BOUND ANTIOXIDANTS IN ELASTOMERS

BY

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Summary

Amine and phenolic antioxidants are found to react with chloroprene (CR) and epichlorohydrin (ECH) rubbers with their reactive chlorine atoms. These reactions take place during high shear mixing in a torque rheometer or in a Winkworth mixer at high temperature or during the vulcanization of the elastomers at 160°C.

Mixed alkyl, aryl secondary amines are shown to react only at the alkyl substituted amino group. Mono substituted sodium salt of dihydric phenols were initially used to facilitate reaction with the rubbers but this was found unnecessary as the free phenols will react to give high yields of bound antioxidant.

The concentration of the bound antioxidants are estimated by I.R. spectroscopy after complete extraction.

Monsanto rheometer studies show that in many cases the cross-linking reaction of CR and ECH rubbers which take place through the chlorine atom are reduced by the presence of the antioxidants.

The effectiveness of the rubber-bound antioxidant is assessed by accelerated oven ageing, U.V. irradiation and stress-relaxation techniques. It is shown that immobilization of amine antioxidants by combining them with the network does not impair their antioxidant activity. Phenolic antioxidants whether free or bound give very good effective protection to chloroprene rubbers but act as pro-oxidant with epichlorohydrin rubber. The effect is increased in the presence of nickel dibutyldithiocarbamate which is commonly employed as an antioxidant for ECH rubber.

Epichlorohydrin rubber bound antioxidant can be used as a very effective polymeric antioxidant in chloroprene rubbers.

Key Words

Rubber bound antioxidant, Polychloroprene,
Polyepichlorohydrin, Thermal-oxidative degradation.

The work described in this thesis was carried out between March 1979 and April 1982. It has been done independently and submitted for no other degree.

M.S. AL-MEHDAWI

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LIST OF FIGURES

Fig. No.	Page
3.1	80
3.2	87
3.3	88
3.4	91
3.5	94
3.6	95
3.7	98
3.8	99
3.9	103
3.10	108
3.11	109
3.12	112
3.13	113
3.14	117
3.15	118
3.16	122
3.17	125
3.18	127
3.19	129
3.20	133
3.21	135
3.22	136
3.23	137
3.24	140
3.25	142
3.26	144
3.27	148
3.28	151
3.29	152
3.30	154
3.31	155
3.32	159
3.33	163
3.34	167
3.35	170
3.36	173
3.37	174
4.1	192
4.2	193
4.3	194
4.4	195
4.5	199
4.6	200
4.7	203
4.8	207
4.9	213
4.10	214
4.11	215
4.12	216
4.13	217
4.14	218
4.15	219

Fig. No.	Page	Fig. No.	Page
4.16	220	5.1	286
4.17	226	5.2	287
4.18	230	5.3	292
4.19	232	5.4	293
4.20	236	5.5	294
4.21	237	5.6	297
4.22	243	5.7	298
4.23	245	5.8	303
4.24	246	5.9	305
4.25	247	5.10	306
4.26	248		
4.27	254		
4.28	257		
4.29	261		
4.30	264		
4.31	266		
4.32	270		
4.33	271		
4.34	272		
4.35	277		
4.36	279		

LIST OF TABLES

Table No.	Page
2.1	45
3.1	79
3.2	82
3.3	85
3.4	86
3.5	90
3.6	100
3.7	101
3.8	104
3.9	107
3.10	110
3.11	111
3.12	119
3.13	123
3.14	124
3.15	128
3.16	131
3.17	132
3.18	141
3.19	143
3.20	147
3.21	150
3.22	156
3.23	157
3.24	160
3.25	162
3.26	166
3.27	168
3.28	169
3.29	175
3.30	176
4.1	189
4.2	191
4.3	198
4.4	198
4.5	204
4.6	205
4.7	210
4.8	223
4.9	227
4.10	229
4.11	233
4.12	234
4.13	238
4.14	241
4.15	242
4.16	253
4.17	256
4.18	258
4.19	260
4.20	263
4.21	265
4.22	268
4.23	269
4.24	269
4.25	276

Table No.	Page
5.1	284
5.2	285
5.3	290
5.4	291
5.5	295
5.6	299
5.7	302
5.8	304

CONTENTS

Page

Chapter One

INTRODUCTION 1

1.1 DEGRADATION OF POLYMERS 1

1.2 OXIDATIVE DEGRADATION 3

1.3 ANTIOXIDANTS 5

1.3.1 PREVENTIVE MECHANISMS 5

1.3.1.1 Light Absorbers 6

1.3.1.2 Metal Ion Deactivators 6

1.3.1.3 Peroxide Decomposers 7

1.3.1.3.1 Metal Dithiocarbamates 7

1.3.1.3.2 Transition Metal Dithiophosphates 8

1.3.1.3.3 Mono and Disulphides 9

1.3.2 CHAIN BREAKING ANTIOXIDANTS 10

1.3.2.1 Phenolic Antioxidants as Chain Terminators 10

1.3.2.2 Amines as Chain Breaking Antioxidants 13

1.3.3 SYNERGISM 15

1.3.3.1 Homosynergism 15

1.3.3.2 Heterosynergism 16

1.3.3.3 Autosynergism 16

1.3.4 LONGEVITY OF ANTIOXIDANTS 17

1.3.4.1 Introduction 17

1.3.4.2 High Molecular Weight Antioxidants 20

1.3.4.3 Bound Antioxidants 23

1.3.4.3.1 The Chemical Binding of an Antioxidant to the Polymer before vulcanization 24

Page

1.3.4.3.2 By the Grafting of Vinyl Group Antioxidants in Rubber Lattice 24

1.3.4.3.3 Reaction of Non-reactive Antioxidants with the Rubbers in the Presence of Free Radicals. 25

1.3.4.3.4 Thiol Antioxidants Adducts in Rubber 27

1.3.4.3.5 Chemically Binding an Antioxidant to a Modified Rubber. 29

1.3.4.3.6 Chemical Binding of an Antioxidant to the Base Polymer during Compounding or Vulcanization. 31

1.3.4.3.7 The Binding of an Antioxidant to a Reactive Group in the Polymer 35

1.4 ASSESSMENT OF AGEING 37

Chapter Two

GENERAL EXPERIMENTAL TECHNIQUES 39

2.1 MATERIALS 39

2.1.1 SYNTHESIS OF MATERIALS USED IN THE WORK 41

2.1.1.1 Preparation of the Sodium Salt of 2,4-dihydroxybenzophenone 41

2.1.1.2 Preparation of the Sodium Salt of 4,4¯-butyliene (6-tert-butyl-m-cresol). 41

2.1.1.3 Preparation of N,N¯-chloro-propyl-p-phenylene diamine 42

2.2 APPARATUS USED FOR MODIFICATION OF RUBBERS 43

2.2.1 LABORATORY TWO ROLL MILL 43

2.2.2 WINKWORTH "2"BLADE MIXER 43

2.2.3 RAPRA VARIABLE TORQUE RHEOMETER 43

Page

2.2.4 BANBURY MIXER 44

2.3 PREPARATION OF VULCANIZATES 45

2.3.1 COMPOUNDING 45

2.3.2 MONSANTO OSCILLATING DISC RHEOMETER 46

2.3.3 VULCANIZATION OF COMPOUNDS 48

2.3.4 EXTRACTION OF VULCANIZATE 49

2.4 ACCELERATED AGEING TESTS 50

2.4.1 STRESS-RELAXATION 50

2.4.2 ULTIMATE-TENSILE STRENGTH AND ELONGATION AT BREAK 53

2.4.3 THE HARDNESS 54

2.4.4 MODULUS AT 100% AND 50% EXTENSION 55

2.4.5 ULTRA-VIOLET IRRADIATION 57

2.4.6 INFRA-RED SPECTROSCOPY 58

2.4.6.1 Characterisation of Synthesised Compounds 58

2.4.6.2 Estimation of Amount of Bound Antioxidant 58

2.4.6.3 Measurement of Carbonyl-Index for Ageing Assessment 61

2.4.7 OIL AGEING 61

Chapter Three

POLYCHLOROPRENE 64

3.1 INTRODUCTION 64

3.1.1 SULPHUR MODIFIED POLYCHLOROPRENE (TYPE-G) 65

3.1.2 MERCAPTO MODIFIED POLYCHLOROPRENE (TYPE-W) 66

3.1.3 POLYMER STRUCTURE 67

3.1.4 VULCANIZATION OF POLYCHLOROPRENES 70

3.1.5 OXIDATION AND AGEING OF POLYCHLOROPRENES 73

Page

Further Reactions of Polychloroprenes 76

Experimental Work 76

3.2 REACTIONS OF ANTIOXIDANTS WITH POLYCHLOROPRENE 78

3.2.1 REACTION OF CR TYPE-W WITH AMINES 78

3.2.1.1 Reactions of CR Type-W with IPPD 78

3.2.1.1.1 Assessment of Amount of Reaction of IPPD 78

3.2.1.1.2 Reaction of CR Type-W with IPPD during Mixing in the Torque Rheometer 81

3.2.1.1.3 Reaction of IPPD during Vulcanization 81

3.2.1.1.4 Mechanism of Reaction of IPPD with CR Type-W 82

3.2.1.1.5 Effect of IPPD on the Vulcanization Characteristics of CR Type-W in the Absence of other Accelerators 85

3.2.1.1.6 Effect of IPPD bound to CR Type-W by Pre-Mixing on Vulcanization Characteristics. 89

3.2.1.1.7 Assessment of Effectiveness of Bound IPPD on CR Type-W 92

3.2.1.1.7.1 Stress Relaxation 92

Results and Discussion 93

3.2.1.1.7.2 Accelerated Oven Ageing of Vulcanizates 96

3.2.1.1.7.2.1 UTS and Elongation at Break 97

3.2.1.1.7.2.2 Hardness 97

Results and Discussion 102

3.2.1.2 Reaction of CR Type-W with DPPD 105

3.2.1.2.1 Reaction of CR Type-W with DPPD on Milling 106

Page

3.2.1.2.2 Effect of DPPD on Vulcanization Characteristics of CR Type-W Rubber 107

3.2.1.2.3 Attempted Detection of Bound DPPD by Means of Antioxidant Activity 111

3.2.1.2.3.1 Stress Relaxation 111

Results and Discussion 111

3.2.1.2.3.2 Accelerated Oven Ageing 115

3.2.1.2.3.2.1 UTS and Elongation at Break 115

Results and Discussion 116

3.2.1.3 Reaction of Santoflex-13 with CR Type-W 120

3.2.1.3.1 Proof of Absence of a Cross-Linking Reaction 121

3.2.1.3.2 Infra-Red Absorbtion Studies 121

3.2.1.3.3 Effect of Santoflex-13 on the Vulcanization Characteristics of CR Type-W 123

3.2.1.3.4 Assessment of Effectiveness of Santoflex-13 on CR Type-W 126

3.2.1.3.4.1 Stress Relaxation 126

Results and Discussion 126

3.2.2 REACTIONS OF AMINES WITH CR TYPE-G 128

3.2.2.1 Reaction of CR Type-G with IPPD 130

3.2.2.1.1 Effect of IPPD on Vulcanization Characteristics of CR Type-G 130

3.2.2.1.2 Assessment of Effectiveness of IPPD for CR Type-G 132

3.2.2.1.2.1 Monsanto Rheometer Studies 132

Page

3.2.2.1.2.2 Stress Relaxation 134

Results and Discussion 134

3.2.2.1.2.3 UTS and Elongation at Break 138

Results and Discussion 138

3.2.2.1.2.4 I.R. Confirmation of the Reaction Between CR Type-G and IPPD during Vulcanization 139

3.2.2.2 Reaction of Santoflex-13 with CR Type-G 141

3.2.2.2.1 Effect of Santoflex-13 on Vulcanization Characteristics of CR Type-G 141

3.2.2.2.2 Proof of Absence of Cross-Linking 143

3.2.2.2.3 Stress Relaxation 143

Results and Discussion 143

3.2.3 REACTION OF PHENOLS WITH CR TYPE-W 146

3.2.3.1 Reactions of CR Type-W with Topanol CA 146

3.2.3.1.1 Effect of Topanol CA on the Vulcanization Characteristics of CR Type-W 147

3.2.3.1.2 Assessment of Effectiveness of Topanol CA for CR Type-W 149

3.2.3.1.2.1 Stress Relaxation 149

Results and Discussion 150

3.2.3.1.2.2 Accelerated Oven Ageing of the Vulcanizates 153

3.2.3.1.2.2.1 UTS and Elongation at Break 153

3.2.3.1.2.2.2 Hardness Measurements 158

Results and Discussion 158

3.2.3.1.2.2.3 Determination of Extent of Reaction of Topanol CA with CR Type-W 162

Page

3.2.3.2 Reactions of CR Type-W with Santowhite Powder 165

3.2.3.2.1 Effect of Santowhite Powder on the Vulcanization Characteristics of CR Type-W. 165

3.2.3.2.2 Attempted Detection of Bound Santowhite Powder by Means of Antioxidant Activity 168

3.2.3.2.2.1 Stress Relaxation 169

Results and Discussion 169

3.2.3.2.2.2 Accelerated Oven Ageing of Vulcanizates 171

3.2.3.2.2.2.1 UTS and Elongation at Break 172

Results and Discussion 172

Chapter Four

POLYEPICHLOROHYDRIN (ECH) 179

4.1 INTRODUCTION 179

4.2 POLYMER STRUCTURE 182

4.3 VULCANIZATION OF ECH 183

4.4 AGEING OF ECH 185

Further Reaction of ECH 187

4.5 EXPERIMENTAL 188

4.5.1 TO ASSESS THE FUNCTION OF THE VARIOUS COMPOUNDING INGREDIENTS 188

4.5.1.1 The Vulcanization Characteristics of ECH Homopolymer 189

Results and Discussion 190

4.5.1.2 Stress Relaxation 190

Results and Discussion 191

Page

4.5.1.3 Oven Ageing 197

Results and Discussion 198

4.5.2 REACTION OF ECH WITH AMINES 202

4.5.2.1 Reaction of ECH with IPPD Antioxidant 202

4.5.2.1.1 Assessment of Amount of IPPD Bound into ECH 202

4.5.2.1.2 Reaction of IPPD with ECH Rubber During Mixing in the Winkworth Machine 202

4.5.2.1.3 Effect of Milling on the Reaction Between IPPD and ECH Homopolymer 205

4.5.2.1.4 Reaction of IPPD with ECH During Vulcanization 205

4.5.2.1.5 The Effect of IPPD on the Vulcanization of ECH with and without Diak No. 1 206

4.5.2.1.6 The Mechanism of the Reaction Between IPPD Antioxidant and ECH Rubber 206

4.5.2.1.7 Effect of IPPD on the Ageing of ECH. 209

4.5.2.1.7.1 Introduction 209

4.5.2.1.7.2 Effect of the IPPD on the Vulcanization Characteristics of ECH Homopolymer 211

4.5.2.1.7.3 Assessment of Effectiveness of Bound IPPD as an Antioxidant to ECH Polmer. 211

Results and Discussion 212

4.5.2.1.7.4 The Effect of Extraction on ECH Homopolymer Before Compounding. 225

Results and Discussion 227

4.5.2.2 Reaction of ECH with Santoflex-13 229

Page

4.5.2.2.1 Proof of Absence of a Cross-Linking Reaction Between Santoflex-13 and ECH Homopolymer 229

4.5.2.2.2 Assessment of Amount of Santoflex-13 Bound into ECH 231

4.5.2.2.3 Reaction of ECH Rubber with Santoflex-13 in the Winkworth Machine 231

4.5.2.2.4 Reaction of ECH with Santoflex-13 in Torque Rheometer 231

4.5.2.2.5 Reaction of ECH with Santoflex-13 during Vulcanization 233

4.5.2.2.6 The Effect of Santoflex-13 on Vulcanization Characteristics of ECH Homopolymer 234

4.5.2.2.7 Assessment of Effectiveness of Santoflex-13 as an Antioxidant on ECH Homopolymer 235

4.5.2.2.7.1 Stress Relaxation 235

Results and Discussion 238

4.5.2.2.7.2 Oil Ageing 240

4.5.2.2.7.2.1 Determination of the Swelling Changed by ASTM Oil No. 1 and 3. 241

Results and Discussion 242

4.5.2.2.7.2.2 UTS and Hardness in ASTM Oils 244

Results and Discussion 244

4.5.3 REACTION OF ECH HOMOPOLYMER WITH PHENOLIC ANTIOXIDANTS 252

4.5.3.1 Reaction of ECH with Santowhite Powder and its Sodium Salt 252

Page

4.5.3.1.1 Assessment of Amount of Santowhite Powder Bound to ECH Homopolymer 253

4.5.3.1.2 Reaction of ECH with Sodium Salt of Santowhite Powder in Torque Rheometer 255

4.5.3.1.3 Reaction of ECH with Sodium Salt of Santowhite Powder During Mixing in a Winkworth Mixer 255

4.5.3.1.4 Reaction of ECH with Santowhite Powder During Vulcanization 255

4.5.3.1.5 Effect of Santowhite Powder on the Vulcanization Characteristics of ECH Rubbers 256

4.5.3.1.6 Assessment of Effectivness of Santowhite Powder as an Antioxidant for ECH Homopolymer 259

4.5.3.1.6.1 Stress Relaxation 260

Results and Discussion 260

4.5.3.1.6.2 Accelerated Oven Ageing of Vulcanizate 262

4.5.3.1.6.2.1 Ultimate Tensile Strength 263

4.5.3.1.6.2.2 Hardness Measurements 265

Results and Discussion 265

4.5.3.2 The Effect of NBC on the Effectiveness of the Phenolic Antioxidants for ECH Rubbers 268

4.5.3.2.1 Stress Relaxation Studies 269

4.5.4 THE EFFECT OF 2,4-DIHYDROXYBENZOPHENONE AS AN ULTRA-VIOLET STABILIZER IN ECH RUBBER 275

4.5.4.1 Determination of the Extent of Reaction of Mono-Sodium Salt of 2,4-dihydroxybenzophenone with ECH Homopolymer 275

Page

4.5.4.2 Reaction Between Mono-Sodium Salt of the 2,4-dihydroxybenzophenone with ECH in the Winkworth Mixer 276

4.5.4.3 Assessment of the Effectiveness of 2,4-dihydroxybenzophenone (free or bound) in ECH to U.V. Irradiation 278

Results and Discussion 278

Chapter Five

THE EFFECT OF ANTIOXIDANT BOUND IN ECH RUBBER ON THE DEGRADATION OF CR RUBBERS 282

5.1 INTRODUCTION 282

5.2 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON CR TYPE-G 283

5.2.1 ON VULCANIZATION CHARACTERISTICS OF CR TYPE-G 283

5.2.2 STRESS RELAXATION 285

Results and Discussion 285

5.3 THE EFFECT OF ECH HOMOPOLYMER ON THE PROPERTIES OF CR TYPE-G RUBBERS 290

5.3.1 MONSANTO RHEOMETER STUDIES 291

5.3.2 STRESS RELAXATION STUDIES 291

5.4 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIXOIDANT ON CR TYPE-W RUBBERS 295

5.4.1 ON VULCANIZATION CHARACTERISTICS 295

5.4.2 STRESS RELAXATION 296

Results and Discussion 296

5.5 THE EFFECT OF ECH-SANTOWHITE POWDER BOUND ANTIOXIDANT ON THE THERMAL OXIDATIVE DEGRADATION OF CR TYPE-W 301

Page

5.5.1 VULCANIZATION CHARACTERISTICS OF CR TYPE-W 302

5.5.2 STRESS RELAXATION 304

Results and Discussion 304

Chapter Six

CONCLUSIONS 308

6.1 BOUND ANTIOXIDANTS IN POLYCHLOROPRENE 308

6.1.1 AMINES 308

6.1.1.1 N,N$^-$-isopropyl-phenyl-p-phenylene diamine (IPPD) 308

6.1.1.2 N,1,3,-dimethyl-butyl-N-phenyl-p-phenylene diamine (Santoflex-13) 309

6.1.1.3 N,N$^-$-diphenyl-p-phenylene diamine (DPPD) 310

6.1.2 PHENOLS 310

6.1.2.1 1,2,3,tris(2-methyl-4-hydroxy-5-tert-butyl phenyl) butane (Topanol CA) 310

6.1.2.2 4,4$^-$-butylidene bis (3-methyl-6-tert-butyl phenol) (Santowhite Powder) 311

6.2 BOUND ANTIOXIDANTS IN POLYEPICHLOROHYDRIN 312

6.2.1 THE FUNCTION OF THE VARIOUS COMPOUNDING INGREDIENTS 312

6.2.2 AMINES 312

6.2.2.1 N,N$^-$-isopropyl-phenyl-p-phenylene diamine (IPPD) 312

6.2.2.2 The Effect of Extraction on the Stability of ECH Rubber 314

6.2.2.3 N,1,3-dimethyl-butyl-N-phenyl-p-phenylene diamine (Santoflex-13) 314

Page

6.2.3 PHENOLS 316

6.2.3.1 4,4¯-butylidene bis(3-methyl-6-tert-butyl phenol) (Santowhite powder) 316

6.2.3.2 The Effect of NBC on the Effectiveness of the Phenolic Antioxidants 317

6.2.3.3 2,4-dihydroxybenzophenone as U.V. Stabilizer 317

6.3 THE USE OF ECH WITH BOUND ANTIOXIDANTS AS POLYMERIC ANTIOXIDANT 318

REFERENCES 319

CHAPTER ONE

INTRODUCTION

1.1 DEGRADATION OF POLYMERS

All rubbers are considerably affected by natural or accelerated ageing processes, such as oxygen, ozone, light, weather and radiation, all of which lead to a deterioration in quality and reduction in service life. The rate of oxidation is not only determined by the chemical structure of the polymer, but also by the physical changes that often take place during oxidation. Hardening of the polymer occurs when oxidative cross-linking predominates in the ageing process, e.g. styrene butadiene (SBR), polychloroprene (CR), polypropylene. Softening occurs when chain scission is the predominant ageing process as in the case of cis 1,4 - polyisoprene (IR) and polyisobutyline isoprene copolymer (IIR). It is not surprising, then, that an antioxidant which offers excellent protection in one rubber is not the most effective stabilizer for another(1).

The atmospheric oxidation of natural rubber (NR) was one of the first polymer ageing processes to be studied in detail from a mechanistic point of view(2).

Polymer characteristics affecting the rate and extent of the degradation reaction include:-

(1) The chemical structure of the polymer(3).

(2) The physical structure of the polymer(4).

(3) The molecular weight of the polymer(5,a,b).

(4) The presence of chemical and physical impurities act as pro-oxidant or anti-degradent (6,7)

(5) The change in stress-strain during service i.e. dynamic or static fatigue (8).

1.2 OXIDATIVE DEGRADATION

Environmental factors affecting the degradation of polymers include:-

(a) Temperature

(b) Concentration of oxygen or ozone

(c) Ultra-Violet or high energy radiation.

In service a rubber is usually subjected to a variety of degrading influences which have a synergistic effect. The damage produced by fatigue, for example, is accelerated in the presence of oxygen, even more by ozone and is worse still if it gets hot in the process.

Oxygen is considered the most important reason for the degradation of rubber. Its attack is often autocatalytic in nature and, therefore, a very small amount of oxygen can cause severe degradation. The major primary cause of oxidation is due to the formation of hydroperoxide, that will decompose under appropriate conditions to give free radicals capable of initiating an oxidation chain reaction which may result in chain scission and/or cross-linking.

The general sequence[(2)] of oxidative attack consists of initiation, propagation and termination reactions.

(1) Initiation

$$RH \xrightarrow[\text{energy}]{\text{activation}} R^{\cdot} + H^{\cdot} \qquad (1.1)$$

(2) Propagation

$$R^{\bullet} + O_2 \xrightarrow{Fast} ROO^{\bullet} \quad (1.2)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad (1.3)$$

$$ROOH \longrightarrow RO^{\bullet} + O^{\bullet}H \quad (1.4)$$

(3) Termination

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R \quad (1.5)$$

$$ROO^{\circ} + OH^{\bullet} \longrightarrow ROH + O_2 \quad (1.6)$$

$$2RO^{\bullet} \xrightarrow{Kt} \text{Non Radical Products} \quad (1.7)$$

During termination, the final products, vary with the structure of the hydrocarbon and the reaction conditions. In general a resonance-stabilised radical would be expected to yield more dimer (R-R) as opposed to reactive radical$^{(9)}$.

1.3 ANTIOXIDANTS

These are substances that may be added to polymers to prevent or reduce the rate of oxygen degradation. There are two mechanistically distinct classes of antioxidants:-

(1) Those that protect the polymer by preventing the formation of hydroperoxide by using surface to prevent contact with oxygen or ozone or the presence of material that absorbs U.V. radiation, for example 2,4-dihydroxybenzophenone. If hydroperoxide are formed, protection may be achieved by either destroying the hydroperoxide as soon as it is formed or by using radical acceptors that remain stable once they have combined with the propagating radicals.

(2) Antioxidants which operate by the chain breaking mechanism.

1.3.1 PREVENTIVE MECHANISMS

The peroxide decomposers, have proved to be the most important antioxidants in rubbers, although metal complexing agents are quite often used. Ultra-violet stabiliser is less often important because of the presence of filler which are effective U.V. screens(10). Compounds that react with peroxides and convert them to stable non-radical products are thus an important class of antioxidants, commonly referred to as peroxide decomposers. Stabilisers of this type include:-

1.3.1.1 Light Absorbers

The most important function of light absorbers is that they prevent or reduce the rate of formation of initiating free radicals in the polymers. Important types of these absorbers are orthohydroxy benzophenones(11,12).

It is now generally accepted(13,14) that photodegradation of polymers involves the same free radical chain mechanism as thermal oxidative degradation and the hydroperoxide are key initiators for the process of oxidative degradation polymer both during thermal and U.V. degradation.

1.3.1.2 Metal Ion Deactivators

The metal ions exert their catalytic effect upon autoxidation by forming unstable co-ordination complexes with alkylhydroxy peroxides, followed by electron transfer to give free radicals(2). Two oxidation-reduction reactions can be involved depending on the metal and its state of oxidation.

$$RO_2H + M^{+n} \longrightarrow R\dot{O} + M^{n+1} + \dot{O}H \qquad (1.8)$$

$$RO_2H + M^{n+1} \longrightarrow R\dot{O}_2 + M^{+n} + H^+ \qquad (1.9)$$

The metal ion deactivators function by deactivating the metal ion thereby, eliminating the catalytic activity of the ion in the decomposition of the hydroperoxide (15). The deactivating process can be achieved in one of the following ways:

(1) By complexing the metal ions to their maximum co-ordination number by various ligands (16,17,18).

(2) By stabilising one valence state at the expense of the other (19).

(3) By forming insoluble products (20).

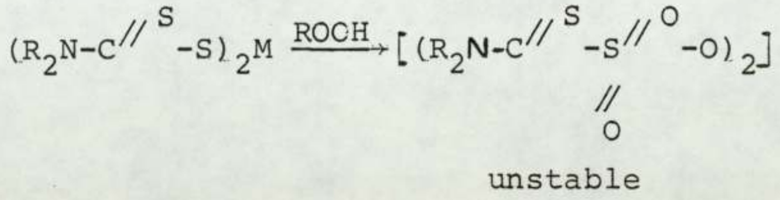
1.3.1.3 Peroxide Decomposers

Materials which contain sulfer, nitrogen and phosphorus promote the decomposition of organic hydroperoxides to form stable products and, thus, function as preventive antioxidants. The peroxide decomposers can be classified as follows:-

(1) Metal dialkyldithiocarbamates.
(2) Cyclic phosphite esters.
(3) Mono- and di- sulphide compounds.

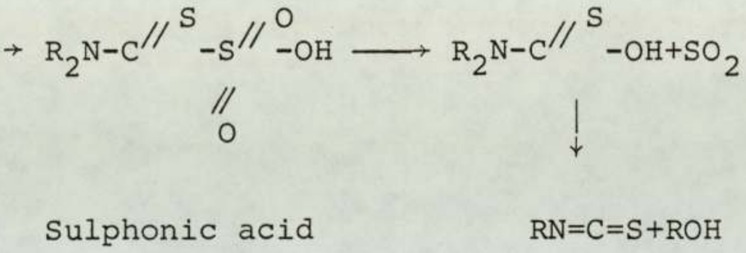
1.3.1.3.1 Metal Dialkyldithiocarbamates

These can react with hydroperoxide to form stable products by a non-radical mechanism (9), by a Lewis acid catalysed reaction involving the evolution of SO_2 and SO_3.



$$(R_2N\text{-}C\overset{S}{/\!/}\text{-}S)_2M \xrightarrow{ROCH} [(R_2N\text{-}C\overset{S}{/\!/}\text{-}\underset{\underset{O}{/\!/}}{S}\overset{O}{/\!/}\text{-}O)_2] \qquad (1.10)$$

unstable



$$\rightarrow R_2N\text{-}C\overset{S}{/\!/}\text{-}\underset{\underset{O}{/\!/}}{S}\overset{O}{/\!/}\text{-}OH \longrightarrow R_2N\text{-}C\overset{S}{/\!/}\text{-}OH+SO_2 \qquad (1.11)$$

$$\downarrow$$

Sulphonic acid

$$RN{=}C{=}S+ROH$$

Husbands(21), showed that sulphur trioxide is an effective catalyst for the decomposition of cumene hydroperoxide to give phenol and acetone and functions as a Lewis acid.

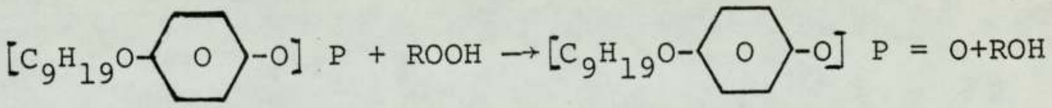
Smith(22), showed that these sulphoxide and sulphones present in the decomposition of hydroperoxide by the dithiocarbamates, are also effective antioxidants and have a higher order of activity than the sulphides.

The formation of sulphur dioxide has been invoked to explain the antioxidant activity of various sulphur containing antioxidants, such as the transition metal dithiocarbamates(23-25).

1.3.1.3.2 Transition Metal Dithiophosphates

The mechanism of oxidation inhibition by zinc dialkyldithiophosphates has been reviewed by Burn(26). These compounds are efficient peroxide decomposers and they are effective as inhibitors of hydrocarbon autoxidation(27).

A polar mechanism of decomposition was suggested, since phenol was the major decomposition product. For example, tri-nonyl phosphate (I) can decompose the hydroperoxide to alcohol without the substantial formation of free radicals.

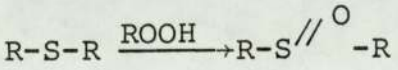


I

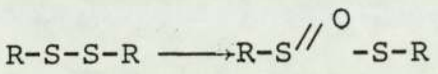
1.3.1.3.3 Mono and Di Sulphides

Denision(28-30) has made a detailed study of the effect of sulphides as antioxidants in hydrocarbon oils. Some of these antioxidants give an initial pro-oxidant effect followed by autoinhibition. The sulphides destroy any hydroperoxide present and are themselves converted to sulphoxide and sulphones.

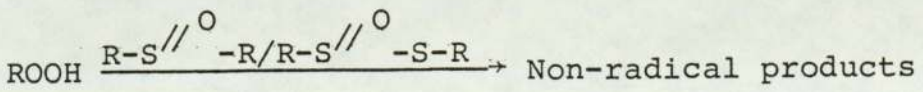
$$R_2S+ROOH \longrightarrow R_2SO \longrightarrow R_2SO_2 \qquad (1.12)$$



$$R\text{-}S\text{-}R \xrightarrow{ROOH} R\text{-}\overset{O}{\overset{/\!/}{S}}\text{-}R \qquad (1.13)$$



$$R\text{-}S\text{-}S\text{-}R \longrightarrow R\text{-}\overset{O}{\overset{/\!/}{S}}\text{-}S\text{-}R \qquad (1.14)$$



$$ROOH \xrightarrow{R\text{-}\overset{O}{\overset{/\!/}{S}}\text{-}R/R\text{-}\overset{O}{\overset{/\!/}{S}}\text{-}S\text{-}R} \text{Non-radical products} \qquad (1.15)$$

Direct addition of the sulphoxide appeared to immediately inhibit the oxidation of squalene in contrast to the delayed stabilisation observed with the corresponding suphides(31)

1.3.2 CHAIN BREAKING ANTIOXIDANTS

Consideration of the free radical chain mechanism of autoxidation suggests the use of materials capable of reacting with either $R^{\bullet}$ or $RO_2^{\bullet}$ free radicals to interrupt the propagation cycle and thus retard the oxidation process. The $R^{\bullet}$ are usually negligible compared to $RO_2^{\bullet}$ radicals.

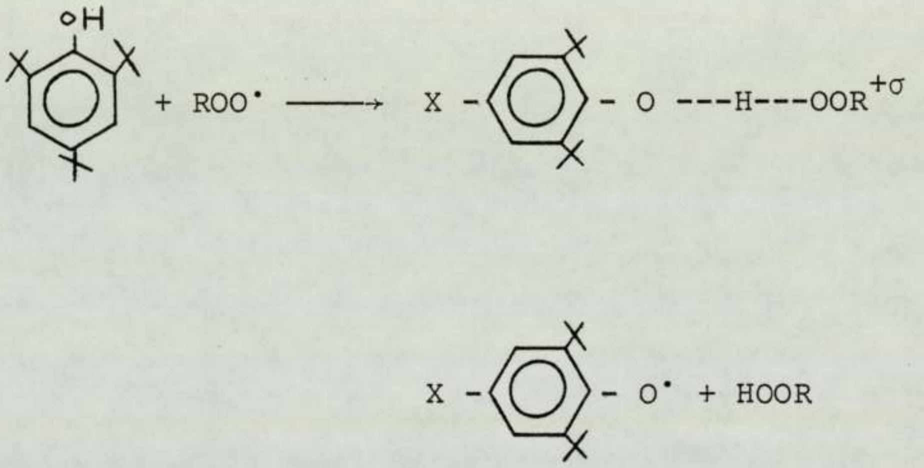
Aromatic amines and hindered phenols are the most important antioxidants of this class. Both types of compounds are themselves easily oxidised and it was initially believed that their role was sacrificial(32), i.e. they would react with oxygen and prevent attack on the polymer. It is now realised that amine and phenolic antioxidants operate by donation of hydrogen to free radicals formed during oxidation(33).

$$ROO^{\bullet}+AH \longrightarrow ROOH+A^{\bullet} \qquad (1.16)$$

where AH is the antioxidant added and $A^{\bullet}$ is the resulting stable radical.

1.3.2.1 Phenolic Antioxidants as Chain Terminators

Phenol itself is a poor antioxidant, but the hindered phenols are very powerful antioxidants, especially those with alkyl groups in the 2, 4 and 6 positions. The efficiency of the phenolic antioxidant is increased by increasing the bulk of the hindering alkyl group in the 2 and 6 positions. This is due to the reduction in the energy of the transition state which involves electron transfer to the peroxy radical and electron delocalisation in the aromatic ring (34).

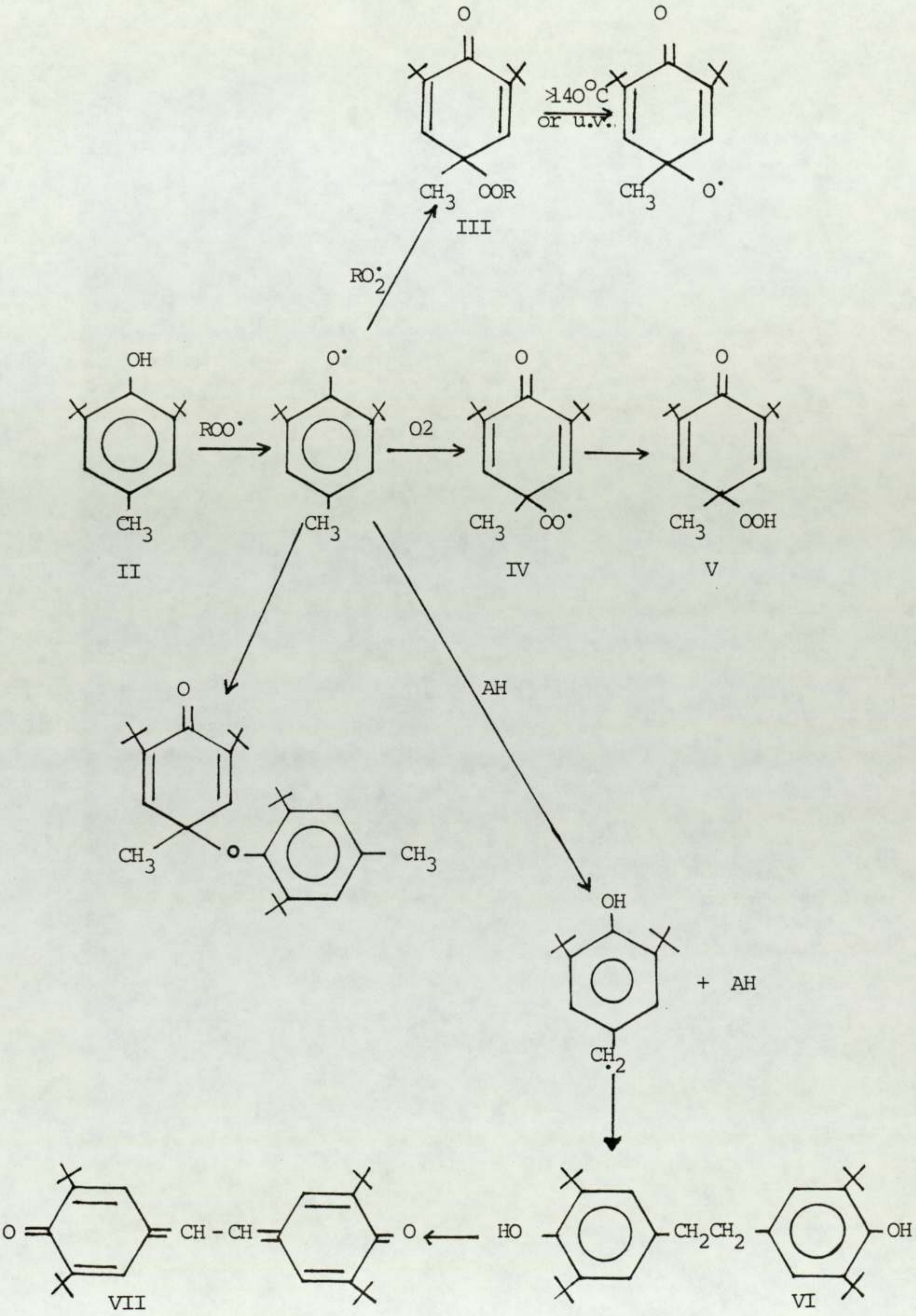


(1.17)

(1.18)

The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity (35).

(35)


O
CH3 OOR
III
>140°C
or u.v.
O
CH3 O•
RO2•
OH
CH3
II
ROO•
O•
CH3
O2
O
CH3 OO•
IV
O
CH3 OOH
V
O
CH3
CH3
AH
OH
CH2•
+ AH
O
CH - CH
O
VII
HO
CH2CH2
OH
VI

The ethylene bis phenol (VI) is an effective antioxidant as the initial phenol (II), and the stilbene quinone (VII) is also effective. The peroxydienones (III and V) are potential pro-oxidants due to the presence of the labile peroxide bond. Stilbene quinonone (VII) is formed in polymer during processing and has been shown to be considerably superior in antioxidant function to the parent phenols under conditions where loss of antioxidant is important(36).

The major effects governing phenolic antioxidant activity are(2):

(1) Electron releasing groups in the ortho and para positions increase the antioxidant activities.

(2) Electron attracting groups decrease activity.

(3) α-branched ortho alkyl group increase antioxidant activity, whereas, such groups in the para position decrease it.

Steric protection of the OH group is essential to prevent too rapid consumption of the antioxidant by direct oxidation and to reduce the activity of the derived radical (phenoxyl) in chain transfer.

1.3.2.2 Amines as Chain-Breaking Antioxidants

In general, the antioxidant action of aromatic amines is similar to that of hindered phenols. For an amine to function as an efficient antioxidant:

(1) The unpaired electron on the nitrogen atom should be delocalised.

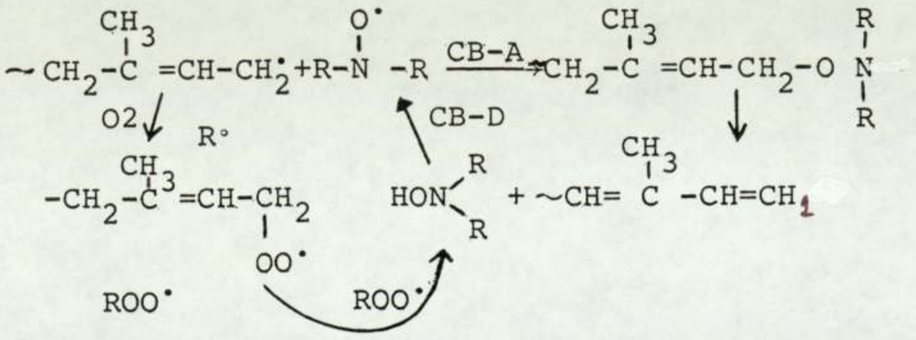
(2) The nitrogen atom should be sterically hindered.

(3) The amine should be able to react with the propagating peroxy radical.

The presence of a hydrogen atom which was earlier thought to be necessary has now been proved to be unimportant(37,38).

Secondary oxidation products formed from aromatic amines are also very powerful antioxidant(34). In particular, nitroxyl radicals which have central importance in stabilization of plastics and rubbers(39-42).

It has recently been observed that the diarylamines e.g. isopropyl-phenyl-p-phenylene-diamine(IPPD) owe their effective antifatigue antioxidant activity due to their conversion to the corresponding nitroxyl radicals. The effectiveness of this species as an antioxidant has been shown to be due to its continual regeneration by a cyclical mechanism involving hydroxylamine(43).



Hindered aliphatic amines behave in the same way although they are less effective. In both cases the parent amines are converted rapidly to the corresponding nitroxyl radicals during the ageing process, and the concentration of the alkyl-peroxy radical which is initially present falls to an immeasurably low value once the nitroxyl radicals begin to be formed in the system.

Unlike the diarylamines, the hindered aliphatic amines are not themselves antioxidants or antiozonants and have been shown to be converted to the effective nitroxy radical in apro-oxidant process(44,45).

1.3.3 SYNERGISM

A combination of antioxidants may show an affect far better than that of either alone at the same concentration. In opposite cases, when the observed effect is weaker, antagonism between the components of the mixture occurs.

G. Scott(46) distinguishes two mechanistically distinct types of synergistic behaviour.

1.3.3.1 Homosynergism

This came from two antioxidants of unequal reactivity, but operating by the same mechanism. A combination of

2-isopropyl-4-methylphenol and 2,6-di-tert-butyl-4-methyl phenol, for example, shows homosynergism due to their different reactivities towards peroxy radicals. The latter is called the inhibitor regenerator since it provides a constant reservoir of hydrogen atoms for the regeneration of the former active antioxidant, other types of hydrogen donors may be used similarly as inhibitor regenerator(47).

1.3.3.2 Heterosynergism

This is derived from the co-operative effect of two or more antioxidants acting by different mechanisms. These synergistic systems may be composed of a chain-breaking antioxidant with either a peroxide decomposer or an ultra-violet absorber with chain-breaking antioxidant(48), for example, this would bring about a reduction in the rate of radical formation and hence the chain-breaking antioxidant would be consumed more slowly.

1.3.3.3 Autosynergism

An important aspect of synergism, known as autosynergism occurs if a stabilizer functions in more than one way as an antioxidant. For example, some amine antioxidants have the ability to complex metal in addition to their chain-breaking activity(2).

The most obvious route to autosynergism is the inclusion of two types of functional capability in the same molecule. A number of phenolic antioxidant which are commercially available also contain either sulphur or phosphorous or both as part of the complex antioxidant molecule, e.g. the thiophenol which include the hindered phenol and a diaryl sulphide linkage.

1.3.4 LONGEVITY OF ANTIOXIDANTS

1.3.4.1 Introduction

Rubber articles such as gloves and protective clothing, particularly for medical use, are being routinely cleansed and high temperature sterilised.

Rubber threads and interlining are subjected to both detergent and solvent during dry cleaning processes, which lead to the rapid leaching of conventional antioxidants from the polymer. The loss of antioxidant by water leaching may play some part in the determining of the effectiveness of antioxidants in tyres.

Three main factors(49) need to be taken into consideration when evaluating antioxidant effectiveness under conditions of service:-

(1) The antioxidants inherent behaviour which is determined primarily by the chemical nature of the antioxidant function.

(2) The microenvironment of the antioxidant in the polymer, this governs the compatibility and ease of migration of the antioxidant.

(3) The rate of loss of antioxidant from polymer during volatilization, extraction, ... etc.

However, in polymer samples which have a high surface area to volume ratio (notably fibres and films), the effect of antioxidant volatility rather than inherent antioxidant activity is the dominant factor in determining stabilisation effectiveness. It is also found that for antioxidants having approximately the same steric hinderance, an increase in the molecular weight considerably reduces the volatility of the antioxidant.(53)

Gordon(50) and Lioÿed(51) have shown that the rate of loss of antioxidants by volatilisation or extraction and the rate of loss of oxidation products, depends to large extent on the thickness and surface area of the sample.

If vulcanizates are used at high temperature or in contact with solvents, the antioxidant may be lost by volatilisation or by leaching out respectively. The antioxidants may also slowly decompose or migrate to the surface(52).

Obviously, the loss of antioxidant will reduce the service life of the polymer i.e. it has been suggested that the reduction of fatigue life and dynamic ozone resistance in tyres is due to leaching out of antioxidant by water(52). Antioxidants, like p-phenylene-diamine, can be extracted from natural rubber and styrene-butadiene rubber stocks by water(54,55).

The performance(56) of antioxidants and antiozonants in rubber is also related to their volatility at high temperature which is effected by their vapour pressure.

Temchin(57), concluded that the predominant factors which determine the volatility of antioxidants is their ability to form a hydrogen bond, their molecular weight, and their dipole moment. It might be supposed that the volatility of an antioxidant would fall as a result of an increase in the force of molecular interaction. This is controlled in particular by a hydrogen bond and by increasing the sterric hinderance of the antioxidant, which is necessary to increase the effectiveness of antioxidants.

The efficiency(58) of sulphur containing antioxidants is reduced by chemical attachment to the vulcanizate. The decrease in the antioxidant efficiency is attributed to the reduction in the mobility of the antioxidant. Nevertheless, more works have shown that the chemical attachment did not effect the efficiency of the antioxidant(59,60).

The approach used to produce non-volatile, non-leaching high molecular weight antioxidant has been two fold:-

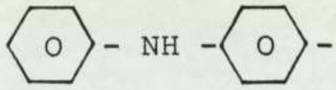
(1) Polymeric antioxidants have been produced for incorporation into rubber and plastics formulations by normal compounding techniques or by the polymerization of species which themselves have antioxidant activity or by attachment of antioxidant group to existing polymers.

(2) By chemically combining the antioxidant with the polymer to form 'bound antioxidant'. This is particularly important in the rubber field, where such groups may be introduced during vulcanization.

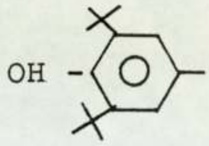
1.3.4.2 High Molecular Weight Antioxidants

As is to be expected an increase in the molecular weight of an antioxidant will reduce its volatility(46,49). The loss of 2,6-di-tert-butyl-4-methyl phenol, for example, is 20 times faster than that of 2-benzyl-4-methyl-6-tert-butyl phenol during the vulcanization of a rubber(61).

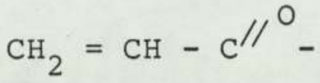
Kline and Miller(62), prepared polymerizable antioxidants by attaching antioxidant function such as 4-diphenylamine (VIII), and 3,5,-di-tert-butyl-4-hydroxy phenol (IX), to α,B- unsaturated acyl groups such as acryloyl (X) and methacryloyl (XI).



(VII)

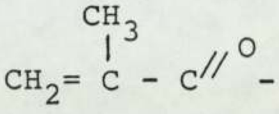


(IX)



$CH_2 = CH - C \overset{O}{/\!/} -$

(X)

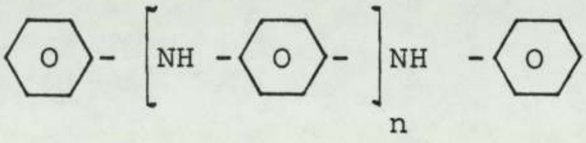


$CH_2 = \overset{CH_3}{\overset{|}{C}} - C \overset{O}{/\!/} -$

(XI)

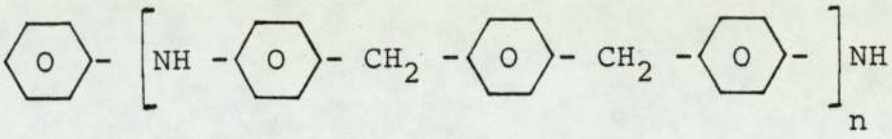
Ladd(63) had reported that the co-polymerization of phenolic substituted monomers in styrene-butadiene rubber system using $2,2^{-}$-azo-isobutyronitrile as initiator (AZBN).

A more recent approach to the production of high molecular weight antioxidants for high temperature rubbers has been pioneered by Thomas(64,65) and his co-workers. Two main types of condensation polymers have been evaluated in a rubber used in aero engines. The first (XII) incorporates the repeating unit of diaryl-p-phenylene diamine structure which is amongst the most effective of the simple aromatic amines as heat stabilizer.



(XII)

The second was a Friedel Craft condensation product containing the di-phenyl-amine function (XIII)

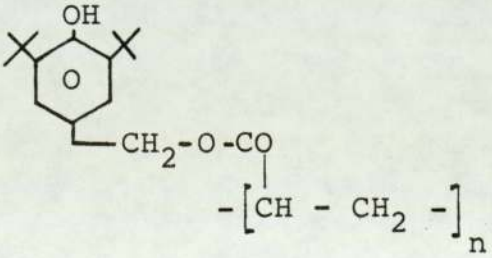


(XIII)

It seems likely that a broad molecular weight distribution for the polymeric antioxidant is an advantage in practice, since the lower molecular weight materials are more compatible with the polymer and will be effective at room temperature whereas, the high molecular weight antioxidants will become soluble at high temperature without being physically lost from the rubber.

Balogh et al(66), concluded that a molecular weight of 400 and higher ensures a low volatility of additive under severe technological conditions provided the thermal stability of the derivatives used is sufficient.

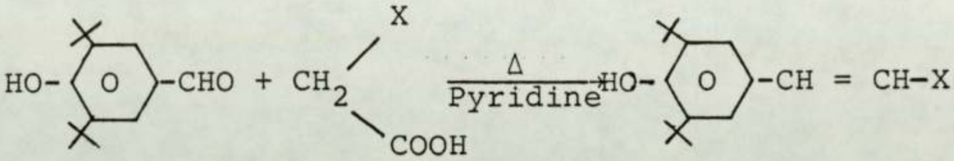
Antioxidants(67) containing a reactive vinyl group can be polymerized to low molecular weight polymers in the complete absence of oxygen. 3,5-di-tert butyl-4-hydroxy benzyl acrylate (DBBA) polymerises to give the polymer (XIV) with a molecular weight of $\bar{Mn} \approx 9500$.



(XIV)

This antioxidant has a similar acitivity to DBBA itself in a model substrate in which it is soluble.

A co-polymerizable phenolic antioxidant(68,69) has been prepared by condensing 3,5-di-tert-butyl-4-hydroxybenzaldehyde with compounds such as ethylhydrogen malonate and cyano acetic acid.



where X = COOR or CN

Phillips et al.(70) have prepared polymeric amine antioxidants by condensing an aromatic amine with a dihalogenomethylaromatic compound with the elimination of hydrogen halide.

1.3.4.3 Bound Antioxidants

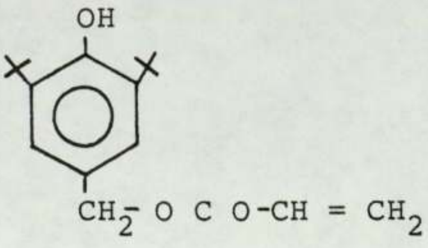
Antioxidant volatility may , also, be reduced by chemical modification of the main polymer so that the antioxidant may be comined with the backbone, thus obviating the need for a separate antioxidant system. This may be achieved by pre-treatment of the polymer prior to processing by reaction of the antioxidant groups with the polymer during processing or reaction with the polymer during vulcanization.

1.3.4.3.1 The Chemical Binding of an Antioxidant to the Polymer before Vulcanization

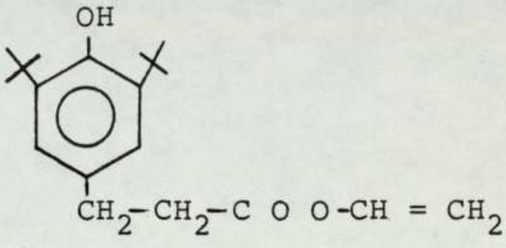
In order to assess possible reactions of the antioxidant that is to be combined with the polymer, reacting with the vulcanizing ingredients and thus interefering with the vulcanization process, it is sometimes better to combine the antioxidant with the rubber before vulcanization.

1.3.4.3.2 By the Grafting of Vinyl Group Antioxidants in Rubber Lattices

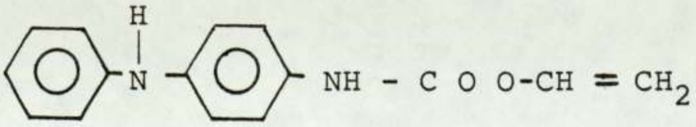
Many vinyl antioxidants have successfully grafted into natural rubber to give effective bound antioxidant using normal radical initiators(71,72). General methods of synthesis have been disclosed. Structures (XV), (XVI) and (XVII) are typical examples.



(XV)



(XVI)



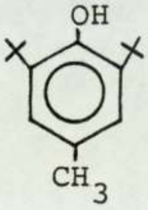
(XVII)

A bound antioxidant such as (XVI) had an almost identical antioxidant activity as the same antioxidant in the unbound form when added in the same concentration(73). The inevitable conclusion is that the segmental motion of the rubber backbone is sufficiently rapid to permit the bound antioxidant to perform its function.

1.3.4.3.3 Reactions of Non-Reactive Antioxidants with Rubbers in the Presence of Free Radicals

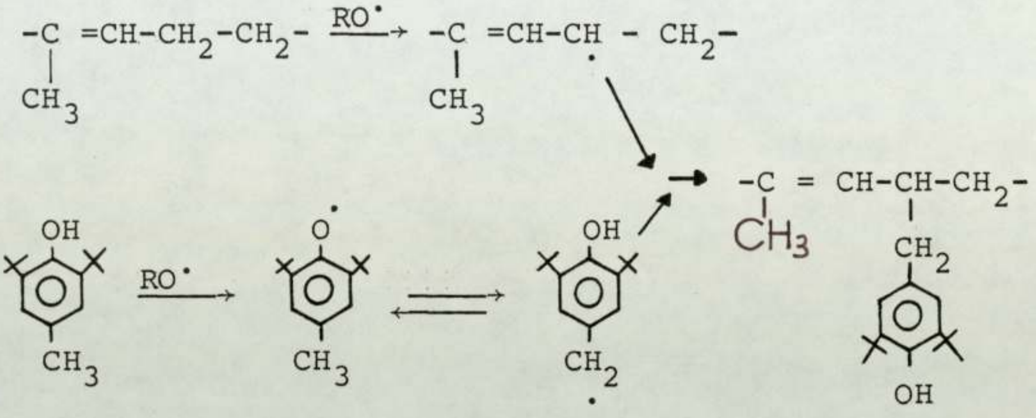
Small amounts of some antioxidants may become bound into rubber during processing or on long term storage(36). The effectiveness of such a process is dependent on the structure of the antioxidant.

It has been shown, for example, that only phenols containing 4-methyl group can be readily bound into the polymer. Up to 20% of 2,6-di-tert-butyl 4-methyl phenol (XV) contained in a formulation combined with natural rubber in the presence of an 'oxyl' radical used in a stoichiometric amount(72). Monophenols are more reactive than the bisphenols.



(XV)

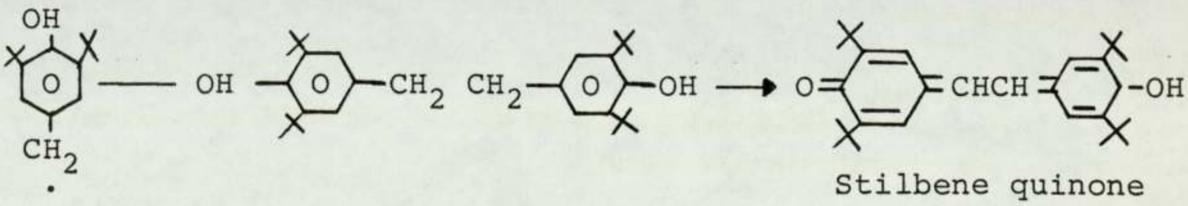
The above process provides a potential means of reacting cheap antioxidant with rubber by means of the radical-pair process.



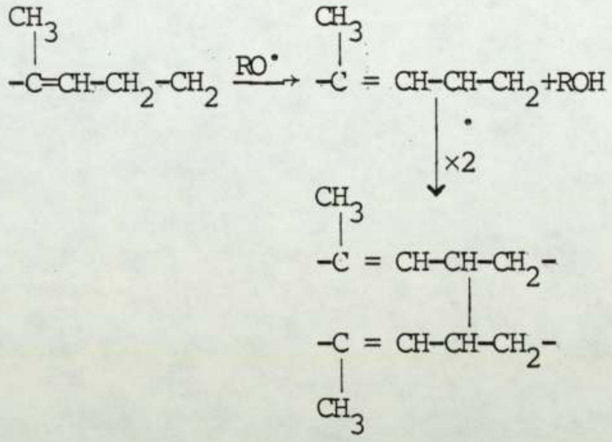
(XV)

This system has some major practical advantages including the cheapness of phenolic antioxidant and its non-interference with the subsequent curing characteristics of the rubbers. However, it has some disadvantages like the occurrence of unwanted reactions such as$^{(72)}$:-

(1) The formation of an intensely coloured stilbene quinone



(2) A parallel dimerization of the allylic rubber radical which will lead to cross-linking.

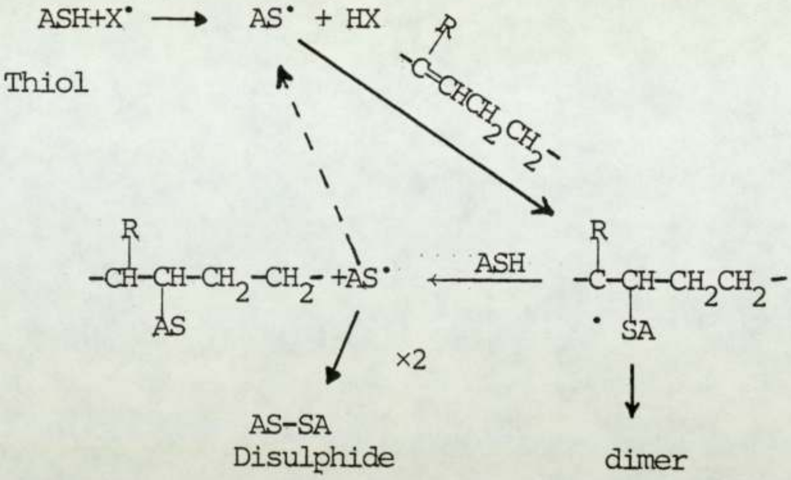


The phenolic antioxidant can inhibit this cross-linking reaction only when the antioxidant/radical generator is present at low concentration.

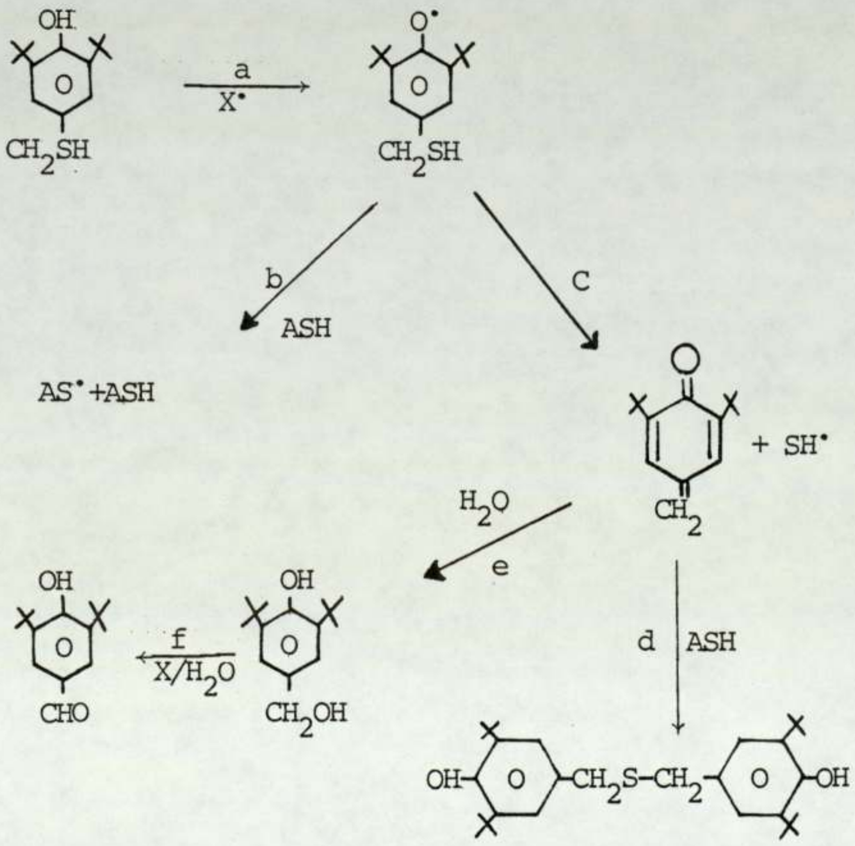
Recently, Evans$^{(67)}$ and Scott , have shown that the antioxidant 3,5-di-tert-butyl-4-hydroxy-benzyl acrylate may be grafted to the surface of a polymer. They claimed that the antioxidant activity is very much higher than that of low molecular weight antioxidants containing the same functional group.

1.3.4.3.4 Thiol Antioxidants Adducts in Rubber

Aliphatic thiols can undergo radical addition to double bonds to form bound antioxidant in the presence of a variety of free radicals ($X^{\cdot}$)$^{(73,74,75)}$. It is conveniently carried out in rubber lattices using a redox initiating system. The mechanism of addition process is as follows:-



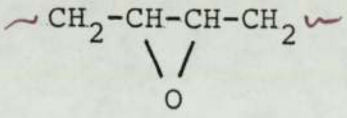
The minor attack of the initiator radical on the hindered phenol leads to a monosulphide and an aldehyde by-product both of which are highly effective anitoxidants. The mono- and di-sulphide by-products are found to react further with rubber latex by a radical initiated process to give bound antioxidants(76)



A major advantage of thiol based bound antioxidants is that relatively a high concentration can be produced which can be used as a master-batch to unmodified rubber, thereby, elminiating the need of reacting all the rubber.

1.3.4.3.5 By Chemically Binding an Antioxidant to a Modified Rubber

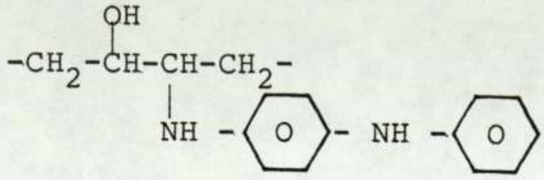
This involves activation of the polymer by prior introduction of an antioxidant-reactive functional group. Such a group may be formed by the epoxidation of the double bond in unsaturated rubbers(77-79). This can be achieved by either direct epoxidation with peroxy benzoic acid or by using a compound such as glycidyl-methacrylate as a comonomer (XVI).



$\sim CH_2-CH-CH-CH_2 \sim$ (O bridging the two CH)

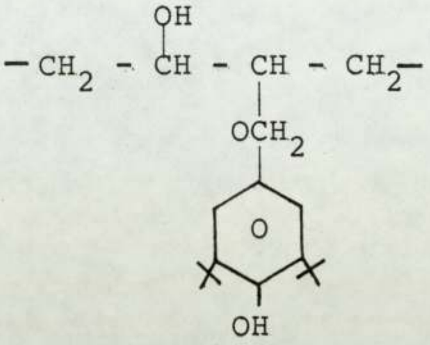
(XVI)

This type of epoxy rubber can be reacted with an amine such as p-amino-diphenylamine or B-naphthylamine in the presence of catalyst such as phenol which acts as acid catalyst to give (XVII) in high yield.



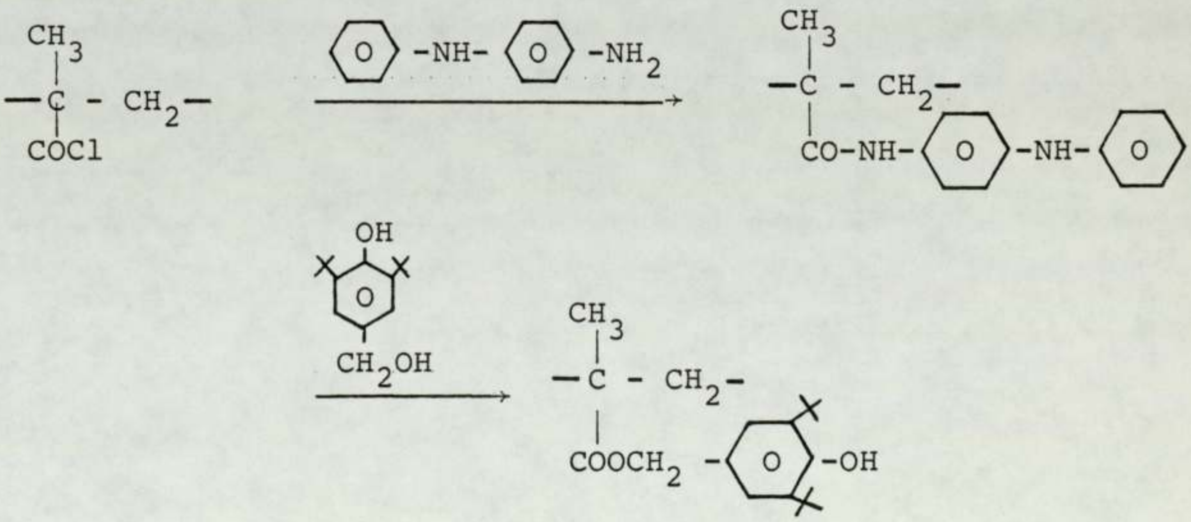
(XVII)

Lorenz(80), reacted epoxy NR or SBR or BR rubbers and 3,6-di-tert-butyl-4-hydroxy-benzyl alcohol and produced the bound antioxidant (XVIII)

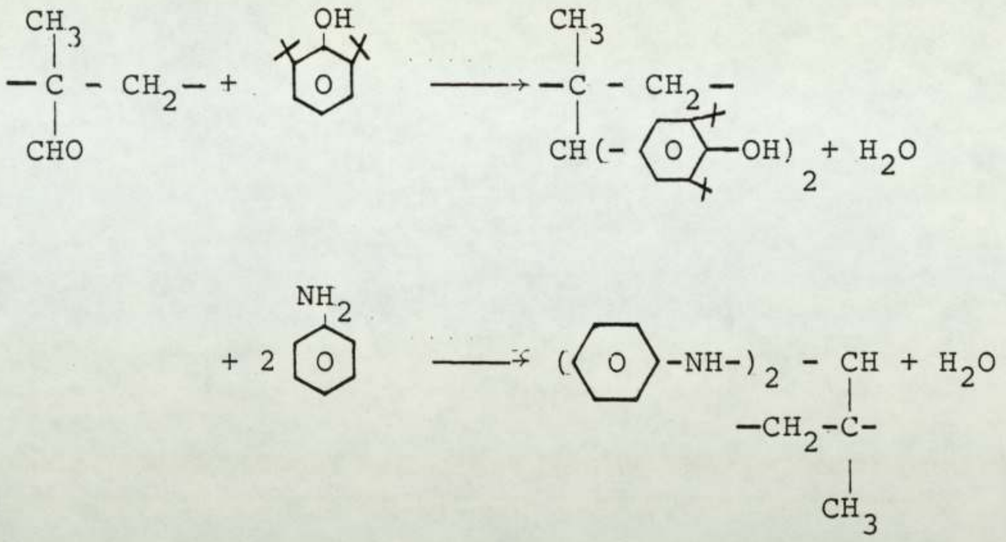


(XVIII)

Blatz and Maloney(81), reacted amine and phenol antioxidants with carboxylic acid halide modified rubber to achieve bound p-phenylene-diamine and phenolic antioxidant.

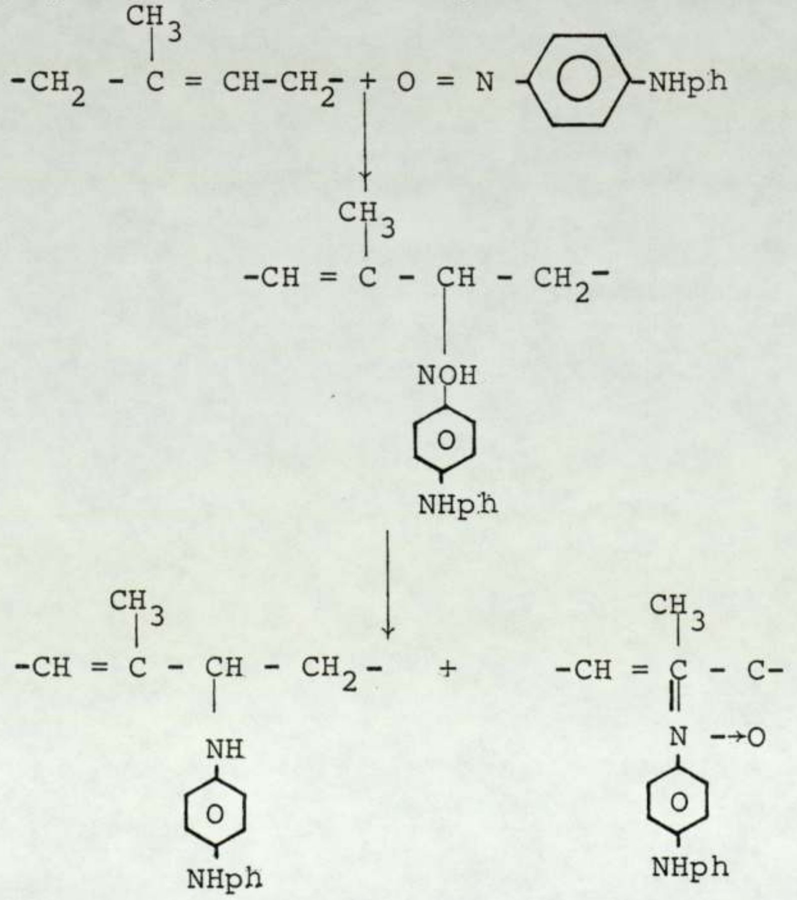


Other studies(82) involve the manufacture of a rubber containing the necessary functional groups by co-polymerisation. For example, a co-polymer of butadiene and methacrolein readily react with aniline and hindered phenols.



1.3.4.3.6 Chemical Binding of an Antioxidant to the Base Polymer during Compounding or Vulcanization

Cain and his co-workers(60,83,84), bound 4-nitroso aniline and 4-nitroso phenol into natural rubber containing α-methylenic hydrogen during the vulcanization process:

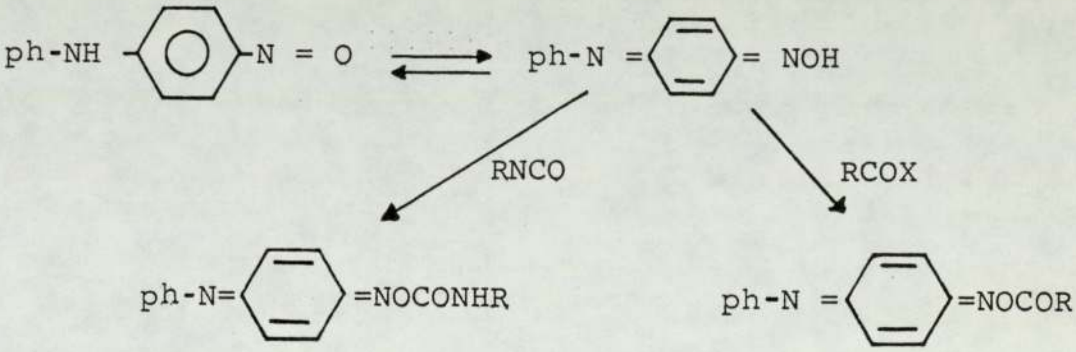


Natural rubber, so treated, has a high antioxidant activity even after solvent extraction.

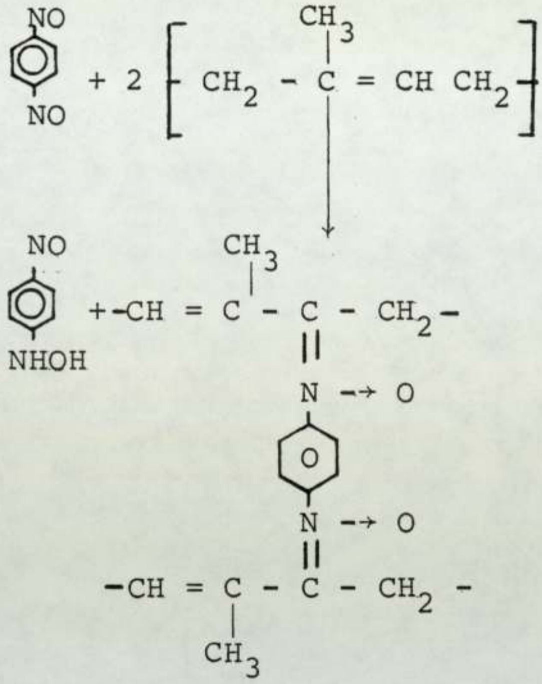
p-phenylene diamine derivatives, such as IPPD, show antifatigue and antiozonant activity but when bound to the natural rubber, the activity is lost due, probably, to the loss of antioxidant mobility(60,85).

Unfortunately, by-products of the binding reaction cause staining and premature vulcanization.

Unhindered nitrosophenol showed some activity as bound antioxidant, but were markedly inferior to the amines. Over-coming the tendancy of premature vulcanization has some success by reaction of the nitrosoamine with an isocyanate or other acylating agent(84).

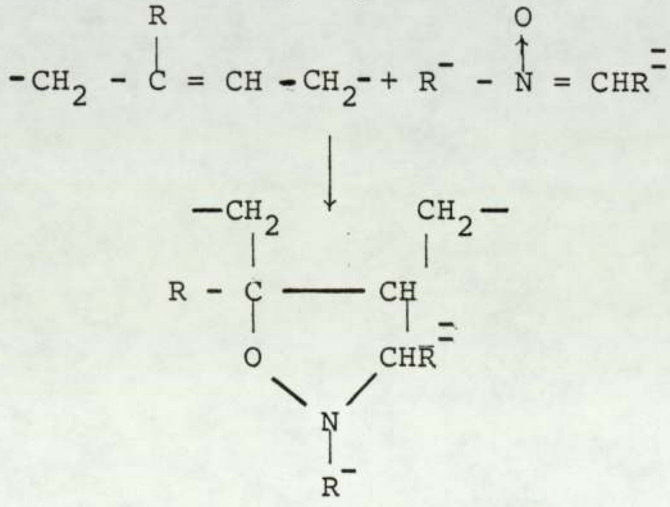


Rehner(86), showed that dinitrosobenzene has been known for many years to cause the cross-linking of butyl rubber. He suggested that reaction occurs at the reactive methylene group to give cross-link containing the dinitrone structure.



There is a little doubt that the extremely good oxidative resistance of nitroso cured rubbers is due to the presence of these nitrones species which are known to be very powerful antioxidants by virtue of their ability to trap radicals (87).

