BONDING OF RUBBER TO
BRASS-PLATED STEEL WIRE

by

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SYNOPSIS

This research is based on a study of the parameters affecting the adhesion of styrene-butadiene rubber (Solprene 1204) and polyisoprene (Natsyn 2200) to monofilament brass-plated steel wire.

Investigations are concentrated on the influence of compounding ingredients and coupling agents on the adhesion between the rubber and wire using H-shape specimens. X-Ray Photo Electron Spectroscopy (ESCA) and Scanning Electron Microscopy (SEM) techniques have been used to identify residues on the wire surface and to interpret the chemical and physical roles of carbon black and silica on the mechanism of bonding rubber to brass-plated wire.

The results show the proportions of carbon black, silica and sulphur in the rubber compound required to give optimum rubber to metal adhesion and optimum rubber mechanical properties. The results also indicate that the lubricant residue on the wire surface, identified by ESCA, has adverse effect on adhesion.

Some organic coupling agents (Titanates) have recently been introduced as adhesion promoters. The effects of these agents on the adhesion characteristics between SBR and brass-plated wire have been investigated by using the titanates both as intermediaries between the rubber and brass layers and when incorporated into the rubber compound. On the latter direct bonding technique the influence of the coupling agents on the bulk SBR properties has also been studied.

The results show that the titanates which were used as intermediaries between rubber and brass-wire exhibited surface activity even though they were observed to produce adverse bond strength values. Titanates incorporated into the rubber also exhibited an effect on physical and bonding properties of SBR.

ACKNOWLEDGEMENTS

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DEDICATION

I am indebted to my family for their encouragement and financial support during the course of my study.

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CHAPTER 1

INTRODUCTION

1.1 Introduction: Rubber-to-Metal Bonding

High polymers, as natural and synthetic rubbers, possess a number of valuable properties: elasticity, absorbency of vibration, resistance to chemical action and high resistance to friction. Metals do not possess such properties, but they do possess high strength and rigidity. Combinations of metal with rubber can have engineering applications which mainly are, to damp out mechanical vibration, to absorb shock loads, to aid in suppression of noise, and to contain liquids.

Earlier methods introduced to bond rubber to metal consisted of attaching the rubber by mechanical means, e.g. by bolting or by encasing in a housing or chemically using a layer of ebonite and recently by the use of various chemical types of bonding agents to adhere rubber to metal.

1.1.1 Identification and Classification of Rubber-to-Metal Adhesives

Ebonite was used as the original bonding agent, it functions by simultaneously cross-linking and forming a strong attachment to metal. It consists essentially of natural rubber with a combined sulphur content of 32% and during its preparation the unsaturated rubber hydrocarbon becomes saturated due to substantial cross-linking. Unlike soft vulcanized rubber, ebonite is thermoplastic, and can be shaped and formed at temperatures over 60^{0}C. This means that the ebonite bond between soft rubber and metal is also sensitive to rises in temperature and will weaken progressively as the unit is heated. Ebonite can be bonded satisfactorily to most metals including iron, zinc, tin, but not to copper and not to certain brass compositions which contain high zinc contents. This technique is still in isolated use today, mainly for roller-covering and chemical plant lining. Typical ebonite mixes which are often used for bonding rubber-to-metal are listed in Table 1.1(1).

These disadvantages challenged scientists to look for more reliable bonding systems. In one approach cyclised derivatives of rubber(2) were prepared, by treating the hydrocarbon with sulphuric acid or with certain sulphonic acids and these were found to have good bonding properties when applied between unvulcanized rubber and metal prior to vulcanizing(3). These compounds were unfortunately thermoplastic and deterioration of the bond occurred at temperatures above 60^{0}C.

A few years later other modified rubber derivatives were developed which showed excellent bonding properties without possessing the major drawback of being thermoplastic. Typically of these were chlorinated and hydrochlorinated rubbers(4). Normally the chlorination process is carried out with the rubber in solution to which chlorine is added and this reacts with the double bonds until complete saturation takes place. During this substitution

TABLE 1.1

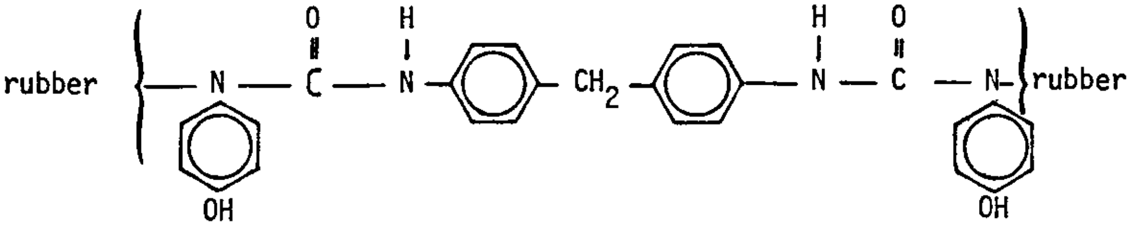
Typical Ebonite Mixes(1)

Ingredients	A	B	C	D
Natural rubber	100	100	100	100
Sulphur	45	35	40	45
Ebonite dust	-	-	40	-
Magnesium carbonate	-	-	-	25
China clay	40	60	50	-
Barytes (barium sulphate)	40	-	-	-
Soft carbon black	-	10	-	5
Lime (calcium hydroxide or calcium oxide)	30	-	10	10
Magnesia (magnesium oxide)	-	-	-	17.5
Crumb rubber	30	-	-	-
Whiting (ground chalk)	-	30	-	-
Red iron oxide (ferric oxide)	-	-	25	-
Boiled linseed oil	10	-	-	-
Brown factice*	5	2	-	-
MBTS (dibenzthiazyl disulphide)	-	2	-	-
DPG (diphenylquanidine)	-	-	2	-
Mineral rubber	4	4	-	-
Litharge (PbO)	-	-	-	3
	304	243	267	202.5

* Brown factice - is manufactured by reacting special vegetable or marine oil with sulphur at 140-160°C

reaction the evolution of hydrochloric acid gas occurs as a by-product which must be removed by washing before the chlorinated product can be used. Chlorinated rubbers which are usually proprietary materials, cannot be applied to all metallic surfaces with equal success. Effective control of their performance and reproducibility was found to be difficult. Cleanliness of the rubber and the metal surfaces is of course extremely important for good adhesion.

Polyisocyanates were also found to be good bonding agents due to their reactivity at the nitrogen-carbon double bond. The di- and tri-isocyanates have proved to be the most interesting from the aspect of rubber to metal bonding. The bonding mechanism of polyisocyanate with rubber and metal is very complicated. The postulated(5) bonding mechanism between rubber and isocyanate is that an adduct form of isocyanate takes place in rubber forming a cross-linking thus:



Bonding of isocyanate to metal might be that isocyanate unites with the hydrated oxide layer on the surface of the metal giving a urethane linkage between the isocyanate and metal surface. The bond is not thermoplastic and when exposed to temperatures as high as 150°C, failure usually occurs within the rubber phase and not between rubber and metal. Triisocyanates can be used to bond all the natural and synthetic types of rubber in common use, with the exception of silicone rubber.

It has been understood for a long time(6) that brass can be used as a bonding medium. The method of brass plating for achieving good adhesion has become one of the most important techniques in industry (rubber to brass-plated metal bonding will be discussed in Section 1.2). In spite of a vast expansion in using brass as a means of rubber adhesion to metal, only a limited size of component could be brass-plated due to handling or manipulation problems and process reproducibility, and therefore chemically based proprietary bonding agents are widely used especially for big items. Such chemical bonding agents are complex mixtures. Their composition has been kept secret because of market competition but they are believed to consist of mixtures of different ingredients such as epoxy resins, oxidized olefins, chlorinated and sulphonated rubbers, cobalt napthenate and other ingredients all of which are normally dissolved in solvent. Some examples of these types of bonding agents are listed according to their trade names, as given below:

a) "Chemlok" rubber-to-metal adhesives(7)
b) "Megum"(8)
c) "Thixon" bond agents(9)

By way of illustration different grades of Chemlok bonding agent for different rubbersand metals are shown in Table 1.2(7).

1.1.2 Preparation of Metal Surface

Proper preparation of the surface of metal to be bonded is one of the most important factors influencing the adhesion in any process. Metal surface preparation methods may be divided broadly into two classes, mechanical methods and chemical methods. Mechanical methods include such operations as blasting with sand, grit, metal oxides or glass beads, abrading with wire brushes, steel wool or baked abrasives and machining or scoring with cutting tools. Chemical methods use inorganic reagents to convert the metal surface from the essentially free metallic state into metallic compounds.

A mechanical cleaning procedure for metal, such as steel, is where the steel surface is immersed in a trichloroethylene vapour degreasing bath to remove the weak oxide residue, mill scale and oil contaminants, as these are detrimental to wetting by the bonding agent and thus adhesion. The second step of a mechanical process is usually blasting with steel or alumina grit. Blasting consists of impinging the abrasive particles against the metal surface with an air stream. The duration of the blast, the shape and size of the blasting material and the hardness and porosity of the metal determine the topography of the resulting surface.

Chemical cleaning methods for steel surfaces may be either acid or base and are normally followed by zinc or iron phosphate

TABLE 1.2

Manufacturer's Recommendations for Bonding Different types of Rubbers to Metals using Chemlok Bonding Agent

Elastomer	Chemlok 1-Coat System	Chemlok 2-coat System		Metals
		Primer	Cover coat	
Butyl	220	205	220 or 233 or 234B	Steel, Stainless Aluminium Brass Copper Zinc Magnesium Titanium Cadmium Lead Silver Platinum Gold
Natural	220	205	220 or 233	
SBR SBR-natural	220 220	205	220 or 233 or 234B	
Polyisoprene	220	205	220 or 233 or 234B	
Nitrile Carboxy modified Vinyl modified	205	205 205 205	220 or 233 233 233	
Polybutadiene	220	205	220 or 233 or 234B	
Fluoro elastomers	607	-	-	
EPDM	Required 2-coat system	205	236	

conversion coating which is water soluble and thus this procedure has to be followed by passivation through dipping into a hot chromic acid solution which forms an insoluble chromic/phosphate complex(10).

1.1.3 Mechanism of Rubber-to-Metal Bonding Using Proprietary Chemical Bonding Medium

The nature of the adhesive bond between metals and rubbers has not been clarified. The situation is complicated because such a bond may have not only a physicochemical character, but also, in adhesion of one high polymer to another, chemical interaction.

Salomon and Schönlau(11) have observed that a higher thermoplasticity in the joint shows that the adhesive bond is brought about by intermolecular interactions. By contrast, heating only slightly affects joint strength and this would indicate that adhesion is based on chemical forces. They gave a diagram, reproduced in Figure 1.1, characterizing the temperature dependence of limiting tensile strength for a rubber stock bonded to metal by different adhesives. As shown, the chemical bonds are responsible for bonding rubber to metal only when rubber stocks are vulcanized to brass-plated metallic surfaces, or, when isocyanate adhesives are used. It is possible that a sufficiently high level of adhesion of rubber to metal may occur in a number of cases because of physical bonding.

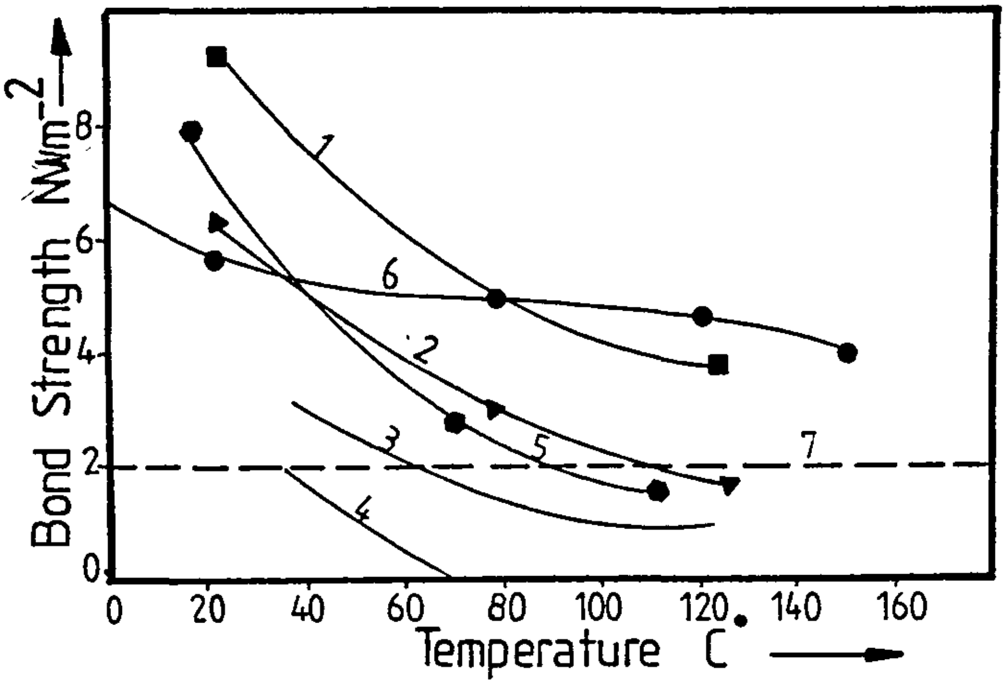


FIGURE 1.1: Effect of Temperature, t, on the Bonding Strength of Rubber to Metals by Different Methods of Bonding:

1. With triphenylmethane tri-isocyanate (Desmodur R);*
2. With rubber hydrochloride ("Ty-ply")**;
3. With latex- albumen mixture containing sulphur;
4. With cyclized rubber;
5. With ebonite;
6. Vulcanization to a brass-plated surface;
7. Lower limit of adhesive strength for a practical application (11).

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* Bayer Chemical

** Anchor Chemicals

A number of factors are known to play an important role in the mechanism of rubber-to-metal bonding. They can be classified as follows:

a) Factors dependent upon the structure and nature of the rubber to be bonded.

b) Factors dependent upon the nature and structure of the combination of polymeric materials, solvent, additives etc. present in the adhesive formulation.

c) Factors dependent upon the metallurgical state and surface nature of the metal to be bonded.

The Rubber Factor

The adhesion of rubber to be bonded to metal is usually related to its polarity. In general it is true that the polar nitrile and polychloroprene rubber compounds can be bonded to metal with greater ease than the non-polar natural or styrene-butadiene rubber. The polarity of rubber can be defined by a number of methods. Contact angle measurement is usually used(12) to indicate polarity characteristics. Contact angle investigations usually measure, the degree of wetting, between the polymer in question and a reference liquid. The degree of adhesion between a polymer and a liquid that wets the polymer is usually higher than that when the polymer and liquid do not wet each other. Two materials of similar polarity will usually wet each other and exhibit a low wetting angle when placed in contact. By measuring the wettability of rubber against a reference liquid we can obtain some idea regarding relative polymer polarity. It has been shown(13) that complete wetting however is usually not sufficient to give adequate adhesion because many polymeric adhesives may wet non-polar butadiene-styrene and natural rubbers, but the physical adhesion is inadequate. Good wetting and a reasonable degree of polarity of the joined materials must characterize the system.

The possibility of adhering butadiene-styrene rubbers or natural rubbers to bonding agents by polar (physical) forces alone is quite remote, and some chemical cross-bridging mechanisms between the rubber and the polymeric adhesive must be introduced into the adhesive-rubber interface system. In most instances the chemical link is sulphur, and the mechanism of cross-linking is probably similar to the mechanism operative during the vulcanization of rubber. The sulphur probably migrates to the interface to participate in a primary chemical bridging mechanism, and produces a chemical union between adhesive and rubber. Sulphur may initially be added to either the rubber or the adhesive (or both) and moves to the interface by either concentration migration or catephoretic effects(13).

The Adhesive Factor

The polarity factor is also important in characterising a polymer adhesive. The bonding agent, however, in addition to demonstrating a high adhesion and low interfacial tension between itself and the rubber, must also demonstrate adhesion to the metal surface. Metal requires for adequate physical adhesion, a highly polar adhesive but this must not possess excessive polarity. The best physical adhesion between metals and polymers usually occurs when polymers have a contact angle against water as a standard of between 25 and 35 degrees(14).

Sometimes there is adequate adhesion between rubber and bonding adhesive, but the adhesion between bonding adhesive and metal is inadequate. This problem can be solved by using a two-coat bonding system in which the most polar coat, known as primer, is applied directly to the metal surface followed by a less polar cover coat. It is important that a type of cross-bridging process happens between cover-coat and elastomer. Sexsmith(15) in his paper has evaluated the adhesion processes that may occur with two-coat bonding agent systems in the formation of rubber-to-metal bond during vulcanization in the following way, Figure 1.2.

1. Adsorption of primer ingredients at the metal surface.
2. Adsorption and/or interdiffusion of cover-coat and primer polymers.
3. Interdiffusion of polymer and crosslinking agents across the rubber interface.
4. Internal vulcanization of the bonding agent.
5. Cross-bridging of the elastomer interface.
6. Internal vulcanization of the elastomer.

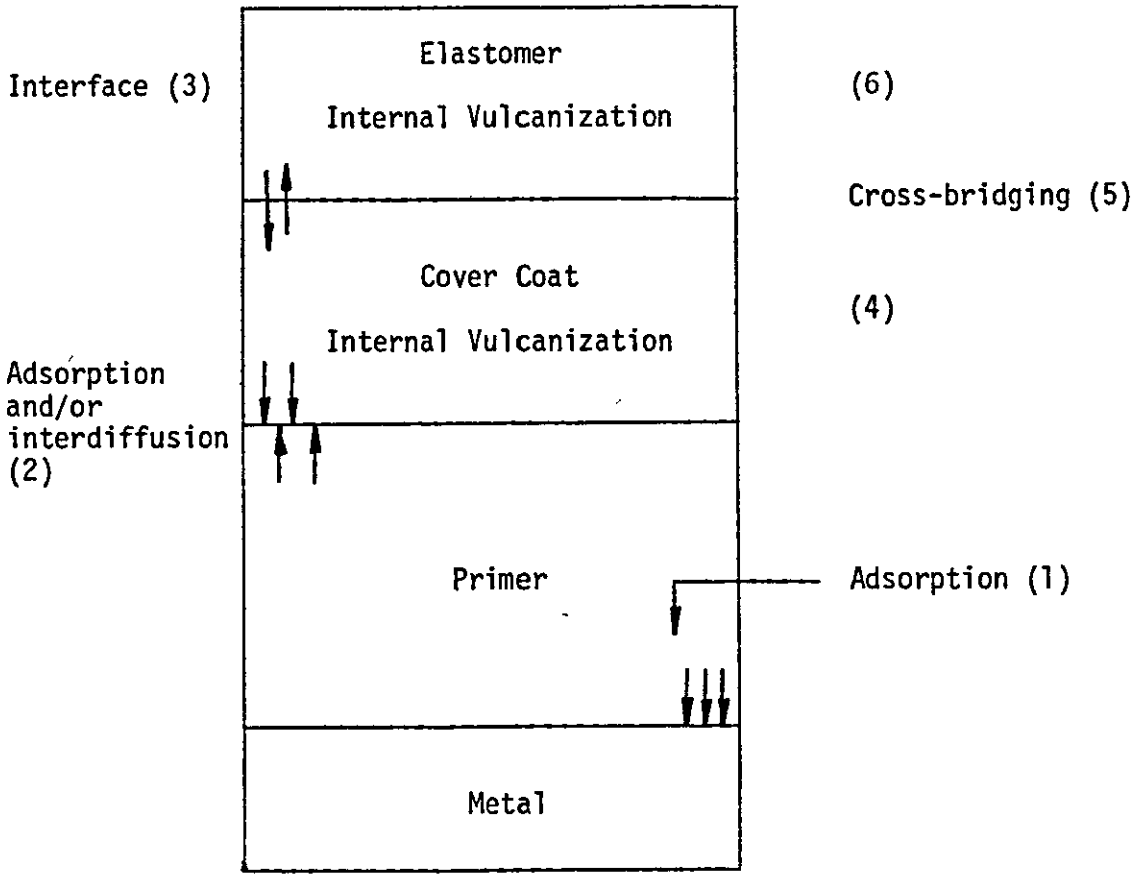


FIGURE 1.2 Concept of Two-coat Bonding Agent System(14)

The Metal Factor

There are a number of surface characteristics of metal which are important in the bonding of the metal to polymer adhesives. The fundamental atomic structure of the metal has been given some consideration by a number of authors. Loughborough and Snyder(16) stated that the magnitude of adhesion of a variety of metals to a reference commercial adhesive was dependent upon the atomic spacing of the metal under consideration. For the adhesive, with measured identity period (lattice spacing) of 0.453 nm, metals with lattice spacings in excess of 0.4 nm gave the best adhesion, while metals with spacings less than this value did not adhere well. Such an observation is in agreement with the statement of Alstadt(13) that the interfacial free energies between adhering phases should be as low as possible; a 'matching' of the micro-dimensional periodicities would contribute to a maximising of the force of attraction and a minimising of the interfacial free energy. A theoretical evaluation of those characteristics of a pure metal surface conducive to the formation of physical adhesion to a reference polymer can be made on the basis of either thermodynamic or electrical considerations(13).

The surface area and the roughness factor of the metal are significant in many adhesive applications. A very rough surface may result in a 'starved joint'; the peaks on the metal surface may actually 'pierce' the adhesive layer and contact the adjacent surface, the total bond area is thereby reduced. In the case of rubber-to-metal adhesion non-conforming surfaces oppose the metal, and starved joints are unlikely.

1.2 Rubber-to-Brass Bonding

1.2.1 Historical Background

As mentioned in the previous section brass can be used as a bonding agent between rubber and metal. It is not known who first observed this phenomena, but as early as 1862 Charles Anderson(6) specified that metal if to be covered with rubber should first of all be coated with a layer of brass applied by electrodeposition. Another scientist(17) adopted in 1911 a brass plating metal technique for obtaining a bond between rubber and metal in the production of rollers.

After the second world war people like Buchan(18) and Blow(19) worked assiduously to explain the theoretical basis of brass adhesion to rubber. When the steel belted radial tyres came on the market brass-plating proved to be a more suitable adhesive for the tyre manufacturer. Since then the method of brass plating for achieving good adhesion has become one of the most important techniques in industry and has attracted much scientific research. Despite the feasibility of bonding rubber to brass-plated steel, many difficulties are associated with getting good reproducible adhesion. Only certain compositions can be employed and with these particular brasses only specific rubber formulations may be used if a vulcanized bond of a consistently high level of adhesion is to be maintained. The brass composition usually quoted as being the most suitable for bonding purposes consists of 70% copper and 30% zinc.

1.2.2 Brass Plating Process

A solution that can be used for producing a brass deposit suitable for bonding to rubber must have properties and capabilities not possessed, necessarily, by solutions employed for producing decorative and protective finishes. The deposit must be uniform in composition and physical structure and it must be reproducible. The solution moreover should be stable in operation so as to reduce to a minimum the amount of control that has to be exercised over it and should be capable of producing a satisfactory brass film over a comparatively wide range of conditions. In other words the solution should be easy to handle. From the economic and productive angles it should deposit rapidly and at a low unit cost.

In production a brass deposit is obtained by plating zinc and copper simultaneously from a solution of the salts of these two metals. When two metallic ions are present in solution the more electropositive will be deposited first of all and unless the two ions have approximately the same potential they will not deposit together to form an alloy. Because of the dissimilarity in their individual potentials, copper and zinc cannot be deposited simultaneously from a solution of their simple salts, such as copper and zinc sulphates or chlorides. By reducing the concentration of copper ions in solution it is possible to make the copper less electropositive and by continuing the process to reach a stage, ultimately, where the copper and zinc would deposit simultaneously from a solution of their simple salts. The concentration of copper ions left in solution after continued dilution combined with the decrease in conductivity would be so small as to render this method impractical when simple copper and zinc salts are combined with other salts so as to form a complex radical. It is possible to prepare solutions of copper and zinc in which the individual potentials of the two metals are equal and in which the electrical conductivity is adequate for electrodeposition. Complex salts formed by dissolving copper and zinc simple salts in sodium or potassium cyanide are probably the most effective for this purpose.

An excess of cyanide, above the amount required to put the metal cyanides into solution, is called the free cyanide, arbitrarily defined as the remaining theoretical concentration after the conversion of copper to $Cu_2(CH)_3^=$ and zinc to $Zn(CN)_4$. Free cyanide is necessary to assist in anode corrosion and as a reserve of cyanide ions to maintain the soluble metal cyanide complexes. Clarke(20) found that 5 gl^{-1} of free cyanide was sufficient to prevent blistering. As the free cyanide is increased, the cathode efficiency decreases and there is also a decrease in the copper content of the deposit.

Ammonium ion is useful for controlling the colour of the brass deposit. Ammonium hydroxide has several functions, it acts as a complexing agent, assists in good anode solution, and acts as a means of pH control, small amounts (0.2-1.5 gl^{-1}) have a remarkable effect in correcting off colour deposits. The effect of ammonia on the composition of the deposit has been studied by several investigators and the curve in Figure 1.3 by Clarke(20) is typical of the results obtained.

A typical brass solution for coating steel prior to rubber bonding is given in Table 1.3(21).

TABLE 1.3

Typical Brass Solution for Coating Steel for Rubber Bonding

	N	gl^{-1}
Cuprous cyanide, CuCN	0.29	26.2
Zinc cyanide $Zn(CN)_2$	0.19	11.3
Sodium cyanide, NaCN	0.90	45.0
Free cyanide, NaCN	0.13	6.4
Copper Cu^I	0.29	18.8
Zinc, Zn	0.19	6.2
Solution ratio , Cu/Zn 3/1		
Temperature, 35-50°C		
Current density, 0.5 amp/dm^2		

Current Density

The cathodic current density controls to a large extent the amount of brass which is deposited, as well as, to a more limited extent, its composition. Ferguson and Sturdevant(22) found that

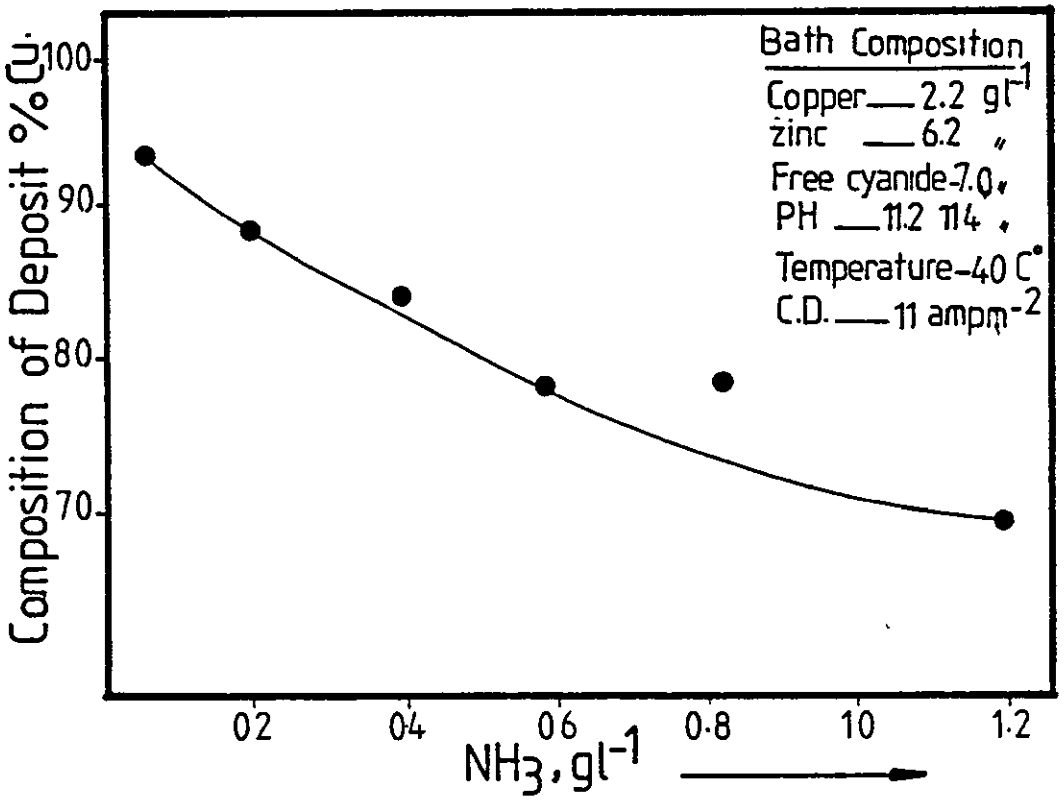


FIGURE 1.3: Effect of Ammonia on the Composition of the Brass Deposit from a Cu/Zn Solution (20)

with increasing current density the percentage of copper in the deposit layer decreased, while the cathodic polarisation increased. This is in agreement with the observation of Compton(23) that as the current density increases, the copper content of the deposit diminishes, passing through a minimum so that further increase in the current density causes the copper content to increase again, Figure 1.4. At higher current densities a dull brass was produced with burnt working along the edges, however operating the solution at a higher temperature was found to combat this tendency to a certain extent.

Temperature

Since the temperature of the plating solution was found to have a marked effect on the composition of the deposit, it has been investigated by several scientists. The copper content increases with increase in temperature(23), Figure 1.5. Zentler-Gordon and Robert(24) state that an increase in the bath of 1°C will increase the copper content by approximately 2%. Efficiency increases with an increase in temperature permitting higher current densities.

Hydrogen Ion Concentration

The degree of alkalinity of the plating solution, controls to a marked extent, the composition of the brass deposited when the pH is high (i.e. the solution is more alkaline) and the percentage of copper in the brass falls. Whereas with a less alka-

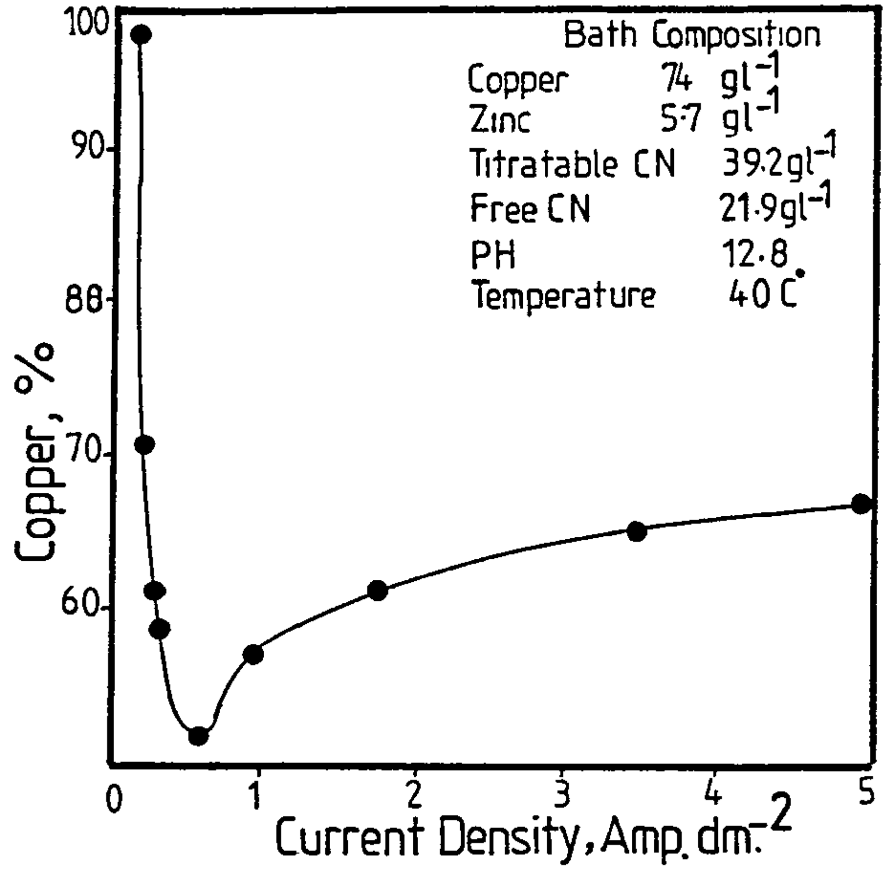


FIGURE 1.4: The Copper Content of the Deposit at Various Current Densities (23)

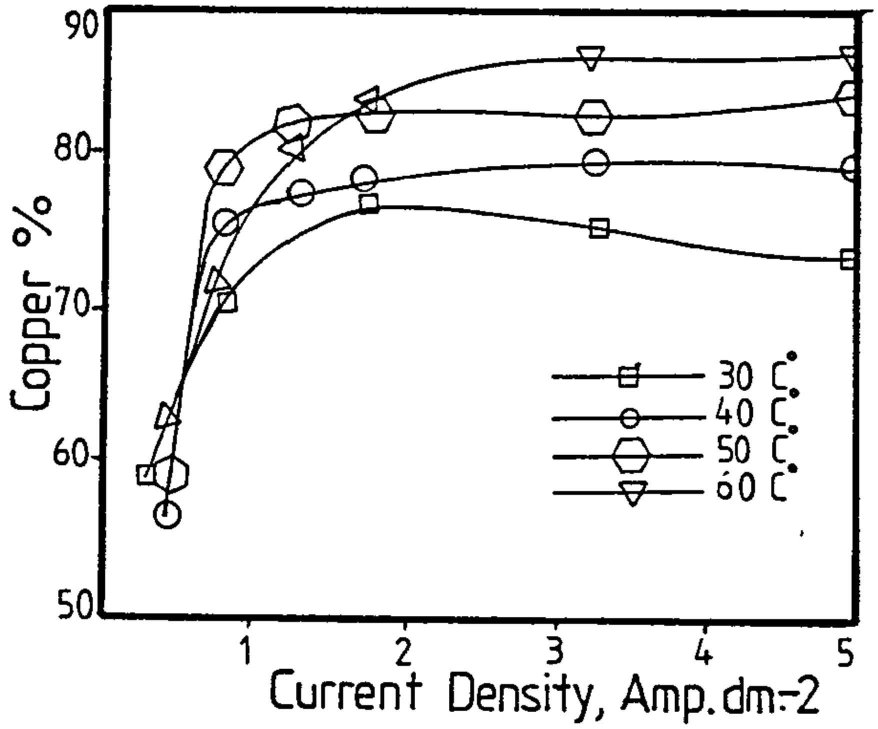


FIGURE 1.5: The Effect of Temperature on the Copper Content in the Deposit (23)

line solution the percentage rises, when a well buffered solution is employed. However it is possible to make a brass plating bath function satisfactorily without actually knowing its pH value. This has been done over a period of years by the addition of ammonia in appropriate amounts coupled with close analytical control of the deposit before and after its addition. The actual addition of ammonia to a buffered solution, which is already alkaline, may not affect its pH to an appreciable extent. It may be that the zinc forms a more ionisable complex with the ammonia than it does with the cyanide and that it deposits more readily under the prevailing conditions. It has been pointed out by Hogaboom(21) that when the pH of brass solution is over 13.6 it will refuse to plate, but addition of a more acid constituent such as $NaHCO_3$ will remedy this condition.

