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CATIONIC SURFACTANTS IN RUBBER COMPOUNDING

by

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ABSTRACT

Cationic surfactants have not been previously known as rubber compounding ingredients. This study examined their use as processing aids, accelerators and crosslinking agents.

The following chemical classes have been investigated, namely:

- i) Commercially available cationic surfactants having the general formula $[\text{RNH}_2(\text{CH}_2)_3\text{NH}_3]^{++} 2 \text{R}'\text{COO}^-$,
where R = tallow
R' = other long chain alkyl groups derived from fatty acids.
- ii) Commercially available cationic surfactants having the general formula $\text{RNH}-(\text{CH}_2)_3\text{NH}_2$
where R = various long chain alkyl groups derived from fatty acids.
- iii) Commercially available hydrophobic materials having the general formula $\text{RCONH}(\text{CH}_2)_2\text{NHCOR}$
where R = long chain alkyl group derived from fatty acid.
- iv) Compounds specially prepared as research intermediates and of general formula $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{++} 2[\text{RCOO}]^-$.

Much of the research has been concentrated on truck tyre sidewall rubber compounds based on NR/SBR blends; however, the effects of the above materials, i.e. the surfactants, diamide compounds and the research intermediate materials, on other rubbers such as NBR, CR, BR, NR and SBR have also been examined. It was discovered that surfactants (i) act as excellent processing aids and were superior in performance to six conventional plasticisers and processing aids. It was also found that the other materials (ii), (iii) and (iv) act as excellent processing aids and behave similar to (i).

Also, and unexpectedly, they can function as cure accelerators without the presence of the conventional cure activation system of zinc oxide and stearic acid. Indeed the use of zinc oxide with surfactants class (i) and research compounds (iv) retarded cure rate. Hydrophobic compounds in class (iii) were found to be cure activated by the addition of triethanolamine. Another new finding was that the surfactants in classes (i) and (ii) and the research materials (iv) act as good crosslinking agents for polychloroprene (CR) rubber and the mechanical properties of the resulting vulcanisate are excellent.

The mechanical properties of vulcanisates cured with a 'surfactant or a research intermediate material-accelerator' and sulphur were found to be superior to those based on conventional thiazole and sulphenamide accelerators in NR, SBR and BR; NBR and CR surfactant containing formulations did not show any significant improvement in vulcanisate properties.

Stress-relaxation and hot air oven techniques were used to study the elevated temperature (100°C) ageing behaviour. Over a period of one week no significant difference with conventional curing systems was found. However for ageing periods of more than one week surfactant containing vulcanisates (without ZnO) were found inferior to conventional rubber cure systems. However addition of zinc oxide was found to be beneficial in improving their ageing behaviour, an unexpected observation. The chemical mechanisms involved were investigated by use of the following techniques: infrared spectroscopy, differential scanning calorimetry, scanning electron microscopy, solvent swelling and extraction, in order to obtain an insight into the behaviour of surfactants when incorporated into a rubber formulation.

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Dedicated to the ones I love:

My parents

My sisters

My wife

and our daughter

Russell

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CHAPTER 1

RUBBER COMPOUNDING

Introduction

The mixture of rubber and ingredients used in rubber manufacture is known as a "compound" and the process of making such a compound as compounding.

The principal raw materials of a compound are: rubber or blend of rubbers, curing system, fillers, plasticiser and/or processing aid. Each one of these components plays an important part in both the processing behaviour and vulcanisate properties of a compound.

The author's research work was to study the behaviour of a cationic surface active agent as plasticiser and/or processing aids for rubber compounds.

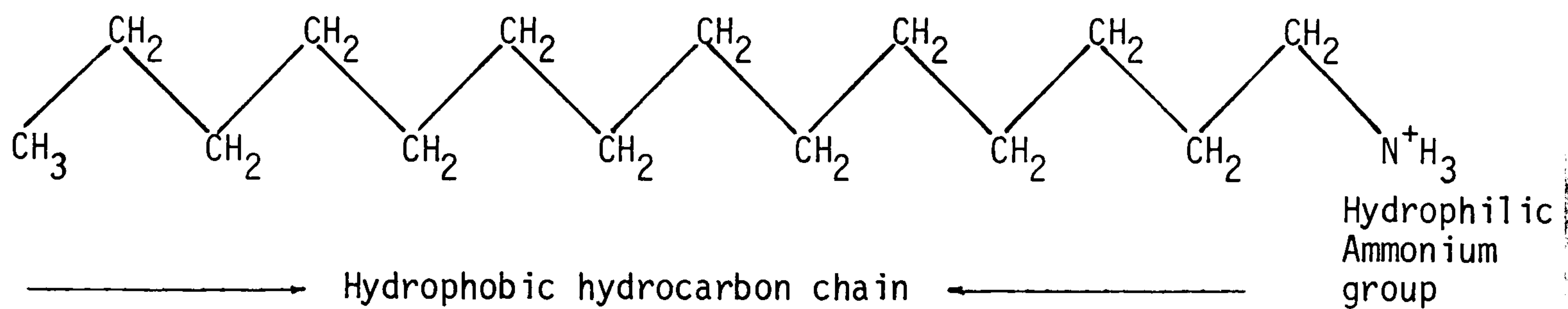
In the course of the study it has been discovered that this type of surfactant has multiple functions and can act as both processing aid and cure activator/accelerator for natural and synthetic rubbers, additionally they can function as crosslinking agents for CR rubber. This chapter describes the present technology of surfactants, plasticisers and/or processing aids, and a brief summary of current rubber vulcanisation theory. Finally the objectives of the present research are stated.

1.1 Surfactants

Some solutes, even present in very low concentration, have the ability of changing the surface energy of their solvents to a considerable degree. The effect is always a lowering rather than an increase of

the surface energy. Such materials have come to be known as Surface Active Agents, and their effect is known as surface activity. A detailed consideration of this effect is given in Appendix 1.

Surface active agents are characterised by their linear structure. One end of this linear structure is composed of radicals which are compatible with the solvent, and the opposite end of incompatible radicals. For example, fatty amines are composed of a hydrophobic (non-polar, water insoluble), hydrocarbon chain, characterised by weak residual valence forces in one end and a hydrophilic (polar, water soluble) cationic nitrogen group which has strong residual valence forces on the other end as shown below:



1.1.1 Classification of Surfactants [1][2][3]

The most common system used to classify surfactants is one which depends on the distribution of electrical charge on the molecules and this system will now be described.

1.1.1.1 Anionic Surface Active Agents

This class of surfactant is characterised by the inclusion of a low-affinity hydrocarbon chain adjacent to anion and is usually soluble in aqueous solution. Sodium stearate (C₁₇H₃₅COONa) is a typical anionic surfactant since it ionises in solution to form Na⁺ and the long-chain

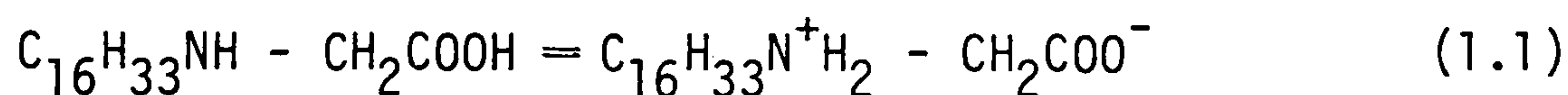
stearate anion, $C_{17}H_{35}COO^-$, which is considered to be responsible for its surface activity. In this class some of the most important end groups are Carboxy ($-COOH$), Sulphonic acid ($-SO_3H$), and Sulphuric ester ($-OSO_3H$). Table 1.0 shows some typical commercially available anionic surfactants [3].

1.1.1.2 Nonionic Surface Active Agents

The non-ionic class has non-ionisable high-affinity end group i.e. no residual electrical charge as for example Dodecylalcohol ethoxylate: $CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOH$. Usually the non-ionic surfactants contain a number of oxygen, nitrogen, or sulphur atoms in non-ionising configurations. Table 1.1 shows some commercially available non-ionic surfactants, their properties, with their main suppliers [3].

1.1.1.3 Amphoteric Surface Active Agents

This class is characterised by the presence of both positive and negative centres in one molecule. Cetylamine acetic acid, for example, comes to the following equilibrium in aqueous solution:



depending on the pH of the medium, cationic, anionic, or nonionic type properties may be exhibited. Table 1.2 shows some commercially available amphoteric surfactants [3].

TABLE 1.0

REPRESENTATIVE COMMERCIAL ANIONIC SURFACTANTS, THEIR PROPERTIES AND USES [3]

Supplier	Trade Name	Code	Cation	Anion	ca. % Activity	Physical Form	Properties and/or Uses	Example of Fields of Application
Akzo Chemie UK Ltd	Elfan	WA Series	Sodium	Dodecylbenzene sulphonate	50	Yellowish liquid to paste	Surfactant	Heavy and light duty, all purpose and dishwashing detergents
	Elfan	280 Powder	Sodium	Coconut fatty alcohol sulphate (C ₁₂ -C ₁₈)	90	Fine, white powder	Detergent	Dishwashing detergents
	Elfan	NS 682 KS	Potassium	Synthetic fatty alcohol (C ₁₆ -C ₁₈) 2EO sulphate	50	Yellowish paste		Shampoo, washing pastes, car shampoos
Hoechst UK Ltd	Hostapur	OS Powder	Sodium	Olefine sulphonates with an alkylene radical (C ₁₅ -C ₁₈)	98	Free-flowing powder, weakly yellow	High foaming, excellent cleaning action with wool. Water hardness stable	Detergents of all kinds; textile leather, auxiliaries, upholstery and carpets
Allied Colloids Ltd	Alcopol	OB Conc. 45%	Sodium	Di-iso-butyl sulphosuccinate	45	Colour less free flowing solution in water/alcohol	Powerful wetting agent in presence of electrolytes	Oils, solvents, waxes and polymer. Wind screen wash concentrate

TABLE 1.1

TYPICAL COMMERCIALY AVAILABLE NONIONIC SURFACTANTS [3]

Supplier	Trade Name	Code	Hydro- Phobe	'n' No.	App. % Active	Physical Form	Cloud Point (°C)	HLB No.	Properties and/ of Uses	Example of Fields of Application
Akzo Chemie UK Ltd	Elfapor	N50	Nony- phenol	5		Clear, nearly colourless liquid	-		Dishwashing det- ergents	Automatic machines
	Elfapor	LP255	C ₁₂ -C ₁₅ Fatty alcohol R-OH	2.5		Clear to slightly turbid liquid			Base material	Ether sulphate manufacture
Croda Chemicals Ltd	Volpo	25D3	C ₁₂ -C ₁₅ Synthetic alcohol	3	100	Liquid	-	7.8	Wetting, disper- sing, solubili- sing, emulsifying antistatic agents	Cosmetic, textiles, agriculture, paper, adhesives etc.
	Volpo	T5	Tridecanol C ₁₃ H ₂₇ OH	5	100	Liquid	-	10.4	Same as above	Detergents, tex- tiles, dustwetting, etc.
ABM Chemicals Ltd	Texofor A2	A2	Higher fatty alcohol "	2	100	Soft waxy solid	-	-	Wide range of surfactants	Glue manufacture, antifoam agents, auxiliaries for emulsion polymeri- sation etc.
	Texofor A60	A60	"	60	100	Brittle waxy solid	-	-	Same as above	

Notes: 'n' No = Average number of ethanol per mole of amine. The 'n' number and the nature of R determine the properties of the derived surfactants.

HLB No = A number representing the balance between the hydrophilic and lipophilic content of the molecule.

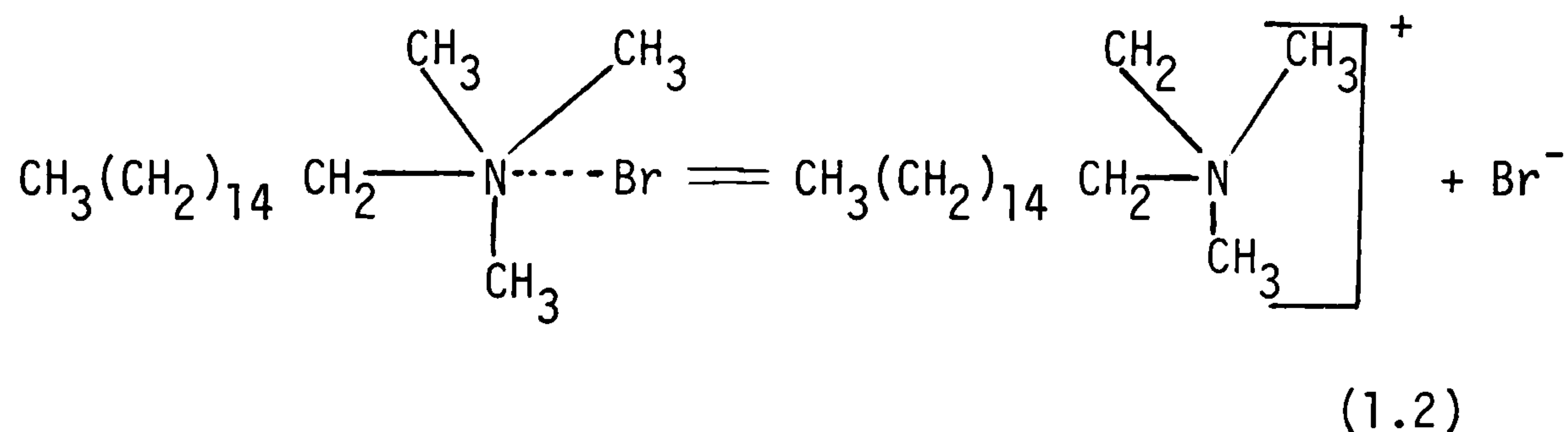
TABLE 1.2

TYPICAL COMMERCIALLY AVAILABLE AMPHOTERIC SURFACTANTS [3]

Supplier	Trade Name	Code	Description	App.% Active	Physical Form	Properties and/or Uses	Examples of Fields of Application
Akzo Chemie UK Ltd	Elfan	A432	Amphoteric surfactant	30	Yellowish, clear liquid		Baby shampoos; bubble baths; strong acid and alkaline cleaning detergents
	Armoteric	LB		30	Yellowish liquid		
	Armoteric	SB		30	Yellowish paste		
KenoGard (UK)Ltd	Ampholyte	SKKP 70				Corrosion inhibitors; dispersing agents	Emulsion paints. Pigment grinding
Croda Chemicals Ltd	IMIDAZOLINE BASED AMPHOTERIC SURFACTANTS						
	Crodateric	0100	Oleic $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	100	Thick paste (fluid at 70°C)	The properties being influenced by pH	Acid and alkali detergents; toilettries; skin cleanser; shaving creams; polymers; textiles; metal treatment, etc.
	"	5	Stearic $\text{C}_{17}\text{H}_{35}\text{COOH}$	50	Pasty solid		
	"	C	Coconut	50	Thick paste (liquid at 50°C)		

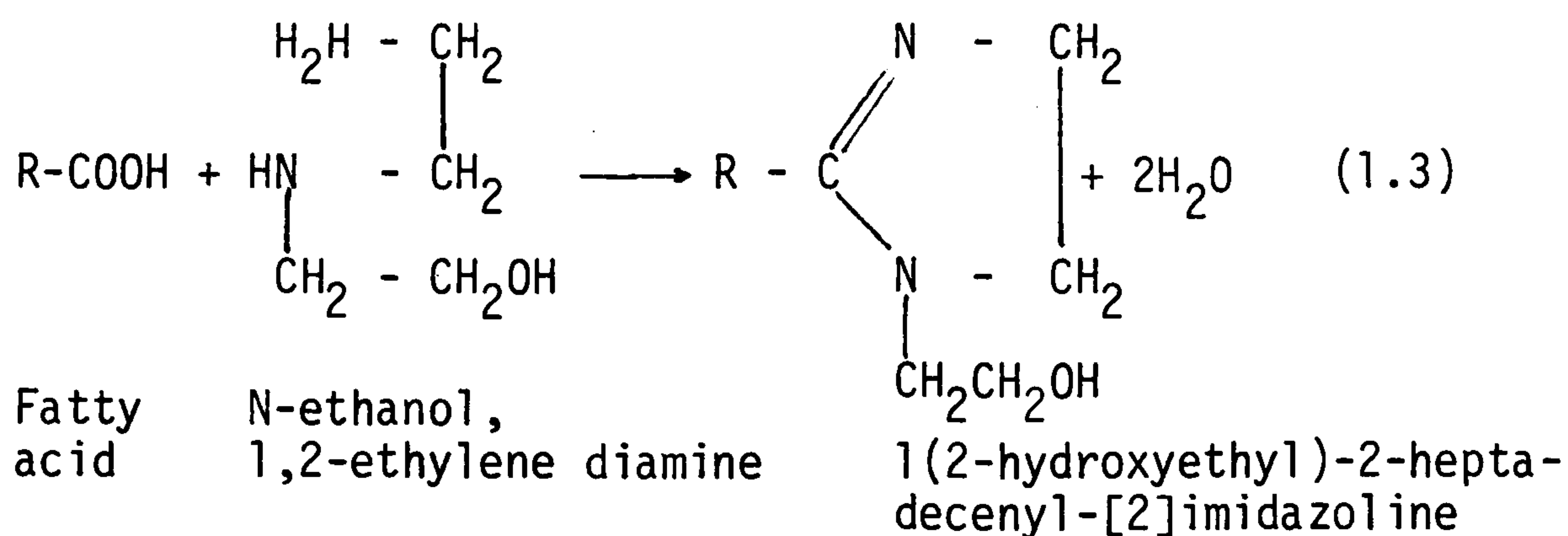
1.1.1.4 Cationic Surface Active Agents

Cationic surface active agents consist of a cation attached to a low water affinity hydrocarbon chain. Cetyltrimethyl ammonium bromide is an example of this class. In aqueous solution it ionises according to equation 1.2:



In this class the most important end groups are primary, secondary, and tertiary amino groups and the quaternary ammonium groups [4]. Phosphonium and sulphonium groups are sometimes used but they are less important.

The hydrophobic, hydrocarbon chain, portion (R) is usually derived from either fatty acids or from petrochemical sources. Fatty acids are usually derived from natural sources such as coconut oil or tallow. Therefore R will vary in both the chain length as well as in the degree of saturation [5]. This is shown in equation 1.3 in which an imidazoline-type cationic surface active agent is prepared from a distilled fatty acid obtained from tallow:



where R can be:

<u>Name of the Group</u>		<u>%</u>
Nonyl	C_9H_{19}	Trace
Undecyl	$C_{11}H_{23}$	0.5
Tridecyl	$C_{13}H_{27}$	3.0
Pentadecyl	$C_{15}H_{31}$	28.4
Heptadecyl	$C_{17}H_{35}$	19.3
Oleyl	$CH_3(CH_2)_7CH=CH(CH_2)_7$	40.7
Linoleyl	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7$	2.8
Palmitoleyl	$C_{16}H_{31}$	4.0
Others		1.3

When R is derived from petrochemical sources, many components have been traced due to variations in molecular weight, degree of branching, the presence of cyclic impurities, or different ring substituents in aromatic system. Variation in the long chain hydrocarbon "R", i.e. in its nature and composition, can significantly affect different characteristics. The analytical methods used to characterise cationic surfactant are explained in Appendix II. Some commercially available cationic surfactants are shown in Table 1.3 [3].

Cationic surfactants can be divided into five different categories. These are namely:

- i) Straight-chain alkyl ammonium compounds
- ii) Polymeric cationic surfactants
- iii) Cyclic alkylammonium compounds
- iv) Petroleum derived cationics
- v) Miscellaneous non-nitrogen containing cationic surfactants.

The first two categories will be discussed in some detail because they represent the majority of presently used cationic surfactants.

TABLE 1.3

SOME COMMERCIALLY AVAILABLE CATIONIC SURFACTANTS [3]

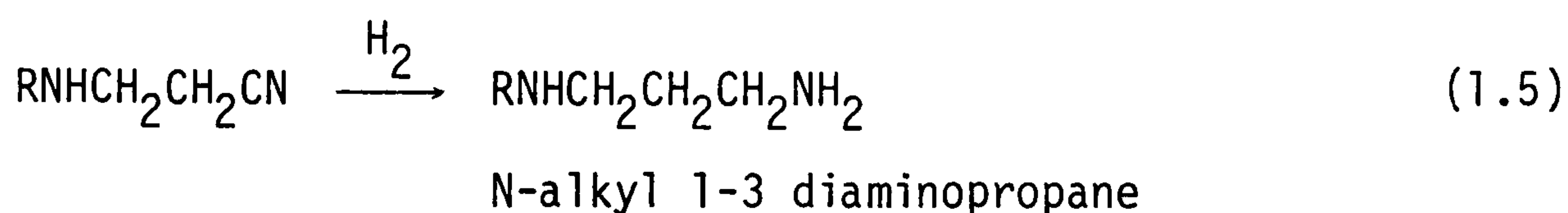
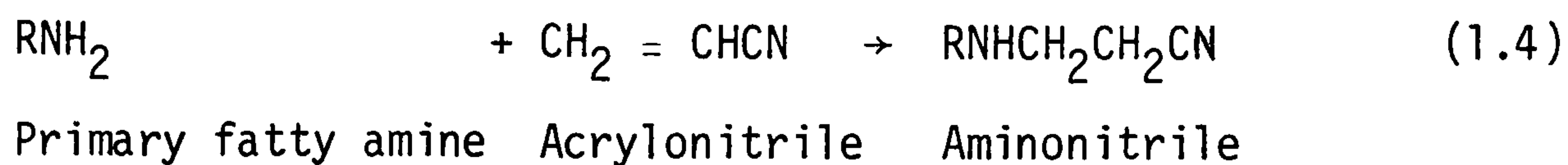
Supplier	Trade Name	Code	Description	App. % Active	Physical Form	Properties and/or Uses	Examples of Fields of Application
Akzo Chemie UK Ltd	General Formula: $\text{RNH}(\text{CH}_2)_3\text{NH}_2$						
	Duomeen	T	R = Tallow	89	Heavy paste	Form strongly bonded films on the surfaces of metal, textiles, plastics, etc.	Metal working emulsion for car under-seals, carbon papers and typewriter ribbons
	Duomeen	C	R = Coconut	89	Liquid		
	Duomeen	CD	R = Coconut	89	Paste		
	Duomeen	S	R = Soya bean	89	Pasty liquid		
	Duomeen	O	R = Oleic	89	Liquid		
Croda Chemicals Ltd	Fatty Alkyl Propylene Diamines ($\text{RNHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)					Strongly cationic and substantive to negatively charged surfaces	Dispersants for pigments, corrosion inhibitors, drawing aids for copper wire and tubing etc.
	Dicrodamine	1.C	R = Coconut				
	Dicrodamine	1.T	R = Tallor				
	Dicrodamine	1.HT	R = Hydrogenated tallow				
	Dicrodamine	1.O	R = Oleic				
KenoGard UK Ltd	Diamine	HBG	R = Hydrogenated tallow			Same as above	Same as above
	Diamine	B11	R = alkyl				

i) Straight-chain alkyl ammonium compounds

Animal fats and vegetable oils were, until the recent development in the petrochemical industry, the main raw materials for the preparation of cationic surfactants. Fatty amines and their derivatives, which may have one, two or three long chains connected directly or indirectly to the nitrogen atom may represent all this class of cationic surfactants. The author will now describe the preparation of cationic surfactants relevant to this research work.

A: Alkyl Diamine Cationic Surfactants

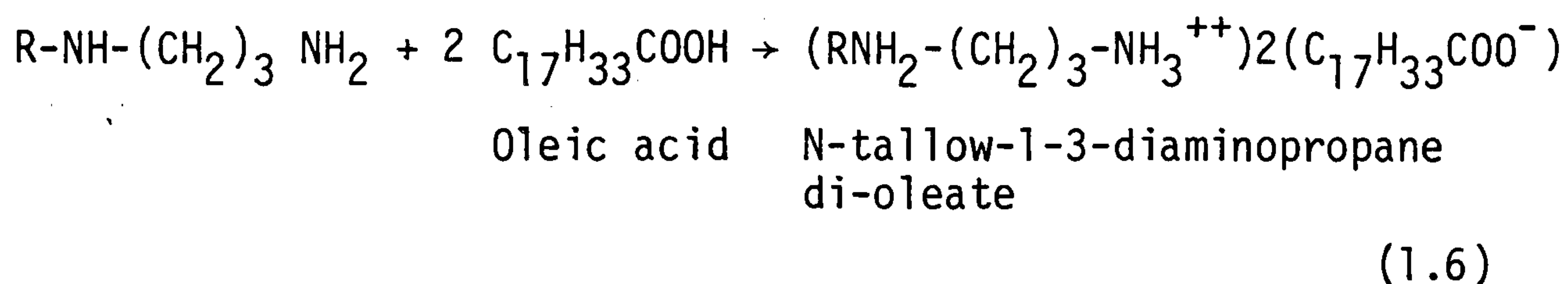
An alkyl diamine cationic surface active agent such as $R-NH(CH_2)_3NH_2$, where R is an alkyl group derived from any fatty acid, is prepared [6] by reacting a primary fatty amine with acrylonitrile as shown in the equations 1.4 and 1.5 below:



The reaction represented by equation 1.4 will take place at 70-80°C in the presence of water.

The diamine produced in equation 1.5 is often called amino-bridged amine [6]. This is because the alkyl group (R) is connected by an amino group to the active amino group at the end of the chain.

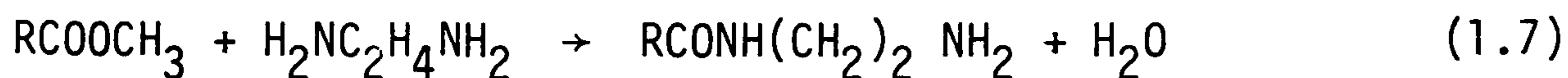
Diamines undergo most of the reactions of primary fatty amines. The principal one is its reaction with oleic acid. When two molecules of oleic acid react with one molecule of diamine the di-oleate is produced [7]:



The di-oleate salts produced in equation 1.6 are considered highly surface active materials and among the important surfactants which are commonly used in various applications such as pigments wetting agents, corrosion inhibitor for epoxy coatings, etc. However, this surfactant was the first material used in this research work.

B: Amide-Bridged Amines

Amide bridged amines have been synthesised where the long aliphatic chain (R) is separated from the amino group by an amide which is another functional group. These cationic surfactants are among the most versatile surface active agents. A great variety of linked amines have been synthesised. Each particular type has its own raw materials and reaction conditions; for example unsymmetrical fatty acyl ethylenediamine is prepared [8] by the action of a fatty acid ester in an excess of ethylenediamine as shown in equation 1.7 below:



It was found [9] that some of the diacyl compound; $\text{RCONH(CH}_2\text{)}_2\text{NHCOR}$, is formed at the same time. This does not behave as a surface active

agent but as a hydrophobic, water-repellent, substance. It is this diamide compound which was used in this research work. This diamide compound was selected mainly because it was thought at the time the research work was started that such a material had not been used before as the author was not aware that such a material had been previously reported in the BLUE BOOK [10] under the trade name Acrawax C* and there its use is described as a processing aid for SBR, butyl and neoprene rubbers. However, during the research work new applications were discovered for this (i.e. EBS) and other derivatives of this class of materials as will be discussed in the forthcoming chapters.

A general method has been reported [11] for the preparation of polyamide compounds such as N,N'-ethylene-bis-stearamide [EBS]. This method may be summarised as follows: polyamides may be prepared by the interaction of polyamines with fatty acids or equivalent acylating agents, as well as by reaction between polybasic acids and primary amines. The reaction product obtained by condensing a polybasic acid with at least 2 moles of an alkylene polyamine or polyalkylene polyamine was further condensed with a long-chain carboxylic acid or equivalent acylating agent in the mole ratio sufficient to establish the required hydrophobic balance. The resulting product is mainly a polyamide. Some commercially available diamides are shown in Table 1.4 from one supplier, their description and uses are mentioned.

* Glyco Chemicals, USA

TABLE 1.4:

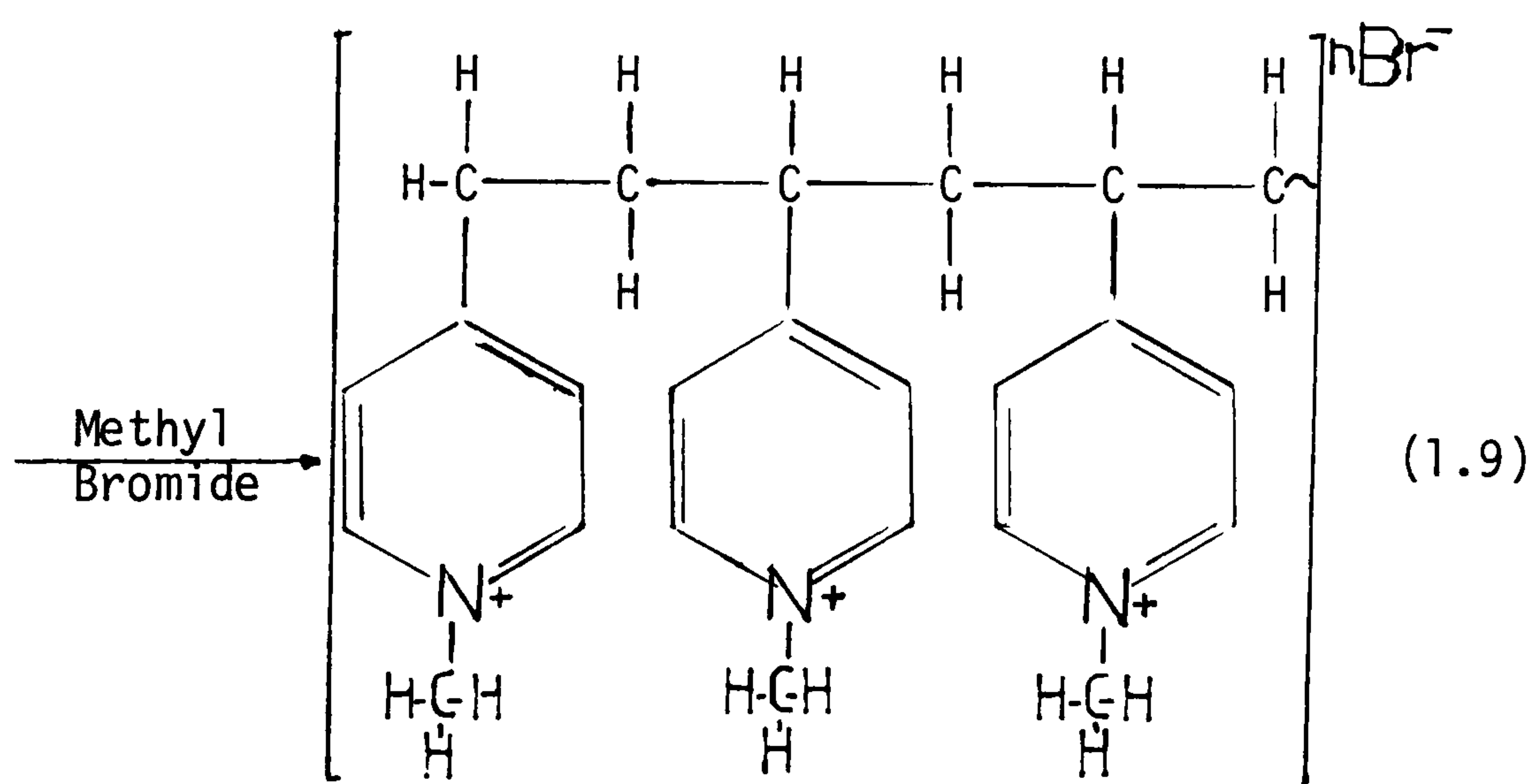
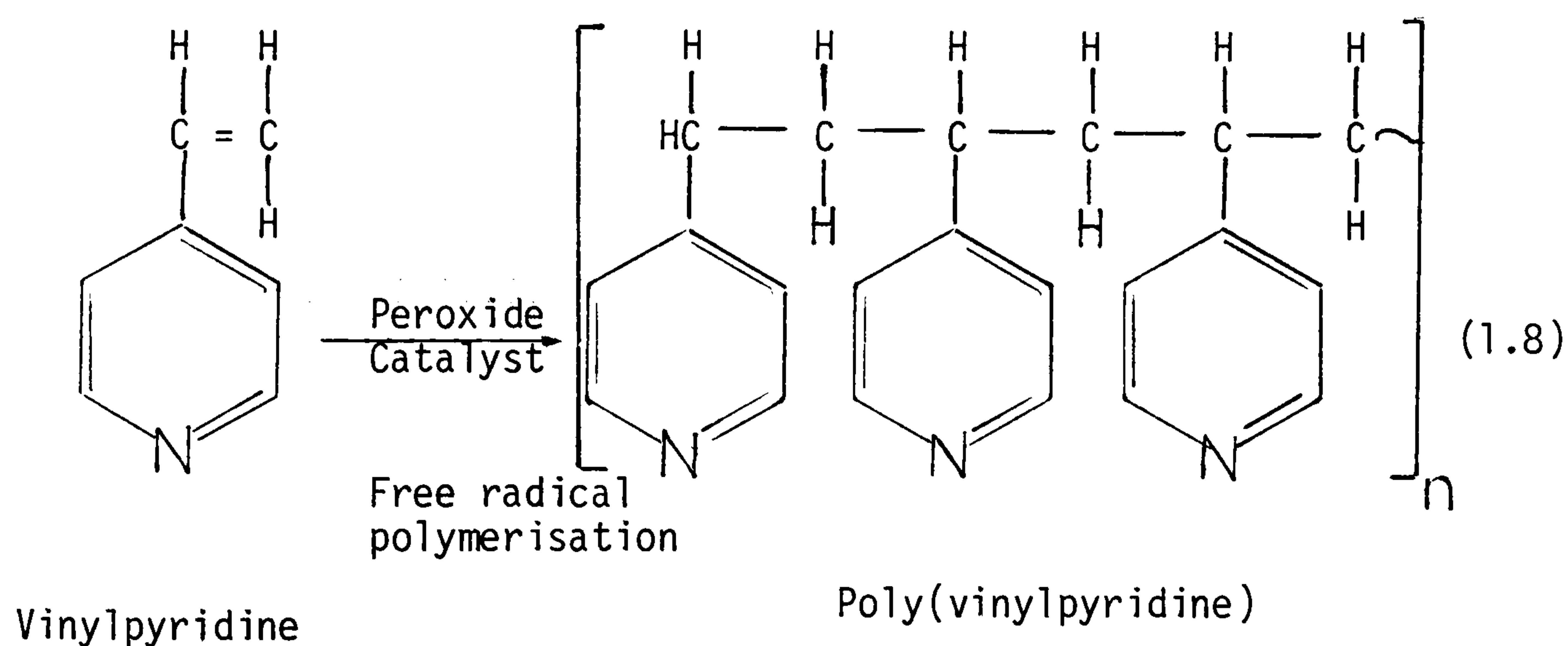
COMMERCIALY AVAILABLE DIAMIDE AND THEIR USES [12]

Supplier	Code	Description	Uses and Field of Application
Croda Chemicals Ltd		General Formula $RCONH(CH_2)_2NHCOR$	
	EBS	$RCO=stearyl$ $= CH_3(CH_2)_{16}CO$	Plastic industry: mould release agents for PVC and other plastics
	EBO	$RCO=oley1$ $= CH_3(CH_2)_7CH=CH$ $(CH_2)_7CO$	Paper industry: water repellent for cardboard and other paper products
	EBL	$RCO=lauroyl$ $= CH_3(CH_2)_{10}CO$	Paint and inks: inhouse stability of the pigment dispersion. Also as corrosion inhibitor for paints and surface coatings.
	EBE	$RCO=erucyl$ $= CH_3(CH_2)_7$ $CH=CH(CH_2)_{10}CO$	Antifoam agents: recommended as an anti- foam in steam genera- tors and in sugar beet liquor evaporators
	EBB	$RCO=behenyl$ $= CH_3(CH_2)_{20}CO$	
	EBM	$RCO=myristyl$ $= CH_3(CH_2)_{12}CO$	Metal drawing: they have the advantage of producing products without surface erosion or residual surface films

ii) Polymeric Cationic Surfactants

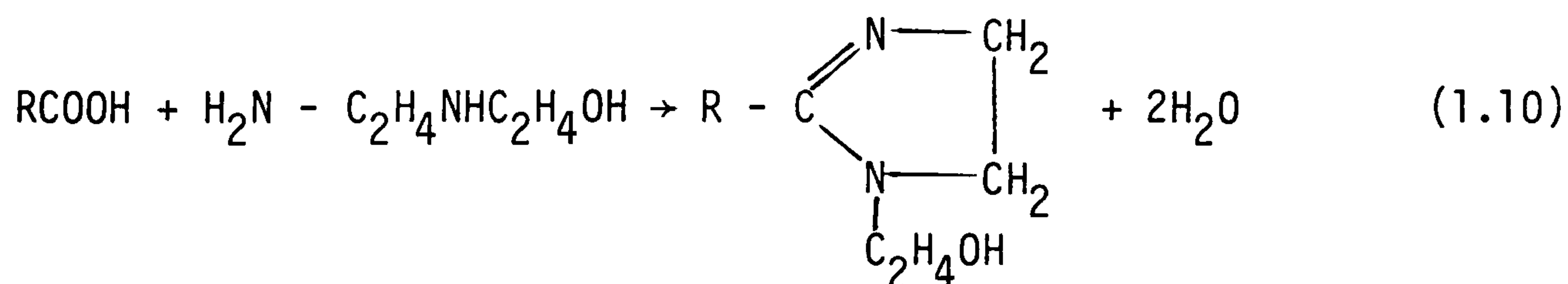
Polymeric cationic surfactants are nearly devoid of many of the typical properties associated with surfactants such as wetting and foaming. However they do have the power to behave as good dispersing agents.

The general structure of the polymeric surface active agents can be divided into two parts; one is that of a high-molecular weight polymer and the other part is that of basic groups, usually either a weak amine or quaternary ammonium ion, distributed along the chain. Therefore, this group of cationic surfactants retain most of the properties of the polymers from which they have been derived, but these properties are significantly modified due to the presence of the basic groups. The preparation of polymeric cationic surfactants, such as poly(vinylpyridine) and poly(vinylmethylpyridinium bromide) is shown in equations 1.8 and 1.9 respectively [5]:



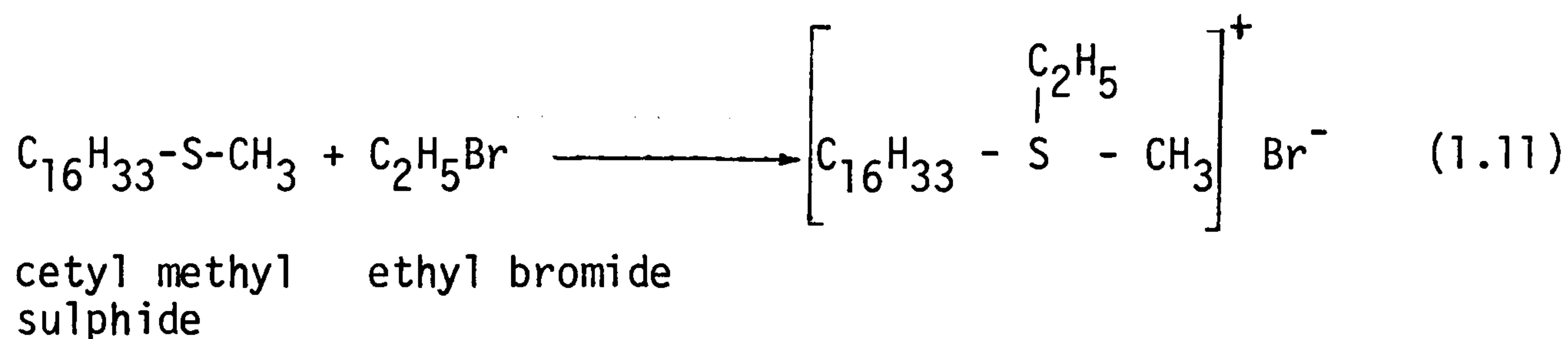
Polymeric surface active agents have relatively limited applications in industry. They are used as antistatic agents on many surfaces; as additives and coagulants to increase the strength of papers. It has been reported [18] that when carbon black is mixed in an organic diluent, such as heptane, with from 0.5 to 50% of its weight of a cationic or nonionic polymeric surfactant and then the mixture is agitated, using a high-speed centrifugal pump, a carbon black gel is formed. This gel when blended with elastomer solution and then the elastomer is coagulated, it was observed that the resulting vulcanisate possess excellent carbon black dispersion and higher tensile properties than those obtained by the conventional rubber mixing methods.

The author will not discuss the further three categories of a cationic surfactant known to exist. However, a brief comment about them can be made as follows; (i) cyclic alkyl ammonium surfactants are compounds in which the nitrogen atom carrying the cationic charge is part of a heterocyclic ring. They are used as wetting agents, dispersing agents, detergents, and fabric softeners. Examples are imidazoline and its derivatives which are particularly useful in many applications such as antiseptic lotions and creams, shampoos, mouth washes, hair rinses, etc. Imidazoline and its derivatives are usually prepared by condensing fatty acids with diamine or its derivatives. The hydroxyethylimidazolines are prepared [14] by condensing a fatty acid with 2-aminoethylethanolamine as shown in equation 1.10 below:



- ii) Petroleum derived cationic surface active agents may possess the same properties, preparation and uses described previously for their straight chain analogs.
- iii) Non-nitrogen containing surface active agents are those surfactants which may consist of compounds of oxygen, phosphorus, sulphur, arsenic, selenium, etc. They are generally prepared in a manner similar to that of the nitrogenous compounds.

Application of these surfactants has been confined to the pharmaceutical field. It has been reported [14] that sulphonium compounds are the only non-nitrogenous cationic surfactants which have received considerable attention in the patent literature. Sulphonium compounds are prepared [14] as shown in equation 1.11 below:



1.1.3 Methods of Evaluating the Properties of Surfactants

Surface active agents are evaluated and utilised for what is called their gross effects [14]. These gross effects can be grouped into five classes as follows: (1) wetting, (2) foaming, (3) detergency, (4) dispersion, (5) emulsification. The author does not wish to discuss these effects in detail. However, a brief comment on each effect will be made.

1. Wetting: The ability of a liquid to penetrate completely into another liquid or solid is called wetting. In textile technology a specific surfactant is usually used to obtain complete wetting i.e. complete penetration of the impregnant through the spaces between individual fibres.

2. Foaming: This property is well known to be possessed by many surfactants. In certain applications such as fire-fighting compositions, cosmetic preparations, ore flotation etc, foaming is very important. Generally foams are formed by passing air or gas under the surface of liquid, or by agitating the surface until it breaks and encloses air. The best materials to form foams are found among the surfactants.
3. Detergency: Generally the enhanced cleaning effect of a liquid bath due to the presence of a special material, the detergent, is known as detergency. This property is regarded as the most important property among surfactants which act as detergents.
4. Dispersion: A solid is usually difficult to disperse uniformly in a liquid due to the tendency of the small particles to remain in the form of aggregates. When the solid particles are heavier than the liquid they tend to settle by gravity. In the manufacture of paints certain surfactants due to their powerful dispersing ability are used to aid in the dispersion of the organic and inorganic pigments in a medium.
5. Emulsification: Emulsion is a suspension or dispersion of liquid particles within another immiscible liquid. Generally the dispersed system, emulsion, will separate out into layers after some time. Certain surface active agents are among the best materials to promote the formation and stabilisation of an emulsion. They are usually known as emulsifying agents.

1.1.3 Some Miscellaneous Applications of Surfactants [15][16]

In addition to what has been mentioned about their uses, many other applications are reported such as in Petroleum, Mining, Fertilizer, Road surfacing, and Pulp and Paper industries. The application of surfactants in most of the processing industries has been reported by Sisely [17] and is given overleaf in Table 1.5.

1.1.4 Rubber and Plastic Industries

Surfactants have long been known to play a very important role in emulsion polymerisation [18]. It is considered to be one of the most important constituents of the emulsion polymerisation basic ingredients. This is mainly because it is essential to use a surfactant to obtain a stable emulsion between monomer and water, both initially and during the polymerisation reaction to give a finished stable latex.

The effect of surfactants on the mechanical and chemical stability of natural rubber latex has been extensively studied. Also the addition of certain surfactants such as n-alkyl triethylammonium bromide as a cationic [19], ethoxylates as non-ionic [20], sodium n-alkyl sulphates and sulphonates as anionic [21] to natural rubber latex has been observed to enhance the mechanical stability of the latex.

Surfactants have also been used as foaming agents in the manufacture of foamed latex and sponge rubber articles.

Surfactants, particularly cationics, being excellent wetting agents, are known to be particularly effective in promoting impregnation of fabrics, with latex and this is established industrial practice.

TABLE 1.5

APPLICATIONS OF SURFACTANTS IN THE PROCESSING INDUSTRIES [17]

Textiles Skins Leather	Laundering and Dyeing	Metallurgy	Mines and Minerals Cement	Paper- making	Paints and Varnish	Food	Agri- culture	Transport	Various	Household
Textiles: Removing skin & wool oil Fully woollen goods. Tanning: Degrea- sing skin	Making of laundry washing compounds and spot removers	Degreasing metal and machine parts		Washing and degr- easing paper felts		Washing & cleaning of apparatus utensils, in brewe- ries, crea- meries, bakeries, preserving plants		Washing of rolling- stock, air- planes, ships, trucks	Cleaning of streets, public buil- dings, hos- pitals. Cosmetics	Dishwashing cleaning tile, pain- ted wood- work, carpets
			Washing and cleaning of workrooms, autostorage, depots, offices, lavatories							
Textiles: Desizing and boi- ling of cottons Carbo- nizing woollens bleaching Dyeing Leather: Re-wett- ing dried skins Tanning Dyeing Finishing	Removal of spots Dyeing	Pickling Cleaning Electro- plating Rotary washer	Mines & minerals: Abate- ment of dust. Washing Cement: Homogeni- zing agent and setting assistant	Wetting of pulp in beater Sizing Coating Water proofing	Making of: water- paint, calco- mines, adhe- sives, water- and fire- proofing compounds		Insecti- cides, herbi- cides, fungi- cides. Treatment of grains and forage Activation of straw manure		Fire- fighting, Photography Fire Extin- guishers Cosmetology	Removing starches, wallpaper cleaning hangings

DETERGENTS

WETTING AGENTS

TABLE 1.5 ... continued

Textiles Skin Leather	Laundering and Dyeing	Metallurgy	Mines & Minerals Cement	Paper- making	Paints and Varnish	Food	Agricul- ture	Transport	Various	Household
Textiles: Kier- boiling Finishing Leather: Fat- liquoring		Making of cutting and soluble oils		Dispersing waxes, pig- ments, for resins, for sizing and printing	Preparation of emulsi- fied paints		Insecti- cides, herbi- cides, fungi- cides. Dispersing dry pow- ders, oils for spraying		Making of bitumen emulsions	

EMULSIFIERS

It has been reported [13] following the development of a non-conventional mixing technique, that certain polymeric cationic and nonionic surfactants can improve carbon black dispersion and consequently enhance the physical properties of rubber vulcanisates. It has also been reported [22] that cyanoethylmethacrylate (a surfactant) was observed to improve the dispersion of the vulcanising agent; azobiscarboxamide, during the vulcanisation of NBR rubber. Recently it has been reported [23] that the addition of 0.5-0.75 phr polyoxyethylene glycol (molecular weight 600 and 5000, denoted as POEG-600 and POEG-5000) enhances the tensile strength of nitrile rubbers and increases the vulcanisation rate. Thus POEG-600 increases significantly the vulcanisation rate of SKN-18 and SKN-26 rubbers, but has essentially no effect on the vulcanisation rate of SKN-40 and SKN-50 rubbers. Unlike POEG-600, POEG-5000 has little effect on the vulcanisation rate of rubbers. POEG-600 behaves in rubber stocks as a surfactant and enters into the rubber network along with the polar vulcanisation agents. Unlike POEG-600, POEG-5000 associates with adjacent rubber macromolecules leading to the formation of physical vulcanisation networks, which account for the improved physicommechanical properties.

In an Akzo technical bulletin [7] it is mentioned that the surfactant ARMEENS 18D, HT and HTD which are primary fatty amines are used as mould release agents in the production of hard rubber articles such as battery cases, combs, etc.

Also the compound N,N'-ethylene bis stearamide is given in the Blue Book [10] as a processing aid for SBR, butyl and neoprene rubbers.

1.2 Plasticisers and/or Processing Aids

Introduction

A plasticiser is any ingredient which, when added to a rubber compound, improves processability without adversely affecting physical or performance properties.

They usually synergise with the rubber compounding ingredients producing noticeable improvements in the various processing steps which involve: (i) mixing with mills and internal mixers; (ii) calendering; (iii) extrusion; (iv) building operations; (v) moulding processes such as compression, transfer and injection methods, and (vii) release from moulds.

The use of plasticisers for rubber is not new. A British patent [24] granted in 1843 described methods of combining asphalt with natural rubber as well as the treatment of the latter with sulfur. In 1935 Rostler and Wilson [25] in an Austrian patent described resinous hydrocarbons as a rubber extender. In 1941 the same authors [26] described the results obtained by mixing these oils with solid natural rubber and with liquid latex.

In 1944 Ludwig et al [27] described the effect of mineral oils and unsaturated petroleum derivatives as plasticisers on the processing and physical properties of rubber stocks [see page 42]. Considerable research work on plasticisers since that time has brought them to a high degree of refinement and versatility.

It should be mentioned here that the plasticisers and/or the processing aids utilised in this study are mainly mineral oils, stearic acid, and Struktol WB 212. Therefore detailed discussion will be given to physical plasticisers and/or processing aids similar to those used in the research.

1.2.1 Methods of Plasticisation

Natural and synthetic rubbers, with the exception of rubber lattices, do not lend themselves easily to fabrication and they must be plasticised to enable easy incorporation of compounding ingredients and to make them readily manipulative in factory processing operations. A rubber can be plasticised by one of the following methods:

1. Mechanical breakdown

This can be divided into two types: thermal softening and mastication.

A: Thermal softening: some rubbers, particularly natural rubber, show a significant decrease in Mooney viscosity under shear forces such as those encountered during Banbury or mill mixing while others such as Butyl and SBR undergo only minor changes as shown in Figure 1.0 [28]. In the case of NR it is difficult and perhaps not possible to separate the effect of thermal softening and mastication.

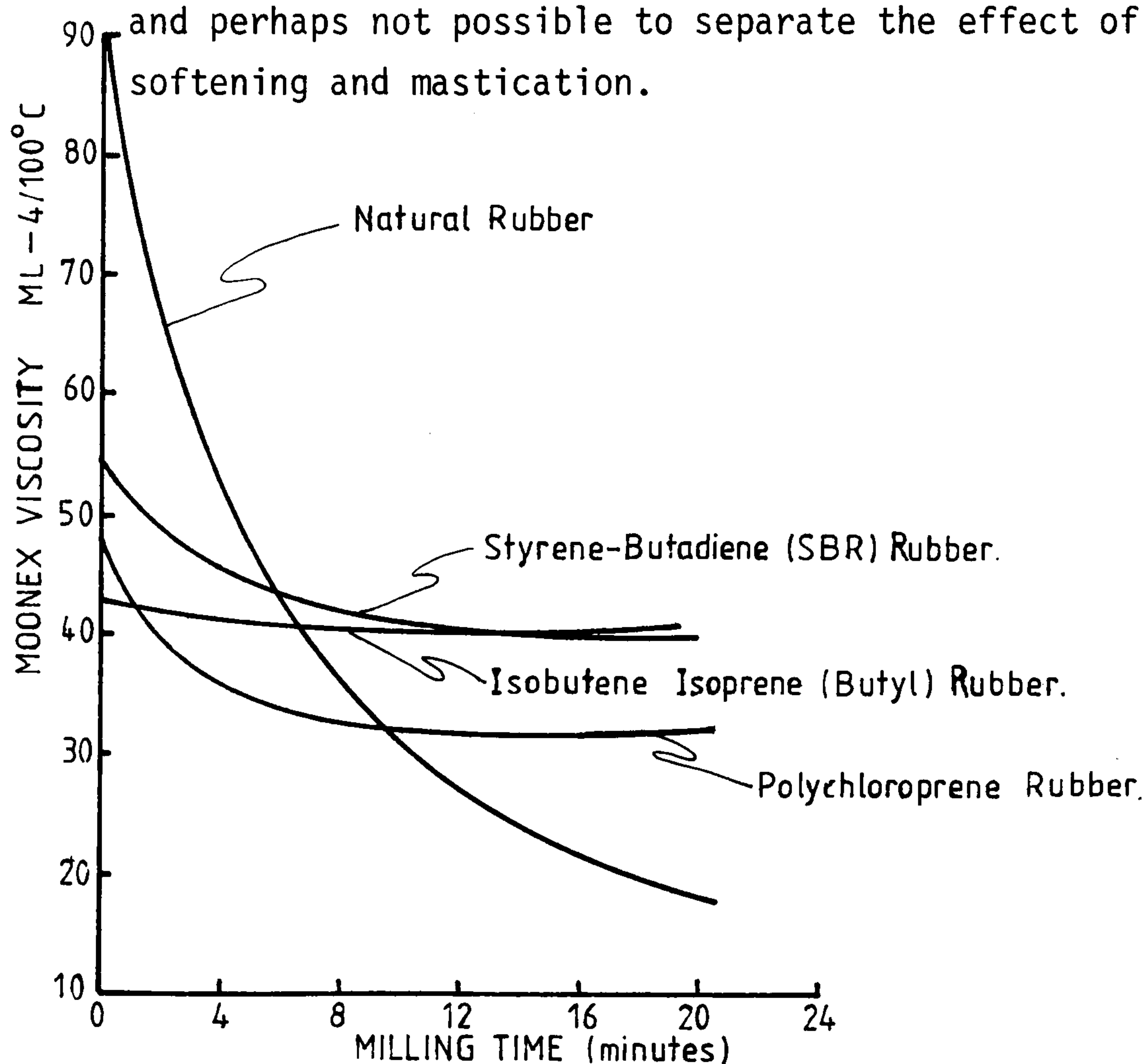


FIGURE 1.0: Effect of milling on viscosity of natural, isobutene-isoprene, polychloroprene, and styrene-butadiene rubbers [28]

B: Mastication: The effect of mastication on rubber, particularly natural rubber, has been studied extensively [29]. A typical example of the effect of mastication i.e. mechanical breakdown, on natural rubber is shown in Figure 1.1 [30], in which the whole curve is a composite one and reflects the occurrence of two independent reactions which would give curves A and B respectively. These two processes are known as "cold mastication" and "hot mastication" due to their predominance at temperatures below 100°C and above 130°C respectively.

Part A is altered by changes in rotor speed and viscosity of the rubber. Part B, on the other hand, is less sensitive to the physical parameters, but is markedly affected by oxidative scission and the generation of in-situ free-radical catalysts for olefin autoxidation. The mechanisms involved in the oxidative degradation are shown below in equations 1.14-1.19.



ROOH is unstable compound

ROH is the degraded rubber

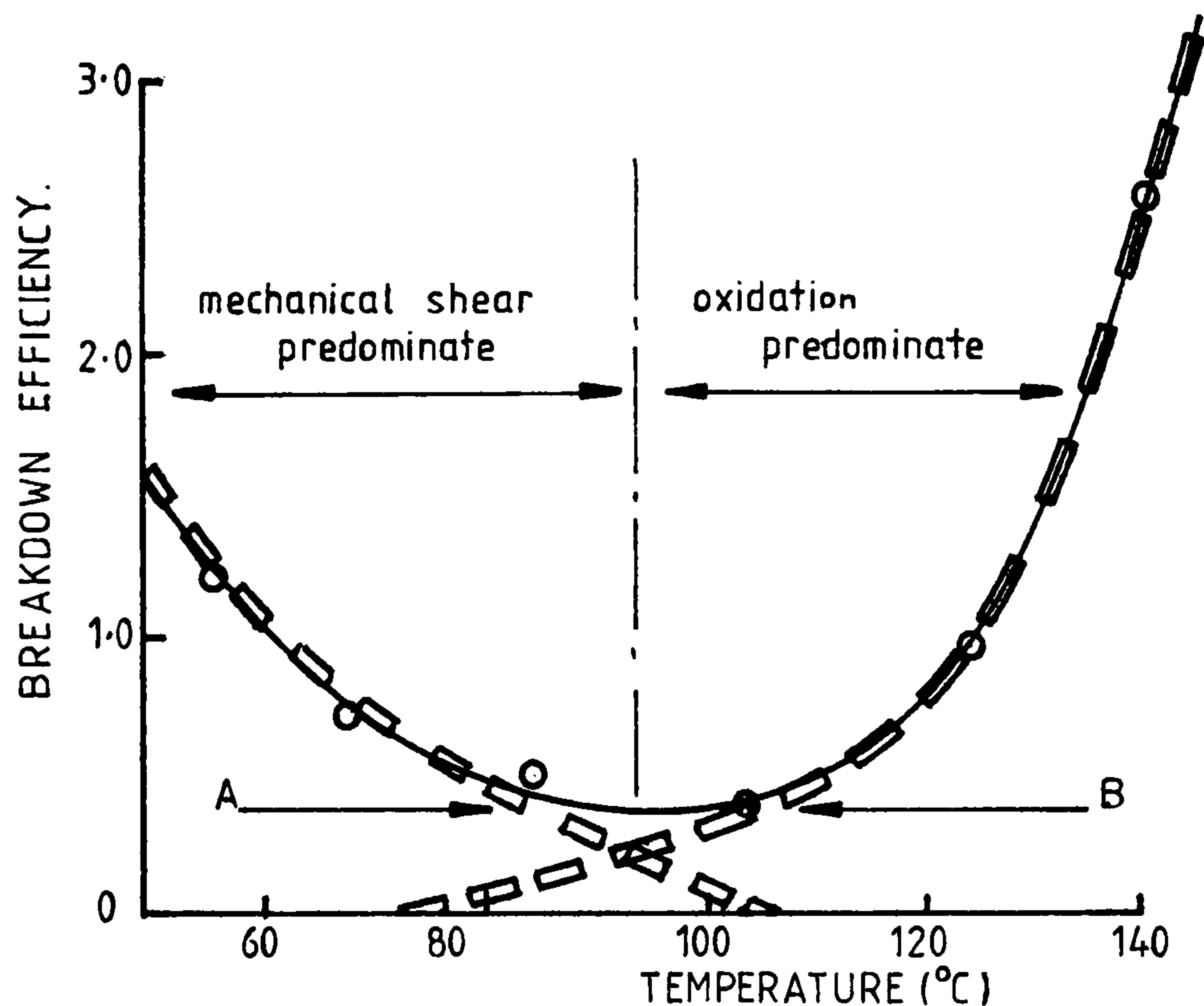


FIGURE 1.1: Breakdown of NR after 30 mins mastication at different temperatures [30]

The different mechanisms responsible for the two parts of the breakdown curve explain why Part B responds to additions of common oxidation inhibitors, while Part A is insensitive to such additions, although the presence of oxygen is important.

In natural rubber, as a result of the mastication phenomenon, this milling action produces low molecular weight segments which make the original high molecular weight mass more plastic and hence makes the rubber more processable.

2. Chemical Plasticiser (Peptisers)

With increasing emphasis in the rubber industry on factory output, chemical plasticisation is considered to be an important means of reducing rubber viscosity and thus increasing production by reducing mixing cycles. These chemicals function as oxidation promoters by

decomposing with heat into free radicals which react with the rubber by removing the free radicals formed during mastication and mixing of the rubber. Recombination of the free radicals from mechanical shear is thus prevented resulting in permanent mastication of the rubber. [See mechanisms given in equations 1.14-1.19].

A typical example of the effect of a chemical plasticiser on the Mooney viscosity and mixing time is shown in Figure 1.2 [28].

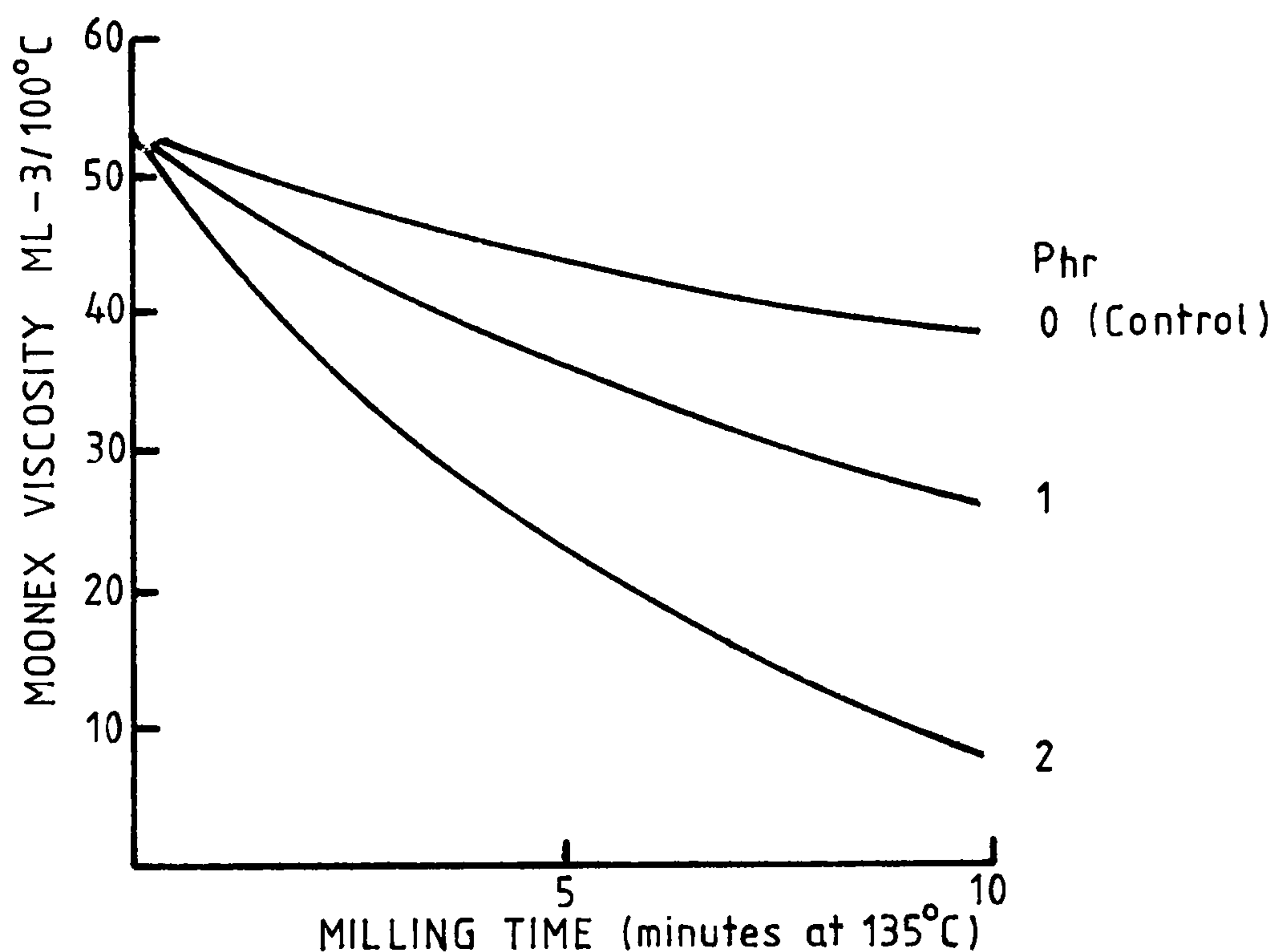


FIGURE 1.2: Effect of chemical plasticiser/pentachlorothiophenol, on the Mooney viscosity and mixing time of SBR rubber [28]

A good review of chemical plasticisers and their use in rubber is reported by Kastein [31]. Some commercially available peptisers are shown in Table 1.6 together with their minimum operative temperature [30].

TABLE 1.6:
SOME COMMERCIALY AVAILABLE PEPTISERS

Producer	Trade Name	Chemical Name	Minimum Operative Temperature (°C)
Anchor Chemicals	Pepton 22	Di(o-benzamido Phenyl) disulphide	115
	Pepton 44	Activated Di(o-benza- mido Phenyl disulphide	70
Bayer	Renacit IV	Zinc salt pentachloro- thio Phenol	70
	Renacit VII	Pentachlorothio Phenol with activating and dispersing additives	70
	Renacit VIII	Metal complex on an organic carrier	70

3. Physical Plasticisers

The intermolecular forces between rubber molecules tend to adhere the molecules together and, hence, make the rubber polymer difficult to process. Also the addition of many ingredients to rubber stiffens up the polymer so that it becomes almost impossible to process without the addition of a plasticiser to lubricate slippage between the macromolecular chains. Chemical plasticisers have limited use due to certain parameters, such as temperature of mixing, type of rubber, cost, etc. Hence physical plasticisers are used in practice as an alternative to function in a physical rather than a chemical manner being sufficiently effective to weaken the intermolecular forces between the rubber molecules and make it much easier for the chains to slip past each other and, hence, for the whole mass to flow.

They act as intermolecular lubricants and perform many important functions as follows:

- i) Decrease viscosity and improve processability of the compound
- ii) Promote wetting and dispersion of fillers
- iii) Reduce sticking to the processing equipment
- iv) Enhancing tack and autohesion
- v) Providing lubrication to improve extrusion, moulding, or other fabricating operations
- vi) Reducing batch temperatures and power consumption during mixing, extrusion etc.
- vii) Modifying properties of the final product.

Mainly, for the above reasons, plasticisers are used in rubber compounds.

1.2.2 Types of Physical Plasticisers

The most common ways of classifying physical plasticisers is by origin because products from a given source tend to have certain properties in common [32].

1.2.2.1 Petroleum Products

This class includes process oils, resins, waxes, asphalts, and mineral rubbers. Among these products the most widely used types are the process oils and for this reason it is convenient to discuss this particular product in more detail.

The types of petroleum oils used as plasticisers are divided into three major categories: aromatic; C_nH_{2n-6} , Naphthenic; C_nH_{2n} , and Paraffinic; C_nH_{2n+2} . Several properties of petroleum oil have been used to assess the performance of these as rubber process oils such as viscosity, chemical composition, specific gravity, volatility, colour

etc. However, the most important properties usually considered are as follows: (i) viscosity of the oil; this property gives an indication of its mobility and volatility because it is a function of the molecular weight of the oil. Low viscosity oil will give a vulcanisate that will remain flexible at low temperature but will show a greater tendency to volatilise when subjected to a high temperature, such as encountered during processing and ageing. The higher the viscosity of an oil, the higher its average molecular weight and density. (ii) Composition of the oil; the composition of an oil can be estimated by the following methods:

A: Clay-Gel Molecular Analysis [33,34, ASTM D2007]

Molecular-type analysis involves the separation of the molecules in the oils, using an adsorbant such as silica gel:

- i) Aromatic hydrocarbon
- ii) Polar compounds
- iii) Saturated hydrocarbons
- iv) Asphaltiness.

Aromatic hydrocarbons are highly compatible with the general purpose rubbers. They are important since they affect rubber properties more than any other constituent [35].

Polar compounds include compounds of nitrogen, sulphur and oxygen. Nitrogen bases can accelerate scorching and cure, however the amount present in an oil is usually too small to exert any noticeable effect on scorch.

Saturated hydrocarbons may be either naphthenic or paraffinic. The compatibility of saturates with most general purpose elastomers is poor. Naphthenes, however, possess greater compatibility than paraffins. for most elastomers. The colour and light stability of saturates make them desirable for light coloured rubber products.

Asphaltenes are high molecular weight bituminous substances. They cause staining of rubber vulcanisates and should not be present in the process oils. It is also essential that rubber processing oils are free from oxidised by products such as peroxide and pro-oxidation catalysts such as Cu and Mn, which can contribute to the degradation of rubber during ageing.

B: Carbon Type Analysis [33,34, ASTM D2140]

This technique determines the percentage of carbon atoms in aromatic rings (C_A), naphthenic rings (C_N) or in paraffinic chains (C_P). The method utilizes a correlation between viscosity-gravity constant (VGC) [36] and refractivity intercept [37]. The viscosity gravity constant is calculated using the equation, according to ASTM D2501:

$$VGC = \frac{10G - 1.0752109 (V-38)}{10 - 109 (V-38)}$$

where G = specific gravity at 15.6°C

V = Saybolt viscosity at 37.8°C

VGC is a measure of the overall aromaticity of an oil and is not dependent on molecular weight.

Refractivity intercept [37] is another characteristic of hydrocarbon type of an oil. It is usually calculated as follows:

$$\text{Refractivity Intercept (RI)} = n_D^{20} - \frac{1}{2} D^{20}$$

where n_D^{20} is the refractive index at 20°C

D^{20} = density at 20°C

When both VGC and Refractivity Intercept (RI) of an oil are determined the composition of that particular oil can be determined using the nomograph of Figure 1.3 [38], shown below:

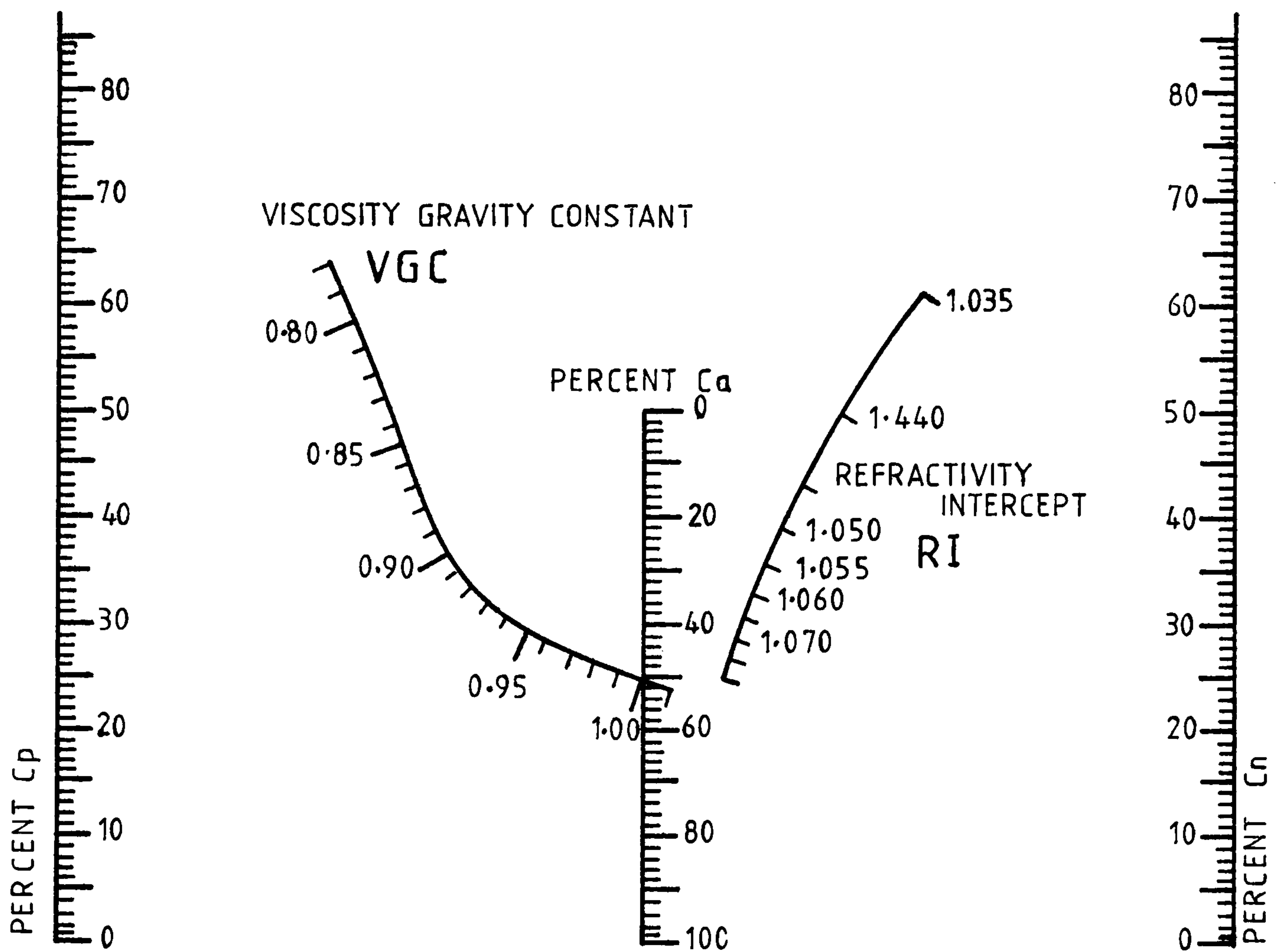


FIGURE 1.3: Carbon atom analysis nomograph used for rubber processing oil characterisation [38]

C: Viscosity-Gravity Constant (VGC) (ASTM D2501)

This constant is explained in connection with the carbon type analysis discussed earlier.

D: Aniline Point

Aniline Point is defined as the temperature at which a mixture of an equal volume of oil and aniline becomes completely miscible on heating. The aniline point of an aromatic oil is lower than that of a naphthenic oil, which in turn is lower than that of a paraffinic oil. The lower the aniline point, the more aromatic the oil becomes. Typical properties for various types of rubber process oils are shown in Table 1.7 [39] below:

TABLE 1.7:

TYPICAL PROPERTIES FOR VARIOUS TYPES OF PROCESS OILS [39]

Property	Paraffinic	Naphthenic	Aromatic
Viscosity, SUS/100°F	310	515	870
Viscosity, SUS/210°F	53.4	52.4	52.0
Specific Gravity 15.6°C (60°F)	0.8713	0.937	0.953
VGC	0.805	0.885	0.908
Refractive index	1.4794	1.5167	1.5416
Refractivity intercept	1.0456	1.0503	1.0671
Carbon type analysis:			
% C _A	4	21	36
% C _N	27	37	19
% C _P	69	42	45
Molecular analysis:	Weight %		
Asphaltenes	0	0	0
Polar compounds	0.4	2.5	4.0
Aromatics	14.8	43.8	68.0
Saturates	84.8	53.7	28.0
Aniline Point °C (°F)	111.7(233)	68.9(156)	51.7(125)

Some commercially available rubber processing oils are given in Appendix III.

Petroleum oils when used as plasticisers reduce the overall viscosity of the compound to a workable level, reduce power consumption in processing equipment, control the heat generation and facilitate dispersion of fillers during mixing. Also they play a part in extrusion by increasing rates, giving smoother stocks and regulating die swell. They are also effective in other processing steps such as calendering where close tolerances must be maintained and in moulding where good flow is important to obtain uniformly filled moulds. Their effect on the cure rate and final physical properties is very important and must be determined on each compound to be sure that the type, aromatic, naphthenic or paraffinic, and amount of the processing petroleum oil is compatible with the final properties required.

1.2.2.2 Natural Fats and Oils

Natural fats and oils were among the first plasticisers used by compounders in the early days of the rubber industry.

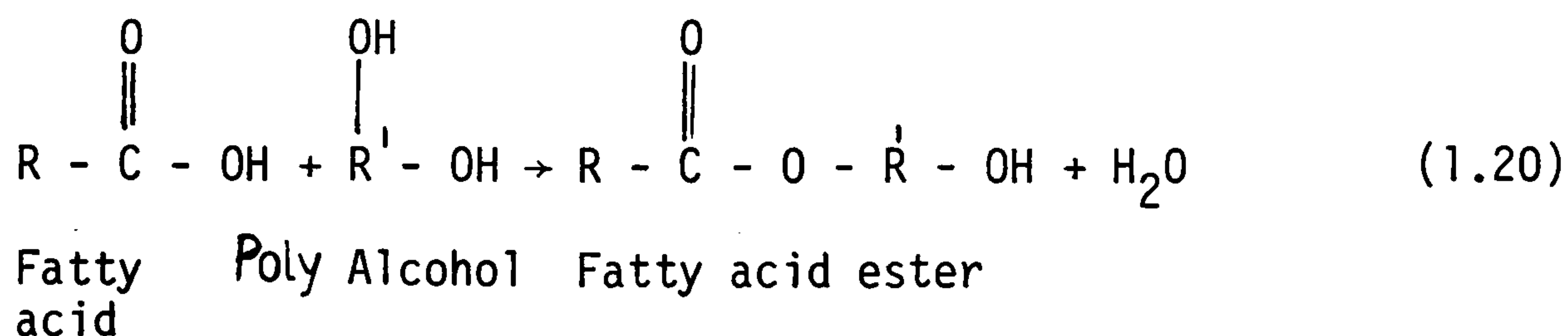
The natural fats and oils are characterised by two opposing effects: a large part of the molecule is made up of long hydrocarbon chains which are rather wax-like in character and therefore tend to limit the compatibility coupled with a lubricating effect; but in the same molecules there are functional groups, for example, ester and carboxylic groups etc, which are polar in nature and hence improve rubber filler compatibility by their possession of high wetting characteristics with respect to fillers.

Fatty acids and their derivatives are widely used in the rubber industry, primarily as components of the emulsifiers used in emulsion polymerisation systems. In compounding to obtain optimum processing and vulcanisation properties, fatty acids and their derivatives also provide significant contributions being an essential part of the vulcanisation activation system.

In most mixing employed in rubber technology, stearic acid is employed either by virtue of its power to form a soluble zinc salt with the zinc oxide added to the rubber and the resulting in situ formation of zinc stearate is essential to obtain good cure state. Also zinc stearate has the ability to function as an excellent processing aid. This is a case of a compounding ingredient possessing a dual function as a plasticiser and also as a cure activator.

It has been reported [40] that the presence of stearic acid improves reinforcement during mixing. There appears to be two reasons for this action: first, free stearic acid lubricates by reducing internal friction, secondly, dissolved stearic acid reduces interfacial tension between rubber and filler thereby increasing wetting or true reinforcement. Stearic acid, because of its low melting point can function as a plasticiser to reduce the nerve of the compounded rubber and provide good processability. The waxy nature of stearic acid also provides release characteristics to the rubber compounds thus preventing excessive sticking to the surfaces of the processing equipment.

Due to the limited solubility of fatty acids in rubber compounds, it is often not possible to use them at the high level needed to fully achieve desirable improvement in processing. To overcome this problem, it has been found [41], that by increasing the molecular weight of the fatty acid it is possible to increase their solubility in rubber and subsequently eliminate this bloom problem, and fatty acid esters offer a solution and are prepared as shown in equation 1.20 below:



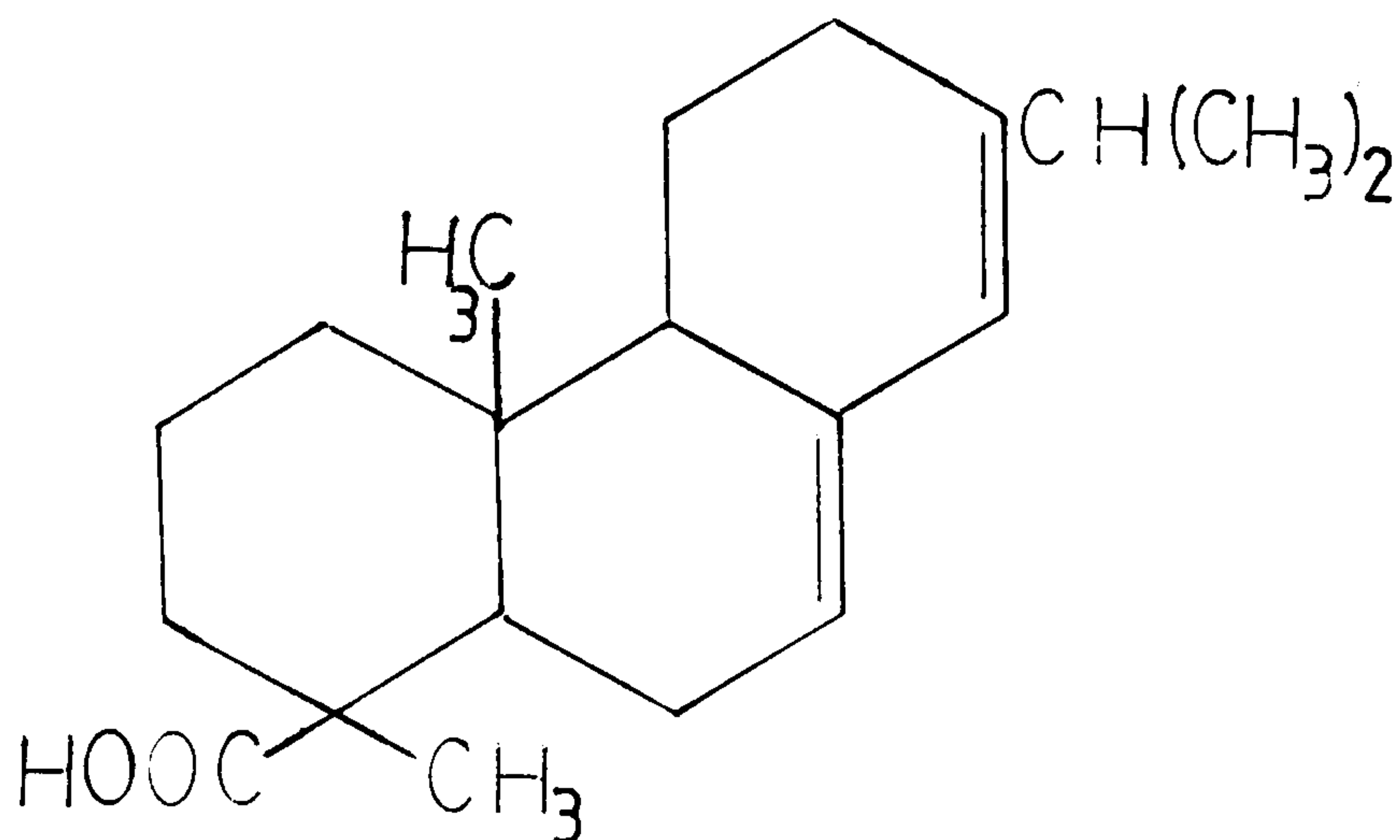
Fatty acid alcohols and fatty acid salts such as zinc oleate and calcium stearate, when mixed in petrolatum or in high molecular weight paraffinic oils, serve as good plasticisers for reducing Mooney viscosity, reducing stickiness, improving mould flow and mould release. They stabilise oxygen chain scission and act as internal chain lubricants during processing [41]. By changing the ratios of the alcohols, acids and salts the relative effectiveness of these plasticisers can be changed.

1.2.2.3 Naturally Occurring Plasticiser

Products from pine trees, pine tar, pitch, rosin and resin are manufactured by the distillation of pine wood. This group of plasticisers is characterised by the presence in their structure of functional groups that will react during vulcanisation to accelerate or retard cure and may also promote or retard ageing of the cured product. For example, pine tar contains organic acid groups that contribute to tack; this tack is semi-permanent, so sidewall, tread and other semi-manufactured tyre components may be kept for a long time in stock and still adhere well to each other when required for use.

Enhanced carbon black dispersion also results from the use of pine tar resins. It is also known that pine tars contain phenolic groups which act as rubber antioxidants. However due to its dark colour and staining properties pine tars are not suitable for use in light-coloured rubber products.

In contrast rosins have an adverse effect on the ageing of natural rubber and they also retard cure. This has been attributed to the presence of unsaturation in the abietic-type acids in rosin [42], see formula below. Nevertheless rosins are reported to have a substantial use [42]:



Abietic acid (in rosin)

Resins are made by polymerising naturally occurring terpenes. Terpenes are usually found in the essential oils of many plants and are made-up of isoprene units joined in a regular, head-to-tail way. It is common to hydrogenate these naturally occurring materials to render them light yellow in colour and remove their staining and discolouration properties.

The use of pine tree products is often limited by price and thus many of them have latterly been replaced by synthetic plasticisers.

1.2.2.4 Plasticisers Based on Coal Tar (Coal Tar Oils, Pitch, Resins) [39][43]

Coal tar products were among the earliest processing aids used in rubber compounding. However, products from coal tar such as the coumarone indene resins, Figure 1.4, are used to produce tack and as a processing aid. Also it was observed [39] that by using these resins a reinforcing effect was produced in rubbers which have low gum tensile strength such as SBR. A significant improvement in tensile strength was noticed when using these resins with fillers

of the non-reinforcing type, such as calcium carbonate, clay, etc. in SBR. This effect is shown in Table 1.8[39]. The reinforcing effect is believed to be due to the improvement in the dispersion of the filler as a result of the wetting action produced by the resins.

TABLE 1.8(a):

TYPICAL ANILINE POINTS OF COAL TAR RESINS [39]

Class	Aniline Point Range °C
Aromatic	-35 to 15
Semi-aromatic	+35 to 75
Aliphatic	Above 100

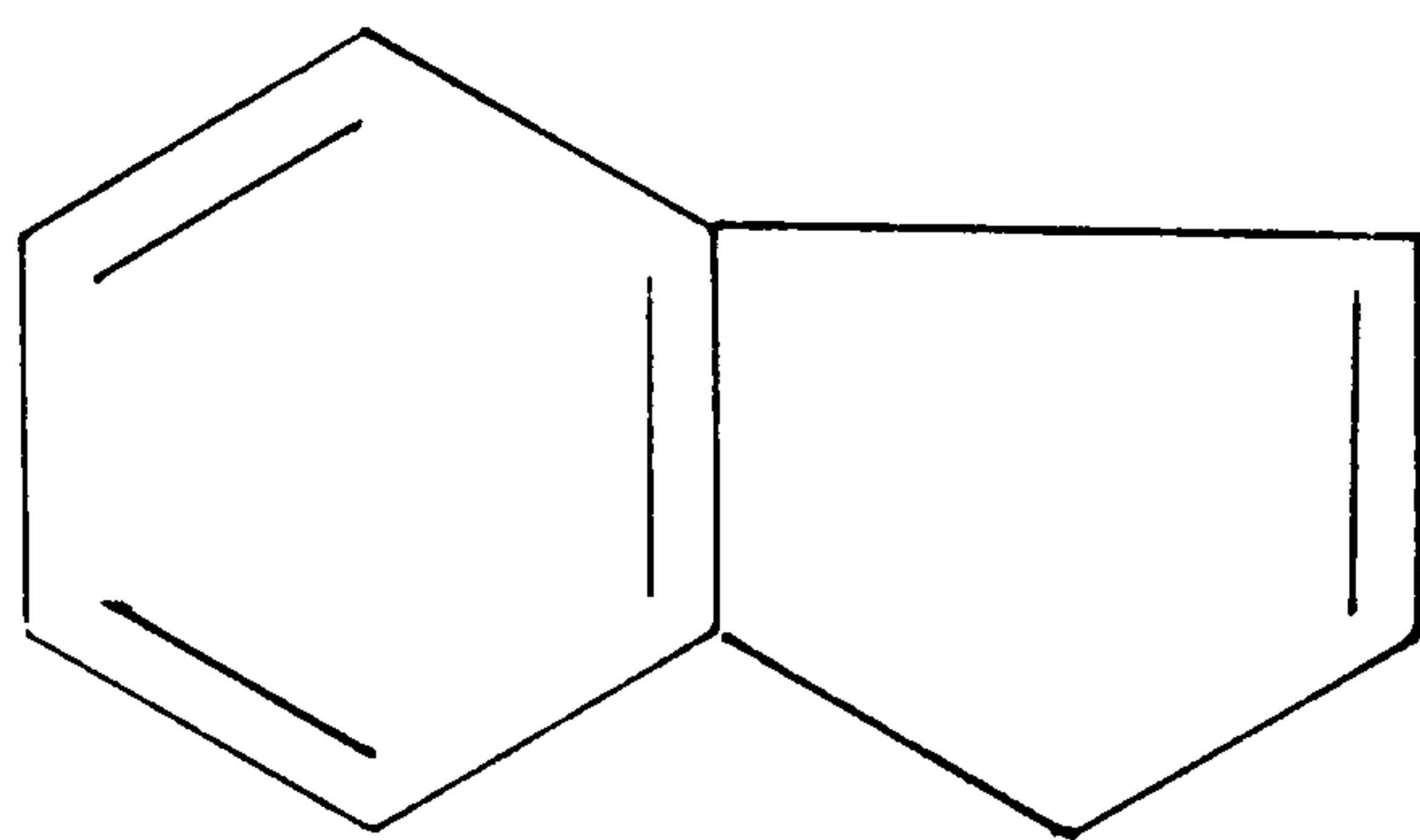
TABLE 1.8(b):

EFFECT OF PLASTICISER AROMATICITY AND ITS REINFORCING EFFECT IN RUBBER WHEN 15 phr IS USED IN MINERAL FILLED SBR

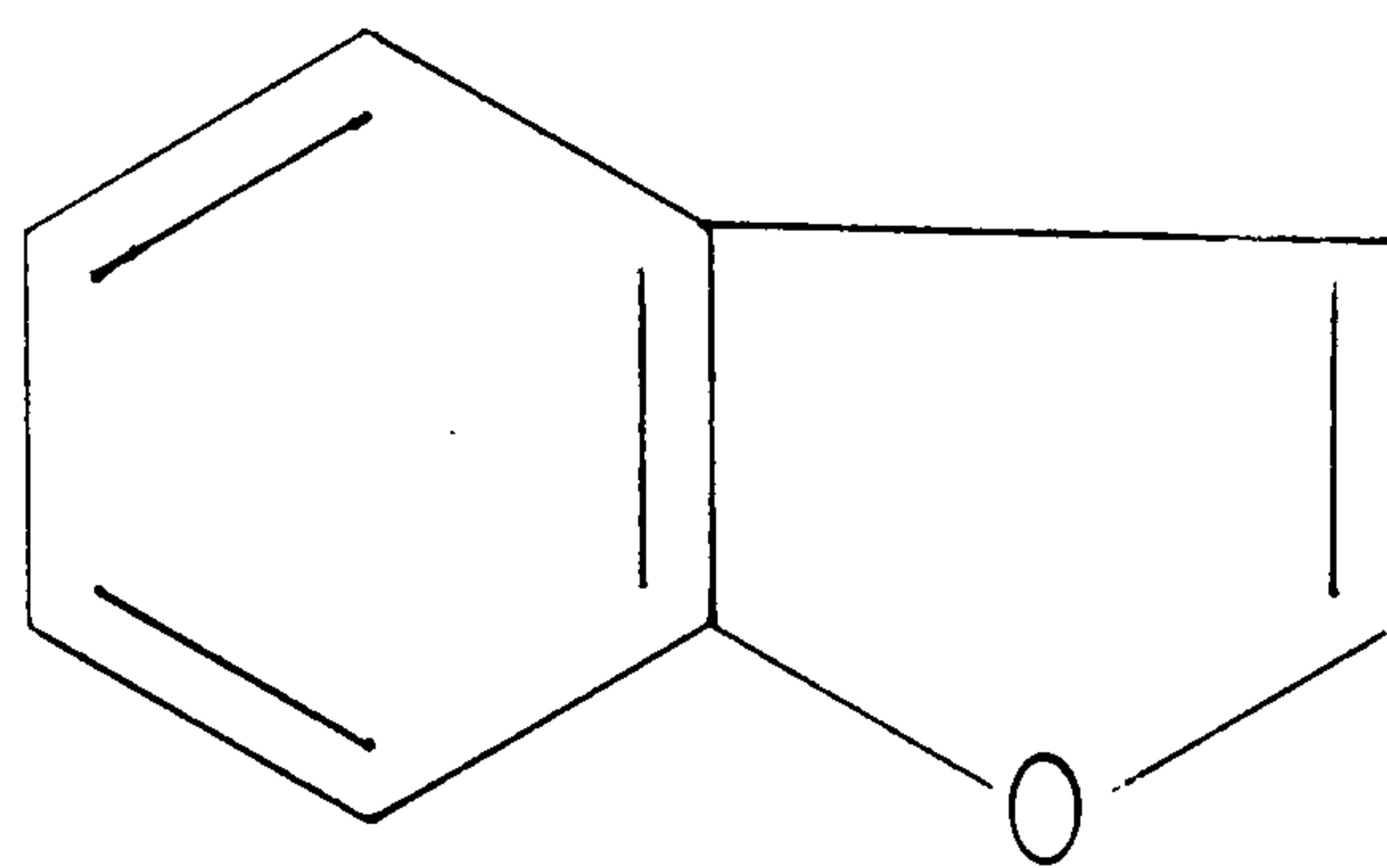
Physical Properties - Cure 10 minutes at 153°C				
Aniline Point of resin used °C	Stress at 300% Elongation (MPa)	Ultimate Tensile (MPa)	Ultimate Elongation %	Shore A Hardness
No resin	2.83	9.97	560	69
0°C	2.00	14.00	720	63
20°C	2.27	14.19	720	63
35°C	1.84	13.26	730	66

Note: All the resins have a softening point of 100°C.

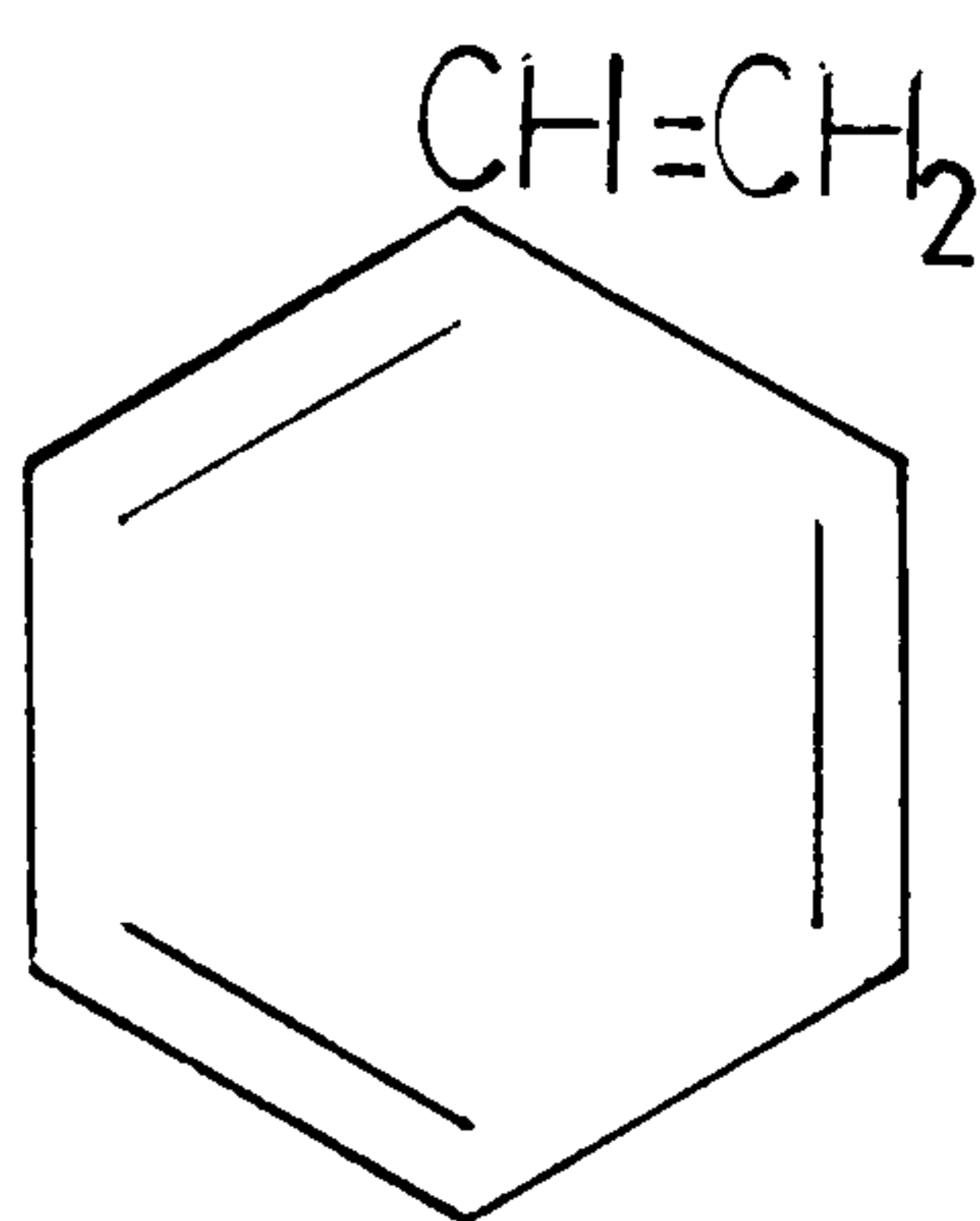
This class of plasticisers contains aromatic hydrocarbons and some other functional groups such as phenolic groups and, in some cases, active nitrogen compounds. These polar groups improve compatibility, but there may also be an accelerating or a retarding effect on the cure in different cases.



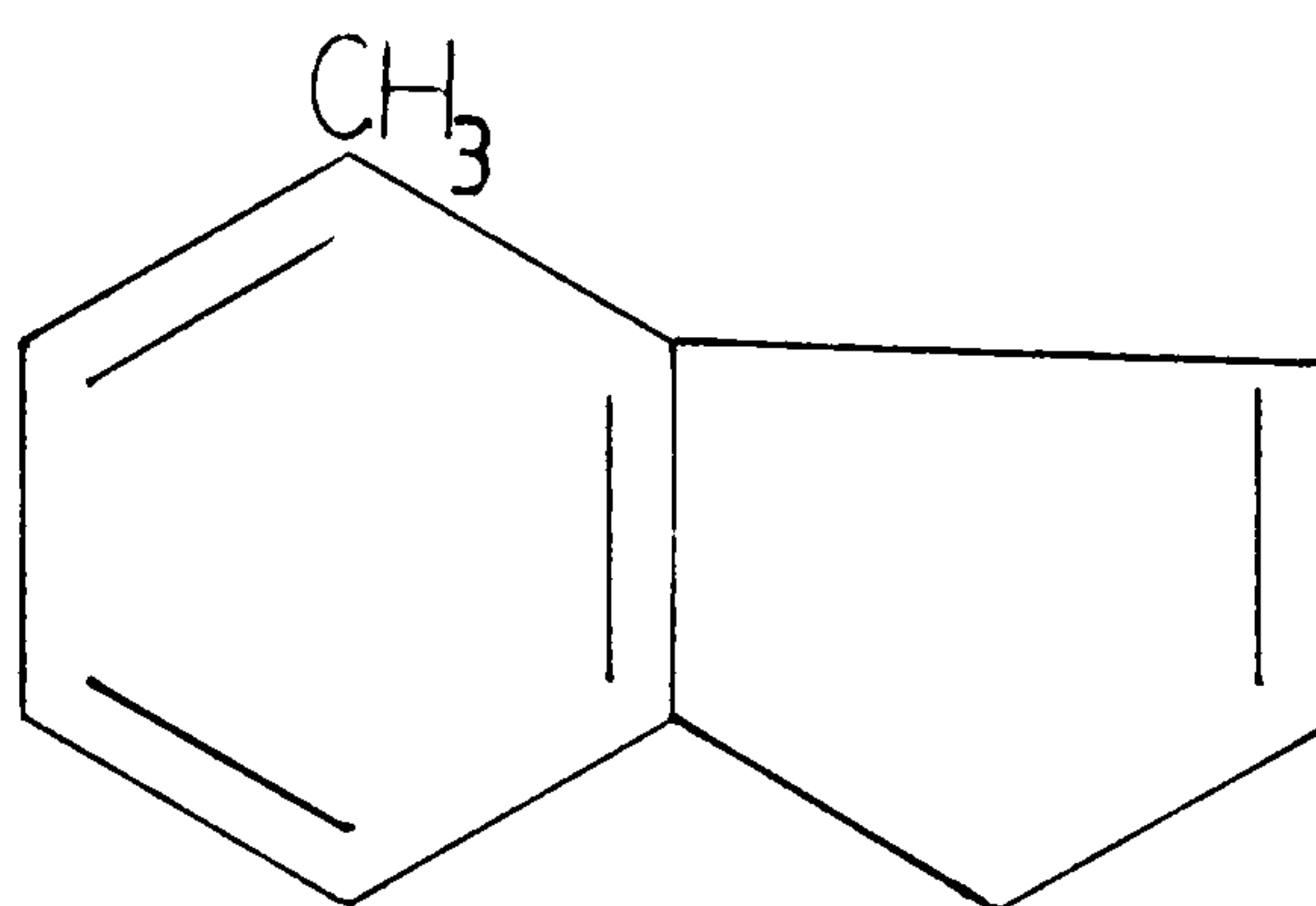
Indene



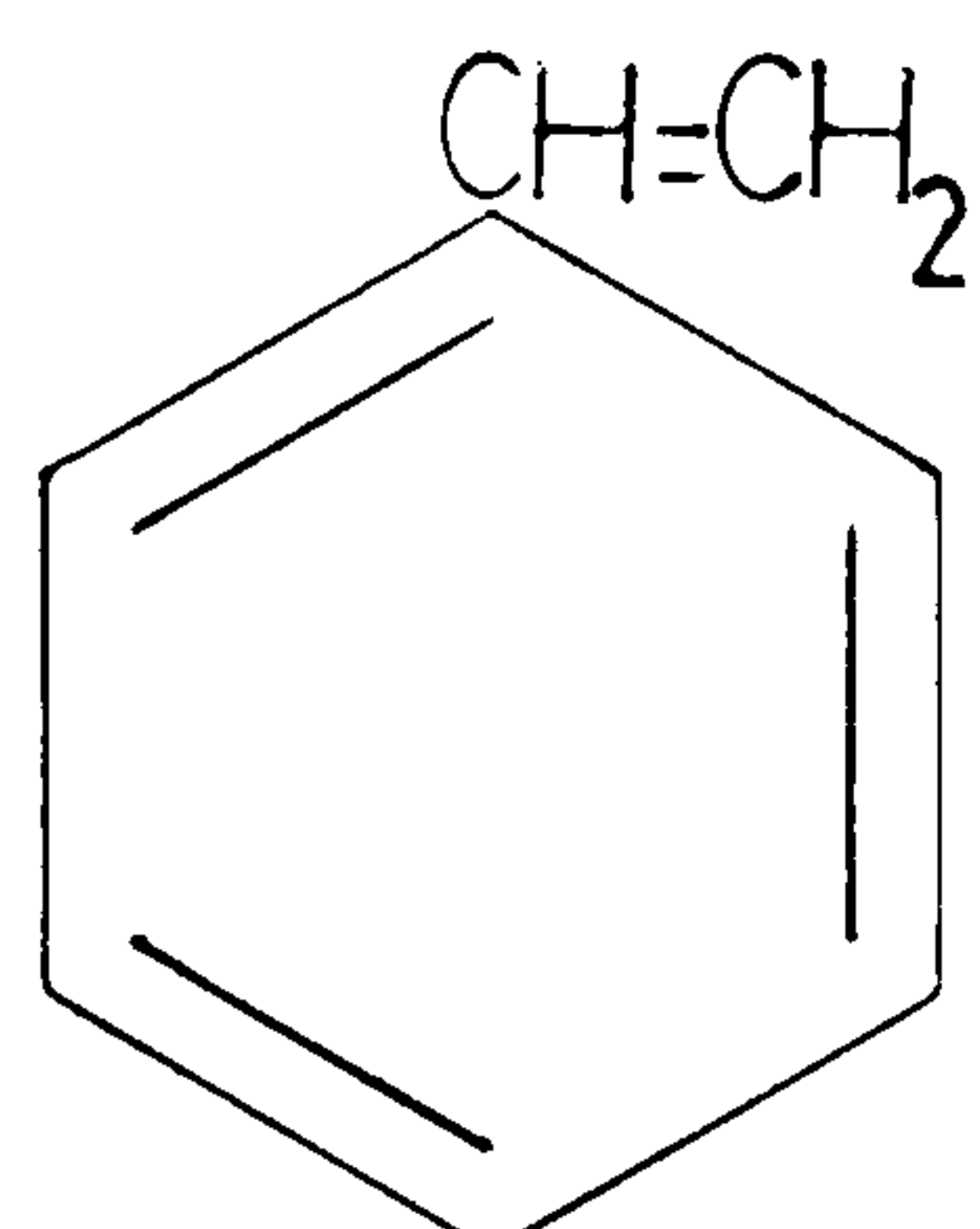
Coumarone



Styrene



Methyl Indene



Vinyl Toluene

FIGURE 1.4: Raw Materials for Coal Tar Resins

The aromatic resins are believed to be [43] the most efficient and active of present plasticisers. They impart greater strength and greater resistance to cut growth in rubber than naphthenic or paraffinic plasticisers and are especially used in the manufacture of mechanical goods.