The nitrone group can also be used as versatile reagents for the attachment of functional groups to the double bond i.e. 1,3 cycle addition reaction (22,87-89).



Isoxazalidine Group.

However, the isoxazalidine has only weak antioxidant activity even when R^{-} is an aromatic ring. Effective bound antioxidant can be produced, however, when R^{-} and $R^{=}$ contains an aromatic amine or hindered phenol function. Amine and phenolic nitrones were found to react readily with rubber during vulcanization.

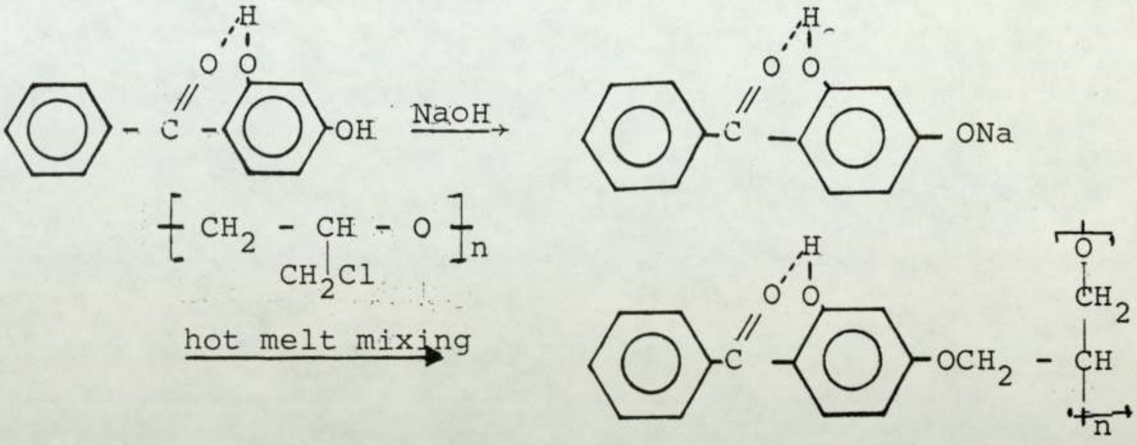
Yet another route(90) by which antioxidants may be bound to unmodified rubber has been described by Yamanoto et al., they found that triallyl phenol, diallyl-p-cresol and allyl-propyl-p-cresol, are useful reactive antioxidants.

1.3.4.3.7 The Binding of an Antioxidant to Reactive Group in Polymer

Stuckey and Tahan(91) have suggested that antioxidant may be bound to polymers containing functional groups such as -COOH, -COOR, $-NH_2$, -OH, -Cl, $-SO_3H$, $-SO_2Cl$, etc., with antioxidants which may themselves contain reactive groups to facilitate reaction with the polymer. Typical reactions include eitherification or thioetherification, amidation or trans-amidation, esterification or trans-esterification. Polymers suitable for these reactions are epichlorohydrin (ECH), chlorosulphonated polyethylene (CPE), polychloroprene (CR), poly vinyl acetate (PVA), ethylene vinyl acetate (EVA), arcylic rubbers, brominated polyisobutylene-isoprene (BII) and chlorinated polyisoprene (CII).

The mechanochemical reaction between Cis-1,4-polyisoprene with amines and phenols has been studied and examined as a possible route for the preparation of bound antioxidants systems(92).

Phenolic antioxidants with at least two reactive hydroxy groups have been reacted with ECH (Epichlorohydrin) elastomers by converting the phenol to the monosodium salt and then reacting the labile chlorine atom of the ECH in a high shear mixer at 140°C. High yields of polymeric antioxidants have been achieved by this way. 4,4′-methylene-bis-2,6-di-tert-butyl-phenol and ECH have been similarly reacted(91).



1.4 ASSESSMENT OF AGEING

As can be seen from the preceding sections the ageing of a rubber (i.e. the changes in molecular structure which occur with the passage of time) include chain scission and cross-linking processes and the introduction of different chemical groups. These cause changes in appearance and in properties. Use is made of these changes to assess the ageing process.

The assessment of ageing is often carried out by accelerated ageing tests in which the rubbers are subjected to ageing conditions or exaggerated severity, (e.g. temperature, concentration of O_2 or O_3, intensity of fatigue, intensity of U.V. irradiation, etc.). The degree of ageing is then assessed by measuring the deterioration of selected physical properties (ultimate tensile strength, modulus, hardness, etc.), by visual inspection (cracking, discolouration, etc.) or by measuring the increase in specific chemical groups resulting from the degradation process (e.g. unsaturation, carbonyl or peroxide groups, etc.). The absorption of oxygen or the measurement of stress relaxation is also used. The ageing process is often monitored at elevated temperatures.

The results of such accelerated ageing tests must always be treated with some suspicion as the accelerating conditions are artificial and may not occur during services e.g. reactions may occur at elevated temperatures that do not take place at room temperature.

In this work thermal oxidative ageing has been accelerated by using high temperatures and assessed by measuring the deterioration of physical properties or by stress relaxation techniques. These are described in section (2.4).

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

2.1 MATERIALS

Unless otherwise stated the materials were used as supplied without further purification.

Neoprene type-G (sulphur modified) and neoprene type-W (mercapto modified) were supplied from Du-Pont Company.

Polyepichlorohydrin (ECH) homopolymer used was supplied by Hercules Powder Company Limited.

Santowhite powder [4, 4^{-} - butylidene bis(3-methyl 6-tert-butyl phenol)] supplied by Monsanto Limited.

Santoflex IP(IPPD)(N,N^{-}, iso propyl-phenyl-p-phenylene-diamine) supplied by Monsanto Limited.

Santoflex - 13, (N,1,3 - Dimethyl butyl-N-phenyl-p-phenylene diamine) supplied by Monsanto Limited.

T.M.T.D. (Tetra-methylene-thiuram disulphide) supplied by Monsanto Limited.

D.P.P.D. (N,N^{-} - diphenyl-phenylene-diamine) supplied by Vulax International Limited.

Diphenyl-amine, supplied by B.D.H.

$\bar{p}$-phenylene-diamine, supplied by B.D.H.

2,4 -dihydroxy benzophenone, supplied by Aldrich Company.

Permanx WSP (2, 2^{-} - Dihydroxy-3,3^{-} Di(α-methyl-cyclo-hexyl)-5,5^{-}, Di-methyl-diphenyl-methane) supplied by V Lnax International Limited.

Topanol CA (1,2,3 tris(2-methyl-4-hydroxy-5-tert-butyl-phenyl) butane) - supplied by Mansanto Limited.

NBC (Nickel dibutyl-dithiocarbamate) supplied by Du-Pont Company.

1,chloro-3-methyl-butane, supplied by B.D.H.

Red lead (lead oxide), supplied by M and B Company.

Diak No. 1 (Hexa methylene diamine carbamate) supplied by Du-Pont Company.

2,chloro-2-methyl propane, supplied by Fison Company Limited.

Mgo-light, supplied by Anchor Chemicals Limited.

Zno, supplied by Anchor Chemicals Limited.

Stearic acid, supplied by Anchour Chemicals Limited.

Zinc stearate, supplied by B.D.H.

Pyrogollol (1,2,3 polyhydroxy benzene) supplied by Hopkin-Williams.

NA-22 (Ethylene thio urea) supplied by Du-Pont Company.

M.B.T.S. (Di-benzothiozol-2-Yl (disulphide)), supplied by Monsanto Limited.

FEF - carbon black, supplied by Sevalco Limited.

Irganox 1076 (n-octadecyl-3(3^{-}-5^{-}-di-tert-butyl-4-hydroxy phenyl) propionate , supplied by Ciba-Geigy.

2.1.1 SYNTHESIS OF MATERIALS USED IN THE WORK

2.1.1.1 Preparation of the Sodium Salt(91) of 2, 4-dihydroxy-benzophenone

2,4-dihydroxybenzophenone (64.2 gm, 0.3M) was dissolved in sodium hydroxide solution (12 gm in 200 ml. of methyl alcohol). The solvent was evaporated using a rotary evaporator to leave the mono-sodium compound. The solid formed was dissolved in acetone and then reprecipitated by n-hexane which yielded a yellow solid (57.8 gm, 90% yield).

2.1.1.2 Preparation of Sodium Salt(91) of 4,4^{-}-butyliene (6-tert-butyl-m-cresol) (Santowhite Powder)

Santowhite powder (0.262 mol, 100 gm) was dissolved in methyl alcohol (1ℓ) and then mixed with sodium hydroxide (10.5 gm in 250 ml of methanol). The mixture was stirred for 30 minutes. The solvent was evaporated using a rotary evaporator to leave the mono sodium compound. The yield was 85% by weight.

2.1.1.3 Preparation of N,N^{-}-chloro-propyl-p-phenylene diamine

This was prepared by reaction of p-phenylene diamine and isopropyl chloride under alkaline conditions as follows.

P-phenylene diamine (10.66 gm) was dissolved in methanol (150 ml). The solution was then stirred with isopropyl chloride (15 ml). Sodium hydroxide (5 gm) was added and the reaction stirred at room temperature for 2 hours. The solvent was evaporated under vacuum using a rotary evaporator. The solid was recrystallined from methanol by n-hexane. The resulting solid (9.09) had a melting point of 110°C, yield = 89%.

2.2 APPARATUS USED FOR MODIFICATION OF RUBBERS

2.2.1 LABORATORY TWO ROLL MILL

A water cooled 12" laboratory two roll mill manufactured by David Bridge Company was used at even speed i.e. no fraction ratio.

2.2.2 WINKWORTH "2" BLADE MIXER

The winkworth blade mixer of approximately three litres capacity consists of a double trough pan fitted with twin z-blades which are rotated by a flame proof one HP motor. The blades revolve in opposite directions and at different speeds. The mixer which may be steam heated or water cooled is fitted with a tight lid which must be in place before the motor can be operated.

2.2.3 RAPRA VARIABLE TORQUE RHEOMETER(93)

This is essentially a small internal mixer, containing contrarotating mixing screws which move at different speeds. It has a precise temperature control and the jackets are heated by oil, circulated by means of a pump. A thermocouple is inserted into the chamber and both the torque and temperature may be recorded during mixing as a function of time on a chart recorder. The chamber may be operated either open to the atmosphere or sealed by means of a ram operated by compressed air at a pressure of 40 PSI. A full charge between 35-40 gms is used with closed chamber.

In this work the rheometer is only used as a mixer.

2.2.4 BANBURY MIXER

The model B Banbury mixer used in this work has a capacity of 1ℓ. It has two powerful water-cooled mixe blades which rotate in opposite directions in a water-cooled shaped chamber (also water-cooled) that are driven by a 35 HP motor. The rubber and compounding ingredients are held in contact with the mixer blades by a shaped ram operated by compressed air. For efficient mixing the chamber should have a full one-litre load. The temperature and the power used by the motor (wattage consumed) are monitored during the mixing process.

When compounding rubbers it is essential that one component of the vulcanising system is added last (usually the sulphur) to prevent pre-mature cross-linking. It is also usual to add softeners at the end of the mixing process so that the maximum viscosity is maintained and this gives better dispersion.

The mixing is accurately timed and the batch immediately dumped onto a two-roll mill and reduced to a sheet which will cool quickly.

2.3 PREPARATION OF VULCANIZATES

2.3.1 COMPOUNDING

The general formulations used for polychloroprene and epichlorohydrin rubbers, unless otherwise stated, are as shown in Table (2.1).

(Table 2.1)

The general formulation of the rubbers used in this work

	Rubber Type		
	CR Type-W	CR Type-G	ECH
Rubber	100	100	100
MgO	4	4	-
Zno	5	5	-
NA-22	1	-	-
M.B.T.S.	1	1	-
Zinc Stearate	-	-	1.0
Read Lead	-	-	5
NBC	-	-	1
Diak No. 1	-	-	1.5
FEF	-	-	30
Antioxidant	2	2	2

Variations on these basic formulations appear in the appropriate sections dealing with specific polymer (Chapters 3 and 4).

The ingredients are mixed on a 12 inch water-cooled laboratory two-roll mill. The total compounding time was kept to the minimum required for a good dispersion. The dispersion was considered adequate when identical Monsanto rheographs (Section 2.3.3) could be obtained from samples taken from different parts of the compounding stock.

2.3.2 MONSANTO OSCILLATING DISC RHEOMETER 100

The Monsanto oscillating disc rheometer 100 is an instrument that enables the curing and processing characteristics of compounded elastomers to be determined.

The rubber specimen is placed in a cylindrical cavity enclosing a biconal rotor which is oscillated sinusoidally through a selected amplitude of between 1° and 5° by means of a motor driver eccentric. The cavity and sample are maintained at the vulcanizing temperature $\pm 0.5^\circ C$ by electric heaters regulated by thermistor controllers. The dies which form the cavity are held together by a force of 3.5 Kg/cm^2 exerted by means of a ram operated by compressed air. On the arm of the eccentric are mounted strain gauges which measure the force required to oscillate the disc.

The motor used in rheometer 100 operates at 100 r.p.m. This 100 cycle per minute signal is too high in frequency to be recorded directly. It is, therefore, first converted to a direct current signal from A.C. to D.C. The resulting direct current signal is recorded to yield a smooth continuous cure curve of elastic modulus versus cure time. It is thus possible to obtain the time of cure which would be expected to produce 90%, 95% or 100% optimum cross-links in a sheet of rubber 2.5mm in thickness.

There are certain factors which must be considered before accuracy can be expected:-

(1) Since the rubber is a relatively poor conductor of heat, the temperature of specimen and hence the extent of cross-linking is not uniform, although the small quantity of rubber required to fill the cavity minimises this.

(2) The work done on the rubber by the oscillating disc in the course of measurement may also cause a rise in the interior temperature of the material.

There is an initial decrease in the viscosity of the stock due to the increasing temperature, which then flattens out until the onset of cross-linking which then produces a sharp rise in viscosity and, therefore, in the torque exerted by the oscillating rotor embedded in the specimen. This torque increases until cross-linking is complete. The curve after optimum cure may show either a decrease in the torque with the time if chain scission takes place during vulcanization or a continued increase if cross-linking reaction is continuous.

It is thus possible to obtain approximately quantitative scorch time based on an arbitrary number of units of torque above the minimum value, and the rate of vulcanization from the slope of the curve. However, a more accurate kinetic analysis has been suggested by Coran(94,95), that allows the rate of reaction to be measured in terms of first order rate constants.

2.3.3 VULCANIZATION OF COMPOUNDS

Vulcanizates were required in the form of sheets of various thickness for determination of ultimate tensile strength (0.25 cm), stress relaxation (0.1 cm), MR 100 (0.1 cm), hardness (1.0 cm) and for infra red spectroscopy (0.02 cm), 60, 30, 30, 30 and 5 grams were used respectively in appropriate cavity moulds.

Vulcanization was carried out in the pre-heated moulds using either the steam heated or induction heated platens of the hydraulic presses. A pressure of 50 tons and 30 tons were used for the steam heated and electrical heated presses respectively.

At the end of the cure time, the mould was removed and plunged into a bath of cold water so that cross-linking was immediately stopped. They were then left for 24 hours at 20 ±5°c before testing.

Vulcanizate samples were taken from the centre of each sheet to eliminate edge effects.

In the case of UTS/EB/MR100 determinations, the specimens were taken in two directions at right angles to each other to reduce orientation effects.

2.3.4 EXTRACTION OF VULCANIZATE

To remove the unbound antioxidant, unreacted accelerators and any other material produced during the vulcanization process, rubbers or vulcanizates were extracted under a nitrogen atmosphere using a soxhlet extractor for 72 hours in the dark. The solvents used were either acetone or methanol as all the antioxidants used in this work were soluble in one of these two solvents. The extracted vulcanizates where then dried under vacuum at room temperature to constant weight.

2.4 ACCELERATED AGEING TESTS

The changes which take place in rubber with the passage of time are defined as ageing. To simulate long term ageing in a conveniently short period of time, laboratory ageing tests are always accelerated to intensify one or more of the factors involved, i.e. temperature, oxygen or ozone concentration, light intensity, etc..

2.4.1 STRESS-RELAXATION

The concept of using stress relaxation measurements to investigate the degree to which antioxidant can protect rubber vulcanizates having a high surface area to volume ratio was originated by Tobolsky et al.(96).

The method is based upon the kinetic theory relationship between the tension, f, exerted by a stretched rubber specimen and the number N of stress-supporting network chains or chain segments between junction points in the network, per unit volume, described by the following:-

$$f = N K T A_o(\lambda - \lambda^{-2})$$

where K is Boltzmann's constant, T is the absolute temperature, A_o is the unstrained cross-sectional area and λ is the ratio of the stretched to the initial length of the sample. If λ, A_o, K and T are kept constant then f is proportional to the N, and if during degradation, a number (N_o-N) of the original number of chains present are broken, the ratio of the final tension f, to original tension f_o, will be as follows:-

$$\frac{f}{f_o} = \frac{N}{N_o}$$

There are two variants of the technique, continuous relaxation in which the sample is held stretched throughout the test, and intermittent relaxation in which the sample is stretched only periodically for a short time to enable measurements to be made.

The decay of stress in continuous relaxation measurements provides a measure of the degradative reaction in the network, while intermittent relaxation measures the net effect of both degradative and cross-linking reactions.

In this work, continuous stress relaxation determinations only were carried out. Six Wallace Shawbury self-recording age-testers (Wallace Instruments Limited) were placed in six cells of an air ageing oven at an elevated temperature. The temperature was selected so that a convenient rate of stress relaxation was produced. A flow of preheated air (1 ft^3 per hour) was maintained during the test. This produced a reduction of the cell temperature of approximately 2^oC

of that of the block, which was constant to $\pm 1^{\circ}C$. Samples were cut from vulcanized sheet using the MR100 cutter (2.4.4). These samples were held between two fixed grips in such a manner that they were enclosed inside the cell of the oven.

The downward force exerted by the specimen is balanced by the upward force applied by a vertical helical stress spring. The change in the force applied by the spring is recorded in the form of a curve on the chart paper. During the test, the force exerted by the spring equals that of the sample. Any change in the state of equilibrium will cause a movement of the beam to maintain the equilibrium.

Procedure

The sample is first clamped in the upper grip and attached to the beam. The instrument is zeroed to eliminate the weight of the sample. The sample is then extended to 60% of its original length by means of a brass collar (1.7 cm depth). The extended rubber is then placed inside the ageing oven, and after allowing 5 minutes for expansion, a pencil lead is placed at the point corresponding to 100% of stress and zero time on the chart paper.

The relaxation in stress necessary to maintain 60% elongation was then recorded over a period of 26 hours.

All experiments for both extracted and non-extracted samples were carried out in triplicate and the results recorded as graphs between the force ratio f/f_o against the time.

2.4.2 ULTIMATE TENSILE STRENGTH AND ELONGATION AT BREAK

The UTS and the percentage of elongation at break were measured according to British Standard BS 5214 Part I, 1975 using a Hounsfield rubber tensometer (Type K301). The rate of jaw separation used was 20 inches per minute.

Procedure

The samples for test consisted of sheets of rubber (13.3×13.3×0.3 cm) that had been left for 24 hours ±2 hours after removal from the press. Dumbell shaped specimens (11.6 cm) long were cut from the sheets using a die cutter. The thickness and width of each specimen was measured using dial gauge.

The samples were then fixed in the jaws of a Hounsfield tensonometer and using a rate jaw separation of 20 inch per minute extended to breaking point. The load and extensions were continuously recorded. The ultimate tensile strength was calculated as the load per unit area (of the parallel portion of the specimen). The percentage extension at break was also recorded.

Five specimens were used for each test and the average recorded. Specimens giving very low results were discarded and another determination made with a new specimen as low values are usually the result of flaws in the specimen that lead to stress concentrations and premature failure.

2.4.3 THE HARDNESS

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber.

Hardness is a property of rubber which must be expressed in terms of instrument parameters rather than in basic units. But as it is a reversible process in rubber, it is related to compression modulus values which in turn are related to cross-link-density.

Better reproducibility is obtained by dead weight loading instruments. The instrument used expressed the hardness in international rubber hardness degrees (I.R.H.D.). These units are directly related to Young's modulus.

Procedure

The hardness determination was carried out according to ASTM D 1415, using a Wallace dead-load hardness tester.

For each formulation, two cylindrical specimens (1×3.7 cm) were compression moulded in a preheated mould in a hydraulic press with steam or electrically heated platens. The platen temperatures were continuously monitored during vulcanization and were constant to $\pm 2^{O}C$. The time and temperature varied according to the type of rubber being used. On removal from the press the samples were quenched in cold water to arrest further cross-linking and were then left for 24 hours ±2 hours before testing.

One sample of each formulation was extracted for 72 hours under nitrogen, followed by vacuum drying for 24 hours at room temperature to constant weight.

The hardness of the specimens was measured before and after ageing at a specific temperature in a Wallace oven.

2.4.4 MODULUS AT 100% and 50% EXTENSION (MR100 AND MR50)

The modulus is defined as the stress required to produce a given elongation and is used to represent the material stiffness. The notation MR100 is used to denote the stress required to produce a 100% elongation.

In this test, which was performed according to British Standard 1673, Part 4, 1953, the test species are exposed to an elevated temperature over a period of time which results in changes in network structure, which may be chain scission, molecular cross-linking or both of these. The predominance of either is reflected in the modulus.

A plot of modulus against time is commonly used.

Procedure

A cutter yielding specimens of (10.2×0.1 cm) was used to cut the dumbell shaped samples from the sheets of rubber vulcanizate.

The test pieces were hung in the Wallace oven so that air had access to all the surface of the test pieces. On removal from the oven the test piece was fixed in the grips with the lower grip in the rest position. An extension of 100% or 50% is obtained by moving the lower grip to a specific position. The time taken for the movement of the lower grip to the extended position was always less than five seconds. The tension of the test piece was balanced by sliding the weight along the beam of the balance and an adjustment made by allowing for any stress relaxation during the first minute.

Three test pieces were used and an average reading was taken.

The test was carried out for both extracted and non-extracted samples, so that the efficiency of bound, partially bound and free antioxidant could be assessed.

2.4.5 ULTRA-VIOLET IRRADIATION

U.V. irradiation of very thin samples was carried out in a U.V. cabinet which consisted of a metal cylinder of 110 cm outside diameter and having a concentric circular rotating sample drum with a circumference of 15 cm from the periphery of the metal cylinder. Thirty-two U.V. fluorescent tube lamps were mounted on the inside of the cylinder. The rotating arrangement of the samples allows an identical amount of total radiation to fall on every sample. The cylindrical cabinet is open to the atmosphere on both the lower and upper sides and the circulation of air in the cabinet is ensured by a drive fan ventilator situated under the rotating frame. The samples are attached separately to cardboard 'window-frames' and arranged vertically on a rotary wheel so that they face the lamps all the time. The irradiation source consists of a cylindrical array of 32×20 watt lamps mounted inside on the wall of the cabinet. 24 lamps - type C (Phillips Actinic blue OS) and 8 lamps - type AI (Westinghouse sunlamps F S20) are used and those are symmetrically distributed so that the combination is one lamp type AI for every 3 lamps of type C. The wavelength of the type AI lamps is mainly 317 nm and that of the type C lamps is 374 nm. The available wavelength distribution with the above combination of lamps is between 290 nm and 500 nm and the radiation intensity I_o at the sample surface is $I_o = 44.3 \ w/m^2$. The tubes are replaced in rotation every 2000 hours of exposure.

The oxidation degradation is followed spectrophotometrically by measuring the increase in the carbonyl groups with time as described in Section 2.4.6.3.

2.4.6 INFRA-RED SPECTROSCOPY

The Perkin Elmer infra-red spectrometer type 599 covering a wavelength range of 4000 to 250 cm^{-1} was used in this work.

2.4.6.1 Characterisation of Synthesised Compounds

This was obtained by measuring the absorption spectra in solution or by the KBr disc method , see Section 2.1.1.

2.4.6.2 Estimation of Amount of Bound Antioxidant

In cases where the bound antioxidant had a suitable functional group which gave an absorption band in the infra red region, it was possible to use this technique for these examinations. Typical examples were phenolic-oH group (3,600 cm^{-1}) and an amino group (NH) in 3,400 cm^{-1} (97,98).

To obtain quantitative calculation, calibration curves were constructed from the peak heights of the absorption curves produced from thin films [(0.02) cm thickness] of the appropriate rubbers containing known added amounts of the compounds under investigation.

The formulations containing the necessary vulcanizing ingredients and varying amount of antioxidant (1,2,4 phr etc.) were mixed on a 12 inch,two roll mill. The samples were vulcanized into transparent thin films and their IR spectra obtained. The intensity of appropriate functional group peaks, such as phenolic or amino groups is proportional to the amount of added antioxidant and was measured as a function of the peak height. To overcome the errors due to sample thickness, an invariant peak at a certain wavelength which is a characteristic of the specific rubber is selected as a peak reference. The absorption due to the functional group and the absorbance due to the invariant group are calculated using the base line technique(97). It is then possible to determine the ratio for a given concentration of antioxidant as follows:-

$$\text{functional group ratio} = \frac{\text{absorbance of functional group}}{\text{absorbance of reference group}}$$

The peak ratio obtained is then plotted as a function of the concentration of the antioxidant added. The calibration curve obtained by this method can now be used to determine the concentration of antioxidant bound to the rubber.

Carbonyl group(99) was not used for calibration curves, however, since it has been already shown that their concentration increases with the extent of oxidation of the rubber during compounding.

In cases when combination of an antioxidant with a rubber occurs before vulcanization e.g. during a mixing process, the rubber must be extracted in the uncross-linked state. The extraction process in this case is different as the rubber is thermo-plastic and must be kept in the form of a relatively thin film so that extraction is efficient. This was achieved by sheeting it on a two-roll mill as a thin sheet which was then wrapped in aluminium foil which was then extracted in an atmosphere of N_2 in an soxhlet extractor, and the solvent was removed under vacuum.

The rubber was then compounded with appropriate ingredients and vulcanized as a thin film in a stainless steel cavity mould at the required temperature. A thin film of vulcanized unmodified rubber was similarly prepared and used as a control.

The films were fixed on cardboard frames and the IR absorption spectra obtained and the peak ratio determined. The percentage of bound antioxidant was then calculated using a calibration curve obtained from rubbers containing known amounts of the antioxidant in its formulation.

2.4.6.3 Measurement of Carbonyl Index for Ageing Assessment

During oxidation ageing scission processes are accompanied by the formation of carbonyl group (see section 1.2). This makes a convenient way in which such ageing can be monitored as carbonyl groups have an absorption wavelength in the region of (1780 cm^{-1}) which can be easily detected by infra-red spectroscopy.

The infra-red spectra of thin films of the vulcanizate rubbers aged by ultra-violet irradiation were determined (Section 2.4.5) and the absorption peak height at (1780 cm^{-1}) measured at time intervals during the U.V. irradiation period. The ratios of the carbonyl absorption peak heights to an appropriate reference peak were then measured.

2.4.7. OIL AGEING

The action of a liquid on rubber may result in absorption of the liquid by the rubber, extraction of soluble constituents from the rubber, and chemical reaction with the rubber. Usually absorption is greater than extraction and an increase in volume results, but this is not always the case (e.g. when large amounts of plasticisers are used in compounding).

At high temperatures, consideration must be given as to whether air is present in the intended application, because oxidation is likely to effect mechanical properties rather more than it does swelling(100). As swelling occurs the rubber is strained, and tensile strength, modulus and hardness decrease.

Two types of oils are used for testing, namely, ASTM oil No. 1 and ASTM oil No. 3. These two oils are different in their viscosities and aniline points. ASTM oil No. 1 has a high viscosity and aniline point of 124°C, while ASTM oil No. 3 has a low viscosity and an aniline point of 70°C. The latter will exhibit a greater swelling effect on rubber than ASTM oil No. 1(101).

Procedure

Samples for UTS and hardness determinations (see sections 2.4.2 and 2.4.3) were cut from vulcanized sheets of ECH rubber. The samples for UTS determination were immersed in 250 ml portions of the ASTM oils at 150°C. Samples for hardness determination were immersed in 50 ml portions of the ASTM oils at 150°C. They were then aged for specific periods of time.

The oil was changed every 72 hours of ageing. After ageing, the samples were removed from the oil, dried on filter paper and left for 24 hours before the UTS and hardness tests were carried out. An average reading of five samples was taken in each case.

The oil ageing was carried out for both acetone extracted and non-extracted samples to study the effect of bound and free antioxidant.

A graph showing the variation of both UTS and hardness with time of immersion was then plotted.

CHAPTER THREE

POLYCHLOROPRENE

3.1 INTRODUCTION

Polychloroprene rubbers were introduced in 1934. They were one of the first synthetic elastomers to be developed(102,103). They are now widely used and are manufactured by seven Western and Japanese manufacturers who produce the rubber under one hundred and eleven trade names(104).

Although CR contains a double bond in its structure the vulcanizates show superior oil, heat and ozone resistance to that exhibited by the hydrocarbon diene rubbers. This is attributed to the deactivating influence of the electronegative chlorine atom attached to the double bond.

The rubbers find wide application where their properties can be utilised and are used for the manufacture of a wide range of articles. Large quantities are also used in adhesives.

There are two main classifications of those rubbers the mercaptan-modified homopolymer (type-W) and the sulphur-chloroprene copolymer (type-G). Both types are made by a free radical emulsion polymerization reaction.

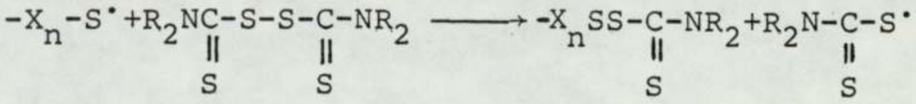
The commonest free radical initiator used is potassium persulphate, although many other materials have been suggested(105).

The reaction is terminated when an appropriate degree of conversion has been achieved by using an alkylmercaptan, thiuram disulfide or phenolic antioxidant as a short-stop(106-109).

3.1.1 SULPHUR MODIFIED POLYCHLOROPRENES (TYPE G)

Sulphur modified polychloroprenes are produced by copolymerization of sulphur and chloroprene. It has been shown that sulphur does not act as a chain-transfer agent but is bound as a linear di- or poly-sulphide in the polymer chain(110,111). Molecular weight control is accomplished by post-polymerization reactions involving thiophilic attack on the polysulphide units by thiuram disulphide which is added during polymerization. The process is carried out at pH above 7, since the thiol anion $(R_2NC(\bar{S})S)$ is probably the active species in the cleaving of the polysulphide segment(112).

$$-X-S_x-X_n-S_x- \xrightarrow[\text{peroxide}]{\text{heat or}} -X_n-S^{\bullet}$$



$$-X_n-S^{\bullet}+R_2N\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-NR_2 \longrightarrow -X_nSS-\underset{\underset{S}{\|}}{C}-NR_2+R_2N-\underset{\underset{S}{\|}}{C}-S^{\bullet}$$

The presence of the weak polysulphide linkage in the copolymer modifies its properties. It is more susceptible to mechanochemical breakdown and this enhances its processibility, produces very high tack and yields polymer solutions with a relatively low viscosity and high solids content.

These G-type rubbers can be vulcanized by Zno/Mgo only, although it has been shown that some of the sulphide in the copolymer can be utilised in cross-linking reactions(113). This increased reactivity results in poor storage stability and the degree of swelling during compounding.

The molecular weight distribution of this type of polychloroprene ranges from 20,000 to 950,000, the major component being with region at 100,000(114).

3.1.2 MERCAPTO MODIFIED POLYCHLOROPREN (TYPE W) (HOMOPOLYMER POLYCHLOROPRENE)

A variety of modifiers have been tested to control the molecular weight of polychloroprene, of these, the alkylmercaptans are the most frequently used(104).

The molecular weight of those homopolymers are controlled by the addition of n-alkyl-mercaptans which act as chain transfer agents according to the reaction sequence:-

$$M_m^{\bullet} + M \xrightarrow{Kp} M_{m+1}^{\bullet} \qquad (3.1)$$

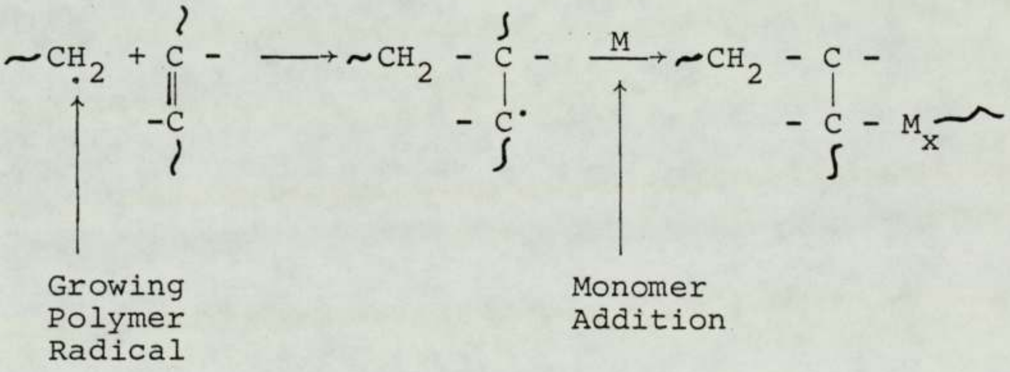
$$M_{m+1}^{\bullet} + RSH \longrightarrow M_nH + RS^{\bullet} \qquad (3.2)$$

$$RS^{\bullet} + M \longrightarrow RSM^{\bullet} \qquad (3.4)$$

where M = monomer

$M^{\bullet}_{m}$ = polymer

The concentration of n-alkyl mercaptans is adjusted to give a molecular weight range of 180,000 to 200,000 and allowed to proceed to about 65% conversion. At higher conversions the homopolymer becomes branched and even cross-linked leading to the formation of networks$^{(115)}$.



The 'W' types have much greater raw polymer stability than the 'G' types. But need the addition of a vulcanizing agent other than Zno/Mgo for adequate cross-linking reactions. The vulcanizates thus produced show better compression set and superior tensile strength than the sulphur modified grades.

3.1.3 POLYMER STRUCTURE

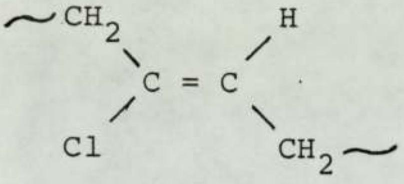
Maynard and Mochel$^{(116-118)}$, have established that the polychloroprene structure consists primarily of linear sequence of:-

A. Trans 2-chloro-2-butylene units arising from 1,4 addition polymerisation.

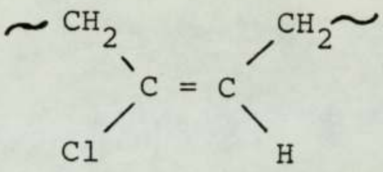
B. Small portions of cis 1,4 - polymerisation.

C. 1,2 - polymerisation.

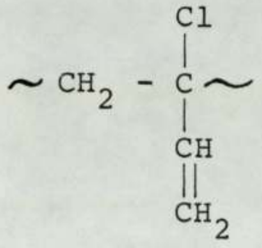
D. 3,4 - polymerisation.



A

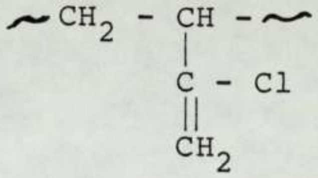


B



$\sim CH_2 - C(Cl)(CH{=}CH_2) \sim$

C

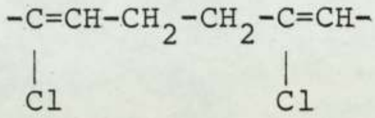


$\sim CH_2 - CH(C(Cl){=}CH_2) - \sim$

D

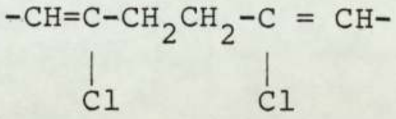
The proportion of structures B and C increases with polymerization temperature from a total of about 5% in polychloroprene polymerised at -40^{O}C to about 30% in those prepared at 100^{O}C. While structures B, C and D comprise a relatively minor fraction of the chloroprene structure, physical and chemical properties of the polymer are profoundly effected by their presence in the polymer chain.

NMR evidence(119), has recently been found for sequence isomerization in 1,4 polychloroprene units as a consequence of "head-to-tail" E, 'head-to-head" F, and "tail-to-tail" G.



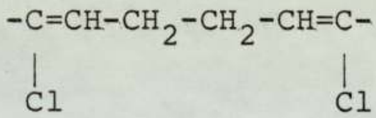
$$-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}=\mathrm{CH}-$$

E



$$-\mathrm{CH}=\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}-\mathrm{CH_2CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}} = \mathrm{CH}-$$

F



$$-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH}=\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}-$$

G

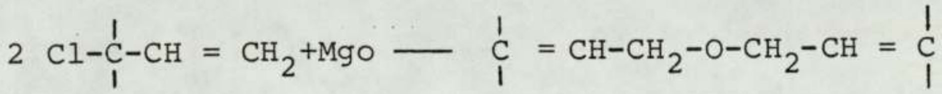
The structure E accounts for approximately 75% and the other structures account for the rest in equal portions.

The possibility of the polymer to crystallise is reduced when the irregularity of the monomer units or if the sequence of these units, increases. The number of these irregularities in the polymer increases with polymerization temperature and this offers a practical means by which the extent of crystallinity can be controlled, e.g. the polymer prepared at -40°C is approximately 38% crystalline and has a Tm of about +73°C. Polymer prepared at +40°C is only 12% crystalline and has a Tm of about +45°C. Such differences are reflected in the mechanical properties of the polymer(116-118).

3.1.4 VULCANIZATION OF POLYCHLOROPRENES

Vulcanization of the polychloropenes involves the highly reactive tertiary allylic chlorine atom which results from the small amount of 1,2-polymerization. The allylic bonds of the chloroprene unit, however, are deactivated by the electronegative chlorine atom, so that reactivity towards sulphur moieties is limited. The average allylic chloride content of mercapto polychloroprene is about 1.5% of total chlorine present. This corresponds to an active cure site for every 67 monomer units. For practical vulcanizates, metallic oxide must be used in the curing system. Many metallic oxides have a vulcanizing effect on CR rubber but the most useful system found is a combination of magnesium and zinc oxides.

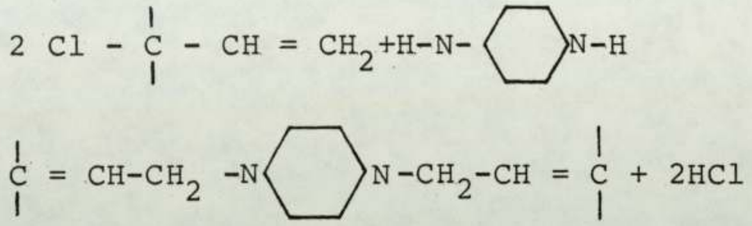
It has been suggested that metal oxides can generate an ether cross-link between two allylic sites



$$2\ Cl\text{-}\overset{|}{\underset{|}{C}}\text{-}CH = CH_2 + Mgo \text{ —— } \overset{|}{\underset{|}{C}} = CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH = \overset{|}{\underset{|}{C}}$$

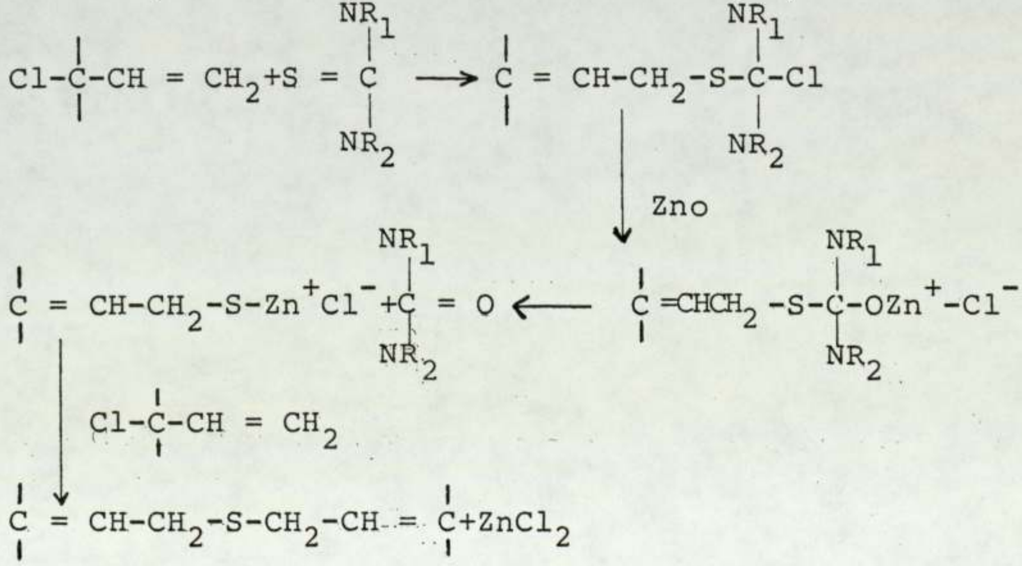
but the reality of this has never been established. Regardless of the cross-linking role of metal oxides, their presence is essential for controllable vulcanization and for good ageing of the vulcanizate. The type-G rubber can be vulcanized by Zno-Mgo alone, but the type-W rubber requires the use of organic accelerators which are in reality vulcanizing agents. These are believed to operate by either of the two mechanisms:-

(A) Difunctional cross-linking agents such as diamines and bisphenol, can be alkylated by active chlorine units in the polymers probably by 1,3-allylic shifts to yield stable cross-links(120).



The hydrochloric acid formed is then neutralised with the magnesia and zinc oxide. The latter acting as a strong Lewis acid which further catalyses the reaction(121).

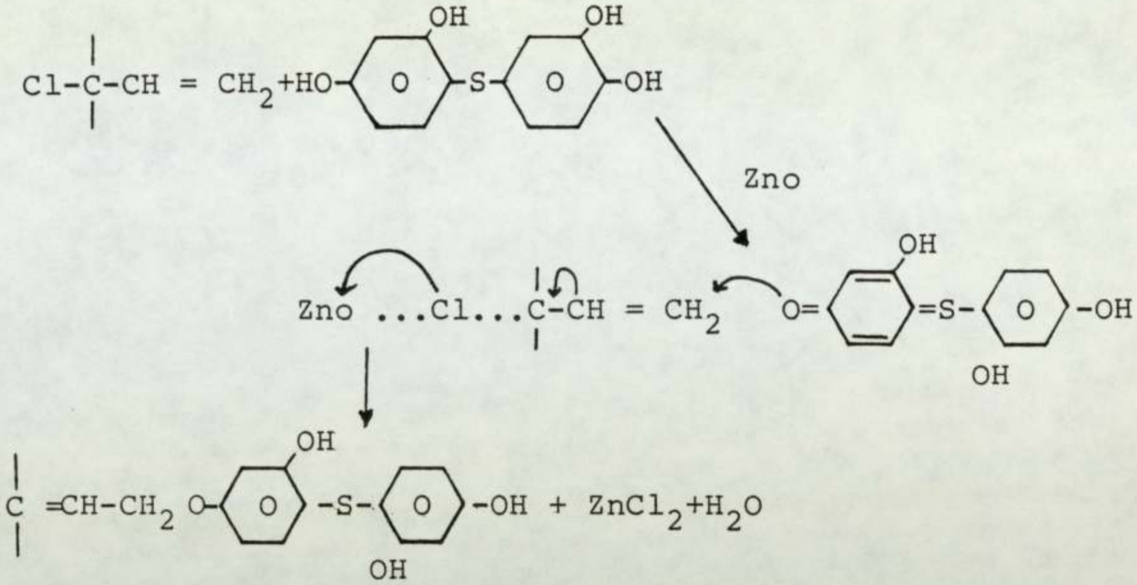
(B) <u>Substituted thiourea</u> Substituted urea such as ethylene thiourea (NA-22) react with the tertiary allylic chlorine via an isothiuronium intermediate. The following reaction mechanism has been proposed(122);



The vulcanization (113,123) of type-G involves rearrangement of backbone polysulphide segments as well as the above reactions of allylic chlorine structures. Free radical sulphur moieties such as $RS^{\cdot}$ and $S^{\cdot}S^{\cdot}$ are believed to arise from the interaction of the polysulphide segments and the thiuram disulphide present in the polymer. These radicals react with each other or with the polymer backbone to yield sulphidic cross-links.

In recent years the use of ethylene thiourea (NA-22) has become restricted since it has been shown to be carciogenic. This has led to renews interest in systems involving poly hydroxylated aromatics and heterocyclic amines as possible alternatives.

It was found (124) that $2,2^{-},4,4^{-}$ tetrahydroxy diphenyl sulphide gave cure data similar to NA-22 except that in this case the cure rate was not greatly effected by the presence of M.B.T.S. In the same work, it was found that pyrogollal (1,2,3-trihydroxy benzene) was similarly effective if a sulphur donor such as M.B.T.S., T.M.T.D. or even elemental sulphur was present. They suggested that in this case the polyhydroxy compound has reacted with the sulphur donor to form a polyhydroxylated diphenyl sulphide similar to the tetra hydroxy diphenyl sulphide. They suggest that in their system the following scheme may be operative.



A part of the hypothetical intermediate may undergo further reaction with another chlorine atom to form a cross-link, but the subsequent reactions involved in vulcanization are so complicated that the overall mechanism remains unknown.

3.1.5 OXIDATION AND AGEING OF CR

The deactivating influence of the chlorine atom attached to the double bond, besides effectively preventing conventional sulphur vulcanization, also results in better heat and oxidation resistance than is shown by other diene hydrocarbon rubbers. Such thermal stability can be improved further by the use of suitable antioxidants. Several major restrictions exists since neoprene is chemically a more reactive and complicated polymer. The antioxidants added must be chosen with great care, or destabilization actually occurs(125).

Properly compounded neoprene vulcanizates (125) have outstanding resistance to natural or accelerated ageing, but if they are not protected by an antioxidant their physical properties will deteriorate.

Polychloroprene compounds have moderate heat resistance much better than natural rubber, but not quite as good as butyl rubber. Non-sulphur modified (type-W) of the polymer are better than the sulphur modified (type-G).

The polymer shows much better ageing in the absence of air, which indicates its ability to withstand thermal degradation.

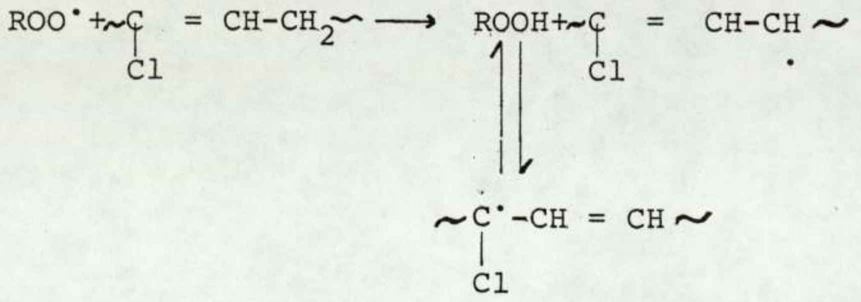
Common compounding ingredients may effect heat resistance e.g. the use of Zno in amounts greater than 5 phr up to 25 phr improves heat resistance (126).

The oxidative degradation of polychloroprene has been studied at temperatures up to 150°C. Hydrogen chloride is eliminated during the oxidation at a rate which is closely related to that of oxygen uptake (127). The activation energy for hydrogen chloride loss has been reported as 9.2, 12 (127,128) and 15.8 Kcal/mole (127). The reaction has a short induction period and is autocatalytic (127,129). During polychloroprene oxidation a variety of C=O and C-O chromophores has been detected by infra-red spectroscopy (130).

During oxidation, the molecular weight may either increase through cross-linking or decrease by chain scission. The latter is more important in accelerated oxidation at raised temperatures (127,131), but at ambient temperatures both processes take place (131). The cross-links are most likely to be peroxide bonds since they are broken easily by ultrasound (132) or even on a precipitation chromatography column. Crystallization studies on polychloroprene aged in air between 65°C and 100°C suggest that cross-linking at these temperatures is not very important (128).

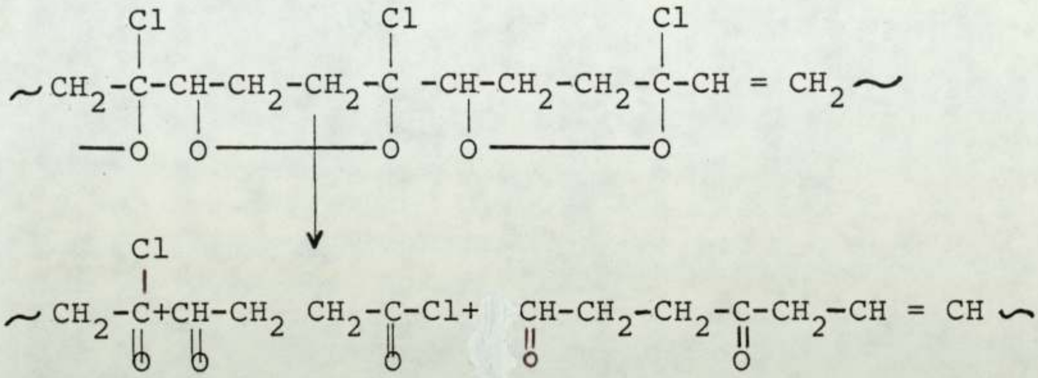
Verbance (125), showed that the simultaneous elimination of hydrogen chloride from the backbone skeleton during the oxidation process serves to complicate any study of protective agent since the elimination of HCl with compounding ingredients serve as catalysts for additional side reactions, including cross-linking.

Bailey (127,133), showed that the oxidation of neoprene leads to the formation of hydroperoxide and peroxides and proposed a mechanism involving the attack of the α-methylene hydrogen by a peroxy radical followed by rearrangement.



$$ROO^{\bullet} + \sim\underset{Cl}{\underset{|}{C}} = CH-CH_2\sim \longrightarrow ROOH + \sim\underset{Cl}{\underset{|}{C}} = CH-\underset{\cdot}{CH}\sim \rightleftharpoons \sim\underset{Cl}{\underset{|}{C^{\bullet}}}-CH = CH\sim$$

Further peroxidation leads to β-alkoxy peroxide radicals which decompose to carbonyl compounds by the following reaction:-



These reactions are stated to account for the majority of the polychloroprene oxidation products, including those found by decomposing oxidized specimens under nitrogen.

The thermal degradation of CR rubber has been reviewed by Gardner(134-136) and McNeill, who confirm that 90% of the available chlorine is removed by dehydrochlorination.

Further Reactions of Polychloroprene Rubbers

It may be possible to react the chlorine atoms in the polychloroprene rubbers with the reactive groups of phenolic and amine antioxidants. This may possibly be carried out by reaction of the raw polymer before compounding or during the mixing of the vulcanization process. Thus producing either:

(a) Linear polymeric antioxidant which can be used to protect CR rubber or other rubbers.

or

(b) Antioxidants bound to CR rubber network.

The remainder of this chapter deals with the attempts made to carry out such reactions.

3.2 EXPERIMENTAL WORK

REACTIONS OF ANTIOXIDANTS WITH POLYCHLOROPRENE

Consideration is only to be given to the two main types of antioxidants i.e. amines and phenols.

3.2.1 REACTION OF CR TYPE-W WITH AMINES

The tendency of the allylic chlorine atoms of CR type-W rubber to react with the amine antioxidants has been discussed(137).

Kalil and his group(137,138), found that the reaction of CR type-W with amines decreases as the substitution on the nitrogen atoms changes from dialkyl to alkyl-aryl to alicyclic aryl and to diaryl. The extent of reaction is related , among other factors, to the base strength of the diamines.

3.2.1.1 Reactions of CR Type-W with IPPD Antioxidant

3.2.1.1.1 Assessment of Amount of Reaction of IPPD

To assess the amount of IPPD bound into CR type-W a calibration curve was produced using vulcanisates prepared from formulations shown in Table (3.1).

TABLE (3.1)

Formulations for CR Type-W with IPPD Antioxidants to be used for the IR Calibration Curve

	1
CR Type-W	100
MgO	4
IPPD	0,1,3,5 and 7.5 phr respectively
NA-22	1
MBTS	1
Zno	1

The ingredients were mixed on a two roll mill until sufficient dispersion was obtained. Thin films were vulcanised at 160°C for 30 minutes. Infra-red anlysis was then carried out on the film in duplicate as described in Section 2.4.6.2. A peak ratio at 3,400 cm^{-1} to 2020 cm^{-1} was measured for each concentration and a graph between this peak ratio and the concentration of IPPD added was drawn as shown in Fig. 3.1.

A thin film of the modified CR type W was formed using the same conditions as above and this was then acetone extracted to remove any free antioxidant, dried under vacuum and the infra-red spectrum obtained. The

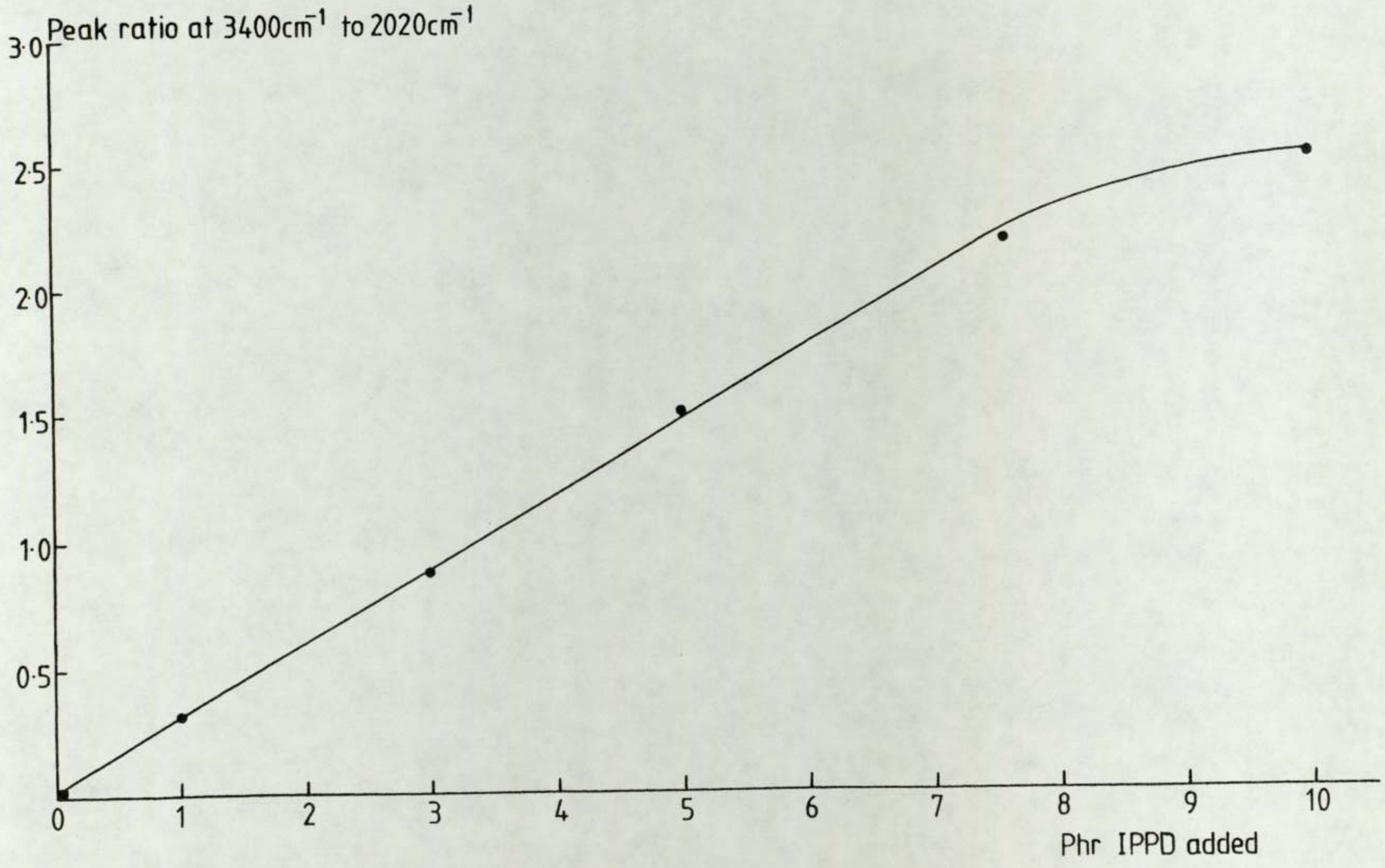


Fig 3:1 Calibration curve of IPPD with CR-G type polychloroprene

amount of bound antioxidant was determined by measuring the peak ratio of this film and by comparing it with the known peak ratio of the spectrum of the vulcanizate containing a known concentration of IPPD.

3.2.1.1.2 Reaction of CR Type-W with IPPD during Mixing in the Torque Rheometer

The CR type-W and IPPD (10 phr) were mixed at 80°C for five minutes in the torque rheometer (2.2.3) using a motor speed of 60 r.p.m. Infra-red analysis of the acetone extracted vulcanized film (2.4.6.2) used in conjunction with the calibration curve, showed that 6.35 phr of IPPD is bound into the polymer. This is equivalent to one molecule of antioxidant for each 37 chloroprene units.

3.2.1.1.3 Reaction of IPPD during Vulcanization

The possibility of reaction between IPPD antioxidant and CR type-W rubber during mixing and vulcanization was assessed using the formulation shown in Table (3.2).

The ingredients were mixed on a two roll mill until good dispersion was obtained. Thin films of thickness 0.02 cm were prepared at 160°C for 30 minutes. The film was then acetone extracted under a nitrogen

TABLE (3.2)

Formulation used to Study the Amount of IPPD Bound into CR-Type-W during Vulcanization

	2
CR Type-W	100
Mgo	4
IPPD	2
NA-22	1
MBTS	1
Zno	5

atmosphere to remove any unbound antioxidant and any other acetone soluble materials. Infra-red analysis of these films showed that there was 1.4 phr of IPPD bound to CR type-W during processing and vulcanization. This amount corresponds to 70% of the original amount of added antioxidant and is equivalent to one unit of IPPD per 176 chloroprene repeat units.

3.2.1.1.4 Mechanism of Reaction of IPPD Antioxidant with CR-Type-W

The chemistry of vulcanization of CR type-W is discussed in Section 3.1.4, which shows that reaction occurs at the tertiary allylic chlorine atoms resulting from the occasional 1,2-additions produced during the polymerization process.

It has been shown (3.4.1.1.2 and 3.2.1.1.3) that IPPD will react with CR type-W. To determine the point of reaction , e.g. the isopropyl - or the phenyl substituted amino groups or both on the IPPD, the following experiments were carried out.

(1) IPPD (2 phr) was mixed with 100 gm of CR type-W on a two roll mill at room temperature. The mixture was found to be completely soluble in CCl_4.

(2) Five grams of the above mixture was pressed in a very shallow mould at 160°C for 20 minutes. The mixture would not vulcanize and was still tacky.

(3) Monsanto rheometer tests did not show any vulcanization.

(4) The corresponding unsubstituted amine, p-phenylene diamine, however, showed a very good cross-linking activity in CR Type-W as shown by the Monsanto rheometer results.

(5) N,N^- diisopropyl-p-phenylene-diamine, prepared by reacting IPPD with 2-chloro-propane (Section 2.1.1.3) also cross-linked the CR type-W (Monsanto rheometer and solubility tests).

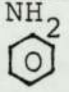
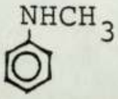
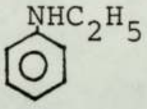
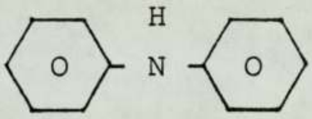
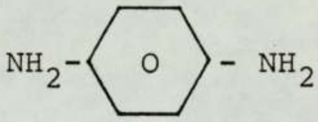
(6) N,N$^-$, diphenyl-p-phenylene diamine (DPPD) did not show any cross-linking action as assessed by solubility and Monsanto rheometer. Infra-red measurments also could not detect any reaction.

The reason for the lack of cross-linking reactivity of IPPD and DPPD, is probably due to the low base strengths of the amino groups when situated between two benzene rings. This is due to the delocalisation of the unpaired electron on the nitrogen atom with the benzene rings. It is also quite likely that reactivity is further restricted by steric hinderance offered by the phenyl groups.

Although the base strengths of the N,N$^-$ substituted p-phenylene diamines have not been measured, prediction of their relative reactivities can be made from the known base strengths of the analogous substituted anilines. This data is listed in Table (3.3) and shows that diphenylamine has the lowest base strength. This is in agreement with the finding that the DPPD is completely unreactive. The IPPD must, therefore, react via the isopropyl substituted amino group, but as this is monofunctional, no cross-linking takes place.

TABLE (3.3)

Base Strength of Substituted Anilines Compound(137)

		pKb
Aniline		9.42
Mono Methyl Aniline		9.16
Mono Ethyl Aniline		8.87
Diphenyl Amine		13.28
P-Phenylene Diamine		9.02

3.2.1.1.5 Effect of IPPD on the Vulcanization Characteristics of CR Type-W in the Absence of Other Accelerators

To study the effects of IPPD antioxidant on the vulcanization characteristics of CR type-W, the formulations shown in Table (3.4) were mixed on a two roll mill at room temperature until a good dispersion was obtained. They were then tested in the Monsanto rheometer at 160°C using a torque range of 100 in -ℓb, and a time range of 30 minutes.

TABLE (3.4)

Formulations of CR type-W with Different Concentration of IPPD Antioxidant

CR Type-W	100
Mgo	4
IPPD	0,3,5,7 and 10 phr respectively
Zno	5

The effect of IPPD concentration on the time required to obtain a 90% modulus and on the scorch time is shown in Figs 3.2 and 3.3 respectively. It can be seen that there is a decrease in the modulus as the concentration of IPPD increases. This decrease in the modulus can be attributed to the decrease in the cross-linking density of the vulcanizate due to the removal of some of the tertiary allylic chlorine atoms by the reaction with IPPD during the vulcanization (Section 3.2.1.1.3).

When a small concentration of IPPD is used (up to 3 phr), there is an increase in the modulus but this then decreases as the concentration increases. The initial increase is probably due to the fact that the basic IPPD acts as an accelerator, but increasing amounts

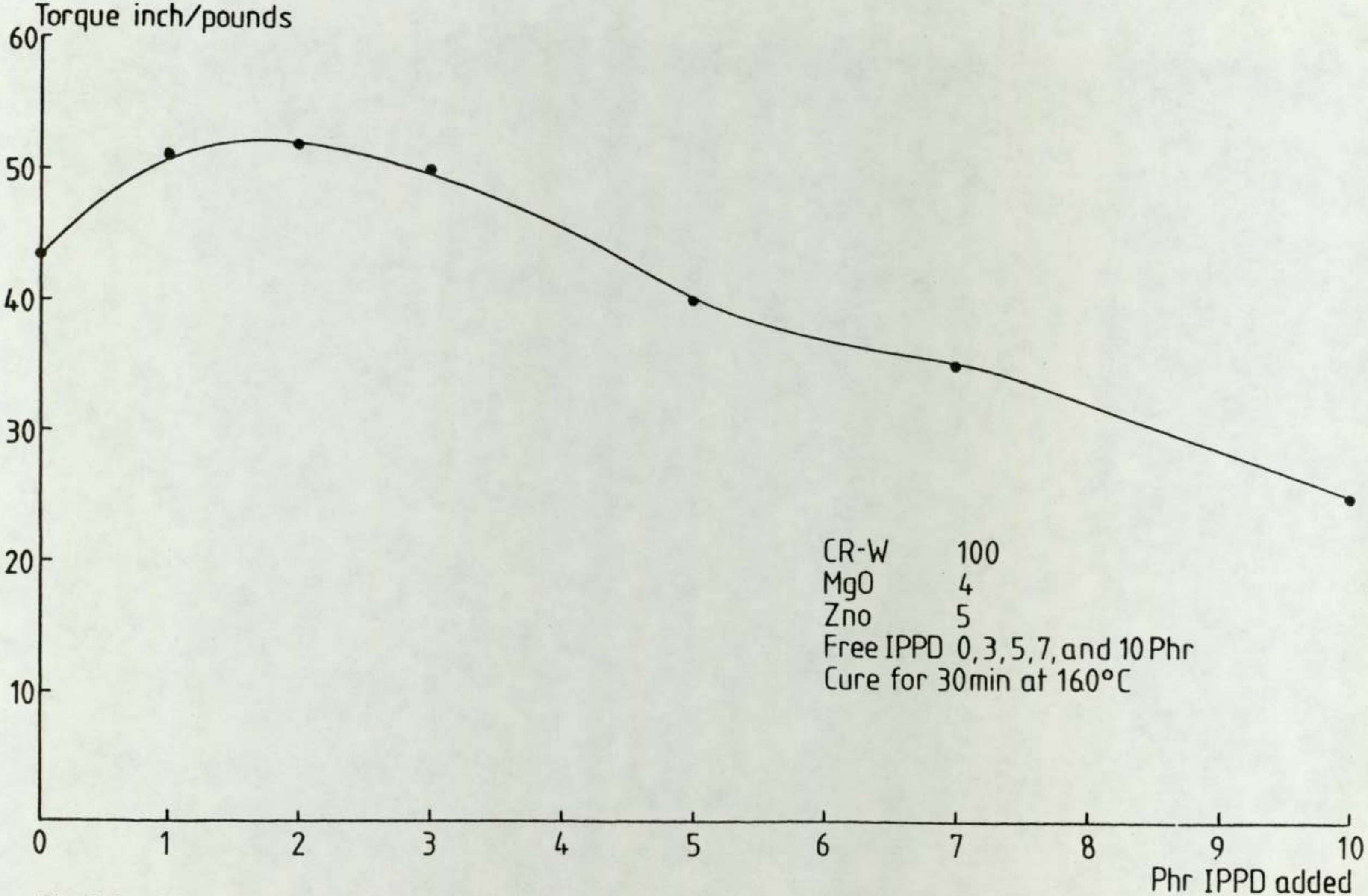


Fig 3:2 The effect of IPPD on vulcanization of CR-type W

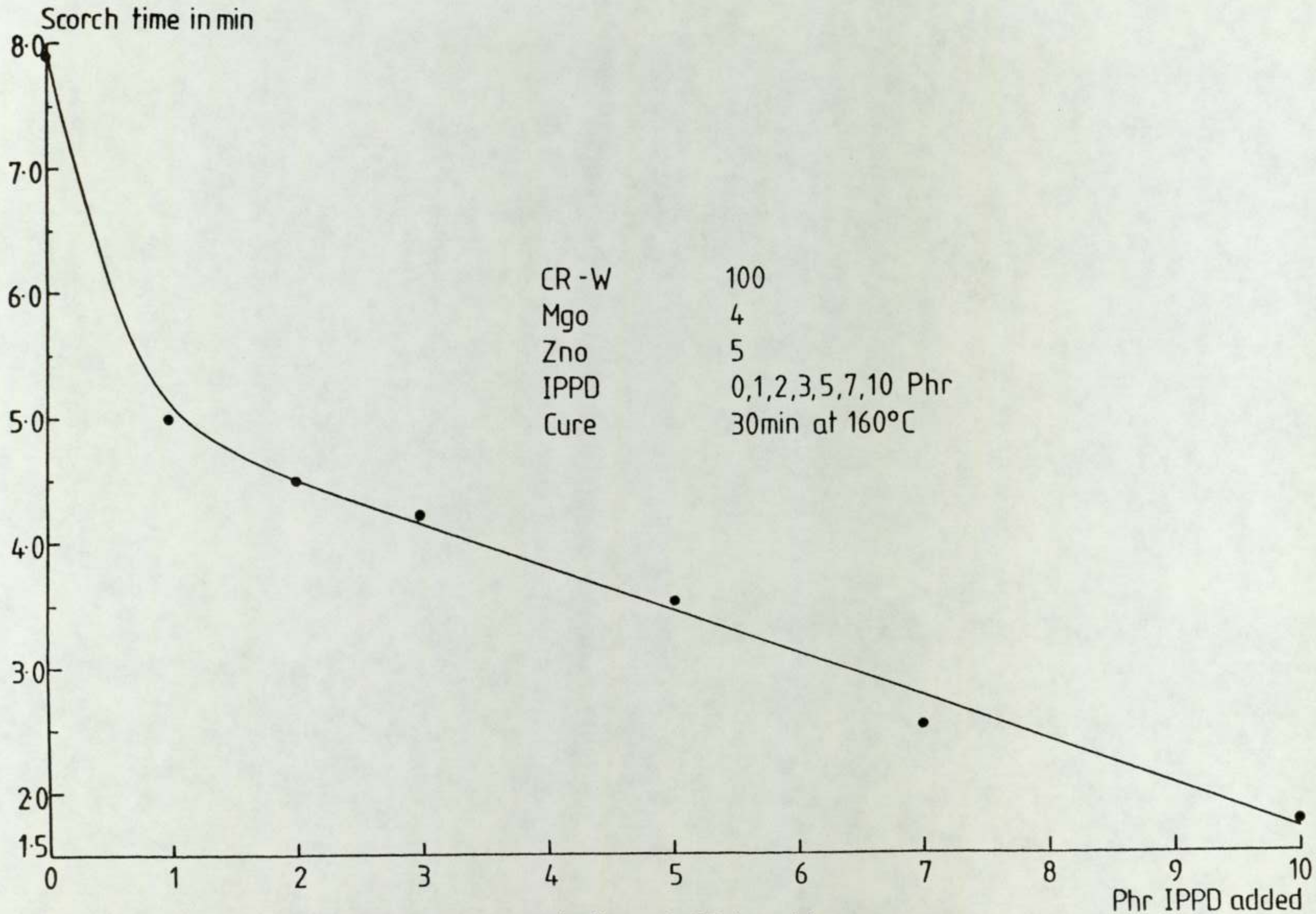


Fig 3:3 The effect of IPPD on the scorch time of CR type W

block the reactive chlorine atoms and reduce its overall reactivity.

The scorch time is reduced as the concentration of IPPD is increased due to the acceleration produced by the basic IPPD in the initial stage of the reaction and this is not effected by the blocking produced by the higher concentration of IPPD which only takes place at the late stage of the reaction.

3.2.1.1.6 Effect of IPPD Bound to CR Type-W by Pre-Mixing on Vulcanization Characteristics

As it was shown in Section 3.2.1.1.5 the presence of free IPPD antioxidant with CR type-W rubber led to a decrease in the cross-linking density due to the reaction between the two components through the tertiary allylic chloring atoms. To assess the affect of IPPD already bound to the rubber by pre-mixing, CR type-W was reacted with IPPD in the torque rheometer (Section 3.2.1.1.2) and the free IPPD removed by extraction with acetone under N_2 (2.3.4). The vulcanization characteristics of this modified polymer were then compared with those of CR type-W containing no antioxidant and with CR type-W containing IPPD added as a compounding ingredient using the formulations shown in Table (3.5). These were mixed on a two roll mill and cured in the Monsanto rheometer at 160°C using a time span of 30 minutes and a torque

TABLE (3.5)

Formulations of CR Type-W with IPPD 'in situ' or Containing Bound IPPD

	3	4	5
CR Type-W	100	100	68.5
Mgo	4	4	4
IPPD	-	2	-
CR +6.35 phr IPPD(ext)	-	-	31.5
NA-22	1	1	1
MBTS	1	1	1
Zno	5	5	5
Modulus at 90% cure (in-lb) at 160°C	45	39	40
Scorch time (min) at 160°C	5.0	5.0	5.5

range of 100 in-lb. The results are shown in Fig. 3.4 and Table (3.5).

It can be seen that in the presence of the CR type-W accelerator NA-22, the free IPPD reduces the time required for 90% cure (as assessed by the modulus) but has no effect upon the scorch time, i.e. the effect of basic IPPD is masked by the strong accelerating effect of the NA-22.

Binding the IPPD to the CR type-W before vulcanization

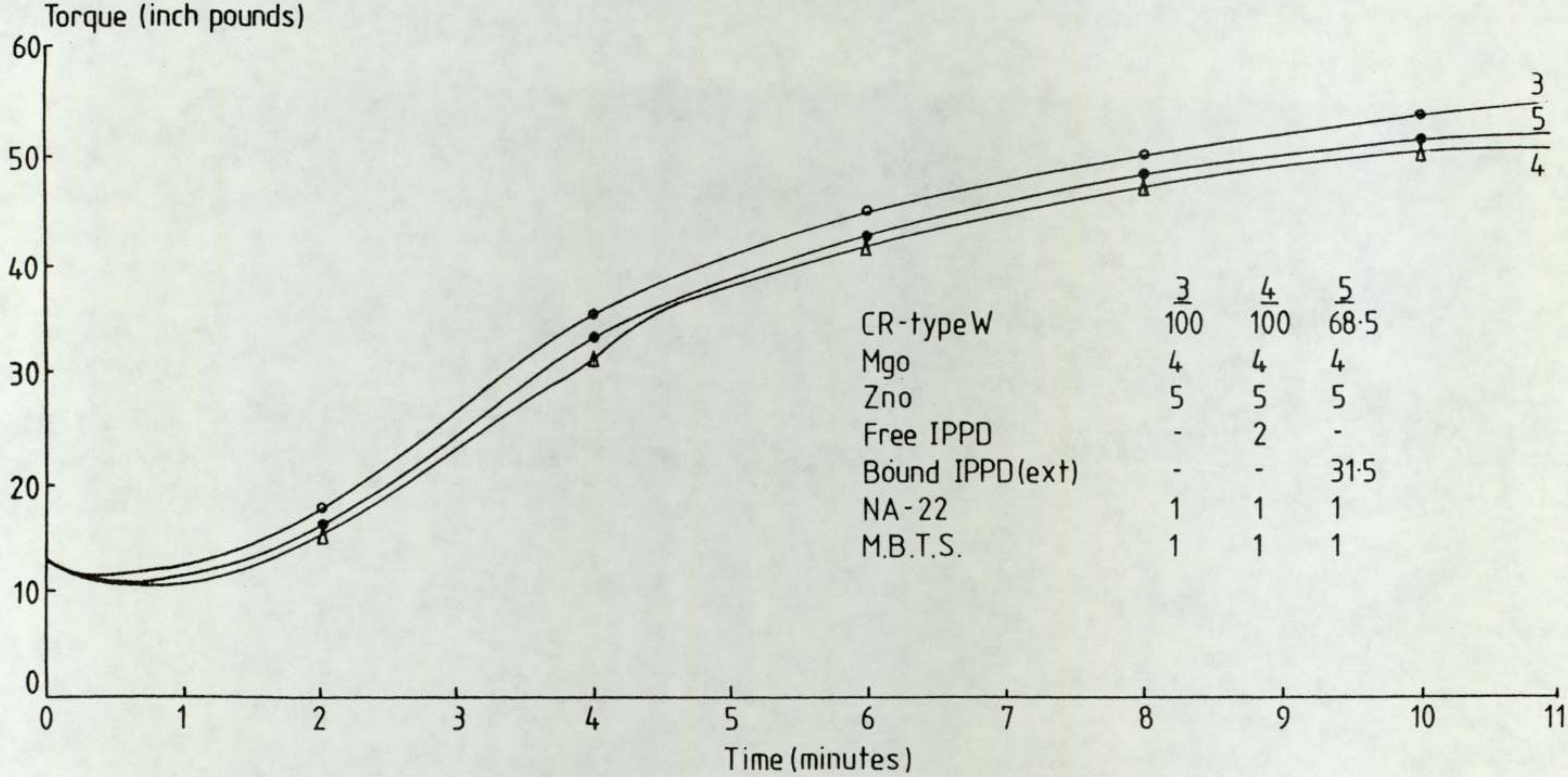


Fig 3:4 The effect of IPPD antioxidant (free or bound) on the vulcanization characteristics of CR-type W, cure for 30 minutes at 140°C

makes no difference to the vulcanization characteristics compared with those obtained when using free IPPD. These results are as expected as active allylic chlorine sites are blocked by the IPPD and whether this occurs during mixing in the torque rheometer or in the vulcanization reaction the Monsanto rheometer should make no difference to the rate of cure.