The technique of wire or cord plating is different from the ordinary plating technique. A helical coil method of wire plating in rod form is used followed by subsequent consecutive redrawing and heat treatment to the required finished diameter(25). The open coil is passed through external roller and comb guide members spirally along a rotating shaft held down by a similar roller shaft, as illustrated in Figure 1.6. Electrical contact to the wire is accomplished by a roller contact on the rod opposed by a roller guide, functioning external to the plating bath. The internal anodes are semi-cylindrically disposed to the rod coil shape. Current

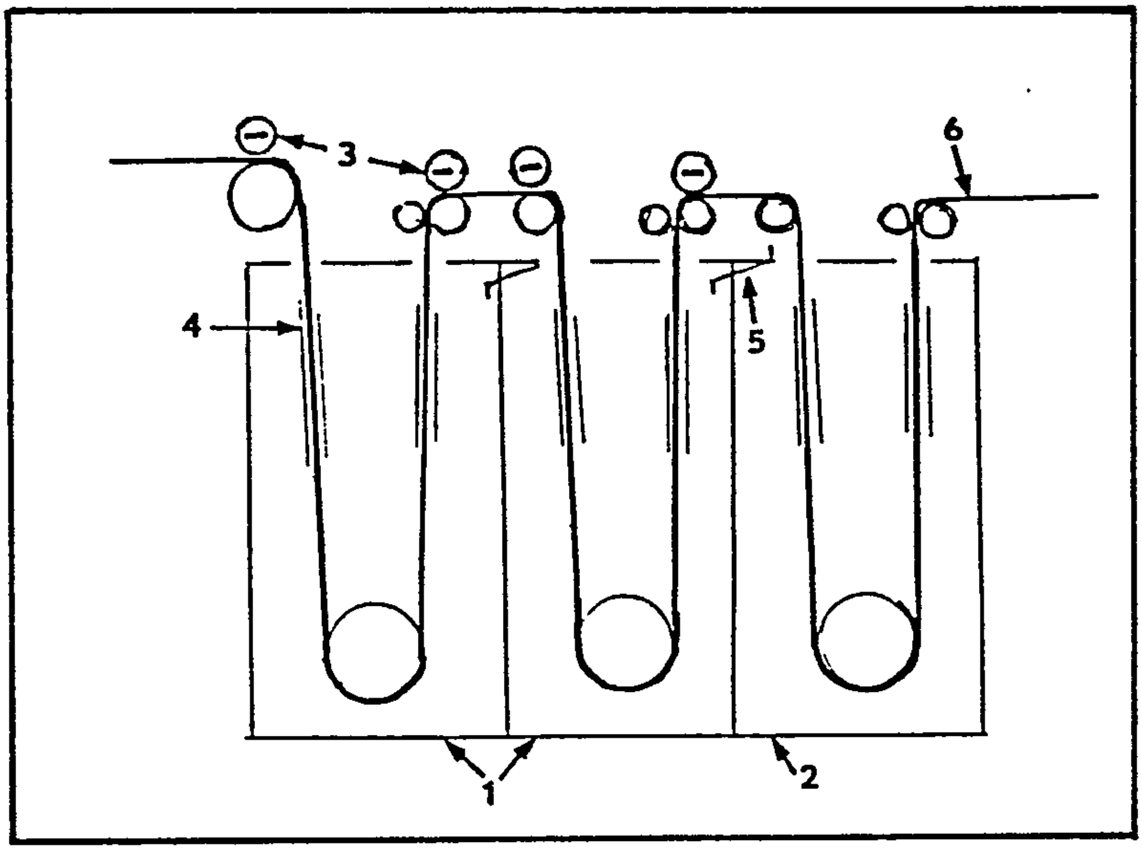


FIGURE 1.6: Vertical Pass Plating and Rinsing Cell Designed for Wire or Cord Plating:

1. Plating cells
2. Rinse tank
3. Contact rolls
4. Special insoluble anode grids
5. Drip collection tray
6. Strip

densities up to approximately 55 amps m^{-2} are said to be employed.

1.2.3 Wire Drawing Process

The brass-plated wire or cord used as a reinforcing material in rubber (especially in tyres) is in the drawn form. The wire is usually produced by drawing of a high carbon steel hillet through a shaped die so that the wire is forced to conform to the size and shape of the die orifice. Although the deformation per pass is limited, it is possible to build up an enormous total deformation by using many dies in sequence. Extreme measures often have to be taken before drawing and includes the use of various pretreatments such as coatings because it has been found that(26) coated steel can be drawn better than uncoated steel. These coatings include metallic copper, brass, tin and phosphate. The wire used for the reinforcement of rubber is usually coated with brass since it exhibits good bonding properties to rubber(6).

During the wire drawing process, the surface of wire and die is in contact with each other. The contact area will be only possible at the tip of their asperities(27) because most surfaces are rough on an atomic scale. The real area of contact will generally be much smaller than the apparent, Figure 1.7.

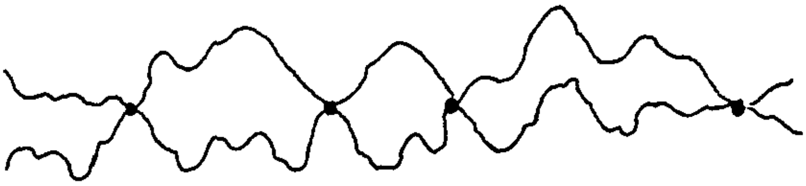


FIGURE 1.7 Contact between Flat Surfaces is Considered to occur only at Asperity Tips

At these regions of real contact, the atoms on one surface will attract those on the other and produce strong adhesion. When drawing occurs, this adhesion has to be overcome, that is the junctions have to be sheared. The force to shear the junction is the cause of primary friction between surfaces. In addition one surface is harder (die) than the other (wire) hence any roughness of the die will plough out grooves in the softer materials and this constitutes a second case of friction. We may write:

Force of friction (F) = Force to shear Junctions (A)
+ Force to plough (S)

The most effective way of reducing friction and surface damage is to prevent contact between the surface of the wire and die by the use of lubricants. Usually a lubricant, which is able to prevent undesirable friction and surface damage has also a number of functions notably given as follows:

1. To penetrate between the two contacting surfaces thus reducing friction and changing the surface to surface contact phenomenon by distributing the pressure uniformly along the surfaces and thus preventing localised wear due to surface-surface pressure.
2. To prevent corrosion of the drawn wire.
3. To aid dissipating heat caused by friction.

In industry many different techniques are in use according to the metal being drawn, the size range, and the volume of production. There are two broad divisions in wire-drawing techniques: wet drawing and dry drawing. The differences largely revolve around the pretreatment and lubrication methods used, but they also extend to the design of the wire drawing machine. Dry drawing is normally used for large and intermediate wire sizes. The main characteristics of wet drawing as opposed to dry drawing are that efficient cooling of the wire is possible and the product has a better finish(26). While tremendous quantities of steel wire (such as tyre cord wire) have been drawn by the wet drawing technique and since in the high temperature drawing of wire, the lubricant reacts with the brass surface giving surface 'staining' which is considered detrimental to wire-rubber adhesion(28).

The mechanism of wet drawing for wire is of a boundary type. A lubricant layer penetrates between the surfaces of the two bodies (die and wire) moving in contact against each other. A protective layer can be formed by physical (adsorption) and chemical reaction between the solid and surrounding bulk lubricants (see Figure 1.8).

The thickness of the protective layer is often as small as 2 nm (10^{-7} in) and the coefficient of friction for surface operating with a good boundary lubricant is 0.05 to 0.01 and the amount

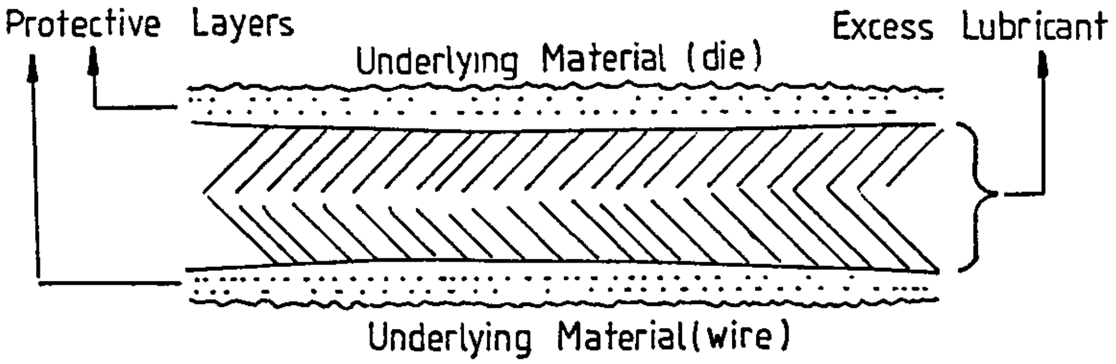


FIGURE 1.8 The Formation of Protective Layer of Lubricant between the Two Solid Surfaces Formed from Wire Drawing Die and Wire

of wear may be 1000 to 10 000 times less than for unlubricated surfaces(27). In the boundary mechanism, the chemical and physical nature of the surface and lubricant is of major importance. Such films (protective layers) may contain only one or two layers of lubricant molecules.

Good wire drawing lubricants for tyres must have certain properties and the most important of those properties are given as follows:

1. 'Stability' of drawing lubricant emulsion. The lubricant used for tyre cord is generally an oil-in-water emulsion. This emulsion consists of at least one immiscible liquid intimately dispersed in the form of droplets. Such a system possesses only low stability, but it can be improved by chemical additives, such as mixtures of soap and fatty acid which are often called "emulsifiers". McDonough(29) describes an emulsifier as a material which possesses surface active properties and which affects the stability of the oil-in-water emulsion. Emulsifiers can act as wetting agents and increase the adhesion of lubricants to solid surfaces.

2. 'Film Strength'. The term of film strength in a drawing process is defined as the property of a lubricant to prevent metal-metal contact between die and wire being drawn, to prevent excessive die wear, and to promote a smooth bright finish. In other words, film strength is the 'ability' of the lubricant to draw the wire. The purpose of using extreme-pressure additives (such as organic chlorine or sulphur compounds) is to increase film strength of lubricant. It is generally known in the wire drawing industry that high pressures are generated on the die approach angle when the wire is processed.

3. Adhesion of rubber to drawn wire. Some researchers consider that, after drawing the wire, the residue of drawing lubricant remaining on the wire surface is considered detrimental to the adhesion of rubber to wire(28,30) (this will be discussed in Chapter 3).

Typical wire drawing lubricant ingredients, and their functions as modern wet drawing lubricants, are given in Table 1.4.

1.2.4 Mechanism of Rubber-to-Brass Bonding

Although the discovery of the adhesion of brass to sulphur-vulcanizable rubber dates back some 115 years(6), interest in the mechanism of the bond formation is only fairly recent.

An interesting oxidation theory was developed by Blow(19) who suggested that during the cure of rubber in contact with brass,

Additive	Function
Synthetic emulsifier	Emulsify, wet metal surface, deterge, lubricate
Amine soaps	Maintain pH
Liquid fats, chemically modified fats or oils	Lubricant Lubricant and provide anti-wear or extreme pressure properties
Mineral oils	Lubricate, reduce foaming
Defoamers	Reduce foaming
Chelating agents	Deactivate hard water salts, reduce metallic soap formation
Water	Product of reactions, assist in coupling
Coupling agents	Solubilize incompatible ingredients
Inhibitors	Prevent metal corrosion Inhibit lubricant oxidation Retard bacterial degradation

TABLE 1.4 Wire Drawing Lubricants Ingredients and their Function in the Formulation of Wet Drawing Lubricants(26)

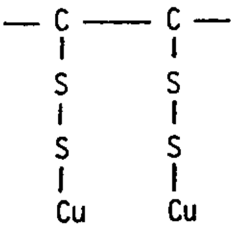
copper atoms diffuse into the compound and oxidise the rubber which leads to an increased surface polarity of the rubber phase and it is this oxidised film that provides the adhesion. He considered the fact that copper and cobalt are at their most effective in catalysing the oxidation of rubber when in the form of their fatty acid soaps (which are soluble in hydrocarbons) as good evidence for the support of the oxidation theory insofar as brass deposits suitable for bonding contain copper in a form active towards stearic acid and therefore readily soluble in the rubber. In such a form these elements would promote the oxidation of the rubber.

The second theory was based on the existence of chemical linkages between the rubber, sulphur and brass. This was first put forward by Hayford and Rogers(31), and with experimental evidence provided later by Buchan and Rae(32). According to this theory, there are four possible reactants viz copper, zinc, sulphur and rubber. They established that sulphur bridges exist between Cu atoms at the brass surface and rubber molecules. Copper possesses a variable valency and can therefore form more than one chemical compound with sulphur and two stable sulphides are known to be formed, cuprous sulphide (Cu_2S) and cupric sulphide (CuS). It was shown(33) that sulphur alone in carbon disulphide solution reacts with copper powder to give mostly cuprous sulphide. Subsequently later reaction to the higher sulphide is slow and is thought to be governed by a diffusion process(34). This cuprous sulphide can react in three ways while in contact with the matrix of vulcanizing rubber, as shown by the following reactions:

1. It reacts with free sulphur to form the higher sulphide namely cupric sulphide.
2. It can attach itself to a sulphur atom already bonded to the rubber.
3. It can react directly to the rubber at one of the points of unsaturation in the dienes structure.

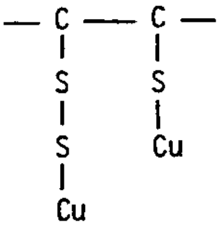
Reaction (1) will take place to an appreciable extent only when in an excess of uncombined sulphur. Reaction (2) can take place at all concentrations of sulphur, but when there is excess present there will be an added tendency for formation of sulphur chains between the copper and the rubber as shown below:

Formula I



$$\begin{array}{ccc} -\mathrm{C} & \text{---} & \mathrm{C}- \\ | & & | \\ \mathrm{S} & & \mathrm{S} \\ | & & | \\ \mathrm{S} & & \mathrm{S} \\ | & & | \\ \mathrm{Cu} & & \mathrm{Cu} \end{array}$$

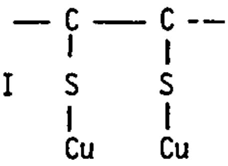
Formula II



$$\begin{array}{ccc} -\mathrm{C} & \text{---} & \mathrm{C}- \\ | & & | \\ \mathrm{S} & & \mathrm{S} \\ | & & | \\ \mathrm{S} & & \mathrm{Cu} \\ | & & \\ \mathrm{Cu} & & \end{array}$$

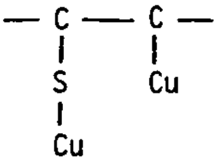
From a stereo-chemical point of view, structure (II) is less likely than structure I, hence the greater probability of a sulphur-sulphur linkage occurring. If reaction (2) occurs, weak bond formation is likely to result due to the low strength of these chains as the chemical forces creating them are weak. With reaction (3), however, two possible structures are:

Formula III



$$\begin{array}{cccc} - & \mathrm{C} - & \mathrm{C} & -- \\ & | & | & \\ & \mathrm{S} & \mathrm{S} & \\ & | & | & \\ & \mathrm{Cu} & \mathrm{Cu} & \end{array}$$

Formula IV



$$\begin{array}{cccc} - & \mathrm{C} - & \mathrm{C} & - \\ & | & | & \\ & \mathrm{S} & \mathrm{Cu} & \\ & | & & \\ & \mathrm{Cu} & & \end{array}$$

Again from stereochemical considerations structure (III) is more probable than structure (IV). It can be seen, therefore, that less sulphur is required to enter into combination with copper in reaction (3) than in reactions (1) and (2), and that, consequently, bad bonding brasses will be characterised by excessive sulphide formation. By the same reasoning, reaction (2) will be more likely to occur when fast curing stocks are vulcanized against brass, because of rapid saturation with sulphur at the reactive double bonds.

Stuart has also observed(35) that a sulphide film is formed on the brass surface in spite of the oxide film initially present and that this film acts as the actual adhesive between metal and elastomer. According to his observation, good and poor bonding brasses differ in that they form different types of sulphide but he was not able to characterise these films further or to differentiate between structural differences of areas on the brass surface with good and poor properties due to the lack of suitable techniques.

The advent of sophisticated laboratory equipment in the early 1970's has enabled researchers to study the surface composition and structure of brass and brass-plated tyre cord a great deal.

Ooij was the first to apply the ESCA (Electron Spectroscopy for Chemical Analysis) technique to analyse the brass sheet, brass-plated steel cord and rubber-brass interfaces. Although most present day applications for the brass-to-rubber bond involves the use of brass-plated steel wire or cord, Ooij used 0.5 mm brass sheet at well defined surface composition which could be bonded to rubber and separated smoothly under liquid nitrogen. Figure 1.9 shows the bonding specimens and method of preparation.

The properties of the brass coating on steel cord or wire cannot really be imitated adequately by using massive brass sheets because:

1. The brass coating on cord is more deformed and contains lattice defects and a different texture(36).
2. The high curvature of the brass-plated filament probably increases their reactivity in corrosive media and may be different for different filament diameters(37).
3. The cords contain lubricant residues which may affect the adhesion between wire and rubber(38).

But Ooij claims that the trends observed by varying parameters such as compound recipes are similar to those observed when using brass-plated cord. His conclusion is probably correct on a qualitative basis and in particular is of interest in the identification of the mechanism of adhesion. However the results of interface

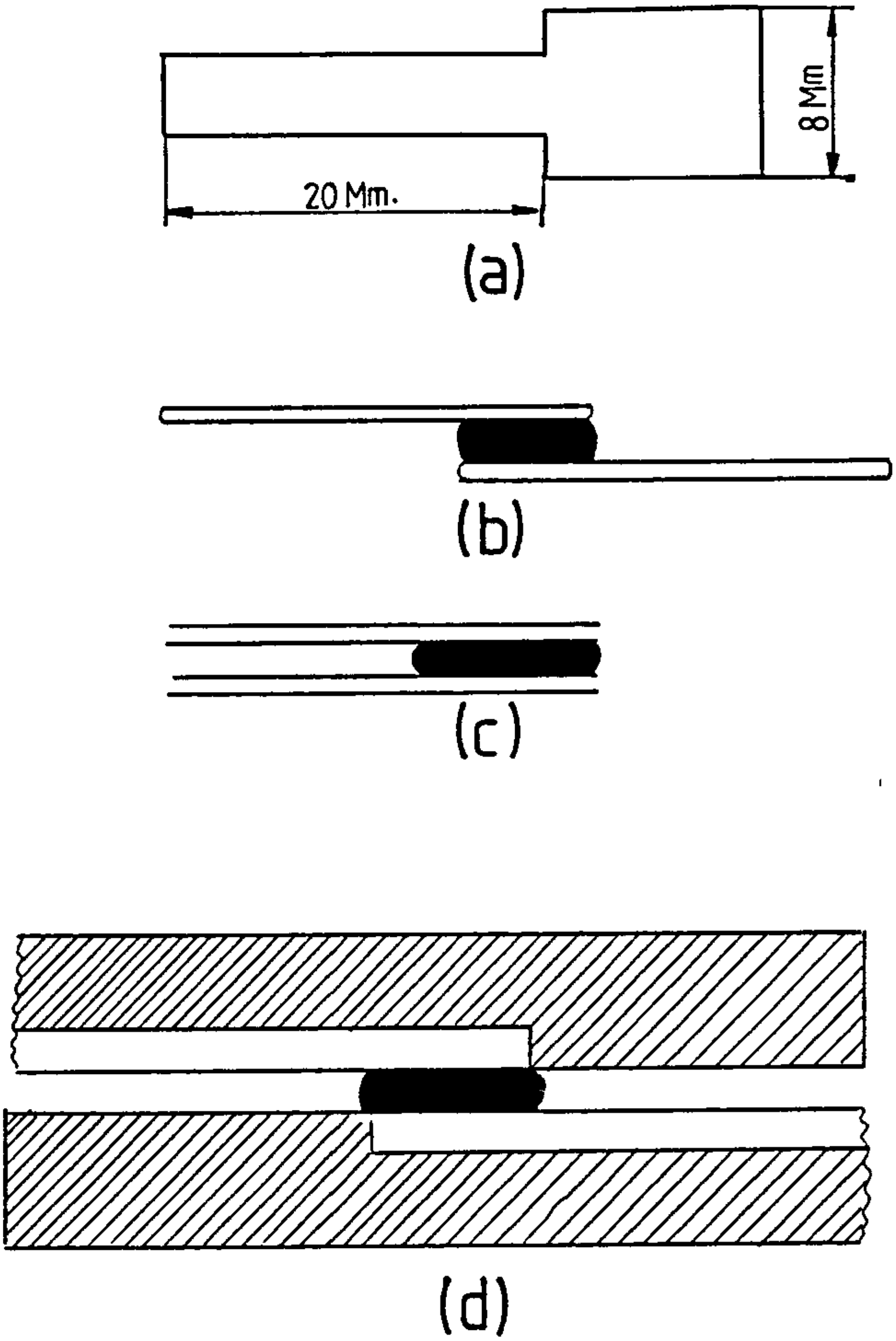


FIGURE 1.9: Preparation of Specimen (Ooij Experiment)

a) Brass specimen (thin flat plate)
b) Vulcanized rubber-brass sample for interface analysis
c) Vulcanized rubber-brass sample for adhesion test
d) Test fixture

analysis and depth profiling of rubber-to-brass sample are shown in Figure 1.10(39). The adhesion level was such that the bond strength would exceed the rubber strength if tested at room temperature. Therefore the result of Figure 1.10 is typical of a sample with good adhesion. Analysis of the rubber-brass interface has shown that an interfacial film of reaction product is always formed. By means of the chemical shift principle (binding energy) this layer was identified as a duplex film consisting of ZnO and ZnS at the interface-metal-interlayer and Cu_2S at the interface-rubber-interlayer. The ESCA measurements indicate that adhesion is a bonding between a Cu_2S-coated brass surface and rubber(40). No other chemical state of copper (e.g. CuS or Cu-S-rubber bonds) was observed. Haemers(41) has evaluated the same observation that during the vulcanization, a stable bond has to be obtained between the brass coating and rubber. This bond must be at its optimum when the rubber reaches its optimal properties with increasing vulcanization time at given temperature-pressure conditions. During vulcanization the free "S" decreases, while, the cross-linked sulphur (poly-di or mono sulphide) increases; simultaneously there occurs a gradual increase of sulphides on the cord side and an increasing amount of Cu at the rubber side, this is the adhesion process. The detected "S" on the cord side has been identified as Cu_2S, by X-ray diffraction. In Figure 1.11 some events occurring during the vulcanization are summarised.

Modelling. Some modelling experiments have been performed on copper plates immersed in a paraffin bath containing sulphur(40)

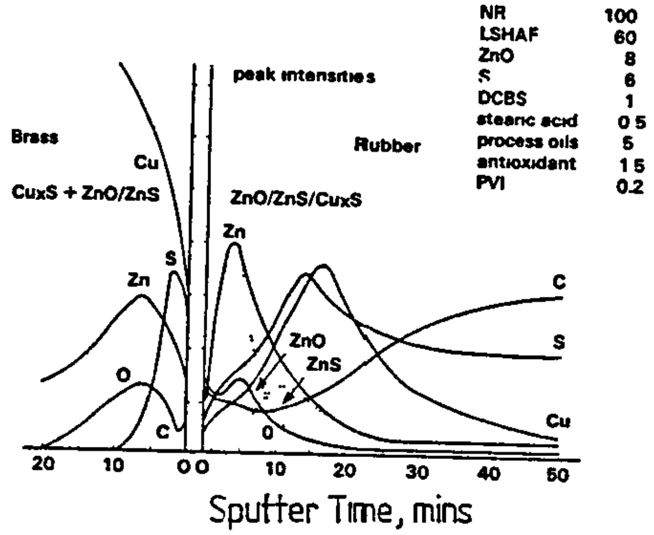


FIGURE 1.10: Analysis by XPS and Argon Ion Depth Profiling of Rubber-Brass Interface; Compound as Indicated; Polished brass of 65/35 Composition, Cured 25 mins at 150°C; Sampling broken in liquid nitrogen, 1 min of Argon Ion Sputtering Corresponds to 2 nm Material Removed (39)

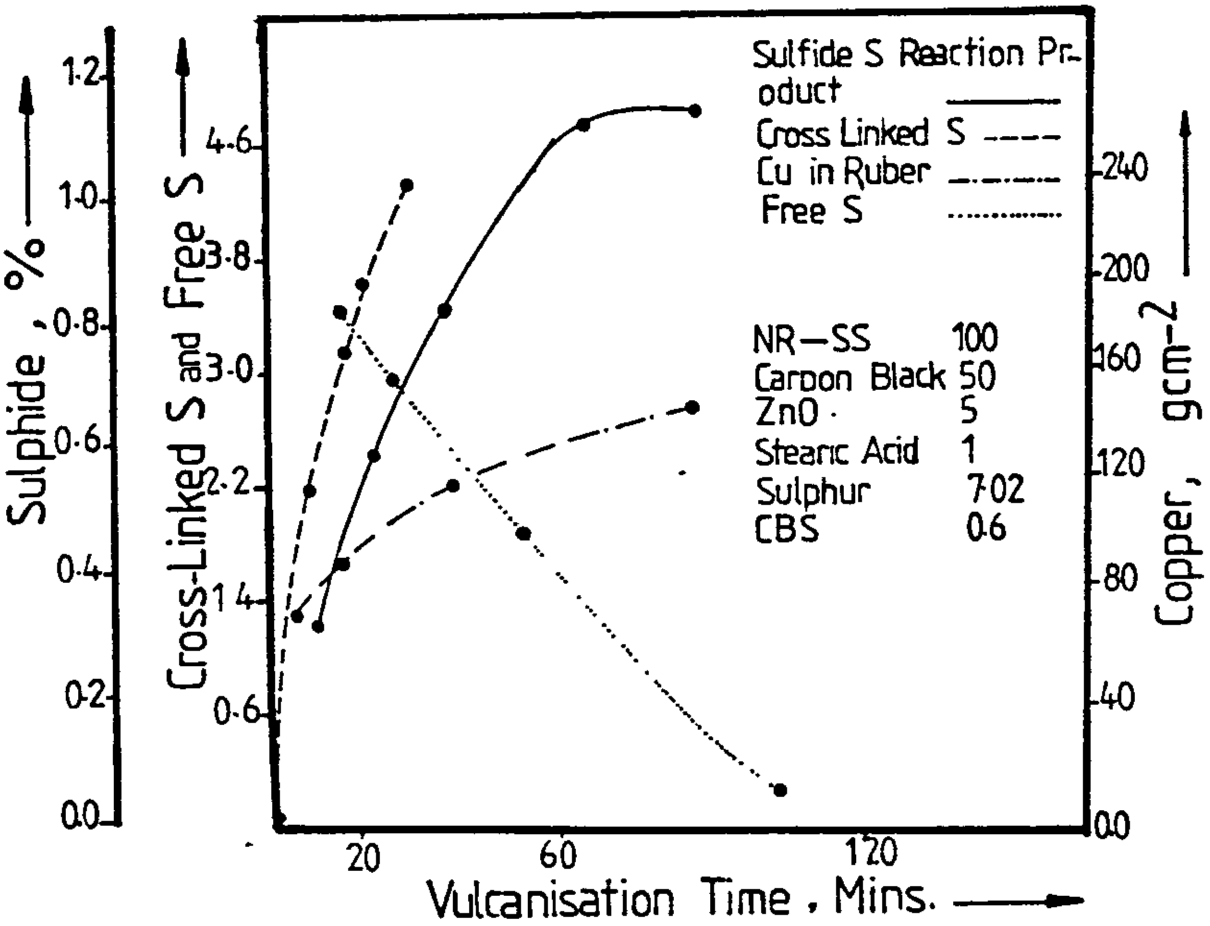


FIGURE 1.11: Change in Free Sulphur, Cross-Linked S, Sulphide Sulphur and Cu in the Rubber During Vulcanization (41)

using ESCA for quantitative analysis of thin films, identification shows that the composition of the film is Cu_xS. The $Cu_{2P_{3/2}}$ photo line observed for Cu at the interface with brass showed a negative shift when contrasted with controls based on metallic copper and Cu_2S powder, Figure 1.12. The negative shift shown in (c) and (d) of Figure 1.12 can be explained on the basis of the non-stoichiometric composition of a sulphide film grown on brass. For good adhesion the value of x in Cu_xS ought to be 1.97. This implies that the surface of the growing Cu_xS film contains an excess of sulphur atoms. In the later stages of the vulcanization the brass is corroded by O_2, OH and other groups, present in the rubber. Hence other phases are formed such as $Cu_{2-x}S$ with x gradually changing from 0.18 to 0.45.

A series of adhesion experiments were carried out with various metals and alloys which show the involvement of Cu_xS in the adhesion reaction(42). Some results are given in Table 1.5. They indicate that good adhesion is only obtained with metals which form a thin film of Cu_xS at the surface, and Cu_xS is identified as the actual bonding agent. As the films grow thicker different phases of Cu_xS are formed and this leads to a complete loss of adhesion.

The mechanism of adhesion of Cu_xS to rubber is considered an autocatalytic effect(40) i.e. during vulcanization the brass surface is corroded by sulphur which is assumed to diffuse by continuous adsorption-desorption process to the sulphide film and reaction (1.1) occurs:

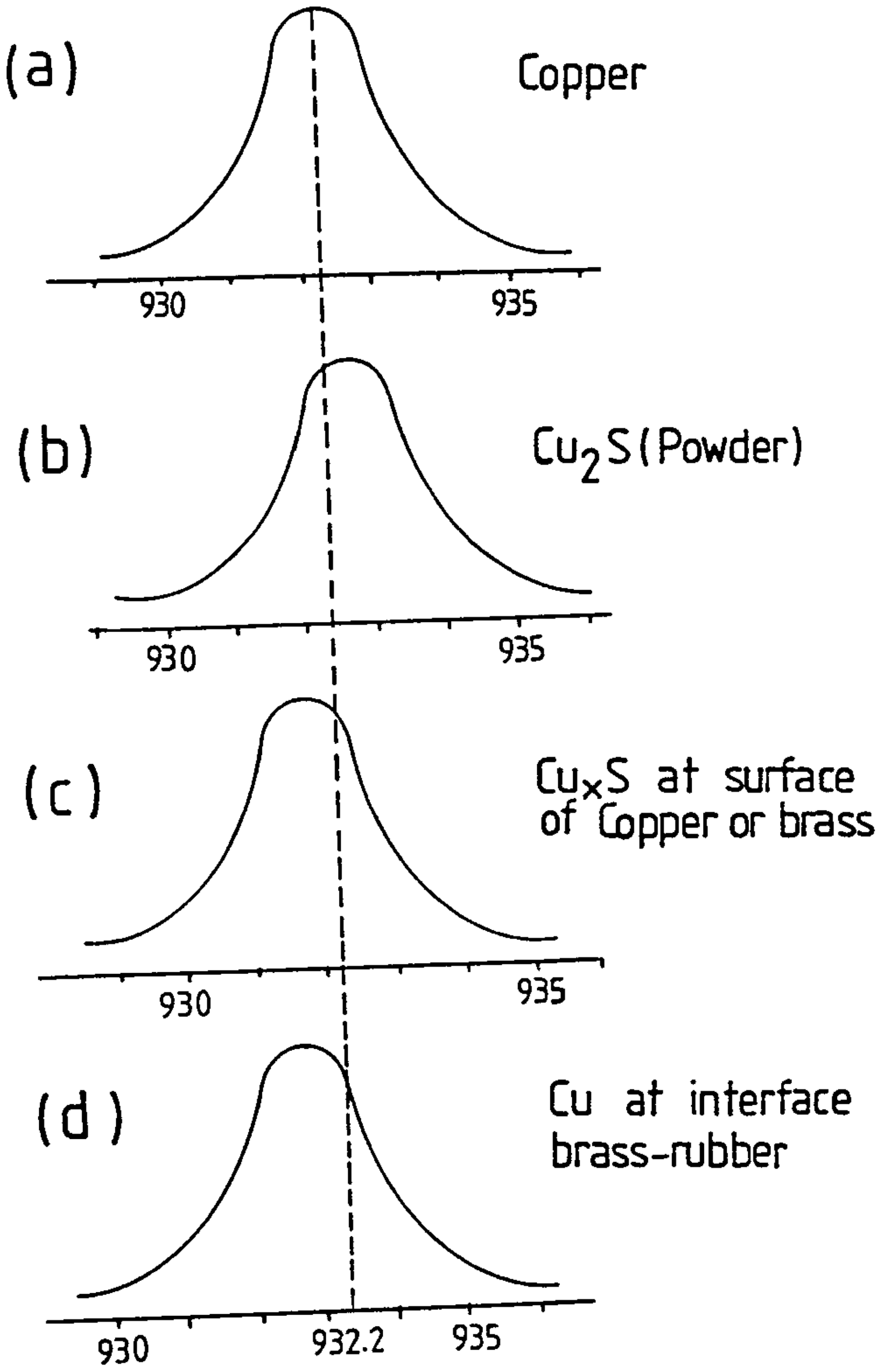


FIGURE 1.12: $Cu_{2p_{3/2}}$ Photoline in Some Selected Samples Indicating that Cu at the Interface (see (d)) of Brass-rubber is in the Form of Cu_xS (see (c))

TABLE 1.5

Adhesion of Various Metals and Alloys to Rubber(42)

	Material(1)	Adhesion Level (2)	XPS of Interface	Remarks
1	Iron, steel	0	-	No adhesion
2	Copper sheet	0	Excess Cu_2S	Some adhesion if undercured
3	Copper-plated steel (3)	700-900	-	Good adhesion if plating thickness <50 nm
4	Steel+Cu_2S coating (4)	700-800	-	Good adhesion for fresh Cu_2S layer (<50 nm)
5	Zinc sheet	100-200	ZnS formation	Poor adhesion
6	Copper-plated zinc (4)	700-800	Cu_2S formation	Good adhesion if plating thickness <50 nm
7	70/30 brass sheet	700-1000	Formation of Cu_2S and ZnS	Good adhesion level depends on surface preparation

1. Vulcanized at 150°C for 25 mins
2. N/64 mm^2
3. Electroless immersion plating
4. Prepared from sample 3 by reaction with sulphur in liquid paraffin at 180°C

$$S + 2e^{-} \rightarrow S^{--} \qquad (1.1)$$

and also at the sulphide-metal interface the reaction (1.2) takes place

$$2\,Cu \rightarrow 2\,Cu^{++} + 2e^{-} \qquad (1.2)$$

As Cu_xS grows, it participates in the rubber vulcanization leading to high rubber surface polarity. This polar surface bonds to the cuprous sulphide-coated surface by physical interaction (physical bonding). Figure 1.13 shows schematically the film grown of Cu_xS and its adhesion to rubber during the vulcanization process. This theory is in good agreement with the effect of temperature on the bond strength of rubber to brass(32) where low temperatures give high bond strength and vice versa.

The mechanism of adhesion of rubber to brass can be summarized as follows: the formation of Cu_xS is necessary for good adhesion, and the total amount of Cu_xS should not exceed a certain value at the end of vulcanization process. Since we are dealing with the formation of a crucial film thickness, all factors which may accelerate or retard sulphide formation will thus affect the adhesion performance.

1.2.5 Parameters which Affect the Adhesion of Rubber-to-Brass

As mentioned in the previous section, the bonding of rubber-to-brass involves the formation of Cu_xS and bond strength depends on the

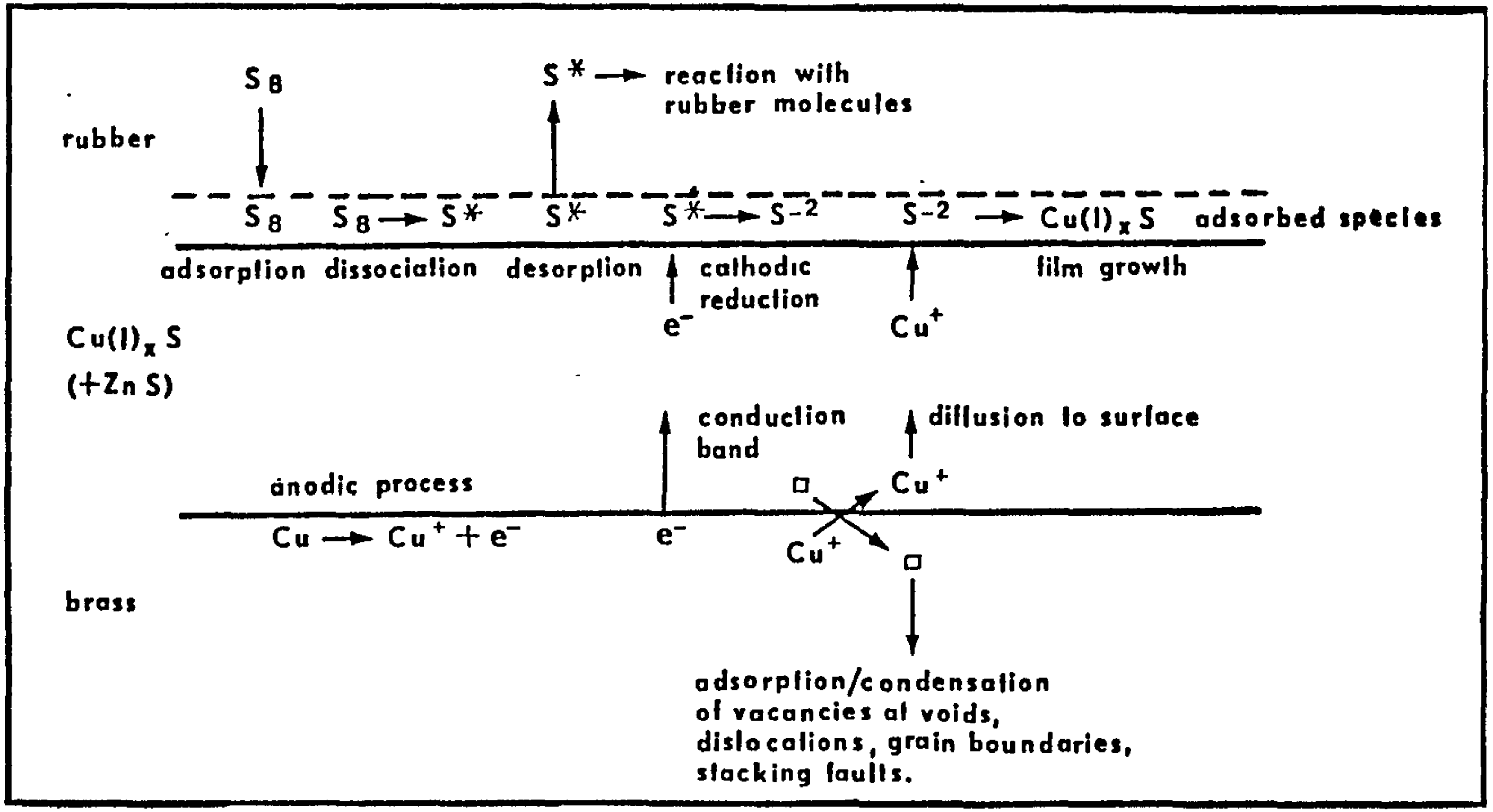


FIGURE 1.13: Reaction at Rubber-Brass Interface During Vulcanization (40,42)

Cu_xS film thickness. The parameters which affect the rate of Cu_xS formation therefore, will have an effect on the bonding phenomena.