1.2.2.5 Synthetic Organic Plasticisers

Certain rubbers such as acrylonitrile-butadiene, polychloroprene rubbers, etc. with polar groups may require polar plasticisers for efficient plasticisation because of compatibility considerations. Ester-type plasticisers such as diisooctyl phthalate, dibutyl sebacate, etc. are recognised as very effective plasticisers for these rubbers [44]. This type of plasticiser has a definite wetting effect between filler and rubber and their presence in compounds provides many valuable characteristics such as faster and improved filler dispersions, gives the required curing stiffness and flexibility at low temperature.

Polymerisable plasticisers are another important group of synthetic plasticisers which have the unique ability to increase the physical properties of the rubber vulcanisate by being polymerised in situ. These plasticisers are nearly always used in combination with a peroxide vulcanising agent which brings about the in situ polymerisation of the plasticiser in the rubber during cure and, hence, increases the modulus of the vulcanisate due to its conversion to a rigid plastic within the matrix of the rubber. This gives rise to high hardness and high stiffness in the cured vulcanisate. Also as they are in the liquid state during processing they act as plasticisers and tackifiers. Some examples of these plasticisers are shown in Table 1.9 [30] below:

TABLE 1.9:
SOME POLYMERISABLE ESTER PLASTICISERS; THEIR TRADE NAMES AND SUPPLIERS

Supplier	Trade Name	Chemical Name
Anchor Chemicals	Anchomer ATM 3	Ethylene glycol dimethacrylate
	Anchomer ATM 9	1,3-Butylene glycol dimethacrylate
	Anchomer ATM11	Trimethylol propane trimethacrylate
Lenning Chemical	Monomer X-970	1,3-Butylene glycol dimethacrylate
	Monomer X-980	Trimethylol propane trimethacrylate

Another special class of synthetic plasticisers are the low molecular weight liquid rubber. Examples of these are liquid polybutadiene, liquid polybutylene , liquid NBR, liquid CR, liquid polysulphides, depolymerised natural rubber etc. This group of plasticisers is usually confined to speciality uses due to their high cost and are only used where special performance characteristics are needed.

1.2.3 Parameters Involved in Selecting Plasticisers for Use in Rubber Compounds

To aid processing of a compound during mixing, extrusion, calendering, moulding or other fabrication operations it is necessary to mix with the rubber and other compounding ingredients liquids and low melting solids which act as internal lubricants causing a reduction in viscosity, easing filler incorporation and reducing the heat and power consumption during the processing operations.

These plasticisers are considered to function in a physical rather than a chemical manner, i.e. their function is independent of the temperature of mixing or vulcanisation.

The prime factors governing the selection of these plasticisers are as follows:

- B: Rubber compatibility: compatibility between polymer and a plasticiser is considered important. If a plasticiser is not miscible with rubber it will sweat out giving vulcanisate with poor physical properties and a sticky surface; also poor adhesion properties between uncured layers of the rubber may result.

Compatibility between rubber and its plasticisers is usually considered related to their relative solubility parameters and this parameter can be defined as a measure of the intermolecular attraction forces within a material and can be calculated from the equation shown below [45]:

$$\delta = \left[\frac{\Delta E}{V} \right]^{\frac{1}{2}}$$

where δ is the solubility parameter $(\text{cal.cm}^{-3})^{\frac{1}{2}}$ or $(\text{MJ.m}^{-3})^{\frac{1}{2}}$

ΔE is the energy of vaporisation cal. or Joule

V is the molecular volume cm^3 or m^3

The general rule is that rubbers and plasticisers having closely similar solubility parameter values are likely to be compatible.

Typical values of solubility parameters for a range of plasticisers [30] and rubbers [45] are shown in Table 1.10.

TABLE 1.10:
SOLUBILITY PARAMETERS FOR SOME RUBBERS AND PLASTICISERS [30,45]

Materials	Solubility Parameters	
	$(\text{Cal/cc})^{\frac{1}{2}}$	$(\text{MJ/m}^3)^{\frac{1}{2}}$
<u>Processing aids</u>		
Paraffinic oil	7.2	14.7
Naphthenic oil	8.2	16.7
Aromatic oil	9.2	18.7
Stearic acid	8.5	17.3
Paraffinic wax	7.7	15.7
Dioctyl sebacate	8.7	17.8
Dibutyl sebacate	8.9	18.2
<u>Rubber</u>		
Natural rubber (NR)	8.15	16.6
SBR	8.54	17.5
Cis-polybutadiene (Br)	8.35	17.0
Polychloroprene (CR)	9.38	19.1
Acrylonitrile butadiene (NBR)	9.25	19.0
Butyl (IIR)	7.5 (approx)	15.3 (approx)
EPDM	7.5	15.3

In 1944, Ludwig [27] and co-workers published two articles on SBR plasticisers. They investigated 650 different materials in a single SBR formulation. One of the general principles that resulted from their study was that the mutual solubility between plasticiser and rubber has a significant effect on both processing behaviour and final vulcanisate properties. Plasticisers highly soluble in rubber give the softest, but nerviest (i.e. most elastic) uncured rubber compounds; with intermediate solubility plasticisers the effect known as lubrication begins to be observed (this usually results in a less nervy

or smoother running compound), and with plasticisers of relatively low solubility, the lubricating factor becomes quite pronounced with only small amounts of such plasticisers being used to reduce nerve, giving smoother extrusions and prevent sticking to the rolls of mills and other processing equipment.

It must be recognised that no one function such as the solubility parameter, can be a complete guide to a multivariable situation. In rubber process oils the solubility parameter approach is very helpful in getting a first approximation in regard to what will or will not be a good plasticiser, but it has not been widely used in selection or comparison of these oils for rubber compounds. Instead the behaviour of such oils is clearly, as explained earlier in this chapter, dependent on their composition and therefore it has been the standard practice to measure the compatibility of a process oil as the time in which a particular process oil could be mixed into the basic rubbers. This oil take-up time [28] is in turn a function of the physical characteristics of the petroleum oil such as molecular weight, viscosity, viscosity-gravity constant, aniline points etc. Figure 1.5 shows the rate of oil take-up as a function of its viscosity gravity constant (VGC) and its molecular weight; SBR rubber was used and the compound mixed into Amodel B Banbury.

As a generalisation, the shorter the oil take-up time, the shorter the mixing cycle. This will result in less power consumption and higher productivity.

It is also recognised that efficient and/or compatible plasticisers can affect the processability of the compound after Banbury mixing i.e. the down line operations which may include:

1. Mill mixing: the general appearance and feel of the compound on the mill are good indications of its milling behaviour.

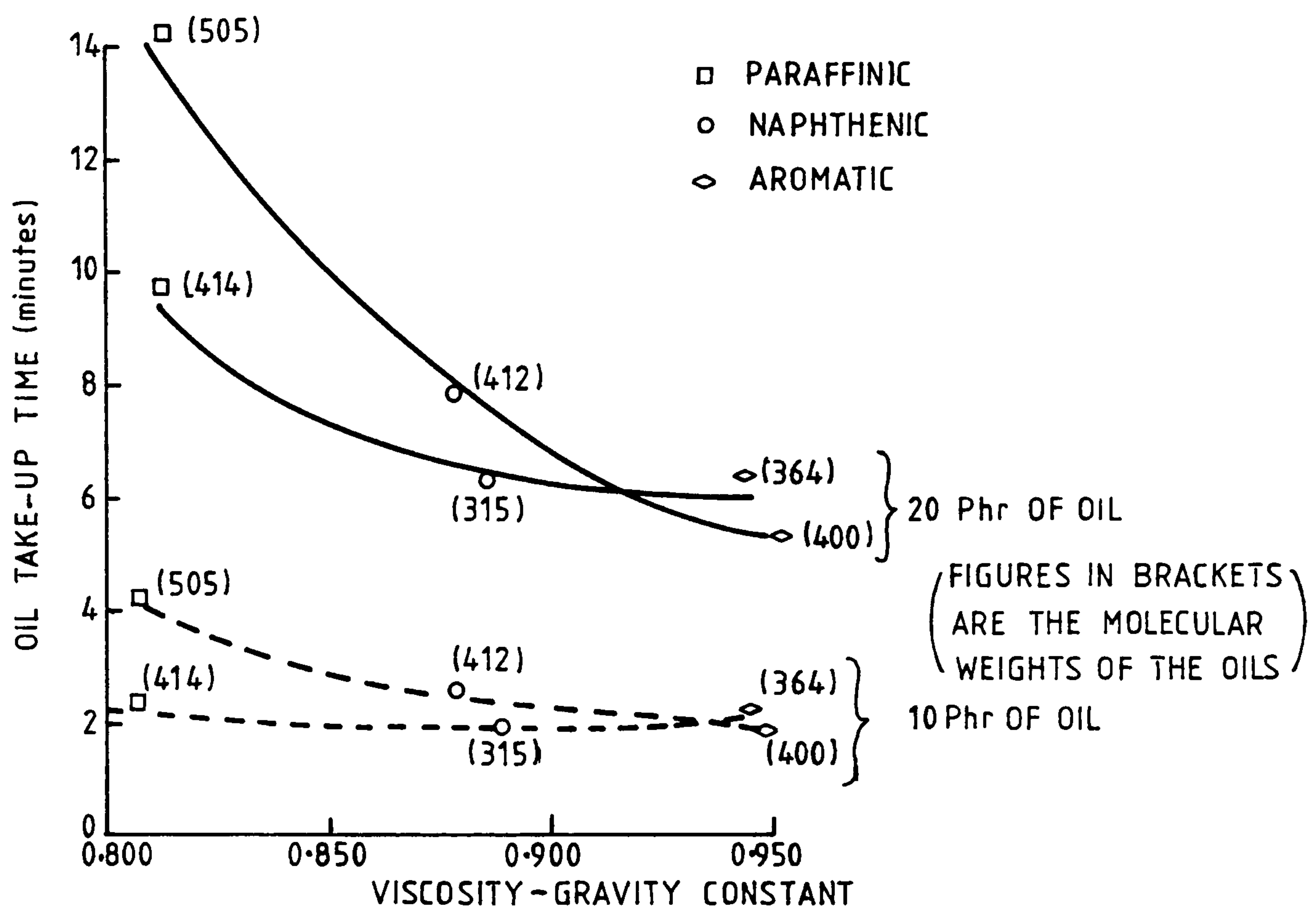


FIGURE 1.5: RATE OF OIL TAKE-UP AS A FUNCTION OF V.G.C. AND MOLECULAR WEIGHT [28]

A compatible plasticiser gives the compound a smooth shiny band on the mill roll which can be pulled and cut easily into strips.

2. Extrusion: stocks are frequently extruded to a needed form, as for example, a tyre tread. A good plasticiser i.e. compatible, could increase the extrusion flow rate, improve the smoothness of the extrudate, and reduce die swell.

For polybutadiene Macey [46] has reported the effect of three different plasticisers at variable concentrations on the extrusion characteristics; rate of extrusion, die swell, and roughness, as well as the Mooney viscosity of cis-polybutadienes. The conclusion that may be drawn from the data in Table 1.11 is that the more compatible plasticisers are those which have higher viscosity, in this example factice, has a considerable effect on die swell and a noticeable effect on the rate of extrusion.

Another important factor used to characterise the compatibility of a plasticiser with rubber is the effects imparted by the plasticiser on the curing behaviour and final properties of the vulcanised product. As explained earlier in this chapter, with certain plasticisers there are some reactive functional groups, for example: organic acid groups, phenolic groups and active nitrogen compounds. These reactive groups improve compatibility, but there may also be either a retarding effect or an accelerating effect on cure in different circumstances. As a generalisation, cure retardation is regarded as undesirable leading to a loss of properties and costs.

Most of the plasticisers, with the exception of polymerisable and crosslinkable plasticisers, reduce the physical properties of the vulcanised products to a certain degree depending on the type and concentration of the plasticiser used.

TABLE 1.11
EFFECT OF DIFFERENT PLASTICISERS ON THE EXTRUSION CHARACTERISTICS OF CIS-POLYBUTADIENE

Raw Rubber ML-10	Softener		Softened ML-10	ISAF Added (phr)	Compounded ML-10	ΔML	Garvey Die Extrusion at 100°C		
	Type	phr					Rate in/min	Swell cm ²	Rough- ness
45	Oil*	3	36	55	90	45	28	1.22	2
		6	29		84	39	27	1.31	3
		9	27		81	36	30	1.29	3
	Resin**	3	37	55	95	50	28	1.24	2
		6	35		94	49	27	1.17	3
		9	32		87	42	27	1.17	4
	Brown Factice	3	37	55	91	46	29	1.21	2
		6	37		92	47	29	1.19	3
		9	36		89	44	31	1.17	4

* Naphthenic petroleum oil
** P-octyl phenol formaldehyde resin

Hence, the relative effect of different plasticisers on the physical properties of a rubber mix is commonly used to assess its compatibility.

An investigation was carried out [47] looking into the effect of naphthenic oil and dehydrated castor oil (DCO) plasticisers on the physical as well as processing properties of SBR 1502 rubber. The formulations used in the study are tabulated in Table 1.12, their physical and extrusion behaviour are shown in Table 1.13, and Figure 1.6 respectively.

TABLE 1.12:

FORMULATION USED TO STUDY THE EFFECT OF VARIOUS LEVELS OF DEHYDRATED CASTOR OIL (DCO) AND NAPHTHENIC OIL IN COMPARISON WITH A CONTROL MIX WHERE THERE IS NO PLASTICISER

Material	A	B	C	D	E	F	G
Level	phr	phr	phr	phr	phr	phr	phr
SBR 1502	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
HAF Black	50	50	50	50	50	50	50
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75	1.75
MBTS	1	1	1	1	1	1	1
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2
PBNA	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Dehydrated castor oil (DCO)	0	5	10	15	-	-	-
Naphthenic oil	0	-	-	-	5	10	25

TABLE 1.13:

PROCESSING, CURING AND PHYSICAL PROPERTIES OF SBR RUBBER BASED ON FORMULATION OF TABLE 1.12

Formulation	A	B	C	D	E	F	G
Physical Properties:							
Modulus (100%) MPa	2.94	2.3	1.96	1.47	1.96	1.6	1.4
Modulus (300%) MPa	16.672	12.65	10.98	7.9	11.3	9.6	8.34
Tensile strength MPa	21.1	19.6	18	16.67	19.6	17.65	17.2
Elongation at break (%)	370	410	450	560	410	460	510
Hardness (IRHD)	66	61	58	54	63	60	57
Tear strength N/mm	36.3	39.2	34.3	34.3	53	51	46
Compression set at 70°C/72 hrs	32	35	37	39	44	47	50
Resilience %	65	64	62	60	54	53	53
Mooney Viscosity (ML + 4)100°C	73	60	51	47	68	57	54
Curing Properties:							
Optimum curing time (t_{90}) at 150°C (min)	22	24	24	25	20	19	19
Mooney scorch at 120°C	20	23	24	26	28	30	32

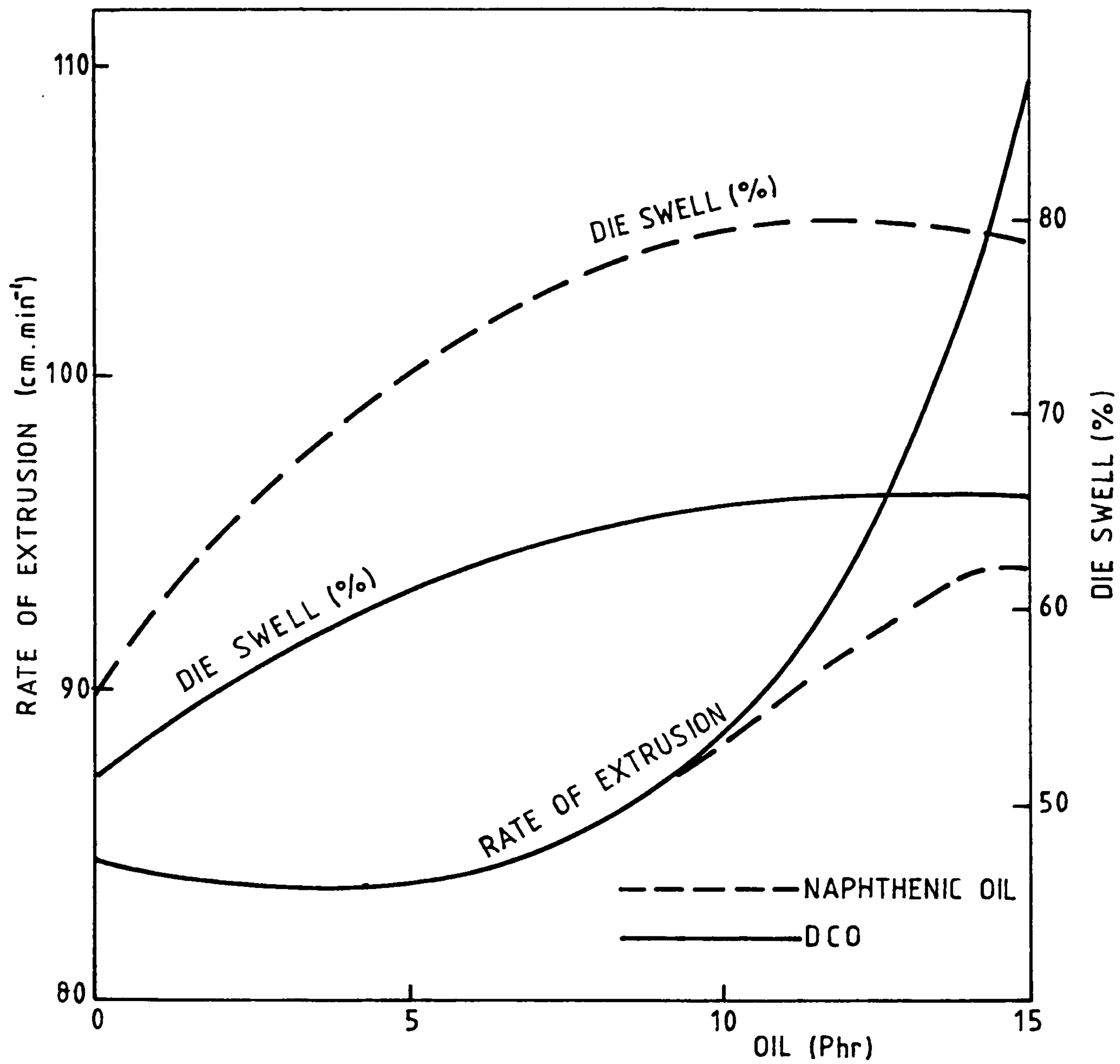


FIGURE 1.6: PROCESSABILITY CHARACTERISTICS AT THE EXTRUSION STAGE FOR COMPOUNDS OF TABLE 1.12 FORMULATIONS AS A COMPARISON BETWEEN DEHYDRATED CASTOR OIL AND NAPHTHENIC MINERAL OILS

The interpretation of the results given in Table 1.13 and Figure 1.6 indicate that DCO plasticiser shows more rubber compatibility than naphthenic oils as a result of which higher physical properties and extrusion behaviour were obtained. However DCO plasticiser has a longer cure time and Mooney scorch than naphthenic oil. These effects could be caused by some retarding groups that might be present in the DCO plasticiser. However, these retarding groups must favour compatibility and probably carbon black dispersion. Extrusion parameters, i.e. extrusion rate and die swell, are clearly enhanced by the presence of the DCO plasticiser. Again this may be attributable to the efficiency, or compatibility of the DCO plasticiser.

B: Handling Properties of a Plasticiser (i.e. volatility and flow)

Various physical properties of plasticisers have definite effects on rubber compounds. For example, very high vapour pressure plasticisers are obviously undesirable because of evaporation during processing, curing and service.

Viscosity affects the ease of incorporation during mixing: in general lower viscosity plasticisers are incorporated with more difficulty, while those plasticisers with the lowest viscosity give the softest stocks. Moreover plasticisers with a very low viscosity are too volatile for most applications whereas those above a certain viscosity give rise to an acceptable behaviour.

Other parameters often used to select plasticisers are: staining, ageing resistance, fluid extractability and retention of flexibility at low temperatures.

1.3 Sulphur Vulcanisation

Introduction

Vulcanisation is a process by which the long chains of the rubber molecules become crosslinked by reacting with the vulcanisation agent to form three-dimensional structures. This reaction transforms the predominantly plastic nature of rubber into a strong elastic product. Consequently the rubber loses its tackiness and becomes insoluble in solvents and is more resistant to heat, light, and ageing processes.

The most generally favoured vulcanisation methods today are merely elaborations of the original method of heating rubber with sulphur discovered by Goodyear in 1839. Despite the extensive research since that time no other generally accepted method has been found which gives vulcanisates with as good a balance of mechanical and chemical properties. Most research work dealt with accelerated sulphur vulcanisation only and hence it is this which is now discussed in detail. However, as a preliminary a brief summary about unaccelerated sulphur vulcanisation will be given.

1.3.1 Unaccelerated Sulphur Curing

Sulphur will cure rubber alone, but the reaction requires considerable time, and it produces vulcanisates with poor resistance to ageing. This is attributed to the incorporation of sulphur in a variety of crosslinks such as long polysulphide, cyclic monosulphide, cyclic disulphide, vicinal crosslinks, etc. which can be represented pictorially as in Figure 1.7 [48].

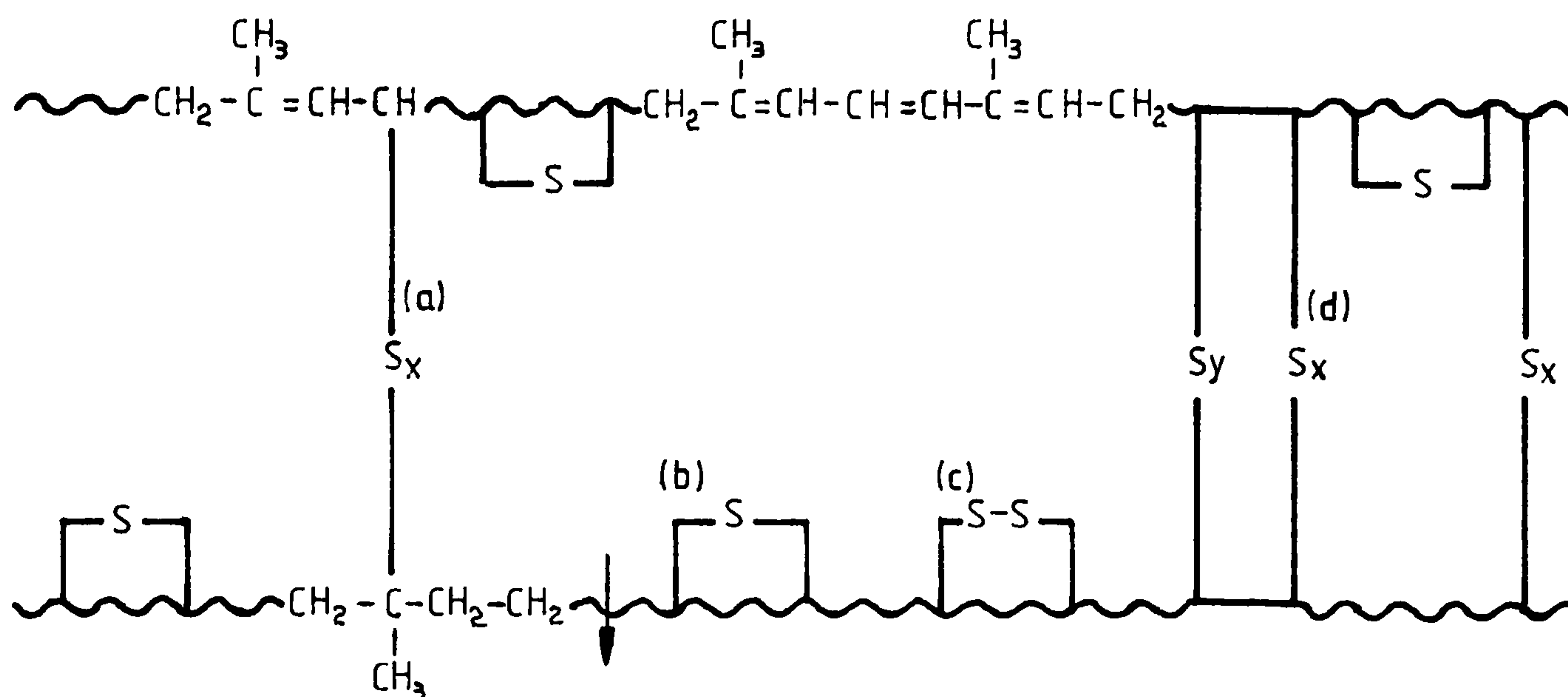


FIGURE 1.7: Typical Chemical Groups Present in an Unaccelerated Sulphur NR Vulcanisate Network [48]

- (a) Polysulphide crosslink ($X = 3-6$);
- (b) Cyclic monosulphide crosslink;
- (c) Cyclic disulphide;
- (d) Vicinal crosslink ($Y = 1-6$).

The relative proportions and composition of these crosslinks change considerably with reaction (or cure) time to give predominantly short sulphurated crosslinks with a substantial proportion of cyclic monosulphide, together with trienes at mature cure states [48].

Vulcanisate obtained from unaccelerated sulphur systems are not used for the following reasons:

- i) Vulcanisation time is very long i.e. long cure time of typically 8 hours at 140°C .
- ii) Large proportions of sulphur are necessary.
- iii) The storage stability and ageing resistance are very poor.
- iv) Generally they are dark in colour and show severe sulphur blooming.
- v) They have a strong tendency to revert.

It is mainly for reason (i) above that accelerators were introduced.

1.3.2 Accelerated Sulphur Vulcanisation

The formation of an accelerator-sulphur vulcanisate network is a result of different thought. However, the present part deals with two different mechanisms for two different accelerators. The accelerators selected are namely: sulphenamide and amine types. These accelerators are selected mainly because they were used throughout the research work. Also they are among the most commonly used accelerators in the rubber industry.

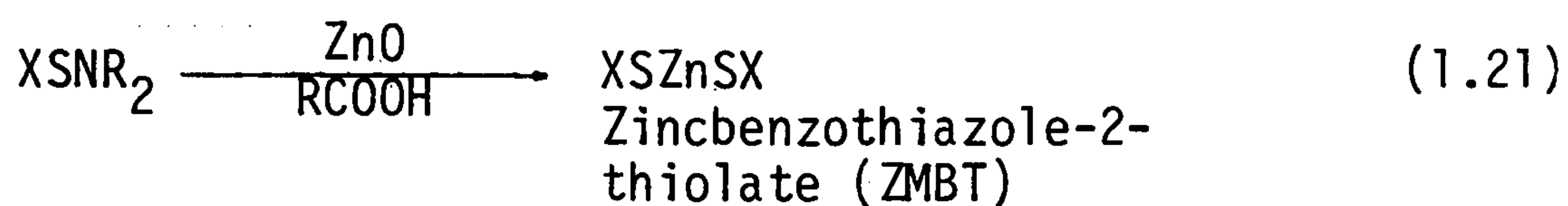
A: Sulphenamide accelerator

The sulphenamide accelerator used is N-cyclohexyl benzothiazole-2-sulphenamide.

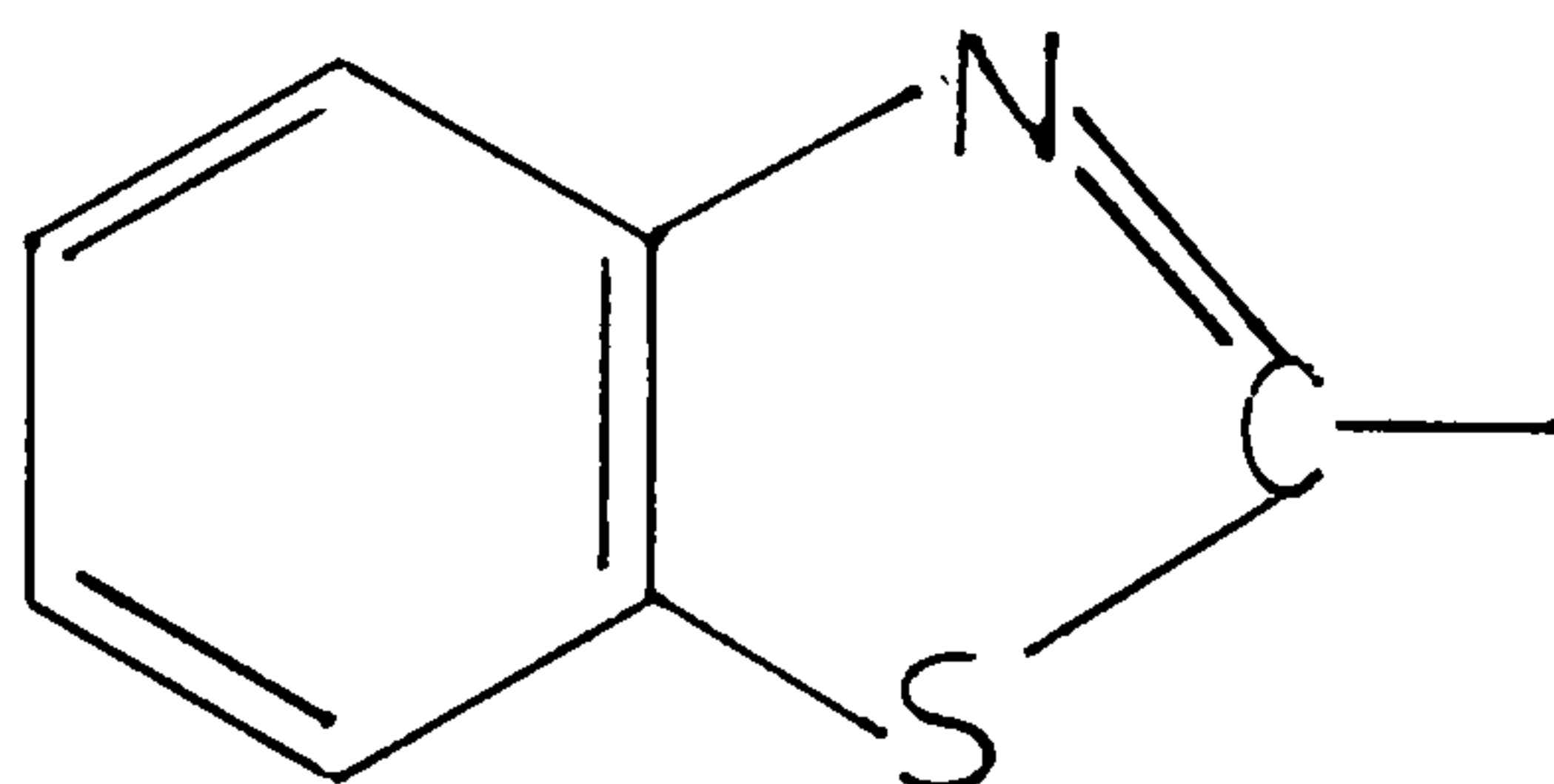
Consider a typical vulcanisation recipe which contains the following components: NR (100), ZnO (3), Stearic acid (1), CBS (0.5), S(2).

Step 1:

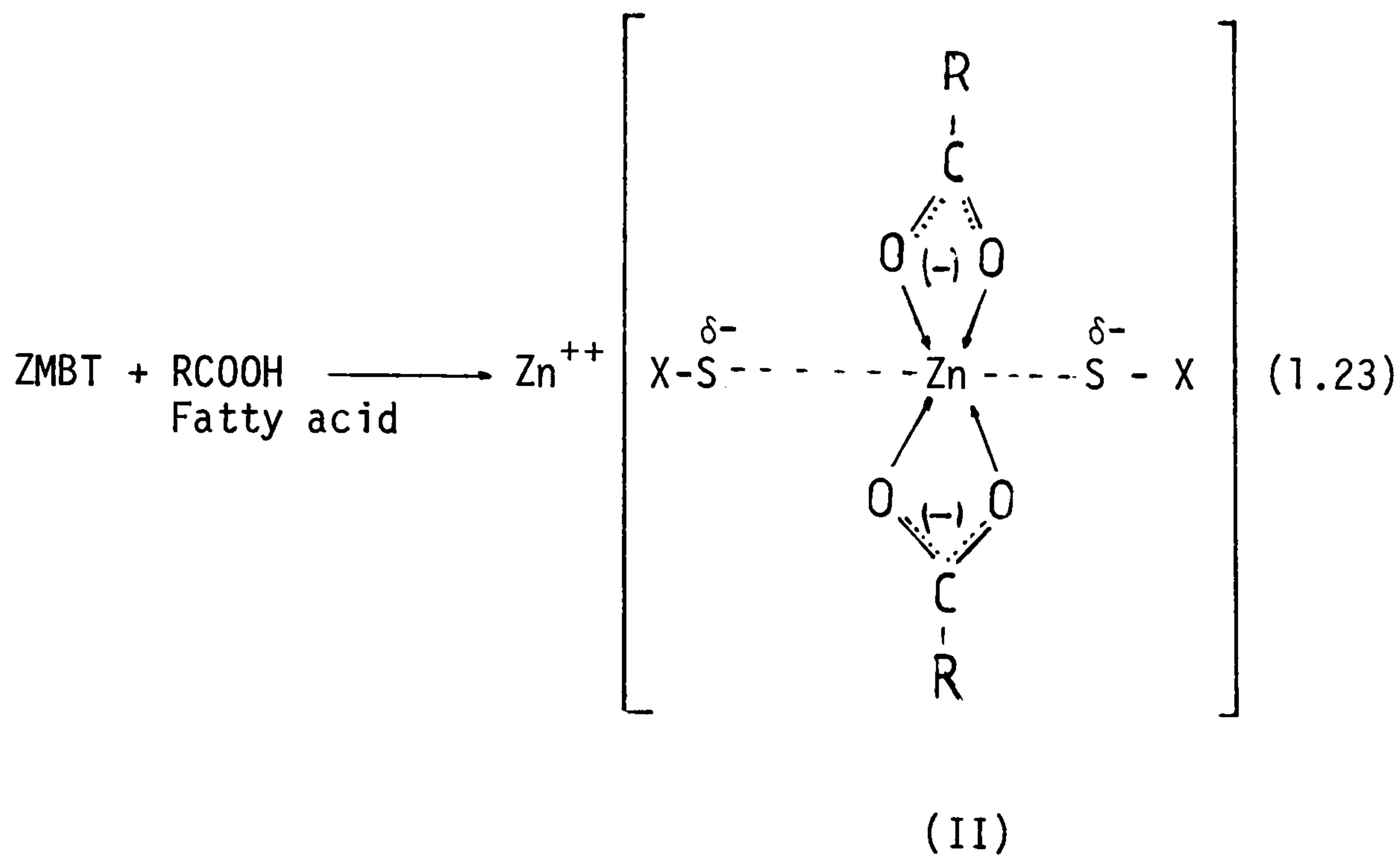
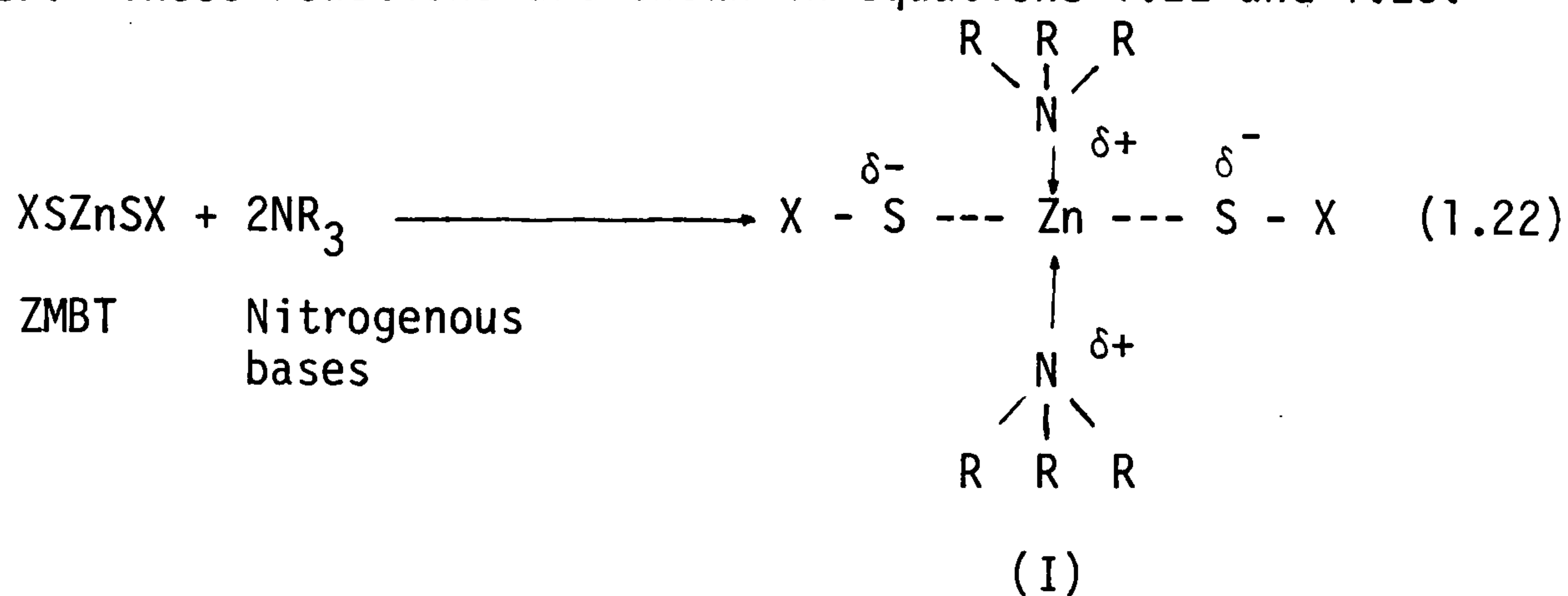
The first step involves the reaction of ZnO, stearic acid, and CBS to produce zincbenzothiazole-2-thiolate (ZMBT) [48-51] as shown in equation 1.21.



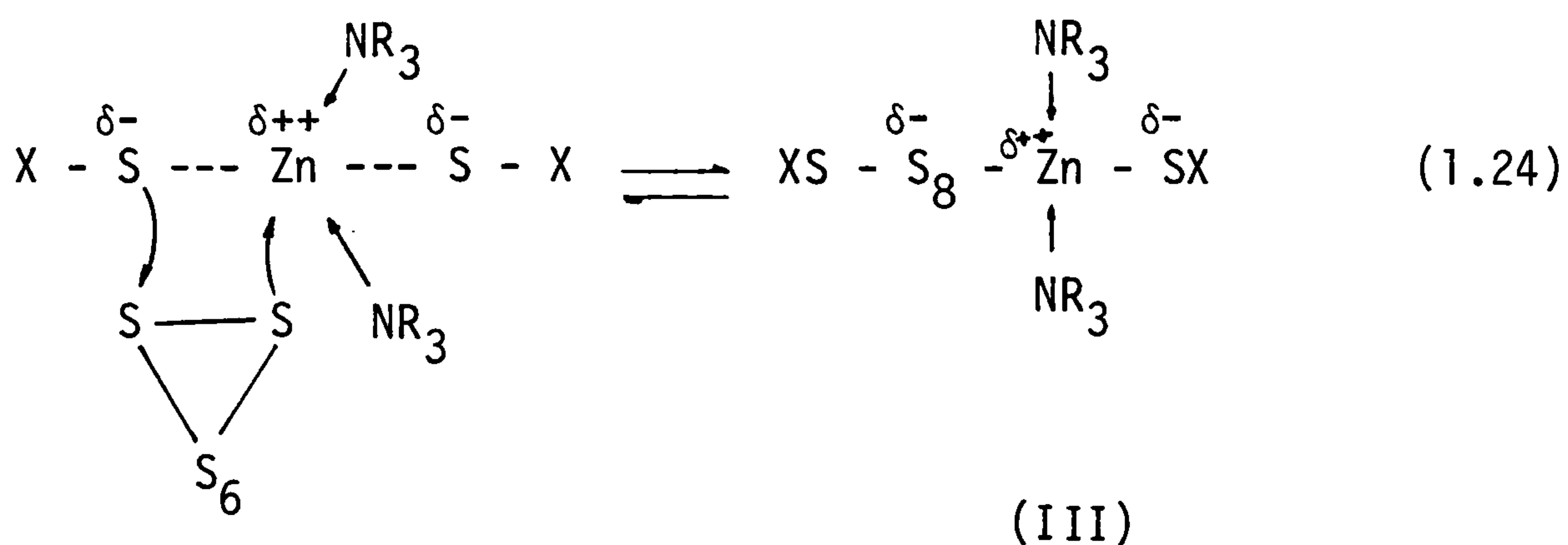
where X =



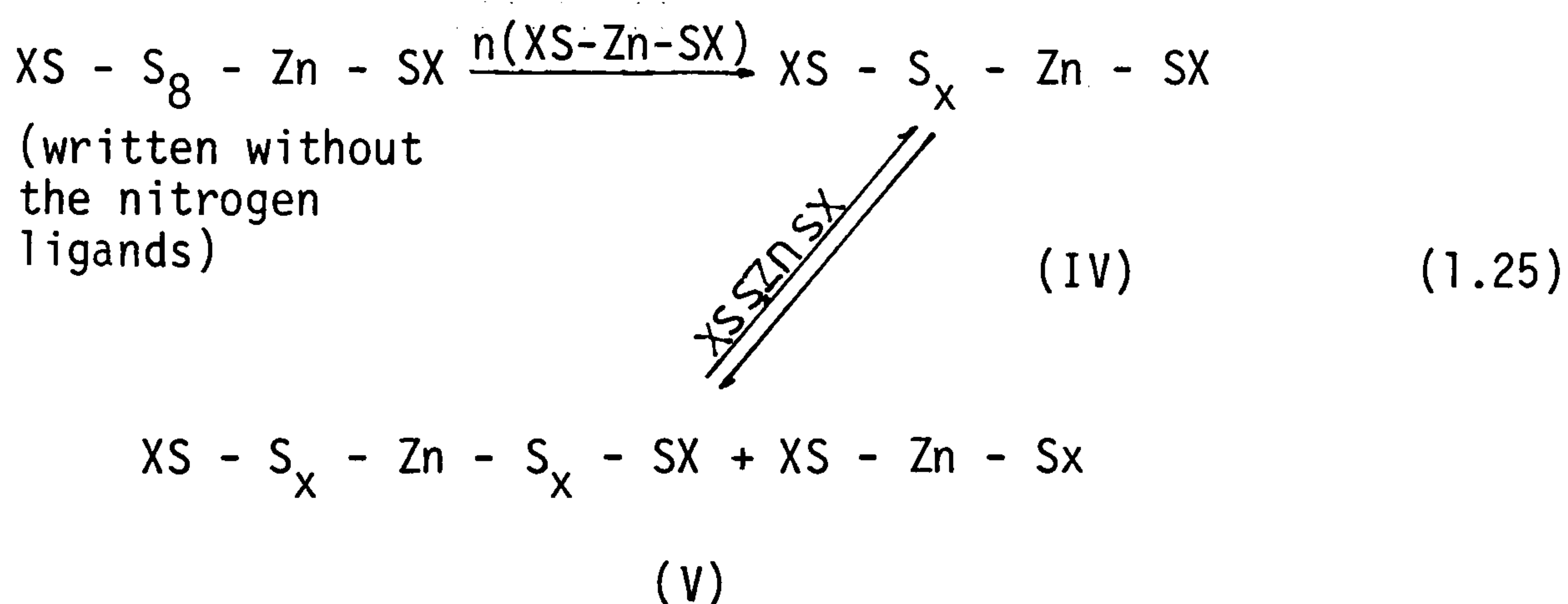
ZMBT is only sparingly soluble in rubber but the coordination of it with the amine or carboxylate ligands renders it very soluble. Nitrogenous bases are produced either from the nitrogenous proteins of natural rubber or from dissociation of the sulphenamide accelerator. Carboxylate ligands are derived from the fatty acid present in the formulation or that naturally occurring in the natural rubber. These reactions are shown in equations 1.22 and 1.23:



The complexes formed above (I and II of equations 1.22 and 1.23) react with sulphur to form zinc perthiomercaptides which are believed to be active sulphurating agents as shown in equation 1.24 below:



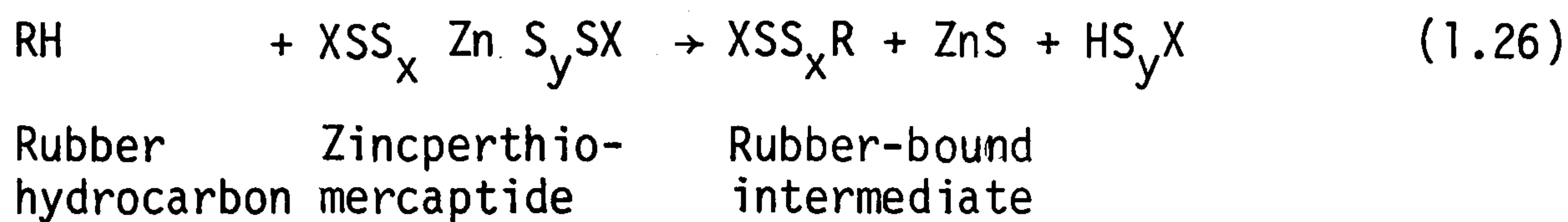
The sulphurating complex (III) is then reacted with other ZMBT molecules to produce sulphurating complexes of varying sulphur chain length which are also considered as sulphurating agents as shown in equation 1.25:



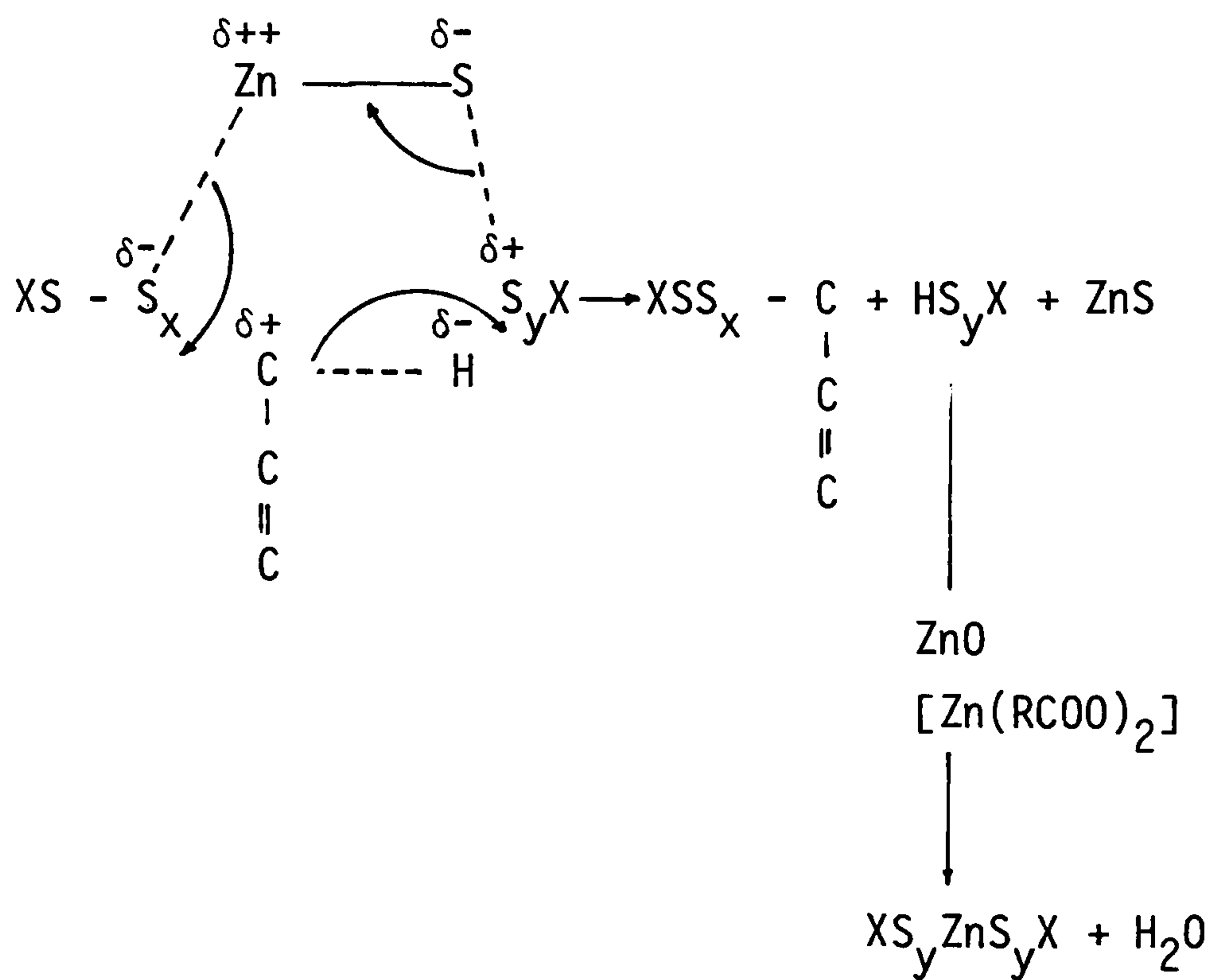
Step 2:

In the second stage of the vulcanisation the sulphurating agent (V) reacts with the rubber hydrocarbon to produce a rubber-bound intermediate (RS_xSX). Bateman and his associates proposed that the formation

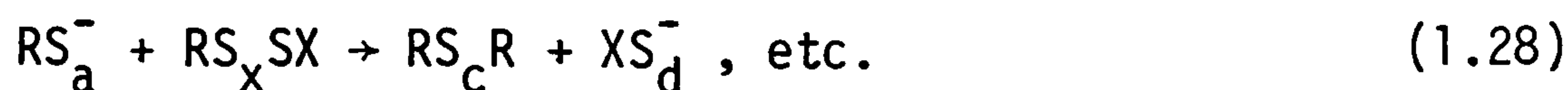
of (RS_xSX) involves nucleophilic attack of a terminal perthiomer-captide sulphur atom at the side-chain methylic carbon or backbone α -methylenic carbon atom in the rubber hydrocarbon. This is shown in equation 1.26:



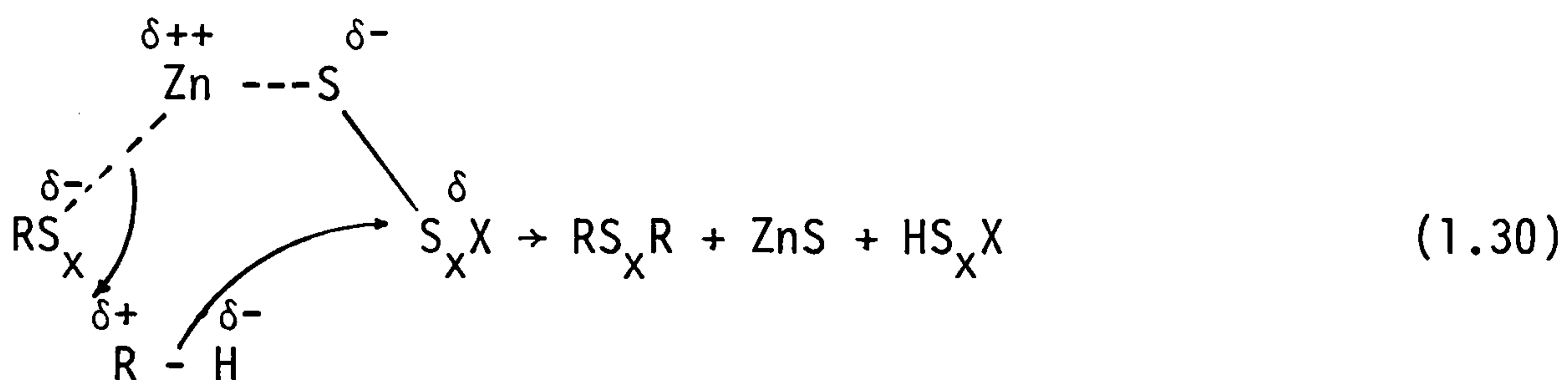
The above reaction can be described as follows:



The conversion of the rubber-bound intermediate (RS_xSX) into initial crosslinks may be formed either by nucleophilic displacement as shown below in equations 1.27 and 1.28:



where XS^- is derived from the zinc perthiomercaptide or interchange between the rubber-bound intermediate and zinc perthiomercaptide (equation 1.29). This is then followed by sulphuration of another rubber chain (equation 1.30):



Continued heat and action of ZMBT complex strip sulphur from the polysulphide initially formed (equation 1.30) and produce an end product having higher percentage of monosulphidic crosslinks than the other type of crosslinks. However, recent structural features of an accelerated sulphur vulcanisate based on natural rubber have been reported [52] to be as given below in Figure 1.8:

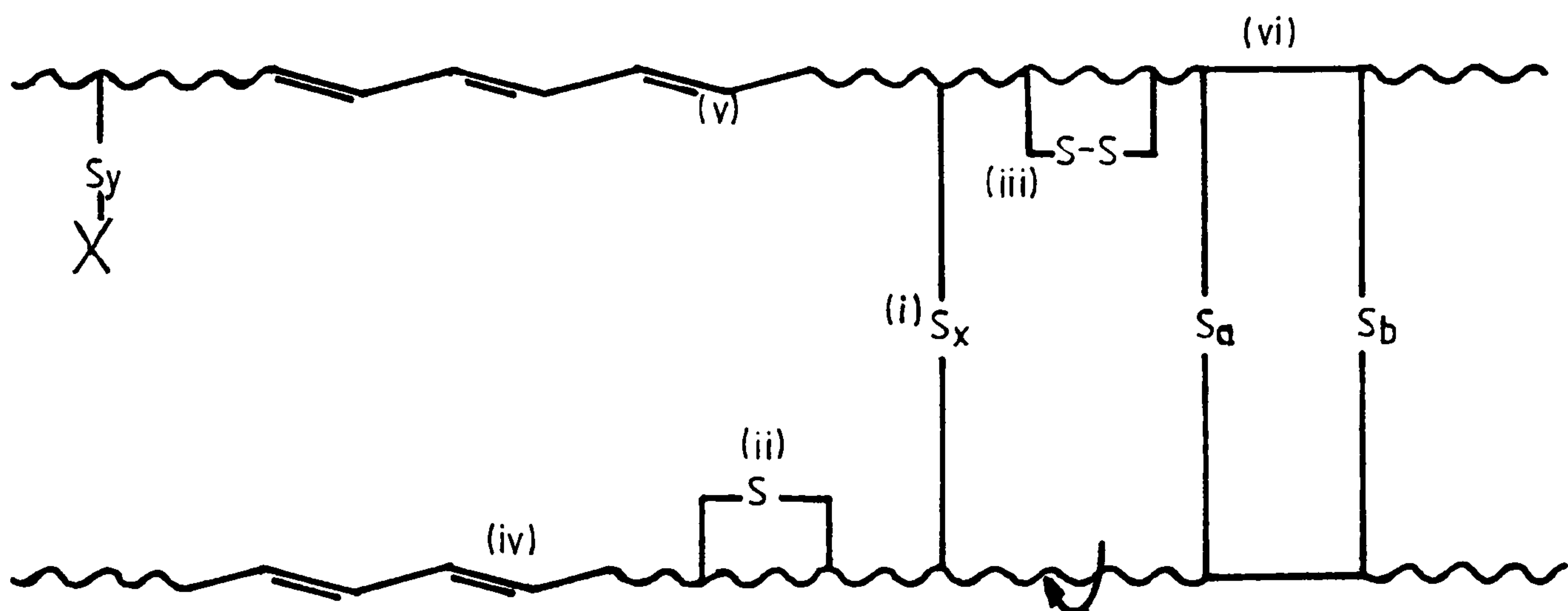


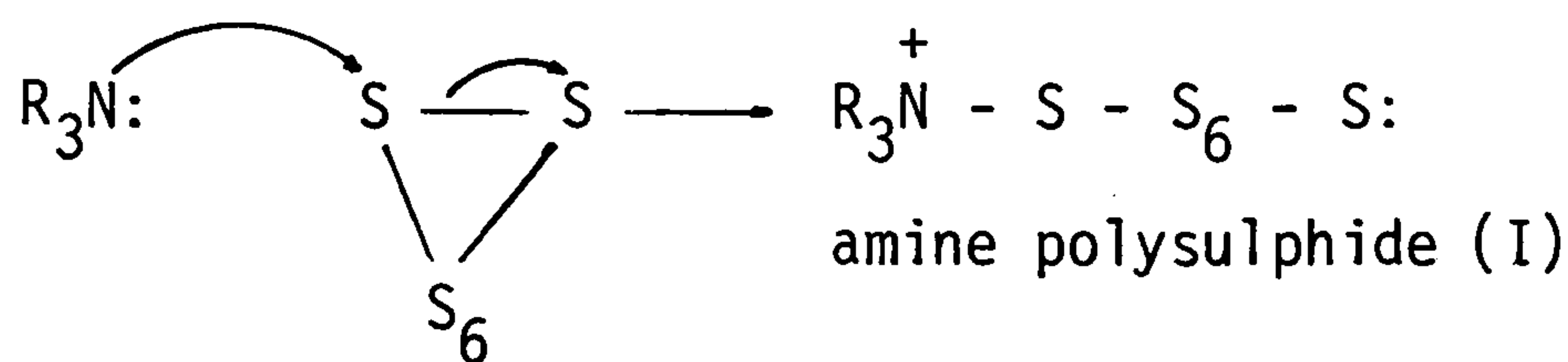
FIGURE 1.8: Structural feature of an accelerated sulphur vulcanisate of natural rubber.

a,b,x,y = 1,6; X = accelerator residue; (i) long polysulphide crosslink; (ii) cyclic monosulphide; (iii) cyclic disulphide; (iv) conjugated diene; (v) conjugated triene; (vi) vicinal crosslink, curved arrow signifies cis, trans-isomerisation,

Two extra reaction mechanisms are postulated to account for the sulphur vulcanisation accelerated by sulphenamide in addition to the polar mechanism just discussed. These are namely: the free radical mechanisms and mechanisms with a combined polar/radical nature. These are not discussed here mainly because the polar mechanism is generally accepted as the best way of explaining the numerous features of accelerated sulphur vulcanisation.

B: *Amine Type Acceleration*

The mechanism of sulphur vulcanisation by amino type accelerators is thought to be [53] as follows: amine with their free pair of electrons, are capable of entering the electron gap of the ionically split sulphur as follows:



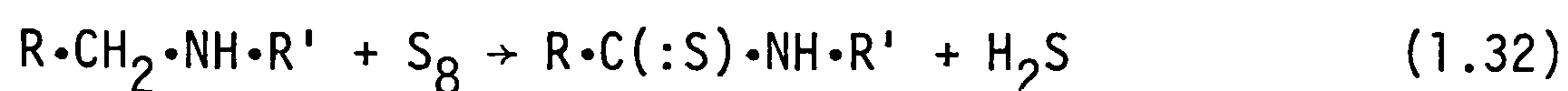
Then shortly after the formation of (I) they split off reactive sulphur which is capable of reacting with the rubber hydrocarbon. The above mechanism was doubtful mainly because it is believed that the electron gaps referred to in this mechanism do not form easily and require a large amount of energy [54].

Recently Bartlett and co-workers [55,56] have put forward very satisfactory assumptions which suggest that the sulphur-sulphur bond can only be opened by the thiophilic substances such as hydrosulphide, sulphide, and sulphite ions derived from the reaction of the amine with

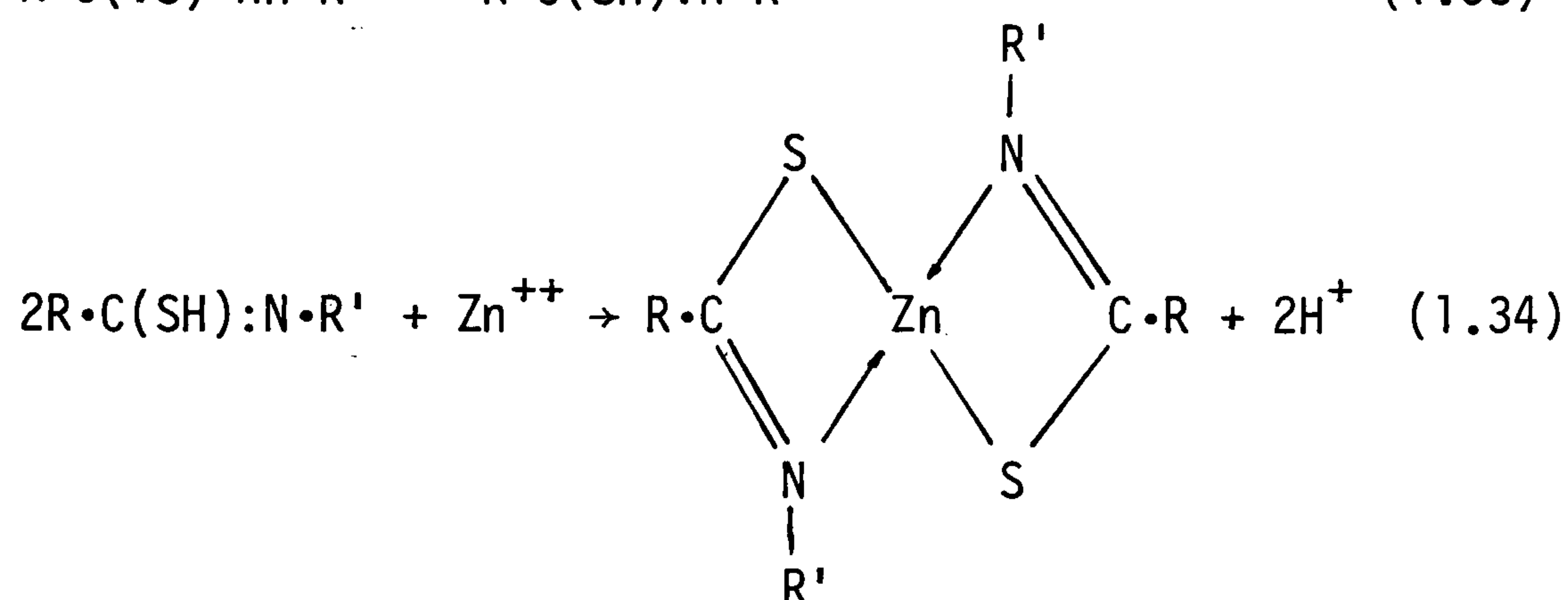
trace amount of hydrogen sulphide or sulphurous acid present in the sulphur (equation 1.31):



Additional hydrogen sulphide is necessary for equation 1.31 to be possible and this is believed to be formed from the reaction between sulphur and amine [48] as shown in equation 1.32 below:



In the presence of zinc ions a zinc accelerator complex, formally similar to [I] of equation 1.22, forms from the reaction of the thioamide formed in equation 1.32 with zinc ions as shown below:



This complex is able to activate sulphur in a similar manner to that shown in connection with sulphenamide accelerator just discussed.

1.4 Objectives of the Research

The purpose of this research work was to study the effect of cationic surfactants as rubber plasticisers and/or processing aids or dispersion aids on processability, curing characteristics and physical properties of rubber formulations.

Earlier pioneering efforts had studied the use of polymeric cationic surfactants as dispersing agents for carbon black using a special technique [13].

Against this background a research programme was planned to investigate whether fatty diamine salts classified as cationic surfactants, and which have not been studied before, could be used as plasticisers for rubber compounds. Cationic surfactants were chosen following an observation made in a previous research programme of Rahman [57]. The programme had the following sequence:

1. To investigate the effect of variable concentration of fatty diamine surfactant on the physical and curing properties in a standard NR/SBR type rubber, based on a truck tyre sidewall recipe and to compare its properties with some common rubber plasticisers. When optimum levels of a particular plasticiser are known a study in detail of its effect as a plasticiser on the following rubber technology parameters will be made: these are to be processability during mixing, extrusion and moulding, curing characteristics, physical properties, and cyclic deformation fatigue. Controls will be the common plasticising agents.
2. Synthesis of various diamine salts and the investigation of their ability as plasticisers.
- 3a. To examine these commercially available cationic surfactants and the experimentally prepared salts as processing aids in rubber.

- b. Study the effect of fatty diamine, fatty diamine salts, prepared salts and ethylene bis fatty amides in gum natural rubber, carbon black filled natural rubber and filled SBR compounds in different formulations; curing characteristics, mechanical properties and ageing behaviour of rubbers will be examined.
4. To extend the use of the fatty diamine, fatty diamine salts, diamide and the prepared salts in other types of unsaturated rubbers such as polybutadiene, acrylonitrile-butadiene and polychloroprene rubbers.

In the course of this research it was realised that these materials have, when incorporated in rubber, demonstrated unique and useful characteristics. Accordingly another programme was put forward to examine whether they could also be used as curing activators, it had the following sequence:

1. A study of their ability as accelerators for NR/SBR compounds.
2. Examine the effect of zinc oxide and stearic acid on the curing performance of these substances.
3. Extension of their use in other rubbers such as NR, SBR, BR and NBR and to study their behaviour as accelerators compared to conventional accelerators.
4. To investigate their ability as crosslinking agents for chloroprene rubber.

CHAPTER 2

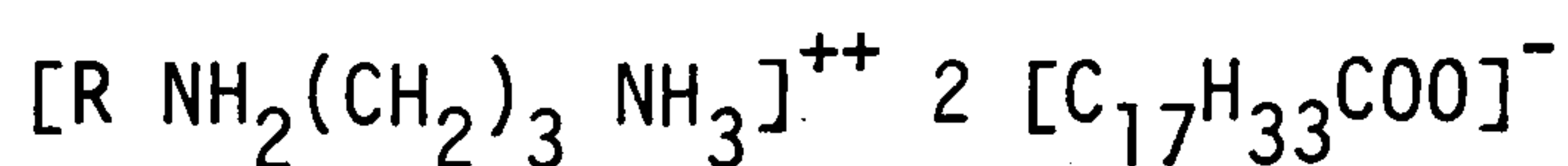
CONVENTIONAL PLASTICISERS AND A CATIONIC SURFACTANT IN AN NR/SBR TYRE SIDEWALL COMPOUND

Introduction

The effect of conventional plasticisers and/or processing aids on the properties of rubber compounds, in their unvulcanised and vulcanised states, has been discussed in Chapter 1, Section 1.2. Cationic surface active agents, particularly the fatty diamine salts, have not as far as the author is aware, been studied before as plasticisers or processing aids in rubber compounds. Their synthesis, properties, and general applications have been given previously in Chapter 1, Section 1.1.

Why cationic surfactants? The main reason to study cationic surfactants as plasticisers or processing aids is the fact that these materials are derivatives of fatty acids and usually fatty acids and their derivatives (see Section 1.2) are known as one of the common plasticisers and processing aids for rubber. Also these materials are cheap compared to many of the other expensive commercially available processing aids. Another important factor is that these compounds are alkaline in nature due to the presence of nitrogen groups in their structure and this assists in making surface active towards the usual fillers used in rubber whereas conventional plasticisers are usually inactive as surfactants. Finally cationics are known as excellent wetting and dispersing agents and therefore they may enhance filler dispersion.

In this chapter the cationic surface active agent, N-tallow-1,3-propane-diamine di-oleate, having the structural formula



where R = tallow

has been selected for evaluation as a plasticiser in a truck tyre sidewall compound based on an NR/SBR rubber; it is used in comparison with six conventional plasticisers and processing aids. The effect of different levels of each individual plasticiser and surface active agent on curing and physical properties is first studied. Then an optimum level is chosen from each plasticiser and surface active agent and studied in detail.

The plasticisers and processing aids used in this study are selected because they are the most commonly used plasticisers and processing aids in the rubber industry and are commercially available. These plasticisers and processing aids are shown in Table 2.1.

2.1 Performance of Individual Plasticisers in a Truck Tyre Sidewall Rubber Compound

Each individual plasticiser and processing aid has been studied in four different proportions given in Table 2.1 below:

TABLE 2.1:
PLASTICISER, PROCESSING AIDS AND SAPA 1/1 PROPORTIONS STUDIED

Plasticiser and/or Processing Aids	Type	Supplier	Proportions in phr used
Dutrex 729 (UK)	Aromatic petroleum oil	Shell Oil	5-7.5-10-12
Sundex 790	Aromatic petroleum oil	Sun Oil	5-7.5-10-12
Iraqi Oil	Aromatic petroleum oil	Iraq	5-7.5-10-12
Circosol 4240	Naphthenic petroleum oil	Sun Oil	= = = =
Stearic acid	-	Anchor Chemicals	5-7.5-10
Struktol WB212	Emulsion of water and fatty acid	Schill and Seilacher	5-7.5-10
SAPA* 1/1	Fatty diamine salts	Akzo Chemie	2.5-5-7.5-10
Iraqi oil + stearic acid			5 parts + 5 parts
Iraqi oil + Struktol WB212			5 parts + 5 parts
Iraqi oil + SAPA 1/1			5 parts + 5 parts

* Note: SAPA 1/1 is an abbreviation for surface active plasticiser and this term will be used in the forthcoming sections.
SAPA 1/1 chemical structure is $[RNH_2(CH_2)_3NH_3]^{++} 2[C_{17}H_{33}COO]^{-}$

An NR/SBR truck tyre sidewall type compound was used as the base mix as shown in Table 2.2 below:

TABLE 2.2:
TRUCK TYRE SIDEWALL COMPOUND FORMULATION STUDIED

Materials	phr
1. NR(SMR20)	30.00
2. SBR 1500	70.00
3. Zinc oxide	4.00
4. Sulphur	2.00
5. CBS	0.25
6. Santocure MOR	0.25
7. Flectol-H	0.75
8. IPPD	2.00
9. Antiozone wax	3.00
10. Stearic acid	2.00
11. Carbon black FEF	51.00
12. Processing oil	Variable (see Table 2.1)

The specific rubber grades and other ingredients employed are given in Appendix III with their suppliers name and other relevant technical information.

Traditionally, time of mixing and temperature rise have been the mixing process criteria for determining when any individual batch should be dumped. Recently however there has been increasing evidence that more precise and reproducible control of the mixing cycle can be obtained by using the energy input as the major dump criteria [58,59] and throughout this programme time of mixing has been used as the main criteria to dump the batch with energy input being compared as power consumption for each mix.

All the rubber mixes prepared in this investigation used a laboratory-size internal mixer (Farrel Bridge BR model of 1200 ml capacity); mixing of sulphur into the compound was always carried out on a two-roll rubber mill (450 mm x 225 mm and friction ratio 1.1:1), after the batch was dumped from the mixer.

Mixing conditions and mixing cycle are described as follows:

Mixing conditions:

Rotor speed	=	58 rpm
Ram pressure	=	2.5 kg/cm ²
Fill factor	=	0.8
Cooling water	=	ON

Mixing Cycle:

	<u>Time</u>	<u>Operation</u>
A.	0	NR (SMR 20) + SBR 1500, ram down (r.d)
B.	1'	Black + all ingredients (r.d)
C.		After one and a half minutes from the second addition the plasticiser is added
D.	4'30"	CBS + Santocure MOR (r.d)
E.	7	Clean (r.d)
F.	7'30"	Dump

Each batch was then completed by mixing in the sulphur on the two roll mill for two minutes. Finally each batch was refined for an extra one minute through a tight nip and then sheeted off at a thickness, normally approximately 3.0 mm, for subsequent tests. A short account of the testing procedures used is given in Appendix IV.

Curing characteristics of the NR/SBR compounds containing the plasticisers and processing aids of Table 2.1 are shown in the ODR curing curves of Figures 2.1-2.6. Each mineral oil and processing aid is

compared at different levels with the control mix in which there is no plasticiser. Generally these figures are in agreement with the results obtained by many workers where the increase in concentration of processing aid causes a decrease in the state of the cure. Although this decrease in the state of the cure is not large, it is significant with almost all the mineral oil plasticisers, whose performance is given in Figures 2.1-2.4, compared to the control mix in which there is no plasticiser. The reduction in the state of the cure in Figure 2.4 with Circosol 4240; naphthenic oil, is quite pronounced at the oil levels of 10 phr and 12.5 phr compared with the other mineral oils and processing aids.

The ODR cure characteristics, shown in Figure 2.6, of cationic surfactant SAPA 1/1, are very exceptional enabling it to be easily distinguished from all the other mineral oils and processing aids ODR curing curves. The SAPA 1/1 curves are characterised by their high state of cure and enhancement of cure rate. This result may be due to the presence of nitrogen groups that may allow SAPA 1/1 to act as a cure rate and a cure state promoter. Processing safety i.e. scorch time with all the SAPA 1/1 mixes is dramatically reduced; this is considered an undesirable effect with respect to processing.

The effect of increasing the level of individual mineral oils, processing aid and SAPA 1/1 compared with the control mix on; uncured properties, cure characteristics, and on physical properties, is shown in Table 2.3. This table shows that the physical properties and Mooney viscosity in each mix based on the respective mineral oils and processing aids and SAPA 1/1 decrease as the level of the additive increases. This result agrees with those of many other workers. However, the physical properties obtained from SAPA 1/1 containing rubber vulcanisates are significantly higher than those of all the mineral oils and processing aids used by between 5-20%. Tensile properties of SAPA 1/1 mix at 10 phr level are similar to those of the flow additives Struktol WB 212 and stearic acid. The physical properties, particularly the

modulus at the 2.5 phr SAPA 1/1 are higher than the modulus of the non-oil containing mix by about 50% in the case of 100% modulus and about 48% in the case of 300% modulus. These particular results make SAPA 1/1 perform as a unique plasticiser because usually the presence of a plasticiser, with the exception of polymeric plasticisers, reduces the physical properties of a rubber. Whilst the physical properties and curing characteristics of SAPA 1/1 mixes were better than the zero containing oil mix, mineral oils, combination of mineral oil and processing aid, and processing aids containing rubber vulcanisates, the Mooney viscosity of the SAPA 1/1 mixes were greater than all the other mixes. This unexpected result is confirmed later in Section 2.3.

FIGURE 2.1: EFFECT OF THE IRAQI AROMATIC OIL CONCENTRATION ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

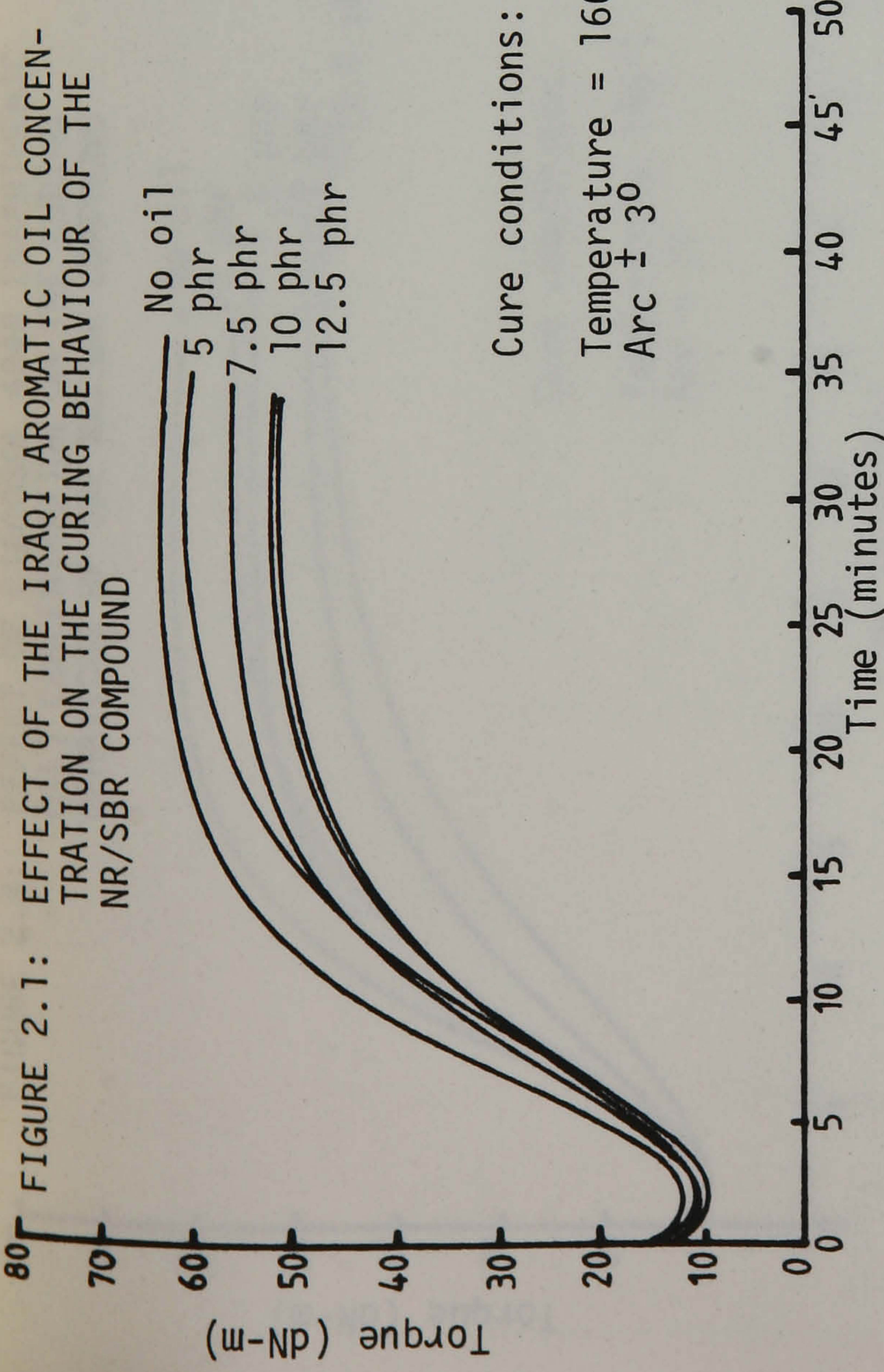


FIGURE 2.2: EFFECT OF THE DUTREX 729, AROMATIC OIL, CONCENTRATION ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

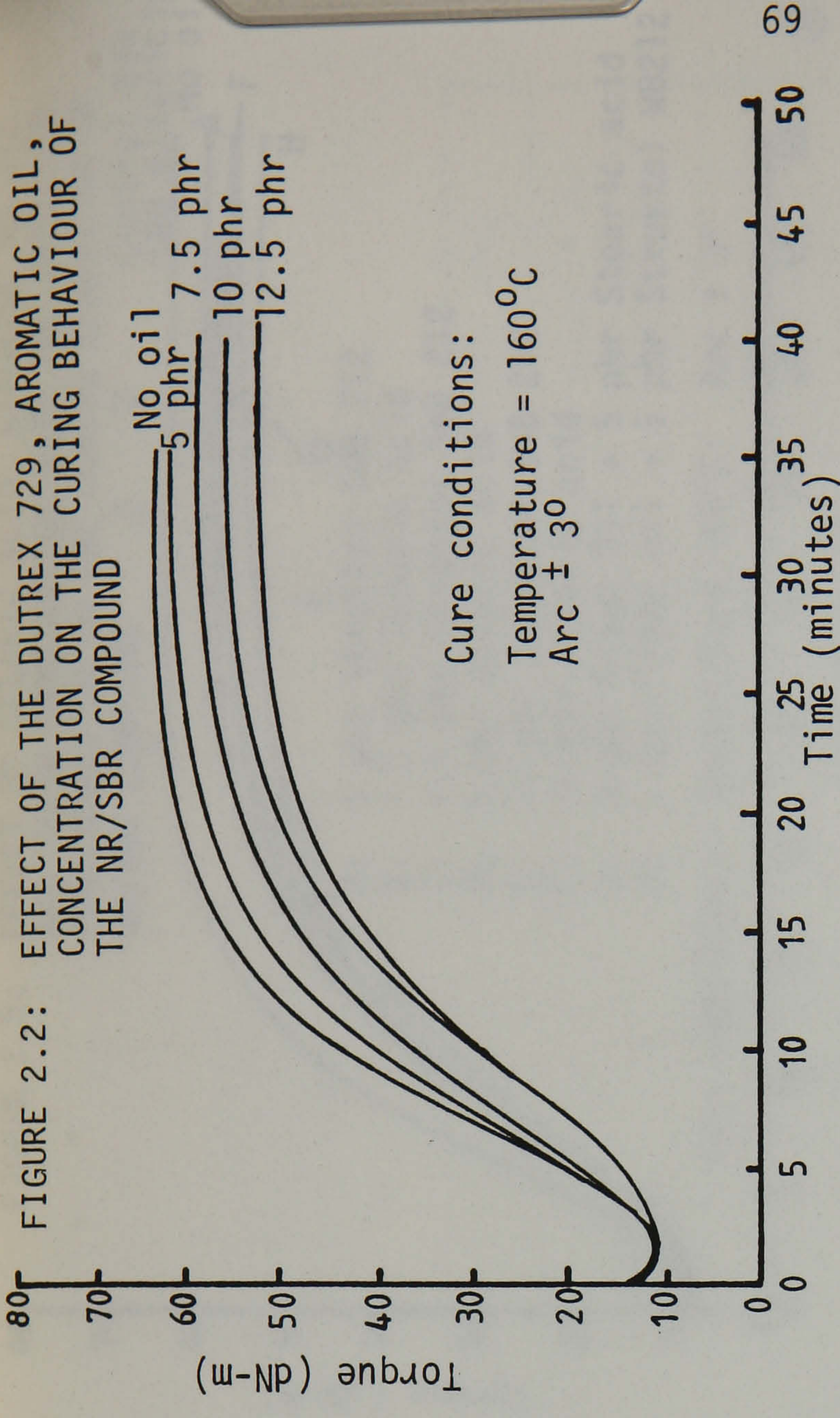


FIGURE 2.3: EFFECT OF SUNDEX 790, AROMATIC OIL, CONCENTRATION ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

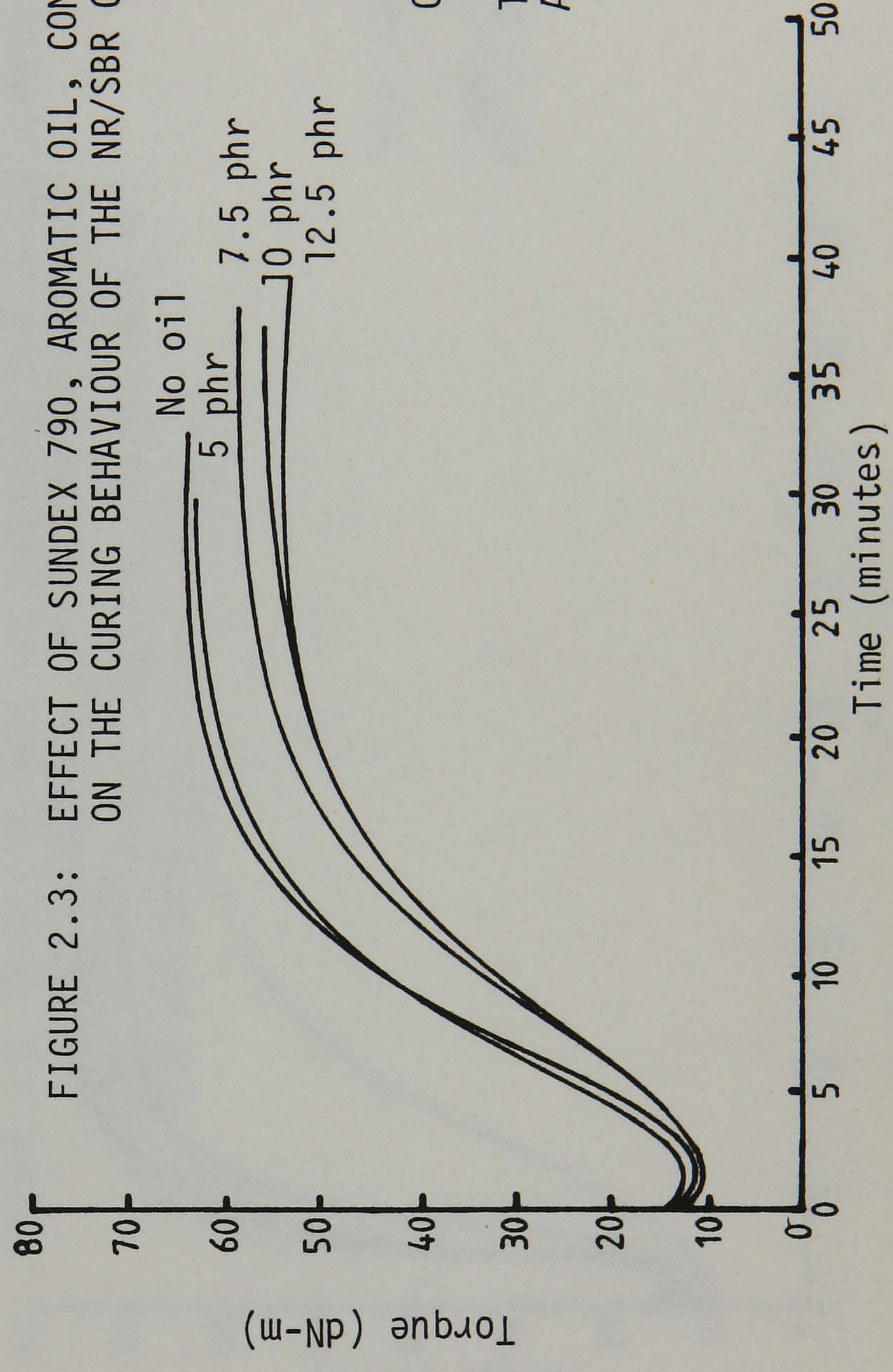


FIGURE 2.4: EFFECT OF CIRCOSOL 4240 (NAPHTHENIC OIL) CONCENTRATION ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

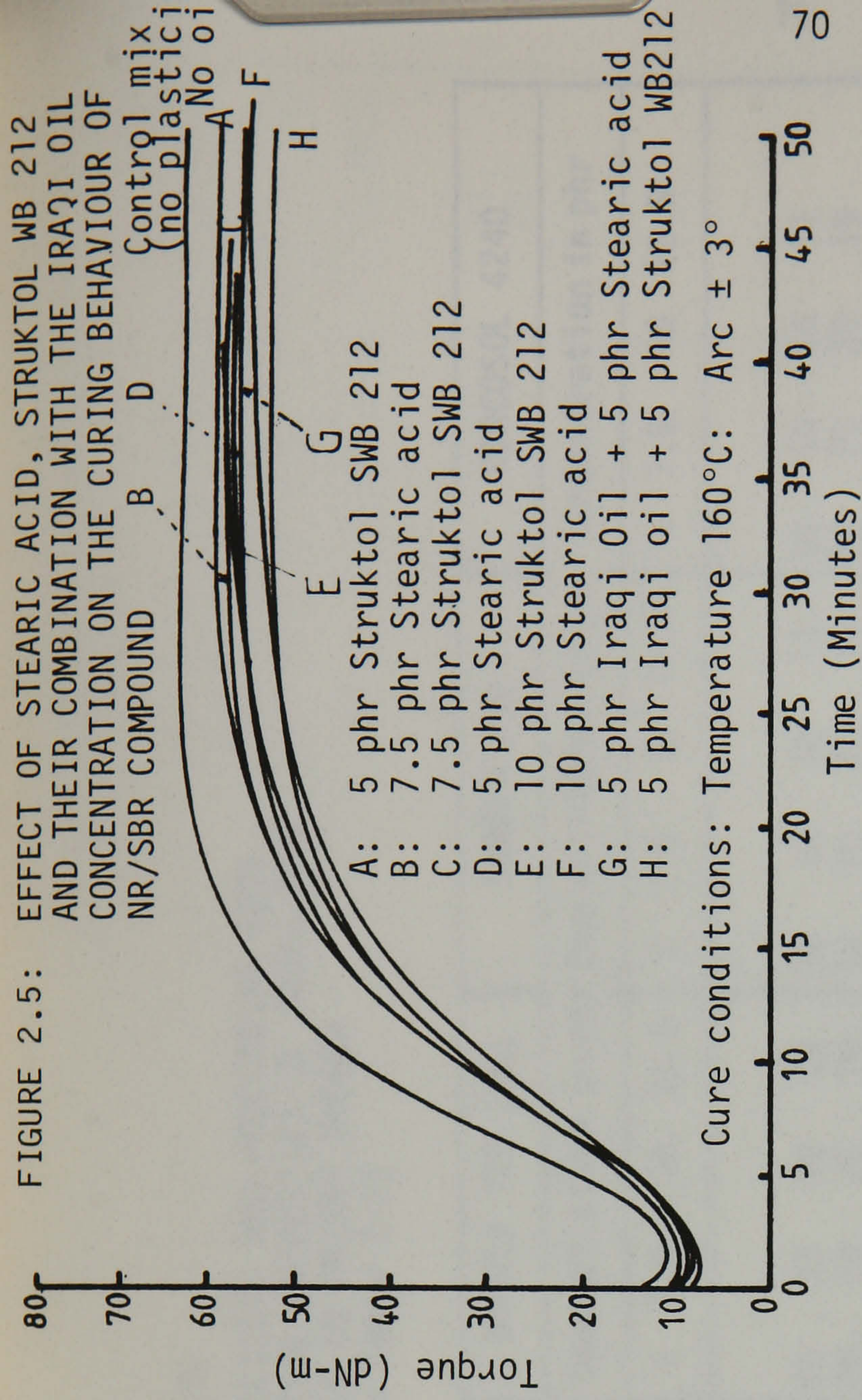
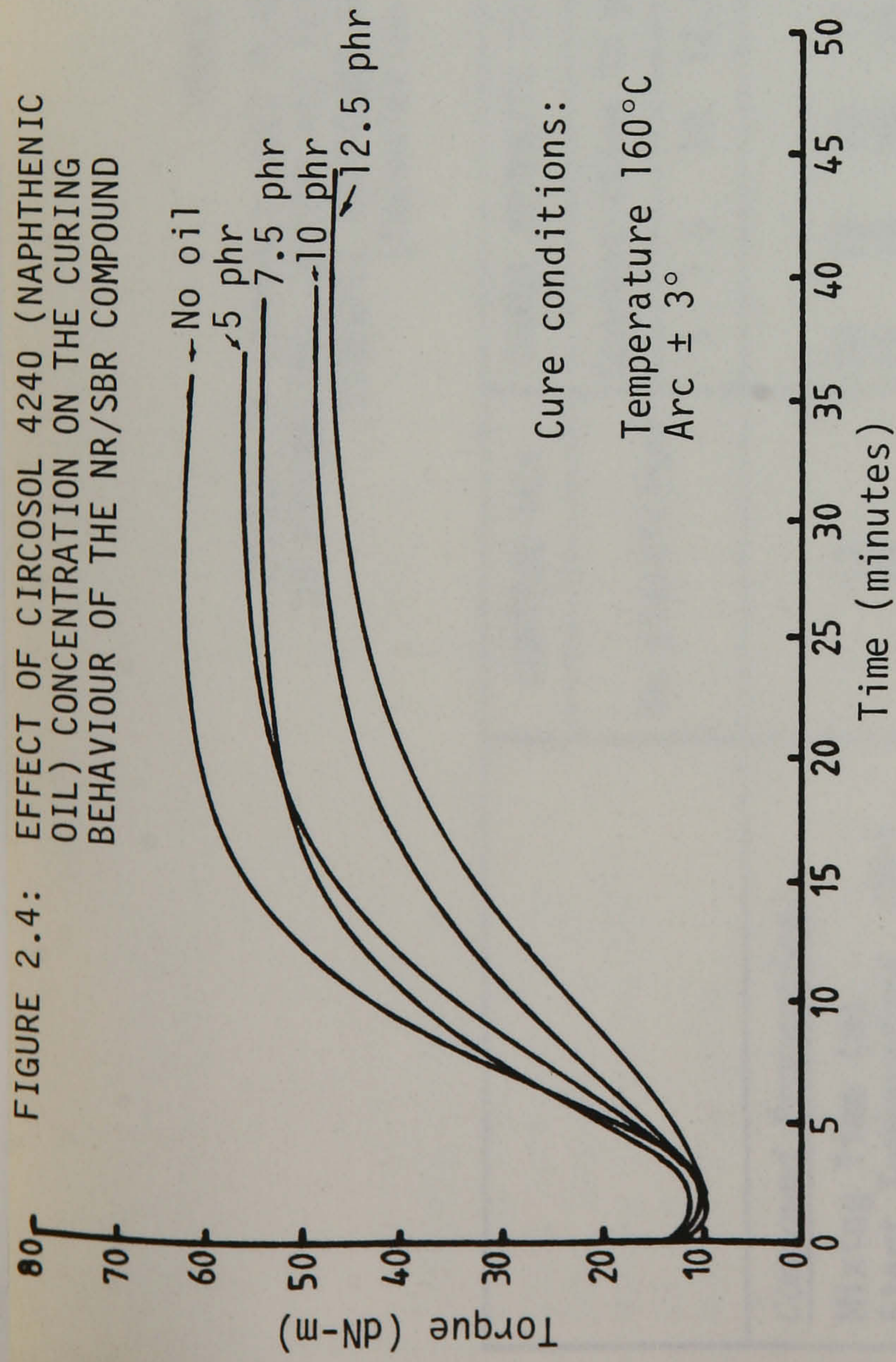


FIGURE 2.6: EFFECT OF SAPA 1/1 CONCENTRATION ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

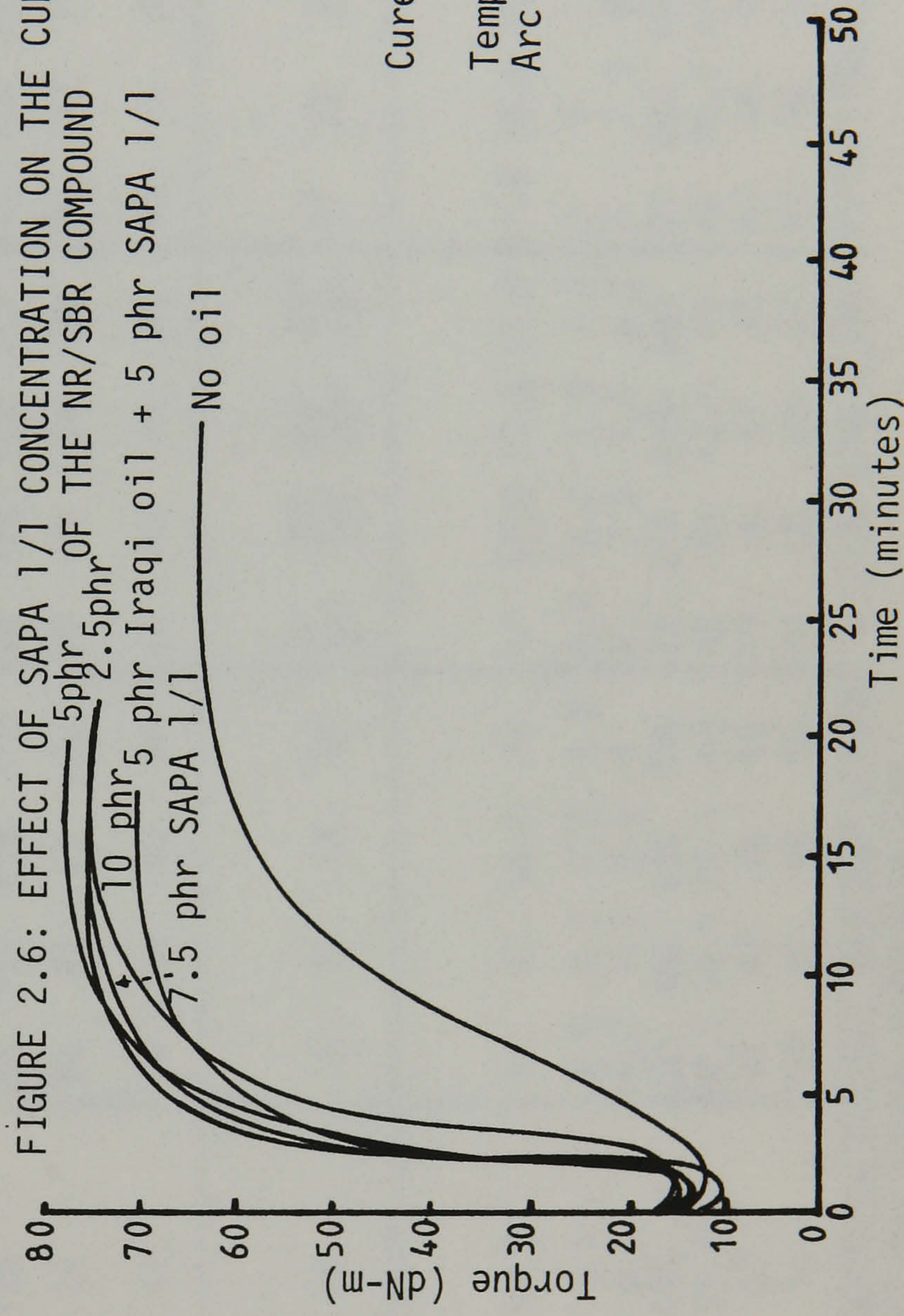


TABLE 2.3:

EFFECT OF COMMONLY USED PLASTICISERS AND PROCESSING AIDS
ON PROCESSING, CURING AND PHYSICAL PROPERTIES OF TRUCK TYRE
SIDEWALL COMPOUND BASED ON NR/SBR RUBBER
(Formulation on Table 2.2)

	CONTROL MIX	IRAQI AROMATIC OIL	DUTREX 729 (UK)			SUNDEX 790			CIRCOSOL 4240				
	No plasticiser	Concentration in phr			Concentration in phr			Concentration in phr					
		5	7.5	10	12.5	5	7.5	10	12.5	5	7.5	10	12.5
<u>Compound Properties:</u> Mixing Time (m) Start Temperature (°C) Dump Temperature (°C) Mooney Scorch at 1250C (m) Mooney Viscosity ML(1+4) 1000C	13	10	10	10	11	10	10	10	11	10	10	10	11
	20	18	18	20	20	20	20	20	18	20	21	20	19
	135	121	119	119	119	120	115	117	120	119	119	118	122
	19	20	21	22	22	19	21	24	24	20	22	24	21
	47	44	41	40	38	48	45	43	40	49	45	43	41
<u>Curing Properties:</u> Optimum Curing Time t ₉₀ at 1600C (m)	16	18	18	18	18	18'	20'	20'	20'	17	20	20	19
						18"	20"	20"	20"	18'	18'	30"	22
<u>Mechanical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa % Elongation at break Tear Strength kN m ⁻¹ Rebound Resilience % Hardness (IRHD)	19.3	18	17	16.5	16	17	17.6	17.9	17.8	17.5	18.8	18.4	17.7
	2.4	2.4	2.2	1.8	1.8	1.8	2.2	1.9	1.7	2	2	1.7	1.7
	8.4	8.2	7.4	5.5	5	6	7.4	6.5	6.2	7	7.3	5.8	6
	582	630	660	690	710	635	612	660	681	597	642	688	675
	45.5	52.5	50.5	47.5	43	48	44	42.5	50	49	49.5	50.5	45
	47	45	47	46	45	47	46	44	43	47	46	46	45
	61	58	57	56	54	54	55	53	53	57	55	52	51

* Other curing properties such as maximum torque, minimum torque, scorch time t₂ etc can be found directly from the ODR trace for each individual plasticiser at any given concentration

TABLE 2.3 continued

	SAPA 1/1				STRUKTOL WB212			STEARIC ACID			SAPA 1/1 + IRAQI OIL	STRUKTOL+ IRAQI OIL	STEARIC ACID + IRAQI OIL
	Conc. in phr				Conc. in phr			Conc. in phr			Conc.in phr	Conc.	Conc.in phr
	2.5	5	7.5	10	5	7.5	10	5	7.5	10	5 phr each	5 phr each	5 phr each
<u>Compound Properties:</u> Mixing time (min) Start Temperature °C Dump Temperature °C Mooney Scorch at 125°C in min Mooney Viscosity ML(1+4) 100°C	10	10	10	10	10	10	10	10	10	10	10	10	10
	18	21	20	20	20	19	20	20	21	18	19	21	18
	124	122	120	120	129	127	126	130	127	124	117	114	112
	9'30"	4'30"	3'45"	3	2 4	2 4	24'30"	22	22	22'30"	4'15"	19	18'30"
	55	53	50	50	46	44	42	48	44	40	40	48	44
<u>Curing Properties:</u> Optimum Curing Time t ₉₀ at 160°C in min	8	7	6'30"	5	19	19'30"	20	20	20	21'30"	7	20'30"	21'30"
<u>Mechanical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus, MPa 300% Modulus, MPa % Elongation at break Tear Strength kN m ⁻¹ Rebound Resilience % Hardness (IRHD)	21.4	20	20	19.5	20	19.7	19.5	20	20	19.5	17	18.7	18
	3.6	2.8	2.5	2.2	2.7	2.5	2.4	2.9	2.7	2.6	2.5	2.3	2
	12.4	10	8.7	8	8.8	8.8	8.3	9.0	8.6	8.6	7.7	8	7.4
	477	515	545	596	525	540	570	518	575	583	625	590	599
	46.5	54.8	59.5	64.5	46	47	47	53	56	57	67	55.5	54.5
	55	53	50	50	45	45	44	42	44	44	48	45	46
	62	61	59	57	65	65	62	67	65	65	50	58	46

2.2 Optimisation of Plasticiser Proportions for NR/SBR Compounds

A prime factor used to assess any particular plasticiser is its effect on the processability of the rubber compound. The basis used in this investigation for deciding on an optimum level, out of those shown in Table 2.1, for processability evaluation, is simply:

- a) each plasticiser should not have a dramatic effect on curing and physical properties
- b) the level selected should be economically acceptable over the total cost of the final products.