3.2.1.1.7 Assessment of Effectiveness of Bound IPPD as an Antioxidant to CR Type-W

To assess the effect of IPPD as antioxidant on CR type-W rubber, vulcanizates were prepared containing 2 phr IPPD either pre-bound by mixing in torque rheometer or by binding 'in situ' and then assessed by measuring their physical properties before and after ageing at elevated temperatures.

Samples for stress relaxation, ultimate tensile strength and hardness were prepared for the formulations shown in Table (3.5).

3.2.1.1.7.1 Stress Relaxation

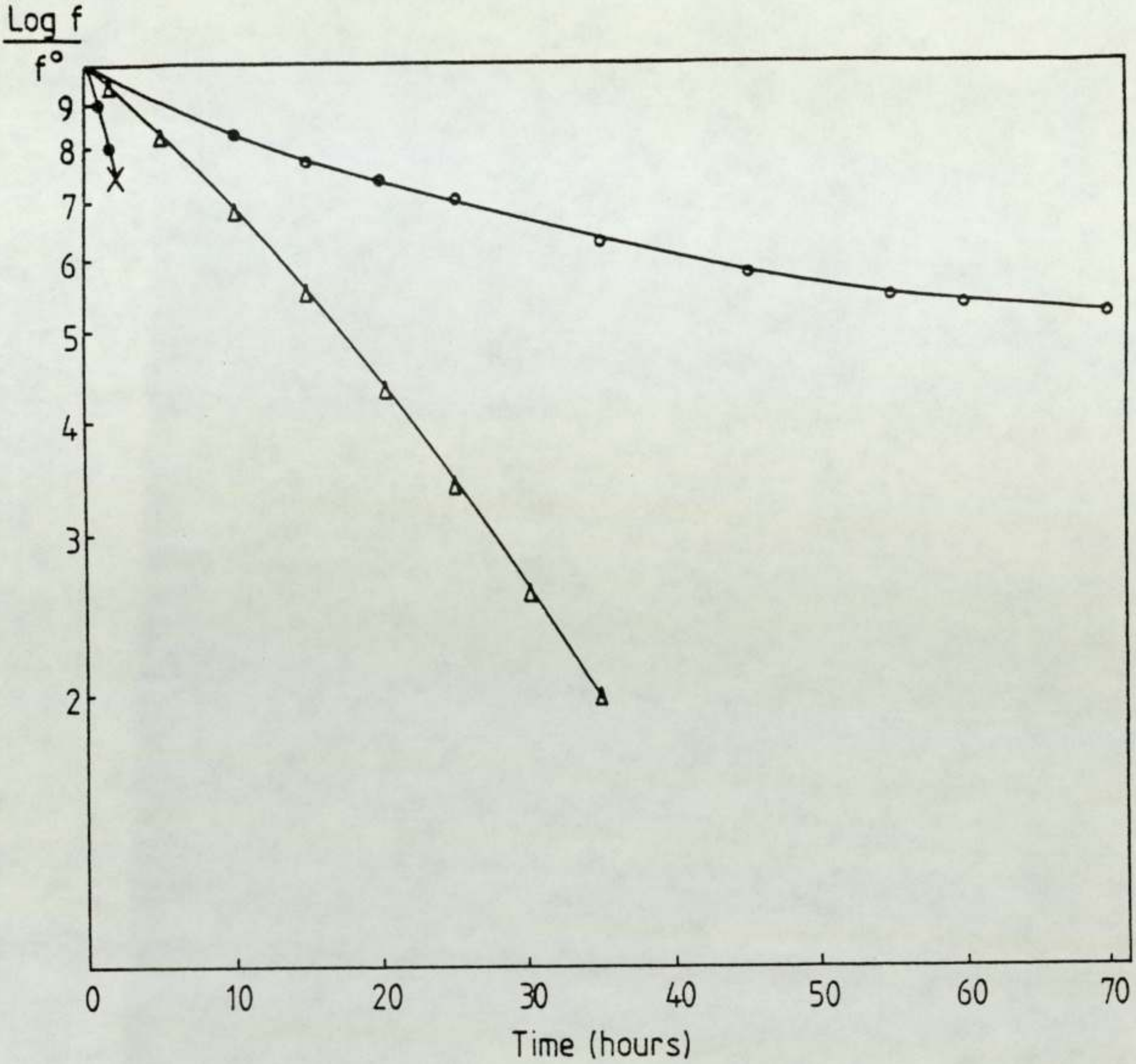
Thin films of 0.1 cm thickness were prepared at 160°C for 30 minutes, (Section 2.3.3). Samples were cut using MR100 cutter (Section 2.4.4). Half of the samples were acetone extracted under N_2 (Section 2.3.4).

Continuous stress relaxation was carried out at 120°C for both acetone extracted and non-extracted samples (2.4.1). The results are shown in Figs 3.5 and 3.6 respectively.

Results and Discussion

From Fig. 3.5 it can be seen that the control curve is autocatalytic in the absence of any antioxidant. It becomes soft after 35 hours of ageing. In the presence of IPPD the shape of the relaxation curve becomes auto-retarting due to antioxidant activity. Therefore, IPPD is considered a very good antioxidant for CR type-W when it is added 'in situ'.

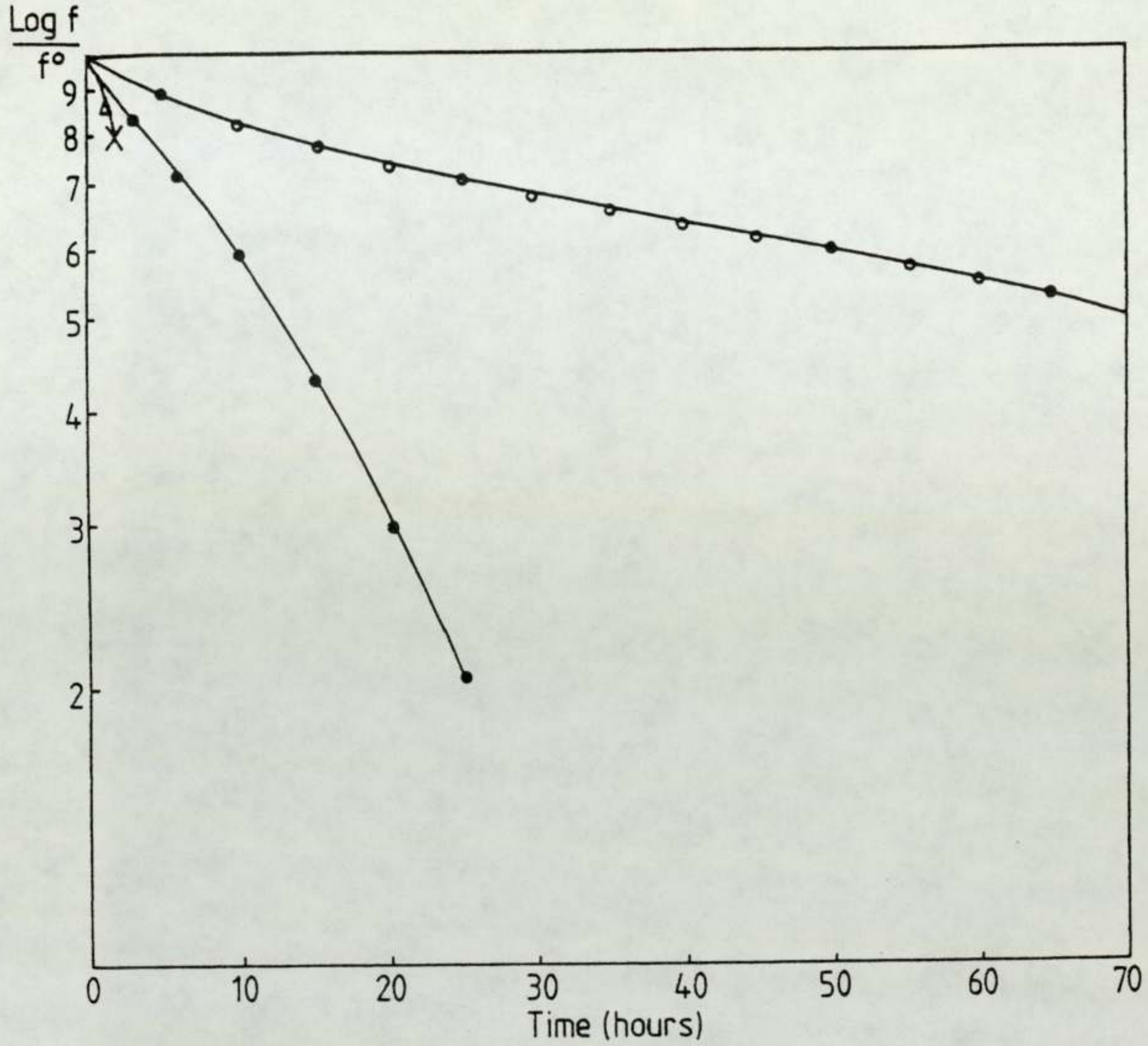
The stress relaxation curves for samples containing 2 phr antioxidant bound to CR type-W by pre-mixing in the torque rheometer (Section 3.2.1.1.2) could not be obtained as they broke before any recording was obtained. This might be due to cross-linking processes occurring during the mixing in the torque rheometer(Section 3.2.1.1.2) followed by mechano-chemical degradation. In addition to this there is the possibility of excessive HCl evolution due to the dehydrochlorination and this would, then, attack the rubber main chain. Yet another possibility is the formation of hydroperoxide groups which subsequently produce free radicals which can take part in further ageing. The presence of IPPD which is capable of destroying hydroperoxide makes this less likely.



	3(Δ)	4(○)	5(●)
CR type W	100	100	68·5
Mgo	4	4	4
Zno	5	5	5
Free IPPD	–	2	–
Bound IPPD (ext)	–	–	31·5
NA - 22	1	1	1
M.B.T.S.	1	1	1

Fig 3:5

Continuous stress relaxation of CR type W with IPPD antioxidant (free and bound) aged at 120°C before extraction



	3(•)	4(○)	5(Δ)
CR-W	100	100	68·5
Mgo	4	4	4
Zno	5	5	5
Free IPPD	–	2	–
Bound IPPD (ext.)	–	–	31·5
NA-22	1	1	1
M.B.T.S.	1	1	1

Fig 3:6
Continuous stress relaxation of CR type W with IPPD antioxidant (free or bound) after acetone extraction, aged at 120°C

On acetone extraction under N_2 (Section 2.3.4) some of the control samples were broken after 2 hours of ageing although some of them lasted for 25 hours. This indicates that the control lost some of its resistance on extraction due to the removal of some ingredients from the vulcanizate which have antioxidant activity, or alternatively it might be due to the swelling effect of vulcanizate during extraction. This swelling may cause rupture of the network and decrease the cross-linking density.

The effect of IPPD mixed 'in situ' on the stress relaxation after acetone extraction,is shown in Fig. 3.6. After the acetone extraction, the vulcanizate still shows a very good thermal oxidative resistance. This must be attributed to the binding of the antioxidant to the rubber during vulcanization (Section 3.2.1.1.3) and this would not be removed by acetone extraction. The shapes of the relaxation curves, however, are similar to those obtained prior to extraction.

The stress relaxation of vulcanizates with IPPD bound in the torque rheometer and after acetone extraction were too weak to withstand the ageing.

3.2.1.1.7.2 Accelerated Oven Ageing of Vulcanizates

The efficiency of IPPD as an antioxidant, whether free or bound, to CR type-W was assessed by ageing vulcanizates in air at 130°C in a Wallace multicell oven.

The deterioration of the vulcanizate at different times during this ageing was monitored by measuring the decrease in selected physical properties, i.e. UTS/ elongation at break and hardness.

3.2.1.1.7.2.1 UTS and Elongation at Break

Formulations listed in Table (3.5) were mixed on a water-cooled laboratory 12" mill and moulded at 160°C for 30 minutes in the form of sheets of 0.2 cm thickness. They were quenched in cold water after being removed from the press and left for 24 hours before testing. Samples were cut from the sheets using the standard cutter for UTS (Section 2.4.2). Half of the samples were acetone extracted under N_2 (Section 2.3.4).

Ageing was carried out at 130°C in a multicell oven to avoid contamination between the samples. The graphs of the UTS and elongation at break against time of ageing, for both acetone extracted and non-extracted samples are shown in Figs 3.7 and 3.8, respectively. The percentage decrease in UTS and elongation at break are shown in Table (3.6) and (3.7) respectively.

3.2.1.1.7.2.2 Hardness Measurement

Samples of one cm thickness were prepared for all the formulations shown in Table (3.5) vulcanized for 30 minutes at 160°C. Two samples for each formulation were

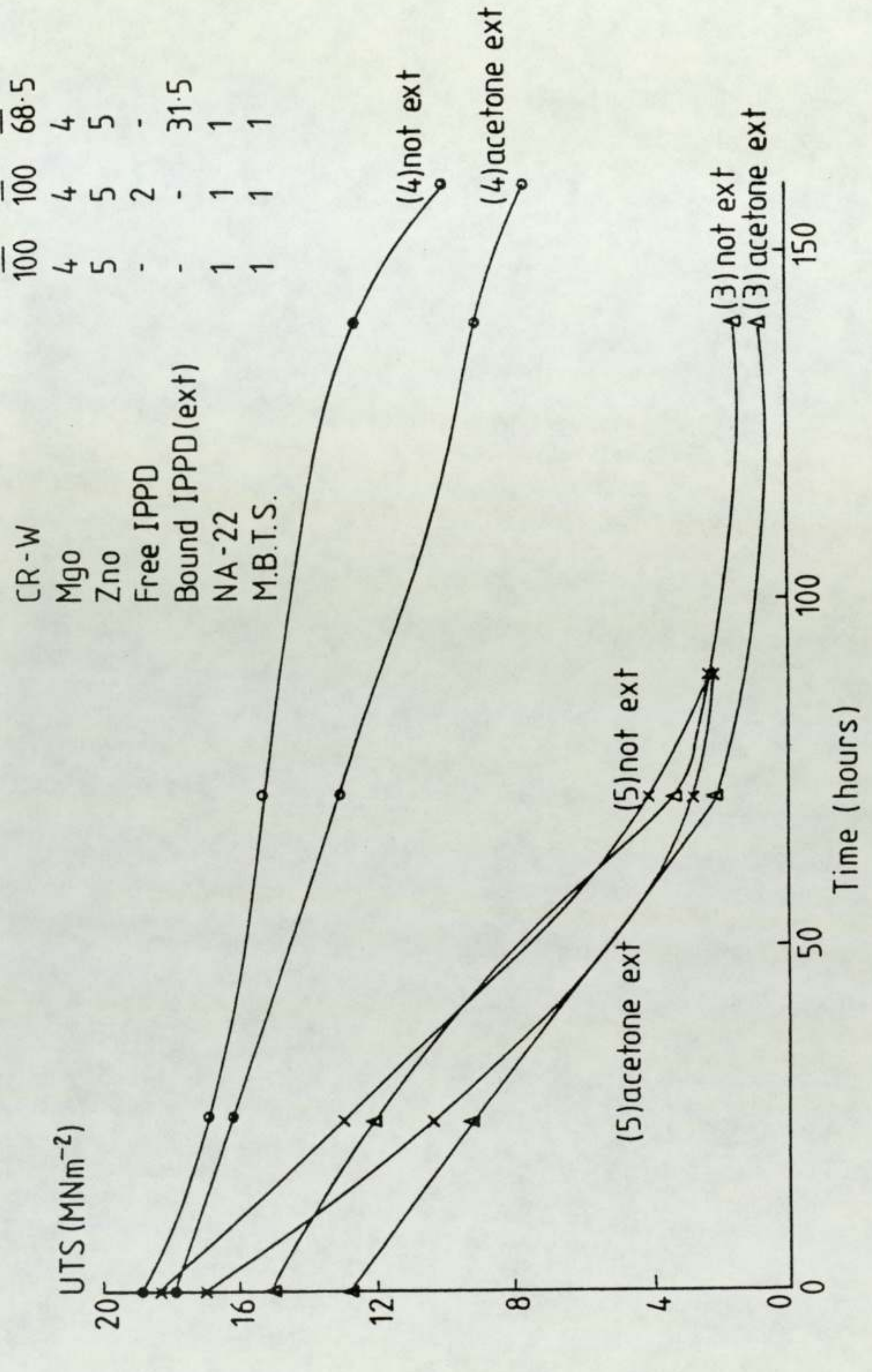


Fig 3 : 7

The effect of IPPD (free or bound) on the UTS of CR-type W rubber aged at 130°C.

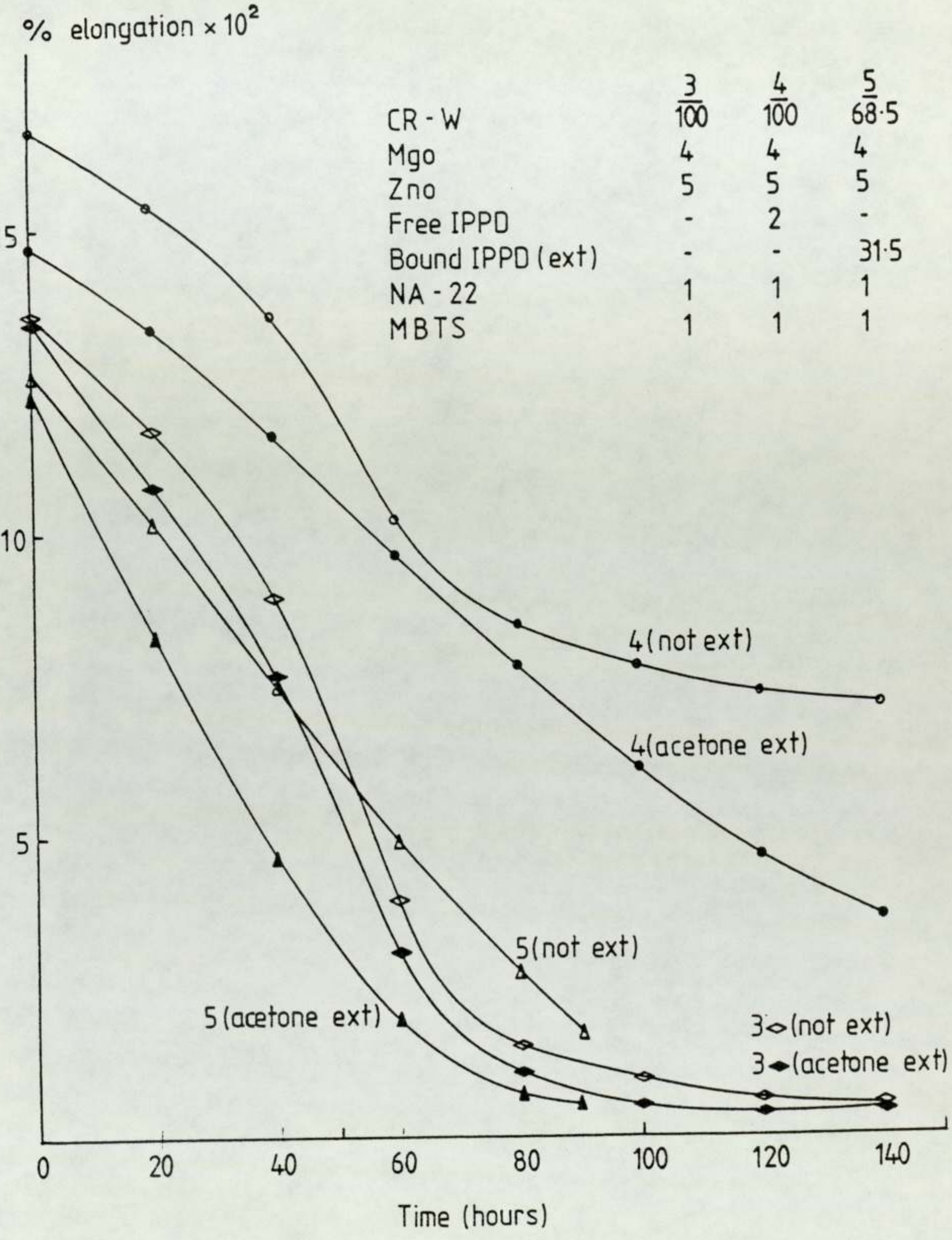


Fig 3:8 The effect of IPPD antioxidant (free or bound) on the % elongation, aged at 130°C

TABLE (3.6)

% Decrease of UTS (MNm^{-2}) of CR Type-W Vulcanizates Aged at 130°C

Formulations Number	Ageing Period							
	Non-Extracted				Acetone Extracted			
	Ohr	72hr	140hr	160hr	Ohr	72hr	140hr	160hr
3		-79	-88	embrittle		-85	-96	embrittle
4		-19	-32	-47		-28	-50	-57
5		-78	embrittle	embrittle		-82	embrittle	embrittle

TABLE (3.7)

% Decrease of % Elongation at Break of CR Vulcanizates Aged at 130°C

Formulations Number	Ageing Period							
	Non-Extracted				Acetone Extracted			
	0hr	72hr	140hr	160hr	0hr	72hr	140hr	160hr
3		-87	-96	-		-91	-97	
4		-47	-56			-42	-76	
5		-72	embrittle			-91	embrittle	

prepared. One of them was acetone extracted and dried in each case (Section 2.3.4).

Ageing was carried out in a Wallace oven at 130°C for different intervals of time for both acetone extracted and non-extracted samples. The instrument and procedure used to study the hardness are described in Section 2.4.3.

The effect of ageing on the hardness of CR type-W was shown in Fig. 3.9 and the percentage changes in the hardness is shown in Table (3.8).

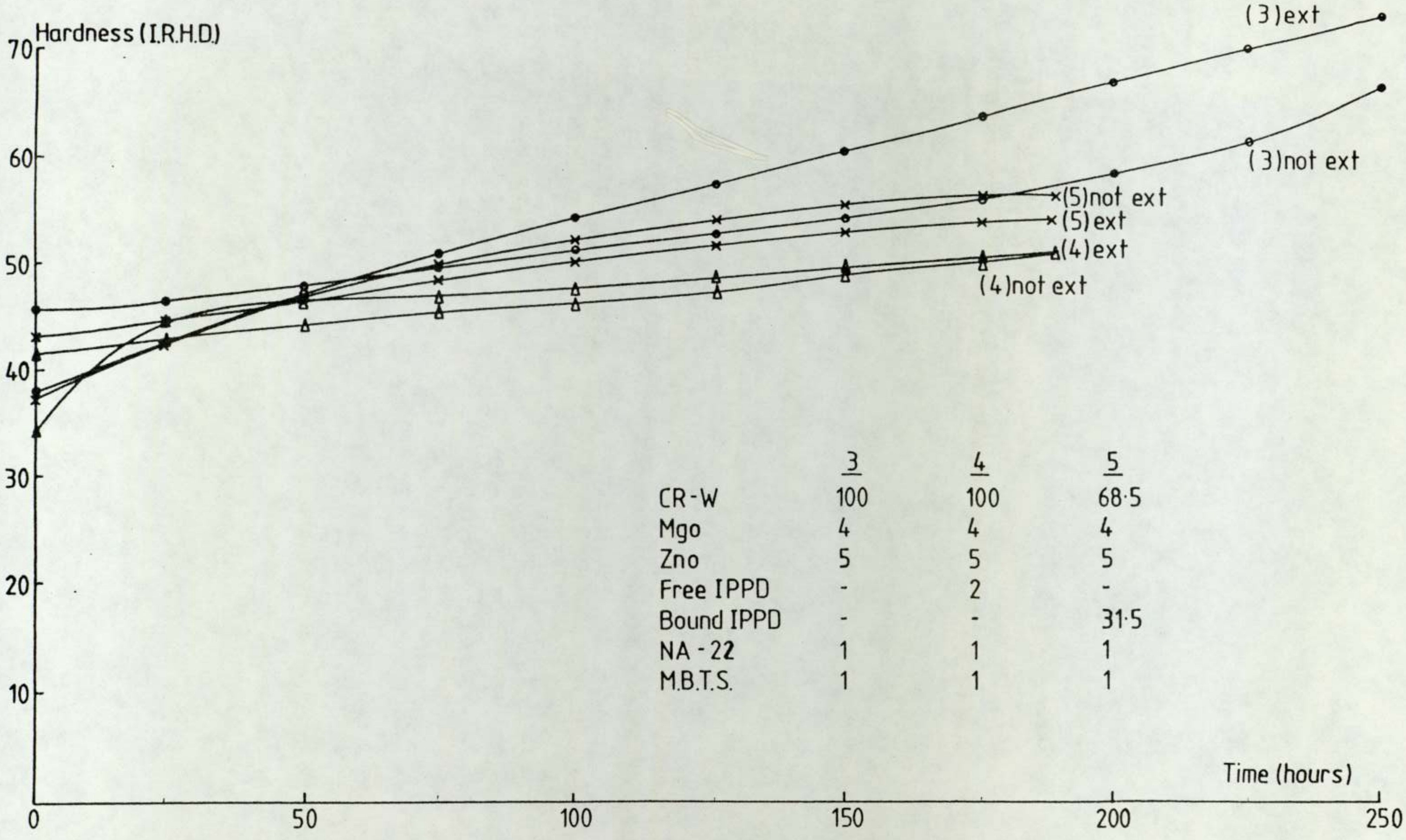
Results and Discussion

Ultimate tensile strength, elongation at break and hardness are broadly in agreement with the stress relaxation results (Section 3.2.1.1.7.1).

The conclusions to be drawn from these results are as follows:-

(1) IPPD is a good antioxidant for CR type-W rubber even after acetone extraction. This must be due to the fact that some of IPPD becomes combined with the rubber and cannot be removed by acetone extraction (see Section 3.2.1.1.3).

(2) The protection given by the IPPD bound by processing before vulcanization is very inferior to that produced when the IPPD is bound 'in situ' during



	3	4	5
CR-W	100	100	68·5
Mgo	4	4	4
Zno	5	5	5
Free IPPD	-	2	-
Bound IPPD	-	-	31·5
NA-22	1	1	1
M.B.T.S.	1	1	1

Fig 3:9 The effect of IPPD (free or bound) on the hardness of CR-type W aged at 130°C

TABLE (3.8)

% Loss of Hardness of CR Vulcanizate (IRHD) Aged at 130^{o}C

Formulations Number	Ageing Period							
	Non-Extracted				Acetone Extracted			
	0hr	72hr	130hr	190hr	0hr	72hr	130hr	190hr
3		+8.7	+15.2	+26		+33.0	+53.3	+73.3
4		7.0	+13.0	+21.0		+31.4	+37.2	+45.2
5		+13.9	+22.1	+27.9		+31.6	+43.4	+51.3

vulcanization. As explained in Section 3.2.1.1.7.1 this may be due to adverse reactions occurring in the torque-rheometer.

(3) Acetone extraction decreases the ageing resistance only slightly for formulation (4) in Table (3.5) containing free IPPD,again,supporting the belief that the IPPD is bound to the network during vulcanization process. This is also the case with formuation (3) containing no IPPD and formulation (6) with bound IPPD. The slightly lesser ageing resistance after extraction is probably due to loss of antioxidant added to the raw polymer to increase storage and processing stability or due to the leaching out of soluble compounding ingredients or of products of the vulcanization reaction with mild antioxidant properties. Oxidation is occurring during the extraction (although the extraction is carried uned N_2 there must always be some oxygen present) or a weakening of the rubber due to swelling may cause some deterioration in these cases.

(4) The removal of some of the allylic chlorine atoms by the IPPD is reflected in the high hardness of the control vulcanizate when compared with those containing IPPD (either free or bound).

3.2.1.2 Reaction of CR Type-W with N, N¯-Diphenyl P-Phenylene Diamine (DPPD)

DPPD is widely used as an antioxidant for CR rubber(137,138).

In addition to its effectiveness as an antioxidant the low reactivity of the phenyl substituted amino groups (Section 3.2.1.1.4) ensures that it will not react during storage of the compounded stock (i.e. have low bin scorch and freedom from an increase of viscosity on storage).

These properties, in addition to its low cost, would make it an attractive bound antioxidant.

Although it has been shown to have no detectable reaction with CR type-W rubber either on mixing or vulcanization (Section 3.2.1.1.4) there is a possibility that it may be bound in a very small amount (but sufficient to show antioxidant activity) in a different vulcanization system.

3.2.1.2.1 Reaction of CR Type-W with DPPD Antioxidant on Milling

CR type-W (100 phr) was mixed on a two roll mill at room temperature with 2 phr or DPPD. This was then used to prepare very thin films of a vulcanizate using the formulation shown in Table (3.9).

The film was then acetone extracted under N_2 and examined by infra-red (Section 2.4.6) which showed that no antioxidant could be detected in these vulcanizates.

TABLE (3.9)

Formulation of CR Type-W with 2 phr DPPD

6	
CR Type-W	100
Mgo	4
DPPD	2
Pyrogollol	1
MBTS	0.5
Zno	5

It was felt, however, that very low concentrations of DPPD may be combined (which are below the level capable of being detected by IR techniques) and may produce some antioxidant activity.

3.7.1.2.2. Effect of DPPD on the Vulcanization Characteristics of CR Type-W Rubber

In order to assess the effect of DPPD antioxidant on the vulcanization characteristics of CR Type-W the formulations shown in Table (3.10) were prepared, and then tested in the Monsanto rheometer at 160°C, Fig. 3.10.

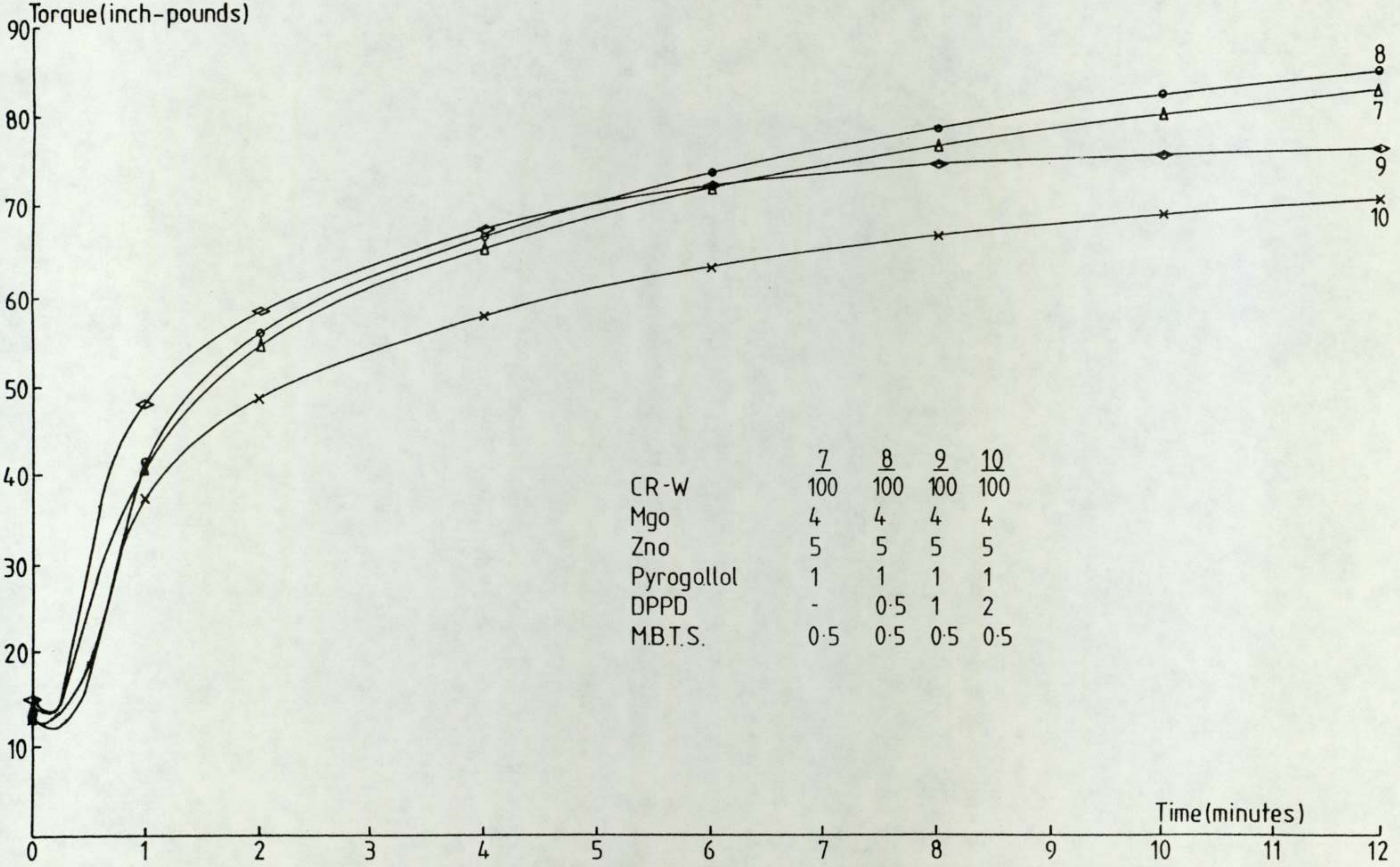


Fig 3:10 The effect of DPPD on the vulcanization characteristics of CR-type W cure for 30minutes at 160°C

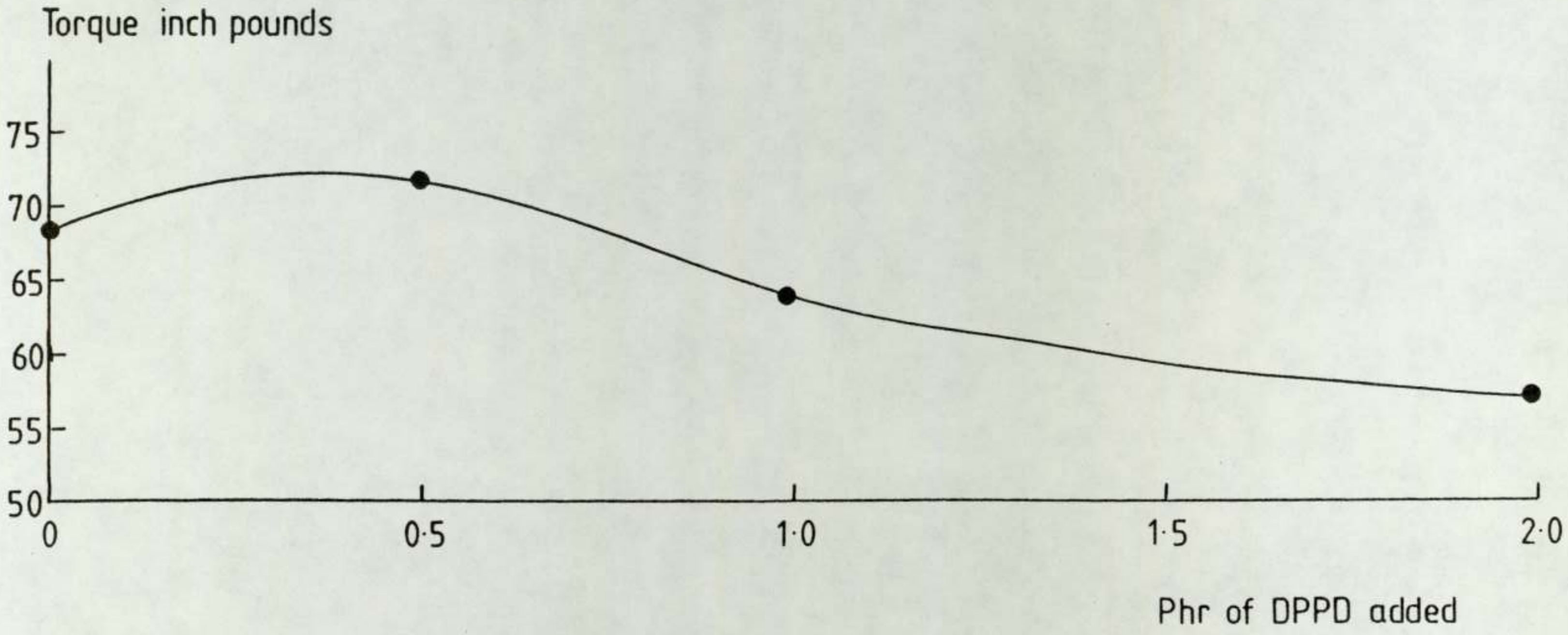


Fig 3:11
The effect of p-phenyl-diphenylene diamine on the vulcanization characteristics of CR type W
(Cured for 30min at 160°C)

TABLE (3.10)

Formulations of Ingredients of CR Type-W with DPPD

	7	8	9	10
CR Type-W	100	100	100	100
Mgo	4	4	4	4
Pyrogollol	1	1	1	1
MBTS	0.5	0.5	0.5	0.5
Zno	5	5	5	5
DPPD	-	0.5	1.0	2.0
Modulus at 100% cure (in-lb)	68	72	64	57

The results are shown in Figs. 3.10 and 3.11 and Table (3.10) shows that there is an increase in the modulus of CR type-W when 0.5 phr of DPPD is used. Although their is a decrease in modulus at higher concentrations the initial increase cannot be attributed to DPPD acting as a cross-linking agent since the mixture of the rubber and the antioxidant alone did not show any vulcanization reaction (3.2.1.1.4). It must be due to the DPPD acting as an accelerator which increases the extent of vulcanization. When the concentration of DPPD increases above 0.5 phr it causes a decrease in the modulus. This decrease may be due to the reaction between the curative agent (pyrogollol) which is acidic and the antioxidant which is basic.

3.2.1.2.3 Attempted Detection of Bound DPPD by Means of Antioxidant Activity

The antioxidant activity of CR type-W formulations containing DPPD Table (3.10) was assessed by stress relaxation and by oven ageing techniques.

3.2.1.2.3.1 Stress Relaxation

Films of 0.1 cm thickness were vulcanized at 160°C for 30 minutes (2.3.3) and used to prepare test samples. Half of the samples were acetone extracted under N_2.

Continuous stress relaxation (2.4.1.) was carried out at 130°C for both before and after the extraction. A plot of Log f/f^o against time of ageing are shown in Figs. 3.12 and 3.13 respectively. The values of Log f/f^o after 900 minutes of ageing are shown in Table (3.11).

Results and Discussion

TABLE (3.11)

The Values of Log f/f^o of CR Type-W after 900 Minutes of Ageing at 130°C, in the Presence of DPPD Antioxidant

	Formulation Number			
	7	8	9	10
Not extracted	0.18	0.73	0.73	0.73
Acetone extracted	0.08	0.68	0.68	0.68

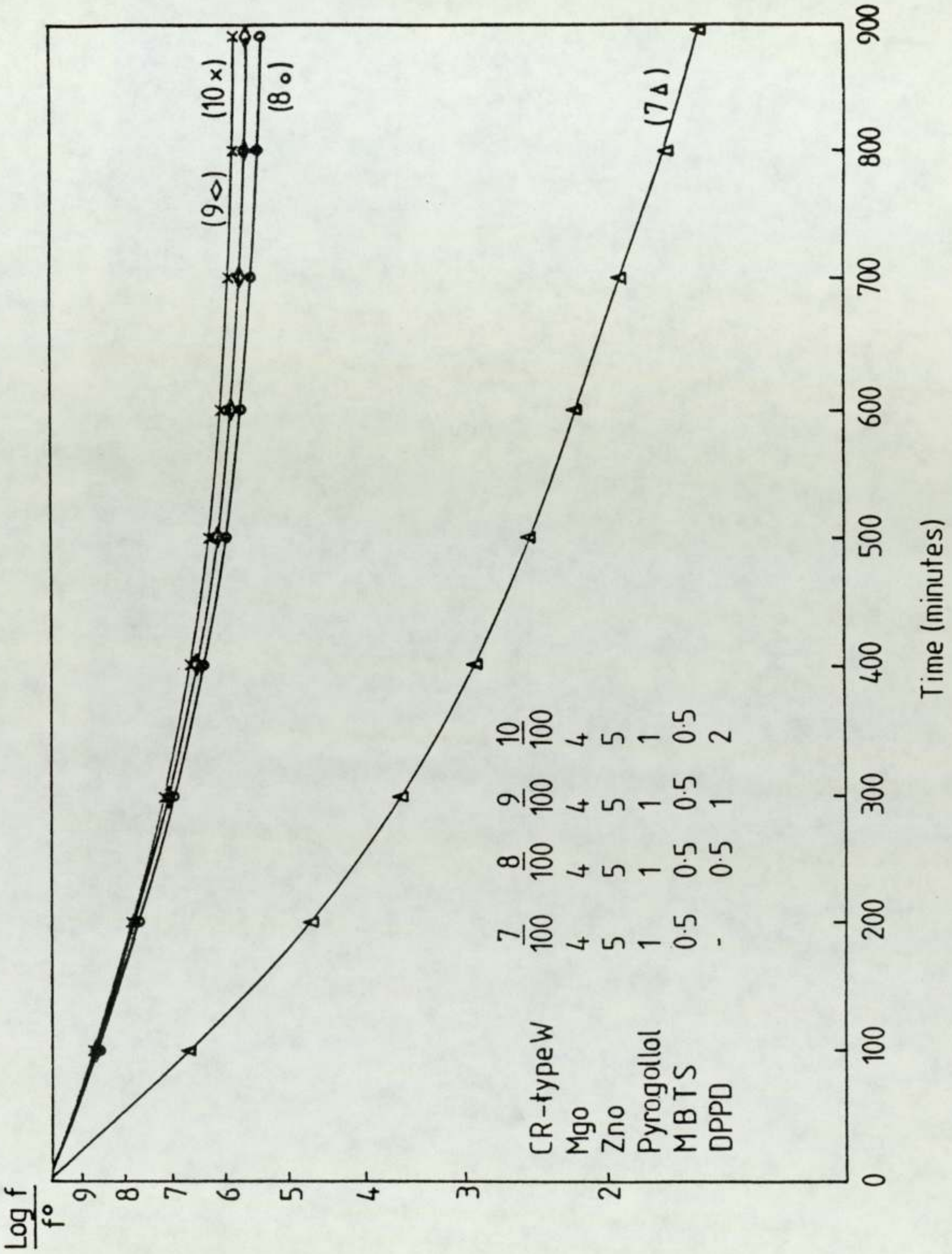
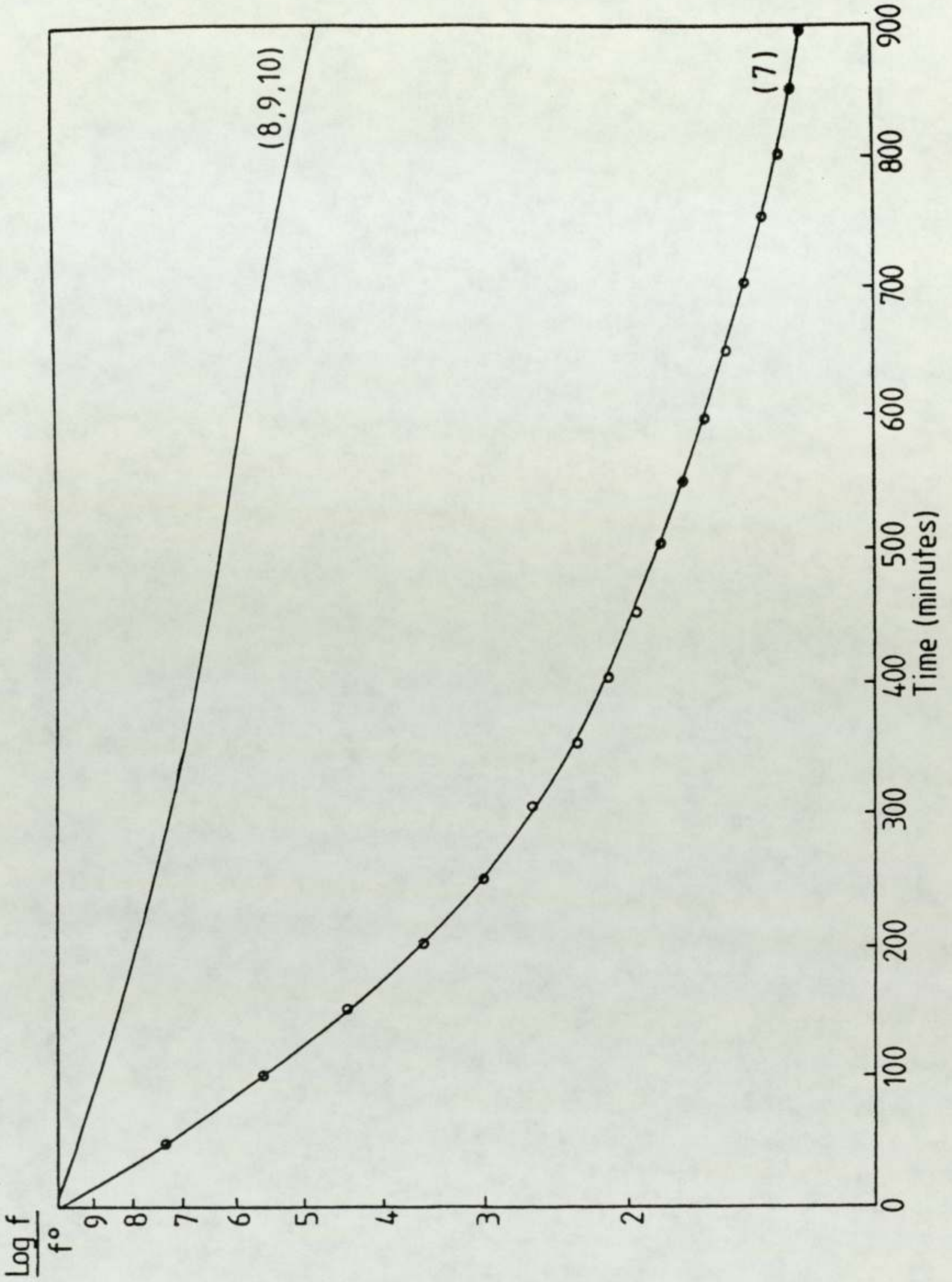


Fig 3:12

Continuous stress relaxation of CR-type W in the presence of different concentrations of DPPD, before extraction, aged at 130°C.



	7	8	9	10
CR-W	100	100	100	100
Mgo	4	4	4	4
Zno	5	5	5	5
Pyrogollol	1	1	1	1
M.B.T.S.	0·5	0·5	0·5	0·5
DPPD	—	0·5	1	2

Fig 3:13 Continuous stress relaxation of CR typeW in the presence of different concentrations of DPPD, after acetone extraction, aged at 130°C.

Table (3.11) shows that DPPD is a very good antioxidant to CR type-W. The thermal oxidative resistance of CR type-W increases even in the presence of a very low concentration of DPPD (0.0033 mole, 0.5 phr). The thermal oxidative resistance is not effected by the increasing of the concentration of DPPD above 0.5 phr. This is due to the fact that DPPD has very limited solubility in polychloroprene vulcanizates and tends to bloom and remain on the surface as a white waxy deposit if present in a concentration more than about 0.5 phr. The antioxidant activity of these low concentrations of DPPD is retained after acetone extraction under N_2 (2.3.4) as shown in Figs. 3.12 and 3.13 and Table (3.11).

The loss of antioxidant activity in the control (formulation 7) after acetone extraction,may be due to

(1) The removal of pyrogollol and MBTS both of which are antioxidants.

(2) The effect of swelling on the network of the vulcanizate.

(3) The possibility of the presence of oxygen in the solvent leading to oxidative degradation.

The reduction of ageing resistance after acetone extraction suggests that a very small amount of the antioxidant has become bound into backbone of the rubber during the mixing and vulcanization processes, even though the amount is too small to be detected by infra-red spectroscopy. It is possible, however, that the basic DPPD has reacted with the acidic pyrogollol to form a compound that is insoluble in acetone but retains its antioxidant activity.

3.2.1.2.3.2 Accelerated Oven Ageing of CR Type-W Vulcanizate Containing DPPD

The effect of DPPD as an antioxidant and the possibility of binding it to CR type-W rubbers was studied by ageing vulcanizates in air at 130°C in a Wallace multicell oven (2.4.2). The changes in the selected physical properties of the vulcanizate were measured at different times of ageing.

3.2.1.2.3.2.1 Ultimate Tensile Strength (UTS) and Elongation at Break

Sheets of 0.2 cm thickness were vulcanised using the formulations (7) and (10) shown in Table (3.10) at 160°C for 30 minutes and dumbell UTS specimens were then cut (2.4.2) and half of them were acetone extracted under N_2 (2.3.4).

Ageing was carried out at 130°C in a Wallace oven and the UTS and elongations at break after different periods of ageing were determined. The average values of 5 samples against time of ageing in hours is shown in Figs 3.14 and 3.15 for both acetone extracted and non-extracted samples, respectively.

Results and Discussion

The results obtained from UTS and elongation at break were in agreement with those obtained from the stress relaxation results (Section 3.2.1.2.3.1). The results of ageing at 130°C in the air oven are shown in Figs. 3.14 and 3.15. The percentage decrease in UTS and elongation at break with time of ageing is shown in Table (3.12).

The following results are obtained from the above figures and the table:

(1) The initial UTS and elongation at break values for both formulations were the same before extraction. Hence, the presence of the DPPD did not have any effect on the initial UTS values and on percentage of elongation. This supports the evidence that there is no reaction of the DPPD to block the chlorine cross-linking sites in the CR type-W.

(2) From Table (3.12) it is noticed that the control lost all its properties and become soft, while the samples with 2 phr DPPD can withstand the ageing. Therefore, DPPD

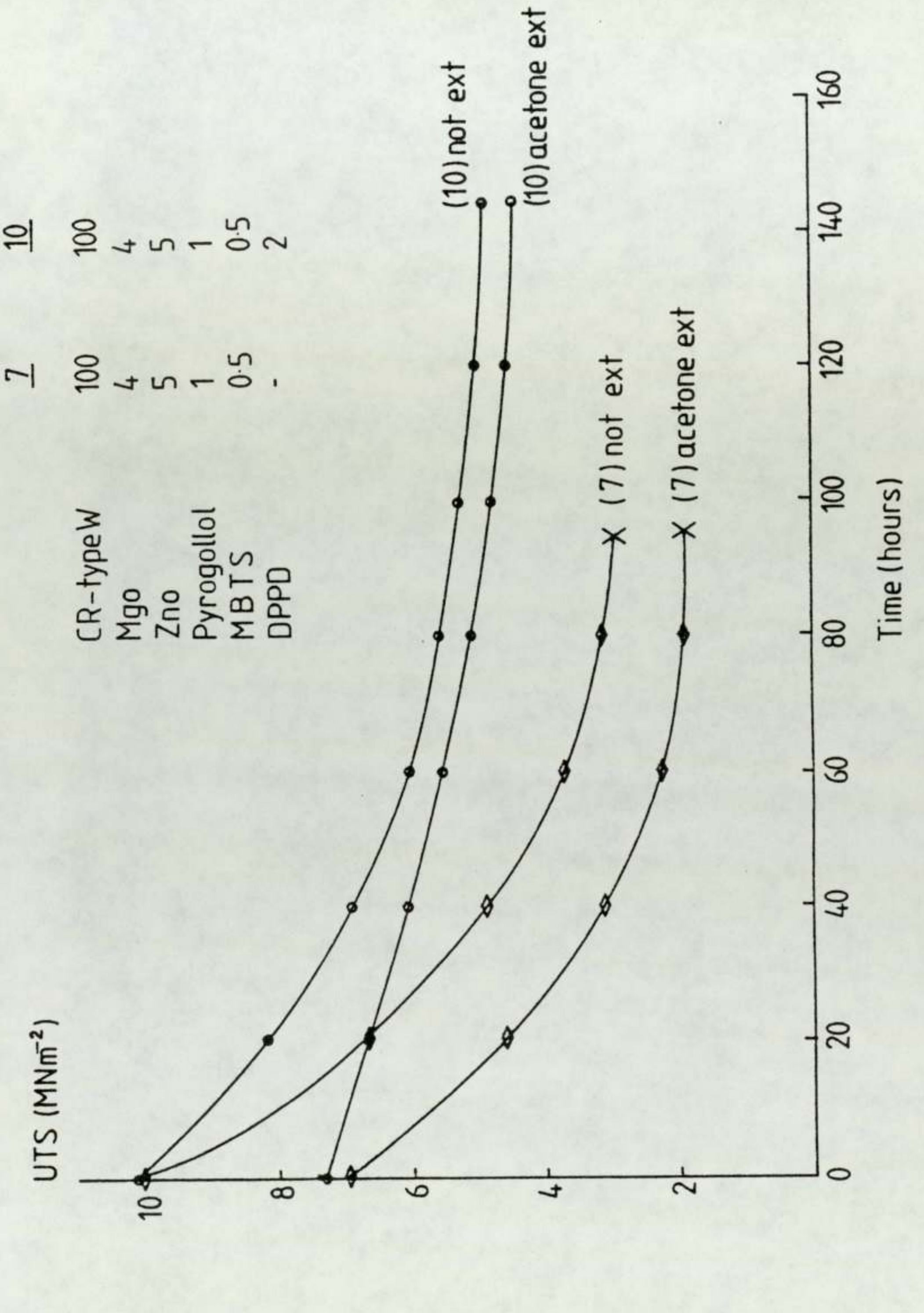
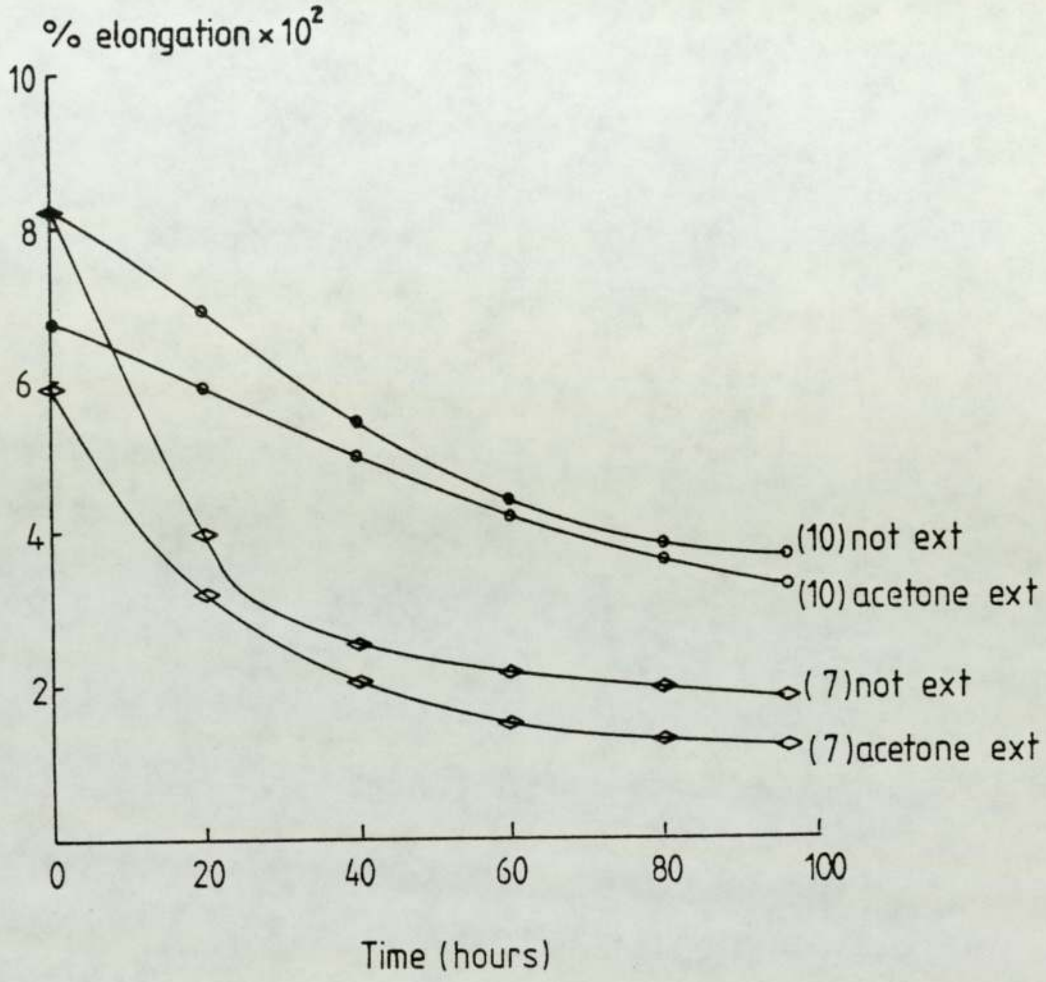


Fig 3:14

The effect of DPPD on the UTS of CR-typeW aged at 130°C



	7	10
CR-typeW	100	100
Mgo	4	4
Zno	5	5
Pyrogollol	1	1
MBTS	0·5	0·5
DPPD	-	2

Fig 3:15

The effect of DPPD on the elongation of CR-typeW aged at 130°C

TABLE (3.12)

% Decrease in UTS and % of Elongation of CR Type-W in the Presence of DPPD, Aged in Oven at 130°C Before and After Acetone Extraction

Formulation Number	UTS								% Elongation							
	Ageing Period in Hours								Ageing Period in Hours							
	Non-Extracted				Acetone Extracted				Non-Extracted				Acetone Extracted			
	0	55	95	145	0	55	95	145	0	55	95	145	0	55	95	145
7		-59	-70	melt		-61	melt	melt		-74	-78			-75	-83	
10		-36	-46	-50		-20	-34	-39		-46	-55			-35	-50	

is a good antioxidant for CR type-W before extraction process.

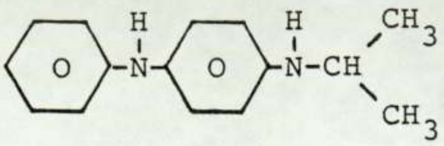
(3) Acetone extraction of samples containing 2 phr DPPD decreases the ageing resistance only slightly which again supports the idea that some of the DPPD may be bound to the network during vulcanization or that an insoluble antioxidant has been formed by reaction of the DPPD with one of the other compounding ingredients.

(4) There is a drop in the initial physical properties after acetone extraction for both the control and the vulcanizate containing DPPD. This drop after extraction may be attributed to the removal of uncured CR type-W, or due to bond-rupture caused by swelling during the extraction process.

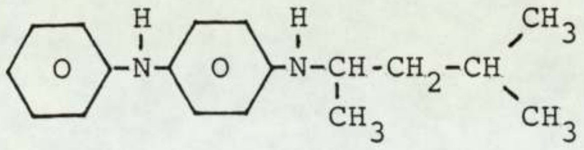
3.2.1.3 Reaction of N-1,3-Dimethyl Butyl-N-Phenyl-P Phenylene Diamine (Santoflex 13) With CR Type-W

As stated before(137,138), p-phenylene diamine derivatives have a tendency to cause bin scorch and this is a function of the base strength of the diamine.

Santoflex 13 is an antioxidant with a similar structure to IPPD antioxidants, i.e. the amine groups are substituted



IPPD



Santoflex 13 (M.wt = 268)

by a phenyl and an alkyl group respectively. The different alkyl group may change the reactivity of the amino group with the tertiary allylic chlorine atoms in the polychloroprene rubber.

3.2.1.3.1 Proof of Absence of a Cross-Linking Reaction Between CR Type-W and Santoflex 13

The set of experiments carried out on IPPD (3.2.1.1.4) to try and detect cross-linking reactions were repeated for Santoflex 13. They showed there was no cross-linking detected with Monsanto rheometer,no formation of insoluble rubber and no vulcanization detectable on moulding at 160°C.

By analogy with IPPD, the phenyl substituted amino group will be unreactive, however, it is possible that the alkyl substituted group reacts.

3.2.1.3.2 Infra-Red Absorption Studies

Thin films of CR type-W vulcanizates were prepared (3.2.1.1.3) using the formulations shown in Table (3.13) and a calibration curve of the ratio of 3,400 cm^{-1} peak height to 3,300 cm^{-1} peak height plotted against concentration of Santoflex 13, Fig. 3.16.

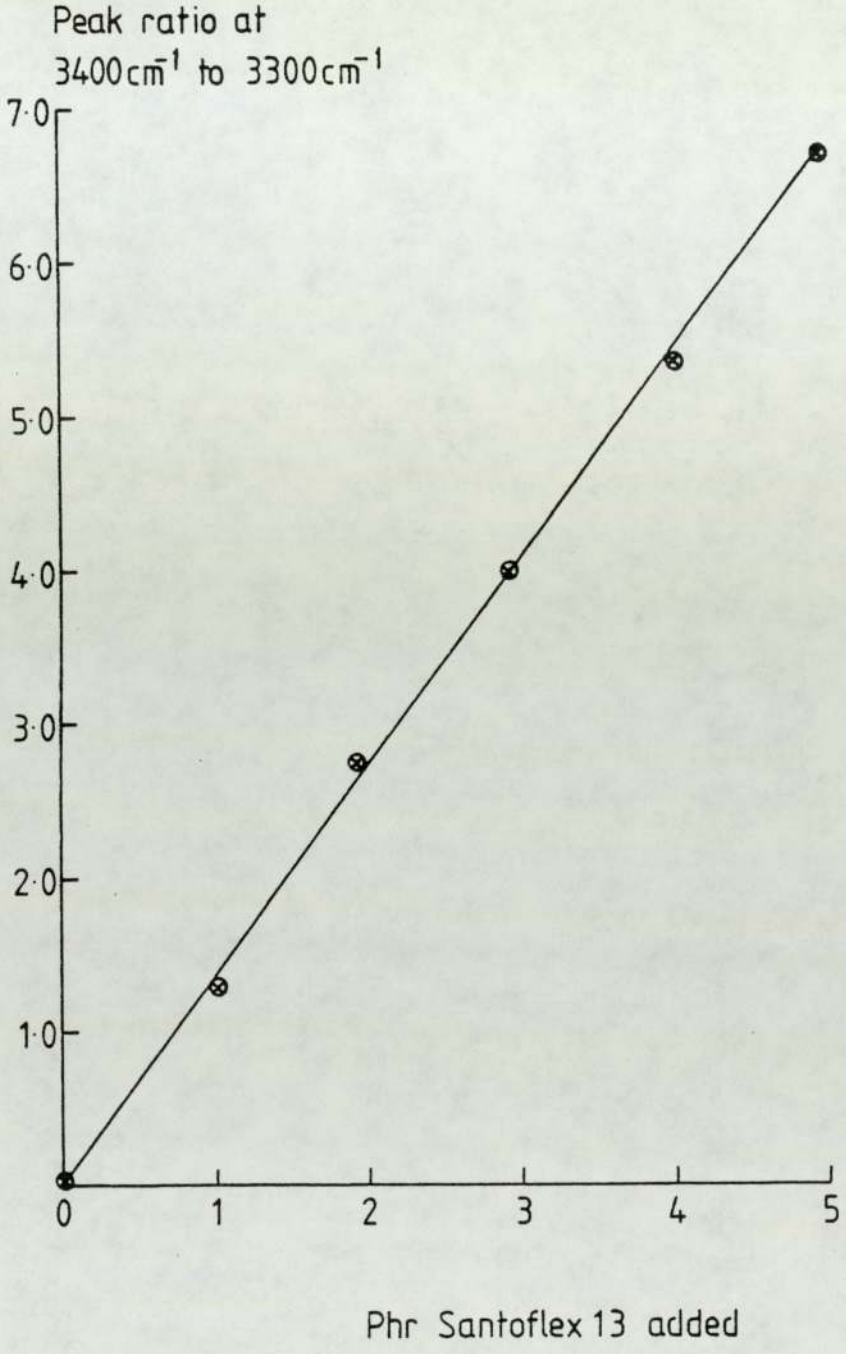


Fig 3:16
Calibration curve for Santoflex 13 in CR type W rubber

TABLE (3.13)

Formulations for CR Type-W with Santoflex-13 for the I.R Calibration Curve

11	
CR Type-W	100
Mgo	4
Zno	5
Santoflex-13	0,1,3,5 and 7.5 respectively
NA-22	1
MBTS	1

The film containing 2 phr of Santoflex-13 was then acetone extracted under N_2 for 48 hours, dried and the infra-red absorption again determined. An absorption in the 3,400 cm^{-1} region was obtained giving a ratio of 1.9 which corresponds to a concentration of Santoflex-13 combined with the CR type-W of 1.4 phr which is equivalent to one unit of Santoflex-13 per 213 units of chloroprene. The point of attachment being via the alkyl substituted amino group.

3.2.1.3.3 Effect of Santoflex-13 on the Vulcanization Characteristics of CR Type-W

In view of the fact that 1.4 phr of Santoflex-13 is shown to combine with the rubber (3.2.1.3.2) there is a corresponding decrease in the number of allylic chlorine sites available for cross-linking reaction and this, may therefore, interfere with the vulcanization process.

In order to study the effect of this antioxidant on the vulcanization characterisitics of CR type-W, the formulations shown in Table (3.14) were mixed on a two roll mill and the vulcanization characteristics tested in the Monsanto rheometer using a torque range of 100 in-lb, a time span of 30 minutes at a temperature of 160°C. The results are shown in Fig. 3.17 and Table (3.14).

TABLE (3.14)

Formulations of CR Type-W with Santoflex-13

	12	13
CR Type-W	100	100
Mgo	4	4
Zno	5	5
Santoflex-13	-	2
NA-22	1	1
MBTS	1	1
Modulus at 90% cure (in-lb)	40	36
Scorch Time (min)	5	5

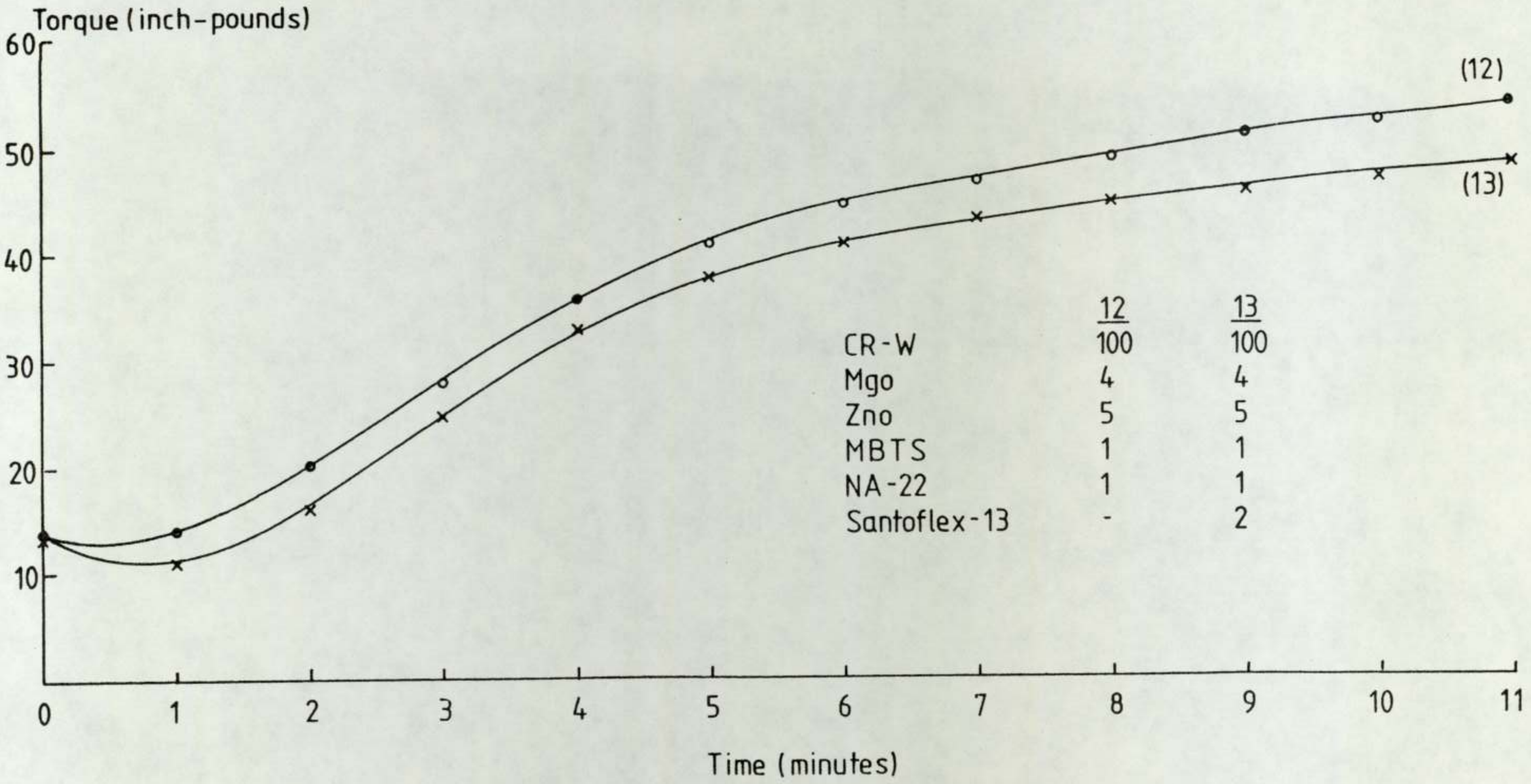


Fig 3:17 The Monsanto rheometer of CR-type W with 2Phr Santoflex-13

It can be seen that there is a slight decrease in the modulus i.e. a decrease in the cross-linking density, but this is not great enough to be of practical significance

3.2.1.3.4 Assessment of Effectiveness of Santoflex-13 on CR Type-W

To assess the effectiveness of Santoflex-13 on CR type-W, samples for stress relaxation determination were prepared for the formulations shown in Table (3.14).

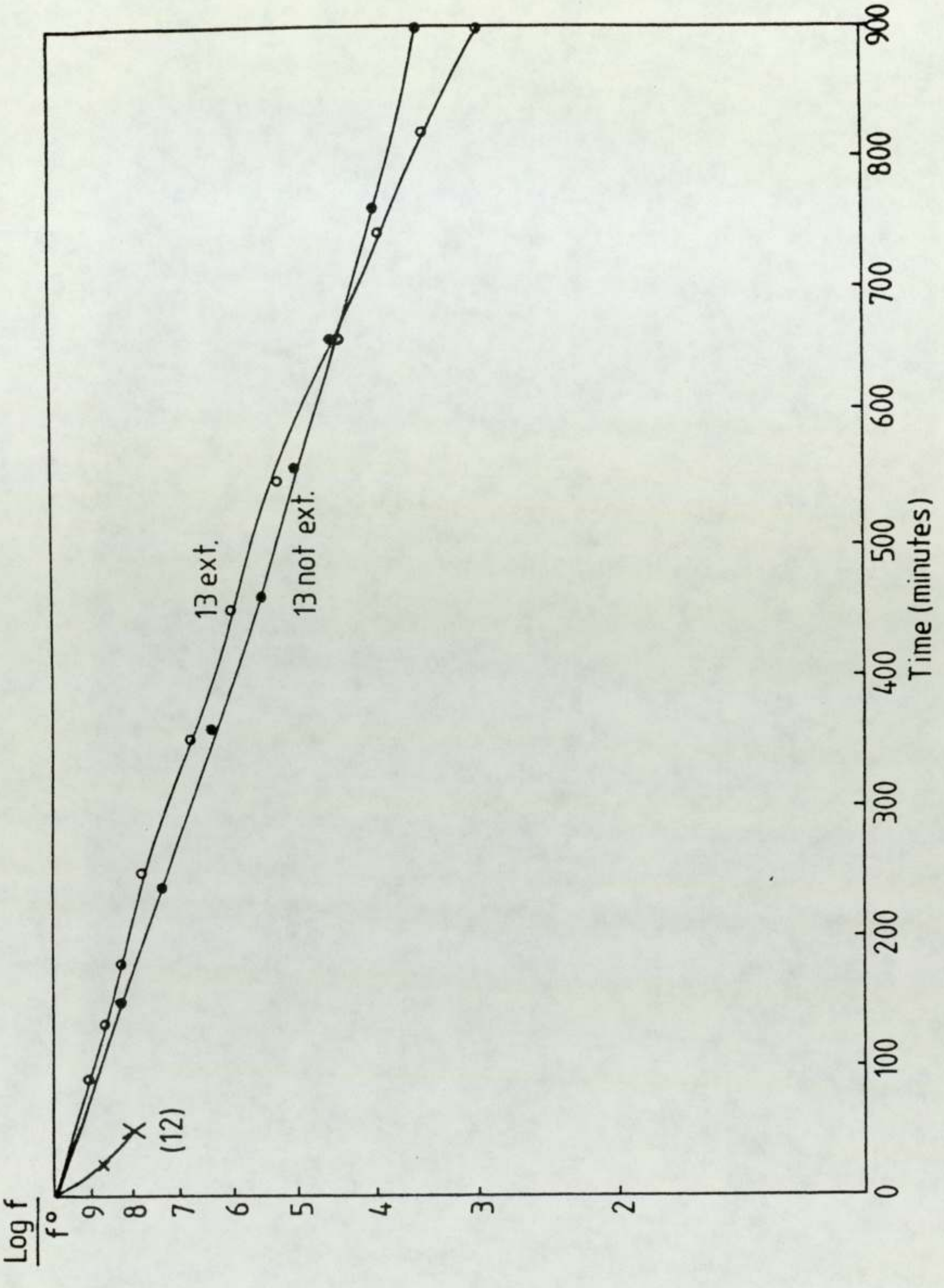
3.2.1.3.4.1 Stress Relaxation

Thin films of 0.1 cm thickness were prepared at 160°C for 30 minutes as described in Section 3.2.1.1.7.1 and used to prepare samples for stress relaxation. Half of the samples were methanol extracted under N_2 (2.3.4).

Continuous stress relaxation (2.4.1) was carried out at 140°C in a Wallace oven for both methanol and for the non-extracted samples. The results are shown in Fig. 3.18 and Table (3.15).

Results and Discussion

The values of Log f/f^{o} after 400 minutes of ageing at 140°C is shown in Table (3.15).



	12	13
CR-W	100	100
Mgo	4	4
Zno	5	5
Santoflex 13	–	2
NA-22	1	1
M.B.T.S.	1	1

Fig 3:18 Continuous stress relaxation of CR type W with Santoflex 13 before and after methanol extraction, aged at 140°C.

TABLE (3.15)

The Values of Log f/f^o of CR Type-W with Santoflex-13 After 400 Minutes of Ageing at 140°C

	Formulation Number	
	12	13
Not extracted	Broken	0.79
Acetone extracted	Broken	0.81

From the above table the following results may be deduced:

(1) Santoflex-13 is a good antioxidant for CR type-W rubber when judged by its performance in stress relaxation tests at 140°C both before and after the methanol extraction.

(2) The fact that much of the antioxidant activity remains after extraction shows that Santoflex-13 combines with the rubber and that even when extracted it is still a good antioxidant.

(3) The control which did not contain any antioxidant degraded so quickly that stress relaxation could not be carried out which again shows how effective the antioxidant is.