1.2.5.1 Effect of Brass Surface Parameters

Copper Content

The most obvious parameter which determines the rate of cuprous sulphide formation is the copper content of the brass alloy. As stated before, several authors have observed that poor adhesion is accompanied by relatively large amounts of copper sulphide formation which results when too high a copper contents occur at the brass-rubber interface. Maeseele and Debruyne(43) have studied the effect of copper content in the brass and observed that the optimum copper content of a brass coating of constant plating thickness to give maximum adhesion depends on the rubber compounds. 65-72% of copper content will usually give good adhesion with most types of rubber compounding practice.

The effect of copper content on the sulphidisation rate of brass has been investigated by Ooij(40). His experiment is based on sulphidisation of brass sheets of different copper concentration in a paraffin medium at 180°C, see Figure 1.14. The experimental curves show a pronounced dependence of sulphidisation rate on copper content. As can be seen as the copper content increases, the rate of reactivity deviates from linearity. This effect is probably caused by differences in oxide formation.

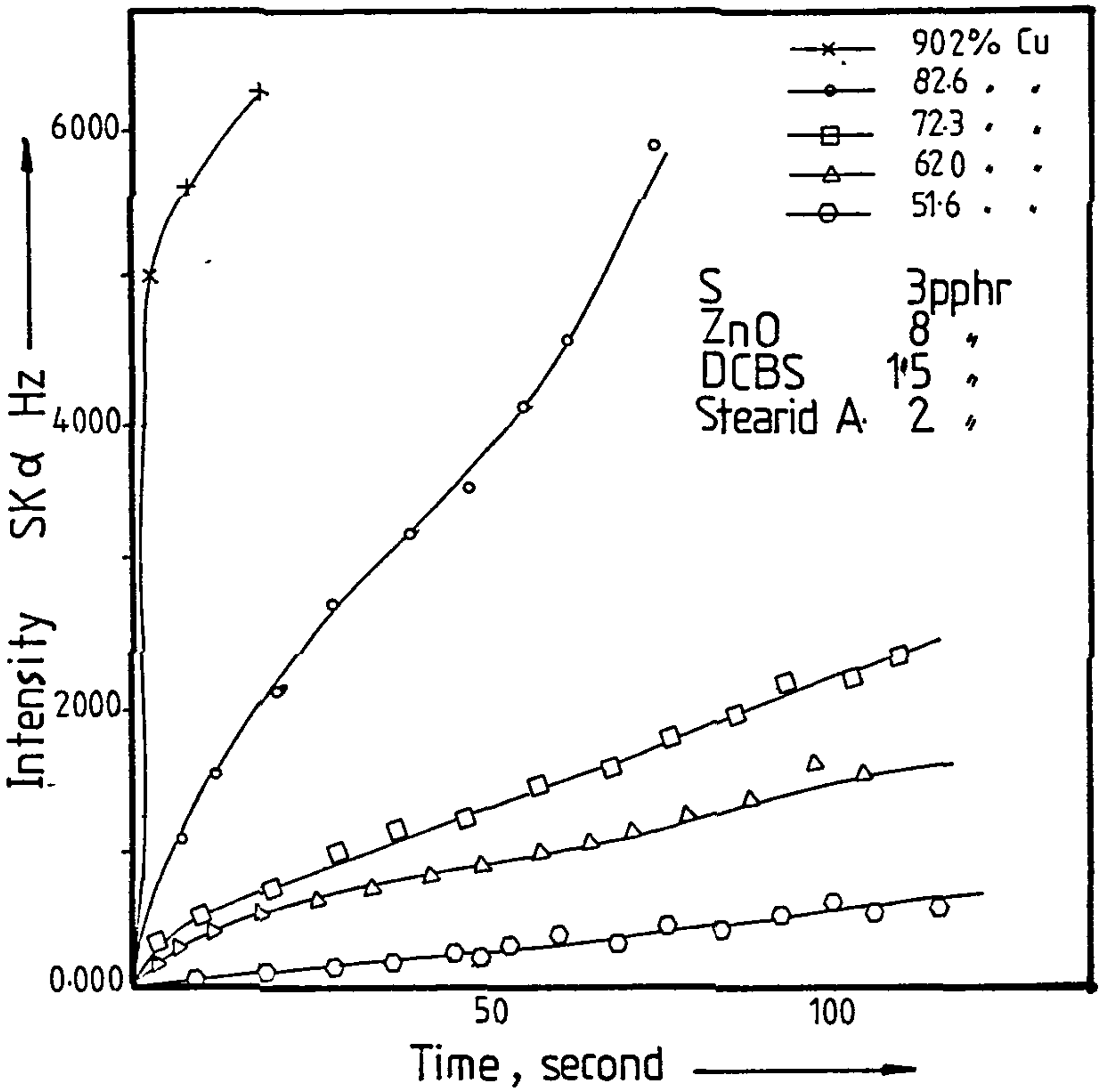


FIGURE 1.14: Effect of Bulk Copper Content on the Sulphidation Rate of Brass in the Presence of the Above Reactants in a Paraffin Medium, at 180°C (40)

Plating Thickness

The brass-plating thickness may have a pronounced effect on the adhesion. This effect is, however, strongly dependent on the compound composition(43). For higher copper content (> 70%), a thin coating is required (i.e. less than 0.2 μm) and for low copper content a higher plating weight (i.e. more than 0.2 μm) is needed for optimum adhesion. A combination of low plating weight and low copper content is very difficult to bond satisfactorily. The effect of plating weights on cords are most likely caused by an increase of brass oxidation if the plating weight is reduced. This effect has been stressed by Weening(44), Murray(45) and Ooij(42). Brassed cords of 2g/Kg plating weight show a considerably lower surface copper content and a lower reactivity than cords with 8g/Kg. The underlying cause of this effect can be understood if one considers that drawing of brass-plated cords is an example of cold co-extrusion where the outer alloy (brass) can more easily be deformed than the actual material of the wire (steel). Therefore, the steel deformation produces more heat per unit of volume than brass deformation. The brass layer is not only coated onto the wire in order to confer adhesive properties, but it also improves the drawability of the steel, partly by absorbing and dissipating some of the deformation energy. If the thickness of the brass coating is reduced, its heat capacity decreases and so the surface temperature will be higher. For the cord producer this implies that in an optimized process he cannot simply reduce the plating weight keeping all other conditions constant. This may adversely affect the adhesive properties of his material. In order to restore optimum bonding behaviour, the lubricant will have to be adjusted in such a way that it will dissipate heat from the brass surface more efficiently.

1.2.5.2 Effect of Rubber Compounding

Many investigations have been done on the effect of rubber compounding variations on the adhesion of rubber to brass cord. These studies were mostly empirical and not fundamental since knowledge of the mechanism of adhesion has only recently become available. A rubber mix usually contains sulphur, zinc oxide, stearic acid, filler, accelerators, etc. The effect of some of these ingredients is to be discussed as follows.

Sulphur and Sulphur/Accelerator Ratio

It is generally accepted that sulphur is an essential ingredient for adhesion of rubber-to-brass due to its involvement in the formation of Cu_xS. As was mentioned the formation of Cu_xS is based on the corrosion of brass by sulphur. Van Ooij(40) studied the reaction of Cu or Cu/Zn (brass) with sulphur in a paraffin medium instead of rubber to eliminate the bonding reaction. Although the result obtained differs from the within rubber result, it can give useful information to the understanding of brass corrosion by sulphur and the relative effects of sulphidisation. Some typical results of the sulphidation of copper and brass by sulphur in paraffin are given in Figure 1.15. For both metals parabolic curves are obtained which indicate the rate determining step in the mechanism of film growth is the diffusion of copper atoms to the surface of the film and not the diffusion of sulphur molecules in the solution(46). Another observation is that a variation of sulphur concentration from 0.2 to 2.0 pphr has no effect on the rate of sulphidation. These results are in agreement with the model mentioned in Section 1.2.4 (Figure 1.13) that the surface of the growing Cu_xS film is completely covered with absorbed sulphur atoms.

Other literature deals with empirical findings. It was found that the minimum amount of sulphur to give satisfactory adhesion is 2 pphr. Ayerst(47) observed that up to at least 10 pphr of sulphur gave a high bond strength. He also demonstrated that at a constant sulphur level, the adhesion drops to a very low value as the accelerator level increases above about 1 pphr. This effect is confirmed in several publications(48,49).

Stearic Acid

The effect of stearic acid dosage on adhesion has been studied by Hicks and Lyon(50). They reported a well-defined optimum stearic acid of 2 pphr for thiazole accelerated systems. Van Ooij(40) found that up to 2 pphr stearic acid markedly accelerated the rate of brass sulphidation in a paraffin medium (the model mentioned earlier). The omission of stearic acid was found to have two effects: first, that the zinc oxide particles in the reaction mixture are no longer

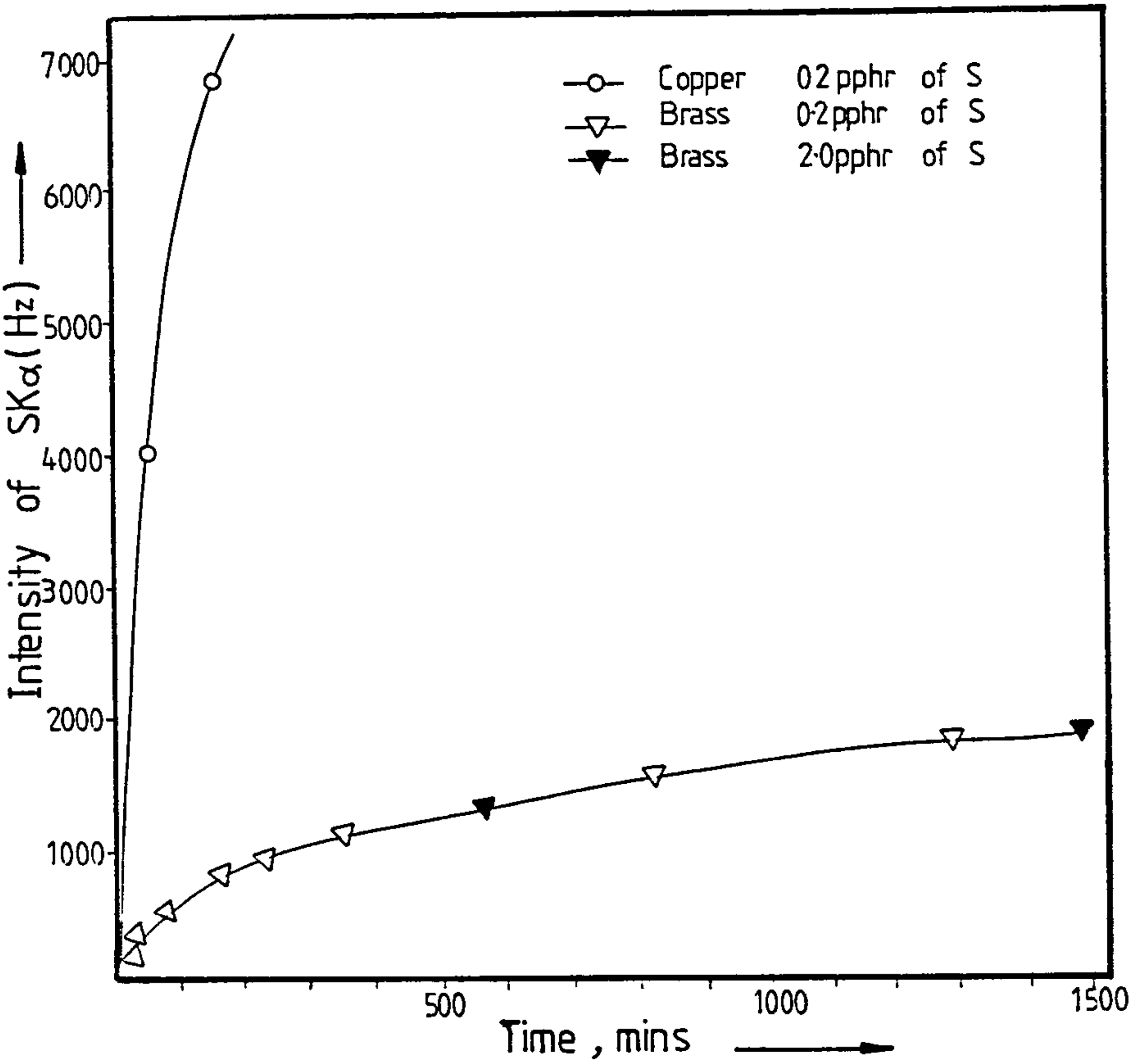


FIGURE1.15: Sulphidation of Copper and a 65/35 Cu/Zn (Brass) by Sulphur in Paraffin Medium at 180°C (40)

suspended and tend to settle; second, the rate of sulphidation is decreased markedly. Also it was noticed that the curve deviates from linearity which indicates a different growth mechanism. Consequently, it was also found that the addition of stearic acid to a sulphidation mixture has two effects: it is adsorbed by the ZnO particles via the polar groups in the molecules thus keeping the ZnO particles in suspension; on the other hand, the corrosion of brass by sulphur is noticeably accelerated due to the effect of stearic acid on brass corrosion(46).

Zinc Oxide

A few authors have studied the effect of ZnO loading to rubber-brass adhesion. Rutz(51) in his experiments concluded that some ZnO, about 3 pphr, is required for activation of the cure system. Any additional ZnO had little effect on adhesion. Hick and Lyon(52) reported an optimum ZnO content of 15 pphr. Quantitatively a 10% gain in adhesion resulted when the ZnO content increased from 4 pphr to the optimum level. Ulbrich and Backhaus(53) state that adhesion to metal is influenced by the shape and purity of the zinc oxide as well as the degree of dispersion. Zinc oxide particles have traditionally been described as being acicular, molecular, or round because of their appearance under the optical microscope. A statistical study of the effect of ZnO was recently reported by Carpenter(54). He concluded that the adhesion increased with ZnO loading especially for cures longer than the optimum cure, Figure 1.16. He comments that when there is not enough ZnO in the compound

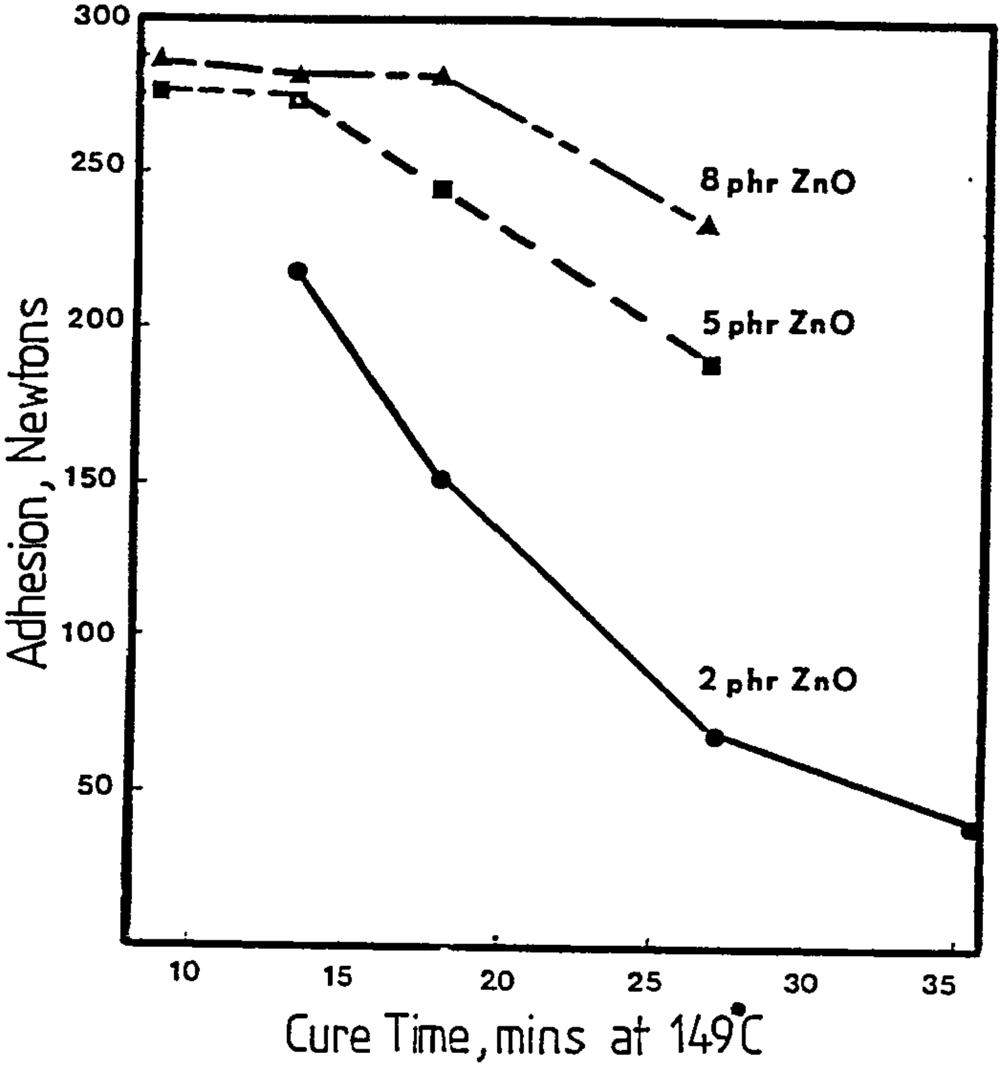


FIGURE 1.16: Adhesion as a Function of Cure Time and ZnO Proportion

for vulcanization, then ZnO on the brass surface will be used so adhesion decreases because it has been known that the ZnO controls the Cu_xS formation. When ZnO is available in the rubber, the attack on the ZnO layer on the brass is reduced and adhesion increased.

He also shows that decreasing the particle size of ZnO will increase the adhesion. This effect is considered due to the small particle size of the ZnO increasing the availability of ZnO so the ZnO on the brass surface will not be used. This effect is shown schematically in Figure 1.17 where the upper part of the figure represents compounds containing large ZnO particles, the lower part of the figure represents compounds containing small ZnO particles. Vulcanizing agents are considered to react with the closest available ZnO particle. Both dashed lines in Figure 1.17 represent a division between rubber-wire. Above the dashed line, vulcanizing agents will react with particles in the rubber. Below the dashed line, they will attack the ZnO layer on the brass. A comparison of the area under the dashed line is probably a good indication of the severity of the attack of the ZnO layer and consequently, the level of adhesion.

Van Ooij found no effect of ZnO type or concentration on the rate of brass sulphidisation in his paraffin medium reaction, if the mixture contained no stearic acid. If the mixture did contain stearic acid, addition of some ZnO led to a higher rate of brass sulphidisation(40).

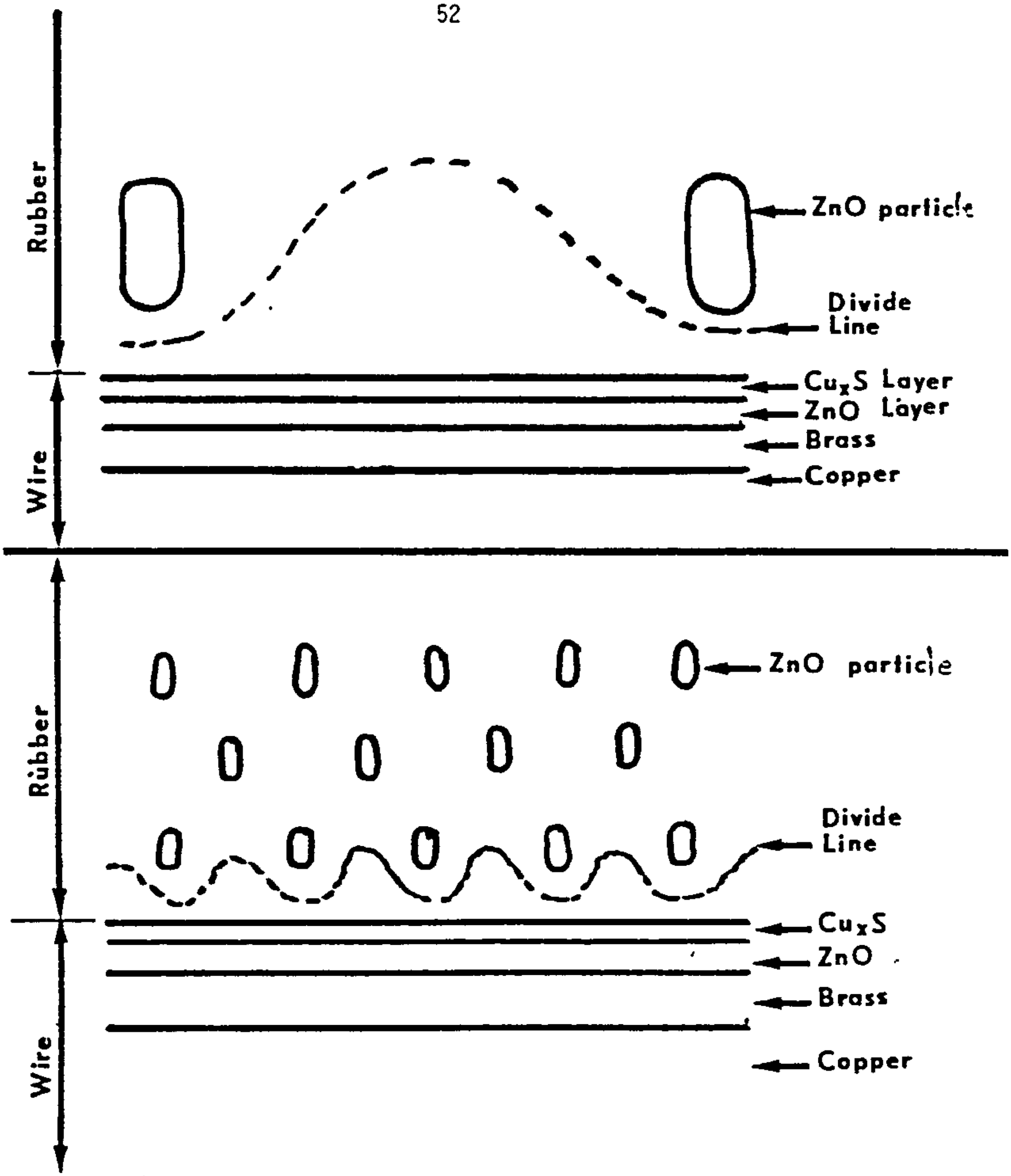


FIGURE 1.17: Schematic Drawing of Wire-Rubber Interface Using Large ZnO Particles (Top) and Small ZnO Particles (Bottom) (54)

Accelerators

Sulphenamide type accelerators are the most widely used for bonding of rubber to brass-plated cord since it has been reported that a sulphenamide accelerator gives high adhesion. Bertrand(55) compared 10 accelerators and concluded that only the sulphenamides CBS, TBBS, MBS and DCBS can give high bond strengths. Albrecht(48) explained the good performance of sulphenamides on the basis of their longer scorch times, which resulted in a better wetting of the metal surface. He also reported that higher doses of sulphenamide will increase the rate of cross-linking and reduce the scorch time so adhesion should be reduced. Other publications(56) confirm that there will be a reduction in adhesion at levels of accelerator higher than 1 pphr, Figure 1.18. The ultra-accelerators such as ZDEC, TMTM, or TMTD, even if added in small amounts or in combination with sulphenamide accelerators lead to very low bond strengths. Hicks(50) suggested a qualitative adhesion rating of these ingredients given in Figure 1.19.

Van Ooij has studied the effect of sulphenamide accelerators on the rate of sulphidisation. He explained that sulphenamide-types have a pronounced effect on the sulphidisation reaction. They initially retard the reaction, but in a later stage an acceleration is observed(40). These results indicate that the accelerator is initially an inhibitor of brass corrosion by sulphur, probably as a result of a strong adsorption at the Cu_xS surface.

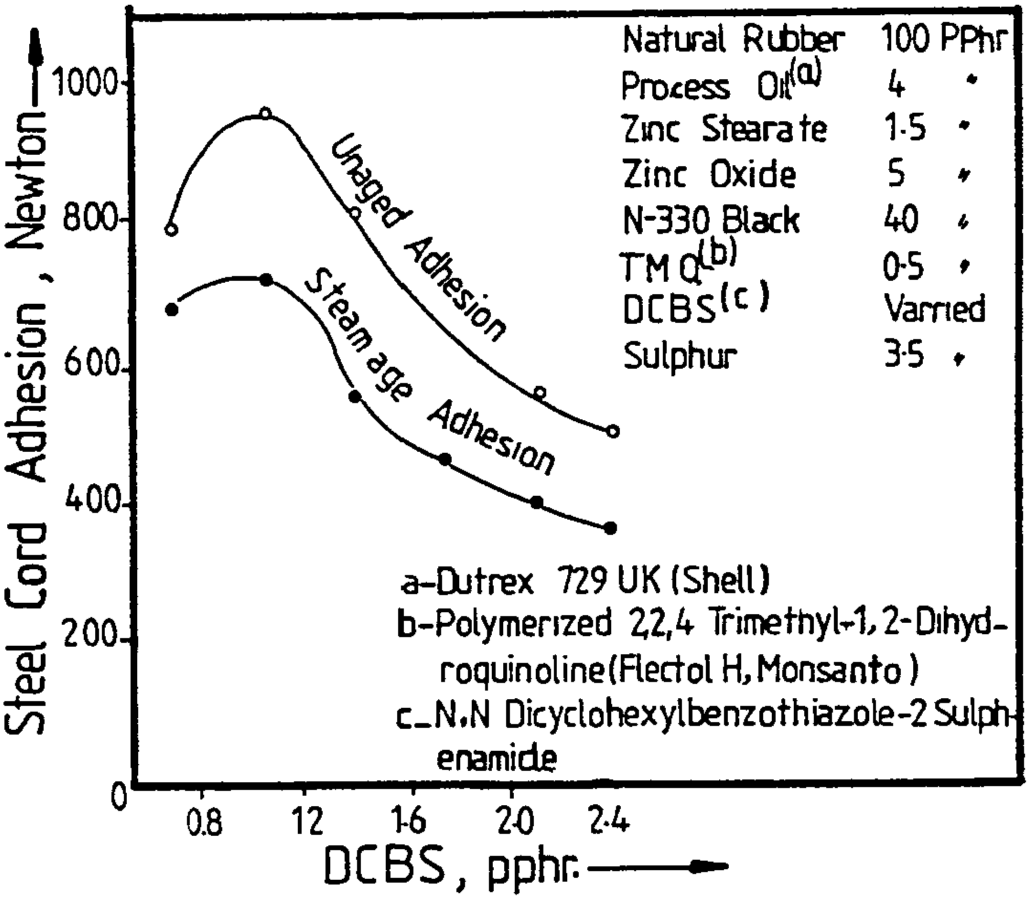


FIGURE 1.18: Effect of DCBS Accelerator on Adhesion (56)

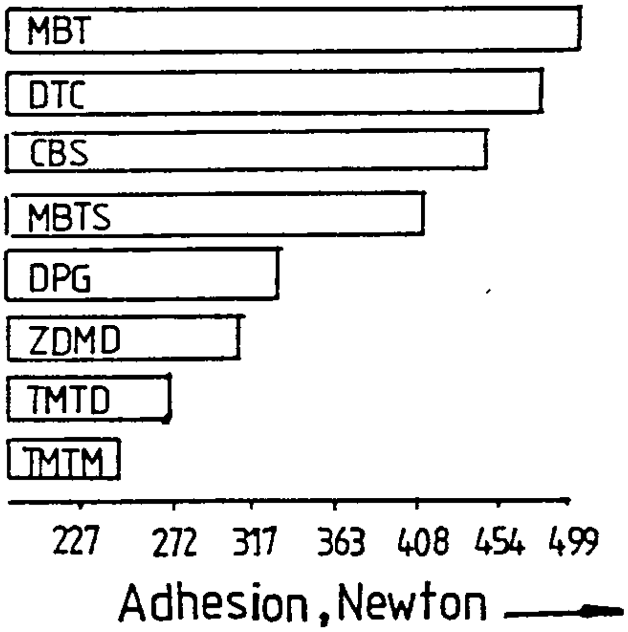


FIGURE 1.19: Accelerator Rating for Rubber/Brass Adhesion

Fillers

Filled rubbers generally have better adhesion to brass than unfilled rubbers. Each filler has an optimum loading for maximum adhesion usually giving in the range of 50-75 compound hardness (IRHD). Carbon black is the preferred loading or reinforcing agent for rubber when it has to be bonded to brass. It has been found that increasing carbon black proportions always increases the bonding of rubber to brass up to an optimum level and the bond strength depends upon the type and properties of the carbon black. Its first effect is by altering the rate of vulcanization in a direction that favourably affects the competing reactions of the rubber and brass for sulphur and second, it increases the reinforcementof the rubber. Hick and co-workers(50) published a comprehensive study of carbon black loading and properties on the adhesion. Above 50 pphr, additional black hardly affects adhesion (Figure 1.20). Black properties such as dispersion, structure, porosity, activity, sulphur content, and concentration of volatiles were all found to affect adhesion quite noticeably. Hicks(52) explained these effects on the basis of the well-known effect of black properties on compound stiffness and, inasfar as volatiles were concerned on the pH of the mix. Poyarkova, Maloenko and Timofeeva also reported that the pull-out force increases with carbon black loading, reaching an optimum at 50-60 pphr(57). They found that at this loading the type of black had no marked effect. In a technical bulletin published by Monsanto it is reported that the type of carbon black has only a small effect on adhesion, but can have a major influence whenever certain adhesion promoters are used(49).

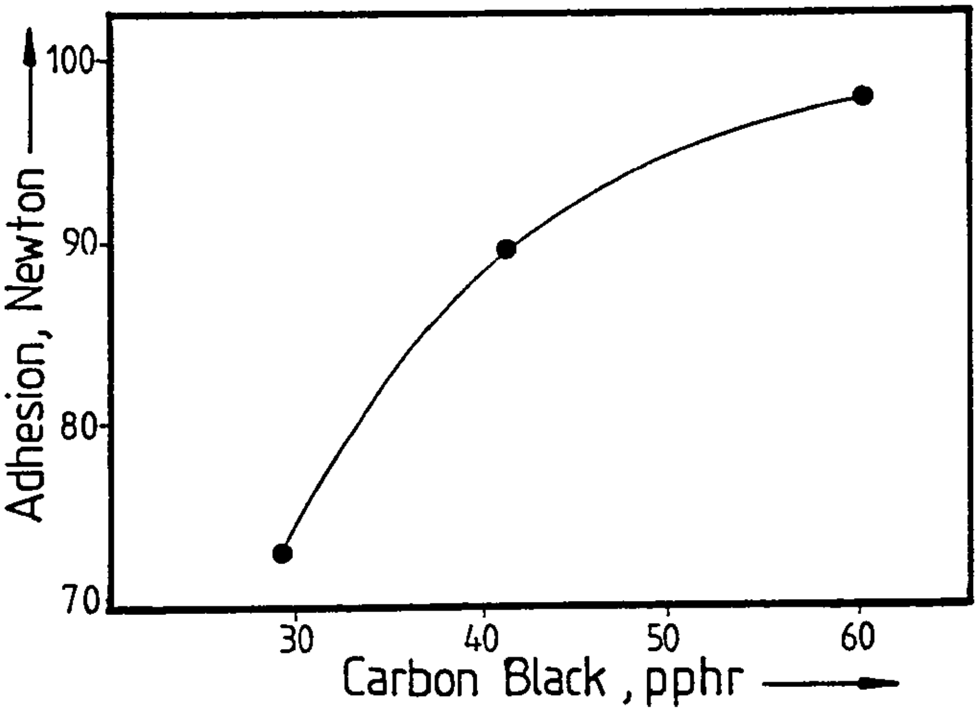


Fig.

FIGURE 1.20: Effect of Carbon Black Loading (HAF) on the Bond Strength of Natural Rubber to Brass-Wire (50)

Van Ooij was unable to detect any effect of low structure HAF black on the rate of brass sulphidisation in a DCBS system(40). On the other hand, the presence of HAF black increases the overall rate of reaction between rubber and sulphur and promotes desulphuration, thus leading to an increase of cross-link efficiency (58).

The effect of silica and silicates fillers were studied by Creasy and co-workers(59). They observed that adhesion of natural rubber compounds to brass-plated wire was improved through the use of silica or silicates. The increase was only 10-30 percent, but, addition of resorcional and hexamethylene tetramine greatly improved adhesion. So silica should always be used with resorcional and hexamethylene tetramine. The increase in adhesion was claimed due to an improvement in wetting and hydrogen-bonding between the rubber compound and substrate to which it adheres(59). Van Ooij(60) argues in a different way that the NR compound with an HRH system forms the usual $ZnO-ZnS-Cu_xS$ interfacial layer, and it does not seem likely that wetting, hydrogen bond and surface energy change play a significant role in determining rubber-brass strength.

1.3 Bonding of Synthetic Rubber to Brass

Natural rubber has been used in most investigations of bonding to brass-wire. A few papers are concerned with the adhesion of synthetic to brass-wire. Generally synthetic rubbers can be divided into two general classes: those which have been developed to act as replacements for natural rubber, and those which are classed as "special purpose" rubbers. The various grades of copolymer butadiene and styrene have acted as substitutes for natural rubber, while polychloroprene, acrylnitrile-butadiene copolymer, butyl rubber exemplify the special purpose synthetics.

In order to produce qualities which will bond to brass-plating, the same general principles are followed as with natural rubber, but the proportion of ingredients must be adjusted largely by trial and error, so that the speed of vulcanization of the rubber balances the rate of reaction of the sulphur in the rubber with the brass. With styrene-butadiene rubber and acrylnitrile-butadiene the proportion of sulphur, as a percentage of the total hydrocarbon, is usually less and the accelerator content higher. In butyl rubber stocks the sulphur may be normal but the accelerator or accelerator combination is very fast curing compared with natural rubber usage. Buchan(61) compared the bond strength between natural rubber and SBR which consisted of a copolymer containing usually 70% of butadiene and 30% of styrene to brass-plated wire, under the same condition. He concluded that the bond strength was less than that obtained from natural rubber.

Generally, the rubber compounding additives play the more important role in the bonding of rubber to brass and the type of rubber is not so important.

1.4 Objectives of Present Work

The purpose of this present work is to study parameters affecting the adhesion of solution polymerised styrene-butadiene rubber (Solprene 1204) and synthetic polyisoprene (Natsyn 2200) to monofilament brass-plated wire. These parameters are as follows:

1. The effect of drawing lubricant residue on the adhesion between SBR and brass-plated wire.
2. Optimization of the proportion of carbon black (HAF) and silica (VN3) and also sulphur proportion in filled SBR, filled IR and their gum form, according to their adhesion to brass-plated wire and to mechanical properties.
3. Some recently introduced coupling agents (Titanates) may perhaps be useful as adhesion promoters hence the effect of some selected titanates on the adhesion characteristics between rubber and brass-plated wire will be investigated.