By inspection of the data in Table 2.3 and using the above basis a suitable level selected for further property examinations of each individual plasticiser, plasticiser plus processing aid, and SAPA 1/1 is shown in Table 2.4 below:

TABLE 2.4:

SHOWING THE LEVEL SELECTED FOR EACH PLASTICISER, PLASTICISER/PROCESSING AID COMBINATION, AND SAPA 1/1 FOR PROCESSABILITY TESTING

Plasticiser Type	Level Selected for Processability Evaluation
*1. Aromatic Oil (Iraqi)	7.5
*2. Aromatic Oil (Sundex 790)	7.5
*3. Aromatic Oil (Dutrex 729 UK)	7.5
*4. Naphthenic Oil (Circosol 4240)	7.5
*5. Aromatic Oil (Iraqi) + Stearic Acid	5 Parts + 5 Parts
*6. Aromatic Oil (Iraqi) + Water-in-fatty acid-emulsion (Struktol WB 212)	5 Parts + 5 Parts
**7. SAPA 1/1	3

* The base formulation used was that of Table 2.2

** The base formulation used was that of Table 2.2 with the activators and accelerators omitted (this will be discussed later in Chapter 4).

2.3 Effect of SAPA 1/1 and Various Plasticisers on the Processability of a Truck Tyre Sidewall Compound

It is first useful to try and identify the meaning of the term 'processability'; this term has been defined by many rubber processors including the ASTM Standards [60-62]. From these definitions the following definition is derived; processability is the ease with which a rubber compound can be processed throughout the production steps. It depends on the stage of the process. For instance in mixing, it means the way with which fillers and other compounding ingredients can be mixed and dispersed properly, while in extrusion it means the ease with which the compound can be extruded provided that good dimensional stability of the extrudate can be maintained.

2.3.1 Methods Used to Study Processability

One particular process cannot simulate the behaviour of a compound in other processes. For example, mixing cannot simulate extrusion. The methods used to study the effect of SAPA 1/1 and the other plasticisers on processability now discussed under the following three main headings:

I: Mixing:

The mixing process has been discussed satisfactorily in a number of papers [63-66]. However, the objective of the mixing process is mainly to obtain a material which is rheologically satisfactory with an acceptable degree of filler and other ingredient dispersion. Plasticisers and/or processing aids play important roles in the mixing process as explained earlier in Section 1.2. There are a number of methods which can be used to study the effect of any plasticiser on this stage. In this work the following methods were used:

- A: Power Consumption: This test could also represent the total work done by the mixer on the rubber compound. It is calculated as follows:

$$\text{Unit work mJ/m}^3 = \frac{\text{Total work (mJ)}}{\text{Mixer volume} \times \text{Fill factor}}$$

The total work is calculated as follows:

A counter is directly connected to a domestic meter which counts the number of revolutions made by the circular disc of the domestic meter. It was found that each 200 revolutions is equivalent to 1 kWh. Therefore total work = number of counts x 18000J.

- B: Dump Temperature: If time is selected to be the dump criteria for any batch then dump temperature could very well be used to give an indication of the efficiency of a plasticiser in the mixing process.
- C: Laboratory Viscosity Test: ASTM D1646-72: This method uses the Mooney shearing disc plastometer to measure the Mooney viscosity which is a measure of shearing torque averaged over a range of shearing rates. The Mooney viscometer does not adequately characterise the performance of a rubber compound at the high shear rates encountered in all the processing stages. It also makes no estimate of elastic properties. However, despite these limitations, it is still regarded, by the rubber industry, as a very useful processability tester.
- D: Milling Behaviour: The behaviour of any rubber compound, after shelf ageing, on a mill is a very important factor used to assess its processability.

II. Extrusion

Extrusion can be taken as fairly typical of the processing operations required subsequent to the original mixing stage. Evaluation of processability of rubber compounds at this stage takes into account important factors such as dimensional stability, pressure drop, rate of extrusion and surface roughness. These factors, particularly the dimensional stability, are very important parameters in many applications e.g. tyre components, inner tubes and unreinforced hoses. Therefore processability evaluation by extrusion is vital in this technology. In this work two techniques have been adopted for evaluation, these are as follows:

A: Extrusion Processability measured by Capillary Rheometer:

The capillary rheometer used in this investigation was the Davenport extrusion rheometer. Its basic working principle is shown in Figure 2.7 below:

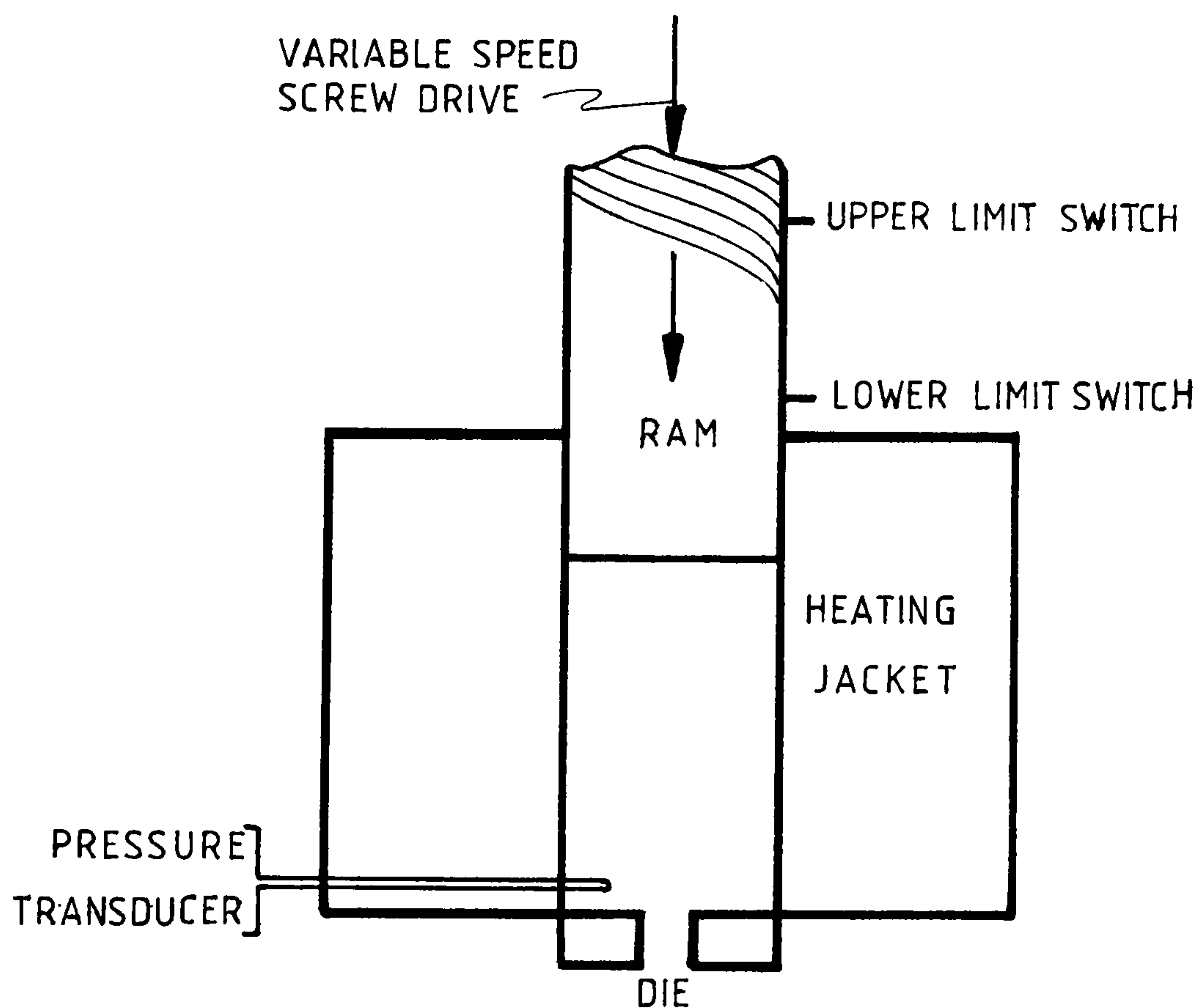


FIGURE 2.7: Shows the Basic Mode of the Davenport Extrusion Rheometer

This instrument was used to extrude a volume of material at fixed rates under controlled temperature conditions. Pressure developed throughout compound extrusion was measured at different rates and thus shear stresses (τ_w). Shear rate ($\dot{\gamma}$) and its corresponding shear stress were calculated as shown below:

$$\text{Shear rate } \dot{\gamma} \text{ (sec}^{-1}\text{)} = \frac{4Q}{\pi r^3}$$

where Q = output rate = $\pi R^2 V$

r = radius of die

R = radius of ram

V = velocity of ram

$$\text{Shear stress } \tau_w = \frac{\Delta P r}{2L} \text{ kN m}^{-2}$$

ΔP = pressure in the barrel

L = length of die

B: Extrusion Processability Measured by a Garvey-type Die:

Several types of dies have been used to assess extrusion processability [67-69]. The most generally accepted one is the Garvey type shown in Figure 2.8 overleaf. It has been designed to show typical faults that can occur in an extrudate having a five-sided cross section, with one thin edge, similar to the thin edge of an extruded tyre tread sidewall combination. This test has been recognised by the ASTM under the designation: D2230-73.

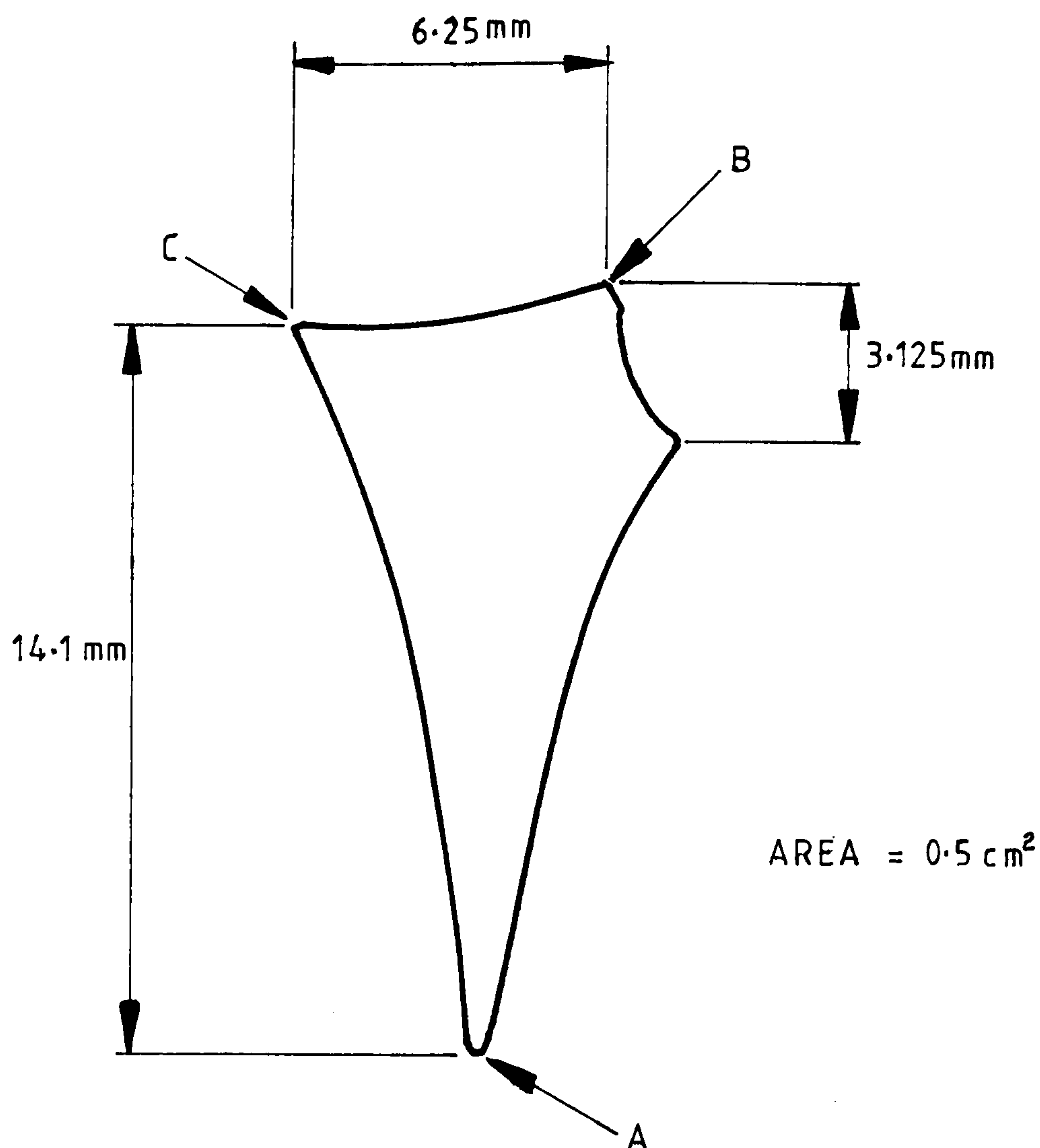


FIGURE 2.8: Cross-section of Garvey Die [13]
 A Sharpness of the edge
 B and C the two corners.
 ASTM D2230-73

III: Moulding

The most important compound properties relevant to the moulding stage are: scorch sensitivity, curing rate, mould flow and mould release. The first two properties are usually related to the curing system. However they could be very easily affected by certain additives such as plasticisers and/or processing aids. This subject has been discussed briefly in Chapter 1 (Section 1.2). Mould flow is considered a very important characteristic of a rubber compound. It has been found, in most of the rubber industries, that inclusion of mould flow additives to certain compounds is sometimes essential to reduce scrap levels. This is particularly true when the shape of

the final product is not uniform such as the shape of curing bladders for tyres. Most rubber compounds require the application of mould release agents to the curing moulds. This is mainly to prevent sticking of the final products to the curing moulds, also to minimise the pressure required to open curing moulds. Certain plasticisers and processing aids have the ability to sweat out during the vulcanisation process forming very thin films between the mould and the final product. In such cases the application of a mould release agent is not important.

2.3.2 Experimental

The plasticisers used in this investigation are those of Table 2.4 incorporated into the main formulation given before in Table 2.2 with a special mix used for the SAPA 1/1 (i.e. no activators and accelerators used). The formulation used with SAPA 1/1 is shown below in Table 2.5.

TABLE 2.5:

FORMULATION*USED TO ASSESS SAPA 1/1 AS A PLASTICISER IN NR/SBR COMPOUND

Material	phr
NR (SMR 20)	30
SBR 1500	70
Sulphur	2
Flectol-H	0.75
IPPD	2
Microcrystalline wax	3
SAPA 1/1	3
FEF Black	51

* The reason for using this formulation will be discussed in detail in Chapter 4.

Mixing cycle and conditions followed the same mixing conditions adopted earlier in Section 2.1.

To assess the processability of a mix's milling behaviour, the compound was returned to the mill, usually within 24 hours of removal of the compound when first mixed. On the first pass through the nip the compound crumbled but eventually it began to soften, cohere and finally band on the mill rolls. Milling was continued until the sample attained a good level of processability which was assessed as the total time taken, in minutes, to form a coherent smooth sheet of rubber with a rolling band at the nip. The test was carried out on a two-roll rubber mill (450 x 225 mm and friction ratio 1.1:1). Nip opening was kept constant at about 3 mm. Temperature at the two roll was kept constant at about 40°C by cold water cooling of the mill.

Extrusion utilised a Garvey die. The extruder used was a cold feed 37.5 mm (1½") extruder made by Farrel-Bridge Ltd which has a length to diameter ratio of 20:1.

The conditions used throughout the extrusion process were as follows:

1. The temperature of the two roll mill was kept constant at about 20°C. Mixing of the compounds was kept constant for a period of 4 minutes with constant cutting intervals of 30 seconds from each side.
2. Extruder conditions:
 - i) Temperature of the barrel = 70°C
 - ii) Temperature of the head = 110°C
 - iii) Temperature of the die = 110°C
 - iv) Screw speed = 20 rpm

3. Take off conveyor speed = 0.5 m/min. This is to prevent any stretching of the extrudate.

In the Davenport rheometer the barrel was set to a temperature of 100°C. The die used had a length of 15 mm and a diameter of 2 mm.

Mould flow was assessed visually. Mould release was evaluated by assessing the physical strength required to open the mould after curing.

2.3.3 Results and Discussion

Internal Mixing

Table 2.7 summarises the results of processing in the internal mixer. The table allows direct comparison of the effect of mineral oils, combination of mineral oil and processing aid, and SAPA 1/1 with a control mix where there is no plasticiser. The results prove that although the concentration of SAPA 1/1 is quite low, 3 phr, compared to 7.5 phr of mineral oil and 5 phr of each mineral oil and processing aid, SAPA 1/1 is a very efficient plasticiser when the total mixing energy, power consumption and dump temperature are considered. It is noticeable that the increase in Mooney viscosity of the SAPA 1/1 containing mix is once again (see Table 2.7) quite pronounced and higher by 7-14 points than the control mix, in which there is no plasticiser, and all the mineral oils, combination of mineral oil and processing aid, containing mixes. This is considered to indicate that as a result of the heat generated in the rubber by mixing, the SAPA 1/1 is undergoing or promoting a chemical reaction between itself and the rubber mix which results in an increase in Mooney viscosity. It is postulated that the SAPA 1/1 is, to some extent, functioning as a coupling agent between the filler and the rubber and, or, perhaps as a surfactant between the filler and the rubber. This effect is examined in Section 3.3.

Milling Behaviour

Table 2.8 shows the results of the milling behaviour performance of an NR/SBR compound mixed with various mineral oils, combination of mineral oil and processing aid, and SAPA 1/1. These mixes are compared with a mix without plasticiser. After internal mixing and resting for 24 hours in a refrigerator the mixes were milled and visually assessed for flow and mill banding behaviour. The superiority of SAPA 1/1 containing compound in comparison with all other mixes was very noticeable in that it formed a smooth band and rolling back on the mill within a 9 minute period whereas the non-plasticiser containing mix took 15 minutes, and those which contained mineral oils as plasticiser required 11 minutes (see Table 2.8). Throughout the milling process SAPA 1/1 containing compounds always showed excellent milling behaviour, i.e. there was no sagging, bagging or crumbling on passage through the nip; also extreme ease of release of the rubber from the mill was observed with SAPA 1/1 mix. The Iraqi oil and stearic acid containing mix showed bagging and sagging; this was thought to be due to the presence of a high level (7 phr) of stearic acid causing a severe reduction in its sticking tendency to the two rolls of the mill which gave rise to sagging and bagging.

Extrusion

Capillary rheometer: Table 2.8 and Figure 2.9 give the extrusion results. The increase in shear stress imparted by SAPA 1/1 containing mix is higher than that of the non-containing plasticiser mix. This behaviour emphasises once again the observation of high Mooney viscosity values of SAPA 1/1 containing compounds (see Table 2.3). The results apparently show that the use of a cationic surface active agent SAPA 1/1, as an alternative to mineral oils for processing purposes, gives an unvulcanised NR/SBR compound with a high capillary extrusion shear stress of 351 kN m^{-2} . This is to be compared with the range of $243\text{--}278 \text{ kN m}^{-2}$ for equivalent mixes containing conventional plasticisers and processing aids. Die swell is reduced and

flow rate is enhanced in the SAPA 1/1 containing mixes. Although the improvement in the flow rate and die swell is not very great, the observation established that SAPA 1/1 is an efficient plasticiser at the relatively low levels used compared to the other plasticisers and processing aids which were incorporated in much greater proportions.

Extrusion:

Garvey Die: The ASTM standard, Designation D2230-73, test results for the extrudability of NR/SBR compound mixed with mineral oils, mineral oils plus processing aids, SAPA 1/1 and a control mix with no plasticiser are shown in Table 2.10. The results of this table, particularly the flow rate, die swell, and the temperature of the SAPA 1/1 containing extrudate, are comparable to the results of the conventional mineral oils, combination of mineral oils and processing additives containing extrudates. Head pressure of the SAPA 1/1 containing extrudate is considerably higher than that of all other plasticiser containing mixes by as much as 1869 kN m^{-2} . It compares with the value of 621 kN m^{-2} obtained for the zero plasticiser mix. Figure 2.10 shows the Garvey die extrudates for three selected mixes. The results shown in this figure indicate that the SAPA 1/1 containing mix has an excellent profile i.e. its surface roughness is low; thin edge, corners, and swelling are superior to all other mixes. For example, the mineral oil containing mix has a good surface, good corners, and low die swell, but only an intermediate quality thin edge finish (see part X in Figure 2.10). It therefore lies between the good overall surface of the SAPA 1/1 containing mix and the poor thin edges quality (see Y in Figure 2.10) of the zero plasticiser containing mix. Extrudates combining mineral oil and processing aid have an excellent profile and are similar to that of the SAPA 1/1 mix shown in Figure 2.10.

Table 2.11 gives moulding properties. The results show the pronounced release and flow properties of SAPA 1/1 containing mix compared to all other mixes.

All this data confirms the observed excellent processability of SAPA 1/1 mixes compared with conventional rubber formulations demonstrating that no abnormal or adverse processing phenomena result from the use of the cationic surface active agent SAPA 1/1.

Curing and physical properties for these mixes are given and discussed in Chapter 4.

TABLE 2.6

INTERNAL MIXING STUDIES OF SAPA 1/1 COMPARED WITH HYDROCARBON MINERAL OILS, PROCESSING AIDS
AND A CONTROL MIX WHERE THERE IS NO PLASTICISER

Mix No.	Formulation	Starting Temperature °C	Dump Temperature °C	Mooney Viscosity	Power Consumption kWh	Unit Work mJ.m ⁻³	Mixing Cycle mins.
1(A)	Control. No plasticiser	20	135	47	0.535	1533	13 First stage only
2(A)	7.5 phr Iraqi oil (Aromatic oil)	18	119	41	0.38	1089.2	10
3(A)	7.5 phr Naphthenic oil Circosol 4240	21	117	42	0.3625	1039	10
4(A)	7.5 phr Dutrex 729 Aromatic oil	19	115	45	0.3875	1110	10
5(A)	7.5 phr Sun oil Sundex 790 Aromatic oil	20	119	45	0.39	1117	10
6(A)	5 phr Iraqi oil + 5 phr Stearic acid	18	112	44	0.3575	1024	10
7(A)	5 phr Iraqi oil + 5 phr Struktol WB 212	21	114	48	0.3675	1053	10
8(B)	SAP 3 phr (+ 0.5 phr ZnO)	20	112	55	0.385	1103	10

Note: A indicates the use of the formulation in Table 2.5
B indicates the use of the formulation in Table 2.6

Unit work = total mixing energy mJ/m³

TABLE 2.7:

MILLING BEHAVIOUR OF SAPA 1/1 COMPARED WITH MINERAL OILS, PROCESSING AIDS AND A CONTROL MIX (WITHOUT PLASTICISER)

Mix No.	Plasticiser	Level in phr	Process-ability Time	Remarks
1(A)	None	-	15	The compound remains dry, difficult to cut into uniform strips
2(A)	Iraqi	7.5	11	Good behaviour throughout the milling process
3(A)	Circosol 4240	7.5	11	Good
4(A)	Dutrex 729	7.5	11	Good
5(A)	Sundex 790	7.5	11	Good
6(A)	Iraqi + Stearic acid	5 each	12	Bagging was observed. Sweat out of plasticiser was felt
7(A)	Iraqi + Struktol	5 each	10	Very good behaviour throughout the milling process
8(B)	SAPA 1/1	3	9	Excellent process-ability

Note: A indicates the use of the formulation mentioned in Table 2.5
 B indicates the use of the formulation mentioned in Table 2.6

TABLE 2.8:

EXTRUSION CHARACTERISTICS MEASURED BY DAVENPORT CAPILLARY RHEOMETER FOR SAPA 1/1 CONTAINING MIXES, MINERAL OIL CONTAINING MIXES, COMBINATION OF MINERAL OIL AND PROCESSING ADDITIVE CONTAINING MIXES, AND A CONTROL MIX WITHOUT PLASTICISER

Mix No.	Formulation	Flow Rate* g/min	Die Swell* Ratio	Shear Stress τ_w kNm ⁻²
1(A)	No plasticiser	3.99	1.15	277
2(A)	7.5 phr Iraqi oil (Aromatic oil)	3.99	1.20	243
3(A)	7.5 phr Naphthenic oil Circosol 4240	3.99	1.20	253
4(A)	7.5 phr Dutrex oil 729 Aromatic	3.99	1.17	260
5(A)	7.5 phr Sun oil Sundex 790 Aromatic oil	3.99	1.17	260
6(A)	6 phr Iraqi oil + 5 phr Stearic acid	4	1.20	243
7(A)	5 phr Iraqi oil + 5 phr Struktol SWB 212	4	1.15	278
8(B)	3 phr SAP + 0.5 phr ZnO	4.11	1.15	351

* Flow rate and die swell was calculated at a shear rate of 58.3 sec⁻¹

Note: A indicates the use of the formulation in Table 2.5

B indicates the use of the formulation in Table 2.6

TABLE 2.9

EXTRUSION-PROCESSABILITY EVALUATION BY THE USE OF GARVEY TYPE DIE OF SAPA 1/1, MINERAL OIL,
MINERAL OIL/PROCESSING AID AND A CONTROL MIX WITHOUT PLASTICISER

Mix No	Formulation	Flow Rate m/min	Die Swell Index g/cm	Die Swell Ratio	Head Pressure kN/m ²	Temp.of Extrudate	Grading*			
							Swelling and Porosity	Edge	Surface	Corners
1(A)	No plasticiser	4.22	0.833	1.463	4343	98	4	2	4	4
2(A)	7.5 phr Iraqi oil (Aromatic oil)	4.24	0.842	1.486	3723	95	4	3	4	4
3(A)	7.5 phr Naphthenic oil. Circosol 4240	4.25	0.838	1.484	4033	95	4	3	4	4
4(A)	7.5 phr Dutrex 729 Aromatic oil	4.30	0.842	1.486	3095	95	4	3	4	4
5(A)	7.5 phr Sundex 790 Aromatic oil	4.24	0.842	1.484	3909	94	4	3	4	4
6(A)	5 phr Iraqi oil + 5 phr Stearic acid	4.24	0.84	1.489	3971	94	4	4	4	4
7(A)	5 phr Iraqi oil + 5 phr Struktol SWB212	4.26	0.84	1.479	4288	94	4	4	4	4
8(B)	3 phr SAPA + 0.5 phr ZnO	4.31	0.835	1.476	4964	95	4	4	4	4

Note: A indicates the use of the formulation in Table 2.5

B indicates the use of the formulation in Table 2.6

* Grading followed is that of the ASTM D2230-73

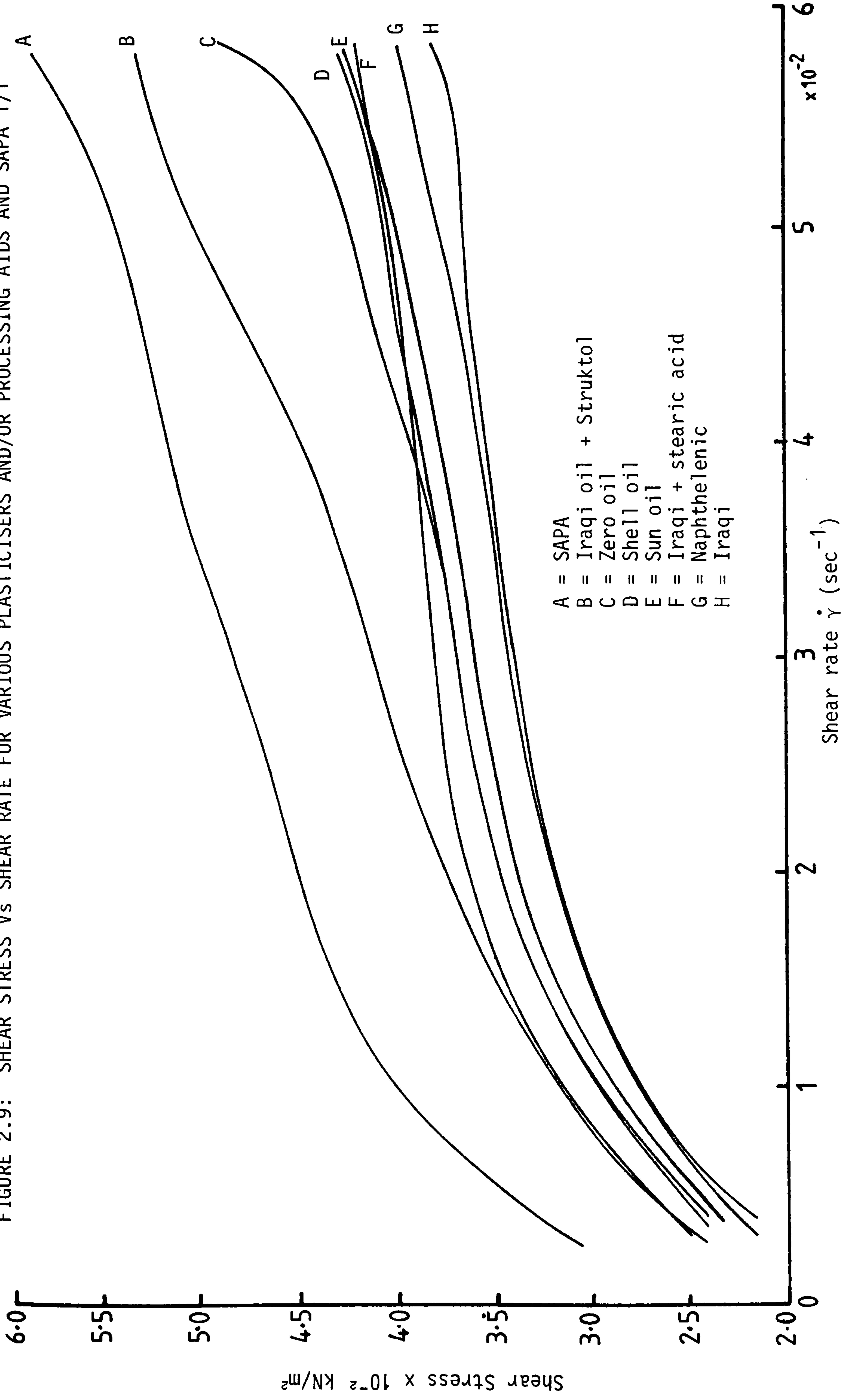
TABLE 2.10

PROCESSING PROPERTIES AT THE MOULDING STAGE OF MINERAL OILS, COMBINATION OF MINERAL OIL AND PROCESSING AID,
SAPA 1/1, AND A CONTROL MIX WITH NO PLASTICISER

Note: A indicates the use of the formulation in Table 2.5
B indicates the use of the formulation in Table 2.6

Mix No.	Formulation	Mould Flow	Mould Release
1(A)	Control. No plasticiser	Poor surface finish on compression moulded sheet; stress lines and small depressions present	Release is a major problem. High force was required to open the mould
2(A)	7.5 phr Iraqi oil (Aromatic Oil)	Intermediate dull finish flow lines visible	Release is essential. Mould needed quite high force to open
3(A)	7.5 phr Circosol 4240 (Naphthenic oil)	Dull finish. Stress lines are visible	Release is essential. Force needed quite high.
4(A)	7.5 phr Dutrex 729 (Aromatic Oil)	Intermediate dull finish. Flow lines visible	Release is essential. Force needed was quite high to open the mould
5(A)	7.5 phr Sundex 790 (Aromatic Oil)	Intermediate dull finish. Flow lines visible.	Release is desirable. Force is almost the same as required for the other aromatic oil
6(A)	5 phr Iraqi oil + 5 phr Stearic acid	Stress lines are visible. Good finish	Release is acceptable. Low force was required to open the mould
7(A)	5 phr Iraqi oil + 5 phr Struktol SWB 212	Good finish. Some flow lines visible	Release is good. Relatively low force was required to open the mould
8(B)	SAPA 1/1 3 phr	Glossy finish with no faults present. Stress free moulding.	Release excellent. Mould fell open

FIGURE 2.9: SHEAR STRESS VS SHEAR RATE FOR VARIOUS PLASTICISERS AND/OR PROCESSING AIDS AND SAPA 1/1



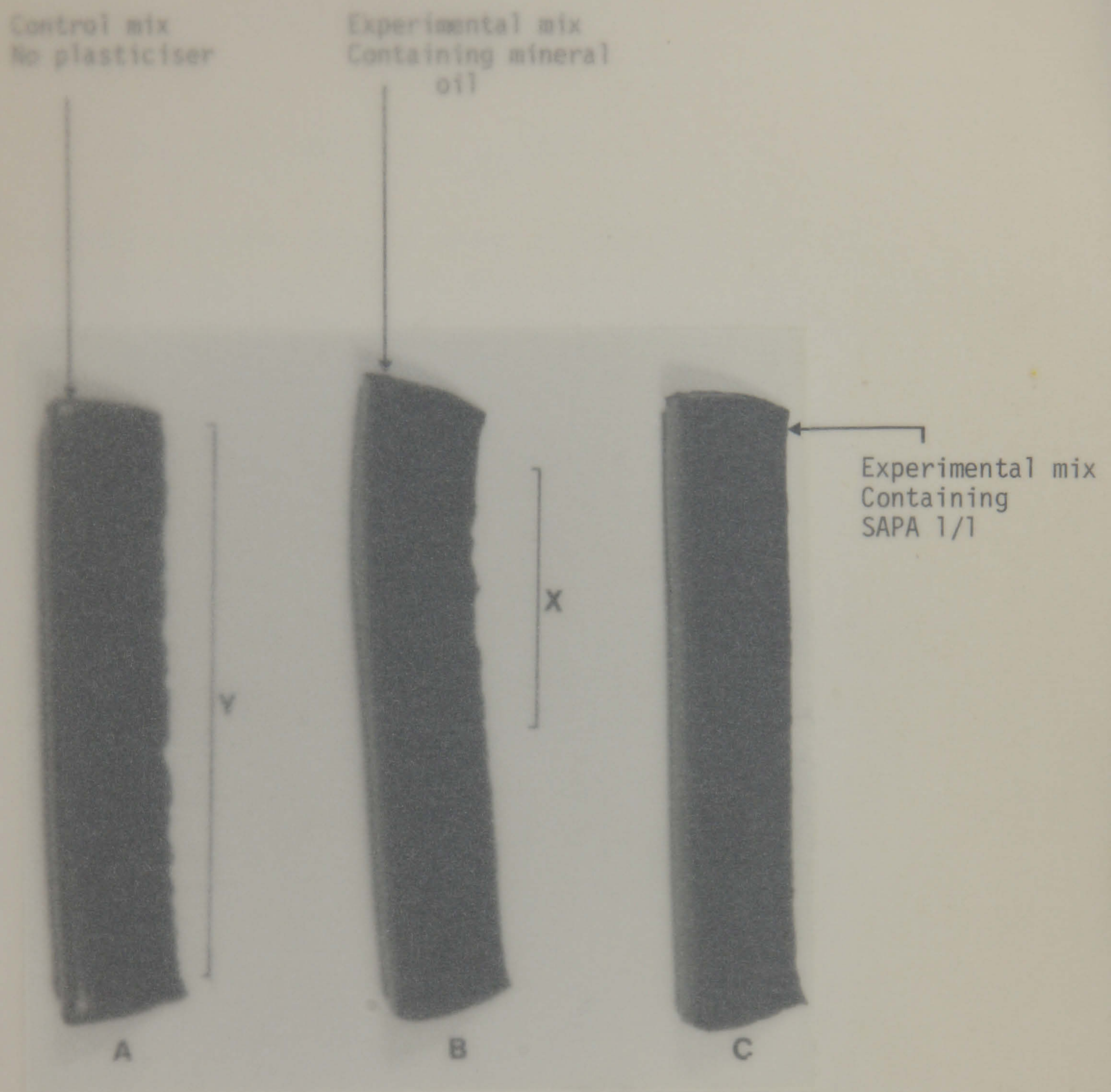


FIGURE 2.10: EXTRUDATES PRODUCED THROUGH GARVEY DIE
A: ZERO PLASTICISER CONTAINING EXTRUDATE
B: MINERAL OIL CONTAINING EXTRUDATE
C: SAPA 1/1 CONTAINING EXTRUDATE

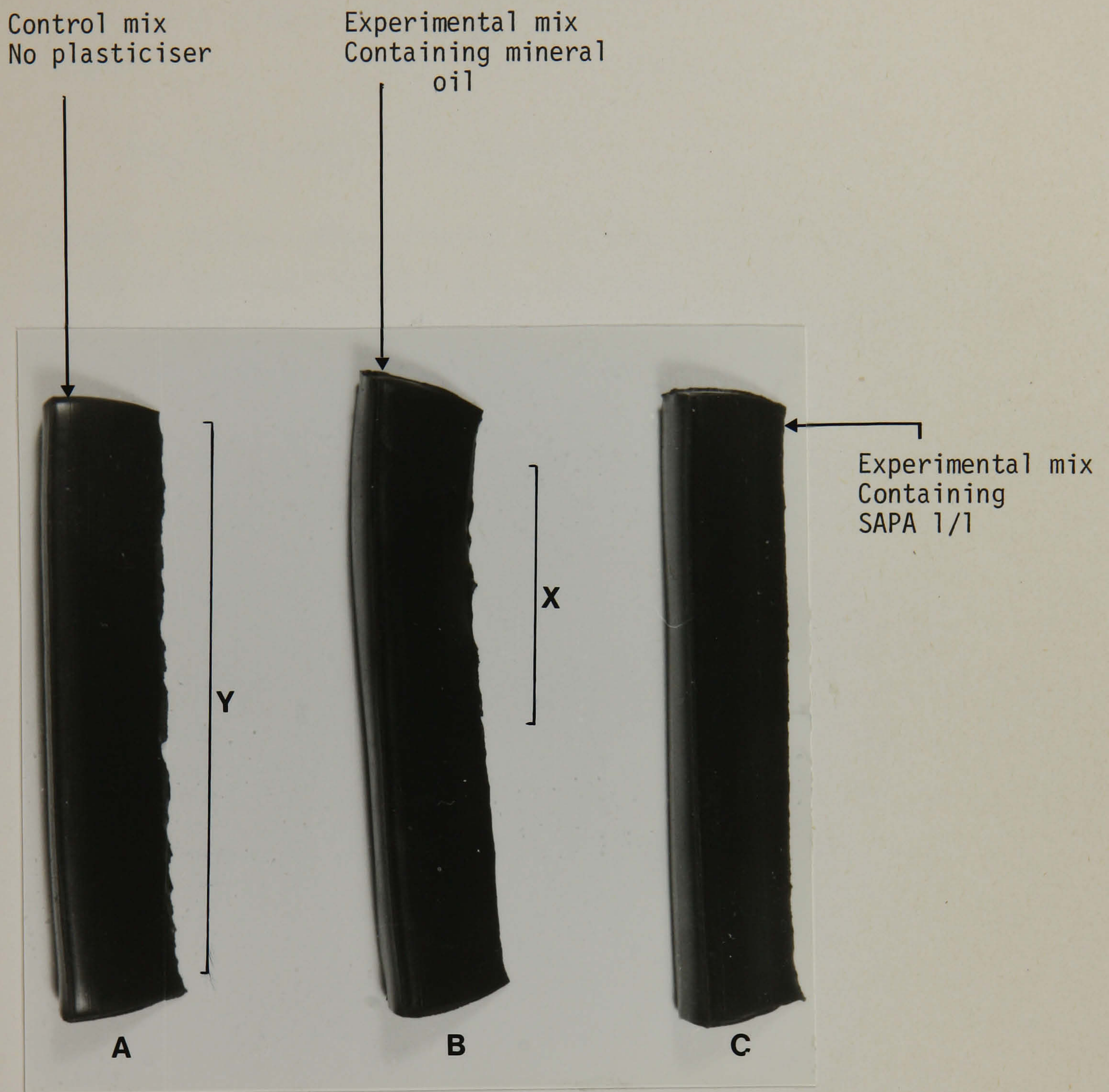
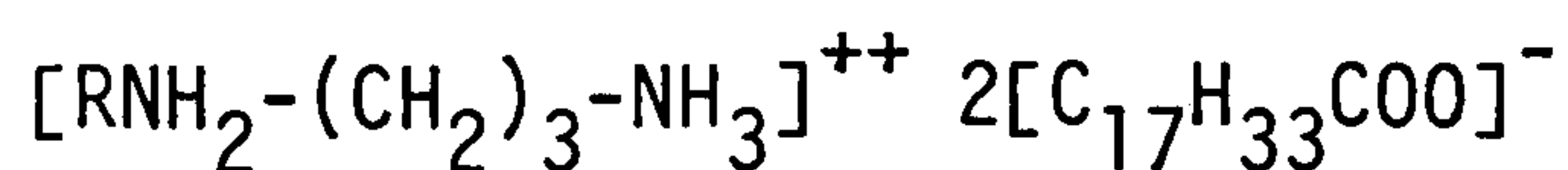


FIGURE 2.10: EXTRUDATES PRODUCED THROUGH GARVEY DIE
A: ZERO PLASTICISER CONTAINING EXTRUDATE
B: MINERAL OIL CONTAINING EXTRUDATE
C: SAPA 1/1 CONTAINING EXTRUDATE

2.4 Conclusion

1. The cationic surface active agent, SAPA 1/1, of the general formula



where R = tallow, offers promise as a replacement for part or all of the usual aromatic oils, napthenic oils, and conventional processing aids such as stearic acid, and Struktol WB 212, in NR/SBR vulcanisates.

2. The SAPA 1/1 imparts increased modulus and other physical properties (see Table 2.3).
3. These surfactants enhanced the curing rate and the curing state of NR/SBR compound to a considerable degree compared to conventional plasticisers and processing aids. However, scorch time has been reduced dramatically. Therefore it is not advisable to use this surfactant as a plasticiser at high concentration.
4. There is a noticeable increase in the Mooney viscosity of the NR/SBR mix which has been confirmed by many techniques such as the capillary rheometer and the Garvey die extrusion process.
5. Processability of SAPA 1/1 containing mixes at all the three basic processing stages: mixing, extrusion, and moulding, has been confirmed to be superior to all mineral oils, combination of mineral oils and processing additives containing mixes.

CHAPTER 3

CATIONIC SURFACTANTS AS PROCESSING AIDS FOR RUBBER COMPOUNDS

Introduction

Many terms have been used in the rubber industry to describe the liquids and low melting solids which are used to improve compound processability. Among these terms the following are the most commonly used: (a) Processing aids, (b) Plasticisers, and (c) Extenders. The distinction between these various terms is not a sharp one [71]. However, as a generalisation, the use of a small amount of one of these materials may be referred to as a processing aid, and the usage of larger amounts as extenders or plasticisers. In this chapter the term processing aid will be used to cover the range of materials used up to 5 phr.

The effect of the SAPA 1/1 surfactant on the processability and the mechanical properties of one particular NR/SBR compound has been studied in Chapter 2. The result proved that this type of surfactant is superior in its overall effect to some very well known plasticisers and processing aids. In this chapter an attempt is made, in the first place, to describe the performance of other SAPA 1 types, specially prepared research diamine salts and also to the use of a wider series of commercially available hydrophobic, fatty diamide materials, which are shown in Table 3.1, as processing aids in NR/SBR, NR, CR, NBR, SBR and BR type compounds.

3.1 Synthesis of Diamine Salts

Many complex mixtures of fatty diamine and ammonium salts are available as commercial surfactants (Section 1.1). However, these materials are

TABLE 3.1

GENERAL FORMULA AND THE STRUCTURE OF THE SURFACTANTS, DIAMIDE MATERIALS AND THE PREPARED SALTS
STUDIED THROUGHOUT THE RESEARCH

Class No.			Surfactants Used in the Research	Abbreviation	Trade Name and Physical Form	Melting Point
1	RNH(CH ₂) ₃ NH ₂ Alkyl Propylene Diamines (SAPA2-series)	I	CH ₃ (CH ₂) ₁₆ CH ₂ NH(CH ₂) ₃ NH ₂ N-stearyl-1,3-propane diamine	SAPA 2/A	Dicrodamine 1.18 ^(a) Waxy solid, acceptable odour	70-74°C
		II	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₈ NH(CH ₂) ₃ NH ₂ N-oley1-1,3-propane diamine	SAPA 2/B	Dicrodamine 1.0 Amber liquid, acceptable odour	-
		III	RNH(CH ₂) ₃ NH ₂ N-tallow-1,3-propane diamine	SAPA 2/C	Dicrodamine 1-T Waxy solid, acceptable odour	46-50°C
		IV	CH ₃ (CH ₂) ₁₄ CH ₂ NH(CH ₂) ₃ NH ₂ N-palmityl-1,3-propane diamine	SAPA 2/D	Dicrodamine 1.16 Soft waxy solids, acceptable odour	46-50°C
		V	CH ₃ (CH ₂) ₁₀ CH ₂ NH(CH ₂) ₃ NH ₂ N-lauryl-1,3-propane diamine	SAPA 2/E	Dicrodamine 1.12 Pale yellow liquid, sharp ammonia odour	-
2	RCONH(CH ₂) ₂ NHCOR Ethylene bis fatty amides (EBF-series)	I	CH ₃ (CH ₂) ₁₆ CONH(CH ₂) ₂ NHCO(CH ₂) ₁₆ CH ₃ N,N'-ethylene-bis-stearamide	EBF-S	Crodamide EBS ^(a) Creamy solid, no odour	140-145°C
		II	C ₈ H ₁₇ CH=CH(CH ₂) ₇ CONH(CH ₂) ₂ NHCO(CH ₂) ₇ CH=CHC ₈ H ₁₇ N,N'-ethylene-bis-oleamide	EBF-O	"	107-110°C
		III	C ₈ H ₁₇ -CH=CH(CH ₂) ₁₁ CONH-(CH ₂) ₂ NHCO (CH ₂) ₁₁ CH=CH-C ₈ H ₁₇ N,N'-ethylene-bis-erucamide	EBF-E	Crodamide EBS Creamy solid, no odour	110-113°C
		IV	CH ₃ (CH ₂) ₂₀ CONH-(CH ₂) ₂ NHCO(CH ₂) ₂₀ CH ₃ N,N'-ethylene-bis-behenamide	EBF-B	"	138-140°C
		V	CH ₃ (CH ₂) ₁₂ CONH(CH ₂) ₂ NHCO(CH ₂) ₁₂ CH ₃ N,N'-ethylene-bis-myristamide	EBF-M	"	140-144°C
		VI	CH ₃ (CH ₂) ₁₀ CONH(CH ₂) ₂ NHCO(CH ₂) ₁₀ CH ₃ N,N'-ethylene-bis-lauramide	EBF-L	"	146-150°C
3	[RNH ₂ (CH ₂) ₃ NH ₃] ⁺² 2[RCCO] ⁻ Fatty diamine Salt (SAPA 1 series)	I	[R ^b NH ₂ (CH ₂) ₃ NH ₃] ⁺² 2(C ₁₇ H ₃₃ COO) ⁻ N-tallow-1,3-propane diamine dioleate	SAPA 1/1	Duomeen TDO Paste and Cenfort RPO1	30- 40°C
		II	[R ^b NH ₂ (CH ₂) ₃ NH] ⁺² 2(C ₁₇ H ₃₅ COO) ⁻ N-tallow-1,3-propane diamine di-stearate	SAPA 1/2	Solid Acceptable odour	60°C
4	Specially prepared salts as research intermediates	I	CH ₃ -CH(N ⁺ H ₃)-CH ₂ -N ⁺ H ₃ 2[C ₁₇ H ₃₃ COO] ⁻ 1,2-propane diamine di-oleate	NS1	Soft paste Acceptable odour	35-40°C
		II	CH ₃ -CH(NH ₂)-CH ₂ N ⁺ H ₃ [C ₁₇ H ₃₃ COO] ⁻ 1,3-propane diamine oleate	NS2	"	35-40°C
		III	N ⁺ H ₃ -(CH ₂) ₃ -N ⁺ H ₃ 2[C ₁₇ H ₃₃ COO] ⁻ 1,3-propane diamine di-oleate	NSC/1	Stiff amber paste Acceptable odour	40-45°C
		IV	NH ₂ -(CH ₂) ₃ -N ⁺ H ₃ C ₁₇ H ₃₃ COO ⁻ 1,3-propane diamine oleate	NSC/2	"	40-45°C
		V	CH ₃ -CH(N ⁺ H ₃)-CH ₂ -N ⁺ H ₃ 2C ₁₇ H ₃₅ COO ⁻ 1,2-propane diamine di-stearate	NSA/1	Creamy solid (waxy) Acceptable odour	85°C
		VI	N ⁺ H ₃ -(CH ₂) ₃ -N ⁺ H ₃ 2[C ₁₇ H ₃₅ COO] ⁻ 1,3-propane diamine di-stearate	NSA/2	"	88°C
		VII	NH ₂ -(CH ₂) ₃ -N ⁺ H ₃ C ₁₇ H ₃₅ COO ⁻ 1,3-propane diamine stearate	NSA/3	"	72°C

a) Trade Name of Croda Chemicals Ltd;

b) R is tallow which consists exclusively of the glycerides (C₃H₅ O.R O.R') of R Palmitic, R' stearic and R" oleic acids O.R"

c) Trade name of Akzo Chemie Chemicals Ltd.

d) Trade name of Central Chemicals Co. Ltd.

e) NS - an abbreviation for 'New Salts'

NS1: is the reaction product of 2 moles of the oleic acid with one mole of the 1,2 diamino propane

NS2: is the reaction product of 1 mole of the oleic acid with one mole of the 1,2 diamino propane

NSC/1: is the reaction product of 2 moles of the oleic acid with one mole of 1,3 diamino propane

NSC/2: is the reaction product of 1 mole of the oleic acid with one mole of 1,3 diamino propane

NSA/1: is the reaction product of 2 moles of stearic acid with one mole of 1,2 diamino propane

NSA/2: is the reaction product of 2 moles of stearic acid with one mole of 1,3 diamino propane

NSA/3: is the reaction product of 1 mole of stearic acid with one mole of 1,3 diamino propane

difficult to synthesise as their preparations involve more than one stage and require specific reaction conditions. For these reasons it was decided to synthesise simple diamine salts which have similar structure to SAPA 1/1 and then compare their behaviour with SAPA 1/1 in rubber compounds.

3.1.1 Materials

Stearic acid

Two grades were used (a) pure stearic acid. This acid had the following properties:

Minimum stearic acid content by assay	99%
Melting point range	68-71°C
Sulphated ash - not more than	0.05%

It was obtained from BDH Chemicals Ltd.

(b) Commercially available stearic acid: This is the type usually used in the rubber industry as an accelerator activator and as a processing aid. Although commonly called stearic acid, it is usually a mixture of myristic acid, palmitic acid, stearic acid and oleic acids. It has a melting point range of 52-58°C. The material used was obtained from Anchor Chemicals Ltd.

Oleic acid

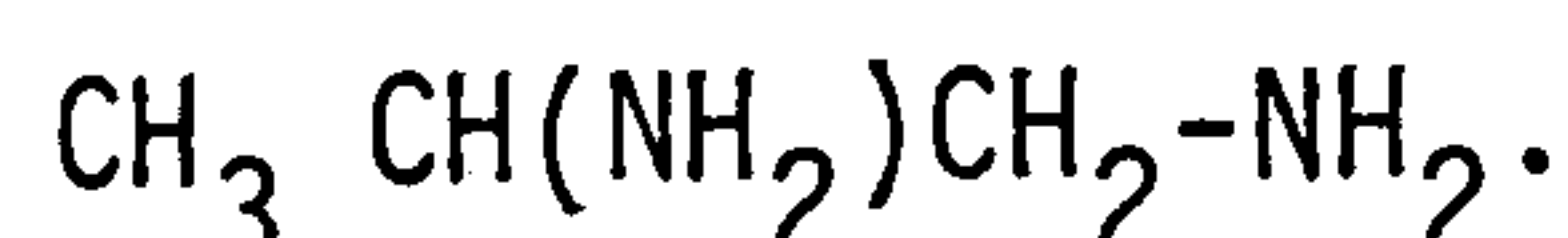
This acid was obtained from BDH Chemicals Ltd, it has the following properties:

Assay	56-70%
Congeaing point	3-7°C
Sulphated ash - not more than	0.1%

Iodine value	85-93
Weight per ml at 20°C - about	0.891g

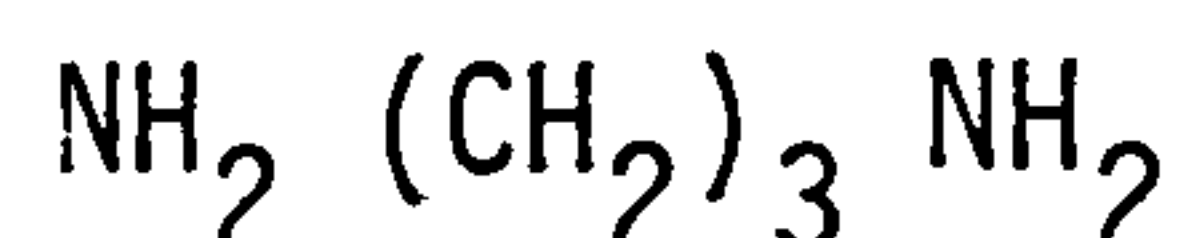
1,2-diaminopropane

BDH Chemicals Ltd. SG = 0.87 at 20°C



1,3 diaminopropane

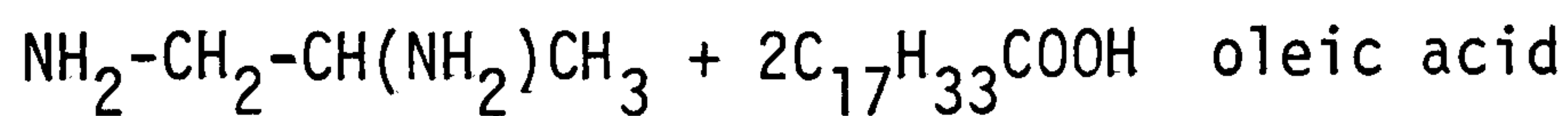
BDH Chemicals Ltd. SG = 0.89 at 20°C



3.1.2 Preparation of Diamine Fatty Acid Salts

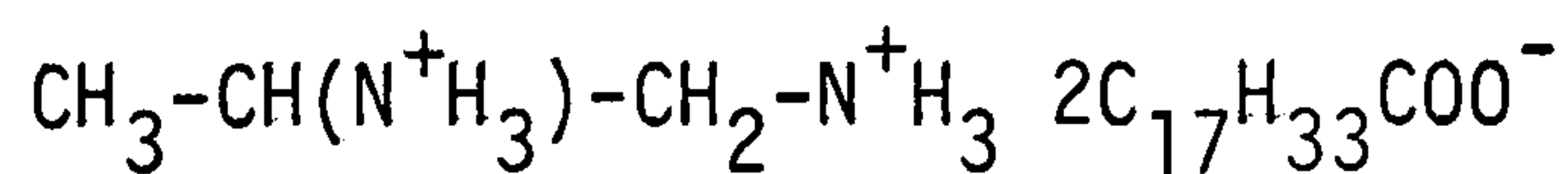
This was carried out in a 500 ml reaction flask fitted with a stirrer at room temperature. The acid, for example two equivalents of oleic acid, was placed in the reaction flask and the liquid diamine, 1,2 propylene diamine, was added dropwise from a burette with continuous stirring of the reaction mixture. The reaction is exothermic and therefore the reaction flask was kept cool by partial immersion in a cold water bath. Once all the amine base had been added the product was obtained in the form of a viscous paste. The concentrations of acid and base used were varied as appropriate (see Table 3.1). However, as an example the product obtained by reacting two equivalents of oleic acid with one equivalent of 1,2 diaminopropane is discussed. The product obtained was used without further purification.

The reaction is believed to proceed by the following route:



1,2 diaminopropane

↓



1,2 diaminopropane di-oleate

Product (I)

For convenience this product is called new salt number 1 and abbreviated to NS1.

Product (I) is therefore seen to be the result of reacting 2 moles of the oleic acid and this involves two functional -COOH groups, with one mole of the diamine which already has two functional -NH₂ groups.

The various experimental materials prepared in this research programme are given in Table 3.1, see class 4.

3.1.3 Identification of the Reaction Product

The infra red spectrum of the reaction product NSC/1 is shown in Figure 3.1 which clearly shows the absence of the characteristic bands of the oleic acid, i.e. the -COOH band which absorbs at 1730 cm⁻¹, and also the amine, -NH₂ band, which absorbs at 3400-3200 cm⁻¹.

Comparing the NSC/1 spectrum with that of the SAPA 1/1 spectra, Figures 3.2, 3.3 and 3.4, which represent the products of two different suppliers, it appears that the differences between the laboratory and commercial products are not significant although equally the SAPA 1/1 structure (see Table 3.1) is not identical to the NSC/1 chemical structure.

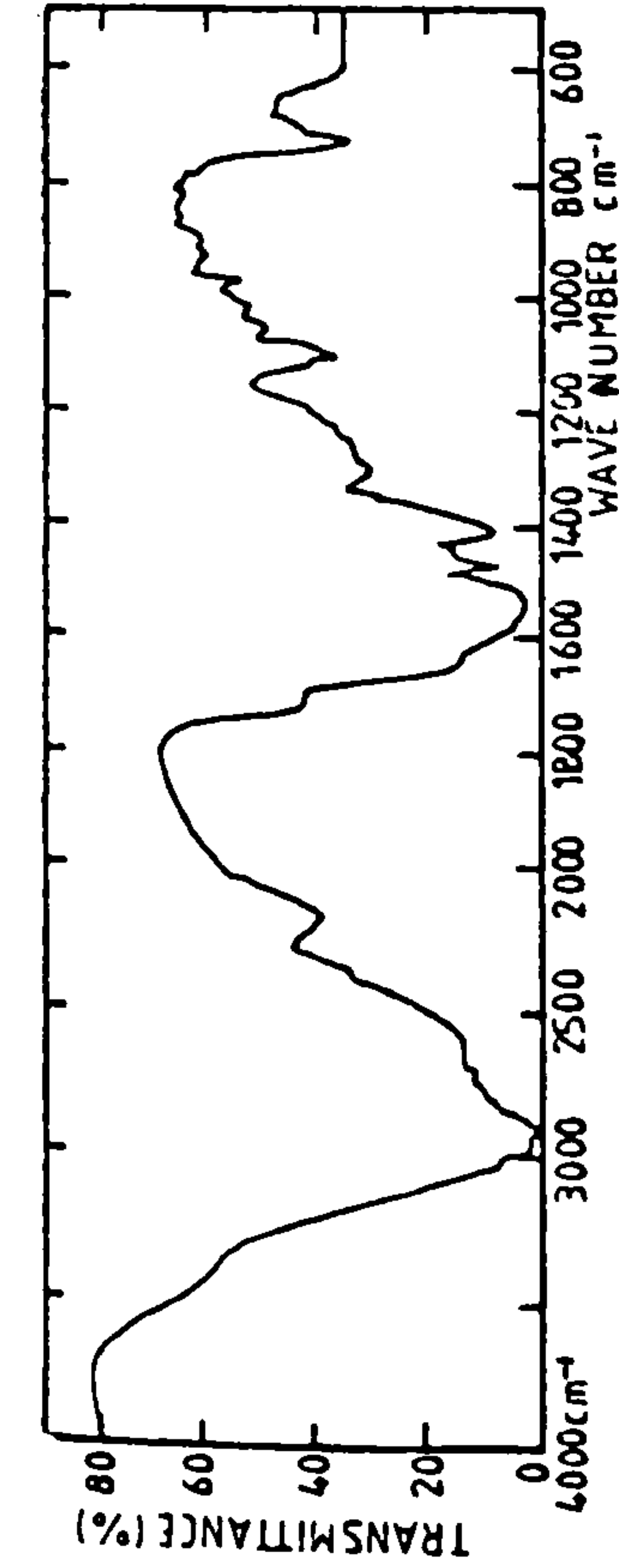


FIG. 3. 1. INFRA-RED SPECTRUM OF 1,3 PROPANE DIAMINE DI-OLEATE (NSC/1) (LABORATORY PREPARED MATERIAL)

THIN FILM ON A NaCl DISC.

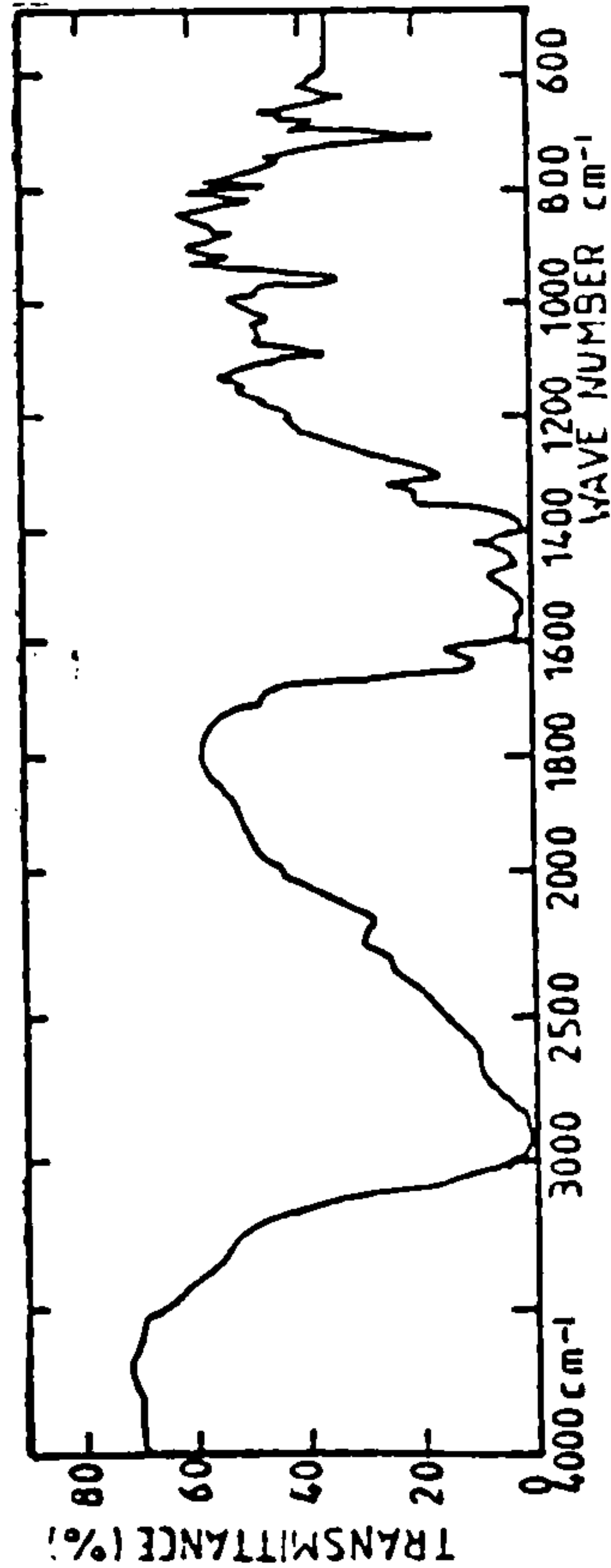


FIG. 3. 3. INFRA RED SPECTRUM OF SAPA1/1 (IN PASTE FORM) OF AKZO CHEMIE (DUOMEEN TDO). THIN FILM ON A NaCl DISC

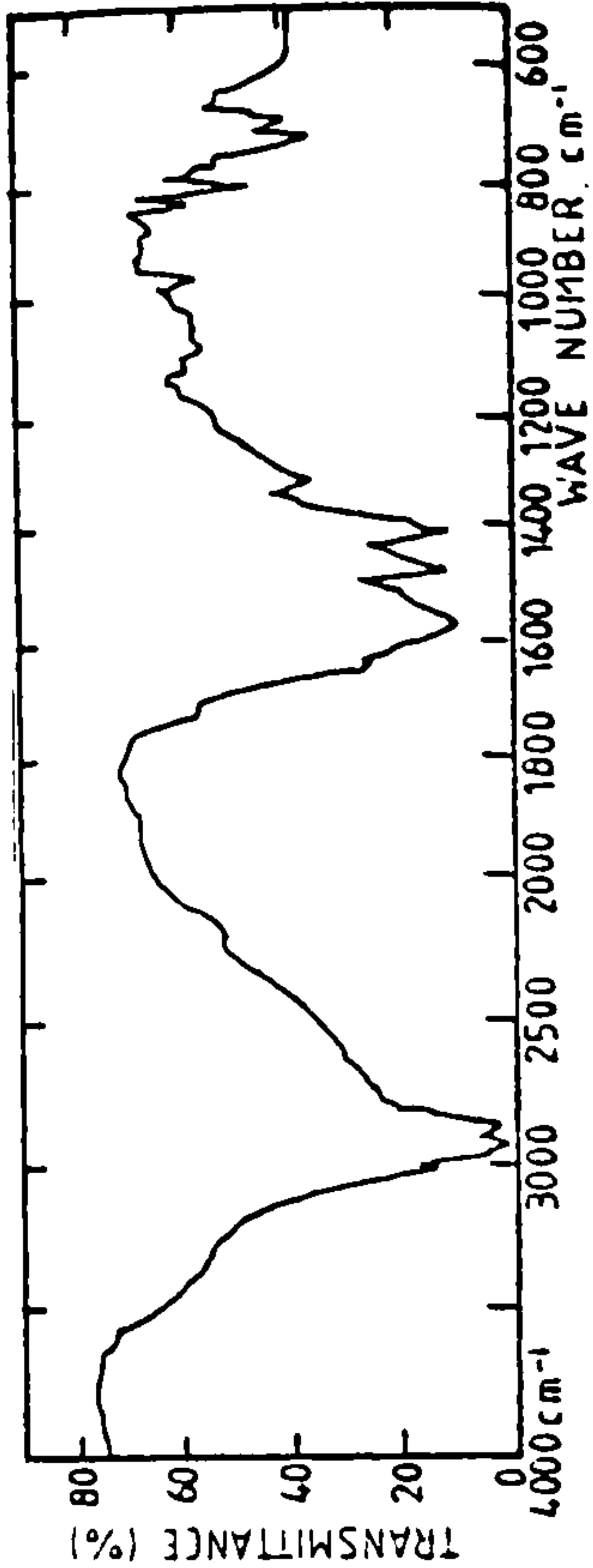


FIG.3. 2. INFRA-RED SPECTRUM OF SAPA1/1 (IN VISCOUS LIQUID FORM) OF CENTRAL CHEMICALS Ltd. THIN FILM

ON A NaCl DISC

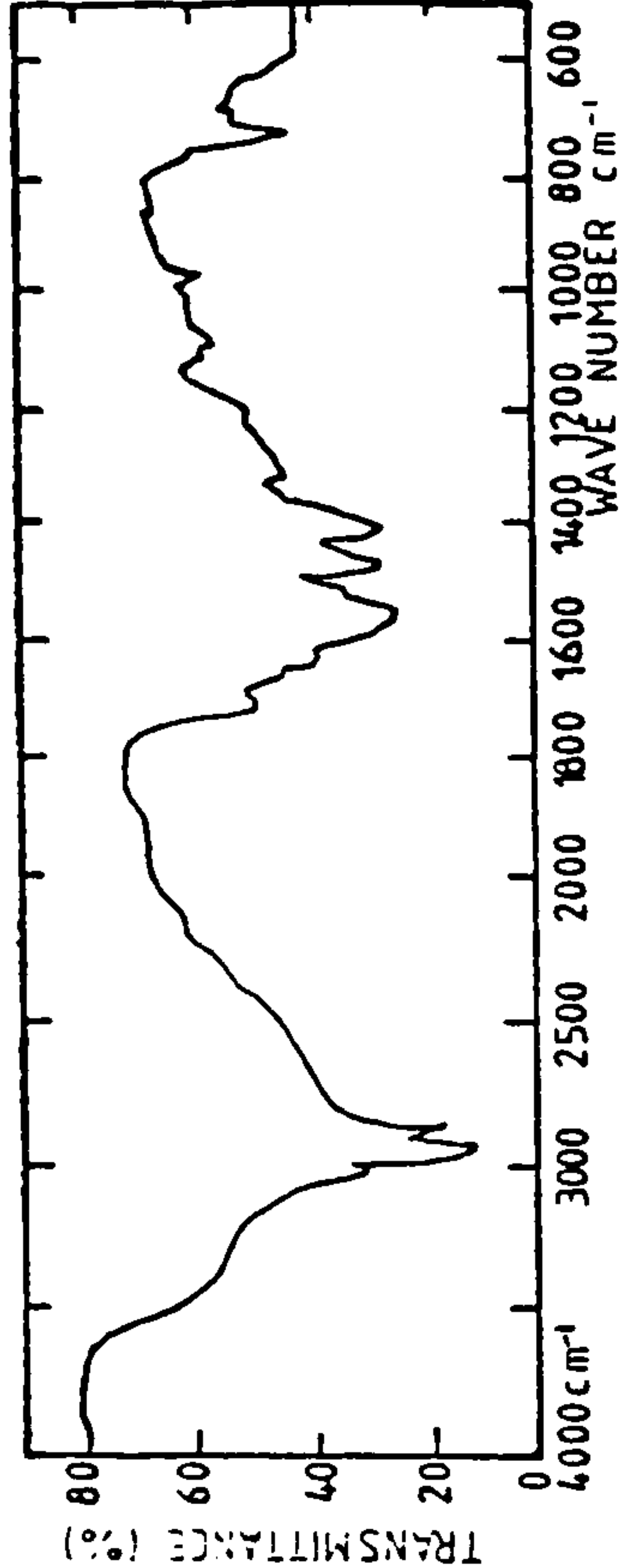


FIG 3. 4. INFRA-RED SPECTRUM OF SAPA1/1 (IN VISCOUS LIQUID FORM) OF ACTOSURF P1 OF AOCM CHEMICALS (WHICH IS THE SAME MATERIAL AS CENFORT RP01 OF CENTRAL CHEMICALS Ltd.)

THIN FILM ON A NaCl DISC

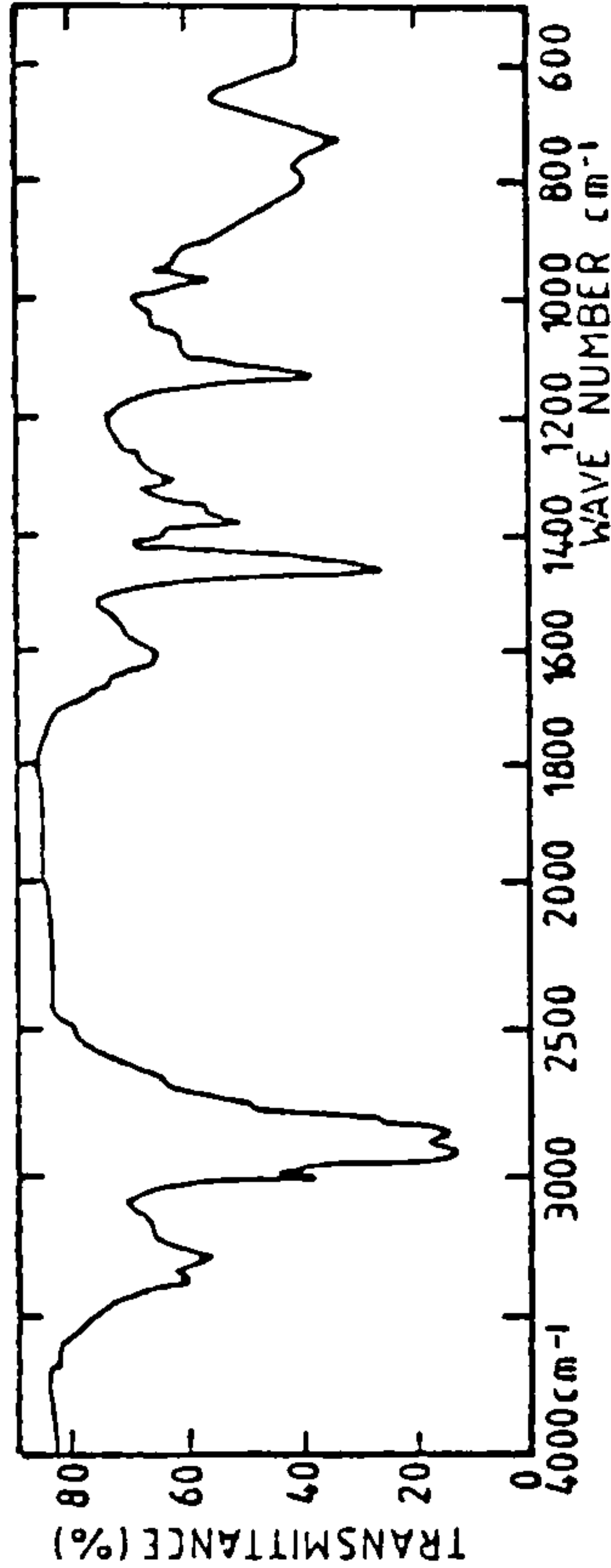


FIG. 3. 5. INFRA-RED SPECTRUM OF A TYPICAL MEMBER OF THE SAPA2 SERIES REPRESENTED BY OLEYL PROPYLENE DAMINE (IN LIQUID FORM). THIN FILM ON A NaCl DISC.

(FOR STRUCTURE SEE TABLE 3. 1.)

Figure 3.5 is the IR spectrum of the N-oley1 1-3 propane diamine surfactant (SAPA 2/B) which is representative of the class 1 series of Table 3.1. This spectrum is significantly different from those of Figures 3.2-3.4. It is clear in this class that the NH_2 group predominates and absorbs at $3200\text{-}3400\text{ cm}^{-1}$, 1610 cm^{-1} , and 1130 cm^{-1} . Hence it is established that the SAPA 1 and SAPA 2 series of surfactants have quite different chemical functional groups available for reactions. Also that the experimental product NSC/1 is similar to the products of the SAPA 1 series.

3.2 Performance of Surfactants, Prepared Salts, and Diamide Material as Processing Aids for an NR/SBR Compound

In this investigation the effect of SAPA 1/1, SAPA 2/A, EBF-S and NSC/1 as processing aids on the processing, curing and physical properties of an NR/SBR compound is examined.

The formulations used as shown in Table 3.2 below.

TABLE 3.2:

FORMULATIONS USED FOR EVALUATING THE EFFECT OF THE SURFACTANTS,
DIAMIDE MATERIAL AND THE PREPARED SALT IN AN NR/SBR COMPOUND

Material	Mix 1 phr	Mix 2 phr	Mix 3 phr	Mix 4 phr	Mix 5 phr
NR "SMR 20"	30	30	30	30	30
SBR 1500	70	70	70	70	70
Sulphur	2	2	2	2	2
Zinc oxide	4	4	4	4	4
Stearic acid	2	2	2	2	2
CBS	0.25	0.25	0.25	0.25	0.25
Santocure MOR	0.25	0.25	0.25	0.25	0.25
Flectol H	0.75	0.75	0.75	0.75	0.75
IPPD	2	2	2	2	2
Microcrystalline wax	3	3	3	3	3
Aromatic Oil, Dutrex 729	5	5	5	5	5
Carbon black FEF	51	51	51	51	51
SAPA 1/1	-	2	-	-	-
SAPA 2/A	-	-	2	-	-
EBF-S	-	-	-	2	-
NSC/1	-	-	-	-	2

The above formulations were mixed and tested as explained earlier in Chapter 2.

Results and Discussion

Figure 3.6 and Table 3.3 summarise the results for the effect of the SAPA 1/1, SAPA 2/A, EBF-S and the NSC/1 upon the processability of this NR/SBR compound and give its curing and physical properties.

These substances are compared with a conventional mix where there is used 5 phr aromatic (Dutrex 729) oil, i.e. no surfactant. First the results clearly show that there are almost no differences between the vulcanisate properties obtained from the respective use of SAPA 1/1, SAPA 2/A and NSC/1. However, the optimum curing times (t_{90}) and the scorch times of SAPA 1/1 and NSC/1 are nearly similar; also they differ considerably from that of SAPA 2/A. This may be attributed to the chemical structure differences between these materials as SAPA 1/1 and NSC/1 are salts while SAPA 2/A is a diamine base and hence differences in performance may occur due to the greater ^{Pr}stearic hindrance effects considered present in both SAPA 1/1 and NSC/1 when compared with SAPA 2/A where stearic effects are thought to be relatively lower (see the structures of Table 3.1). Hence, the activity of the hindered amino groups in SAPA 1/1 and NSC/1 is observed to be lower than that of SAPA 2/A where the amine groups are free and therefore exhibit a shorter optimum curing time, t_{90} , and scorch time than is observed from the SAPA 1/1 and NSC/1 mixes. stearic

EBF-S

Secondly the EBF-S containing mix (mix 4) has essentially no adverse effects on the physical properties of the control mix 1 of Table 3.3. Also the effect of EBF-S on the optimum curing time, t_{90} , and the scorch time is not pronounced. This may be attributed to the chemical structure of EBF-S which has two amide groups present whose reactivities are lower than those of the amino groups present in SAPA 1/1, SAPA 2/A and NSC/1.

Effect of alkyl groups

An important observation was made when the effect of various alkyl groups were studied. Figures 3.7 and 3.8 examine the effect of various alkyl groups in the EBF series, SAPA 2 series, and NS series on the curing properties of the NR/SBR compound (for formulation details see Table 3.2). It is obvious from these results that varying

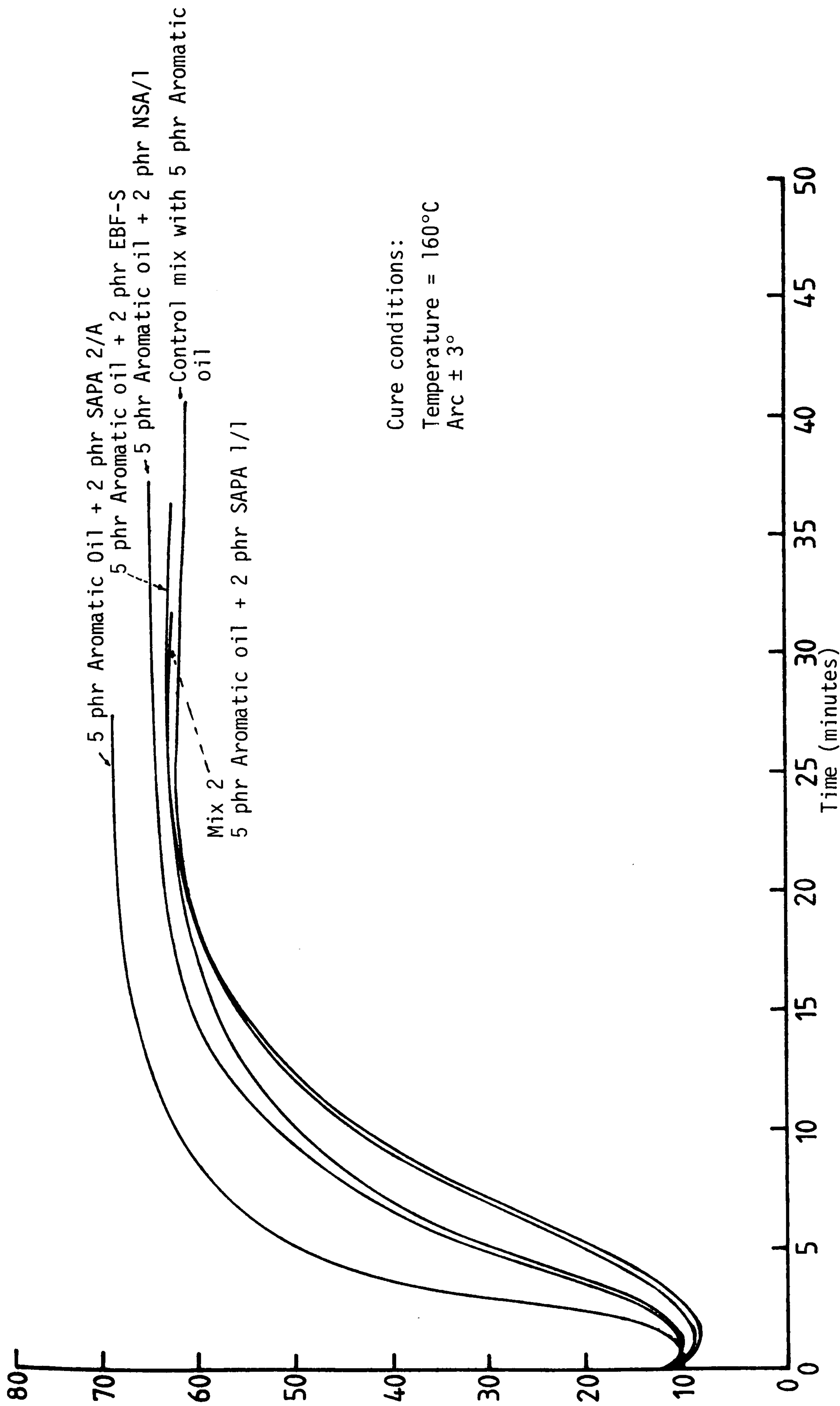


FIGURE 3.6: CURING BEHAVIOUR OF SAPA 1/1, SAPA 2/A, NSA/1, AND EBF-S IN NR/SBR COMPOUND (SEE TABLE 3.2)

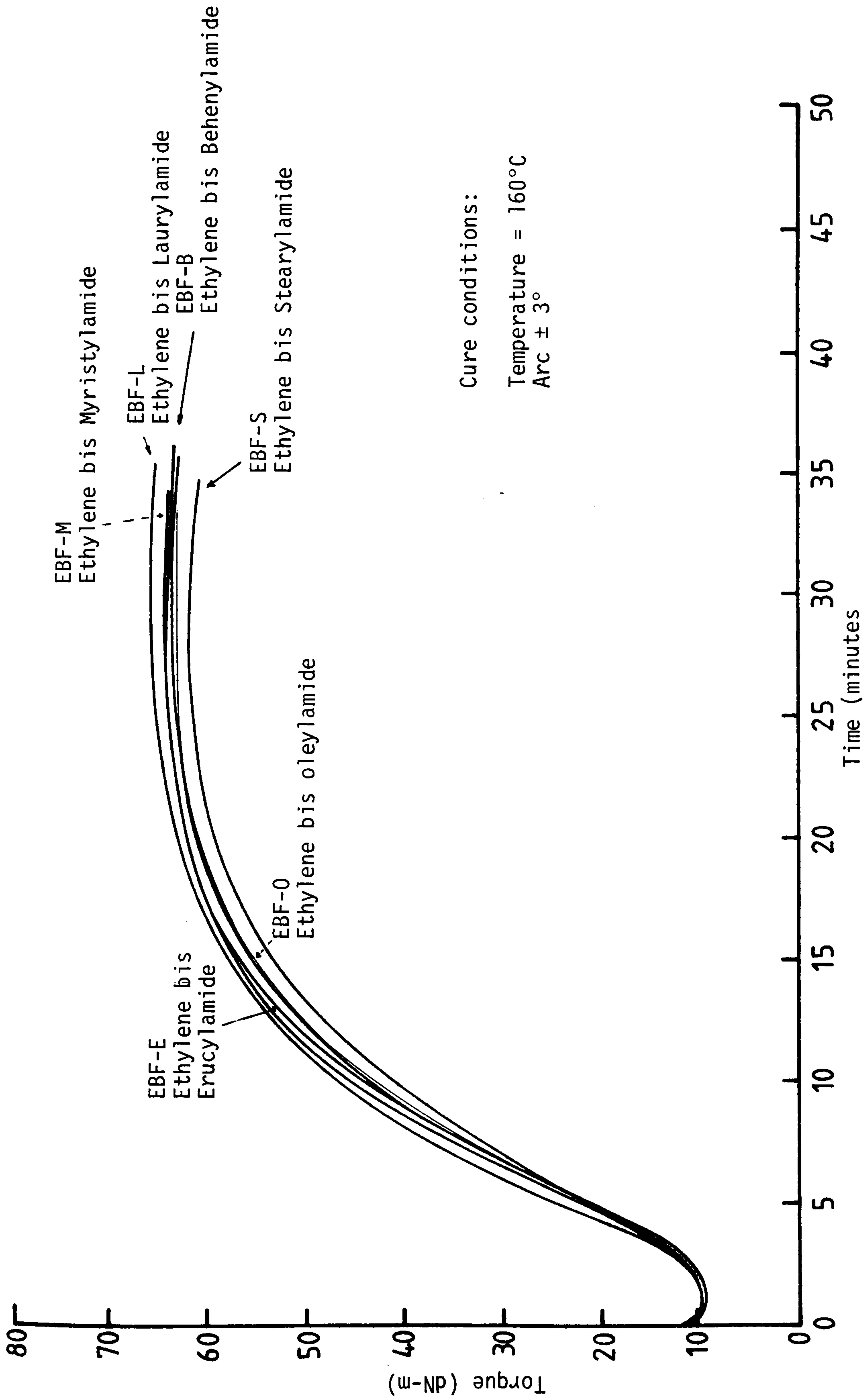


FIGURE 3.7: CURING BEHAVIOUR OF VARIOUS ETHYLENE BIS FATTY AMIDES ON NR/SBR COMPOUND

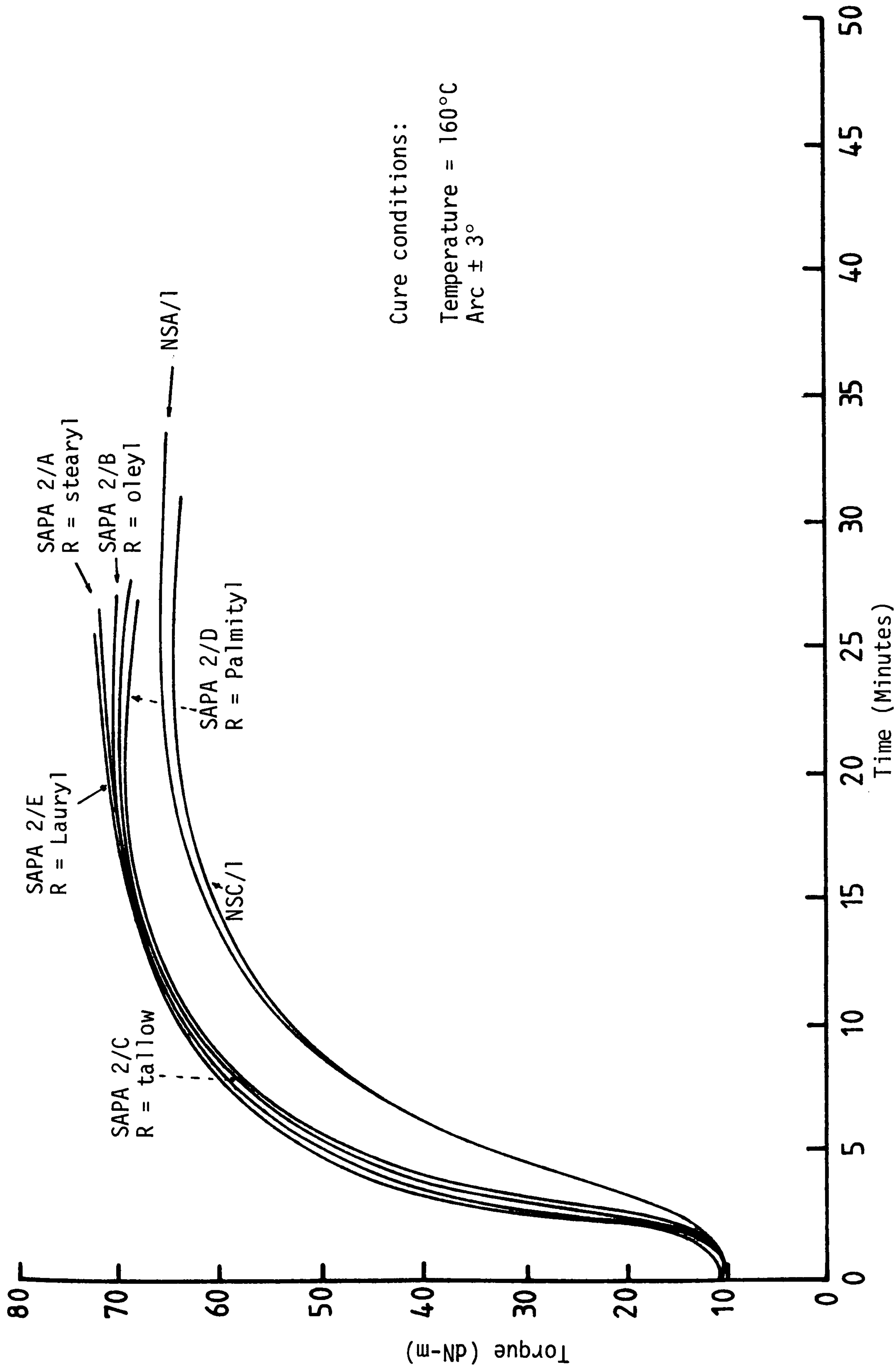


FIGURE 3.8: CURING BEHAVIOUR OF SAPA 2 and NS TYPE SUBSTANCES WITH DIFFERENT ALKYL GROUP

TABLE 3.3

EFFECT OF THE SURFACTANTS, DIAMIDE MATERIALS, AND THE PREPARED SALT AS PROCESSING AIDS ON THE PROCESSING AND VULCANISATE PROPERTIES OF THE TABLE 3.2 COMPOUNDS

	Control Mix with 5 phr Aromatic Oil Mix No. 1	5 phr Aromatic Oil + 2 phr SAPA 1/1 Mix No.2	5 phr Aromatic Oil + 2 phr SAPA 2/A Mix No.3	5 phr Aromatic Oil + 2 phr EBF-S Mix No.4	5 phr Aromatic Oil + 2 phr NSA/1 Mix No.5
<u>Compound Properties:</u> Banbury Mixing Time (m) Start Temperature °C Dump Temperature °C Mooney Scorch at 125°C (m) Mooney Viscosity ML(1+4) 100°C	10 21 123 20 50	10 22 121 11' 48	10 20 118 7' 48	10 19 120 18'30" 52	10 19 120 10'30" 50
<u>Curing Properties:</u> Optimum curing time t ₉₀ at 160°C, minutes	18	10'30"	8'	17'30"	9'30"
<u>Mechanical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa % Elongation at break Tear Strength kN m ⁻¹ % Compression Set at 70°C for two days Hardness, IRHD % Rebound Resilience	17 2 6 630 48 30 55 46	17 2.5 8.5 595 53 27 56 46	17.5 2.5 8.3 590 27 26 56 45	17 2.2 7.3 600 46 28 57 45	16.7 2.8 8.0 590 48 26 56 45

the alkyl group has no effect either on the curing properties or the vulcanisate properties of the rubber. However, in the EBF series it has been observed that there is a considerable difference in the processability, particularly at the mixing stages of the rubber, between the various alkyl groups. Such differences are great when the alkyl group is unsaturated as for example in the case of EBF-0 and EBF-E. These two diamide materials were found to be superior in the processing advantages conveyed to the rubber mixes over all the other types in the EBF series. This is believed to be due to their lower melting points (107/110°C and 110/113°C) compared with all the other types of the EBF series (see Table 3.1, Class 2 series).

3.3 Examination of Surfactants, Prepared Salts, Diamide Material in Natural and in some Further Synthetic Rubbers

The performance of SAPA 1, SAPA 2, NS and EBF have been studied as processing aids in different rubber classes and formulations which are now given in the following subsections.

3.3.1 Unfilled (Gum) and Filled Natural Rubber

SAPA 1/1, SAPA 2/A, NSI and EBF-S were examined in gum and black filled natural rubber utilizing two different types of formulation for each series. The effect of SAPA 1/1 on carbon black dispersion has also been investigated.

The formulations used to assess SAPA 1/1 as a processing aid are shown in Tables 3.4 and 3.5.

TABLE 3.4:

THE 'A' FORMULATION SERIES USED TO EXAMINE SAPA 1/1 AS A PROCESSING AID

	Mix 1	Mix 2	Mix 3	Mix 4
Natural Rubber (SMR5)	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulphur	2.5	2.5	2.5	2.5
CBS	0.5	0.5	0.5	0.5
Permanax BL	1.5	1.5	1.5	1.5
SAPA 1/1	-	2	-	2
HAF Black	-	-	30	30

TABLE 3.5:
The 'B' FORMULATION SERIES USED TO EXAMINE SAPA 1/1 AS A PROCESSING AID

	Mix 5	Mix 6	Mix 7	Mix 8
Natural Rubber (SMR20)	100	100	100	100
Zinc oxide	4	4	4	4
Stearic acid	2	2	2	2
Sulphur	2	2	2	2
Santocure MOR	1.5	1.5	1.5	1.5
Santogard PV1	0.15	0.15	0.15	0.15
Flectol-H	1	1	1	1
IPPD	1.5	1.5	1.5	1.5
Antiozone wax	2	2	2	2
Aromatic oil (Dutrex 729)	-	-	7	7
SAPA 1/1	-	1.5	-	1.5
ISAF Black	-	-	48	48

Mixing of the gum natural rubber, mixes 1, 2, 5 and 6 of Tables 3.4 and 3.5 were carried out on a cooled two-roll rubber mill (300 mm x 150 mm and friction ratio 1:1.25), where roll temperatures became constant at about 50⁰C. The order of mixing the ingredients was as follows:

- Natural rubber
- ↓
- Zinc oxide + stearic acid + SAPA 1/1 if present
- ↓
- Antioxidant
- ↓
- Accelerators
- ↓
- Sulphur

Mixing was continued until adequate dispersion of all ingredients was achieved and each mix was then refined by passing 6 times through a tight nip: each mix was then sheeted off the mill at a thickness of approximately 3 mm which was appropriate for subsequent tests. The carbon black filled natural rubber mixing was carried out in a model BR Banbury using the following conditions:

Rotor speed = 77 rpm
 Ram pressure = 2.5 kg/cm²
 Fill factor = 0.7
 Cooling water full on.

Mixing cycle*

0	: SMR 5
1'	: Black + Zinc oxide + stearic acid + Antioxidants
1'45"	: Processing oil + SAPA 1/1 when present
4'45"	: Accelerators
5	: Clean
7'30"	: Dump

Sulphur was added on the open mill.

All tests were carried out on the uncured and cured natural rubber following the same techniques adopted earlier in Chapter 2. Scanning electron microscopy was used to gain information about the size of the carbon black agglomerates in both the conventional control compound (mix 5) and the SAPA 1/1 containing compound (mix 5) using test specimens carefully taken from one of the two broken pieces of the failed tensile test specimen, the fractured end of the specimen was used in the SEM examination.

* Mixing cycle includes the time taken for the ram to go up and down.

SEM test specimens were stored in a dessicator to avoid contamination. Later each specimen was mounted on an aluminium stub and gold sputter-coated in an Edwards 150 sputter coater. SEM micrographs of the test specimen were taken using a 'Cambridge Stereoscan' S2A scanning electron microscope.

Results and Discussion

It was observed that mixes of gum natural rubber which do not contain surfactant, SAPA 1/1, i.e. mix 1 of Tables 3.4 and 5 of Table 3.5, tend to badly stick to the mill rolls and consequently were difficult to release. This mill sticking was observed to be completely absent in mixes 2 and 6, both of which contained SAPA 1/1.

Extrusion

Figure 3.9(a) and (b) demonstrate the use of SAPA 1/1 as a processing aid in carbon black and silica filled natural rubber extrusions.

Carbon black extrudates

From a comparison of the two extrudates appearing in Figure 3.9(a) it can be established that the inclusion of SAPA 1/1 results in a considerable improvement in its extrudate appearance. As can be seen the extrudate containing SAPA 1/1 possesses a uniform thin edge free from cuts and roughness which is not obtained in the extrudate containing no SAPA 1/1 in its recipe (mix 7 of Table 3.5).

Silica extrudates

As it can be seen in Figure 3.9(b) the inclusion of SAPA 1/1 in the recipe has resulted in a significant reduction in the otherwise

rough surface of such an extrudate. Also inclusion of the SAPA 1/1 has resulted in a considerable improvement in the dimensional stability of the extrudate. Therefore, this observation confirms the previous one concerned with improvement in the appearance of the carbon black filled natural rubber extrudate. This is all the more significant because silica filled rubber is more difficult to process than its carbon black analogue.

Processing, Curing and Physical Properties

The results of the processing, curing and physical properties for both series of formulations A and B (Tables 3.4 and 3.5) are given in Tables 3.6 and 3.7 respectively. The following observations can be made:

It can be seen from these results that the inclusion of SAPA 1/1 has, once again, increased the Mooney viscosity by small amounts. Hence, investigations using the formulations of Table 3.5 (mixes 7 and 8), were conducted to try and explain this phenomena. These investigations included: swelling tests (percentage change in volume (BS 903: Part A16: 1971) and acetone extract tests (ASTM D297). The results of these tests are given in Table 3.8. The inclusion of SAPA 1/1 has reduced the swelling by about 18% from that of the vulcanisate which does not contain SAPA 1/1 (mix 7, Table 3.5). The acetone extraction results show that both the non-SAPA 1/1 and SAPA 1/1 containing mixes have the same acetone extraction values. Two possibilities have been suggested to account for these results. The first one is that possibly all the SAPA 1/1 has been reacted with the rubber, carbon black and other ingredients in the mix and therefore is not available for extraction. The second explanation is that possibly SAPA 1/1 might have caused all the sulphur to be utilised in the crosslinking process. Therefore, no free sulphur is available for extraction.

Taken as a whole, these results agree with the suggestions made earlier that SAPA 1/1 may either act as a coupling agent between the filler and the rubber or react directly with the rubber molecule itself to produce, in situ, a few chemical crosslinks and therefore increase the Mooney viscosity.

Cure rates and cure states are increased by the inclusion of SAPA 1/1, in both the formulations, i.e. mixes 2, 4, 6 and 8 as denoted by the shorter scorch times (t_2) and higher ODR torque values (see Figures 3.10 and 3.11). The physical properties, particularly tensile strength, and modulus, are significantly improved in all the mixes (save mix 8 where a small reduction is observed) which contain SAPA 1/1.

The enhancement in the physical properties of the carbon black filled natural rubber (mixes 4 and 8) is thought to be as a result of improved carbon black dispersion created by the inclusion of the surfactant e.g. SAPA 1/1. Hence, an investigation using the scanning electron microscopy (SEM) technique was carried out to explore this suggestion. The results of this investigation are given in Figures 3.12(a) and (b). These micrographs show that the torn surface of rubber vulcanisates containing no SAPA 1/1 (mix 7 of Table 3.7) show relatively many surface rugosities and voids on their torn surfaces, whilst a SAPA 1/1 containing vulcanisate (mix 8, Table 3.7), has almost a smooth surface relatively free from protrusions and voids. This observation could also be taken to indicate superior filler aggregate breakdown, filler dispersion and also better filler/rubber surface wetting when SAPA 1/1 is contained in the formulation.