3.2.2 REACTIONS OF AMINES WITH CR TYPE-G

Polychloroprene type-G is a copolymer of chloroprene and sulphur (3.1.1). The chemistry, properties and

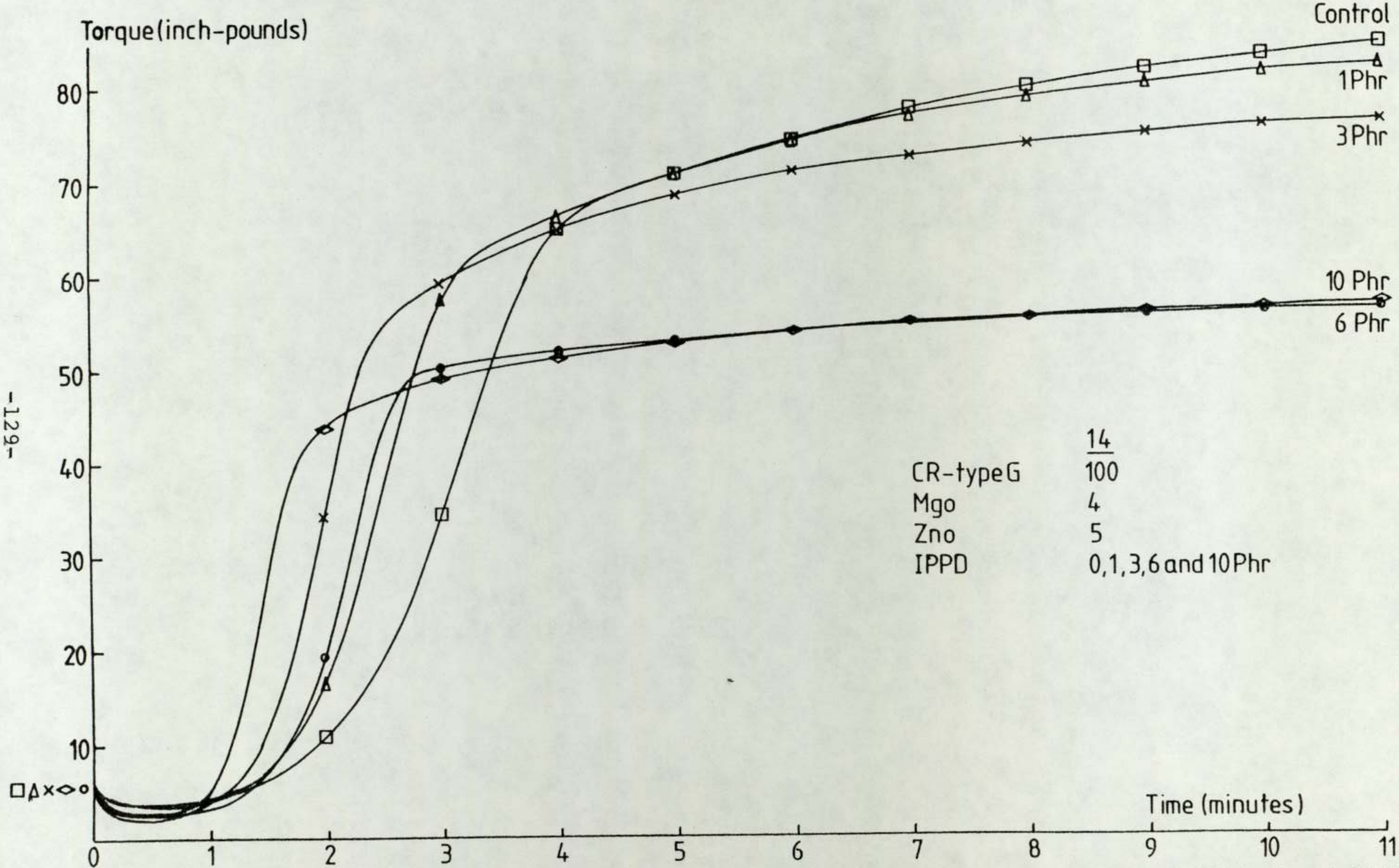


Fig 3:19 The Monsanto rheometer of CR-type G with different concentrations of IPPD. Cure for 30minutes at 160°C

differences of this type of rubber have been discussed.

Diamine compounds act as cross-linking agent for CR type-W as long as both the amino groups are active enough to combine with the tertiary chlorine atom. The differences in these reactivities has been determined in Section 3.2.1.1.4.

It has been shown (3.2.1.1.4) that amines such as IPPD will react with the allylic chlorine atom of CR type-W via the isopropyl substituted amino group (the phenyl groups is unreactive). This reaction takes place during high temperature mixing (3.2.1.1.2) and/or during the vulcanization reaction (3.2.1.1.3).

To see whether this applies to CR type-G the following experiments were carried out.

3.2.2.1 Reactions of CR Type-G with IPPD Antioxidant

3.2.2.1.1 Effect of IPPD on Vulcanization Characteristics of CR Type-G

In order to study the effect of IPPD on the vulcanization characteristics of CR type-G the formulations shown in Table (3.16) were mixed on a two roll mill and vulcanized at 160°C in a Monsanto rheometer using a torque of 100 in-lb and a time span of 30 minutes (Fig. 3.19).

TABLE (3.16)

Formulations to Study the Effect of Different Concentrations of IPPD on CR Type-G

14	
CR Type-G	100
Mgo	4
Zno	5
IPPD	0,1,3,6 and 10 phr respectively

The results shown in Fig. 3.19 show that there is a decrease in the modulus when the concentration of IPPD increases above 1.5 phr. This is attributed to the reaction between the active chlorine atoms and IPPD which decreases the number of cross-linking sites.

It can be seen that IPPD has more effect on type-W than type-G (3.2.1.1.5) and this is probably due to the fact that type-W only cross-links by reaction with the allylic chlorine atoms in the presence of organic accelerators, but the cross-linking of the type-G involves the sulphur atom in the polymer main chain as well as the metallic oxide reaction.

As the amino group of IPPD will react with the allylic chlorine atom in both types of neoprene and, therefore, prevent them from taking part in the vulcanization process, but the effect on the type-W is more dramatic as it is the only cross-linking reaction available.

3.2.2.1.2 Assessment of Effectiveness of IPPD as an Antioxidant to CR Type-G

The effect of the antioxidant IPPD on the ageing behaviour of CR type-G was studied by mixing the formulations shown in Table (3.17) on a two roll mill (6 minutes) and in a Banbury mixer (6 minutes) respectively.

TABLE (3.17)

Formulations of CR Type-G with IPPD Antioxidant

	15	16
CR type-G	100	100
Mgo	4	4
Zno	5	5
IPPD	-	2

3.2.2.1.2.1 Monsanto Rheometer Studies

Because of the great differences in shear ratio and temperatures produced during mill mixing and Banbury mixing, the effect of IPPD on the vulcanization characteristics when compounded by these two methods was studied by Monsanto rheometry.

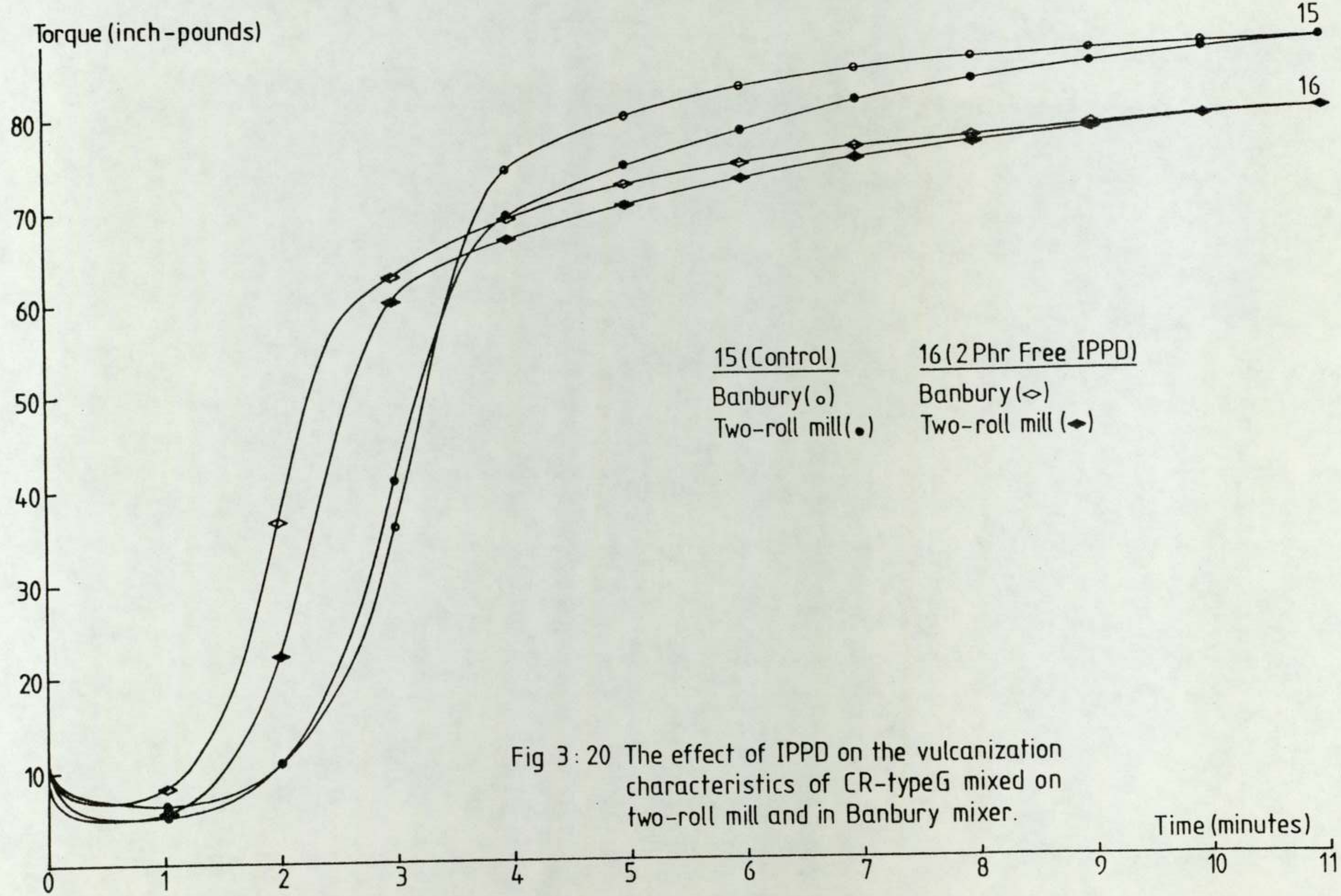


Fig 3 : 20 The effect of IPPD on the vulcanization characteristics of CR-typeG mixed on two-roll mill and in Banbury mixer.

The tests were carried out at 160°C, a torque of 100 in-lb, and a time span of 30 minutes were used. The results, Fig. 3.20, show that no difference could be detected.

3.2.2.1.2.2 Stress Relaxation

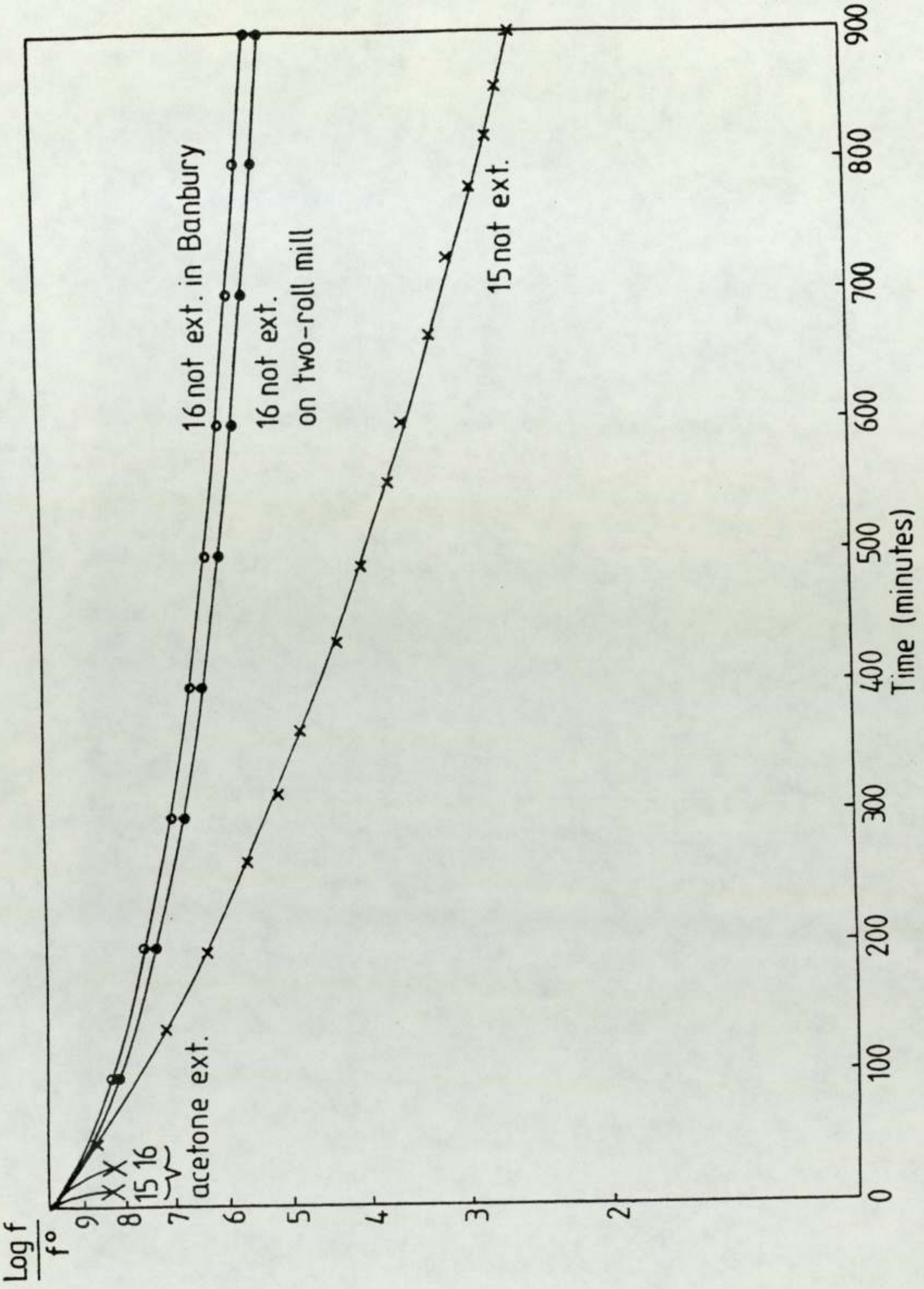
Thin films of 0.1 cm thickness were prepared as described in (3.2.1.1.7.1) for the formulations shown in Table (3.17) which were mixed on a two roll mill and on a Banbury mixer. Samples were cut using MR100 cutter . Half of the samples were then acetone extracted under N_2 (2.3.4).

Continuous stress relaxation (2.4.1.) was carried out at 130°C for both acetone extracted and non-extracted samples. The results are shown in Fig. 3.21.

Results and Discussion

From Fig. 3.21 it can be seen that the control curve has little autoretartation due to the absence of any antioxidant, while in the presence of IPPD the shape of the relaxation curve becomes atuoretarting due to antioxidant activity of IPPD. Therefore, IPPD is a good antioxidant for CR type-G. The antioxidant shows the same extent of protection to CR type-G irrespective of the method of mixing.

On acetone extraction under N_2, the samples deteriorated rapidly which suggest that the IPPD



	15	16
CR-G	100	100
Mgo	4	4
Zno	5	5
IPPD	-	2

Fig 3:21

The effect of IPPD on the continuous stress relaxation of CR type G mixed on both two-roll mill and Banbury mixers, aged at 130°C.

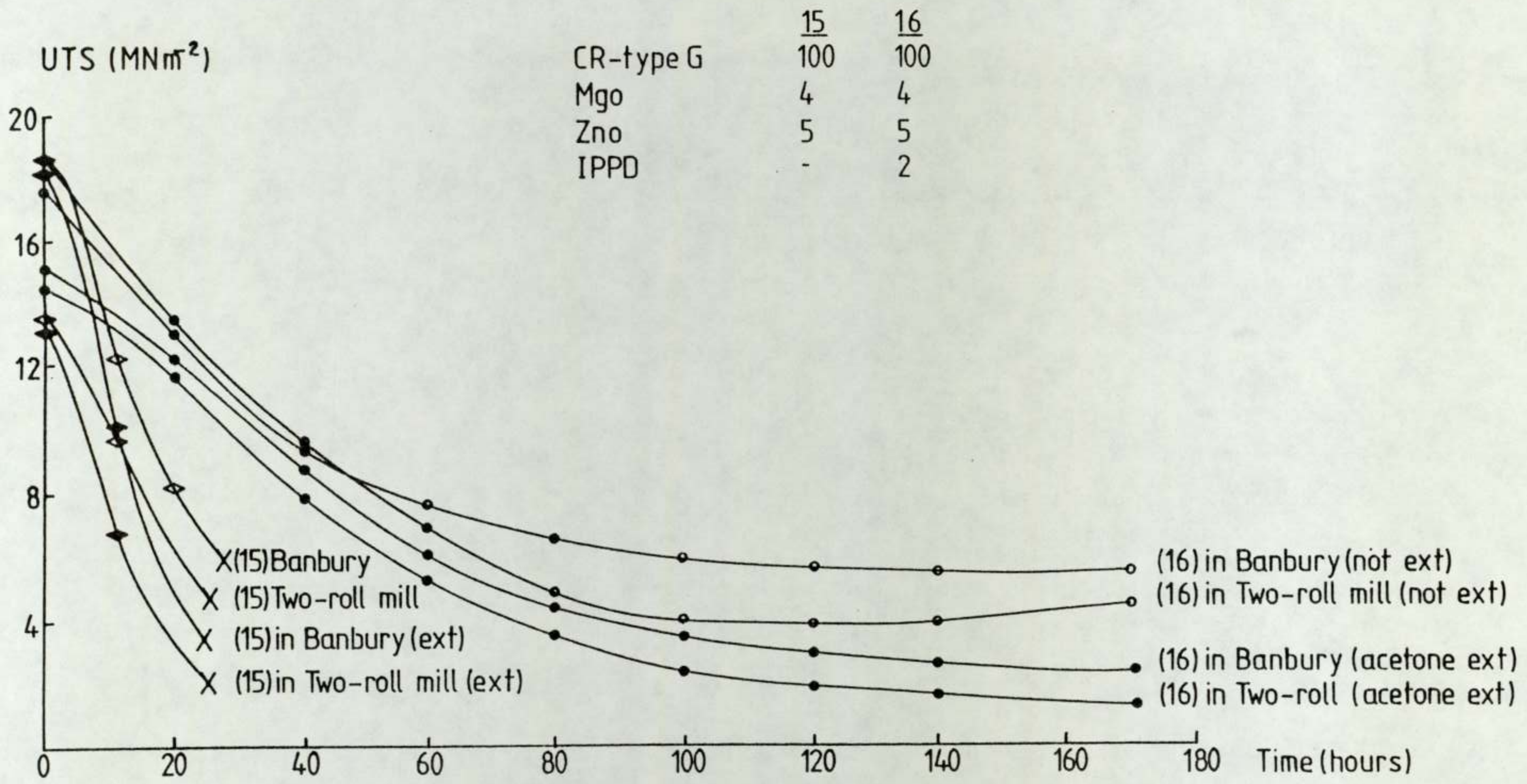


Fig 3:22
The effect of IPPD on the UTS of CR-type G mixed on two-roll mill and Banbury mixer, aged at 130°C.

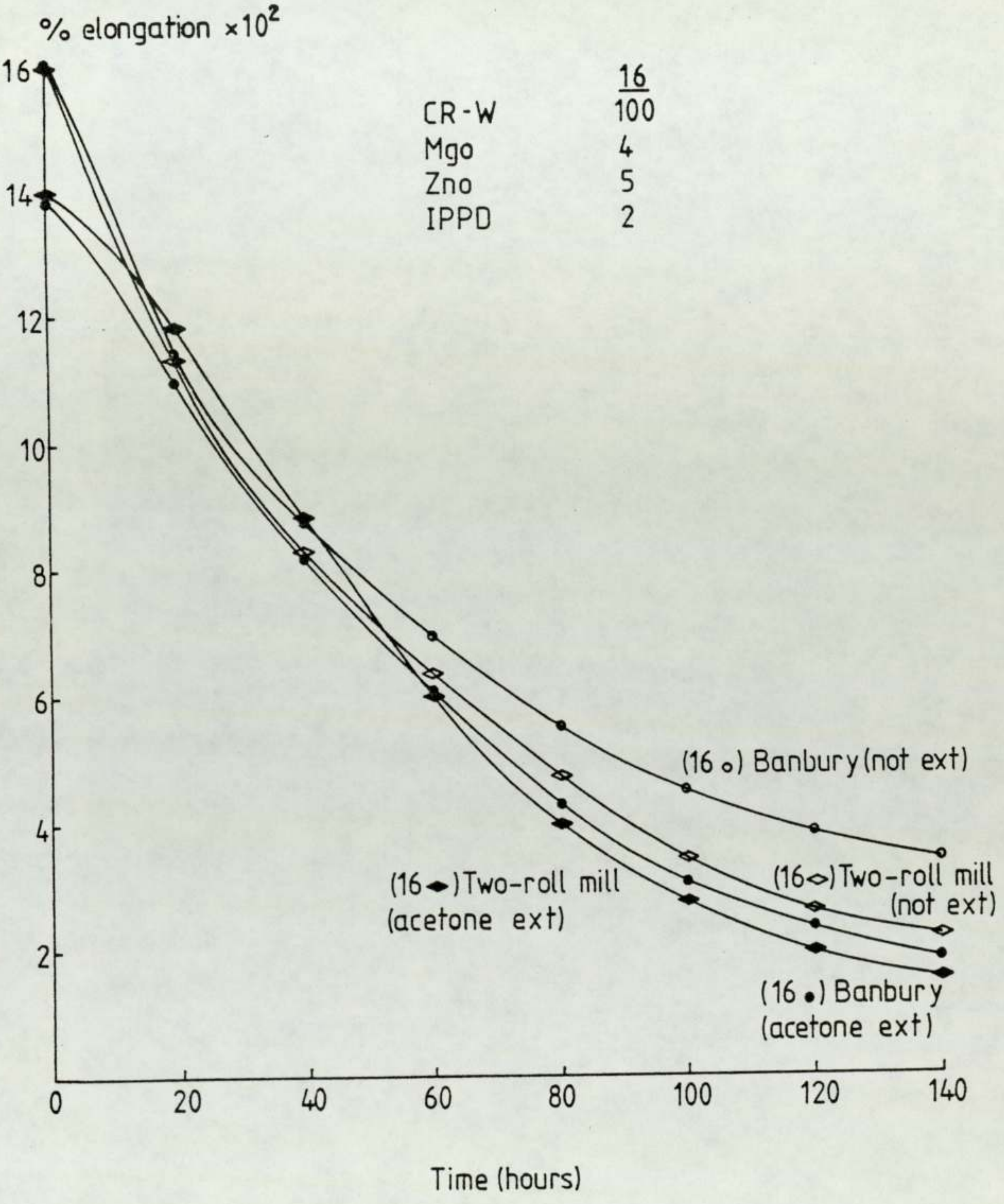


Fig 3:23

The effect of IPPD on the % of elongation of CR-type G mixed on two-roll mill and Banbury mixer, aged at 130°C.

antioxidant had not reacted with the rubber. But it has been shown to combine (Infra-red and effect on vulcanization Section 3.2.2.1.1)

3.2.2.1.2.3 Ultimate Tensile Strength and Elongation at Break

Formulations listed in Table (3.17) were mixed on a water-cooled laboratory 12" two roll mill and in a Banbury mixer respectively. The mixtures were then moulded at 160°C for 30 minutes and used to prepare dumbell shaped tensile strength specimens as described in Section 3.2.1.1.7.2.1. Half of the samples were acetone extracted under N_2 (2.3.4).

Ageing was carried out at 130°C ±2°C in a Wallace oven. The graphs between the UTS and elongation at break respectively against the time of ageing for non-extracted and acetone extracted samples, are shown in Figs 3.22 and 3.23.

Results and Discussion

The conclusions to be drawn from the results shown in Figs 3.22 and 3.23 are as follows:-

(1) IPPD is a very effective antioxidant for polychloroprene type-G.

(2) There is little difference between mill mixing and Banbury mixing, although the Banbury mixed samples

are slightly better. This is probably due to the restricted excess of oxygen in the Banbury or due to more mechano-chemical degradation on the two roll mill which is known to produce a higher rate of shear.

(3) Acetone extraction removed some of the protection given by the IPPD but it is still very much better than the control. Thus providing evidence that the antioxidant becomes bound with the CR type-G during mixing and vulcanization (3.2.2.1.2.4).

3.2.2.1.2.4 Infra-Red Confirmation of the Reaction between CR Type-G and IPPD Antioxidant during Vulcanisation Processes

To determine the amount of IPPD bound into CR type-G, a calibration curve was produced using vulcanizate films (3.2.1.1.1) as shown in Fig. 3.24.

A thin film of the modified CR type-G was formed using formulation number 16, and then acetone extracted under N_2, dried and the infra-red spectrum obtained. The amount of bound antioxidant was determined by measuring the peak ratio of this film and by comparing it with the known peak ratio of the spectrum of the vulcanisate contianing a known concentration of IPPD. The amount of IPPD bound to CR type-G was found to be 1.4 phr, which is equivalent to one IPPD unit per 131 chloroprene repeat units.

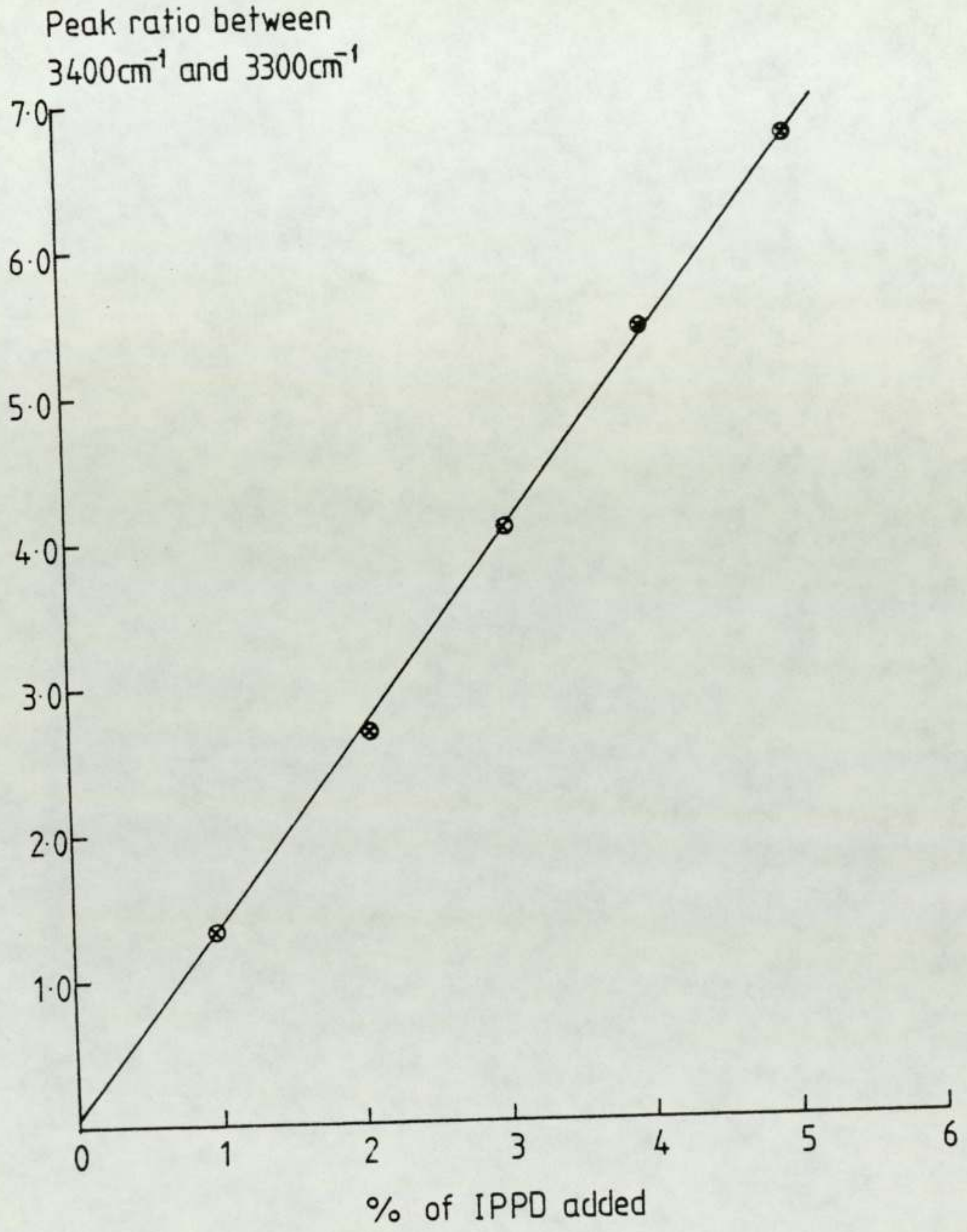


Fig 3:24
Calibration curve for CR type G with IPPD

3.2.2.2 Reaction of Santoflex-13 with CR Type-G Rubber

The formulations shown in Table (3.18) were mixed on a water-cooled 12" laboratory mill and tested in a Monsanto rheometer at 160°C, using a torque of range of 100 in-lb and a time span of 30 minutes.

TABLE (3.18)

Formulations of CR Type-G with Santoflex-13

	17	18
CR Type-G	100	100
Mgo	4	4
Zno	5	5
Santoflex-13	-	2
Induction period (min)	7	5
Torque after 30 min (in-lb)	57	57

3.2.2.1 Effect of Santoflex-13 on Vulcanization Characteristics of CR Type-G

The Monosanto rheograph Fig. 3.25 shows that 2 phr of Santoflex-13 causes a 30% reduction in scorch time, increases the rate of cure but has no affect upon the cross-link density. This is as expected because the basic Santoflex-13 will accelerate the rate of vulcanisation but its reaction with the allylic chlorine atoms does not

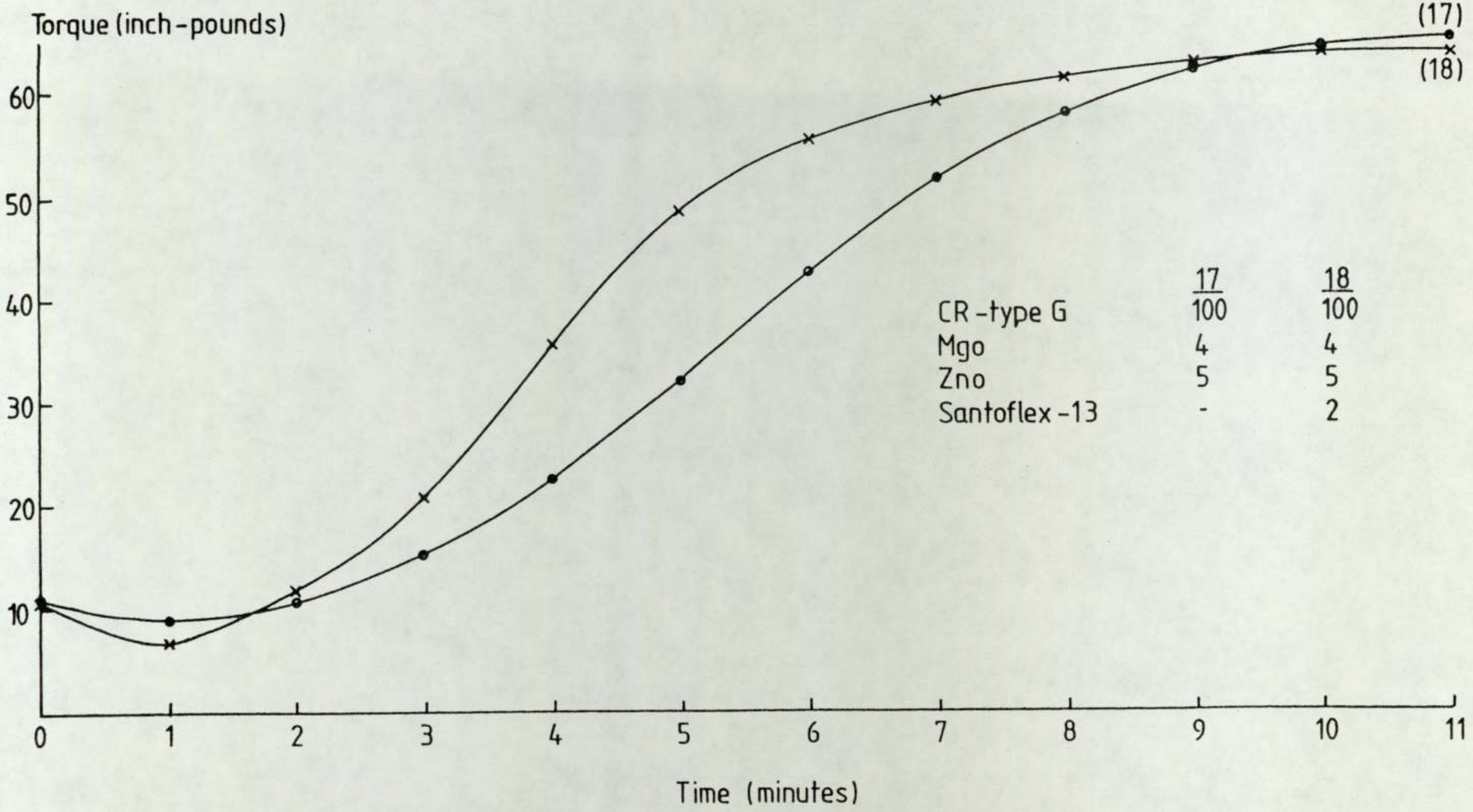


Fig 3:25 Monsanto rheograph of CR-type G with Santoflex-13 antioxidant. Cure at 160°C for 30minutes.

interfere with the vulcanization since much of the cross-linking takes place via the sulphur atoms(39). This is not the case with CR type-W which vulcanized via the allylic chlorine atoms only.

3.2.2.2.2 Proof of Absence of Cross-Linking Reaction Between CR Type-G and Santoflex-13

The same set of experiments carried out with IPPD (3.2.1.1.4) were carried out on Santoflex-13 with CR type-G. No cross-linking would be detected.

3.2.2.3 Assessment of Effectiveness of Santoflex-13 on CR Type-G by Stress Relaxation

Films for stress relaxation were prepared from formulations shown in Table (3.18) and used for stress relaxation determinations which were carried out at 140°C using the Wallace age tester, Fig. 3.26 (Section 2.4.1). Half of the samples were acetone extracted with methanol under N_2 (2.3.4).

Results and Discussion

The values of log f/f^o after 400 minutes of ageing at 140°C are as shown in Table (3.19).

TABLE (3.19)

Values of Log f/f^o of CR Type-G after 400 Minutes of Ageing at 140°C with Santoflex-13

	17	18
Not extracted	Broken	0.61
Methanol extracted	Broken	0.63

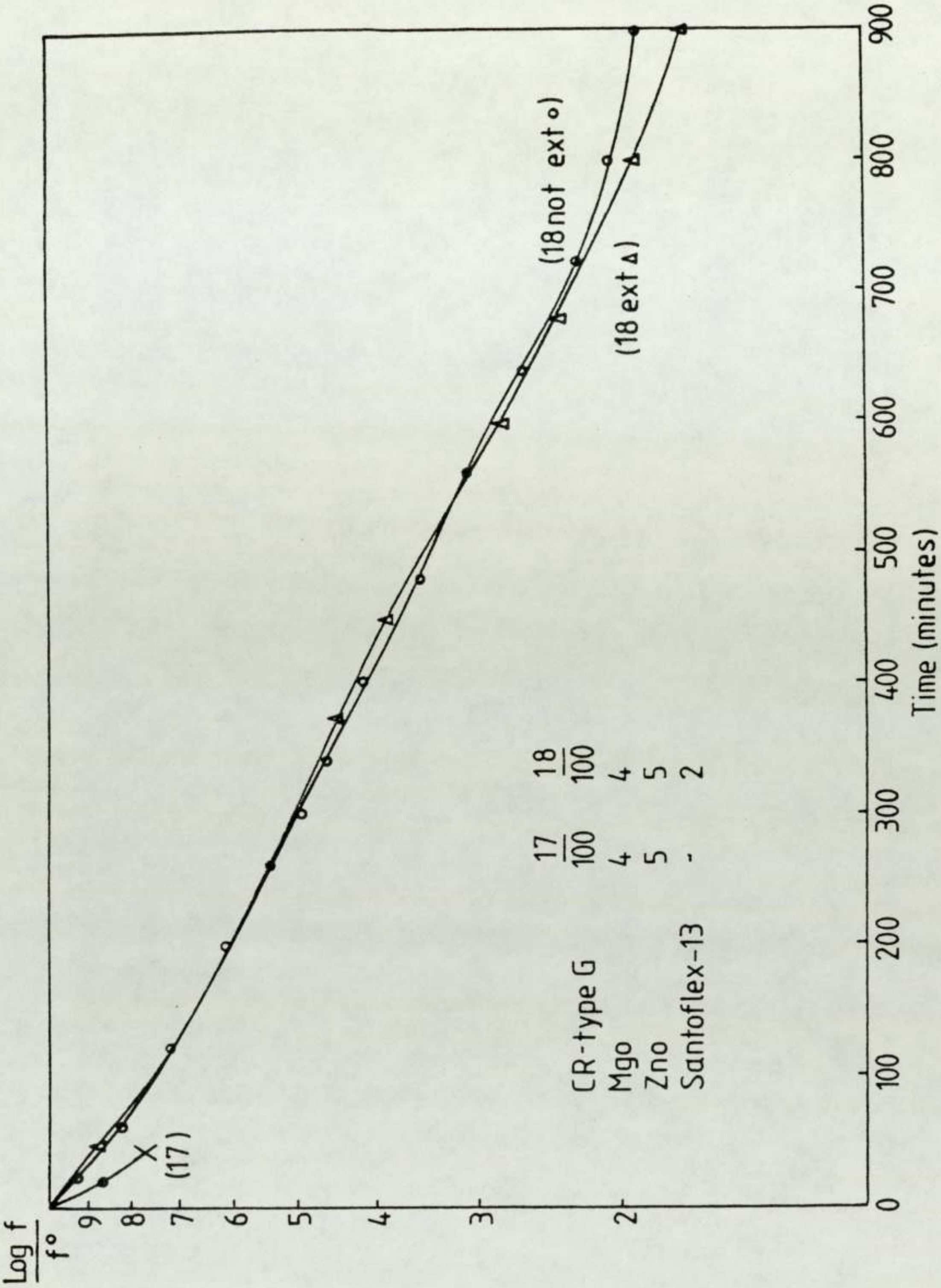


Fig 3:26
Continuous stress relaxation of CR type G with Santoflex 13 at 140°C
for not extracted and methanol extracted vulcanizate

From the Table (3.19), the following results are obtained:-

(1) Santoflex-13 is a very good antioxidant for CR type-G before and after methanol extraction process.

(2) Santoflex-13 becomes bound into CR type-G during mixing and vulcanization as is shown by the fact that activity could not be removed by extraction.

(3) The control lost all its properties after a few minutes under these conditions which is further proof of the effectiveness of Santoflex-13 as an antioxidant and that it becomes bound into CR type-G.

Summary of Reaction of Diamines with CR rubbers

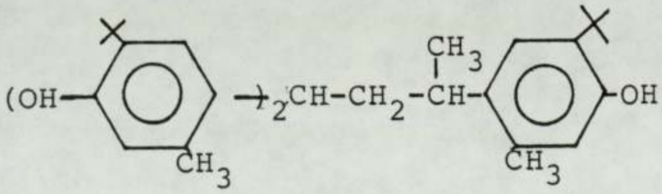
Amine	Type of Rubber	Method of Binding	% Bound	Unit of Amine per Unit of CR
IPPD	W	Torque rheometer	63.5%	1:37
		Vulcanization	70%	1:176
DPPD	W	Mixing	not detectable	-
		Vulcanization	not detectable	-
Santoflex 13	W	Vulcanization	70%	1:213
IPPD	G	Vulcanization	70%	1:131

3.2.3 REACTION OF PHENOLS WITH CR TYPE-W

In view of the fact that polychloroprene rubbers may be protected with phenolic antioxidants, it was decided to attempt to bind these to the rubbers as was attempted with the amines antioxidants.

The allylic chlorine atoms in the CR, resulting from the 1,2 polymerization of the monomer, are able to react with the phenolic additives through the hydroxyl group(125). This leads to HCl elimination and, if they are difunctional gel formation. Therefore, if phenolic antioxidants are to be used they must be monofunctional.

3.2.3.1 Reactions of CR Type-W with 1,2,3 tri (2-Methyl-4-Hydroxy-5-Tert.Butyl-Phenyl) Butane (Topanol-CA).



Topanol-CA

Topanol-CA is an antioxidant which offers good thermal stability due to its function as a chain breaking antioxidant. The possibility of reaction between CR type-W rubber and Topanol-CA is feasible because the hydroxyl groups are not completely blocked by alkyl sites in the position ortho to the hydroxyl groups.

3.2.3.2.1 The Effect of Topanol CA Antioxidant on the Vulcanization Characteristics of CR Type-W Rubber

To study the effects of Topanol CA antioxidant on the vulcanization characteristics of CR type-W, the formulations shown in Table (3.20) were mixed on a two roll mill at room temperature.

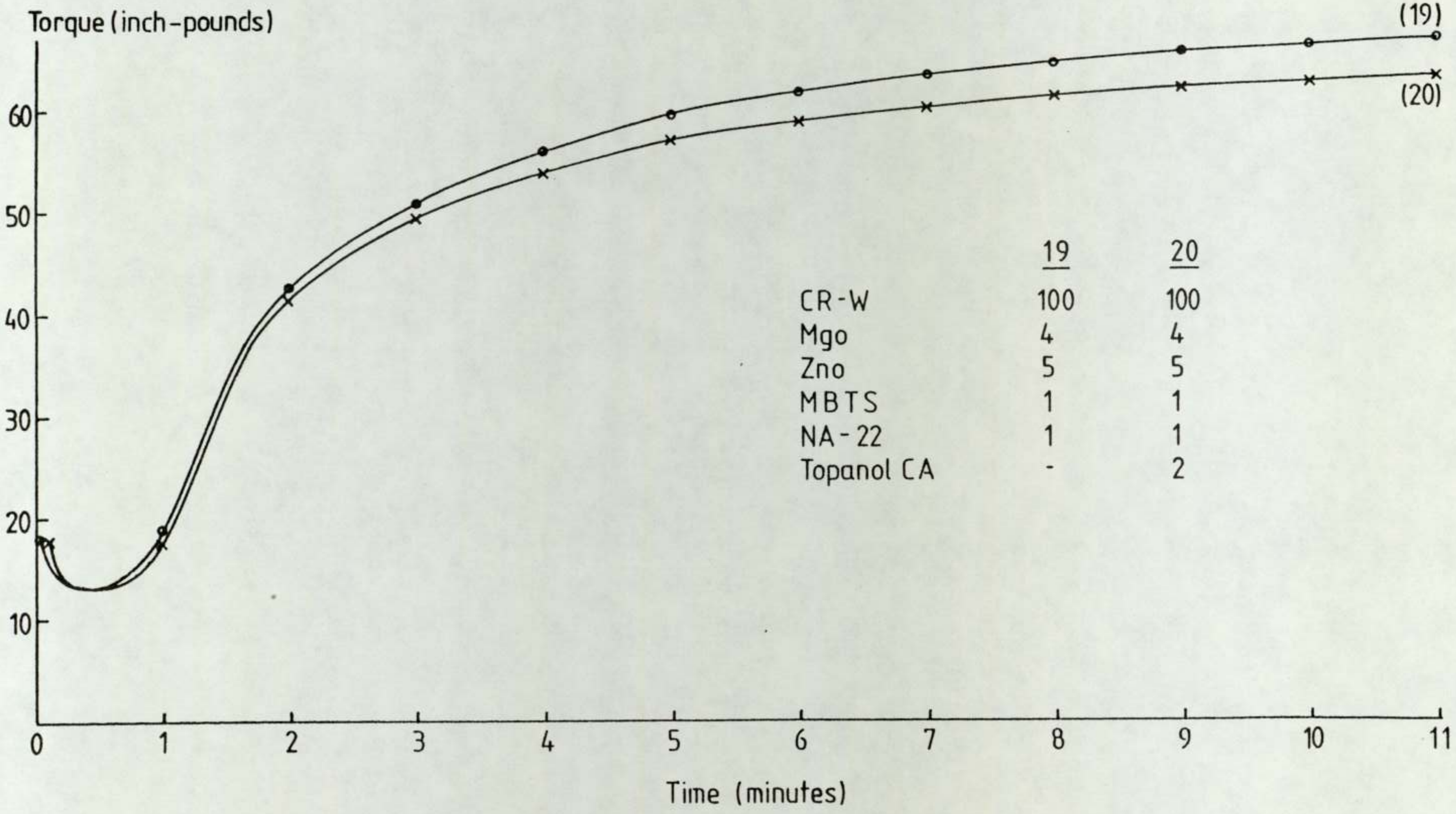
TABLE (3.20)

Formulations for CR Type-W with Topanol CA

	19	20
CR Type-W	100	100
Mgo	4	4
Topanol CA	-	2
NA-22	1	1
MBTS	1	1
Zno	5	5
Induction time (minutes)	2.25	2.5
Modulus at 30 minutes (inch-lbs)	56	49

They were then tested in the Monsanto rheometer at 160°C using a torque range of 100 in-lb and a time range of 30 minutes as is shown in Fig. 3.27.

From the above Table (3.20) and Fig. 3.27, it is seen that the presence of Topanol CA does not affect the induction period or rate of vulcanization , but it



	19	20
CR-W	100	100
Mgo	4	4
Zno	5	5
MBTS	1	1
NA-22	1	1
Topanol CA	-	2

Fig 3 : 27 Monsanto rheograph of CR-type W with 2Phr Topanol CA. Cure at 160°C for 30minutes does slightly reduce the modulus. This decrease in the modulus can be attributed to the decrease in the cross-linking density of the vulcanizate due either to the reaction between the rubber and the antioxidant through the tertiary allylic chlorine atoms which are responsible for the vulcanization, or due to the acidic behaviour of the antioxidant which would decrease the extent of vulcanization.

3.2.3.1.2 Assessment of Effectiveness of Topanol CA as an Antioxidant for CR Type-W

To assess the effectiveness of Topanol CA as an antioxidant on CR type-W, vulcanizate samples were prepared containing 0 and 2 phr Topanol CA. They were assessed by measuring their physical properties before and after ageing at 130°C. Samples for stress relaxation, UTS, and hardness were prepared for the formulations shown in Table (3.20). The thickness of the moulded sheets for these determinations are 0.1 cm, 0.2 cm and 1.0 cm respectively.

3.2.3.1.2.1 Stress Relaxation

Thin films of 0.1 cm thickness were prepared in the induction heated press at 160°C for 30 minutes (Section 2.3.3). Half of the samples were acetone extracted under N_2 (2.3.4).

Continuous stress relaxation (2.4.1) was carried out at 130°C for both non-extracted and acetone extracted samples. The results are shown in Figs 3.28 and 3.29 respectively.

Results and Discussion

From Figs. 3.28 and 3.29 the values of Log f/f^o after 15 hours of ageing is shown in Table (3.21).

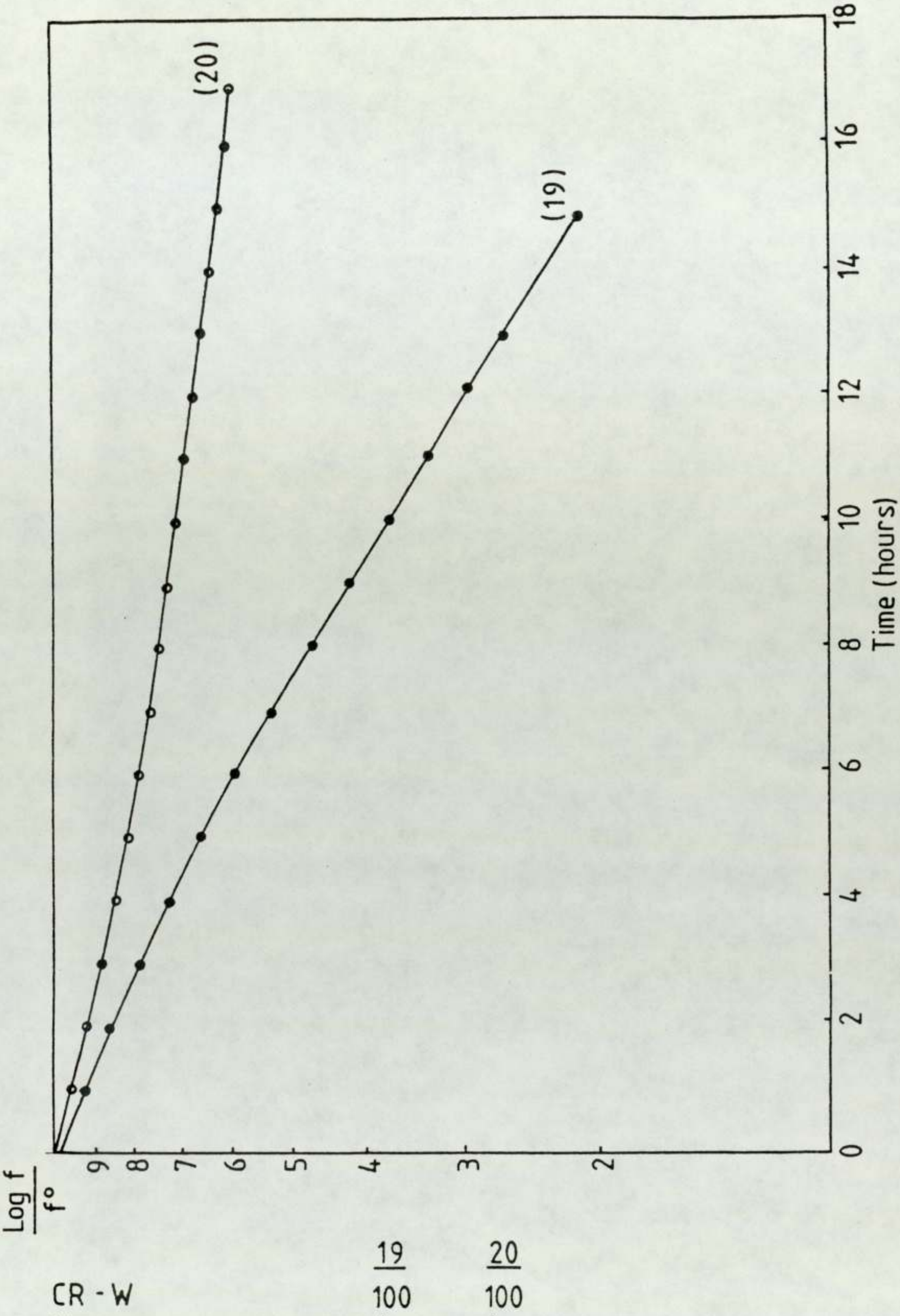
TABLE (3.21)

The Values of Log f/f^o of CR Type-W with 2 phr Topanol CA Aged at 130°C, After 15 Hours

	Formulation Nos	
	19	20
Not extracted	0.34	0.79
Acetone extracted	0.30	0.71

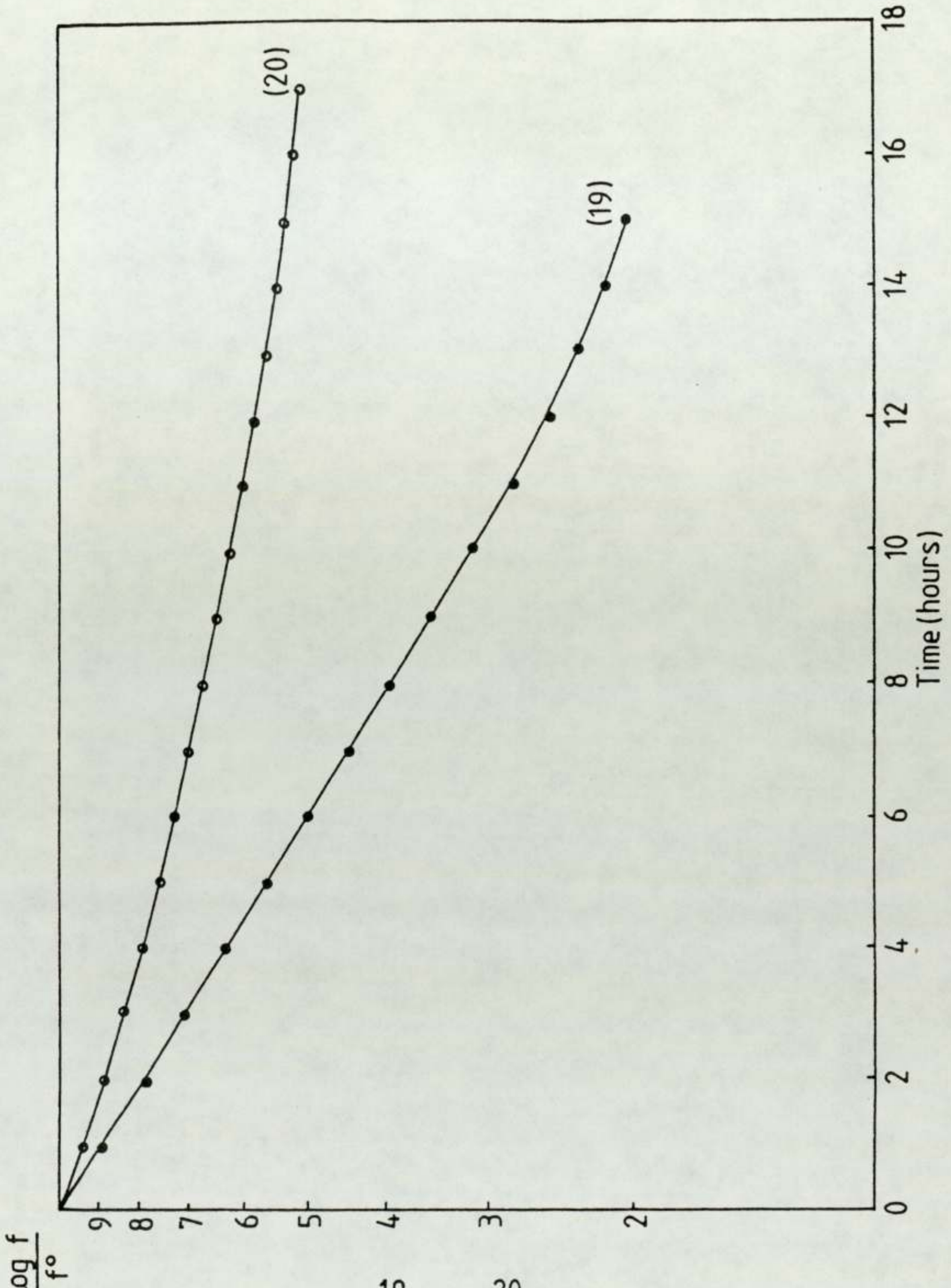
From Figs. 3.28 and 3.29 it is seen that the control curve decay and is autocatalytic in the absence of any antioxidant (The rubber becomes soft after 15 hours of ageing at 130°C). In the presence of Topanol CA the relaxation curve shows less decay and becomes autoretarting due to antioxidant activity of the Topanol CA. Therefore, Topanol CA is considered as a good antioxidant for CR type-W when it is added 'in situ'.

On acetone extraction under N_2 there is very little difference in the stress relaxation curve for the formulation containing 2 phr of Topanol CA or for the



	19	20
CR - W	100	100
Mgo	4	4
Zno	5	5
Topanol CA	-	2
NA - 22	1	1
M.B.T.S.	1	1

Fig 3:28 The effect of Topanol CA on the stress relaxation of CR type W aged at 130°C before extraction.



	19	20
CR type W	100	100
Mgo	4	4
Zno	5	5
Topanol CA	-	2
NA-22	1	1
M.B.T.S.	1	1

Fig 3:29 The effect of Topanol CA on the stress relaxation of CR type W, aged at 130°C after acetone extraction.

control. This means that the Topanol CA is very firmly bound to the polymer and is still an effective antioxidant.

3.2.3.1.2.2 Accelerated Oven Ageing of Vulcanizates

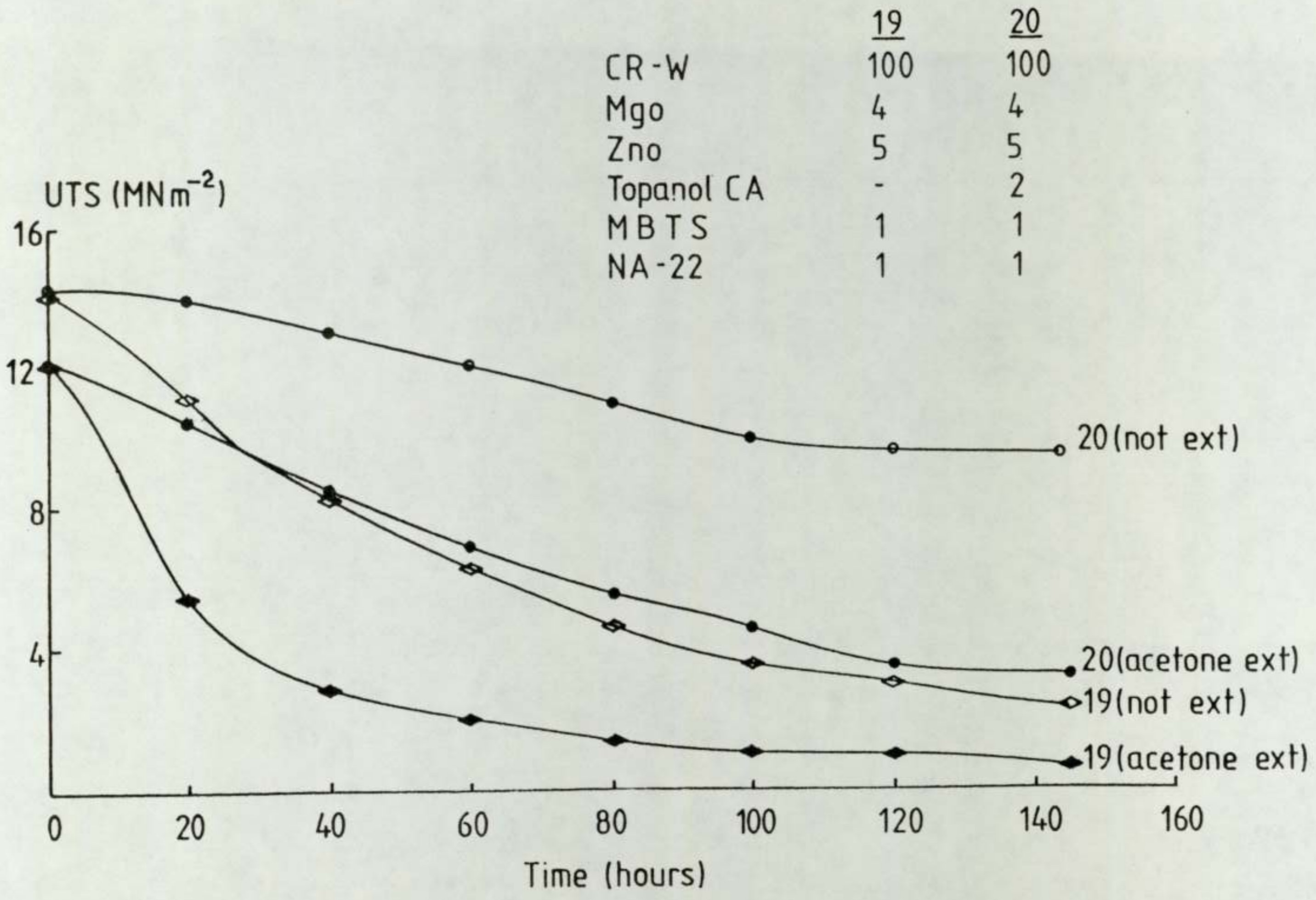
An alternative assessment of the efficiency of Topanol CA as an antioxidant and the possibility of it becoming bound into CR type-W rubber was made by ageing vulcanizates in air at 130°C in a Wallace multicell oven.

The deterioration of the vulcanizates at different times during this ageing was monitored by measuring the decrease in UTS, elongation at break and hardness.

3.2.3.1.2.2.1 UTS and Elongation at Break

The formulations shown in Table (3.20) were mixed on a water-cooled laboratory 12" mill and moulded at 160°C for 30 minutes in the form of sheets of 0.2 cm thickness. Dumbell shaped samples were cut from the sheets using the standard cutter for UTS (2.4.2). Half of the samples were acetone exctracted under N_2 (2.3.4) and then dried in a vacuum oven until constant weight.

Ageing was carried out at 130°C in a multicell oven and the UTS and elongation at break determined. The graphs between UTS and elongation at break against ageing time for both before and after acetone extraction are shown in Figs 3.30 and 3.31 respectively. The percentage decrease



	19	20
CR-W	100	100
Mgo	4	4
Zno	5	5
Topanol CA	-	2
MBTS	1	1
NA-22	1	1

Fig 3 : 30
The effect of Topanol CA on the UTS of CR-type W aged at 130°C, for both not extracted and acetone extracted vulcanizates.

	19	20
CR -W	100	100
Mgo	4	4
Zno	5	5
Topanol CA	-	2
MBTS	1	1
NA -22	1	1

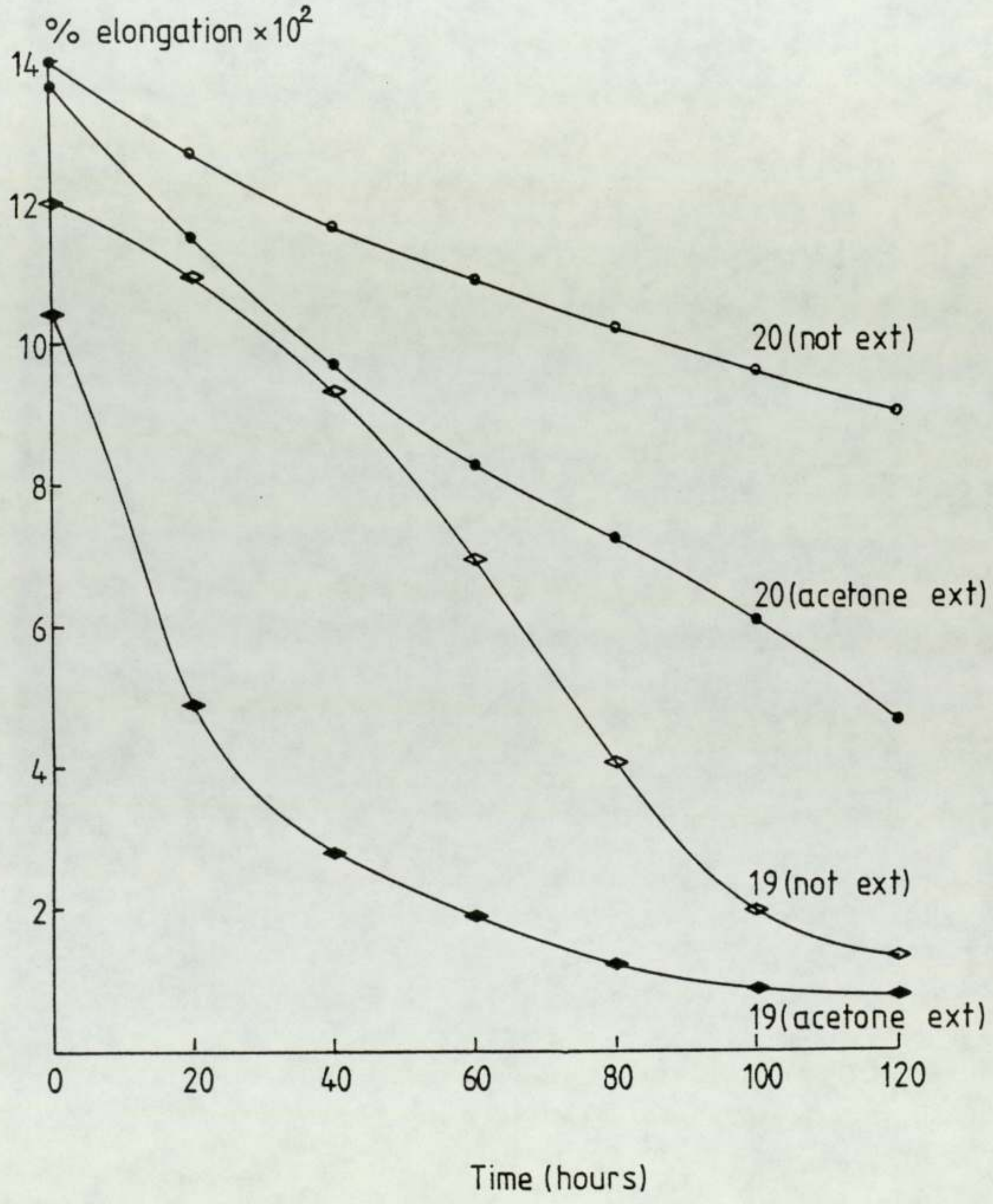


Fig 3 : 31
The effect of Topanol CA on the % elongation of CR-type W, aged at 130°C, before and after acetone extraction.

in UTS and elongation at break are shown in Tables (3.22) and (3.23).

TABLE (3.22)

% Decrease of UTS (MNm^{-2}) of CR Type-W Vulcanizate in the Presence of Topanol CA, at 130^{o}C

Formulation Number	Ageing Period							
	Non-extracted				Acetone Extracted			
	Ohr	24hr	96hr	144hr	Ohr	24hr	96hr	144hr
19		-29	-74	-84		-66	-91	-96
20		-3	-28	-33		-16	-58	-73

TABLE (3.23)

% Decrease of Elongation at Break of CR Type-W in the

Presence of Topanol CA, aged at 130^{o}C

Formulation Number	Ageing Period							
	Non-extracted				Acetone Extracted			
	Ohr	24hr	96hr	144hr	Ohr	24hr	96hr	144hr
19		-13	-81	-90		-62	-92	-92
20		-11	-31	-36		-19	-52	-67

3.2.3.1.2.2.2 Hardness Measurements

Samples of one cm thickness were prepared for the formulations shown in Table (3.20). The same conditions as in Section 3.2.3.3.2.1 were used. Two samples for each formulation were prepared. One of them was acetone extracted and dried in each case (2.3.4).

The hardness was determined before and after ageing in a Wallace multicell oven at 130°C for different times for both before and after acetone extracted vulcanizates (2.4.3).

The results are shown in Fig. 3.32 and Table (3.24).

Results and Discussion

The effect of Topanol CA as an antioxidant on the CR type-W studied by UTS, elongation at break and hardness, Figs. 3.30, 3.31 and 3.32 respectively. The percentage decrease in the physical properties of the CR type-W after ageing is shown in Table (3.22), (3.23) and (3.24) respectively. These results are in agreement with the stress relaxation results (3.2.3.1.2.1).

The following conclusions could be drawn:-

(1) Topanol CA is a good antioxidant for CR type-W even after acetone extraction under N_2. Therefore, some of the Topanol CA has either combined with the CR type-W rubber or become insoluble and cannot be removed by

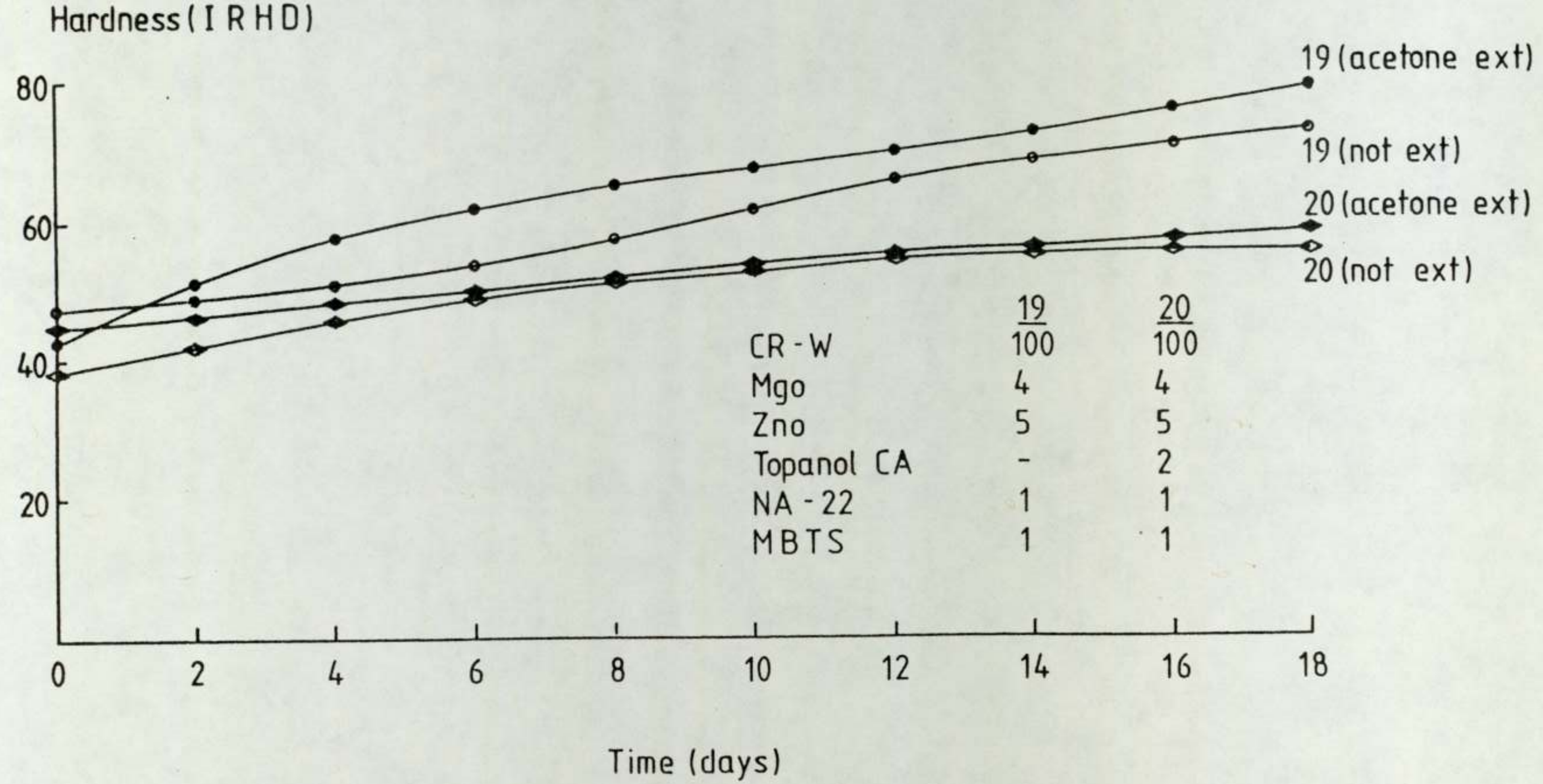


Fig 3: 32 The effect Topanol CA on the hardness of CR-type W aged at 130°C, before and after acetone extraction.

TABLE (3.24)

% Change of Hardness of CR Vulcanizate (IRHD) in the Presence of Topanol CA, Aged at 130°C

Formulation Number	Ageing Period							
	Non-extracted				Acetone extracted			
	0 days	4 days	9 days	18 days	0 days	4 days	9 days	18 days
19		+8.5	+23	+55		+35	+57	+88
20		+4.5	+13.3	+22.2		+18.4	+37	+55

acetone extraction.

(2) Acetone extraction decreases the ageing resistance of both, the control and the samples with 2 phr Topanol CA, but the thermal oxidative resistance of the samples with 2 phr Topanol are still much better than the control shows that even when combined or insoluble it is still a sufficient antioxidant.

(3) The decrease in the thermal oxidative resistance by acetone extraction is probably due to loss of some of the antioxidant added to the raw polymer to increase storage and processing stability or due to the leaching out of soluble compounding ingredients or of products of the vulcanization reaction with mild antioxidant properties.

(4) There is a decrease in the initial physical properties on acetone extraction which might be due to the removal of uncured rubber or any other acetone soluble ingredients which decrease the rubber strength. Oxidation process occurring during the extraction or a weakening of the samples due to swelling may also cause some deterioration in their physical properties.

(5) In both cases, before and after acetone extraction, the controls become soft due to degradative scission.

3.2.3.1.3 Determination of Extent of Reaction of Topanol CA with CR Type-W

Thin films (0.02 cms) thick were prepared by moulding the formulations shown in Table (3.25) in an induction heated press for 30 minutes at 160°C.

TABLE (3.25)

Formulations for CR Type-W with Different Concentrations of Topanol CA

	21
CR Type-W	100
Mgo	4
Zno	5
NA-22	1
MBTS	1
Topanol CA	0,1,3,5, and 7 phr respectively.

I-R determination of the ratio of the peak height due to aromatic absorption (1620 cm^{-1}) and the constant absorption (2,300 cm^{-1}) were made and plotted against concentration of Topanol CA and this was used as a calibration curve (2.4.6.2). The infra-red analysis of the acetone extracted films containing 2 phr of Topanol CA was then carried out. This showed a peak high ratio of 1.8 which corresponded to 1.4 phr of bound Topanol CA

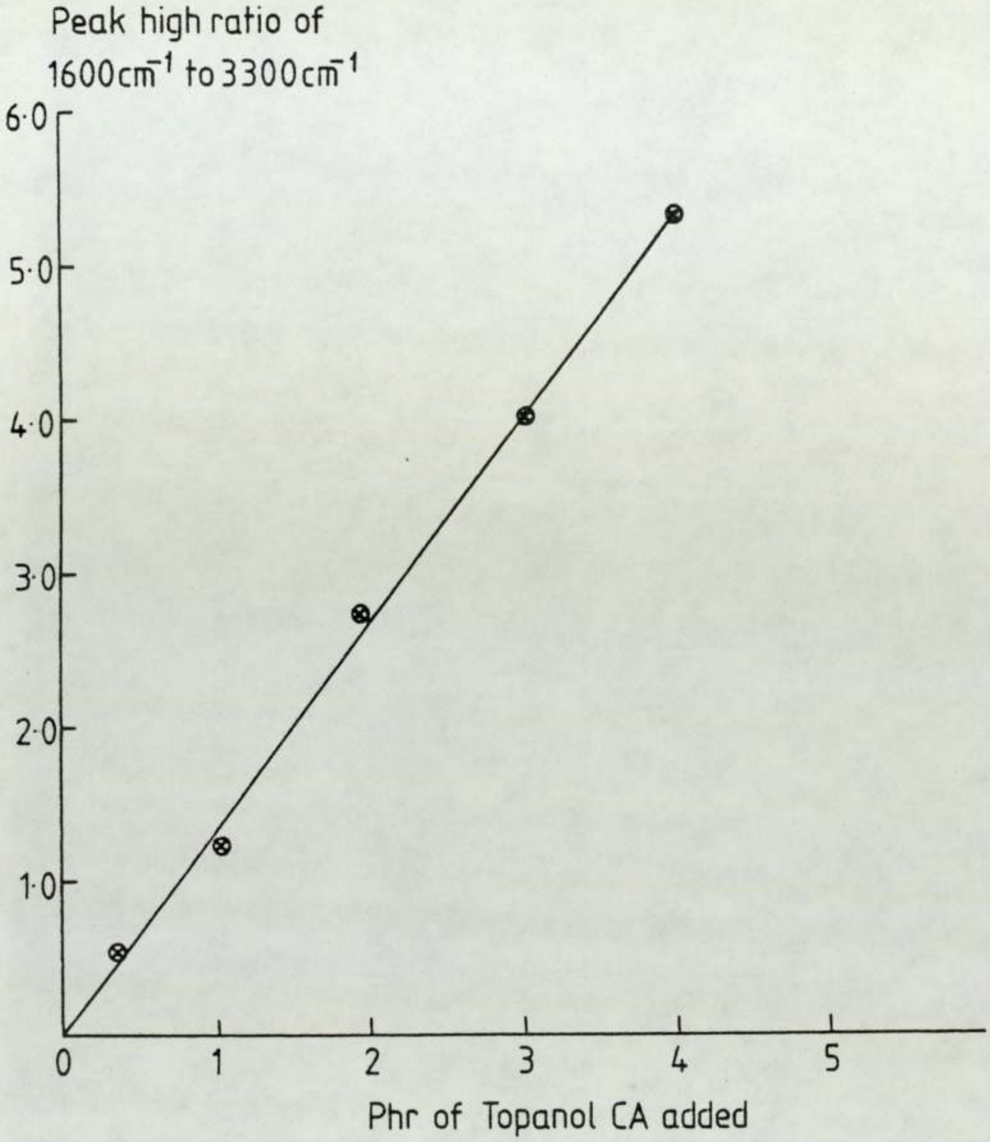


Fig 3: 33
Calibration curve for Topanol CA with CR type W rubber

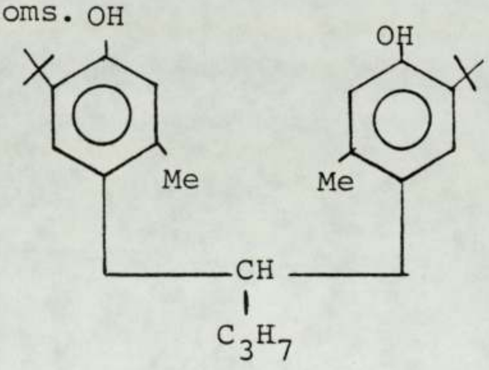
which is equivalent to 1 phenyl group per 228 chloroprene unit.