CHAPTER 2

SPECIMEN PREPARATION AND TESTING

2.1 Introduction

The present work aimed to study adhesion of rubber to brass-plated wire which finds its application in the tyre industry, much research work has been carried out on the adhesion of natural rubber to brass wire. As natural rubber is being increasingly substituted by synthetic rubber due to its high cost, it was considered useful to study the adhesion of synthetic rubber to brass-plated wire. Two different types of synthetic rubber commonly used for tyres, styrene-butadiene rubber and polyisoprene rubber were chosen for this investigation.

The techniques used for mixing, moulding, physical and adhesion testing are described in the following sections.

2.2 Materials

2.2.1 Brass-Plated Steel Wire

Throughout this work a single filament type of brass-plated wire* of 0.3 mm diameter and 5-6 g/Kg (0.3μ) thickness of brass-coating was used.

2.2.2 Styrene-Butadiene Rubber (Solprene 1204)**

This is a solution type of SBR with random structure in which the ratio of butadiene to styrene is 75/25. It was selected due to

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* Supplied by Steel Cord Limited, Spondon, Derby

** Supplied by Philips Petroleum Chemical SA, B-1000 Brussels, Belgium the relative absence of non-rubber additives, it has 98-99% purity compound to the emulsion grades of 92% purity. Due to its lower unsaturation curing being slower than with natural rubber, it requires higher accelerator levels. Solprene elastomers can be reduced in viscosity by mastication and by addition of stearic acid (see Figure 2.1).

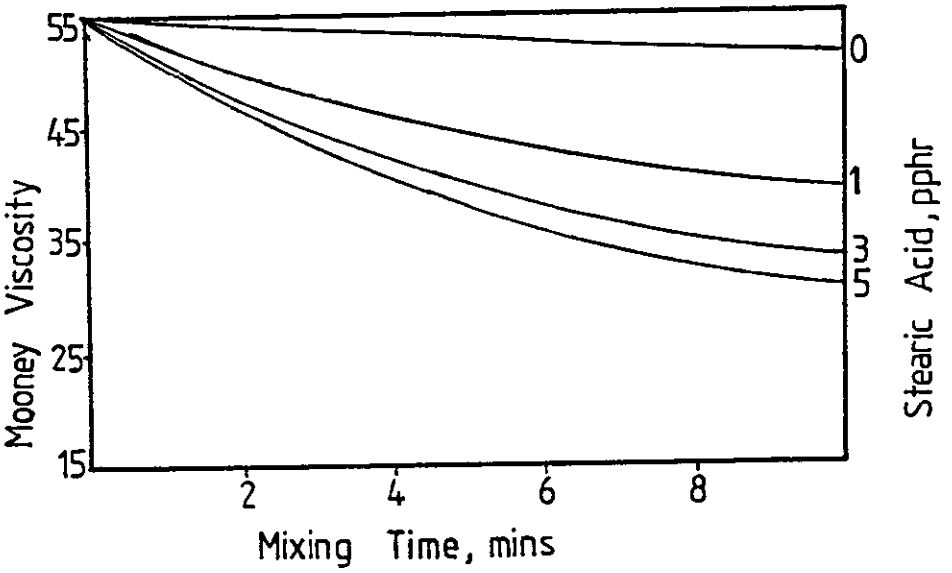

FIGURE 2.1 Polymer Breakdown Characteristics

This is an important characteristic and used to control the Mooney Viscosity. Such a breakdown is temperature dependent and can be terminated by the addition of reinforcing filler(62).

Another characteristic of Solprene 1204 is its low nerve, i.e. elastic recovery, hence it sometimes tends to bond loosely on mills and occasionally it tends to stick to the mill rollers.

2.2.3 Polyisoprene (Natsyn 2200)*

This is a high cis 1-4 polyisoprene of stereo specific structure which has a 96% cis content. The processing characteristics of Natsyn 2200 under normal mill mixing conditions forms a smooth band, usually after one minute, at which point filler and other ingredients may be added. Filler incorporation is very rapid and the minimum of cross-cutting and folding is required.

2.2.4 Fillers and Other Ingredients

The two fillers used are given in Table 2.1 with nominal values of particle size and specific surface area and their supplier's name.

Type of Filler and Commercial Name	Classification	Particle Size (nm)	Specific Surface Area m^2/g	Supplier
Carbon black HAF (Vulcan 3)	N330	29	75-88	Cabot Carbon
Silica Ultrasil (VN3)	-	11 - 19	175	I.D. Chemical (Degussa)

TABLE 2.1 Fillers Used, their Names and Properties

Other compoundings used were zinc oxide(1), stearic acid(2), sulphur(3) and N,N-dicyclohexyl-2-benzothiazole sulphenamide accelerator (DCBS)(4).

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* Goodyear Compaigne, Francaise. Goodyear BP 31-91402, Orsey.

1. Anchor Chemical Co. Ltd.
2. Anchor Chemical Co. Ltd.
3. Anchor Chemical Co. Ltd.
4. Vulcafor, Vulnax International Ltd.

2.3 Preparation of Test Specimens

2.3.1 Mixing of Rubber Compounds

Rubber (SBR) or IR) and other ingredients were compounded on a two roll mill of 850 cc capacity. SBR tended to bond loosely on the mill; it was found that mixing of SBR at 90-100°C roll temperature improves its mixing behaviour.

Addition of compounding ingredients was done in two different ways, depending on the identity of the mix. The following mixing order was used for non-silica containing formulations:

SBR → Activator (Zinc oxide/Stearic acid) + Filler (Carbon black (HAF))
→ Accelerator → Curing agent

IR → Activator (Zinc oxide/Stearic acid) + Filler (Carbon black (HAF))
→ Accelerator → Curing agent

In silica containing formulations, the activators (zinc oxide/stearic acid) were added after silica in order to avoid any silica/activator interaction as reported(63). The order of mixing used for such silica containing formulations was:

SBR → Silica (VN3) → Coupling agent (Si 69) → Activator (Zinc oxide/
stearic acid) → Accelerator → Curing agent

It was found that SBR/silica without coupling agent gives poor physical properties (see Chapter 4, Section 4.3.1).

2.3.2 Curing Characteristics

After compounding the rubber, it was stored for 48 hours to allow any unknown chemical reactions to go to completion before vulcanization occurred.

A Monsanto ODR, TM100 was used to measure curing characteristics. This instrument consisted of a die cavity located between electrically heated platens as shown in Figure 2.2. The temperature of the platens and dies are maintained to within ± 0.5°C by proportional temperature controllers. A rubber mix is placed within the vulcanization chamber so that a reciprocating biconical disc is embedded in the mix and the mix is maintained under high pressure throughout the test. The sinusoidal oscillation of the biconical disc at constant amplitude exerts a shear strain on the mix. As vulcanization proceeds the torque required to shear the mix increases and a curve of torque versus cure time is generated. The idealised forms of cure curves are given in Figure 2.3.

Scorch and cure time were calculated as follows:

Scorch time = time taken to raise torque value of 2 units above the minimum point on the cure curve

Cure time = 90 or 95% criterion was adopted calculating from the formula:

$$T_{90} \text{ or } T_{95} = M_L + \frac{(M_M - M_L) \times (90 \text{ or } 95)}{100} \text{ minutes}$$

Cure rate index = $\frac{100}{t_c(x) - t_{sx}}$ is proportional to the average slope of the cure rate in the steep region.

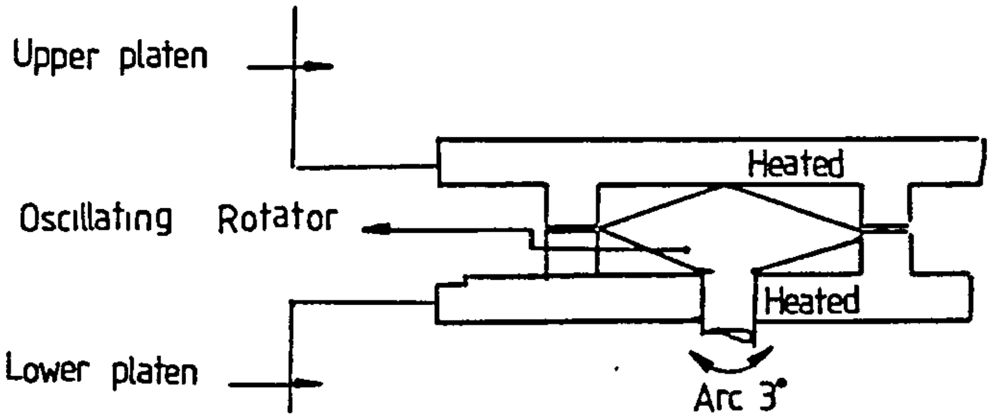


FIGURE 2.2: Basic Principle of the Monsanto ODR

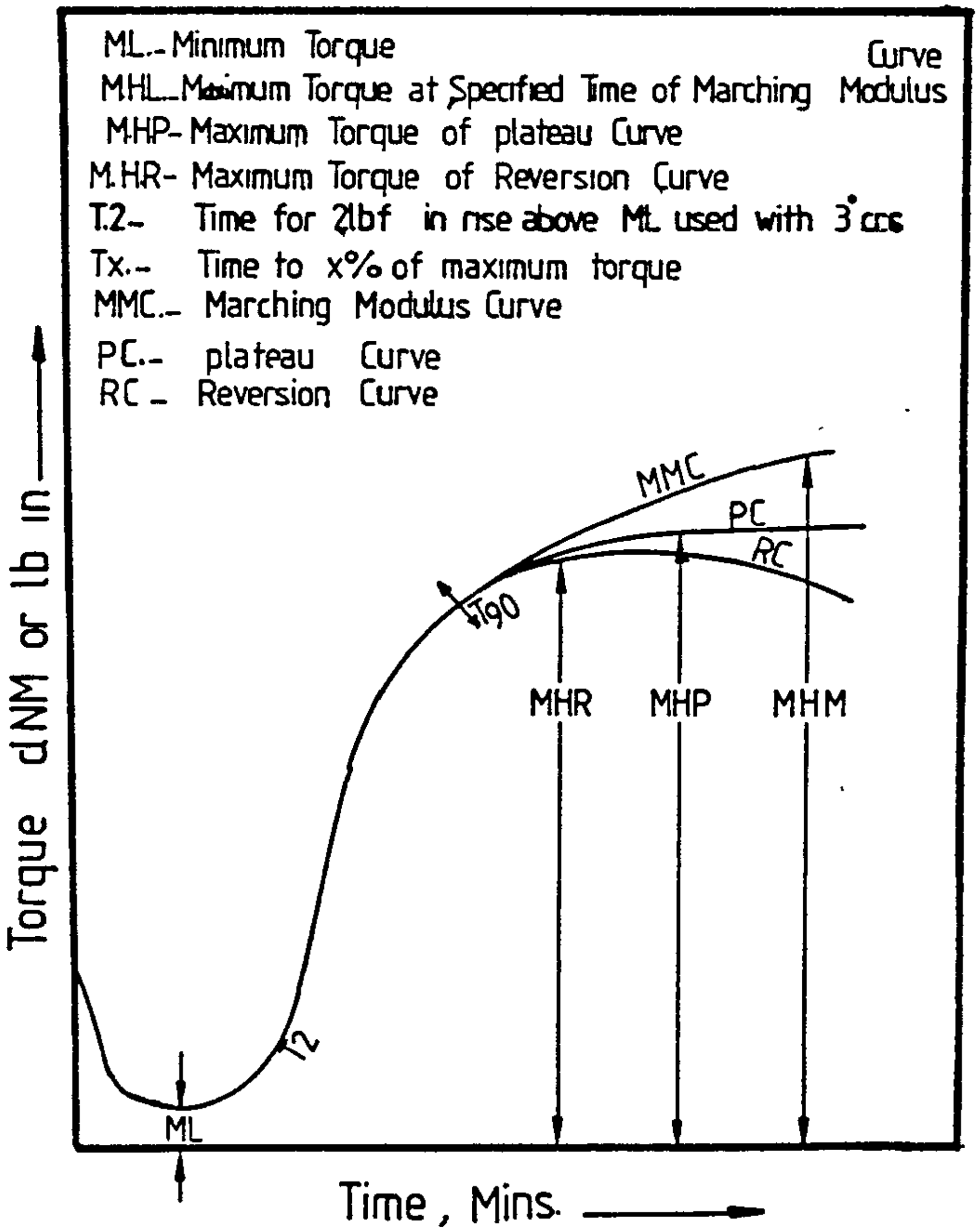


FIGURE 2.3: Typical Types of Rheometer Traces of a Rubber Compound

2.4 Moulding Methods

2.4.1 Physical Testing Samples

Vulcanized rubber sheets were prepared using a mould with 93 cm^3 cavity volume where the blank produced was 2 ± 0.2 mm in thickness. The cured sheets were stored for 24 hours in polythene bags for curing prior to testing in accordance with British Standards BS 903 procedures.

2.4.2 Adhesion Samples

Adhesion specimens were prepared using a specially designed mould (see Figure 2.4). The actual bonding of rubber to the brass-plated wire takes place in tension as a sandwich between the two layers of rubber. The roll of brass-plated steel wire used for test specimen preparation was always kept in a dessicator with dry silica gel to prevent any moisture attack. The wire was normally taken out from the dessicator just before use and moulding. A special cleaning procedure was used for both the wire and the rubber. Wiping the wire with toluene several times was necessary to give consistent results (see Chapter 3) and the final wash was with acetone to remove the last bit of contamination. Unvulcanized rubber was cut to the same shape as the mould and placed in the mould cavity so that the clean surface of the rubber had contact with the wire (it was found that using solvent to clean the rubber surface affected bond strength). Moulding was always carried out at a pressure of 20 tons/m^2 and a temperature of 170°C.

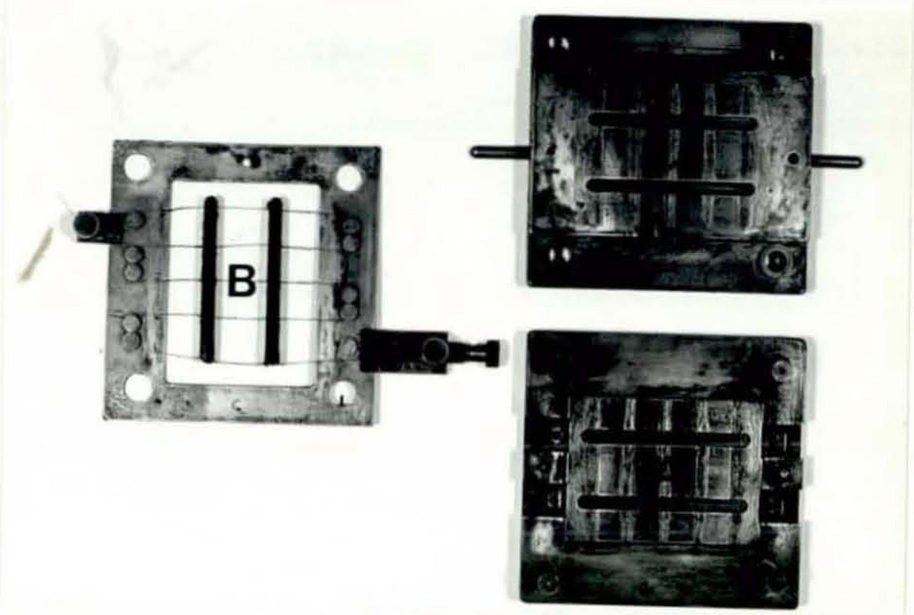


FIGURE 2.4 Showing the Compression Mould used in the Present Investigation where it Consists of Three Parts A, B and C. Those parts are Designed to Fit one Over the Other.

2.5 Rubber Testing

2.5.1 Physical Testing

For determining the vulcanized rubber compound properties, British Standard methods were employed. The JJ Tensile Testing machine of model T5002 (JJ Lloyd Instruments Ltd) was used in conjunction with an X-Y plotter (PL 100 of JJ). All tests were carried out at a speed of 500 mm/min.

2.5.1.1 Tensile strength (BS 903 A2 1971)

Two different types of specimens were used. A dumbell shape and a spherical ring shaped sample for polyisoprene due to its unusually high elongation at break, which the JJ extensometer was not able to otherwise measure.

A. *Dumbell shape*

A dumbell shape cutter was used to prepare specimens for tensile strength and elongation at break (Figure 2.5(a)). Tensile strength is calculated as the applied force per unit area of the original cross-section of the test length (unit MPa). The formula used to calculate the tensile strength is as follows:

$$\text{Tensile strength} = \frac{\text{Force to break}}{\text{Cross-sectional area}}\ \text{MPa}$$

where the force to break is the stress applied so as to stretch the test piece.

B. *Ring-Shaped Tensile Strength Specimen*

This shape was only used to measure the tensile strength of gum polyisoprene due to its high elongation which the JJ was unable to measure and a micro-dumbell shape was shown to undergo slippage in the standard grips and hence no reliable data could be obtained by this technique. Hence a micro-ring of internal diameter 23 mm and external diameter 27 mm was used and rings were cut by ring die (see Figure 2.5(b)).

Ultimate tensile strength was calculated from the recorded load at break using the following formula:

$$\text{UTS} = \frac{\text{Force to break}}{2 \times \text{Sample thickness} \times \text{Sample radial width}} \text{ MPa}$$

Sample width = 2 mm (from dimensions of cutting die)

$$\therefore \text{UTS} = \frac{\text{Force to break}}{4 \times \text{Sample thickness}} \text{ MPa}$$

2.5.1.2 Tear strength (BS 903 Part A3: 1972)

A crescent shape cutter was used for the tear strength test (see Figure 2.5(c)). In this the force measured is that required to cause a nick, cut in a rubber test piece, to extend by tearing of the rubber; the force acts in a direction substantially normal to the plane of the cut. The following equation was used to calculate the tear strength:

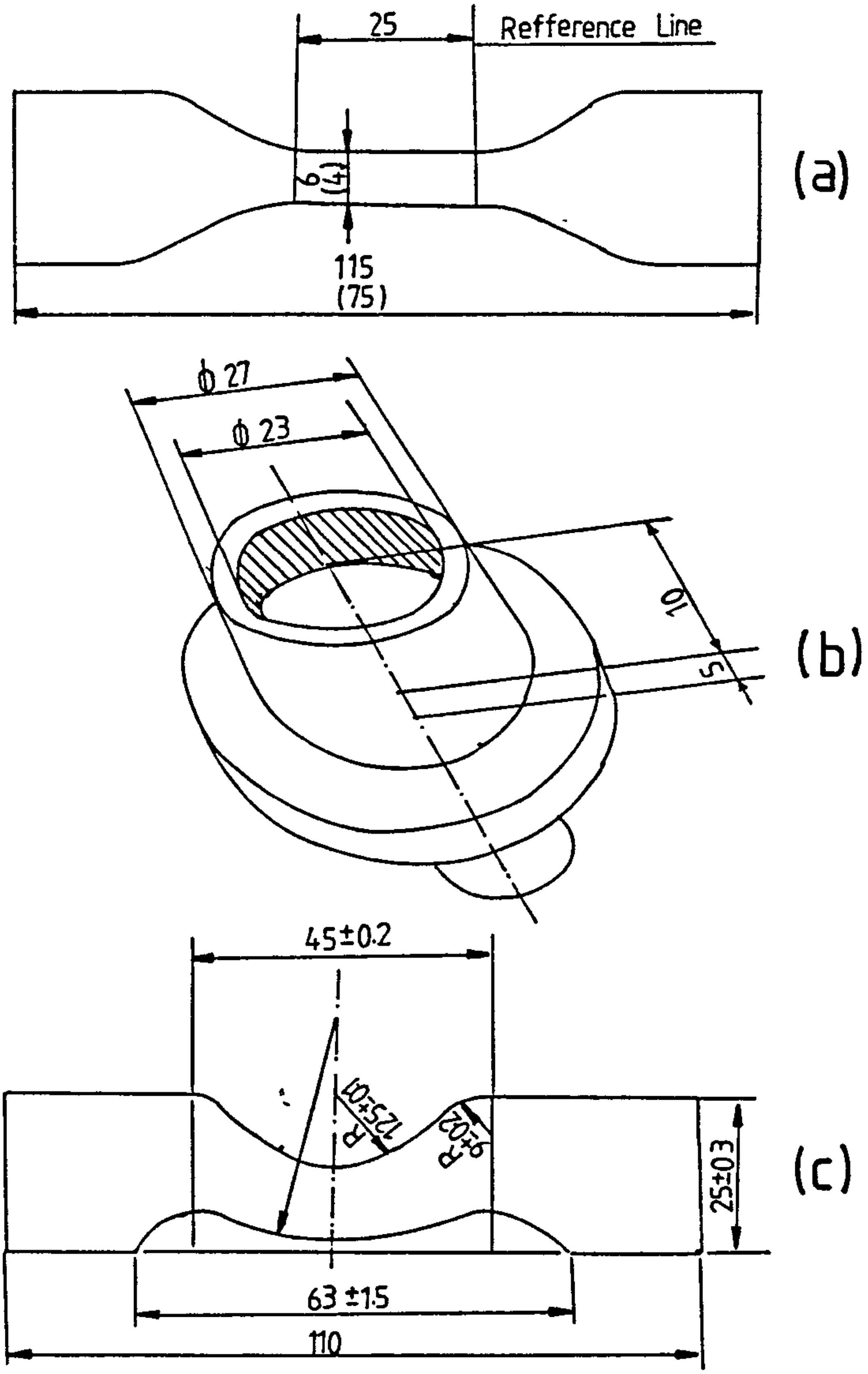


FIGURE 2.5: Cutter Design for Tensile Strength and Tear Strength

$$\text{Tear Strength} = \frac{t_s F}{t} = \frac{2F}{t} \quad (\text{KN m}^{-1})$$

$\frac{2m\ F}{t}$

where: F = maximum force in KN

t = thickness in m of test piece

t_s = standard thickness of test piece, 2 mm

KN/2mm

KN/2mm

2.5.1.3 Elongation at break (BS 903 Part A2: 1971)

A. Dumbell test piece method

In this technique elongation at break is defined as the tensile strain in the test length at the breaking point (unit %). It was calculated by subtracting the initial distance between the reference lines on the dumbell test piece from the distance between the line at breaking point.

B. Ring shape

In this the sample elongation (%) is calculated from the following equation:(64)

$$E\% = \frac{100}{M}(2D + G - M)$$

where: M = mean circumference of sample

G = constant of grip geometry (see Figure 2.6)

D = vertical separation of grip spindle centres

For grips used, G = 38.74 mm

For ring samples used, M = 78.55 mm

$\therefore$ $E\% = 2.5462D - 50.682$ (A)

where D = extension recorded on the chart (mm) (i.e. vertical displacement of grip) + 15 mm (initial setting of grip separation)

Elongation at break is obtained from equation (A) by inserting the value of D at break.

2.5.1.4 Hardness (BS 903 Part A26)

In this the modulus is measured at very small deformations, commonly by the use of a hemispherical indentor device. The apparatus used was the British Standard micro-hardness (IRHD).

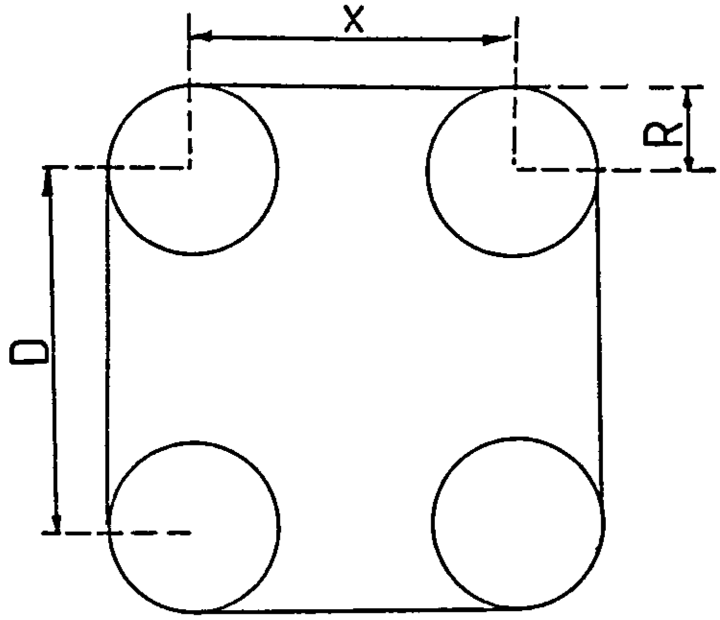
2.5.1.5 Rupture energy

This is related to the area under the stress-strain curve. Hence rupture energy was calculated by measuring the area under stress-strain curve by cutting chart paper and weighing this on an analytical balance.

2.5.1.6 Tensile product

In industry, tensile product is often used for quality control purposes as a measure of rupture energy. It can be calculated by multiplying ultimate tensile strength with elongation at break.

Tensile product = tensile strength x elongation at break



$$\text{Sample length} = 2D + 2X + 2\pi R$$

$$2X + 2\pi R = \text{Constant, } G$$

$$\therefore \text{Sample length} = 2D + G$$

FIGURE 2.6: Ring Sample Geometry Around Grips

2.5.2 Adhesion Testing

From the bonding mould described in the previous section (Figure 2.4), a bonded brass-plated steel to rubber adhesion sample was obtained, as shown in Figure 2.7(a). To prepare the samples, all the wires between the solid arrows were cut as well as cutting through all the dotted arrows. An H-shape specimen was prepared (Figure 2.7(b)). Bond strength was determined by means of a JJ Tensile Testing machine, Model T5002, using a rate grip separation speed of 20 mm/min. Special grips were used(65) for holding the H-shape samples in the tensile machine. Bond strength was calculated from the expression:

$$\text{Bond Strength} = \frac{\text{Force to rupture}}{\pi . d . \ell} \text{ MPa}$$

where d and ℓ are the diameter and the length of the wire in contact with the rubber. In addition to the mechanical strength measurement of bond strength observation, an assessment was made of the amount of rubber left attached to the surface of the wire after bond failure and this is referred to as rubber coverage. The wire was considered to have four sides (each covers 25% of the total % coverage) each of which was examined for percentage rubber coverage over the bonded areausing a stereo zoom microscope and the total percentage coverage of all four sides summed to give the rubber coverage. Figure 2.8 illustrates the different types of failures which occurred between the rubber and the wire. All bond strength results were reported as the average of 10 test specimens. A typical sequence of such photographs is shown in Figure 2.7.

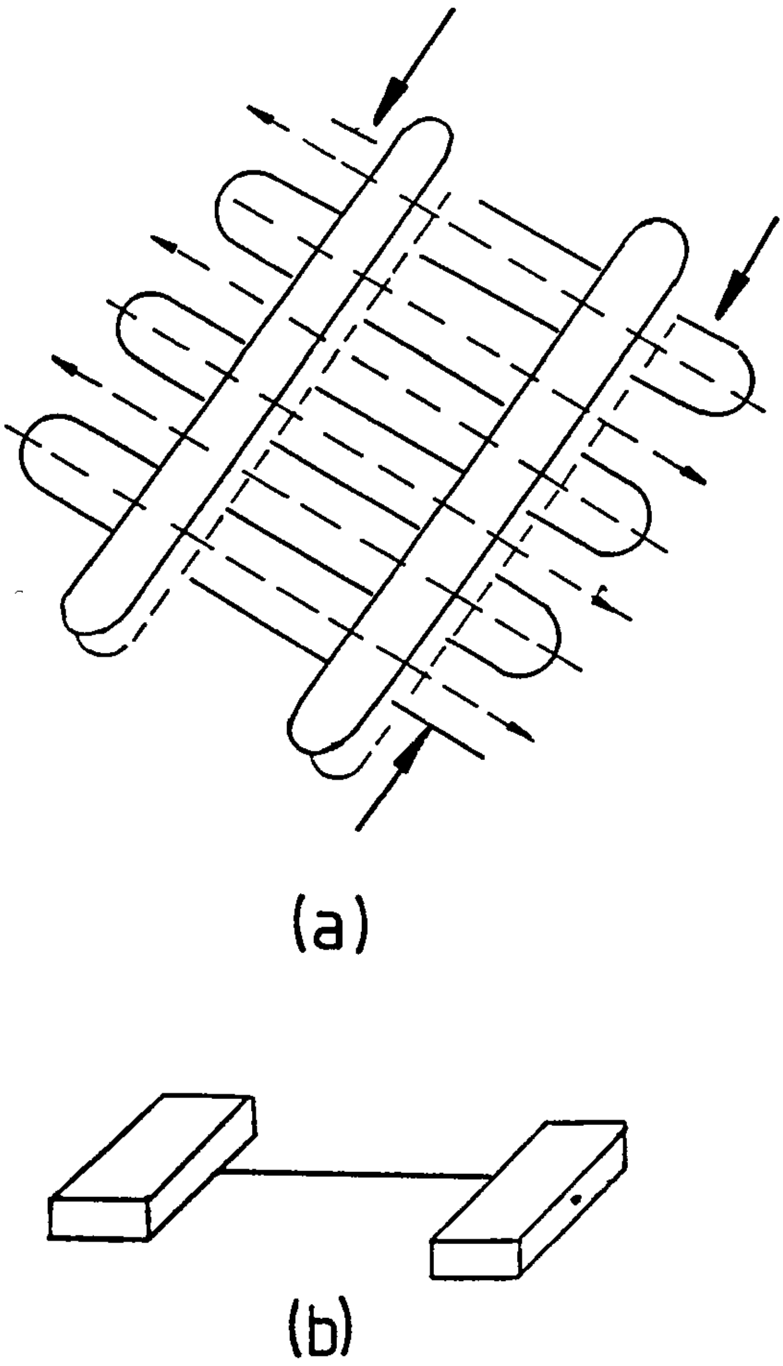
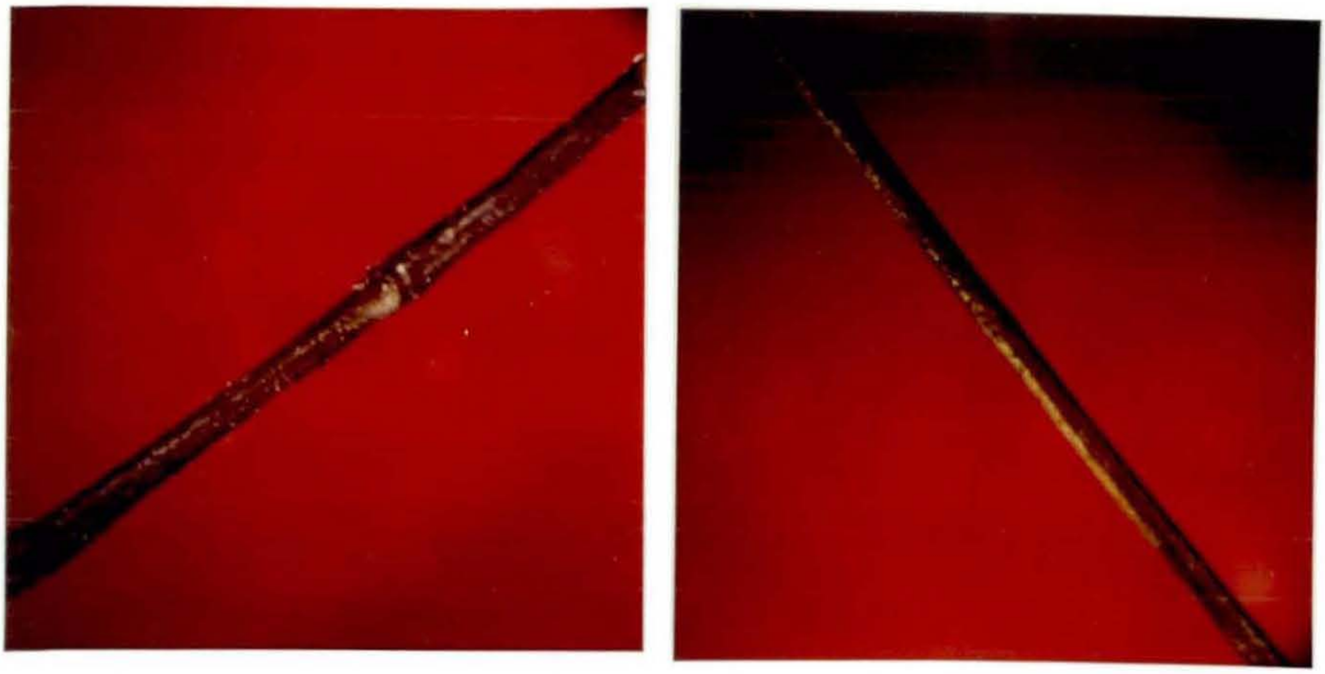


FIGURE 2.7: Showing a Test Specimen coming out from the Mould (a) By Chopping the Wire between the Arrows from Both Sides and then Cutting the Rubber Along the Dotted Line, Five Test Pieces in the Shape of (b) will be Formed

wire samples were prepared for examination by ESCA by different technique illustrated on p. 164.



(a) with rubber failure of the adhesive bond

(b) rubber brass interfacial adhesion failure

(c) partially with rubber failure and partially interfacial failure

2.8: Different Types of Failure Between Rubber and Brass-Plated Wire

CHAPTER 3

INFLUENCE OF WIRE DRAWING LUBRICANT ON THE ADHESION OF RUBBER TO BRASS-PLATED WIRE

3.1 Introduction

The adhesion between rubber and brass-plated wire is a vital factor that can be affected by many parameters. One such parameter is the residue left by the wire drawing lubricant on the surface of the wire. During the manufacture of this special wire it is essential to apply a lubricant to reduce friction heat build-up between the wire and its drawing-to-size die.

The effect which such lubricants have on adhesion can be divided into two categories. First, there is believed to occur some chemical interaction between the lubricant and the brass surface caused by the drawing process particularly when a hot drawing process is utilised. Smith(28) has observed that the wire surface during the drawing operation can become chemically activated because of displacement of copper and/or zinc metal grains to form micro-sized galvanic cells. The formation of these extremely small cells is considered the major reason for the surface of freshly drawn wire to react with lubricant with the formation of isolated dark coloured spots. The existence of such a stained area is known to inhibit the formation of a good and consistent adhesive bond between rubber and wire, as such coloured spots are not readily wetted by the hot molten rubber during the moulding and vulcanization process. The greater the number of stained spots the lower the overall bond strength. The second category is less readily defined. In this instance the physical presence of the lubricant residue on the wire surface is considered to produce bond strengths which are inconsistent, being sometimes excellent and sometimes indifferent and of poor quality. Literature reports on the effect of wire drawing lubricant on rubber to wire adhesion arrive at inconsistent conclusions. McConnel and Richards(38) determined that the commonly used wire lubricants have a negative effect on the bond strength 'pull out' adhesion forces. They also reported that there was no consistent decrease in adhesion with increasing quantity of lubricant residue and interpreted this observation as an indication that some degree of chemical reaction was occurring between the rubber and wire drawing lubricant. Equally, Haemers and Mollet(66) have found no difference in adhesion due to the presence of lubricant residue on wire.

Information published concerning typical wire drawing lubricants(26,67) show them to consist of one or several combinations of fatty acid soaps e.g. calcium or zinc stearate, triethanolamine with either a vegetable oil or mineral oil. Also the use of a special poly siloxane-ethylene oxide condensation as an anti-foaming agent has been noted*.

3.2 Experimental

3.2.1 Acetone Extraction of Wire

This experiment was done to find out which type of drawing lubricant or additives within the lubricant had been used in industry.

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* Private communication

For this purpose a quantity (100g) of the brass-plated wire was refluxed with 300 ml of analytical quality acetone for 48 hours, after which the solvent was decanted into a watch-glass and evaporated to dryness and the residue subjected to infra-red spectroscopic analysis using Pye Unicam SP 200, and, also thermal analysis using Du Pont 990 Thermal Analyser with an empty aluminium pan as a reference standard sample weight was 3 mg and the heating rate used was 20°C/min.

3.2.2 Preparation of Specimen for Adhesion Test

Examination of the uncleaned wire showed that there was no black or coloured spots on its surface visible to the unassisted human eye. However, when this wire was wiped with clean white filter paper a black deposit was obtained, presumably due to wire drawing lubricant being wiped off the wire (Figure 3.1). Due to this observation, it was decided to clean some wire prior to bonding so that it could be compared with the "as received" wire.

Cleaned wires were produced by the following procedures:

1. The wire was wiped with cotton wool soaked in cold solvent with any solvent residue remaining being removed using an acetone wash.
2. The wire was cleaned using the repeated condensation of freshly evaporated solvent, produced using a Soxhlet type apparatus. The solvents were used in sequence, toluene and carbon tetrachloride. Solvent residue of CCl_4 remaining on the wire surface was removed by using a final acetone solvent wash.