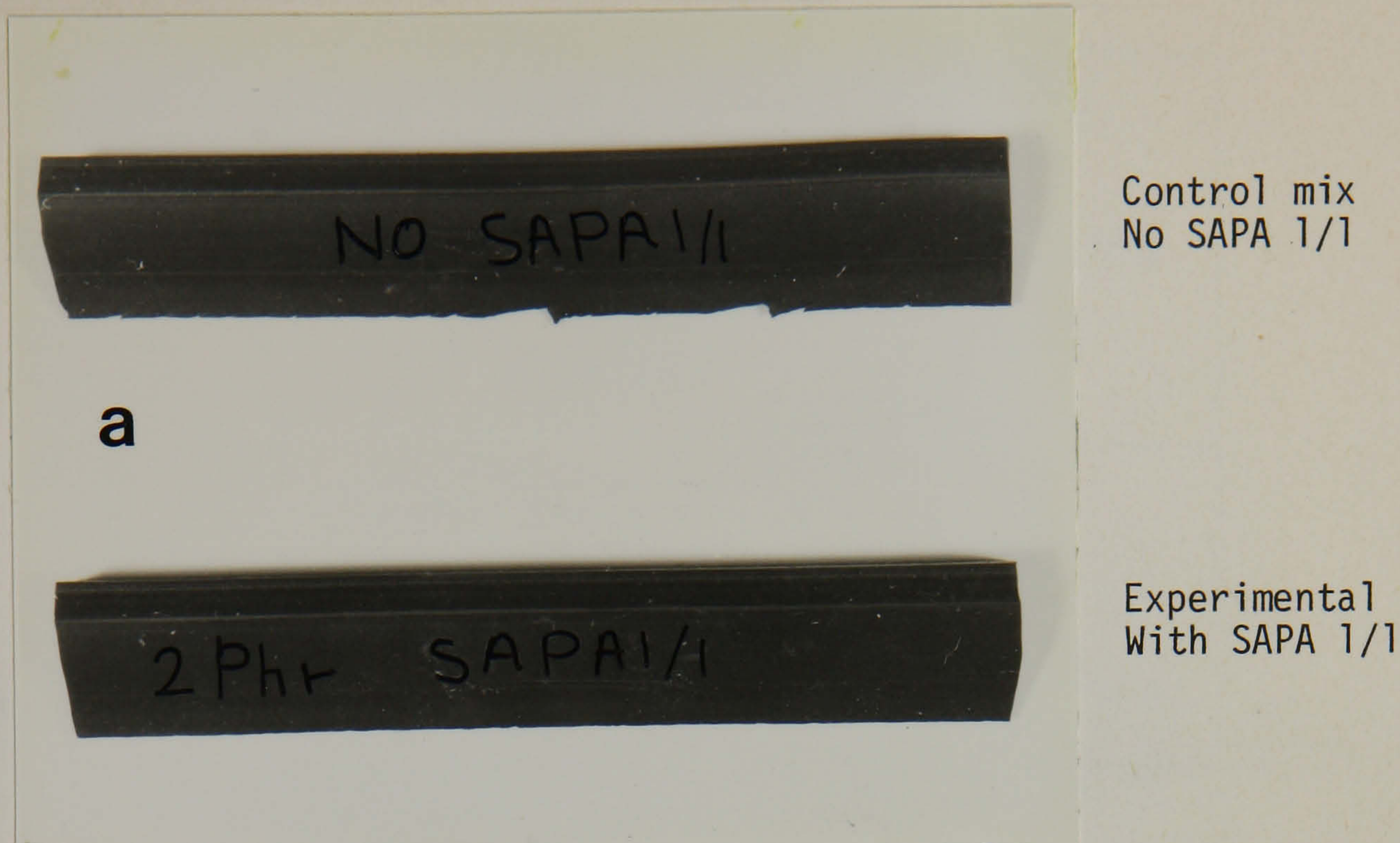


FIGURE 3.9(a): EFFECT OF SAPA 1/1 ON THE EXTRUDATE APPEARANCE OF CARBON BLACK FILLED NATURAL RUBBER (NR 100/ZnO 5, STEARIC ACID 2, SULPHUR 2.5, CBS 0.5, PERMANAX BL 1.5, HAF 30, SAPA 1/1 2)

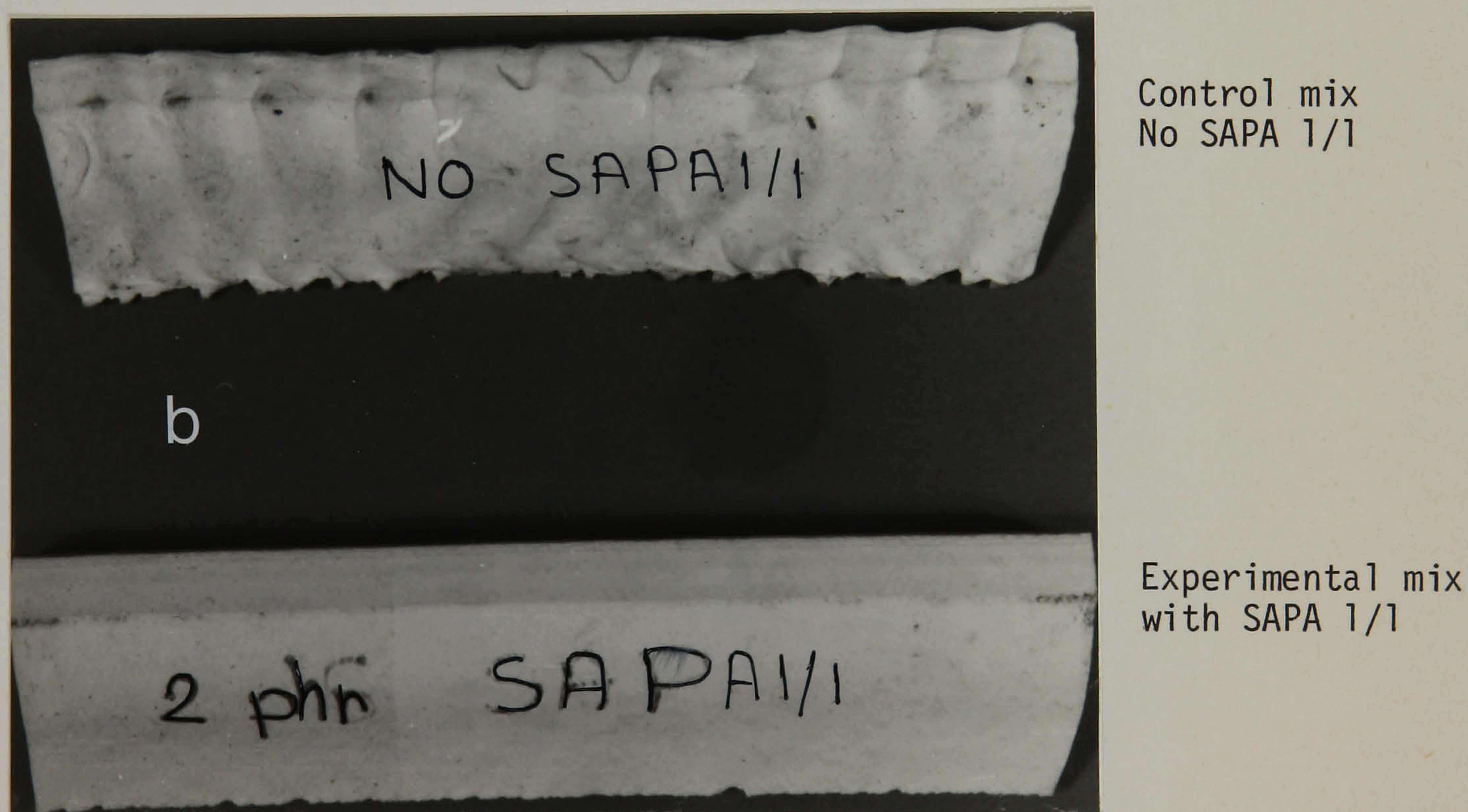


FIGURE 3.b(b): EFFECT OF SAPA 1/1 ON EXTRUDATE APPEARANCE AND DIMENSIONAL STABILITY OF SILICA FILLED NATURAL RUBBER (NR 100, ZnO 5, STEARIC ACID 2, SULPHUR 2.5, CBS 0.5, SILICA VN3 30, SAPA 1/1 2)

TABLE 3.6

EFFECT OF SAPA 1/1 ON GUM AND CARBON BLACK FILLED NATURAL RUBBER (SMR5); PROCESSING, CURING AND PHYSICAL PROPERTIES (FOR FORMULATION SEE TABLE 3.4)

Properties	Unfilled (gum stock) Formulation (A)		Carbon Black Filled Natural Rubber. Formulation (A)	
	Control Mix 1	Mix 2 with SAPA 1/1	Mix 3	Mix 4
<i>Processing Properties:</i> Mooney Viscosity ML (1+4) 100°C ODR Scorch time, t ₂ (m) at 150°C Optimum curing time, t ₉₅ , at 150°C	16 8 17	18 3.5 12.5	27 5 14	28 3 11
<i>Physical Properties:</i> Cure conditions	—————15m at 150°C—————			
Ultimate Tensile Strength, MPa % Elongation at Break 300% Modulus MPa Hardness, IRHD	17 760 1.4 39	21 750 1.8 42	25.6 610 8.2 52	26.0 530 9.9 56
Cure conditions	—————20m at 150°C—————			
Ultimate Tensile Strength, MPa % Elongation at break 300% Modulus MPa Tear Strength kN m ⁻¹ % Compression set at 70°C for 24 hrs	19.6 735 1.6 50 46	28.4 690 1.85 55 41	26 600 8.7 60 50	30.4 500 10.5 62 46

TABLE 3.7

EFFECT OF SAPA 1/1 ON GUM AND CARBON BLACK FILLED NATURAL RUBBER (SMR20) PROCESSING,
CURING AND PHYSICAL PROPERTIES

Properties	Unfilled (gum stock) Formulation (B)		Carbon Black Filled Natural Rubber. Formulation (B)	
	Mix 5	Mix 6	Mix 7	Mix 8
<u>Processing and Curing Properties:</u> Mooney Viscosity ML (1+4) 100°C Mooney scorch at 125°C (m) Optimum curing time, t ₉₀ , at 160°C (m)	19 37 10'	19 19 6'30"	56 20 6	58 9 4
<u>Physical Properties:</u> Tensile Strength, MPa 100% Modulus, MPa 300% Modulus, MPa % Elongation at break Tear Strength kN m ⁻¹ * Hardness IRHD Rebound Resilience %	25 0.6 1.0 1000 44 40 75	26.5 0.68 1.7 945 43.5 41 76	27 2.6 10.6 590 80 72 37	25 4.6 16 450 76 75 36

* An occasional very high value was observed

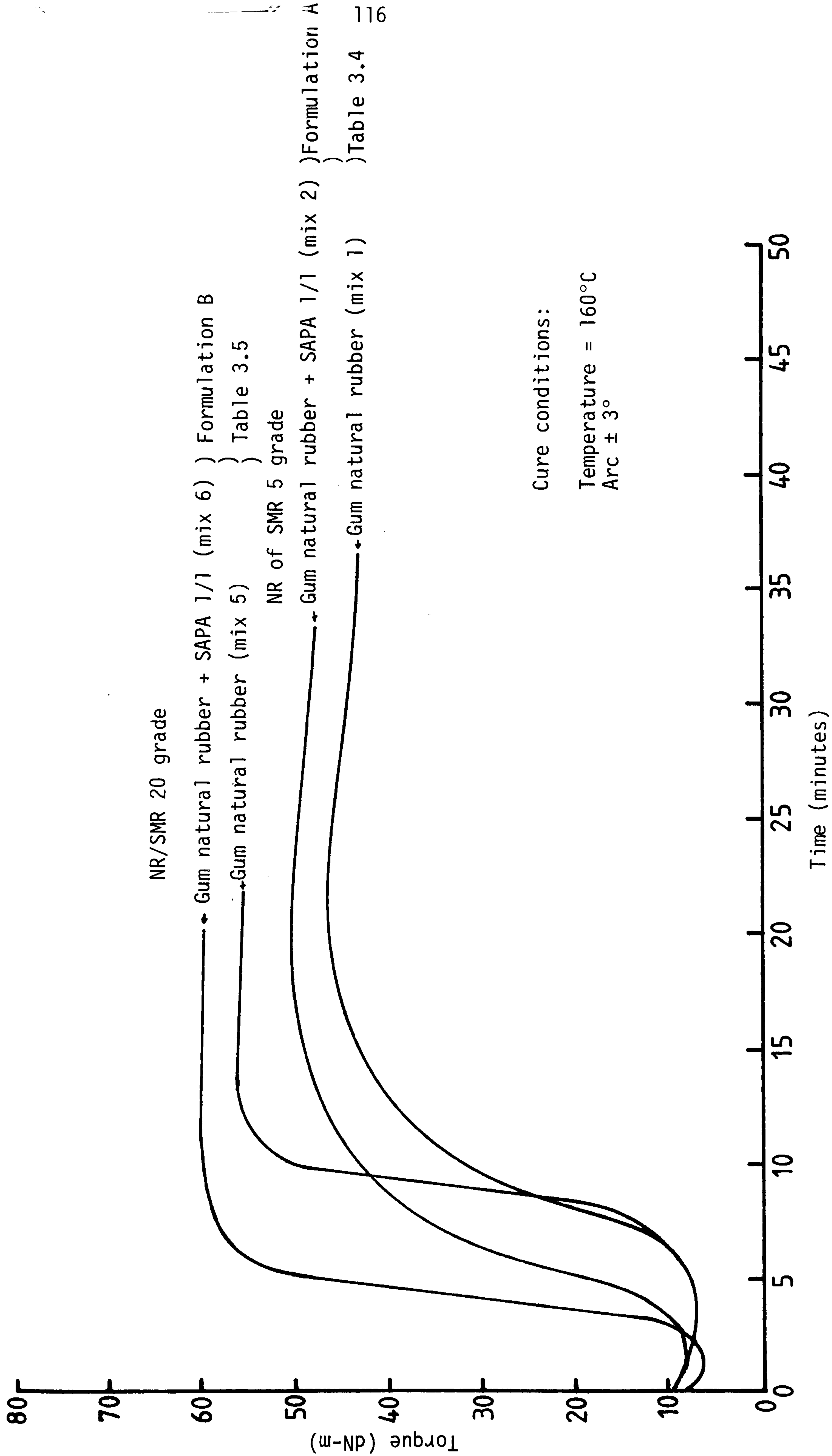


FIGURE 3.10: THE EFFECT OF SAPA 1/1 ON THE CURING BEHAVIOUR OF GUM TYPE NR MIXES. DATA FOR TWO GRADES OF NR ARE DEMONSTRATED

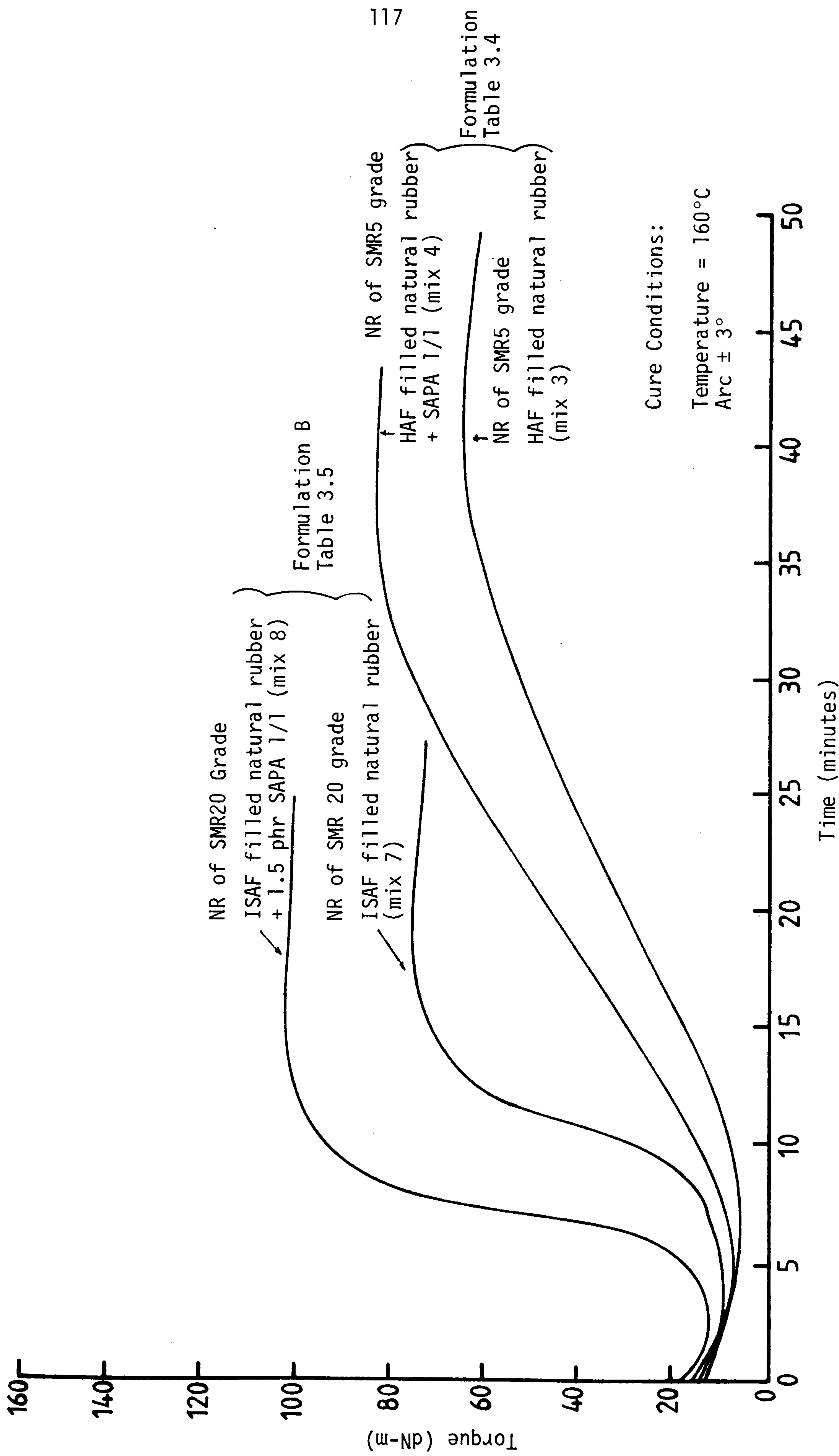


FIGURE 3.11: THE EFFECT OF SAPA 1/1 ON THE CURING BEHAVIOUR OF CARBON BLACK FILLED NR MIXES. DATA FOR TWO GRADES ARE DEMONSTRATED

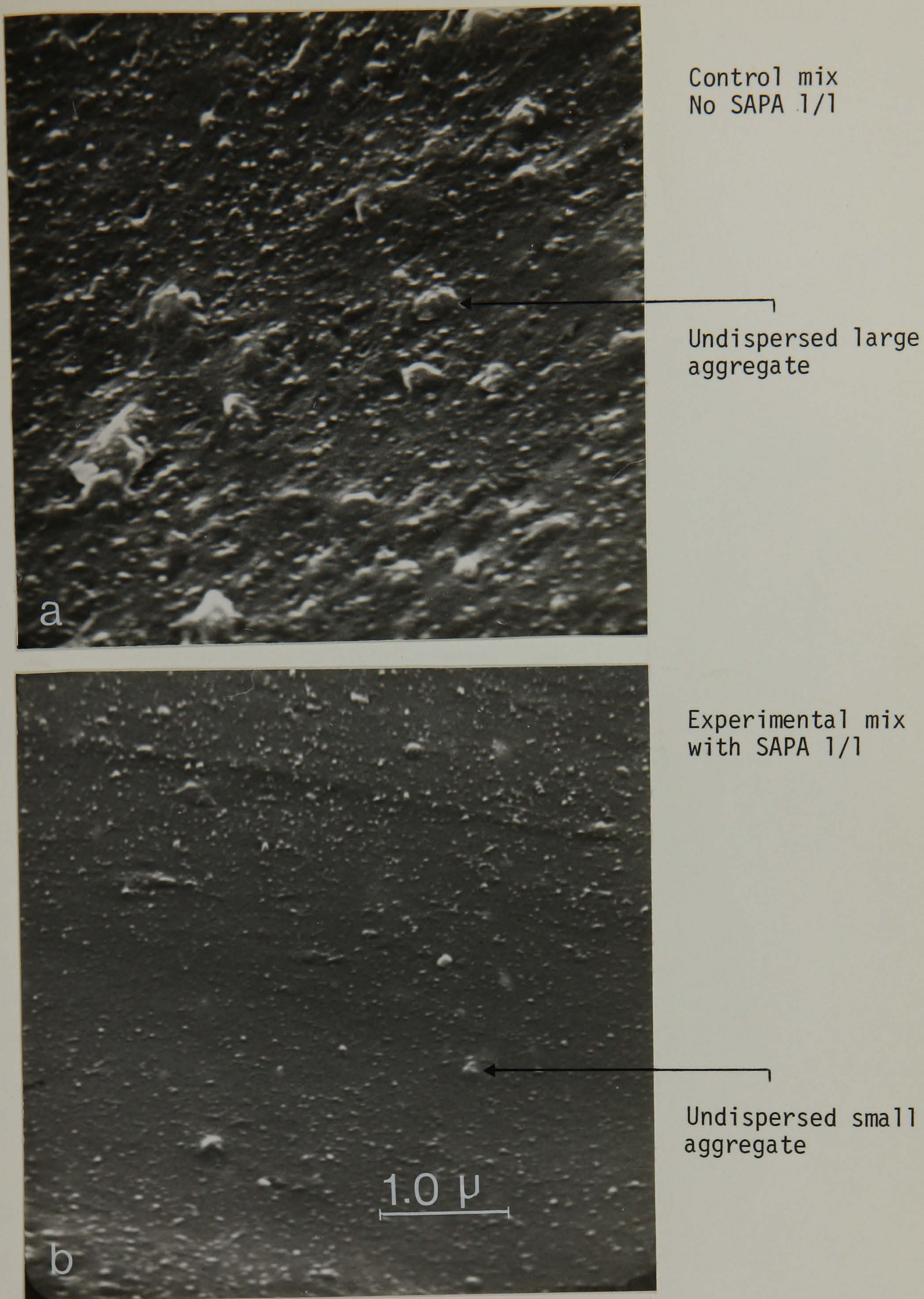


FIGURE 3.12: SEM MICROGRAPHS ($\times 7000$ MAGNIFICATION) OF A TORN VULCANISATE SURFACE ILLUSTRATING THE EFFECTS OF SAPA 1/1 AS A FILLER DISPERSION AND WETTING AGENT IN NATURAL RUBBER

a) CONTAINS NO SAPA 1/1, b) CONTAINS 2 phr SAPA 1/1

(FORMULATION: NR 100, FEF BLACK 50, AROMATIC OIL 5, FLECTOL-H 2, CBS 0.5, SULPHUR 2)

TABLE 3.8:

SWELLING AND ACETONE EXTRACT RESULTS FOR NR RUBBER WITH AND WITHOUT SURFACTANT SAPA 1/1 (FOR FORMULATIONS SEE TABLE 3.5, MIXES 7 AND 8)

	Formulation B (Table 3.5)	
	Vulcanisate Without Surfactant Mix 7	Vulcanisate With Surfactant Mix 8
% Change in volume*	280	237
% Acetone extract	4.575	4.575

* The immersion period was 7 days using toluene as a test liquid.

SAPA 2/A, NS1, and EBF-S Materials

These substances have been examined in a gum type natural rubber based on the base formulation of Table 3.5 (mix 5). The effect of SAPA 2/A, NS1, and EBF-S materials on the curing behaviour of the gum natural rubber are shown in the rheometer curves in Figure 3.13. As can be seen NS1 and SAPA 1/1 have almost identical effects on the curing behaviour of natural rubber and they exhibit considerably different effects from that of SAPA 2/A. The latter was found to give a shorter scorch time, t_2 , and optimum curing time, t_{90} , than SAPA 1/1 and NS1.

The EBF-S material is observed to have only a slight effect on the curing behaviour, particularly optimum curing time, t_{90} , and scorch time, t_2 , of the natural rubber. However, use of the EBF-S material in the gum NR was shown to demonstrate a considerable improvement in the processability of the natural rubber which was mainly observed at the mixing and moulding stages.

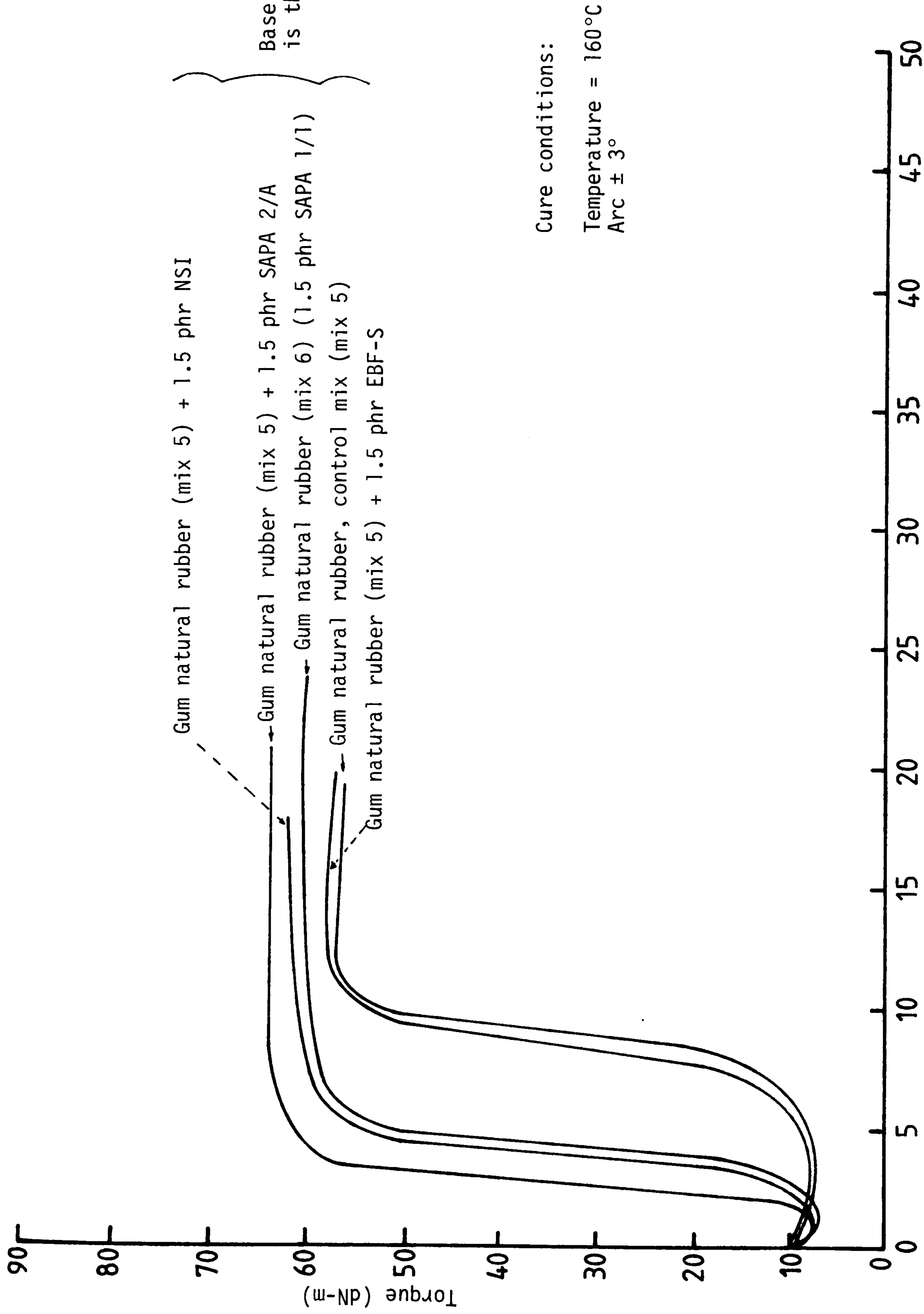


FIGURE 3.13: EFFECT OF SAPA 2/A, NSI, AND EBF-S ON THE CURING BEHAVIOUR OF GUM NATURAL RUBBER IN COMPARISON WITH SAPA 1/1 MATERIAL

3.3.2 Chloroprene Rubber (CR)

In addition to natural rubber another strain crystallisable rubber was selected to be examined in combination with a surfactant and prepared salt as processing aids.

Two grades of CR were tested in two series of formulations. The (I) series of formulations and the (II) series of formulations are given in Tables 3.9 and 3.10 respectively.

TABLE 3.9:

THE "I" FORMULATION SERIES USED TO EXAMINE SAPA 1/1 AS A PROCESSING AID

	Gum CR		Carbon Black Filled CR	
	Control Mix 1	Mix 2	Control Mix 3	Mix 4
Neoprene GRT	100	100	100	100
ZnO	5	5	5	5
Magnesia (MgO)	4	4	4	4
ETU* (Robac 22)	0.5	0.5	0.5	0.5
HAF Black	-	-	-	-
Permanax B	1	1	1	1
DOP	2	-	2	-
SAPA 1/1	-	2	-	2

* Denotes ethylene thiourea

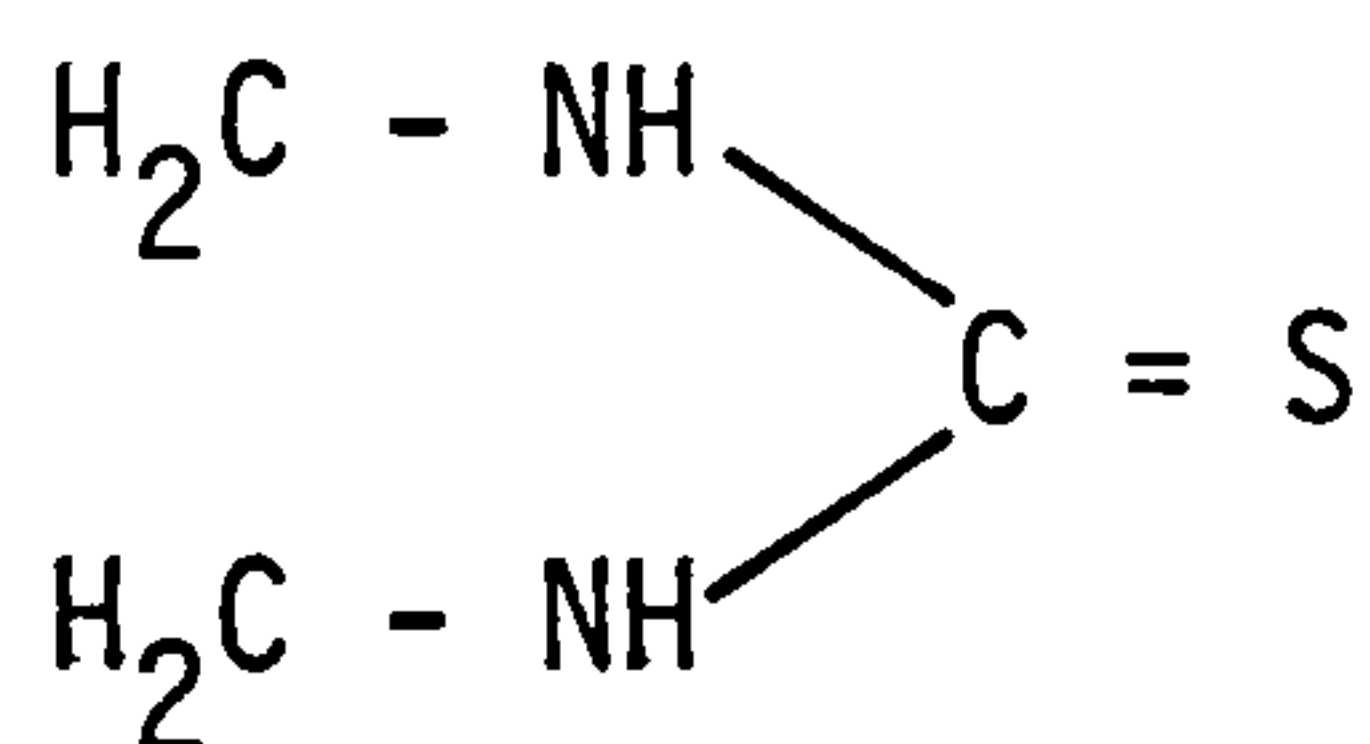


TABLE 3.10:

THE "II" FORMULATION SERIES USED TO EXAMINE SAPA 1/1 AND NS1 AS PROCESSING AIDS

	Mix 5	Mix 6	Mix 7
Neoprene WRT	100	100	100
ZnO	5	5	5
MgO	4	4	4
Stearic Acid	0.5	0.5	0.5
Robac 22	0.75	0.75	0.75
Aromatic Oil (Dutrex 729)	12	12	12
SRF Black	58	58	58
SAPA 1/1	-	2	-
NS1	-	-	2

Both series were prepared in a model B Banbury at a rotor speed of 58 rpm, ram pressure 4.5 kg/cm² and a fill factor of 0.65. Each mix was then refined 6 times on a laboratory mill roll (450 mm x 225 mm, friction ratio of 1:1.125). The following mixing cycle was adopted throughout.

Mixing Cycle:

Operation:	:	Time:
Neoprene	:	0
Magnesia and antioxidants	:	1
$\frac{1}{2}$ Black + $\frac{1}{2}$ Oil added	:	2'30"
Rest of black + $\frac{1}{2}$ oil + SAPA 1/1 or NS1 when present	:	5'30"
Clean down	:	6
Zinc oxide + accelerators	:	7'30"
Dump onto mill	:	9

The results of this investigation are summarised as follows:

GRT Grade (Formulation I Series)

Table 3.11 and Figure 3.14 summarise and compares the results for the effect of SAPA 1/1 upon the processing, curing and vulcanisate properties of CR rubber based on series I formulation of Table 3.9. The following observations can be made. The effect of SAPA 1/1 on the Mooney viscosity of CR is similar to that of a conventional processing aid in both unfilled and filled rubbers. Cure rate is not significantly affected by the SAPA 1/1 but the cure state (t_{95} modulus) of the unfilled CR is considerably enhanced; the cure state of the filled CR is only marginally enhanced. Processing of the SAPA 1/1 containing rubbers is markedly improved by the presence of SAPA 1/1 both during milling and moulding with mouldings possessing flow mark free surfaces and being free of stress and distortion problems. Physical properties are not improved by the presence of SAPA 1/1 in CR where its effect seems similar to that of a conventional processing aid.

WRT Grade

Table 3.12 and Figure 3.15 give the processing, curing and physical properties of carbon black filled CR rubber (WRT grade) based on series II formulation of Table 3.10. The results clearly show that the Mooney viscosity is significantly lower than the control, e.g. between 11-15% lower, indicating that SAPA 1/1 and NS1 are similar in their effect to any conventional processing aid.

It was observed that the inherent tendency of CR rubber mixes to stick to mill rolls was eliminated entirely by the use of SAPA 1/1 and NS1. Flow of the rubber compound during moulding was dramatically enhanced and the resulting vulcanisates remarkably free from the usual moulding stresses and distortion tendencies even when the

deliberate use of poor blank preparation methods was adopted to test flow properties. Further no mould release was necessary when SAPA 1/1 or NSI containing mixes (mixes 6 and 7 of Table 3.10) were cured whereas the control mix (mix 5 of Table 3.10) required the use of a mould release agent. This remarkable mould release phenomena is believed to be due to the formation of fatty acids as a result of heating SAPA 1/1 or NSI during mixing. Therefore, an extra amount of fatty acid is formed in addition to that already present in the mix (0.5 phr). Usually fatty acids are very effective release agents for rubber and are widely used in CR compounding for this purpose. Hence mixes containing SAPA 1/1 or NSI showed excellent mill and mould release characteristics. However, fatty acids are known to retard the cure of CR rubber. This retardation in the cure might have been the reason for getting the longer scorch time in the mixes containing SAPA 1/1 and NSI (mixes 6 and 7 of Table 3.10).

The physical properties are again marginally improved in vulcanisates containing surfactant. However, it is noteworthy that the SAPA 1/1 and NSI containing mixes, in both the CR grades, have better (i.e. lower) compression set than their controls which do not contain surfactant (SAPA 1/1) or NSI.

TABLE 3.11:

COMPARISON OF EFFECTS OF A CONVENTIONAL PLASTICISER (DOP) AND SAPA 1/1 UPON PROCESSING, CURING AND MECHANICAL PROPERTIES OF GUM AND CARBON BLACK FILLED CHLOROPRENE RUBBER BASED ON FORMULATION (I) OF TABLE 3.10

	Unfilled (gum stock)		Carbon Black Filled	
	Control Mix 1	Mix 2	Control Mix 3	Mix 4
<u>Processing and Curing Properties:</u>				
Mooney Viscosity ML (1+4) at 100°C	25	23	48	46
	Poor flow and mill roll release. Difficult to mill & mould. Stress lines on cured moulding	Mill flow and roll release excellent. No stress lines or distortion of cured mouldings	Mill flow difficult due to high black content. High shear heat generation during mixing. Distorted mouldings if black preparation not accurate	Easy processing rubber; low heat generation during mixing. Moulds readily with no flow or stress problems in final moulding
Optimum Curing Time t_{90} , at 160°C	33	30	28	28
<u>Physical Properties:</u>				
Tensile Strength MPa	9.4	9.9	19.7	19.8
Elongation at break (%)	580	610	350	330
Hardness, IRHD	42	45	80	81
Tear Strength kNm^{-1}	44	44	58	56
Compression set at 70°C for 48 hr %	20	18	10	9
<u>Physical Properties at 7 days ageing at 70°C:</u>				
Tensile Strength	5.9	4.8	18.4	18.3
Elongation at break (%)	480	500	305	235
Hardness, IRHD	43	47	81	82

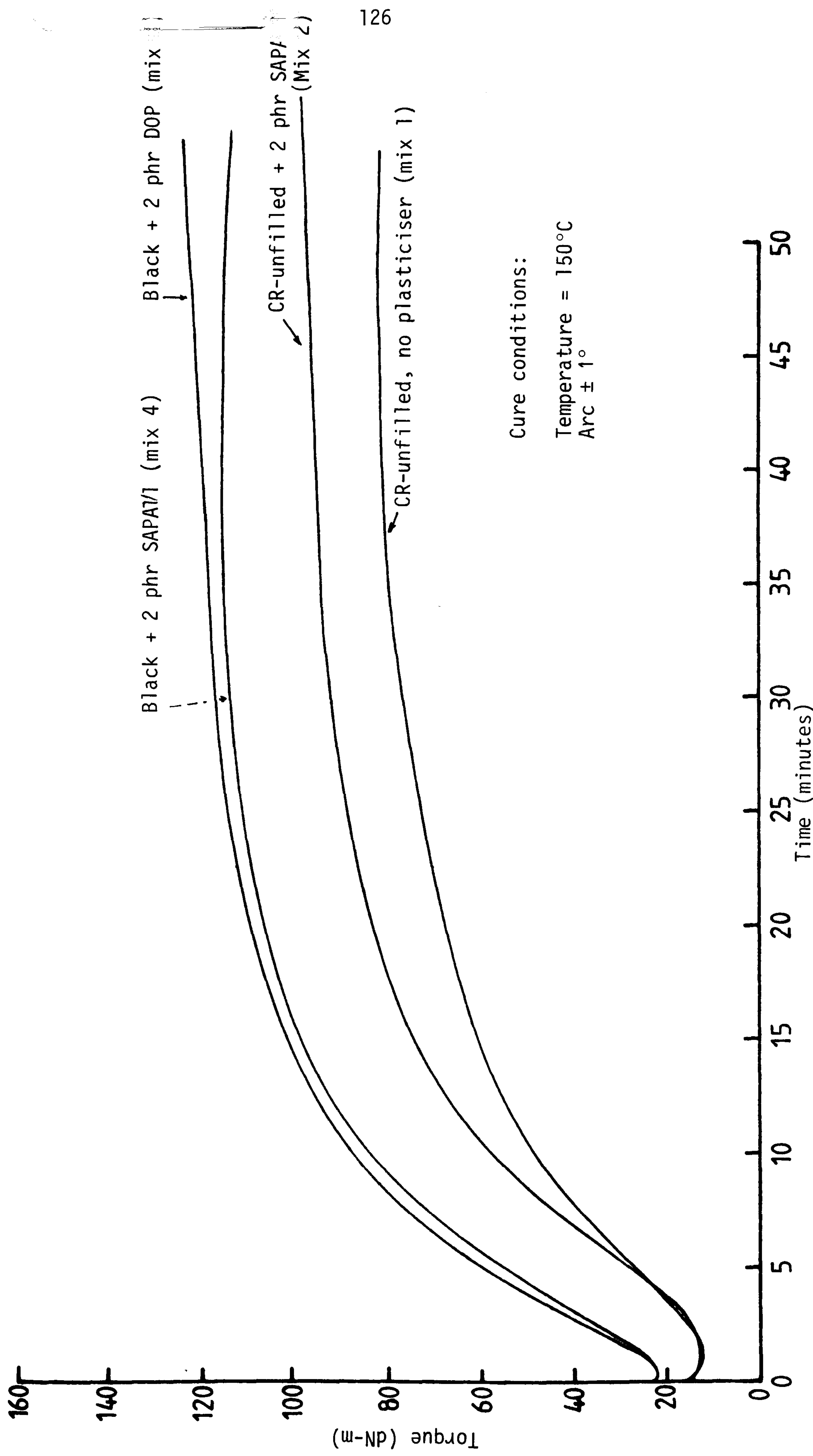


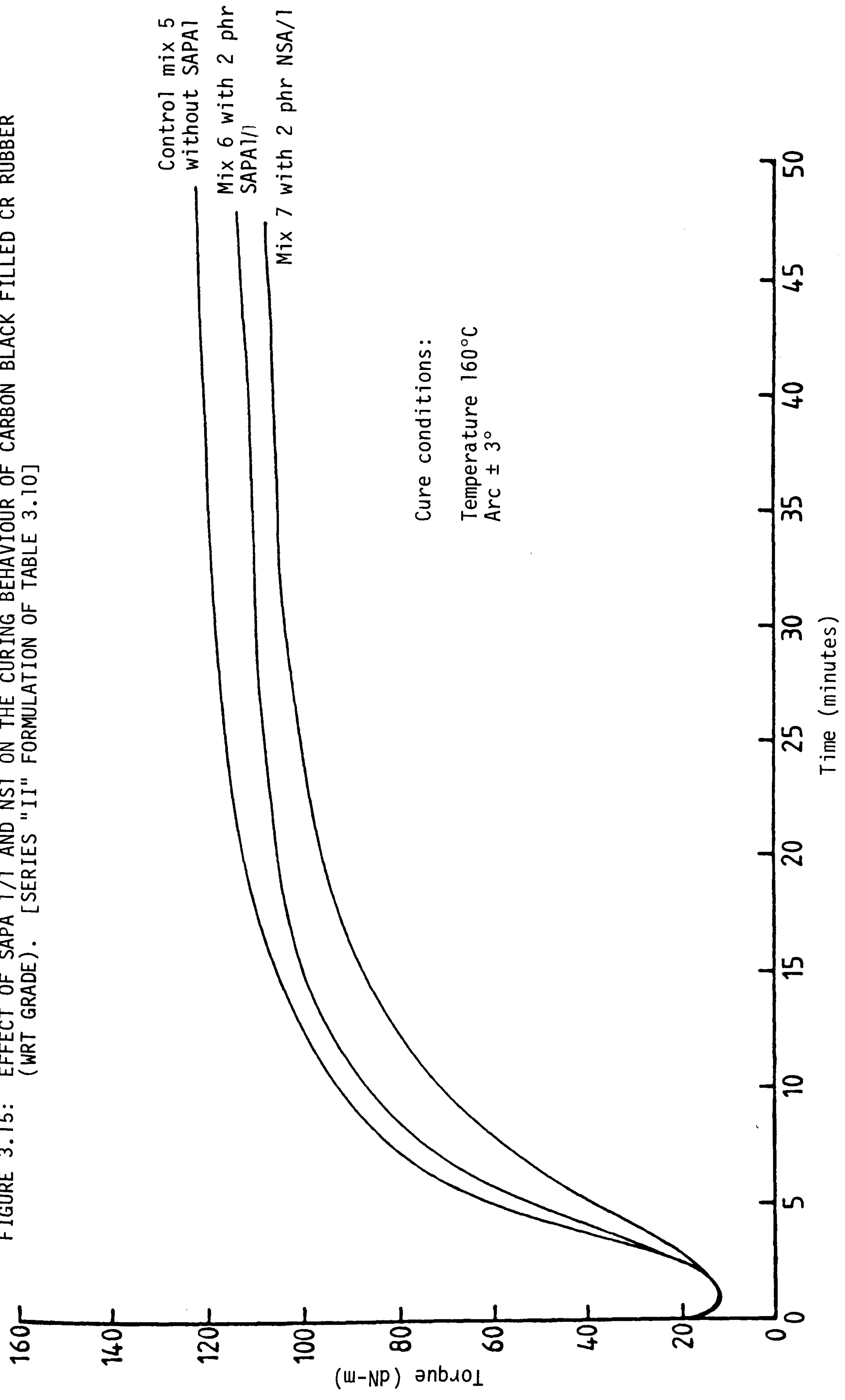
FIGURE 3.14: EFFECT OF SAPA 1/1 ON CURING PROPERTIES OF GUM AND CARBON BLACK FILLED CR RUBBER (GRT GRADE) BASED ON SERIES "I" FORMULATION OF TABLE 3.10

TABLE 3.12:

EFFECT OF SAPA 1/1 AND NS1 AS PROCESSING AIDS ON CHLOROPRENE RUBBER BASED ON FORMULATION (II) OF TABLE 3.10

	Mix 5	Mix 6	Mix 7
<u>Processing and Curing Properties:</u>			
Mooney Viscosity ML (1+4) 100°C	62	53	55
Scorch time at 125°C (m)	5	6	7'30"
Optimum curing time, t_{90} , at 160°C (m)	25	22	25
<u>Mechanical Properties:</u>			
Tensile Strength MPa	17	18	18
100% Modulus MPa	5	5	5.7
200% Modulus MPa	12.5	12	14
% Elongation at break	255	265	250
Tear Strength kN m^{-1}	50	40	40
Hardness, IRHD	75	73	77
Compression set at 70°C for 48 h. %	12	9.5	9
Rebound Resilience %	34	31	35

FIGURE 3.15: EFFECT OF SAPA 1/1 AND NS1 ON THE CURING BEHAVIOUR OF CARBON BLACK FILLED CR RUBBER (WRT GRADE). [SERIES "II" FORMULATION OF TABLE 3.10]



3.3.3 Nitrile Rubber (NBR)

Acrylonitrile-Butadiene rubber, usually known as nitrile rubber, was selected to be examined with a surfactant and a prepared salt in addition to CR rubber which was examined before; this group of rubbers, NBR and CR, is classified as a group of rubbers which contain significant proportions of polar groups. Therefore, an impression may be gained about the effect of surfactants on such rubbers.

The formulations used to assess the performance of SAPA 1/1 and NSA/1 are shown in Table 3.13.

TABLE 3.13:

RECIPE USED TO EXAMINE THE BEHAVIOUR OF SAPA 1/1 AND NSA/1 AS PROCESSING AIDS IN NBR RUBBER

	Control Mix 1	Mix 2 with SAPA 1/1	Mix 3 with NSA/1
NBR (Breon 1042)	100	100	100
ZnO	5	5	5
MC* Sulphur	1.5	1.5	1.5
Stearic acid	1.0	1.0	1.0
CBS	0.75	0.75	0.75
SRF Carbon Black	40	40	40
SAPA 1/1	-	2	-
NSA/1	-	-	2

* Denotes magnesium carbonate coated sulphur

Mixing was carried out in a laboratory size internal mixer (BR Banbury). The following conditions were followed throughout the mixing cycle:

Rotor speed : 60 rpm
 Fill factor : 0.75
 Ram pressure : 3 kg/cm²
 Cooling water : on

Mixing Cycle:

Operation:	Time:
Add NBR (Breon 1042) :	15"
Add $\frac{1}{2}$ SRF + Zinc oxide + SAPA 1/1 :	2'45"
Add $\frac{1}{2}$ SRF + Stearic acid :	4'45"
Clean :	5'
Dump :	5'30"

Sulphur and CBS accelerator were added on a cool rubber mill (450 mm x 225 mm and friction ratio 1.1:1). Each mix was then refined six times through a tight nip and finally sheeted off at approximately 3 mm thickness for preparation of test specimens.

Table 3.14 and Figure 3.16 summarise the results for the effect of SAPA 1/1 or NSA/1 as processing aids for the NBR rubber compound. The effect of SAPA 1/1 and NSA/1 on the Mooney viscosity is believed to be similar to that of a conventional processing aid. Ease of processability at all the processing stages; Banbury, mill and moulding, was very evident compared to the control mix which did not contain SAPA 1/1 or NSA/1.

From a comparison of the Mooney scorch values in Table 3.14, the fact that emerges is that a definite action of a chemical nature takes place; otherwise there can be no accounting for the high reduction in the scorch time of both SAPA 1/1 and NSA/1 containing compounds (reduction of about 69%). In order to explain this effect two possibilities have been suggested. The first one is

that possibly there is some free unreacted diamine, with SAPA 1/1 or NSA/1, which could accelerate the cure rate and reduce the scorch time. This hypothesis has not been found to be correct as after washing thoroughly the NSA/1 with water gave identical results to that reported in Figure 3.16. The second explanation is that possibly the heat developed during the mixing or the curing process causes a dissociation in SAPA 1/1 or NSA/1 into a diamine and fatty acids. Hence, the diamine will, of course, reduce the scorch time and the curing time. This hypothesis was found to agree with some experimental results, hence it will be discussed later in Chapter 5 in some detail.

Most of the physical properties are not affected by the presence of SAPA 1/1 or NSA/1. Noticeable increase in the hardness can be observed with NBR containing SAPA 1/1 or NSA/1.

The effect demonstrated by the surfactant (SAPA 1/1) and NSA/1 on the processing and physical properties of NBR rubber is similar to that of the CR rubber reported earlier. Therefore, surfactants improve considerably the processability of polar rubbers, such as NBR and CR, without affecting their vulcanisates physical properties. These surfactants have different effects, as expected, on the curing characteristics, particularly the scorch time, of these rubbers. This is mainly because CR rubber has fundamentally different vulcanisation chemistry from that of the NBR rubber.

TABLE 3.14
EFFECT OF SAPA 1/1 AND NSA/1 AS PROCESSING AIDS ON THE PROCESSING, CURING AND
PHYSICAL PROPERTIES OF THE NBR COMPOUND

	Control mix no processing aid (Mix 1)	2 phr SAPA 1/1 as a processing aid (Mix 2)	2 phr NSA/1 as a processing aid (Mix 3)
<u>Processing and Curing Properties:</u> Banbury Dump Temperature °C Mooney Viscosity ML (1+4) 100°C Mooney Scorch at 125°C (m) Optimum Curing Time, t ₉₀ , at 160°C (m)	124 68 16 22'30"	116 65 5 30	115 63 4'30" 30
<u>Physical Properties:</u> Tensile Strength (MPa) 100% Modulus (MPa) 300% Modulus (MPa) Elongation at break (%) Tear strength kN m ⁻¹ Compression set at 70°C for 48 hr % Hardness, IRHD Rebound Resilience, %	19 2.7 7.5 530 41 20 62 23	18.5 2.7 7.9 525 39 20 66 23	18.5 2.6 8 530 38 20 66 23
Vulcanisate appearance	Distorted and stressed moulded sheet with poor surface finish	Undistorted moulding with high gloss. Defect free surface	Undistorted moulding with high gloss. Defect free surface

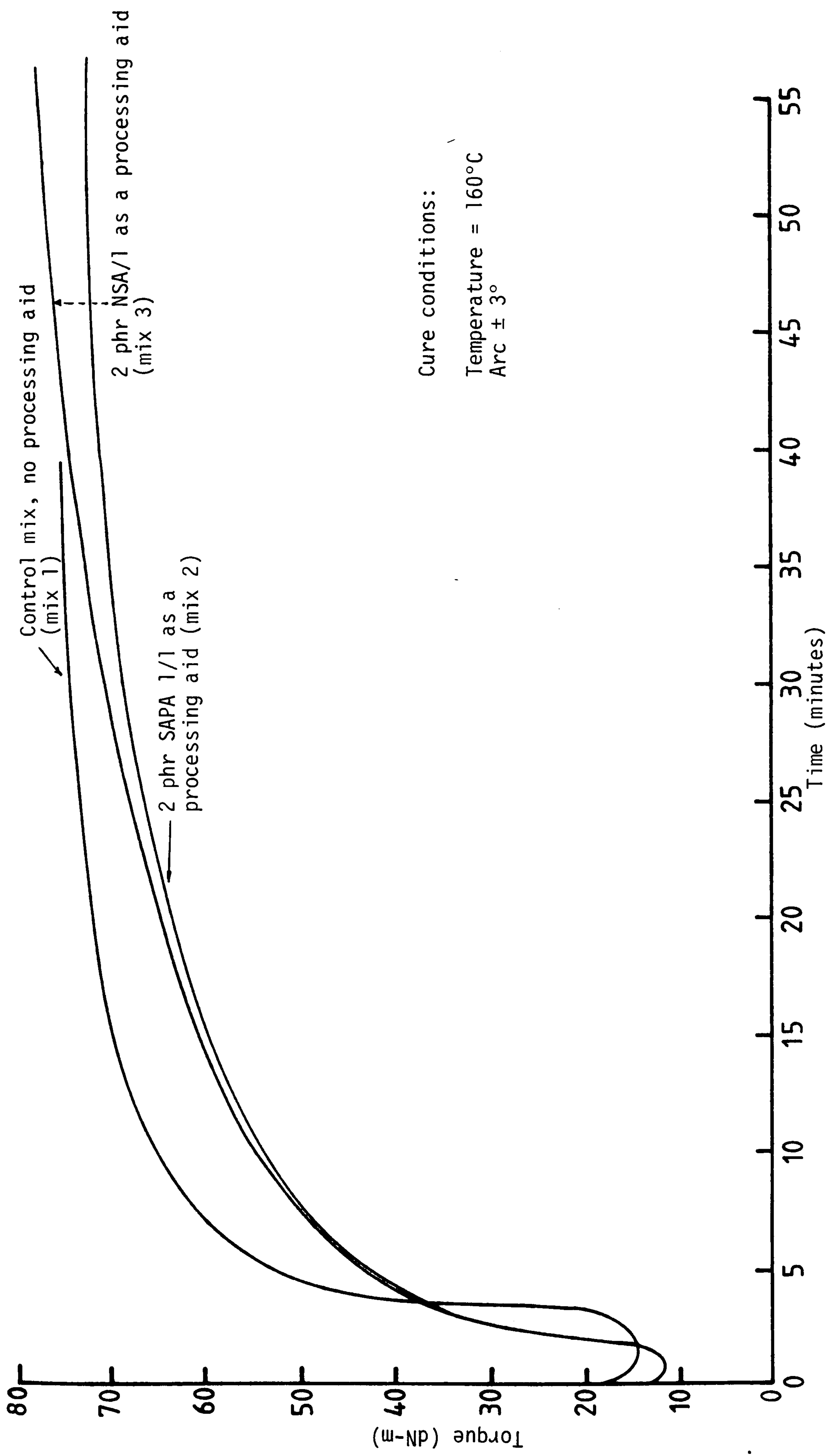


FIGURE 3.16: CURING BEHAVIOUR OF SAPA 1/1 AND NSA/1 IN NBR RUBBER

3.3.4 Styrene-Butadiene Rubber (SBR)

The performance of SAPA 1/1, NSA/1, SAPA 2/B and EBF-S as processing aids in a non-polar synthetic rubber, SBR, is reported here. This investigation also includes a comparison study between the performance of two conventional processing aids and two types of the EBF class of materials in SBR rubber. The formulations used in this investigation are shown below in Tables 3.15 and 3.16 respectively.

TABLE 3.15:

FORMULATIONS USED TO STUDY THE PERFORMANCE OF SAPA 1/1, NSA/1, SAPA 2/B AND EBF-S AS PROCESSING AIDS IN SBR RUBBER

	Control Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
SBR 1500	100	100	100	100	100
ZnO	4	4	4	4	4
Stearic Acid	2	2	2	2	2
S	2	2	2	2	2
CBS	0.25	0.25	0.25	0.25	0.25
Santocure MOR	0.25	0.25	0.25	0.25	0.25
Flectol-H	1	1	1	1	1
FEF Carbon Black	50	50	50	50	50
Dutrex 729 (aromatic oil)	5	5	-	-	-
SAPA 1/1	-	2	-	-	-
SAPA 2/B	-	-	2	-	-
NSA/1	-	-	-	2	-
EBF-S	-	-	-	-	2

TABLE 3.16:

FORMULATIONS USED TO EXAMINE THE PERFORMANCE OF EBF-0 AND EBF-S
VERSUS AROMATIC OIL AND STRUKTOL WB 212

	Mix 6	Mix 7	Mix 8	Mix 9	Mix 10
SBR 1500	100	100	100	100	100
ZnO	3	3	3	3	3
Stearic Acid*	2	2	2	-	-
Sulphur	2	2	2	2	2
Santocure MOR	1	1	1	1	1
DPG	0.7	0.7	0.7	0.7	0.7
Flectol-H	2	2	2	2	2
ISAF-Black	50	50	50	50	50
Aromatic Oil (Dutrex 729)	-	2	-	-	-
Struktol SWB212	-	-	2	-	-
EBF-0	-	-	-	2	-
EBF-S	-	-	-	-	2

* Stearic acid was omitted from mixes 9 and 10. The reason for this will be explained later in Chapter 5.

All compounds were mixed in a laboratory Banbury (Size BR) according to the following conditions and mixing cycle.

Mixing Conditions:

Rotor speed : 60 rpm
 Ram pressure : 2.7 kg/cm²
 Fill factor : 0.7
 Cooling water : full on

Mixing Cycle: *

Operation:	Time:
SBR 1500	: 0
$\frac{1}{2}$ Carbon black + $\frac{1}{2}$ processing oil (when present)	: 30"
$\frac{1}{2}$ Carbon black + $\frac{1}{2}$ processing oil (when present) + surfactant + zinc oxide + stearic acid + antioxidants	: 1'30"
Accelerators	: 2'30"
Clean	: 4'
Dump	: 4'15"

Sulphur was then added on a 150 mm x 300 mm mill. Curing and testing were carried out as before.

Die swell is measured using the Monsanto plastimeter, (the B270 Atkinson-Nancarrow Extrusion Plastimeter) which was designed to be used in conjunction with a tensometer. Rubber is extruded through a standard orifice of 2.344 mm diameter at a constant speed. Ageing of the rubber vulcanisates of Table 3.16 utilised the accelerated circulated hot air oven test method at the following conditions:

Air temperature	: 100°C
Period of the tests	: 7 days

Results and Discussion

Table 3.17 and Figure 3.17 summarise the results obtained for the effect of SAPA 1/1, SAPA 2/B, NSA/1 and EBF-S on processing, curing and vulcanisate properties in comparison with the control compound

* The above mixing cycle accounts for the effective mixing time only.

which contains no SAPA (mix 1, Table 3.15). These results show that the processing, curing, and physical properties of SAPA 1/1 and NSA/1 containing mixes are once again identical. The SAPA 2/B containing compound (mix 3, Table 3.15) differs from SAPA 1/1 and NSA/1 containing mixes (mixes 2 and 4, Table 3.15) only in its effect on the curing behaviour. As can be seen in Table 3.17 the compound containing SAPA 2/B (mix 3) has shorter scorch time and shorter optimum cure time, t_{90} , than all the other mixes. This behaviour of SAPA 2/B has been observed previously with natural rubber. However, all the mixes which contain the following types of material, namely: SAPA 1/1, SAPA 2/B, and NSA/1 are observed to possess superior processability over that of the control compound (mix 1 of Table 3.15). As can be seen in Table 3.17, the Banbury power consumption is reduced by 19% as well as the dump temperature, by about between 5-7°C, with compounds containing SAPA 1/1, SAPA 2/B and NSA/1 than that of the control compound (mix 1). These materials have also affected the curing properties; they improved the optimum curing time, t_{90} , by between 44-61% and the state of the cure by between 10-14%. However, compounds containing these materials showed considerable reduction in their processing safety; about 26% with SAPA 1/1 and NSA/1 containing mixes and about 63% with SAPA 2/B containing mix. The stress-strain properties are improved by these surfactants and prepared salt; tensile strength by between 10-15%, 100% modulus by between 18-32%. However, they have caused the tear strength to be reduced by about between 8-12%.

The EBF-S type of material, incorporated in mix 5, Table 3.15, has not shown the considerable improvements in processability at the Banbury mixing stage as that demonstrated by the SAPA series. The reason for this is thought to be due to its high melting point (about 140°C), which is thought to prevent the EBF-S material from melting at the Banbury mixing stage. Hence it could not show its effect as a processing aid at the mixing stage. The EBF-S material produced undistorted

stress free test specimen sheets when compression moulded hot from a cold thick round blank by the simple application of pressure at 160°C. The equivalent control rubber (mix 1) gave sheets possessing defects due to flow problems. The improvement in the flow of the EBF-S containing rubber is believed to be as a result of using a moulding temperature of 160°C as such a temperature will obviously cause the EBF-S material to melt and therefore act as a lubricant by improving the compound flow.

The curing and physical properties of the EBF-S containing compound (mix 5, Table 3.17) are similar to those obtained with the control compound (mix 1, Table 3.17).

EBF-S and EBF-O Versus Aromatic Oil and Struktol WB 212

The effect of 2 phr of EBF-S has not shown significant improvement in the processability at the Banbury mixing stage of the SBR rubber. Hence, it was decided to run another set of experiments to study the effect of equal levels (2 phr) of EBF-S and another derivative in this class namely EBF-O which has a low melting point, about 107-110°C, aromatic oil (Dutrex 729 UK), and the processing additive Struktol WB 212. These were compared with a control mix which does not contain processing additives (see Table 3.16 for the formulations).

Therefore, this investigation is designed to assess the relative efficiency of EBF-S and EBF-O versus aromatic oil and Struktol WB 212. In Table 3.18 and Figure 3.18 are given the processing, curing, and physical properties of all the mixes under investigation. From a comparison of the figures in the table, it can be observed that EBF-O containing mixes have a better softening action than the aromatic oil mix. The EBF-O material reduced the total work input at the Banbury mixing stage by 61 mJ/m³ and reduced the dump temperature by 6°C from that of the aromatic oil containing compound (mix 7). It also showed

higher softening action than EBF-S mixes (mix 10) but similar to that of the Struktol WB 212 compound (mix 8). The die swell of EBF-0 and EBF-S containing mixes are better than all the other mixes by between 7-11%.

The curing behaviour is almost similar for all the mixes except that of the non-processing aid containing compound (mix 6) which showed a higher stage of cure (see Figure 3.18). The Struktol WB 212 containing mix showed better processing safety than all the other mixes by between 11-20% without affecting the cure rate. The physical properties of all the mixes are similar except the compression set results. The compound which contained no processing additives (mix 6) has a compression set value lower than all the other mixes by between 11-20%. This result confirms the previous observation made that the zero processing aid containing compound reaches a higher state of cure than all the other mixes containing processing additives. The EBF-S and EBF-0 containing mixes have the next best values of 46% and 44% compression sets respectively. The EBF-S containing compound, once again, tended to have a lower softening action, at the Banbury mixing stage, than all the other processing aid containing mixes. The reason for such behaviour was explained in the first part of this study. The aromatic oil has the next lowest softening action. This is possibly because insufficient aromatic oil has been added to the SBR mix which contains 50 phr of ISAF black.

Table 3.19 summarises the results of the effect of hot air ageing on the vulcanisates of all mixes given in Table 3.16. These results demonstrate quite clearly that vulcanisates containing EBF-0 or EBF-S have significantly better resistance to thermal oxidation than all the other vulcanisates. This is believed to be due to the formation of a thin film of EBF-S or EBF-0 on the surface of their vulcanisates. These films are thought to help the rubber resist ageing which because of their high melting point, EBF-0 $\approx 107-110^{\circ}\text{C}$, EBF-S $\approx 140^{\circ}\text{C}$, form a bloom barrier on the rubber surface which prevents the ingress of oxygen.

During the tensile testing of the aged samples which contain EBF-S and EBF-0 materials, the following features were observed:

- i) A thin film of the EBF-S material on the vulcanisate aged sample surface has been observed.
- ii) No thin film of the EBF-0 material on the aged sample surface was observed.

This was believed to be due to the presence of some unsaturation in the EBF-0 material (see its chemical structure in Table 3.1) which is thought to promote adhesion of the EBF-0 with the rubber and hence, reduces blooming. Therefore, a very thin film might have formed which could not be seen by the naked eye.

Considering the results as a whole demonstrated by the EBF-S and EBF-0 materials, it can be seen that only advantages and no adverse effects have resulted from using these substances as processing aids. Hence, these materials can be regarded as unique additives for another reason which is that recipes containing them do not need to contain stearic acid (see mixes 9 and 10, Table 3.16). This dual action as processing aid and cure activator (i.e. no stearic acid is needed) demonstrated by the EBF-S and the EBF-0 is discussed later in Chapter 5.

TABLE 3.17

EFFECT OF SAPA 1/1, SAPA 2/B, NSA/1 AND EBF-S AS PROCESSING ADDITIVES IN SBR RUBBER
[COMPOUNDS BASED ON FORMULATIONS SHOWN IN TABLE 3.15]

	Control Mix 1	SAPA 1/1 Mix 2	SAPA 2/B Mix 3	NSA/1 Mix 4	EBS Mix 5
<u>Processing and Curing Properties:</u> Power consumption kWh Unit work mJ/m ³ Start temperature °C Dump temperature °C Mooney viscosity ML (1+4)100°C Mooney scorch, t ₅ at 125°C (m) Optimum curing time, t ₉₀ at 160°C (m)	0.25 764 20 125 62 67' 32'	0.21 642 22 120 62 49'30" 18'	0.215 657 20 121 62 25' 12'30"	0.215 657 21 122 62 48' 18'	0.25 764 19 125 62 65' 31'
<u>Physical Properties:</u> Ultimate tensile strength MPa % Elongation at break 100% Modulus MPa 300% Modulus MPa Tear strength kN m ⁻¹ Hardness, IRHD Rebound resilience, %	20 525 2.8 10.6 59 60 50	23 500 3.5 11.5 54 64 51	22 500 3.7 11 52 64 51	22.5 510 3.3 11 54 65 51	19.4 530 2.7 10.5 57 61 50

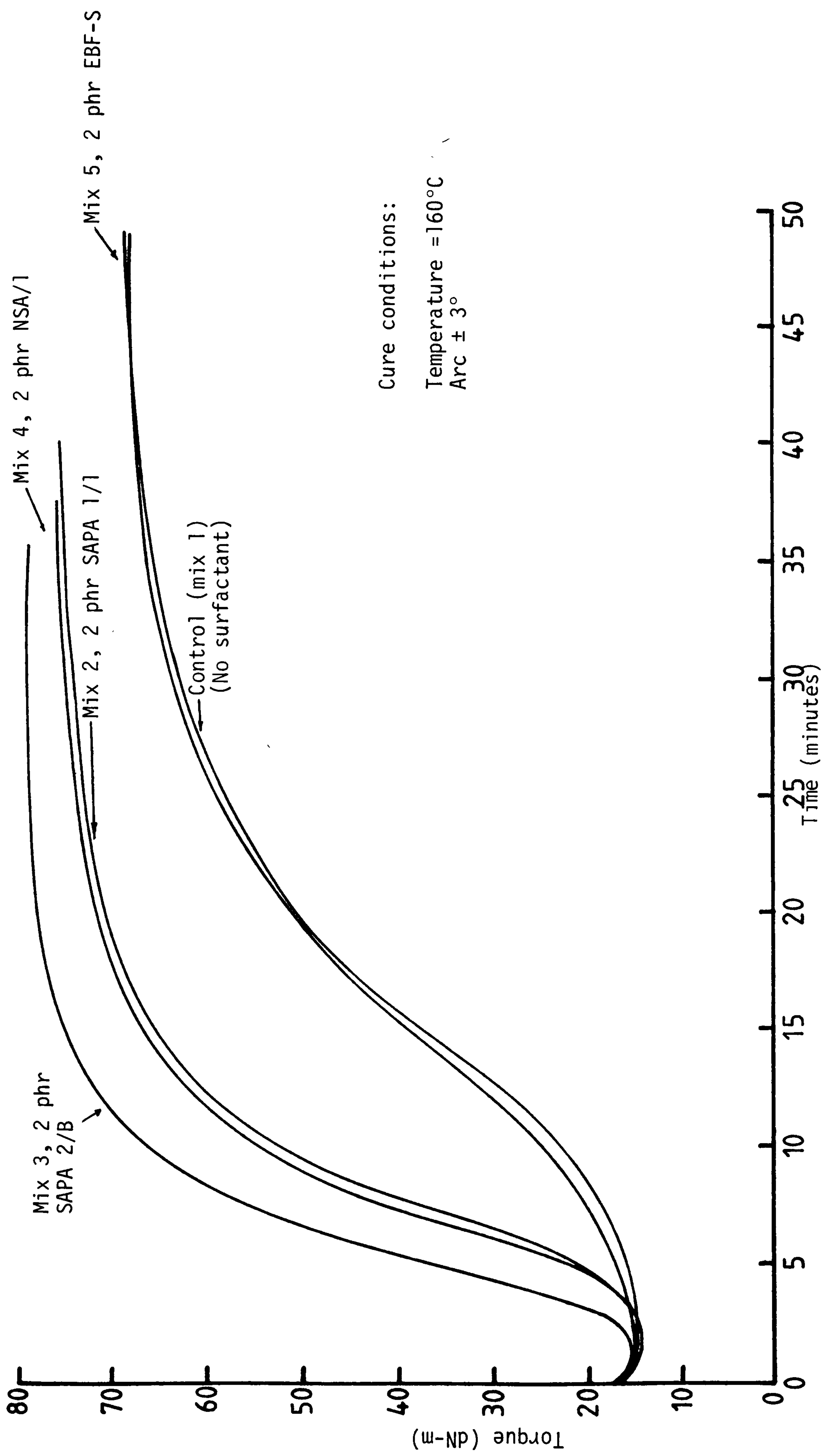


FIGURE 3.17: EFFECT OF SAPA 1/1, SAPA 2/B, NSA/1 AND EBF-S AS PROCESSING AIDS ON SBR RUBBER VULCANISATION (FORMULATIONS ARE SHOWN IN TABLE 3.15)

TABLE 3.18
EFFECT OF EBF-S AND EBF-0 AS PROCESSING AIDS FOR SBR RUBBER IN COMPARISON WITH AROMATIC OIL
AND STRUKTOL WB 212

	Control No processing aid Mix 6	2 phr Aromatic Oil (Dutrex 729) Mix 7	2 phr Struktol SWB 212 Mix 8	2 phr EBF-0 Mix 9	2 phr EBF-S Mix 10
<i>Processing and Curing Properties:</i> Energy consumed at the Banbury mJ/m ³ Dump temperature °C Mooney viscosity ML(1+4)100°C Die swell % at 70°C Mooney scorch, t ₅ , at 125°C (m) Optimum curing time, t ₉₀ , at 160°C (m)	1101 129 75 27 28 15	1055 126 72 27 28 10	978 119 70 28 31 10	994 120 70 25 27 10	1044 125 73 25 26 10
<i>Physical Properties:</i> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa % Elongation at break Compression set at 100°C for 2 days % Tear strength kN m ⁻¹ Hardness, IRHD Rebound resilience, %	24.8 3.8 16.4 400 39 43 77 39	23.4 3.6 14 430 48 49 75 37	22.6 3.2 15 450 49 49 75 38	24.5 3.4 15 430 44 44 75 39	24.8 3.9 15.2 430 46 46 75 40

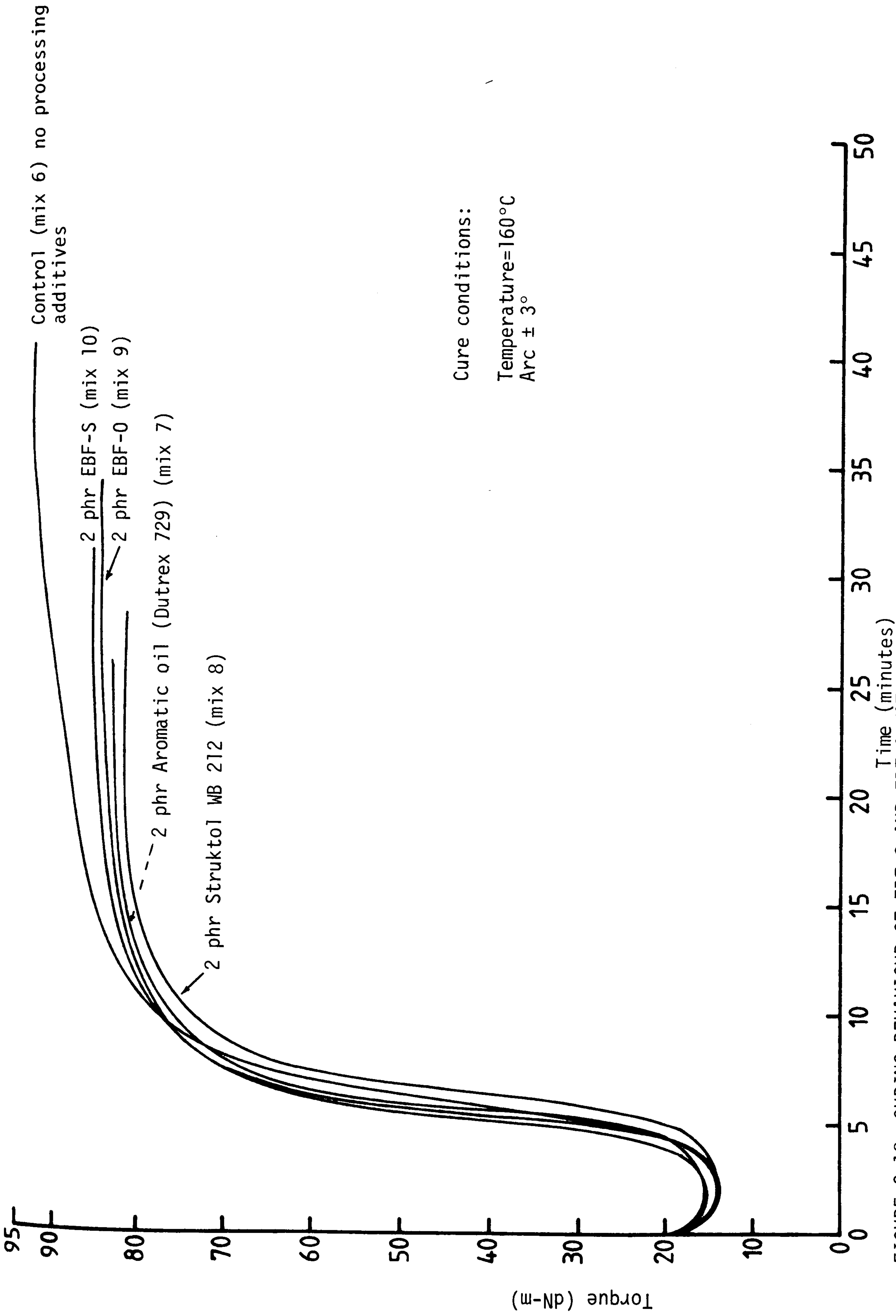


FIGURE 3.18: CURING BEHAVIOUR OF EBF-S AND EBF-0 MATERIALS IN COMPARISON WITH AROMATIC OIL AND STRUKTOL WB 212

TABLE 3.19

AGEING BEHAVIOUR OF EBF-S AND EBF-O IN COMPARISON WITH AROMATIC OIL AND STRUKTOL WB 212

	Mix 6		Mix 7		Mix 8		Mix 9		Mix 10	
		% Change		% Change		% Change		% Change		% Change
Tensile Strength MPa	19	-23.4	17	-27	17	-25	22.6	-8	23	-7
100% Modulus MPa	8.8	+132	9.6	+167	9.5	197	6.5	91	7.8	100
% Elongation at break	173	-57	158	-63	158	-65	264	-39	250	-42
Tear Strength kN m ⁻¹	28	-35	31.5	-36	22	-55	37	-16	35	-20
Hardness, Points Change	83	+6	84	+9	84	+9	77	+2	77	+2
Rebound Resili- ence %	40	+3	38	+3	39	+3	42	+8	40	-

3.3.5 Polybutadiene Rubber (BR-CIS)

Polybutadiene rubber (BR) is regarded as a member of the non-polar rubber class. It is generally used as a blend with other rubbers. This is mainly because of its poor processing and mechanical properties. For these reasons BR rubber was selected to be studied in combination with SAPA 1/1 and NSA/1.

The formulations utilised throughout this investigation are given below in Table 3.20.

TABLE 3.20:

BR RECIPES USED TO EXAMINE THE EFFECT OF SAPA 1/1 AND NSA/1 AS COMPOUNDING INGREDIENTS

	Control Mix 1	With SAPA 1/1 Mix 2	With NSA/1 Mix 3
Polybutadiene	100	100	100
Sulphur	2	2	2
ZnO	4	4	4
Stearic Acid	2	2	2
DPG	0.75	0.75	0.75
Flectol-H	1.5	1.5	1.5
Dutrex 729 (Aromatic oil)	5	5	5
SAF Black	50	50	50
SAPA 1/1	-	2	-
NSA/1	-	-	2

All the BR rubber mixes, given in Table 3.20, were prepared using a laboratory BR type Banbury operated at the following conditions:

Rotor speed : 60 rpm
Ram pressure : 2.5 kg/cm²
Fill factor : 0.75
Cooling water : Full on

The mixing cycle adopted for all mixes was:

Operation:	Time:
BR rubber + $\frac{1}{2}$ carbon black + $\frac{1}{2}$ Processing oil	: 0
$\frac{1}{2}$ Carbon black + $\frac{1}{2}$ Processing oil + SAPA 1/1	: 1'30"
Accelerator	: 3'00"
Clean	: 4'15"
Dump	: 4'30"

Results and Discussion

Table 3.21 and Figure 3.19 summarise the results of the effects of SAPA 1/1 and NSA/1 on the processing, curing and physical properties of a typical BR compound compared with a control mix which did not contain SAPA 1/1 or NSA/1. Processability, at the Banbury mixing stage of SAPA 1/1 and NSA/1 containing mixes was superior to that of the control compound (mix 1). The inclusion of SAPA 1/1 or NSA/1 caused a reduction in the total energy (unit work) of about 20% and a reduction in the mixing dump temperature of about between 22-23⁰C. Processability at the mill mixing stage of the control compound (mix 1, Table 3.20) was observed to be very poor; the mix tended to sag and bag on the mill with formation of high amounts of nerve. No improvement in the processability at the mill mixing stage was observed to occur even at lower mill temperature (about 30⁰C). This was believed to be as a result of the high Mooney viscosity of the control compound (about 105). SAPA 1/1 and NSA/1 containing mixes (mixes 2 and 3) have relatively lower Mooney viscosities (of between 9-10 units) than the control compound (mix 1). This reduction in the

Mooney viscosity has resulted in a considerable reduction in the amount of nerve formed in comparison to the control compound which did not contain SAPA 1/1 or NSA/1. Also some improvement was observed to take place at this, the mill mixing stage, with SAPA 1/1 and NSA/1 containing mixes in comparison with the control compound (mix 1). However, considerable improvement in the appearance of vulcanisates was observed with SAPA 1/1 and NSA/1 containing compounds which all had a glossy surface finish and gave test sheets with no surface defects or stresses. The equivalent control compound (mix 1) gave moulded sheets possessing flow defects due to flow problems.

The inclusion of SAPA 1/1 or NSA/1 has improved the optimum curing time t_{90} by about 18% from that of the control compound (mix 1) which did not contain SAPA 1/1 or NSA/1. However, these additives have reduced the processing safety (as judged by Mooney scorch) dramatically (by about 50% from that of the control compound). However, a scorch time of 15-16 minutes is usually considered industrially acceptable.

The inclusion of SAPA 1/1 or NSA/1 increases the 100% modulus (30%), 300% modulus (28%) and the hardness (20%) over the control compound (mix 1) which did not contain SAPA 1/1 or NSA/1. The 20% increase in the hardness agreed with the previous suggestion made earlier, Section 3.3.5, that SAPA 1/1 may cause all the sulphur to be involved in the crosslinking process.

According to these results addition of SAPA 1/1 or NSA/1 to a BR rubber compound is beneficial particularly when processability at the Banbury and moulding stages are considered. Also their presence has no deterrent effect on the other properties such as the curing and physical properties.

TABLE 3.21
EFFECT OF SAPA 1/1 AND NSA/1 ON PROCESSING, CURING AND PHYSICAL PROPERTIES OF A CIS-
POLYBUTADIENE COMPOUND [FOR FORMULATIONS SEE TABLE 3.20]

	Control Mix 1	2 phr SAPA 1/1 Mix 2	2 phr NSA/1 Mix 3
<u>Processing and Curing Properties:</u> Power Consumption kWh Unit Work mJ/m ³ Start temperature °C Dump temperature °C Mooney viscosity ML(1+4) 100°C Mooney scorch t ₅ at 125°C (m) Optimum curing time t ₉₀ , at 160°C (m)	0.21 642 20 120 105 31 45	0.175 535 22 95 95 15 38	0.175 535 20 98 96 16 36
<u>Physical Properties:</u> Ultimate Tensile Strength MPa % Elongation at break 100% Modulus MPa 300% Modulus MPa Tear Strength (kN m ⁻¹) Hardness IRHD Rebound Resilience %	14 530 2 5.8 46 59 53	14.5 490 2.5 7.4 49 71 56	15 490 2.7 7.5 48 70 55

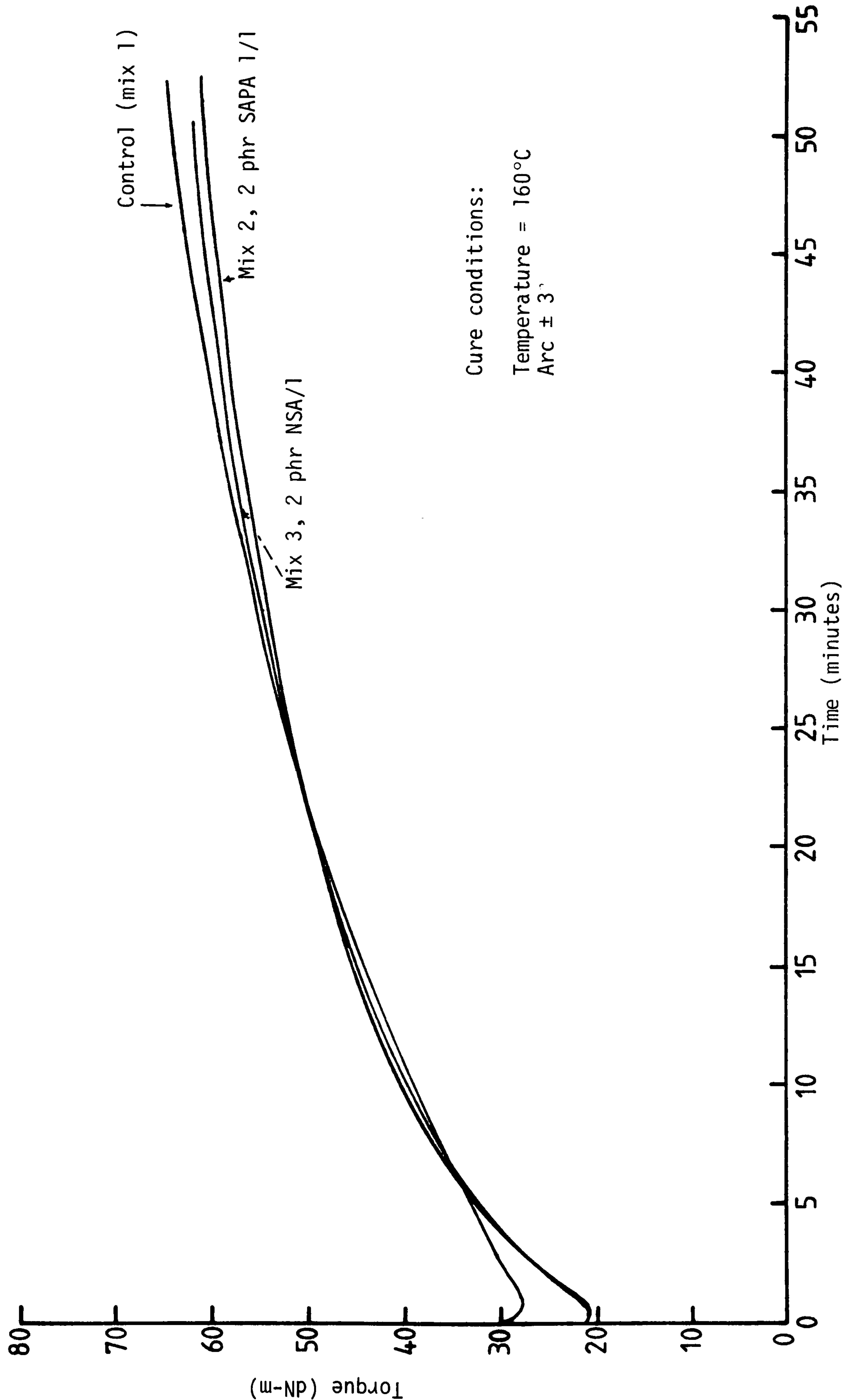


FIGURE 3.19: EFFECT OF SAPA 1/1 AND NSA/1 ON CURING PROPERTIES OF BR RUBBER BASED ON FORMULATION IN TABLE 3.20

3.4 Conclusion

Accordingly the results demonstrated for the various rubber classes show that the surfactants and the other materials given in Table 3.1 all function as excellent processing aids or flow additives when used in low proportions (ca. 0.5-2.0 phr). With certain rubbers such as NR, and NR/SBR blends these materials increase Mooney viscosity and hence green strength; in other rubbers such as SBR, CR and NBR they function as a flow additive only and do not increase the green strength.

Surfactants are universal in their effect as processing flow additives with all the common rubbers; they provide excellent green strength dimensional stability with carbon black and silica filled rubbers; they also provide excellent roll release and mould release properties.

Curing properties are enhanced by the inclusion of these materials with almost all the various types of rubber studied. However, their effect on processing safety of any one particular rubber compound is dependent on the type of the surfactant or the salt itself. From the results demonstrated in this chapter, it is shown that the effect of these materials on the scorch time can be arranged in the following order:

SAPA 2 > SAPA 1 or NS > EBF

Greatest effect
on cure rate

Lowest effect
on cure rate

The physical properties of vulcanisates of non-polar rubbers such as NR, NR/SBR, SBR and BR are all increased by the inclusion of the SAPA 1, SAPA 2, and NS series. This increase in the physical properties was found to be due to better filler dispersion. The EBF type of

materials, particularly the EBF-S and EBF-0 types, were found not to have any adverse effect on the physical properties of NR/SBR blends, and SBR rubber vulcanisates. The presence of these diamide compounds was also found to have no adverse effect on the ageing properties of those rubbers in which they were incorporated (Table 3.16). However, some of the EBF series, the EBF-S and EBF-0, were found to have improved considerably the ageing behaviour of the SBR rubber compound (Table 3.19) and therefore apparently make an anti-oxidant contribution to stability.

CHAPTER 4
SURFACTANTS AS CURE ACCELERATORS FOR
TRUCK TYRE SIDEWALL COMPOUNDS

Introduction

The organic accelerators discovered in the early 1900's revolutionised the rubber industry. They cut curing times to a fraction of their former periods and also they improved the quality of the compound by increasing the resistance of rubber to heat, abrasion, oxidation, ageing etc.

In order to maximise the efficiency of an organic accelerator, almost always the presence of organic and/or inorganic activators is essential. Stearic acid is normally used in combination with zinc oxide to increase the vulcanisation rate by activating the accelerator so that it performs more effectively. The mechanisms involved have been explained in detail in Chapter 2 (section 1.3.2, equations 1.21-1.30).

It has been discovered that the SAPA 1/1 surfactant, which showed excellent behaviour as a processing aid for various rubbers (Chapters 2 and 3), can act also as an accelerator for an NR/SBR rubber compound. Uniquely this accelerator, SAPA 1/1, was found to function without the conventional cure activator system i.e. zinc oxide and stearic acid. This discovery is reported in this chapter.

All the rubber mixes prepared in this chapter followed the same mixing procedure adopted earlier in Section 2.1.1, unless otherwise stated.

4.1 Elimination of the Cure Activation and Acceleration Systems From a Rubber Formulation

It was observed from the results of Table 2.3, section 2.1, that the processing behaviour and the physical properties of SAPA 1/1 containing NR/SBR compound were excellent compared to all the other plasticisers and processing additives. However, the scorch time of SAPA 1/1 mixes was observed to be very short at the relatively high proportions of SAPA 1/1 in comparison with all the other plasticisers and processing aids. Hence, an investigation, using the base compound of NR/SBR rubber, was conducted to try and resolve this scorch problem. The method was first to omit the zinc oxide/stearic acid activator system and next to reduce the concentration of the conventional organic accelerator system in the rubber formulation; initially some PVI (N-cyclohexylthiophthalimide) retarder was retained to evaluate this as a cure retardation method.

The formulations used in this investigation are given in Tables 4.1 and 4.2 respectively.

Results and Discussion

Effect of PVI Retarder

Table 4.3 and Figure 4.1 summarise the results obtained for the effect of two levels of PVI; N-cyclohexylthiophthalimide retarder on the curing behaviour, particularly the optimum curing time, t_{90} , and on the Mooney scorch of the NR/SBR compound containing 7.5 phr SAPA 1/1. These results clearly indicate that the PVI retarder did not show any considerable effect, at both the levels used, on the curing behaviour and the Mooney scorch of the NR/SBR compound. These results do not therefore agree with the results obtained by Leib and co-workers[72] that PVI is a highly effective retarder with all sulphenamide accelerator systems. This change from the previous situation may be due to the presence of the SAPA 1/1 which might

have altered the vulcanisate mechanism. This means that the pre-vulcanisation inhibitor PVI is ineffective and not required in a mix which uses a combination of sulphenamide accelerators and a SAPA 1/1 surfactant.

Elimination of the Activators and Accelerator Systems from the Rubber Formulation

Table 4.4 and Figure 4.2 show the behaviour of an NR/SBR compound which contains 7.5 phr of SAPA 1/1 when the activators, ZnO/stearic acid, and the accelerators, CBS/MOR, are eliminated from the formulations. Unexpectedly, the elimination of zinc oxide and stearic acid from mix 4, Table 4.2, has resulted in shorter scorch times and optimum curing time, t_{90} (by about one minute in both cases), compared with its control compound which contains ZnO and stearic acid. More surprisingly, the elimination of the main accelerators systems, CBS and MOR from mixes 5 and 6, has reduced the scorch time and the optimum curing time, t_{90} , even further without affecting the state of cure.

The compound which has neither cure activators i.e. ZnO and stearic acid, nor cure accelerators, CBS and MOR, was found to cure well by SAPA 1/1 only (comparing mix 6 with mix 1 in Figure 4.2).

This remarkable behaviour of SAPA 1/1 as a combined cure activator/accelerator indicated that it can cure an NR/SBR compound without the presence of activators and accelerators. However, further investigations were considered necessary to confirm these observations.

TABLE 4.1

FORMULATIONS USED TO EXAMINE THE EFFECT OF PVI RETARDER
IN THE NR/SBR COMPOUND CONTAINING SAPA 1/1

	Control Mix 1	0.25 phr PVI Mix 2	0.5 phr PVI Mix 3
NR (SMR 20)	30	30	30
SBR 1500	70	70	70
Zinc oxide	4	4	4
Stearic acid	2	2	2
Sulphur	2	2	2
CBS	0.25	0.25	0.25
Santocure MOR*	0.25	0.25	0.25
IPPD	2	2	2
Flectol-H	0.75	0.75	0.75
Microcrystalline wax	3	3	3
FEF Carbon Black	51	51	51
SAPA 1/1	7.5	7.5	7.5
Santogard PVI**	-	0.25	0.5

* Monsanto trade name for 2-(morpholinothio) benzothiazole sulphenamide

** Monsanto trade name for N-cyclohexylthiophthalimide

TABLE 4.2

FORMULATIONS USED TO EXAMINE THE EFFECT OF ELIMINATING THE
CURE ACTIVATORS AND ACCELERATORS SYSTEMS FROM RUBBER

Mix No	1	4	5	6
	← SAPA 1/1 = 7.5 phr →			
	Control ZnO = 4 phr Stearic acid = 2phr CBS=0.25phr MOR=0.25phr	ZnO = 0 Stearic acid = 0 CBS=0.25phr MOR=0.25phr	ZnO = 0 Stearic acid = 0 CBS = 0 MOR=0.25phr	ZnO = 0 Stearic acid = 0 CBS = 0 MOR=0
Natural Rubber SMR 20)	30	30	30	30
SBR 1500	70	70	70	
Sulphur	2	2	2	2
IPPD	2	2	2	2
Flectol-H	0.75	0.75	0.75	0.75
Microcrystalline wax	3	3	3	3
FEF Black	51	51	51	51
SAPA 1/1	7.5	7.5	7.5	7.5
ZnO	4	-	-	-
Stearic acid	2	-	-	-
CBS	0.25	0.25	0.25	-
Santocure MOR*	0.25	0.25	-	-

* Monsanto trade name for 2(morpholinothio)benzothiazole sulphenamide

TABLE 4.3

EFFECT OF PVI RETARDER ON OPTIMUM CURING TIME, t_{90} ,
AND MOONEY SCORCH OF AN NR/SBR COMPOUND CONTAINING 7.5 phr SAPA 1/1

	Control Mix 1	0.25 phr PVI Mix 2	0.5 phr PVI Mix 3
Optimum curing time, t_{90} at 160°C (m)	7'30"	8'30"	10'
Mooney scorch, t_5 , at 125°C (m)	4'	4'30"	6'

TABLE 4.4

EFFECT OF ELIMINATING THE CURE ACTIVATORS AND ACCELERATORS
SYSTEMS FROM NR/SBR COMPOUND CONTAINING 7.5 phr SAPA 1/1

	Control Mix 1	No ZnO and stearic acid Mix 4	No CBS Mix 5	No CBS and MOR Mix 6
Optimum curing time, t_{90} at 160°C (m)	7'30"	6'30"	6'30"	6'
Mooney scorch, t_5 , and 125°C (m)	4'	3'	3'	3'

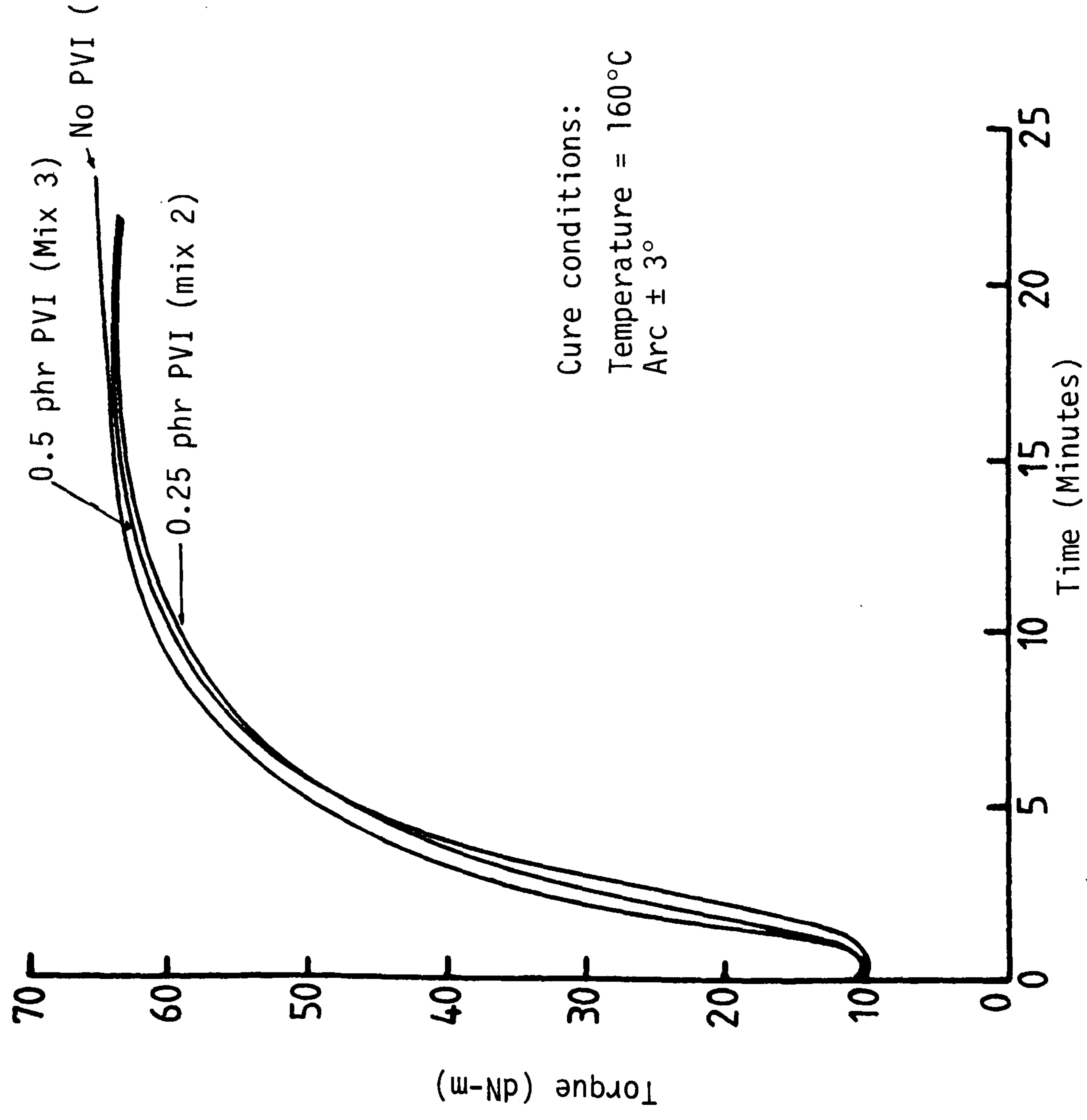


FIGURE 4.1: EFFECT OF PVI PREVULCANISATION RETARDER ON THE CURING BEHAVIOUR OF NR/SBR COMPOUND CONTAINING 7.5 phr SAPA 1/1

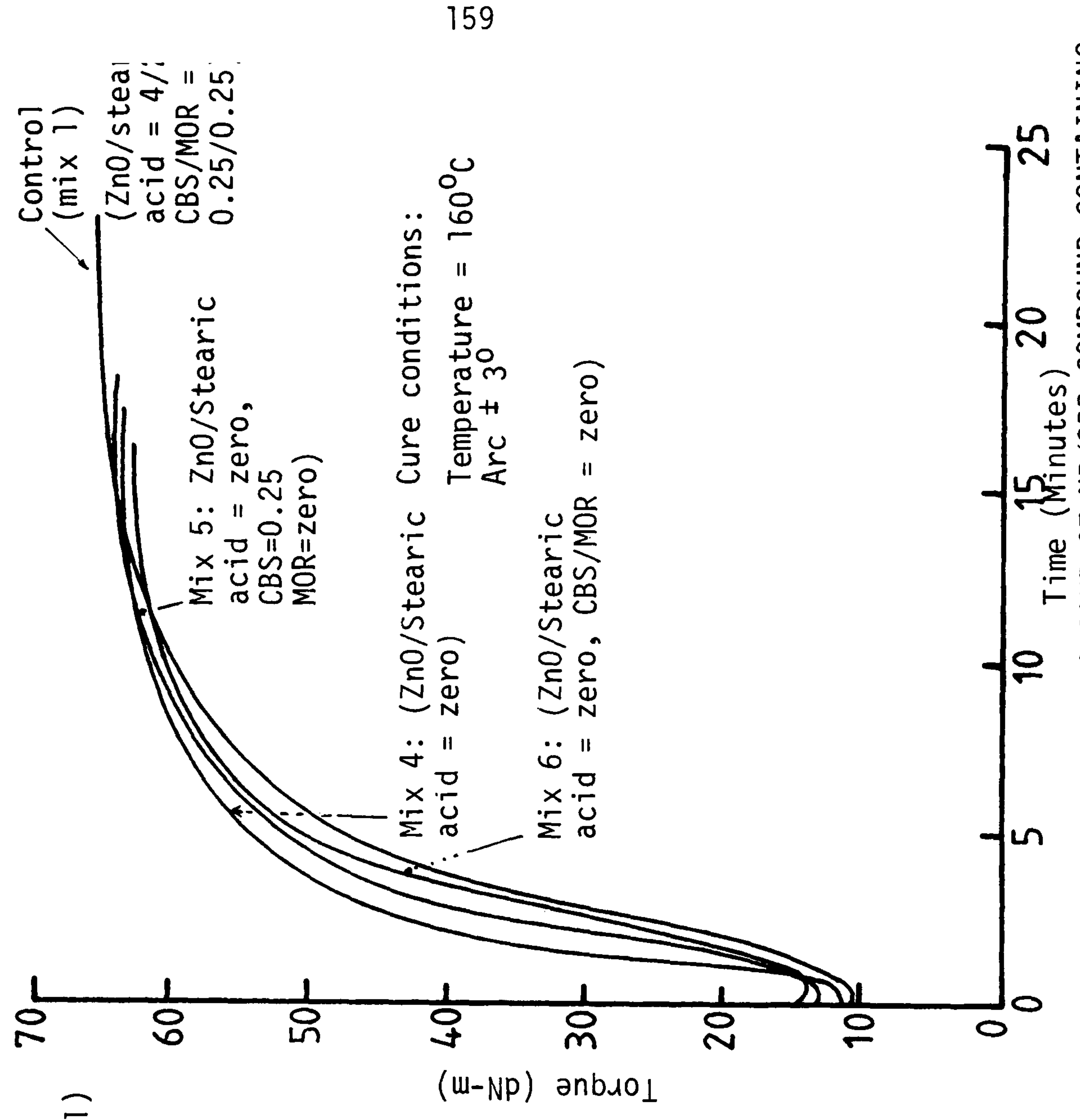


FIGURE 4.2: CURE BEHAVIOUR OF NR/SBR COMPOUND CONTAINING 7.5 phr SAPA 1 AND THE EFFECT OF ELIMINATING THE ACTIVATORS AND ACCELERATOR SYSTEMS

4.2 SAPA 1/1 as a Combined Cure Activator and Accelerator System for NR/SBR Compound

The curing behaviour demonstrated by the SAPA 1/1/sulphur curing system in the NR/SBR compound (Section 4.1) was observed to be similar to the curing behaviour obtained by the conventional CBS/MOR/ZnO/Stearic acid/Sulphur curing system. In order to confirm this observation it was decided to design a series of experiments to find out whether SAPA 1/1 can be used as cure activator and accelerator systems in general for NR/SBR compounds. It was also decided to examine the effect of the Santogard PVI retarder on such curing systems (i.e. the sulphur/SAPA 1/1 system).

The formulations used in this investigation are given below in Table 4.5:

TABLE 4.5:

FORMULATIONS USED TO EXAMINE VARIOUS LEVELS OF SAPA 1/1 AS A CURE ACTIVATOR/ACCELERATOR SYSTEM

Mix No	1	2	3	4	5
	7.5 phr SAPA 1/1	3.0 phr SAPA 1/1	2.0 phr SAPA 1/1	1.5 phr SAPA 1/1	1.0 phr SAPA 1/1
NR (SMR 20)	30	30	30	30	30
SBR 1500	70	70	70	70	70
Sulphur	2	2	2	2	2
SAPA 1/1	7.5	3	2	1.5	1
Santogard PVI	0.5	0.5	0.25	-	-
Flectol-H	0.75	0.75	0.75	0.75	0.75
IPPD	2	2	2	2	2
Microcrystalline wax	3	3	3	3	3
FEF Carbon black	51	51	51	51	51

A master batch of NR/SBR/carbon black (30/70/51) was prepared in a laboratory size internal mixer (BR Banbury) for an effective mixing of 3 minutes at rotor speed of 70 rpm. The other ingredients including SAPA 1/1 were mixed with the master batch as in the formulations of Table 4.5 on a two-roll mill (300 x 150 mm, friction ratio 1.1:1). Each mix was then refined 6 times through a tight nip and then sheeted off at a thickness of about 3 mm ready for further preparations.

Results and Discussion

Table 4.6 and Figure 4.3 summarise the results for the effect of various levels of SAPA 1/1 as cure activators/accelerator systems on the processing, curing and physical properties of the NR/SBR rubber compound. These results show that relatively high SAPA 1/1 proportions (e.g. 7.5 phr) give short scorch times (4.5 minutes). Reducing the SAPA 1/1 level to 1-3 phr level increases the scorch time, to 17-13 minutes which is usually considered industrially acceptable, and the optimum curing time, t_{90} , from 10'30" to 23'. This behaviour of SAPA 1/1 follows the general behaviour usually observed by most of the conventional organic accelerators. Additionally the effect of various concentrations of SAPA 1/1 on the curing behaviour has been further examined and will be discussed in Section 4.7.

The results also show that the prevulcanisation inhibitor PVI can be omitted from the formulations as its effect is not beneficial.

The physical properties remain consistently good over the range of SAPA 1/1 proportions used, 1-7.5 phr, with only a reduction in hardness becoming apparent at the higher (7.5 phr) SAPA 1/1 levels.

These results, therefore, confirm the previous observation made earlier in Section 4.1 that by using SAPA 1/1, it is possible to eliminate the

conventional cure activation system (ZnO and stearic acid) and the delayed action accelerators (CBS and MOR) and, the prevulcanisation inhibitor PVI, whilst retaining the principal crosslinking agent, sulphur, at the modest proportion of 2 phr.