3.2.3.2 Reactions of CR Type-W with 4,4′-Butylidene bis (3-methyl-6-tert.butyl-phenol) (Santowhite Powder)

The two hydroxyl groups of Santowhite powder are not sterically hindered to prevent reaction of the hydroxyl group with the polymer. Two possible reactions may, therefore, occur:-

(1) The reaction of the acid OH groups of the phenolic antioxidant with the vulcanizing agent(i.e. NA-22) which is basic.

(2) The reaction of the unhindered phenolic hydroxyl groups with the polymer through the reactive allylic chlorine atoms.



Santowhite Powder

3.2.3.2.1 Effect of Santowhite Powder on the Vulcanization Characteristics of CR Type-W Rubber

In order to study the effect of the presence of Santowhite powder on the vulcanization characteristics of CR type-W formulation shown in Table (3.26) were mixed on a water-cooled laboratory two roll mill.

TABLE (3.26)

Formulations of CR Type-W with Different Concentrations of Santowhite Powder

	22
CR Type-W	100
Mgo	4
NA-22	1
MBTS	1
Santowhite Powder	0,2,4,8 and 10 phr
Zno	5
Modulus at 100% cure in in-lb	50,47,45,43 and 42 in-lb
Induction time in min.	2.5,2.5,2.5,2.5,2.5 min

The tests were carried out on Monsanto rheometer (2.3.2) at 160^{O}C, a torque range of 100 in-lb, and time span of 30 minutes were used as shown in Fig. 3.34.

From Fig. 3.34 and Table (3.26), it is seen that the change in the Santowhite powder concentrations does not have any effect on the iduction period of CR type-W rubber, but causes a small decrease on the modulus of the vulcanizates. This decrease must be due to the interference between the antioxidant and other ingredients in the formulations which in turn leads to a decrease in

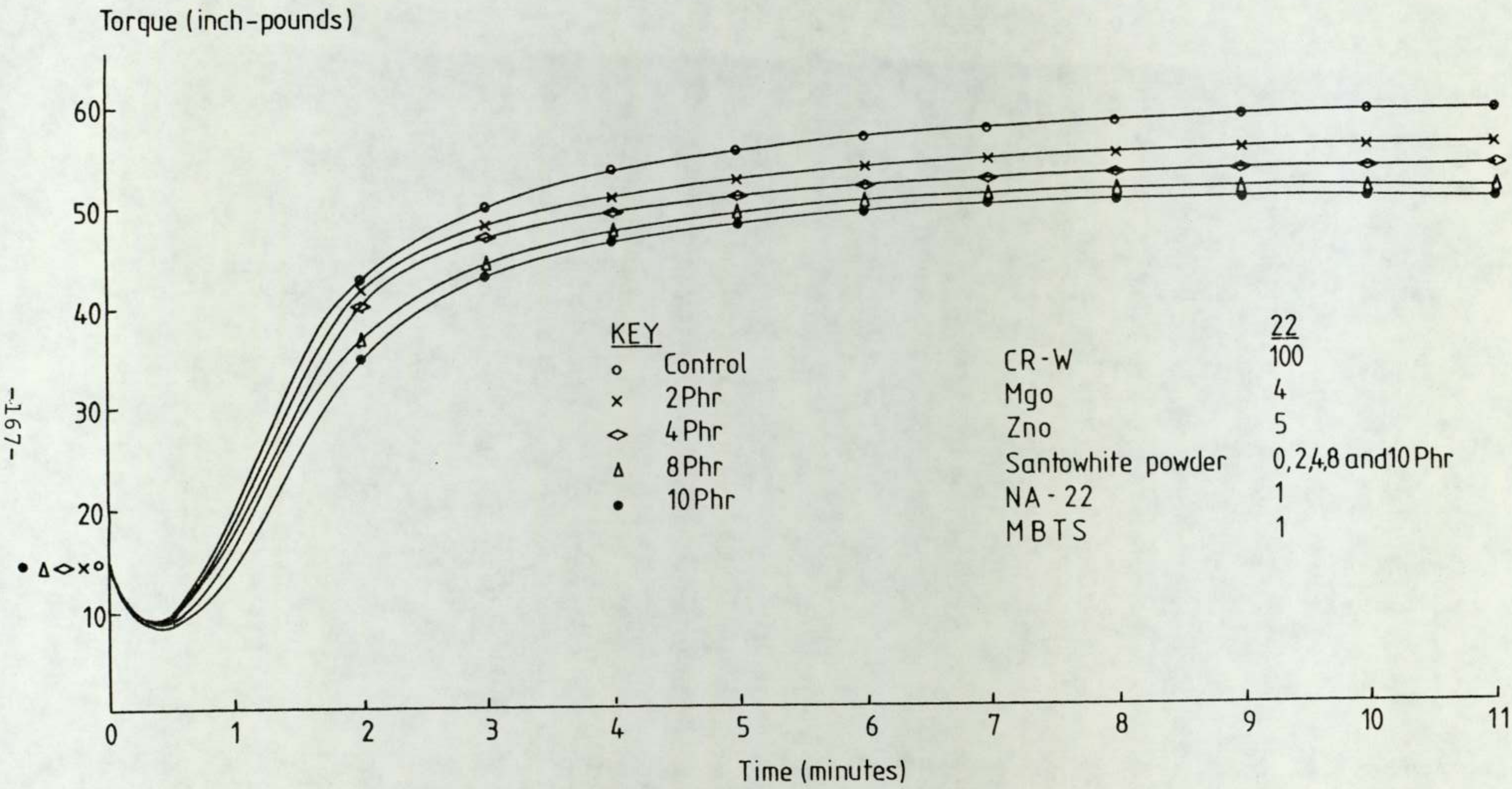


Fig 3:34 The effect of different concentrations of Santowhite powder on the vulcanization characteristics of CR-type W, cure at 160°C for 30 minutes.

in the extent of vulcanization. This interference might be due to the acidity of the Santowhite powder antioxidant or it might be due to some reaction that takes place between the tertiary allylic chlorine atoms of the polymer and the hydroxyl groups of the antioxidant to form a bound antioxidant.

The interference is lower than that shown with the amine antioxidants (3.2.1). This is due to the high reactivity of amino groups in amine antioxidants towards tertiary allylic chlorine atoms.

3.2.3.2.2 Attempted Detection of Bound Santowhite Powder by Means of Antioxidant Activity

In order to assess the possibility of reaction of Santowhite powder with CR type-W by antioxidant activity formulations in Table (3.27) were mixed on a water-cooled laboratory two roll mill at room temperature, and then ageing reactions assessed.

TABLE (3.27)

Formulations of CR Type-W to Study the Antioxidant Activity of Santowhite Powder

	23	24
CR Type-W	100	100
Mgo	4	4
NA-22	1	1
MBTS	1	1
Santowhite Powder	-	2
Zno	5	5

Films for stress relaxation and oven ageing were produced for the two above formulations.

3.2.3.2.2.1 Stress Relaxation

Films of 0.1 cm thickness were prepared as in Section 2.3.2. Samples were cut using MR100 cutter (2.4.4). Half of the samples were acetone extracted under N_2 (2.3.4).

Continuous stress relaxation was carried out at 140°C in a Wallace oven (2.4.1) for both non-extracted and acetone extracted samples. A plot of Log f/f^o against time of ageing is shown in Fig. 3.35. The values of Log f/f^o after 400 minutes of ageing are shown in Table (3.28)

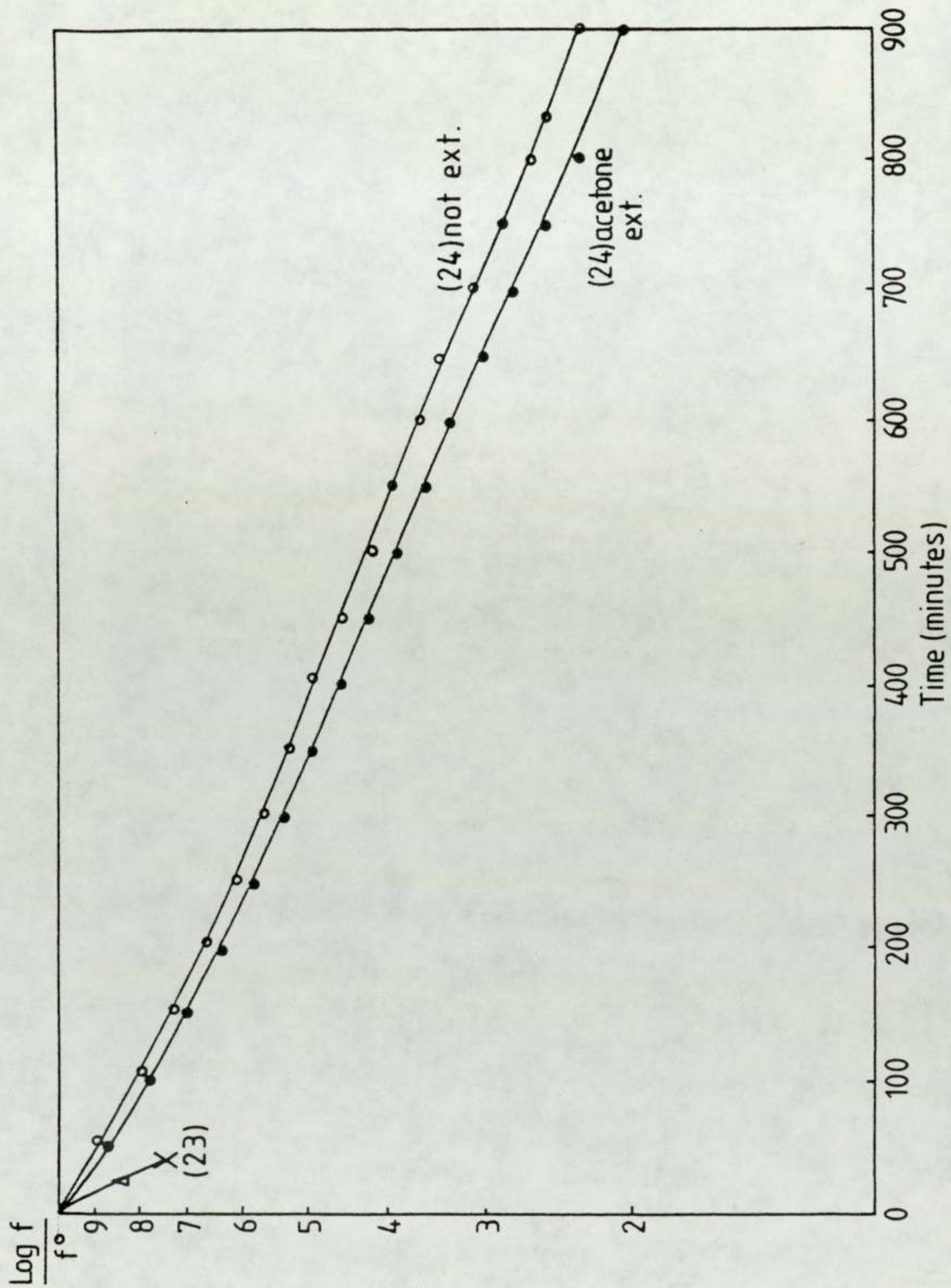
TABLE (3.28)

The Values of Log f/f^o After 400 Minutes of Ageing for CR Type-W with Santowhite Powder Aged at 140°C.

	Formulation No.	
	23	24
Not extracted	melted	0.68
Acetone extracted	melted	0.67

Results and Discussion

(1) Table (3.28) showed that the control could not withstand the ageing and it became very soft after a few minutes of ageing. This is due to the absence of any



	23	24
CR type W	100	100
Mgo	4	4
Zno	5	5
Santowhite powder	-	2
NA - 22	1	1
M.B.T.S.	1	1

Fig 3:35 The effect of Santowhite powder on the continuous stress relaxation of CR type W aged at 140°C before and after acetone extraction.

antioxidant.

(2) The presence of 2 phr Santowhite powder greatly increases the thermal oxidative resistance of the polymer.

(3) On acetone extraction the control still cannot withstand the ageing and it melts after a few minutes. The sample which contained 2 phr Santowhite powder still shows a good thermal oxidative resistance which suggests that the Santowhite powder has combined with the polymer or become insoluble in acetone.

(4) Despite its retention of antioxidant activity, there is a small decrease in the sample containing 2 phr of antioxidant after acetone extraction. This may be due to removal of some of the antioxidant, uncured rubber or any other compounding ingredients which are soluble in acetone. The other possible reason for this decrease may be due to the presence of some soluble oxygen in the acetone which oxidizes the rubber during the extraction process. The swelling of the rubber during extraction is another possible reason for the decrease in the ageing resistance.

3.2.3.2.2.2 Accelerated Oven Ageing of Vulcanizates

The efficiency of Santowhite powder as an antioxidant and the possibility of reaction with CR type-W during vulcanization processes was investigated by ageing the vulcanized rubber in an oven at 130°C for different interval time and then, measuring the deterioration in the selected physical properties.

3.2.3.2.2.2.1 Ultimate Tensile Strength and Elongation At Break

Test-samples from formulations listed in Table (3.27) were prepared as in Section 3.2.3.1.2.2.1. Half of the samples were acetone extracted under N_2 (2.3.4) and dried.

Ageing was carried out in a Wallace multicell oven at 130°C for both non-extracted and acetone extracted samples. The graphs between UTS in (MNm^{-2}) and the elongation at break against time of ageing are shown in Figs 3.36 and 3.37 respectively.

The percentage decrease in UTS and the elongation at break are shown in Tables (3.29) and (3.30) respectively.

Results and Discussion

The effect of the presence of Santowhite powder on CR type-W and the possibility that some binding would take place during the vulcanization process is studied by oven ageing as is shown in Tables (3.29) and (3.30) and Figs. 3.36 and 3.37.

From the above figures and tables the following deductions can be made:

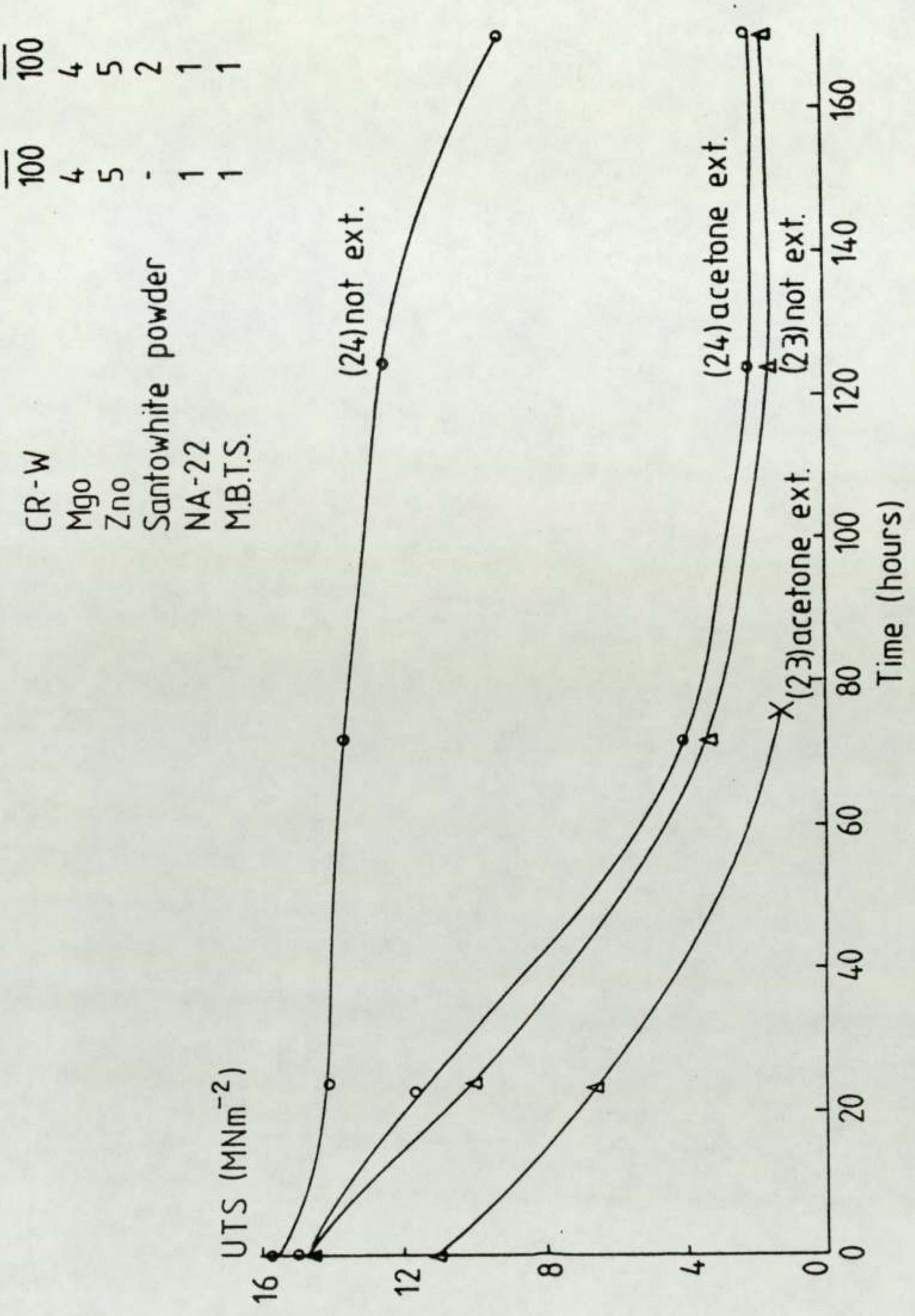
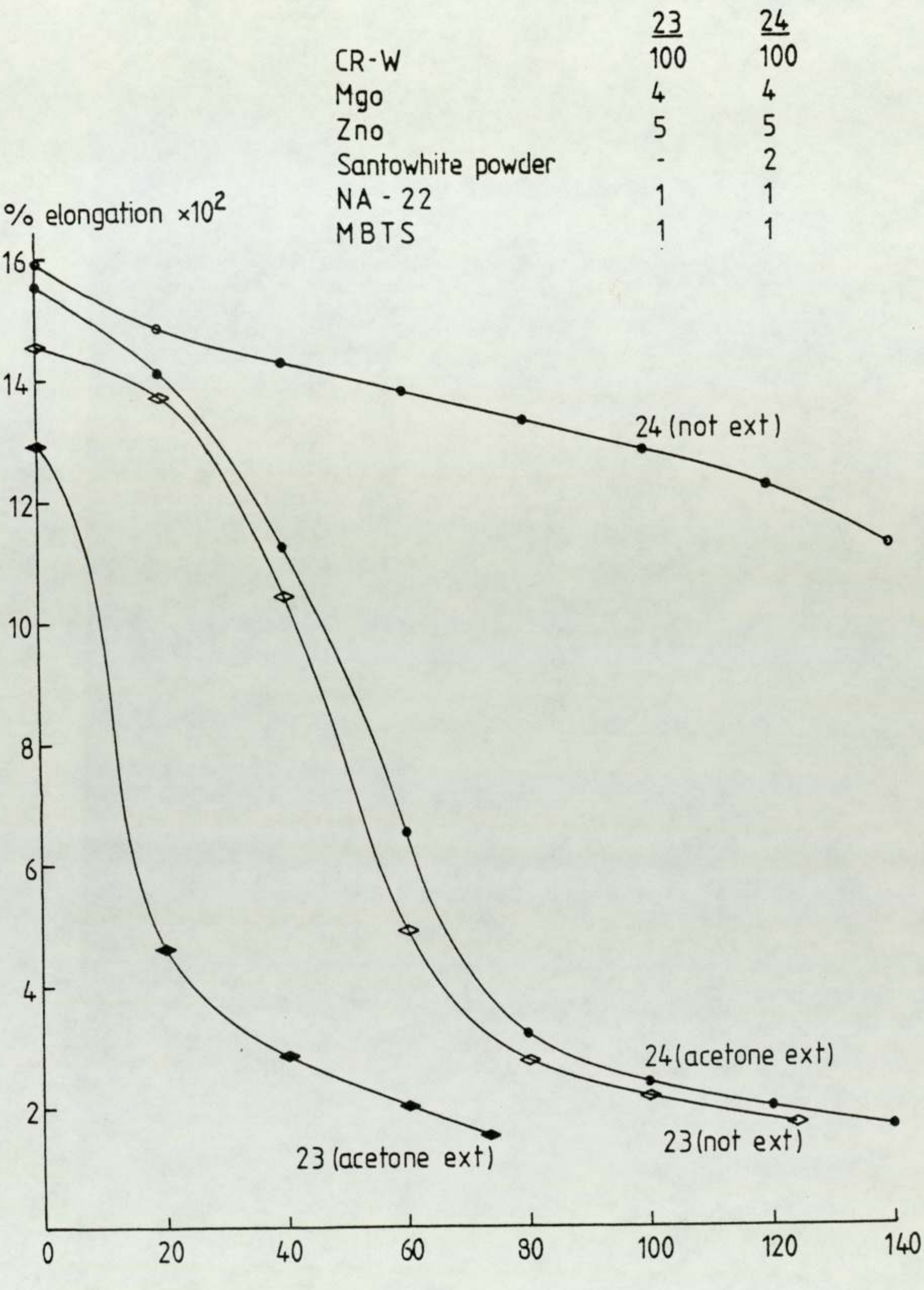


Fig 3:36
The effect of Santowhite powder on the UTS of CR type W aged at 130°C before and after acetone extraction.



	23	24
CR-W	100	100
Mgo	4	4
Zno	5	5
Santowhite powder	-	2
NA - 22	1	1
MBTS	1	1

Fig 3 : 37
The effect of Santowhite powder on the % elongation of CR-type W aged at 130°C before and after acetone extraction

TABLE (3.29)

% Decrease of UTS (MNm^{-2}) of CR Type-W Vulcanizate in the Presence of Santowhite Powder, Aged at 130°C

Formulation Number	Ageing Period							
	Non-extracted				Acetone Extracted			
	Ohr	24hr	72hr	124hr	Ohr	24hr	72hr	124hr
23		-33.3	-77.3	-89.3		-40	melted	melted
24		-9.6	-11.5	-21.7		-19.2	-72.6	-86.3

TABLE (3.30)

% Decrease of Elongation at Break of CR Type-W in the Presence of Santowhite Powder

Formulation Number	Ageing Period							
	Non-Extracted				Acetone Extracted			
	0hr	24hr	72hr	124hr	0hr	24hr	72hr	124hr
23		-7.6	-79.3	-88.2		-69.5	melted	melted
24		-8.1	-16.2	-25		-11.6	-76.1	-87

(1) The samples for both the control and that with 2 phr Santowhite powder have approximately the same initial UTS which indicates no degradation has taken place during the processing and vulcanization.

(2) Santowhite powder is a very active antioxidant for CR type-W rubber. This is due to the ability of this antioxidant to donate its hydrogen atom to the free radicals or to the peroxy radicals, (3.2).

(3) Acetone extraction of the control leads to a decrease in the thermal oxidative resistance of CR type-W for the same reasons already studied (Section 3.2.3.2.2.1). Therefore, although the control before extraction lost 88% of its initial UTS values after 124 hours of ageing it still had sufficient strength to be tested, but the extracted control had become soft and tacky within 72 hours.

(4) Acetone extraction of the samples containing 2 phr Santowhite powder led to a remarkable decrease in the phsyical properties of the vulcanizates on ageing. This is due to the removal of most of the antioxidant during extraction process as well as due to the same reasons mentioned in Section 3.2.3.2.2.1.

(5) The samples with 2 phr Santowhite powder still have much better thermal oxidative resistance than the control even after acetone extraction. This indicates that some of the antioxidant must have combined with the

rubber during the vulcanization process.

(6) The oven ageing results are not in agreement with the results obtained from stress relaxation (Section 3.2.3.2.2.1). This is due to the fact that in stress relaxation the ageing is carried out only for 15 hours and, therefore, even the small amount of Santowhite powder which becomes bound into the rubber during vulcanization will have a great effect on the thermal oxidative for a short period. In the oven ageing the period of ageing is very long and the efficiency of Santowhite powder as an antioxidant soon vanishes.

CHAPTER 4

POLYEPICHLOROHYDRIN RUBBER

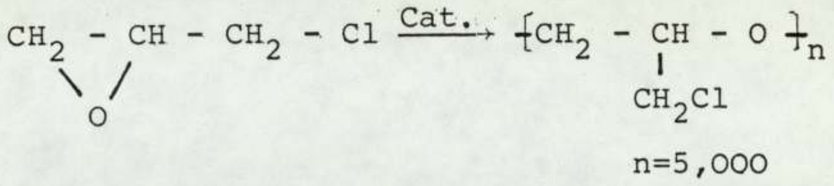
4.1 INTRODUCTION

The discovery of the ECH elastomers was announced in 1965 (139) and they were manufactured under the trade mark 'hydrin' (Goodrich) and later under the trade mark 'Herclor' (Hercules Limited).

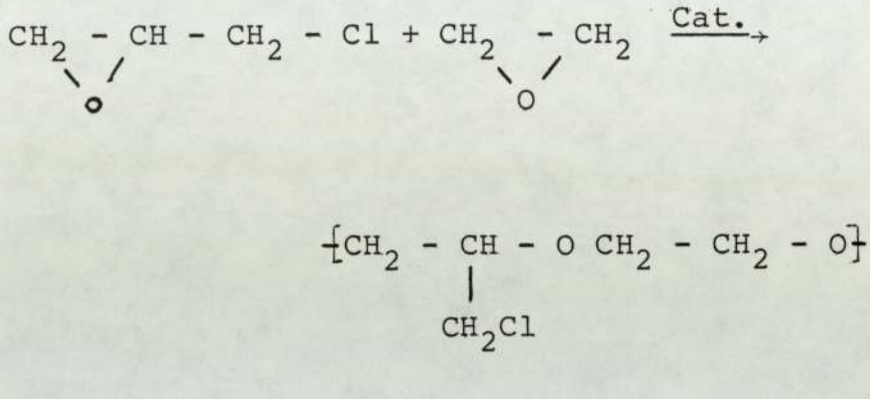
Two members of this new elastomer were produced namely, the homopolymer of epichlorohydrin and a copolymer of epichlorohydrin and ethylene oxide (1:1 mole). These rubbers are amorphous and have good processing and vulcanizate properties. The absence of unsaturated double bonds in their structure and the presence of the chlorine produces vulcanizates with a good resistance to oil, heating and ozone superior to that shown by the nitrile and polychloroprene rubbers. The high chlorine content also confers flame retardancy and increases the reactivity of the rubber during vulcanization.

These rubbers are used in many applications such as seals and gaskets, diaphram, hose, belting, wire and cable jackets, printing rolls and blankets, and mechanical goods. They are also used in adhesives.

The polymers are derived from the ring opening polymerization of epichlorohydrin and in the case of copolymer with epichlorohydrin and ethylene oxide.



n=5,000



n = 20,000.

The molecular weight of the polymer depends on the type of catalyst system employed in the polymerization process. Such catalyst include: aluminium alkyl-transition metal salt combinations, aluminium alkyl-water systems and aluminium alkyl system with a chelating agent in hydrocarbon solvent (140). Solution polymerization in benzene, toluene, or methylene chloride are used.

In general, these polymer are prepared in an inert organic solvent at moderate temperature with a minor amount of an appropriate aluminium based catalyst. The optimum catalyst composition and preparation conditions vary with the nature of the product desired.

The copolymer is more easily prepared than homopolymer due to the presence of ethylene oxide which is about seven times more reactive than epichlorohydrin. Molecular weight can be controlled by the addition of carbonium ion precursors such as various organic halides, acid halides, ... etc.

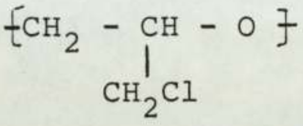
The presence of the ether oxygen confers flexibility to the molecule because of the free rotation about the oxygen in the backbone and is responsible for the excellent low temperature flexibility (-40°C of the copolymer and -18°C for homopolymer). This combination of oil resistance and low temperature flexibility is very unusual.

The homopolymer has better flame resistance, is less permeable to gases and has better heat resistance than the copolymer. This is due to the increases in the chlorine content (homopolymer 38.4% cl and for copolymer 26% cl).

The homopolymer is used in this investigation because of its superior thermal stability.

4.2 POLYMER STRUCTURE

The asymmetrical monomer units can exist either in random stereo sequences (a tactic polymer) or in stereoregular sequences (isotatic polymer (I)).



$$-\!\left[CH_2 - \underset{\underset{\displaystyle CH_2Cl}{|}}{CH} - O \right]\!-$$

(I)

The monomers can be arranged head-to-head, tail-to-tail, and as it is found in Herclor H elastomers is more than 97% head-to-tail. The stereoregular isotatic, crystalline rubber can be detected by conventional methods such as X-ray spectroscopy.

4.3 VULCANIZATION OF POLYEPICHLOROHYDRIN (ECH)

Vulcanization of ECH occurs through the pendent chloromethyl groups(139) as there are no double bonds in the main chain, the polymer cannot be vulcanized by using the conventional sulphur accelerator covulcanization.

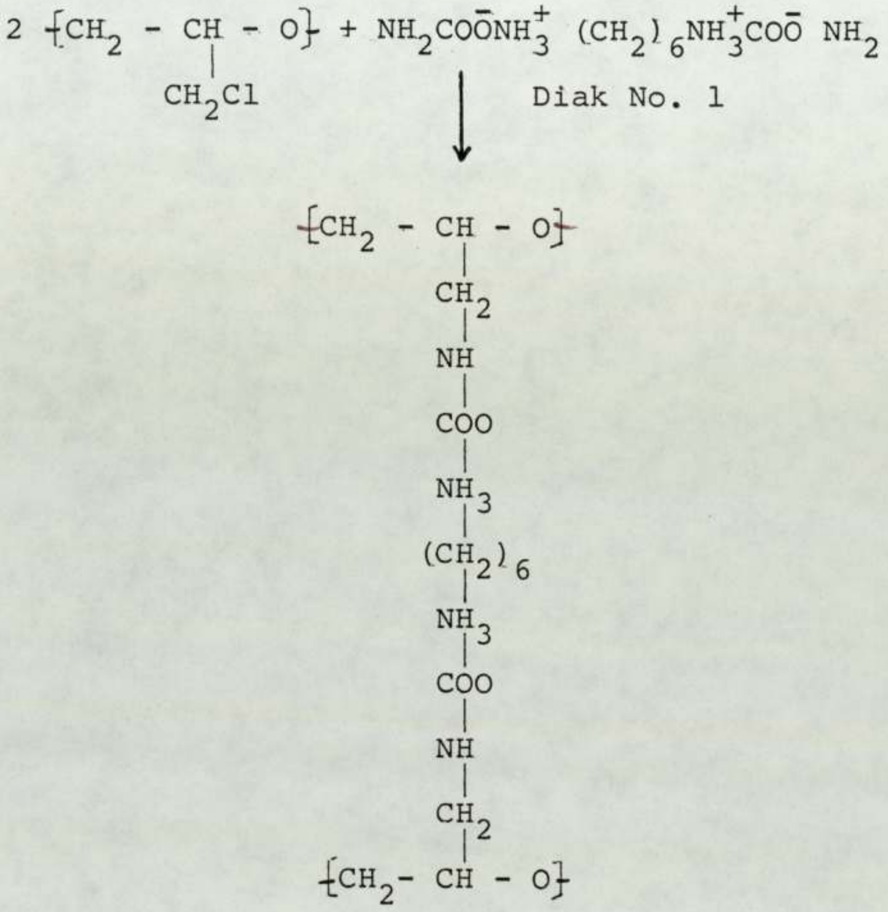
Unlike neoprene (Chapter 3), the chlorine groups of ECH are not reactive enought to be cross-linked using Zno and Mgo(141) alone, but will cross-link in the presence of difunctional compounds such as thiourea, poly-functional amine, 2-mercaptoimidazoline (NA-22), and hexamethylenediamine carbamate (Diak No. 1).

The curing mechanism of ECH with thiourea, is believed to be similar to that proposed for neoprene(142) in which an intermediate isothiuronium salt is first formed and then reacts with metal oxide to form a sulphur cross-link and urea (see Section 3.5).

The use of sulphur with NA-22 markedly enhances the tensile strength of ECH. Such systems are useful for covulcanization of ECH with other elastomers which are cured by sulphur.

In this work the vulcanisation process is carried out using Diak No. 1. This gives relatively fast cures but there is sufficient scorch time for normal compounding and processing.

Diak No. 1 reacts with epichlorohydrin through the two reactive amino groups of the curative agent with the chlorine atoms of the polymer.



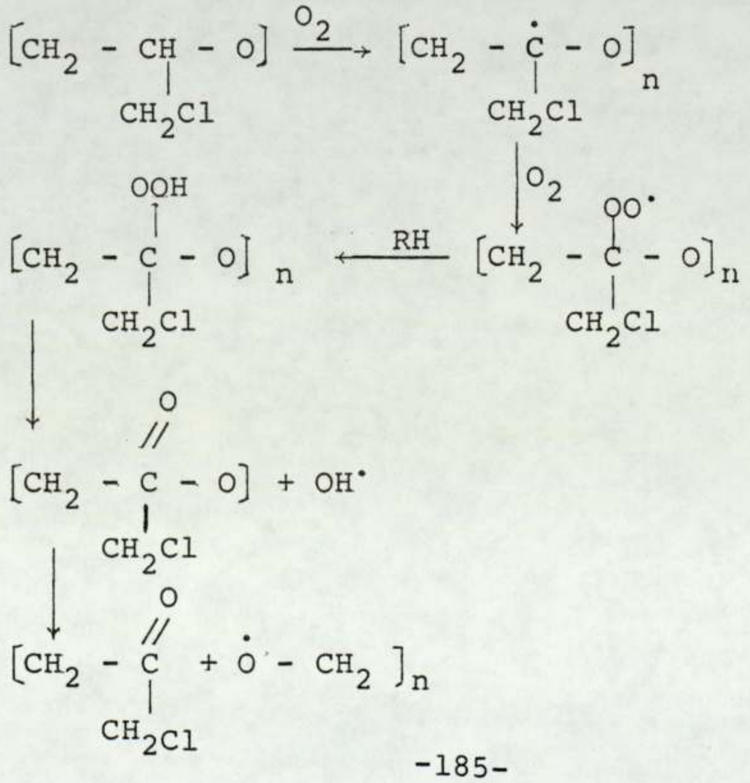
$$2\,\left[CH_2 - \underset{\displaystyle CH_2Cl}{CH} - O\right] + NH_2CO\bar{O}NH_3^{+}\,(CH_2)_6NH_3^{+}CO\bar{O}\,NH_2 \xrightarrow{\text{Diak No. 1}} \begin{array}{c} \left[CH_2 - CH - O\right] \\ | \\ CH_2 \\ | \\ NH \\ | \\ COO \\ | \\ NH_3 \\ | \\ (CH_2)_6 \\ | \\ NH_3 \\ | \\ COO \\ | \\ NH \\ | \\ CH_2 \\ | \\ \left[CH_2 - CH - O\right] \end{array}$$

Since polyepichlorohydrin elastomers require basic condition to cure properly, an acid acceptor such as red lead (ph_3O_4) or dibasic lead phosphite is used with the curative agent. These compounds will eliminate HCl which is evolved during the vulcanization process which will otherwise cause mould adhesion problems and produce vulcanizates with low heat resistance and poor physical properties.

4.4 AGEING OF POLYEPICHLOROHYDRIN

The thermal degradation of the raw or vulcanized homopolymer has been studied in air or N_2 by thermogravimetry(143). The evolution of HCl from the homopolymer as a function of temperature and compounding formulation with different types of acid acceptors have been studied. It was found that samples were more stable in N_2 than in air, and the raw rubber was more stable in both atmospheres than the vulcanizate. In all cases, HCl-evolution commenced at temperatures greater than 290°C and proceeded at a rapid rate in the temperature range of 310°C-330°C. The final HCl yield at 400°C amounted 30-35% of the available chlorine.

An autoxidation mechanism involving the formation of hydroperoxide groups followed by scission of the ether link has been suggested(144,145), e.g.



If the polymer is heated in the presence of an organic peroxide drastic chain scission rapidly takes place(146). The presence of certain metals such as Zn, Fe, Sn and Cu, present in either the rubber or in the acid acceptor, cause a considerable acceleration of degradation.

The Japanese workers(147), found that ECH cleaves much more readily in the air in the presence of Mgo than with other acid acceptors.

Oetzel(148), suggests that in order to improve the heat resistance of ECH, the recipe should contain an acid acceptor and an antioxidant in addition to the curative agent. The type of acid acceptor used was found to influence the properties of the vulcanizate. Oetzel, found that ECH polymers gradually lose their tensile strength while the elongation and hardness values tend to plateau in long term ageing tests. This is in direct contrast to some other elastomers which continuously harden on ageing and eventually fail embrittlement.

Vadenberg(140), found that the physical properties of ECH vulcanizates varied with the change in the amount of curative agent used, the type and amount of filler as well as with the type of acid acceptor used.

Improving the heat resistance of ECH with compounding ingredients can be achieved by the following:-

(1) Selection of vulcanizing agent (140)

(2) Selection of the acid acceptor (148)

(3) Selection of an antiageing compound (149)

(4) Selection of the stabilizer (148)

(5) Selection of the filler (150)

(6) Selection of processing acids (150).

The thermal ageing resistance of ECH can also be improved by blending with other polymers e.g.

(1) Acrylic rubbers,

(2) Unsaturated epoxy copolymer.

Further Reactions of Polyepichlorohydrin

It has been shown in Section (4.4) that the thermal oxidative resistance of ECH rubber may be improved by the addition of an antioxidant. The loss of such antioxidant due to volatilization or leaching may be overcome if the antioxidant is combined with the polymer via the chloromethyl group reacting with phenolic or amine antioxidants as inthe case of the polychloroprene (Chapter 3). It may possibly be carried out by reaction of the raw rubber before compounding or during vulcanization.

The remainder of this chapter describes our attempts to combine antioxidants with the polymer.

4.5 EXPERIMENTAL

4.5.1 TO ASSESS THE FUNCTION OF THE VARIOUS COMPOUNDING INGREDIENTS

There is much confusion in the literature as to the function of the various compounding ingredients (NBC for example is sometimes described as an accelerator and again as an antioxidant). As we have to assess the ageing properties of ECH vulcanizates we must know the effect of the other compounding ingredients upon its ageing behaviour. It was, therefore, decided to determine this before we commenced with bound antioxidant preparation and evaluation.

The formulations listed in Table (4.1) were prepared.

The master batch was prepared using the Banbury mixer at room temperature for 6 minutes. The formulations were, then, finished on a two-roll mill at room temperature for 5 minutes.

TABLE (4.1)

Formulations used to Assess the Function of the ECH Compounding Ingredients

		Formulation Number						
		1	2	3	4	5	6	7
ECH	Master Batch	100	100	100	100	100	100	100
FEF		30	30	30	30	30	30	30
pb$_3$O$_4$		5	5	5	5	5	5	5
IPPD		-	-	-	2	2	2	2
Zinc stearate		1.0	-	1.0	-	1.0	-	1.0
NBC		-	1.0	1.0	-	-	1.0	1.0
Diak No. 1		1.5	1.5	1.5	1.5	1.5	1.5	1.5
Monsanto Rheometer data Induction Period in min		2	2	2	2	2	2	2
Time to 90% cure		79	69	76	56	79	64	79
Torque at 60 min		88	77	85	57	88	72	88

4.5.1.1 The Effect of Various Compounding Ingredients on the Vulcanization Characteristics of ECH Homopolymer

The vulcanization characteristics of the formulations shown in Table (4.1) were tested in a Monsanto rheometer at 160°C using a time span of 60 minutes and a torque range of 100 in-lb. The values of induction period, time to 90% vulcanization and torque after one hour of curing, were determined and are shown in Table (4.1).

Results and Discussion

The largest torque values are obtained when zinc stearate is present (formulations 1, 3, 5 and 7), although it has no effect on the rate of vulcanization. This is attributed to the ability of the zinc stearate to act as an acid acceptor and to catalyze other aspects of the curing reaction(151).

Zinc stearate also acts as a lubricant which give good milling processing characteristics(140).

From Table (4.1) it is seen that the presence of zinc stearate has a greater effect on the extent of vulcanization than nickel dibutyl-dithiocarbamate. This is due to the basicity of zinc stearate increasing the extent of vulcanization, or through its action as a scavenger to eliminate the effect of evolved HCl from polyepichlorohydrin rubber.

The IPPD antioxidant showed only a small effect on the extent of vulcanization due to the reaction of the amino groups and the chlorine atom of the polyepichlorohydrin. This reaction leads to a decrease in the number of chlorine atoms available for vulcanization reaction, see Section 4.3.

4.5.1.2 Stress Relaxation Studies

Continuous stress relaxation was used to assess the ageing behaviour of ECH rubbers and the effect of some of the compounding ingredients on ageing.

Films of (0.1) cm thickness were prepared from the formulations, Table (4.1), using a steam press (2.3.3) at 160°C for 45 minutes. Samples were cut from the films. Half of the samples were acetone extracted for 48 hours under N_2 (2.3.4) and then dried.

Continuous stress relaxation (2.4.1) was determined in a Wallace age-tester at 160°C for both before and after the acetone extraction. The results are shown in Figs 4.1 to 4.4.

Results and Discussion

The values of log f/f^o after 400 minutes of ageing are shown in Table (4.2).

TABLE (4.2)

The Log f/f^o Values of ECH after 400 minutes of Ageing at 160°C with Different Compounding Ingredients

	Formulation Number						
	1	2	3	4	5	6	7
Not extracted	0.290	-	0.34	0.19	0.54	0.07	0.55
Acetone extracted	0.13	-	-	0.65	0.62	0.59	0.64

It can be seen that the highest resistance to thermal oxidative ageing is obtained with the formulations which contain IPPD. This is due to the ability of IPPD to act as an hydrogen doner to the free

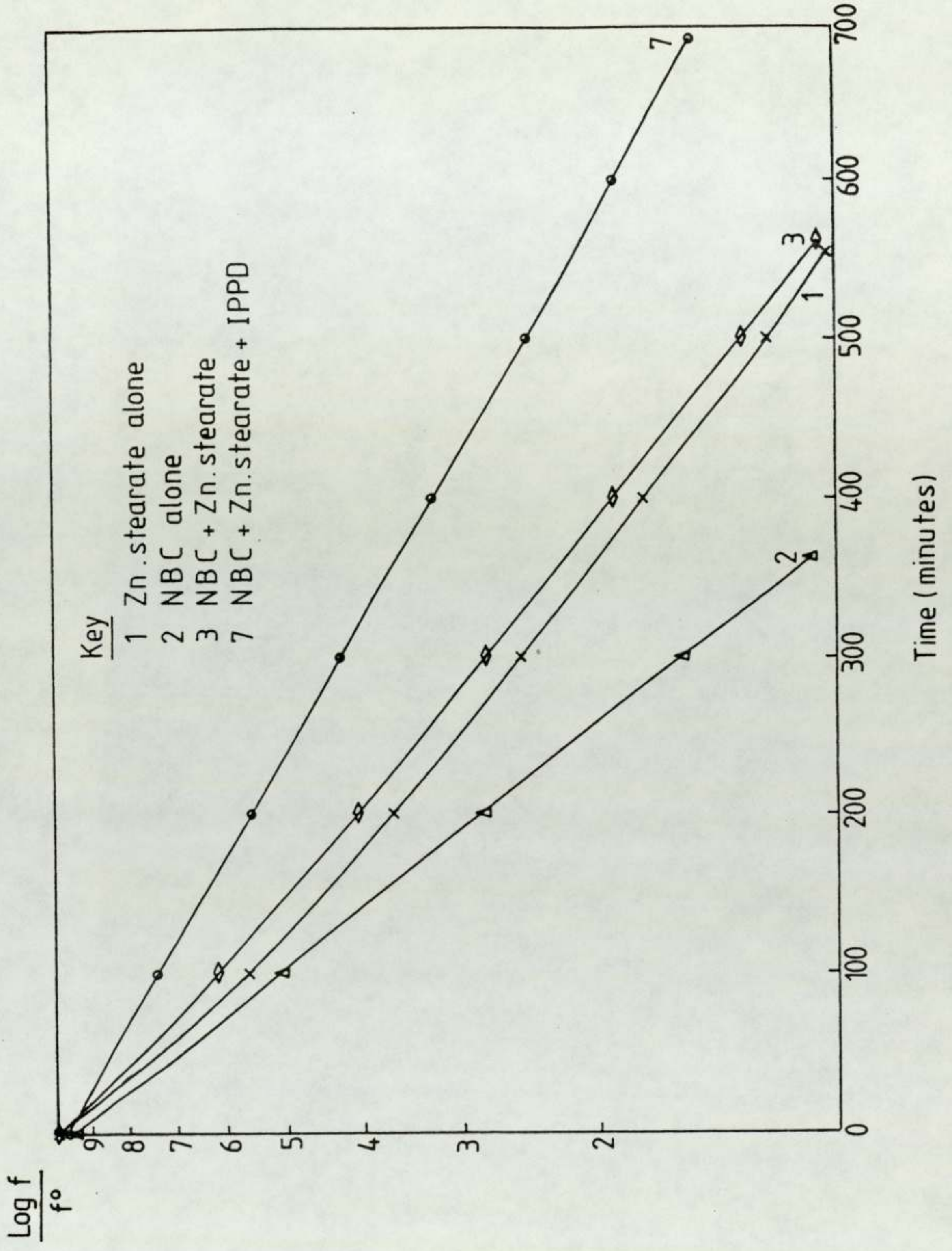


Fig 4:1

Continuous stress relaxation of ECH at 160°C, not extracted

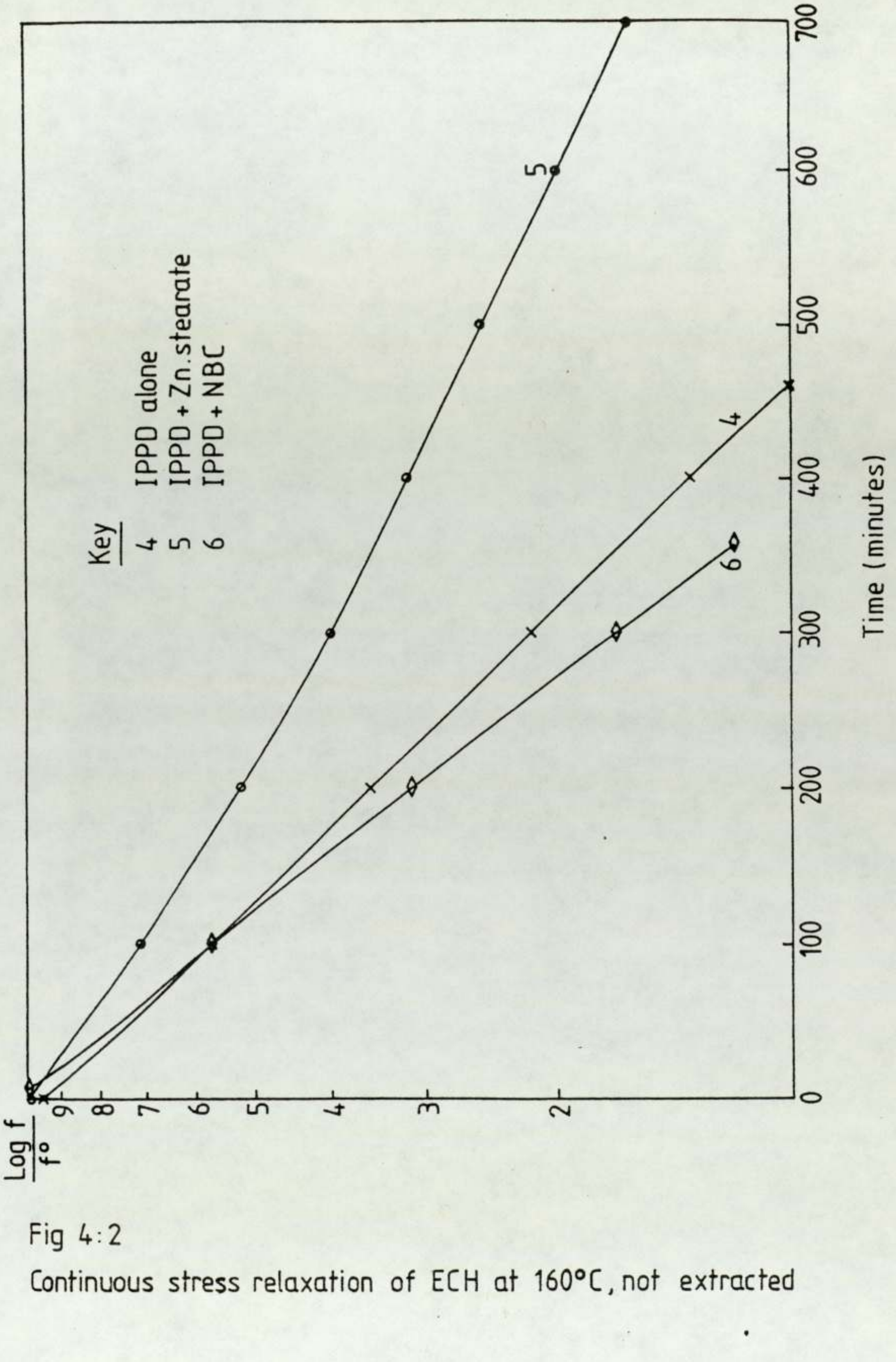


Fig 4:2

Continuous stress relaxation of ECH at 160°C, not extracted

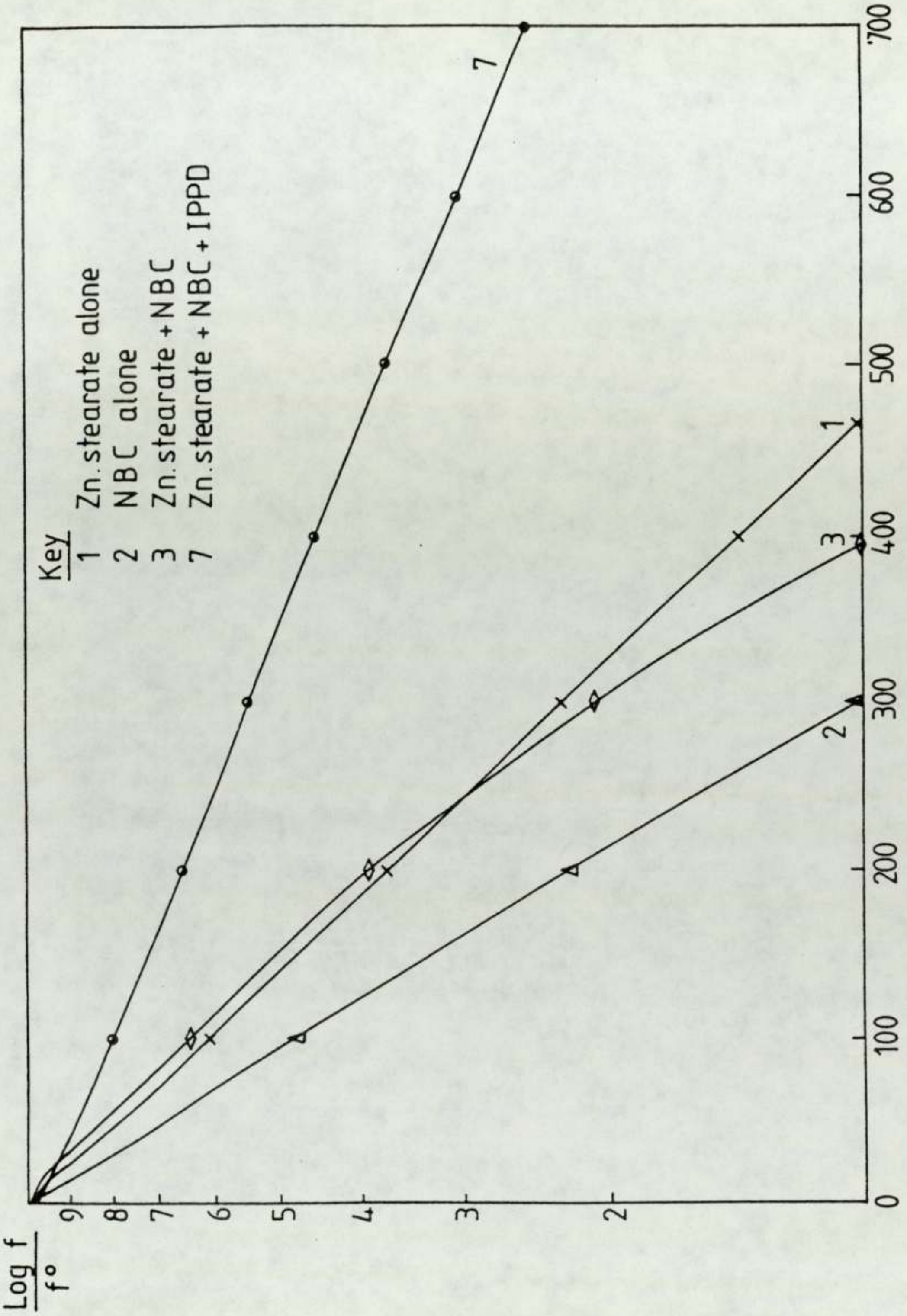


Fig 4:3

Continuous stress relaxation of ECH at 160°C, after acetone extraction.

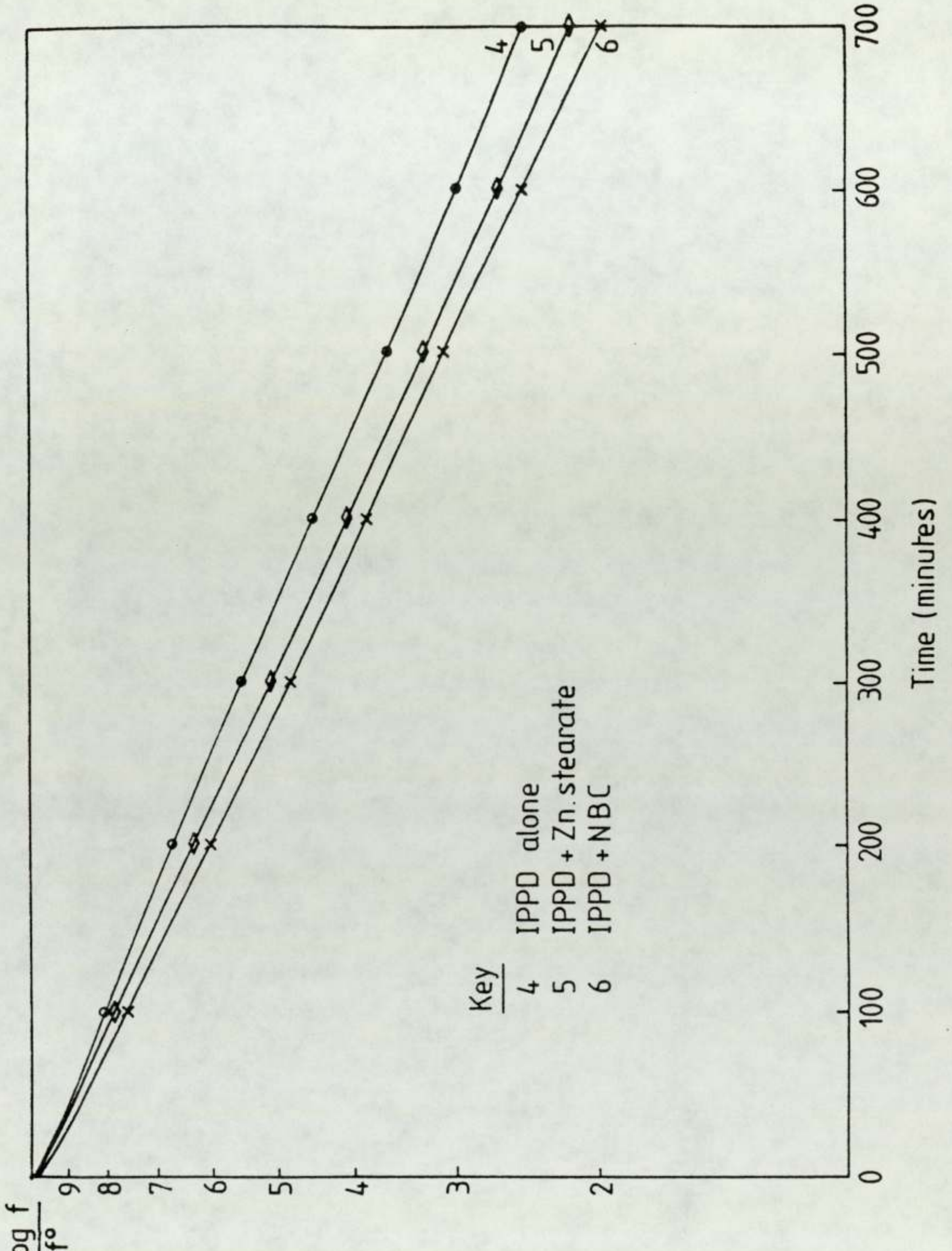


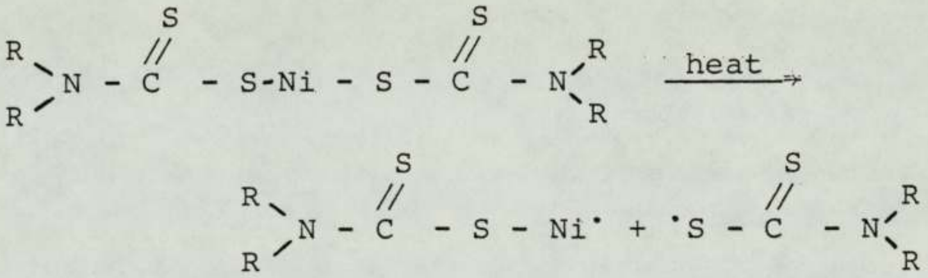
Fig 4:4

Continuous stress relaxation of ECH at 160°C, after acetone extraction radicals and therefore, decrease the extent of degradation of ECH rubbers.

The uneffectiveness of NBC as an antioxidant can be seen from the comparison of formulation (2) with (1) and (4) (Table (4.2) and Fig. 4.1). This is in contradiction with the function of NBC as hydroperoxide decomposer. This could be explained on the basis that the effectiveness of an antioxidant depends on the ratio of the chain termination and initiation stages. The latter process is characterized by a greater activation energy. When the temperature increases, it is found that for most antioxidants, the rate of initiation increases more rapidly than the rate of chain termination and, therefore, the effectiveness of the antioxidant should decrease with increasing temperature (See section 4.5.3.2). This must be the case with NBC in ECH rubbers aged at 160°C since it is known to be a good hydroperoxide decomposer and is used to protect polyethylene and has been incorporated into latex sponge as a protective agent against deterioration caused by light (152).

The effect of zinc stearate on ageing resistance is shown in Table (4.2). It is clear that zinc stearate has a great effect on the stabilization of the polymer. This is due to its ability, like pb3O4, to remove the HCl produced during the cross-linking process.

There is an synerigestic effect between IPPD and zinc stearate, while IPPD and NBC together have an antagonistic effect as shows in Table (4.2). The synerigestic effect is due to the fact that both IPPD and zinc stearate act as good stabilisers and can remove the free radicals and HCl, while in the case of IPPD and NBC, the combination of two of them decrease the effectiveness of IPPD due to the formation of more free radicals by the NBC decomposition which initiate the degradation process.



Acetone extraction shows improvements in the ageing resistance, this is attributed to the removal of the extra network material, like NBC, or pro-oxidant combination of NBC and IPPD but it is possible that some of the IPPD has combined with the polymer during the vulcanization process and is exerting a powerful antioxidant effect.

4.5.1.3 Oven Ageing Studies

The effect of NBC and IPPD in the presence of zinc stearate on the thermal-oxidative ageing of ECH rubbers was further studied by oven ageing vulcanizate prepared from formulations (1), (3) and (7) in Table (4.1).

Samples for UTS and hardness measurement were prepared as described in Section s 2.4.2 and 2.4.3. Ageing was carried out in a Wallace oven at 160°C.

Results and Discussion

The percentage decrease in UTS and the hardness are shown in Tables (4.3) and (4.4) respectively.

TABLE (4.3)

The % Decrease of UTS (MNm^{-2}) of ECH use at 160°C

Formulation Number	Ageing Period (in days)				
	0	1	3	4	6
1		- 7.4	-55.9	-77.7	-97.7
7		+50	+ 5	-23	-58
3		+22	-15.4	-42.3	-76

TABLE (4.4)

% Loss of Hardness (IRHD) of ECH Aged at 160°C

Formulation Number	Ageing Period (in days)						
	0	1	6	8	11	18	20
1		+16.0	-8.0	-16.0	-17.7	melted	melted
7		+17.7	+4.8	zero	- 0.8	- 7.2	-15.3
3		+16.1	+3.2	- 4.8	- 6.5	-31.5	-36.3

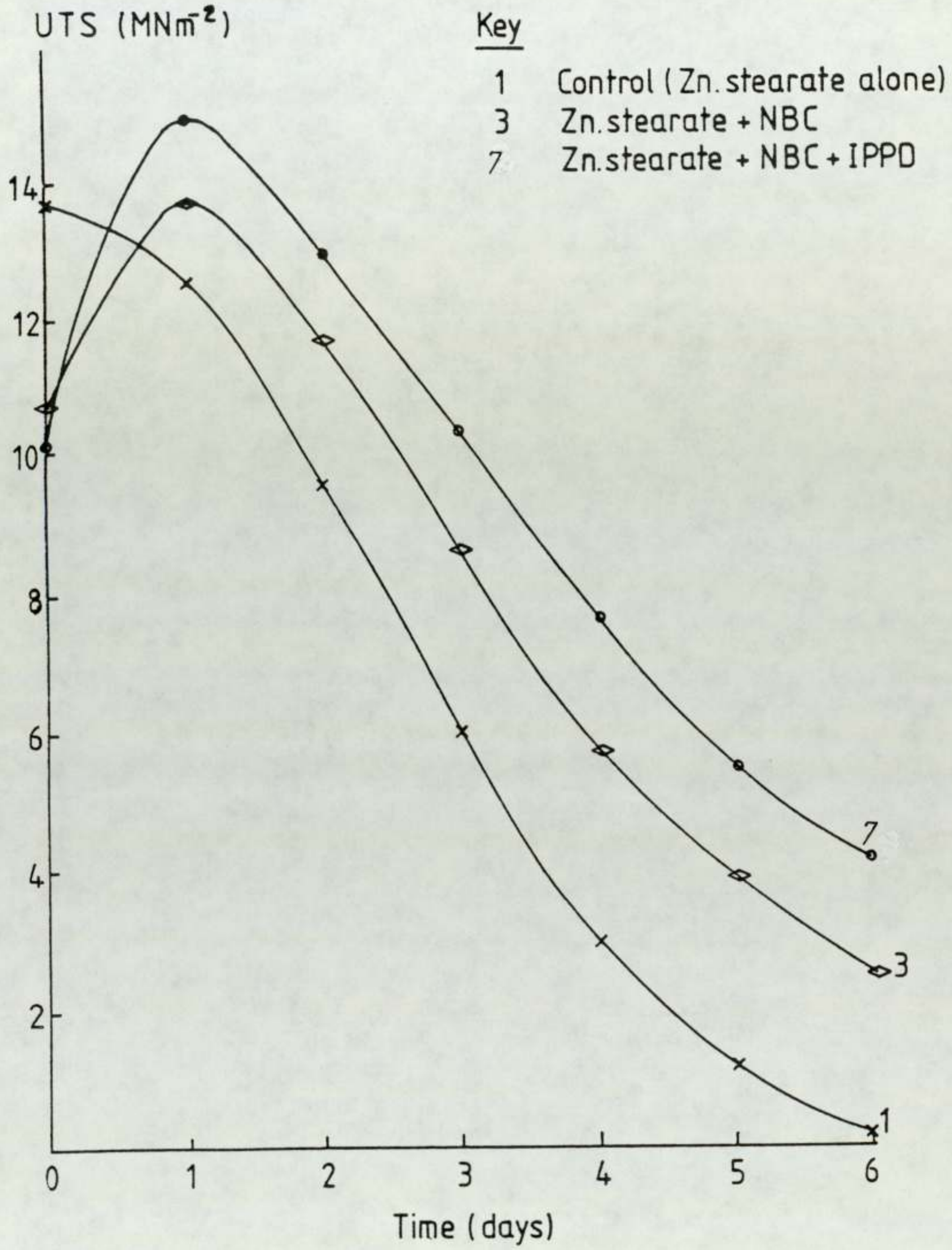


Fig 4:5

The changes in the UTS of ECH aged at 160°C in the presence of NBC or IPPD

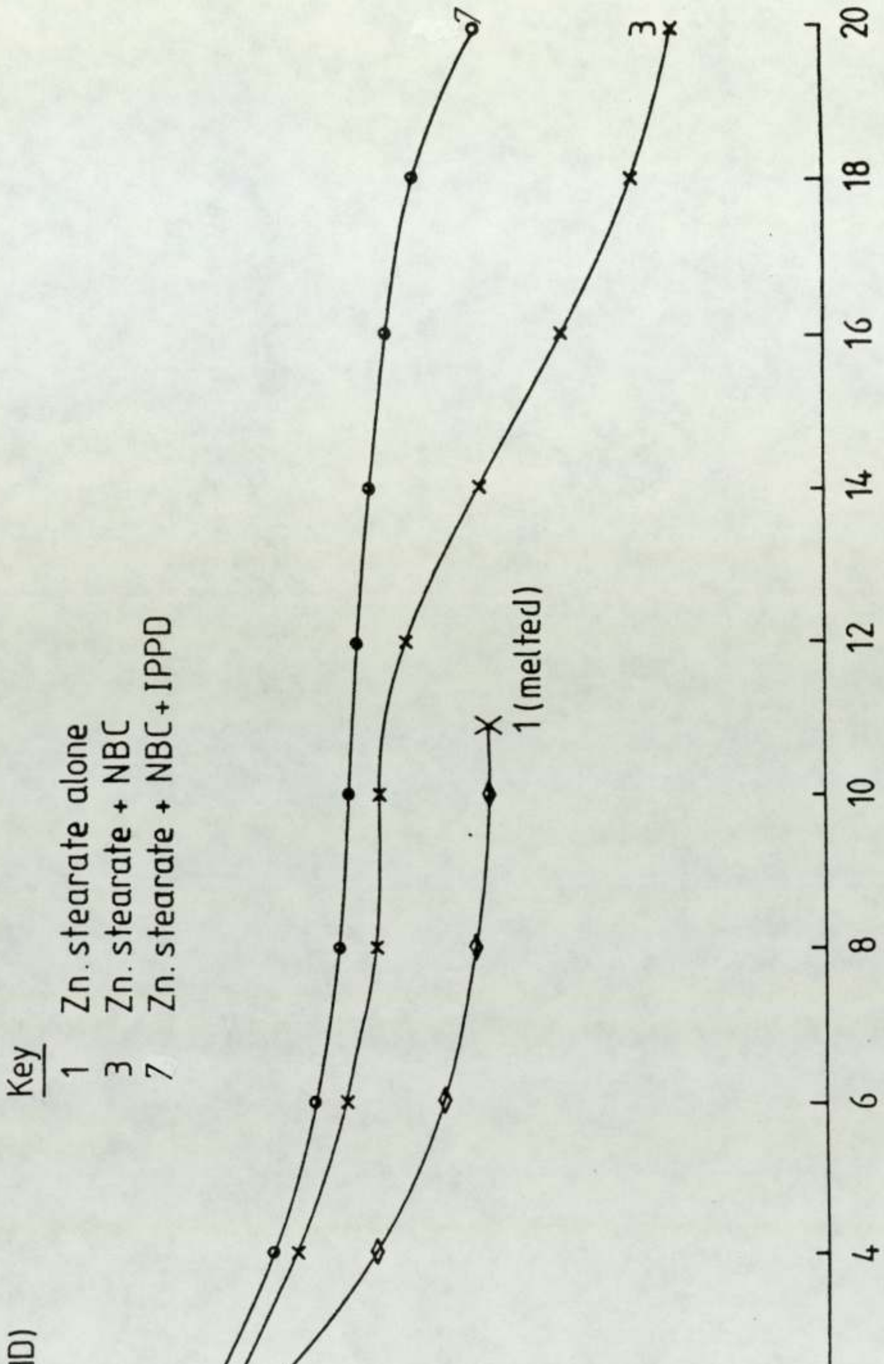


Fig 4 : 6

The effect of NBC and IPPD on the hardness of ECH aged at 160°C in a Wallace oven

The ultimate tensile strength and hardness are broadly in agreement with the stress-relaxation results Section 4.5.1.2.

From graphs (4.5) and (4.6) and also from Tables (4.3) and (4.4) it is noticed that a very good protection is obtained when IPPD is used. This is due to its activity as a chain breaking antioxidant which donates a hydrogen atom to the free radicals produced during the degradation and convert them to the corresponding nitroxyl radicals. These have an antioxidant activity due to their continual regeneration in a cyclical mechanism involving the hydroxyl amine (1.3.2.2.).

It is shown that NBC has some activity as an antioxidant, but it is inferior to the IPPD (Section 4.5.1.2).

4.5.2 REACTIONS OF ECH WITH AMINES

As the chlorine atoms in ECH are sufficiently active to become the cross-linking points during vulcanization it thought likely that we would be able to react these reactive groups with suitable amine antioxidants and bind them to the rubber.

4.5.2.1 Reaction of ECH with IPPD Antioxidant

4.5.2.1.1 Assessment of Amount of IPPD Bound into ECH

A calibration curve was produced as described in Chapter 3, Section 3.2.1.1.1. A peak ratio at 3,380 cm^{-1} to 1600 cm^{-1} was measured for each concentration and a graph between these peak ratios and the concentration of IPPD added was drawn as shown in Fig. 4.7.

The amount of bound antioxidant was determined by measuring the peak ratio of an extracted modified film and then comparing it with the known peak ratio of the spectrum of the vulanizate containing a known concentration of IPPD.

4.5.2.1.2 Reaction of IPPD with ECH Rubber During Mixing in the Winkworth Machine

ECH (1000 gm) was mixed with IPPD (100gm) in the Winkworth machine (Section 2.2.2) at 140°C for 30 minutes

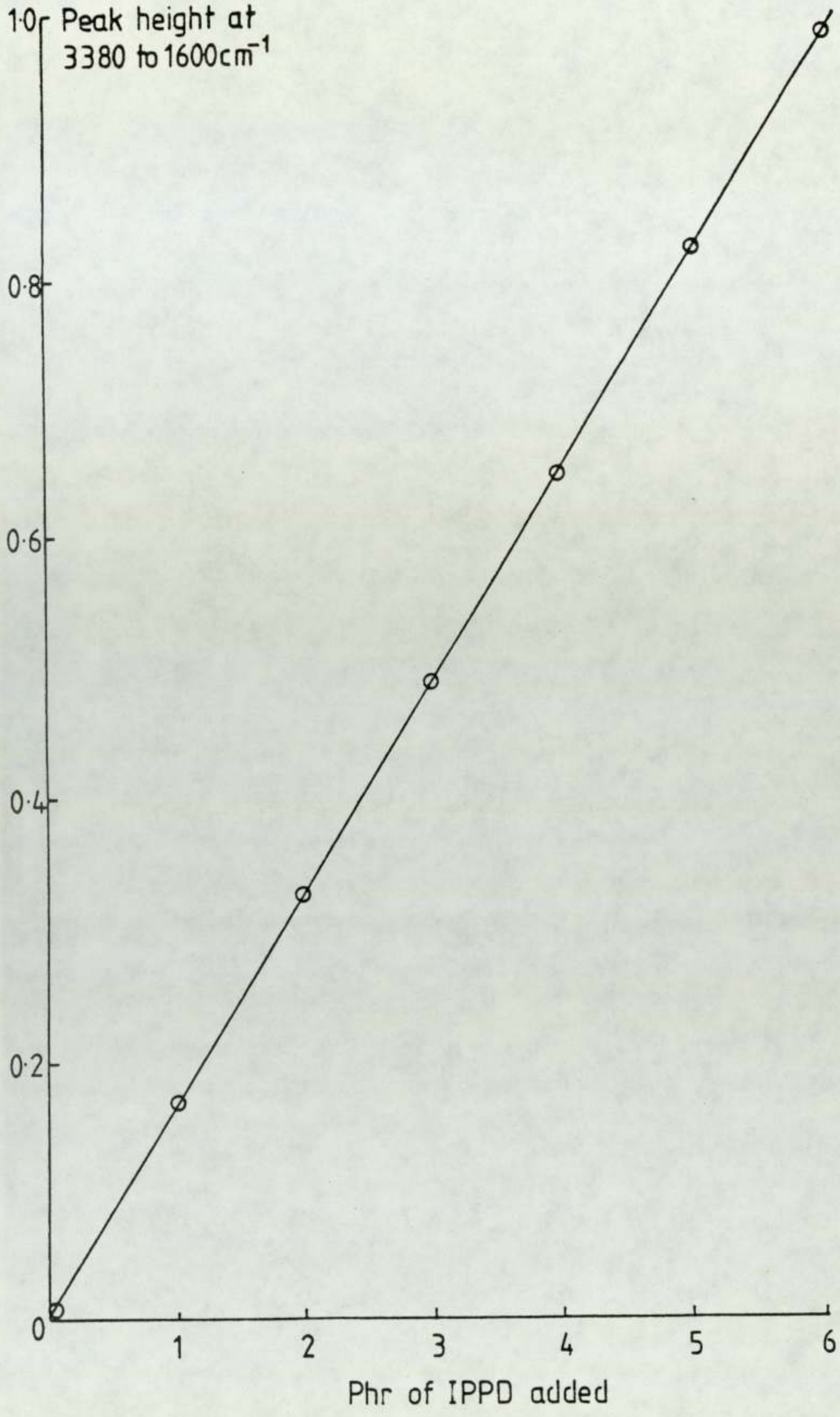


Fig 4:7

Calibration curve for IPPD with ECH homopolymer

1 hour and 2 hours respectively, and then extracted with methanol under N_2 (Section 2.3.4) to remove any free antioxidant. This was then used to prepare thin films by pressing between preheated stainless steel plates at 160°C for 15 minutes. Infra-red absorption measurements showed that IPPD had reacted with ECH. The results are shown in Table (4.5).

TABLE (4.5)

The Effect of Processing Time in the Binding of IPPD to ECH in a Winkworth Machine

Time of Mixing in Hours	phr of IPPD Bound
½ hour	2.0
1 hour	3.1
2 hours	2.5

When the mixing is carried out for one hour, 3.1 phr of IPPD is bound to the ECH which is equivalent to 0.0137 mole of IPPD to one mole of ECH rubber, i.e. one molecular of antioxidant for each 73 epichlorohydrin units.

The decrease in bound IPPD on extended mixing is attributed to mass action effect and to the degradation caused by the excessive evolution of HCl. The modified polymer was completely soluble in acetone showing that no cross-linking reaction had taken place.

4.5.2.1.3 Effect of Milling on the Reaction Between IPPD and ECH Polymer

ECH (100 gm) was mixed with IPPD (2 gms) on a two-roll mill for different times at room temperature i.e. 5, 10 and 15 minutes respectively. Unbound IPPD was removed by methanol extraction under N_2. Infra-red absorption spectra of thin films of vulcanizate prepared from the modified polymer failed to show that any combination had taken place.

4.5.2.1.4 Reaction of IPPD with ECH during Vulcanization

We have seen that amine antioxidants will combine with polychloroprene rubber (Section 3.2.1.1.3) during the vulcanization process. To assess the possibility of such a reaction with ECH, the following formulations shown in Table (4.6) were prepared.

