2 The problems encountered in using rubber goods in the unvulcanized form

This primitive industrial application of raw rubber had posed a big industrial research problem to the industrialists, technologists, and scientists. Because the unvulcanized natural rubber became soft and sticky in the hot summer days, stiff and hard in the cold winter days and resinous and brittle after using for a short period due to ageing, i.e. oxidation of the rubber hydrocarbon by atmospheric oxygen. These undesirable qualities of the raw natural rubber became the main handicap and obstacle for the development of the rubber industry and even retarded the progress of industrial applications of rubber as most of the manufacturers of rubber goods during that period of 1800-1844 had to think of abandoning their industries due to the numerous claims, complaints and criticisms by their customers<sup>4</sup>. One can imagine the extent of frustration and disappointment of the helpless customers of that period, in comparison to a present day customer who claims full replacement of the tyre for a small patch of undervulcanized rubber due to bad mixing or some other reason.

### 2.3 What is Vulcanization ?

Vulcanization is the process of heating raw rubber with a suitable substance like sulphur, or any treatment of compounded rubber which produces chemical crosslinking of the macromolecules of rubber and thus introducing changes in the physical properties and chemical nature of rubber. Rubber which is essentially plastic before vulcanization becomes essentially elastic after vulcanization. It changes the solubility characteristics of rubber markedly. Even though vulcanized rubber swells to over 300%, it is insoluble in the common solvents for raw unvulcanized rubber, such as, benzene, toluene, hexane, chloroform and carbon tetra chloride. Vulcanized rubber has much better physical and mechanical properties such as higher modulus, higher hardness, higher resilience, higher tensile and tear strength, higher abrasion resistance, higher resistance to temperature changes (does not become soft and sticky in hot summer days and hard and brittle in cold winter days), higher resistance to solvents and chemicals and even oxidation.

Hence, vulcanization is the most important and

the key technological process in the manufacture of rubber goods serviceable to mankind, from the raw rubber, which if not vulcanized, poses many problems in the usage and is unsuitable for any industrial applications.

The other terms generally used for vulcanization are 'cure' and 'crosslinking'. It is the discovery of this vital technological process which emerged as a rejuvenator to the dying rubber industry of 1830's and gave it a long new lease of life with rapid progress and a bright and prosperous future.

#### 2.4 Discovery of vulcanization

Goodyear of America is generally considered as the father of vulcanization, even though the same discovery was made almost at the same time in England by Thomas Hancock who is rightly regarded as the father of the British rubber industry.

Once the industrial potential of rubber had been realised by the more developed countries, they started manufacturing rubber goods from raw rubber. But the problems posed by the undesirable qualities

of unvulcanized rubber goods had made the scientists, technologists and industrialists in Europe and America to search for a suitable chemical or process which could eliminate these problems. Metallic oxides such as lead oxide, magnesium oxide, calcium oxide, and iron oxide were the first substances to be tried out.

The two outstanding figures who were the pioneer workers for the discovery of vulcanization were Goodyear of America and Thomas Hancock of England. Goodyear was born on the 29th December, 1800<sup>4</sup>. Goodyear was apprenticed in hardware business but he took up to rubber goods manufacture after his first contact in 1836 with the Roxbury Company (rubber goods manufacturers) which wanted to buy a new type of valve for an air cushion devised by Goodyear.

He received an order from the United States Government for a considerable quantity of mailbags. The mailbags were manufactured and finished in the warm season. But a few weeks later these bags deteriorated and dropped off the handles. This

caused a great loss to Goodyear. Nevertheless he applied himself alone with unabated ardour and diligence, devoting a lot of time and money towards the search, for an additive or a process which could eliminate these undesirable properties of crude rubber, which caused a great loss for him in connection with the United States Government order for the mailbags.

Goodyear tried mixing into rubber, everything that he could possibly think of<sup>5</sup>. After many trials magnesia seemed to give him good results. But a spell of hot weather quickly disposed of this theory. Later, boiling lime with rubber seemed to have solved his problem but again he was disappointed. Once by accident while using nitric acid to remove some bronze powder from rubber, he noticed that the acid left the rubber surface hard and thought nitric acid was the answer and obtained a patent calling this process as acid gas process. But this also did not stand the test of time, as the action by nitric acid on rubber was only superficial. When he sold this patent on acid gas process to Nathaniel Hayward of Roxbury company, he came to know about Hayward's patent for the solarization process. Hayward used

sulphur containing solvents like turpentine for preparing rubber films coated on fabrics which were exposed to sunlight after coating. This treatment was found to remove the undesirable properties of rubber to some extent. He developed this idea by preparing a film of a mixture of rubber and sulphur, i.e. by adding sulphur into the solvents, or by using solvents with higher sulphur content. But even such treatment did not remove considerably or satisfactorily the undesirable properties of raw unvulcanized rubber.