TABLE 4.6

ELIMINATION OF THE CONVENTIONAL CURE ACTIVATOR AND ACCELERATOR SYSTEM FROM SAPA 1/1 CONTAINING RUBBER FORMULATIONS [BASE MIX AS SHOWN IN TABLE 4.5]

Mix No	Reducing SAPA				
	1	2	3	4	5
	7.5 phr SAPA 1/1	3 phr SAPA 1/1	2 phr SAPA 1/1	1.5 phr SAPA 1/1	1 phr SAPA 1/1
No conventional accelerator/activator present in the mix	*PVI = 0.5 phr ZnO = 0 **St.A = 0 CBS = 0 MOR = 0	PVI = 0.5 phr ZnO = 0 St.A = 0 CBS = 0 MOR = 0	PVI = 0.25 phr ZnO = 0 St.A = 0 CBS = 0 MOR = 0	PVI = 0 phr ZnO = 0 St.A = 0 CBS = 0 MOR = 0	PVI = 0 phr ZnO = 0 St.A = 0 CBS = 0 MOR = 0
Mooney scorch at 125°C (t ₅) mins	4'30"	13	12	12	17
Mooney Viscosity ML (1+4)100°C	38	41	44	44	46
Optimum curing time, t ₉₀ , at 160°C mins	5'30"	10'30"	19	20	23
Tensile Strength MPa % Elongation at break 100% Modulus MPa 300% Modulus MPa Tear Strength kN m ⁻¹ Hardness, IRHD Rebound Resilience, %	<i>Processing and Curing Properties</i>				
	<i>Physical Properties</i>				
	15	17	17.5	17	16.3
	580	520	500	460	480
	2.2	2.5	2.6	3.0	3.3
	7.0	8.5	9.5	9.5	8.8
	41	39	35	30	30
	55	59	59	60	60
	47	46	47	46	45

* PVI = Pre Vulcanisation inhibitor (retarder). Santoguard (Monsanto)

** St.A = Stearic acid

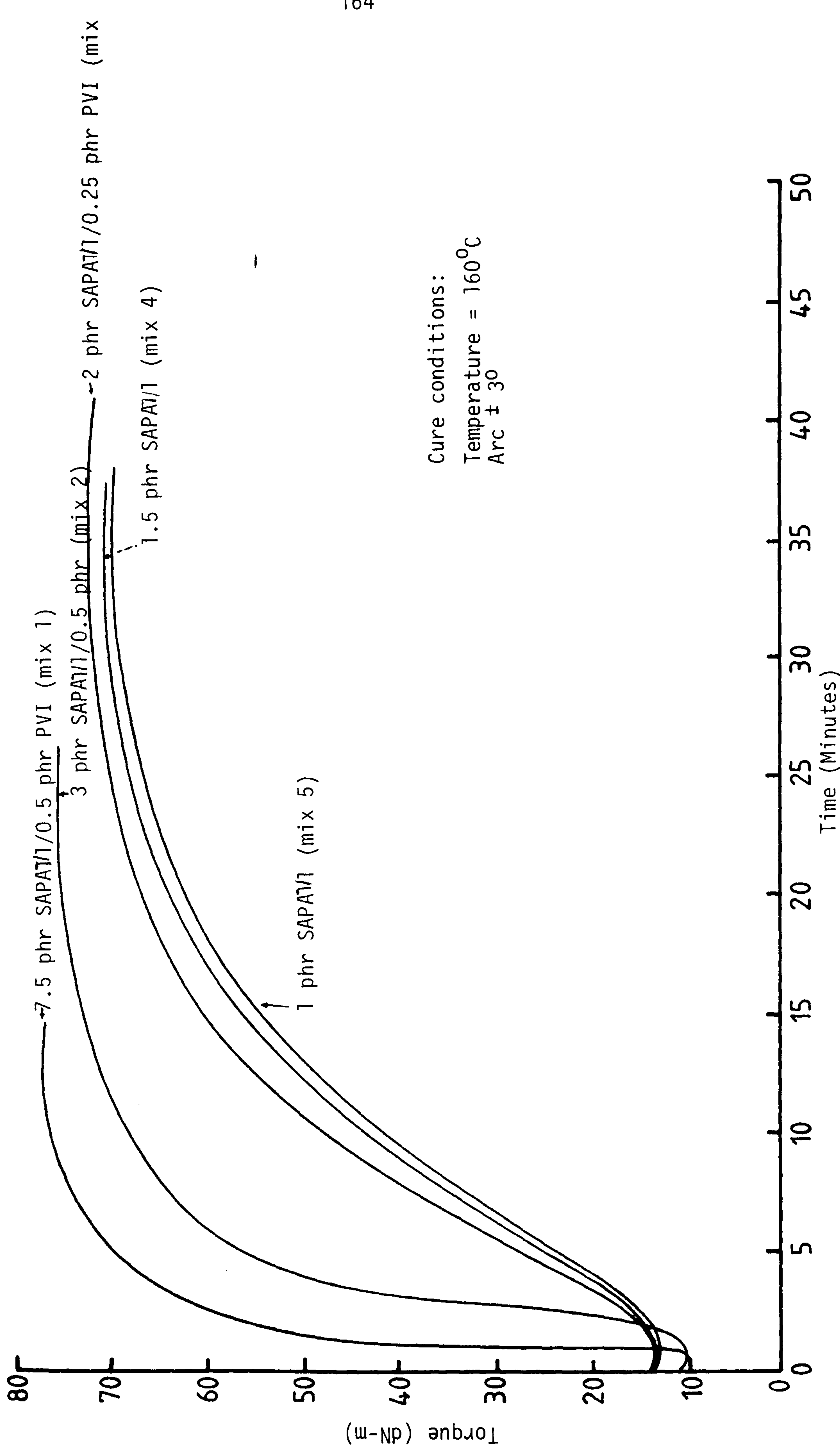


FIGURE 4.3: ODR TRACES OF THE NR/SBR COMPOUND CONTAINING VARIOUS LEVELS OF SAPA 1/1 AS A COMBINED CURE ACTIVATOR/ACCELERATOR SYSTEM

4.3 Zinc Oxide as a Scorch Control Additive in an NR/SBR Compound Accelerated by the SAPA 1/1 System Only

It was observed from the results of Table 4.4, Section 4.1, that when zinc oxide and stearic acid were eliminated, the scorch time was reduced. Hence, an investigation was carried out, based on the NR/SBR rubber, to find out the effect of zinc oxide and stearic acid on the SAPA 1/1 sulphur curing system when used in the NR/SBR rubber compound.

The formulations used in this investigation are given below in Table 4.7.

TABLE 4.7:

EFFECT OF ZINC OXIDE AND STEARIC ACID ON THE PROPERTIES OF THE SAPA 1/1/ SULPHUR CURING SYSTEM

Mix No	1	2	3	4
	← 1.5 phr SAPA 1/1 →			
	ZnO = 4phr Stearic acid = 2phr	ZnO = 2phr Stearic acid = 1phr	ZnO = 1phr Stearic acid = 0	ZnO = 0 Stearic acid = 0
NR (SMR 20)	30	30	30	30
SBR 1500	70	70	70	70
Sulphur	2	2	2	2
SAPA 1/1	1.5	1.5	1.5	1.5
ZnO	4	2	1	-
Stearic acid	2	1	-	-
IPPD	2	2	2	2
Flectol-H	0.75	0.75	0.75	0.75
Microcrystalline wax	3	3	3	3
Aromatic oil (Dutrex 729 UK)	7.5	7.5	7.5	7.5
FEF Carbon black	51	51	51	51

4.3.1 Results and Discussion

Table 4.8 summarises the results of reducing the zinc oxide and stearic acid on the processing, curing, and the physical properties of the NR/SBR compound cured with the SAPA 1/1/sulphur curing system. Figure 4.4 shows the ODR rheographs obtained when zinc oxide and stearic acid are systematically reduced to zero level. It can be seen from these results that the SAPA/1/1/sulphur curing system (mix 4, Table 4.7), which does not contain zinc oxide and stearic acid, has a scorch time of 12' and an optimum curing time, t_{90} , of 17'30". Introducing 1 phr of zinc oxide (mix 3) increases the scorch time from 12' to 100' and the t_{90} cure time from 17'30" to 42'. The addition of a further amount of ZnO and stearic acid (mixes 2 and 1 of Table 4.7) has little to no effect on the further extension of scorch time or t_{90} curing time. These results can be seen very clearly in the cure response curves of Figure 4.4 which demonstrate that zinc oxide acted as a cure retarder and significantly increased the scorch time of the NR/SBR compound. This behaviour of zinc oxide as a cure retarder in NR/SBR compounds cured by the SAPA1/1/sulphur curing system is believed to be exceptional. This is because no results have been reported before, as far as the author is aware, showing that ZnO can be used as a cure retarder.

It is worth noting from the results of Figure 4.4, that the inclusion of zinc oxide with the SAPA 1/1/sulphur curing system shows no reversion in the ODR curing curves. This was particularly observed when the ODR curing curves of all the mixes containing zinc oxide (mixes 2 and 3 of Table 4.8) were extended to cure times of 90 minutes. The SAPA 1/1/sulphur curing system by itself i.e. without zinc oxide, shows noticeable reversion (compare curves 1, 2 and 3 with curve 4 of Figure 4.4).

The inclusion of ZnO has resulted in some reduction in the physical properties of the NR/SBR vulcanisates. However the results show that the inclusion of zinc oxide has resulted in a considerable reduction

in the 300% modulus of the vulcanisate. The reason for this reduction is believed to be due to an altering in the cure mechanism of the SAPA 1/1/sulphur curing system when zinc oxide is present.

The use of stearic acid as a part of the activator system does not seem to be necessary in the NR/SBR formulation which only contains SAPA 1/1.

TABLE 4.8:

ZINC OXIDE AS A SCORCH RETARDER FOR THE SAPA 1/1/SULPHUR CURING SYSTEM IN THE NR/SBR COMPOUND (FOR FORMULATIONS SEE TABLE 4.7)

Mix No:	1	2	3	4
	← 1.5 phr SAPA 1/1 →			
	ZnO = 4 phr Stearic acid = 2 phr	ZnO = 2 phr Stearic acid = 1 phr	ZnO = 1 phr Stearic acid = 0	ZnO = 0 Stearic acid = 0
<i>Processing and Curing Properties:</i>				
Mooney Viscosity ML(1+4)100°C	43	42	43	44
Mooney Scorch, t_5 at 125°C (m)	110	100	100	12
Optimum Curing Time, t_{90} , at 160°C(m)	41'30"	40	42'30"	17'30"
<i>Physical Properties:</i>				
Tensile Strength MPa	13.3	14.2	15	16
Elongation at Break %	570	535	505	500
100% Modulus MPa	2	2	2.3	3.0
300% Modulus MPa	6	7	7.7	9.3
Tear Strength kN m^{-1}	36	35	34	30
Hardness IRHD	56	54	57	59
Rebound Resilience %	48	48	49	53

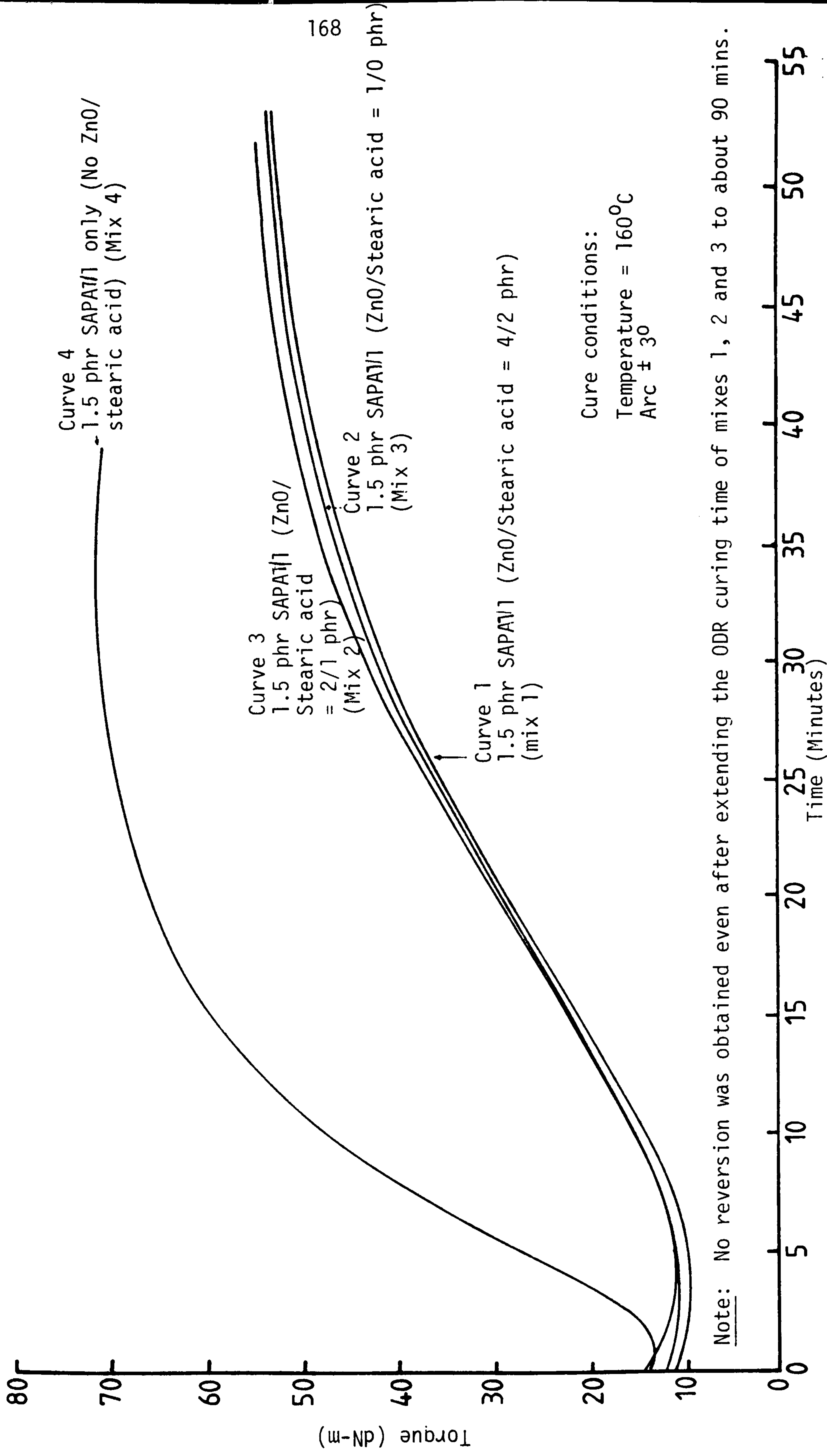


FIGURE 4.4: ZINC OXIDE AS A SCORCH CONTROL ADDITIVE IN NR/SBR COMPOUND CURED WITH SAPA 1/1/SULPHUR CURING SYSTEM

4.4 Zinc Oxide Versus Benzoic Acid as Cure Retarders for SAPA 1/1/ Sulphur Curing System in NR/SBR Compound

Zinc oxide was observed to increase, significantly, the scorch time of the NR/SBR compound cured by the SAPA 1/1/sulphur curing system (Table 4.8, Section 4.3). However, it also had an adverse effect on the cure rate and cure state. Such effects are always regarded as undesirable mainly because they are directly related to the quality and the productivity of the products. So for these reasons it was decided to examine the effect of an acidic retarder, Benzoic acid, on the SAPA 1/1/sulphur curing system in the NR/SBR blend in comparison with zinc oxide.

The formulations used are given in Table 4.9.

TABLE 4.9:

FORMULATIONS USED TO STUDY THE EFFECT OF BENZOIC ACID AS A RETARDER IN COMPARISON WITH ZINC OXIDE ON SAPA 1/1/SULPHUR CURING SYSTEM

Mix No.	1	2	3
	Control No retarder	0.5 phr ZnO	0.5 phr Benzoic acid
NR (SMR 20)	30	30	30
SBR 1500	70	70	70
Sulphur	2	2	2
Aromatic Oil (Dutrex 729 UK)	5	5	5
Flectol-H	0.75	0.75	0.75
IPPD	2	2	2
Microcrystalline wax	3	3	3
FEF Carbon black	51	51	51
SAPA 1/1*	2	2	2
Zinc oxide	-	0.5	-
Benzoic acid	-	-	0.5

* SAPA 1/1 is referred to as: N-tallow 1,3 propane diamine-di-oleate (see Table 3.1 for chemical structure)

Results and Discussion

Figure 4.5 and Table 4.10 demonstrate the results of the effect of benzoic acid as a retarder compared with a control compound (mix 1) which does not contain retarder and a compound retarded by zinc oxide. These results clearly show that the response of processing safety to the addition of 0.5 phr zinc oxide is significant, being increased by about 190% from that of the control compound (mix 1). However, the cure rate and state are, once again, adversely affected; optimum curing time, t_{90} , is increased by about 93% and the maximum torque was reduced by about 10% from that of the control compound (mix 1). It can also be seen that zinc oxide has reduced the 300% modulus by about 12% from the control mix. This reduction of properties was also observed before in Section 4.3.

The results obtained with benzoic acid show that the scorch time is increased by about 64%, while maintaining, almost, the same fast cure time of the unretarded SAPA 1/1/sulphur system (mix 1). The benzoic acid retarder can also be observed to have no detrimental effect on the vulcanisate properties of the NR/SBR compound.

Hence, benzoic acid can be used as a retarder for SAPA 1 series accelerators without affecting the curing or the physical properties of the NR/SBR compound.

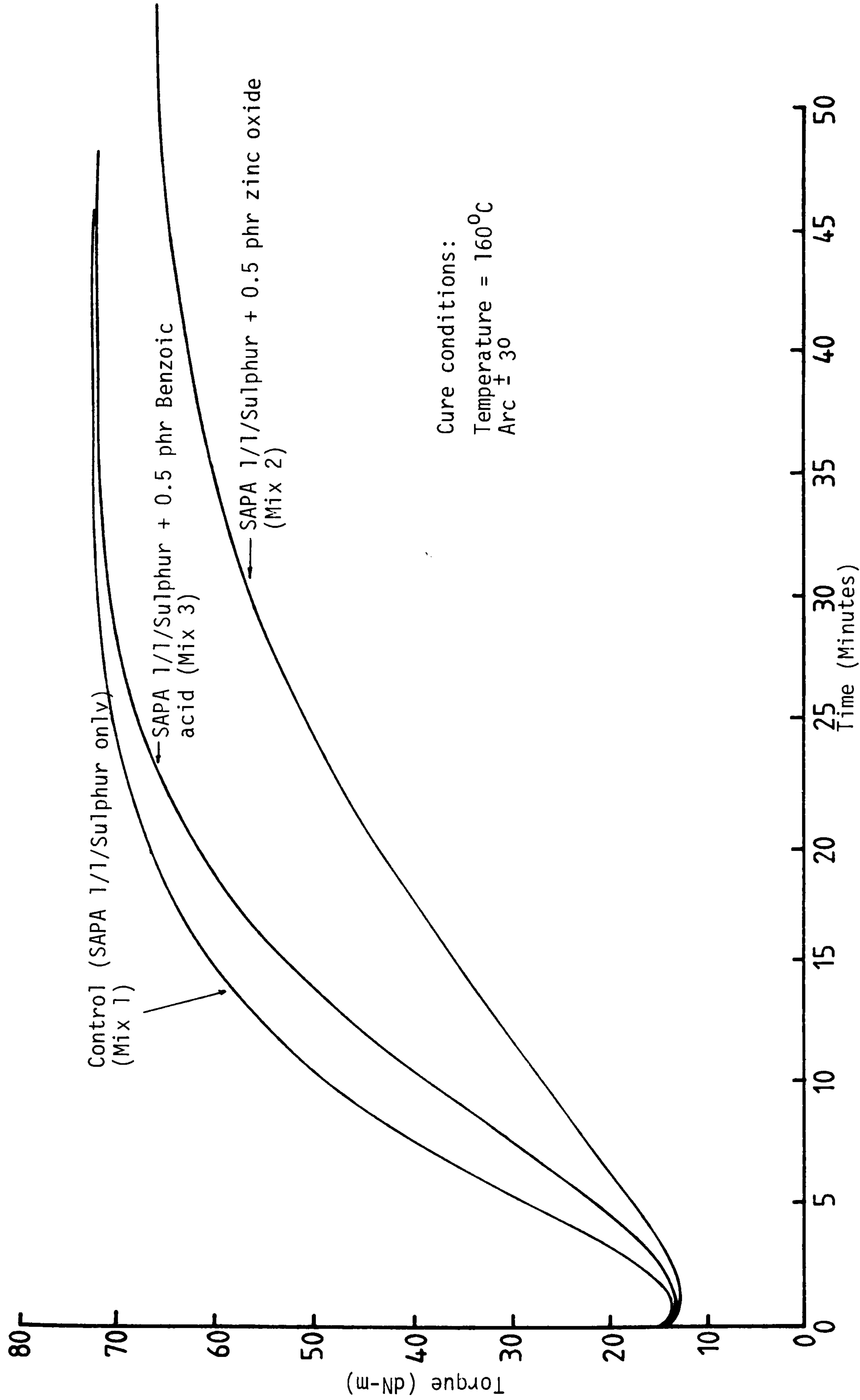


FIGURE 4.5: BENZOIC ACID VERSUS ZINC OXIDE IN NR/SBR COMPOUND CURED WITH SAPA 1/1/SULPHUR SYSTEM ONLY

TABLE 4.10:

EFFECT OF ZINC OXIDE AND BENZOIC ACID ON PROCESSING, CURING AND PHYSICAL PROPERTIES OF NR/SBR COMPOUND CURED WITH SAPA 1/1/SULPHUR SYSTEM

	Control Mix 1 (No retarder)	Mix 2 (Zinc oxide)	Mix 3 (Benzoic acid)
<u>Processing and Curing Properties:</u>			
Mooney Viscosity ML (1+4) 100°C	53	52	53
Mooney Scorch, t_5 , at 125°C (m)	9'30"	26	15
Optimum Curing Time, t_{90} , at 160°C (m)	19	36'30"	23
<u>Physical Properties:</u>			
Tensile Strength, MPa	17	16.7	17
100% Modulus, MPa	2.5	2.2	2.5
300% Modulus, MPa	9.7	8.5	9.6
Elongation at break %	445	445	445
Tear Strength, kN m^{-1}	32	31	30
Hardness, IRHD	58	58	59
Rebound resilience, %	55	54	55

4.5 SAPA 1/1 as a Combined Processing Aid and Acceleration System for Truck Tyre Sidewall Compound Based on NR/SBR Rubber

The formulation given in Table 2.5, Chapter 2, was designed after it had been discovered that SAPA 1/1 can, effectively, completely replace the cure activator and accelerator systems of the NR/SBR compound. Therefore, the original recipe contained 3 phr SAPA 1/1 which acted as a combined plasticiser and a cure accelerator system and also 0.5 phr ZnO as a scorch control additive.

The performance of SAPA 1/1 as a plasticiser was explained previously in Section 2.1. In this part of the research work the effect of SAPA 1/1 as a combined cure activator and accelerator system, on the curing and vulcanisate properties is examined in comparison with the more conventional CBS/MOR/sulphur curing systems.

Curing Behaviour

The ODR traces of Figure 4.6 illustrate the curing behaviour of the NR/SBR compound containing 3 phr SAPA 1/1 as a plasticiser and a cure accelerator system compared with the same base rubber containing a conventional curing system (ZnO/stearic acid/CBS/MOR/sulphur) plasticised with various processing aids. These two systems are also compared with a non-plasticiser containing NR/SBR compound.

These results show that the SAPA 1/1 containing compound reaches a higher state of cure than all its analogous plasticisers and non-plasticiser containing NR/SBR compounds which are cured by the conventional sulphenamide/sulphur system. The scorch time of the SAPA 1/1 system is better than the conventional system by about 13%. This increase in the scorch time is, of course, due to the presence of 0.5 phr zinc oxide. However, the optimum curing time, t_{90} , of the SAPA 1/1/sulphur/0.5 phr ZnO system is longer than that of the conventional curing system by about 42%. This increase in the t_{90} is obviously

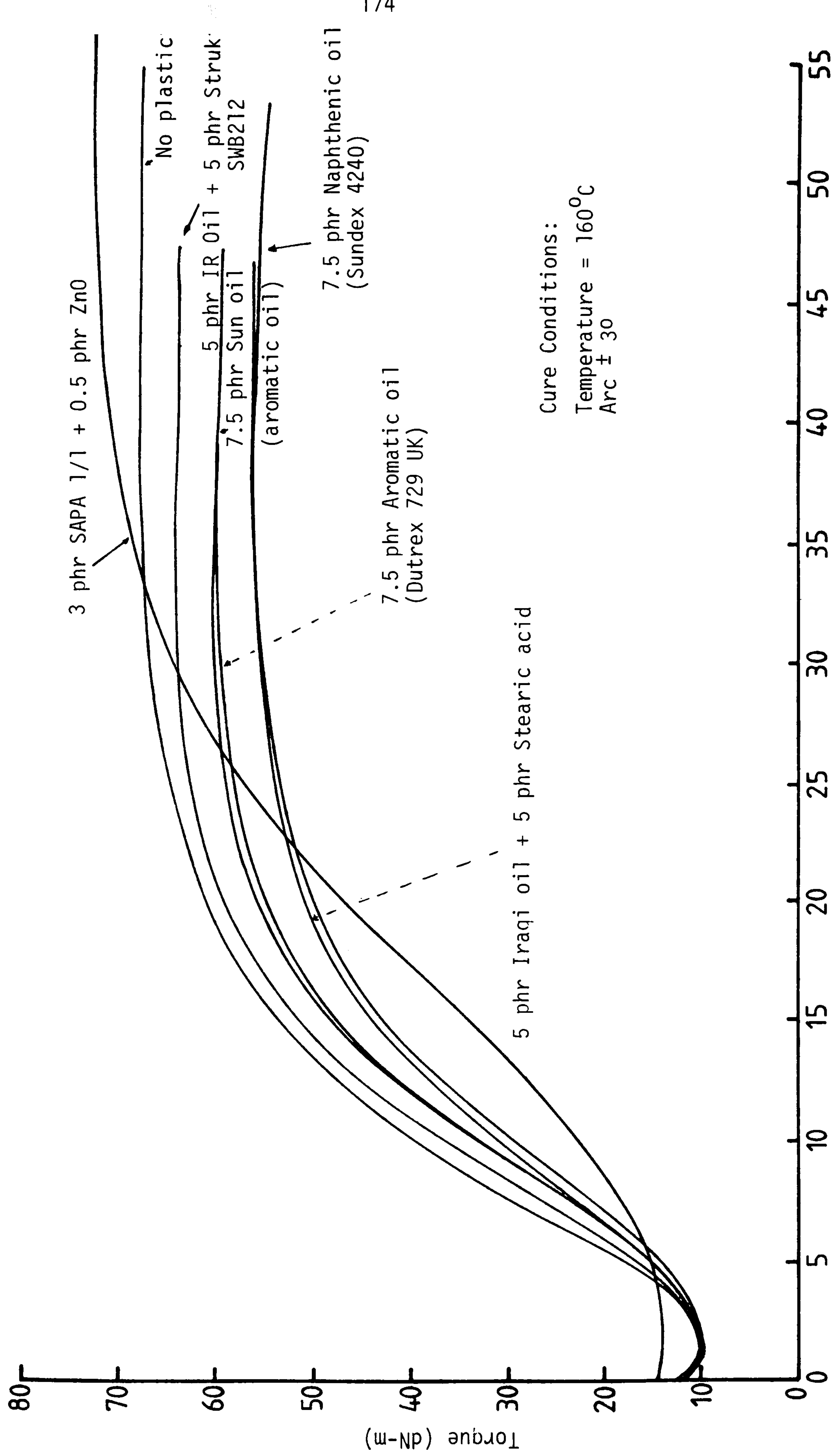


FIGURE 4.6: COMPARATIVE CURE PROPERTIES OF THE SAPA1/1/SULPHUR SYSTEM WITH SULPHENAMIDE/SULPHUR SYSTEM PLASTICISED WITH VARIOUS PLASTICISERS AND PROCESSING AIDS. BASE FORMULATIONS ARE SHOWN IN TABLE 4.5

due to the presence of zinc oxide (0.5 phr).

Physical Properties

The observation made earlier that SAPA 1/1/sulphur curing system has a higher state of cure than the conventional accelerators/sulphur system is confirmed by the lower compression set value for SAPA 1/1 mix shown in Table 4.11. The SAPA 1/1 containing mix has a compression set value of about 15% better (i.e. 25.5%) than the non-plasticiser containing compound cured by the conventional curing system, which has the next best value of 30% compression set.

A further point of interest, see Table 4.11, is that the specific gravity (SG) of the SAPA 1/1 mix was less than that of all the NR/SBR compounds, cured by the conventional system plasticised with various

TABLE 4.11

EFFECT OF SAPA 1/1 AS A PLASTICISER AND A COMBINED CURE ACTIVATOR ACCELERATOR SYSTEM COMPARED WITH A CONVENTIONAL CURING SYSTEM IN AN NR/SBR COMPOUND PLASTICISED WITH VARIOUS PLASTICISERS. (FOR FORMULATIONS SEE TABLE 2.5, SECTION 2.1)

	Compression Set*	Specific Gravity
Zero oil i.e.no Plasticiser	30	1.1385
7.5 phr Ir.**Oil (Aromatic)	31	1.1328
7.5 phr Naphthenic Oil (Circosol 4240) ¹	31	1.1293
7.5 phr Sundex ² 790 (Aromatic Oil)	32	1.1393
7.5 phr Dutrex ³ 729 (Aromatic Oil)	31.5	1.1383
5 phr Ir. Oil + 5 phr Strukto ⁴ SWB 212	32	1.1356
3 phr SAPA 1/1 (+ 0.5 phr ZnO)	25.5	1.1166

* Compression set was performed at 25% strain and 70°C for 48 hours

**Ir = An abbreviation of Iraqi

1&2 = Trade name of Sun Oil Company

3 = Trade name of Shell Oil Company

4 = Trade name of Schill and Sielacker

plasticisers. This, of course, indicates that the SAPA 1/1 containing mix has relatively lower volume cost potential than the other NR/SBR mixes containing conventional plasticisers and curing system.

In Table 4.12 it can be seen that the stress-strain properties of the SAPA 1/1 system are better (e.g. 100% modulus is about 13% better, 300% modulus about 21% better) than the conventional curing system in combination with various plasticisers. However, the tear strength seems to be lower than that of the conventional system by about 18%. This may be due to the higher state of cure achieved by the SAPA 1/1 system.

Resistance to flex-cracking, BS 903: Part A10, of the vulcanisates obtained from both the curing systems was observed to be similar as both samples did not show any sign of crack until 800 kilocycles. However, the resistance to cut growth, BS 903: Part A11, of the vulcanisate obtained by the conventional curing system was observed to be better than those obtained by the SAPA 1/1 system (see Figure 4.7). The test was carried out in the De Mattia machine which compared the results at equal extension. Such results can be meaningless because vulcanisates differing in modulus will have different stresses acting on cuts at the same extension. This case may, therefore, be applied to the vulcanisates obtained by the SAPA 1/1 system which had a higher modulus than those obtained by the conventional curing system.

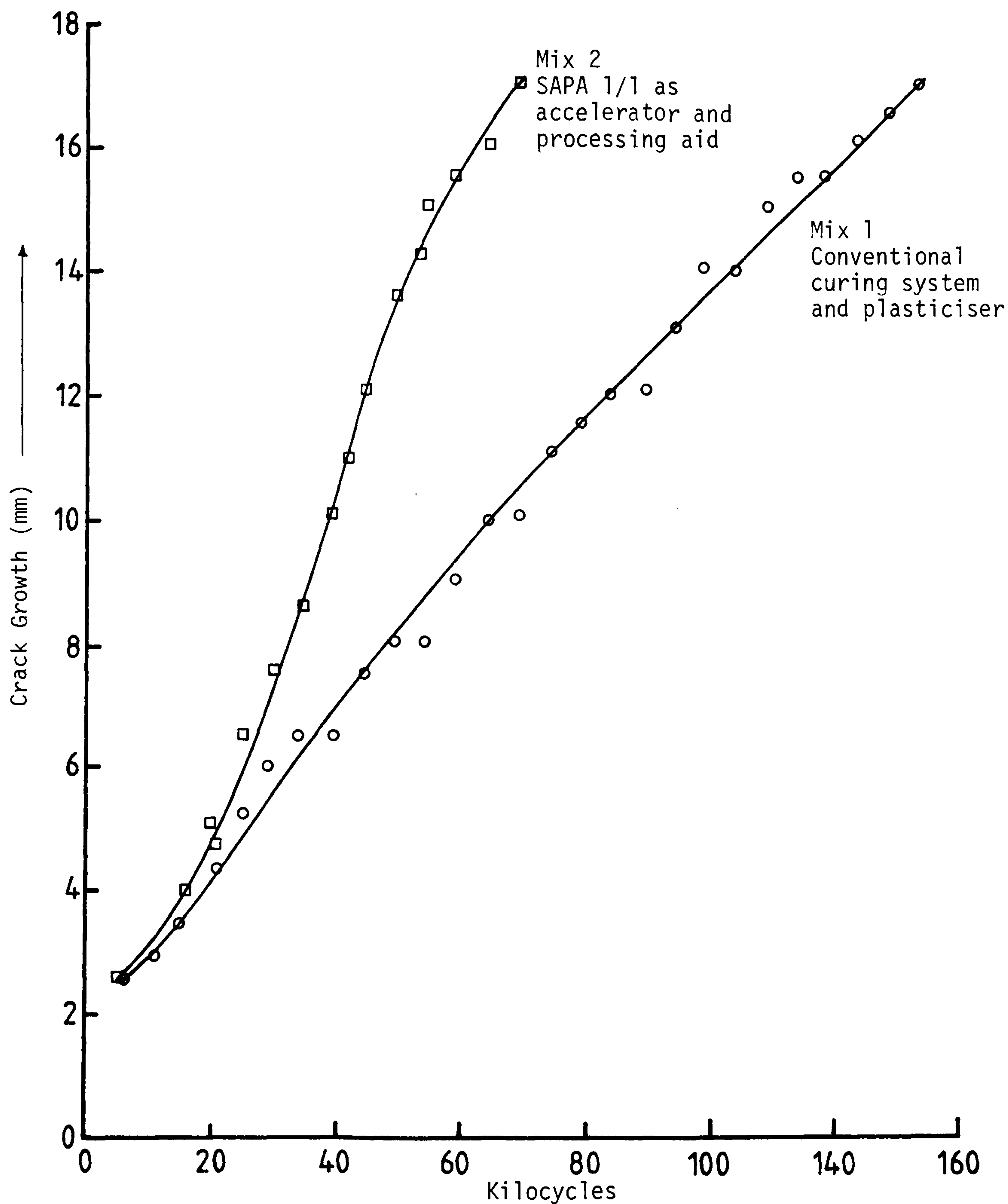
TABLE 4.12:

PROCESSING, CURING AND VULCANISATES. PROPERTIES OF NR/SBR COMPOUND CONTAINING 3 phr SAPA/1 AS A PLASTICISER AND ACCELERATOR SYSTEMS COMPARED WITH A CONVENTIONAL ACCELERATOR AND PLASTICISER SYSTEMS

Mix No.	1	2
	Conventional Curing System and Plasticiser	SAPA 1/1 as Accelerator System and Plasticiser
Natural rubber (SMR 20)	30	30
SBR 1500	70	70
Sulphur	2	2
Flectol-H	0.75	0.75
IPPD	2	2
Microcrystalline wax	3	3
FEF Black	51	51
Aromatic oil (Dutrex 729 UK)	7.5	-
Zinc oxide	4	0.5
Stearic acid	2	-
CBS	0.25	-
Santocure MOR	0.25	-
SAPA 1/1	-	3
<i>Processing and Curing Properties:</i>		
Mooney Viscosity ML(1+4)100°C	45	55
Mooney Scorch, t ₅ , at 125°C (m)	24	27
Optimum curing time, t ₉₀ at 160°C (m)	24'	34'
<i>Physical Properties:</i>		
Tensile Strength MPa	18	19
100% Modulus MPa	2.2	2.5
300% Modulus MPa	7.4	9.0
Elongation at break %	612	510
Tear Strength kN m ⁻¹	44	40
De Mattia* Flex Cracking (k.cycle)	800	800
Hardness IRHD	55	57
Rebound Resilience %	46	47

* The test stopped at 800 kilocycles because both samples did not show any sign of cracking

FIGURE 4.7: CUT GROWTH RESISTANCE OF A CONVENTIONAL CURING SYSTEM VULCANISATE COMPARED WITH SAPA 1/1/SULPHUR CURING SYSTEM VULCANISATE (DE-MATTIA)



4.6 Examination of Various Surfactants, Prepared Salts and Diamide Material as Cure Activator/Accelerator Systems in the NR/SBR Compound

In this investigation it has been decided to include the following studies:

- A: Performance of SAPA 1/2, NSC/1, SAPA 2/B and the EBF-S material as cure activator/accelerator systems for the NR/SBR compound in comparison with a conventional sulphenamide curing system.
- B: Effect of varying the type of alkyl groups in the SAPA 2 class of activator/accelerators.
- C: Effect of ZnO on the curing behaviour of the NSC/1 and SAPA 2/B system.

The formulation used in this investigation is given in Table 4.13.

Results and Discussion

- A: Table 4.14 and Figure 4.8 summarise the results for the performance of SAPA 1/2, NSC/1, SAPA 2/B and EBF-S materials as combined cure activator/accelerator systems for the NR/SBR compound compared with a conventional activator/accelerator system in the same base compound.

Curing Behaviour

From an examination of the results of Table 4.14 and Figure 4.8 it can be seen that the SAPA 1/2 and the NSC/1 activator/accelerator systems have similar effects on the curing properties. However, the optimum curing time, t_{90} , of the NSC/1 system is shorter than that of the SAPA 1/2 system by 4 minutes. This may be due to the presence of some free, unreacted, diamine within the NSC/1 material which could,

TABLE 4.13

FORMULATIONS USED TO EXAMINE VARIOUS SURFACTANTS, DIAMIDE MATERIAL AND A PREPARED SALT AS CURE ACTIVATOR/
ACCELERATOR SYSTEMS IN COMPARISON WITH A CONVENTIONAL SULPHENAMIDE
IN AN NR/SBR COMPOUND

Mix No	1	2	3	4	5
	Conventional Accelerator System	SAPA 1/2 System	NSC/1 System	SAPA 2/B System	EBF-S System
NR (SMR 20)	30	30	30	30	30
SBR 1500	70	70	70	70	70
Sulphur	2	2	2	2	2
ZnO	4	-	-	-	-
Stearic acid	2	-	-	-	-
CBS	0.25	-	-	-	-
Santocure MOR	0.25	-	-	-	-
Flecto1-H	0.75	0.75	0.75	0.75	0.75
IPPD	2	2	2	2	2
Microcrystalline wax	3	3	3	3	3
Aromatic oil (Dutrex 729UK)	7.5	7.5	7.5	7.5	7.5
FEF Carbon black	51	51	51	51	51
SAPA 1/2*	-	1.5	-	-	-
NSC/1*	-	-	1.5	-	-
SAPA 2/B*	-	-	-	1.5	-
EBF-S*	-	-	-	-	1.5

*For chemical structure see Table 3.1, Section 3.1

obviously, affect the curing properties. The processing safety of the SAPA 1/2 or the NSC/1 system is shorter than that of the conventional curing system (mix 1) by 8 minutes. However, a scorch time of 20 minutes is acceptable by most of the rubber industries. The optimum curing time, t_{90} , and the scorch time of the SAPA 1/2 or the NSC/1 system are shorter than those of the conventional activator accelerator system by 23% and 16% respectively.

The compound cured by the SAPA 2/B system (mix 4) has a shorter optimum cure time, t_{90} , by about 46%, than that of the SAPA 1/2 or the NSC/1 system. Also, the scorch time of the SAPA 2/B compound is considerably lower than that of the SAPA 1/2 or NSC/1 mixes (lower by about 77%). This significant difference in the curing behaviour between SAPA 1/2 or NSC/1 and SAPA 2/B is mainly due to their different chemical structures (see Table 3.1). This observation has been explained earlier in Section 3.2.

The EBF-S activator/accelerator system has a very long scorch time, more than 100 minutes, and an optimum curing time, t_{90} , (130 minutes). This behaviour is thought to be due to its chemical structure as amides are relatively thermally stable materials (see Table 3.1) compared to diamines. In Chapter 5 further investigations are carried out to confirm this observation.

Physical Properties (Table 4.14)

The physical properties of the NR/SBR vulcanisate cured by SAPA 1/2/sulphur and NSC/1/sulphur systems are similar. Comparing these results with those obtained from a conventional curing system the following observations can be made:

- i) There is a significant difference in the modulus values between the conventional curing system and that of the SAPA 1/2 or NSC/1 system. These latter systems give vulcanisates with higher 100% modulus and 300% modulus values (typically 36% and 58% for SAPA 1/2 and NSC/1 respectively) than the former sulphenamide system.
- ii) The elongation at break and the tear strength of the SAPA 1/2 or the NSC/1 system are observed to be lower than those of the conventional curing system by about 20% and 32% respectively. This difference in the properties suggests that the cure mechanisms that apply to the SAPA 1/2 and the NSC/1 systems are different from that of the conventional sulphenamide curing system.
- iii) The compression set value obtained from the SAPA 1/2 or the NSC/1 system is lower than that of the conventional curing system by about 10%. This low compression set value is believed[73] to indicate a more uniform state of vulcanisation.

The SAPA 2/B system seems to have physical properties midway between those of the conventional curing system and those achieved by the SAPA 1/2 or the NSC/1 systems.

The physical properties of the vulcanisate obtained by the less reactive accelerator/activator system, i.e. the EBF-S, are lower than those of the conventional curing system. These are clearly indicated by the lower tensile strength, about 22%, tear strength, about 36% and elongation, about 27%, from the vulcanisate obtained by the sulphenamide curing system. However, the 100% modulus, 300% modulus, hardness, resilience, and the compression set of the EBF-S system are almost similar to those obtained by the sulphenamide curing system.

TABLE 4.14:

PERFORMANCE OF SAPA 1/2, NSC/1, SAPA 2/B AND EBF-S SUBSTANCES AS A COMBINED CURE ACTIVATOR/ACCELERATOR SYSTEM COMPARED WITH A CONVENTIONAL ACTIVATOR (ZnO/Stearic Acid) ACCELERATORS (Sulphenamide) SYSTEM IN NR/SBR COMPOUND.

	Control Mix 1	SAPA 1/2 Mix 2	NSC/1 Mix 3	SAPA 2/B Mix 4	EBF-S Mix 5
<u>Processing and Curing Properties:</u>					
Mooney Viscosity ML (1+4) 100°C	45	56	56	57	53
Mooney Scorch at 125°C (m)	24	13	13	4'30"	More than 100
Optimum Curing Time t_{90} at 160°C (m)	24	19	18	10	130
<u>Physical Properties:</u>					
Tensile Strength MPa	18	18	17	17	14
100% Modulus MPa	2.2	3	3	2.6	2
300% Modulus MPa	7.4	11.7	12	9.6	8
Elongation at break %	612	485	450	476	446
Tear Strength kN m ⁻¹	44	30	29	40	28
Compression Set at 70°C for 48 hours	20	18	18	19	21
Hardness IRHD	55	62	64	59	55
Rebound Resilience %	49	51	50	57	49

B: Effect of various alkyl groups on SAPA 2 class of activator accelerator systems

Figure 4.9 and Table 4.15 summarise the results for the effect of various alkyl groups in the SAPA 2 class of surfactants, which have the general chemical structure of $\text{RNH}(\text{CH}_2)_3\text{NH}_2$, on its performance as a cure activator/accelerator system in the NR/SBR rubber base of formulation 4 of Table 4.13. These results indicate that the chain

length or the degree of unsaturation of any alkyl group does not produce any noticeable difference in the curing and physical properties usually obtained by any group of the SAPA 2 series.

C: Effect of ZnO on the performance of the NSC/1 and the SAPA 2/B systems

Figure 4.10 illustrates the results for the effect of 0.5 phr ZnO on the curing behaviour of the NSC/1 and the SAPA 2/B systems in the NR/SBR compound (formulations 3 and 4 of Table 4.13). These results show that the NSC/1 system seems to be affected by the ZnO in a similar way reported earlier with SAPA 1/1 system (Section 4.4, Figure 4.5). Unlike the NSC/1 system, the SAPA 2/B system seems to be unaffected by the 0.5 phr of the zinc oxide. However, the presence of ZnO was found to be beneficial if heat resistant compounds are required. This remark is explained later in Chapter 7.

FIGURE 4.8: CURING BEHAVIOUR OF SAPA 1/2, NSC/1, SAPA 2/B AND EBS SURFACTANTS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS COMPARED WITH A CONVENTIONAL SULPHENAMIDE CURING SYSTEM IN THE NR/SBR COMPOUND

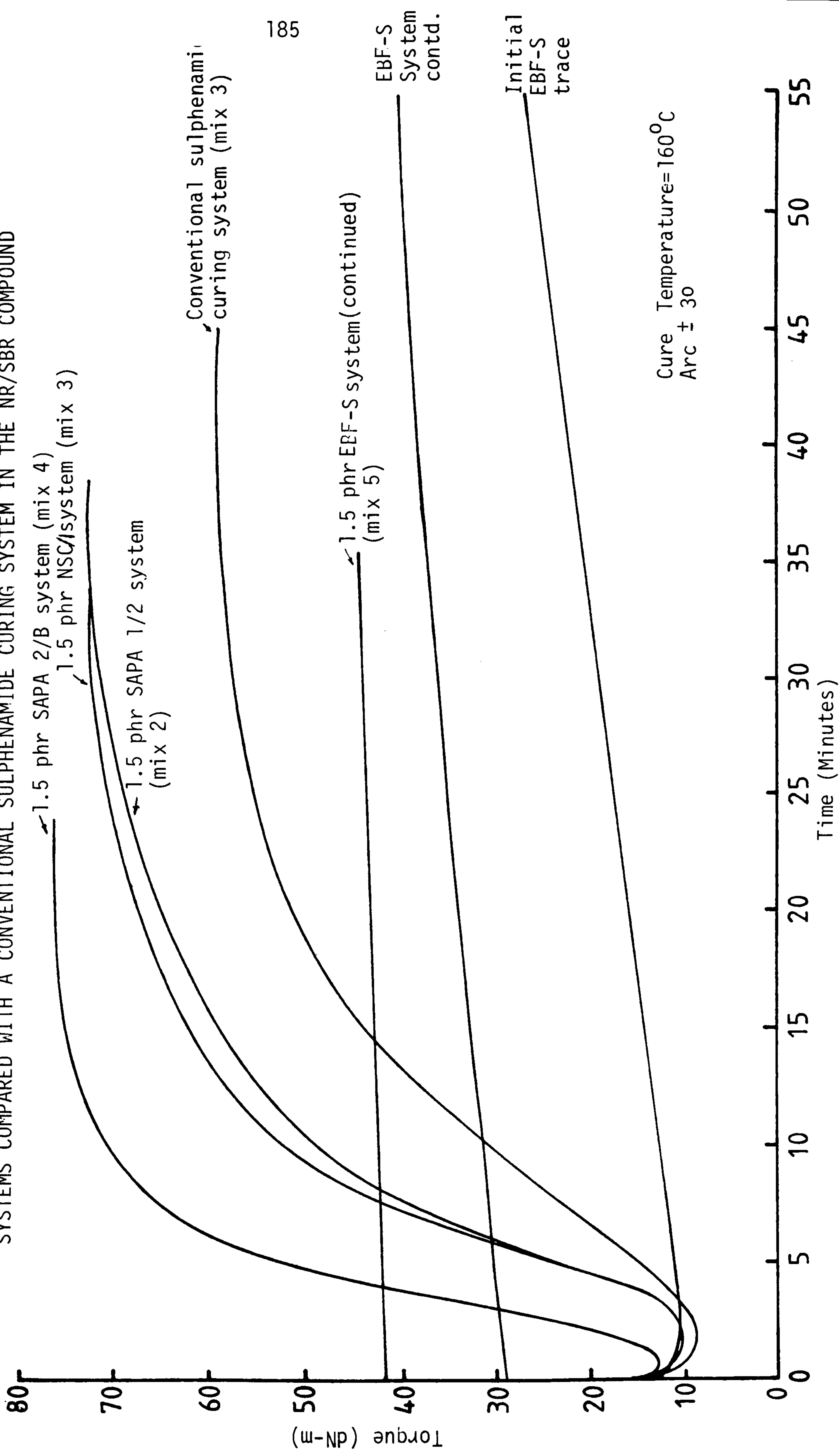


FIGURE 4.9: EFFECT OF VARIOUS ALKYL GROUPS OF SAPA 2 SERIES ON THE CURING BEHAVIOUR OF THE NR/SBR COMPOUND

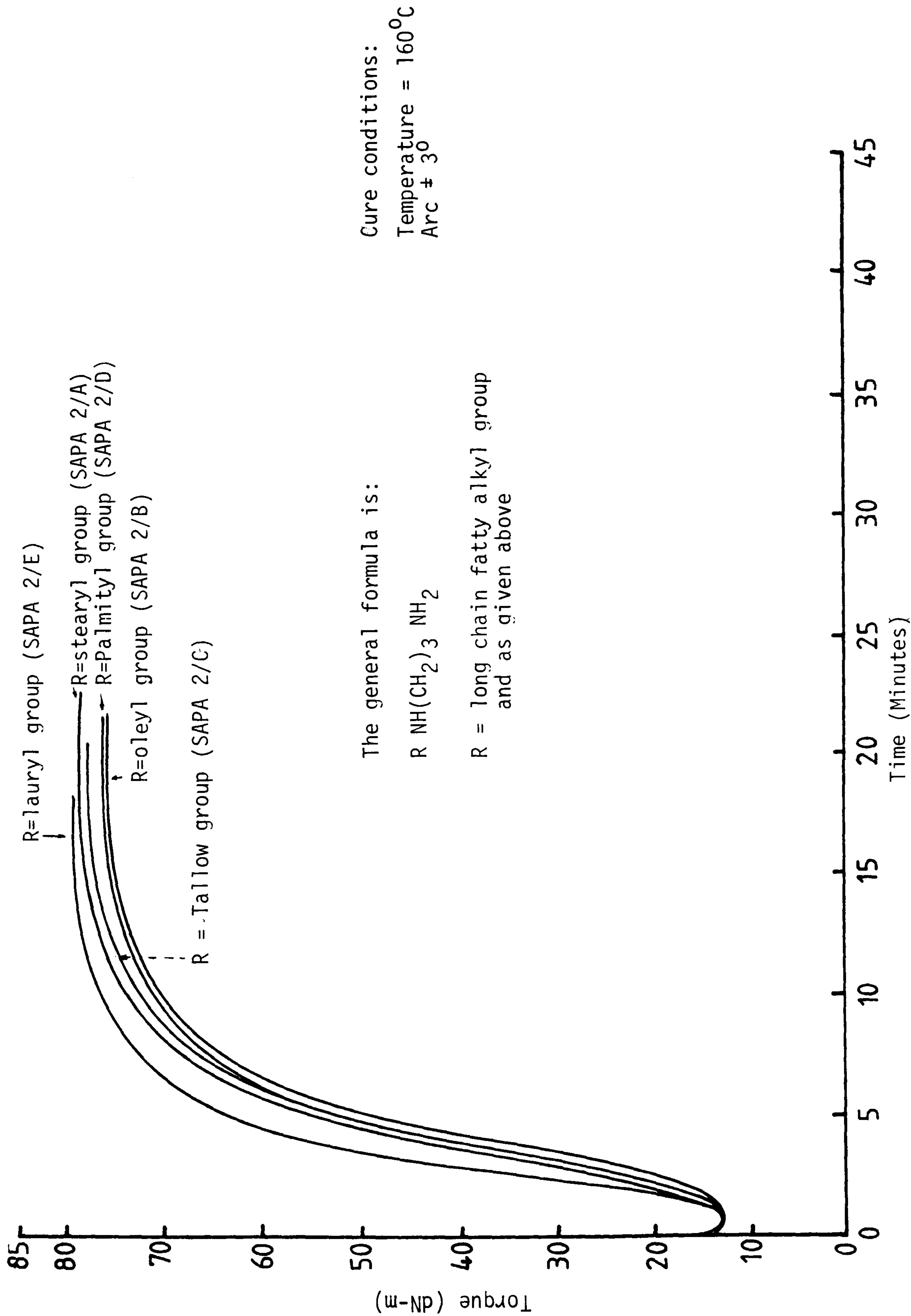
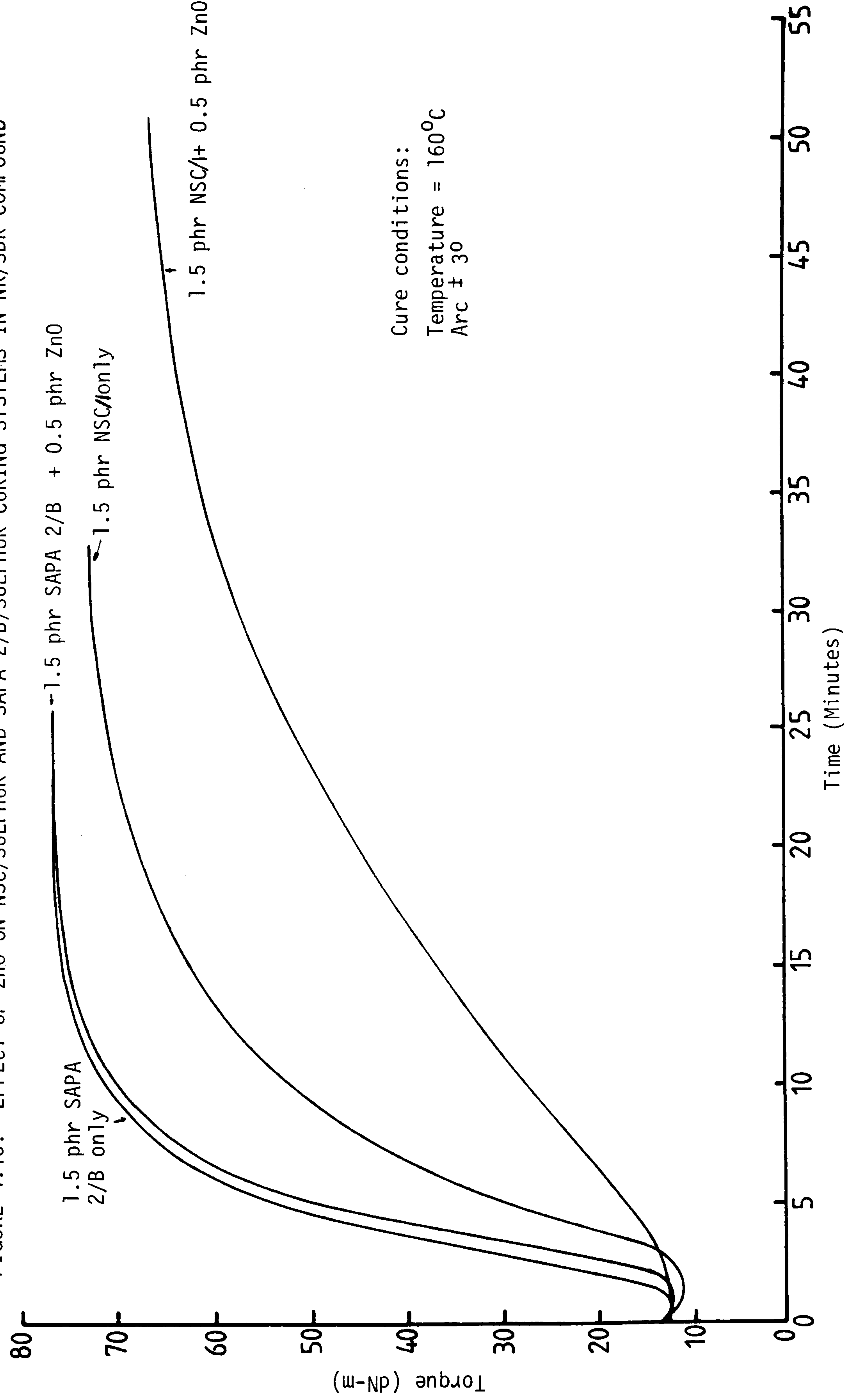


TABLE 4.15
EFFECT OF VARIOUS ALKYL GROUPS OF SAPA 2 SERIES ACTIVATOR/ACCELERATOR SYSTEM ON THE CURING
AND PHYSICAL PROPERTIES OF THE NR/SBR COMPOUND

Mix No	1	2	3	4	5	Notes
	R=oleyl SAPA 2/B	R=stearyl SAPA 2/A	R=palmityl SAPA 2/D	R=tallow SAPA 2/C	R=lauryl SAPA 2/E	
<u>Processing and Curing Properties:</u> Mooney Viscosity ML (1+4) ₁₀₀ Mooney Scorch, t ₅ , at 125°C (m) Optimum Curing Time, t ₉₀ at 160°C (m)	50 4'30" 10	52 4'30" 9	51 5 10	51 5'30" 9'30"	50 4'30" 8	SAPA 2 has the general formula of RNH(CH ₂) ₃ NH ₂ . R = alkyl group of fatty acid. For formulation see Table 4.13, mix 4.
<u>Physical Properties:</u> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness, IRHD Rebound Resilience %	17 2.6 9.6 476 40 59 57	16 2.7 10.5 430 40 59 58	17 2.7 10.4 445 42 59 58	16 2.5 9.8 430 38 59 58	16 2.5 10.2 445 42 58 58	

FIGURE 4.10: EFFECT OF ZnO ON NSC/SULPHUR AND SAPA 2/B/SULPHUR CURING SYSTEMS IN NR/SBR COMPOUND



4.7 Effect of Various Concentrations of SAPA 1/1 and Some of the NS Series on Cure Characteristics

In this investigation the effect of various concentrations of the SAPA 1/1, NSC/1, NS1 and the NSA/3 activator/acceleration systems on the curing characteristics, t_{90} and t_{95} , and the Mooney scorch, t_5 , at 125°C, are examined.

The formulation used was as follows: NR (SMR 20) 30, SBR 1500 70, sulphur 2, FEF carbon black 51, surfactant and prepared salts were varied. The results of this investigation are given in Figures 4.11-4.13. On examining these results the following observations can be made:

SAPA 1/1 and NSC/1:

The results given in Figures 4.11 and 4.13 show that the effect of concentration of the SAPA 1/1 and the NSC/1 systems on t_{90} , t_{95} and t_5 times are almost similar. The slight differences that exist between them may be as a result of some dissociation in the SAPA 1/1 that might have occurred during the long storage period (more than 3 years which it underwent during this investigation). Such dissociation is believed to result in the formation of some free diamine which could be expected to adversely (shorten) affect the scorch time.

NSA/3 System:

The system is seen to have shorter t_{90} , t_{95} and t_5 times than all the other systems (Figures 4.12 and 4.13). This may be because in its chemical structure only one of its two amino groups has been reacted with a fatty acid group, namely stearic acid, with the other remaining free.

NSI System:

Figures 4.12 and 4.13 show that this system had longer t_{90} , t_{95} and t_5 times than those obtained from the NSA/3 system but were similar to those of the NSC/1 system. This may be because in its chemical structure both of its two amino groups have been reacted with fatty acid groups, namely oleic acid.

Taken as a whole, these results show that as the concentration of a surfactant or a prepared salt increases, then cure rate increases and scorch times decrease. Hence, these materials follow the general pattern usually adopted by most of the conventional accelerators.

FIGURE 4.11: EFFECT OF SAPA 1/1 AND NSC/1 SYSTEMS ON t_{90} , AND t_{95} OF THE NR/SBR COMPOUND

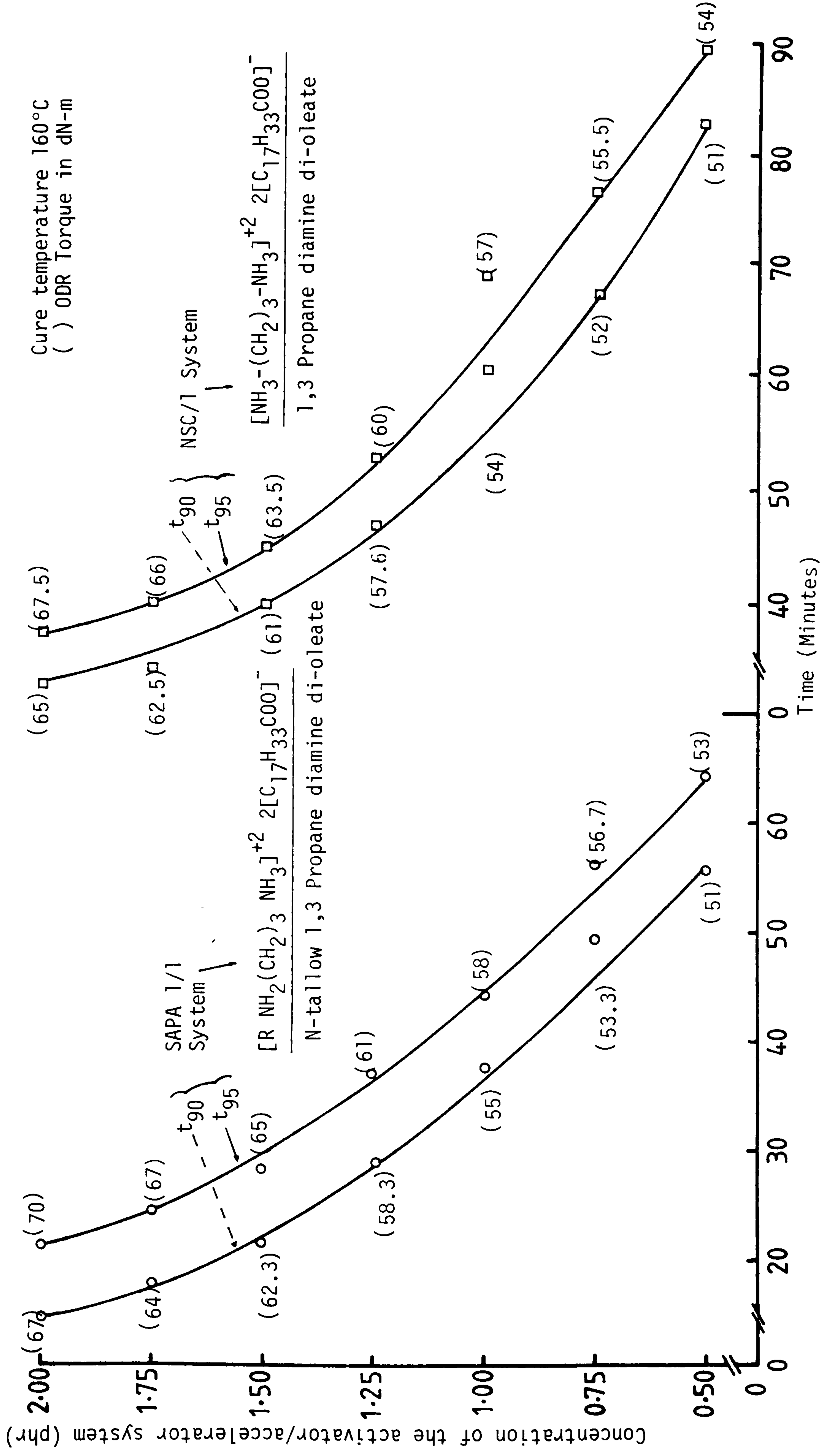


FIGURE 4.12: EFFECT OF NS1 AND NSA/3 SYSTEMS ON t_{90} AND t_{95} OF THE NR/SBR COMPOUND

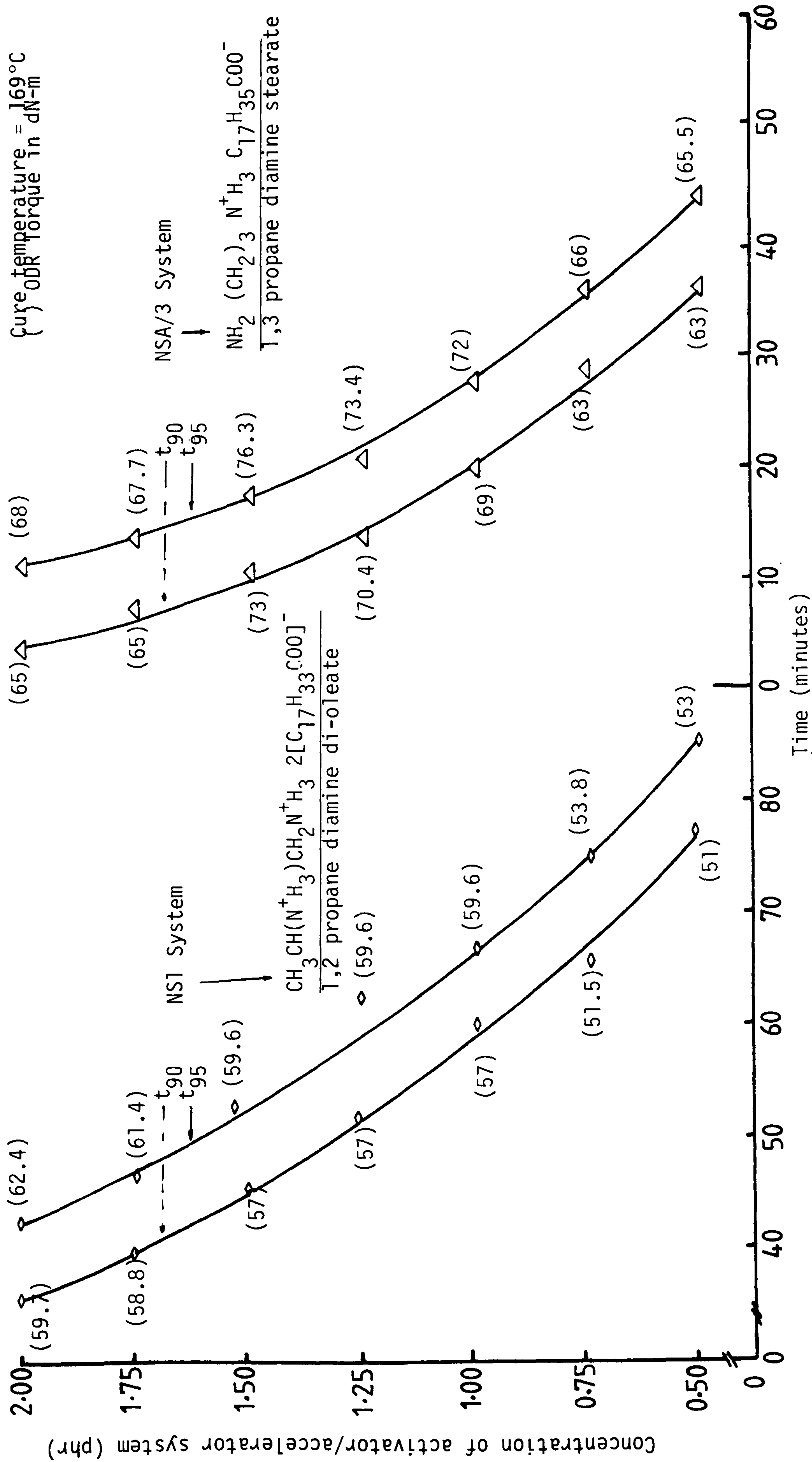
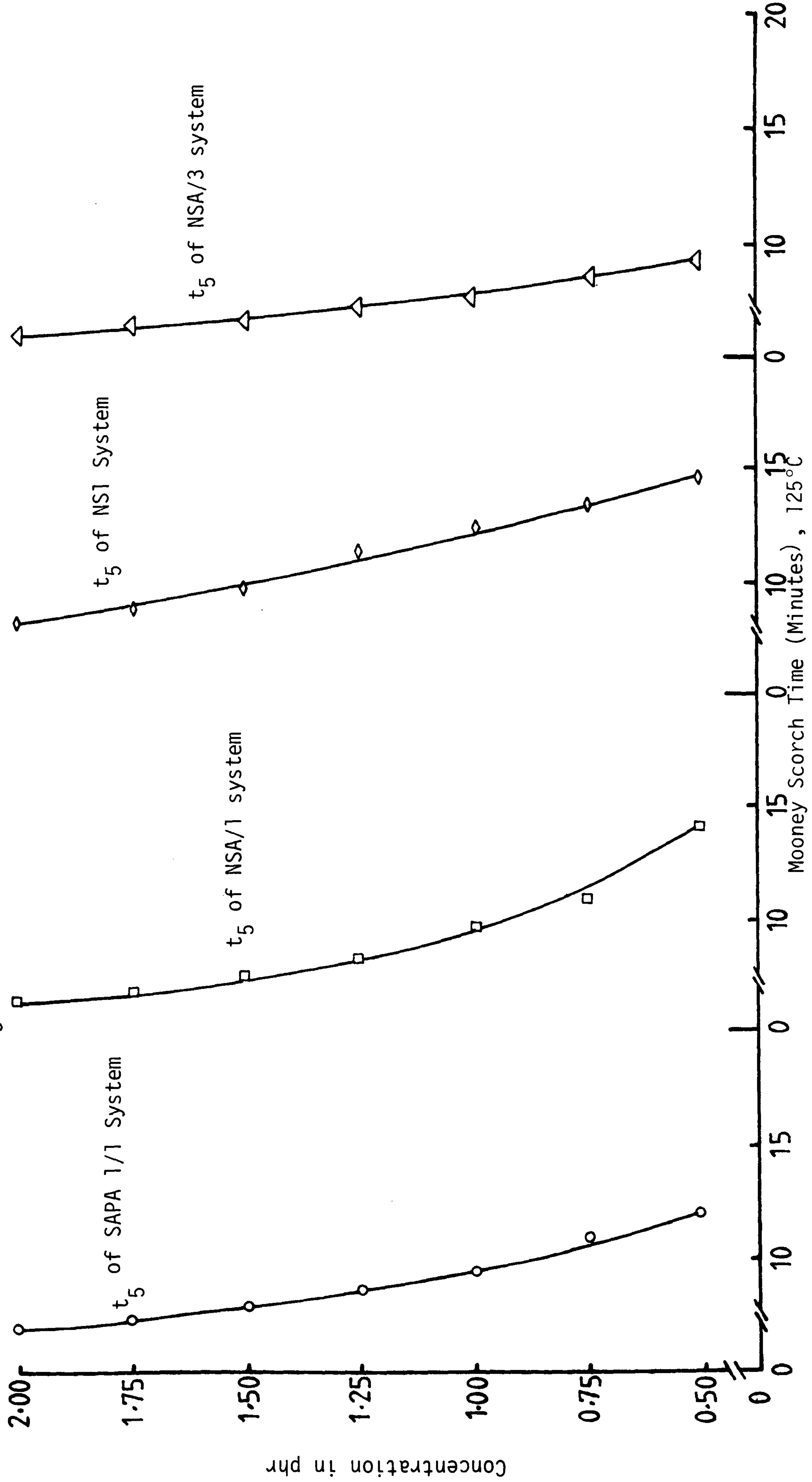


FIGURE 4.13: EFFECT OF CONCENTRATION OF SAPA 1/1, NSA/1, NS1 and NSA/3 SYSTEMS ON THE MOONEY SCORCH TIME, t_5 , OF THE NR/SBR COMPOUND



4.8 Effect of Antioxidants on the SAPA 1/1 Sulphur Curing System in the NR/SBR Compound

As SAPA 1/1/sulphur is a new type of curing system, it was decided to study the effect of antioxidants on such a system compared with a conventional curing system using an NR/SBR compound. The formulation used is given in Table 4.16.

TABLE 4.16:

FORMULATIONS USED TO EXAMINE THE EFFECT OF ANTIOXIDANTS ON THE SAPA 1/1 SYSTEM IN COMPARISON WITH A SULPHENAMIDE SYSTEM IN THE NR/SBR COMPOUNDS

	Conventional Curing System ZnO/St.A*/CBS/MOR/Sulphur		SAPA 1/1/Sulphur Curing System	
	With Antioxidant Mix 1	Without Antioxidant Mix 2	With Antioxidant Mix 3	Without Antioxidant Mix 4
NR (SMR20)	30	30	30	30
SBR 1500	70	70	70	70
Sulphur	2	2	2	2
ZnO	4	4	-	-
Stearic Acid	2	2	-	-
CBS	0.25	0.25	-	-
Santocure MOR	0.25	0.25	-	-
Aromatic Oil (Dutrex 729UK)	7.5	7.5	7.5	7.5
FEF Carbon black	51	51	51	51
SAPA 1/1	-	-	1.5	1.5
IPPD	2	-	2	-
Flectol-H	0.75	-	0.75	-
Microcrystal- line Wax	3	-	3	-

* Stearic acid

Accelerated hot air oven ageing tests were run on all vulcanisates at 70°C for 48 hours. All vulcanisates were cured at their optimum curing times, t_{90} , before the ageing test commenced. This is mainly to achieve a reasonable comparison between them after ageing. The hot air oven ageing test was used to conduct a preliminary examination of the accelerated ageing for evaluation of rubber products which are exposed to the conditions existing in service. Also it is considered to provide better correlation with natural ageing data than did other accelerated ageing tests such as the oxygen and air bombs [74,75].

A very interesting paper [76] proposed a method of characterising the ageing behaviour of rubber using a single expression called the fractional strain energy at break (TE)_f. This expression describes an aged vulcanisate in terms of its retained tensile strength and its retained elongation as follows:

$$\text{Fractional Strain Energy (TE)}_f = \frac{\text{Aged tensile strength} \times \text{aged elongation}}{\text{Original tensile strength} \times \text{original elongation}}$$

It should be noted that if tensile strength and elongation remain unchanged after the ageing period, the value of (TE)_f will be unity. In general, vulcanisates which have good resistance to ageing and suffer only small changes in tensile strength and elongation will have (TE)_f values slightly over or slightly under unity. Vulcanisates which deteriorate more readily will have very small (TE)_f values. This expression is used throughout this investigation.

4.8.1 Results and Discussion

Table 4.17 summarises the results of the effect of antioxidants on a vulcanisate cured by the SAPA 1/1/sulphur system compared to a vulcanisate cured by a conventional curing system; ZnO/stearic

TABLE 4.17

EFFECT OF ANTIOXIDANTS ON THE AGEING PROPERTIES OF THE VULCANISATE CURED BY THE SAPA 1/1/SULPHUR CURING SYSTEM COMPARED TO THOSE OBTAINED FROM A SULPHENAMIDE/SULPHUR SYSTEM AGED 2 DAYS AT 70°C

	Conventional Curing System ZnO/Stearic acid/CBS/MOR/Sulphur						SAPA 1/1/Sulphur Curing System					
	1			2			3			4		
	With Antioxidants			Without Antioxidants			With Antioxidants			Without Antioxidants		
Mix No:	Not Aged	Aged	% Change in Property	Not Aged	Aged	% Change in Property	Not Aged	Aged	% Change in Property	Not Aged	Aged	% Change in Property
Tensile Strength MPa	18	17.0	(-) 6	18	16.7	(-) 7	17.5	16.0	(-) 9	17.5	16.4	(-) 6
100% Modulus MPa	2	2.5	(+) 25	2.3	3	(+) 30	3	3.8	(+) 26	3	3.6	(+) 20
300% Modulus MPa	7	8	(+) 14	7.4	8.5	(+) 15	9.5	10.8	(+) 14	10	11	(+) 10
Elongation at break %	610	560	(-) 8.5	610	550	(+) 10	506	470	(-) 6	500	470	(-) 6
Tear Strength kNm ⁻¹	44	39	(-)(11)	45	40	(-) 11	40	36	(-) 10	41	38	(-) 7
Hardness IRHD	55	57	(+) 2 units	55	59	(+) 4 units	58	60	(+) 2 units	57	58	(+) 1 unit
Rebound Resilience %	49	49	-	49	48	(-) 2	52	52	-	52	52	-
(TE)f*	0.87			0.84			0.85			0.88		

(TE)f = Fractional strain energy

acid/CBS/MOR/sulphur in an NR/SBR compound. These results show that the addition of antioxidants to the conventional sulphenamide system are beneficial. This is clearly shown by the decrease in the fractional strain energy $(TE)_f$, of about 4% when the antioxidants were eliminated from the formulation (mix 2, Table 4.16). Vulcanisates cured by the SAPA 1/1/sulphur system which contain antioxidants exhibit less resistance to ageing than those cured by the conventional sulphenamide system containing antioxidants. However, aged vulcanisate cured by the SAPA 1/1/sulphur system which did not contain antioxidants, seems to have better thermal resistance, its $(TE)_f$ is better by about 4%, than those which contained antioxidants. The following suggestions have been put forward to account for this unusual behaviour. The first one is that the type of antioxidant used is not effective with the SAPA 1/1/sulphur system. The second suggestion is that the ageing conditions of temperature and time, are not severe enough to show the full effect of the antioxidants used. The third proposal is that the SAPA 1/1 activator/accelerator system may be acting as antioxidant by itself and therefore does not need antioxidants. However, the effect of antioxidants on the ageing behaviour of SAPA type system is further examined, at various ageing conditions, in Chapter 7.

4.9 Conclusion

The results presented in this chapter have shown that SAPA 1, SAPA 2, and the NS series can act, very effectively, as a cure activator/accelerator system, for the NR/SBR compound cured with sulphur as a curing agent. Any one of these materials was found to function as an accelerator system in its own right enabling fast curing of the NR/SBR compound to be obtained without the presence of any organic or inorganic accelerators (e.g. CBS/zinc oxide/stearic acid). Delayed action curing of SAPA 1/1 and NS systems (i.e. longer

scorch times) can be obtained by using zinc oxide e.g. 0.5 phr or less, or benzoic acid. The cure rate properties of SAPA 2 systems were found to be unaffected by the presence of zinc oxide.

The EBF systems showed longer scorch delay and slower overall cure rates than all the other systems used in this chapter. This is thought to be as a result of its stable structure (see Table 3.1).

The results concerned with the ageing behaviour of the SAPA 1/1 vulcanisate showed that the presence of the antioxidants used is not important. However, further examination was considered necessary to confirm these preliminary observations.

CHAPTER 5

SURFACTANTS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS FOR NATURAL AND SOME SYNTHETIC RUBBERS

Introduction

In Chapter 4 it has been established that the surfactants and the prepared salts of Table 3.1 could function very effectively as cure activator/accelerator systems for the NR/SBR typical blend compounds. Surprisingly these materials were found to function without the inclusion of the conventional activators i.e. ZnO and stearic acid.

This chapter reports work which was carried out to examine whether these materials can also be used as cure activator/accelerator systems for individual rubbers such as NR, SBR, BR and NBR.

5.1 SAPA 1/1 as a Cure Activator/Accelerator System for Natural Rubber

SAPA 1/1 was selected to be examined as the cure activator/accelerator for natural rubber. The formulations used are given in Table 5.1. All the mixes used in this investigation were prepared in a laboratory size BR Banbury at the following conditions:

Rotor speed = 60 rpm
Ram pressure = 2.5 kg/cm²
Fill factor = 0.75
Cooling water : full on

Mixing cycle:

Time:	Operation:
0	NR (SMR 20)
45"	$\frac{1}{2}$ FEF Black + SAPA 1/1
2'0"	$\frac{1}{2}$ FEF Black + Oil + Flectol-H
5'0"	Clean
5'15"	Dump

Sulphur was added on a two-roll rubber mill (450 mm x 225 mm and friction ratio 1.1:1) and mixed for 2 minutes. Each mix was refined six times through a tight nip and then sheeted off at 3 mm thickness for preparations of test specimens.

TABLE 5.1:
RECIPES USED TO EXAMINE SAPA 1/1 AS A CURE ACTIVATOR/ACCELERATOR
SYSTEM FOR NR RUBBER

Mix No.	1	2	3	4
	SAPA1/1 0.5phr Sulphur 2 phr	SAPA1/1 1.5phr Sulphur 2 phr	SAPA1/1 0.5phr Sulphur 3.5phr	SAPA1/1 1.5phr Sulphur 4 phr
NR (SMR 20)	100	100	100	100
Sulphur	2	2	3.5	4
Flectol-H	2	2	2	2
Aromatic Oil (Dutrex 729UK)	5	5	5	5
FEF Carbon black	50	50	50	50
SAPA 1/1	0.5	1.5	0.5	1.5

Figure 5.1 is the rheographs obtained for the curing behaviour of the mixes given in Table 5.1. Comparison of curve A with B in Figure 5.1 shows that as the SAPA 1/1 level increases (from 0.5 to 1.5 phr) the optimum curing time, t_{90} , and the scorch time decrease considerably. Such behaviour is usually observed with almost all the conventional

accelerators. However, the crosslinking efficiency i.e. the state of the cure, achieved by the SAPA 1/1 system, at both the concentrations used, is very low compared to what can usually be obtained by any conventional accelerator system. This low crosslinking efficiency has been confirmed as when a test sheet from each mix (mixes 1 and 2 of Table 5.1) were prepared by compression moulding then the compression mould was extremely difficult to open as the test sheet stuck to the upper and lower parts of the mould preventing it from being opened. The vulcanised sheets were very tacky and not fully cured, as a result physical testing was not possible.

This unexpected behaviour was thought to be due to the presence of the natural high percentage of the unsaturation in the natural rubber. Hence higher proportions of sulphur were considered necessary to achieve good state of cure with the SAPA 1/1 system. This suggestion was confirmed in practice with the results obtained with the higher sulphur contents of mixes 3 and 4 of Table 5.1.

As can be seen in Figure 5.1 curves C and D have a considerably higher state of cure (at their 3.4 and 4 phr levels of sulphur) than that of curves A and B at the 2 phr level of sulphur. This improvement in the state of the cure has resulted in fairly good overall physical properties (see Table 5.2). This higher level of sulphur, 3.5-4 phr, used in this investigation, is not usually used in the present technology for various reasons such as sulphur blooming and formation of excessive polysulphide linkage. However, this investigation has shown that for SAPA 1/1 to successfully act as a cure activator/accelerator system for natural rubber then the use of these higher sulphur proportions (i.e. > 3.0 phr) is necessary.

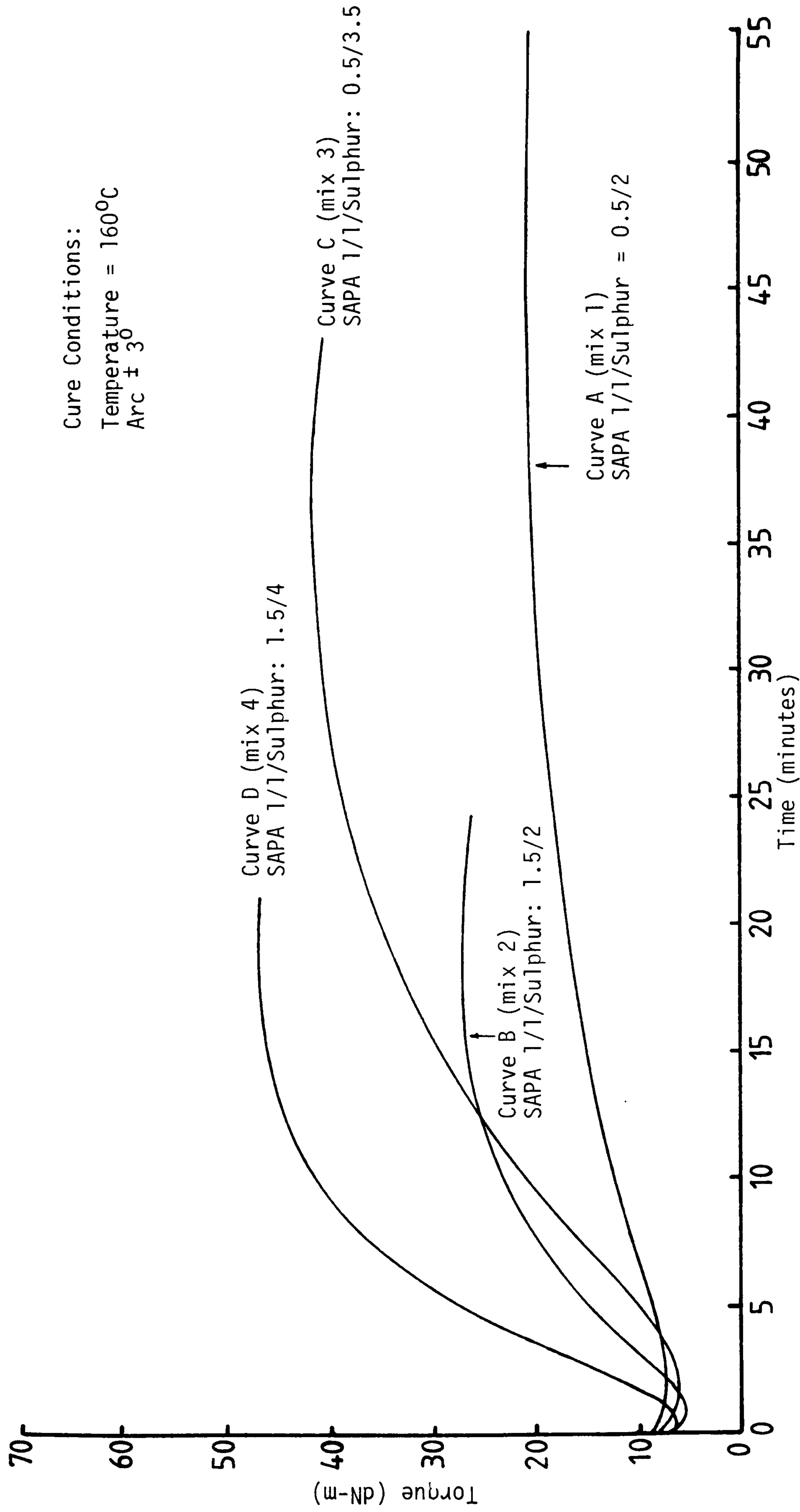


FIGURE 5.1: CURING BEHAVIOUR OF NATURAL RUBBER CURED BY SAPA 1/1/SULPHUR SYSTEM

TABLE 5.2:

PROCESSING, CURING AND PHYSICAL PROPERTIES OF NATURAL RUBBER CURED WITH THE SAPA 1/1/SULPHUR SYSTEM [FOR FORMULATIONS SEE TABLE 5.1]

	Mix 1	Mix 2	Mix 3	Mix 4
<u>Processing and Curing Properties:</u>				
Mooney Viscosity ML (1+4) 100°C	42	40	46	42
Mooney Scorch at 125°C (m)	>60	10	41	6'30"
Optimum Curing Time, t_{90} at 160°C (m)	27'30"	12'	25	11
<u>Physical Properties:</u>				
Tensile Strength MPa	No property was measured	No property was measured	14	16
100% Modulus MPa			1.7	2
300% Modulus MPa			6	7
% Elongation at break	See Section 5.1		536	510
Tear Strength kNm^{-1}			30	36
Hardness, IRHD			48	45
Rebound Resilience %			51	53

5.1.1 Effect of Zinc Oxide and Stearic Acid on the Performance of SAPA 1/1 in Natural Rubber

This investigation was conducted to ascertain whether the scorch retardation effect of zinc oxide, apparent in the NR/SBR blend given in Chapter 4, also applied to a single polymer system, namely NR.

The formulations used are given below in Table 5.3.

TABLE 5.3:

COMPOUND RECIPES USED TO EXAMINE THE EFFECT OF ZINC OXIDE AND STEARIC ACID ON SAPA 1/1/SULPHUR CURING SYSTEM

	I	II
Natural rubber (SMR 20)	100	100
Sulphur	2	2
FEF Black	50	50
Flectol-H	1	1
Aromatic oil (Dutrex 729)	5	5
SAPA 1/1	0.5	1.5
Zinc oxide	Variable	Variable
Stearic acid	Variable	Variable

The results are given in Figures 5.2 and 5.3 and Table 5.4. It can be seen from these results that decreasing the zinc oxide content progressively from 4 parts to 1 part, increases the scorch time in a regular and uniform manner from 14' to 24' in mixes containing 0.5 phr SAPA 1/1. However, at the higher SAPA 1/1 levels, i.e. 1.5 parts, the effect of the ZnO on reducing scorch, whilst apparent, is not so pronounced. This observation confirms, in principle, the ability of ZnO to control scorch in SAPA 1/1 containing rubber formulations. It is considered that stearic acid plays no role in scorch control

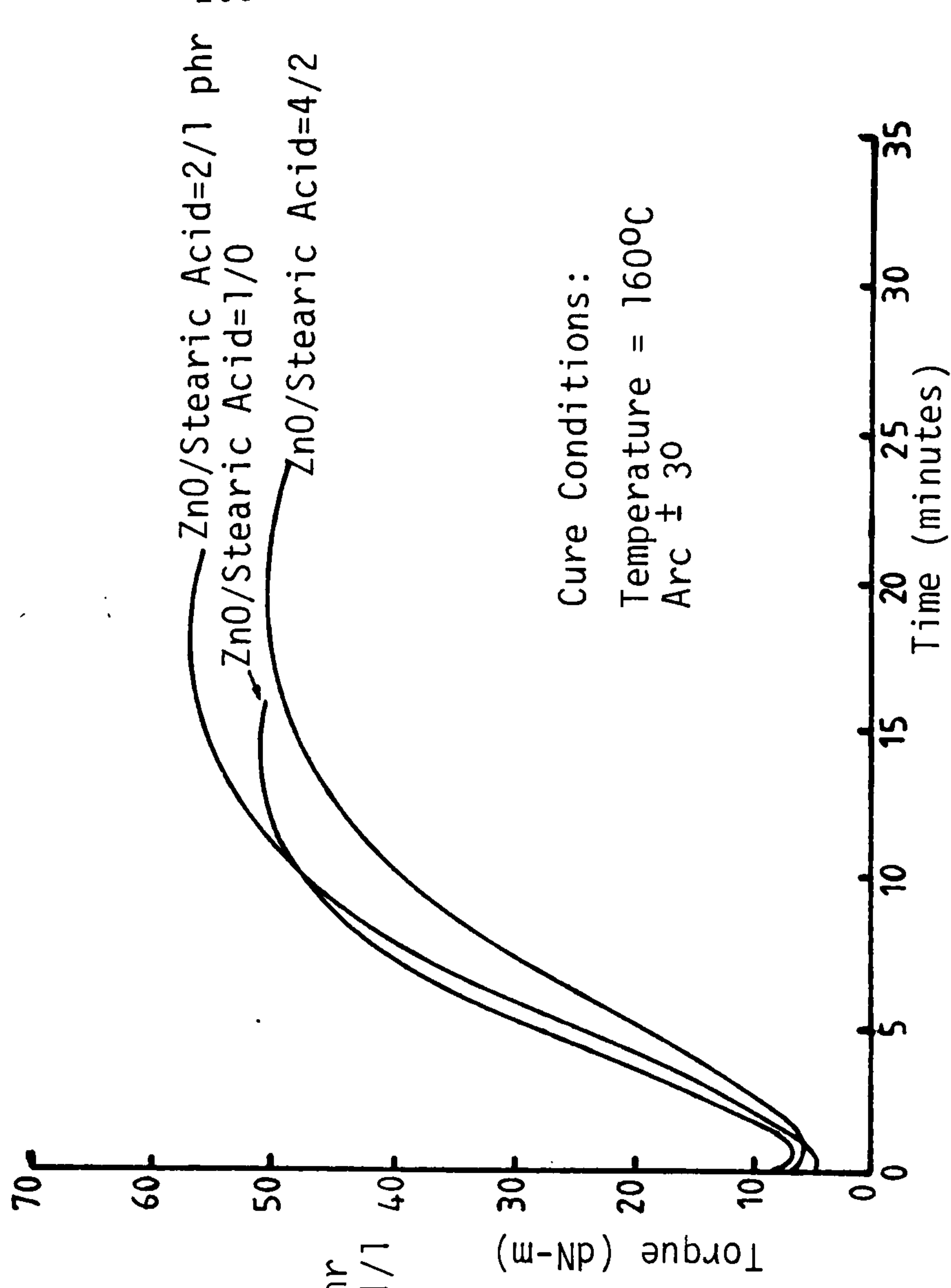


FIGURE 5.2: EFFECT OF VARIOUS LEVELS OF ZnO AND STEARIC ACID ON THE PERFORMANCE OF NATURAL RUBBER CURED WITH 0.5 phr SAPA 1/1/SULPHUR (2 phr) CURING SYSTEM

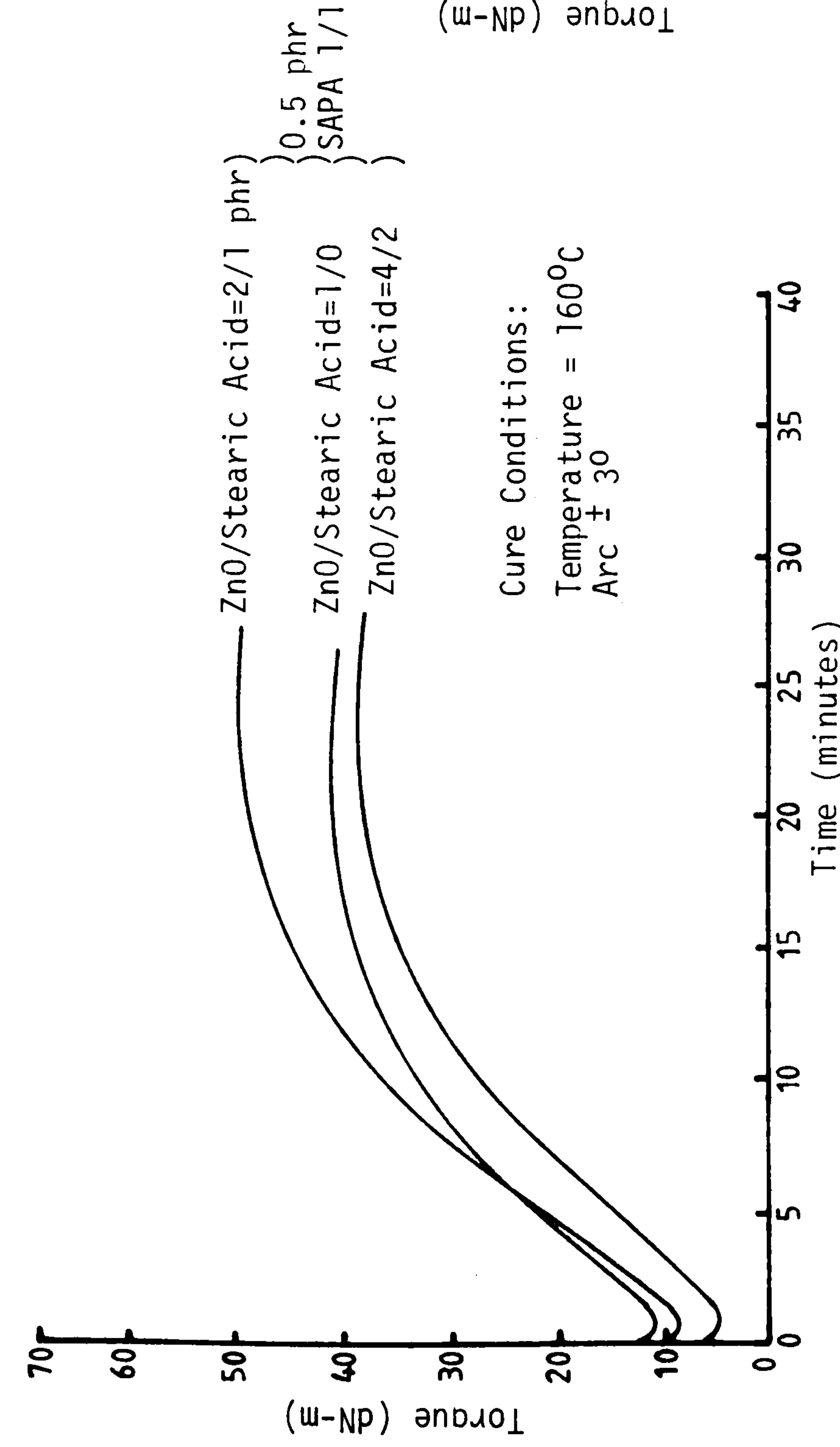


FIGURE 5.3: EFFECT OF VARIOUS LEVELS OF ZnO AND STEARIC ACID ON THE PERFORMANCE OF NATURAL RUBBER CURED BY THE 1.5 phr SAPA 1/1/SULPHUR (2 phr) CURING SYSTEM

TABLE 5.4

EFFECT OF ZnO AND STEARIC ACID ON THE PERFORMANCE OF THE SAPA 1/1/SULPHUR CURING SYSTEM IN NATURAL RUBBER
[FOR FORMULATIONS SEE TABLE 5.3]

	Reducing ZnO and Stearic Acid Proportions			Reducing ZnO and Stearic Acid Proportions		
	0.5 phr SAPA 1/1			1.5 phr SAPA 1/1		
	ZnO = 4 phr St.A= 2 phr	ZnO = 2 phr St.A= 1 phr	ZnO = 1 phr	ZnO = 4 phr St.A= 2 phr	ZnO = 2 phr St.A= 1 phr	ZnO = 1 phr
Mix No.	1	2	3	4	5	6
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4)100°C Mooney Scorch at 125°C (m) Optimum Curing Time, t ₉₀ at 160°C (m)	41 24 15'30"	44 16 15'30"	41 14 14	38 14 12'40"	39 12 12'30"	38 9 9'50"
<u>Physical Properties:</u> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa %Elongation at break Tear Strength kN m ⁻¹ Hardness, IRHD Rebound Resilience, %	13 2 9 385 56 51 53	14.3 2.4 10 370 53 53 55	12 1.6 7 430 47 49 50	13.4 2 9.2 375 66 52 54	16 2 9.3 415 65 52 54	13 2 8 410 62 48 50

in this instance. All the mixes given in Table 5.4 have showed good processability at the moulding stage as they exhibited good flow behaviour and excellent release properties after compression moulding. Also all the vulcanisates were observed to be highly elastic and resilient and hence well cured. These observations were confirmed when the physical properties of the vulcanisates were tested. However, Table 5.4 shows that the physical properties of the 0.5 phr and the 1.5 phr of SAPA 1/1 containing mixes are best when 1 phr of stearic acid and 2 phr of zinc oxide are used in both the formulations. This observation indicates that inclusion of specific levels of ZnO and stearic acid are beneficial to achieving good curing and physical properties with the natural rubber when cured by the SAPA 1/1/sulphur curing system.

5.1.2 An Accelerator Study of SAPA 1/1 Vs a Sulphenamide Accelerator in NR

In this investigation SAPA 1/1 is compared with a conventional sulphenamide accelerator; 2-(morpholinothio)benzothiazole, in NR based on sulphur as the curing agent. The evaluation of these accelerators was made using the formulations given below in Table 5.5. The experimental recipe (mix 1) was designed as a truck tyre tread compound.

TABLE 5.5:

RECIPES USED TO EXAMINE SAPA 1/1 AS A CURE ACCELERATOR IN COMPARISON WITH A SULPHENAMIDE ACCELERATOR IN NR RUBBER

Mix No:	1	2
	Santocure MOR	SAPA 1
NR (SMR 20)	100	100
ZnO	4	4
Sulphur	1.5	1.5
Santocure MOR	1.5	-
Santogard PVI	0.15	-
Flectol-H	1.0	1.0
IPPD	1.5	1.5
Microcrystalline wax	2	2
Stearic acid	2	-
Aromatic Oil (Dutrex 729)	7	7
ISAF-Black (N220)	48	48
SAPA 1/1	-	1.5

Mixing conditions and mixing cycles are described as follows:

Mixing conditions:

Rotor speed = 72 rpm
 Ram pressure = 4.5 kg/cm²
 Fill factor = 0.75
 Cooling water = full on

Mixing cycle:

Time:	Operation:
0	NR
1	FEF black + (ZnO + stearic acid + Flectol-H + IPPD + wax + SAPA 1/1)
2	Aromatic oil (Dutrex 729 UK)
4	Clean
4'15"	Dump

Santocure MOR, Santogard PVI, and sulphur of mix 1 were added on a two roll rubber mill and mixed for 2 minutes. For mix 2 only the sulphur was added on the mill. Each mix was then refined 6 times through a tight nip and then sheeted off the mill at a thickness, normally approximately 3.0 mm, appropriate for subsequent tests.

The results of this investigation are summarised in Figure 5.5 and Table 5.6. It can be seen from these results that the SAPA 1/1 accelerator containing mix has higher Mooney viscosity, by about 6 units, than the sulphenamide accelerator containing mix. This increase in the Mooney viscosity may be in agreement with the previous suggestion of Section 2.3 that as a result of the heat generated during mixing the SAPA 1/1 promoted a chemical reaction between itself and the natural rubber molecule to produce in situ a few chemical crosslinks; should such a process occur it would be analogous to the in situ formation of a slightly gelled rubber similar to SP types of natural rubber or the divinyl benzene SBR series. The improvement in the processability, at the milling stage, of the NR mix contained SAPA 1/1 over the sulphenamide mix was quite noticeable. The latter mix used to run on the rear roll which had a lower temperature than the front roll and it also used to stick to both the rolls. These processing difficulties were almost entirely eliminated with the SAPA 1/1 containing mix.

The curing and the vulcanisate properties of the sulphenamide containing compound were superior to those of the SAPA 1/1 containing mix. However, the SAPA 1/1 mix showed significantly better thermal stability than the sulphenamide mix which reverted (see Figure 5.4).