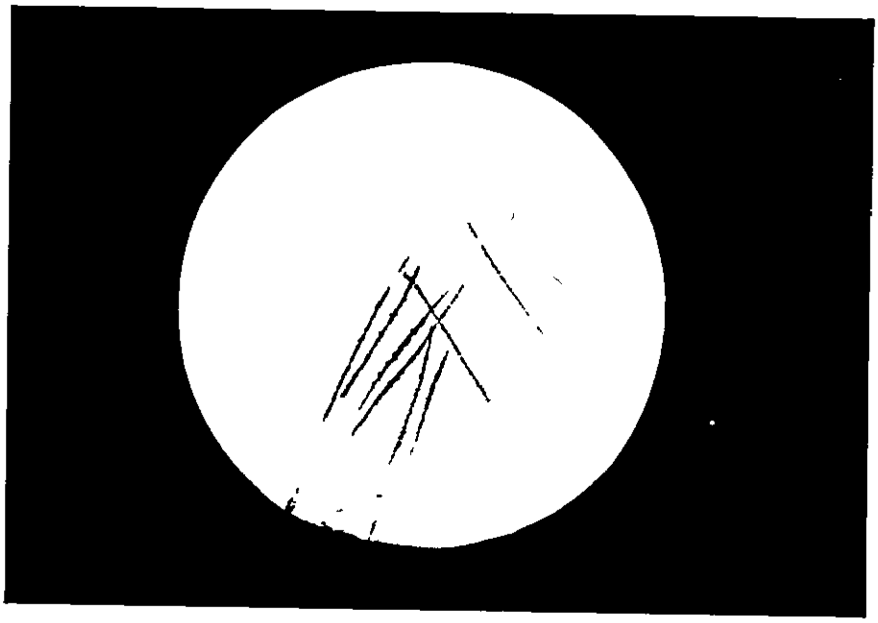
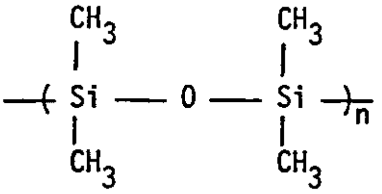


FIGURE 3.1 Lubricating Oil Resides on Filter Paper after Wiping the Wire with Toluene

3.3 Results and Discussion

3.3.1 Infra-red Analysis of Lubricant Residue

The residue of extracted wire subjected to infra-red spectroscopic analysis. Figure 3.2 shows the spectrum obtained from which the following assignations of wave-number are made: Si-O-Si at 1000-1100 $\mathrm{cm^{-1}}$ and an aliphatic group at 2900-3000$\mathrm{cm^{-1}}$. These IR spectra assignments correspond with those of Haslam and Willis$^{(68)}$ for silicones which are known probably to consist of dimethylsiloxanes whose typical structure is as follows:



$$-\!\!\left(\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{Si} \\ | \\ \mathrm{CH_3} \end{array} - \mathrm{O} - \begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{Si} \\ | \\ \mathrm{CH_3} \end{array} \right)_n$$

poly (dimethyl siloxane)

3.3.2 Effect of Lubricant Residue on the Adhesion of Rubber to Brass-Plated Wire

Bond strength and rubber coverage of ruptured bonds that are given in Tables 3.2-3.4 reveal that most of the various solvent cleaning procedures increased bond strength by about 10%. The coefficient of variation, however, between uncleaned and cleaned wire remained approximately constant at about 10-14%. Only in the case where $\mathrm{CCl_4}$ was used as a hot extract, and as the wire cleaning agent, did the bond strength decrease and the coefficient of variation increase. In this instance it is considered that the $\mathrm{CCl_4}$ solvent, although of good quality, contained some trace of chlorine impurity which attacked the brass and reduced its bonding activity.

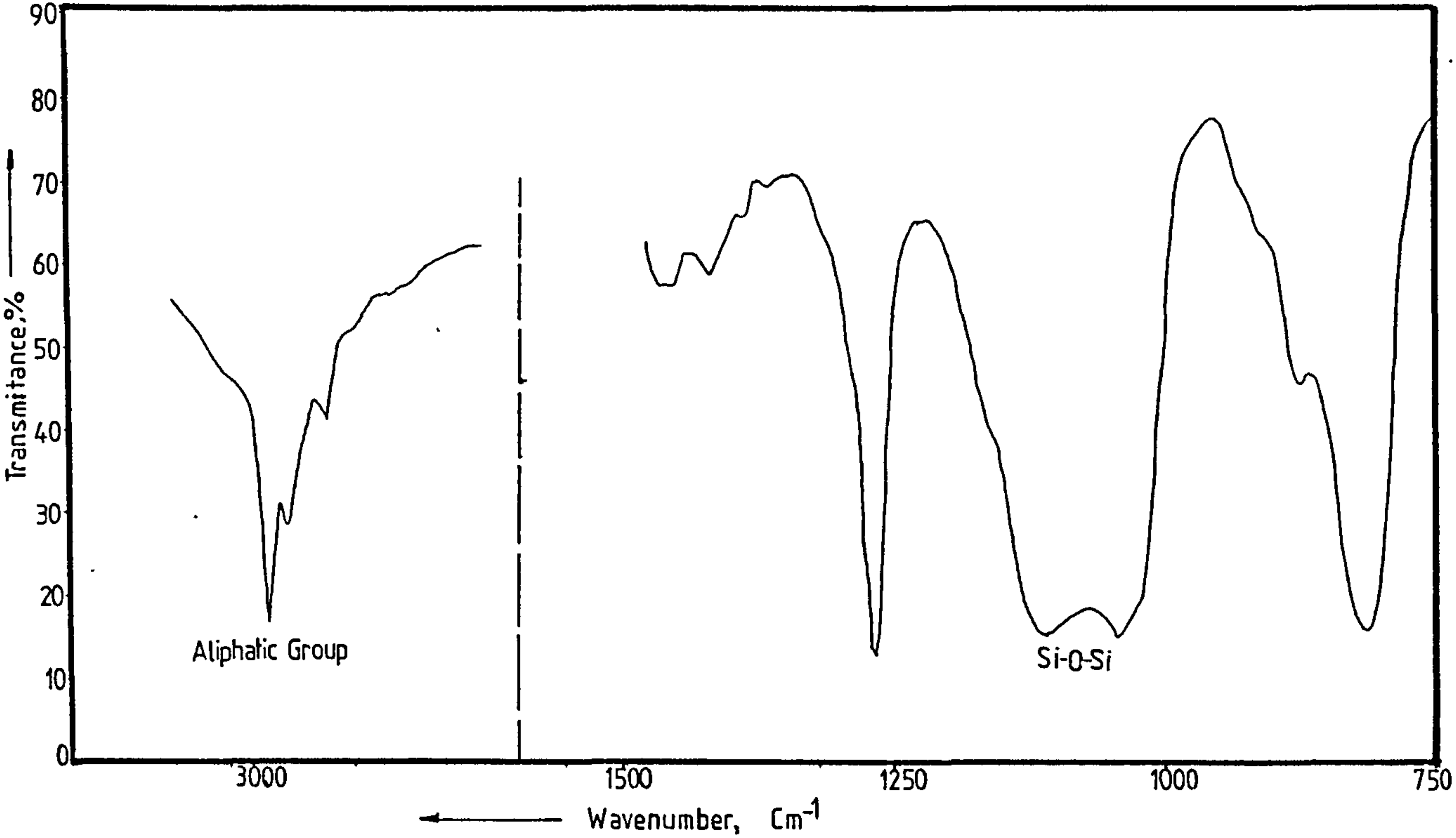


FIGURE 3.2: Infra-red Spectra of the Wire Drawing Lubricant Residue Extracted by Hot Acetone from the Surface of Brass-Plated Steel Wire. This shows a Siloxane to be Present in the Wire Drawing Lubricant

TABLE 3.2: Brass-Plated Wire Surface Cleaned using a Cold Solvent Wash-Wipe Procedure Plus a Final Acetone Wash

Solvent Treatment	Bond Strength MPa	Standard Deviation of bond Strength MPa	Coefficient of variation Bond Strength %	Rubber Coverage %	Standard Deviation of rubber Coverage %	Coefficient of variation rubber coverage %	Change in bond Strength %	Change in rubber coverage %
Untreated	12.9	1.9	14.7	48	8	15	-	-
Carbon tetra-chloride	14.4	2.0	13.9	60	11.8	19.6	+11.6	+25
Tri-chloro-ethylene	14.2	1.4	9.8	55	7.6	13.8	+10.1	+14.6
Toluene	14.0	2.0	14.2	60	9.6	16	+8.5	+25

TABLE 3.3: Wire Surface Cleaned by Condensation of Hot Solvent into a Soxhlet Thimble Plus a Final Cold Acetone Wash

Solvent Treatment	Bond Strength MPa	Standard Deviation of bond Strength MPa	Coefficient of variation Bond Strength %	Rubber Coverage %	Standard Deviation of rubber Coverage %	Coefficient of variation rubber coverage %	Change in bond Strength %	Change in rubber coverage %
Toluene	14.8	1.6	10.8	60	10.2	17	+14.7	+25
Carbon tetra-chloride	9.4	2.0	21.3	25	5.0	20	-27	-51

TABLE 3.4: Wire Treated as Given Belowthen Finally Wiped with Trichloroethylene and Acetone Wash

Solvent Treatment	Bond Strength MPa	Standard Deviation of bond Strength MPa	Coefficient of variation Bond Strength %	Rubber Coverage %	Standard Deviation of rubber coverage %	Coefficient of variation rubber coverage %	Change in bond strength %	Change in rubber coverage %
CCl_4 + $CHClCCl_2$+ CH_3COCH_3	14	1.7	12	60	13.8	23	+8.5	+25
$C_6H_5CH_3$+ $CHClCCl_2$+ CH_3COCH_3	13.8	1.8	13	60	2.5	15.8	+7.0	+25

An explanation for two of these observations (bond strength and rubber coverage) was now sought, namely the approximate 10% increase in bond strength and 25% increase in rubber coverage together with no change due to cleaning of their respective coefficients of variation, i.e. the cleaned wire is as variable in its response to rubber as the uncleaned wire.

3.3.3 Surface Microscopy of Brass-Plated Wire

Uncleaned and solvent cleaned wire (toluene of cleaning procedure (1)) was examined using a Scanning Electron Microscope (SEM) and the observations are shown as photomicrographs in Figure 3.3(a) and 3.3(b). These reveal the presence of irregularly shaped dark patches (arrowed on the micrograph) which it is thought to represent areas of unremoved wire drawing lubricant.

3.3.4 Analysis of Wire Surface by Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA technique has been widely used to examine the brass-plated wire-rubber bonding(60) and it is now used to try to determine whether any reaction was occurring between the wire drawing lubricant, now known to contain some siloxane, on the wire surface. The ESCA spectra are given in Figure 3.4. Figure 3.4(a) is the ESCA spectra of the unbonded wire which contains lubricant on its surface, and Figure 3.4(b) the wire surface after it was bonded to rubber and then the bond was broken by freezing the specimen in liquid N_2 and then removing the brittle rubber by a sharp blow with a hammer. It can be seen that the two binding energies for Si_{2p}, Si_{2s} of

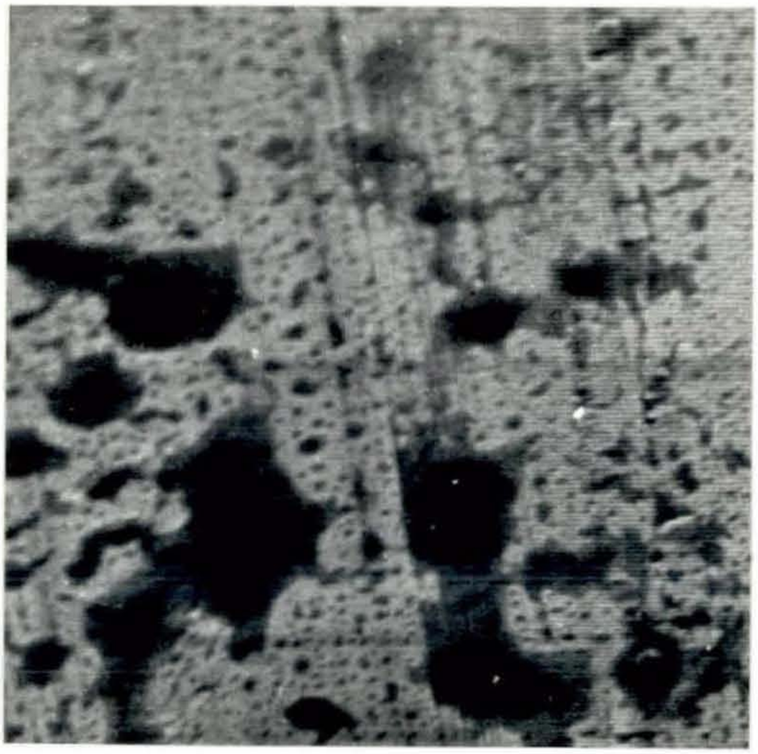


FIGURE 3.3(a) SEM Micrograph of Uncleaned Brass-plated Wire showing what appears to be a Very Heavy Deposit of Wire Drawing Lubricant Recognised as a Dark Colour where shown by the Arrows (Magnification 1.2K)

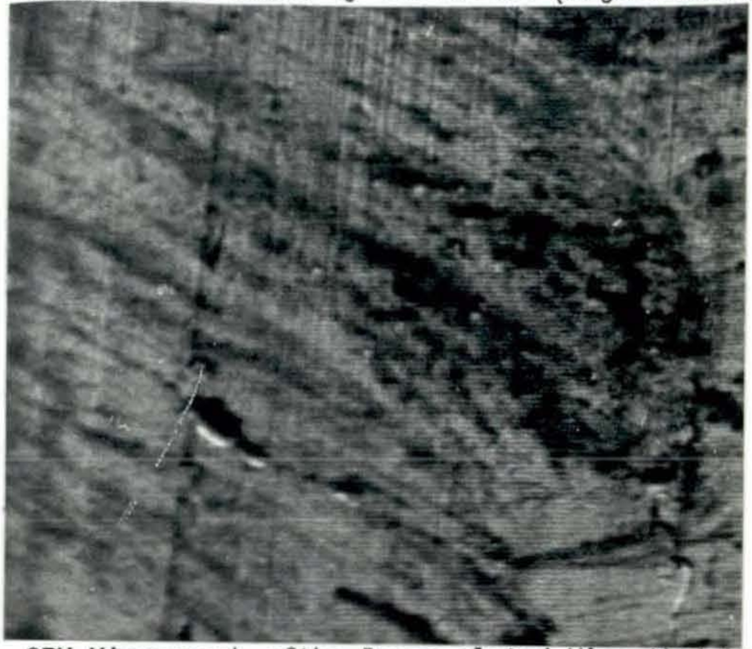


FIGURE 3.3(b) SEM Micrograph ofthe Brass-plated Wire that has been Cleaned with a Toluene Wipe. Long Dark Streaks can be seen Running Diagonally across the Micrograph (see Direction of Arrow). It is thought that these Streaks Represent Drawing Lubricant Remaining Behind on the Wire Surface after Cleaning (Magnification 1.2K)

104.3 eV and 154.3 eV, clearly seen in Figure 3.4(a), have almost disappeared in Figure 3.4(b) showing that most, but not all, of the siloxane has taken part in the bond forming vulcanization process. It is also to be noted that the debonded wire surface was not covered with rubber and is thus thought to be free from the deposit of vulcanisation by-products as it had a bright shiny surface.

The Cu_{3p} and Zn_{3p} peaks in Figure 3.4(a) cannot be used to form an internal reference standard as in Figure 3.4(b) the Cu_{3p} and Zn_{3p} peak intensity has changed relative to the Si during the wire-rubber bonding reaction. An internal reference standard which can be used is that of carbon, and this is seen in both Figures 3.4(a) and 3.4(b) at 284.7 eV; the intensities observed are identical on the wire surface before and after bonding.

3.3.5 Thermal Analysis of the Wire Drawing Lubricant Residue

The result is shown in Figure 3.5. This reveals the presence of a sharp exothermic event in the siloxane lubricant which commences between 110-130°C. Normal vulcanization temperatures for rubber are greater than 130°C hence this DSC thermogram may be evidence that this siloxane wire drawing lubricant is chemically active over the conventional curing range for rubber.

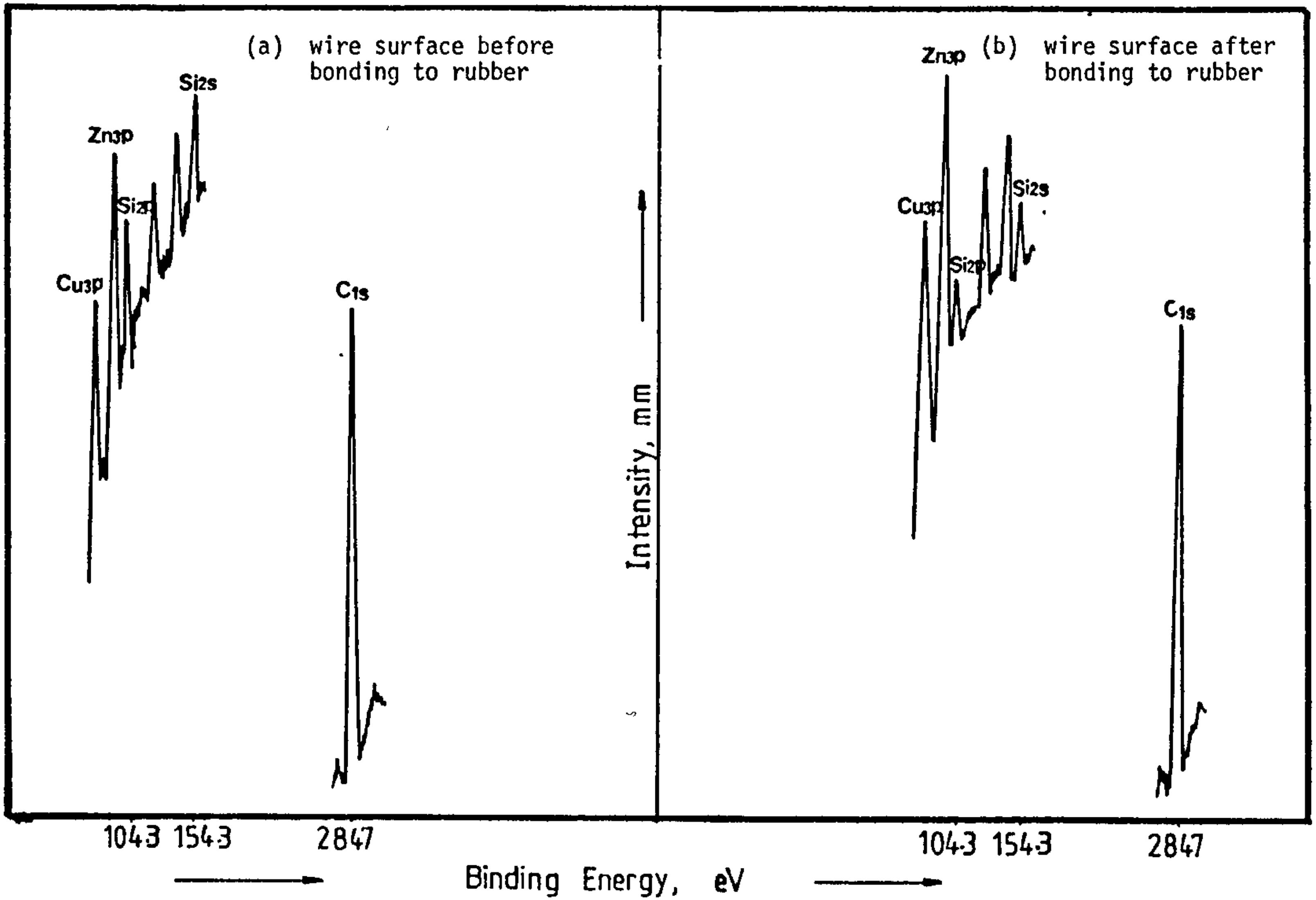


FIGURE 3.4: Electron Spectroscopy for Chemical Analysis (ESCA). Analysis by X-Ray Photoelectron Spectroscopy of the Wire Surface (a) before bonding to rubber, and (b) after bonding to rubber. In ESCA Spectra (a) the presence of Si on the wire surface is dominating, in (b) the presence of Si is much reduced by the rubber bonding process

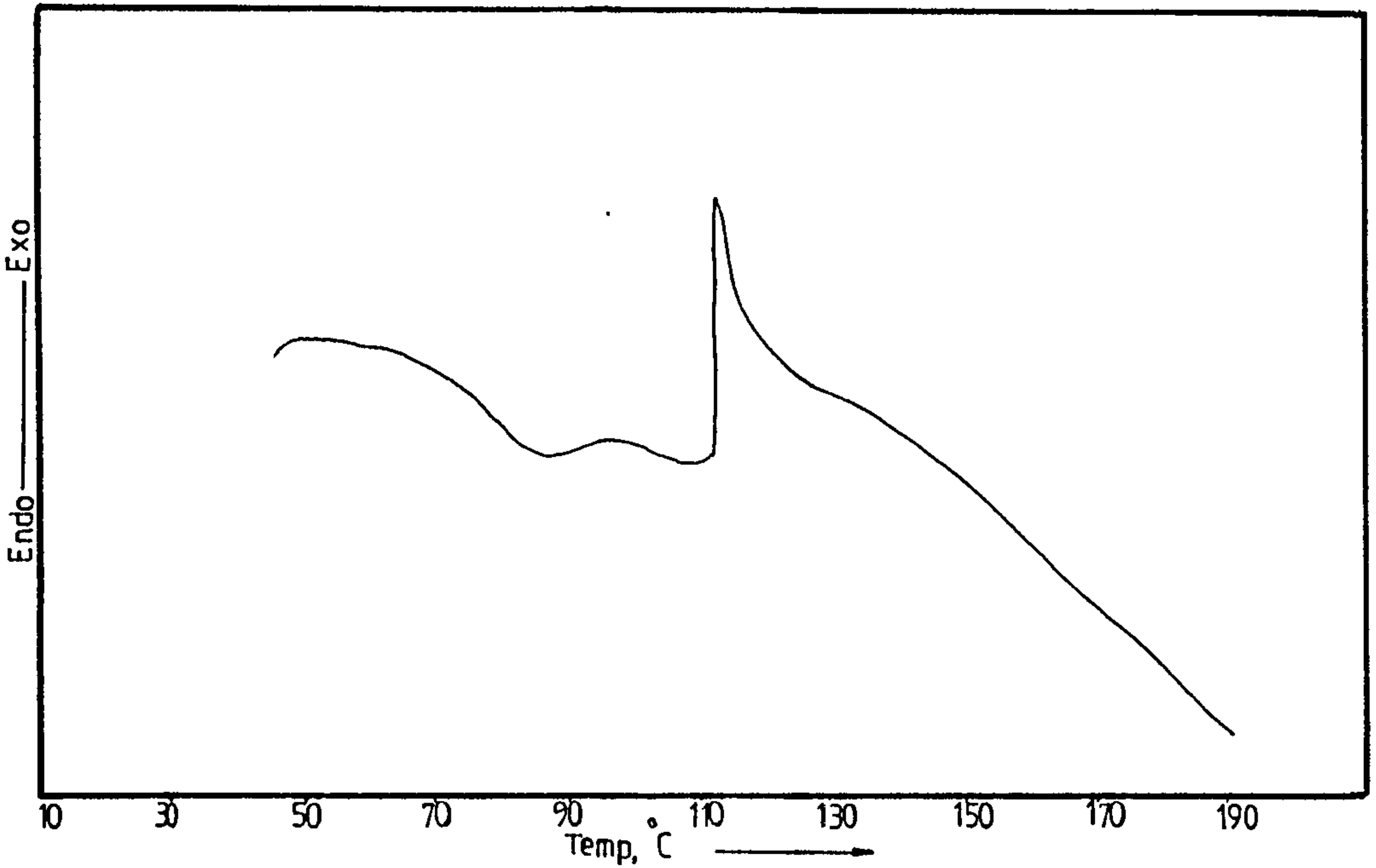


FIGURE 3.5: Thermal Analsysis of the Acetone Extracts from the Uncleaned Wire. The Thermogram shows that an Exothermic Process Occurs at 130°C and Above

CHAPTER 4

EFFECT OF COMPOUNDING ADDITIVES ON PHYSICAL PROPERTIES OF SBR, IR WITH RESPECT TO THEIR ADHESION TO BRASS-PLATED WIRE

4.1 Introduction

Since the brass-plated steel belted radial tyres came on the market, and as the adhesion between rubber and brass is a vital factor in the performance of a tyre, many investigations have been carried out by researchers to understand and find better bonding systems.

There is no systematic and universal approach or model of compounding which gives the rubber high bond strength to brass-plated wire since often a small amount of each compounding ingredient has a disproportionate effect on bond performance. Hence it is necessary to determine by experiment the adhesion of each specific rubber mix formulation to brass-plated wire. Sometimes the effect of some rubber compounding ingredients can be predicted from previous knowledge. For instance a delayed action type accelerator, such as a sulphenamide type usually gives good adhesion. The ultra accelerators such as ZDEC, TMTM or TMTD cannot be used, because even if added in small amounts low bond strength results. Bertrand(55) found that only the sulphenamides CBS, TBBS, MBS and DCBS can give high bond strengths.

Sulphur is also an essential ingredient for adhesion of rubber to wire. The minimum sulphur loading before a high bond strength can be formed is around 2 pphr and often up to at least 10 pphr is needed. A conventional and used industrial level of sulphur is 4 pphr.

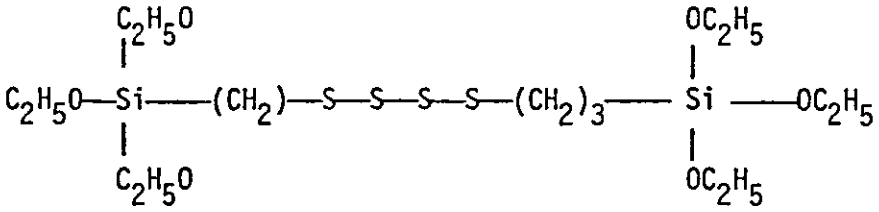
Adhesion seems to be less affected by zinc oxide proportions and up to 15 pphr shows good adhesion(50). Stearic acid should be low due to its well known internal lubrication function.

Filler such as carbon black is an important ingredient in rubber. Several investigators have suggested 40 to 50 pphr of carbon black as a satisfactory range, but this depends on the particular carbon black properties(50). Silica is another filler for reinforcement of rubber after carbon black and due to its white colour finds application in a wide range of coloured products. Because of its high polarity and its hydrogen bonding capacity, silica is often added to enhance its adhesion between dissimilar rubbers, between rubber and textiles or metals.

4.2 Experimental

In this chapter the effect of a wide range of compounding ingredients on the physical properties and bond strength of solution styrene-butadiene rubber (Solprene 1204) and synthetic polyisoprene (Natsyn 2200) to brass-plated steel wire is investigated. Carbon black (HAF) and silica (Ultrasil VN3) in proportions of between 10-70 pphr and at a sulphur proportion varying between 1-10 pphr in both unfilled (gum) and filled rubbers was examined. The effect of DCBS accelerator dosage on SBR and the effect of antioxidant on IR were also investigated.

A mercapto silane (Si 69)* with following structure:



$$C_2H_5O-\overset{C_2H_5O}{\underset{C_2H_5O}{Si}}-(CH_2)-S-S-S-S-(CH_2)_3-\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}-OC_2H_5$$

Bis-(3-(triethoxisilyl)-propyl)-tetrasulphane.

was used in the SBR/silica mix as it was found that SBR reinforced with silica gives poor physical properties. The amount of silane used was 4% by weight of silica content (as recommended by the manufacturers).

Silica is well known to retard cure time. The cure retarding effect of silica has been shown to be due to its tendency to absorb the accelerator. To overcome this problem, either the amount of accelerator should be increased or a secondary accelerator or activator should be used(58,69). In the SBR/silica formulation a secondary accelerator was used.

4.3 Results and Discussion

4.3.1 Effect of Hot Mixing and Coupling Agent (Si 69) on the Physical Properties and Bond Strength of the SBR/silica Mix

The mix formulations are given in Table 4.1. Mix No. 1 was

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prepared on a two roll mill with roll temperature of about 70°C, mix No. 2 at 150-180°C and in mix No. 3 the mercapto coupling agent (Si 69) was added at 70°C. The vulcanizate properties and bond strength results are given in Table 4.2. Poor physical properties and bond strength were observed in mix No. 1. This is considered due to the combination of insufficient adherence between the SBR molecules and silica and insufficient dispersion of silica in SBR(70).

In mix No. 2 which was treated at 150-180°C, the physical properties and bond strength increased by comparison with mix No.1. This might be due to the fact that during mixing at high temperature some silica adsorbed molecules (e.g. water or other low molecular-weight absorbates) can be removed (or released) which may enhance the silica-polymer interaction and also improve the dispersion of silica in SBR. An interesting observation was that although the bond strength increased from 4.2 to 8.5 MPa, the rubber coverage was still low (10-25%). The literature offers an explanation that heat treatment of silica filled rubber reduces adhesion(71).

In these results mix No. 3 has the highest properties (tensile strength, tear strength and bond strength) due to the use of the silane. This silane has an alkoxysilyl group which is considered to react with the silica surface to form a stable siloxane linkage, and its organic functionality can participate in reactions that lead to linkages with rubber, so it appears that silanes with the appropriate functionality provide chemically bonded coupling between the silica and the rubber network. Such coupling is apparently responsible

TABLE 4.1: Evaluation of the Filler Treating Agent (Si 69) together with the Effect of a Hot Mixing Process using an SBR/Silica Formulation

Formulation	Mix No.		
pphr	1	2	3
SBR* (1204)	100	100	100
Zinc oxide	10	10	10
Stearic acid	3	3	3
Silica (VN3)	40	40	40
Sulphur	4	4	4
DCBS	1.4	1.4	1
DPG	-	-	1
Si 69	-	-	2

* Solprene

combined

TABLE 4.2: Effect of Si 69 and Hot Mixing on the Physical Properties and Bond Strength of SBR/Silica Mix

Physical Properties	Formulation No. (Table 4.1)		
	1	2	3
Tensile strength (MPa)	5.2	9	11.8
Elongation at break (%)	360	340	310
Tear strength (kN m^{-1})	40.3	58	60.8
Bond strength (MPa)	4.2	8.5	12.8
Rubber coverage (%)	0-10	10-25	50-60

for the fully reinforcing action of the silica. Also improved dispersion of the silica in the SBR may result.

It was also found that using Si 69 was an effective means of reducing viscosity.

4.3.2 Effect of Compounding Additives on the Physical Properties and Bond Strength of SBR and IR

4.3.2.1 Influence of the Accelerator DCBS Proportions on Bond Strength of SBR to Brass-plated Wire

This experiment was done to optimize the proportion of DCBS to give the highest bond strength (Table 4.3) which was found to be obtained at the level of 1 pphr of DCBS (see Table 4.4 and Figure 4.1). An explanation for the rapid reduction in adhesion that occurs when the optimum proportion of DCBS is exceeded is now attempted.

For an ideal bond strength to develop complete contact between rubber and brass surface is necessary. To achieve this condition sufficient time must be allowed to elapse for the rubber to wet the wire surface during the vulcanization process. Since higher amounts of DCBS will increase the rate of cross-linking and reduce the scorch time then this will result in shorter periods of time being available for wire surface wetting and consequently the rubber to wire bonding should be reduced(48). But as is shown in Table 4.4 the scorch time at 2.5 pphr of DCBS is still 5 minutes which is a long scorch time hence the above explanation cannot be correct. The drop in the bond strength as DCBS level rises might be due to interference in the sulphidisation of sulphur with copper during vulcanization.

TABLE 4.3: Formulation used to Evaluate DSBC Proportions in SBR on Bond Strength

Formulation	Mix No.					
pphr	1	2	3	4	5	6
SBR (1204)	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3
Carbon black (HAF)	40	40	40	40	40	40
Sulphur	4	4	4	4	4	4
DSBC	0.5	0.7	1	1.5	2	2.5

TABLE 4.4: Effect of DSBC Proportions on Bond Strength of SBR to Brass-Plated Wire

Physical Properties	Formulation No. (Table 4.3)					
	1	2	3	4	5	6
Bond Strength (MPa)	13.5	15.1	15.4	14.8	14.1	11.5
Rubber coverage (%)	80	100	90-100	100	70	30
Scorch time t_2 (mins) @ 170°C	7	7	6	5	5	5
Cure time t_{95} (mins) @ 170°C	25	18	17	14.5	12	11.5

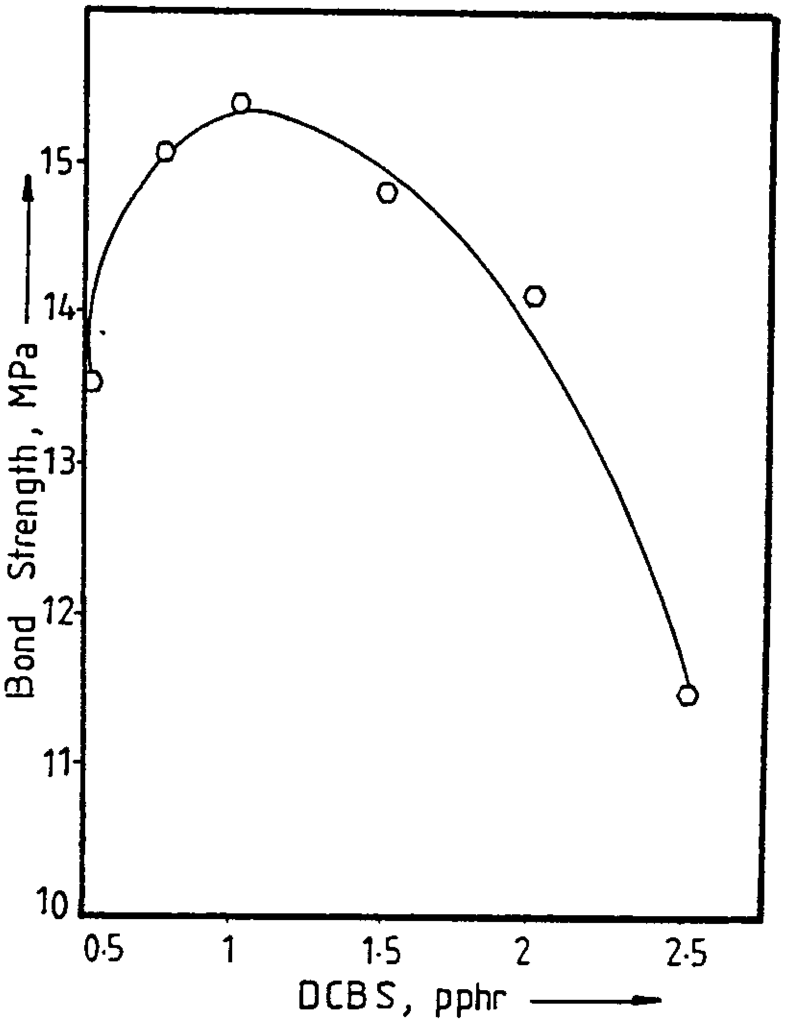

FIGURE 4.1: Effect of Accelerator (DCBS) Proportions on the Bond Strength of SBR to Brass-plated Wire

4.3.2.2 Effect of Sulphur Proportions on Bonding and Physical Properties of Unfilled SBR and IR

Mix formulations are given for SBR and IR in Tables 4.5 and 4.6 respectively. Results are shown in Table 4.7, Figure 4.2(a), 4.2(b) for SBR and Table 4.8, Figures 4.3(a), 4.3(b) for IR.

SBR

Poor physical properties were obtained due to the absence of a reinforcing filler in the non-strain crystallisable SBR. Bond strength and rubber coverage are also low (<3 MPa and 5-20% respectively) which indicates that no adhesion is formed between the SBR and the wire. Low strength and non-polarity of rubber might be the reason for this poor adhesion. Also it is not possible to draw conclusions from the results of these sulphur levels in SBR due to the low properties of the vulcanizates. A later experiment will determine the effect of sulphur proportions on a filled reinforced SBR.

IR

Unlike SBR, IR is a self-reinforcing rubber which has high strength in gum form due to its ability to strain crystallize. Ring samples were used to measure tensile strength and elongation since IR has a high elongation and the JJ machine was unable to measure it using the normal dumbell.