TABLE (4.6)

Formulation for ECH to Study the Binding of IPPD to ECH During Vulcanization

	11
ECH homopolymer	100
Zinc stearate	1.0
IPPD antioxidant	2
pb3O4 (Red lead)	5
NBC	1.0
Diak No. 1	1.5

The ingredients were mixed at room temperature on a two-roll mill, vulcanized as a thin film for 40 minutes at 160°C and then extracted with acetone under N_2 to remove any unbound antioxidant. Infra-red measurements showed that 1.2 gm of IPPD was bound during vulcanization. This is equivalent to 0.005 mole, i.e. equivalent to 200 units of ECH monomer per one unit of IPPD.

4.5.2.1.5 Effect of IPPD on the Vulcanization of ECH with Diak No. 1

The formulations shown in Table (4.6) with and without Diak No. 1 were vulcanized in the Monsanto rheometer at 160°C using a range of 100 in-lb and a time span of 30 minutes. The rheograph shows that the IPPD did not act as a cross-linking agent, Fig. 4.8.

4.5.2.1.6 The Mechanism of the Reaction Between IPPD Antioxidant and ECH Rubber

In view of the presence of CH_2-Cl group in epichlorohydrin and the two secondary amino groups in IPPD, reaction between the polymer and the antioxidant can take place, in the following ways:

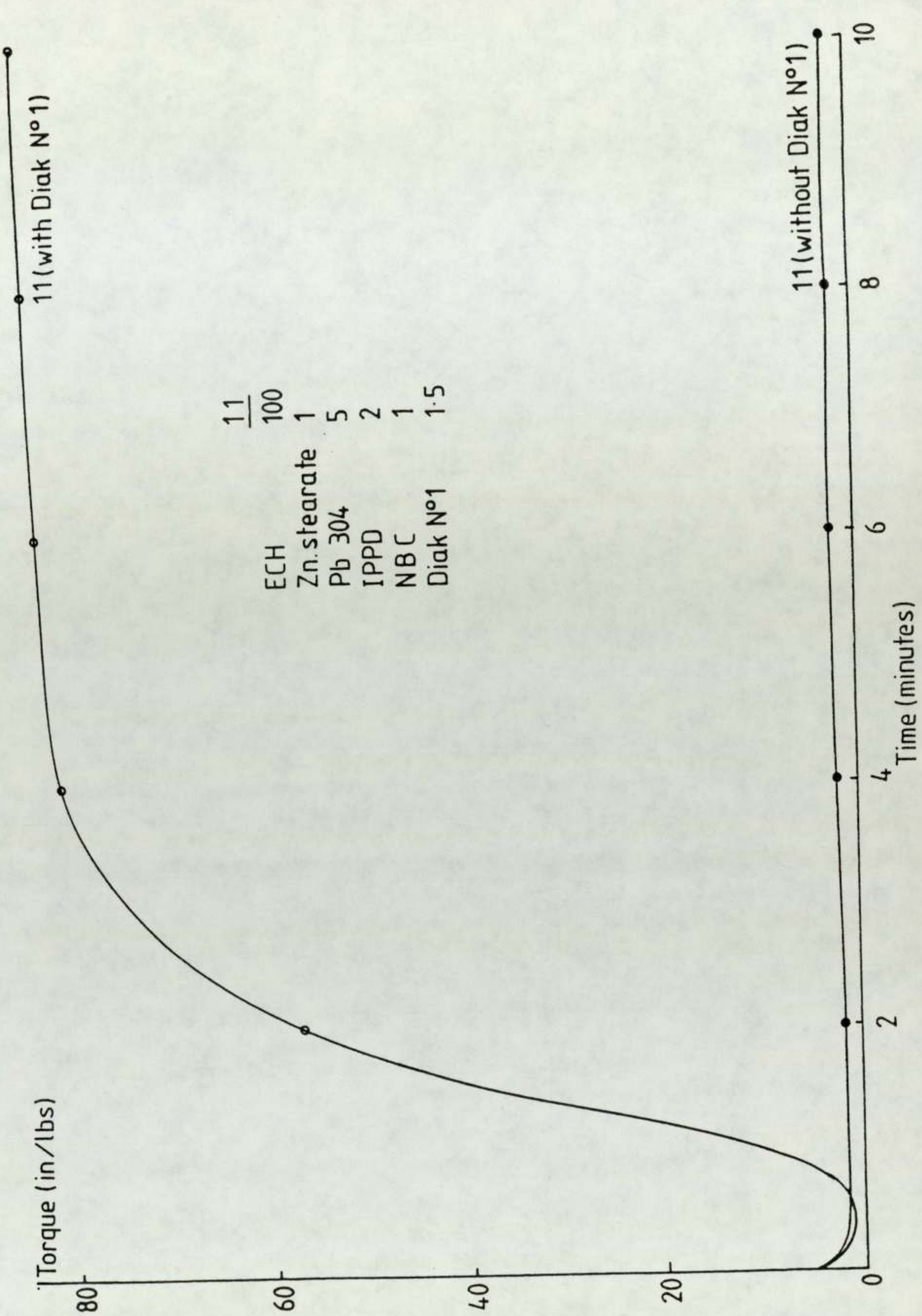
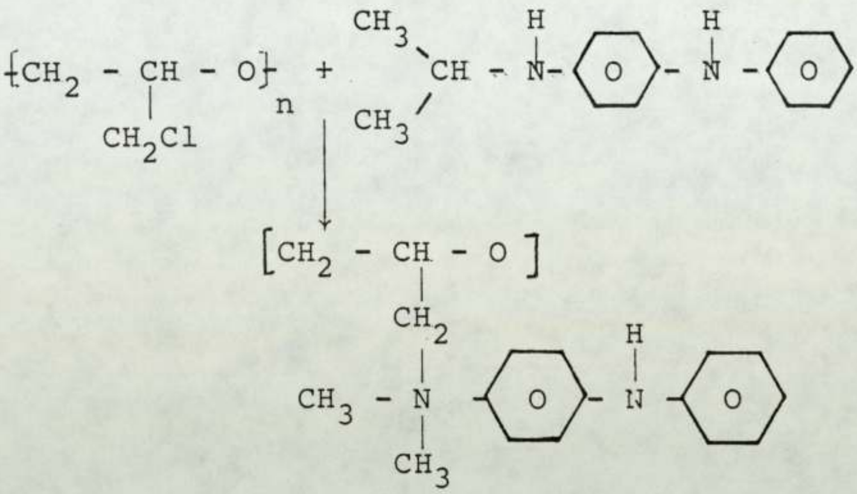


Fig 4:8

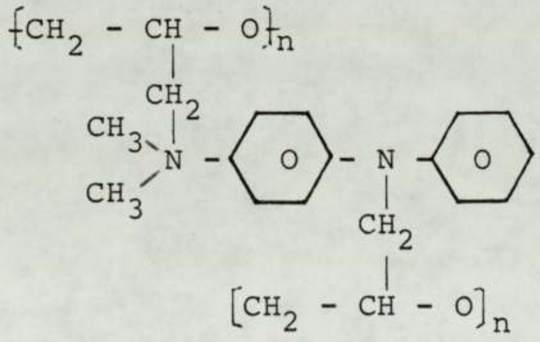
The effect of IPPD on the vulcanizing process of ECH rubber

(1) Reaction of one amino group of IPPD with a pendent chloromethyl group of ECH

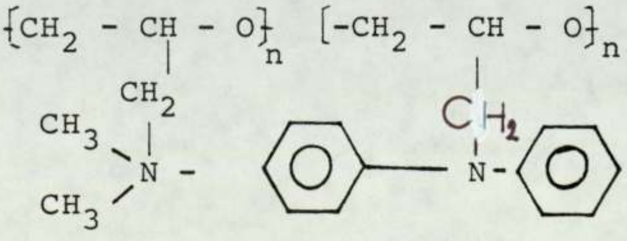


(2) Reaction of the two amino groups of the IPPD with pendent chloromethyl group of ECH to give either

(a) Cross-linking (intermolecular)



(b) Ring Formation (intramolecular)



As shown before, IPPD can be bound into ECH rubber either by mechanochemical reaction or during vulcanization (Sections 4.5.2.1.2 and 4.5.2.1.4).

The extent to which reaction (1), (2a) and (2b) take place depends upon the relative reactivities of the phenyl substituted and isopropyl substituted amino group on the IPPD.

It has been shown in Section 3.2.1.1.4 that the chlorine groups in polychloroprene rubbers react with isopropyl substituted group but not with the phenyl substituted group because of steric hinderance and the delocalisation effect of the unpaired electron in the benezene ring (the base strength).

As no cross-linking can be detected in the IPPD/ECH reaction (Section 4.5.2.1.5), reaction No. 1 must take place.

4.5.2.1.7 Effect of IPPD on the Ageing of ECH

4.5.2.1.7.1 Introduction

The degree to which the vulcanizates are protected by the bound antioxidant was assessed by extracting unbound antioxidant with an organic solvent and then comparing the physical properties before and after heating in air for both extracted and non-extracted vulcanizates.

To study the efficiency of bound IPPD antioxidants in ECH rubbers the following formulations were prepared as shown in Table (4.7).

TABLE (4.7)

Formulations for ECH used to Study the Efficiency of Bound IPPD

	12	13	14	15
Virgin ECH	100	100	33	50
Zinc stearate	1	1	1	1
FEF (carbon black)	30	30	30	30
Free IPPD	-	2	-	-
Bound IPPD (extracted)	-	-	67[x]	-
Bound IPPD (not extracted)	-	-	-	50[■]
pb3O4	5	5	5	5
Diak No. 1	1.5	1.5	1.5	1.5
Monsanto Rheometer info.				
Induction time in mins.	1.5	1.5	1.5	1.5
Torque at 90% cure	77	81	81	81
Torque at 30 mins	79	82	82	81

[x] 2 phr IPPD (3.1% bound)

[■] 2 phr IPPD (3.1% bound + 0.9% free)

The ingredients were mixed at room temperature on a two-roll mill (Section 2.2.1) for the minimum time required for a good dispersion. Sheets for UTS, hardness and for MR100 were prepared using a steam press at 160°C for 45 minutes (Section 2.3.3).

4.5.2.1.7.2 Effect of the IPPD Antioxidant on the Vulcanization Characteristics of ECH Homopolymer

The effect of free and bound IPPD on the cure of ECH with Diak No. 1 was studied in the Monsanto rheometer at 160^{o}C using a time span of 30 minutes and a torque range of 100 in-lb. The results are shown in Table (4.7).

As can be seen, the effect of IPPD on the rate and extent of vulcanization was small. This means that there was little interference between the antioxidant and the other ingredients.

Binding the IPPD to the polyepichlorohydrin before vulcanization makes no difference to the vulcanization characteristics compared with those obtained when using free IPPD.

4.5.2.1.7.3 Assessment of Effectiveness of Bound IPPD as an Antioxidant to ECH Polymer

The effect of bound or free IPPD antioxidant on the ageing processes of ECH is studied in this section. Samples for UTS, MR100 and hardness were prepared for the formulations listed in Table (4.7). The vulcanization process is carried out at 160^{o}C using a steam press for 45 minutes (Section 2.3.3).

Half of the samples are acetone extracted under a nitrogen atmosphere (Section 2.3.4) and dried under vacuum for 24 hours.

The ultimate tensile strength, modulus at 100% and 50% extensions, and the hardness of the samples were measured before ageing and after ageing at 140°C in a Wallace oven (Sections 2.4.2, 2.4.4, 2.4.3). The ageing was carried out for both acetone extracted and non-extracted samples and is shown in Figs 4.9-4.16. The physical values after different times of ageing are shown in Table (4.8).

Results and Discussion

Table (4.8) and Fig. 4.9 shows that the control lost its properties very rapidly (before and after the acetone extraction). The degradation is reduced when IPPD is present and more so after acetone extraction as is shown in Table (4.8) and Figs. 4.10, 4.11 and 4.12. These results show that IPPD is a good antioxidant to ECH homopolymer due, no doubt, to its ability to remove alkyl and alkylperoxy radicals formed during thermal oxidative degradation(144,145).

Acetone extraction of the control does not have a great effect on the degradation of ECH. There is an initial increase in theUTS before extraction, this is attributed to the presence of unreacted materials which cause post cure (e.g. unreacted Diak No. 1). Acetone extraction removes all these unreacted materials and

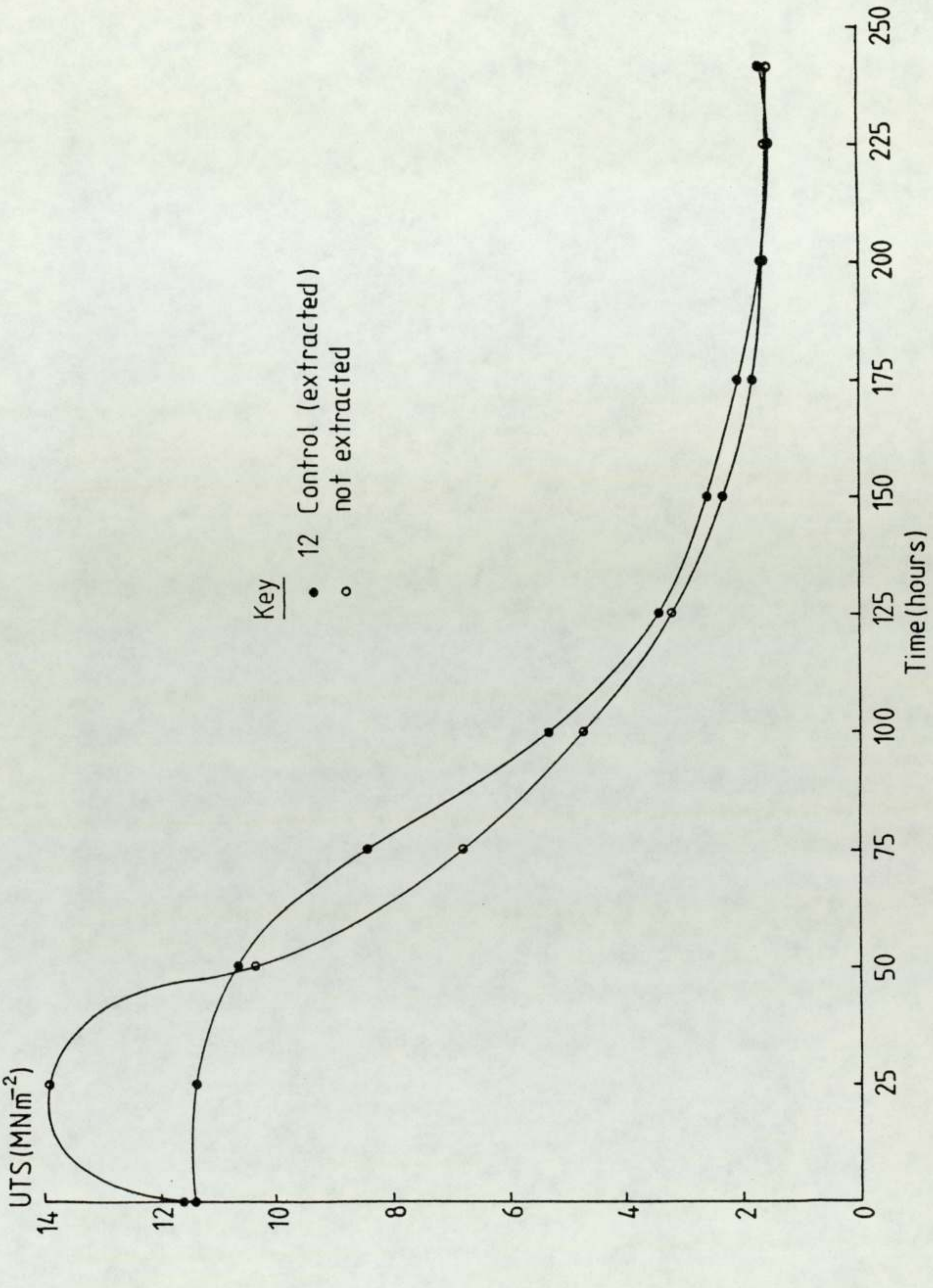


Fig 4:9

UTS change of ECH aged at 140°C before and after acetone extraction

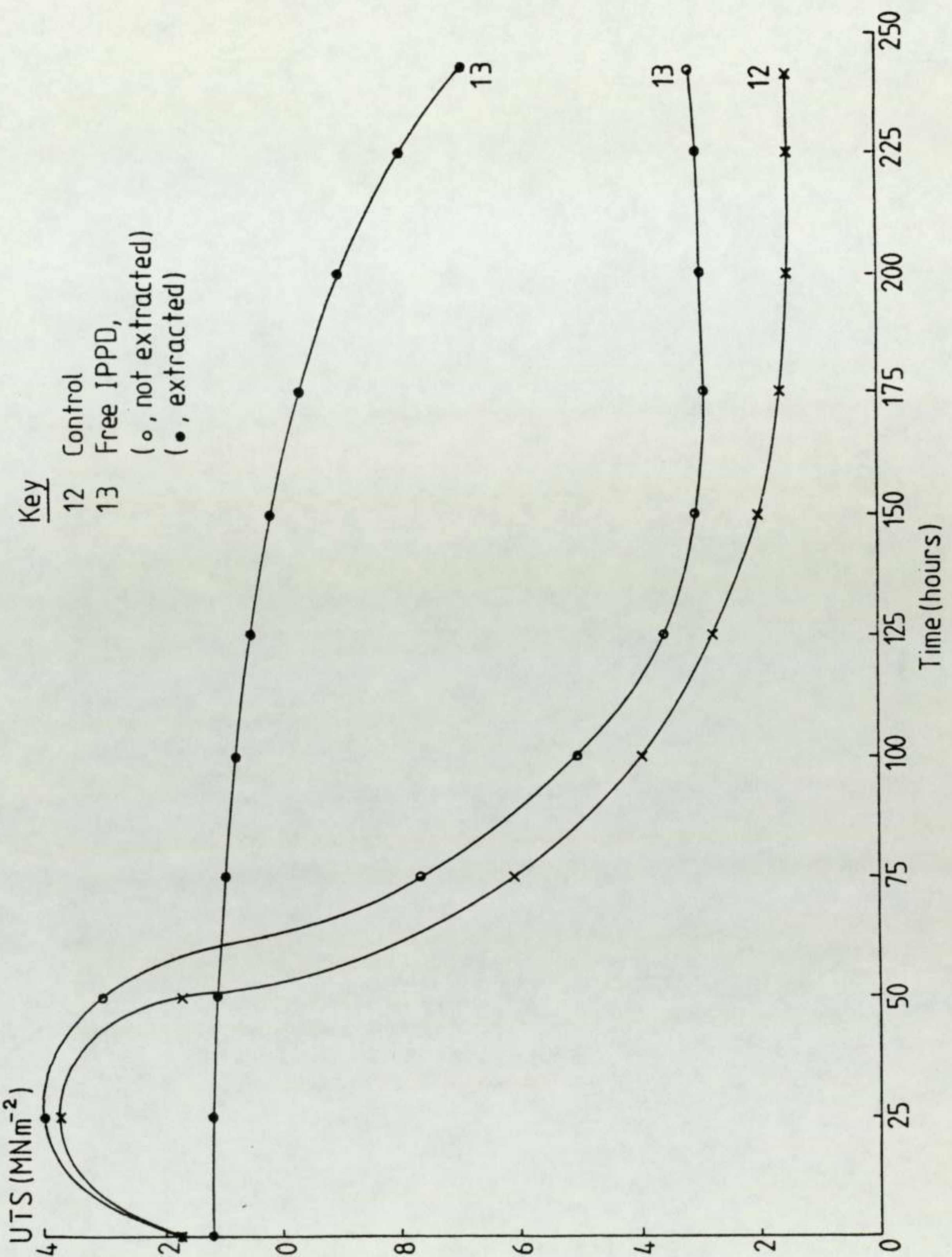
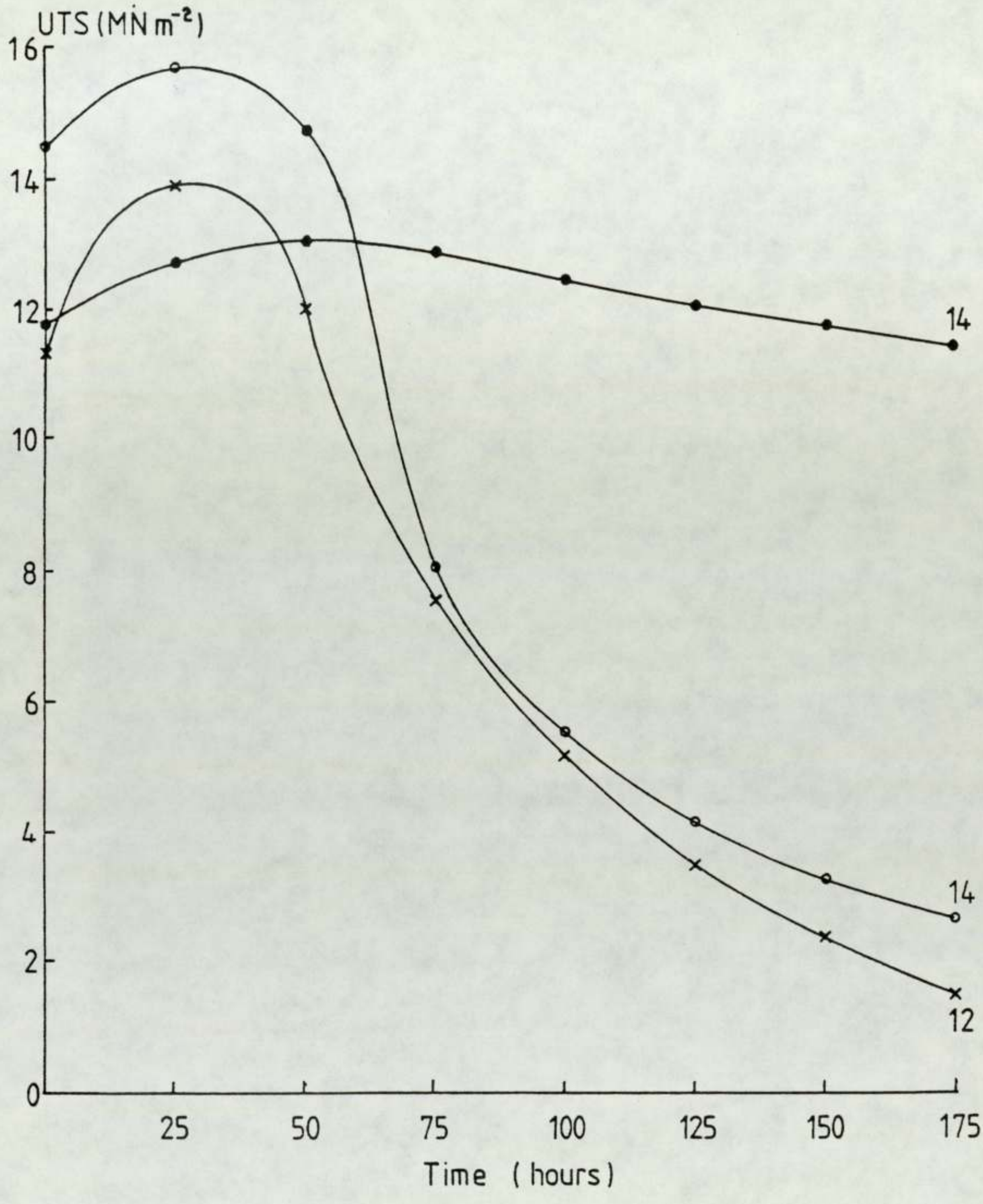


Fig 4:10

UTS change of ECH aged at 140°C before and after acetone extraction



Key

12 Control

14 Bound IPPD (ext)
(○, not extracted)
(●, extracted)

Fig 4:11 UTS change of ECH aged at 140°C before and after acetone extraction

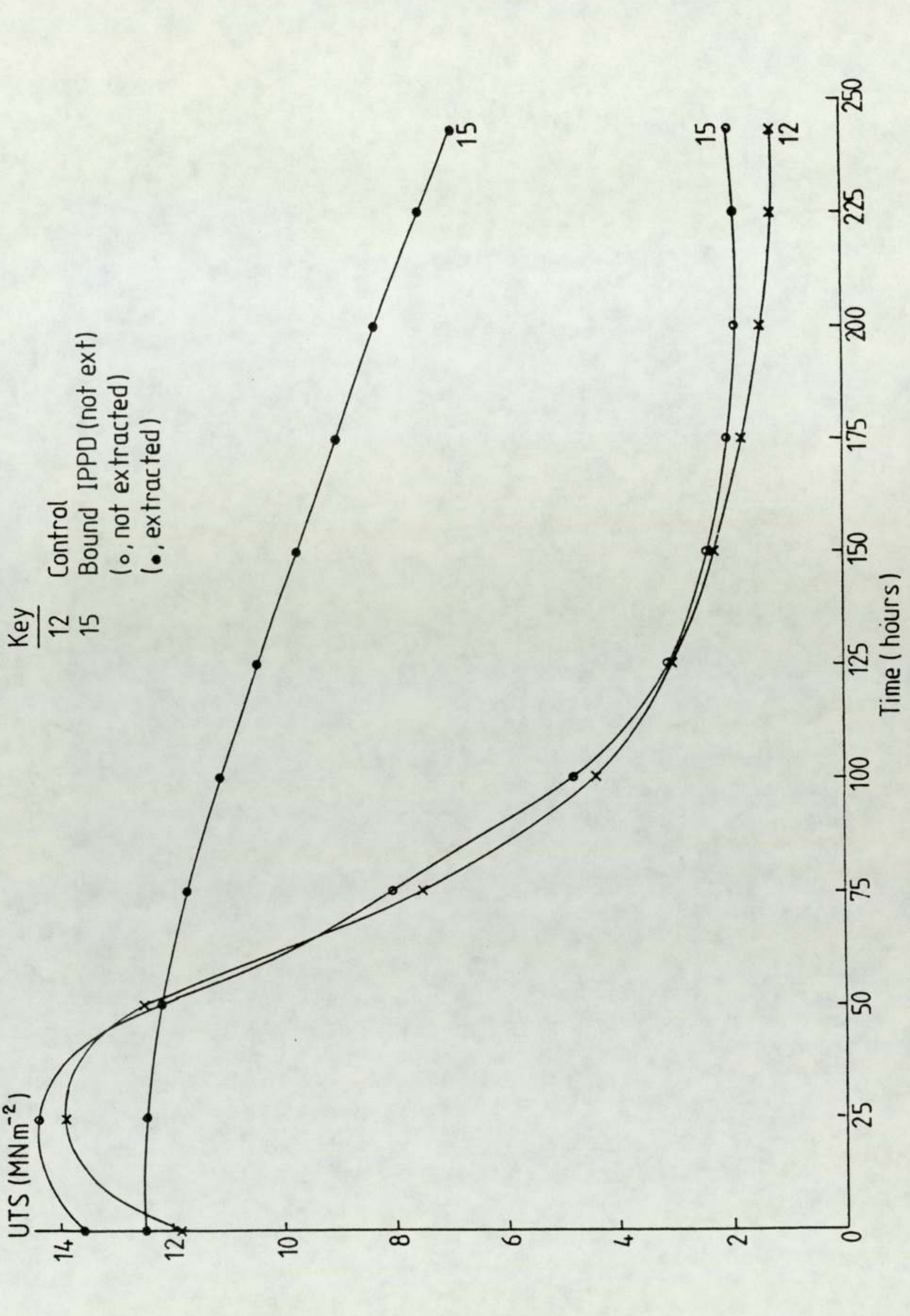
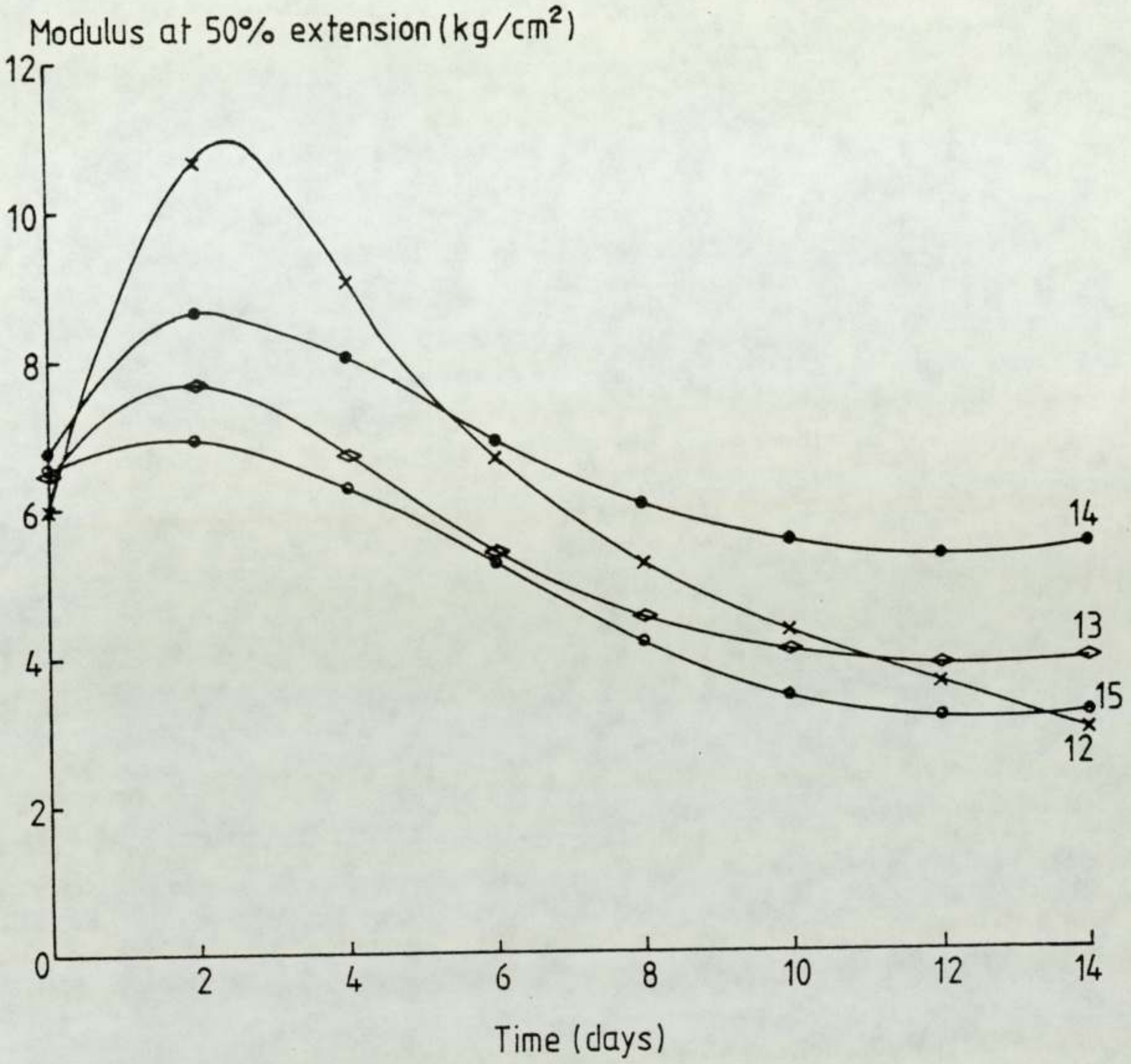


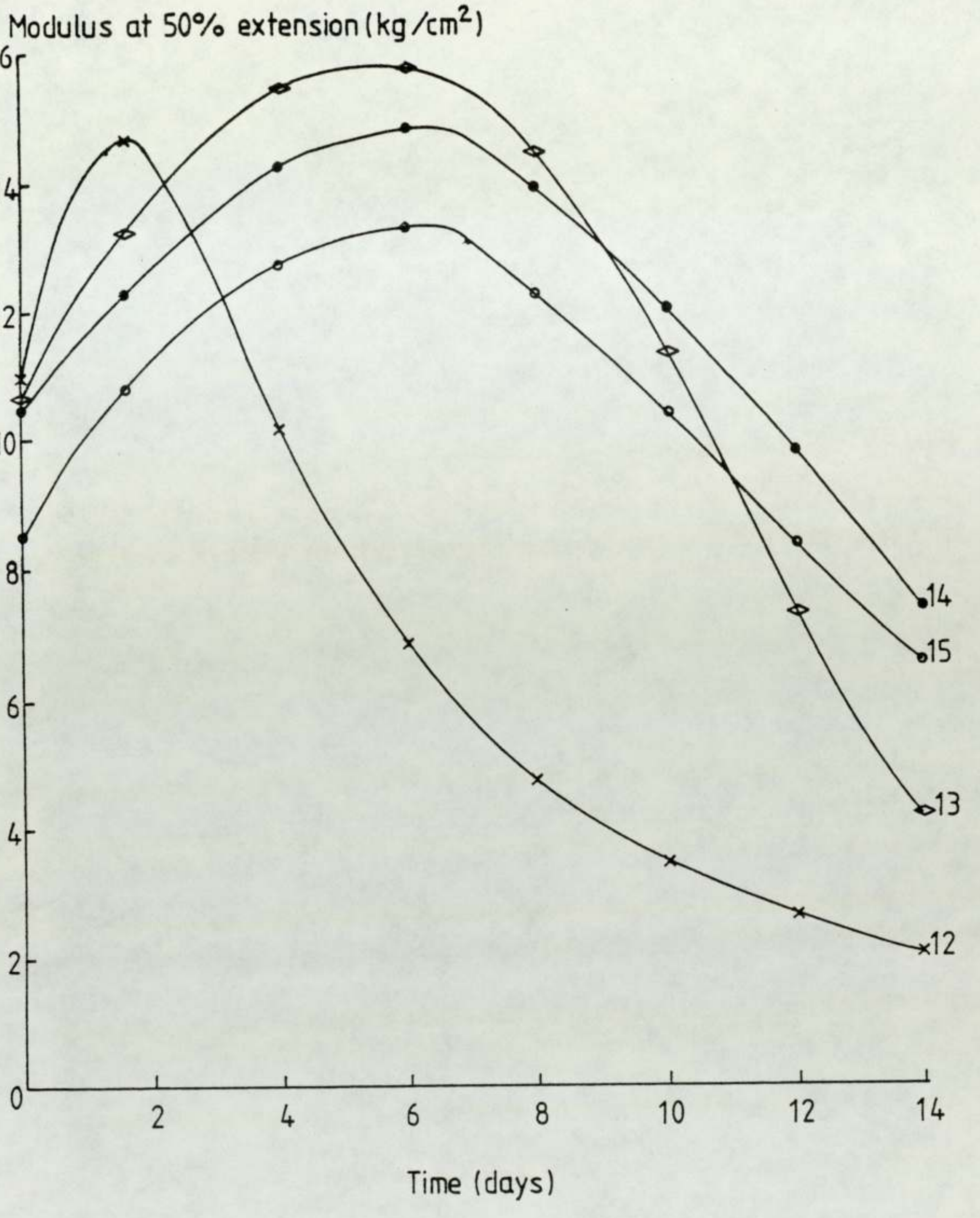
Fig 4:12
UTS change of ECH aged at 140°C before and after acetone extraction



Key

12 Control
13 Free IPPD
14 Bound IPPD (ext)
15 Bound IPPD (not ext)

Fig 4:13
MR 50 measurement of ECH aged at 140°C with or without IPPD before acetone extraction



Key

12	Control
13	Free IPPD
14	Bound IPPD (ext)
15	Bound IPPD (not ext)

Fig 4:14

MR 50 measurements of ECH aged at 140°C with and without IPPD after acetone extraction

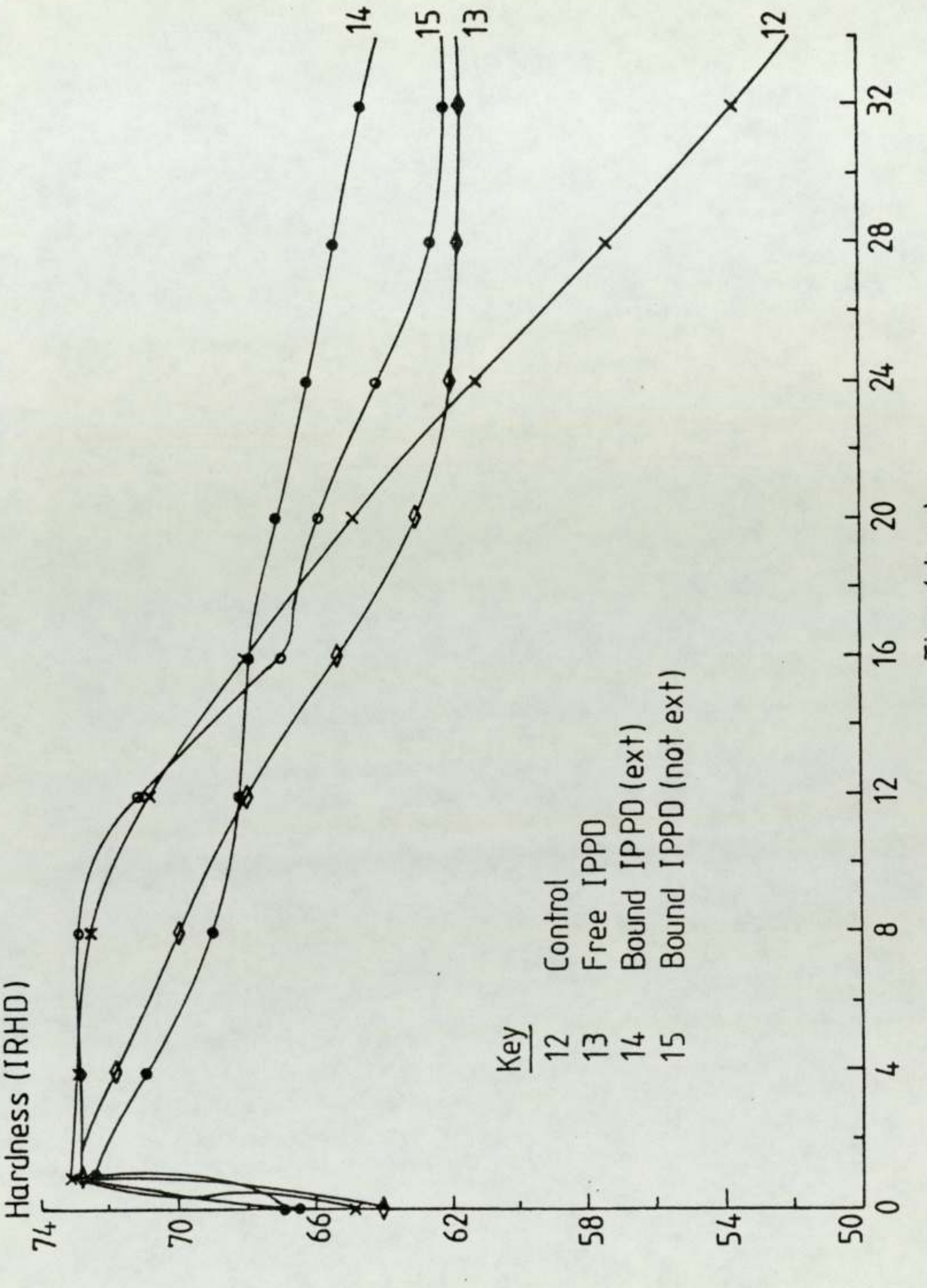


Fig 4:15

The effect of IPPD on the hardness of ECH aged at 140°C for non-extracted vulcanizates

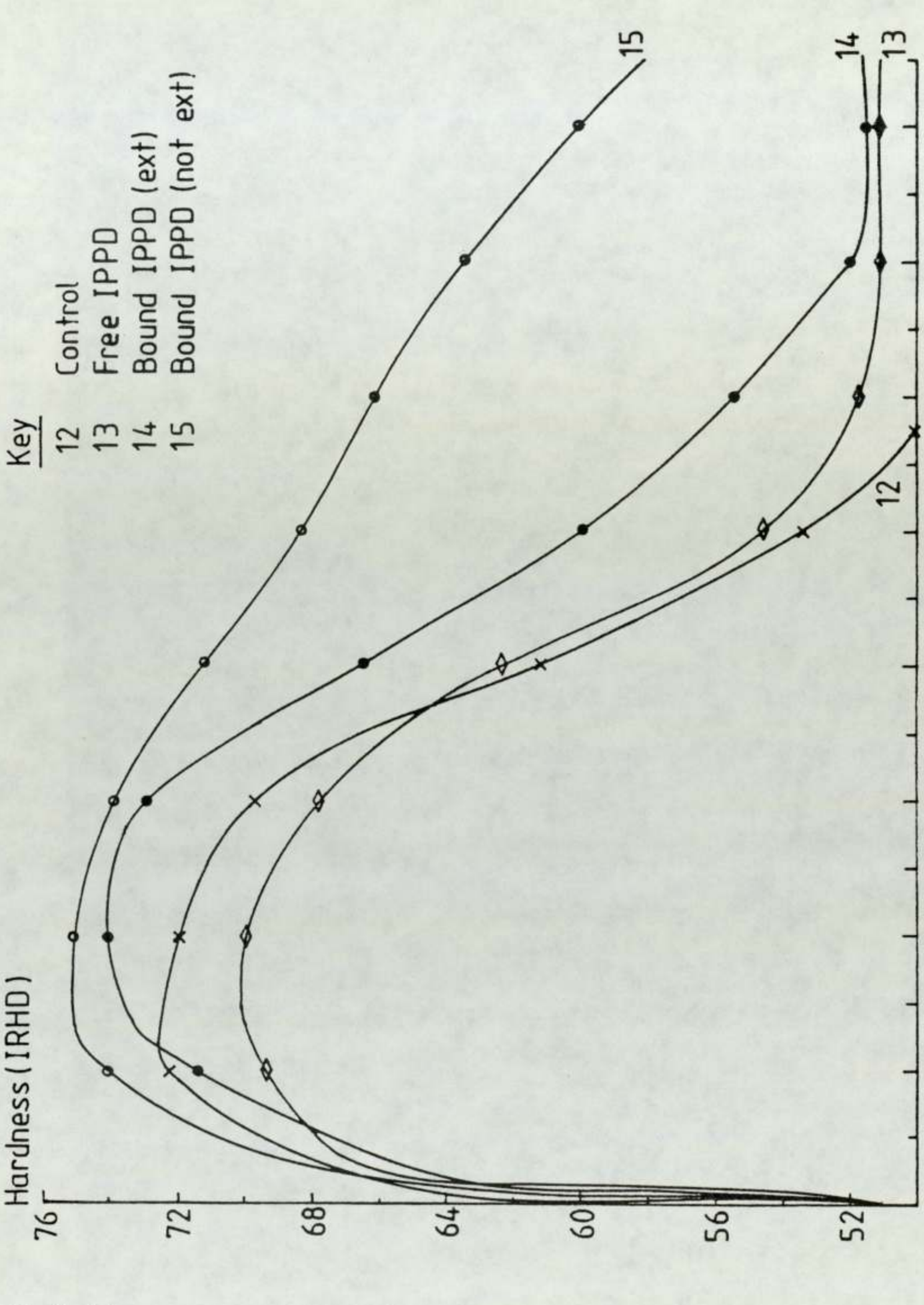


Fig 4:16

The effect of IPPD on the hardness of ECH aged at 140°C for extracted sample elminates the post cure reactions.

In the presence of IPPD (2phr free), it is found that there is a small increase in the ageing resistance (before extraction) which is increased on extraction. This is shown in Fig. 4.10 and Table (4.8). This improvement in the ageing resistance can be attributed to the removal of unreacted materials (such as the phenolic antioxidant that are added to improve the processing stability of the polymer and have been shown to be antagonistics, see Section 4.5.3.2) which inhibit the antioxidant function of IPPD. The increase in the ageing resistance of ECH after acetone extraction must be due to the fact that some of the antioxidant is bound to the rubber during the vulcanization process (Section 4.5.2.1.4).

The presence of 2 phr rubber bound antioxidant improves the ageing resistance of ECH to a small extent Table (4.8) and Fig. 4.11. After acetone extraction the improvement is much greater, Table (4.8) and Fig. 4.11. The removal of the extra network materials during the acetone extraction of the formulation containing bound IPPD, formulation No. 14 greatly improves the ageing resistance. The inactivity of antioxidant before extraction must be due to this extra network material interfereing with the antioxidant activity. The extent of protection of ECH by rubber bound antioxidant is greater than that given by the same amount of free IPPD.

When IPPD is mixed with ECH in Winkworth machine (Section 4.5.2.1.2), 3.1 gm of the added 4 gm is bound to ECH, while 0.9 gm remains as free antioxidant (as extra network material) which can be removed by acetone extraction. Therefore, formulation No. 15 in Table (4.8) contains rubber bound antioxidant in addition to free antioxidant.

The effect of such antioxidant on the oven ageing of ECH is shown in Table (4.8) and Fig. 4.12. The results show that there is little improvement in ageing resistance before extraction. On acetone extraction this ageing resistance is increased due to the removal of the extra network material.

The same result is obtained when MR50 values are measured for non-extracted and acetone extracted samples (Section 2.4.4) as is shown in Table (4.8) and Figs. 4.13 and 4.14.

The hardness results before and after ageing at 140°C are shown in Figs. 4.15 and 4.16 for both extracted and non-extracted samples. The values of hardness after 34 days of ageing at 140°C are shown in Table (4.8).

It can be seen that the presence of IPPD improves the ageing resistance of ECH before extraction i.e. both free or bound IPPD show good ageing resistance.

(TABLE 4.8)

The Effect of IPPD Bound or Added by Conventional Way on the Physical Properties of ECH after Ageing in a Wallace Oven at 140^{O}C.

	Not Extracted				Acetone Extracted			
	12	13	14	15	12	13	14	15
UTS in MNm^{-2} after 10 days of ageing	1.50	3.50	2.25	2.0	1.65	7.1	10.6	7.0
Hardness of IRHD after 34 days	52	62	62	64	-	51	52	58
MR50 in KG/cm^{2} after 14 days of ageing	3.0	4.0	5.6	3.2	2.0	4.0	7. 2	6.25

The vulcanizates with bound non-extracted IPPD (formulation 15) shows the best ageing resistance. This is due to the fact that the polymer has not been subjected to any degradation process such as may occur by mechanochemical reaction or during the extraction process before ageing.

Samples containing IPPD, 60% of which has become bound during vulcanization, proves to be almost as effective as acetone extracted IPPD bound in the Winkworth mixer. This shows that the immobilisation of IPPD by binding does not change its activity as an antioxidant in ECH polymer.

When acetone extraction is carried out there is a decrease in the hardness, Fig. 4.16 and Table (4.8), which can be attributed to the removal of the uncured rubber as well as any other extra network material. It may also be due to the swelling effect of the acetone or due to thermal oxidative degradation occurring during extraction. These factors would lead to rupture of cross-links and cause a reduction in the modulus.

4.5.2.1.7.4 The Effect of Extraction on ECH Homopolymer Before Compounding

From the previous results (4.5.2.1.7.3) it is shown that on extraction of the ECH vulcanizates the physical properties are improved. This improvement may be attributed to the following:

(1) The presence of stabilizer in the commercial ECH which is always added to increase the storage stability and compounding or due to the presence of some impurities resulting from the polymerization process.

(2) The presence of by-products, such as HCl, resulting from the vulcanization process that may lead to an acceleration in the degradation of the rubber.

In order to study these effects formulations No. 5 and 7 in Table (4.1) were prepared. Another formulations were also prepared with exactly the same ingredients except that the commercial polymer was methanol extracted under N_2 and dried before compounding.

Sheets of 0.1 cm thickness were prepared in a steam press at 160°C for 40 minutes as described in (2.3.3). Samples for stress relaxation determination were cut from the sheets using MR100 cutter.

Continuous stress relaxation (2.4.1) was carried out at 160°C in the Wallace age tester. The results are shown in Fig. 2.17. The values of log f/f^o after 400

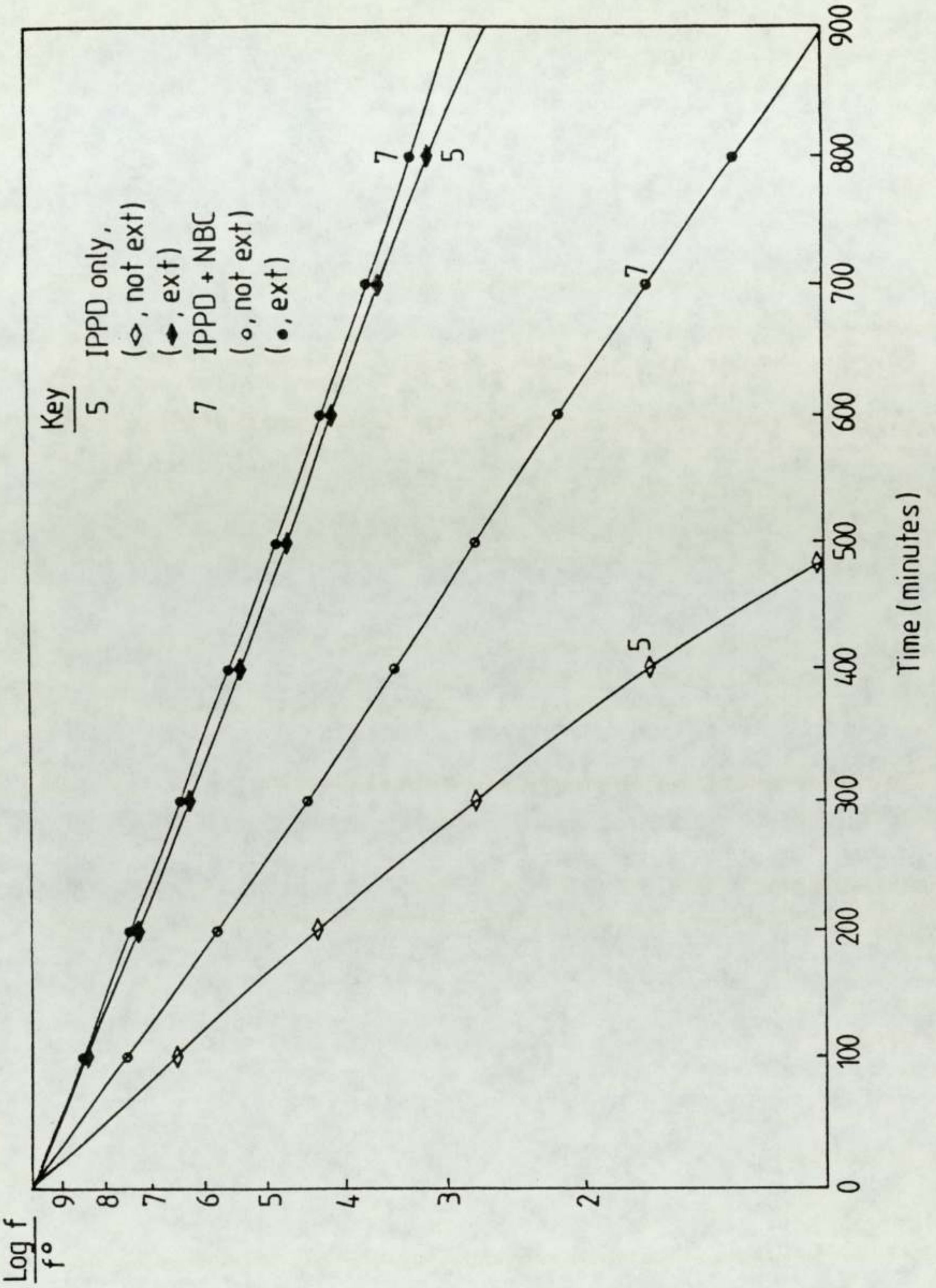


Fig 4:17

The effect of extraction on the continuous stress relaxation of ECH aged at 160°C for both extracted and non-extracted samples minutes of ageing are shown in Table (4.9)

TABLE (4.9)

The Values of Log f/f^o for ECH with IPPD Before and After Extraction the Commercial ECH Rubber

	Formulation Number	
	5	7
Not extracted	0.25	0.55
Methanol extracted	0.74	0.74

Results and Discussion

ECH rubber contains phenolic antioxidant that are added as processing stabilizers.

From Table (4.9) the following conclusions may be drawn:-

(1) NBC gives some thermal oxidative resistance to unextracted commercial ECH rubber. This is due to the ability of the NBC to destroy hydroperoxide by a catalytic process. Since it is known that the major reaction products of phenolic antioxidants added as stabilizers to the ECH are stilibene quinones and peroxydienones (1.3.2.1), these products will inhibit the NBC from being an antioxidant by preventing the initial radical generation step. These radicals, then, form a Lewis acid which destroys the hydroperoxides by

an ionic process (157,158).

(2) When the commercial ECH rubber is extracted before compounding its thermal-oxidative resistance is increased and the effectiveness of IPPD as an antioxidant is increased. This is due to the removal of the phenolic stabilizer or impurities present in the commercial ECH which are formed during the polymerization process.

(3) IPPD shows much better protection to ECH rubber after extraction (i.e. in the absence of phenolic antioxidant and the impurities) and in the absence of NBC.

(4) Before extraction NBC and IPPD have an additive effect on the thermal oxidative-degradation. But after extraction of the ECH before compounding (i.e. in the absence of phenolic antioxidant and any other impurities) the NBC has not effect at all.

The explanation for this will be discussed in Section 4.5.3.2 as it was only resolved when we carried out work with phenolic antioxidants.

4.5.2.2 Reactions of ECH with Santoflex-13

For the same reasons given in Section 3.2.1.3 which deals with the reaction of Santoflex-13 with CR type-W, an attempt was made to react this antioxidant with ECH homopolymer and so to form a rubber-bound antioxidant.

4.5.2.2.1 Proof of Absence a Cross-Linking Reaction Between Santoflex-13 and ECH Homopolymer

Attempted reaction of Santoflex-13 with ECH homopolymer, as described in Section 4.5.2.1.6, failed to produce any cross-linked insoluble material and were shown not to interfere with the vulcanization characteristics as deduced from Monsanto rheographs, Fig. 4.18. The formulations used are shown in Table (4.10). By comparison with IPPD, the phenyl substituted amino group will be unreactive and the only way that Santoflex-13 will react with ECH is through the amino group attached to alkyl group.

TABLE (4.10)

Formulations used to study the effect of Santoflex-13 on the Vulcanization Characteristics of ECH Homopolymer

	16	17
ECH	100	100
Zinc Stearate	1	1
FEF	30	30
pb304	5	5
Santoflex-13	-	2
Diak No. 1	1.5	–

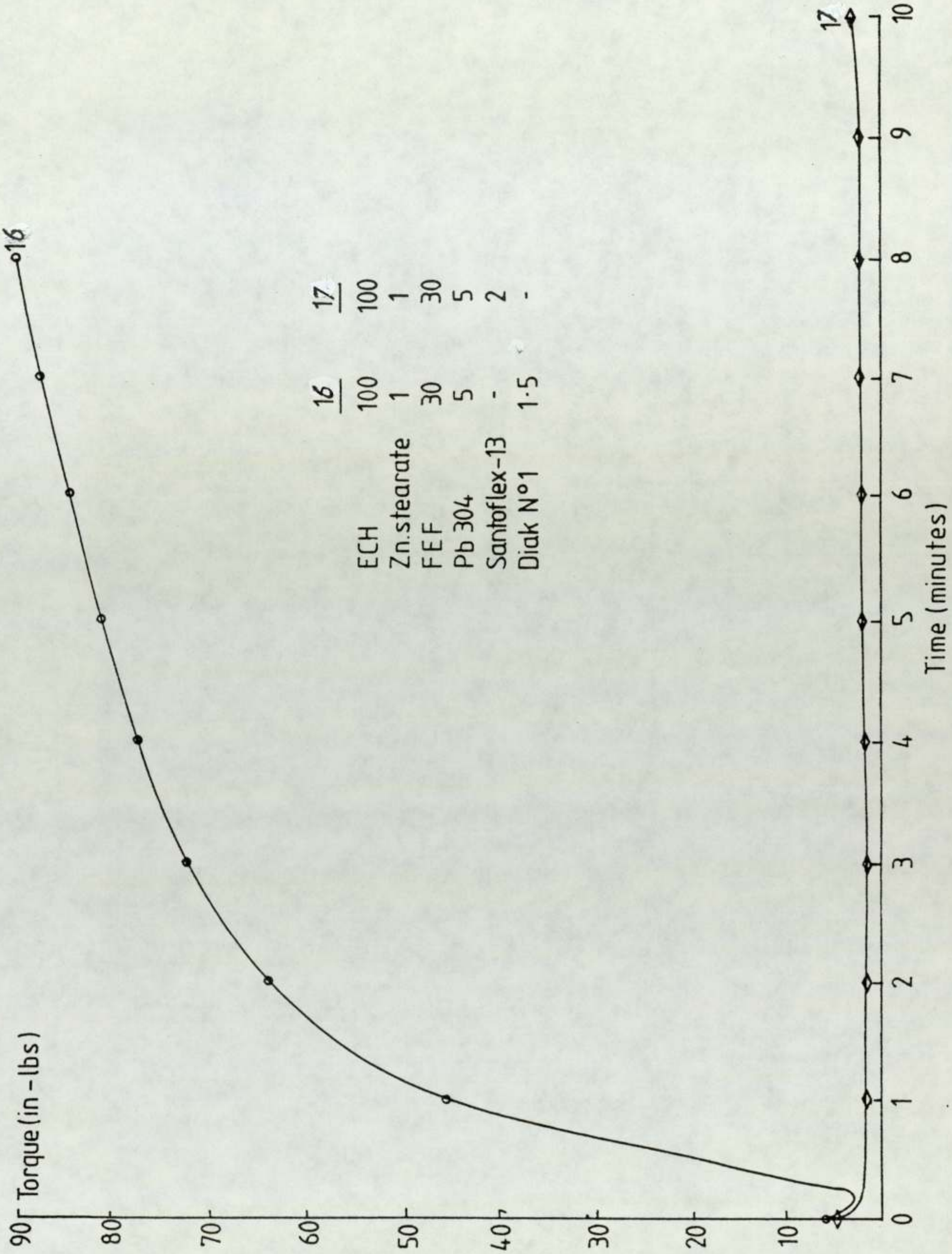


Fig 4:18
The effect of Santoflex-13 on the vulcanization characteristics of ECH

4.5.2.2.2 Assessment of Amount of Santoflex-13 Bound into ECH

As in Section 4.5.2.1.1 a calibration curve was produced between the peak ratio at 3,400 cm^{-1} to 2,120 cm^{-1} for different concentrations of Santoflex-13 in ECH. This curve was then used to determine the amount of bound antioxidant, Fig. 4.19.

4.5.2.2.3 Reaction of ECH Rubber with Santoflex-13 in the Winkworth Machine

ECH (1000 gm) was mixed with Santoflex-13 (100 gm) at 100°C for one hour (2.2.2). It was then methanol extracted under N_2 (2.3.4) to remove any free antioxidant. The mixture was then dried. Infra-red analysis was then carried out on a thin film of the modified rubber and this showed that the amount of bound antioxidant was 3.75 gm of Santoflex-13 combined with 96.25 gm of the ECH, i.e. a mole ratio of 1:75 Santoflex-13:ECH.

4.5.2.2.4 Reaction of ECH with Santoflex-13 in Torque Rheometer

ECH (35 gm) and Santoflex-13 (3.5 gm) were mixed in the torque rheometer for 15 minutes at 100°C. Infra-red analysis after methanol extraction showed that there was the same extent of reaction as occurred in the

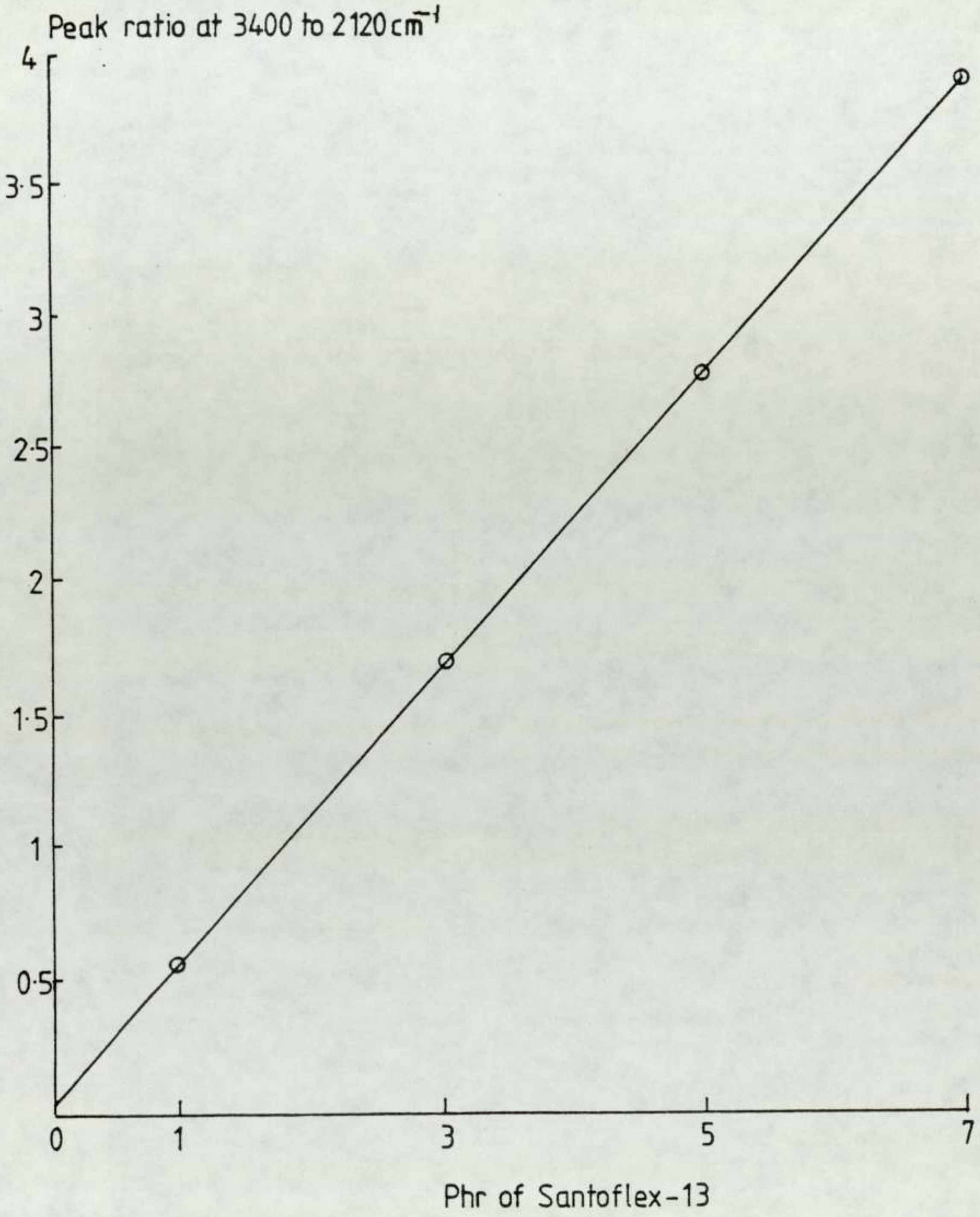


Fig 4:19

Calibration curve for Santoflex-13 with ECH

Winkworth mixer (4.5.2.2.3). The reaction times were varied from 15 minutes to one hour and the reaction temperature for a standard reaction time of 30 minutes, was varied from 60^{O}C to 120^{O}C. The amount of Santoflex-13 combined was the same in all cases.

4.5.2.2.5 Reaction of Santoflex-13 with ECH during Vulcanization

In order to investigate whether Santoflex-13 becomes bound to ECH during the vulcanization process, the formulation shown in Table (4.11) was vulcanized for 40 minutes at 160^{O}C in the form of a thin film 0.02 cm thick, and subjected to infra-red analysis after acetone extraction.

TABLE (4.11)

Formulation used to Determine the Amount of Santoflex-13 Combined to ECH During Vulcanization Process

	18
ECH	100
Zinc Stearate	1
Santoflex-13	2
Diak No. 1	1.5

Comparison with the peak ratio in Fig. 4.19, the calibration curve, showed that 1.2 phr of Santoflex-13 was bound to ECH during the vulcanization process. This amount corresponds to 60% of the original amount of added antioxidant and it is equivalent to 1:238 of Santoflex-13 :ECH units.

4.5.2.2.6 The Effect of Santoflex-13 on Vuclanization Characteristics of ECH Homopolymer

In order to study the effect of Santoflex-13 antioxidant on the vulcanization characteristics of ECH, the formulations shown in Table (4.12) were mixed on a two-roll mill and the vulcanization characteristics tested on the Monsanto rheometer at 160°C using a torque range of 100 in-lb and a time span of 30 minutes. The results are shown in Table (4.12)

TABLE (4.12)

Formulations of ECH with Santoflex-13

	Formulation Number				
	19	20	21	22	23
ECH Virgin	100	100	100	100	46.7
ECH bound with Santoflex-13 and acetone extracted	-	-	-	-	53.33
FEF carbon black	30	30	30	30	30
Zinc stearate	1	1	1	1	1
pb3O4	5	5	5	5	5
Diak No.1	1.5	1.5	1.5	1.5	1.5
Santoflex-13 (free)	-	-	2	2	-
NBC	-	1.0	-	1.0	-
Induction time (min)	2.0	2.0	2.0	2.0	2.0
Torque at 90% vulcanization	100	93	93	88	93

From Table (4.12) it can be seen that the Santoflex-13 causes a decrease in the modulus of the vulcanizate but this is not great enough to be of significance. This decrease in modulus is attributed to the decrease in the cross-linking density due to the removal of some of the chlorine groups through the reaction with ECH.

Binding the Santoflex-13 to ECH before vulcanization makes no difference to the vulcanization characteristics compared with those obtained when using free antioxidants.

4.5.2.2.7 Assessment of Effectiveness of Santoflex-13 as an Antioxidant on ECH Homopolymer

The effectiveness of Santoflex-13 as an antioxidant in ECH homopolymer was studied by using Stress-relaxation techniques (2.4.1.)

4.5.2.2.7.1 Stress Relaxation

Thin sheets, 0.1 cm thickness, were prepared from formulations shown in Table (4.12) by vulcanizing at 160°C for 40 minutes. These sheets were used to prepare samples for stress relaxation (3.2.1.1.7.1). Half of the samples were acetone extracted under N_2 (2.3.4).

Continuous stress relaxation was carried out at 160°C in the Wallace age tester for both before and after the acetone extraction. The results are shown in Fig. 4.20 and Fig. 4. 21, and in Table (4.13).

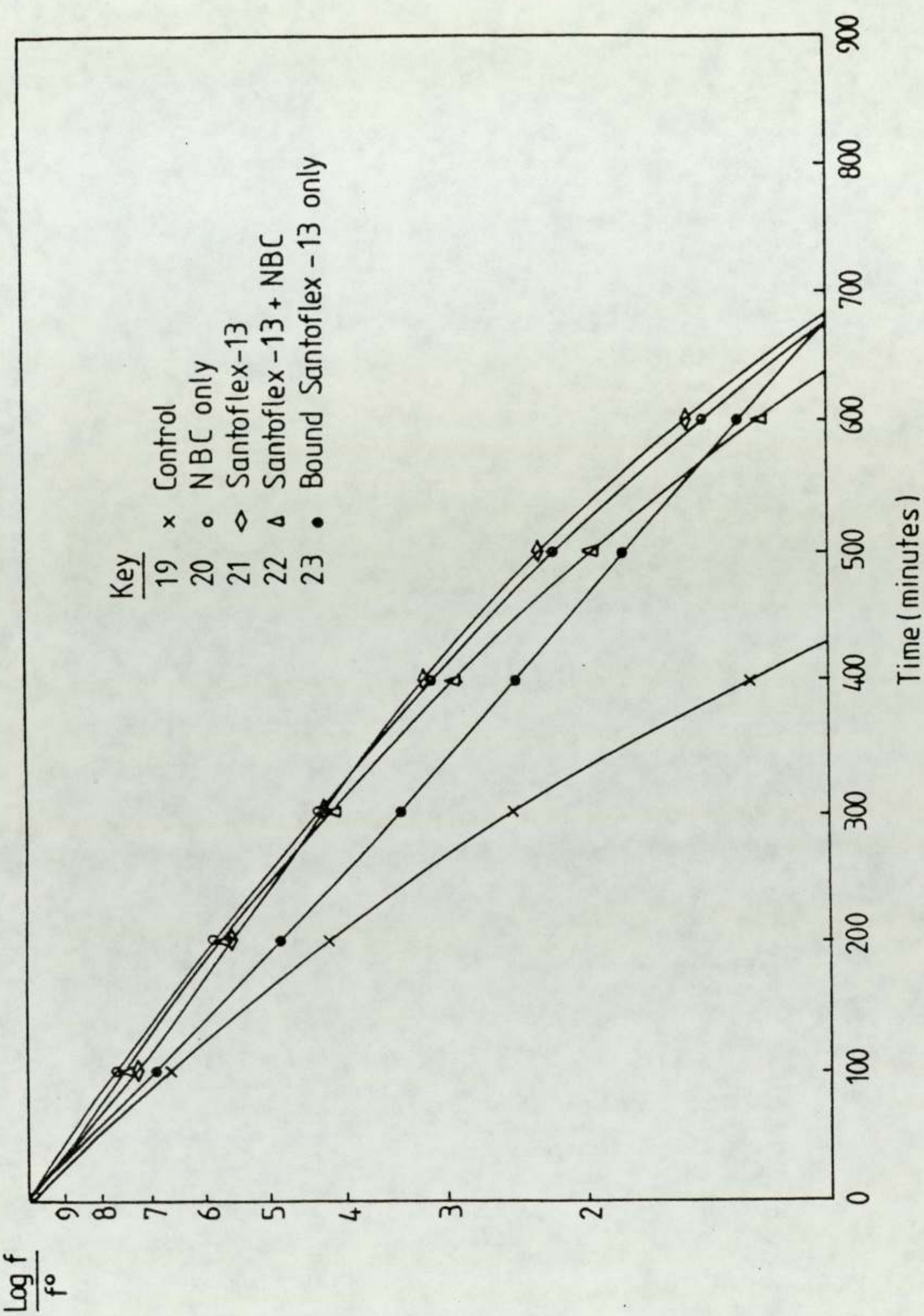


Fig 4:20

The effect of Santoflex-13 on the continuous stress relaxation of ECH aged at 160°C, not extracted

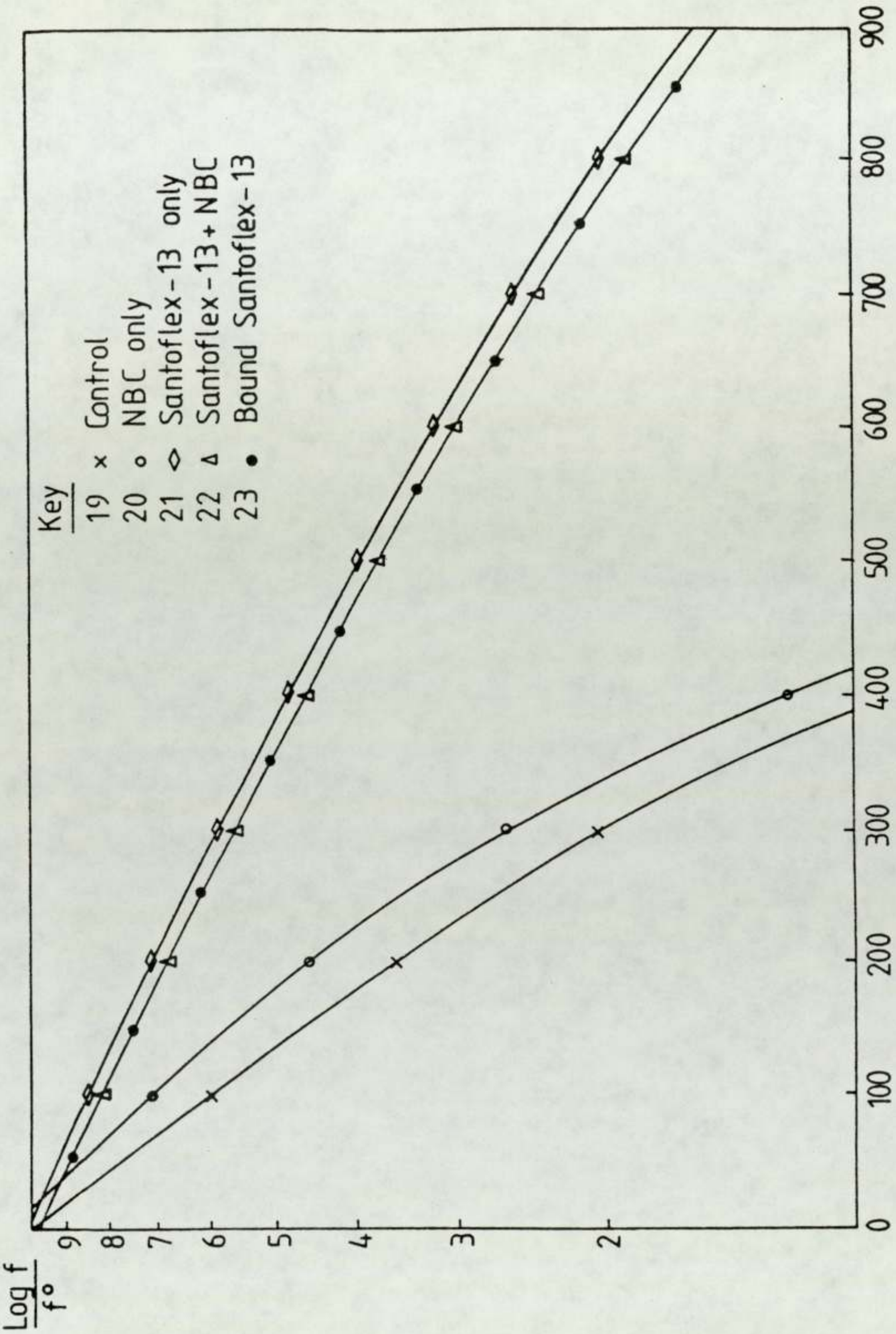


Fig 4:21

The effect of Santoflex-13 on the stress relaxation of ECH aged at 160°C after acetone extraction

TABLE (4.13)

The Values of Log f/f^{o} for ECH with Santoflex-13

After 400 Minutes of Ageing at 160°C

	Formulation Number				
	19	20	21	22	23
Not extracted	0.01	0.50	0.51	0.48	0.40
Acetone extracted	melted	0.08	0.68	0.65	0.65

Results and Discussion

It can be concluded from Table (4.13) that:-

(1) The control lost all its properties after 400 minutes of ageing before and after acetone extraction. This is shown by its autoxidation curve in Fig. 4.20. This drastic deterioration is due to the absence of any antioxidant.

(2) NBC gives some protection to ECH before extraction. After extraction, the samples lost all their resistance due to the complete removal of the NBC.

(3) Santoflex-13 is a good antioxidant for ECH when judged by stress relaxation at 160°C both before and after the acetone extraction.

(4) The good antioxidant activity of Santoflex-13, even after the acetone extraction, shows that some of the added antioxidant combines with the rubber.

(5) The Santoflex-13 bound to ECH before vulcanization (Formulation No. 23 in Table (4.13)) has the same effect on the ECH as that with formulation No. 22. Therefore, the ECH Santoflex-13 bound antioxidant shows a very good antioxidant activity on ECH homopolymer.

(6) There are always improvements in the activity of Santoflex-13 (free or bound) as an antioxidant on acetone extraction. This is attributed to the presence of acetone-soluble antagonistic extra network material e.g. phenolic antioxidant in the commercial polymer (See Section 4.5.3.2).

4.5.2.2.7.2 Oil Ageing

Many rubber articles come into contact with organic liquids or water. This leads to either an absorption process or the leaching out of the plastizers and other soluble constituents (See Section 2.4.7). These may be associated with chemical changes because rubber in the swollen state is more prone to oxidation. When oils come into contact with rubbers they often swell or lose their physical properties.

There is a specific relationship between the chemical composition of a rubber and the chemical composition of oil being considered. The closer these two compositions are to each other, the more effect there is of the oil on the rubber(153). For instance, the polar rubbers are badly swollen by polar oils, while they are virtually unaffected by the non-polar paraffinic oils.

The polarity of hydrocarbon oils is dependent upon their aromaticity. This is usually expressed in terms of the aniline point i.e. the temperature at which aniline become missible with the oil.