Goodyear bought this patent from Hayward and continued with his experiments of combining crude rubber and sulphur. In the latter part of 1839 while on one of his visits to his factory for the purpose of closing down and discontinuing operations, he conducted some experiments to ascertain the effect of heat upon the same compound that had decomposed in the mailbags and other articles<sup>6</sup>. He was surprised to find that a specimen of a mixture of sulphur and crude rubber accidentally brought in contact with a hot stove, charred like leather<sup>5</sup>. Then he heated a rubberised fabric before an open fire and observed



a layer of cured rubber. Thus he had found the object of his search, the result of his agonising, strenuous and exhausting research towards the process of "vulcanization" which undoubtedly became an important milestone and a prosperous turning point in the history of the service of rubber to mankind, and the progress of the rubber industry. This became the first of many experiments which culminated in the discovery of vulcanization which could render the crude rubber very much less affected by heat, cold, solvents and atmospheric oxidation. He extended his discovery to industrial applications by mixing 100 parts of crude rubber with 20 parts of sulphur and 23 parts of white lead and using this compound to coat or rubberise textile fabrics to be used in mailbags and raincoats. He obtained a patent for this in 1844<sup>7</sup>. His patent specifies that a temperature of 270<sup>o</sup>F is necessary for best effect of vulcanization of this compound of rubber, sulphur and white lead. It also states that natural rubber could be combined with the sulphur and white lead by mixing on heated cylinders or calender rollers.

What Goodyear was to the American rubber world, Thomas Hancock was to the British rubber industry. They both being contemporaries discovered the process of vulcanization almost simultaneously but independently in their own countries.

Thomas Hancock began manufacture of rubber articles in England in 1819 and the following year he invented the masticator for rubber. Sometimes in the early part of the autumn of 1842, one of his friends, Mr. Brockedon showed him some pieces of rubber brought from America by an agent for Goodyear who invented vulcanization<sup>s</sup>. These pieces had sulphur smell and were unaffected by cold, heat and solvents. These were the requirements Hancock was searching for in order to make his rubber goods serviceable and durable. Hence he started to experiment the effect of sulphur in crude rubber. He gradually increased the temperature of molten sulphur bath in which he dipped the rubber sheet and observed the improved results. While he discussed this subject amongst his friends, Mr. Brockedon suggested the term "vulcanization" for this process which brought about valuable changes in the

properties of crude rubber, which was essential for the progress of rubber industry. Hancock obtained a patent for this process in 1843<sup>9</sup>.

The discovery of the process of vulcanization of rubber laid the foundation of the modern rubber industry. Two men had vested interests in the early development, progress and commercial use of rubber. They worked hard to make rubber of greater commercial value as evidenced by their fascinating personal descriptions of their discovery in Goodyear's "Gum Elastic" and Hancock's "Personal narrative of the origin and progress of the coutchouc or India rubber manufacture in England"<sup>10</sup>. Both were crowned with success for their strenuous efforts but the latter part of their lives were unpleasant due to the litigations which sometimes happen to be the price of the achievements of genii.

Discovery of vulcanization is a remarkable technological achievement as it is the key process in the technology of manufacture of rubber goods serviceable to mankind, from the raw polymers.

## 2.5 Vulcanizing Agents

Any chemical or agent which could initiate the chemical reaction of crosslinking of the macromolecules of rubber resulting in a three dimensional network of the rubber, is called a vulcanizing agent. The first known and the most common vulcanizing agent is sulphur. The other vulcanizing agents used are: Sulphur Chloride, Sulphur Dioxide plus Hydrogen Sulphide, Selenium, Tellurium, Halogens of Selenium and Tellurium, Benzoyl Peroxide, Dicumyl Peroxide, Disulphides of tetra alkyl thiurams, thiocyanates, isocyanates, phenol formaldehyde resins, amines plus oxidising agents, Quinones, Quinone dioximes, Quinoxalines, sulphur donors such as morpholine derivatives, organometallic compounds, metallic oxides and high energy radiations.

The selection of vulcanizing agents depends on the type of polymer and the end use. For example, for natural rubber tyre compound, sulphur is used in combination with suitable accelerators, for chloroprene rubber, zinc and magnesium oxides are used and for a heat resistant rubber compound, thiuram disulphide is used.

## 2.6 Other compounding ingredients

The other ingredients of rubber which are closely related to the vulcanizing agents are: accelerators of vulcanization, retarders and activators. Fillers, softeners and antidegradants are also ingredients present in most of the industrial rubber compounds.

### 2.6.1 Accelerators of vulcanization

As the name implies, these are organic compounds which can speed up the rate of vulcanization of rubber with sulphur. As the rate of vulcanization is dependent on temperature, accelerators can lower the temperatures of vulcanization. Besides this, accelerators are capable of promoting more efficient utilisation of sulphur for crosslinking and imparting better physical and mechanical properties to the rubber vulcanizates. Examples are, mercapto benzo thiazole, dipehnylguanidine, thiuram disulphides and sulphenamides.

### 2.6.2 Retarders

These are organic or inorganic compounds (generally but not necessarily acidic) which slow down the rate of vulcanization. These are used in compounds which are scorchy (i.e. compounds which undergo prematured vulcanizing during processing stages before the compound is purposely heated for vulcanization). Examples: Salicylic Acid, Phthalic Anhydride, Benzoic Acid and N-Nitrosodiphenylamine.

### 2.6.3 Activators

These are organic or inorganic substances which improve the effectiveness of the accelerators, not only by speeding up the rate of vulcanization but also by imparting better physical and mechanical properties to the rubber vulcanizates (vulcanized rubber). They take part in the chemical reaction of crosslinking possibly through the formation of complexes with the accelerators, which are more soluble in rubber than the accelerators themselves. Examples of activators: metallic oxides such as zinc oxide and fatty acids such as stearic, lauric and oleic acids.