Bond strength of unfilled IR to wire was found to be higher than that obtained with unfilled SBR due to higher rubber strength and this indicates that bond strength can be related to the strength of rubber. The failure is mostly interfacial (i.e. between rubber and

TABLE 4.5: Formulation Used to Evaluate Sulphur Proportions in Unfilled (gum) SBR

Formulation	Mix No.							
pphr	1	2	3	4	5	6	7	8
SBR (1204)	100	100	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3	3	3
DCBS	1	1	1	1	1	1	1	1
Sulphur	0.5	1	1.5	2	3	4	6	8

TABLE 4.6: Formulation Used to Evaluate Sulphur Proportions in Unfilled (Gum) IR

Formulation	Mix No.					
pphr	1	2	3	4	5	6
IR (2200)	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3
DCBS	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	1	2	3	4	6	8

TABLE 4.7: Effect of Sulphur Proportions on Physical Properties and Bond Strength of Unfilled (Gum) SBR

Physical Properties	Formulation No. (Table 4.5)							
	1	2	3	4	5	6	7	8
Hardness (IRHD)	38	40	43	48	48	50	50	53
Tear strength (kN m^{-1})	14.1	17.5	18.1	20.5	20.4	22.3	20	18.8
Tensile strength (MPa)	1.4	1.6	1.6	1.6	1.8	1.9	2.2	2.2
Elongation at break (%)	880	690	560	580	450	360	235	230
Tensile product (MPa x %) 10^2	12.3	11	8.9	9.3	8.1	6.8	5.2	5.1
Rupture energy (J)	0.6	0.75	0.71	0.74	0.66	0.5	0.52	0.35
Bond strength (MPa)	-	-	1.7	2.2	2.2	2.4	2.4	2.5
Rubber coverage (%)	-	-	0-5	0-5	0-5	5-15	5-20	15-25
Scorch time t_2 (mins) @ 170°C	21	17.5	16	12	13.5	8	8	6
Cure time t_{95} (mins) @ 170°C	55	44	36	27.5	27	25	25	22

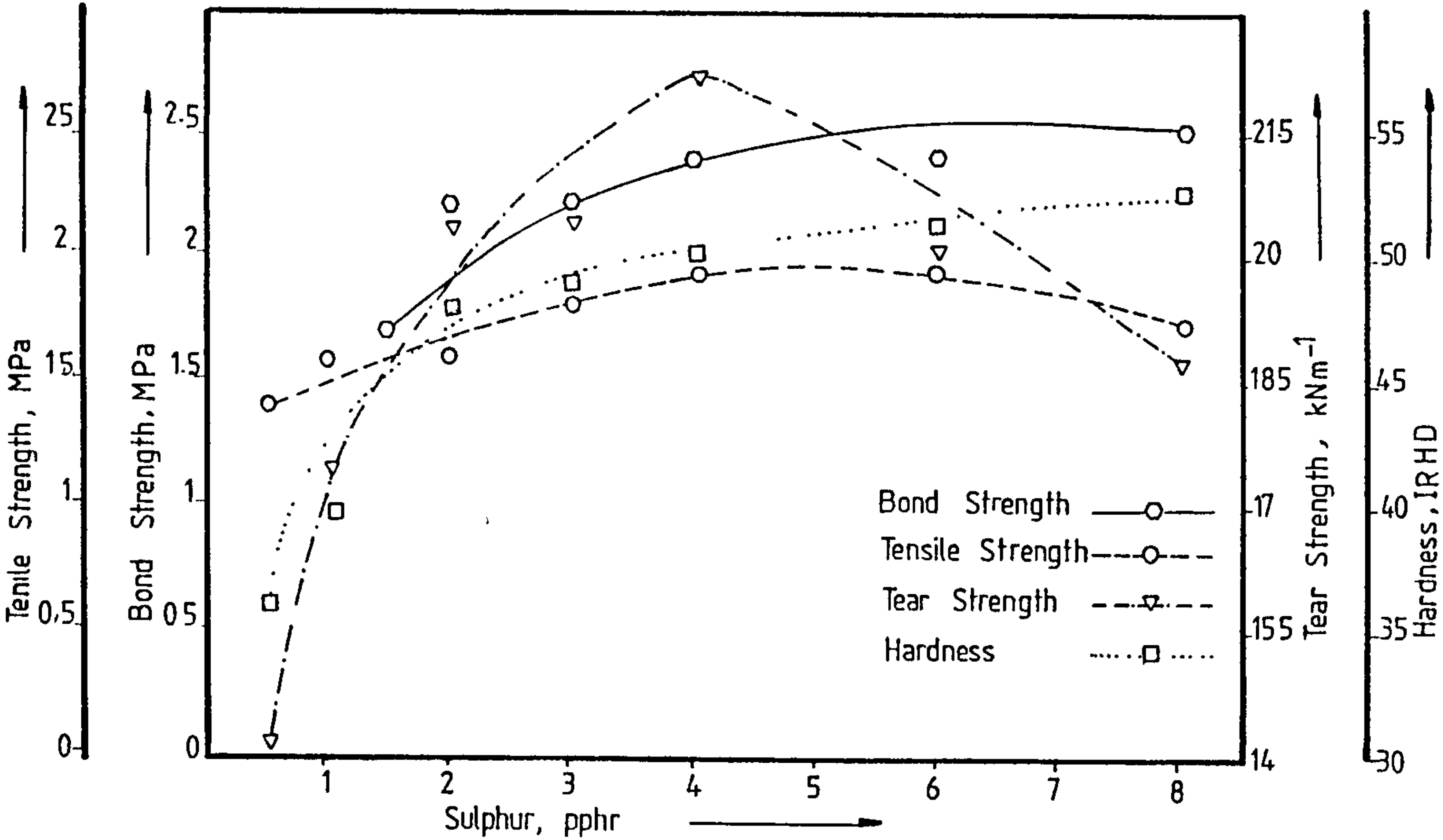

FIGURE 4.2(a) Effect of Sulphur Proportions on Physical Properties and Bond Strength of Unfilled (Gum) SBR

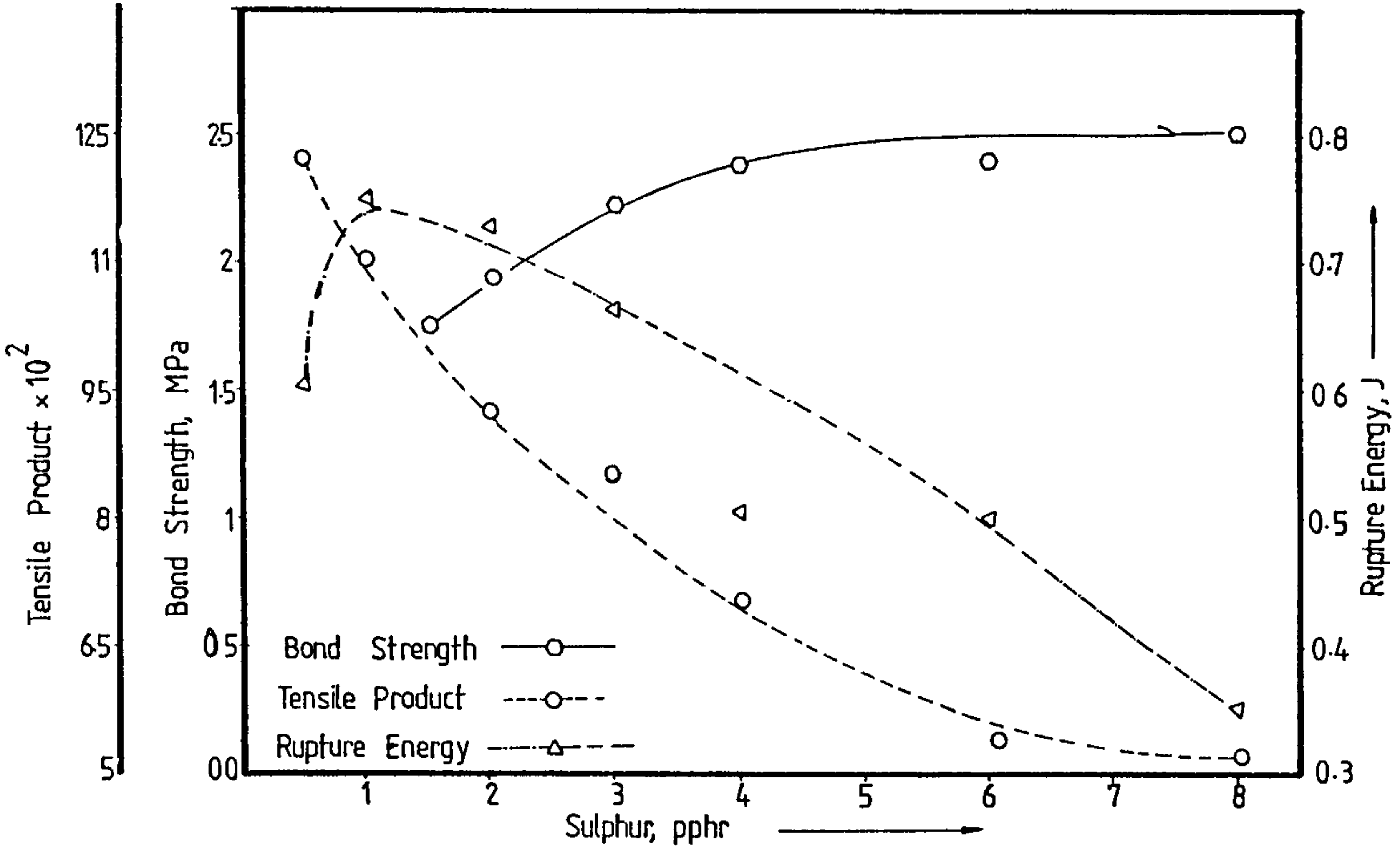

FIGURE 4.2(b): Relationship Between Sulphur Proportions Versus Bond Strength, Rupture Energy and Tensile Product in Unfilled (Gum) SBR

TABLE 4.8: Effect of Sulphur Proportions on Physical Properties and Bond Strength of Unfilled (Gum) IR

Physical Properties	Formulation No. (Table 4.6)					
	1	2	3	4	5	6
Hardness (IRHD)	30	32	34	37	41	43
Tear strength ($kN\ m^{-1}$)	38.9	51.9	61.0	66.7	37.2	24
Tensile strength (MPa)*	3	4.5	7.9	8	4.6	1.7
Elongation at break (%)	1000	945	920	870	340	280
Tensile product (MPa x %) 10^2	30	42.5	72.7	69.6	15.6	4.8
Rupture energy (J)	0.72	0.72	0.92	1.15	0.6	0.23
Bond strength (MPa)	4.1	5.2	8.8	9.4	6.9	6.2
Rubber coverage (%)	0	20	40	40	40	30
Scorch time t_2 (mins) @ 170°C	8.5	6.5	6	5.5	4.5	4
Cure time t_{95} (mins) @ 170°C	25	18	15	14	14	13

* Ring sample

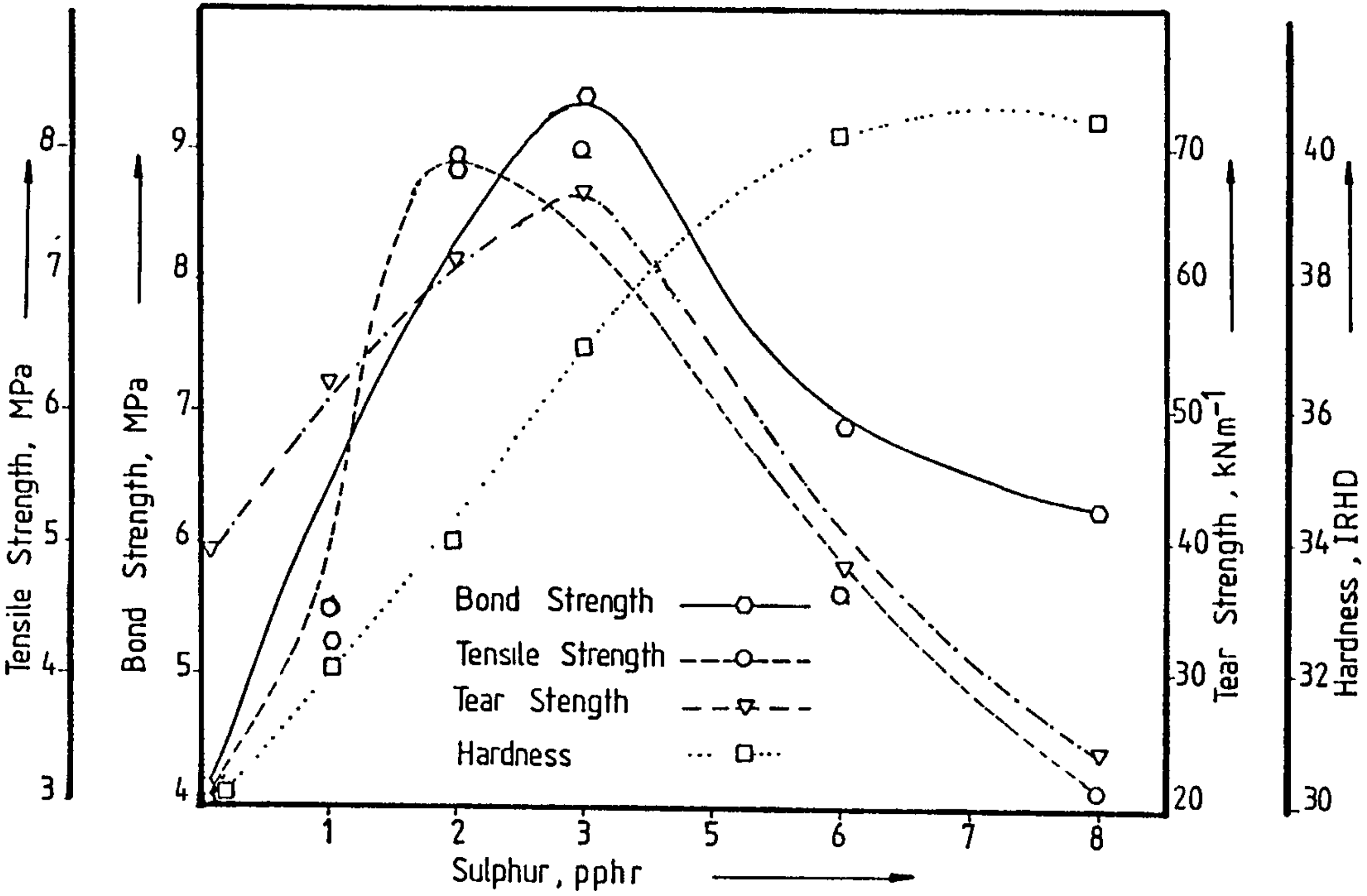

FIGURE 4.3(a) Effect of Sulphur Proportions on Physical Properties and Bond Strength of Unfilled (Gum) IR

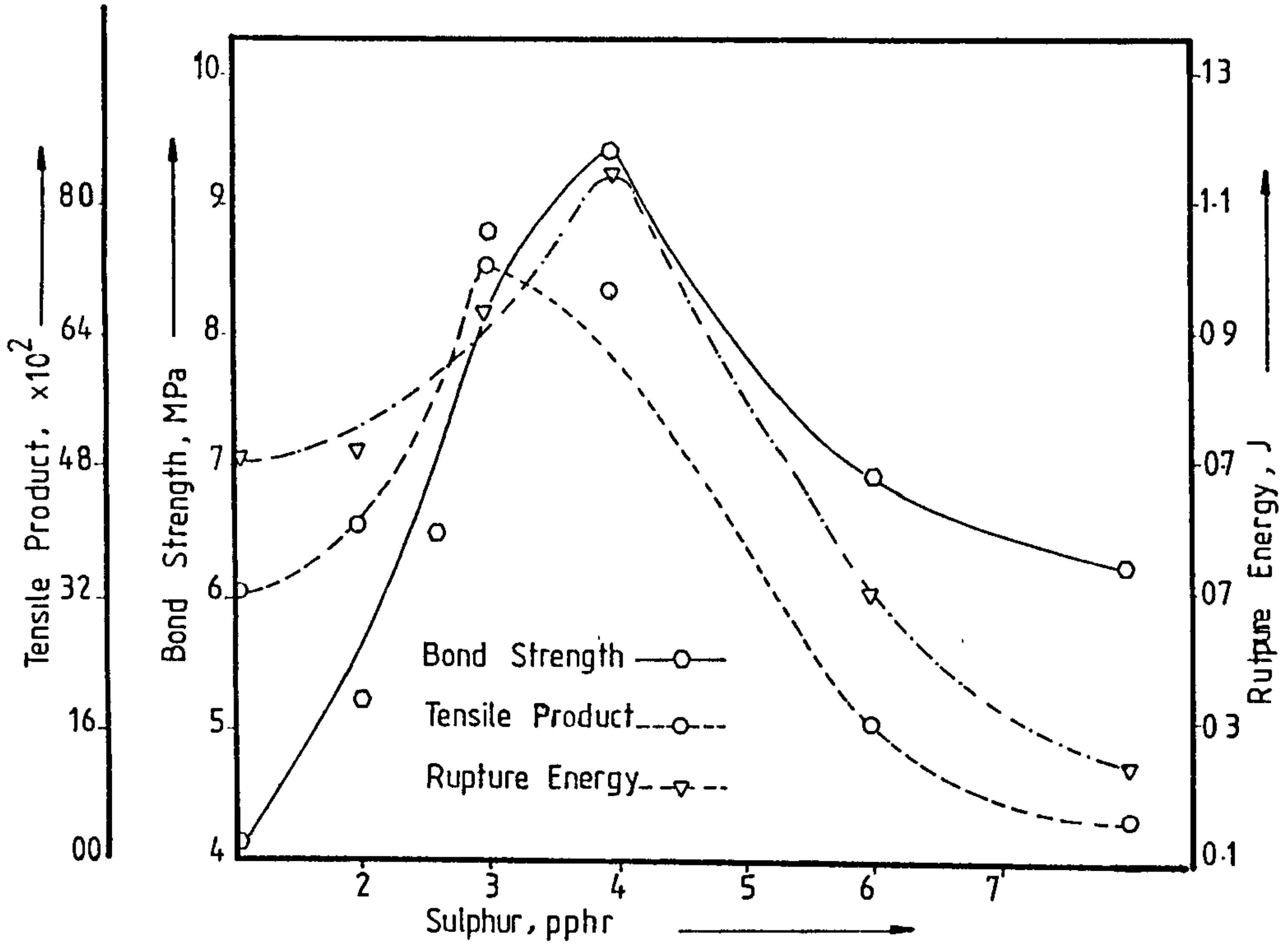

FIGURE 4.3(b): Relationship Between Sulphur Proportions Versus Bond Strength, Rupture Energy, and Tensile Product in Unfilled (Gum) IR

wire) which shows that there is only poor adhesion between the unfilled IR and the wire. However, bond strength achieves its optimum value (9.4 MPa) at 3-4 pphr of sulphur then drops rapidly as the sulphur proportion exceeds the 4 pphr level.

Results show that bond strength can be related to the tensile strength, tear strength, rupture energy and tensile product (see Figures 4.3(a) and 4.3(b)).

4.3.2.3 Effect of Carbon Black (HAF) Proportions on Bonding and Physical Properties of SBR and IR

Mix formulations for SBR and IR are given in Tables 4.9 and 4.10.

SBR

HAF carbon black, having a particle size of 29 nm, was used at different levels of loading in order to determine the optimum level which gives the highest bond strength and physical properties. Results are shown in Table 4.11, and Figures 4.4(a), 4.4(b), for SBR where a sharp increase was observed in physical properties and bond strength. 15 pphr of carbon black increased tensile strength and bond strength about 6 and 5 times respectively in comparison with the gum form. Bond strength and tensile strength progressively increased each to its own optimum level then decreased as carbon black content further increased. An optimum bond strength of 15.5 MPa and tensile strength of 23.2 MPa respectively were achieved at the 45 and 55 pphr of carbon black levels. Also rubber coverage increased from 0-5% level of gum form of SBR to 100% when a 35 pphr of carbon black content was used. However as an increase in bond strength and rubber coverage occurs it can be considered that carbon black has a large effect on the bonding of SBR to brass-plated wire. Over 35 pphr, carbon black loading is shown to have a small effect on bond strength and rubber coverage which remains approximately constant.

IR

Carbon black increases the bond strength of IR to brass-plated wire from 9 MPa in unfilled rubber to 15.9 MPa and rubber coverage from 40% to 100% at the optimum level of carbon black, indicating again its ability to give good bonding. The mechanical values for the tensile strength and bond strength at optimum filler level had similar values to those of the SBR/carbon black mixes, however a lower content (35 pphr) of carbon black gave optimum bonding with IR (compared with 45 pphr for SBR)(see Tables 4.11 and 4.12). Increasing the carbon black content over the optimum level caused a big drop in bond strength with IR. This might be due to the large decrease in tensile strength (see Figure 4.5(a)).

Investigations using HAF carbon black on bond strength of SBR (1204) and IR (2200) to brass-plated wire have now been shown to have beneficial effects on bond strength. SEM (Scanning Electron Microscopy) photomicrographs of wire surfaces debonded from unfilled SBR (Figure 4.6(a)) and carbon black filled SBR (Figure 4.7(b)) provide good evidence for the influence of carbon black on the adhesion of rubber to brass-plated wire. To explain the increase in bond strength from these results and SEM observations it is suggested that carbon black loading has two effects, first is that it reinforces (increases the strength of) rubber, hence with this enhanced strength progressively more energy to deform the rubber-wire interface is needed, thus leading to a higher bond strength. Second increasing carbon black content might have an effect on the sulphidisation between copper and sulphur. Because it was observed that the colour of the wire surface debonded from the carbon black filled SBR was greenish-blue (see Figure 4.7(a)) which indicated the formation of copper sulphide. The colour of the wire surface which was debonded from the unfilled rubber was yellow (see Figure 4.7(b)) (this will be discussed in detail in Chapter 7).

A good relationship appears to exist between bond strength, tensile strength, rupture energy and tensile product (see Figures 4.4(a), 4.4(b) and Figures 4.5(a), 4.5(b)). Tear strength did not show any correlation to bond strength in SBR/carbon black mixes, but it did demonstrate a correlation in IR/carbon black mixes.

In summary the maximum bond strength was obtained for SBR/carbon black and IR/carbon black between 35-65 pphr and 25-45 pphr of carbon black content respectively. Rubber coverage in this range was 100% i.e. failure is within the rubber. The highest bond strength for SBR/carbon black and IR/carbon black was achieved at values of 15.5 MPa and 15.9 MPa which indicated that the type of rubber i.e. non-strain crystallisable or strain crystallisable does not make a significant difference.

TABLE 4.9: Formulation Used to Evaluate Carbon Black (HAF) Proportions in SBR

Formulation	Mix No.						
pphr	1	2	3	4	5	6	7
SBR (1204)	100	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3	3
Carbon black (HAF)	15	25	35	45	55	65	75
DCBS	1	1	1	1	1	1	1
Sulphur	4	4	4	4	4	4	4

TABLE 4.10: Formulation Used to Evaluate Carbon Black (HAF) Proportions in IR

Formulation	Mix No.						
pphr	1	2	3	4	5	6	7
IR (2200)	100	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3	3
Carbon black (HAF)	15	25	35	45	55	65	75
DCBS	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	4	4	4	4	4	4	4

TABLE 4.11: Effect of Carbon Black (HAF) Proportions on Physical Properties and Bond Strength of SBR

Physical Properties	Formulation No. (Table 4.9)						
	1	2	3	4	5	6	7
Hardness (IRHD)	54	59	64	70	74	80	82
Tear strength ($kN\ m^{-1}$)	31.3	39.2	46.6	53	57.7	60.4	61.2
Tensile strength (MPa)	8.5	13.7	16.6	20.5	23.2	21.5	20.5
Elongation at break (%)	470	440	450	375	337	300	253
Tensile product (MPa x %) 10^2	40	60.3	74.7	76.9	78.2	64.5	51.9
Rupture energy (J)	2.37	4.1	5.35	5.75	5.77	5.35	5.4
Bond strength (MPa)	9.5	12.1	15.2	15.5	15.2	15.5	14.1
Rubber coverage (%)	60	90	100	100	100	100	70
Scorch time t_2 (mins) @ 170°C	8.5	7	7	5.5	5	5	4.5
Cure time t_{95} (mins) @ 170°C	28	24	22.5	22	22	22	20

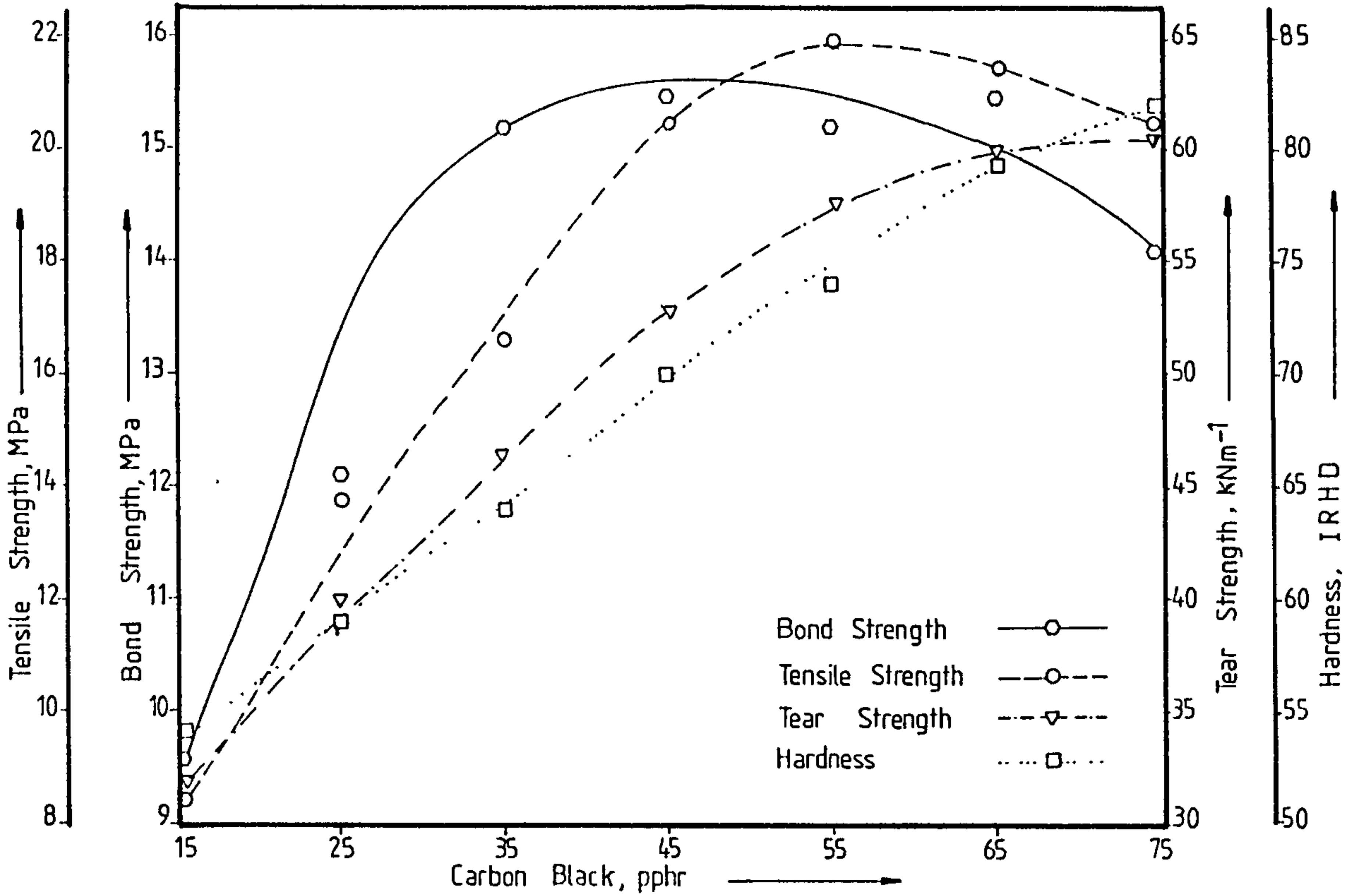

FIGURE 4.4(a): Effect of Carbon Black (HAF) Proportions on Physical Properties and Bond Strength of SBR

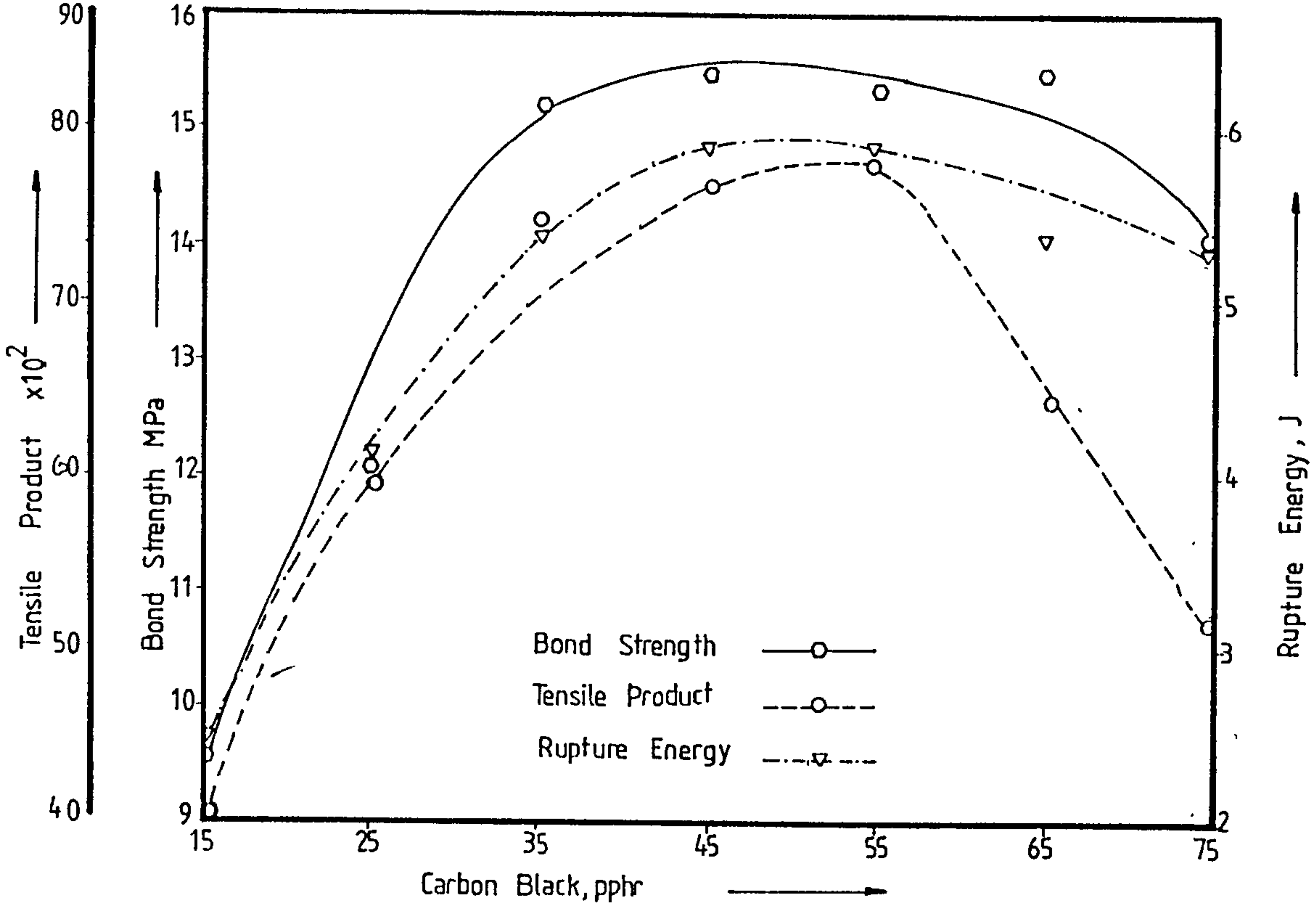

FIGURE 4.4(b): Relationship Between Carbon Black (HAF) Proportions Versus Bond Strength, Rupture Energy, and Tensile Product in SBR

TABLE 4.12: Effect of Carbon Black (HAF) Proportion on Physical Properties and Bond Strength of IR

Physical Properties	Formulation No. (Table 4.10)						
	1	2	3	4	5	6	7
Hardness (IRHD)	41	52	59	62	64	68	70
Tear strength (kN m^{-1})	44.5	60.3	69	67.5	63.8	61	52.4
Tensile strength (MPa)	15.8	19.1	22	20.6	18.9	18.7	16.5
Elongation at break (%)	620	540	500	440	430	390	350
Tensile product (MPa x %) 10^2	97.9	103	110	90.6	81.3	71	57.8
Rupture energy (J)	6	6.5	7.15	6.23	5.81	5.13	3.8
Bond strength (MPa)	11.7	15.9	15.2	14.3	13.2	9.8	9.5
Rubber coverage (%)	50-60	90-100	100	100	80	60	30
Scorch time t_2 (mins) @ 170°C	6.5	5.5	5.5	5	5	4.5	4
Cure time t_{35} (mins) @ 170°C	16	14	13	12.5	11	11.5	10

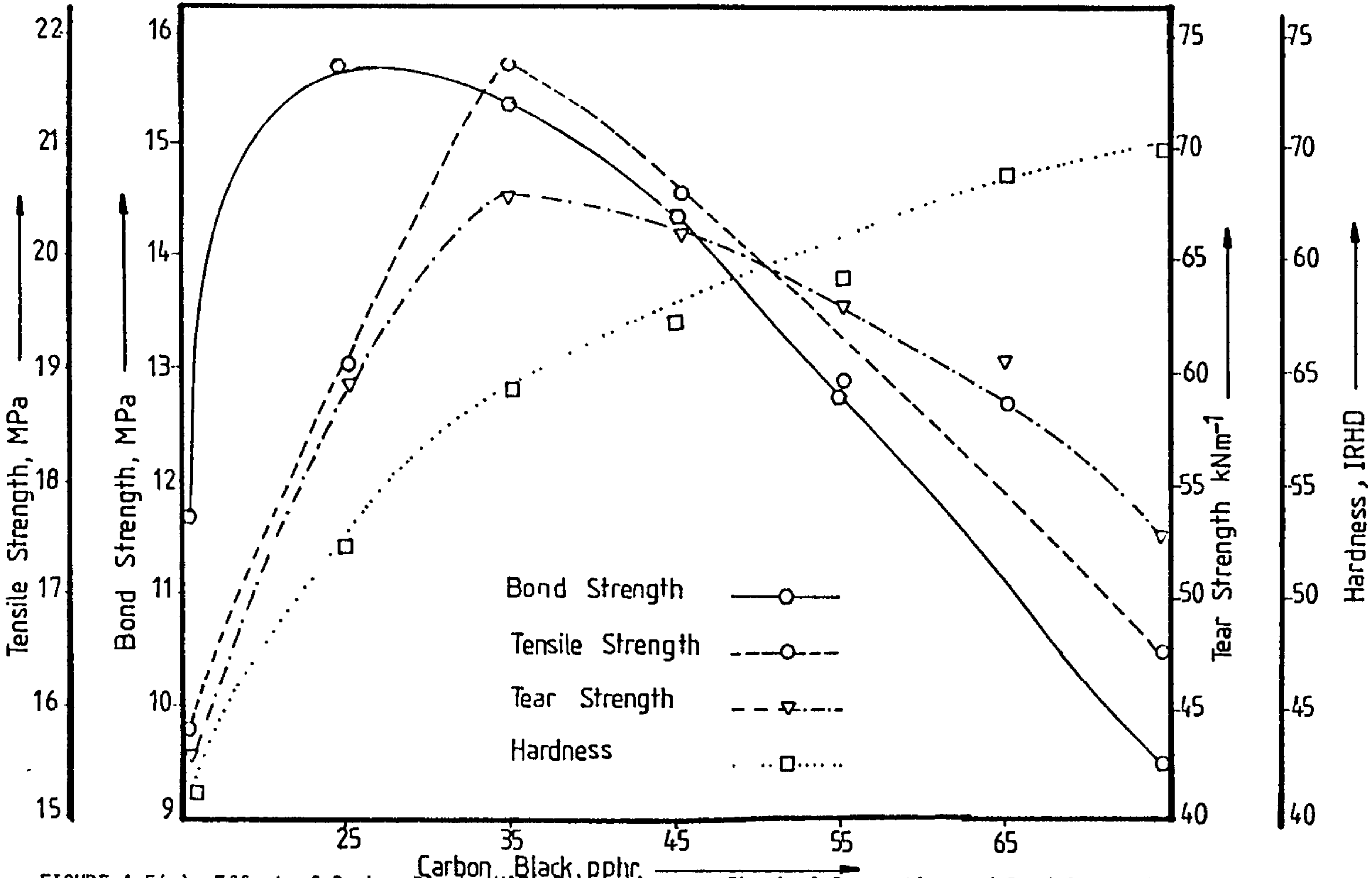

FIGURE 4.5(a) Effect of Carbon Black (HAF) Proportions on Physical Properties and Bond Strength of IR