An oil with a low aniline point (e.g. ASTM oil No. 3) is more polar or aromatic and swells ECH rubber to greater extent than an oil with a high aniline point, e.g. ASTM oil No. 1.

In order to study the effect of Santoflex-13 (free or bound) on the oil-ageing of ECH rubber, the formulations shown in Table (4.14) were mixed on a two-roll mill at room temperature.

TABLE (4.14)

Formulations used for Oil-Ageing of ECH Rubber in the Presence of Santoflex-13 (free of bound)

	Formulation Number		
	24	25	26
ECH	100	100	46.7
ECH/Santoflex-13 (ext)	-	-	53.3
Zinc stearate	1	1	1
FEF	40	40	40
pb3O4	5	5	5
Free Santoflex-13	-	2	-
Diak No. 1	1.5	1.5	1.5

4.5.2.2.7.2.1 Determination of the Swelling Changed by ASTM Oil Nos. 1 and 3

Sheets of 0.2 cm thickness were prepared from formulation 24 (Table 4.13) in an induction heated press and vulcanised for 40 minutes at 160°C. Dumbell shaped test pieces were cut from the sheets using a dumbell cutter (BS No 5214 Part I, 1975).

For swelling determinations the samples were accurately weighed and immersed in 150 ml of ASTM oil at 150°C, in separate beakers. The weights of the samples were measured at different intervals of time, after drying them on filter paper, and the percentage increase or decrease in weight with time recorded. The results are shown in Fig. 4.22 and Table (4.15).

Results and Discussion

The specification of ASTM oils No. 1 and 3 respectively are shown in Section 2.4.7. From Table(4.15) it can be seen that ECH rubber is quite resistant to ASTM oil No. 1 and shows a decrease in weight due to the leaching out of soluble material, Fig. (4.22).

ASTM oil No. 3 which is more polar than ASTM oil No.1, causes substantial swelling of ECH as shown in Fig. 4.22 and Table (4.15).

TABLE (4.15)

The Percentage Change in Weight of ECH

Immersed in ASTM Oil Nos. 1 and 3

	In ASTM Oil No. 1						In ASTM Oil No. 3					
	Time of Ageing in days											
	1.8	5	6	7	8.3	11.3	1.8	5	6	7	8.3	11.3
Change in weight	-0.04	-0.06	-0.06	-0.07	-0.08	-0.11	0.15	0.50	0.51	0.53	0.54	0.58
% Change in weight	-0.7%	-1%	-1.1%	-1.4%	-1.4%	-2%	7.8%	7.9%	8.1%	8.3%	8.3%	9.1%

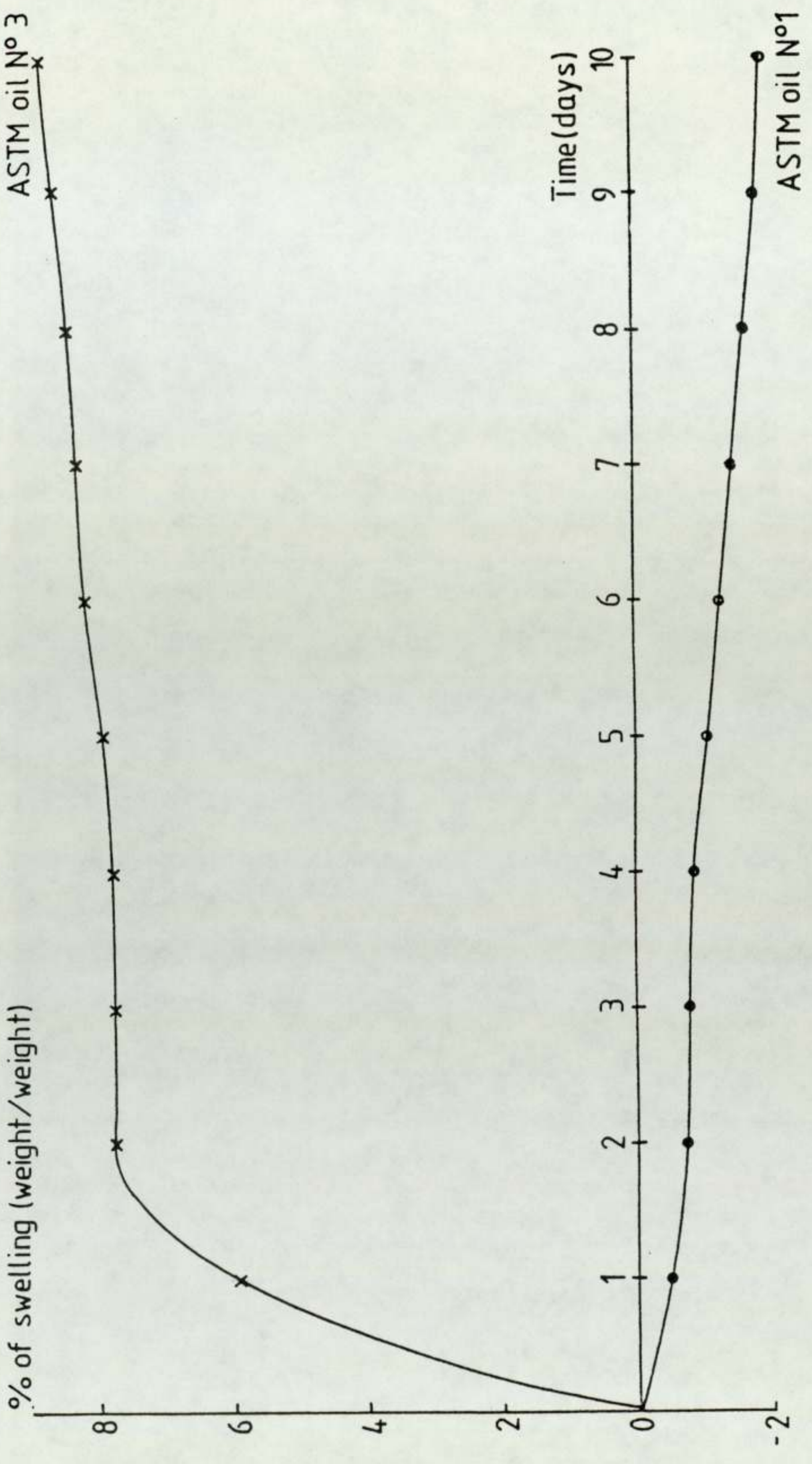


Fig 4: 22

% of swelling of ECH rubber in ASTM oil N° 3 and N° 1 at 150°C

4.5.2.2.7.2.2 Ultimate Tensile Strength and Hardness Ageing in ASTM Oils

Samples were prepared for UTS and hardness from the formulations shown in Table (4.14) by vulcanizing at $160^{\circ}C$ for 40 minutes as described in 2.4.2 and 2.4.3 respectively.

Ageing was carried out at $150^{\circ}C$ on samples immersed in ASTM oil Nos. 1 and 3 respectively. The changes in the UTS and the hardness values with ageing time during the period of 13 days are shown in Figs. 4.23, 4.24, 4.25 and 4.26 respectively.

Results and Discussion

ASTM Oil No. 1

This oil of low aromaticity (e.g. high aniline point) does not swell the ECH rubber but it does leach out soluble materials, Fig. 4.22.

(1) Ultimate Tensile Strength

The control vulcanizate containing no added antioxidant suffered a 50% loss in UTS after 6 days. The samples containing the free Santoflex-13 or the bound Santoflex-13 lasted 11 and 12 days respectively, see Fig. 4.23. The fact that there is little difference between the vulcanizates containing free and bound Santoflex-13 antioxidant is probably because some of

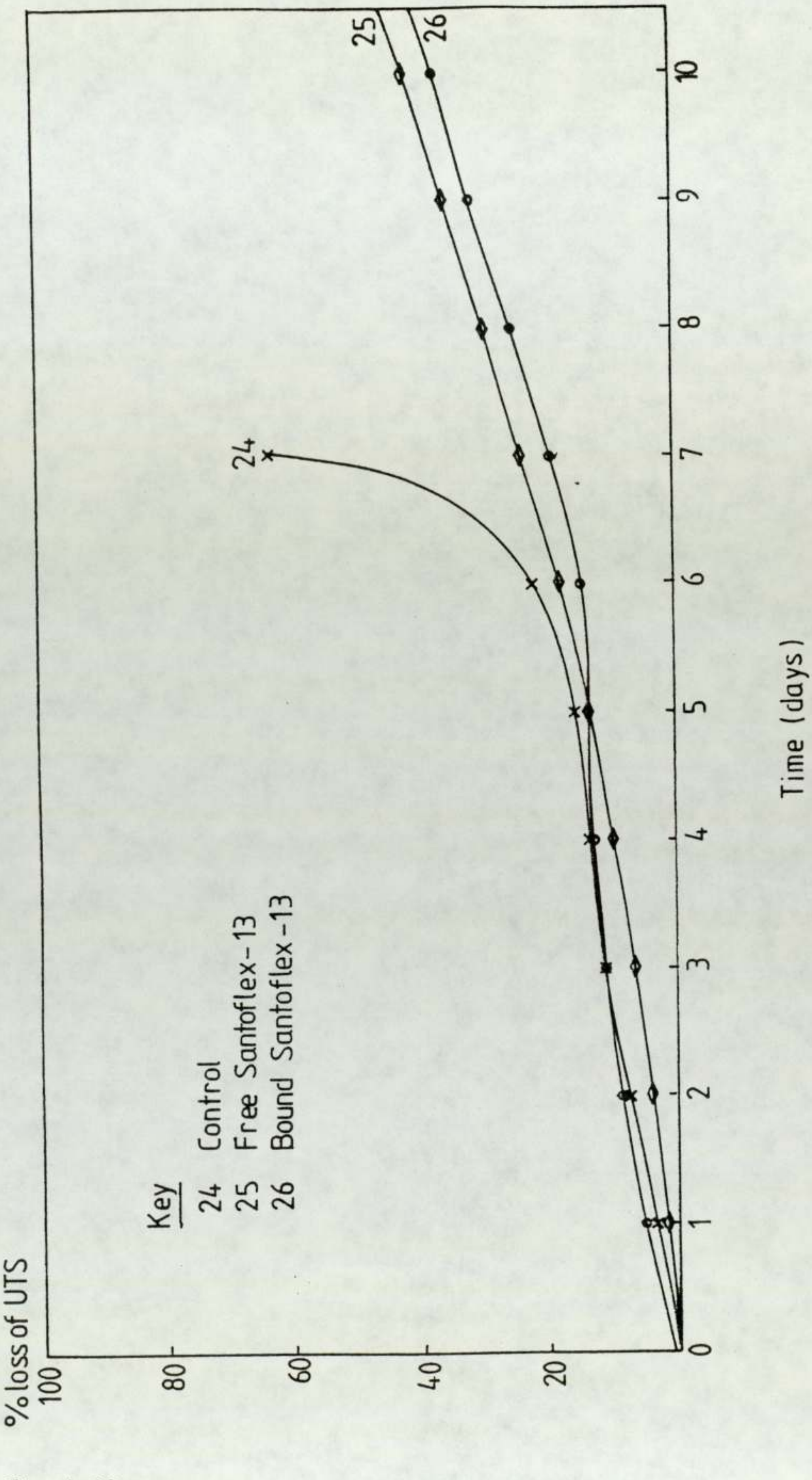


Fig 4:23

UTS oil ageing of ECH aged at 150°C in ASTM oil N°1

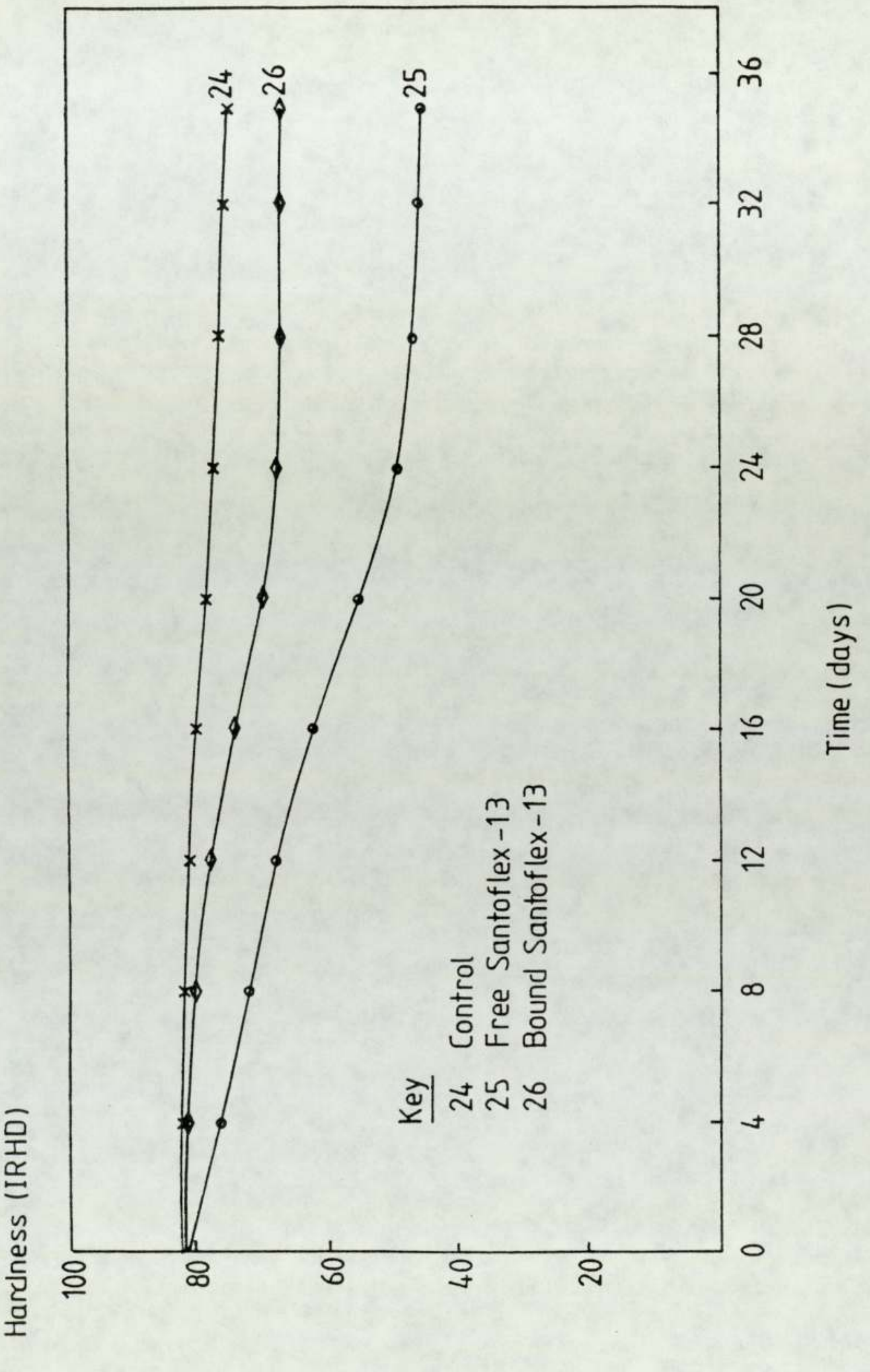


Fig 4:24

The effect of Santoflex-13 on the hardness of ECH in ASTM oil N°1 aged at 150°C

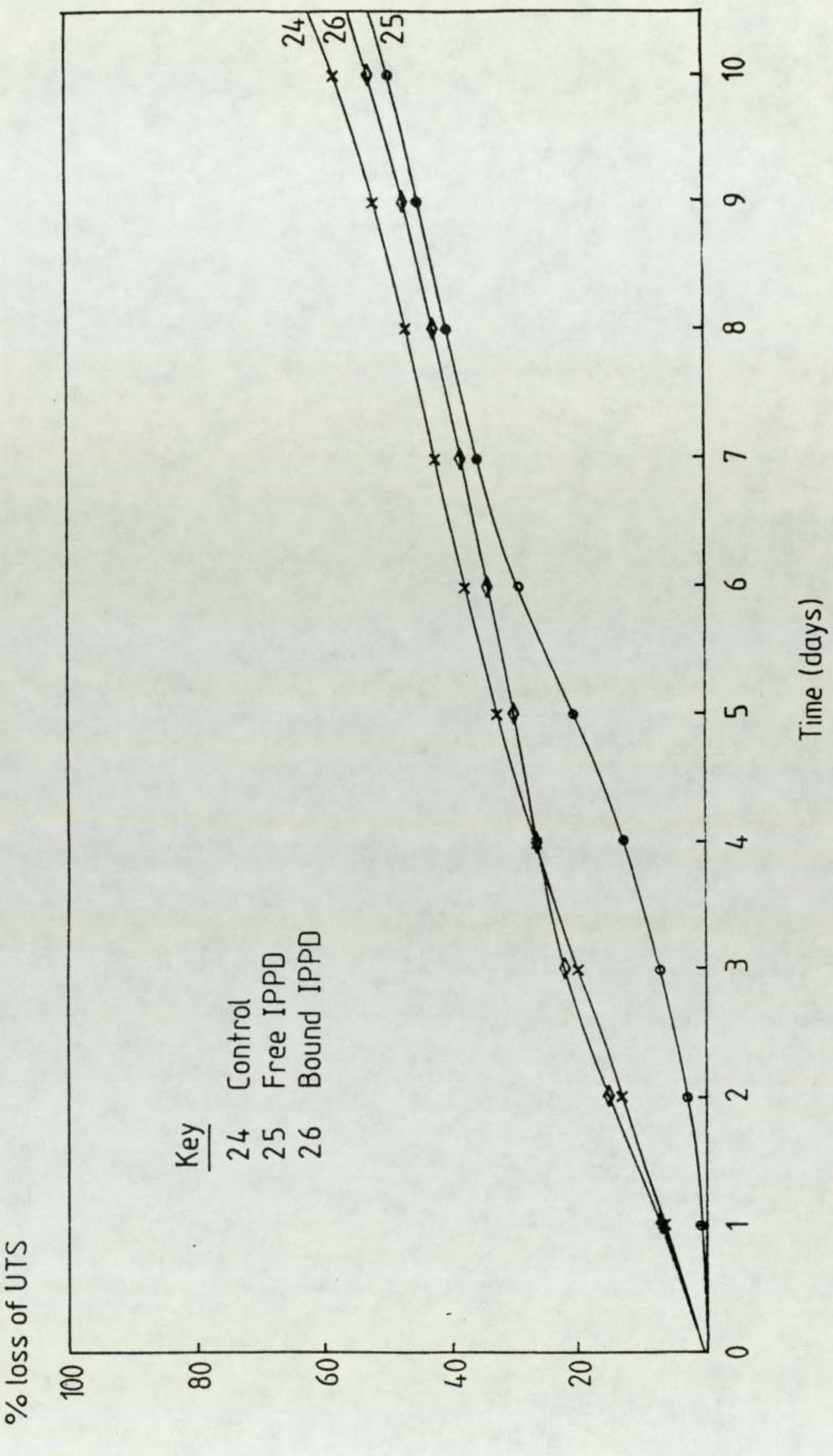


Fig 4:25

UTS oil ageing of ECH at 150°C in ASTM oil N° 3

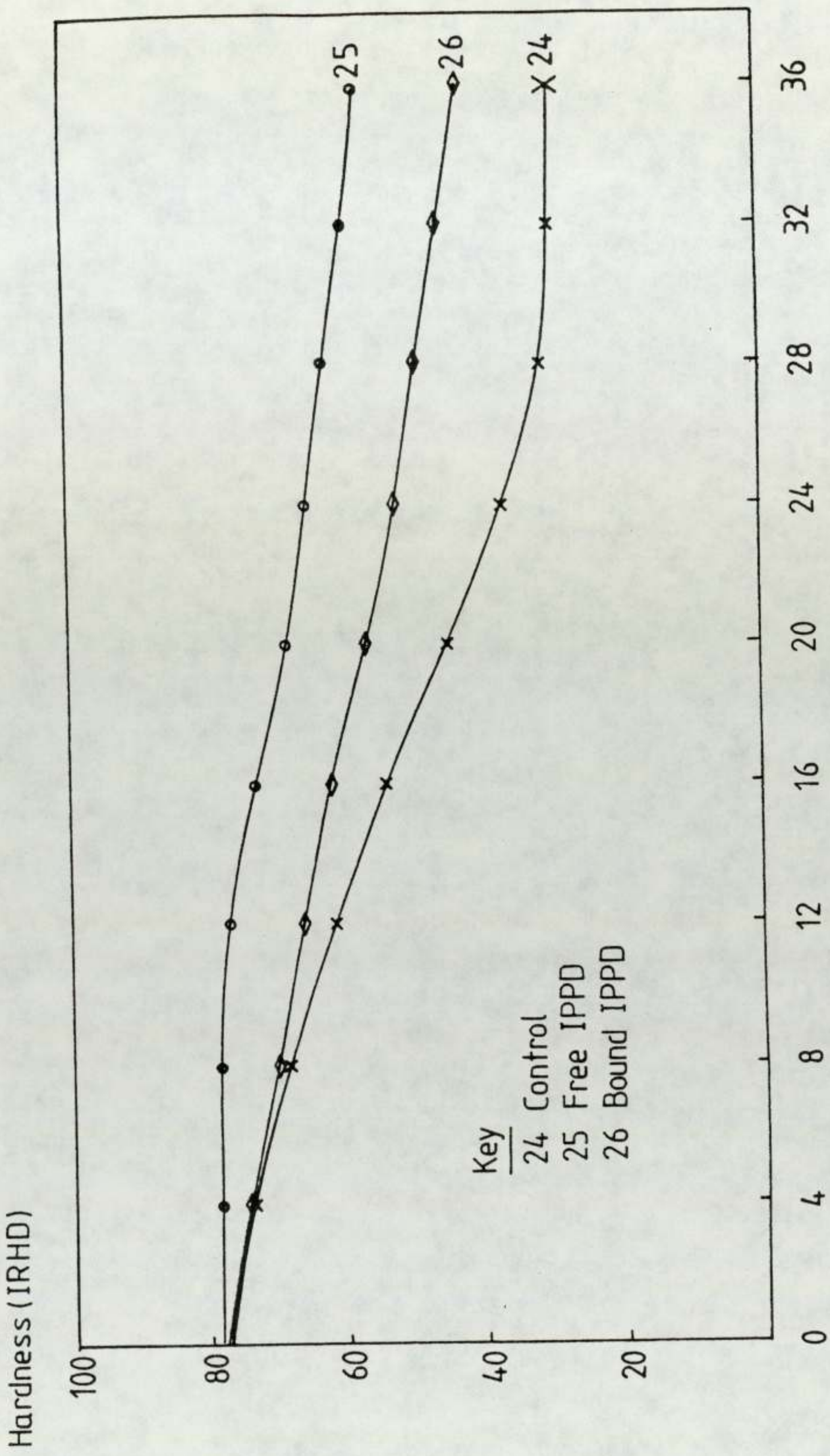


Fig 4: 26

The effect of free or bound IPPD on the hardness of ECH in ASTM oil N°3 aged at 150°C the 'free' Santoflex-13 becomes chemically combined with the ECH during vulcanization (see Section 4.5.2.2.5) otherwise it would have been leached out by the oil.

The slightly superior performance of the sample containing the 'bound' Santoflex-13 is due to the fact that none of it is soluble in the oil.

Visual inspection showed that the sample with no antioxidant i.e. the control, was soft and degraded after ageing but the sample with free or bound Santoflex-13 were comparatively unaffected, therefore, Santoflex-13 must be giving some protection.

(2) Hardness

The presence of 'free' Santoflex-13 causes a greater reduction in hardness on ageing than the bound Santoflex-13. There is even less of a reduction of hardness in the control. The changes in hardness do not reflect ageing processes in the oil, but are merely the result of extraction of soluble materials which vary in the following order: control (the most), bound Santoflex-13 and vulcanizate containing free Santoflex-13 (the least).

Visual inspection of the samples after ageing show that the control had degraded and become embrittled while the vulcanizates containing free or bound Santoflex-13 were unaffected. This embrittlement must be due to a cross-linking process which takes place during ageing.

ASTM Oil No. 3

This oil, of higher aromatic content, swells the ECH rubbers as well as leaching out soluble material.

(1) Ultimate Tensile Strength

There is a very little difference between the samples containing no antioxidant, free Santoflex-13, and bound Santoflex-13.

The swelling process is complete after 2 days, Fig. 4.22, and therefore, the continuous decrease in UTS must be due to degradation. The degradation of ECH is due to the absorption of the oil rather than to thermal oxidative degradation.

Any leaching out or degradation is being masked by the high swelling, but apparently the presence of Santoflex-13 has very little effect on ageing of ECH in ASTM oil No. 3.

(2) Hardness

The control suffers the most degradation and this is reflected in the hardness results in ASTM oil No. 3 as this causes much greater swelling than the ASTM oil No. 1. The sample containing the free Santoflex-13 is apparently superior to that containing the bound Santoflex-13. This is probably due to the leaching out of the free antioxidant which causes some shrinkage and reduces the overall swelling.

The large dimensions of the hardness sample minimises the effect of degradation.

4.5.3 REACTIONS OF ECH HOMOPOLYMER WITH PHENOLIC ANTIOXIDANTS

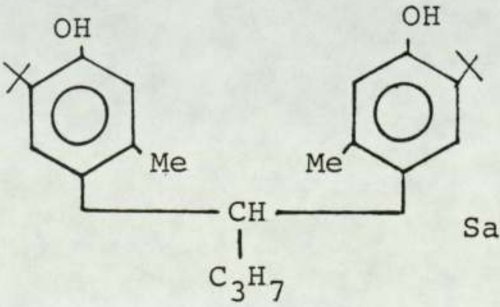
Phenols are classified as non-staining antioxidants which function by a chain-breaking mechanism. They have been discussed in detail in Chapter 1.

The possibility of binding phenolic antioxidants to ECH rubber and their effectiveness as antioxidants will now be considered.

The presence of active chlorine groups on ECH polymer and the hydroxyl groups on the antioxidant make such reactions possible with the elimination of HCl.

4.5.3.1 Reactions of ECH Rubber with 4,4$^-$-Butylidene bis (3-methyl-6-tertiary-butyl-phenol) (Santowhite Powder) and its Sodium Salt

Santowhite powder is made by condensing alkylated phenol with butylaldehyde.



Santowhite Powder

To facilitate the reaction of Santowhite powder with the chlorine atoms in ECH rubber the sodium salt was prepared as in Section 2.5.4.

4.5.3.1.1 Assessment of Amount of Santowhite Powder Bound to ECH Homopolymer

To assess the amount of Santowhite powder bound into ECH, a calibration curve was produced using vulcanizates prepared from the formulations shown in Table (4.16).

TABLE (4.16)

Formulations used for Calibration Curve of ECH with Santowhite Powder

	27
ECH	100
Zinc stearate	1.0
Sodium salt of Santowhite Powder	0,1,2,5,7 and 10 phr respectively
Diak No. 1	1.5

The ingredients were mixed on a two-roll mill and thin films were prepared at 160°C for 5 minutes. Infra-red anlaysis was carried out (2.4.6.2). A peak ratio at relative absorption peaks at 3,420 cm^{-1} to 2,120 cm^{-1} was measured for each concentration and a graph was drawn between the peak ratio and the concentration of antioxidants as shown in Fig. 4.27.

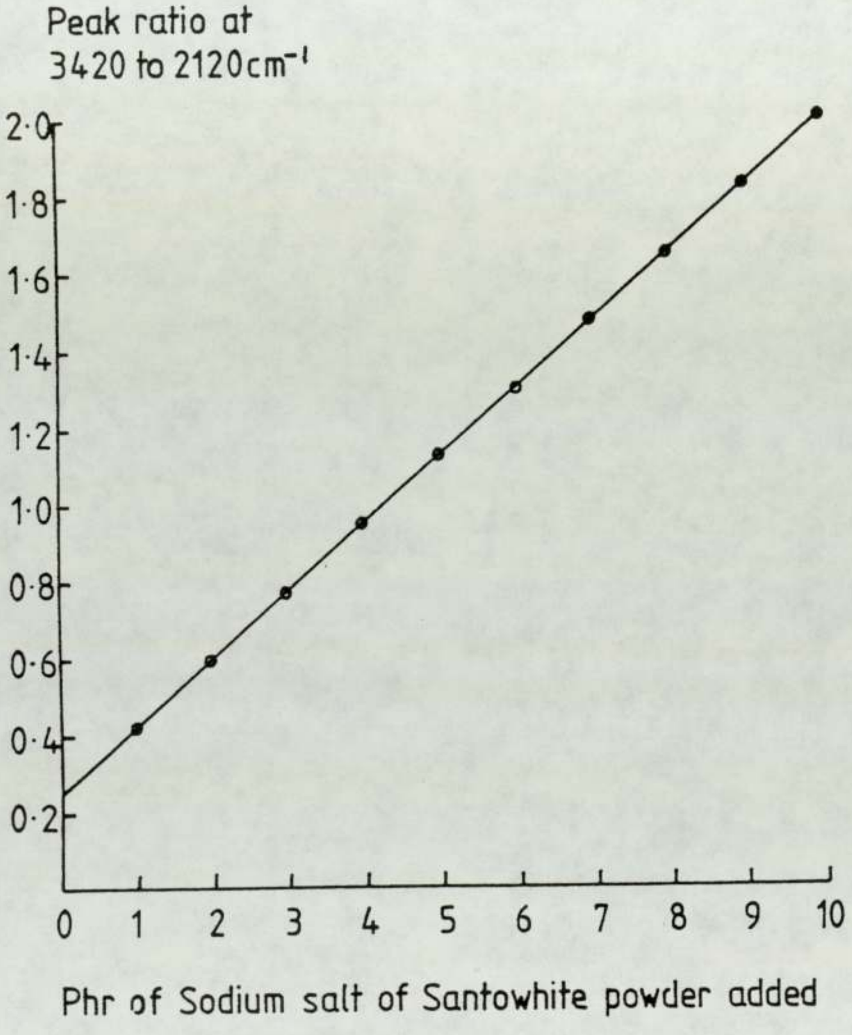


Fig 4:27

Calibration curve for Sodium salt of Santowhite powder with ECH

4.5.3.1.2 Reaction of ECH Homopolymer with Sodium Salt of Santowhite Powder in Torque Rheometer

The ECH polymer (35 gm) and Santowhite powder (3.5 gm) were mixed at 110°C for 19 minutes in MK_3 torque rheometer (2.2.3) using a motor speed of 60 rpm. Infra-red anlysis of the acetone extracted film used in conjunction with the calibration curve, showed that 2.9 gm of Santowhite powder is bound into the rubber. This is equivalent to a molar ratio of 1:152 antioxidant to repeat units of polyepichlorohydrin.

4.5.3.1.3 Reaction of ECH homopolymer with Sodium Salt of Santowhite Powder during Mixing in a Winkworth Mixer

ECH polymer (1000 gm) and the antioxidant (100 gm) were mixed in a Winkworth mixer for 30 mins at 80°C. Infra-red analysis and the calibration curve showed that 1.94 gm is bound to rubber during mixing. This is equivalent to 1:220 antioxidant to ECH rubber.

4.5.3.1.4 Reaction of ECH with Santowhite Powder during Vulcanization

The use of the sodium salt of the antioxidant was thought necessary to facilitate reaction between it and the chlorine atom of the rubber. In order to assess the extent of such reaction the formulation shown in

Table (4.17) was mixed on a two-roll mill and vulcanized at 160°C for 40 mins in the form of thin film. The thin film was acetone extracted under N_2 and its infra-red absorption spectra measured. In conjunction with the calibration curve the amount of bound Santowhite powder was found to be equal to 1.0 phr. This is equivalent to one antioxidant molecula per 432 epichlorohydrin units.

TABLE (4.17)

Formulation used to Study the Amount of Santowhite Powder Combined to ECH Rubber during Vulcanization

	28
ECH	100
Zinc stearate	1
Sodium salt of Santowhite Powder	2
Diak No. 1	1.5

4.5.3.1.5 Effect of Santowhite Powder (free or pre-mixed in the Torque Rheometer) on the Vulcanization Characteristics of ECH Rubber

In order to assess the effect of free or bound Santowhite powder on the vulcanization characteristics of ECH rubber the formulations shown in Table (4.18) were mixed on a two-roll mill and cured in the Monsanto rheometer at 160°C using a time span of 60 minutes and a torque range of 100 in-lb as shown in Fig. 4.28.

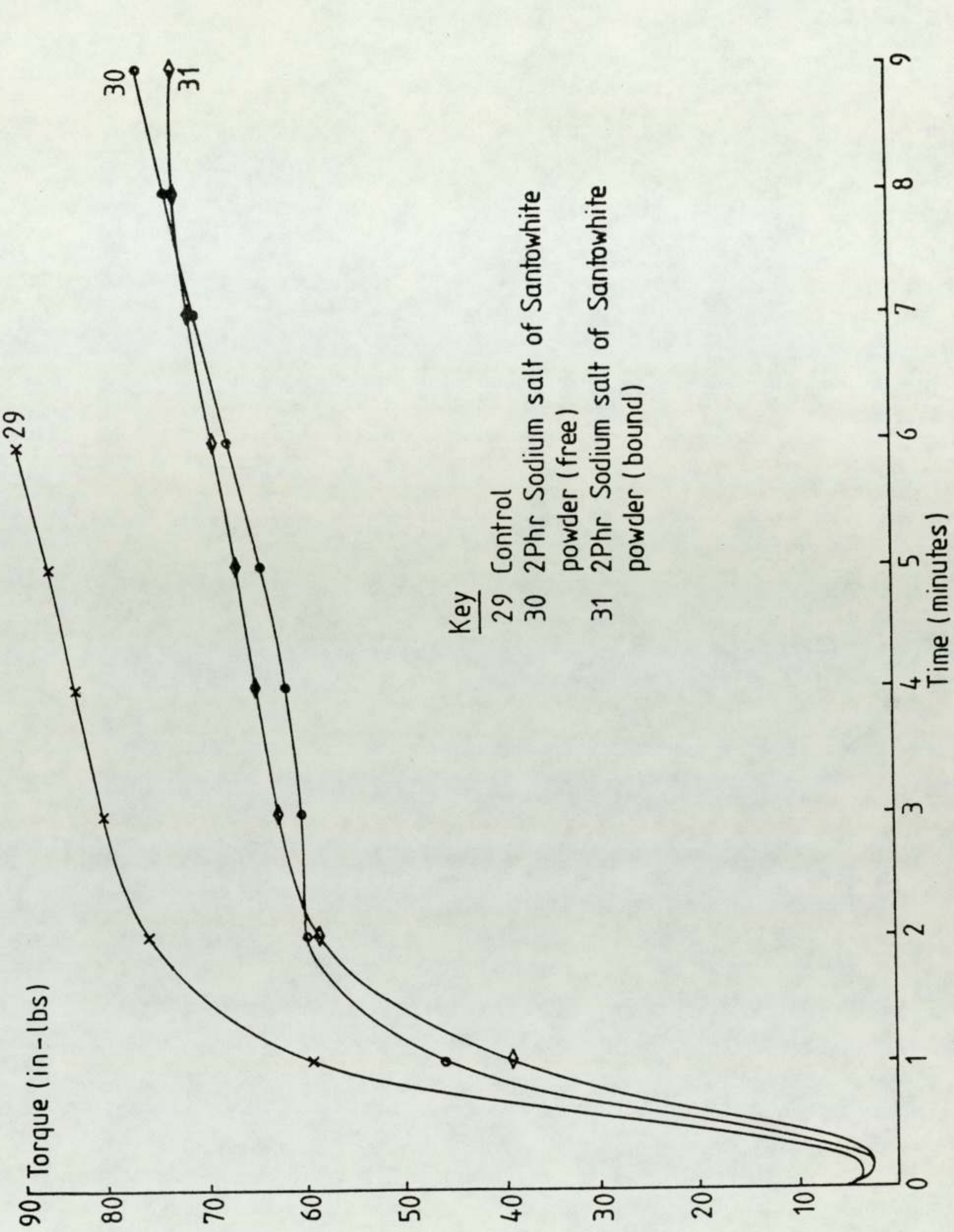


Fig 4:28

Monsanto rheograph of ECH with free or bound Sodium salt Santowhite powder

TABLE (4.18)

Formulations of ECH Homopolymer with Santowhite Powder, Free or Bound, before Vulcanization

	29	30	31
ECH Virgin	100	100	75
ECH/Santowhite Powder (extracted)	-	-	25
Zinc Stearate	1	1	1
FEF Carbon black	30	30	30
NBC	1	1	1
Free Santowhite Powder	-	2	-
Bound Santowhite Powder	-	-	2
pb3O4	5	5	5
Diak No. 1	1.5	1.5	1.5
Induction time in mins	1.5	1.5	1.5
Torque after 100% cure	100	83	80

From the above Table (4.18) and Fig. 4.28 it is seen that the presence of Santowhite Powder has little effect on the induction period and the rate of vulcanization but it does decrease the modulus. This decrease in the modulus is attributed to the decrease in the cross-linking density of the vulcanizate due to either a decrease in the number of curative sites by the reaction with the antioxidant or due to the acidic characteristics of the antioxidant which could react with the basic curative agent (Diak No. 1) and, therefore, decrease the effective concentration of the cross-linking agent.

The presence of Santowhite powder bound to ECH rubber as the sodium salt before vulcanization in the torque rheometer (Section 4.5.3.1.2) shows more decrease in the modulus than free Santowhite powder added 'in situ'. This is due to the effect of mechanochemical reactions which took place during mixing in the torque rheometer which leads to a chain scission and a decrease in the modulus of the vulcanizate rubber. Another reason for this is because the bound Santowhite powder is present at a concentration of 2 phr but only part of the free antioxidant added will react. In the bound antioxidant more of the reactive chlorine atoms have been blocked and this will result in a lower modulus.

4.5.3.1.6 Assessment of Effectiveness of Santowhite Powder as an Antioxidant for ECH Homopolymer

The effectiveness of Santowhite powder as an antioxidant for ECH rubber was assessed by comparing the physical properties of vulcanizate samples containing bound or free antioxidants with the control as shown in Table (4.18). Samples for UTS (0.2 cm thick), MR100 (0.1 cm thick), hardness (1.0 cm thick) and for stress relaxation (0.1 cm thick) were prepared as described in Section 3.3.3 using a steam press at 160°C for 40 minutes.

4.5.3.1.6.1 Stress Relaxation

Thin films were prepared and samples for stress relaxation were cut using MR100 cutter. Half of the samples were acetone extracted under N_2 (Section 2.3.4).

Continuous stress relaxation (2.4.1) was carried out at 160°C in a Wallace age tester, both before and after the acetone extraction. The results are shown in Fig. 4.29 and in Table (4.19).

Results and Discussion

The log f/f^o values after 200 minutes of ageing for all the vulcanizates, is shown in Table (4.19).

TABLE (4.19)

The Values of Log f/f^o of ECH Rubber with Santowhite Powder Aged at 160°C After 200 minutes.

	29	30	31
Not extracted	0.74	0.58	0.70
Acetone extracted	Zero	0.17	0.47

The following conclusions can be drawn:-

(1) The graph shows that the oxidation of vulcanizate samples is slightly autocatalylic in the presence of Santowhite powder (free or bound).

(2) The autocatalylic behaviour of the sample

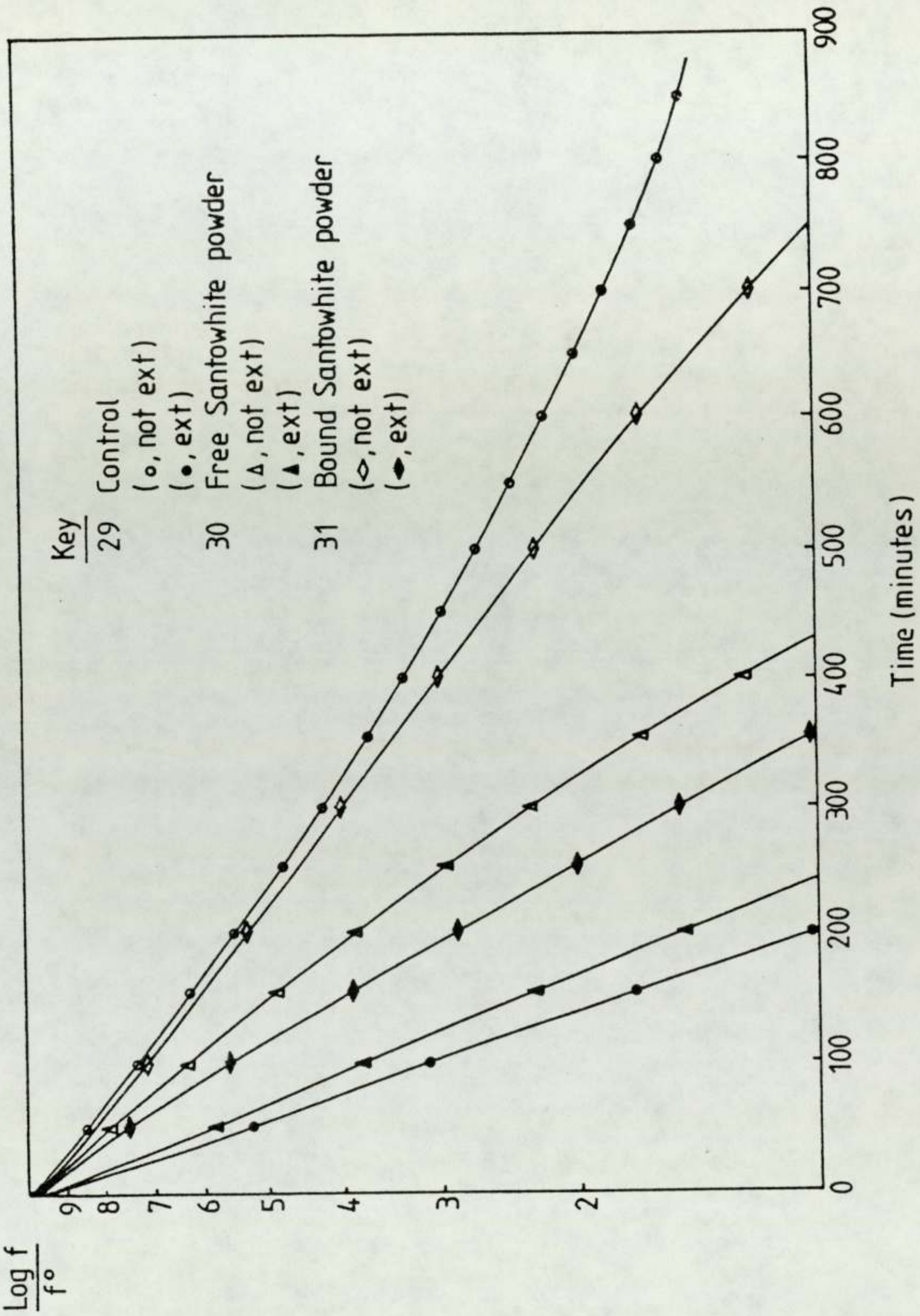
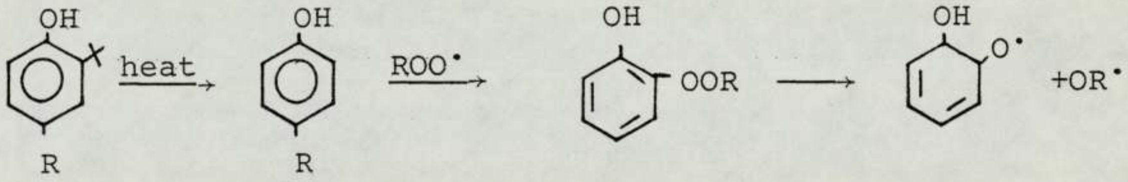


Fig 4:29 Continuous stress relaxation of ECH with Sodium salt of bound or free Santowhite powder, at 160°C for acetone extracted and non-extracted samples

increased when 2 phr free Santowhite powder was present. This is because that the tertiary alkylated phenols, such as Santowhite powder, when heated in the presence of acidic material (HCl) are de-alkylated and a loss in antioxidant activity, and it may even become a proxidant. When the phenol loses its tertiary alkyl groups, the peroxy radicals become capable of reacting with the hydrogen atoms in the ortho position to the hydroxyl groups which then decompose to give more free radicals which initiate the degradation(154).



(3) A vulcanizate sample containing bound Santowhite powder shows a better resistance to ageing than the free Santowhite powder. This improvement is attributed to the extraction process on the ECH containing bound antioxidant which was carried out before vulcanization, which removed the impurities or the stabilizer added to raw rubber, see Section 4.5.2.1.7.4.

4.5.3.1.6.2 Accelerated Oven Ageing of Vulcanizates

The assessment of Santowhite powder as an antioxidant for ECH homopolymer was also made by ageing the vulcanizate in a Wallace oven at 160°C. The deterioration of the vulcanizates at different times during this ageing was monitored by measuring the decrease in ultimate tensile strength,MR100 or MR50 and hardness, see Sections 2.4.2, 2.4.3 and 2.4.4.

4.5.3.1.6.2.1 Ultimate Tensile Strength

The formulations shown in Table (4.18) were mixed on a two-roll mill at room temperature and moulded at 160°C for 30 minutes in a steam heated press in the form of sheets of 0.2 cm thickness, (2.4.2). Dumbell shape samples were cut by the standard cutter for UTS (2.4.2).

Ageing was carried out in a Wallace multi-cell oven at 160°C and the UTS was measured. The graph between the UTS and ageing time is shown in Fig. 4.30.

The percentage decrease in UTS is shown in Table (4.20).

TABLE (4.20)

% Decrease of UTS (MNm^{-2}) of ECH Vulcanizate with Santowhite Powder (free or bound) aged at 130°C in Oven Ageing

Formulation Number	Ageing Period (hrs)				
	0	26	45	66	88
29		+13	+ 4.5	-13	-77
30		+21	- 1.2	-46.5	-93
31		-45.3	-62.3	-73.6	-90.5

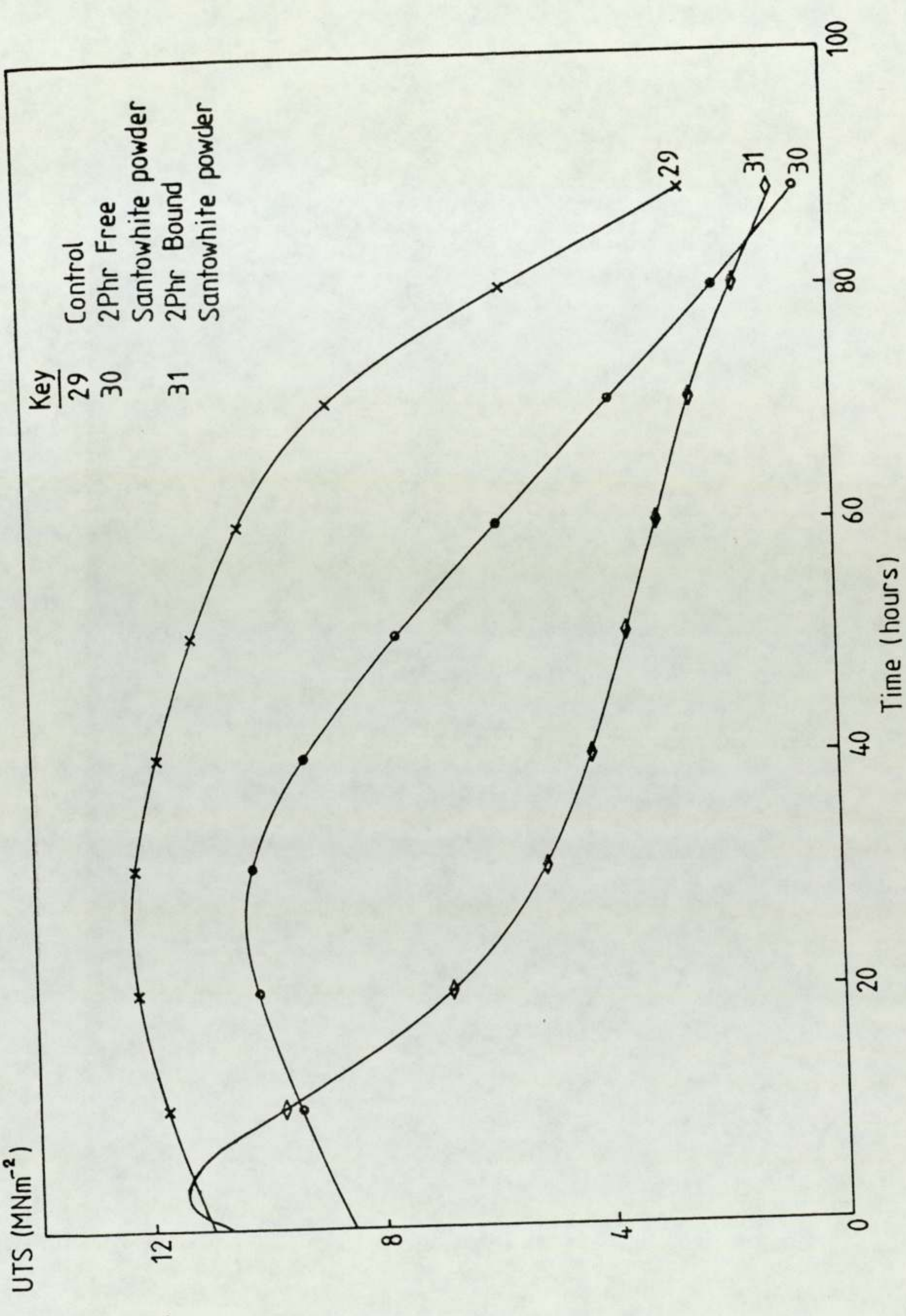


Fig 4:30

The effect of Santowhite powder and its Sodium salt on the UTS of ECH rubber aged at 160°C, not extracted

4.5.3.1.6.2.2 Hardness Measurements

Samples of one cm thickness were prepared for the formulations shown in Table (4.18) at 160°C for 40 minutes (2.3.3). The hardness was determined before and after ageing in a Wallace oven at 160°C for different intervals of time as described in Section 2.4.3. The results are shown in Fig. 4.31 and Table (4.21).

TABLE (4.21)

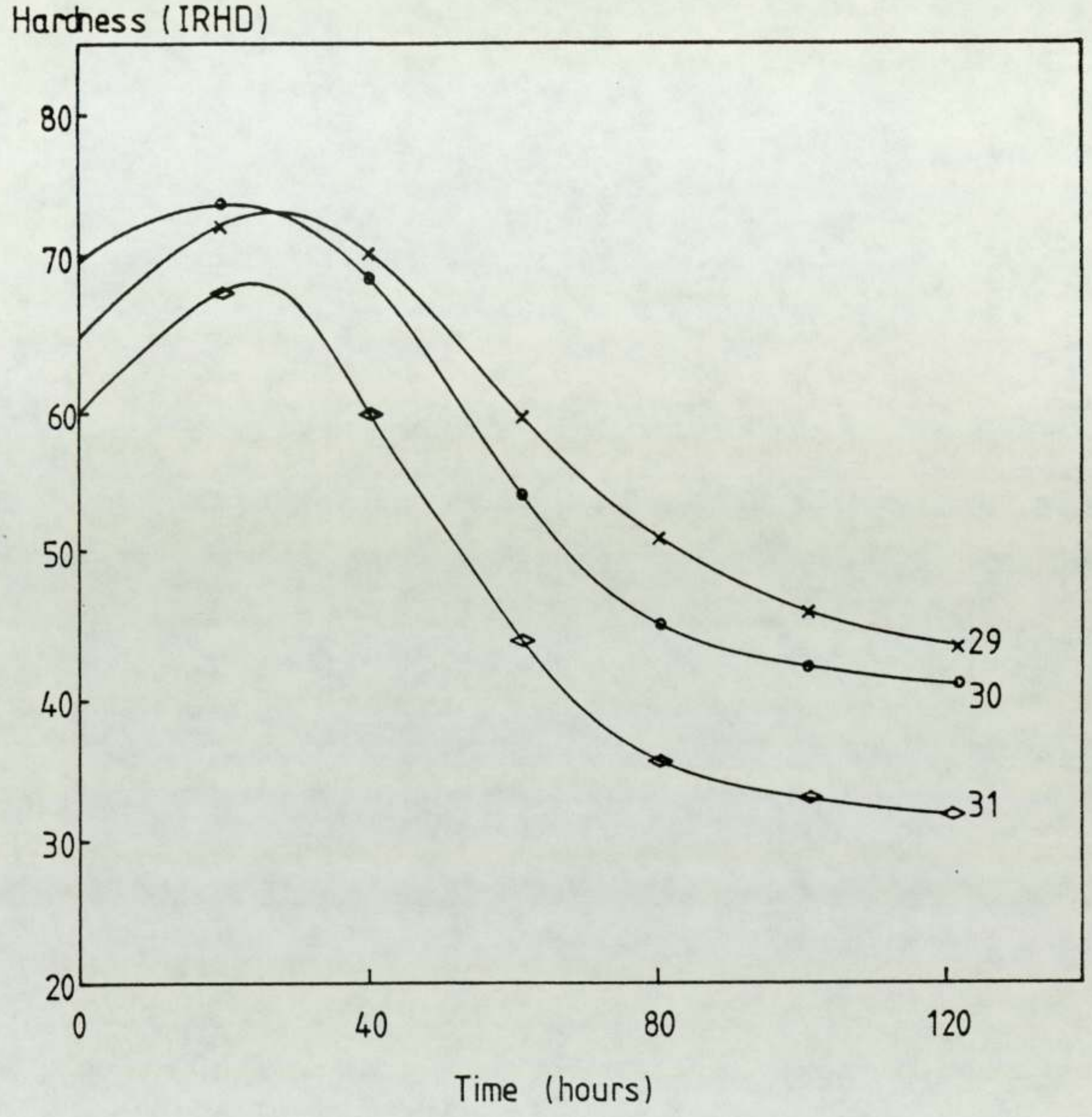
% Change of Hardness of ECH Vulcanizate (IRHD) in the Presence of Santowhite Powder, Aged at 160°C in a Wallace Oven

Formulations	Ageing Period (hrs)				
	0	24	50	72	120
29		+12.3	+ 0.8	-18.5	-34
30		+ 5.7	-11.3	-34.8	-40.4
31		+13.3	-13.3	-37.5	-46.7

Results and Discussion

The results obtained for UTS and hardness, Fig. 4.30 and Fig. 4.31 respectively, and Tables (4.20) and (4.21) are in agreement with the stress relaxation results (4.5.3.1.6.1) and the following conclusions can be drawn:-

(1) Santowhite powder in the presence of NBC is found to accelerate the thermal-oxidative degradation of ECH rubber.



Key

29	Control
30	2Phr Free Santowhite powder
31	2Phr Bound Santowhite powder

Fig 4:31

The effect of Santowhite powder (free or bound) on the hardness of ECH aged at 160° C

(2) There is an increase of the degradation of ECH in the presence of bound Santowhite powder which is pre-bound in the torque rheometer. This is attributed to the mechanochemical degradation which took place during mixing and, therefore, reduced the physical properties of ECH homopolymer and to the presence of 2 phr of the antioxidant bound into the backbone.

(3) The initial values of UTS decrease in the presence of 2 phr free Santowhite powder. This may be due either to a reaction taking place between this antioxidant through its hydroxyl groups and the ECH by the active chlorine groups, or due to the interference of the acidic antioxidant and the vulcanizing system which is basic. In either case a reduction in the cross-link density and consequently the initial value of UTS would take place.

(4) It can be seen from the results that Santowhite powder (free) will combine with the ECH rubber during the vulcanization process and the use of the sodium substituted antioxidant is an unnecessary step.

4.5.3.2 The Effect of the Presence of NBC on the Effectiveness of the Phenolic Antioxidants for ECH rubber

It has been shown previously that the effectiveness(23, 155,156) of NBC is at least in part due to its ability to destroy hydroperoxides in a catalytic process, Section 1.3.1.3.

It has been shown (Section 4.5.3.1) that the Santowhite powder (free or bound) accelerates the thermal oxidative degradation of ECH rubber in the presence of NBC. Therefore, in order to study the effect of NBC on the activity of phenolic antioxidants in ECH, the formulations shown in Tables (4.22) and (4.23) were mixed on a water-cooled, two-roll mill. These were moulded as thin sheets of 0.1 cm thickness in a steam press at 160°C for 40 minutes (Section 2.3.3) and used for stress relaxation measurements.

TABLE (4.22)

Formulations to Study the Effect of NBC on the Activity of the Phenolic Antioxidant Santowhite Powder for ECH Rubber

	32	33	34	35
ECH	100	100	100	100
Zinc stearate	1	1	1	1
pb3O4	5	5	5	5
FEF	30	30	30	30
Santowhite powder	-	-	2	2
NBC	-	1.0	-	1.0
Diak No. 1	1.5	1.5	1.5	1.5

TABLE (4.23)

Formulations to Study the Effect of NBC on the Activity of the Phenolic Antioxidant Permanx WSP and Irganox 1076 for ECH Rubber

	36	37	38	39
ECH	100	100	100	100
Zinc stearate	1	1	1	1
pb3O4	5	5	5	5
FEF	30	30	30	30
Permanx WSP	2	2	-	-
NBC	-	1.0	-	1.0
Diak No. 1	1.5	1.5	1.5	1.5
Irganox 1076	-	-	2	2

4.5.3.2.1 Stress Relaxation Studies

Continuous stress relaxation was carried out at 160°C in a Wallace Age tester Figs. 4.32 -4.34 and the values of Log f/f^o after 400 minutes of ageing are shown in Table (4.24).

TABLE (4.24)

The Values of Log f/f^o of ECH with NBC in the Presence of Phenolic Antioxidants After 400 Minutes of Ageing at 160°C

	Formulation Number							
	32	33	34	35	36	37	38	39
Log f/f^o	0.25	0.35	0.21	-	0.11	-	-	0.36

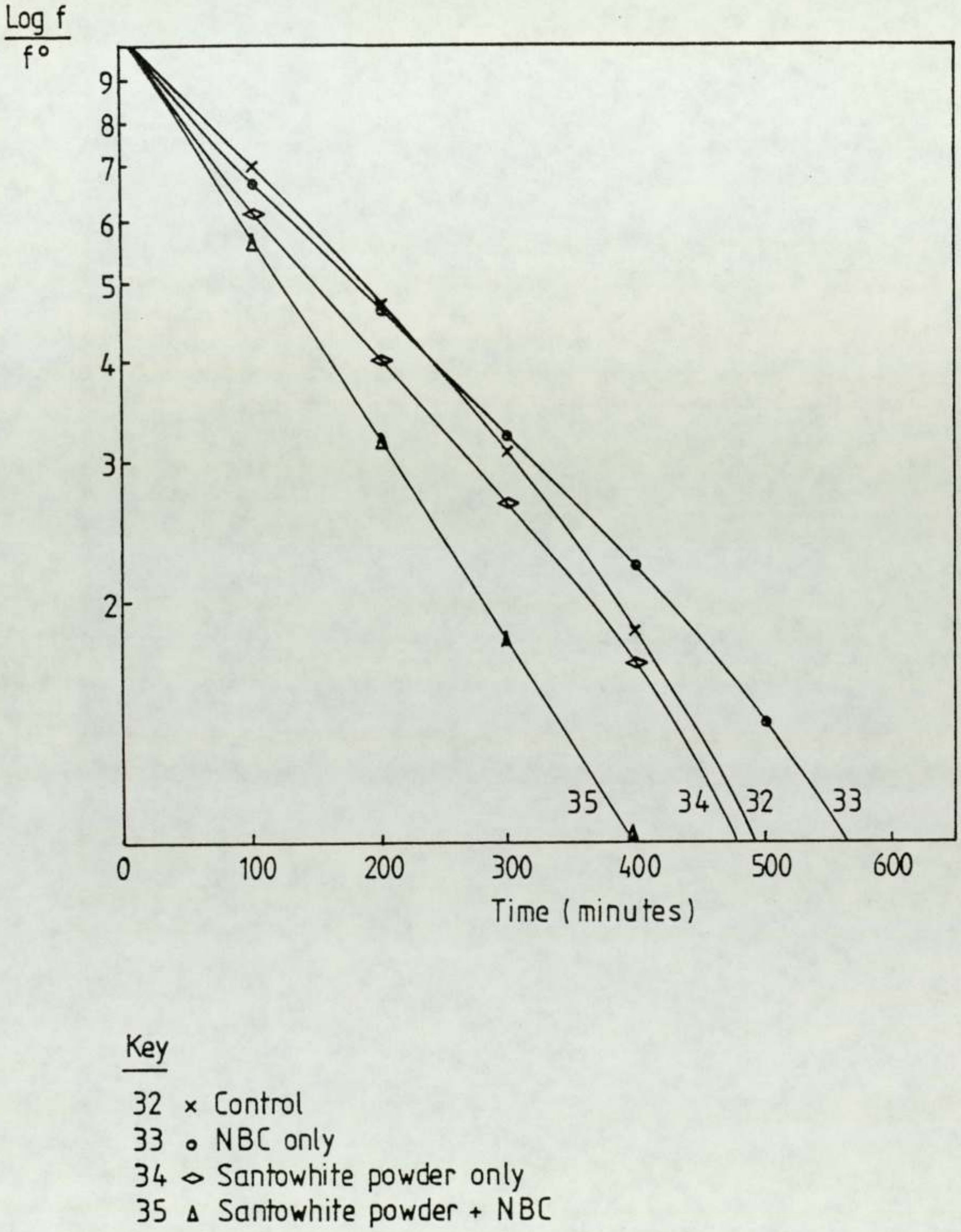
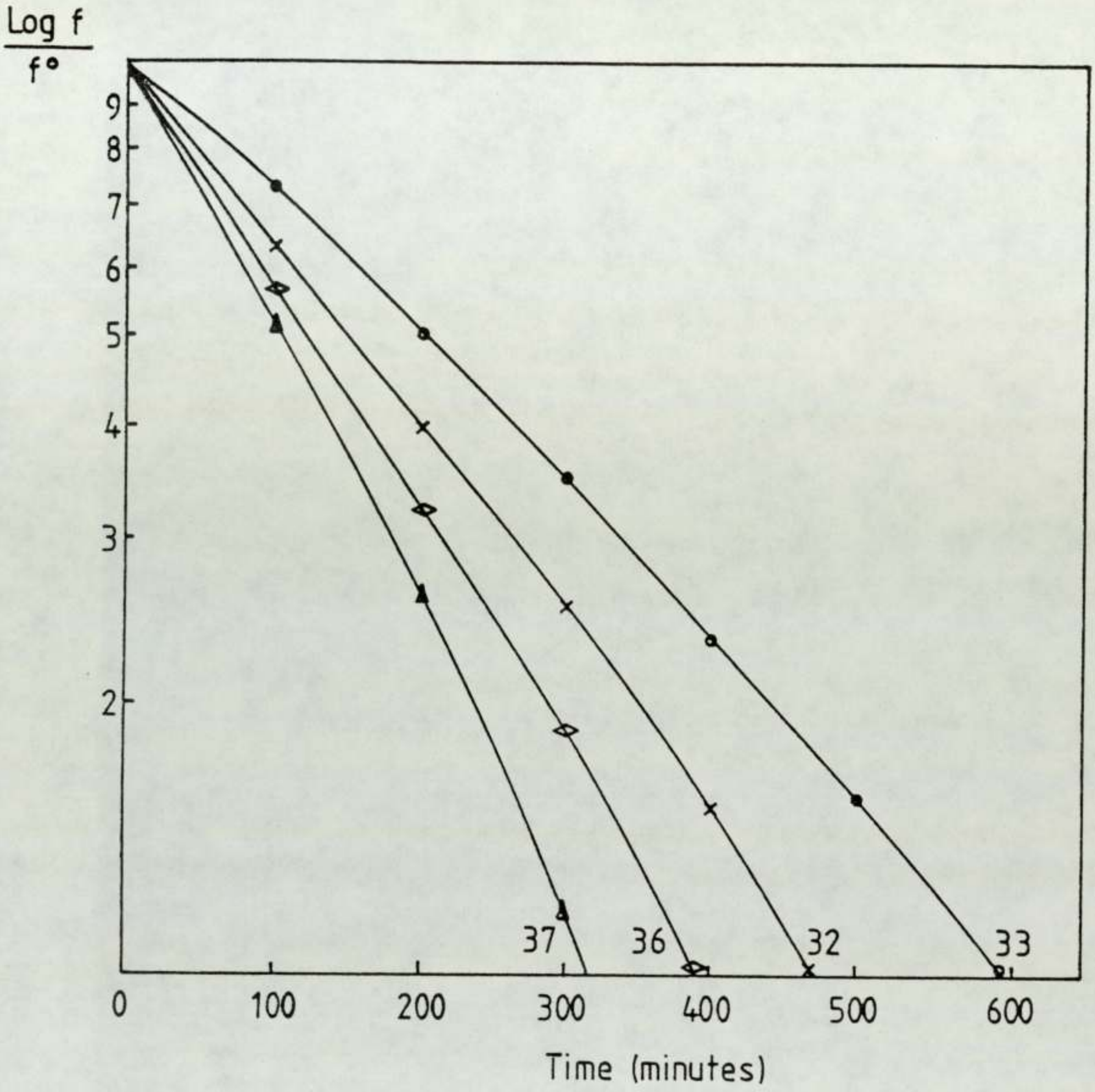


Fig 4:32

The effect of NBC and Santowhite powder on the continuous stress relaxation of ECH rubber aged at 160°C

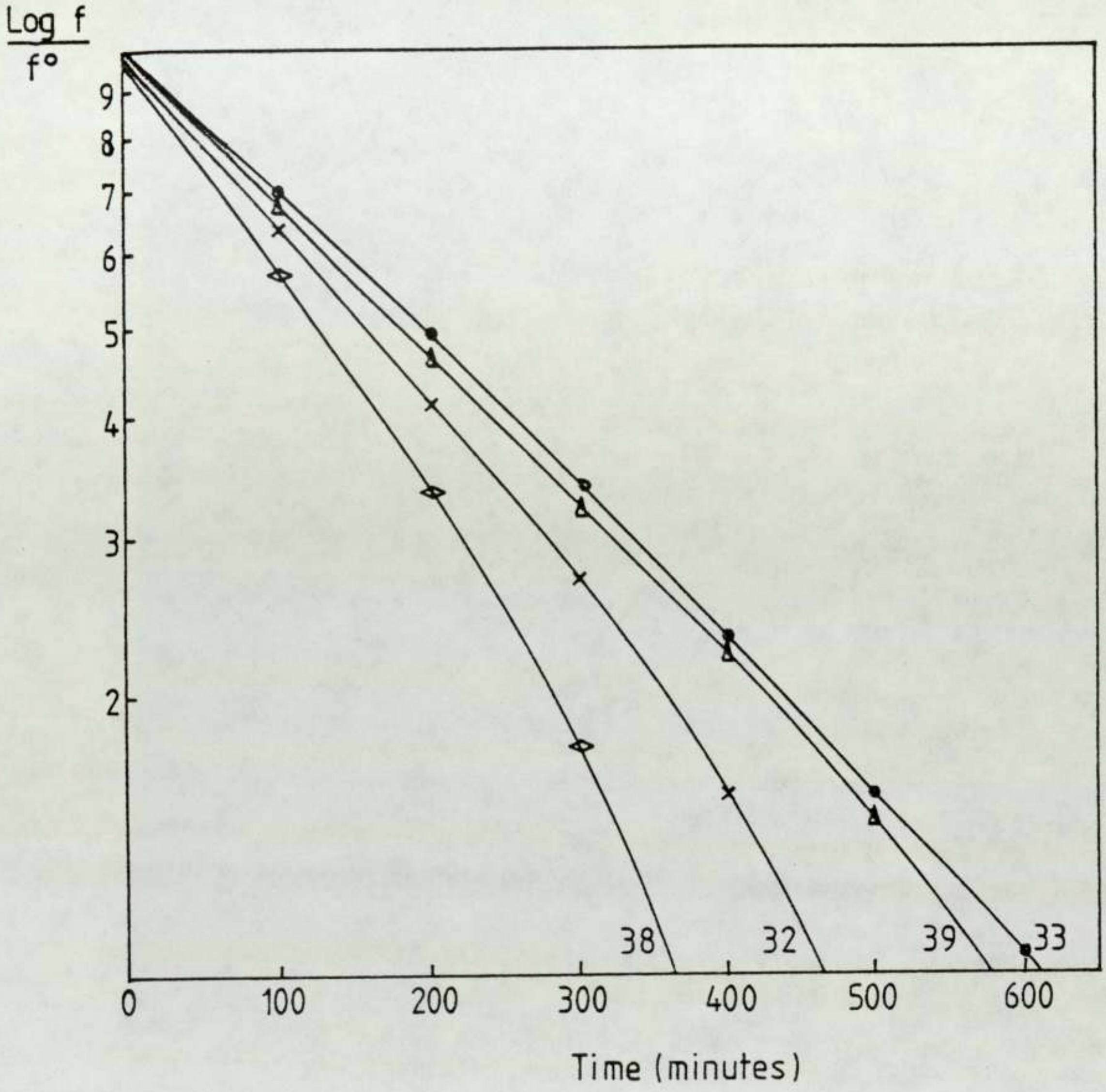


Key

- 32 × Control
- 33 ○ NBC
- 36 ◇ Permanx WSP
- 37 ▲ Permanx WSP + NBC

Fig 4: 33

The effect of NBC and Permanx WSP on the continuous stress relaxation of ECH rubber aged at 160°C



Key

32 × Control
33 ∘ NBC
38 ◇ Irganox 1076
39 △ Irganox 1076 + NBC

Fig 4:34

The effect of NBC and Irganox 1076 on the continuous stress relaxation of ECH rubber aged at 160°C

From the above table the following conclusions can be drawn:-

(1) All the curves show autocatalytic stress relaxation. Therefore, the presence of NBC and the phenolic antioxidants does not stop the thermal oxidative degradation.

(2) NBC when it is used alone shows some antioxidant activity.

(3) The presence of Santowhite powder alone increases the thermal oxidative degradation of ECH rubber. This might be due to the reaction between the Santowhite powder and ECH which produces HCl that will increase the degradation and convert the antioxidant into products which accelerate the degradation(154).

(4) When Santowhite powder and NBC are present in the same sample, the thermal oxidative degradation of ECH increases due to the antagonism between the hydroperoxide decomposer and the chain breaking antioxidant. This is because NBC like other sulphur antioxidants is involved in an initial radical generation step before the formation of the Lewis acid antioxidant which destroys hydroperoxides by an ionic process(8, 157, 158). An important function of chain breaking antioxidant (Santowhite powder) in this situation is to inhibit the initial radical generation. Therefore, the Santowhite powder accelerates the decomposition of NBC leading to a

decrease in their ability to function as a hydroperoxide decomposer. This is almost certainly due to the presence of quinonoid products (stilbene quinones and peroxy dienones) which are major products of the normal function of phenols as antioxidants (Section 1.3.2.1).

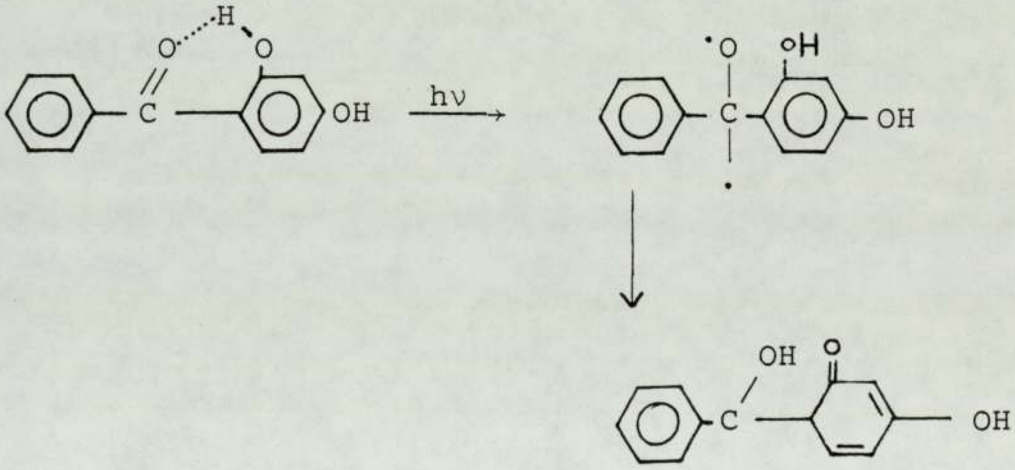
(5) Permanx WSP has the same effect as Santowhite Powder.

(6) Irganox 1076 has a pro-oxidant effect on the ECH rubber when it is used alone. When a combination of NBC and Irganox 1076 was used there was some improvement in the thermal-oxidative degradation of ECH, which is approximately equal to that found in the sample containing NBC only.

(7) From the above results it can be concluded that phenolic antioxidants are not good antioxidants for ECH rubber and an antagonism effect is produced between these phenolic antioxidant and NBC.

4.5.4 THE EFFECT OF 2,4-DIHYDROXYBENZOPHENONE AS AN UV STABILIZER ON THE AGEING OF ECH RUBBER

2,4-Dihydroxybenzophenone is a UV absorber. These are believed to function by absorbing most of the UV light and dissipate the absorbed energy in a harmless manner in the form of heat. The capacity of this compound as a UV stabilizer is associated with the presence of intramolecular hydrogen bond in its structure which permits energy transfer and probably hydrogen transfer(159)



In order to study the effectiveness of this compound on stabilizing ECH homopolymer during UV irradiation and the possibility of reaction (i.e. becoming bound) to ECH, the stabilizer is converted into its sodium salt as described in Section 2.5.3.

4.5.4.1 Determination of Extent of Reaction of Mono-Sodium Salt of 2,4-Dihydroxybenzophenone with ECH Homopolymer

Thin films 0.02 cm thickness were prepared by moulding the formulations shown in Table (4.25) in a steam heated press at 160°C for 5 minutes.

TABLE (4.25)

Formulations for ECH with Different Concentration of Mono-Sodium 2,4-Dihydroxybenzophenone

	40
ECH	100
Zinc stearate	1
Mono-sodium salt of 2,4-dihydroxybenzophene	0,1,2,3,4 and 5 phr.

Infra-red determination of the peak height due to the hydroxyl group at 3,280 cm (broad peak) to the constant peak at 2,120 cm^{-1} were made and plotted against concentration of the compound, this was used as a calibration curve (Section 2.4.6.2) as shown in Fig. 4.35.