TABLE 5.6:
EFFECT OF SAPA 1/1 AS ACCELERATOR IN COMPARISON WITH A SULPHENAMIDE ACCELERATOR ON THE PROCESSING, CURING AND PHYSICAL PROPERTIES OF A TRUCK TYRE TREAD COMPOUND [FOR FORMULATION SEE TABLE 5.5]

Mix No:	1	2
	Sulphenamide System	SAPA 1/1 System
<u>Processing and Curing Properties:</u>		
Mooney Viscosity ML (1+4) 100°C	52	58
Mooney Scorch, at 125°C (m)	20	9
Optimum Curing Time, t ₉₀ , at 160°C (m)	5'30"	12
<u>Physical Properties:</u>		
Tensile Strength MPa	27	19
100% Modulus MPa	2.6	2
300% Modulus MPa	10.7	7.2
Elongation at break %	590	535
Tear Strength kN m ⁻¹	80	65
Hardness, IRHD	72	62
Rebound Resilience %	37	36

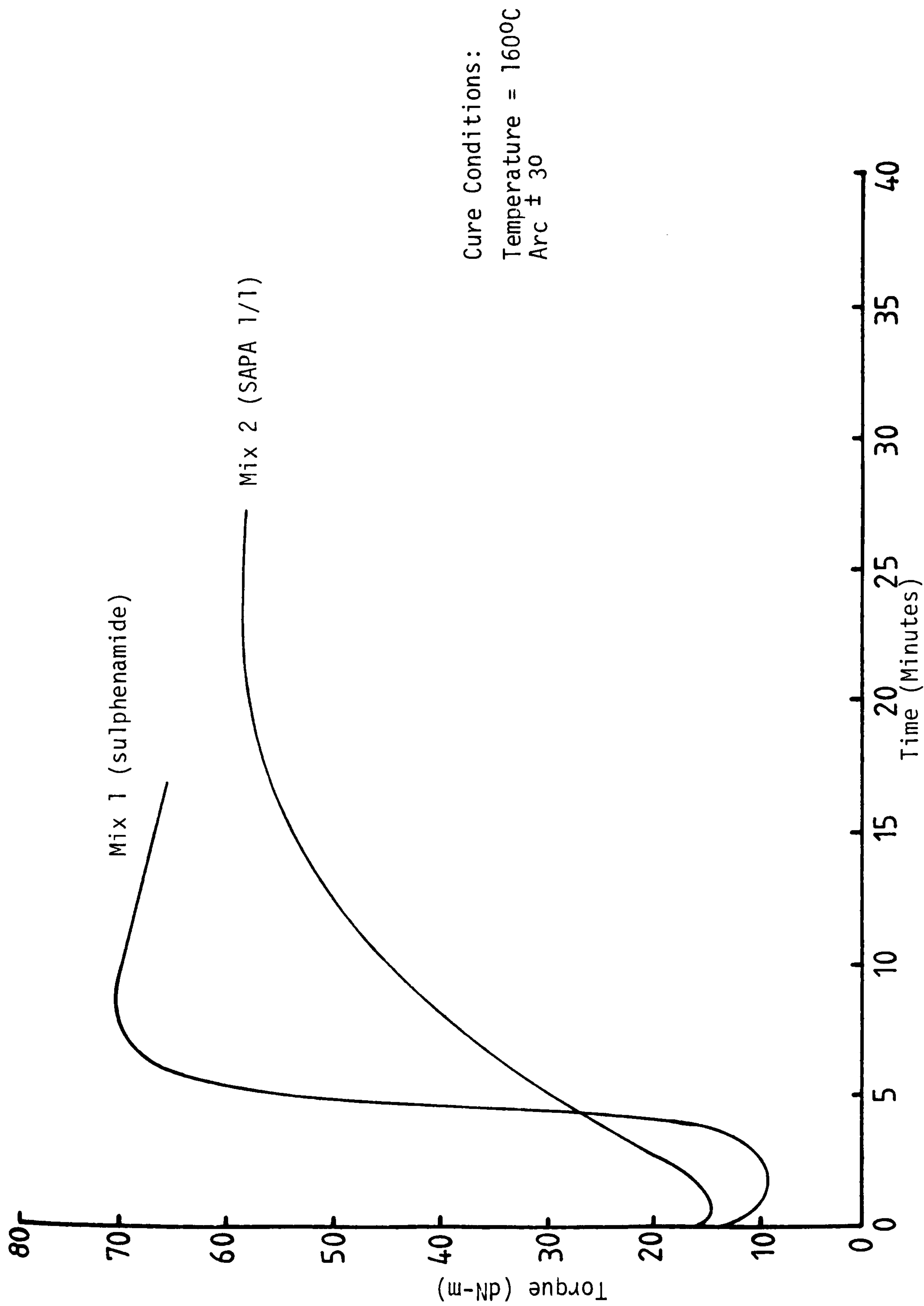


FIGURE 5.4: SALA 1/1 Vs THE SULPHENAMIDE (MOR) IN NR (FOR FORMULATIONS SEE TABLE 5.5)

5.2 Surfactants and SBR Rubber

As a general statement, styrene-butadiene rubbers, because of their lower unsaturation, are slower curing than natural rubber and require more acceleration. The results of Section 5.1 had demonstrated that acceleration by surfactants followed the same mechanism usually adopted by conventional accelerators.

In this part of the research work the use of various surfactants, prepared salts and diamide materials as cure activator/accelerator systems for SBR rubber are reported.

5.2.1 Surfactants, Prepared Salts and Diamide Material Systems Vs Sulphenamide Systems

In this investigation the following systems were selected for study as the cure activator/accelerator systems for SBR rubber in comparison with a conventional sulphenamide accelerator system.

- I: SAPA 1/1.
- II: NSI, NSC/2 and NSA/1.
- III: EBF-S.
- IV: SAPA 2/A, SAPA 2/B, SAPA 2/C, SAPA 2/D and SAPA 2/E.
- V: Sulphenamide; CBS.

The formulations used are given in Table 5.7. Mixing followed the same mixing procedure adopted earlier in Chapter 3.

The ageing behaviour of NSA/1 containing vulcanisate is examined in comparison with a vulcanisate obtained by a conventional sulphenamide accelerator system. Two methods were utilised in evaluating the resistance of these vulcanisates to oxidative degradation.

These are as follows:

- A: Oxidative hot air oven ageing (BS 903: Part A19) at 100°C for 8 days.
- B: Stress-relaxation in tension: using a dumbell test piece, 1.5 mm thick, held at 100% extension at 100°C in the tensile testing machine. The gradual decrease in tension was automatically recorded using a potentiometric recorder (Servoscribe RE 511.20).

In every experiment, the test sample was extended to approximately 100% extension. This is mainly because it has been reported [77] that scission rate is independent of elongation up to about 150%.

Figure 5.5 and Table 5.8 summarise the results for the NS series, SAPA 1/1 and the EBF-S materials as individual cure activator/accelerator systems in comparison with the sulphenamide accelerator system. The rheographs given in Figure 5.5 show that the curing behaviour of the EBF-S and the NSC/2 systems are different from the other surfactant systems. The EBF-S system shows a very long induction period and slow curing rate whilst the NSC/2 system shows shorter scorch time and faster curing rate than all the other surfactant systems. The reasons for such variation in the curing behaviour were explained before in Section 3.2. The optimum curing time, t_{90} , of the surfactant and the prepared salts of Table 5.8 are nearly similar, with the exception of the EBF-S system, to the t_{90} of the CBS system. However, the scorch time of the control mix, the sulphenamide system, is longer by about 47-217%, than all the prepared salts and the surfactant system, with the exception of the EBF-S system. This is believed to be due to the low level (0.5 phr) of the sulphenamide used in comparison with the 1.5 phr level of the surfactants.

It is interesting that all these new systems, except the EBF-S system, exhibited considerably higher states of cure than that of the conventional sulphenamide system (see Figure 5.5).

The physical properties, given in Table 5.8, of all the vulcanisates based on these materials, with the exception of the EBF-S system, are superior to that of conventional sulphenamide systems. Of particular note is the higher stress-strain properties obtained by almost all these new systems, particularly those obtained with the SAPA 1/1 surfactant system, in comparison with those obtained by the conventional sulphenamide system.

An additional concept introduced by the use of the SAPA 1/1 type of accelerator is that of better filler dispersion (see Section 3.3.1). This property is, once again, observed to occur with the SAPA 1/1 system when the tensile fractured surfaces of the sulphenamide and the SAPA 1/1 vulcanisates were examined by the scanning electron microscopy technique whose micrographs are given in Figure 5.6(a) and (b). The presence of large undispersed filler agglomerates (note holes) are evident in the (a) micrograph (CBS) indicating poor rubber penetration and breakdown of the aggregates by the rubber. The (b) micrograph (SAPA 1/1) shows excellent dispersion of the black, and the rubber surface appears continuous, that is there are no gaps or holes which would be indicative of poor wetting of the black. This observation could explain the higher reinforcement effects which were observed to be possessed by the surfactant containing vulcanisates.

The ageing behaviour of the NSA/1 vulcanisates in comparison with the sulphenamide vulcanisate is shown in Table 5.8. The results show that both systems exhibit similar fractional strain energy which may indicate that these systems have similar resistance to thermal oxidative ageing. However the compression set value achieved by the NSA/1 vulcanisate is better (i.e. lower) by about 18%, than that of the sulphenamide vulcanisates. These results, therefore, confirm the previous results of the high ODR modulus and the vulcanisate modulus of the surfactant and the prepared salts system observed before.

The thermal oxidative stress-relaxation behaviour of the vulcanisates obtained by the conventional sulphenamide system and the NSA/1 system are given in Figure 5.7. As can be seen in this figure the thermal oxidative stability of both systems is almost the same up to about 44 hours of ageing after which the sulphenamide exhibited better thermal stability than the NSA/1 vulcanisate. The two systems are believed to form predominantly polysulphidic linkages and hence they should have the same heat stability. The decline in thermal oxidative ageing of the NSA/1 system after about 44 hours is thought to be due to the omission from the formulation of zinc oxide which is known to improve ageing resistance. However, this subject has been studied in detail in Chapter 7.

Figure 5.8 and Table 5.9 summarise the results of the SAPA 2 series cationic surfactants as cure activator/accelerator systems for SBR rubber in comparison with conventional sulphenamide accelerator systems (see formulations in Table 5.7). These results clearly show that the effect of SAPA 2/A, SAPA 2/B, SAPA 2/C, SAPA 2/D and SAPA 2/E as cure activator/acceleration systems on the curing and physical properties of the SBR rubber are similar to each other. Hence, once again, the effect of varying the alkyl group in the surfactant has not resulted in any significant difference in the curing and vulcanisates properties of the SBR rubber. However, the curing and the physical properties of all these new system based compounds are superior to those of the control mix; the conventional sulphenamide based compound.

Comparing the results of the SAPA 2 series with those of the SAPA 1/1 and the NS series it appears that all of these materials have almost similar effects on the processing and physical properties of the SBR rubber. However, their effect on the curing behaviour is considerably different from each other. The reasons for this were explained before (see Section 3.2).

TABLE 5.7:

FORMULATION USED TO EXAMINE VARIOUS SURFACTANT, DIAMIDE MATERIAL AND PREPARED SALTS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS IN COMPARISON WITH A SULPHENAMIDE SYSTEM IN SBR RUBBER

	Control Mix	Test Mix
	Conventional Sulphenamide System	Surfactants Systems
SBR 1500	100	100
Sulphur	2	2
Flectol-H	0.75	2
IPPD	2	2
Aromatic Oil (Dutrex 729)	5	5
FEF-Black	50	50
CBS	0.5	-
ZnO	4	-
Stearic Acid	2	-
New Systems	-	1.5

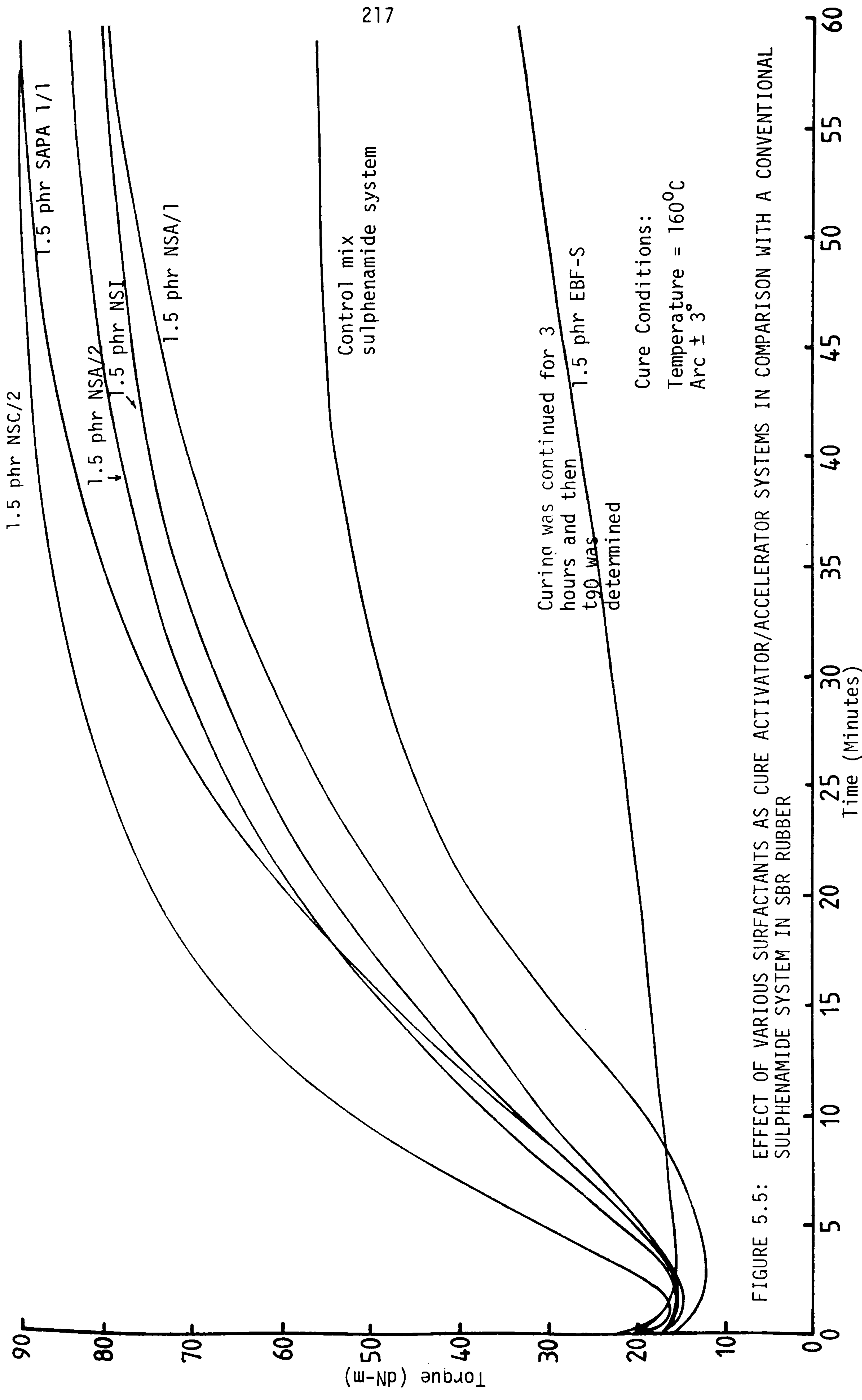


FIGURE 5.5: EFFECT OF VARIOUS SURFACTANTS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS IN COMPARISON WITH A CONVENTIONAL SULPHENAMIDE SYSTEM IN SBR RUBBER

TABLE 5.8

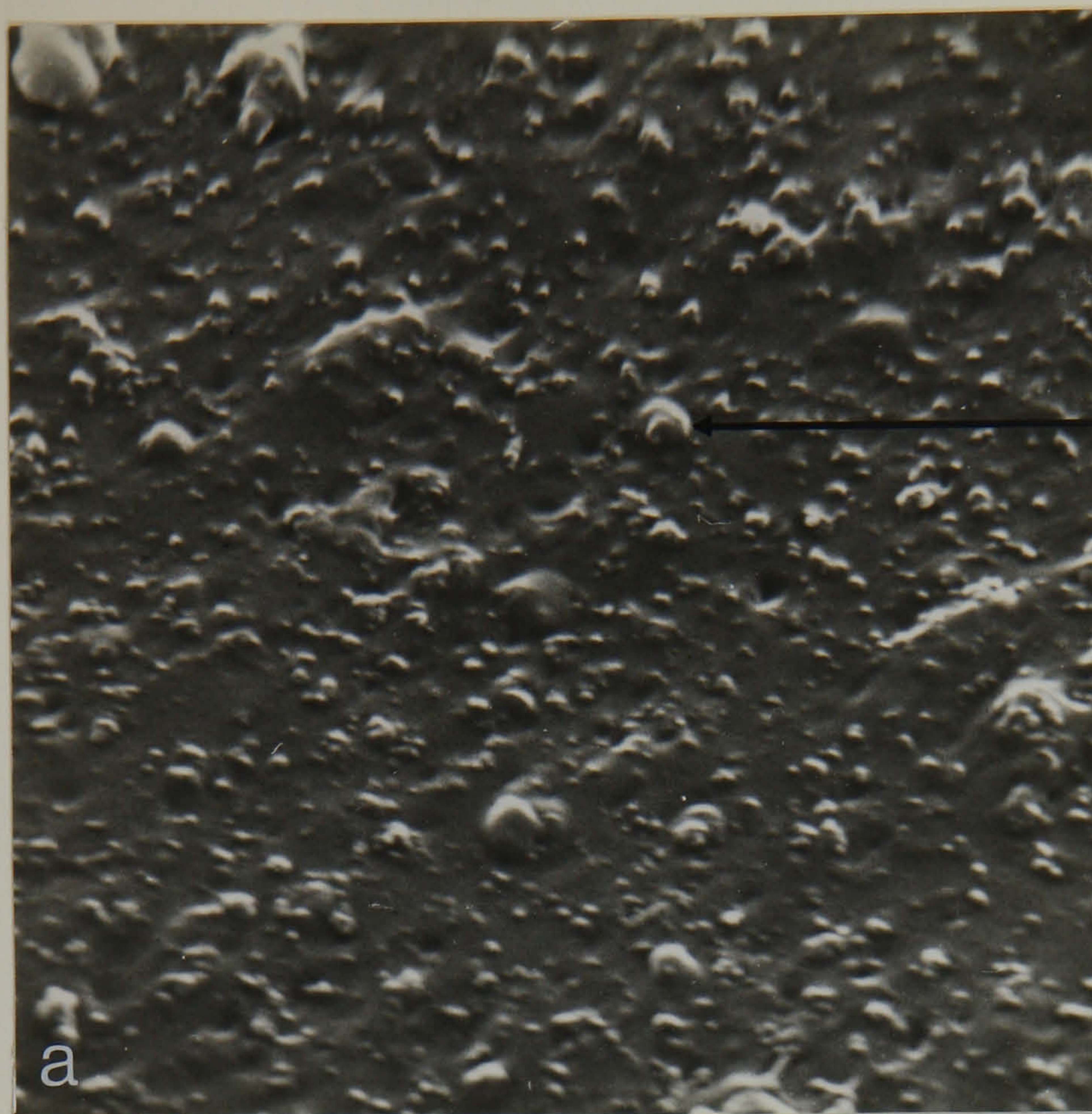
EFFECT OF VARIOUS SUBSTANCES AS CURE ACTIVATOR/ACCELERATOR SYSTEMS FOR SBR RUBBER IN COMPARISON WITH A CONVENTIONAL SULPHENAMIDE (CBS) SYSTEM [FOR FORMULATIONS SEE TABLE 5.7]

Mix No:	1	2	3	4	5	6	7
	Control Sulphenamide System	NSA/1 System	NSA/2 System	NS1 System	SAPA 1/1 System	NSC/2 System	EBF-S System
<u>Processing and Curing Properties:</u>							
Mooney Viscosity ML(1+4)100°C	58	60	61	61	60	60	58
Mooney Scorch at 125°C (m)	53	36	20	36	36	17	More than 2 hours
Optimum Curing Time, t ₉₀ at 160°C (m)	32	40	38	40'30"	38	29	2'15"
<u>Physical Properties:</u>							
Tensile Strength MPa	16	19	18.5	20	21.8	19.5	16
100% Modulus MPa	2	3	2.5	3	3	3	2
300% Modulus MPa	7	11.4	10	10.5	11.2	11	6.5
Elongation at break %	640	475	520	535	540	505	610
Tear Strength kN m ⁻¹	70	63	50	50	55	51	45
Hardness, IRHD	59	62	60	60	62	60	59
Rebound Resilience, %	50	56	52	53	54	53	51

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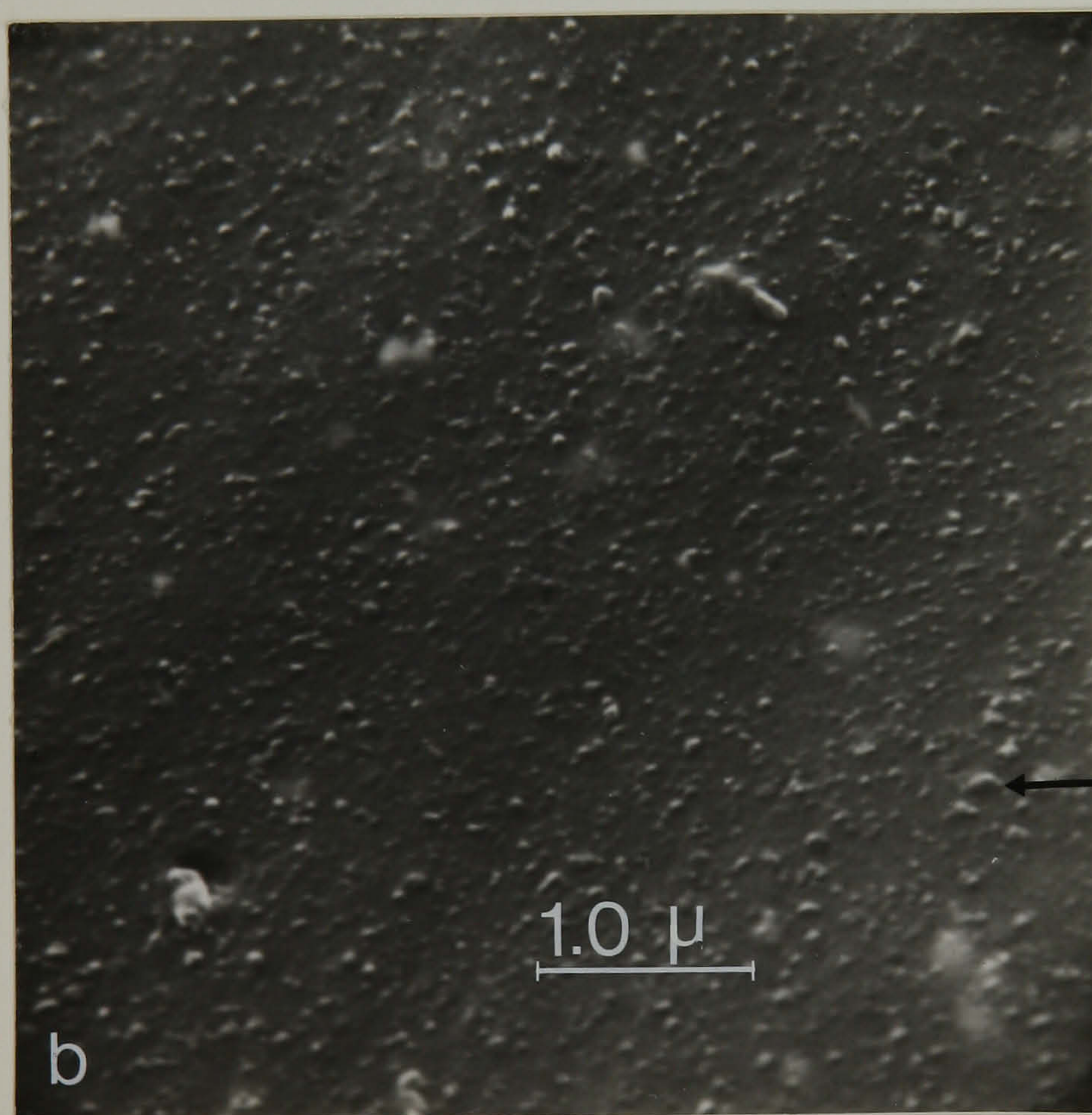
TABLE 5.8 ... continued

Mix No	1		2	
	Control Sulphenamide System		NSA/1 System	
Aged Properties (100°C for 8 days)		% Change in Property		% Change in Property
Tensile Strength MPa	14	(-) 12.5	14	(-) 21
100% Modulus MPa	4.3	(+) 115	4.5	(+) 50
300% Modulus MPa	15	(+) 114	-	-
Elongation at Break %	330	(-) 49	264	(-) 45
Compression set %	68	-	56	-
Fractional Strain Energy (TE)f	0.45	-	0.44	-
Tear Strength kN m ⁻¹	50	(-) 29	48	(-) 24
Hardness, IRHD	68	(+) 9	66	(+) 4 units
Rebound Resilience, %	52	(+) 4	56	No change



Control mix
with sulphenamide
system

Undispersed large
aggregate



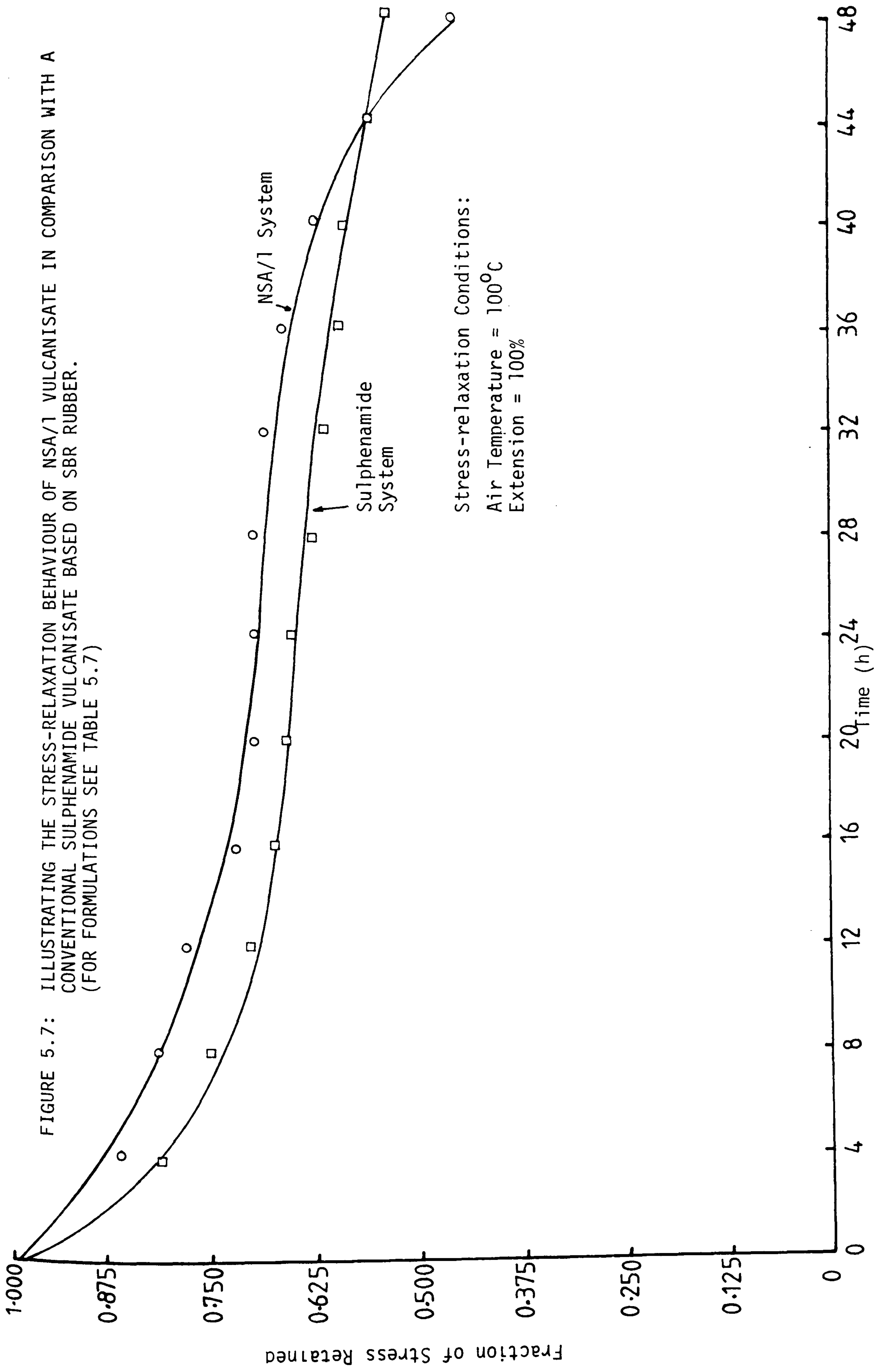
Experimental mix
with SAPA 1/1 system

Undispersed small
aggregate

FIGURE 5.6: SEM MICROGRAPH ($\times 7000$ MAGNIFICATION OF A TORN SURFACE TO ILLUSTRATE THE ABILITY OF THE SAPA 1/1 SURFACTANT AS A FILLER DISPERSION AND WETTING AGENT IN ADDITION TO BEING A CURE ACTIVATOR/ACCELERATOR SYSTEM IN SBR RUBBER

- a) SULPHENAMIDE SYSTEM
- b) WITH 1.5 phr SAPA 1/1 AS A CURE ACTIVATOR/ACCELERATOR SYSTEM

FIGURE 5.7: ILLUSTRATING THE STRESS-RELAXATION BEHAVIOUR OF NSA/1 VULCANISATE IN COMPARISON WITH A CONVENTIONAL SULPHENAMIDE VULCANISATE BASED ON SBR RUBBER. (FOR FORMULATIONS SEE TABLE 5.7)



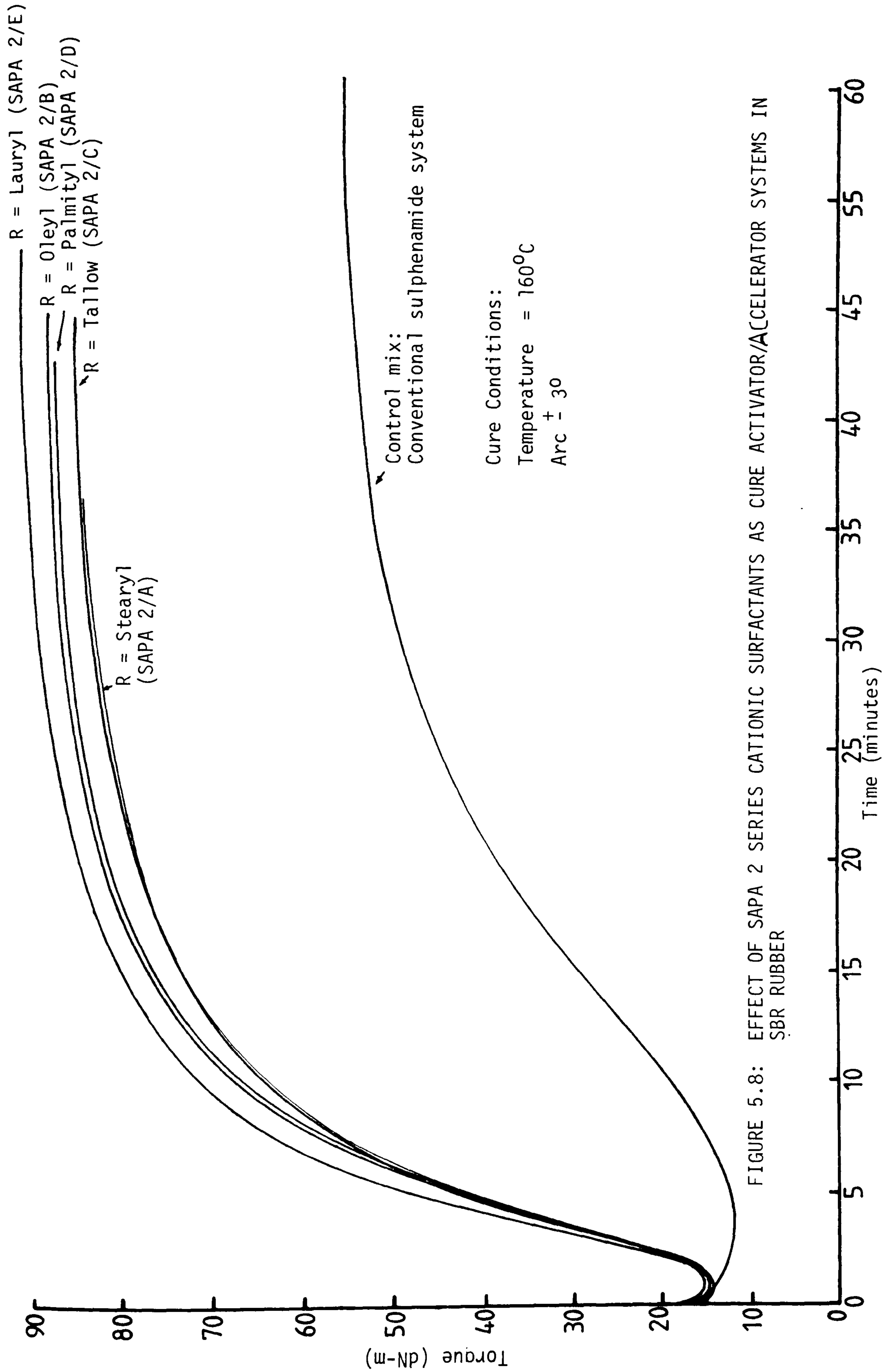


FIGURE 5.8: EFFECT OF SAPA 2 SERIES CATIONIC SURFACTANTS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS IN SBR RUBBER

TABLE 5.9
EFFECT OF SAPA 2 SERIES SYSTEMS AS CURE ACTIVATOR/ACCELERATOR FOR SBR
COMPARED WITH A CONVENTIONAL SULPHENAMIDE ACCELERATOR SYSTEM
[FOR FORMULATIONS SEE TABLE 5.7]

	Control Mix Sulphenamide System	SAPA 2/A System	SAPA 2/B System	SAPA 2/C System	SAPA 2/D System	SAPA 2/E System
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(J+4)100°C Mooney Scorch at 125°C (m) Optimum Curing Time t ₉₀ at 160°C (m)	58 53 32	64 8'30" 19'30"	62 8 19	64 8 21	64 8 20	62 7 19
<u>Physical Properties:</u> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness, IRHD Rebound Resilience, %	16 2 7 642 70 59 50	18.6 2.85 10.85 491 59 61 55	19 3 11.6 460 58 64 57	18 2.9 10.5 491 63 60 54	19.4 3 11 491 61 62 57	19 3 11.6 476 58 64 56

5.2.2 SAPA 1/1 Vs Thiazole Accelerator Systems in SBR

A comparison study was made between SAPA 1/1, as a cure activator/accelerator system, and a thiazole accelerator system in carbon black and silica reinforced SBR rubber. This study is reported here.

The formulations used are given below in Table 5.10

TABLE 5.10:

RECIPES USED TO EXAMINE SAPA 1/1 AS A CURE ACTIVATOR/ACCELERATOR FOR SBR IN COMPARISON WITH A THIAZOLE ACCELERATOR SYSTEM

Mix No:	1	2	3	4
	Conventional Curing System Carbon black	Conventional Curing System Silica	SAPA 1/1/S Curing System Carbon Black	SAPA 1/1/S Curing System Silica
SBR 1500	100	100	100	100
ZnO	5	5	-	-
Stearic acid	2	2		
Sulphur	2	2	2	2
MBT	1.5	1.5	-	-
DPG	0.5	0.5	-	-
SAPA 1/1	-	-	2	2
Flectol-H	2	2	2	2
Aromatic Oil (Dutrex 729 UK)	5	5	5	5
HAF Black	30	-	30	-
Silica (Ultrasil VN3)	-	30	-	30

Mixing conditions and cycles are as follow :

Mixing Conditions:

Rotor speed	=	60 rpm
Ram pressure	=	2.5 kg/cm ²
Fill factor	=	0.75
Cooling water	=	On

Mixing Cycle:

Step:	Time:	Operation:
1	0'	SBR
2	30"	$\frac{1}{2}$ Black + $\frac{1}{2}$ Oil + ingredients r.d.
3	1'30"	$\frac{1}{2}$ Black + $\frac{1}{2}$ Oil + SAPA1/1 if present r.d.
4	3'30"	MBT/DPG r.d.
5	5'	Clean
6	5'30"	Dump r.d.

When the silica was introduced step 3 was extended for one further minute making the total mixing time equal to 6 minutes and 30 seconds.

The results of this study are given in Figure 5.9 and Table 5.11. Scorch times for the SAPA 1/1 system are comparable with those of MBT/DPG though time to optimum (t_{90}) cure is greater. SAPA 1/1 mixes have higher modulus and they do not show cure reversion with the relatively high sulphur level of 2 phr; whereas the MBT/DPG/S system shows conventional reversion. Flow and release properties were superior in the SAPA1/1 formulations (mixes 3 and 4 of Table 5.7) even in the absence of stearic acid. These processing advantages of SAPA containing mixes are now explored.

Deliberately, a bad compression moulding technique was adopted to examine the potential of SAPA 1/1 as a flow additive in addition to

its main purpose as a cure activator/accelerator system. A cold thick round blank (ca. 10 mm thick) was compression moulded by the simple application of pressure to form a standard 2 mm thick test sheet of rubber. The control mixes (numbers 1 and 2 of Table 5.10) all produced moulded sheets possessing defects due to flow problems, whereas by contrast the mixes containing SAPA 1/1 (numbers 3 and 4 of Table 5.10) possessed markedly superior flow and produced undistorted stress free vulcanisates which readily released from the metal surface of the mould without the use of externally applied mould release agent.

TABLE 5.11:

SAPA 1/1 V MBT/DPG ACCELERATORS IN CARBON BLACK AND SILICA FILLED SBR RUBBER

Mix No:	1	2	3	4
	MBT/DPG/S System + Black	MBT/DPG/S System + Silica	SAPA1/1/S System + Black	SAPA1/1/S System + Silica
<u>Processing and Curing Properties:</u>				
Mooney Viscosity by ML (1+4)100°C	57	68	55	70
Scorch time at 125°C(m)	14'30"	>60'	13'30"	>60'
Optimum Curing Time, t_{90} at 160°C (m)	8	46	23	60
<u>Physical Properties:</u>				
Ultimate Tensile Strength MPa	17	17	17.5	17
100% Modulus MPa	2	1.5	2.5	1.7
300% Modulus MPa	7.5	3	8	4
% Elongation at break	590	980	560	920
Tear Strength kN m^{-1}	39	25	35	34
Hardness, IRHD	58	54	58	55
Rebound Resilience %	49	55	52	60

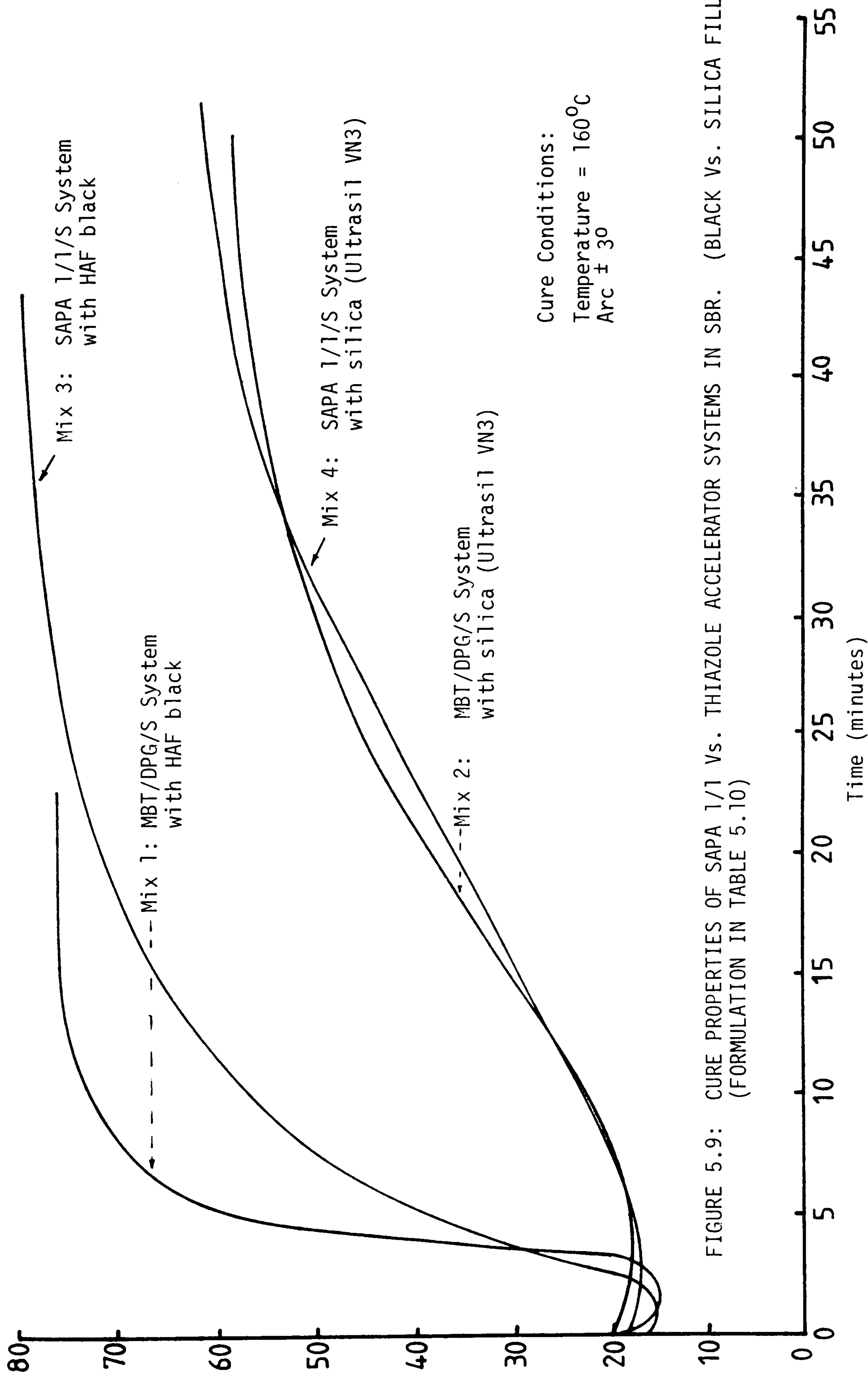
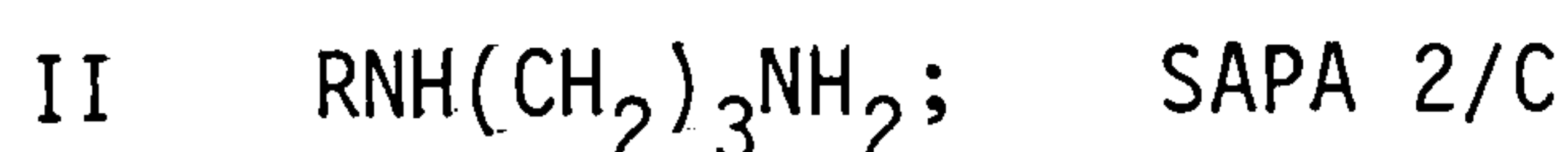
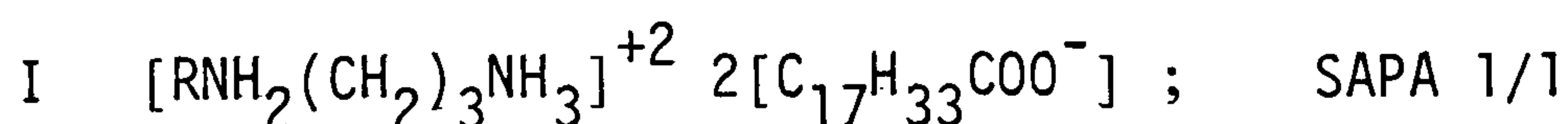


FIGURE 5.9: CURE PROPERTIES OF SAPA 1/1 Vs. THIAZOLE ACCELERATOR SYSTEMS IN SBR. (BLACK Vs. SILICA FILLERS) (FORMULATION IN TABLE 5.10)

5.2.3 Effect of Zinc Oxide on the Performance of Two Different Surfactants/Sulphur Curing Systems in SBR Rubber

The effect of zinc oxide and stearic acid on the performance of two types of surfactants in SBR rubber is reported here. The surfactants selected in this study are of two different chemical structures and they are as follows:



The base formulation used in this part of the research work is the test mix recipe of Table 5.7.

Figure 5.10 and Table 5.12 summarise the results for the effect of zinc oxide and stearic acid on the performance of SAPA 1/1/sulphur and SAPA 2/C/sulphur curing systems in SBR rubber. It can be seen from these results that the effect of zinc oxide on the curing behaviour of the SAPA 1/1/sulphur system is very clear. The addition of 2-4 phr of ZnO increased the scorch time to >120 minutes. This is, however, at the expense of the time to reach optimum cure which is then extended to between 80-90 minutes at 160°C compared with 38 minutes for SAPA 1/1 without zinc oxide.

Concerning the results of the effect of ZnO on the curing behaviour of the SAPA 2/C based compound it can be seen that ZnO has almost no effect on the curing behaviour of the SAPA 2/C/sulphur system as can be seen in Figure 5.11 and Table 5.12.

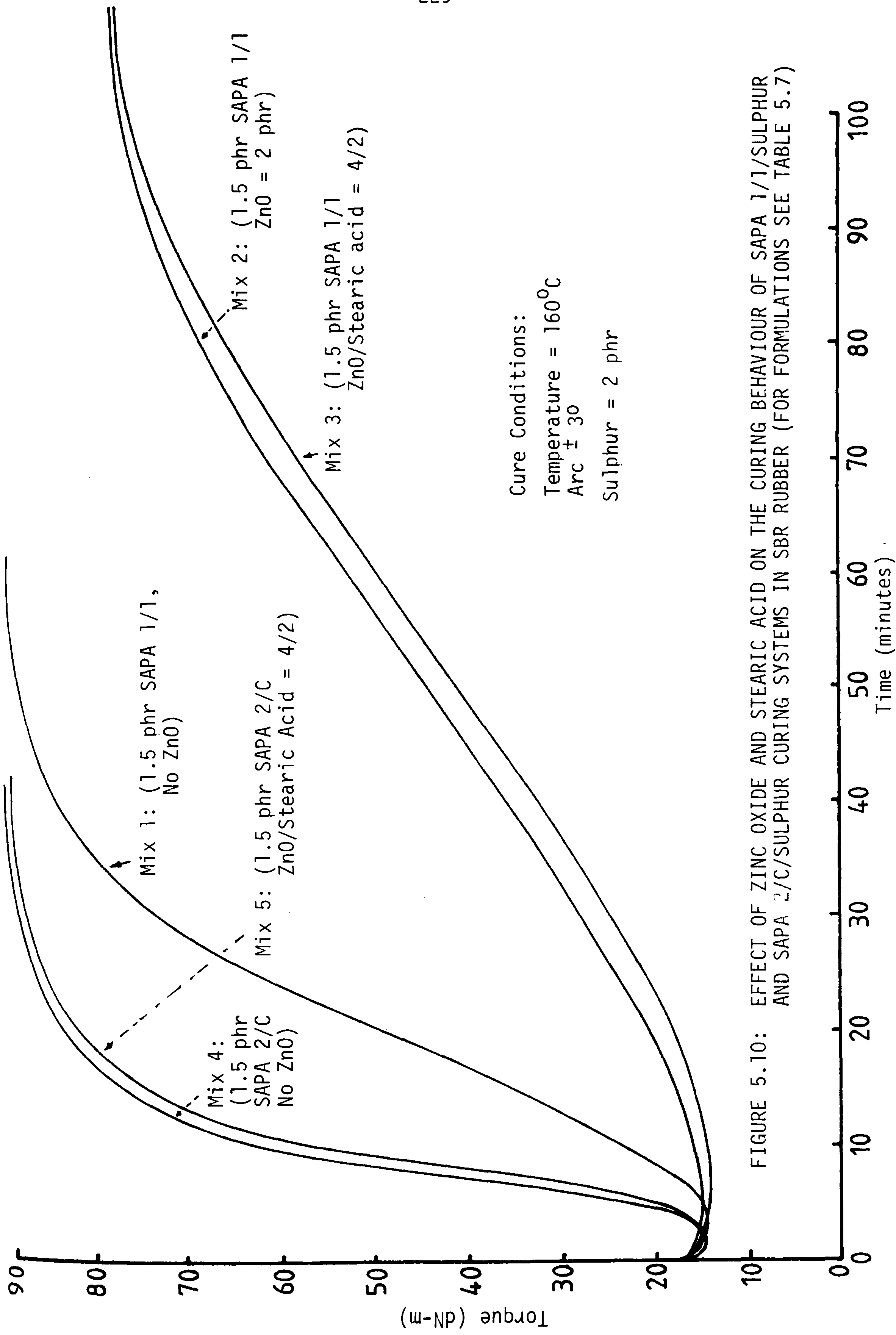


FIGURE 5.10: EFFECT OF ZINC OXIDE AND STEARIC ACID ON THE CURING BEHAVIOUR OF SAPA 1/1/SULPHUR AND SAPA 2/C/SULPHUR CURING SYSTEMS IN SBR RUBBER (FOR FORMULATIONS SEE TABLE 5.7)

TABLE 5.12
EFFECT OF ZnO AND STEARIC ACID ON THE PERFORMANCE OF SAPA 1/1/SULPHUR AND SAPA 2/C/SULPHUR CURING SYSTEMS IN SBR RUBBER

Mix No:	1	2	3	4	5
	1.5phr SAPA 1/1	1.5phr SAPA 1/1 ZnO = 2 phr	1.5phr SAPA 1/1 ZnO = 4 phr St.A= 2 phr	1.5phr SAPA 2/C	1.5phr SAPA 2/C ZnO = 4 phr St.A= 2 phr
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4)100°C Mooney Scorch 1250C (m) Optimum Curing Time, t ₉₀ , at 160°C (m)	60 36 38	60 >120 83	62 >120 89	64 8 21	62 10 22
<u>Physical Properties:</u> Tensile Strength MPa Elongation at break % 100% Modulus MPa 300% Modulus MPa Hardness, IRHD Rebound Resilience, % Tear Strength, kN m ⁻¹	22 540 3 11.2 62 52 54	23 490 3.3 12.5 64 51 50	22.8 535 3 10.7 60 50 56	18 490 2.9 10.5 60 54 63	19 505 3 10.5 60 53 62

The different responses of SAPA 1/1 and SAPA 2/C to ZnO is believed to be due to their different chemical structures. The zinc oxide is thought to react with SAPA 1/1 producing a zinc ion complex which in turn is a stable compound and less reactive than SAPA 1/1 by itself. Hence such a complex will reduce the cure rate. This suggestion, however, is discussed later in Section 5.5.

The use of stearic acid as part of the activator system, once again, does not seem to be necessary in the formulation.

Generally, the results of Table 5.12 clearly show that ZnO has almost no effect on the physical properties of both the SAPA 1/1/sulphur curing system and the SAPA 2/C/sulphur curing system.

5.2.4 Ethylene Bis Stearamide (EBF-S) as a Secondary Accelerator for SBR Rubber

The previous research work has demonstrated that the EBF-S material cannot be used as an activator/accelerator system on its own, for the particular rubbers tested. For this reason it was decided to carry out an investigation to examine whether this diamide material could be used as a secondary accelerator for SBR rubber.

The base formulation used was: SBR 1500 100, S 2, FEF black 50, MBT as given in Table 5.13.

The results of this investigation are reported in Figure 5.11 and Table 5.13. It can be seen that the inclusion of the EBF-S (2 phr) has resulted in a significant reduction in the optimum curing time, t_{90} , (about 196% less than that of mix 1); this occurs when the zinc oxide level is reduced from 4 phr to 1 phr and the stearic acid is completely eliminated with the MBT (1 phr). This reduction in the optimum curing time is accompanied by a considerable reduction

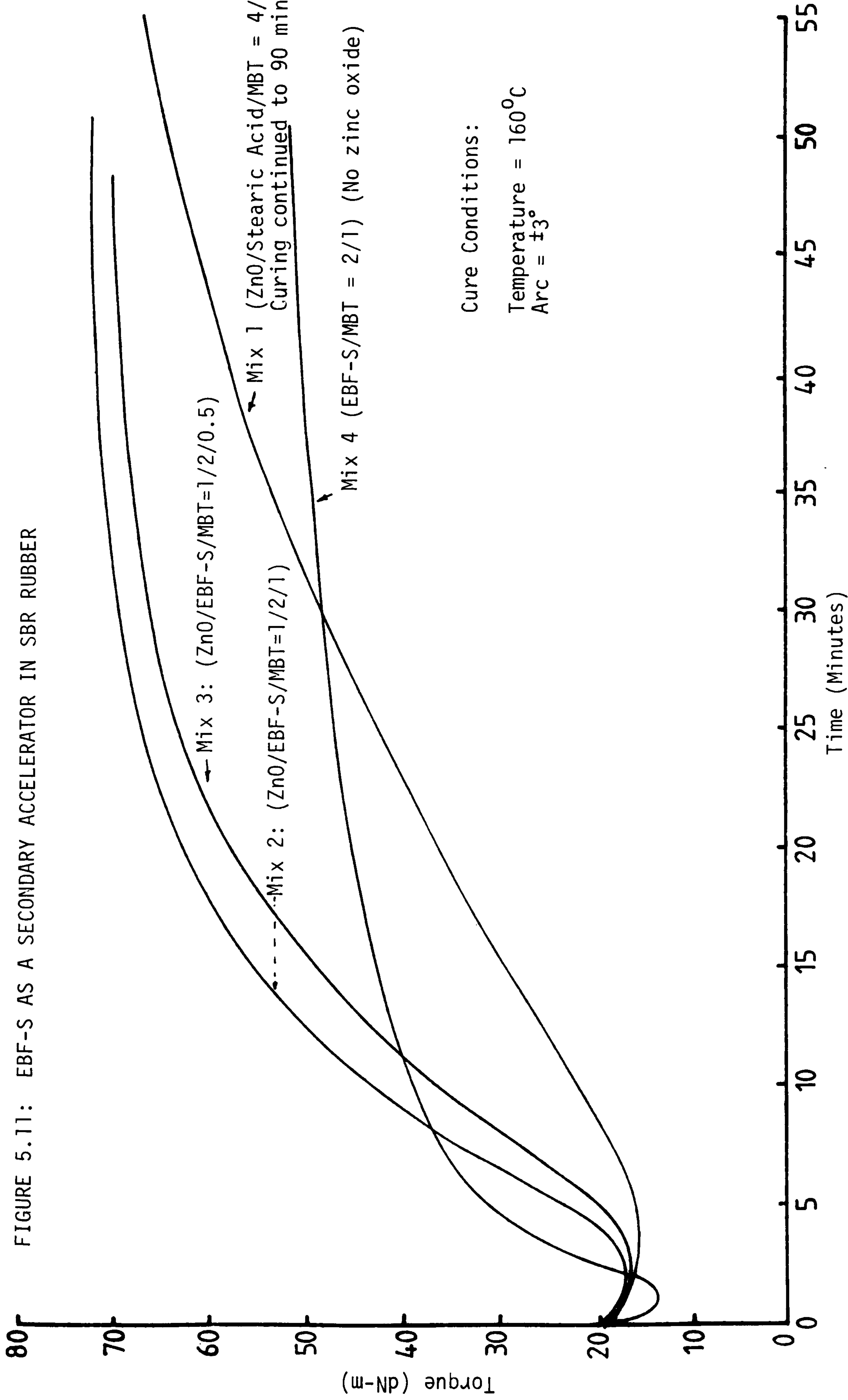


TABLE 5.13:

EFFECT OF THE EBF-S DIAMIDE SYSTEM WHEN USED AS A SECONDARY ACCELERATOR FOR SBR RUBBER

Mix No:	1	2	3	4
	ZnO = 4phr St.A= 2phr MBT = 1phr	ZnO = 1phr EBF-S=2phr MBT = 1phr	ZnO = 1phr EBF-S=2phr MBT=0.5phr	ZnO = 0 EBF-S=2phr MBT = 1phr
<u>Processing and Curing Properties:</u>				
Mooney Viscosity ML/1+4)100°C	61	60	60	58
Mooney Scorch, t_5 , at 125°C (m)	66	28	38	9
Optimum Curing Time, t_{90} , at 160°C (m)	74	25	30	48
<u>Physical Properties:</u>				
Tensile Strength MPa	18.7	18	18	16.8
100% Modulus MPa	2.5	2.4	2.4	1.5
300% Modulus MPa	9.5	8.7	8.5	4.9
Elongation at Break %	529	566	551	748
Tear Strength kN m^{-1}	50	59	61	46
Hardness IRHD	61	60	60	52
Rebound Resi- lience %	52	53	52	52

in the scorch time (ca. 135% below that of mix 1). Such behaviour obviously indicates that the EBF-S system has acted as a secondary accelerator. It can also be observed that no adverse effect on the physical properties of the SBR compound has resulted from using the EBF-S system as a secondary accelerator.

The complete elimination of the zinc oxide from mix 4 has resulted in a significant reduction in the scorch time (by about 211%) from that of mix 2. Also the optimum curing time was increased by about 92% from that of mix 2. These are in addition to the significant reductions which occurred in the ODR modulus of mix 4. This reduction has resulted in poor physical properties. Hence a minimum amount of zinc oxide is important to achieve optimum curing and good physical properties of the EBF-S system if used as a secondary accelerator.

Stearic acid, once again, seems to play no part in the vulcanisation process, therefore its presence is not necessary in the formulation.

5.2.5 Effect of Triethanolamine on the Curing Behaviour of Various Ethylene Bis Fatty Amides in SBR Rubber

Triethanolamine (TEA) and diethylene glycol, together with various waxy polyethylene glycols (Carbowax) are conventionally used as cure activators to enable silica and silicate compounds to be satisfactorily cured with conventional sulphur, accelerator levels. However, it has been reported [78] that zinc oxide is the key factor to achieve good crosslinking levels in the presence of TEA or stearic acid in gum, carbon black and silica filled rubber compounds based on conventional accelerator/sulphur curing systems. In this part of the research work the effect of triethanolamine (TEA) on the curing behaviour of the EBF-S and the EBF-0 systems in a carbon black filled SBR are reported. The study also includes the effect of zinc oxide on the EBF-S/TEA/sulphur and the EBF-0/TEA/sulphur curing systems in SBR

rubber in comparison with a conventional accelerator system. The formulations which were used throughout the study are given below in Table 5.14.

TABLE 5.14:

FORMULATIONS USED TO EXAMINE EBF-S/TEA AND EBF-O/TEA COMBINATION AS CURE ACTIVATOR/ACCELERATOR SYSTEM WITH AND WITHOUT ZINC OXIDE IN SBR RUBBER IN COMPARISON WITH A CONVENTIONAL CURING SYSTEM

Mix No:	1	2	3	4	5
	Control MOR/DPG/S Curing System	Without Zinc Oxide		With Zinc Oxide	
		EBF-S/TEA/S Curing System	EBF-O/TEA/S Curing System	EBF-S/TEA/S Curing System	EBF-O/TEA/S Curing System
SBR (Intol 1500)	100	100	100	100	100
Sulphur	2	2	2	2	2
ZnO	3	-	-	3	3
Stearic acid	2	-	-	-	-
Santocure MOR	1	-	-	-	-
DPG	0.7	-	-	-	-
EBF-S	-	2	-	2	-
EBF-O	-	-	2	-	2
TEA	-	1	1	1	1
Flectol-H	2	2	2	2	2
Aromatic Oil (Dutrex 729)	2	-	-	-	-
ISAF(N220)	50	50	50	50	50

In addition to the standard physical properties the vulcanisates of all the mixes given in Table 5.14 were tested for ageing resistance in a hot air oven at 100°C for 7 days.

The results of this investigation are given in Figure 5.11 and Table 5.15. Examination of these results show the following features.

Processability and Curing Properties

The results of Table 5.15 clearly show that compounds containing the EBF-S/TEA and the EBF-O/TEA without and with zinc oxide have consumed less mixer power, by about between 18-21%, than the control mix containing the conventional curing system. The results also show that the Mooney viscosity of the compounds containing diamide/TEA systems are similar to that of the conventional curing system i.e. the control mix. Moreover, the processability of the diamides/TEA systems without and with zinc oxide as judged by two roll mill mixing behaviour was superior to that of the mix containing the conventional curing system (mix 1 of Table 5.14). It was observed that compounds containing the EBF-S/TEA and the EBF-O/TEA systems possessed significantly less elastic nerve during milling than the mix containing the conventional curing system. The flow of the compound containing the diamides /TEA system was excellent as shown by their compression moulded sheets which exhibited a glossy finish with no surface defects. The conventional accelerator system containing compound gave compression moulded sheets with poor surface finish.

It is known by now that the accelerating effect of the EBF-S material by itself is very low (see Figure 5.5). The inclusion of the 1 phr of triethanolamine with the EBF-S and the EBF-O had resulted in completely different behaviour from that of the sole use of EBF-S or EBF-O. The cure response curves (curves 2, 3, 4 and 5 of Figure 5.12) demonstrate that TEA had, somehow, acted as a cure activator and hence its combination with the EBF-S or EBF-O system demonstrated that a new activator/accelerator system for SBR rubber had been found. The curing characteristics as judged mainly by the scorch

time and the optimum curing time, t_{90} , of the ZnO/stearic acid/Santo-cure MOR/DPG/sulphur system are better than those obtained by the EBF-S/TEA/sulphur and the EBF-O/TEA/sulphur systems. However, it is believed that the curing behaviour of these new accelerating systems is industrially acceptable.

The addition of zinc oxide to the EBF-S/TEA and the EBF-O/TEA activator/accelerator systems increased the scorch times and the times to optimum cure, t_{90} , of these systems (see Figure 5.12).

Physical Properties

The results of Table 5.15 show that the properties of the EBF-S/TEA and the EBF-O/TEA vulcanisates, with and without zinc oxide, are similar to each other. Hence the presence of zinc oxide has almost no effect on the physical properties, particularly the modulus of these EBF type accelerating systems. The vulcanisate properties of the conventional accelerator system, mix 1 of Table 5.14, are similar to those of the diamides/TEA systems except that the MOR/DPG system has higher 100% and 300% modulus values of about 28% and 17% respectively. However, the diamides/TEA systems exhibited better fatigue resistance, at 100% extension, to that of the conventional accelerator system (ca. 68% superiority). This may be because the vulcanisate obtained from the conventional curing system possessed higher modulus. Usually, with constant strain the forces developed in the rubber are greater the higher its modulus, so that stiff rubbers are more severely stressed and will develop more heat build-up and fatigue stresses at the same strain and tend to fail sooner.

Ageing Behaviour

The results of the resistance of all the vulcanisates of Table 5.14 to thermal oxidative hot air oven ageing are illustrated in Table 5.15. These results indicate the following features:

1. The vulcanisates obtained with the EBF-S/TEA or the EBF-O/TEA activator/accelerator systems seem to undergo lower percentage changes in the physical properties as a result of the thermal ageing than those obtained with the conventional accelerator system. This is indicated by the higher fractional strain energy (TE)_f of the EBF/TEA vulcanisates (about 21%), compared with that of the conventional accelerator system based vulcanisate.
2. The inclusion of zinc oxide (3 phr) with the EBF-S/TEA and the EBF-O/TEA accelerator systems had considerably enhanced the resistance of their vulcanisates to heat ageing. As can be seen in the results of Table 5.15 the vulcanisates which were obtained with the EBF-S/TEA/ZnO and with the EBF-O/TEA/ZnO systems exhibited better fractional strain energy (TE)_f, by about 25%, than those obtained by the same systems but without zinc oxide being present.
3. Comparing the ageing behaviour of the EBF-S/TEA/ZnO/S or the EBF/TEA/ZnO/S curing system with that of the conventional curing system; ZnO/stearic acid/Santocure MOR/DPG, it can be seen from the results of Table 5.15, that the former systems have much better fractional strain energy (TE)_f (of about 52%) than the conventional curing system. It is thought that when zinc oxide is present with the EBF-S/TEA or the EBF-S/TEA activator/accelerator system a higher percentage of monosulphidic crosslinks are formed than those obtained with the conventional curing system. Hence, the vulcanisates obtained by these EBF type systems exhibit better ageing behaviour than those of the conventional curing system.

It has been observed before (see Section 3.3.4) during the tensile testing of the aged samples which contained the EBF-S as a processing additive that these samples exhibit severe blooming on their surfaces. This phenomena has, once again, been observed to occur with the samples based on the EBF-S/TEA as an activator/accelerator system with and without zinc oxide.

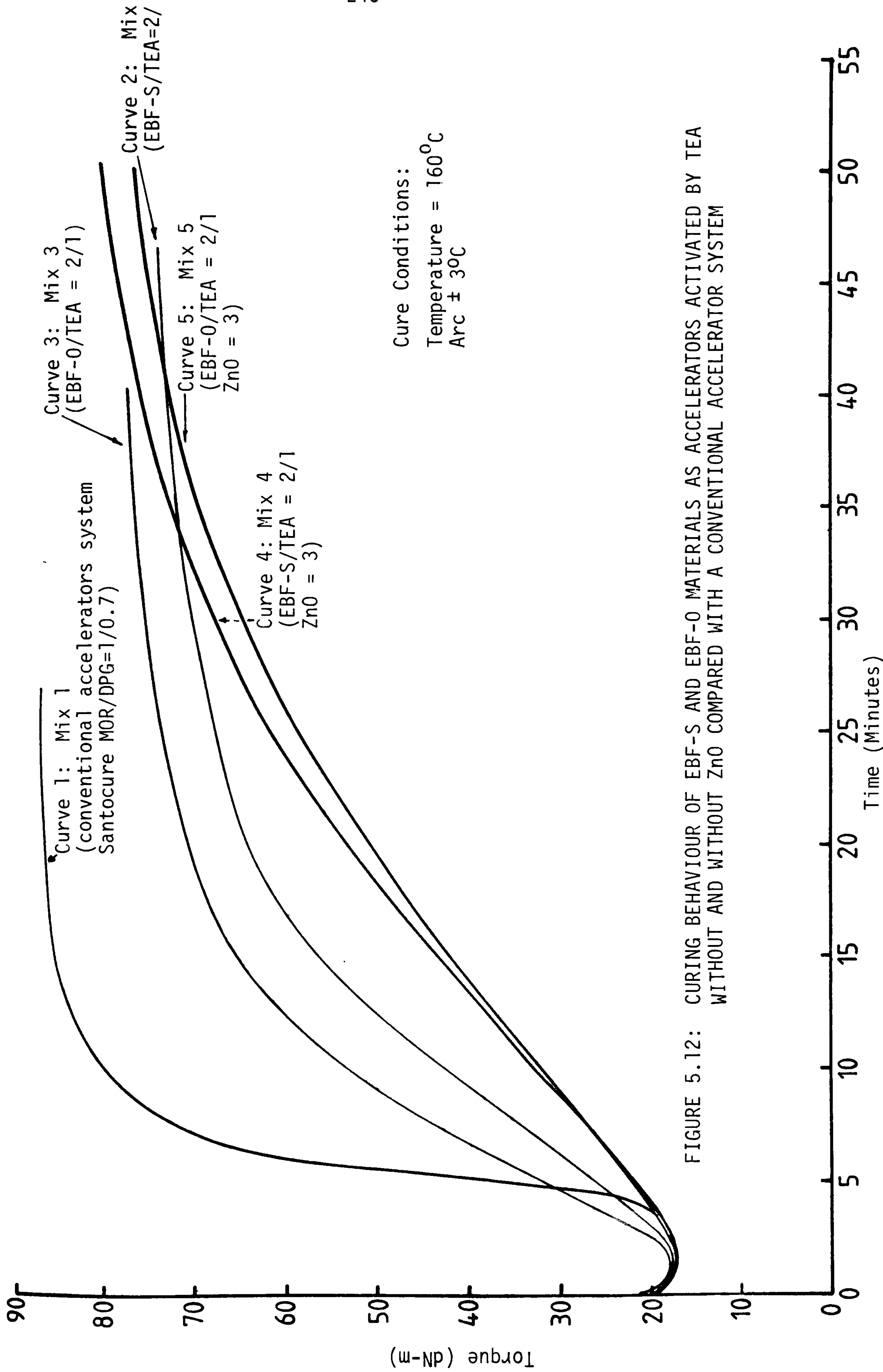


FIGURE 5.12: CURING BEHAVIOUR OF EBF-S AND EBF-0 MATERIALS AS ACCELERATORS ACTIVATED BY TEA WITHOUT AND WITHOUT ZnO COMPARED WITH A CONVENTIONAL ACCELERATOR SYSTEM

TABLE 5.15

EFFECT OF EBF-S AND EBF-O SYSTEMS AS ACCELERATORS ACTIVATED BY TEA WITHOUT AND WITHOUT ZnO
COMPARED WITH A CONVENTIONAL (MOR/DPG) ACCELERATOR BASED COMPOUND [FOR FORMULATION SEE TABLE 5.14]

Mix No:	1	2	3	4	5
	Control Mix 1	EBF-S/TEA = 2/1 (No ZnO)	EBF-O/TEA = 2/1 (No ZnO)	EBF-S/TEA = 2/1 ZnO = 3	EBF-O/TEA ZnO = 3
<i>Processing and Curing Properties:</i> Power Consumption Mooney Viscosity ML(1+4)100°C Mooney Scorch at 125°C (m) Optimum Curing Time, t ₉₀ , at 160°C(m)	0.34 70 28 10	0.283 69 19'30" 25	0.28 67 15' 20	0.287 71 26'30" 42'30"	0.285 70 26'30" 40'
<i>Physical Properties:</i> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at break % Tear Strength kN m ⁻¹ Fatigue Resistance (100% extension)* kilocycle to failure Compression Set at 100°C for 2 days Hardness IRHD Rebound Resilience %	23.4 3.6 14 430 43 95 48 75 37	24.5 2.9 12.7 470 46 150 43 70 39	24.3 2.65 11.4 490 47 160 45 68 40	26 2.8 12 500 51 166 42 70 40	26 2.9 12 505 46 162 41 68 41

/Continued...

TABLE 5.15 ... continued

Mix No:	1	2	3	4	4
	Control	EBF-S/TEA=2/1 (No ZnO)	EBF-O/TEA=2/1 (No ZnO)	EBF-S/TEA=2/1 ZnO = 3	EBF-O/TEA ZnO = 3
<u>Aged Properties:</u> (7 days at 100°C) Tensile Strength 100% Modulus MPa Elongation at break % Tear Strength kN m ⁻¹ Hardness IRHD Rebound Resilience % Fractional Strain Energy (TE)f	% Change in Property	% Change in Property	% Change in Property	% Change in Property	% Change in Property
	17 9.6 158 32 84 38	(-) 27.4 (+) 167 (-) 63 (-) 26 (+) 9 units (+) 3	(-) 22 (+) 202 (-) 59 (-) 40 (+) 17 units -	(-) 19 (+) 171 (-) 50 (-) 37 (+) 7 units -	(-) 19 (+) 152 (-) 49 (-) 28 (+) 11 units (-) 5
		19 8.6 203 25 83 39	19 8 200 32 85 40	21 7.6 249 32 77 40	21 7.3 260 33 79 39
		0.335	0.32	0.4	0.42
	0.27				

*The sample used had the following dimensions:

Length 100 mm
Width 10 mm
Thickness 2 mm

5.3 Surfactant/Sulphur Curing System for BR Rubber

Most of the commercially available polybutadiene rubbers (BR) are produced by solution polymerisation. Hence, polybutadiene rubbers do not contain any fatty acids [79]. Therefore, the presence of a fatty acid, stearic acid, as a vulcanisation activator, is essential in a formulation based on BR only.

For this reason it was decided to try and discover whether a surfactant could be used as a cure activator/accelerator system, without the zinc oxide and the stearic acid in a carbon black filled BR rubber. For comparison a conventional activator/accelerator/sulphur curing system will be used. The formulations used in this study are given below in Table 5.16.

TABLE 5.16:

FORMULATIONS USED TO EXAMINE THE ABILITY OF THE SURFACTANT/SULPHUR AS A CURING SYSTEM FOR SOLUTION POLYMERISED BR RUBBER IN COMPARISON WITH A CONVENTIONAL CURING SYSTEM

Mix No:	1	2
	Conventional Curing System ZnO/Stearic acid/ DPG/Sulphur	Surfactant/ Sulphur Curing System
BR-cis (Intene)	100	100
Sulphur	2	2
ZnO	4	-
Stearic acid	2	-
DPG	0.75	-
SAPA 1/2	-	2
Aromatic oil (Dutrex 729)	5	5
ISAF-black	50	50

Mixing cycle and conditions are as given before in Chapter 3, Section 3.3.5.

The results of this investigation are given in Figure 5.13 and Table 5.17. These results are interpreted as follows:

I: Processing and Curing Properties

It is known that most of the rubbers produced by the solution polymerisation process, mainly BR rubber, undergo significant reduction in their Mooney viscosity when mixed with weak organic acids such as stearic acid. Examination of the Mooney viscosity values given in Table 5.17 shows that the SAPA 1/2 system (mix 2) produced a significant reduction in viscosity even though no stearic acid was added with this system (see Table 5.16). This observation agrees with the general mechanism of action suggested for these surfactants (see Section 5.5).

In Figure 5.1 it can be seen that the conventional curing system of mix 1 has a much longer induction time, slower optimum curing time, t_{90} , and lower level of shear modulus than those obtained by the SAPA 1/2/sulphur curing system (mix 2). Therefore, these results indicate that better curing properties are obtained with the SAPA 1/2/sulphur curing system without the use of zinc oxide and stearic acid than with the conventional curing system. These results agree, also, with the mechanism proposed for the surfactant to act simultaneously as a cure activator/accelerator system which will be explained later in Section 5.5.

II: Physical Properties (Table 5.17)

The vulcanisate properties of the BR compound are significantly improved when the conventional curing system, namely that of DPG/ZnO/stearic acid/sulphur, was replaced by the surfactant system, SAPA 1/2/sulphur.

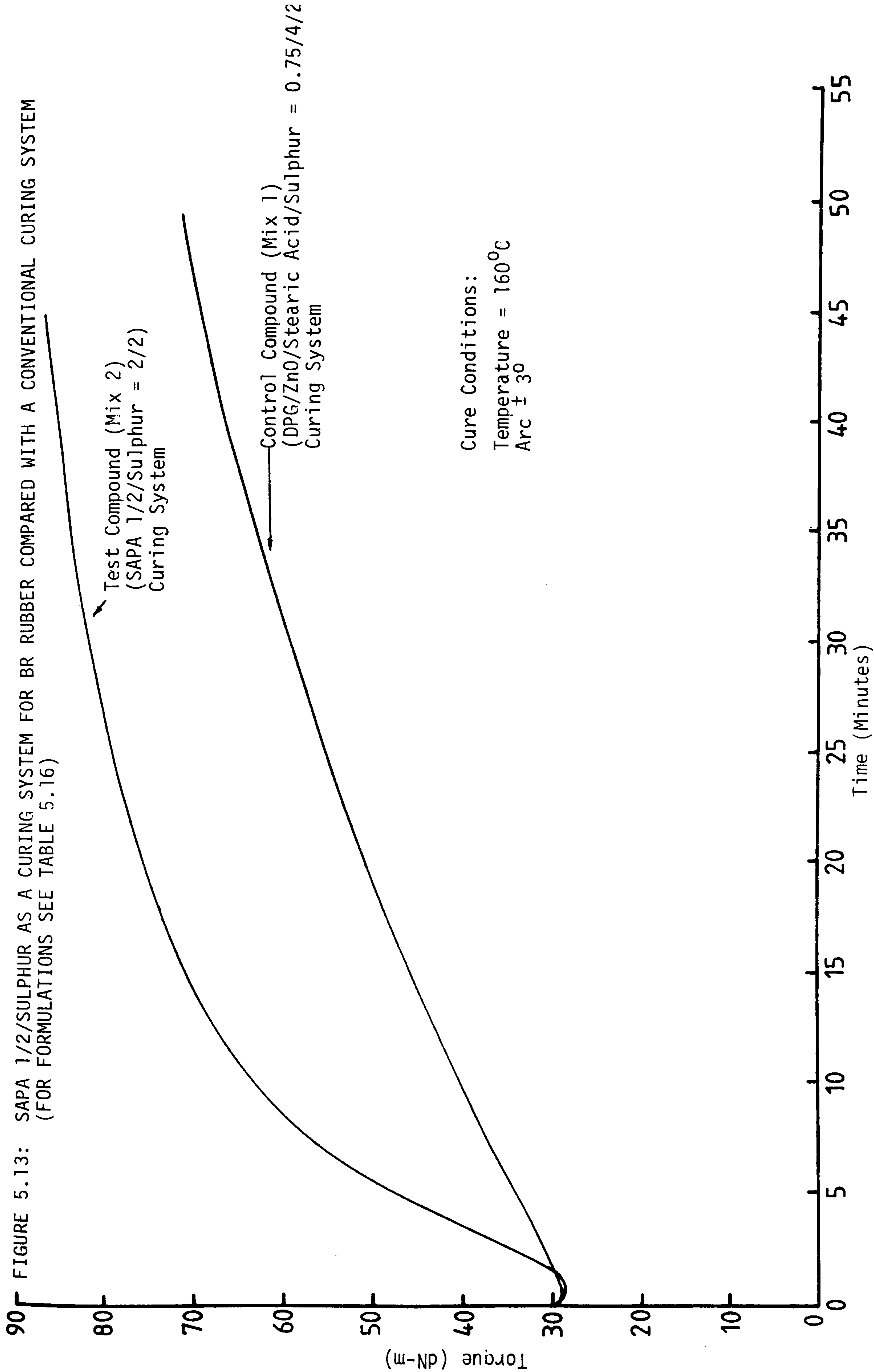
Of particular interest is the higher modulus values obtained with the SAPA 1/2/sulphur cure system. This increase is observed both in the ODR curing curves of Figure 5.14, and in the 100% and 300% modulus values of Table 5.17.

Hence, this experiment proved that the surfactant/sulphur curing system can very effectively be used as a curing system for BR rubber without the use of the conventional activators i.e. zinc oxide and stearic acid.

TABLE 5.17:

PROCESSING, CURING AND PHYSICAL PROPERTIES OF BR COMPOUND CURED BY SURFACTANT/SULPHUR CURING SYSTEM IN COMPARISON WITH A CONVENTIONAL DPG CURING SYSTEM [FOR FORMULATIONS SEE TABLE 5.16]

Mix No:	1	2
	Conventional Curing System ZnO/Stearic acid/ DPG/sulphur	Surfactant/ Sulphur Curing System
<i>Processing and Curing Properties:</i>		
Mooney Viscosity ML(1+4)100°C	105	95
Mooney Scorch, t_5 , at 125°C (m)	31'	16'
Optimum Curing time, t_{90} , at 160°C (m)	45'	27'
<i>Physical Properties:</i>		
Tensile Strength MPa	14	15
Elongation at break %	530	490
100% Modulus MPa	2	2.5
300% Modulus MPa	5.8	7
Tear Strength kN m ⁻¹	46	48
Hardness IRHD	59	68
Rebound Resilience, %	53	57



5.4 The Surfactant/Sulphur Curing System in NBR

The copolymers of butadiene and acrylonitrile are known by the generic name of Nitrile Rubber, NBR. The oil and chemical resistance of nitrile rubber is the major factor dictating the use of such rubbers. In addition to this nitrile rubbers are used in various applications such as those requiring resistance to heat, abrasion, water, gas permeability, etc. The importance of this rubber is increasing as research and industrial experience constantly yield new applications for this rubber. Therefore, it was decided to try and find out the effect of a surfactant and prepared salts as cure activator/accelerator system for this rubber. As a comparison a conventional CBS activator/accelerator system for NBR will be used as a control.

The formulations used are given below in Table 5.18.

TABLE 5.18:

RECIPES USED TO EVALUATE A SURFACTANT AND VARIOUS PREPARED SALTS AS ACTIVATOR/ACCELERATOR SYSTEMS FOR NBR COMPARED WITH A CONVENTIONAL ACTIVATOR/ACCELERATOR SYSTEM

	Conventional System Mix 1	SAPA 1/1 System Mix 2	NSA/1 System Mix 3	NSC/1 System Mix 4
Nitrile Rubber (Breon 1042)	100	100	100	100
MC Sulphur*	1.5	1.5	1.5	1.5
ZnO	5	-	-	-
Stearic acid	1.0	-	-	-
CBS	0.75	-	-	-
SAPA 1/1	2	-	-	-
NSA/3	-	2	-	-
NSC/2	-	-	-	2
SRF Black	40	40	40	40

* MC Sulphur: Magnesium carbonate coated sulphur

Figure 5.14 and Table 5.19 summarise the results of the effects of SAPA 1/1, NSA/3 and NSC/2 systems as activator/accelerators in NBR in comparison with a conventional CBS activator/accelerator system, based on ZnO/stearic acid/CBS. Considering the results of these new systems alone it can be seen that they have the same beneficial effect on the processing, curing and physical properties of NBR as previously found for BR and SBR. However, there is some variation in the curing characteristics of the SAPA 1/1 system from those of the NSA/3 and NSC/2 systems. This variation is thought to occur as a result of the differences in the reactivities of SAPA 1/1 from those of the NSC/2 or NSA/3 systems (see chemical structures in Table 3.1). Comparing the results of these new systems with those of the conventional CBS accelerator system (mix 1 of Table 5.18) it can be observed that the scorch time of both are very similar. However the optimum curing time, t_{90} , of the conventional system is greater than those of the new systems by about 33-56%. Flow and mould release of the SAPA 1/1, NSA/3 and the NSC/2 systems were very much superior to that of the CBS/ZnO/stearic acid mix.

The physical properties of vulcanisates containing the new systems as a cure activator/accelerator system are generally better than those obtained from the vulcanisate which contained the conventional activator/acceleration system; ZnO/stearic acid/CBS.

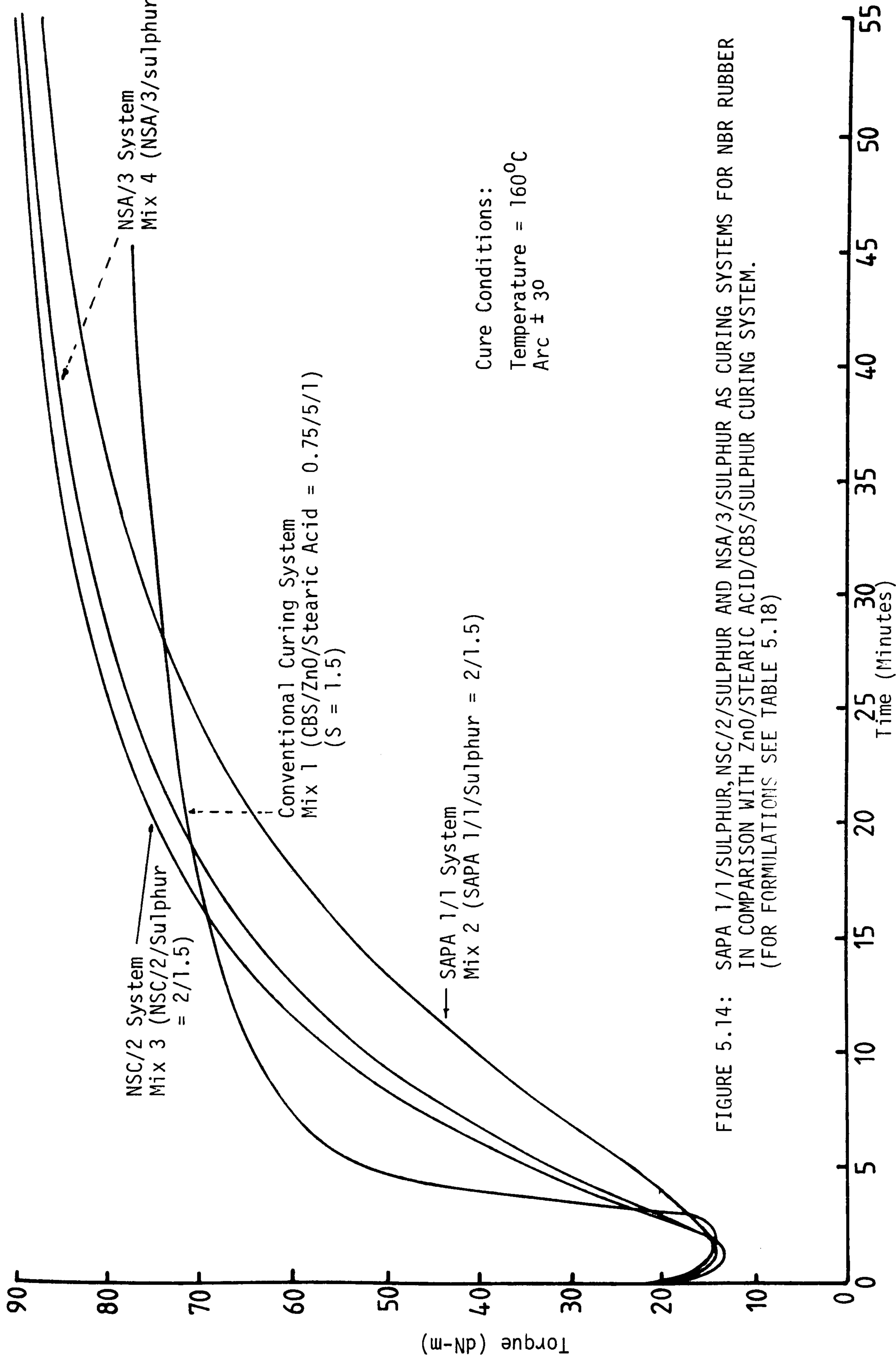


FIGURE 5.14: SAPA 1/1/SULPHUR, NSC/2/SULPHUR AND NSA/3/SULPHUR AS CURING SYSTEMS FOR NBR RUBBER IN COMPARISON WITH ZnO/STEARIC ACID/CBS/SULPHUR CURING SYSTEM. (FOR FORMULATIONS SEE TABLE 5.18)

TABLE 5.19:

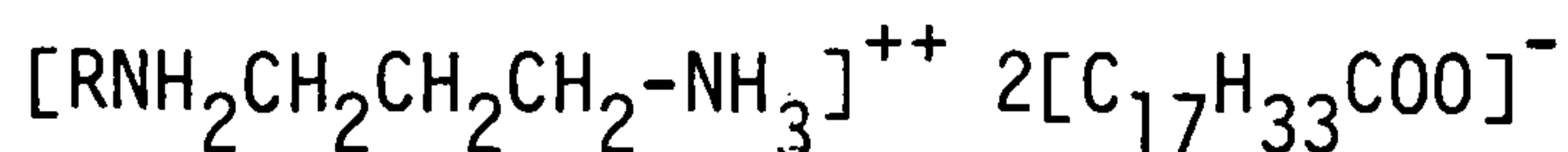
EFFECT OF A SURFACTANT AND PREPARED SALTS SYSTEMS AS CURE ACTIVATOR/ACCELERATOR SYSTEMS ON THE PROCESSING, CURING AND PHYSICAL PROPERTIES OF NBR COMPARED WITH A CONVENTIONAL SYSTEM (CBS/ZnO/Stearic Acid)

Mix No:	1	2	3	4
	Conventional System ZnO/CBS/ Stearic acid	SAPA 1/1 System	NSA/3 System	NSC/2 System
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Mooney Scorch at 125°C (m) Optimum Curing Time t_{90} at 160°C (m)	68 16' 22'30"	69 21' 35'	70 15' 32'	68 15' 30'
<u>Physical Properties:</u> Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break% Tear Strength kN m ⁻¹ Compression Set at 70°C for 48 hours % Hardness IRHD Rebound Resi- lience %	19 2.7 7.5 530 41 20 62 23	21 3 10 550 38 20 66 24	19 3 10.7 496 37 20 66 24	21 2.8 10.7 506 38 20 65 24

5.5 Interpretation of Cure Acceleration by Surfactants

5.5.1 Proposed Mechanism for the Multiplicity of Functions of SAPA 1/1 in Rubber Compounding

The general chemical composition of the SAPA 1/1 used throughout this research work was as follows:



where R is a long chain alkyl group derived from a fatty acid.

To account for the multiplicity of functions demonstrated by this compound, and similar compounds, it has been decided to characterise its chemical structure at high temperatures. For this two methods were used and they are as follows:

I: Differential Scanning Calorimetry (DSC)

The instrument used is a Du Pont 990 Thermal Analyser. A detailed description of the DSC is given in Appendix V. The results obtained from this technique are given in Figure 5.15.

II: Infrared Spectroscopy

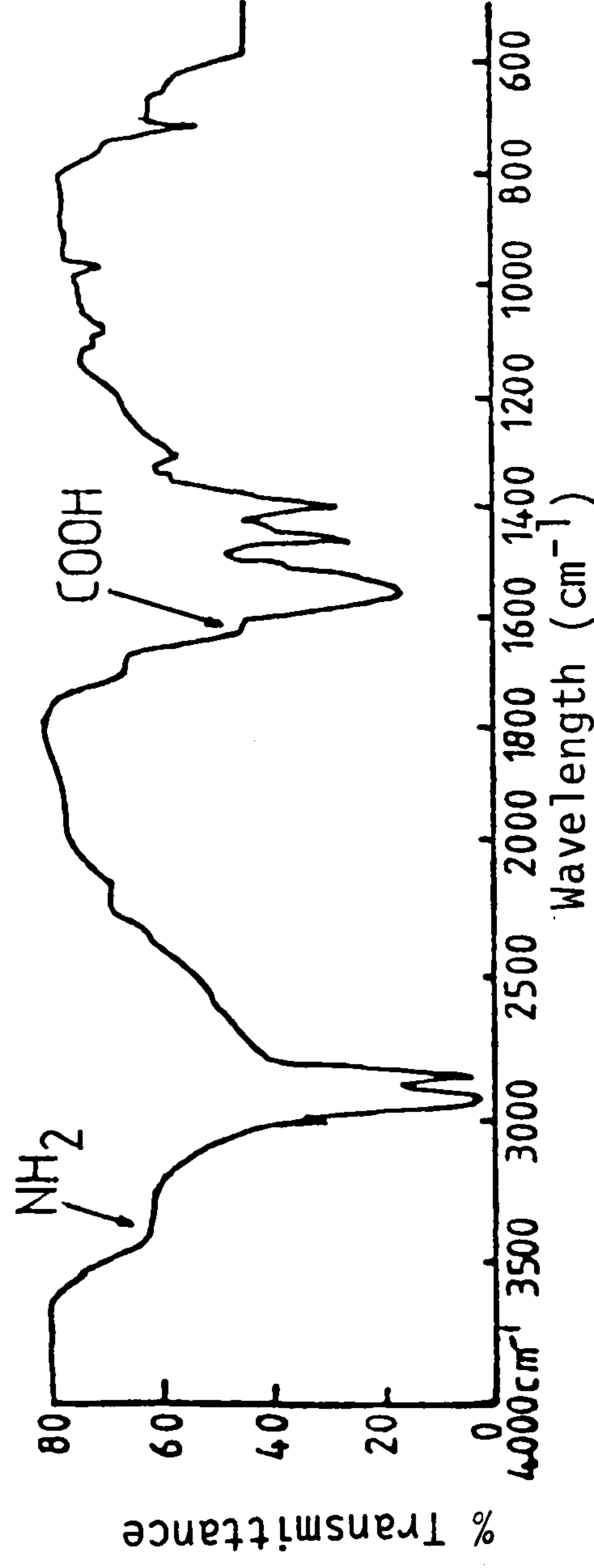
The instrument used was the Pye-Unicam SP 200 Grating Infrared Spectrophotometer. The results of this technique are given in Figure 6.16(a) and (b).

The thermogram of the DSC, Figure 5.15, shows two heat absorption bands at two different temperatures. The first one is at about 39°C which represents the melting range of the SAPA 1/1 compound. The second band occurred at temperatures ranging between 138-143°C. This band is thought to occur as a result of some dissociation of the SAPA 1/1 compound. The infrared technique was then used to confirm

the chemical dissociation occurred around the temperature range of 138-143°C. Two infrared spectras were obtained for SAPA 1/1 compound, the first one was run at room temperature and is given in Figure 5.16(a). The second spectrum was obtained as follows: one gram of SAPA 1/1 was placed in a test tube which was then heated under vacuum at 150°C for about 5 minutes. By using the infrared hot stage technique at 150°C a spectrum was then obtained for the SAPA 1/1 at this temperature. This spectrum is given in Figure 5.16(b).

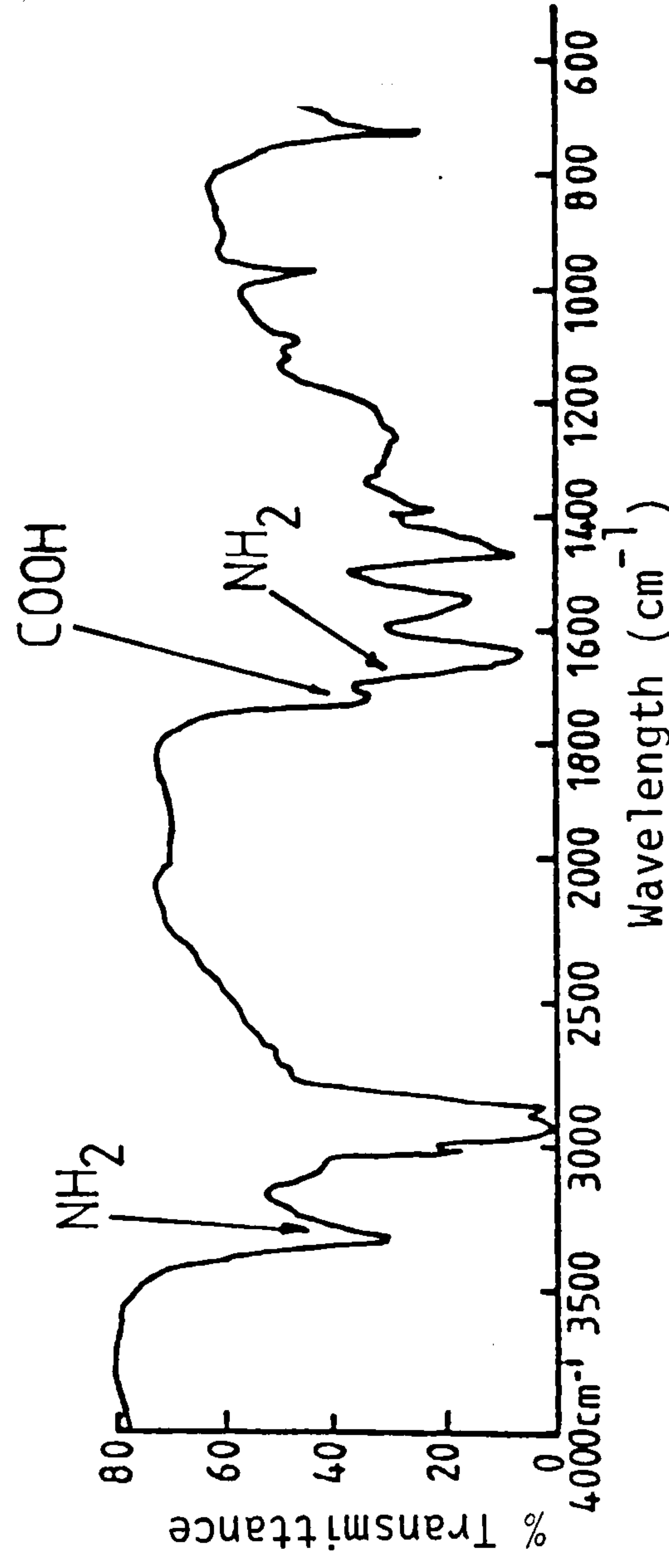
Comparing the infrared spectrum of the SAPA 1/1 at room temperature Figure 5.16(a), with that of the SAPA 1/1 at 150°C Figure 5.16(b), the generation of strong bands at wavelength (cm^{-1}) 3300-3400 (NH_2), 1730 (COOH), and 1650-1700 (NH_2) are very clearly seen in the latter spectrum. The occurrence of these sharp bands therefore confirms the observation made earlier with the DSC results, as follows: these type of compounds whilst stable at room temperature, have the ability to dissociate on heating into their primary components (see Figures 5.15 and 5.16(a) and (b)) and it is this characteristic which is considered to account for its multiplicity of uses as a rubber compounding ingredient. In Figure 5.17 is outlined a mechanism to account for such a multi-purpose role which shows that at ambient temperature SAPA 1/1 can function as a combined internal processing aid and filler/rubber surface active or wetting agent due to its possessing the typical structure of a cationic surfactant. On heating to typical rubber vulcanisation temperatures the SAPA 1/1 molecule is considered to dissociate into both a diamine, which functions as a vulcanisation accelerator, with a fatty acid produced in situ as by-product. Then this fatty acid by-product is considered to have the combined effect of functioning as a processing aid and a mould release agent. The above mechanism is also valid for compounds similar to SAPA 1/1 or SAPA 1/2 such as the NS series.

FIGURE 5.16: INFRARED EVIDENCE FOR THE DECOMPOSITION OF SAPA 1/1 INTO FUNCTIONALLY ACTIVE GROUPS DURING VULCANISATION



(a) Infrared spectrum of SAPA1 unheated. (Thin film on a NaCl disc).

Note: The NH₂ and COOH groups are barely detectable at a wavelength (cm⁻¹) 3300 and 1730.



(b) Infrared spectrum of SAPA 1/1 heated for 5 minutes at 150°C (under vacuum).

Note: The generation of strong bands of new organic groups at wavelengths (cm⁻¹) 3300-3400 (NH₂), and 1730 (COOH), and 1650-1700 (NH₂)

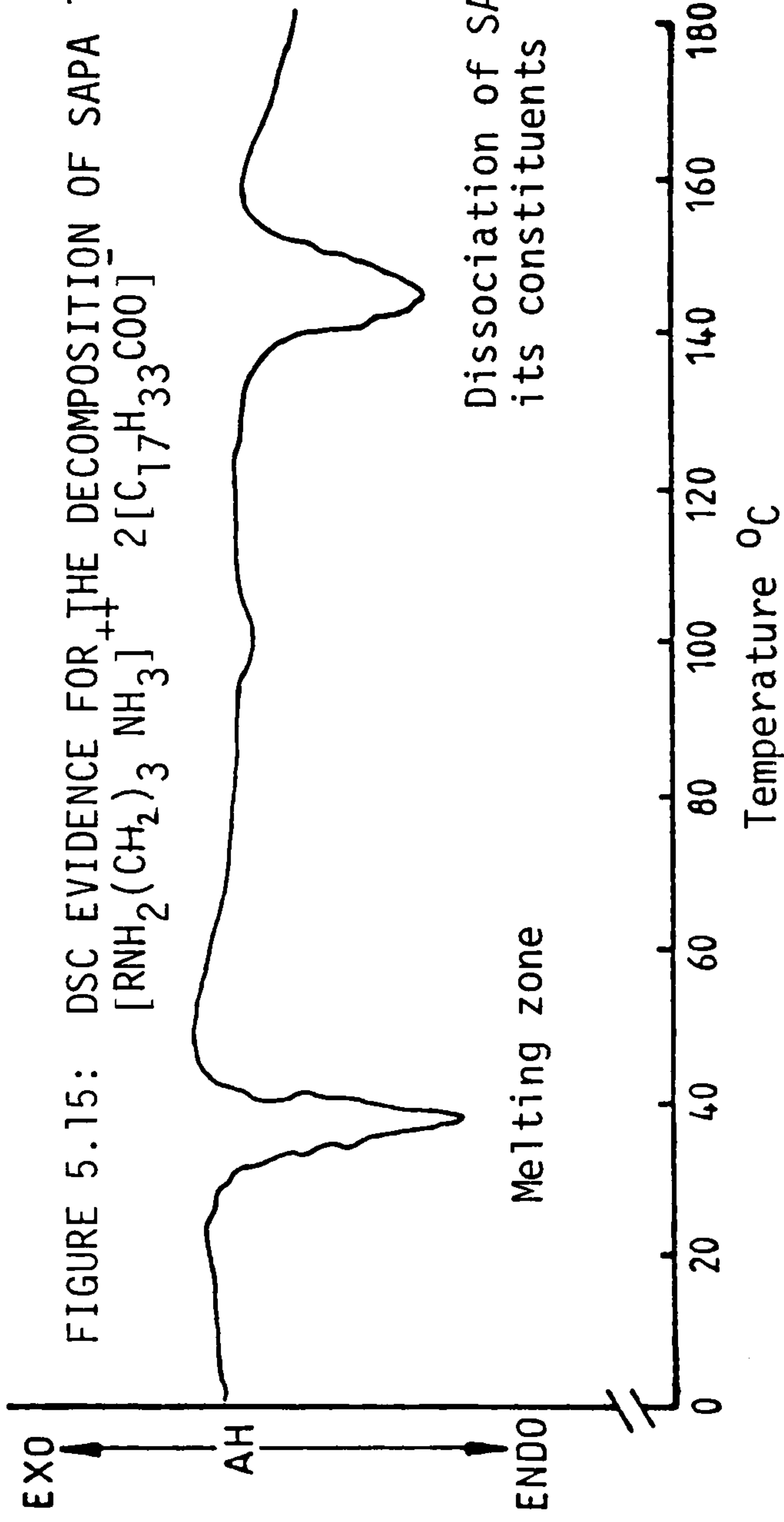
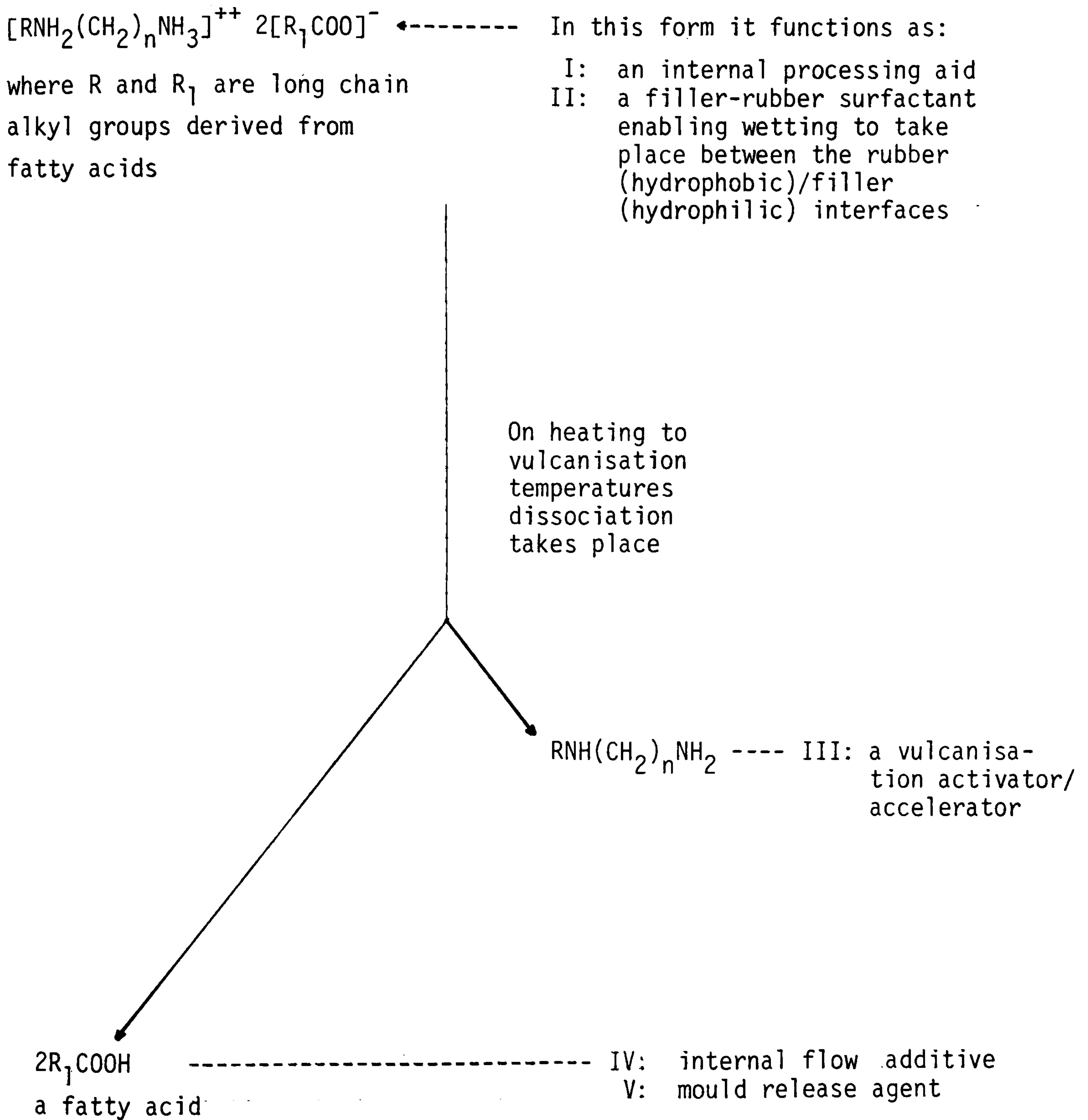


FIGURE 5.15: DSC EVIDENCE FOR THE DECOMPOSITION OF SAPA 1/1

Conditions:
10°C/min
Sample: 10 mg

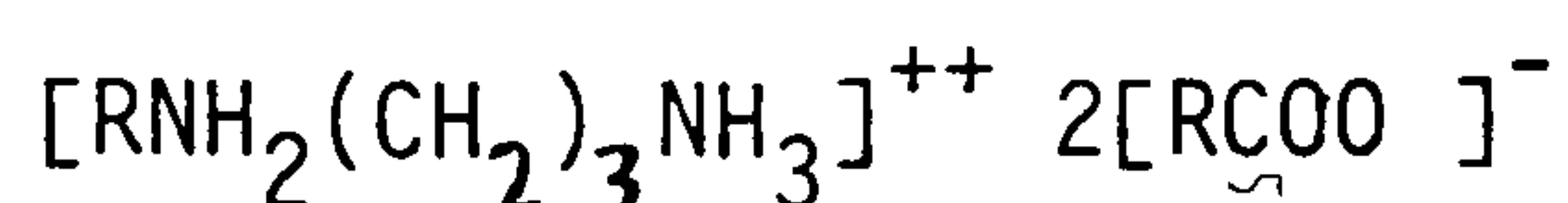
FIGURE 5.17

PROPOSED MECHANISM TO ACCOUNT FOR THE MULTIPLICITY OF FUNCTIONS
OF SAPA 1/1 AND SIMILAR COMPOUNDS



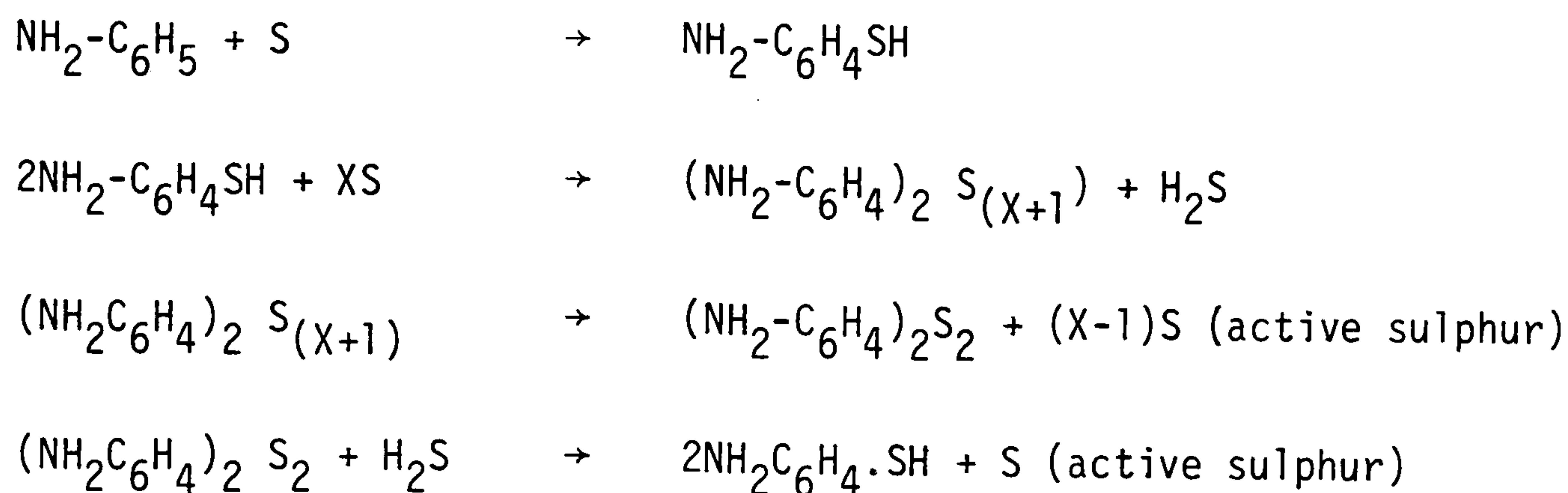
5.5.2 Proposed Hypotheses to Account for the Cure Retardation that Occurs when Zinc Oxide is Used with SAPA 1/1 and Similar Compounds

It has been demonstrated that when zinc oxide is used in conjunction with the SAPA 1/1 activator/accelerator system, or any similar compound, the scorch time was observed to increase significantly. This increase in the scorch time was accompanied by a considerable reduction in the cure rate. It is not clear what might be the mechanism whereby the zinc oxide appears to function as a cure retarder. However, two suggestions have been invoked to explain this effect. The first one is that possibly SAPA 1/1, which has the general formula of:



in the presence of zinc oxide may react with zinc ions to form a complex similar to that known to be capable of existing [80] between ethylene diamine tetraacetic acid and zinc ions, such a complex is believed to be very stable and thus should be able to reduce the activity of SAPA 1/1 to dissociate into the diamine and the fatty acid (see Figure 5.17). However, if such a complex is assumed to be formed it would also retard the cure rate and lengthen the scorch time.