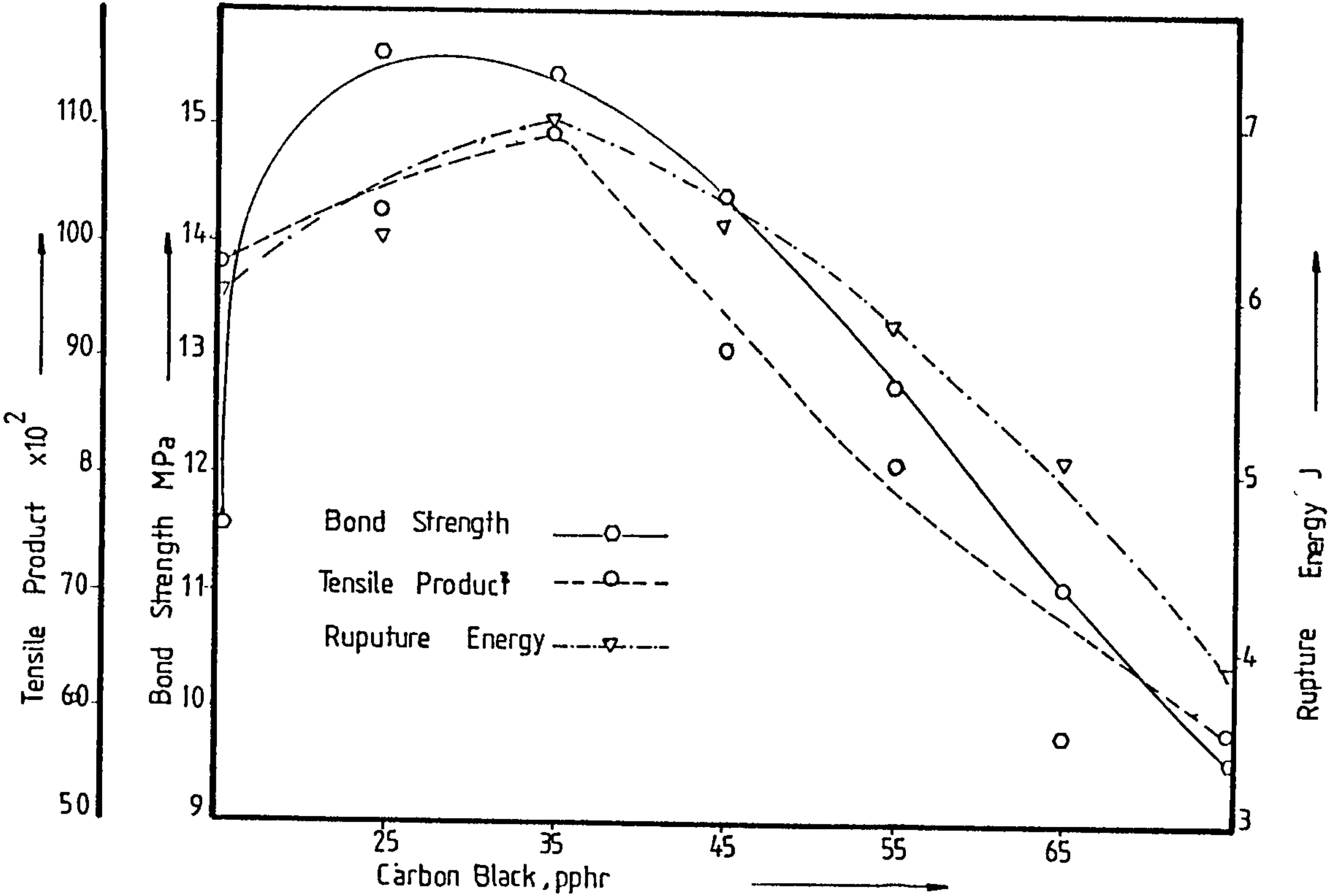

FIGURE 4.5(b): Relationship Between Carbon Black (HAF) Proportions Versus Bond Strength, Rupture Energy and Tensile Product in IR

FIGURE 4.6(a) SEM Micrograph of Wire Surface Debonded from the Unfilled SBR. It shows there is no Rubber Bonded to the Wire Surface (Magnification 100)

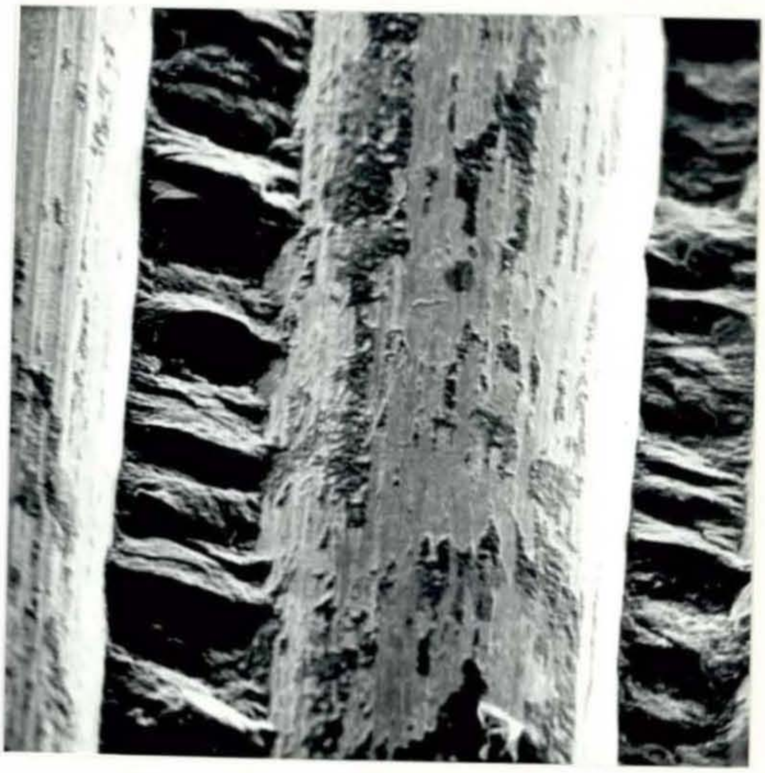

FIGURE 4.6(b) SEM Micrograph of Wire Surface Debonded from the Carbon Black Filled SBR. Marked Areas are Rubber Bonded to Wire (Magnification 160)

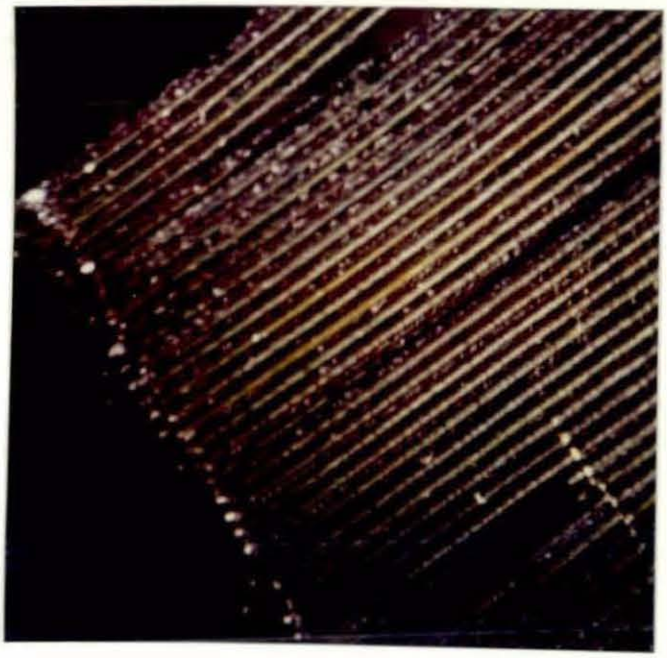

FIGURE 4.7(a) The Wire Surface Debonded from the Carbon Black Filled SBR. The Greenish-Blue is the Sign of Copper Sulphide Formation

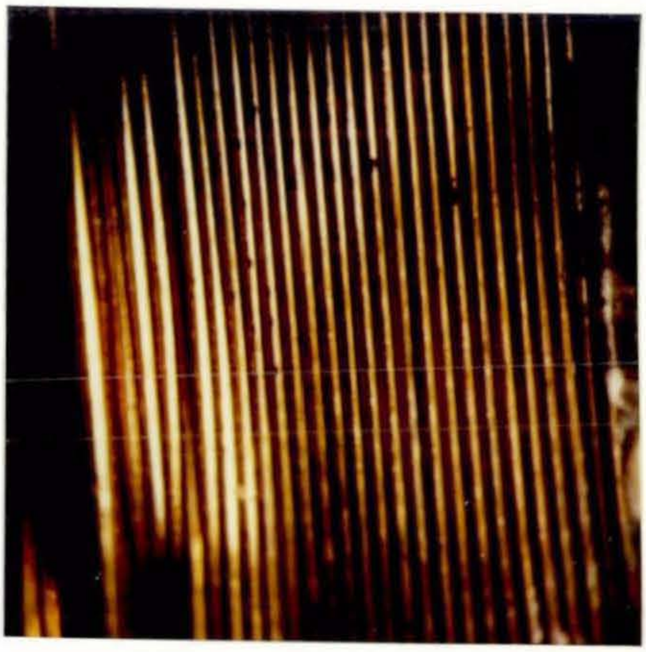

FIGURE 4.7(b) The Wire Surface Debonded from the Unfilled SBR. The Original Colour of the Brass-wire is Unchanged.

4.3.2.4 Effect of Sulphur Proportions on Bonding and Physical Properties of Carbon Black Filled SBR and IR

The mix formulations are given in Tables 4.13 and 4.14 for SBR/carbon black and IR/carbon black respectively.

In this investigation, for a constant accelerator level (1 pphr DCBS), the sulphur dosage was varied between 1-8 pphr in both SBR/carbon black and IR/carbon black to find the highest bond strength. The results are shown in Table 4.15, Figures 4.8(a), 4.8(b) for SBR/carbon black and Table 4.16, Figures 4.9(a), 4.9(b) for IR/carbon black. For both sharp increases were observed in bond strength up to an optimum sulphur level after which an excess of sulphur has a small adverse effect on bond strength in comparison to an adverse effect of sulphur level on physical properties (tensile strength and tear strength). Physical properties slowly increased until the optimum level of sulphur was reached and then a sharp adverse effect was observed on the physical properties. Optimum bond strength was obtained between 3-4 pphr and 4-6 pphr of sulphur level for SBR/carbon black and IR/carbon black respectively. In both cases the maximum physical properties (tensile strength and tear strength) were achieved at the lower sulphur proportion. From these results it can be concluded that for high bond strength relatively large amounts of sulphur is necessary. At optimum levels of sulphur content, rubber coverage in both cases was 100% i.e. failure occurred within the rubber.

Inspection showed that optimum tensile strength, rupture energy, and tensile product values do not exactly correlate with bond strength but do demonstrate a general relationship.

TABLE 4.13: Formulation Used to Evaluate the Effect of Sulphur Proportions on Bonding and Physical Properties in Carbon Black Filled SBR

Formulation	Mix No.					
pphr	1	2	3	4	5	6
SBR (1204)	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3
Carbon black (HAF)	35	35	35	35	35	35
DCBS	1	1	1	1	1	1
Sulphur	1	2	3	4	6	8

TABLE 4.14: Formulations Used to Evaluate Sulphur Proportions in Carbon Black Filled IR

Formulation	Mix No.					
pphr	1	2	3	4	5	6
IR (2200)	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3
Carbon black (HAF)	25	25	25	25	25	25
DCBC	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	1	2	3	4	6	8

TABLE 4.15: Effect of Sulphur Proportion on Physical Properties and Bond Strength of Carbon Black Filled SBR

Physical Properties	Formulation No. (Table 4.13)					
	1	2	3	4	5	6
Hardness (IRHD)	51	60	62	65	68	69
Tear strength (kN m^{-1})	56	60.2	56.5	50.1	46	35.8
Tensile strength (MPa)	16.2	18.5	18	17.4	14.6	12.9
Elongation at break (%)	630	575	450	370	220	160
Tensile product (MPa x %) 10^2	102	106.3	81	64.4	32.1	20.6
Rupture energy (J)	9.1	9.9	8.3	7.35	5.21	4.2
Bond strength (MPa)	11.2	13.6	15.8	15.1	14.3	13.6
Rubber coverage (%)	45	60	90-100	90-100	70	50
Scorch time t_2 (mins) @ 170°C	11	8.5	8	7	6	5.5
Cure time t_{95} (mins) @ 170°C	30	23	22.5	22	20	15

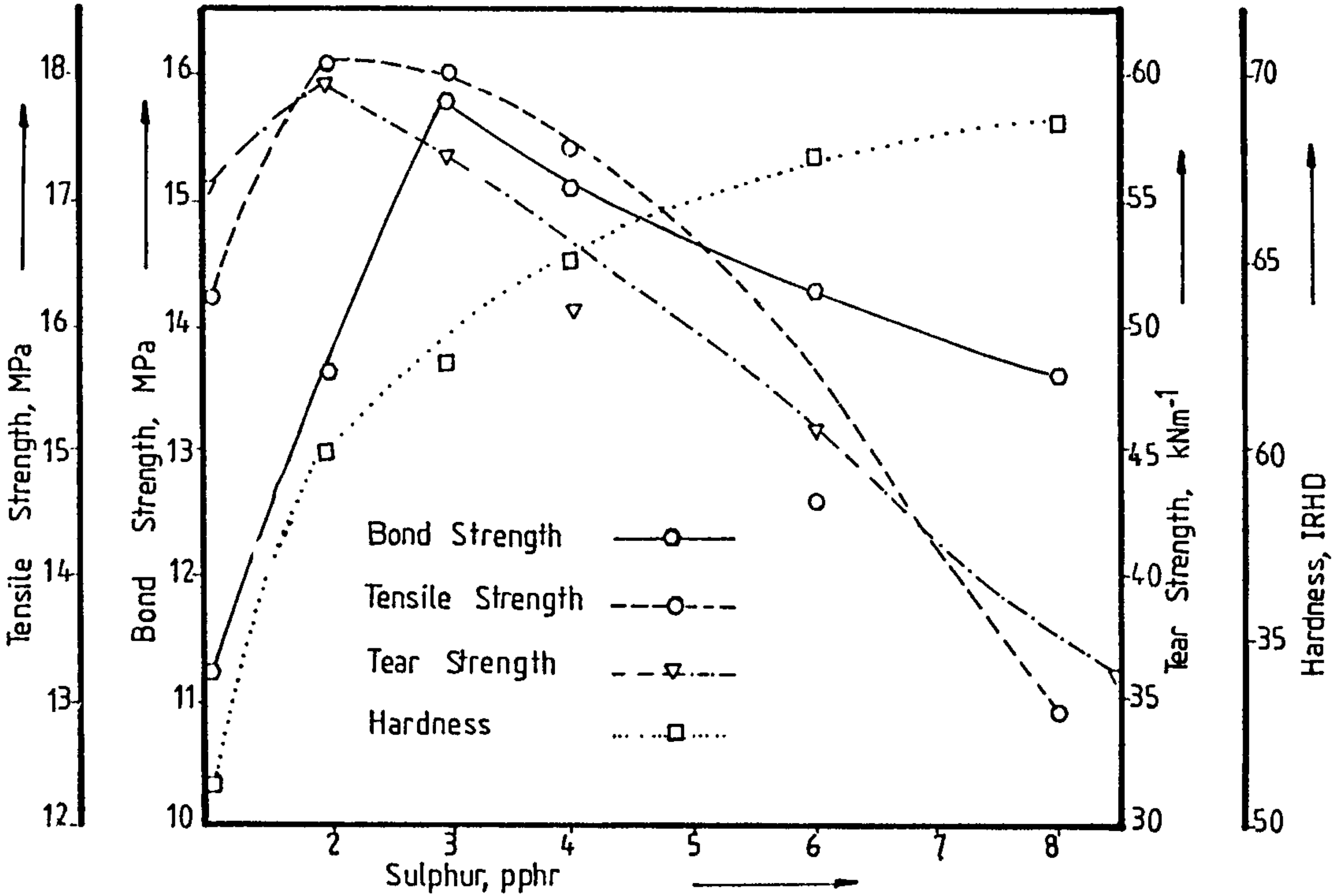

FIGURE 4.8(a): Effect of Sulphur Proportions on Physical Properties and Bond Strength of Carbon Black Filled SBR

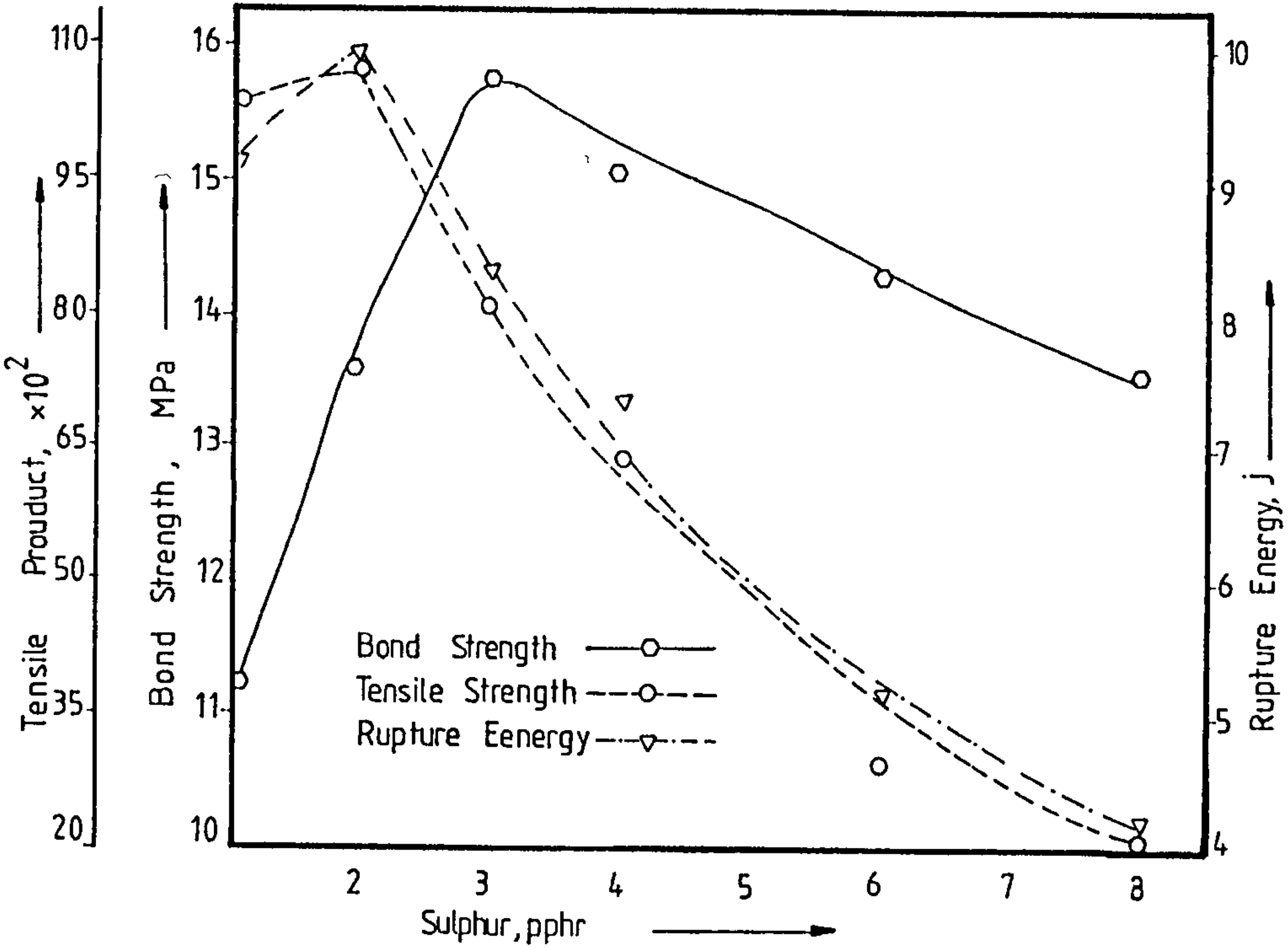

FIGURE 4.8(b): Relationship Between Sulphur Proportions Versus Bond Strength, Rupture Energy and Tensile Product in Carbon Black Filled SBR

TABLE 4.16: Effect of Sulphur Proportions on Physical Properties and Bond Strength of Carbon Black Filled IR

Physical Properties	Formulation No. (Table 4.14)					
	1	2	3	4	5	6
Hardness (IRHD)	43	48	56	59	60	63
Tear strength (kN m^{-1})	49.2	64.1	66.7	73	58.1	59.1
Tensile strength (MPa)	12.2	14.1	16.6	18.0	13.9	10.5
Elongation at break (%)	700	620	580	520	430	330
Tensile product (MPa x %) 10^2	85.4	87.4	96.3	93.6	59.8	36.6
Rupture energy (J)	7.55	7.95	7.8	8	4.35	2.6
Bond strength (MPa)	9.7	10.8	12.9	15.2	15.8	14.1
Rubber coverage (%)	30	50	60	100	100	80
Scorch time t_2 (mins) @ 170°C	4.5	4.2	4	3.5	3	2.5
Cure time t_{95} (mins) @ 170°C	12	12	11.5	10.5	12	14.0

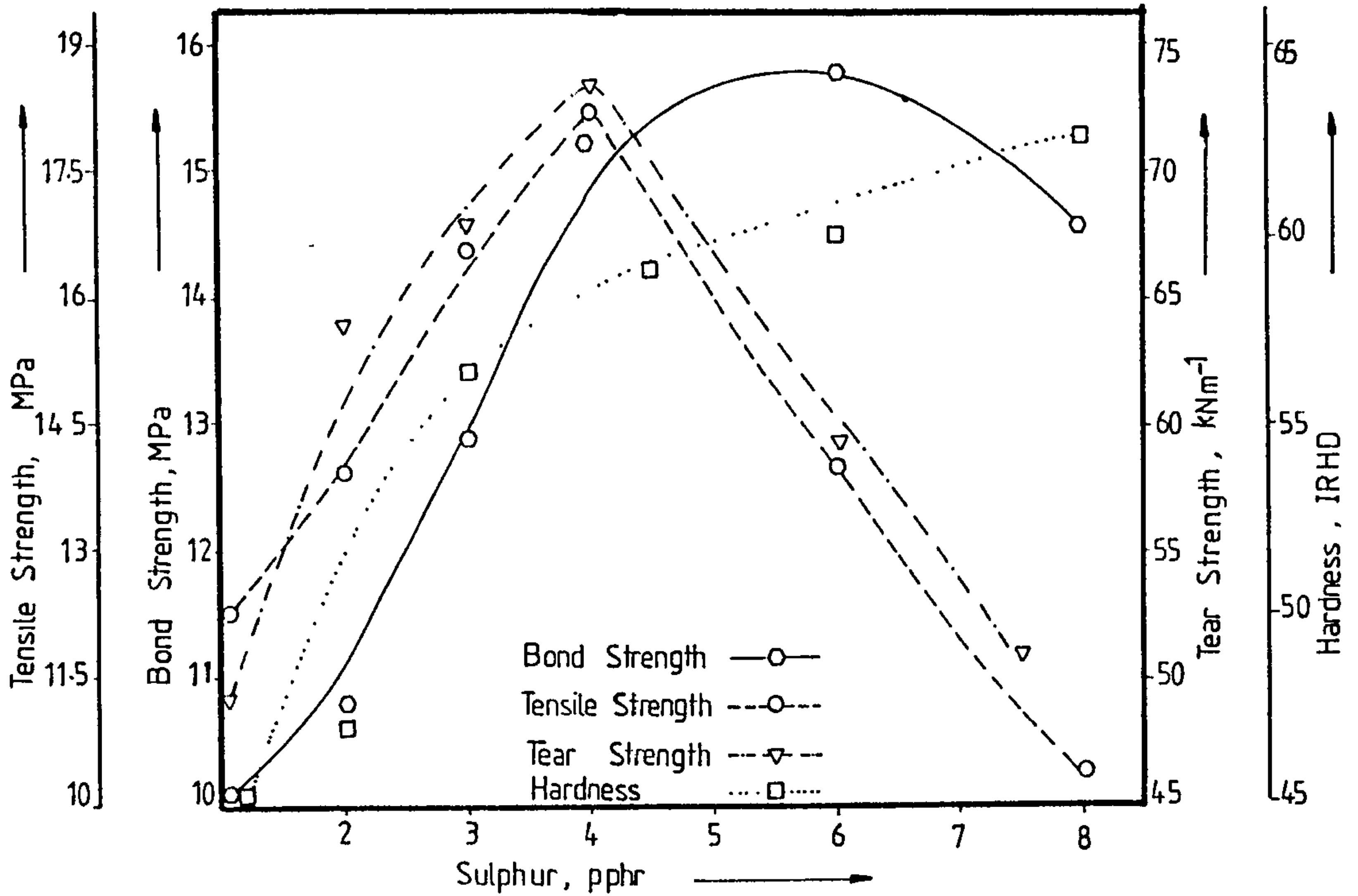

FIGURE 4.9(a): Effect of Sulphur Proportions on Physical Properties and Bond Strength of Carbon Black Filled IR

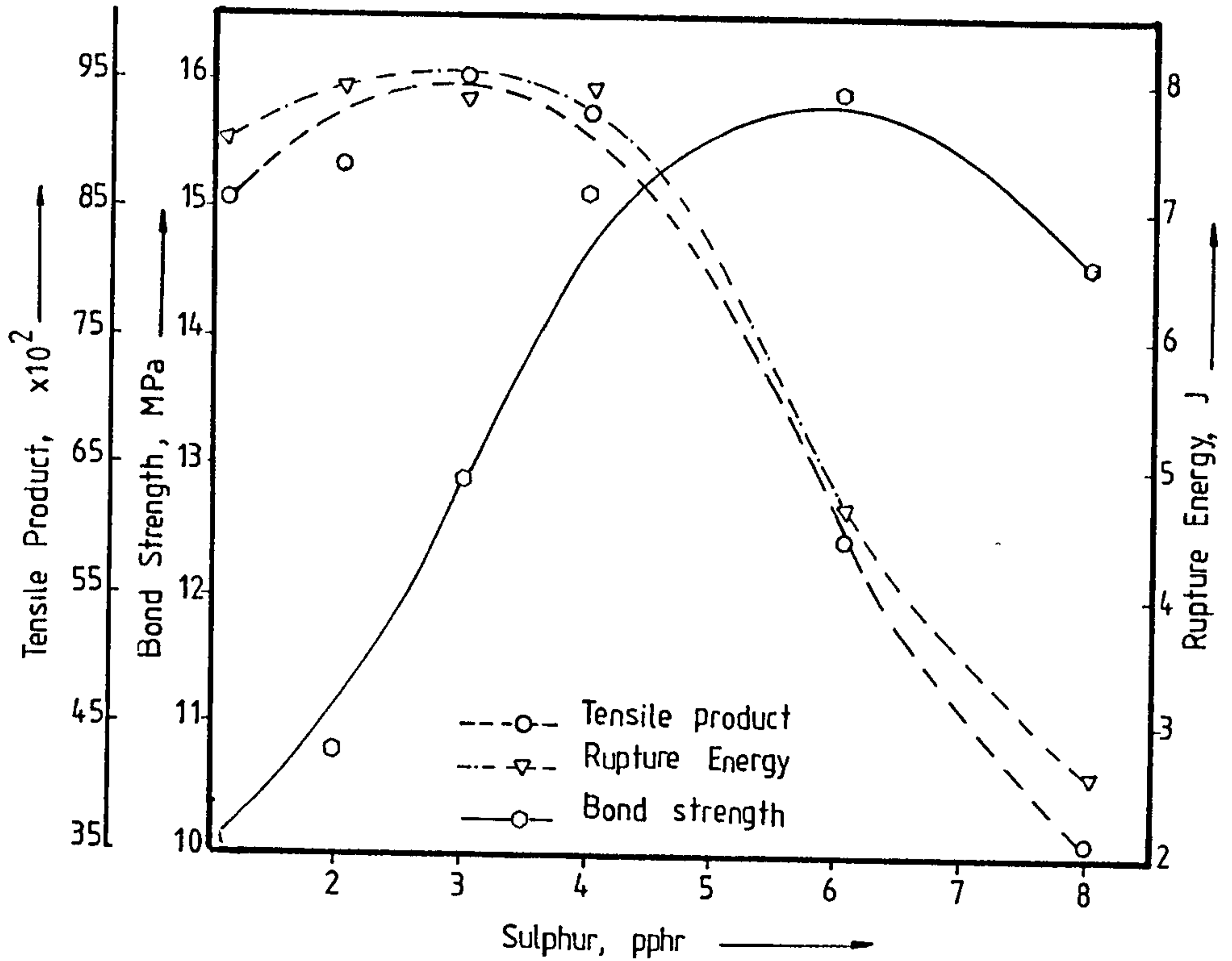

FIGURE 4.9(b): Relationship Between Sulphur Proportions Versus Bond Strength, Rupture Energy and Tensile Product in Carbon Black Filled IR

4.3.2.5 Effect of Silica (VN3) Proportions on Bonding and Physical Properties of SBR

The effect of precipitated silica (VN3) on bonding and physical properties of SBR was studied in the present investigation. The mixing cycle for the silica based mix used was the following order: SBR → Silica → Coupling Agent (Si 69) → Activators (Zinc oxide/Stearic acid) → Accelerators → Curing agent.

This mixing cycle and the use of the coupling agent in SBR/silica mix have already been described in Chapter 2 and Chapter 4 (Section 4.3.1) - mix formulation is shown in Table 4.17.

TABLE 4.17

Formulation Used to Evaluate the Silica (VN3) Proportions in SBR

Formulation	Mix No						
pphr	1	2	3	4	5	6	7
SBR (1204)	100	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3	3
DCBS	1	1	1	1	1	1	1
DPG	1	1	1	1	1	1	1
Sulphur	4	4	4	4	4	4	4
Si 69	0.4	0.8	1.2	1.6	2	2.4	2.8
Silica (VN3)	10	20	30	40	50	60	70

maximum values of 12.5 MPa for tensile strength and 9.9 MPa for bond strength were respectively observed at the 50 and 40 pphr levels of silica content (see Table 4.18 and Figures 4.10(a), 4.10(b). These strength values are lower in comparison with those obtained for the carbon black filled SBR (optimum tensile strength of 23.2 MPa and bond strength of 15.5 MPa). Such low tensile strength might be due to poor interaction of the silica with the SBR during mixing (as will be discussed in Chapter 7): consequently bond strength was lower. A rubber coverage of 40% was the best result obtained with silica thus relatively poor adhesion of the SBR/silica mix to brass-plated wire was expressed (i.e. the failure was partially within the rubber and partially interfacial). Over 35 pphr silica loading is shown to have small effect on bond strength and rubber coverage which remains approximately constant.

The colour of the wire surface debonded from the silica filled SBR was examined to be similar to the colour of the wire surface debonded from the unfilled SBR (see Figure 4.7(b)). Hence it seems that silica has no effect on the sulphidisation of copper and sulphur (as will be discussed in Chapter 7).

Again bond strength can be related to the tensile strength, rupture energy and tensile product.

TABLE 4.18

Effect of Silica (VN3) Proportions on Physical Properties and Bond Strength of SBR

Physical Properties	Formulation No. (Table 4.20)						
	1	2	3	4	5	6	7
Hardness (IRHD)	58	64	70	76	79	79	81
Tear Strength (kN m^{-1})	28.4	38.6	50	60.1	66.6	70.5	73.1
Tensile Strength (MPa)	7.2	8.7	9.2	11	12.5	11.9	10.7
Elongation at break (%)	280	275	280	240	180	120	100
Tensile Product (MPa x %) 10^2	20.2	23.9	25.8	26.4	22.5	14.3	10.7
Rupture Energy (J)	1.2	1.8	2.5	2.9	2.5	1.7	1.5
Bond Strength (MPa)	5.1	6.4	9.5	9.9	9.5	9.4	8.8
Rubber Coverage (%)	50	25	40-50	40	40	40	35
Scorch time t_2 (mins) @ 170°C	4.5	5	5.5	5.5	5	4.5	5
Cure time t_{95} (mins) @ 170°C	25	31	34	35	35	32	34

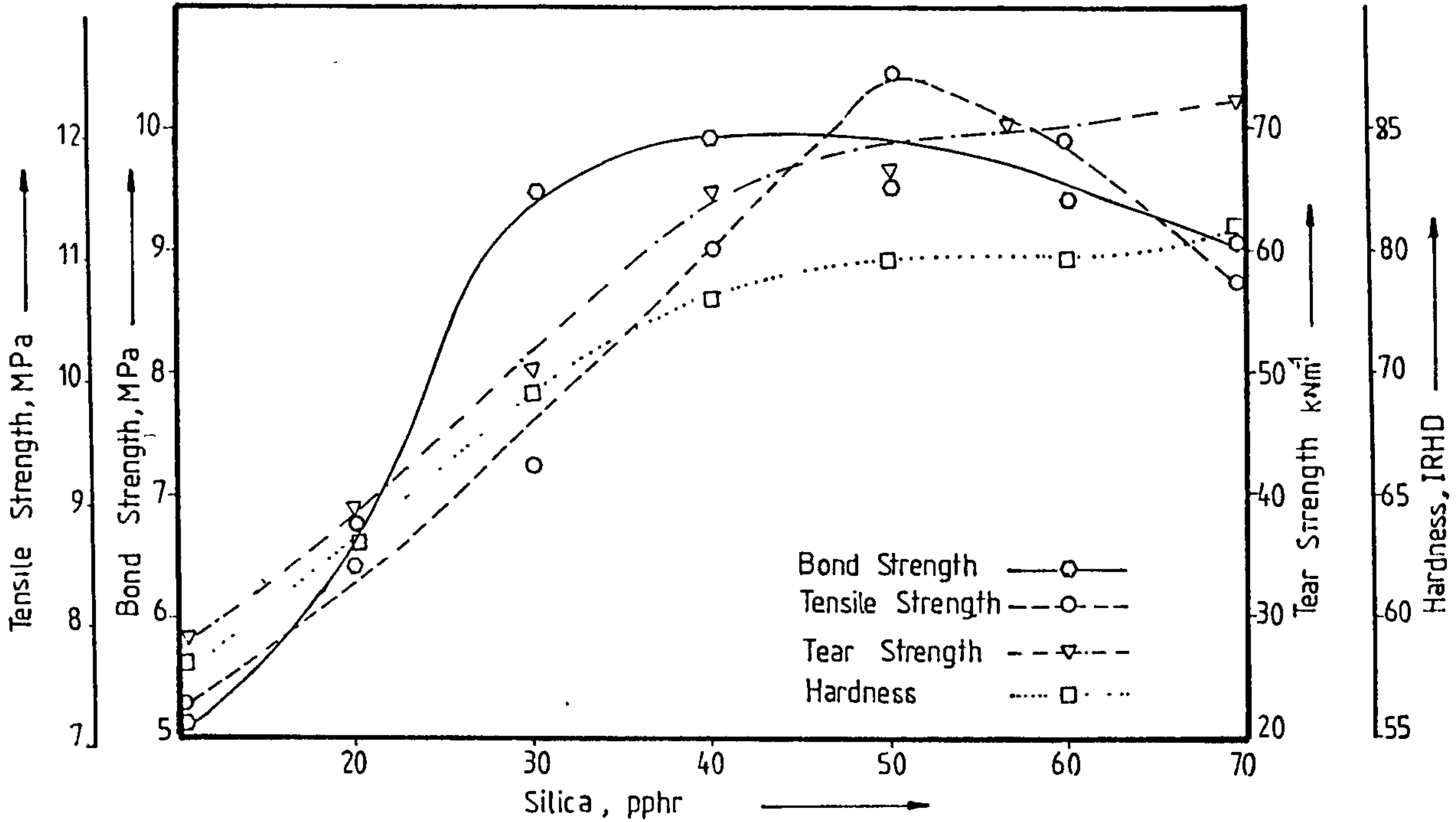

FIGURE 4.10(a) Effect of Silica Proportions on Physical Properties and Bond Strength of SBR

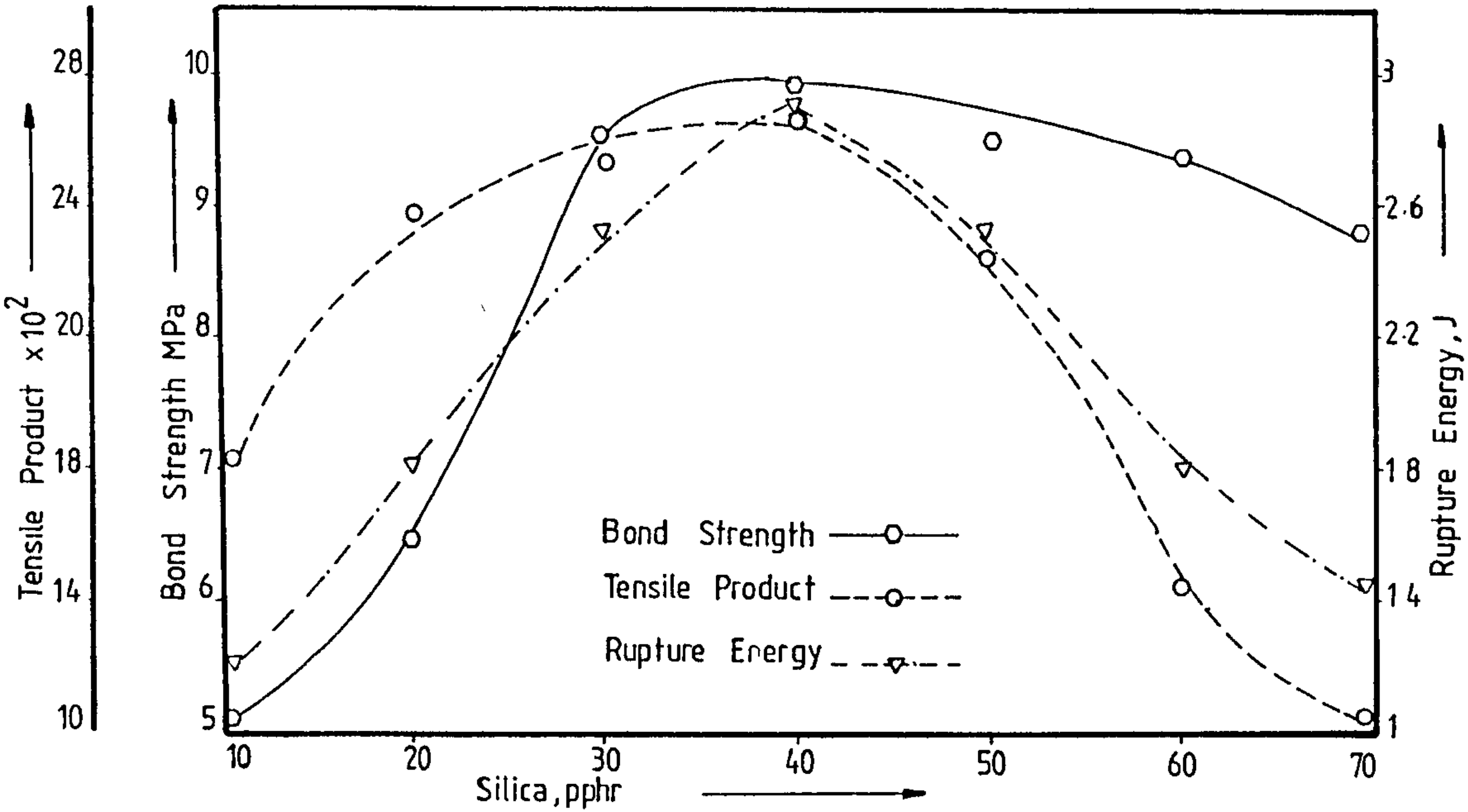

FIGURE 4.10(b): Relationship Between Silica Proportions Versus Bond Strength, Rupture Energy, and Tensile Product in SBR

4.3.2.6 Effect of Sulphur Proportions on Bonding and Physical Properties of Silica Filled SBR

For a constant proportion of accelerators (1 pphr of DCBS and 1 pphr of DPG) the sulphur content was varied between 1-8 pphr (see Table 4.19).