4.5.4.2 Reaction Between Mono-Sodium Salt of 2,4-Dihydroxybenzophenone with ECH Homopolymer in the Winkworth Mixer

Reaction between the stabilizer (45) grams and ECH (1000) grams was carried out in a Winkworth mixer at 80°C for 15 minutes. The mixture was then methanol extracted for 30 days under N_2, and then dried and used to prepare a thin film. Infra-red analysis with conjunction with

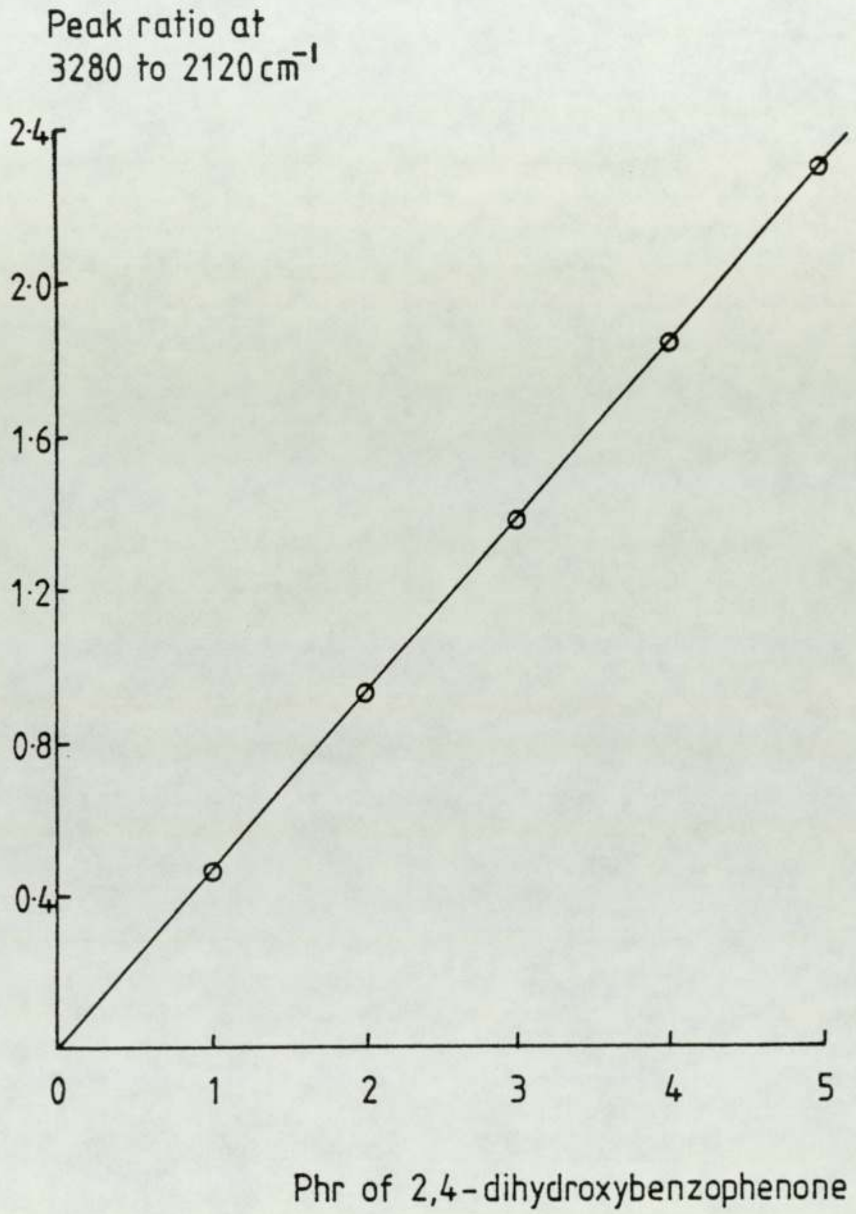


Fig 4 : 35

Calibration curve for 2,4-dihydroxybenzophenone with ECH polymer the calibration curve, showed that 1.8 phr of the stabilizer is bound into ECH. This is equivalent to 1 per 139 epichlorohydrin units.

4.5.4.3 Assessment of the Effectiveness of 2,4-dihydroxybenzophenone (Free or Bound) in ECH to UV Irradiation

In order to assess the activity of 2,4-dihyroxybenzophenone (free or bound) on the photoxidation degradation of ECH homopolymer, formulations shown in Table (4.25) were prepared and moulded into a very thin films of 0.02 cm thickness in a steam press pre-heated at 160^{o}C for 45 minutes. Ultra-violet irradiation was, then carried out as described in Section 2.4.5 for different interval times. The formation of carbonyl group was followed by the infra-red determinations and a peak ratio of the carbonyl group at 1710 cm^{-1} to a standard peak at 2,120 cm^{-1} was plotted against the ageing time as shown in Fig. 4.36.

Results and Discussion

The ageing mechanism of ECH polymer was discussed in Section 4.4 which showed that the main cause of the degradation of ECH polymer is due to the hydroperoxide formation during compounding or during ageing. These hydroperoxides are cleaved homolytically by the U.V. irradiation (Section 4.5.4.3) and this initiates the

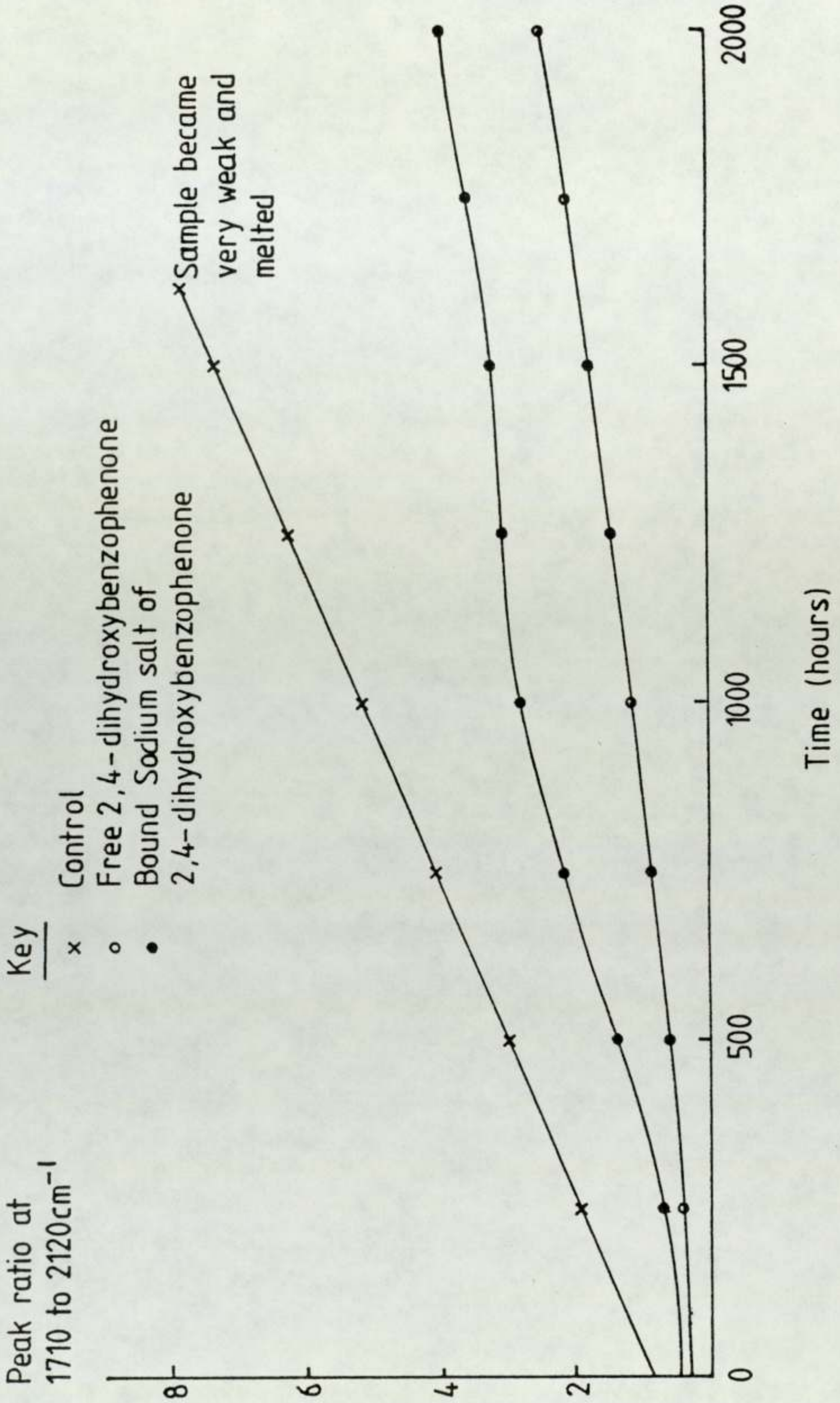


Fig 4 : 36

The U.V irradiation of ECH in the presence of 2,4-dihydroxybenzophenone (free or bound) degradation. This is what happened to the sample without any U.V. stablizer (i.e. the control). The control lost all its properties and melted after 1600 hours of irradiation.

When 2,4-dihydroxybenzophenone is present, the extent of photodegradation is decreased as shown in Fig. 4.36. This is attributed to the activity of the 2,4-dihydroxybenzophenone as a U.V. absorbers.

The sample with 2 phr U.V. absorber (free) retianed its resistance to photodegradation even after 2,200 hours and still had reasonable properties.

The sample with 2 phr bound U.V. absorbers shows a very good activity as a U.V. absorber but it is less than the sample containing the same amount of free absorber. This decrease in the activity of the bound absorbers may be due to the initial thermal degradation which took place during the mixing of ECH polymer and the absorber in the Winkworth mixer or due to its restricted mobility when combined with the rubber.

Summary of Reaction of Amines and Phenols with ECH Rubber

Type of Amine or Phenol	Method of Binding	% Bound	Molar Ratio
IPPD	Winkworth	31%	1:73
IPPD	Milling	no reaction	
IPPD	Vulcanization	60%	1:200
Santoflex-13	Winkworth	37.5%	1:75
Santoflex-13	Torque rheometer	37.5%	1:75
Santoflex-13	Vulcanization	60%	1:238
Sodium salt of Santowhite powder	Torque rheometer	82.8%	1:152
Sodium salt of Santowhite powder	Winkworth	20%	1:220
Sodium salt of Santowhite powder	Vulcanization	50%	1:432
2,4-dihydroxybenzophene	Winkworth	40%	1:139

CHAPTER FIVE

THE EFFECT OF ANTIOXIDANTS BOUND IN POLYEPICHLOROHYDRIN RUBBERS ON THE DEGRADATION OF POLYCHLOROPRENE RUBBERS

5.1 INTRODUCTION

It has been shown in Section 1.3.4 that one way of preventing the loss of antioxidants during service is by binding the antioxidant into the rubber back-bone either before or after the vulcanization process. Binding the antioxidant before the vulcanization process may lead, in some cases, to a high concentration of antioxidant which could be used as a polymeric antioxidant for another rubber.

In Chapters Three and Four it has been shown that the amines and phenols will react with ECH and CR rubbers before vulcanization to form polymeric antioxidants.

In this chapter the efficiency of ECH homopolymer bound antioxidant in protecting polychloroprene rubber is assessed.

5.2 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON CR TYPE-G

The preparation of ECH-Santoflex-13 bound antioxidant is described in Section 4.5.2.2.3. The amount of bound antioxidant (after extraction) is found to be equal to 3.75 phr.

5.2.1 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON THE VULCANIZATION CHARACTERISTICS OF CR TYPE-G

To study the effect of ECH-Santoflex-13 bound antioxidant on the vulcanization characteristics of CR type-G, the formulations shown in Table (5.1) were mixed on a two-roll mill at room temperature. They were then tested in the Monsanto rheometer at 160°C using a torque range of 100 in-lb, and a time span of 30 minutes.

It can be seen from Table (5.1) that there is a decrease in the modulus in the presence of Santoflex-13. This decrease is due to the reaction between the amino group of Santoflex-13 and the reactive chlorine of both polymers. This reaction leads to a decrease in the number of chlorine curative sites which are responsible for vulcanization, see Sections 3.1.4 and 4.3.

The inclusion of ECH Santoflex-13 bound antioxidant makes no difference to the vulcanization characteristics compared with those obtained when using free Santoflex-13.

TABLE (5.1)

Formulations of CR Type-G with ECH Santoflex-13 Bound Antioxidant

	1	2	3	4
CR Type-G	46.67	46.67	46.67	100
ECH Virgin	53.33	53.33	-	-
Mgo	4	4	4	4
Zno	5	5	5	5
ECH Santoflex-13 bound antioxidant	-	-	53.33	-
Free Santoflex-13	-	2	-	-
NA-22	1	1	1	1
MBTS	1	1	1	1
Moduli at 90% in in-lb	47	40	41	57
Induction time (in min)	5	5	5	5

These results are as expected as the chlorine atoms are blocked by the Santoflex-13 whether this occurs during mixing in the Winkworth mixer or during vulcanization.

The presence of ECH homopolymer with CR type-G showed a decrease in the extent of vulcanization Table (5.1). This decrease in the modulus is attributed to the fact that CR type-G have very reactive allylic tertiary chlorine atoms which will react with the curative agent (NA-22) faster than with ECH. Therefore, some of the ECH homopolymer remains uncured. This leads to a decrease in the modulus of the blend.

5.2.2 ASSESSMENT OF EFFECTIVENESS OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON THE AGEING OF CR TYPE-G BY STRESS RELAXATION

Thin sheets of 0.1 cm thickness for the formulations shown in Table (5.1) were prepared at 160°C for 30 minutes (2.3.3). Samples were cut using an MR100 cutter (2.4.4). Half of the samples were methanol extracted under N_2 (2.3.4).

Continuous stress relaxation was carried out in a Wallace age tester at 140°C for both non-extracted and methanol extracted samples (2.4.1). The results are shown in Figs. 5.1 and 5.2 respectively.

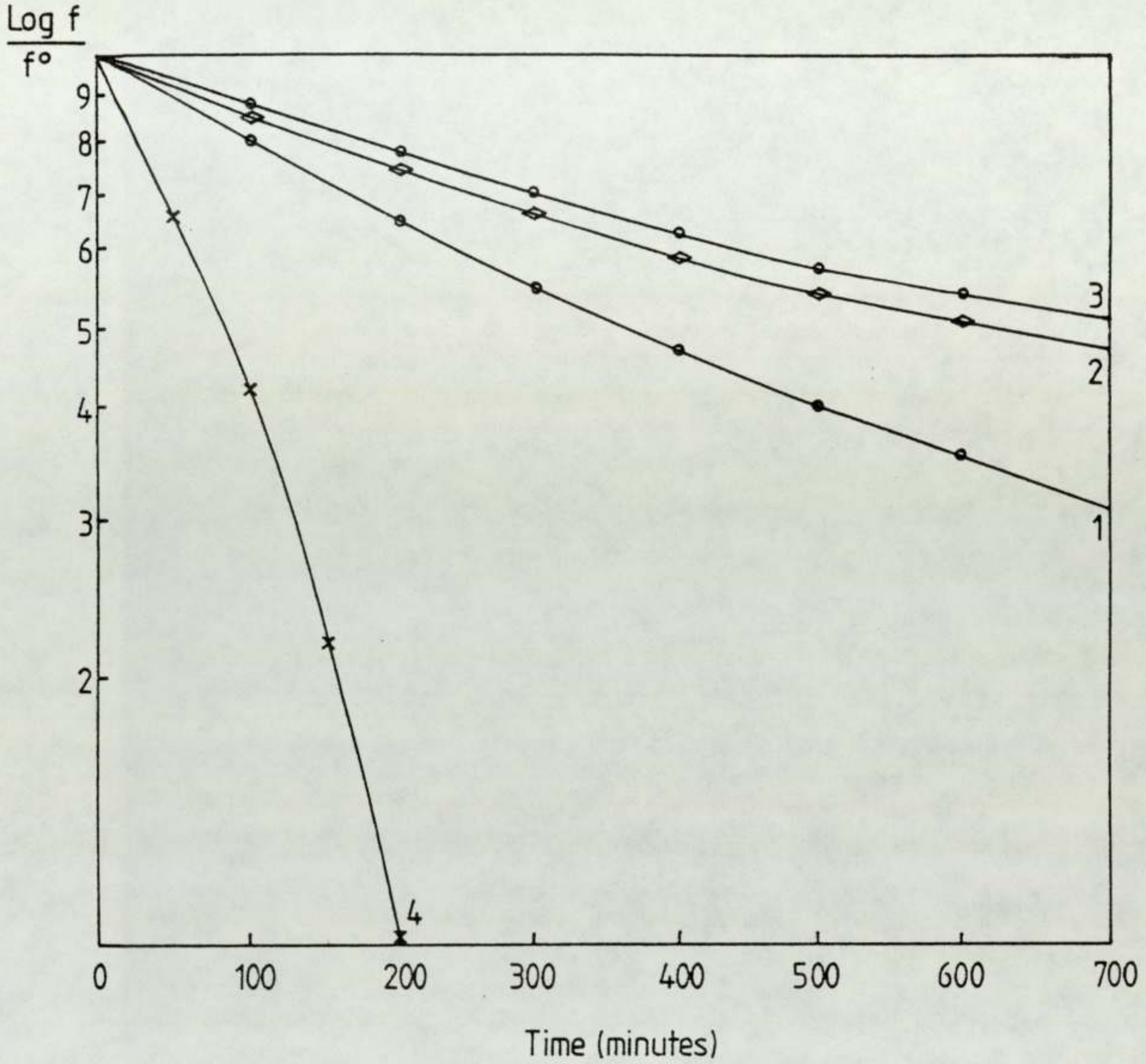
Results and Discussion

From Figs.5.1 and 5.2 the values of Log f/f^o after 900 minutes of ageing at 140°C for both before and after methanol extraction are shown in Table (5.2).

TABLE (5.2)

The Log f/f^o Values for CR Type-G With or Without ECH and Santoflex-13 After 900 Minutes of Ageing at 140°C

	Formulation Number			
	1	2	3	4
Not extracted	0.38	0.61	0.65	Broken in 200 min.
Methanol extracted	0.18	0.48	0.62	Broken in 200 min.

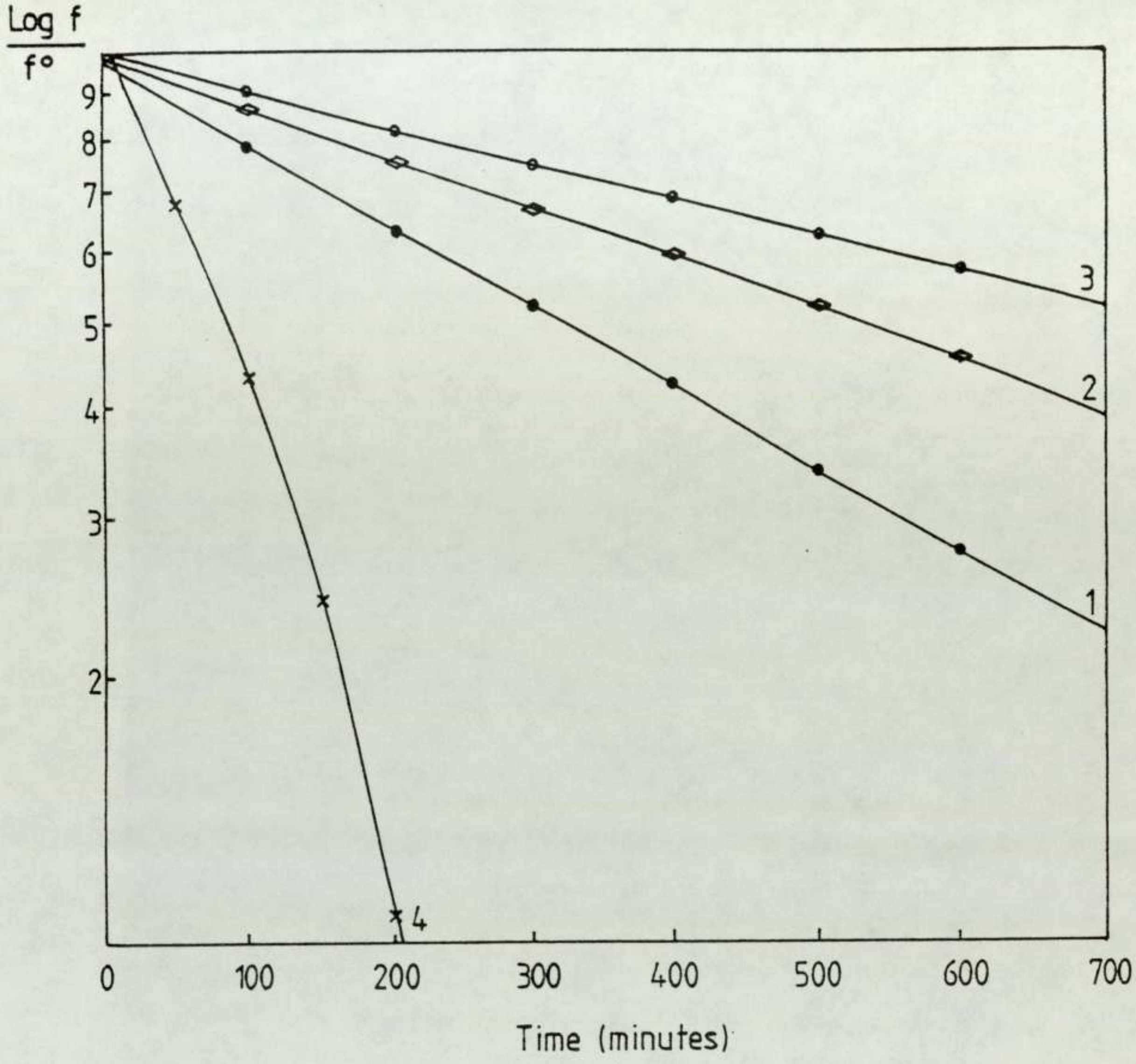


Key

- × (4) CR-G
- • (1) CR-G + ECH
- ◇ (2) CR-G + ECH + Santoflex-13(free)
- ∘ (3) CR-G + bound Santoflex-13 to ECH

Fig 5:1

The effect of Santoflex-13 (free or bound) on the continuous stress relaxation of CR-type G in the presence of ECH polymer before extraction, aged at 140°C



Key

- × (4) CR - G
- • (1) CR - G + ECH (virgin)
- ◇ (2) CR - G + Santoflex - 13 + ECH (free)
- ○ (3) CR - G + bound Santoflex - 13 to ECH

Fig 5:2

The effect of Santoflex-13 (free or bound) on the continuous stress relaxation of CR-type G at 140°C in the presence of ECH, after methanol extraction

From the above table it is clear that the presence of virgin ECH with CR type-G gives considerable protection to CR type-G. This is attributed to the fact that the saturated ECH homopolymer is more resistant to oxidation than CR type-G.

The samples containing only CR type-G lost all its properties after 200 minutes of ageing as is shown in Fig. 5.1 and Table (5.2).

The protection of CR type-G is further increased when free or bound Santoflex-13 is present. The antioxidant activity is due to its ability to react with the free radicals or the peroxy radicals which are produced in the system during degradation of rubber (See Section 3.1.5).

Before extraction the same degree of protection is obtained using free Santoflex-13 or ECH Santoflex-13 bound antioxidant (see Table (5.2)). Therefore, the Santoflex-13 when it combines with ECH, still acts as active antioxidant and its restricted mobility does not reduce the antioxidant activity.

The ageing behaviour of CR type-G after methanol extraction was as poor as the non-extracted sample, see Figs. 5.1 and 5.2 and Table (5.2). The vulcanizate of the CR type-G and ECH without any added antioxidant (Formulation No. 1) lost some of its resistance to oxidation after methanol extraction. This is due to the removal of processing antioxidant added by the manufacturer.

The vulcanizate containing 2 phr free Santoflex-13 (formulation No. 2) still has a good resistance to ageing even after the extraction process, see Table (5.2). This is not surprising as it has been shown that some of the added antioxidant becomes bound to the polymers during the vulcanization process, see sections 3.2.2.2 and 4.5.2.2.5. The decrease in the extent of protection of CR type-G after methanol extraction shows that only a part of the added antioxidant becomes bound during vulcanization.

Vulcanizates with bound Santoflex-13 (Formulation No. 3) show a superior resistance to degradation both before and after methanol extraction, once again showing that immobilisation of the antioxidant does not remove its protection activity.

5.3 THE EFFECT OF ECH HOMOPOLYMER ON THE PROPERTIES OF CR TYPE-G POLYMER

From the previous section 5.2, it is shown that ECH has a great effect on the ageing properties of CR type-G. In order to study in detail these effects, formulations shown in Table (5.3) were prepared on a two-roll mill at room temperature.

TABLE (5.3)

Formulations to Study the Effect of ECH Polymer on CR Type-G Polymer

	Formulation Number			
	5	6	7	8
CR Type-G	98	80	70	46.67
ECH Virgin	2	20	30	53.33
Zinc Stearate	1	1	1	1
FEF Carbon black	30	30	30	30
pb_3O_4	5	5	5	5
Diak No. 1	1.5	1.5	1.5	1.5
Modulus at 90% in-lb	70	66	58	-

These formulations were tested in a Monsanto rheometer at 160°C using a torque range of 100 in-lb and a time span of 30 minutes.

5.3.1 MONSANTO RHEOMETER STUDIES

The Monsanto rheograph, Fig. 5.3, shows that there is a decrease in the extent of vulcanization as the percentage of ECH increases: the induction period is not affected, see Section 5.2.1.

5.3.2 STRESS RELAXATION STUDIES

Thin films for stress relaxation were prepared as described in Section 2.3.3 at 160°C for 45 minutes using an induced heated press.

Continuous stress relaxation was carried out as described in Section 2.4.1 at 140°C. The results are shown in Fig. (5.4). The values of log f/f^{o} after 400 minutes of ageing at 140°C are shown in Table (5.4).

TABLE (5.4)

The Values of log f/f^{o} of CR Type-G with Difference Concentration of ECH Homopolymer

	Formulation Number			
	5	6	7	8
Log f/f^{o}	0.08	0.30	0.46	0.67

As expected increasing in the concentration of ECH homopolymer leads to an increase in the thermal oxidative resistance of CR Type-G rubber. Fig. 5.5 shows that there is a linear relationship between the concentration of ECH added to CR type-G and its thermal oxidative degradation.

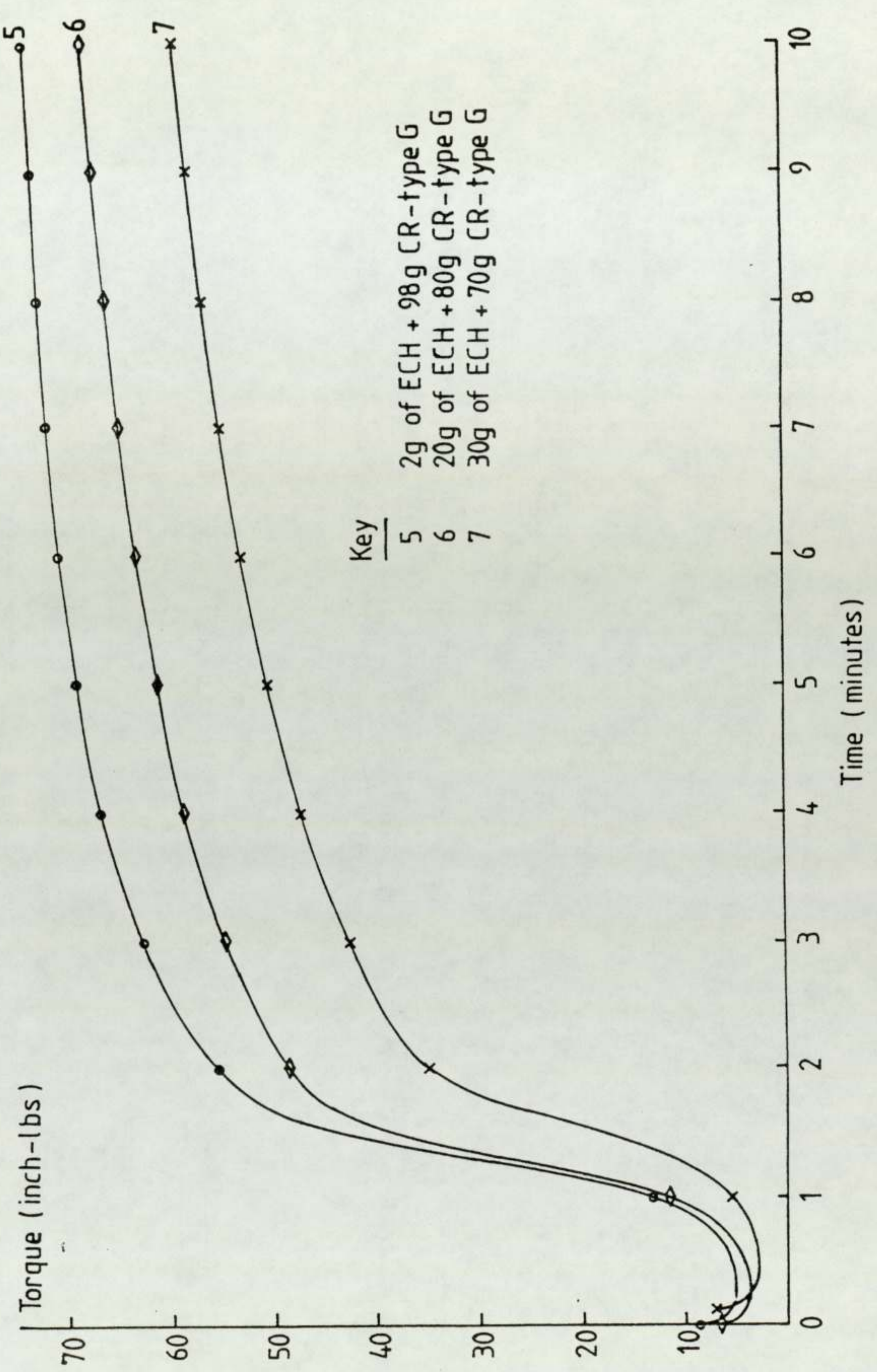
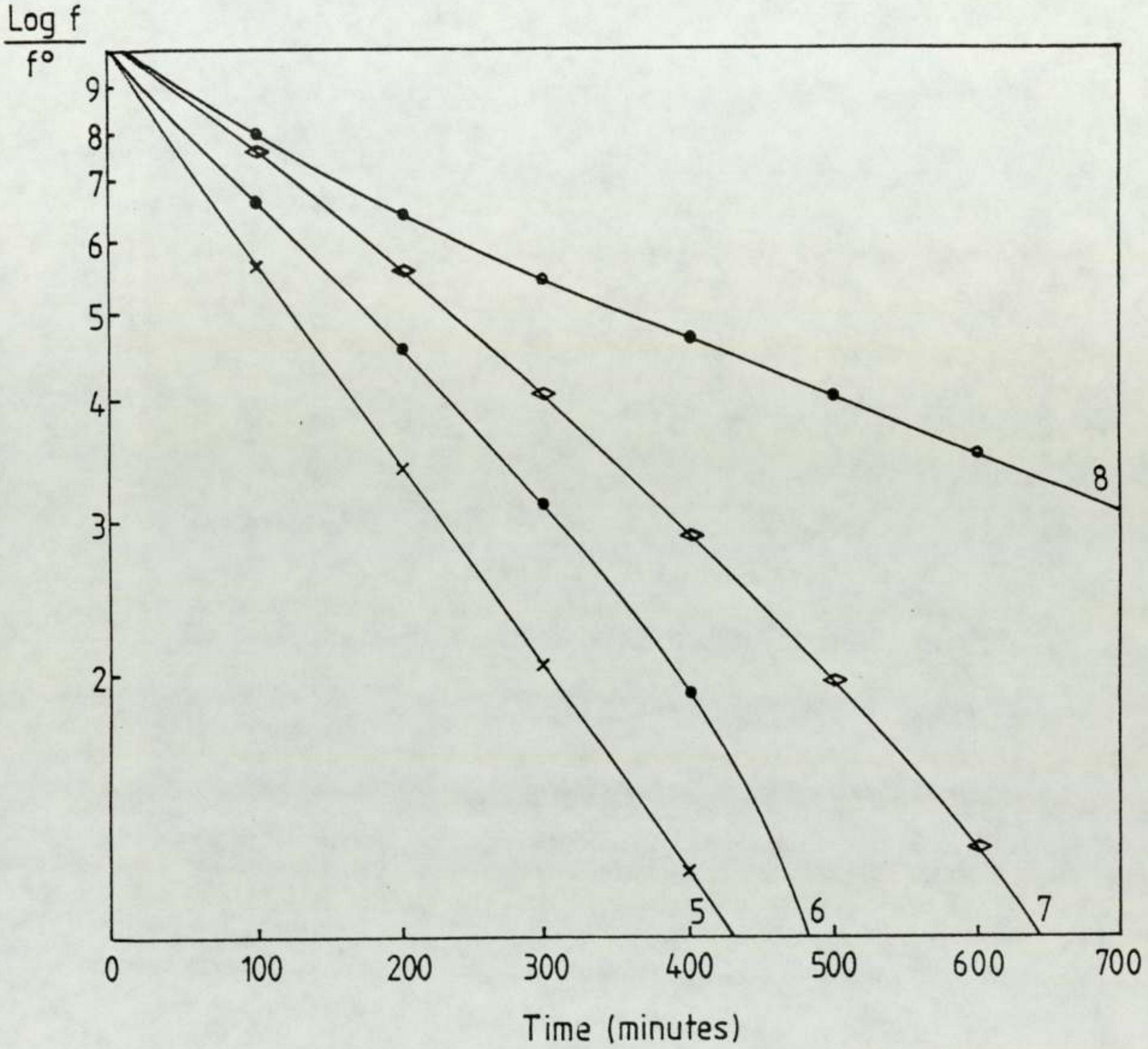


Fig 5:3

Monsanto rheometer of CR-type G with different concentrations of ECH



Key

× (5) 2g ECH + 98g CR-type G
• (6) 20g ECH + 80g CR-type G
◇ (7) 30g ECH + 70g CR-type G
∘ (8) 53·33g ECH + 46·67g CR-type G

Fig 5:4

The effect of different amounts of ECH on stress relaxation of CR-type G aged at 140°C

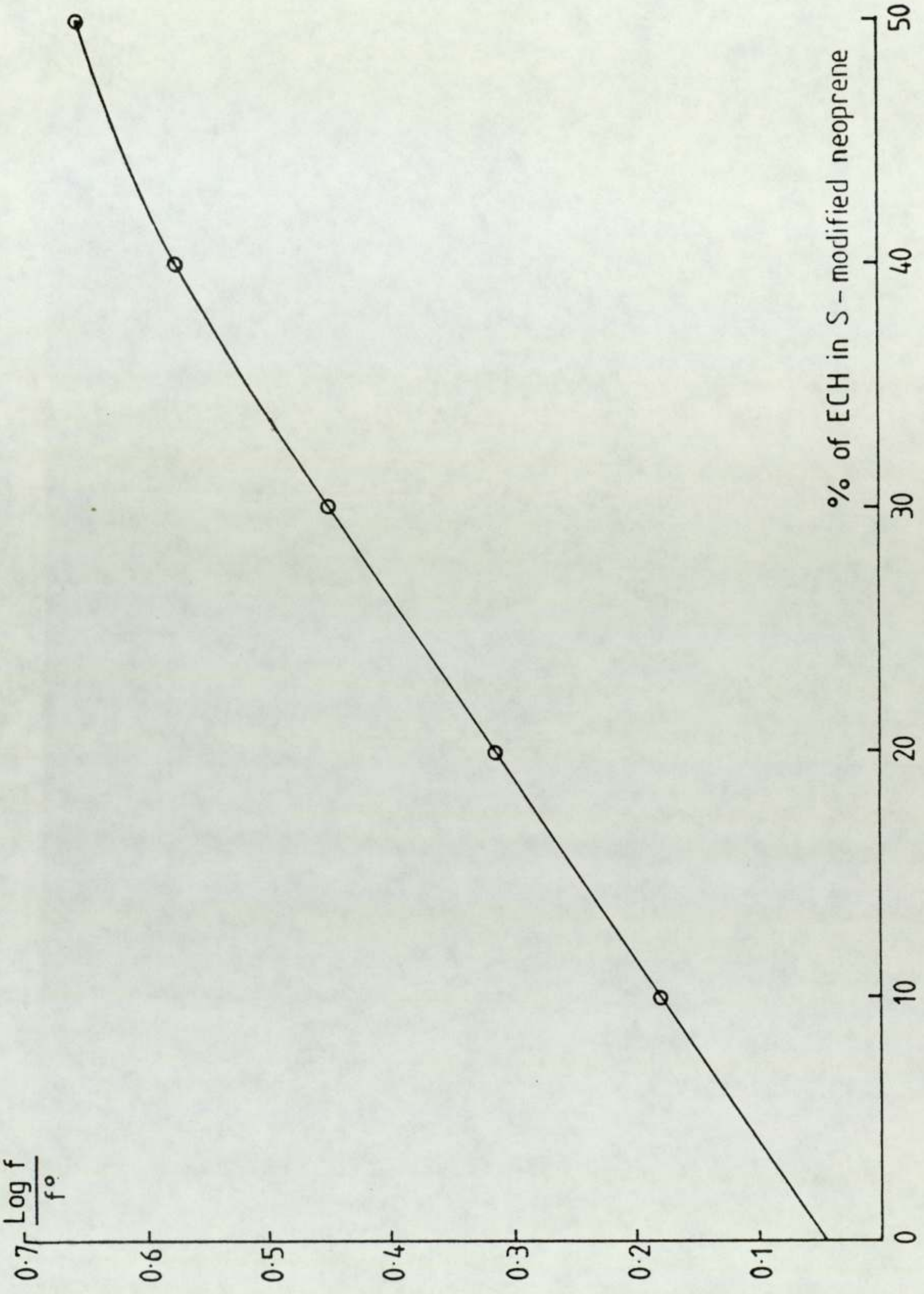


Fig 5:5

Log f/f° values after 400 minutes at 140°C for CR-type G with varying amounts of ECH

5.4 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON THE AGEING OF CR TYPE-W

To study the effect of ECH Santoflex-13 bound antioxidant on the vulcanization and ageing of CR type-W, the formulations shown in Table (5.5) were prepared on a two-roll mill at room temperature.

TABLE (5.5)

Formulations of CR Type-W with ECH-Santoflex-13 Bound Antioxidant

	Formulation Number			
	9	10	11	12
CR Type-W	46.67	46.67	46.67	100
ECH Virgin	53.33	53.33	-	-
Mgo	4	4	4	4
Zno	5	5	5	5
ECH-Santoflex-13 Bound Antioxidant	-	-	53.33	-
Free-Santoflex-13	-	2	-	-
NA-22	1	1	1	1
MBTS	1	1	1	1
Modulus at 90% cure in in-lb	29	29	30	40

5.4.1 THE EFFECT OF ECH-SANTOFLEX-13 BOUND ANTIOXIDANT ON THE VULCANIZATION CHARACTERISTICS OF CR TYPE-W

Formulations shown in Table (5.5) were tested in the Monsanto rheometer at 160°C using a torque range of 100 in-lb and a time span of 30 minutes. The values of the moduli at 90% cure listed in Table (5.5) shows that increasing amounts of homopolymer leads to a decrease in the modulus. Despite the fact that a more reactive curative system is used with CR type-W (i.e. NA-22) the ECH is not completely vulcanized and much of it remains unvlucanized.

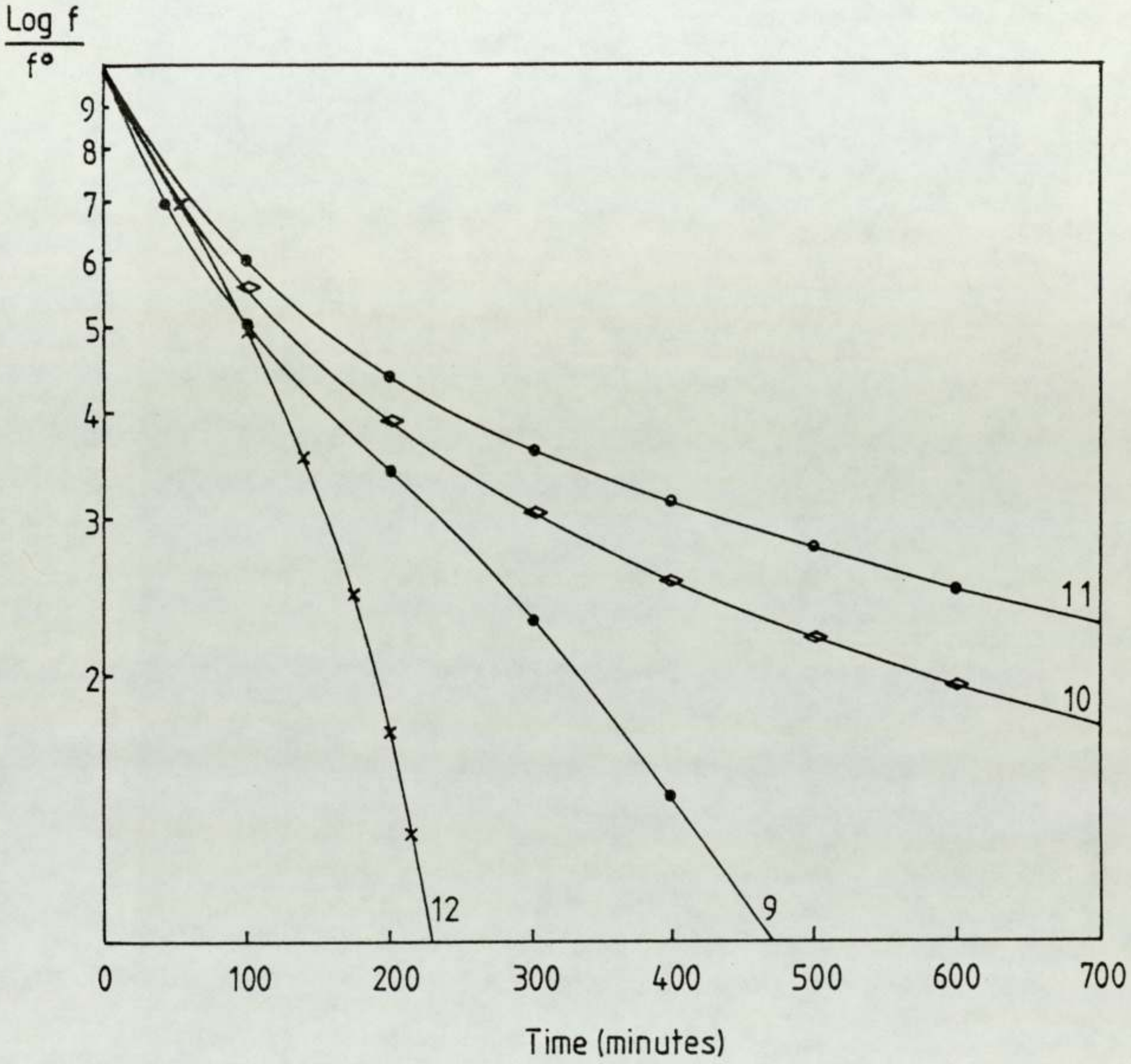
Santoflex-13 (free or bound) does not alter the extent of vulcanization of CR type-W and ECH mixture. This means that the reaction of the free amine which is proven to occur (Section 3.2.1.3.2 and Section 4.5.2.2.5) did not effect the cross-linking density of the vulcanizate or it is masked by the reduction in modulus that occurs when the CR type-W is diluted by the unreactive ECH.

5.4.2 STRESS RELAXATION ASSESSMENT OF EFFECTIVENESS OF ECH SANTOFLEX-13 BOUND ANTIOXIDANT ON CR TYPE-W

Thin sheets of 0.1 cm thickness were prepared as in Section 5.2.2 and continuous stress relaxation was carried out at 140°C for non-extracted and methanol extracted samples as shown in Fig. 5.6 and Fig. 5.7 respectively.

Results and Discussion

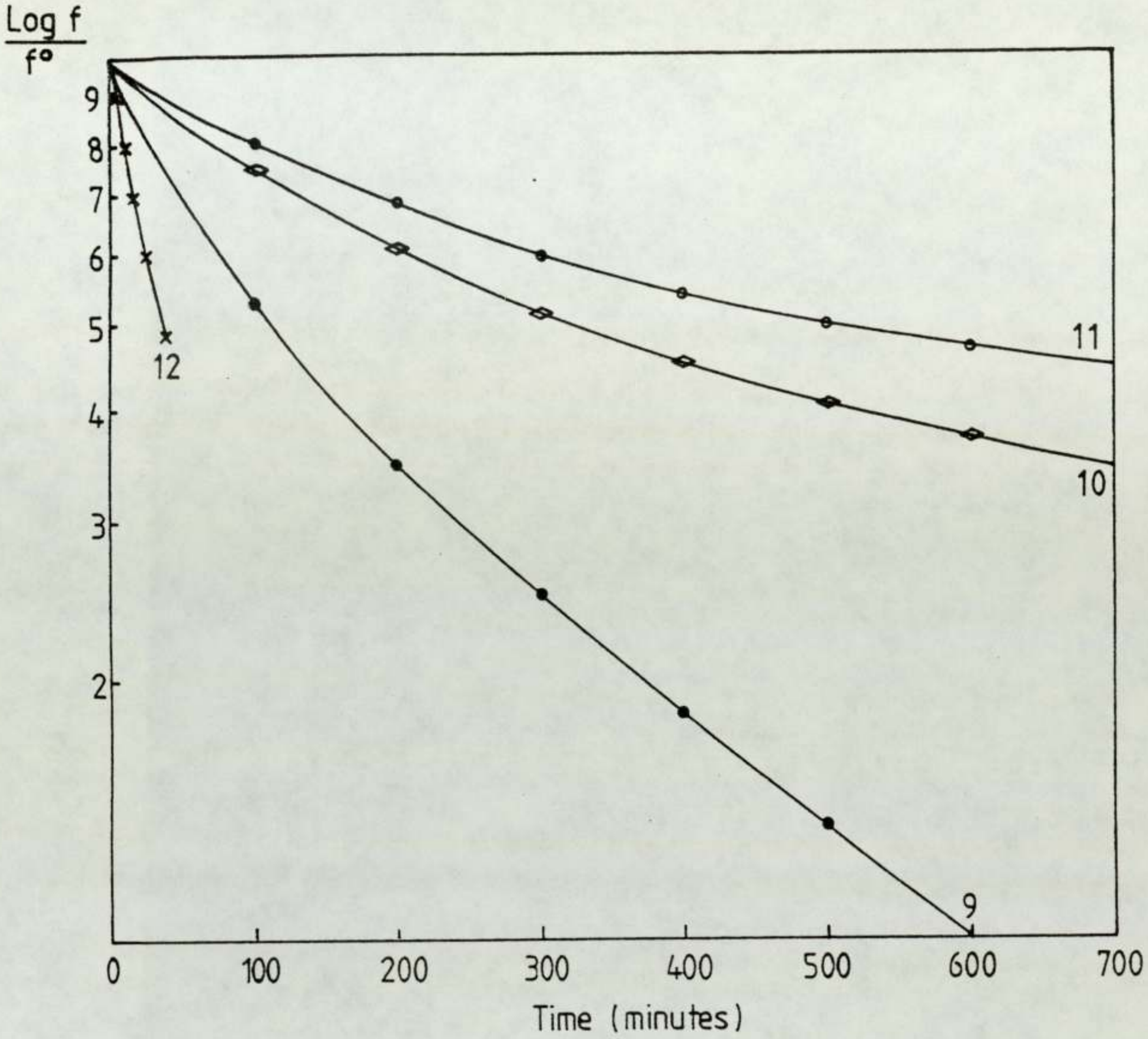
The values of log f/f^{o} after 900 minutes of ageing at 140°C, obtained from Fig. 5.6 and Fig. 5.7 are shown in Table (5.6).



Key

× (12) CR-type W
● (9) CR-type W + ECH
◇ (10) CR-type W + ECH + 2Phr free Santoflex-13
○ (11) CR-type W + ECH + 2Phr bound Santoflex-13

Fig 5:6
Continuous stress relaxation of CR-type W in the presence of Santoflex-13 free or bound to ECH, aged at 140°C for non-extracted samples



Key

- × (12) CR-type W
- • (9) CR-type W + ECH
- ◇ (10) CR-type W + ECH + 2Phr Santoflex-13 (Free)
- ∘ (11) CR-type W + ECH + 2Phr Santoflex-13 (Bound and ext)

Fig 5:7

Continuous stress relaxation of CR-type W in the presence of Santoflex-13, free or bound to ECH, aged at 140°C after methanol extraction

TABLE (5.6)

The log f/f^{o} Values for CR Type-W With or Without Santoflex-13 (free or bound) After 400 Minutes of Ageing

	Formulation Number			
	9	10	11	12
Not extracted	0.16	0.43	0.51	melted
Methanol extracted	0.26	0.67	0.72	melted

As it can be seen from the above table, the vulcanizates containing CR type-W only degrade rapidly.

The presence of virgin ECH gives considerable protection as can be seen by the autoretartation of the stress-relaxation curve of the extracted sample (Formulation No. 9). The corresponding curve of the unextracted sample, although still showing improved oxidative resistance, is still autoaccelerating and this must be due to the phenolic antioxidant added to the ECH by the manufacturer or due to the impurities present in the commercial ECH which has already been shown (Section 4.5.3.2) to act as a pro-oxidant in ECH under these conditions.

The addition of free amine antioxidant (Santoflex-13) gives considerable protection which is not removed by the extraction process, i.e. most of it has been bound in the network during vulcanization and is not lost by volatilization (see Section 3.2.1.3.2). The increase in stability on methanol extraction is due to the removal of the phenolic anitoxidant which we have shown to act antagonistically on ECH (Section 4.5.3.2).

The slightly superior thermal-oxidative resistance given by the Santoflex-13 that has been bound to the ECH before vulcanization is due to the increased concentration of bound antioxidant. Methanol extraction of this improves its resistance due to the removal of phenolic antioxidant and any other materials which inhibit the Santoflex-13 function as an antioxidant (see Section 4.5.2.1.7.4).

5.5 THE EFFECT OF ECH-SANTOWHITE POWDER BOUND ANTIOXIDANT ON THE THERMAL OXIDATIVE DEGRADATION OF CR TYPE-W

It has been shown that (3.2.3.2) Santowhite powder is a very good antioxidant of CR type-W before extraction. When extracted, however, the vulcanizate loses most of its physical properties on oven ageing (3.2.3.2.2.2), as only a small amount of Santowhite powder becomes bound during vulcanization. The small amount of bound phenolic antioxidant shows good antioxidant activity as assessed by stress-relaxation measurements (3.2.3.2.2.1) but is insufficient to give protection during the longer periods of oxidation involved in the oven ageing test (3,2.3.2.2.2).

Santowhite powder, on the other hand, can be bound in a good yield into ECH rubber during mixing before the vulcanization (4.5.3.1.3) but its presence leads to accelerated thermal oxidative degradation of the ECH. Even so, this may act as an antioxidant for polychloroprene rubber.

In order to study the effect of ECH-Santowhite powder bound antioxidant on the ageing of CR type-W, the formulations shown in Table (5.7) were mixed on a two-roll mill and vulcanised as thin sheets for stress relaxation assessment. The effect of the antioxidant on the vulcanization characteristics were first assessed in a Monsanto rheometer at 160°C using a torque of 100 in-lb and a time span of 30 minutes.

TABLE (5.7)

Formulations of CR Type-W with Santowhite

Powder (free or bound)

	Formulation Number			
	13	14	15	16
CR type-W	100	76.75	76.75	76.75
ECH virgin	-	23.25	-	23.25
ECH Santowhite Powder Bound Antioxidant	-	-	23.25	-
Free Santowhite Powder	-	-	-	2
Mgo	4	4	4	4
Zno	5	5	5	5
NA-22	1	1	1	1
MBTS	1	1	1	1
Modulus at 100% cure in-lb	55	36	44	28

5.5.1 THE EFFECT ON THE VULCANIZATION CHARACTERISTICS OF CR TYPE-W

As expected, there is a decrease in the modulus, Table (5.7) due to the presence of virgin ECH polymer, but the presence of 2 phr (free) Santowhite powder with virgin ECH reduced the modulus of CR type-W even more. This must be due to the reaction of the acidic Santowhite powder with the vulcanizing agent (NA-22). This interference is decreased when ECH Santowhite powder

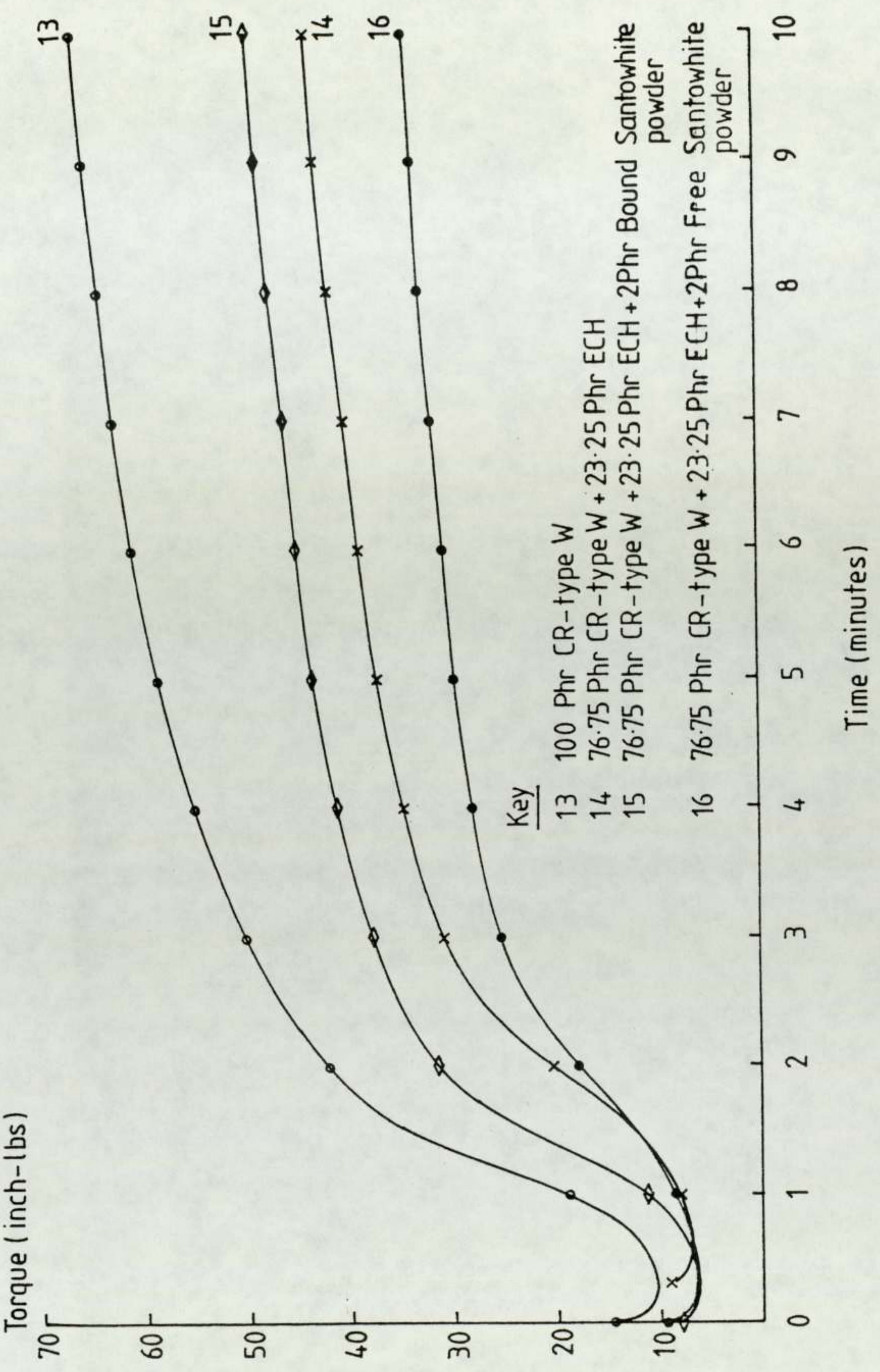


Fig 5:8

The effect of bound Santowhite powder with ECH on the vulcanization characteristics of CR-type W bound antioxidant is co-vulcanized with CR type-W.

5.5.2 THE EFFECTIVENESS OF ECH-SANTOWHITE-POWDER-BOUND ANTIOXIDANT ON THE THERMAL OXIDATIVE DEGRADATION OF CR TYPE-W ASSESSED BY STRESS RELAXATION

Thin sheets were prepared as described in Section 5.2.2 and samples for stress relaxation were cut out with the MR100 cutter. Half of the samples were acetone extracted under N_2 (2.3.4).

Continuous stress-relaxation was carried out at 130°C for both non-extracted and acetone extracted samples using the Wallace age tester.

Results and Discussion

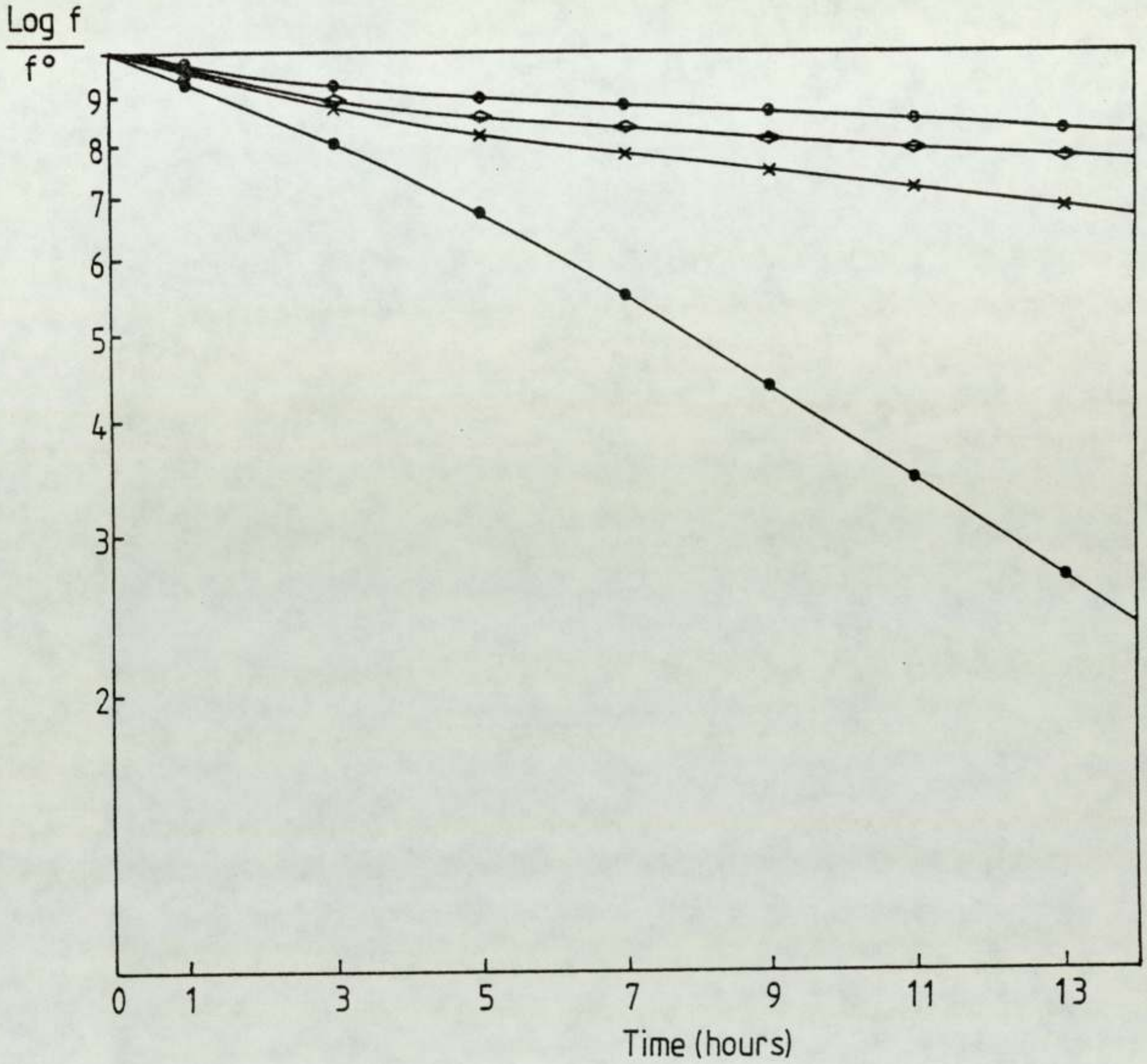
The graphs of the continuous stress relaxation are shown in Figs. 5.9 and 5.10 respectively.

The values of log f/f^o of the vulcanizates after 15 hours of ageing at 130°C are shown in Table (5.8).

TABLE (5.8)

The Values of log f/f^o of CR Type-W After 15 Hours of Ageing at 130°C in the Presence or Absence of Santowhite Powder (Free or Bound)

	Formulation Number			
	13	14	15	16
Not extracted	0.34	0.82	0.88	0.91
Acetone extracted	-	0.16	0.65	0.61

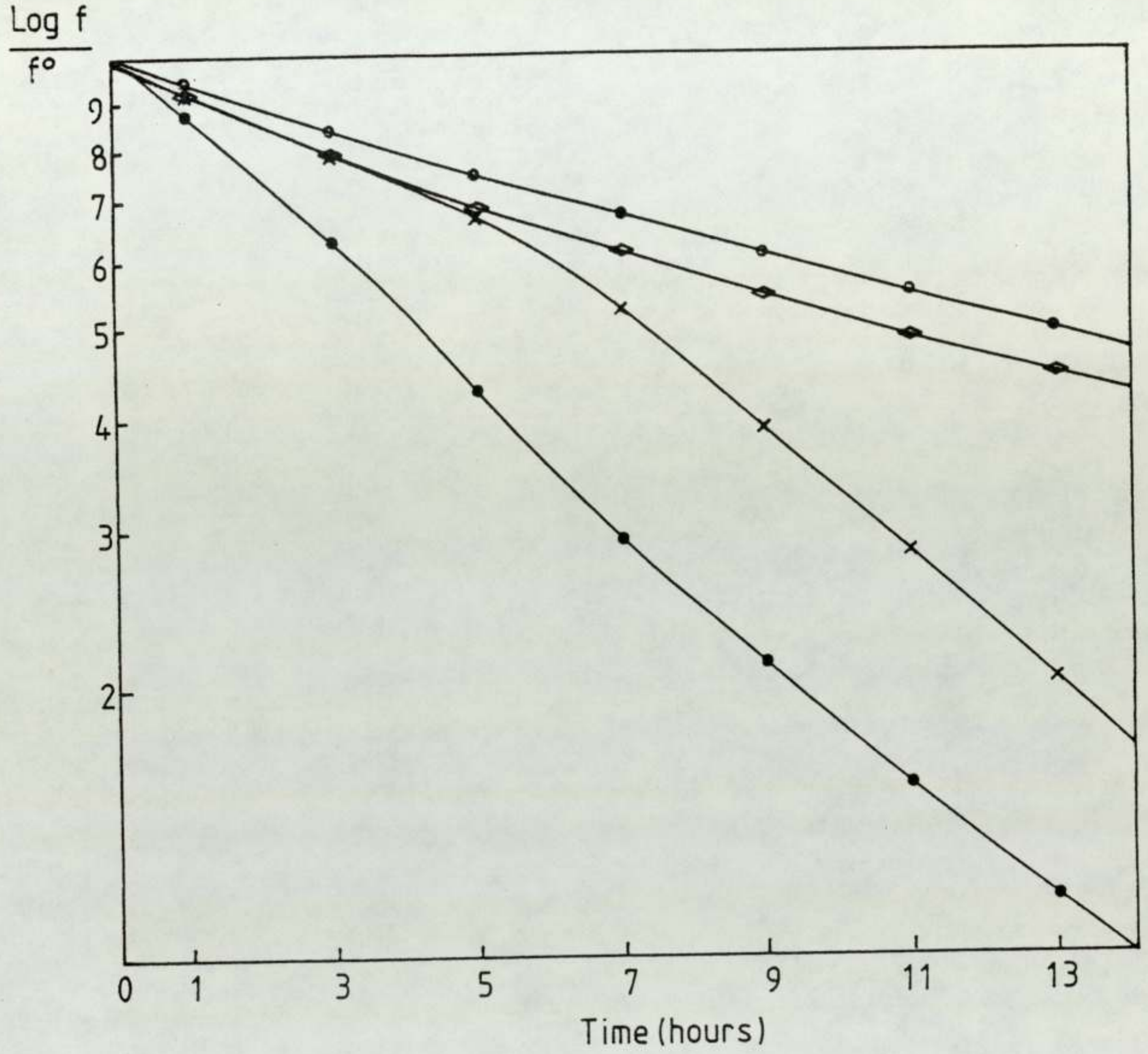


Key

- ● CR - type W
- × CR - type W + ECH homopolymer
- ◇ CR - type W + ECH homopolymer + 2Phr Bound Santowhite powder
- ○ CR - type W + ECH homopolymer + 2Phr Free Santowhite powder

Fig 5:9

Continuous stress relaxation of CR - type W in the presence of Santowhite powder (free or bound) with ECH homopolymer, aged at 130°C, not extracted



Key

- ● CR - type W
- × CR - type W + ECH
- ◇ CR - type W + ECH + 2Phr Bound Santowhite powder
- ○ CR - type W + ECH + 2Phr Free Santowhite powder

Fig 5:10

Continuous stress relaxation of CR-type W in the presence of Santowhite powder (free or bound) with ECH homopolymer, aged at 130°C, acetone extracted

As previously found, the presence of the saturated ECH increases the thermal oxidative resistance of CR type-W.

The presence of Santowhite powder (free or bound) increases the thermal oxidative resistance of CR type-W as shown in Fig. 5.9. The ECH Santowhite powder bound antioxidant still shows considerable antioxidant activity even though it is partially immobilised.

Acetone extraction of the CR type-W reduces its ageing resistance for the same reasons suggested in Section 3.2.3.2.2.1.

The vulcanizate which contains 2 phr (free) Santowhite powder still shows a good thermal oxidative resistance after acetone extraction suggesting that it has combined with the polymer. The amount of bound antioxidant could not be determined by an infra-red spectroscopy due to its low concentration.

From Table (5.8) it is shown that there is a small decrease in the activity of Santowhite powder after acetone extraction, this may be due to the same reasons mentioned in Section 3.2.3.2.2.1.

CHAPTER SIX

CONCLUSIONS

6.1 BOUND ANTIOXIDANTS IN POLYCHLOROPRENE

6.1.1 AMINES

6.1.1.1 N,N^{-}, iso propyl-phenyl-p-phenylene-diamine (IPPD)

IPPD will react with CR type-W during mixing in the torque rheometer to give concentration of bound antioxidant of 6.35 phr (a molar ratio of antioxidant: chloroprene of 1:37). It will also react during the vulcanization process to give a concentration of 1.4 phr (1:176 :: IPPD:CR). Although higher concentrations can be obtained in the latter case, it is impractical to use more than 2.0 phr of IPPD in the vulcanizing reaction as it interferes with the vulcanization process. In the absence of other accelerators, for example, low concentrations of IPPD (upto 3 phr) enhance the extent of the cross-linking density. There is a marked decrease in the scorch time when more than 1 phr IPPD is used. In the presence of accelerators such as NA-22, IPPD causes a reduction in the cross-linking denstiy but the scorch time is unaffected.

The reaction between IPPD and CR type-W takes place through active chlorine atoms and the isopropyl amino groups, i.e. the phenyl substituted amino group is inert.

The antioxidant activity of IPPD is not reduced when it is combined with CR type-W during the vulcanization process even when it is immobilized in the network.

IPPD bound in the rubber by mechanochemical reaction before vulcanization is found to accelerate the thermal oxidative degradation of the vulcanizate. There is no Zno or Mgo present during this mixing process to scavenge the HCl formed during the reaction of the amine with the rubber, as there is in the case of the vulcanization process. HCl is known to cause severe degradation if not removed. In view of this degradation the mechanochemical method of binding was abandoned.

IPPD will combine with CR type-G during vulcanization (1.4 phr $\equiv$ 1: 131 :: IPPD : CR) although the modulus of the vulcanizates reduce with increasing concentrations of IPPD. This reduction in the modulus is not as pronounced as that produced with CR type-W. The type of compounding processes used which were a two-roll mill and Banbury mixer. These do not affect the amount of IPPD combined or its subsequent antioxidant activity which remained unimpaired by its immobilization due to combination with the rubbers.

6.1.1.2 N,1,3-dimethyl butyl-N-phenyl-p-phenylene diamine (Santoflex-13)

Santoflex-13 will react with CR type-W during the vulcanization process by the isopropyl substituted amino group to give a concentration of bound Santoflex-13 of 1.4 phr $\equiv$ 1:213::Santoflex-13:CR. The blocking of some of the active chlorine groups (the cross-linking sites) by the amine, results in a decrease in the modulus of the vulcanizates. The immobilization of the Santoflex-13 by combination in the network does not cause any reduction in the thermal-oxidative antioxidant activity.

Santoflex-13 will similarly react with and give protection to CR type-G.

6.1.1.3 N,N¯-diphenyl-p-phenylene diamine (DPPD)

When attempting to combine DPPD with CR type-W during the vulcanization process the results were confused because pyrogollol was used as the vulcanizing agent.

After acetone extraction these vulcanizates still showed marked antioxidant activity but evidence of bound antioxidant could not be obtained from I.R. absorption spectra. This may be due to the concentration of amine being too low or it may be that the basic amine has reacted with the acidic pyrogollol to produce an insoluble product which retains its antioxidant activity.

6.1.2 PHENOLS

6.1.2.1 1,2,3 tris(2-methyl-4-hydroxy-5-tert-butyl-phenyl) butane (Topanol CA)

Topanol CA is a good antioxidant for CR type-W both before and after acetone extraction indicating that some of it has combined to the rubber. I•R absorption spectra measurement showed that 1.4 phr of Topanol CA has combined

(1:228::Topanol CA:CR).

As in the case of amine the blocking of the cross-linking sites by phenol and its reaction with other ingredients reduces the cross-linking density.

6.1.2.2 4,4^{-}-butylidene bis (3-methyl-b-tert-butyl phenol) (Santowhite Powder)

A little of the antioxidant activity of vulcanizates containing Santowhite powder is still retained after acetone exctraction suggesting that a small amount of it has combined with the rubber or formed an insoluble reaction product which still shows antioxidant properties. Its presence could not be detected from I.R. measurement.

Again there was a decrease in the modulus of the vulcanizates when Topanol CA was added.

6.2 BOUND ANTIOXIDANTS IN POLYEPICHLOROHYDRIN

6.2.1 THE FUNCTION OF VARIOUS COMPOUNDING INGREDIENTS

Zinc stearate increases the extent of cross-linking but does not affect the rate of cross-linking process, while IPPD affects the modulus only slightly.

The presence of NBC does not effect the induction time, however, it does decrease the extent of vulcanization in the absence of zinc stearate.

It is shown that zinc stearate is a good stabilizer for ECH rubbers while NBC shows only slight antioxidant activity in the presence of zinc stearate.

IPPD is a good antioxidant for ECH rubber before and after acetone extraction suggesting that some of IPPD combines with the rubbers during the vulcanization process. The extraction of a vulcanizate containing bound IPPD improves its thermal oxidative resistance due to the removal of extra network material such as phenols which we proved to act as a pro-oxidant.

There is a synergetic effect between IPPD and zinc stearate while IPPD and NBC have an antagonistic effect.

6.2.2 AMINES

6.2.2.1 N,N$^-$-isopropyl-phenyl-p-phenylene diamine (IPPD)

IPPD will react with ECH during mixing in the Winkworth mixer to give a concentration of bound antioxidant of 3.1 phr (a molar ratio of 1:73 antioxidant to epichlorohydrin) It is also shown that there is a decrease in the concentration of bound antioxidant on extended mixing.

The reaction between IPPD and ECH rubbers will take place through the isopropyl substituted amino groups of the antioxidant and the chlorine atoms of the ECH rubbers, therefore, no cross-linking reaction will occur during mixing in the Winkworth mixer.

No reaction will take place if mixing is carired out on a two-roll mill.

The binding of IPPD antioxidant to ECH rubbers will take place during the vulcanization process to give a rubber bound antioxidant of 1.2 phr (a molar ratio of 1:200 antioxidant to epichlorohydrin)

There is a small decrease in the modulus of the ECH vulcanizates in the presence of free or bound IPPD which is due to blocking of the reactive chlorine atoms.

IPPD shows a very good antioxidant activity to ECH rubbers which increases after acetone extraction.

The extent of protection of ECH rubber by rubber bound antioxidant is greater than that given by the same amount of free antioxidant. This suggests that the immobilization of IPPD does not reduce its antioxidant activity on ECH rubbers.

There is some postcure reaction on ageing which does not occur if it is first acetone extracted.

6.2.2.2 The Effect of Extraction on the Stability of ECH Rubbers

The extraction of commercial ECH rubber before the vulcanization process is found to increase the thermal oxidative resistance of the vulcanizate and increase the effectiveness of IPPD as an antioxidant; this is due to the removal of the extra network materials such as phenols which inhibit the IPPD activity.

6.2.2.3 N,1, 3,-dimethyl-butyl-N-phenyl-p-phenylenediamine (Santoflex-13)

Santoflex-13 will react with ECH rubber when mixed in the Winkworth mixer or in the torque rheometer to give a concentrated bound antioxidant of 3.75 phr (a molar ratio of 1:75 antioxidant to epichlorohydrin). The reaction, also, can take place during the vulcanization process to produce vulcanizates containing 1.2 phr (a molar ratio of 1:283 antioxidant to epichlorohydrin).

The presence of Santoflex-13 (free or bound) decreases the modulus of the vulcanizates due to the blocking of some of the cure sites.

No cross-linking takes place during the reaction as only the alkyl-substituted amino group will react with the chlorine atom of the rubber, i.e. the phenyl substituted amino group is unreactive.

Santoflex-13 (free or bound) shows a very good antioxidant activity both before and after acetone extraction suggesting that some of the free antioxidant is combined during the vulcanization process and its activity is not affected by its immobilisation.

The antioxidant activity of Santoflex-13 is increased after acetone extraction due to the removal of phenols which are known to inhibit it.

Santoflex-13 will give some protection to ECH rubber when in contact with ASTM oil No. 1, however, it has no effect on the vulcanizates immersed in high aromatic content oil, i.e. ASTM oil No. 3, due to the absorption of this oil by the rubbers.

6.2.3 PHENOLS

6.2.3.1 4,4^{-}-butylidene bis(3-methyl-6-tert-butyl-phenol) (Santowhite powder)

The sodium salt of Santowhite powder is used to facilitate the reaction which is carried out in the torque rheometer to give bound antioxidant of 2.8 phr (a molar ratio 1:152 antioxidant to epichlorohydrin). The reaction is, also, carried out during the vulcanization process to give 1.0 phr bound antioxidant (a molar ratio of 1:432 antioxidant to epichlorohydrin).

The presence of Santowhite powder (free or bound) decreases the extent of vulcanization due to the reduction in the number of curative sites which are responsible for the vulcanization process; the induction period is not affected.

Santowhite powder accelerates the thermal oxidative degradation of ECH both before and after extraction. Santowhite powder bound into ECH before the vulcanization process is found to accelerate the thermal oxidative degradation of ECH rubber more than the vulcanizates containing the same concentration of free Santowhite powder. This is due to the absence of pb_3O_4 and zinc stearate during the mechanochemical reaction. These compounds will eliminate the effect of HCl which evolves during reaction which is known to accelerate the degradation of ECH rubbers if not removed.

6.2.3.2 The Effect of NBC on the Effectiveness of the Phenolic Antioxidants

NBC, used alone, gives some protection to ECH rubber against thermal oxidative degradation. The presence of other phenolic antioxidant together with NBC accelerates the thermal oxidative degradation of the vulcanizates.

Phenolic antioxidants accelerate the thermal oxidative degradation both before and after extraction. Therefore, phenolic antioxidants are not recommended for these rubbers.

6.2.3.3 2,4-dihydroxybenzophenone as U-V Stabilizer

4.5 phr of 2,4-dihydroxybenzophenone reacts in the Winkworth mixer to give a concentration of 1.8 phr bound antioxidant (a molar ratio of 1:139 stabilizer of epichlorohydrin).

The 2,4-dihydroxybenzophenone (free or bound) is found to be a good U.V. stabilizer for ECH rubber. Some of its reactivity is still retained on binding.

Binding the stabilizer to ECH in the Winkworth mixer accompanied by the production of hydroperoxide which accelerates the degradation. Therefore, bindingof the stabilizer shows less activity than the free stabilizer. Restricted mobility of the stabilizer is another reason for the decrease in its activity as a U.V. stabilizer.

6.3 THE USE OF ECH WITH BOUND ANTIOXIDANT AS A POLYMERIC ANTIOXIDANT

The modulus of CR vulcanizates decreases with each increase in the concentration of ECH rubber in the blends. This decrease in the modulus is greater in the presence of free or bound antioxidants (amines or phenols).

The presence of ECH with CR rubbers, both before and after acetone extraction gives a considerable protection against the thermal oxidative degradation and this protection is increased in the presence of free or bound antioxidants (amines and phenols). This suggests that some of the free antioxidant becomes combined with the rubbers during the vulcanization process and the immobilization of the antioxidant does not reduce its antioxidant activity.

The vulcanizates containing ECH-Santoflex-13 and ECH-Santowhite powder which are bound antioxidants have a superior thermal oxidative resistance than the vulcanizates containing free Santoflex-13 or Santowhite powder.

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