The second possibility of explaining the delayed action of zinc oxide on the cure rate of SAPA 1/1 is based on a report by Kimishima of 1928 [81]. This worker observed that there are certain accelerators, such as aniline, whose action as a cure accelerator is observed to be reduced by the presence of zinc oxide. In order to explain the action of zinc oxide the worker [81] first suggested the following reaction mechanisms to account for aniline as an accelerator:

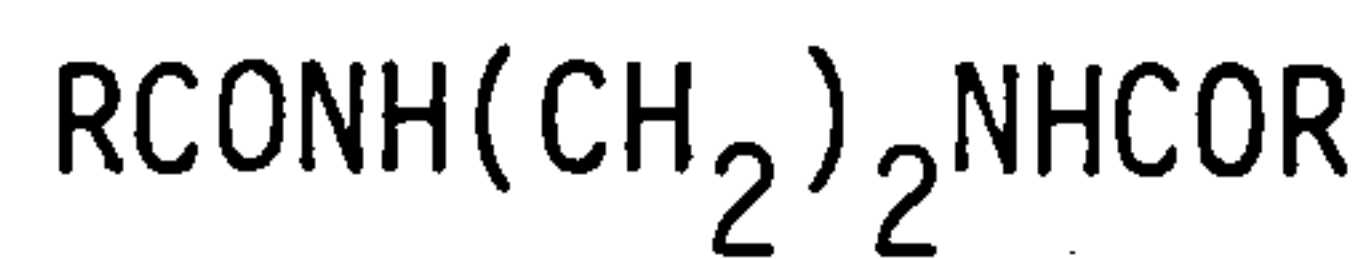


Then he believed that when zinc oxide is present it will act as an absorbant of hydrogen sulphide and hence prevent the action of the disulphide as an accelerator (see equations above).

In the case of SAPA 1/1 the delayed action is thus explained as follows: hydrogen sulphide, produced as discussed before in Section 1.3, reacts with amine to produce hydrosulphide ions. Once these hydrosulphide ions are formed they can react with and open the S_8 rings, forming $\text{H-S-S}_x\text{-S}^-$ chains which are thermally unstable and very reactive. When zinc oxide is present it will react with this H_2S and hence cause a decrease in the quantity of the H_2S normally available and required to produce sufficient hydrosulphide ions. This reduction in the amount of hydrosulphide ions would result in cure retardation.

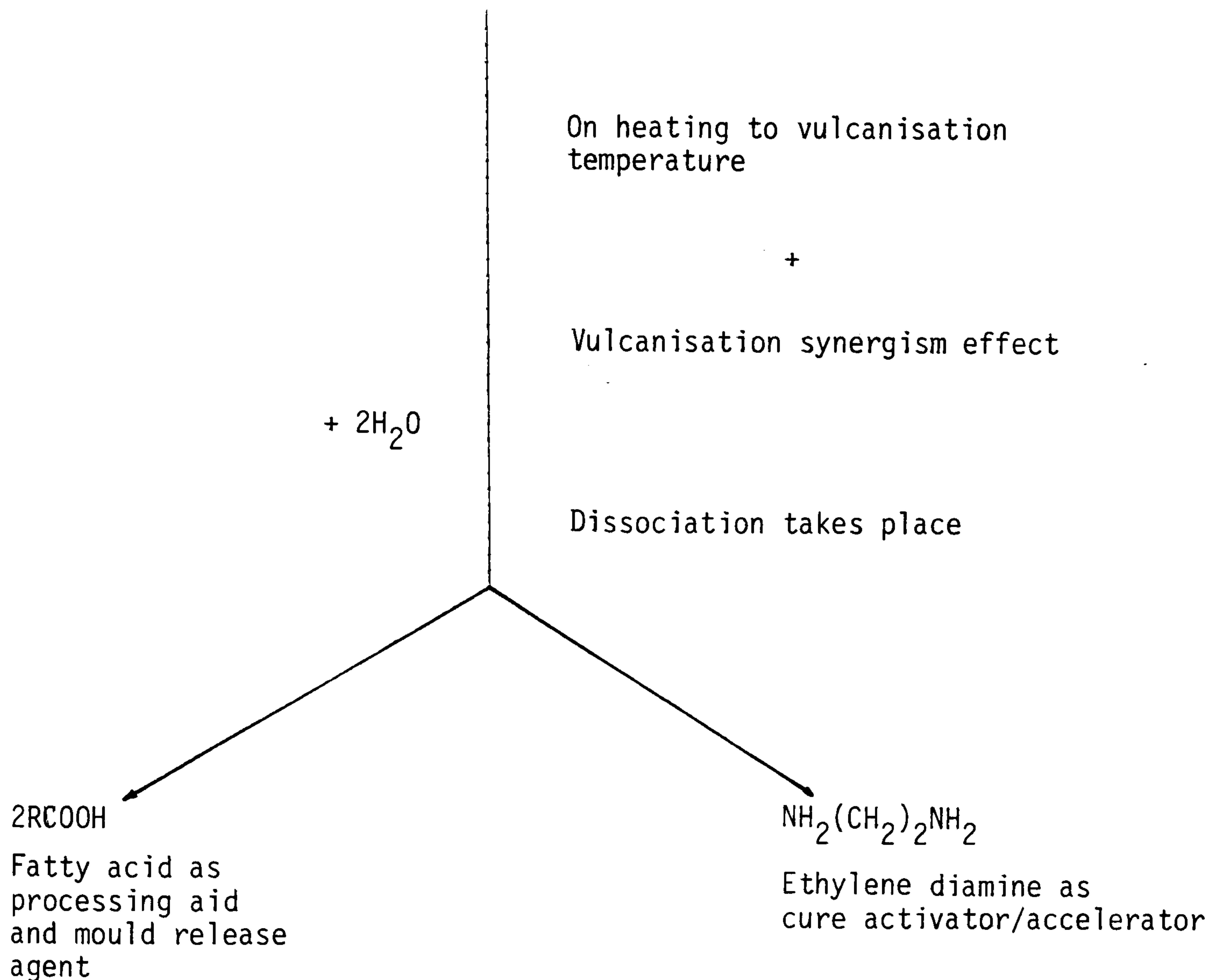
5.5.3 Accelerating Effect of Ethylene Bis Stearamide and Similar Compounds

The results which have been obtained for the effect of ethylene bis stearamide as a cure activator/accelerator system indicate that its effect is very slow compared with the other surfactants. However, it does show some accelerating effect and the rubber eventually cures. To account for this effect the following mechanisms are suggested:



Ethylene bis Fatty Amide

R is a long chain alkyl group derived from fatty acid



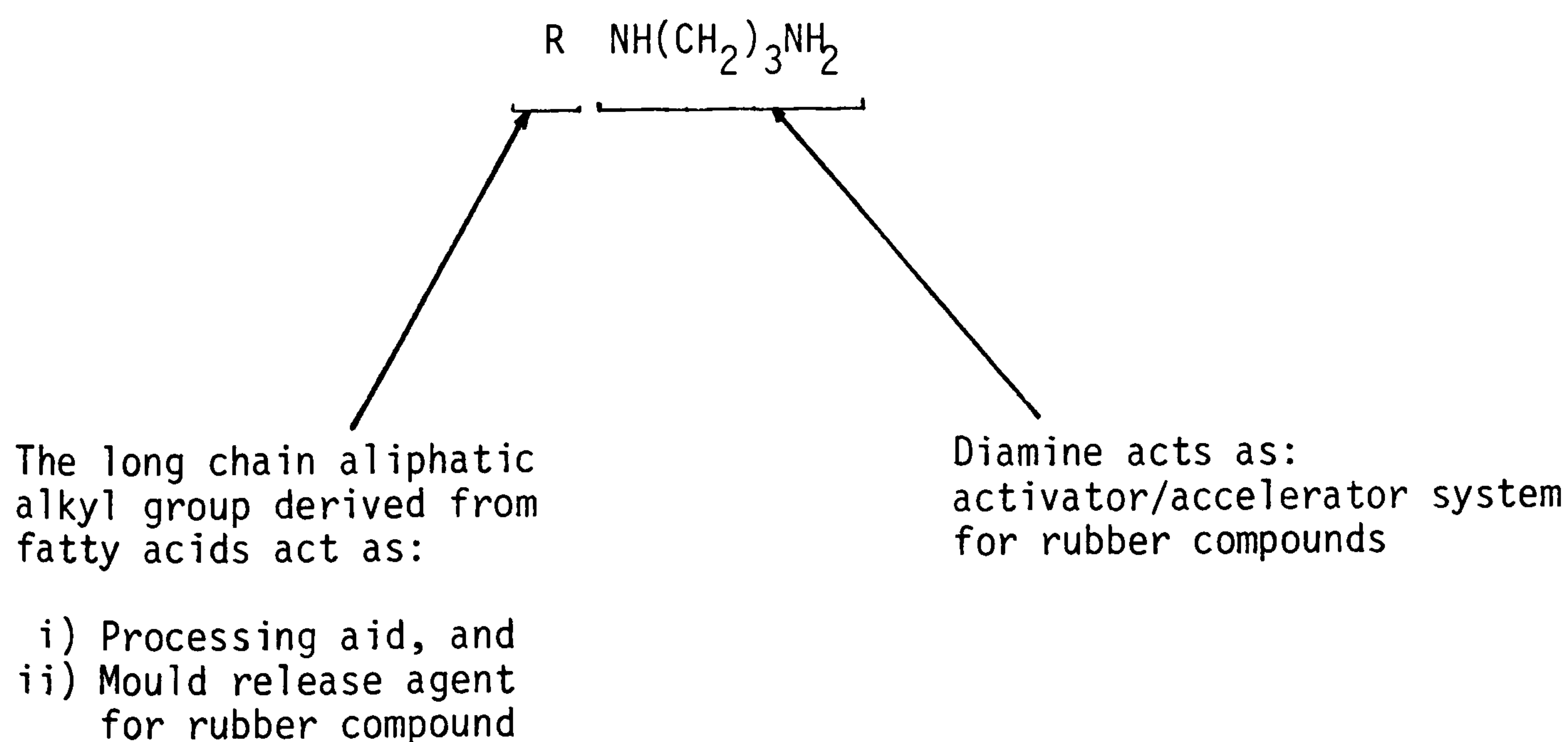
The formation of the ethylene diamine as an accelerator is thought to form gradually and as curing proceeds and this is believed to account for the slow curing characteristics of the EBF-S compound. However, when triethanolamine is present with the EBF-S it is suggested that it acts as a decomposition catalyst and hence accelerates dissociation of the EBF-S, as shown above. Once enough ethylene diamine is formed in situ it will then function as a fast accelerator in its own right (see Section 5.2.4).

It has been reported [82] however that activators such as triethanolamine and ethylene glycol can replace basic accelerators to some extent. This may also explain the fast cure rate achieved by the combination of the EBF-S/triethanolamine.

Obviously this subject of the EBF-S with and without triethanolamine as a rubber accelerator needs further study to determine the details of its reaction mechanism.

5.5.4 Vulcanisation Acceleration Mechanism of SAPA 2/A and Similar Compounds

SAPA 2/A and similar compounds (see Table 3.1) have been demonstrated as very fast curing accelerators for rubber. This is, of course, in addition to their processing advantages as they also function as rubber processing aids and mould release agents. The behaviour of any one of them can be simply explained in relation to their chemical structure as follows:



It is believed that compounds such as SAPA 2/A whose general chemical formula is given above, is stable at the vulcanisation temperature and does not undergo any decomposition which could lead to the formation of free fatty acid. As a result no free fatty acid could be available to react with zinc oxide, as in the case of SAPA 1/1 (see Section 5.5.2) and hence retard the cure. This may explain why zinc oxide does not retard the cure rate of SAPA 2 and similar compounds.

5.6 Conclusions

Compounds such as SAPA 1, NS and SAPA 2 classes were found to act very effectively as activator/accelerator systems without the inclusion of a conventional rubber activator system i.e. zinc oxide and stearic acid, for several rubbers such as NR, SBR, NBR etc. However it was observed that with natural rubber the presence of some zinc oxide (ca. 1 phr) is beneficial to obtain non-reverting cures and good physical property retention after heat ageing. The cure rates of the above surfactants, in all the rubbers studied were found, very often, to be faster than those of some common accelerators. The physical properties of vulcanisates obtained by all classes of the above surfactants were observed to be superior to those obtained by the use of a conventional accelerator system. This reinforcement effect was considered to be as a result of a significant enhancement of the filler dispersion in compounds using these surfactants, either as processing aids or as activator/accelerator systems. The ageing behaviour of NSA/1 and similar systems was observed to be similar to that of the sulphenamide accelerator system. However, the compression set values of almost all the rubbers using the above surfactants, as activator/accelerator systems, were superior to those obtained from the conventional accelerator systems.

Zinc oxide was observed to retard dramatically the curing rate and scorch time of any rubber compound containing SAPA 1/1, SAPA 1/2 or

any one of the NS series (see Table 3.1) in which they were used as a cure activator/accelerator system. However, zinc oxide had almost no effect on the cure rate or scorch times of all the rubber compounds investigated in the SAPA 2 series when these were used as cure activator/accelerators.

The EBF-S and the other compounds of the EBF class are observed to behave quite differently from all the other surfactant and prepared salts classes given in Table 3.1. Rubber compounds containing any material from the EBF class as an activator/accelerator system were observed to possess very slow curing rates and long scorch times. These are in addition to their poor vulcanisate properties. However, it was found that the EBF-S compound can be used successfully as a secondary accelerator, replacing a basic accelerator quite satisfactorily, in SBR rubber.

The EBF-S or the EBF-O when combined with triethanolamine (1 phr) was observed to produce very fast cure rates and excellent physical properties. This system i.e. the EBF-S/triethanolamine was found to give rubber vulcanisates of superior ageing resistance, when zinc oxide is present, to conventional accelerator systems composed of Santocure MOR and DPG. Interestingly the presence of zinc oxide with the EBF-S/triethanolamine system was observed to retard the cure rate and thus could be used as a scorch time cure rate controller.

CHAPTER 6

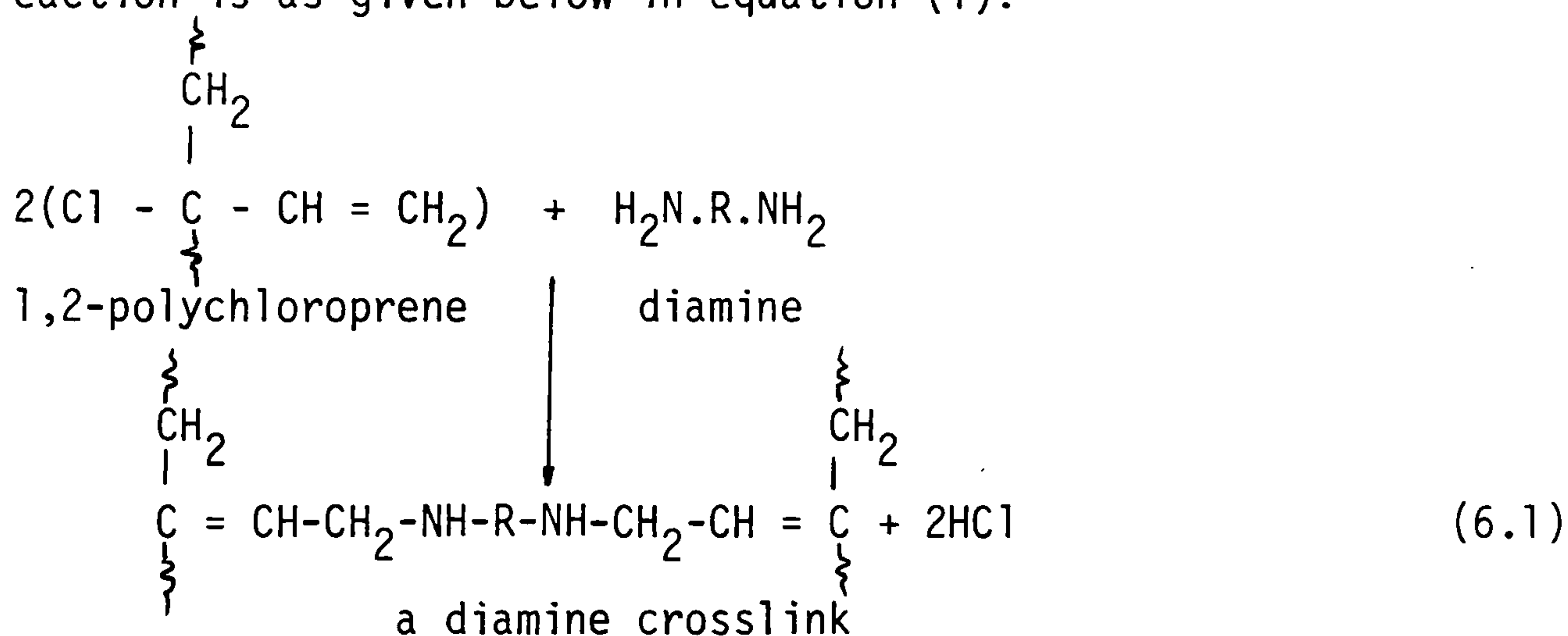
SURFACTANTS AS CROSSLINKING AGENTS FOR

POLYCHLOROPRENE (CR) RUBBER

Introduction

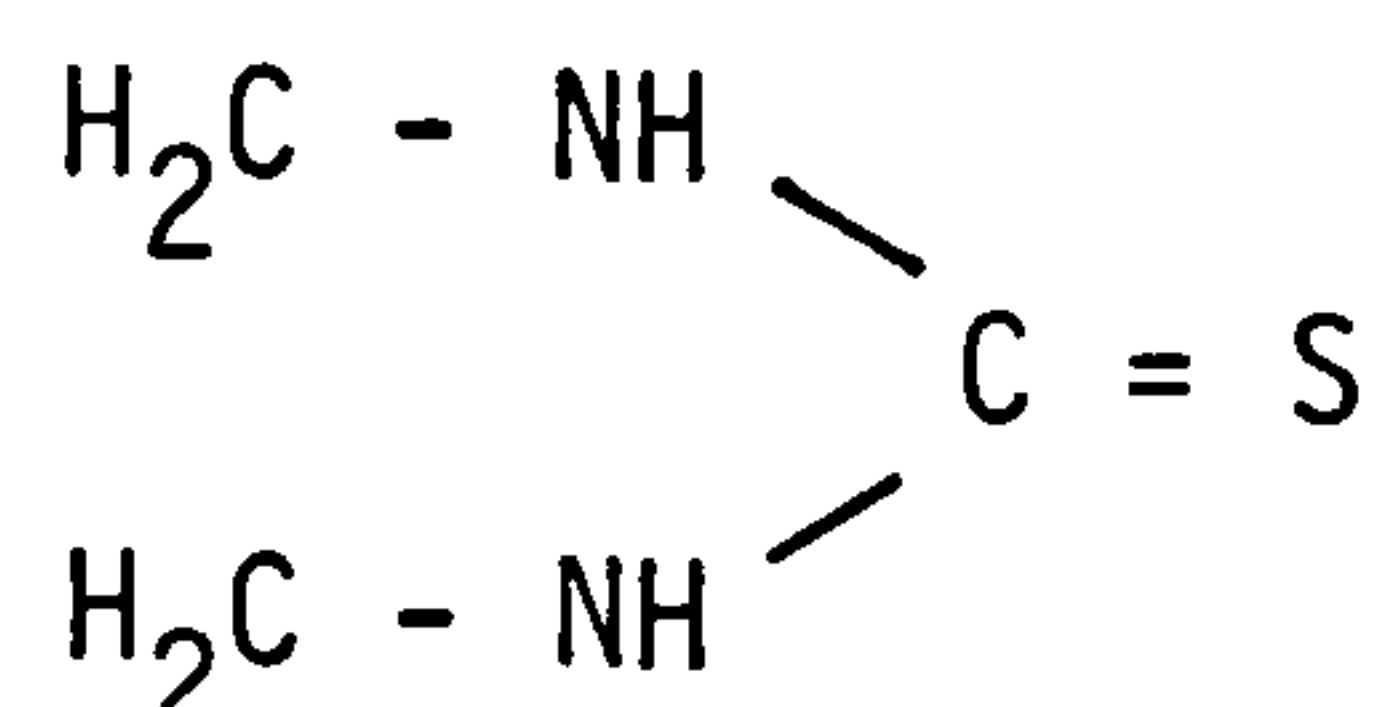
It was first theorised by Kovacic [83] that certain bifunctional diamines become the crosslinks during the vulcanisation of polychloroprene (CR) rubber; the reaction is considered to be accomplished by the active chlorine groups of the CR directly promoting bisalkylation of the difunctional diamine crosslinking agents. These active chlorine atoms, which are present as a result of 1,2 and 3,4 addition polymerisation, comprise about 1.6% of the total chlorine in chloroprene. Therefore, chloroprene crosslinking takes place predominantly through the minor constituent of the CR where the majority component consists of the 1,4-configuration.

The reaction is as given below in equation (1):

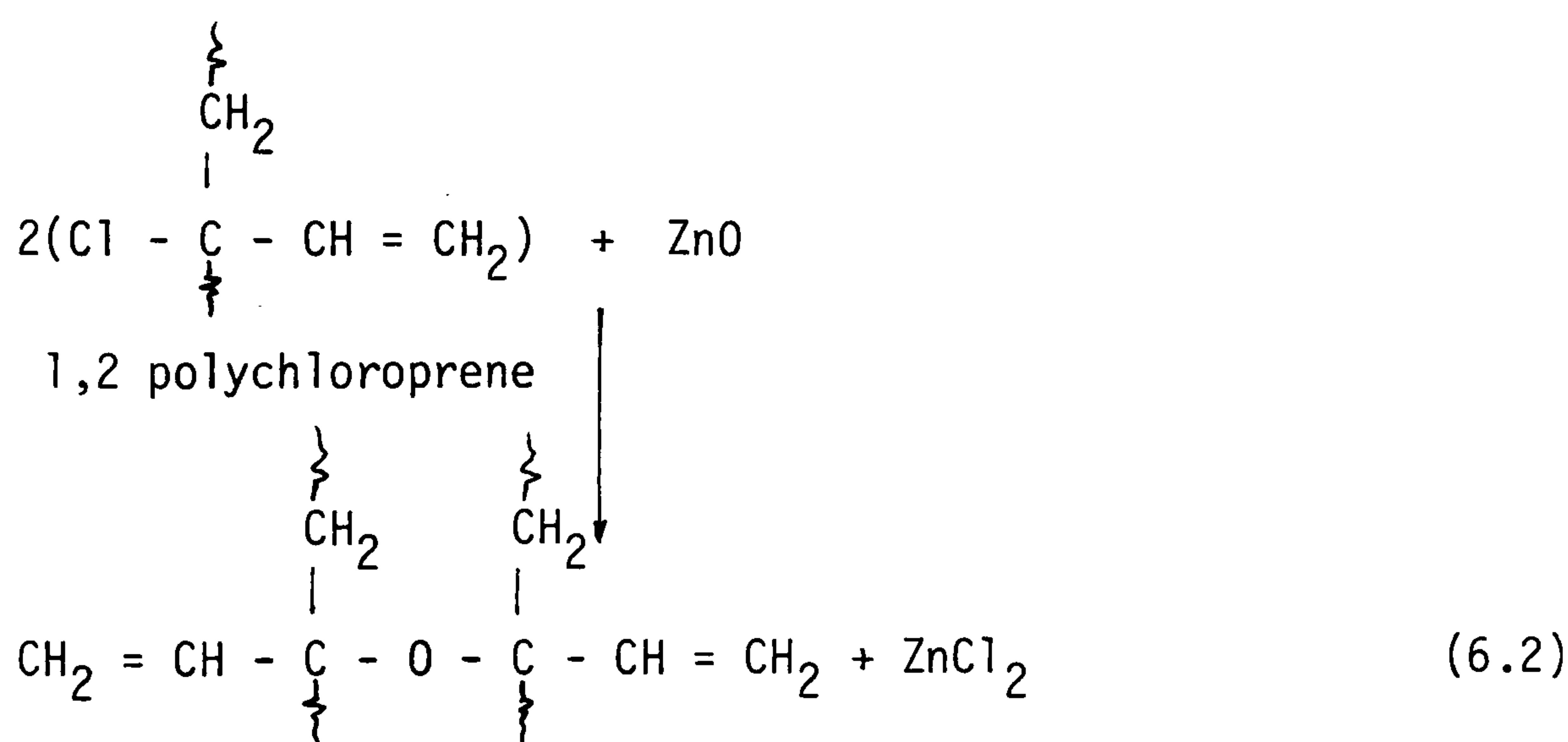


The HCl produced is neutralised by the incorporation of MgO into the rubber formulation. An implication of the mechanism in equation 6.1 is that only the presence of a bifunctional diamine with a neutralising metal oxide is sufficient to crosslink CR. However, in practice

[79,83,84], it is found desirable to have another divalent metal oxide present when a diamine crosslinker is used and the most widely used one is ZnO, though others are also effective such as PbO. For example, if the diamine, ethylene thiourea



is used as the crosslinker without the presence of ZnO then only poorly cured vulcanisates result; the presence of ZnO is therefore desirable for practical cures and implies that the ZnO functions either as a catalyst, or as a crosslinking agent or has both functions. The reaction in which ZnO is considered to function as a crosslinking agent is given in equation 6.2 below:



Combination of diamine (ethylene thiourea), ZnO and MgO as curative systems for CR are summarised in Figure 6.1(a) and 6.1(b) below:

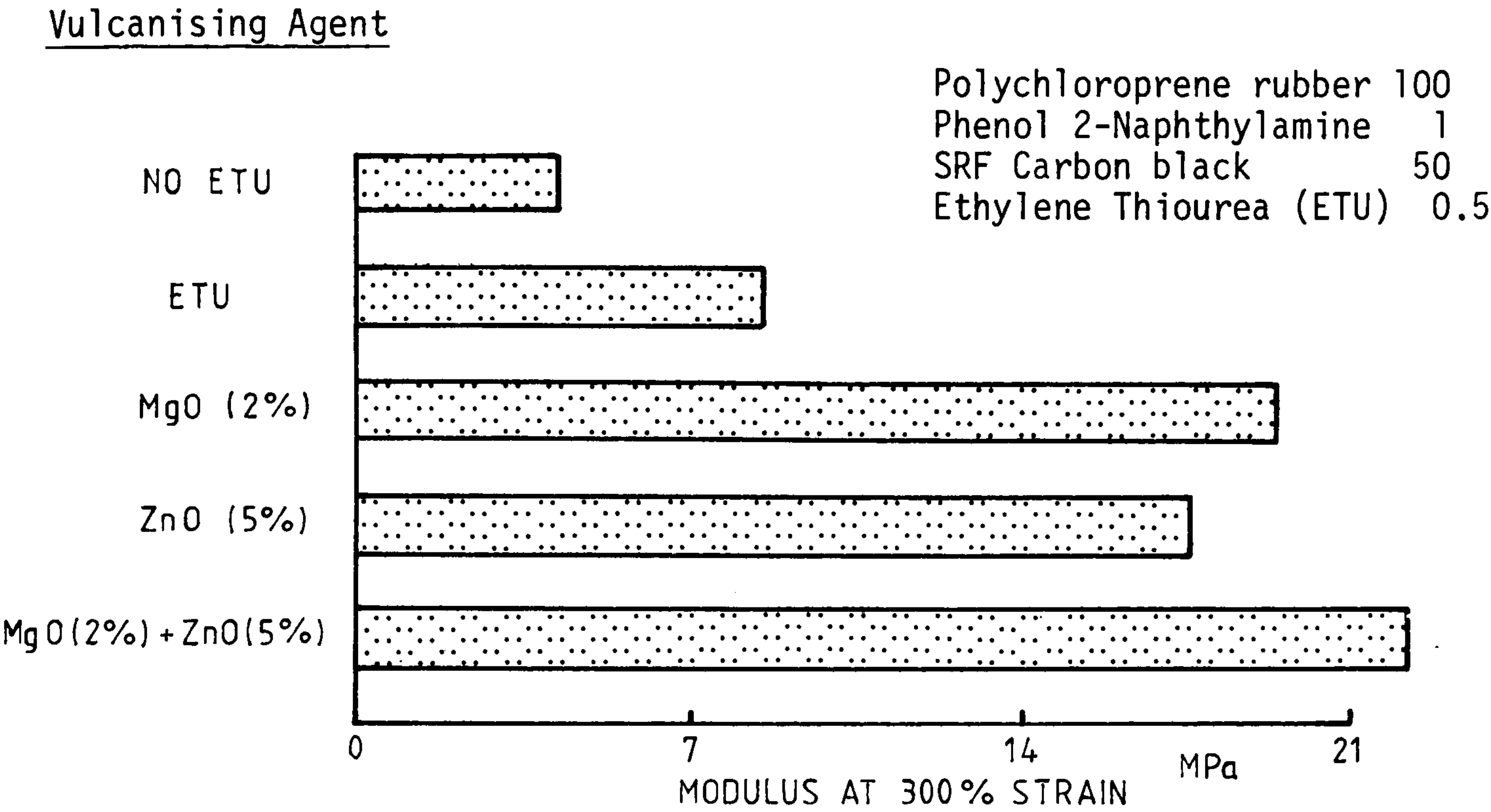


FIGURE 6.1(a): PROGRESSIVE INFLUENCE OF METAL OXIDES ON VULCANISATION PROPERTIES OF ETHYLENE THIOUREA CROSSLINKED CHLOROPRENE RUBBER [83]

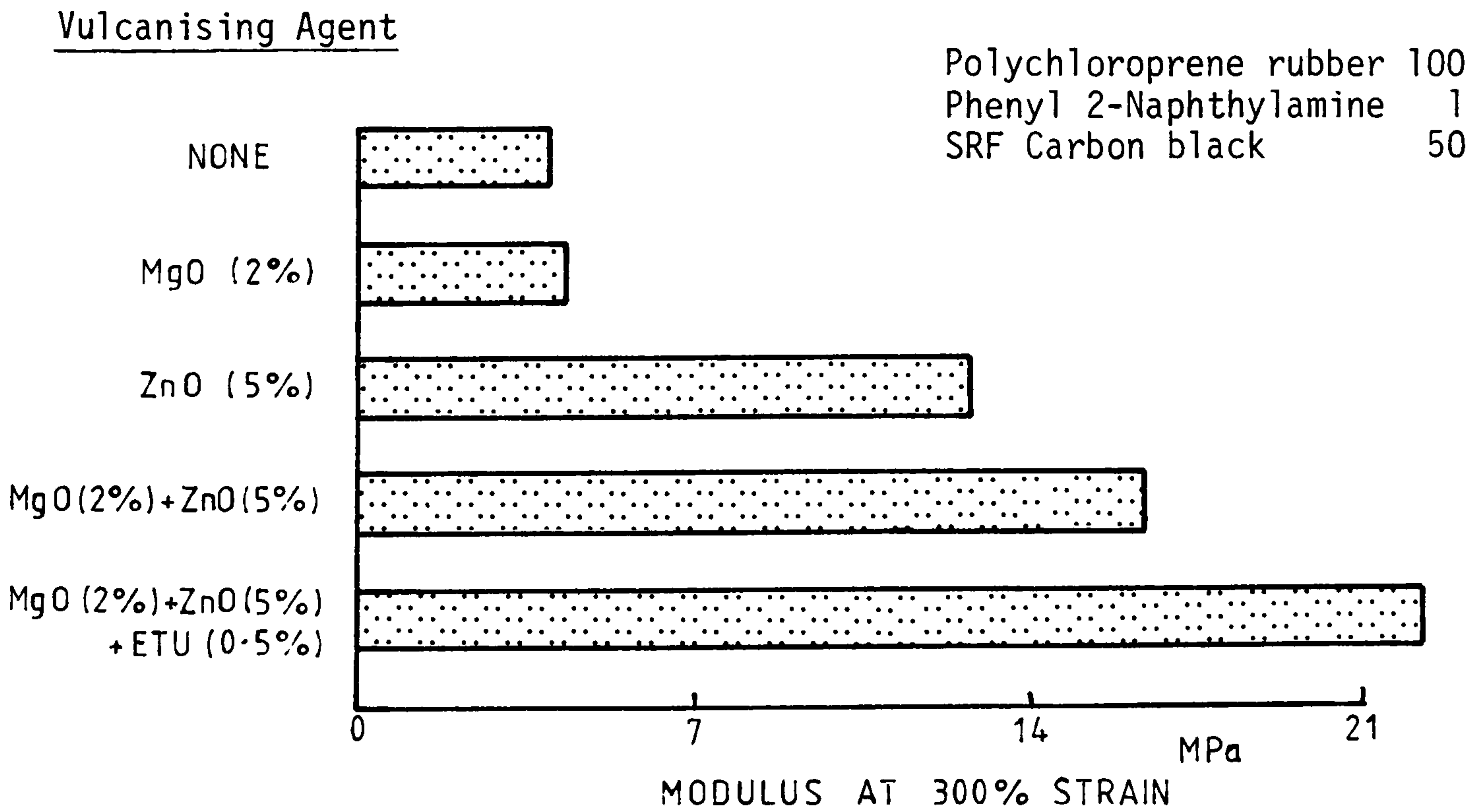


FIGURE 6.1(b): EFFECT OF METAL OXIDES ON CHLOROPRENE VULCANISATION WITHOUT AND WITH ETHYLENE THIOUREA (ETU) [83]

This chapter reports the discovery of diamine surfactants which are able to react with CR and produce well cured vulcanisates which possess good physical properties without ZnO (or MgO) being included in the vulcanisates and thus demonstrate evidence in support of the bisalkylation theory of CR vulcanisation.

The surfactants and the prepared salts used in this investigation as crosslinking agents are given in Table 6.1.

6.1 Vulcanisation of CR with Only a Surfactant and Prepared Salts

Rubber mixes and their properties are given in Table 6.2 where a conventional carbon black reinforced polychloroprene (CR) vulcanised with a standard ZnO/MgO/Ethylene thiourea combination was compared with CRs which contained only a surfactant and prepared salts with the metal oxides of MgO and ZnO omitted; curemeter profiles are given in Figure 6.2.

The results given in Figure 6.2 and Table 6.2 reveal the following features:

1. CR rubber can be crosslinked by the use of a surfactant or prepared salts alone and the resulting vulcanisates have excellent physical strength properties and in particular lower compression set. The presence of a divalent metal oxide such as ZnO and/or MgO is not necessary to obtain a good state of cure.
2. CR rubbers cured with these new curing systems have long scorch times and hence excellent processing safety.
3. The Mooney viscosity of a CR rubber containing these new systems is significantly lower than the control e.g. between 6-12% lower, indicating superior flow properties.

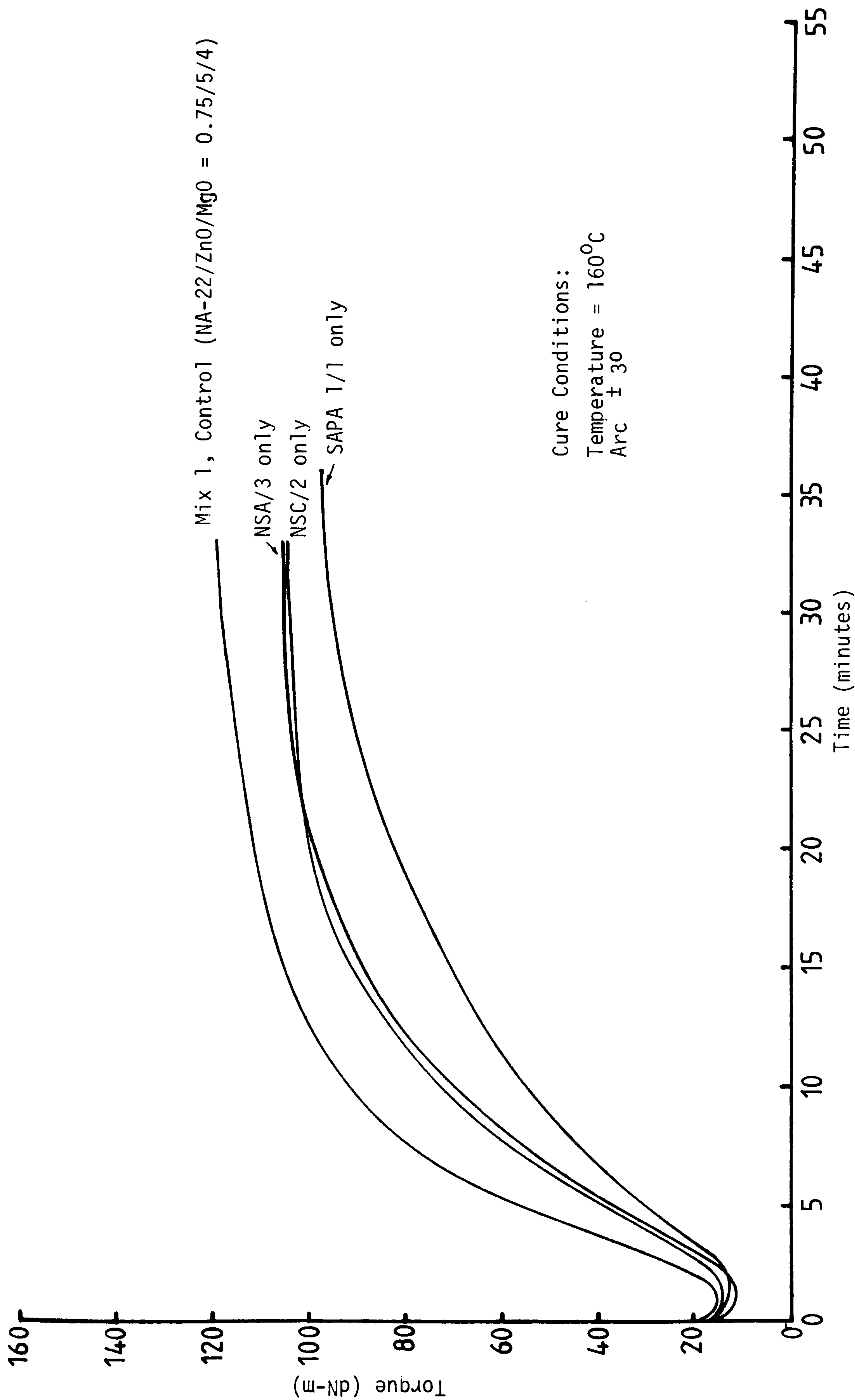


FIGURE 6.2: CURING BEHAVIOUR OF SURFACTANTS AND PREPARED DIAMINE SALTS AS CROSSLINKING AGENTS FOR CR RUBBER IN COMPARISON WITH A CONVENTIONAL (ETU) CROSSLINKING SYSTEM

Also it was observed that the inherent tendency of CR rubber mixes to stick to mill rolls was eliminated entirely by the use of these systems. Further no mould release agent was necessary when the surfactant or the prepared salts rubber mixes were cured, whereas the ethylene thiourea control mix required the use of a mould release agent.

TABLE 6.2:

PROPERTIES OF UNVULCANISED AND VULCANISED CHLOROPRENE CURED WITH A SURFACTANT AND PREPARED DIAMINE SALTS ONLY

Mix Abbreviation	Control Na-22 ZnO+MgO Present	SAPA 1/1	NSA/3	NSC/2
		No ZnO or MgO present		
Mix No:	1	2	3	4
Polychloroprene (Neoprene WRT)	100	100	100	100
SRF Carbon black	58	58	-	-
Aromatic Oil (Dutrex 729)	12	12	-	-
Stearic acid	0.5	-	-	-
MgO	4	-	-	-
ZnO	5	-	-	-
Ethylene thiourea	0.75	-	-	-
SAPA /1	-	3	-	-
NSA/3	-	-	3	-
NSC/2	-	-	-	3
<u>Processing and Curing Properties:</u>				
Mooney Viscosity ML(1+4)100°C	62	58	54	56
Mooney Scorch, 125°C (m)	5	15	9	12
Optimum Curing time, t ₉₀ at 160°C (m)	20	24	15	16
<u>Physical Properties:</u>				
Tensile Strength MPa	17	15	16	16
Elongation at Break %	250	290	250	280
100% Modulus MPa	5	3.6	4	3.7
300% Modulus MPa	12.5	9	11	10
Hardness IRHD	75	63	67	66
Tear Strength kNm ⁻¹	50	43	39	40
Rebound Resilience %	34	31	30	32
Compression set %, 70°C for 48 hrs	12	9.5	10.5	10.5

6.2 Surfactants as Vulcanising Agents in the Presence of ZnO and/or MgO

Table 6.3 and Figure 6.3 compare the processing, curing and vulcanisate properties of surfactant and prepared salts crosslinked vulcanisates with and without the addition of crosslinks from MgO, ZnO and MgO + ZnO combinations. The following observations can be made:

- i) In the control mixes, numbers 1 and 2, the addition of ethylene thiourea as a combined curative and accelerator to a traditional ZnO/MgO crosslinking system is to reduce scorch and increase viscosity (presumably due to the small amount of curing occurring during processing) and also to increase tensile strength (34%), hardness (15%) with other properties changing in sympathy.
- ii) In comparison with the data in Tables 6.2 and 6.3 for the use of a surfactant or a prepared salt material alone and in combination with metal oxides demonstrates that the use of metal oxides in combination with the surfactants type SAPA 2/C gave tensile strength, hardness and modulus equivalent to the best available from an ethylene thiourea system plus advantages of lower compression set, better scorch time and excellent processability.
- iii) Curing system based on a surfactant or a prepared salt alone or in combination with metal oxides, give CR mixes with superior scorch time to their ethylene thiourea analogues.
- iv) The elasticity properties e.g. compression set of these new system vulcanisates, are superior to those of ethylene thiourea by approximately 20%.

- v) A unique property observed to be possessed by these new systems was their ability to improve the flow properties of polychloroprene; this is indicated, to some extent, by the reduction in Mooney viscosity (between 6-12%) of mixes containing surfactants or a prepared salt.
- vi) The effect of the SAPA 1/1 surfactant as a crosslinking agent (mix 4) is generally similar to that obtained by the diamine salt compound NSA/3 (mix 5). However, these compounds seem to be less reactive than the SAPA 2/C compound (mix 7). This is believed to be due to their different reactivities. As can be seen in Table 6.1, SAPA 2/C is a diamine while those of SAPA 1/1 and NSA/3 are diamine salts which obviously are less reactive than the diamine.

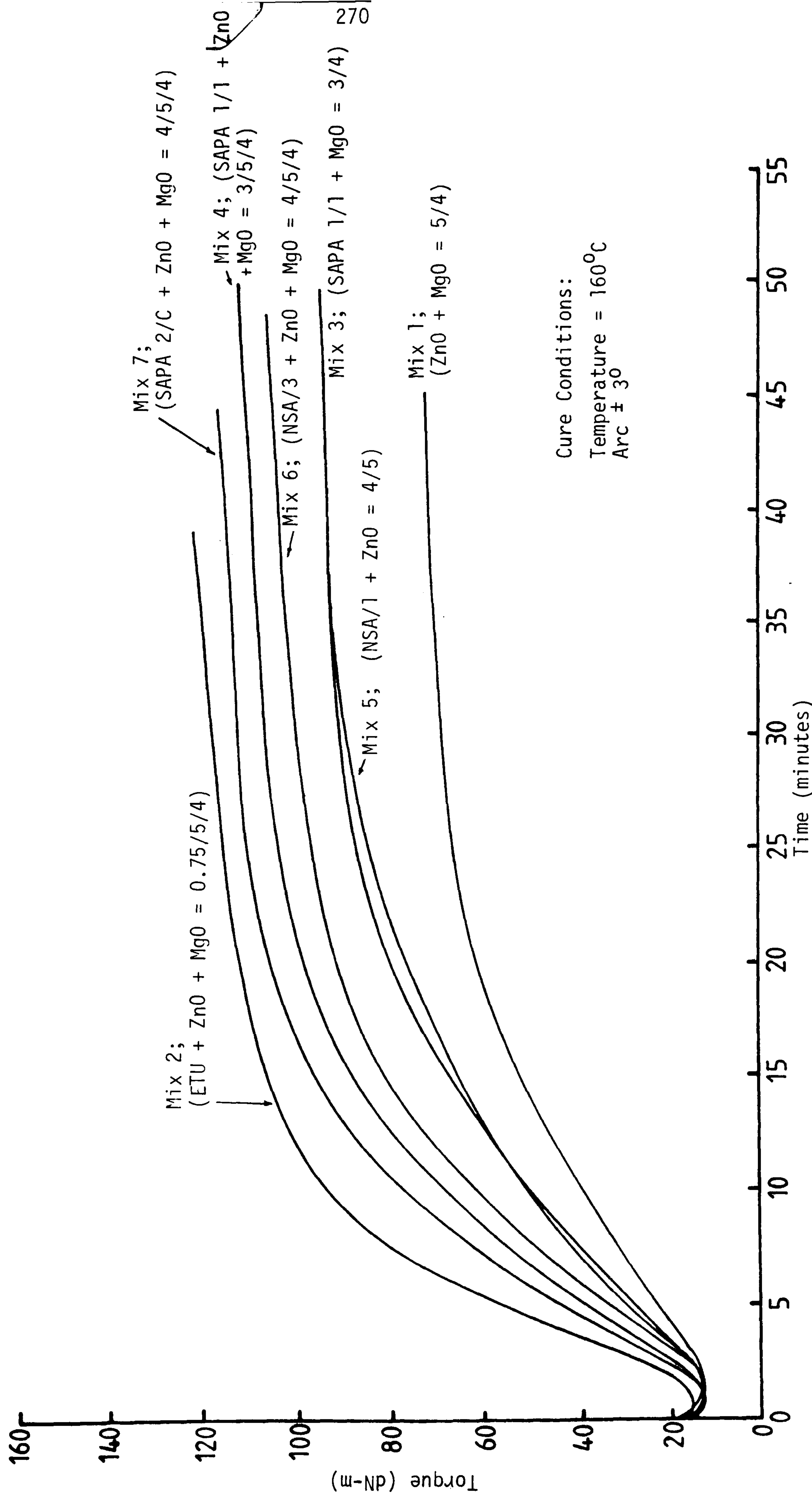


FIGURE 6.3: CROSSLINKING PROPERTIES OF CR RUBBER MIXES (TABLE 6.3)

TABLE 6.3

CHLOROPRENE RUBBER CURED WITH SURFACTANTS AND PREPARED DIAMINE SALTS IN COMBINATION WITH METAL OXIDES

Cure System	Controls		Diamine Systems					
	Metal Oxide Cure ZnO+MgO		Ethylene thiourea + Metal oxides Na-22+ZnO+MgO	SAPA 1/1 + MgO	SAPA 1/1 + MgO+ZnO	NSA/3 + ZnO	NSA/3 + MgO+ZnO	SAPA 2/C + MgO+ZnO
Mix No:	1		2	3	4	5	6	7
Chloroprene (Neoprene WRT) SRF Carbon black Aromatic Oil Stearic Acid MgO ZnO Ethylene Thiourea (Na-22) SAPA 1/1 NSA/3 SAPA 2/C	100		100	100	100	100	100	100
	58		58	58	58	58	58	58
	12		12	12	12	12	12	12
	0.5		0.5	-	-	-	-	-
	4		4	4	4	-	4	4
	5		5	-	5	5	5	5
Processing and Curing Properties: Mooney Viscosity ML(1+4)100°C Mooney Scorch 125°C (m) Optimum Curing Time t ₉₀ , 160°C (m)	-		0.75	-	-	-	-	-
	-		-	3	3	-	-	-
	-		-	-	-	-	4	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
	-		-	-	-	-	-	-
Mooney Viscosity ML(1+4)100°C Mooney Scorch 125°C (m) Optimum Curing Time t ₉₀ , 160°C (m)	58	62		60	58	56	56	56
	18	5		13	9	14	13	8
	29	20		27	30	28	28	23

/Continued

TABLE 6.3 ... continued

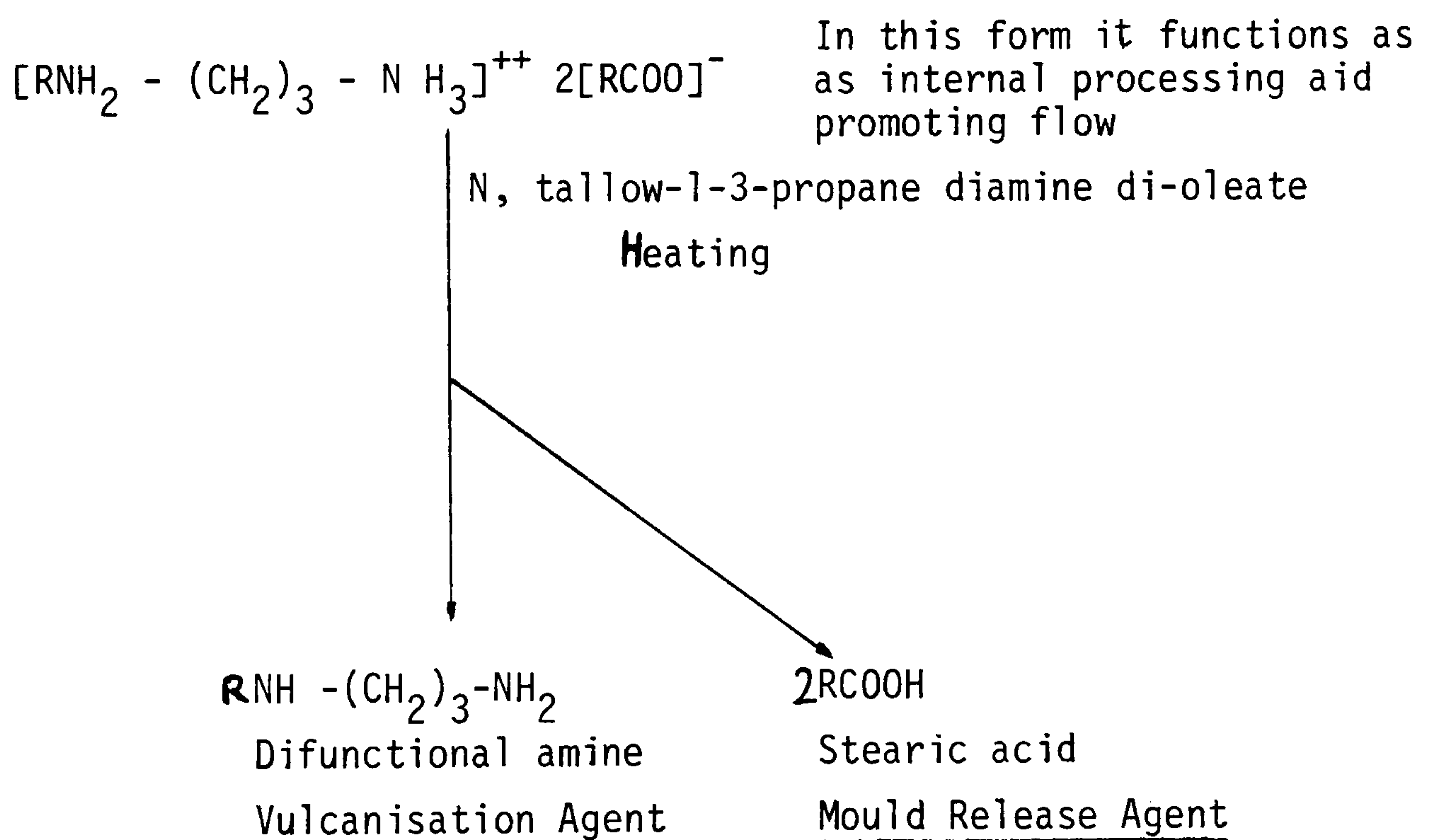
Mix No:	1	2	3	4	5	6	7
<i>Physical Properties:</i>							
Tensile Strength MPa	13.4	17	17	17.4	17	17	17.9
Elongation at break %	475	250	230	345	385	260	300
100% Modulus MPa	2.5	5	5.8	4.4	4	5.4	4.7
300% Modulus MPa	5	12.5	13	10	9.4	12	12
Hardness IRHD	65	75	77	74	70	75	73
Tear Strength kN m ⁻¹	45	50	33	42	44	33	40
Rebound Resilience %	34	34	32	36	36	37	34
Compression Set % (70°C for 48 hours)	13	12	10	10	12	10.5	10

6.3 A Mechanism to Explain the Dual Role Function of Surfactants and Similar Materials as Combined Vulcanisation Agents and Processing Aids

The mechanism proposed is basically divided into four steps. The first step is believed to proceed as explained earlier in Chapter 5. However, a complete mechanism including the first step is explained here.

For the purpose of this mechanism the formula of a typical surfactant can be represented as follows:

Step 1

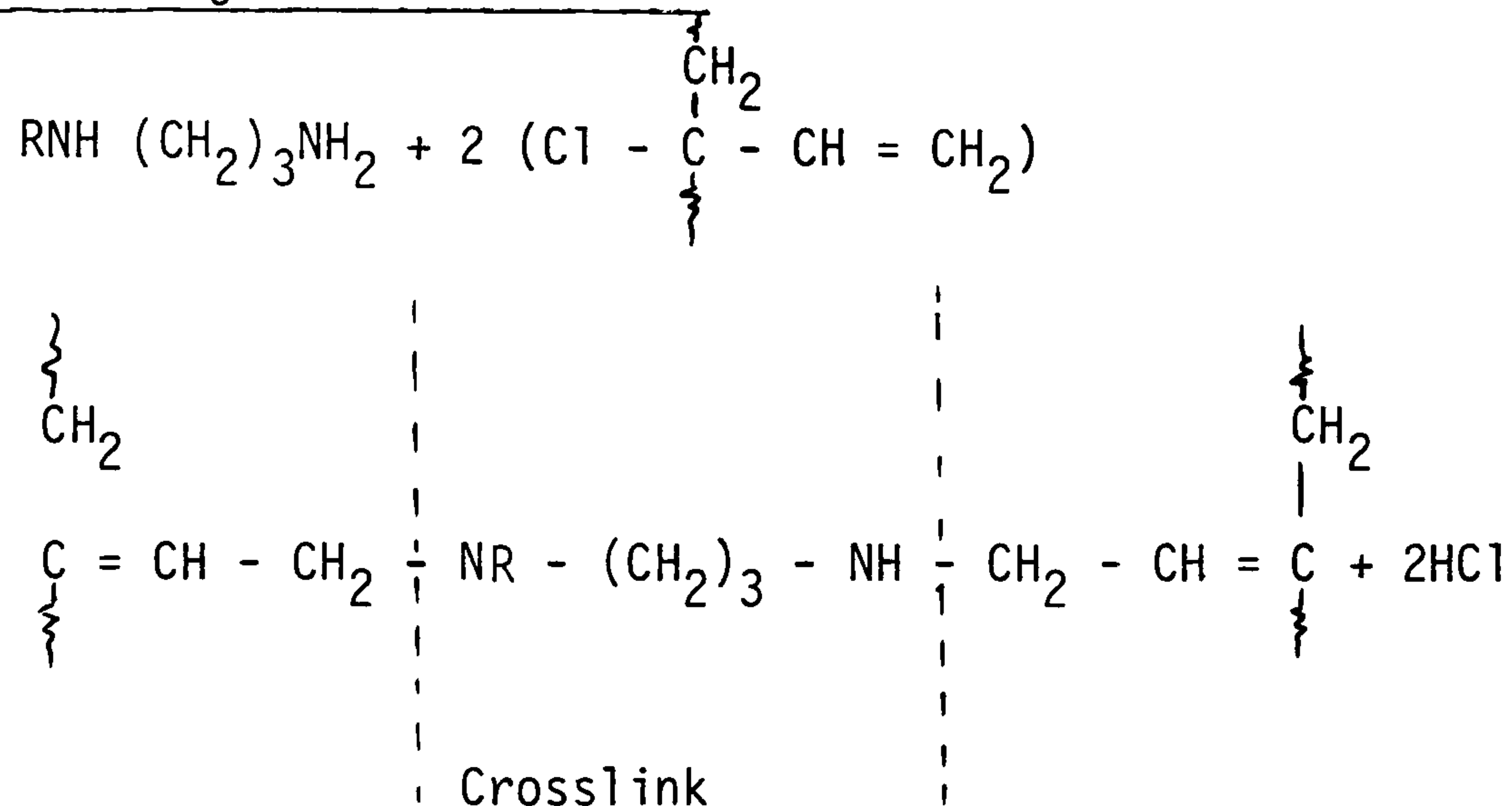


On heating during the vulcanisation process it decomposes as shown, into two constituents; the diamine functions as a combined 'cross-linking agent-accelerator', and the fatty acid as a 'flow promoter-mould release agent'.

Step 2

The $\text{RNH}(\text{CH}_2)_3\text{NH}_2$ produced in situ during the heating of the rubber and during cure can then function alone as a vulcanisation agent; if a divalent metal oxide such as MgO or ZnO (or both) are present then they are also considered to contribute to the cross-linking process (as shown in Steps 3 and 4).

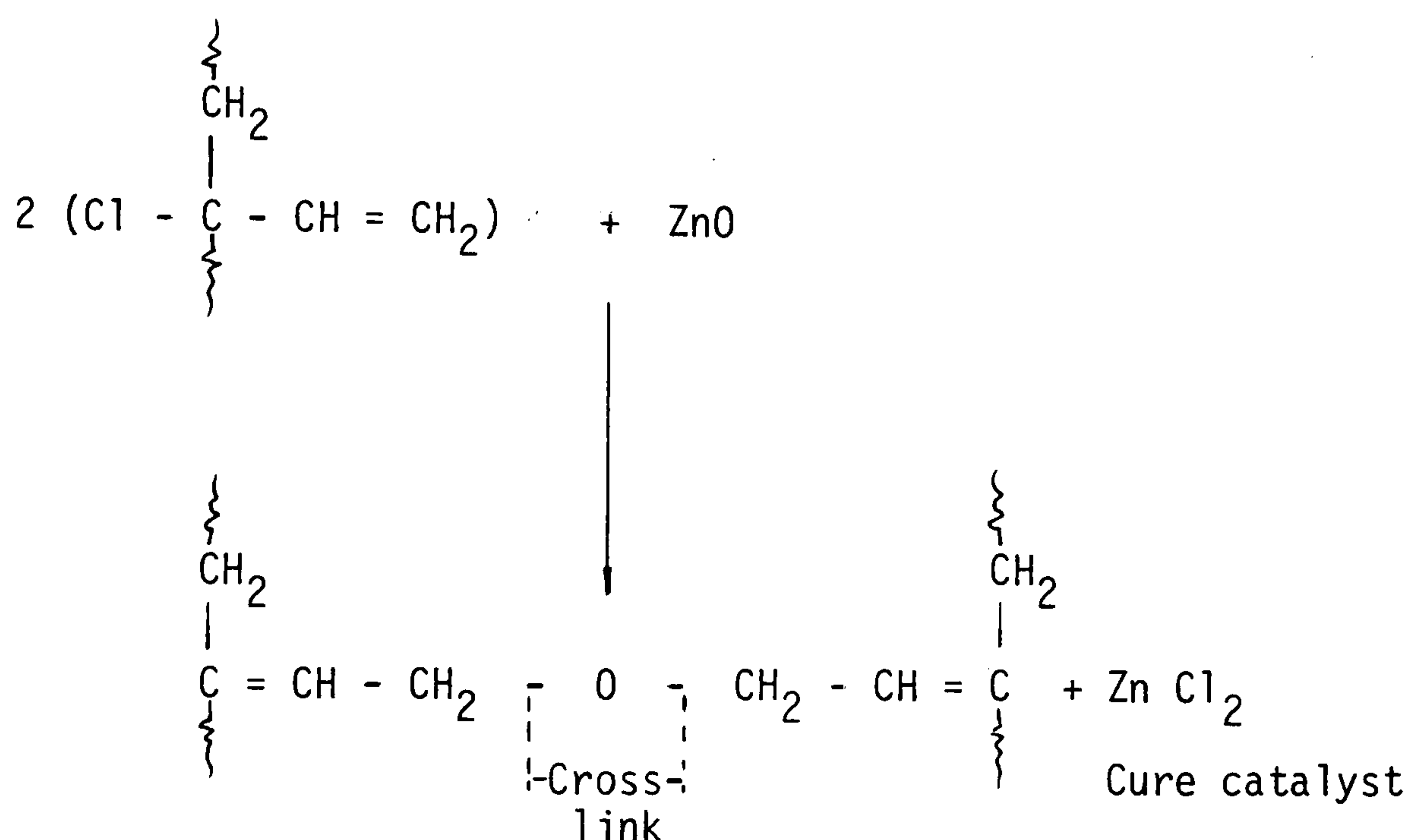
Crosslinking with the Diamine



The occurrence of Step 3 would explain the increase in tensile strength, modulus and hardness (compare mix 3 of Table 6.3 with mix 2 of Table 6.2) when MgO is added to surfactant formulation. The addition of MgO, which is also observed to increase scorch time and retard the onset of cure, can be explained by the in-situ production of MgCl_2 functioning as a retarder of cure.

Step 4: Crosslinking of CR when Zinc Oxide is present

It can be seen by comparing mix 5 of Table 6.3 with mix 3 of Table 6.2



Some Evidence to Support the Above Mechanism

pH changes are known to occur normally in polychloroprene as a result of vulcanisation and it was decided to see if these also occurred in surfactant type cures. The vulcanisates of mixes 1, 2, 3 and 4 of Table 6.2 were extracted using acetone containing 20% of distilled water and then their pH determined. The results are given in Table 6.4.

When surfactants and diamine salts are used to vulcanise CR acidic by-products are produced (see mechanism Step 2); that this occurs can be seen from the data in Table 6.4 which shows surfactant and prepared salts vulcanisates to possess free acidity. It is considered desirable to incorporate some metal oxide in the formulation to reduce this acidity to the level normally achieved in an ethylene thiourea/ZnO/MgO system which is shown in Table 6.4 below:

TABLE 6.4:

COMPARISON OF pH CHANGES IN CHLOROPRENE VULCANISATES CROSSLINKED WITH SURFACTANTS AND PREPARED DIAMINE SALTS

Vulcanisation Systems	Ethylene Thiourea +MgO+ZnO	SAPA 1/1	NSA/3	NSC/2
pH of the solution after extraction	8.5	9.1	9.2	8.8
pH of the solution before extraction	7.1	6.6	6.7	6.3
Difference in pH of the solution	1.4	2.5	2.5	2.5

Comminuted pieces of the vulcanisate were extracted [ASTM D297] with an acetone/water mixture in the ratio of 80/20 by volume.

6.4 Conclusions

Surfactants and prepared salts material alone or in combination with metal oxides, MgO and/or ZnO, crosslink polychloroprene to give vulcanisates with excellent physical properties. The resulting mixes possess processing safety which is superior to their ethylene thiourea analogues; also they have excellent processing flow and ready release from processing equipment surfaces and from mould surfaces; a considerable reduction in mould fouling by formulations containing surfactants or prepared salts is also observed.

The bisalkylation theory of polychloroprene vulcanisation by Kovacic is considered to apply to this vulcanisation by surfactants and this investigation supplies additional evidence for such a mechanism.

CHAPTER 7

SOME RUBBER AGEING CHARACTERISTICS AND SURFACTANTS; SURFACTANTS OF IMPROVED PHYSICAL FORM

This part of the research work is actually composed of two different subjects. The first one deals with the ageing behaviour of some cationic surfactants when used as cure activator/accelerator systems in both carbon black and silica filled SBR rubber. This is compared with a conventional accelerator system.

The second subject covers an attempt which was carried out to improve the physical form of the SAPA 1/1 surfactant and the diamine salt NSA/1 material.

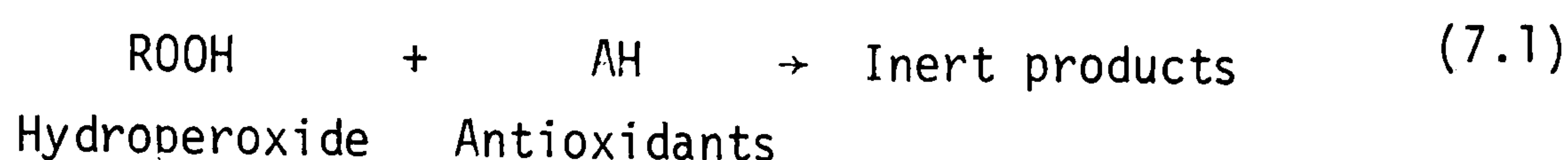
7.1 Ageing Behaviour of the Surfactant/Sulphur Curing Systems in SBR Rubber

Introduction

The term ageing when applied to rubbers includes deterioration in a variety of ways which have been classified and summarised by Buist [85]. These consist of attack by oxygen, heat, flexing fatigue, metal catalysts, light and ozone. The mechanism of the oxidation ageing process has been explained before (see Section 1.2). The nature of the changes that are observed to occur during oxidation or ageing vary considerably, depending on the type of rubber and the ageing conditions to which it is subjected. The net effect upon physical properties is the resultant of two competing processes: chain scission and crosslinking [86].

Natural, polyisoprene and butyl rubbers are known to degrade by chain scission, resulting in a reduction of tensile strength and of average molecular weight. SBR, CR and NBR rubbers degrade by preferential crosslinking producing brittle type rubber vulcanisates.

In order to prevent deterioration of the rubber, it is necessary to either eliminate peroxide initiation, as shown in equation 7.1 below



The antioxidants used at this stage are usually known as preventive antioxidants [88]. Or interrupt the propagation cycle by antioxidant which reacts with the ROO^\bullet radicals thus removing them from the medium as shown in the equations below



These type of antioxidants are known as chain-stoppers or chain breakers [87].

Various methods of accelerated test are used to examine the resistance of rubber compounds to deterioration: the following are the most popular; (a) heat ageing, (b) flexing, (c) light exposure, (d) oxygen absorption, and (e) stress relaxation. However, BS 903-A19 specifically warns against interpreting the results too literally, adding that accelerated ageing tests do not accurately predict the life expectancy of a rubber formulation in its service environment and conditions.

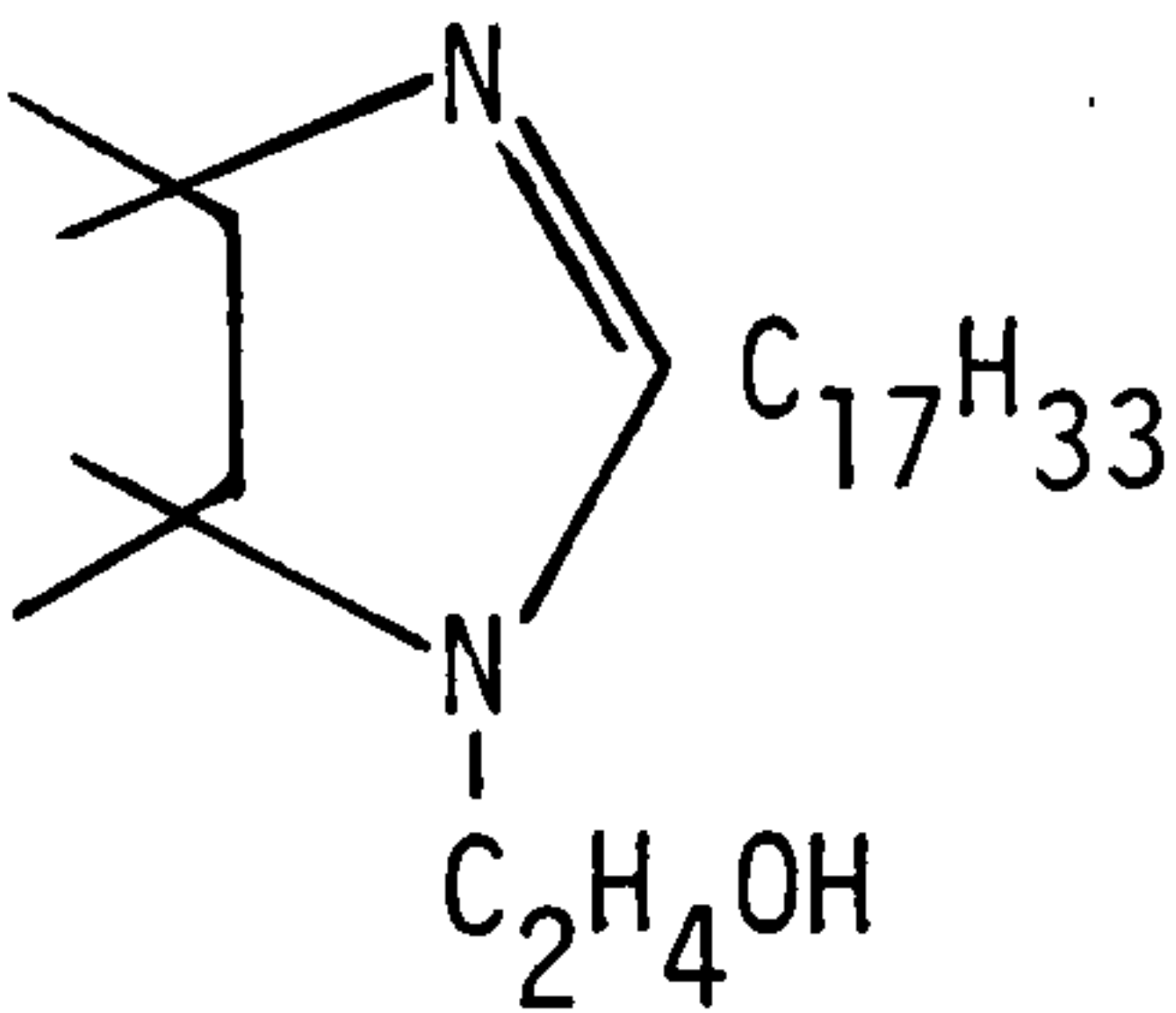
This next part reports the relative ageing behaviour of the surfactant/sulphur curing systems compared with a conventional sulphur curing system, with and without antioxidants, in carbon black and silica filled SBR rubber. Also the effect of zinc oxide on the ageing behaviour of SBR vulcanisates based on the surfactant systems is examined.

7.1.1 Experimental

The ageing behaviour of vulcanisates based on two types of surfactant and a diamide/TEA combination system used as cure activator/accelerator systems. These are given in Table 7.1 below:

TABLE 7.1:

THE SURFACTANTS AND THE EBF-S/TEA SYSTEMS USED IN THIS AGEING INVESTIGATION

Trade Name	Chemical Structure	Supplier	Abbreviation
Diamine HBG	$\text{RNH}(\text{CH}_2)_3\text{NH}_2$ N-tallow-1-3 propane diamine	Kenogard Ltd	SAPA 2/C
Imidazoline (18)OH	 1(2-hydroxyethyl)-2-heptadecenyl [2] imidazoline	Ligand Group Ltd	IM
Crodamines EBS*	$\text{C}_{17}\text{H}_{33}\text{CONH}(\text{CH}_2)_2\text{NHCOH}_{33}\text{C}_{17}$ N,N'-ethylene bis stearamide	Croda Chemicals Ltd	EBF-S

* The EBF-S type of compound was always used in combination with 1 phr TEA.

The rubber formulations used are shown in Table 7.2.

Mixing cycle and conditions adopted were the same as those used previously in Section 5.2.2. All samples were cured to a t_{90} cure state.

Heat ageing tests using the hot air oven technique were run on all vulcanisates at 100°C for one, two and three weeks. The reason for using the above method to study ageing is because some workers [74,75] had indicated that air oven ageing data provided better correlation with natural ageing data than did other accelerated ageing tests such as the oxygen and air bombs.

7.1.2 Effect of Antioxidants on Ageing Behaviour

In this part of the research work the effect of antioxidants was assessed on the ageing behaviour of carbon black and silica filled SBR vulcanisates cured by surfactant/sulphur and EBF-S/TEA/sulphur systems. This was carried out in comparison with a vulcanisate containing a more conventional curing system such as ZnO/stearic acid/MBT/DPG/sulphur.

The results of this investigation are given in Tables 7.3-7.18 respectively. Examination of these results shows the following features:

1. The ageing behaviour of all vulcanisates obtained from the surfactants and the EBF-S/TEA compound of Table 7.1 are similar. The presence of antioxidants confers no apparent additional protection to the thermal oxidation of all the vulcanisates obtained by means of the surfactant and the EBF-S/TEA type cure activator/accelerator systems (see Tables 7.7-7.18).

TABLE 7.2
FORMULATIONS OF SBR RUBBER USED THROUGHOUT THE INVESTIGATION

Cure System	Conventional Curing System				Surfactants System					
	1	2	3	4	5	6	7	8	9	10
Mix No:										
	Carbon Black				Carbon Black		Silica		Carbon Black	Silica
	Without Anti-oxidants	With Anti-oxidants	Without Anti-oxidants	With Anti-oxidants	Without Anti-oxidants	With Anti-oxidants	Without Anti-oxidants	With Anti-oxidants	Without Anti-oxidants	Without Anti-oxidants
SBR 1500	100	100	100	100	100	100	100	100	100	100
Sulphur	2	2	2	2	2	2	2	2	2	2
Aromatic Oil (Dutrex 729)	5	5	5	5	5	5	5	5	5	5
MBT	1.5	1.5	1.5	1.5	-	-	-	-	-	-
DPG	0.5	0.5	0.5	0.5	-	-	-	-	-	-
ZnO	5	5	5	5	-	-	-	-	5	5
Stearic acid	1	1	1	1	-	-	-	-	-	-
Flectol-H	-	2	-	2	-	2	-	2	-	-
Surfactants	-	-	-	-	2	2	2	2	2	2
HAF Carbon black	30	30	-	-	30	30	-	-	30	-
Silica (Ultrasil VN3)	-	-	30	30	-	-	30	30	-	30
EBF-S/TEA	-	-	-	-	2/1	2/1	2/1	2/1	2/1	2/1

2. The most pronounced improvements in heat ageing, resulting from an antioxidant addition, have been observed in vulcanisates obtained with the conventional curing system (compare Table 7.3 with 7.4 and Table 7.5 with 7.6).
3. The vulcanisates obtained from the conventional curing system, without antioxidant addition, exhibit similar ageing behaviour to the vulcanisates obtained by the surfactant and the EBF-S/TEA systems, with and without antioxidant addition over a 2 week ageing period. However, at greater periods of ageing the conventional system vulcanisates, without antioxidant addition, retain better physical properties than the surfactant and the EBF-S/TEA system vulcanisates, with and without antioxidant addition, these latter lost most of their stress-strain properties at the end of three weeks ageing (compare Tables 7.3 and 7.5 with 7.7-7.18).

TABLE 7.3
AGEING BEHAVIOUR OF A CONVENTIONAL CURING SYSTEM (ZnO/stearic acid/MBT/DPG/Sulphur)
WITHOUT ANTIOXIDANT IN CARBON BLACK FILLED SBR VULCANISATES (MIX 1 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Scorch Time, t ₅ , at 125°C in minutes Optimum Curing Time, t ₉₀ at 160°C (m)	57						
	14'30"						
	7						
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus, MPa 300% Modulus, MPa % Elongation at Break Tear Strength, kN m ⁻¹ Hardness IRHD Resilience %	17.5	14.5	-17	9	-48.6	8	-54
	2	2.9	+49	4.3	+115	6	+200
	7.5	12	+60	-	-	-	-
	590	360	-39	193	-67	128	-78
	39	30	-23	23	-41	17.3	-44
	58	62	+ 4 units	66	+8 units	69	+11 units
	49	50	+ 2	47	- 4.0	45	- 8.0

TABLE 7.4

AGEING BEHAVIOUR OF A CONVENTIONAL (ZnO/Stearic acid/MBT/DPG/Sulphur) CURING SYSTEM WITH ANTIOXIDANT (FLECTOL-H) IN CARBON BLACK FILLED SBR VULCANISATES (MIX 2 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Scorch time, t ₅ , at 125°C in minutes Optimum Curing Time, t ₉₀ at 160°C (m)	57						
	15'30"						
	8						
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus, MPa 300% Modulus, MPa % Elongation at Break Tear Strength kN m ⁻¹ Hardness, IRHD Resilience %	17.5	16	-8.6	10	-42.9	9.5	-45.7
	2	2.9	+45	3.7	+85	6	+200
	7.7	10	+29.9	-	-	-	-
	595	420	-29.4	220	-63	160	-73
	40	36.5	-8.75	24.5	-38.75	22	-45
	59	61	+ 2 units	65	+ 6 units	70	+11 units
	48	50	+ 4.2	48	-	45	- 6.25

TABLE 7.5
AGEING BEHAVIOUR OF A CONVENTIONAL (ZnO/Stearic acid/MBT/DPG/Sulphur) CURING SYSTEM WITHOUT ANTIOXIDANT
IN SILICA FILLED SBR VULCANISATES (SEE MIX 3 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Curing Properties:</u>							
Mooney Viscosity ML (1+4) 100°C	70						
Scorch Time at 125°C, t ₅ , in minutes	More than 60'						
Optimum Curing Time, t ₉₀ , at 160°C (m)	45						
<u>Physical Properties:</u>							
Ultimate Tensile Strength MPa	16.7	12.5	-25	9.3	-44.3	7.0	-58
100% Modulus MPa	1.4	2.3	+64	3.9	+178.6	4.8	+243
300% Modulus MPa	3.0	10.8	+260	-	-	-	-
% Elongation at Break	985	390	-60	288	-70.8	253	-74
Tear Strength kNm ⁻¹	26	25	-3.8	44	-7.7	22	-15.4
Hardness IRHD	54	60	+6units	64	+8units	69	+15units
Resilience %	50	50	-	48	-4	45	-10

TABLE 7.6
AGEING BEHAVIOUR OF A CONVENTIONAL (ZnO/Stearic acid/MBT/DPG/Sulphur) CURING SYSTEM WITH ANTIOXIDANT (FLECTOL-H) IN SILICA FILLED SBR VULCANISATES (MIX 4, TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<i>Processing and Curing Properties:</i>							
Mooney Viscosity ML(1+4) 100°C	68						
Scorch Time, t ₅ , at 125°C in minutes	More than 60'						
Optimum Curing Time, t ₉₀ at 160°C (m)	47						
<i>Physical Properties:</i>							
Ultimate Tensile Strength MPa	17	14.5	-14.7	11.7	-31	9.4	-45.3
100% Modulus MPa	1.5	2.3	+53	3.5	+133	4.2	+180
300% Modulus MPa	3	10.3	+243	5.8	93	-	-
% Elongation at Break	980	450	-54	362	-63	287	-70.7
Tear Strength kN m ⁻¹	25	24	-4	23.5	6	22.5	-10
Hardness IRHD	54	58	+4 units	61	+7 units	65	+11 units
Resilience %	50	50	-	48	-4	47	-6

TABLE 7.7

AGEING BEHAVIOUR OF SAPA 2/C SURFACTANT SYSTEM WITHOUT ANTIOXIDANT IN CARBON BLACK FILLED SBR VULCANISATES
(SEE MIX 5 of TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u>							
Mooney Viscosity ML(1+4) 100°C	56						
Scorch Time, t ₅ , at 125°C in minutes	12						
Optimum Curing Time, t ₉₀ , at 160°C (m)	22'30"						
<u>Physical Properties:</u>							
Ultimate Tensile Strength MPa	17.7	13.9	-21.5	7.2	-59	The samples were very brittle	
100% Modulus MPa	2.4	3.5	+45.8	4.5	+87.5		
300% Modulus MPa	7.4	10.6	+43	-	-		
% Elongation at Break	560	333	-40.5	152	-72.8		
Tear Strength kN m ⁻¹	33	25.5	-22.7	19	-42.4		
Hardness IRHD	57	63	+6 units	68	(+)11 units		
Resilience %	52	55	+5.8	50	-3.85		

TABLE 7.8

AGEING BEHAVIOUR OF SAPA 2/C SURFACTANT SYSTEM WITH ANTIOXIDANT (FLECTOL-H) IN CARBON BLACK FILLED SBR VULCANISATES (SEE MIX 6 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<i>Processing and Curing Properties:</i>							
Mooney Viscosity ML(1+4) 100°C	56						
Scorch Time, t ₅ , at 125°C in minutes	13						
Optimum Curing Time, t ₉₀ , at 160°C (m)	23						
<i>Physical Properties:</i>							
Ultimate Tensile Strength MPa	17.5	13.7	-21.7	6	-65.7	The samples were all very brittle	
100% Modulus MPa	2.0	3.0	+50	3.6	+80		
300% Modulus MPa	7.5	8.9	+18.7	-	-		
% Elongation at Break	585	400	-31.6	130	-77.8		
Tear Strength kN m ⁻¹	35	26.5	-24	20	-42.86		
Hardness IRHD	58	63	+5 units	70	(+)12 units		
Resilience %	53	53	-	50	-5.7		

TABLE 7.9

AGEING BEHAVIOUR OF SAPA 2/C SUFFACTANT SYSTEM WITHOUT ANTIOXIDANT IN SILICA FILLED SBR VULCANISATES
(SEE MIX 7 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u>							
Mooney Viscosity ML(1+4) 100°C	72						
Scorch Time, t ₅ , at 125°C in minutes	More than 60 mins						
Optimum Curing Time, t ₉₀ , at 160°C (m)	66'30"						
<u>Physical Properties:</u>							
Ultimate Tensile Strength MPa	16.5	11.7	-29	6.3	-61.8	The samples were all very brittle	
100% Modulus MPa	1.4	2.7	+92.8	4.3	+20.7		
300% Modulus MPa	3.8	7.3	+92	-	-		
% Elongation at Break	975	460	-52.8	189	-80.6		
Tear Strength kN m ⁻¹	32	30.5	-4.7	26	-18.75		
Hardness IRHD	56	62	+6 units	68	+12 units		
Resilience %	60	58	-3.3	57	-5		

TABLE 7.10

AGEING BEHAVIOUR OF SAPA 2/C SURFACTANT SYSTEM WITH ANTIOXIDANTS (FLECTOL-H) IN SILICA FILLED SBR VULCANISATES
(SEE MIX 8 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						
Mooney Viscosity ML(1+4) 100°C	70					
Scorch Time, t ₅ , at 125°C in minutes	More than 60 mins.					
Optimum Curing Time, t ₉₀ , at 160°C (m)	67					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	17	8.66	-49	4.7	-72	The samples were all very brittle
100% Modulus MPa	1.5	4.0	+200	-	-	
300% Modulus MPa	4.0	-	-	-	-	
Elongation at Break %	920	242	-	76	-91.7	
Tear Strength kN m ⁻¹	33.5	29	13.4	25	-25.4	
Hardness IRHD	55	60	(+)5 units	70	(+)15 units	
Resilience %	60	58	-3.3	56	-6.7	

TABLE 7.11
AGEING BEHAVIOUR OF IM SURFACTANT SYSTEM WITHOUT ANTIOXIDANTS IN CARBON BLACK FILLED SBR VULCANISATES
(SEE MIX 5 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						The samples were all very brittle
Mooney Viscosity ML(1+4) 100°C	56					
Scorch Time t ₅ at 125°C in minutes	9					
Optimum Curing Time t ₉₀ , at 160°C (m)	22					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	18	14.6	-18.9	7.2	-60	
100% Modulus MPa	2.5	3.9	+56	5.5	+120	
300% Modulus MPa	10.5	-	-	-	-	
Elongation at Break %	475	263	-44.4	152	-68	
Tear Strength kN m ⁻¹	34.5	22.5	-34.8	17.5	-49	
Hardness IRHD	61	69	+8 units	73	+12 units	
Resilience %	53	50	-5.7	45	-15	

TABLE 7.12

AGEING BEHAVIOUR OF IM SURFACTANT WITH ANTIOXIDANTS (FLECTOL-H) IN CARBON BLACK FILLED SBR VULCANISATES
(SEE MIX 6 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<i>Processing and Curing Properties:</i>						
Mooney Viscosity ML(1+4) 100°C	58					
Scorch Time, t ₅ , at 125°C in minutes	10'30"					
Optimum Curing Time, t ₉₀ , at 160°C (m)	23					
<i>Physical Properties:</i>						
Ultimate Tensile Strength MPa	18.5	14	-24	6.8	-63	The samples were all very brittle
100% Modulus MPa	2.5	4.2	+68	5.8	+132	
300% Modulus MPa	10.5	-	-	-	-	
Elongation at Break %	475	250	-47.4	142	-70	
Tear Strength kN m ⁻¹	35	23.5	-32.8	18.5	-47	
Hardness IRHD	61	70	+9 units	73	+12 units	
Resilience %	53	50	-5.7	42	-20.8	

TABLE 7.13

AGEING BEHAVIOUR OF IM SURFACTANT SYSTEM WITHOUT ANTIOXIDANTS IN SILICA FILLED SBR VULCANISATE
(SEE MIX 7 TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Mooney Scorch at 125°C (m) Optimum Curing Time, t ₉₀ , at 160°C (m)	70					
	More than 60					
	72					
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness IRHD Resilience %	17	11	-35	7.4	-56.5	The samples were all very brittle
	1.75	2.9	+65.7	3.7	+111	
	3.4	7.2	+112	-	-	
	850	455	-46.5	190	-77.7	
	34.5	23.5	-32	18.5	-46	
	57	63	+6 units	68	+11 units	
	50	48	-4	44	-12	

TABLE 7.14
AGEING BEHAVIOUR OF IM SURFACTANT SYSTEM WITH ANTIOXIDANT (FLECTOL-H) IN SILICA FILLED SBR VULCANISATES
(SEE MIX 8 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<i>Processing and Curing Properties:</i>						
Mooney Viscosity ML(1+4)	70					
Scorch Time, t ₅ , at 125°C in minutes	More than 60					
Optimum Curing Time, t ₉₀ , at 160°C (m)	73' 30"					
<i>Physical Properties:</i>						
Ultimate Tensile Strength MPa	17	10.3	-39	7.5	-56	The samples were all very brittle
100% Modulus MPa	1.75	3.0	+71	4.0	+128.6	
300% Modulus MPa	3.5	7.6	+117	-	-	
Elongation at Break %	840	430	-48.8	176	-79	
Tear Strength kN m ⁻¹	35.5	32.5	-8.5	27.5	-22.5	
Hardness IRHD	58	61	+3 units	69	+11 units	
Resilience %	50	48	-4	46	-8.0	

TABLE 7.15
AGEING BEHAVIOUR OF EBF-S/TEA ACTIVATOR ACCELERATOR SYSTEM WITHOUT ANTIOXIDANTS IN CARBON BLACK FILLED SBR
VULCANISATES (SEE MIX 5 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						
Mooney Viscosity ML(1+4) 100°C	50					
Scorch time, t ₅ , at 125°C in minutes	35					
Optimum Curing Time, t ₉₀ at 160°C (m)	45					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	17.5	13.6	-22.3	4.2	-76	The samples were all very brittle
100% Modulus MPa	2	3.8	+90	-	-	
300% Modulus MPa	7.8	12.75	+63.5	-	-	
Elongation at Break %	450	310	-31	81	-82	
Tear Strength kN m ⁻¹	34	31.5	-7.5	12.5	-63	
Hardness IRHD	60	67	+7 units	72	+12 units	
Resilience %	59	52	-11.86	45	-23.7	

TABLE 7.16

AGEING BEHAVIOUR OF EBF-S/TEA ACTIVATOR/ACCELERATOR SYSTEM WITH ANTIOXIDANTS (FLECTOL-H) IN CARBON BLACK FILLED SBR VULCANISATES (SEE MIX 6 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						
Mooney Viscosity ML(1+4) 100°C	50					
Scorch Time, t ₅ , at 125°C in minutes	33'30"					
Optimum Curing Time, t ₉₀ , at 160°C (m)	43					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	17.7	14.8	-16.4	5	-71.8	The samples were all very brittle
100% Modulus MPa	2.2	3.3	+50	-	-	
300% Modulus MPa	8.1	13.3	+64.2	-	-	
Elongation at Break %	445	326	-26.7	90	-79.8	
Tear Strength kN m ⁻¹	33	30	-9	14	-58	
Hardness IRHD	59	68	+9 units	73	+14 units	
Resilience %	61	51	-16.4	48	-21.3	

TABLE 7.17

AGEING BEHAVIOUR OF EBF-S/TEA ACTIVATOR/ACCELERATOR SYSTEM WITHOUT ANTIOXIDANTS IN SILICA FILLED SBR VULCANISATES (SEE MIX 7 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						
Mooney Viscosity ML(1+4) 100°C	68					
Scorch Time, t ₅ , at 125°C in minutes	26'30"					
Optimum Curing Time, t ₉₀ , at 160°C (m)	43'30"					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	16.5	10.5	-36	8.4	-49	The samples were all very brittle
100% Modulus MPa	1.5	2.5	+66.7	3.7	+146.7	
300% Modulus MPa	3.75	8.5	+126.7	-	-	
Elongation at Break %	955	341	-64	227	-76	
Tear Strength kN m ⁻¹	36	30	-16.7	24.7	-31	
Hardness IRHD	62	70	+8 units	75	+13 units	
Resilience %	58	56	-3.4	55	-5	

TABLE 7.18
AGEING BEHAVIOUR OF EBF-S SURFACTANT (TREATED WITH 1 phr TEA) WITH ANTIOXIDANTS IN SILICA FILLED SBR VULCANISATES
(SEE MIX 8 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C
		Value	% Change	Value	% Change	
<u>Processing and Curing Properties:</u>						
Mooney Viscosity ML(1+4) 100°C	68					
Scorch Time, t ₅ , at 125°C in minutes	27'30"					
Optimum Curing Time, t ₉₀ , at 160°C (m)	44					
<u>Physical Properties:</u>						
Ultimate Tensile Strength MPa	16.75	10	-40.3	7.5	-55	The samples were all very brittle
100% Modulus MPa	1.4	2.7	+92.8	3.9	+178.6	
300% Modulus MPa	3.6	8.7	+141.7	-	-	
Elongation at Break %	960	335	-65	198	-79.4	
Tear Strength kN m ⁻¹	36.5	31	-15	25	-31.5	
Hardness IRHD	60	69	+9	73	+13 units	
Resilience %	57	55	-3.5	52	-8.8	

7.1.3 To Explore the Use of Zinc Oxide as a Means of Improving Ageing Behaviour of Vulcanisates Based on Surfactants/Sulphur and EBF-S/TEA/Sulphur Curing Systems

It was decided to investigate this route following the observation made earlier in Section 4.3 that the inclusion of zinc oxide in a surfactant containing mix prevents cure reversion whereas the surfactant system by itself does show conventional reversion. Also it has been generally reported that zinc oxide improves heat ageing [88,89] and acts very effectively as a weathering stabiliser [90].

For the above reasons it was decided to investigate the effect of zinc oxide on the ageing performance of these surfactant/sulphur and EBF-S/TEA/sulphur curing systems in mixes that did not contain antioxidants (see formulations 9 and 10 of Table 7.2).

The results of this investigation are given in Tables 7.19-7.22. These results show that the addition of 5 phr zinc oxide has significantly enhanced the ageing properties of the sulphur-surfactant cured compound although no antioxidants are present in the compound formulations. Comparing these results with those of Tables 7.3-7.6 (which are concerned with the sulphur-conventional accelerator cured compound) it is clear that the ageing behaviour of the surfactant/ZnO/sulphur systems is superior to that of the conventional system without antioxidant and similar when the latter contains antioxidant.

The improvement in the ageing resistance of the surfactant/ZnO/sulphur systems must therefore be due to the action of the zinc oxide. It is believed that the presence of ZnO alters the curing mechanism of vulcanisation and hence produces a network structure that contains a high percentage of monosulphidic crosslinks as compared to the network structure obtained without zinc oxide which is presumed to be predominantly polysulphidic based.

TABLE 7.19

EFFECT OF ZINC OXIDE ON THE AGEING BEHAVIOUR OF SAPA 2/C SURFACTANT SYSTEM, WITHOUT ANTIOXIDANT, IN CARBON BLACK FILLED SBR VULCANISATES (SEE MIX 9 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Scorch Time, t ₅ , at 115°C in minutes Optimum Curing Time, t ₉₀ , at 160°C (m)	55						
	13'30"						
	23						
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness IRHD Resilience %	17.5	15.75	-10	13.2	-24.6	10.5	-40
	2.5	3.6	+44	4.3	+72	5.96	+138.4
	7.5	9.6	+28	-	-	-	-
	560	450	-19.6	230	-58.9	160	-71
	34.5	28	-18.8	25	-27.5	22.5	-34.8
	57	62	+5 units	66	+9 units	70	+13 units
	52	51	-1.9	48	-7.7	48	-7.7

TABLE 7.20

EFFECT OF ZnO ON THE AGEING BEHAVIOUR OF SAPA 2/C SURFACTANT SYSTEM WITHOUT ANTIOXIDANTS IN SILICA FILLED SBR VULCANISATES (SEE MIX 10 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) Scorch Time, t ₅ , at 125°C in minutes Optimum Curing Time, t ₉₀ , at 160°C (m)	73						
	More than 60 mins						
	68						
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness IRHD Resilience %	17	13.54	-20	11.3	-33.5	9.0	-47
	2	3.0	+50	3.7	85	4.1	+105
	3.5	7.4	+111	-	-	-	-
	840	450	-46	280	-	225	-73
	36	305	-15.3	27	-66.7	24	-33.3
	61	66	+5 units	69	+8 units	73	+12 units
	53	52	-1.9	52	-	50	-5.7

TABLE 7.21

EFFECT OF ZnO ON THE AGEING BEHAVIOUR OF IM SURFACTANT SYSTEM WITHOUT ANTIOXIDANTS IN CARBON BLACK FILLED SBR
VULCANISATES (SEE MIX 9 OF TABLE 7.2)

	Not Aged	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
		Value	% Change	Value	% Change	Value	% Change
<u>Processing and Curing Properties:</u> Mooney Viscosity ML(1+4) 100°C Mooney Scorch Time, t ₅ , at 125°C in minutes Optimum Curing Time t ₉₀ , at 160°C (m)	60						
	11'00"						
	23'30"						
<u>Physical Properties:</u> Ultimate Tensile Strength MPa 100% Modulus MPa 300% Modulus MPa Elongation at Break % Tear Strength kN m ⁻¹ Hardness IRHD Resilience %	18.2	15.6	-14	13.8	-24	11.5	-36.8
	2.5	3.3	+32	5.9	+136	7.3	+192
	10.0	11.8	+18	-	-	-	-
	470	370	-21	294	-37	187	-60
	37	26.5	-23	24.5	-33.8	22	-40.5
	63	66	+3 units	69	+6 units	73	+10 units
	52	50	-3.8	48	-7.6	45	-13.5

TABLE 7.22
EFFECT OF ZnO ON THE AGEING BEHAVIOUR OF IM SURFACTANT SYSTEM WITHOUT ANTIOXIDANTS IN SILICA FILLED SBR
VULCANISATES (SEE MIX 10 OF TABLE 7.2)

	Aged one week at 100°C		Aged two weeks at 100°C		Aged three weeks at 100°C	
	Value	% Change	Value	% Change	Value	% Change
Not Aged						
<i>Processing and Curing Properties:</i>						
Mooney Viscosity ML(1+4) 100°C	72					
Scorch Time, t ₅ , at 125°C in minutes	More than 60					
Optimum Curing Time, t ₉₀ , at 160°C (m)	75					
<i>Physical Properties:</i>						
Ultimate Tensile Strength MPa	16.8	-21.4	10.75	-36	8.2	-51
100% Modulus MPa	1.7	+64.7	3.5	+106	3.9	+129
300% Modulus MPa	3.6	+113.8	-	-	-	-
Elongation at Break %	860	-44	297	-65.5	255	-70
Tear Strength kN m ⁻¹	35	-11.4	28	-20	25	-28.6
Hardness IRHD	60	+5 units	69	+9 units	71	+11 units
Resilience %	51	-5.9	47	-7.8	45	-11.7

Effect of various levels of zinc oxide on the ageing behaviour of the EBF-S/TEA system

The effect of 0.5, 1 , 1.5, 2 and 5 phr of zinc oxide are examined in the EBF-S/TEA system in carbon black filled SBR without the presence of antioxidants (see mix 9 of Table 72). The results are given in Table 7.23. It is clear from these results that as the level of zinc oxide increases the ageing resistance improves. Moreover it can be seen that the improvement in the ageing behaviour is at its maximum when the zinc oxide level is between 2 phr - 5 phr. Therefore, zinc oxide is proved to be the key to enhance the ageing characteristics of the surfactant/sulphur curing system.

7.1.4 Conclusions

The results demonstrate that the physical properties of carbon black and silica filled SBR rubber cured by the surfactant/sulphur or EBF-S/TEA/sulphur systems almost completely deteriorate after about two weeks ageing at 100°C. The presence of antioxidants in the surfactant and EBF-S/TEA systems gives no protection against the ageing due to thermal oxidation at 100°C over the respective periods of one, two and three weeks.

The use of an antioxidant has a significant and beneficial effect on the ageing behaviour of the control, carbon black and silica filled SBR compound cured with a conventional ZnO/stearic acid/MBT/DPG/sulphur curing system.

It has been observed that when zinc oxide, 5 phr is present in the surfactant/sulphur curing systems it improves the ageing properties of both the carbon black and the silica filled SBR vulcanisates tremendously without the incorporation of any antioxidants to the extent that a surfactant/ZnO/sulphur system can produce a vulcanisate

TABLE 7.23

EFFECT OF VARIOUS LEVELS OF ZnO ON THE AGEING BEHAVIOUR OF CARBON BLACK FILLED VULCANISATES OBTAINED WITH EBF-S/TEA/
SULPHUR CURING SYSTEM AGED FOR 3 WEEKS AT 100°C (FOR FORMULATION SEE MIX 9 TABLE 7.2)

	Not Aged	0.5 phr ZnO		1 phr ZnO		1.5 phr ZnO		2 phr ZnO		5 phr ZnO	
		Value	% Change	Value	% Change	Value	% Change	Value	% Change	Value	% Change
<i>Processing and Curing Properties:</i>											
Mooney Viscosity ML (1+4) 100°C	51										
Scorch Time t ₅ , at 125°C in mins	39										
Optimum Curing Time t ₉₀ at 160°C (m)	47										
<i>Mechanical Properties:</i>											
Ultimate Tensile Strength MPa	17.5	3.5	(-)80	4.3	(-)75	5.3	(-)70	8.3	(-)53	11.0	(-)37
100% Modulus MPa	2	-	-	-	-	4.9	+149	4.6	+130	7	(+)71
300% Modulus MPa	7.8	-	-	-	-	-	-	-	-	-	-
Elongation at Break %	450	38	92	76	-83	113.6	(-)75	166	-63	190	(-)58
Tear Strength kN m ⁻¹	35	-	(+)17 units	-	-	-	-	17	-52	23	(-)35
Hardness IRHD	60	79	-	79	+17	76	+16 units	73	(+)13 units	70	+10 units
Resilience %	60	Very low	-	Very low	-	Very low	-	43	-28	47	(-)22

which has ageing resistance similar to any conventional accelerator/sulphur system with antioxidants. It has also been observed that a minimum level of 2 phr of ZnO should be present to achieve good ageing resistance.

7.2 Surfactants of Improved Physical Form

Introduction

The physical form of any material to be used in the rubber industry particularly in the tyre field, plays an important part in processing operations, mainly mixing, which control the quality and productivity. It is always desirable to have free flowing, dust free, powder which can easily be weighed and handled in the plant and laboratory. This is to overcome the problems that may arise from using liquids and/or viscous materials which solidify or thicken and therefore create difficulties in factory handling.

For the above reasons it was decided to try and change the physical form of the SAPA 1/1 and the diamine salt compound NSA/1 which were paste like in composition into solid form and study the effect of the new form on the curing behaviour of the rubber.

7.2.1 Experimental

One surfactant was selected to represent the class of those which are in a viscous liquid-cum-paste form, this being the SAPA 1/1 surfactant (see Table 3.1). The following fillers were used as experimental carriers for the SAPA 1/1 compound:

- i) An inert filler - Silica Ultrasil VN3
- ii) An active filler: (a) calcium carbonate; (b) magnesium carbonate; (c) carbon black (N550) FEF

Each one of the above fillers was mixed thoroughly with the SAPA 1/1 compound until all the SAPA 1/1 became completely suspended on the filler such that a dry free flowing powder resulted. It was found that to convert the viscous liquid form of the SAPA 1/1 surfactant into a powder form needed the following relative proportions of surfactant to carrying powder by weight:

	<u>%/%</u>
1. SAPA 1/1/Ultrasil VN3	55/45
2. SAPA 1/1/Calcium carbonate	40/60
3. SAPA 1/1/Magnesium carbonate	50/50
4. SAPA 1/1/Carbon black (N550)	70/30

Then a sample from each of the above suspended SAPA 1/1 filler mixtures was tested for its curing behaviour in comparison with powder free undiluted SAPA 1/1 in an NR/SBR rubber compound.

The diamine salt compound NSA/1 which has a natural waxy form was converted to a free flowing solid following a different procedure from that adopted for converting the paste like SAPA 1/1 to powder form. The procedure used was as follows: 9g of the NSA/1 compound was added to 41g of Ultrasil VN3 placed in a 500 ml beaker. The mixture was then covered with normal tap water and left in an oven at 100°C. Then the mixture was stirred from time to time outside the oven at regular intervals of 10 minutes, until the water had completely evaporated. A thick solid cake was obtained after the product had been left overnight to cool in the beaker at room temperature. A sample from the solid product was then broken into small pieces and tested for the curing behaviour in comparison with the untreated NSA/1 material in an NR/SBR compound.

The formulation used to test this new form of products was that of Table 4.6 (mix 1).

7.2.2 Results and Discussion

SAPA 1/1

Figure 7.1 illustrates the effect of the various carrier powders for SAPA 1/1 on the curing properties of the NR/SBR compound in comparison with powder free SAPA 1/1. It can be seen from these results that calcium carbonate and magnesium carbonate fillers have identical effects on the curing behaviour of SAPA 1/1 in the NR/SBR compound when the above powders are used as carriers for SAPA 1/1 (see ODR curves D and E of Figure 7.1). The carrier powder mixes, C and D, are observed to reduce significantly the state of cure and to possess reversion whereas the carrier powders demonstrated in curves B and C (namely FEF black and silica VN3 powder) show much less reversion. The latter carrier powders (of curves B and C) show similar states of cure to that of the control mix; in this SAPA 1/1 does not contain carrier powder (curve A). However, it is worth noting, from Figure 7.1, that the carbon black FEF carrier (curve B) has similar heat stability to that of the control mix (curve A) and much better heat resistance than all the other powder carriers (compare curve B with those of C, D and E).

NSA/1

Figure 7.2 shows the curing behaviour of the NSA/1 compound with carrier (18% silica) and without carrier in the NR/SBR compound. It can be seen in this figure that the carrier powder has almost no diverse effect on the curing behaviour of the NSA/1 activator/accelerator system.

7.2.3 Conclusions

The results show that the nature of the powder used as a carrier for SAPA 1/1 has an important influence upon its properties even controlling

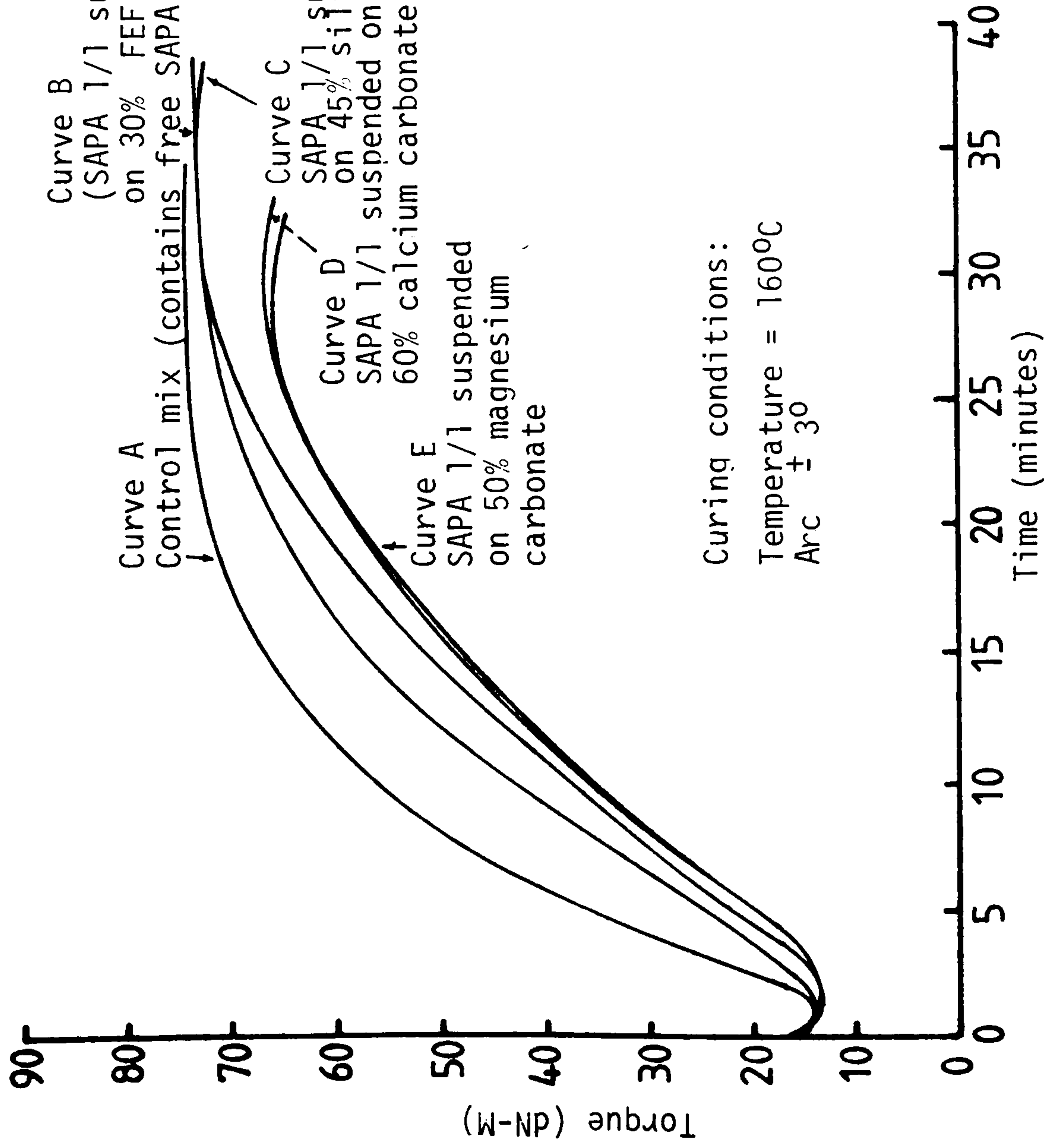


FIGURE 7.1 EFFECT OF VARIOUS CARRIER/ABSORBENT POWDERS FOR SAPA 1/1 ON CURING PROPERTIES (NR/SBR MIX)

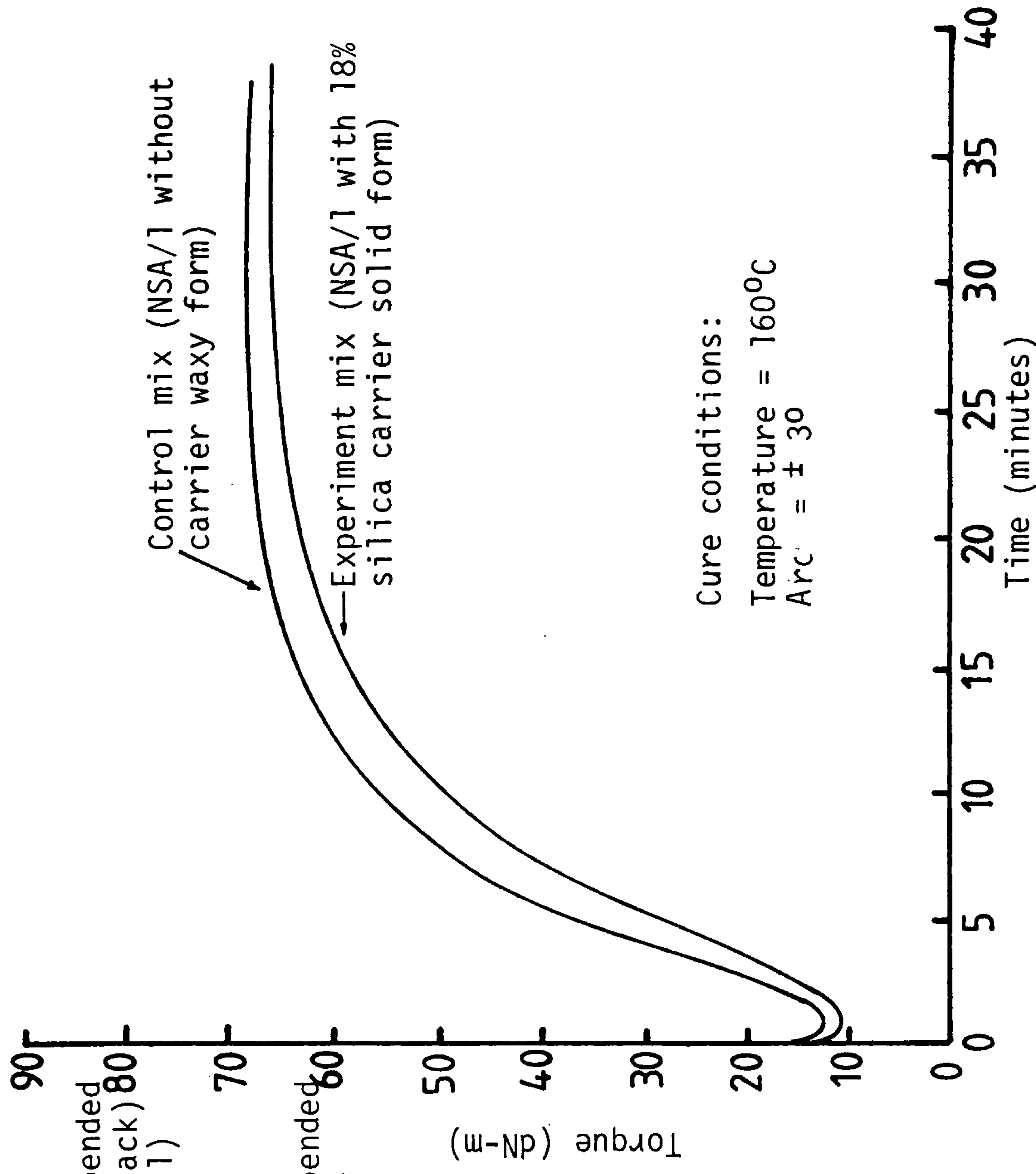


FIGURE 7.2: CURING BEHAVIOUR OF THE NSA/1 ACTIVATOR/ACCELERATOR SYSTEM WITHOUT AND WITH CARRIER IN AN NR/SBR COMPOUND

reversion and maximum torque (i.e. state of cure) values. Of the four types used carbon black (N550) and silica show good overall properties. Calcium and magnesium carbonate however reduce the state of cure more than all the other carriers.

The silica powder carrier used for NSA/1 compound showed no adverse effect on the curing behaviour of the NSA/1 activator/accelerator system.

CHAPTER 8

DISCUSSION, CONCLUSION AND RECOMMENDATIONS

8.1 Discussion and Conclusions

In the author's literature review, it was seen that most of the early studies using the type of cationic surfactants used in this research work concerned their synthesis and use in a great variety of industrial fields of application ranging from textile chemicals to ore flotation, corrosion inhibition, road construction materials, paint and varnish technology, and sanitation.

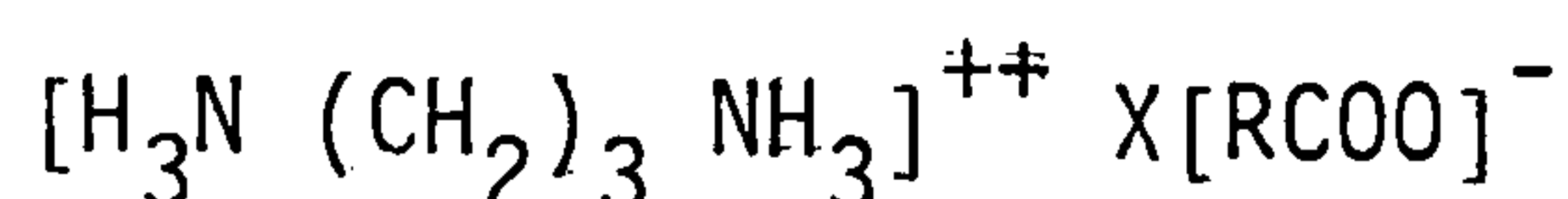
Following the single observation by Rahman [57] that NR containing a cationic surfactant possessed unusually high tensile properties the author initially researched a commercially available fatty diamine salt as a plasticiser to assist the processing of a truck tyre sidewall compound based on an NR/SBR blend.

The particular cationic surfactant was N-tallow-1,3 propane diamine di-oleate (SAPA 1/1). The initial aim of this particular research was to investigate the processability of a rubber compound containing SAPA 1/1 and to compare its performance with six different commonly used plasticisers. However the investigation showed the SAPA 1/1 containing mixes to possess superior processing and physical properties when compared with the controls (Sections 2.1 and 2.3). The only disadvantage observed to occur with the SAPA 1/1 surfactant was that it reduced the scorch time dramatically when it was used at a level of more than 3 phr (Section 2.1).

The improvement in the processability of the NR/SBR compound at all the usual processing stages i.e. mixing, extrusion and moulding, as a result of using the SAPA 1/1 surfactant was remarkable and is

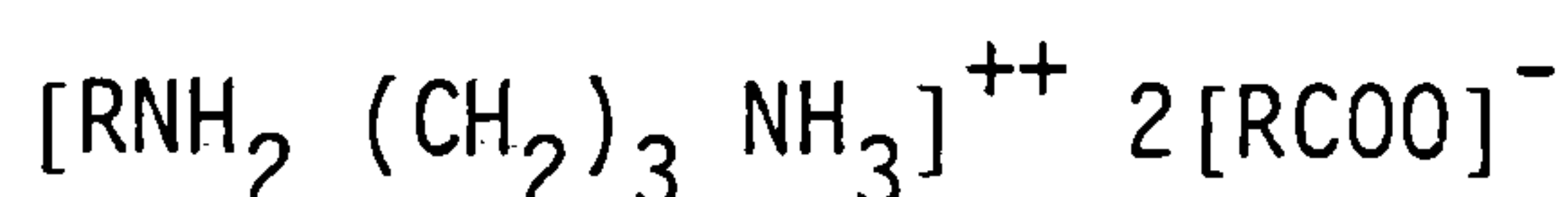
considered unique and it is for this reason the present research work was then directed to synthesis of some other diamine salts to study their performance as rubber processing aids and, in some instances, cure accelerator systems.

Successful attempts were made to synthesise seven diamine salts by reacting propylene diamine with either oleic or stearic acid. These diamine salts which were given the abbreviated name of the NS series (see Table 3.1), can be represented by the following formula:



$$X = 2$$

This general structure is obviously similar to that of the SAPA 1/1:

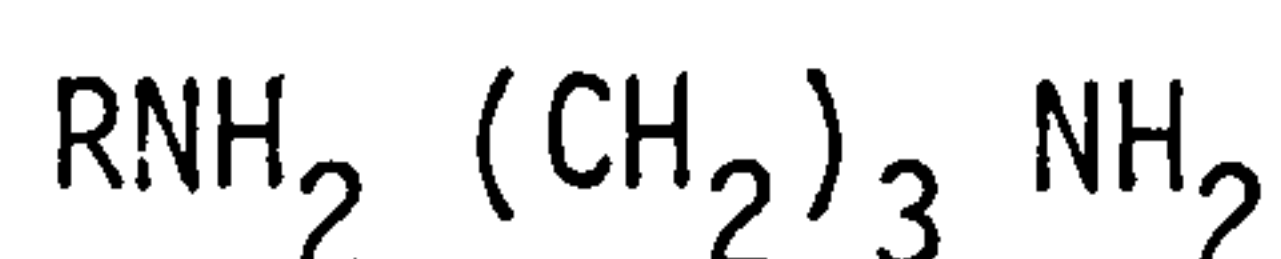


where R = tallow.

The only difference between them is that the tallow group of the SAPA 1/1 surfactant is replaced by a hydrogen group in the structure of the prepared diamine salt. This similarity between the above two structures has also been confirmed when the two materials were characterised for their infrared spectra (Section 3.1).

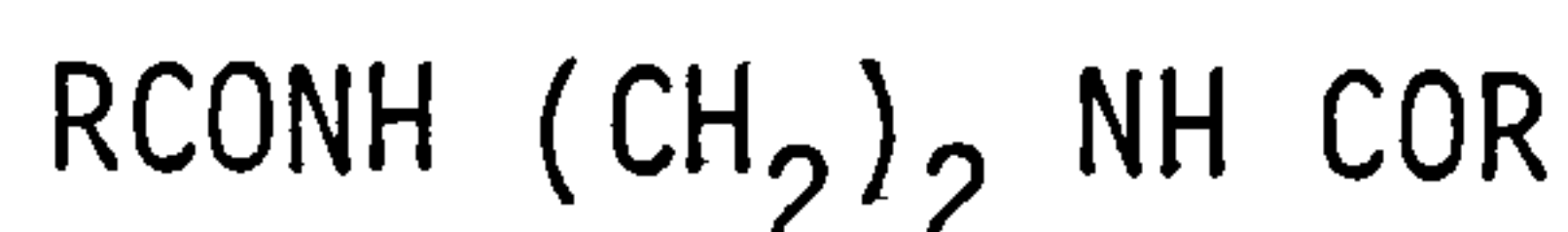
In addition to the SAPA 1/1 surfactant and the prepared salts another two different substances were also selected to be studied in this research work. These were as follows:

- a) Commercially available cationic surfactant having the general formula of



where R = long chain alkyl group derived from fatty acids.
These compounds were given the general abbreviation of SAPA 2 (see Table 3.1).

- b) Commercially available hydrophobic diamide compounds having the general formula of



where R = long chain alkyl group derived from fatty acid.

Compounds of the above formula were given the general abbreviation of EBF.

These compounds (the EBF series) were selected because of their low alkalinity in comparison with the above earlier mentioned surfactants and prepared salts and hence it was presumed would exert less effect on the scorch times of rubber compounds. This assumption was subsequently confirmed by experiment (see Section 3.2).

SAPA 1/1, NSC/1; one of the prepared salts, the cationic surfactant SAPA 2/A, and the diamide EBF-S were initially evaluated as processing aids for the NR/SBR compound used as the control mix. A comparison was made with a 5 phr aromatic oil mix. It was revealed that the improvement in the processability and physical properties brought in by the presence of SAPA 1/1, NSC/1, SAPA 2/A and EBF-S was much superior to that of the aromatic processing oil. Also their relative effects on curing behaviour was found to vary and observed to follow the following sequence:

SAPA 2 > SAPA 1 = NS > EBF

(increasing scorch time)

This behaviour is believed to result from their different chemical structures, as explained above, and hence different chemical reactivities toward the cure process (Section 3.2). It was observed also that varying the alkyl group of the SAPA 1, SAPA 2, NS or EBF material has no effect at all on the curing rate of the mix and physical properties of the final vulcanisate. However significant differences were observed to exist between the processability of compounds containing the different EBF types of substances with superior processability being observed in compounds containing the unsaturated alkyl group, such as that derived from oleic acid i.e. the EBF-0 material, to that containing saturated alkyl group such as that derived from stearic acid (i.e. the EBF-S material).

The use of the surfactants i.e. SAPA 1 and SAPA 2 series, the diamide (EBF) and the prepared salts of the NS series, as processing aids, was then extended to the following rubber classes:

- i) Natural rubber, gum and carbon black filled rubber (Section 3.3.1).
- ii) Polychloroprene (CR) rubber (Section 3.3.2).
- iii) Acrylonitrile-butadiene (NBR) rubber (Section 3.3.3).
- iv) Styrene-butadiene (SBR) rubber (Section 3.3.4).
- v) Polybutadiene (BR) rubber (Section 3.3.5).

It was found that of these substances (i.e. the SAPA 1, SAPA 2, NS and the EBF) all acted as excellent flow additives with all the above rubbers. The extrusion characteristics, particularly the dimensional stability and the surface appearance achieved with natural rubber filled with carbon black or silica fillers in the presence of the SAPA 1 surfactant was considered to be unique rubber

processing property of this surfactant (Section 3.3.1). This was accompanied by a significant improvement in the mould flow and mould release performance particularly with silica filled natural rubber.

They also have enhanced the physical properties of all the above rubber vulcanisates and particularly those of the non-polar type such as NR, SBR and BR. This reinforcement effect is believed to be as a result of better filler dispersion and evidence for this is to be found in the SEM observation of the natural rubber vulcanisate (Section 3.3.1).

With certain rubbers such as NR/SBR blends (Section 2.1) and NR (Section 3.3.1) these substances, i.e. the surfactants (SAPA 1 and SAPA 2 series), diamide (EBF) and the prepared salts (NS series), consistently increase Mooney viscosity by small amounts, in other rubbers such as CR, NBR and SBR they did not increase the Mooney viscosity. This is believed to be because these substances, particularly SAPA 1, react both with the molecules of the natural rubber on the one hand and with the carbon black on the other and hence act as a coupling agent between the rubber and the filler. This suggestion was found to be substantiated by means of the acetone extraction and the volume swelling test results carried out on natural rubber vulcanisates which contained SAPA 1/1 (Section 3.3.1).

Particular note is made concerning the diamide compounds of the EBF series as their presence in rubber has improved the ageing behaviour of the SBR vulcanisates significantly when compared to their controls, the aromatic oil, Dutrex 790, and the processing additive Struktol WB 212. This is in addition to being effective as a cure activator, i.e. no stearic acid was included in their formulations (Section 3.3.4). This observation is believed to be unique and it is explained as follows: the improvement in the ageing behaviour is thought to occur because

these materials (EBF type) bloom to the surface of the vulcanisates and being of relatively high melting point (107-110°C and 140-145°C) they can reduce the action of oxygen (and heat) on the rubber during the ageing process by functioning as a partial barrier to oxygen diffusion into the rubber.

When incorporated into rubber mixes already containing an acceleration system such as a sulphenamide/sulphur combination, then the presence of surfactants i.e. SAPA 1 or SAPA 2, and the prepared diamine salt (NS) was observed to reduce the scorch time dramatically and this was particularly noticeable when the surfactants were used at high proportions (ca. 7.5 phr), (Section 2.1, Table 2.3). To try and resolve this scorch problem the following devices were investigated:

- i) Use of an established scorch retarder such as Santogard PVI (N-cyclohexylthiophthalimide).
- ii) Omission of the cure activator system i.e. zinc oxide and stearic acid, from the formulation.
- iii) Reduction of the proportion of the primary accelerator present in the recipe.

In a systematic way the above suggestions were applied to the NR/SBR compound in which 7.5 phr of SAPA 1/1 was present as plasticiser. None of them was successful. More surprisingly, even the complete elimination of the accelerators (CBS/MOR) did not enhance the scorch time (Section 4.1). At this stage it was realised that a new combined activator/accelerator system for NR/SBR rubber had been discovered based on only the cationic surfactant SAPA 1/1. This was regarded as a new technology simply because at this present time no conventional organic accelerators are used without the inclusion of the basic activator system i.e. zinc oxide and stearic acid. Based on this new technology, it was decided to investigate the same base rubber, i.e. NR/SBR blend, with various proportions of SAPA 1/1

over the range 1 to 7.5 phr and to test the physical properties of their vulcanisates. The reason for using such a high proportion as 7.5 phr was to try and use SAPA 1/1 as a plasticiser in addition to its other function as a cure activator/accelerator system. To prevent the possibility of premature vulcanisation (scorch) the prevulcanisation inhibitor Santogard PVI was also incorporated in the mix. The investigation revealed the following: (a) the curing behaviour of the NR/SBR compound was observed to be in an industrially acceptable range over the SAPA 1/1 proportions of between 1-3 phr; (b) when a high proportion of the SAPA 1/1 (i.e. 7.5 phr) was used the scorch time was very short (4'30") although the retarder PVI was present; (c) the inclusion of the Santogard PVI prevulcanisation inhibitor was not beneficial with respect to scorch time; (d) the mechanical properties were observed to be good over the whole range of the SAPA 1/1 proportions used (Section 4.2).

In order to try and make this new technology similar to conventional technology it was decided to incorporate with the SAPA type system the conventional cure activator system i.e. zinc oxide and stearic acid, and then study their combined effects on cure rate and physical properties. The investigation was carried out (Section 4.3) and it was found that the presence of zinc oxide retarded both the cure rate and the scorch time considerably. In this study it was also found that the presence of stearic acid was not necessary. As it was observed that zinc oxide retarded the cure rate considerably it was decided to also investigate the use of another retarder and see whether the one selected could actually increase scorch time without retarding cure rate significantly. The experiments performed established that benzoic acid (an old traditional rubber cure retarder) could fulfil this purpose i.e. enhance the scorch time (from 9'30" to 15") without affecting cure rate and cure state (Section 4.4). The reason for this scorch improvement is believed to be the result of using an acidic retarder as benzoic acid, being acidic, can reduce the alkalinity and hence cure activity of the SAPA 1/1 which is a basic fatty

diamine salt and hence enhance the scorch time. Additionally, in a separate study (Section 4.5) it was found that the presence of 0.5 phr of zinc oxide produced good cure rate and scorch time at a SAPA 1/1 level of 3 phr, in such a formulation SAPA 1/1 functioned as a combined processing aid and cure activator/accelerator system for the NR/SBR rubber.

After it was proved that surfactants of the SAPA 1 types could act as cure activator/accelerator systems for NR/SBR it was decided to examine whether the surfactant of type SAPA 2, the prepared salts (NS series) and the diamide materials (EBF) can also act as cure activator/accelerators in the same base rubber i.e. NR/SBR. A detailed study accordingly was carried out (Section 4.6) and the following observations were made:

- a) SAPA 2 and the prepared salts (NS) were found to cure NR/SBR rubber very effectively and better physical properties than the conventional sulphenamide accelerator/sulphur system (e.g. CBS/MOR). However, SAPA 2 was observed to produce mixes with a considerably shorter scorch time and optimum cure time, t_{90} , than both the prepared salts (NSC/1) and the SAPA 1 surfactant, the latter two were found to behave similarly in this respect.
- b) The diamide material (EBF-S) was found to behave as an extremely slow cure activator/accelerator system.
- c) The effect of zinc oxide was also studied and it was found that it, i.e. zinc oxide, has almost no effect on the cure behaviour of SAPA 2 systems, but had a significant cure delay effect on NSC/1 system such that in that case it behaved similarly to the SAPA 1 mentioned previously.

- d) The curing behaviour of the NR/SBR rubber was observed not to be affected by varying the nature of the alkyl group of the SAPA 2 series.
- e) The mechanical properties of the vulcanisates obtained with SAPA 1, NS and SAPA 2 were similar to each other and superior to those obtained with the conventional accelerator system (CBS/MOR). However, the EBF-S system exhibited lower physical properties than all of the various systems used including the conventional accelerator system (Section 4.6).

In an investigation to find out the effect of various concentrations of these new activator/accelerator systems on rubber properties, it was found that SAPA 1/1, NSC/1, NSA/3 and NSI follow the same pattern usually observed to be possessed by most conventional accelerators (Section 4.7). It has now been established that the SAPA 1, SAPA 2 and NS series of materials could act as cure activator/accelerator systems for NR/SBR rubber. Accordingly it was decided to examine the behaviour of these new activator/accelerator systems in various other rubbers. The following rubbers were selected and studied in conjunction with the new activator/accelerator systems, in comparison with various conventional accelerators used as controls:

- i) Natural rubber (Section 5.1)
- ii) SBR rubber (Section 5.2)
- iii) BR rubber (Section 5.3)
- iv) NBR rubber (Section 5.4).

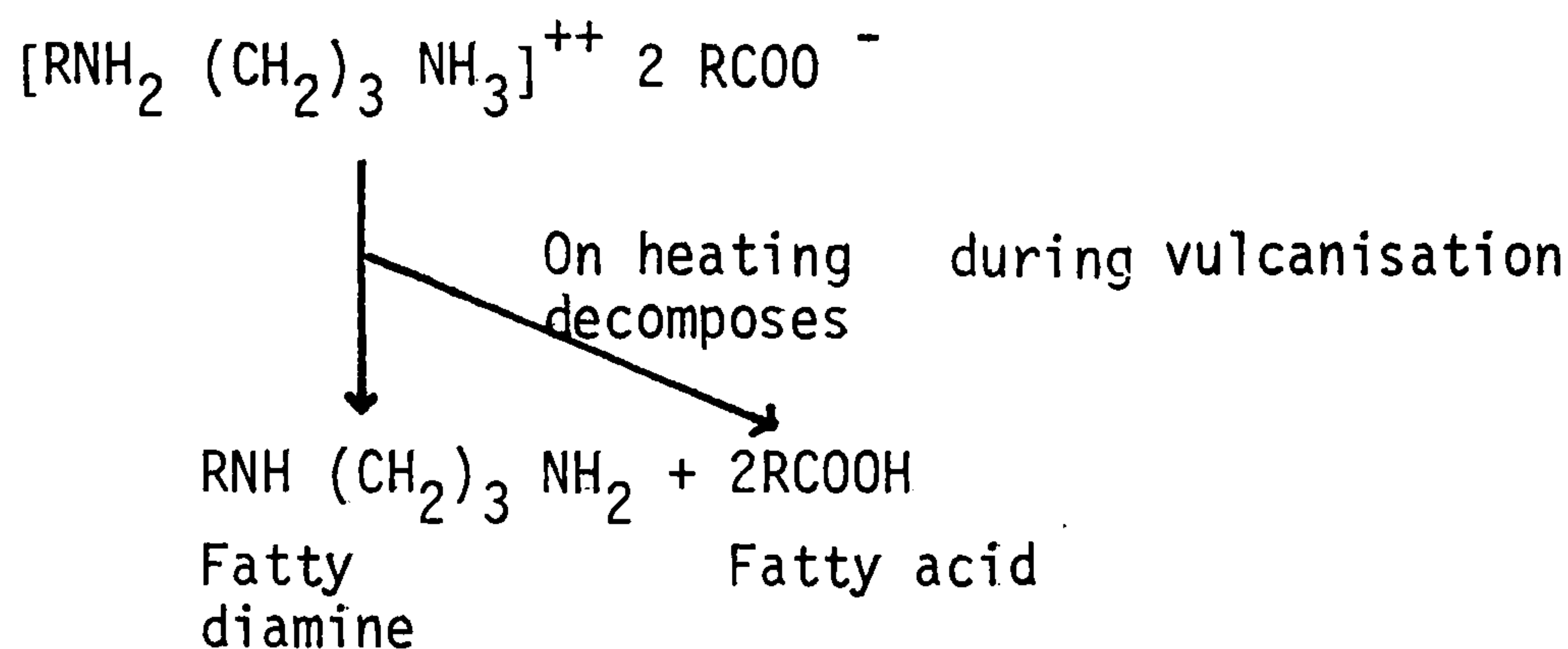
The above investigations revealed the following features:

- a) The SAPA 1, SAPA 2 and NS systems were found to be very efficient cure activator/accelerator systems for all the rubbers tested. The curing and physical properties were very often found to be superior to those of the conventional accelerators.

However, exceptionally with natural rubber (Section 5.1), it was found that the conventional accelerator system gave better curing and mechanical properties than the SAPA 1/1 system. Also it was found that with natural rubber the presence of zinc oxide was beneficial in obtaining an adequate cure state.

- b) A significant increase in the degree of dispersion of carbon black was observed when the conventional accelerator (CBS) system was replaced by the SAPA 1/1 system (Section 5.2). This improvement in carbon black dispersion was believed to be the reason for better physical properties, particularly tensile strength, observed to occur in the SAPA1-containing vulcanisates.
- c) Zinc oxide was, once again, (Section 4.3) observed to retard the cure rate and the scorch time of an SBR compound containing the SAPA 1 type of surfactant and the prepared salts (NS series) but it has almost no effect on the curing characteristics of an SBR compound containing the SAPA 2 type of surfactant (Section 5.2.3).
- d) It was also found that use of the diamide compound (EBF) as the sole accelerator resulted in a slow cure rate and state with the SBR rubber (Section 5.2). Accordingly it was decided to examine the ability of this system (EBF-S) to act as a secondary accelerator for SBR rubber (Section 5.2.4). It was found that the EBF-S diamide material can very successfully act as a secondary accelerator when used in conjunction with MBT as the primary accelerator. In a separate investigation it was found that if the EBF-S system is combined with as little as 0.5-1.0 phr of triethanolamine then the combination is observed to act as an excellent activator/accelerator system without the inclusion of any other accelerator. In addition to this their vulcanisates exhibit superior ageing resistance to the conventional accelerator system (MOR/DPG). Moreover, the presence of zinc oxide is observed to improve significantly the resistance to thermal oxidative ageing of such vulcanisates.

A mechanism is proposed (Section 5.5) to account for the multiplicity of functions demonstrated by the SAPA 1 cationic surfactant and similar materials such as the NS series. This mechanism is believed to be as follows:



The diamine produced is thought to act as the accelerator while the fatty acid acts as the cure activator. The existence of these decomposition products was established using both infrared and DSC techniques (Section 5.5.1).

The cure retardation effect of zinc oxide in a SAPA 1 type vulcanisate is believed to be the result of either the formation of a complex between the SAPA 1/1 and zinc ions which deactivate the accelerating action of SAPA 1, or as a result of the reaction between zinc oxide and H_2S which is known to be produced during all sulphur type cures, particularly with amine type accelerators. This reaction would lead to a decrease in the quantity of the H_2S normally available and essential for the sulphur vulcanisation process to be completed (Section 5.5.2). Based on the same mechanism proposed for the SAPA 1/1 system a similar mechanism has been proposed to account for the cure rate accelerating action of EBF containing rubber compounds (Section 5.5.3).

The mechanism which was suggested to account for the multiplicity of functions of SAPA 1, NS and SAPA 2 was further confirmed when these systems demonstrated that they are able, effectively, to act as crosslinking agents for chloroprene (CR) rubber (Chapter 6).

The chloroprene vulcanisates thus obtained by incorporating these surfactants, particularly those using the SAPA 2 class of surfactant as a crosslinking agent, exhibited excellent processing, curing and physical properties.

The performance of carbon black and silica filled SBR vulcanisates based on surfactant systems were evaluated for thermal oxidative hot air oven ageing, with and without the presence of antioxidants, and compared with vulcanisates based on a conventional sulphenamide accelerator system (see Chapter 7). It was shown that the presence of antioxidant, in the vulcanisates containing the conventional accelerator system, was important to maintain good ageing behaviour. This observation was also made that the presence of antioxidants was not found to be important in any of the vulcanisates using surfactant as the cure activator/accelerator system. However, the presence of zinc oxide (of between 2-5 phr) was found to be essential as a means of inhibiting the premature degradation of crosslinking (i.e. reversion), observed to occur in all the vulcanisates obtained using only a surfactant/sulphur curing system. This improvement in the heat ageing is considered to be due to the production of soluble zinc ions which convert the pendant sulphur side chains produced during vulcanisation into true crosslinks of the polysulphidic, disulphidic and monosulphidic type [52,91].

8.2 Recommendations

1. During the course of this research work, it was observed that vulcanisates based on the surfactant/sulphur curing system had a glossy finish. Therefore it is considered worthwhile to investigate the effect of this shiny vulcanisate surface on the following subjects:
 - a) Adhesion: a detailed study would include: rubber-to-metal bonding (ASTM D429), bonding of rubber to brass-plated steel wire (ASTM D413), bonding of rubber to fabrics such as nylon, rayon, polyvinyl acetate, etc. (ASTM D413).
 - b) Friction: this subject is particularly important for those applications in which friction of rubber is among the required properties. Friction coefficients range from very low coefficients such as those in antifriction bearings, to very high coefficients usually required in tyre treads and shoe heels. The tests could be carried out by using the British portable skid tester for road surfaces.

The above two studies could be made in comparison with vulcanisates obtained by a conventional activator/accelerator system based on car tyre tread compounds.

The following formulations are suggested as suitable:

	Control Mix phr	Test Mix (A) phr
SBR (Intol 1500)	35	35
SBR (Intol 1712)	30	30
BR cis (Polysaw 1220)	35	35
Zinc Oxide	2.5	2.5
Stearic Acid	2.0	-
Sulphur	1.5	1.5
CBS	1.0	-
DPG	0.1	-
Surfactant	-	2.0
Flectol-H	1.0	-
IPPD	1.0	-
Antiozone Wax	1.5	1.5
Aromatic Oil	10	10
ISAF (N220) Black	49	49

It would be considered useful if a car tyre from the test mix could be made to be tested in comparison with a car tyre based on the control mix.

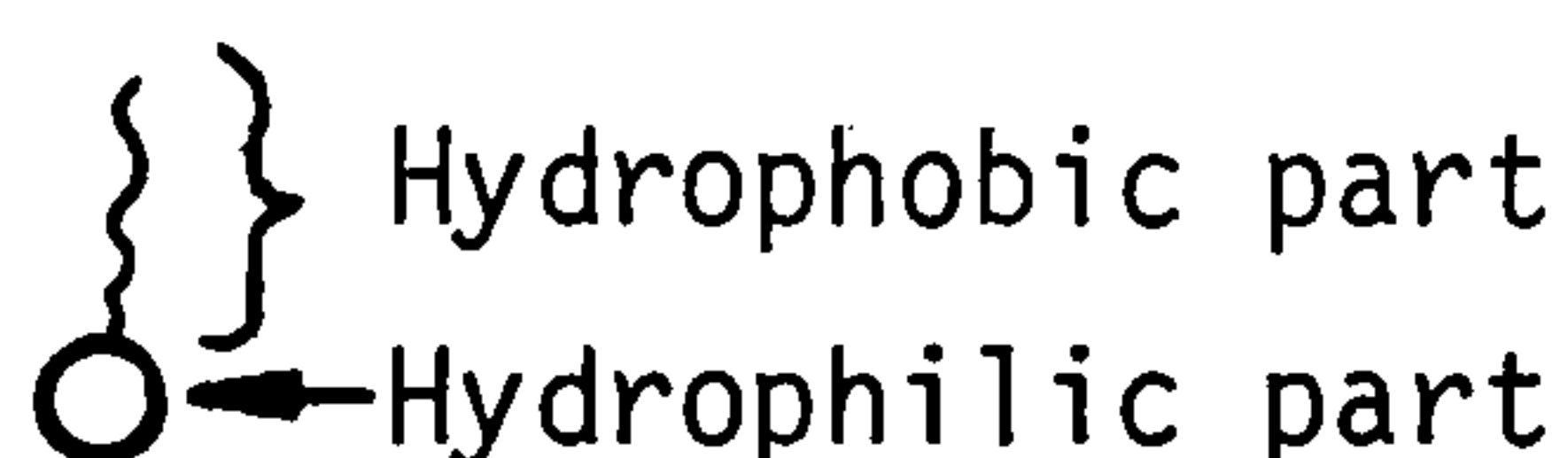
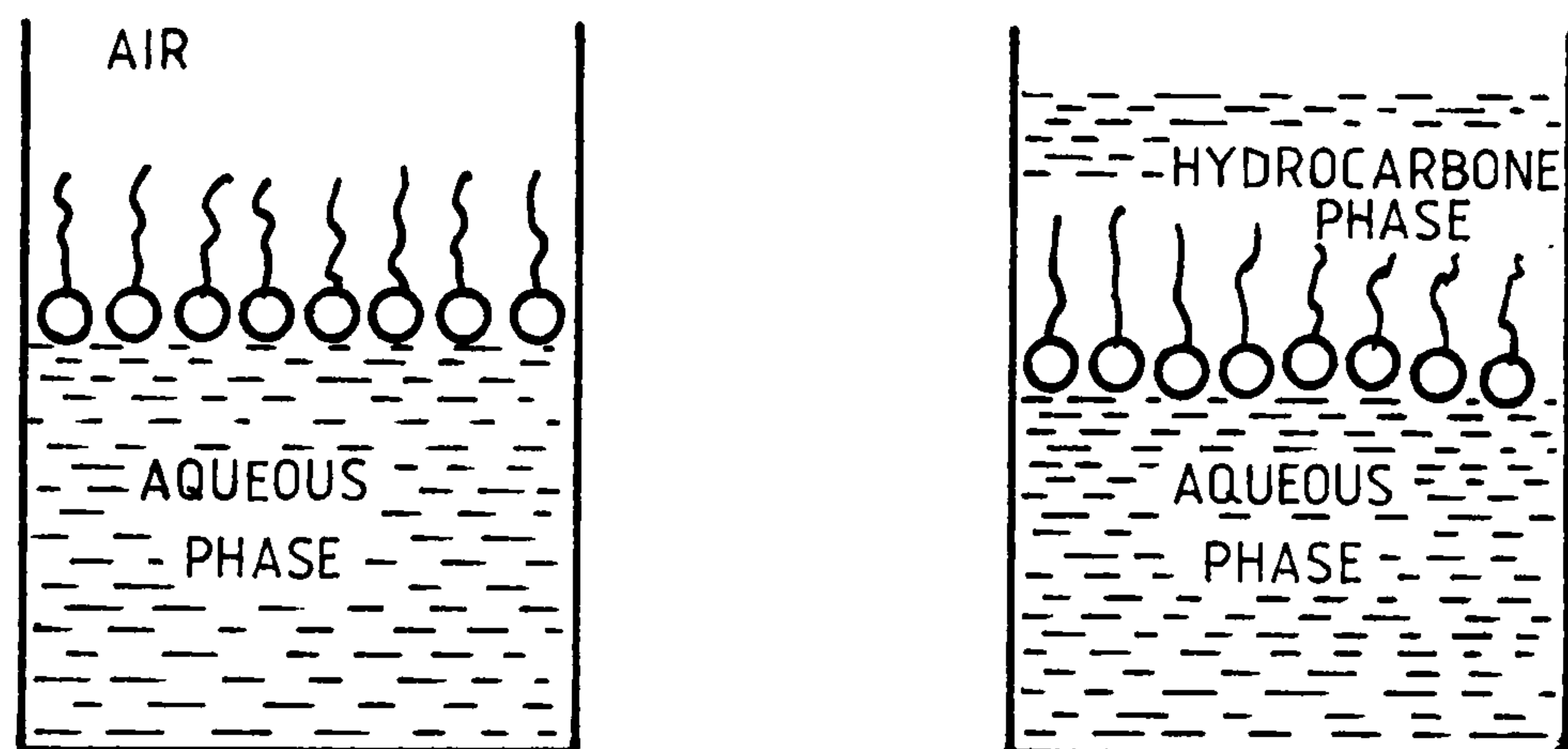
2. It was observed that the surfactant, particularly SAPA 1/1, had improved the dispersion of carbon black and also the mechanical properties of the resulting vulcanisates. It would be interesting to investigate the effect of SAPA 1/1 or any other system, on the dispersion and physical properties of several rubbers containing various carbon black and other filler loadings.
3. To carry out a comparison study of the effect of SAPA 1/1 and a coupling agent such as vinyl triethoxysilane; $\text{CH}_2=\text{CH}-\text{Si}-(\text{OC}_2\text{H}_5)_3$, on the processing, curing and physical properties of carbon black and silica filled SBR rubber based on a conventional curing system.

4. To explore the ability of the surfactants and the compounds given in Table 3.1 as activator/accelerator/crosslinking agents or processing aids for other rubbers such as EPDM, Butyl (IIR), Epichlorohydrin etc.
5. In the present research work mainly two groups of cationic surfactants were examined as rubber compounding ingredients. It would be useful to investigate other types of cationic surfactants such as those based on quaternary ammonium salts which contain long aliphatic hydrocarbon chains, polymeric quaternary ammonium compounds etc. as vulcanisation activator/accelerator systems.

APPENDIX I

SURFACE ACTIVITY OF SURFACTANT [1]

The surface activity of surfactant depends on the presence of a hydrophobic (non-polar, water-insoluble) hydrocarbon chain and a hydrophilic (polar, water-soluble) group. If surfactant molecules become located at an air-water or oil-water interface, they are able to locate their hydrophilic groups in the aqueous phase and allow the hydrophobic hydrocarbon chains to escape into the vapour or oil phase (see below).



The strong adsorption of surfactants at surfaces or interfaces in the form of an oriented monomolecular layer (or monolayer) (see above), is called surface activity.

The tendency for surfactant molecules to pack into an interface favours an expansion of the interface; this must therefore be balanced against the tendency for the interface to contract under normal surface tension forces. If π is the expanding pressure (or surface pressure) of an adsorbed layer of surfactant, then the surface (or

interfacial) tension will be lowered to a value

$$\gamma = \gamma_0 - \pi$$

If the interfacial tension between two liquids is reduced to a sufficiently low value on addition of a surfactant, emulsification will readily take place because only a relatively small increase in the surface free energy is involved. If $\pi \geq \gamma_0$, either the liquids will become miscible or spontaneous emulsification will occur.

Reference:

1. Shaw, D.J. Introduction to colloid and surface chemistry, Second Edition, Butterworths, 1970.

APPENDIX IIANALYTICAL METHODS USED FOR THE ANALYSIS OF CATIONIC SURFACTANTS

A short description of important analytical methods used for the analysis of fatty amino derivatives is shown below:

Definition

The amine number is the amount of hydrochloric acid (in mg) needed for the neutralization of a sample weighing one gram

$$N = A \cdot M_{\text{HCl}}$$

N = amine number (mg HCl/g)

A = milliequivalents of amine in one gram sample

M_{HCl} = molecular weight of HCl, 36.46.

The amine value (AV) is the amount of potassium hydroxide (in mg) that would be equal to the number of milliequivalents of amine present in one gram sample

$$AV = A \cdot M_{\text{KOH}}$$

AV = amine value (mg KOH/g)

M_{KOH} = molecular weight of potassium hydroxide, 56.11.

Consequently the amine number is easily converted to the amine value and vice versa

$$AV = N \cdot \frac{M_{\text{KOH}}}{M_{\text{HCl}}} = N \cdot \frac{56.11}{36.46}$$

$$AV = N \cdot 1.539$$

$$N = AV \cdot 0.6498$$

i) Total amine numbers

An amine sample is dissolved in chloroform and salicylaldehyde is added. After heating in a water bath, all primary amine groups have reacted with the aldehyde and salicylaldimines have been formed. The sample is then diluted with additional chloroform and methylisobutylketone and potentiometrically titrated using perchloric acid in dioxane.

$$\text{Hence, total amine number } (N_{\text{total}}) = \frac{V_2 C}{m} \cdot 36.46$$

where V_2 = ml perchloric solution for total neutralization
 C = concentration of perchloric acid (mol/l).

ii) Acid value (I_A)

The term acid value is normally used to express the percentage of free fatty acids present in fatty compounds.

The acid value (I_A) expresses the weight in mg of potassium hydroxide required to neutralize one gram of fatty material

$$\text{Acid value } (I_A) = \frac{56.1 \cdot C \cdot V_a}{m}$$

where C = concentration of potassium hydroxide
 V_a = number of ml of potassium hydroxide solution
 m = weight of sample in g.

iii) Iodine value I_I

The iodine value of a fat compound is a measure of its degree of unsaturation.

The standard method by Wijs [1] is used. The fatty amine is reacted with acetic anhydride. To the product amine is added an excess of iodomonochloride dissolved in glacial acetic acid. After addition of potassium iodide solution to the iodine is titrated with thio-sulphate. A parallel experiment with the fatty amine omitted is run to determine the total amount of iodomonochloride added.

Hence

$$I_I = \frac{M_I \cdot C (V_0 - V)}{10 \cdot m}$$

where M_I = molecular weight for iodine = 126.9

C = concentration of thiosulphate solution (mol/l)

V_0 = ml thiosulphate solution for blank sample

V = ml thiosulphate solution for amine sample

m = sample weight (g).

iv) Moisture content

Volatile matter present in a fatty amine compound is defined as the total quantity of substances volatile at 105°C, and includes any moisture present.

$$\text{Moisture \%} = \frac{(p - a)}{p} 100$$

where p = weight in g of sample

a = weight in g of the heated sample

Reference:

1. TUPAC "Oils, fats and soaps", Standard Method for Analysis, 5th Edition 1965.

APPENDIX III

COMMERCIALLY AVAILABLE RUBBER PROCESSING OILS IN GREAT BRITAIN

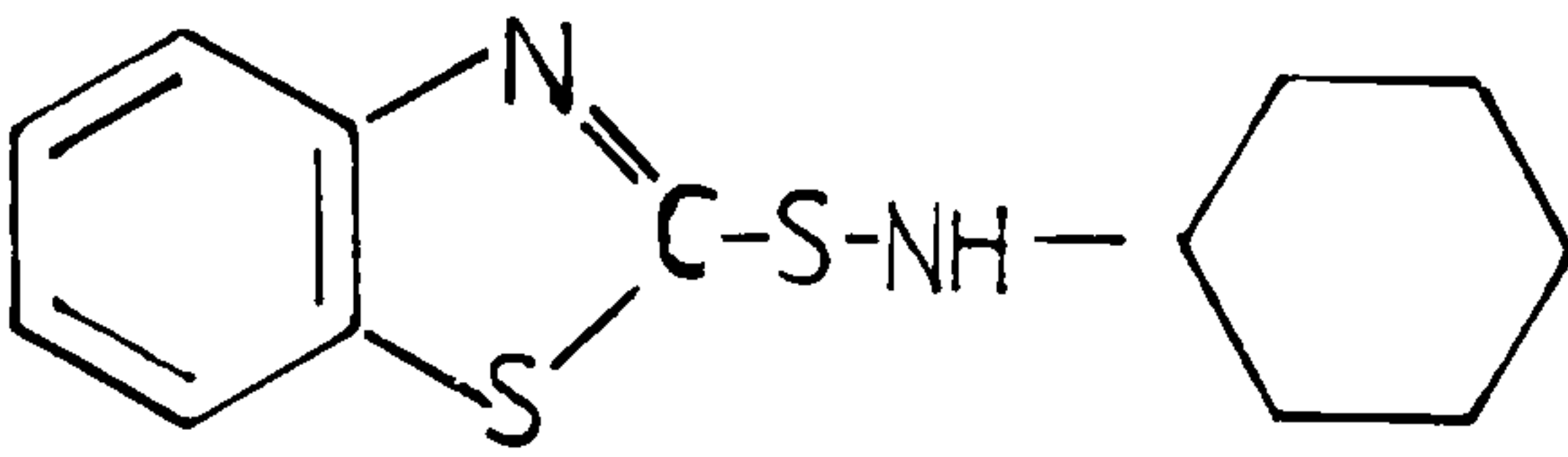
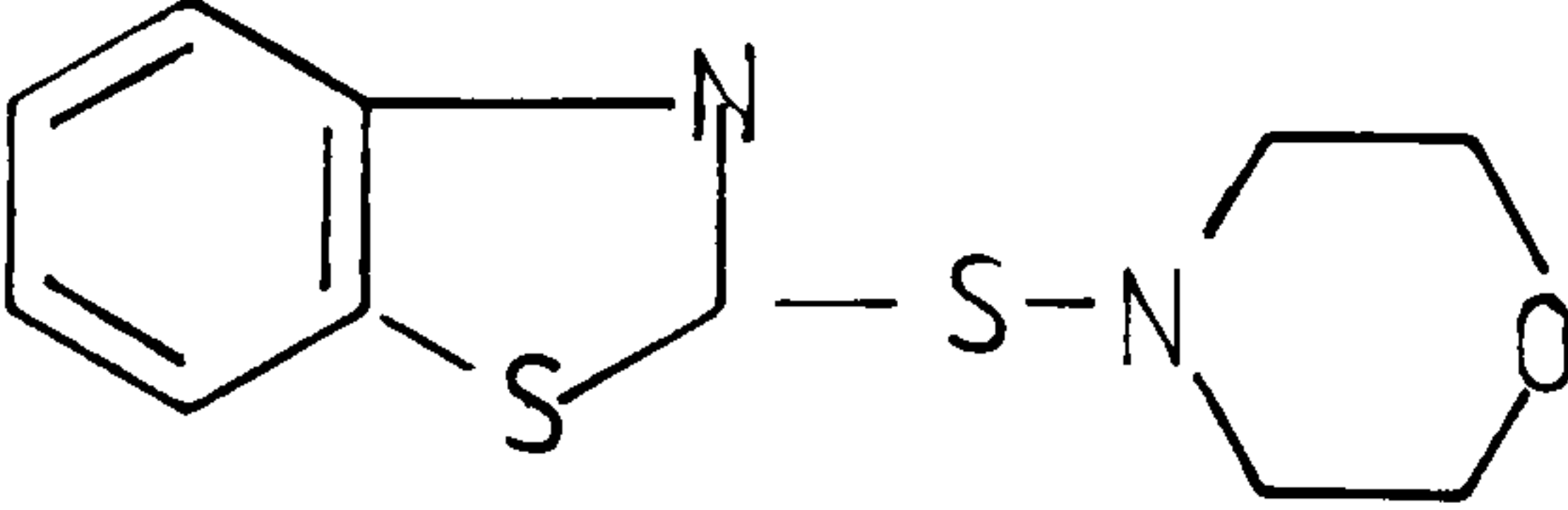
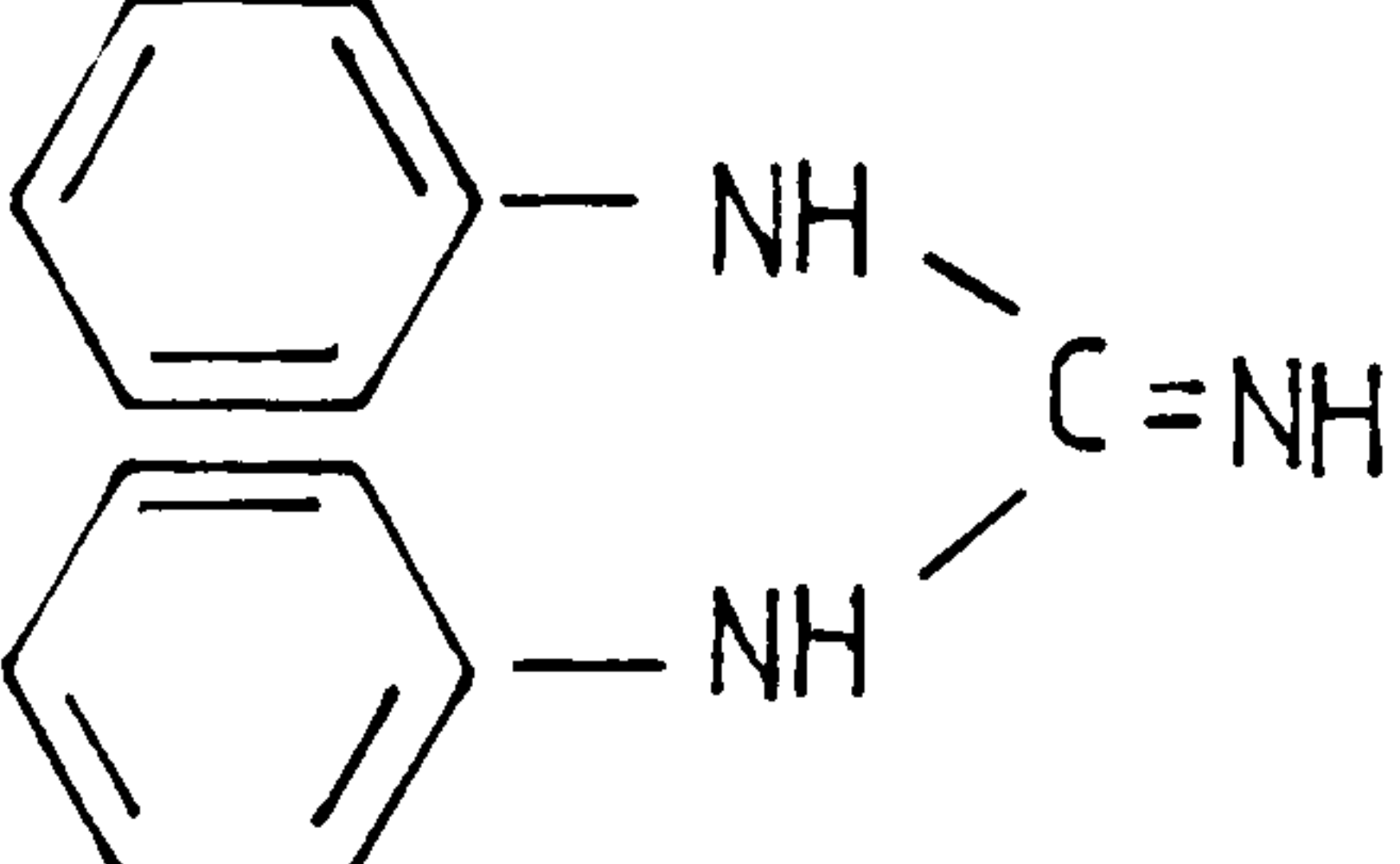
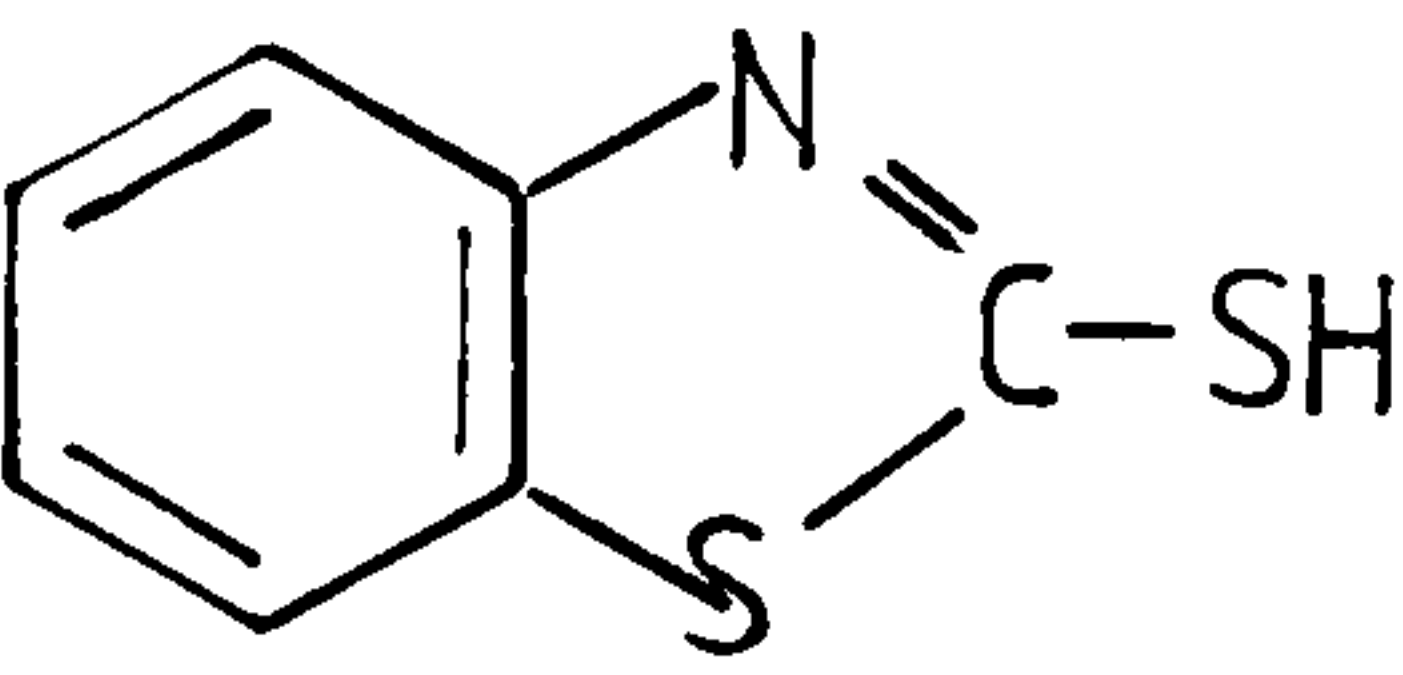
Viscosity-Gravity Constant Range	Manufacturer	Oil Trade Name	VGC ASTM D501	Specific Gravity, 60°F ASTM D1520	Aniline Point ASTM D611	Viscosity ASTM : D2161		Refractive Index ASTM: D1747	Molecular Weight ASTM: D2502	Volatility % Wt. Loss 22hr @ 225°F	Flash Point ASTM: D92	Clay-Gel Analysis wt. % ASTM: D2007			Carbon Type Analysis wt. % ASTM: D2140			
						SUS/100F	SUS/210					Polar Compounds	Aromatics	Saturates	Paraffins	Naphthenics	Aromatics	
Paraffinic Oil Range 0.790-0.819	Sun Oil	Sunflex	150	0.798	0.8762	242 °F	535	65.2	1.4808	540	0.12	500	0.6	12.9	86.5	72	25	3
			130	0.800	0.8735	235	320	53.1	1.4800	470	0.18	450	0.5	14.0	85.5	69	29	2
			2280	0.800	0.8899	267	2540	154	1.4900	700	0.03	565	3.8	21.5	74.7	72	23	5
		Sunpar	2100	0.800	0.8816	249	975	87	1.4847	580	0.05	515	0.9	23.6	75.5	71	25	4
			2150	0.800	0.8860	254	1494	110	1.4865	650	0.03	540	1.1	24.8	74.1	71	25	4
			2280	0.800	0.8911	262	2562	155	1.4895	720	0.02	580	2.5	21.6	75.9	71	25	4
			150	0.802	0.8740	240	495	63.1	1.4805	530	0.08	495	0.4	15.5	84.1	72	25	3
			130	0.804	0.8702	231	370	53.5	1.4785	475	0.19	455	0.4	18.6	81.0	69	27	4
			120	0.806	0.8665	226	208	46.9	1.4764	440	0.27	435	0.3	16.7	83.0	68	28	4
			115	0.807	0.8618	222	155	43.5	1.4752	400	0.33	425	0.3	16.2	83.5	68	28	4
			110	0.807	0.8571	215	108	40.0	1.4719	370	2.5	390	0.3	14.1	85.6	67	29	4
		Sunprime	200	0.802	0.8623	230	200	47.3	1.4730	440	0.2	435	0.0	1.8	98.2	66	34	0
			100	0.808	0.8602	221	118	41.2	1.4710	380	1.2	430	0.0	1.8	98.2	65	35	0
		Sunflex	125	0.810	0.8708	227	260	50.0	1.4782	440	0.14	440	0.5	16.0	83.6	66	32	2
			120	0.810	0.8681	227	210	47.8	1.4769	435	0.40	425	0.4	13.3	86.3	66	32	2
			115	0.813	0.8649	216	133	41.9	1.4749	400	0.51	400	0.4	14.7	84.9	66	32	2
			110	0.815	0.8571	215	110	40.4	1.4719	385	1.5	385	0.3	16.2	83.5	67	29	4
			3340	0.814	0.9042	246	3289	165	1.4961	680	0.06	565	7.4	27.4	65.2	67	24	9
			270	0.814	0.8877	229	714	70.1	1.4891	520	0.09	505	3.8	27.0	69.2	65	30	5
			250	0.817	0.8855	222	515	62.0	1.4876	-	0.17	470	2.0	25.8	72.2	65	30	5
	Esso Oil	Flexon	845	0.808	0.870	98.6°C	29.6°C	5.2	1.4795	-	0.2	216	0.5	23.1	76.4	63.2	28.4	8.4
			855	0.810	0.811	101	63.82	8.51	1.4865	-	0.4	246	0.5	30.5	69.0	65.4	26.0	8.6
			842	0.814	0.859	96.3	18.4	3.90	1.4740	-	0.34	204	0.3	27.7	72.0	65.5	25.7	8.8
			815	0.815	0.902	121.4	458.0	30.5	1.4930	-	0.1	302	3.3	40.5	56.2	68.4	22	9.6
			876	0.815	0.889	107	110	71.8	1.4895	-	0.05	266	0.5	38.0	61.5	67.2	24.0	8.8
	Shell Oil	No oil in this range of VGC																
Relatively Naphthe- nic Oil Range 0.820-0.849	Sun Oil	Sunflex	107	0.820	0.8524	201	65.0	35.5	1.4733	320	3.0	350	0.4	17.1	82.5	63	32	4
			LM107	0.830	0.8681	197	73.0	36.2	1.4752	290	2.2	360	0.2	10.0	89.8	58	38	4
		Sunflex	230	0.821	0.8816	216	305	51.4	1.4859	445	0.18	440	1.6	25.0	73.4	64	30	6
			210	0.822	0.8639	208	108	39.4	1.4776	350	1.95	365	0.6	18.8	80.6	62	32	6
			207	0.823	0.8540	194	68	35.9	1.4743	320	3.30	345	0.5	18.4	81.1	62	32	6
			216	0.824	0.8751	206	146.1	42.4	1.4810	400	0.67	395	1.1	23.0	75.9	56	35	9
			3150	0.826	0.9042	236	1530	100	1.4964	575	0.37	485	2.9	29.7	67.4	62	32	6
		Sunthene	210	0.824	0.8811	220	230	47.6	1.4823	400	1.0	400	0.3	13.9	85.8	60	36	4
			255	0.837	0.8950	205	435	55.2	1.4926	445	0.2	445	0.6	25.5	73.9	58	33	9
			210	0.840	0.8816	195	105	39.3	1.4828	330	3.8	330	0.2	18.1	81.7	55	38	7
	Esso oil	No oil in this range																
	Shell Oil	Shellflex 451UK	0.844	0.908	197	659.0	60.7	1.4966	-	-	420	0.9	35.2	68.9	-	-	-	
Naphthenic Oil Range 0.850-0.899	Sun Oil	Sunthene	310	0.861	0.9007	167	100	39.0	1.4938	325	6.20	330	1.0	30.0	69.0	48	40	12
			480	0.869	0.9340	169	760	60.8	1.5085	385	1.7	410	1.8	37.0	62.0	46	39	15
			410	0.871	0.9088	160	104	38.0	1.4986	300	5.4	330	0.2	34.8	65.0	43	42	15
			5600	0.873	0.9402	193	5047	126.5	1.5174	450	0.02	470	2.0	41.0	56.2	46	36	18
			450	0.878	0.9303	164	502	52.0	1.5104	355	2.53	385	0.7	42.3	57.0	42	43	15
			4130	0.881	0.9371	174	1275	67.7	1.5146	380	0.35	400	1.0	39.1	59.9	45	39	16
			4240	0.882	0.9449	176	2206	84.7	1.5170	400	0.23	440	1.1	43.9	53.0	41	41	18
		Circosol Circo Lt RP0	5600	0.875	0.9522	185	5830	136	1.5241	455	0.02	495	4.2	44.7	51.1	46	34	20
			4240	0.878	0.9188	156	156	41.0	1.5069	325	6.0	330	1.2	40.5	58.3	44	37	19
			420	0.883	0.9490	173	2520	85.9	1.5216	395	0.2	435	2.7	44.8	52.5	41	38	20
			415	0.884	0.9248	153	208	43.2	1.5121	325	5.4	345	1.8	44.0	54.2	42	37	21
			4130	0.885	0.9218	148	155	40.6	1.5121	325	5.4	345	1.8	44.0	54.2	42	37	21
			410	0.885	0.9133	166	1275	68	1.5104	312	7.0	330	1.4	44.0	54.6	41	38	21
			410	0.886	0.9159	149	110	38.2	1.5086	380	1.67	405	3.0	44.0	53.0	46	36	22
			430	0.886	0.9309	156	310	46.2	1.5138	295	7.6	325	1.4	41.6	57.0	43	37	20
			450	0.886	0.9371	161	515	52.4	1.5170	355	4.5	355	1.9	44.0	54.1	41	38	21
480			0.888	0.9402	164	775	58.4	1.5122	355	3.1	360	2.5	43.8	53.7	42	36	22	
Sundext		8600T	0.882	0.9626	165	-	300	1.5391	325	1.9	370	1.5	43.6	54.8	41	38	21	
		7260T	0.897	0.9600	149	27000	260	1.5480	575	0.07	575	15.9	57.9	26.2	49	22	30	
Esso Oil	Flexon	641	0.859	0.894	78°C	19.71	3.48	1.4930	470	0.08	490	17.6	59.3	23.0	48	19	30	
Shell Oil	D	0.894	0.97	66	-	75	1.545	-	0.95	166	1.0	34.5	64.3	51.6	31.5	16.9		
Relatively Aromatic Oil Range 0.900-0.939	Sun Oil	Sundex	7135T	0.902	0.9626	145	6000	135	1.5437	450	0.08	465	12.0	62.3	25.7	42	26	32
			T-65	0.914	0.9574	126	625	56.5	1.5365	385	2.8	360	5.4	59.3	35.3	38	31	31
			790T	0.916	0.9705	117	3000	92.0	1.5487	385	0.2	445	12.0	63.2	23.8	33	37	30
			750T	0.920	0.9593	121	450	50.2	1.5382	340	0.3	400	5.2	66.5	28.3	36	30	34
			780T	0.9														

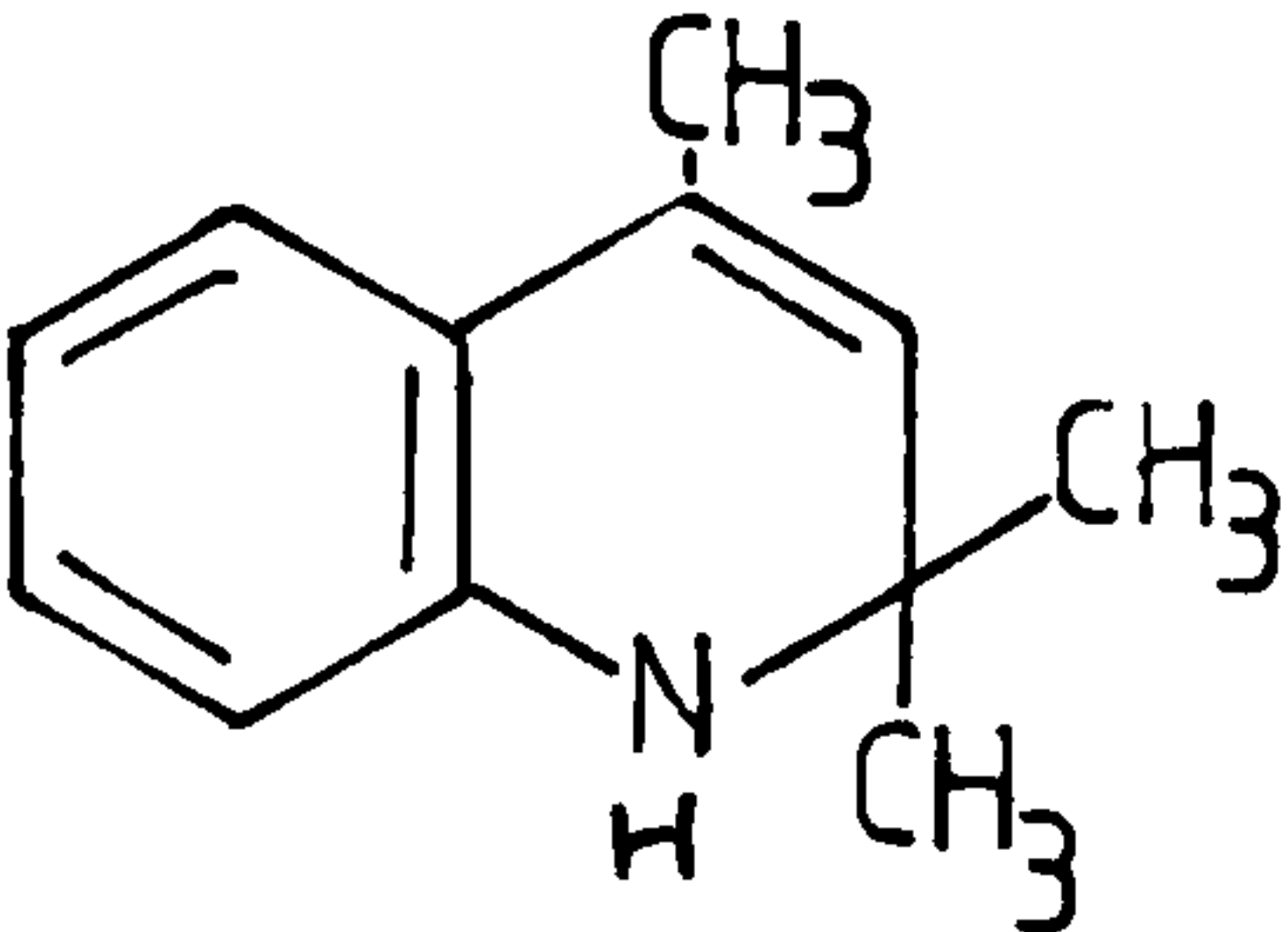
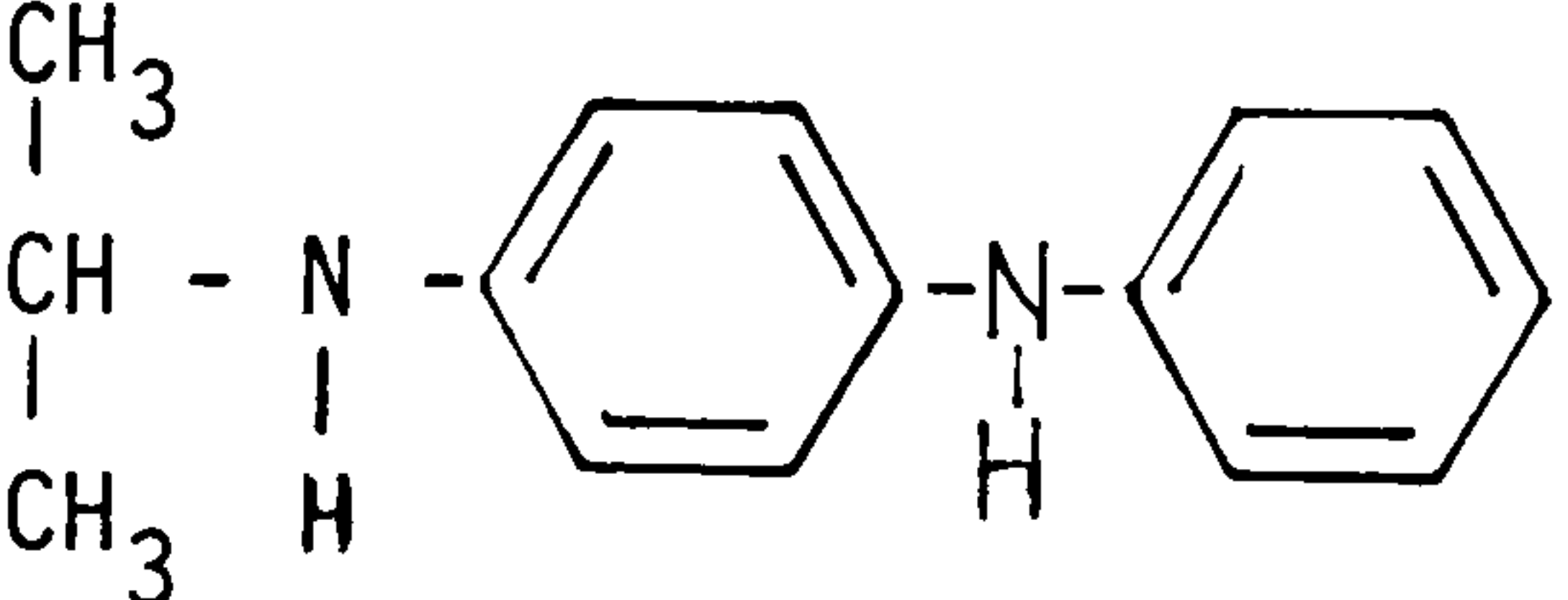
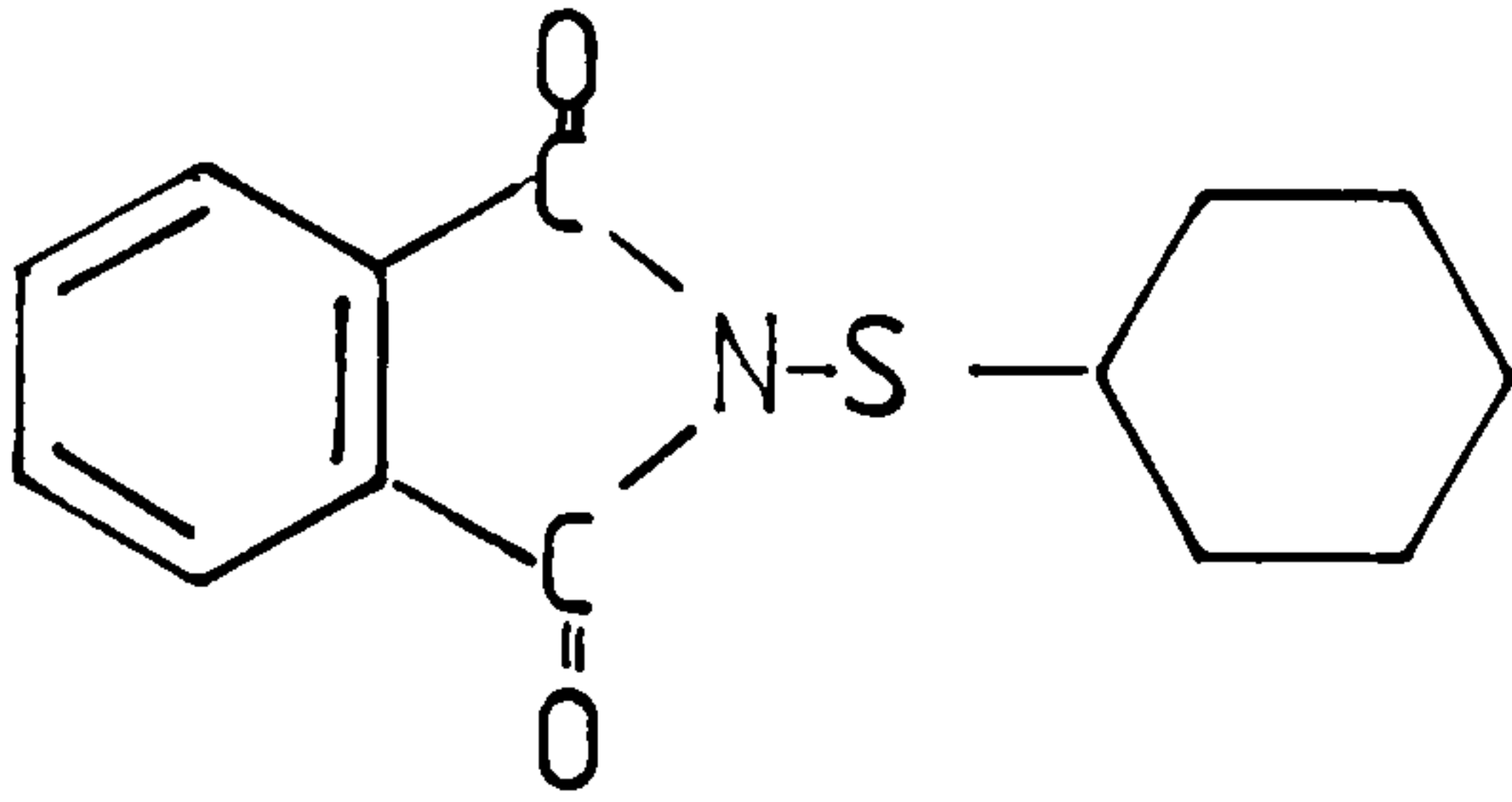
APPENDIX IV

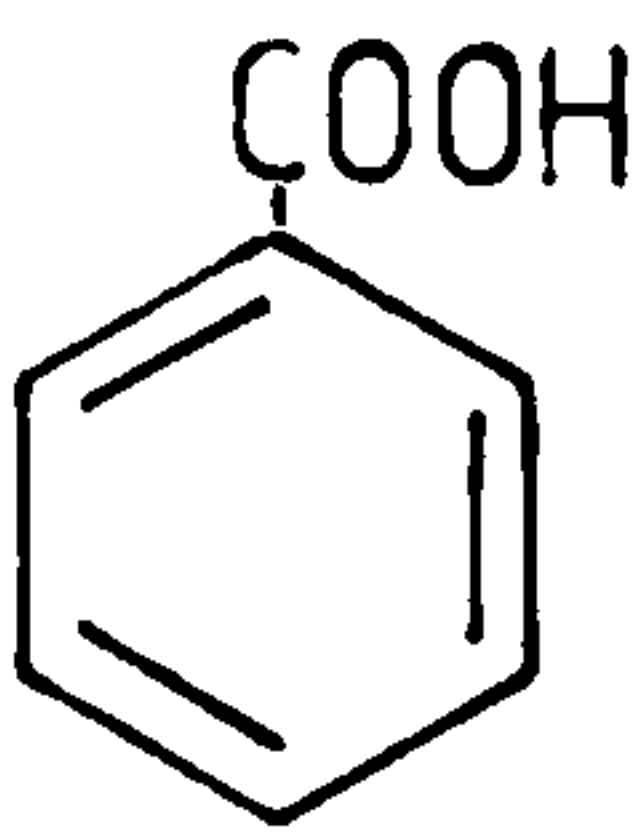
LIST OF MATERIALS USED WITH THEIR RELEVANT TECHNICAL INFORMATION

1. Rubber Used

Type and Trade Name	Specifications	Chemical Structure	Supplier
NR (SMR20)	Nitrogen (max.wt%) 0.6 Volatile matter (max wt%) 0.8 Ash (max.wt%) 1.0 Dirt 0.2 PRI (min.%) 40 Rapid plasticity no. 30	$\begin{array}{c} \text{CH}_3 \\ \\ \sim \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \sim \end{array}$	Hubron Ltd
NR (SMR5)	Nitrogen (max.wt%) 0.6 Volatile matter (max.wt%) 0.8 Ash (max.wt%) 0.6 Dirt 0.05 PRI (min.%) 60 Rapid plasticity no. 30	$\begin{array}{c} \text{CH}_3 \\ \\ \sim \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \sim \end{array}$	Hubron Ltd
SBR(Cari-flex S-1500)	Volatile matter, % wt. 0.75 Ash, % wt 1.5 Organic acid, %wt 7.5 Soap, % wt 0.5 Bound styrene, % 24.5 Viscosity ML (1+4) 100°C 58	$(\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2)_n (\text{CH}_2 - \underset{\substack{ \\ \text{C}_6\text{H}_5}}{\text{CH}})_m$	Shell Chemicals Ltd
BR (Intene)	Volatile matter, % wt. 0.2 Ash, % wt 0.07 Structure purity, % cis 1,4 93 Viscosity, ML (1+4) 100°C 42	$\sim \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \sim$	ISR
NBR (Breon 1042)	Ash content, % wt. 0.5 Bound acrylonitrile, % 34 Viscosity, ML (1+4) 100°C 58-78	$\sim \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \underset{\substack{ \\ \text{CN}}}{\text{CH}} \sim$	BP Chemicals Ltd

CR (Neoprene WRT)	Volatile matter, 1.0 % wt Ash content, % wt. 1.0 Viscosity, ML (1+4) 100°C 50	$\sim \text{CH}_2 - \underset{\text{Cl}}{\underset{ }{\text{C}}} = \text{CH} - \text{CH}_2 \sim$	Du Pont & Co. Inc
2. <u>Chemical Ingredients</u>			
Type and Trade Name	Chemical Structure	Supplier	
<u>Accelerators</u> Vucafor CBS	 N-cyclohexyl benzthiazyl sulphenamide	Vulnax International Ltd	
Santocure MOR	 2-(Morpholinothio)benzothiazole (MBS)	Monsanto Company	
Vulcafor DPG	 N,N'-diphenyl guanidine	Vulnax International Ltd	
Vulcafor MBT	 2-mercaptobenzothiazole	Vulnax International Ltd	

<u>Activators</u> Zinc oxide Stearic acid Triethanolamine	ZnO $\text{C}_{17}\text{H}_{35}\text{COOH}$ $\text{N}(\text{C}_2\text{H}_2\text{OH})_3$	Anchor Chemicals Ltd Anchor Chemicals Ltd Fisons Ltd
<u>Antioxidants</u> Flectol-H	 1,2-dihydro-2,2,4 trimethyl-quinoline	Monsanto Company
Anchor IPPD	 N-isopropyl-N'-phenyl-para-phenylenediamine	Anchor Chemicals
<u>Scorch retarders</u> Santogard PVI	 N-(cyclohexylthio)phthalimide	Monsanto Company

Benzoic acid	<div><div></div><div>Benzoic acid</div></div>	BDH Ltd
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Fillers

Type and Trade Name	ASTM No.	Type Name	Supplier
FEF (Statex M550)	N550	Fast extrusion furnace	Columbian Ltd.
HAF (Statex R)	N330	High abrasion furnace	"
ISAF (Statex 125)	N220	Intermediate super abra- sion furnace	"
SRF (Furnex 765	N765	Semi-reinforcing furnace	"
		Chemical Name	
Precipitated Silica Grade Ultrasil VN3		Precipitated Silica type VN3	ICI

Type and Trade Name	Specification	Supplier
<u>Processing Aids</u> Struktol WB212	Specific gravity 1.15 g/cm ³ Melting point 50°C Ash content 20% Acid value 5 H ₂ O 10%	Schill and Sellacher (GmbH & Co)
Aromatic Oil Iraqi Oil	Specific gravity 1.008 Redwood at 60°C 275 secs Refractive index 1.559 20°C Flash point (open cup) 252°C Ash at 550°C 0.05% Loss at 180°C for 15 mins. 2% Loss at 150°C for 60 mins 0.5% Viscosity gravity constant 0.96 Aniline point 33°C	Dura Refinery Iraq

APPENDIX V

A SHORT ACCOUNT OF THE PROCESSING, VULCANISATION AND PHYSICAL TESTS USED THROUGHOUT THE RESEARCH WORK

A: Processing and Curing Characteristics

a) Processing properties

Mooney viscosity: viscosity of rubber compounds were determined by using the Mooney viscometer (BS 1673: Part 3: 1969). In the viscosity measurements, the sample was allowed to warm up for one minute after the platens were closed. The temperature of the platens was set at 100°C. The motor was then started and a reading taken after 4 minutes. The results were expressed as [ML 1+4 (100°C)], where M is the Mooney viscosity number, L indicates the use of large rotor (1.5 in), 1 is the time in minutes that the specimen was permitted to warm up in the machine before starting the rotor, 4 is the time in minutes after starting the motor at which the reading was taken, and 100°C is the temperature of the test.

For the measurement of scorch time, the viscometer was set up similarly as in the viscosity measurement, except that the temperature of the platens was set at 125°C. The scorch time was taken as the time when the viscosity rose 5 points above the minimum assigned as t_5 .

b) Curing characteristics by ODR

Curing characteristics for all the rubber mixes were measured by Monsanto ODR, Model TM100. This equipment consisted of a die cavity located between electrically heated platens as shown in Figure AV.1a. The temperature of the platens and dies is maintained to within $\pm 0.5^\circ\text{C}$ by means of temperature controllers. A rubber mix of about 9 gms is placed in the lower platen so that a reciprocating biconical disc is embedded in the mix and the mix is then maintained at a high

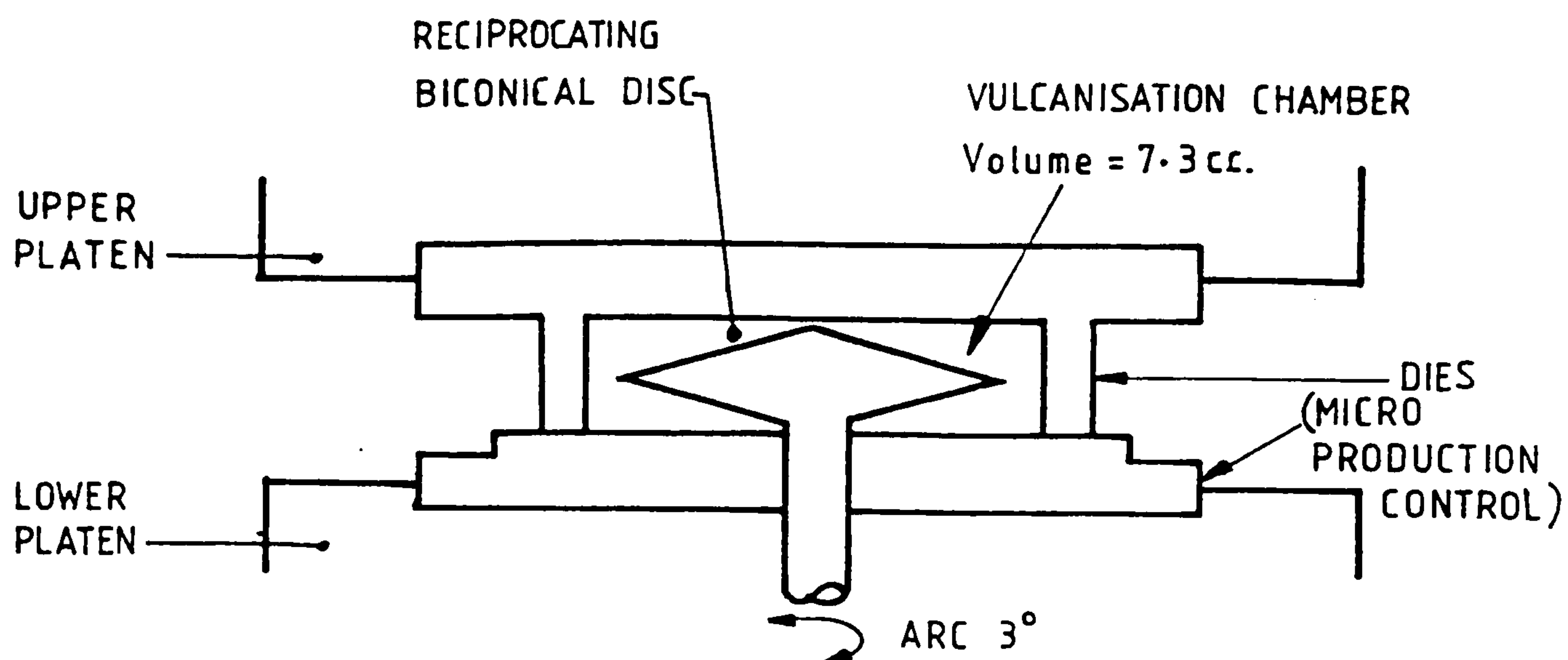


FIGURE AV.1a: SHOWING THE MAIN PARTS OF THE MONSANTO ODR

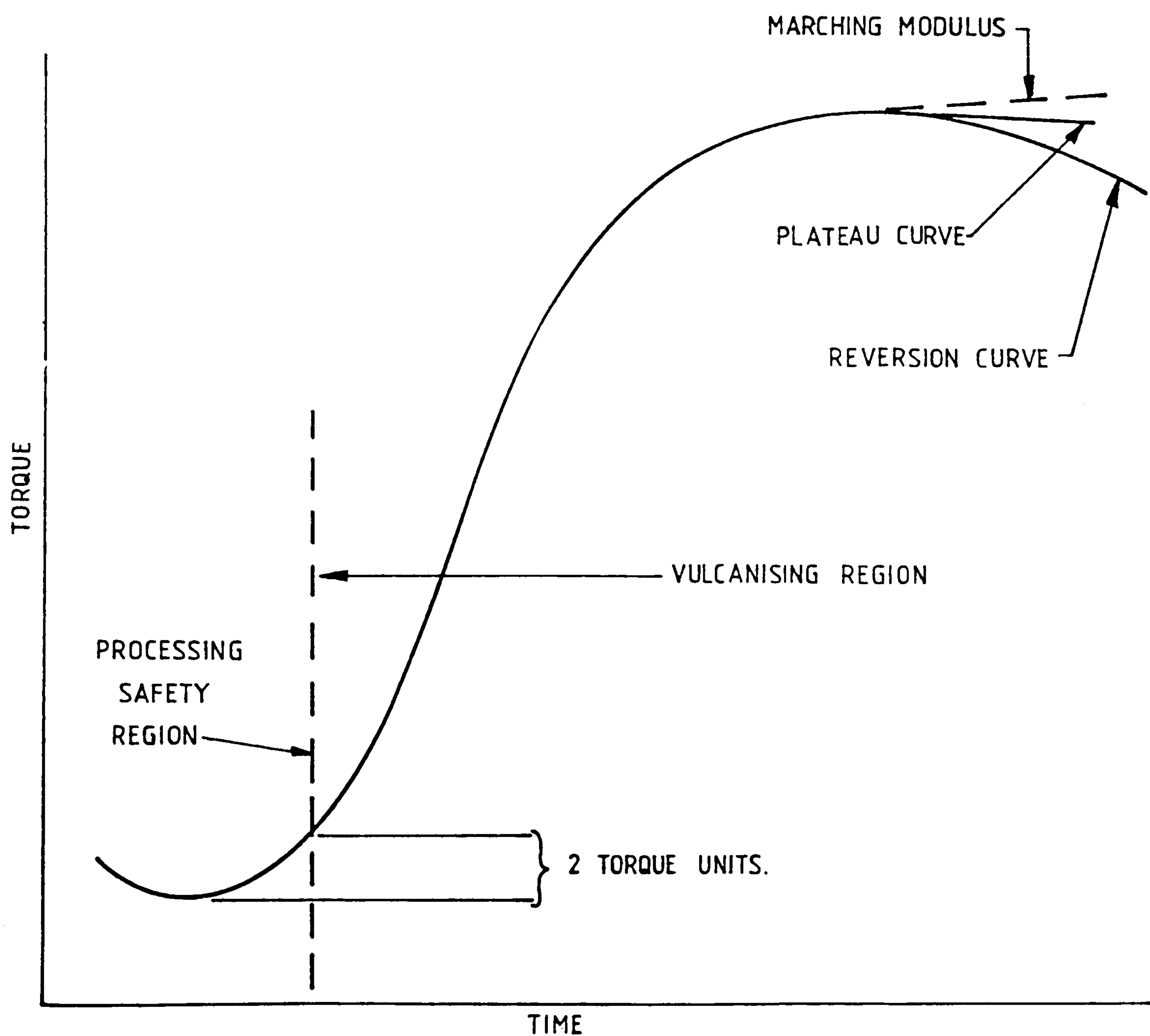


FIGURE AV.1b: TORQUE V CURE TIME GENERATED DURING THE CURING IN THE MONSANTO ODR

pressure, approximately 3.5 kg/cm^2 , throughout the test. The sinusoidal oscillation of the biconical disc at constant amplitude exerts a shear strain on the mix. As curing proceeds the torque required to shear the mix increases and a curve of torque versus cure time is generated. The torque value is directly related to the shear modulus of the mix at any given arc; see Figure AV.1b for properties available from an ODR.

The standard procedure described in ASTM Designation D2084-75 was employed in which an oscillation angle of 3° , an oscillation frequency of 1.7 Hz, a die temperature of 160°C .

B: Physical Testing

a) Determination of stress-strain properties

This test was carried out in accordance with BS 903: Part A2: 1971. The JJ tensile testing machine of model T5002 (JJ Lloyd Instruments Ltd) in conjunction with an X-Y plotter (PL 100 of JJ) was used for this test. The details of the machine set up are as follows:

Tensile speed	=	500 mm/min
Load cell	=	500N

The test piece used in this test was the dumbbell type 1 as specified in British Standards.

i) Tensile strength:

It is defined as the maximum tensile stress reached in stretching the test piece to breaking point. The value is calculated as follows:

$$\text{Tensile strength} = \frac{\text{Force at break}}{\text{Initial cross-sectional area}} \text{ MPa}$$

ii) Modulus at a given tensile strain (100% or 300%):

It is a tensile stress at a given strain and obtained as follows:

$$\text{Modulus (at 100\% or 300\%)} = \frac{\text{Force at a given strain}}{\text{Initial cross-sectional area}} \text{ MPa}$$

iii) Elongation at break:

It was calculated by subtracting the initial distance between the reference lines on the dumbbell test piece from the distance between the lines at breaking point and expressing the result as a percentage of the initial distance. For type 1 test pieces, the initial distance is 25 mm.

b) Determination of tear strength

In a normal tensile stress-strain test, the force to produce failure in a nominally flawless test piece is measured. However, in a tear test the force is not applied evenly but concentrated on a deliberate flaw or sharp discontinuity and the force to continuously produce a new surface is measured. This force to start or maintain tearing will depend on the geometry of the test piece and on the nature of the discontinuity, which may be a cut, notch or re-entrant angle.

Using a crescent test piece, the values obtained indicate the force required to propagate a nick already produced in the test piece. Testing was carried out by using the JJ tensile testing machine set at 500 mm/min.

The following equation was used to calculate the tear strength (BS 903: Part A3: 1982)

$$\text{Tear Strength} = \frac{F}{t}$$

where F = maximum force in kN

t = thickness in m of the test piece.

The result was expressed in kN/m.

c) Hardness

A hardness measurement is a simple way of obtaining a measure of the elastic modulus of a rubber by determining its resistance to a rigid indenter to which is applied a force. It is a measure of modulus at very small deformation. The measurement was carried out using a standard dead-load hardness tester of the Wallace Company which is in accordance with BS 903: Part A 26: 1969.

d) Rebound resilience %

The test is used to assess the elastic behaviour of rubbers in the range of 30-85 IRHD in the case of shock stressing according to DIN 53512. The resilience is determined as follows:

$$R = \frac{\text{Recovery energy}}{\text{Expended energy}}$$

This can be read off directly from the scale in %. The instrument used is of Zwick-Werkstoff Company.

e) Compression set at constant strain (25%); Method A of BS 903: Part A: 1969

This test is intended to measure the ability of rubbers to retain elastic properties after prolonged compression.

The test piece used was a cylindrical disc of 13.0 ± 0.5 mm diameter. At the end of the compression period, the compression set at constant strain was calculated as follows:

$$\text{Compression set at constant strain} = \frac{t_o - t_r}{t_o - t_s} \times 100$$

where t_o = original thickness of test piece

t_r = thickness of test piece after recovery

t_s = thickness of spacer (4.73 ± 0.01 mm).

f) Swelling in liquids (BS 903: Part A16: 1971)

In this method the percentage change in volume which a test piece of given initial dimensions undergoes when immersed in toluene for a period of one week at room temperature is calculated.

Expression of results;

$$\% \text{ change in volume} = \frac{[W_3 - (W_4 - W_5)] - [W_1 - (W_2 - W_5)]}{[W_1 - (W_2 - W_5)]} \times 100$$

where W_1 = initial weight of rubber in air

W_2 = initial weight of rubber in water

W_3 = weight of rubber in air after immersion in the test liquid

W_4 = weight of rubber in water after immersion in the test liquid

W_5 = weight of the sinker in water.

g) Flex cracking and cut growth test

A: Resistance to flex cracking (BS 903: Part A10)

B: Determination of resistance to cut growth (BS 903: Part A11).

The De Mattia-type machine is used. The test piece which is a strip with a transverse groove is fixed in two clamps which move towards each other to bend the strip into a loop. Repeated bending or flexing causes cracks to develop in this part of the surface where tension stress is set up during flexing or, if this part of the surface contains a crack or cut, causes this to extend in a direction perpendicular to the stress.

For the flex-cracking test, cracking is graded according to the scale of grade 1-6 given in the above mentioned British Standards.

h) Differential scanning calorimetry (DSC)

DSC is a technique which measures the heat flow into or out of a sample relative to an inert reference material as both are subjected to a linear increase or decrease in temperature. The temperature difference between the sample and the reference is measured using thermocouples connected in position. When the temperature of the sample is equal to the reference, the two thermocouples produce identical voltages and therefore the net voltage equals zero. When the temperatures differ there is a net voltage which is proportional to the difference in temperature. This net voltage is amplified and recorded on the y-axis of an x-y recorder. The temperature of the experimental material and reference, which is varied at a programmed constant rate, is monitored on the x-axis.

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PATENTS AND PUBLICATIONS ARISING FROM THIS THESIS

A: Patents

I: SAPA in Rubber, a Process for Treating Rubber.
PCT/GB 84/00168.

II: Polychloroprene Rubber, Crosslinking Agents and Processing
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B: Papers

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