TABLE 4.19

Formulation Used to Evaluate the Sulphur Proportions in Silica Filled SBR

Formulation	Mix No					
pbw	1	2	3	4	5	6
SBR (1204)	100	100	100	100	100	100
Zinc oxide	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3
Silica (VN3)	40	40	40	40	40	40
DCBS	1	1	1	1	1	1
DGP	1	1	1	1	1	1
Si 69	1.6	1.6	1.6	1.6	1.6	1.6
Sulphur	1	2	3	4	6	8

An optimum bond strength was obtained at the 4 pphr of sulphur content (similar to carbon black filled SBR) but the optimum tensile strength was achieved at lower sulphur proportions. Again it can be considered that for high bond strength a relatively large amount of sulphur is necessary. Excessive sulphur contents over the optimum level had only a small adverse effect on bond strength. The rubber coverage at maximum bond strength is 60% (i.e. failure is partially within rubber and partially interfacial).

Again, tensile strength, rupture energy and tensile product values do not exactly correlate with bond strength but do demonstrate a general relationship (Figures 4.11(a), 4.11(b)).

4.3.2.7 Effect of Antioxidant on Adhesion of IR to Brass-Plated Wire

An interesting and surprising observation was made when a new batch of polyisoprene (Natsyn 2200) was obtained half way through the project. It showed an unusually low bond strength to the wire compared to earlier deliveries of IR (which had been stored at least 6 years, on the shelf, in our laboratory).

It was thought that the poor adhesion of new IR to wire could be due to the presence of an antioxidant which is usually added to synthetic rubber.

According to the literature the majority of antioxidants in use have been found not to exert a great effect on brass adhesion. Rutz(51) found no significant effect of PBN at up to 6 pphr; at higher contents of antioxidant blooming occurred and a drastic decrease

TABLE 4.20

Effect of Sulphur Proportion on Physical Properties and Bond Strength of Silica Filled SBR

Physical Properties)	Formulation No. (Table 4.19)					
	1	2	3	4	5	6
Hardness (IRHD)	59	69	74	75	76	76
Tear Strength (kN m^{-1})	52.4	57.5	57.3	50	43.9	36.9
Tensile Strength (MPa)	5.9	10.2	10.9	9.4	8	7.2
Elongation at break (%)	510	440	320	220	200	140
Tensile product (MPa x %) 10^2	30.1	44.9	34.9	20.7	16	10.1
Rupture Energy (J)	3.25	4.65	4.1	2.4	1.65	1.05
Bond strength (MPa)	4.2	7.2	9	9.5	8.5	7.4
Rubber coverage (%)	10	40-50	40	60	50	50
Scorch time t_2 (mins) @ 170°C	5	5	5	4.5	4	3.5
Cure time t_{95} (mins) @ 170°C	40	32.5	31.5	30	24	18

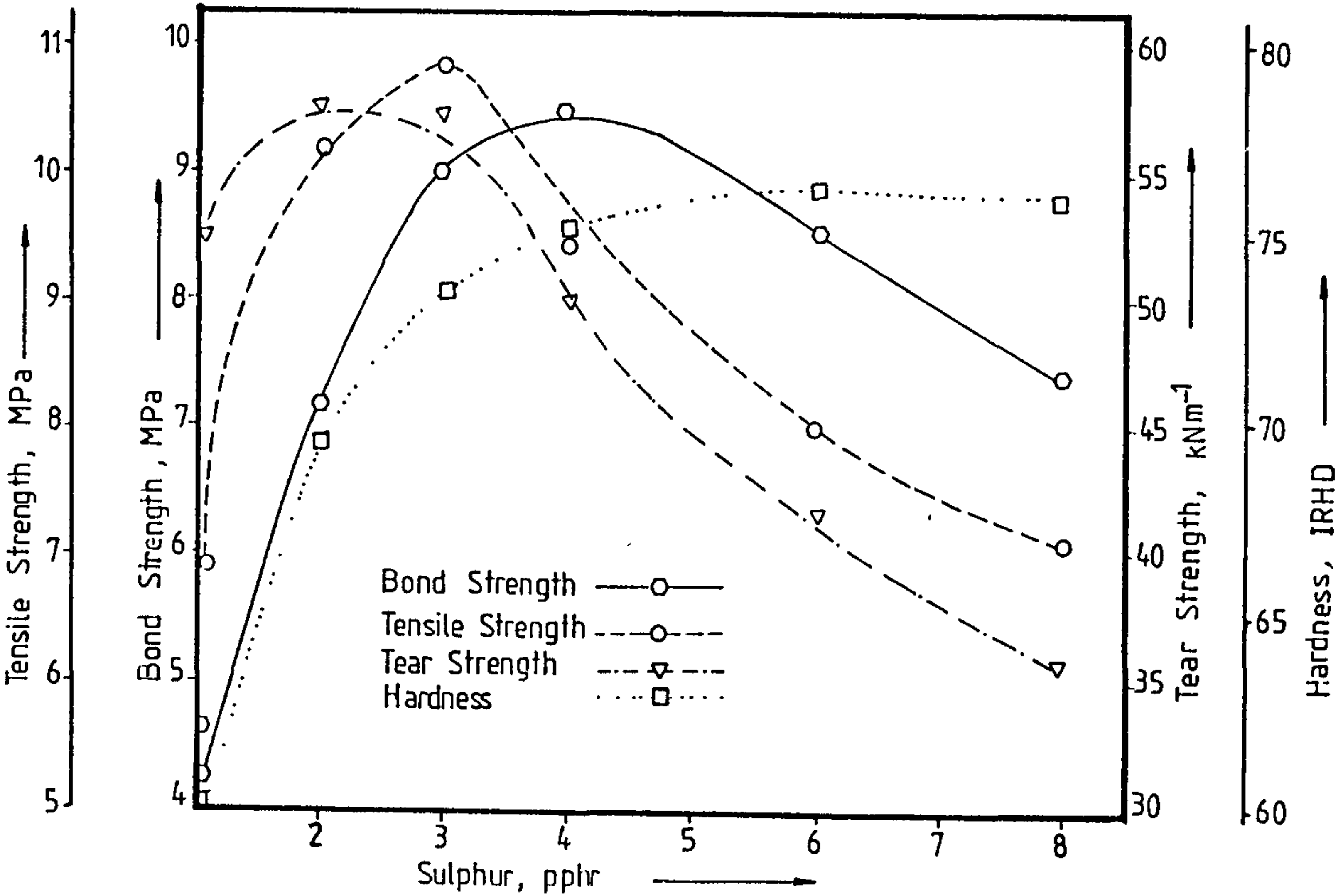

FIGURE 4.11(a): Effect of Sulphur, Proportions on Physical Properties and Bond Strength of Silica Filled SBR

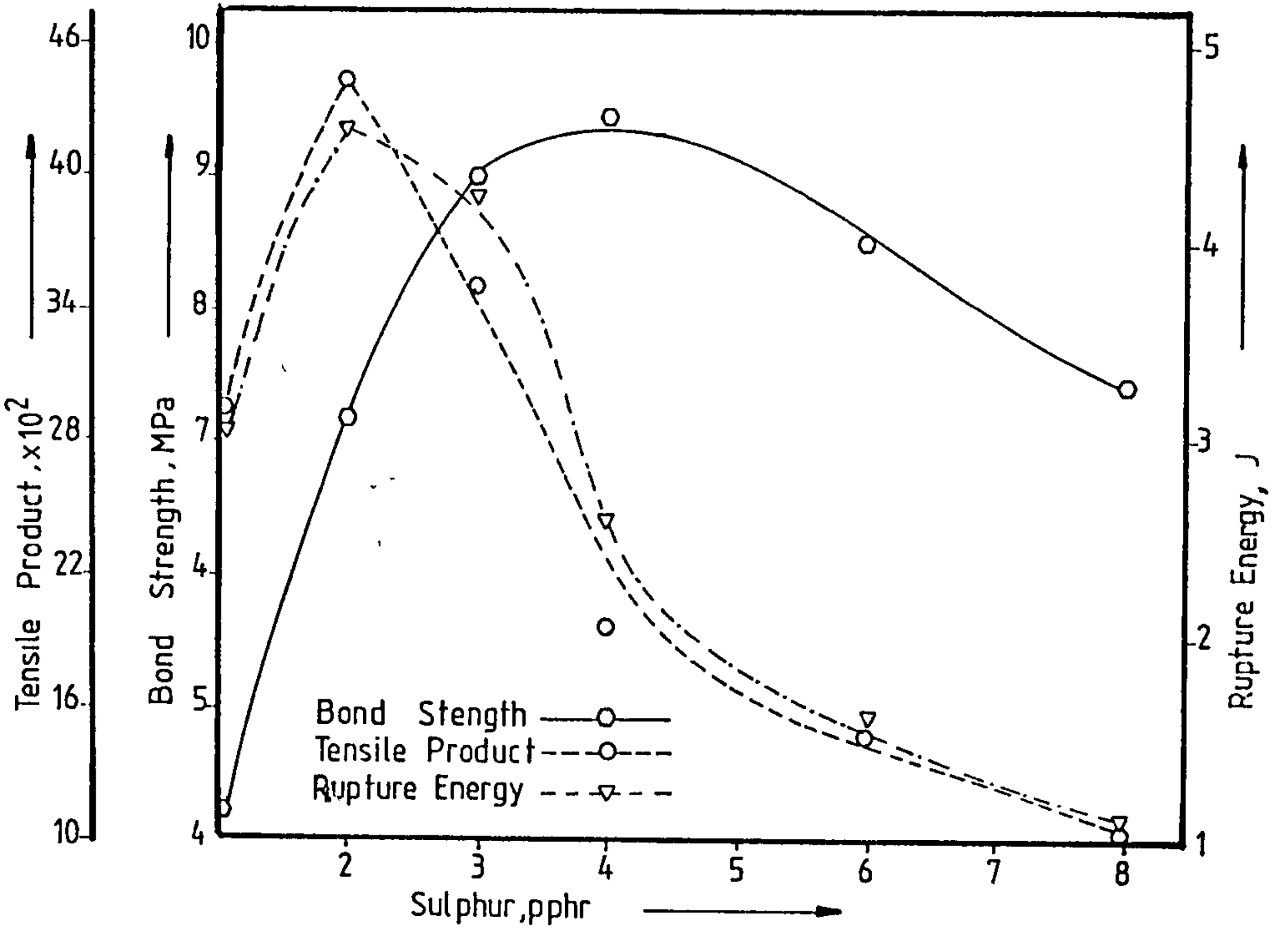

FIGURE 4.11(b): Relationship Between Sulphur Proportions Versus Bond Strength, Rupture Energy and Tensile Product in Silica Filled SBR

of adhesion was the result. Albrecht(48) found an adverse effect of MBT on bonding due to its strong reduction of the Mooney scorch time. This postulation seems to be correct, in view of the negative effect on bonding of accelerators with very short scorch times. Bertrand(72), who used a black NR/BR compound with DCBS and cobalt naphthenate reported no effect of several antioxidants on initial adhesion.

In this study the investigation was carried out using three mixes (Table 4.21). Mix No. 1 contained old IR, mix No. 2 contained new IR and specially extracted new IR (acetone extraction) was used in mix No. 3. The results are given in Table 4.22. According to the results the physical properties (hardness, tear strength, tensile strength) of the old IR and new IR were the same only the small difference recorded is due to testing variation. But the bond strength results are contradictory. The new IR gave a very poor bond strength of 3.2 MPa and rubber coverage of 0-5%. Some improvement in bond strength (8.3 MPa) and rubber coverage (40%) were observed when the extracted IR was compared with its counterpart. From these results it can be considered that the deterioration of bond strength might be due to the presence of antioxidant in the new IR which is known from the supplier to be BHT*.

The old and new IR were analysed ** and the antioxidant amounts in old and new IR found to be as follows:

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* BHT = 2,6-di-t butyl-p-cresol

** They were sent to Goodyear Research Centre to be analysed.

	% antioxidant
Old IR	0.59% by weight
New IR	0.40% by weight

The above does not support a postulation of better adhesion with diminishing levels of residual stabiliser so this observation thus remains a mystery. There was no more old IR to carry out further investigation. Due to this reason the effect of silica (VN3) proportions on the physical and bonding properties of IR rubber to brass-plated wire was not studied.

TABLE 4.21

Formulation Used to Evaluate the Effect of Antioxidant on Bond Strength of IR

Formulation	Mix No.		
	1 old IR	2 New IR	3*
IR (2200)	100	100	100
Zinc oxide	10	10	10
Stearic acid	3	3	3
Carbon black (HAF)	35	35	35
Sulphur	4	4	4
DCBS	0.7	0.7	0.7

* New IR with antioxidant extracted

TABLE 4.22

Effect of Antioxidant on Bond Strength of IR to Brass-Wire

Physical Properties	Formulation No. (Table 4.21)		
	1	2	3
Hardness	58	57	-
Tear strength (kN m^{-1})	66.2	68	-
Tensile Strength (MPa)	20.9	21.3	-
Bond Strength (MPa)	15.3	3.2	8.3
Rubber Coverage (%)	100	0-5	40
Scorch time t_2 (mins) @ 170°C	5.5	5.5	5.5
Cure time t_{95} (mins) @ 170°C	14	14	14

CHAPTER 5

AN INVESTIGATION INTO THE EFFECT OF TITANATES ON THE PHYSICAL PROPERTIES OF SBR AND ITS ADHESION TO BRASS-PLATED WIRE

5.1 Introduction

Before the development of 'integral' or 'direct' rubber-to-metal bonding systems the conventional method of adhesion in use to bond rubber to metal was where one or more adhesive layers were applied as a sandwich between the rubber and metal. In the recently developed so-called direct rubber-metal adhesion systems, a bonding promoter is mixed with the rubber which tends to enhance the affinity of the rubber to metal substrate resulting in effective adhesion. Many tyre manufacturers use either cobalt salts, usually cobalt naphthenate or a hexamethylene tetramine-resorcionol-silica system (HRH) or both of these together in their steel cord skim compounds. These bonding promoters are usually incorporated by mixing into the rubber. Another way to possibly improve rubber to steel wire adhesion is to dip the wire or cord into a solution of bonding promoter in imitation of the procedure which is usually used for textile cords; this method was investigated for a number of silane coupling agents but the results were rather poor(73). The dipping method has also been used by employing a solution of inorganic or organic phosphates, preferably tricresyl phosphate and various sulphur-containing rubber vulcanization accelerating agents(74).

A new class of coupling agents was recently introduced by Kenrich Petrochemical Inc*. They can be considered to function as a molecular

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* Kenrich Petrochemicals Inc.
Foot of East 22nd Street, Bayonne, N.J. 07002, USA

bridge between the interface of the inorganic and the organic matrix. They are unique in their reaction enabling the free protons at the inorganic (filler, metal, etc) interface to form organo-functional monomolecular layers on the inorganic surface. Then these monomolecular layers can link to the polymer through either organic groups with titanates acting as a bridge between polymer and inorganic surfaces (filler, substrate).

The design of the molecule is similar to that of a siloxane coupling agent with additional complications and may be represented as follows:(75)

$$(R'O)_m\text{—Ti—}(O\text{—}X\text{—}R''\text{—}Y)_n$$

The R'O groups are considered to react with protons on the filler or metal surface, the remainder of the molecule can then react with functional groups in the polymer. X can be phosphite or phosphate, carboxyl or sulphonyl thus donating, at will, antioxidant, corrosion inhibition, flame retardant, or thixotropic properties to the polymer, R" is the group which is thought able to bond to thermoplastic polymers and may be aliphatic or aromatic in character whilst Y has the function of bonding to thermoset and may be amino, or merely a non-reactive hydrogen termination. Appendix I shows in detail the titanates various structures and functions.

Titanate coupling agents have been suggested principally for use in plastics, although examples of their use in rubber have been cited(76). But the use of these coupling agents in rubber compounding has not been widely practised.

Some of these titanate coupling agents have been suggested as bonding promoters and also by permitting the formation of a monolayer on the steel surface, to prevent corrosion(77,78).

A preliminary investigation was carried out to find the effect of several types of titanates on the physical properties of SBR and its adhesion to brass-plated steel wire.

5.2 Experimental

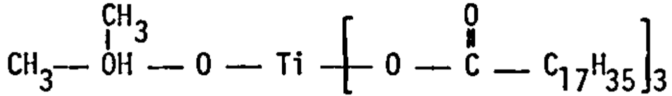
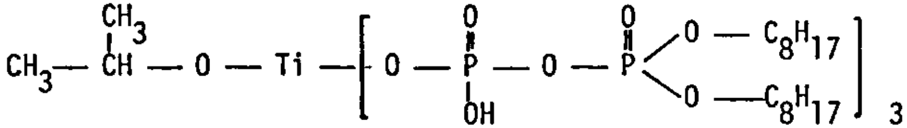
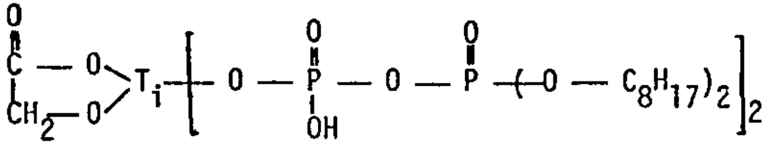
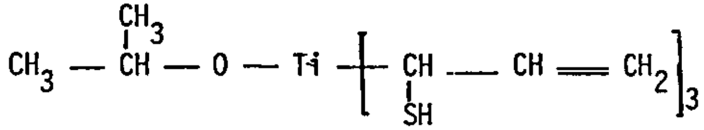
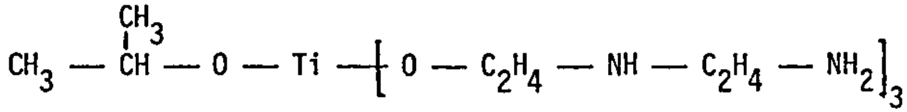
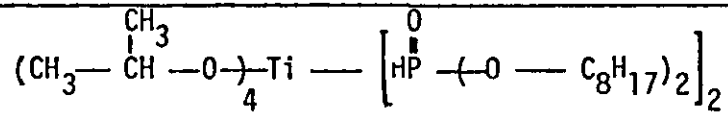
Seven different types of titanates were selected according to their structure. The Kenrich Petrochemical Inc. code names are quoted and their structure and their code names are presented in Table 5.1. These titanates have been used in two different ways.

i) Applied directly to the wire surface.
ii) Incorporated by mixing into the rubber.

5.2.1 Titanate Applied Directly to the Wire Surface

In the wire industry, a surface lubricant it used to cool down the wire during the drawing process and this generates high frictional heat. Usually such a lubricant leaves a residue which reduces the adhesion between the rubber and wire. The purpose of this work was to determine if these titanium coupling agents would enhance the strength and permanence of the bond between rubber and brass-plated wire. If so, they may perhaps be used as a wire drawing lubricant either alone or in a special formulation modified using this additive.

TABLE 5.1: Chemical Structure of Titanate Coupling Agents

Code	Chemical Description	Chemical Structure	
		Wire or filler active group	Polymer active group
TTS	Isopropyl triisostearoyl titanate	 $CH_3-\overset{CH_3}{\overset{\vert}{OH}}-O-Ti-\left[O-\overset{O}{\overset{\Vert}{C}}-C_{17}H_{35}\right]_3$	
KR-38S	Isopropyl tri(dioctylpyrophosphato) titanate	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-O-Ti-\left[O-\underset{OH}{\underset{\vert}{\overset{O}{\overset{\Vert}{P}}}}-O-\overset{O}{\overset{\Vert}{P}}\begin{matrix}O-C_8H_{17}\\O-C_8H_{17}\end{matrix}\right]_3$	
KR-138S	Titanium di(cumylphenylate)oxyacetate	 $\begin{matrix}\overset{O}{\overset{\Vert}{C}}-O\\ \vert \\ CH_2-O\end{matrix}\rangle Ti\left[O-\underset{OH}{\underset{\vert}{\overset{O}{\overset{\Vert}{P}}}}-O-\overset{O}{\overset{\Vert}{P}}(O-C_8H_{17})_2\right]_2$	
KR-66S	Isopropyl tri(3-mercaptopropionyl) titanate	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-O-Ti-\left[\underset{SH}{\underset{\vert}{CH}}-CH=CH_2\right]_3$	
KR-44S	Isopropyl tri(N-ethylamino-ethylamino) titanate	 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-O-Ti-\left[O-C_2H_4-NH-C_2H_4-NH_2\right]_3$	
KR-41B	Tetraisopropyl di(dioctylphosphito) titanate	 $\left(CH_3-\overset{CH_3}{\overset{\vert}{CH}}-O\right)_4Ti-\left[H\overset{O}{\overset{\Vert}{P}}(O-C_8H_{17})_2\right]_2$	

The method used to apply the titanate to the wire surface was derived from the work of McConnell(38) and Smith(28) who have investigated the effect of different types of lubricant on the adhesion of rubber to wire.

For this experiment a 2% solution* of the selected titanates were prepared, Table 5.2. Their surface tension and interfacial tension with the wire was measured with a Du Nuoy Torsion Balance. Also, any change in their structure over the temperature (ambient - 170°C) was measured by Du Pont Thermal Analyser 990 (DSC) at a heating rate of 20°C/min. To examine the effects of these titanate solutions on adhesion, each piece of wire was first cleaned with toluene to remove the lubricant residue and the contamination from the surface of the wire with absorbant paper until no black residue shows on the paper. These cleaned wires were weighed and one was kept as a standard sample. The rest were dipped in the titanate test solutions and then washed with the same solvent to remove the unreacted titanate, and suspended vertically and allowed to dry. Then they were weighed to determine the amount of solution retained on the wire. The retained solution on the wire surface varied between 1-4 mg/g of wire. The mix formulation used to evaluate bonding is shown in Table 5.3(a).

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* Kenrich normally recommend use of a 1% solution for direct application to a surface

5.2.2 Titanate Incorporated into the Rubber

Addition of compounding ingredients followed one of the following cycles:

Carbon black mixing cycle

SBR → Activators (Zinc oxide/Stearic acid) + Carbon black (HAF)
+ Titanate → Accelerator → Curing agent

Silica mixing cycle

SBR → Silica (VN3) + Silane (Si 69) + Titanate + Activators
(Zinc oxide/Stearic acid) → Accelerators → Curing Agent

It was found that the addition of titanate in the early stages of mixing made the processing easy. A recommended amount of titanate for use with a small particle size filler such as carbon black (HAF) and silica (VN3) is ½ - 1½% of the filler weight(77) but in this experiment, the amount used was 4% of the filler weight to enable a broad assessment of its effects to be made. The mix formulation used is given in Table 5.3(b).

5.3 Results and Discussion

5.3.1 Wetting the Wire Surface

Results as shown in Table 5.4 indicate that the addition of titanate did not make any difference to the interfacial tension between the wire and solutions. It is the solvent which wets the wire surface and due to its low interfacial tension most parts of the wire surface were wetted by the solutions (i.e. there is good wettability between wire and solutions).

TABLE 5.2: Solvents Used for Different Types of Titanates

Solvent	Titanate
Isopropanol	KR-138S, KR-38S, KR-44, KR-41B
Chloroform	KR-TTS

TABLE 5.3: Mix Formulation Used to Evaluate the Bonding Ability of Titanates

(a)		(b)		
pphr	1	pphr	1	2
SBR (1204)	100	SBR (1204)	100	100
Zinc oxide	10	Zinc oxide	10	10
Stearic acid	3	Stearic acid	3	3
Carbon black (HAF)	35	Carbon black (HAF)	35	-
Sulphur	2	Silica	-	30
DCBS	1	DCBS	1	1
Titanate applied as a 2% solution on the wire surface		DPG	-	1
		Si 69	-	1.2
		Titanate	1.4	1.2

(a) Titanate applied directly to the wire surface

(b) Titanate incorporated directly into the rubber for direct bonding examination.

5.3.2 DSC Analysis of Titanates

According to the DSC thermogram of titanates, Figure 5.1, titanates KR-TTS, KR-38S, KR-138S and KR-66S show little change in state over the temperature ambient -170°C. However, KR-44S and KR-41B are seen to show thermal transitions below 170°C (170°C is the vulcanization temperature) and hence indicates that some bonding response may occur with these materials.

5.3.3 Effect of Titanates on Adhesion of Rubber to Wire (Titanate Solution Applied Directly to the Wire Surface)

The results are given in Table 5.5. By reference to the table it can be seen that all the titanates applied to the wire surface reduced the bond strength in comparison with the control. The poorest were isopropyl tri(N-ethylamino-ethylamino) titanate (KR-44S), and tetra isopropyl di(dioctylphosphito) titanate (KR-41B) which reduced both bond strengths from 12.2 MPa to 1.9 MPa and rubber coverage from 45% to 0%. This is considered due to the thermal transitions of these titanates below the vulcanization temperature (170°C) see Figure 5.1. During the vulcanization process the titanates apparently decompose so no surface activity probably occurs between titanates and wire or rubber and hence they may remain at the interface between wire and rubber acting as a lubricant. In the case of isopropyl di(4-aminobenzoyl) isostearoyl titanate (KR-38S) and titanium di(dioctylpyrophosphate) oxyacetate (KR-138S), the bond strength values were slightly lower than the control values. The relatively slight deterioration in bond strength that is observed

TABLE 5.4: Surface Tension and Interfacial Tension Measurements of Titanate Solutions

Titanate Solution	Solvent	Surface Tension $Nm^{-1} \times 10^{-3}$	Interfacial Tension $Nm^{-1} \times 10^{-3}$
-	Isopropanol	22	7
-	Chloroform	28	8
KR-TTS	Chloroform	28	8
KR-138S	Isopropanol	22	7
KR-38S	Isopropanol	22	7
KR-44	Isopropanol	22	7
KR-41B	Isopropanol	22	7

TABLE 5.5: Effect of Titanates on Bond Strength (Titanate Solution Applied to the Wire Surface)

Titanate	Bond Strength MPa	Rubber Coverage %	Comments
Control No titanate	12.2	45	-
KR-TTS	11.8	43	Equal to control
KR-138S	10.3	26	Slightly poorer
KR-38S	10.9	29	Slightly poorer
KR-44	1.9	0	No bonding
KR-41B	1.9	0	No bonding

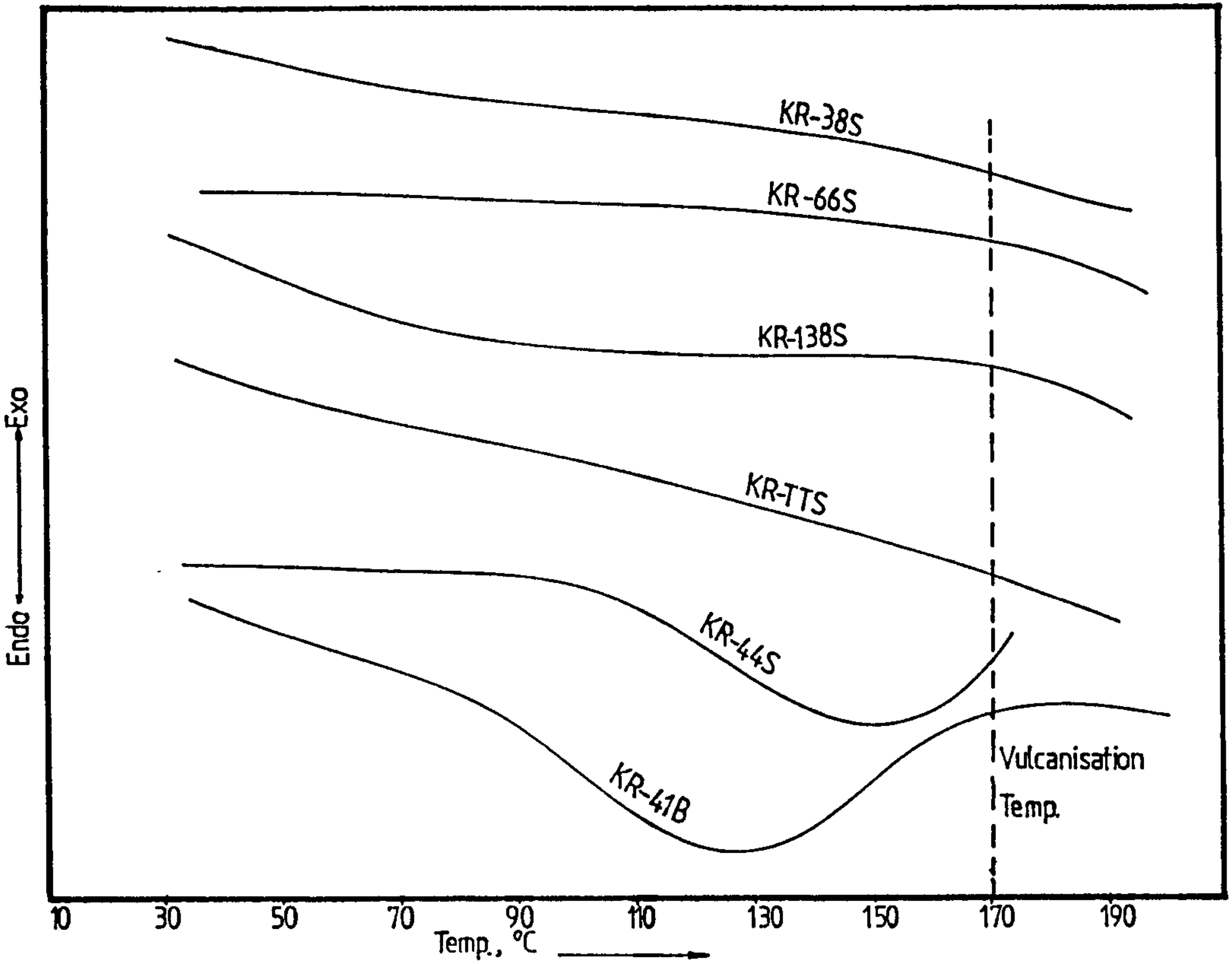


FIGURE 5.1: DSC Thermogram of Titanates Used

when KR-38S and KR-138S are used may be due to hydrolyzation of the titanates at the metal-titanate interface by the presence of water in that region (there is little water present in all rubber compounds). Cotton and Wilkinson(79) state that titanium alkoxide can be hydrolyzed by small traces of water. Isopropyl triisostearoyl titanate (KR-TTS) shows an adhesion result equal to the control indicating some surface activity of KR-TTS between wire and rubber surface.

In general it is concluded that the titanates which were studied exhibited some surface activity but were observed to produce adverse bond strength values.

5.3.4 Effect of Titanates (Incorporated into the Rubber) on the Physical and Bonding Properties of Filled (Carbon Black and Silica) SBR

As stated earlier, the titanates which were applied to the wire surface exhibited surface activity since they produced negative results. It was decided to investigate the effect of these titanates on the adhesion of SBR to wire and on the physical properties of the rubber when they are incorporated into the rubber.

The results are given in Table 5.6. Reference to the results of these titanates show positive and negative results compared with the control. Negative results with respect to bond strength were obtained with KR-44S (2 MPa bond strength and 0-5% rubber coverage), K-41B (7.7 MPa bond strength and 8% rubber coverage) and KR-66S (9.5 MPa bond strength and 30% bond strength), see Figure 5.2.

TABLE 5.6: Effect of Different Types of Titanates on Physical Properties of Carbon Black Filled SBR and on its Adhesion to Brass-plated Wire

Titanate	Cure rate properties at 170°C		Mooney Viscosity 4(ML+1)	Hardness (IRHD)	Tear Strength kN m^{-1}	Tensile Strength (MPa)	Elongation at break (%)	Bond Strength (MPa)	Rubber Coverage (%)	Comments on bond strength and rubber coverage
	Scorch time t_2 (mins)	Cure time t_{95} (mins)								
Control	10	27	63	58	56.4	18.5	670	13	45	-
KR-TTS	13	33	58	56	57.7	19.3	710	15.8	95-100	Better than control
KR-138S	13.5	43	60	56	56.8	18	730	13.5	95-100	"
KR-38S	13.5	43	58	57	56.6	21.6	810	14.2	95-100	"
KR-66S	2.5	17	59	58	78.2	16.6	700	9.5	30	Poorer
KR-44	2	17.5	70	61	80	11.3	760	2	0	Much poorer
KR-41B	13	32	58	57	59.8	21.3	810	7.7	8	Poorer

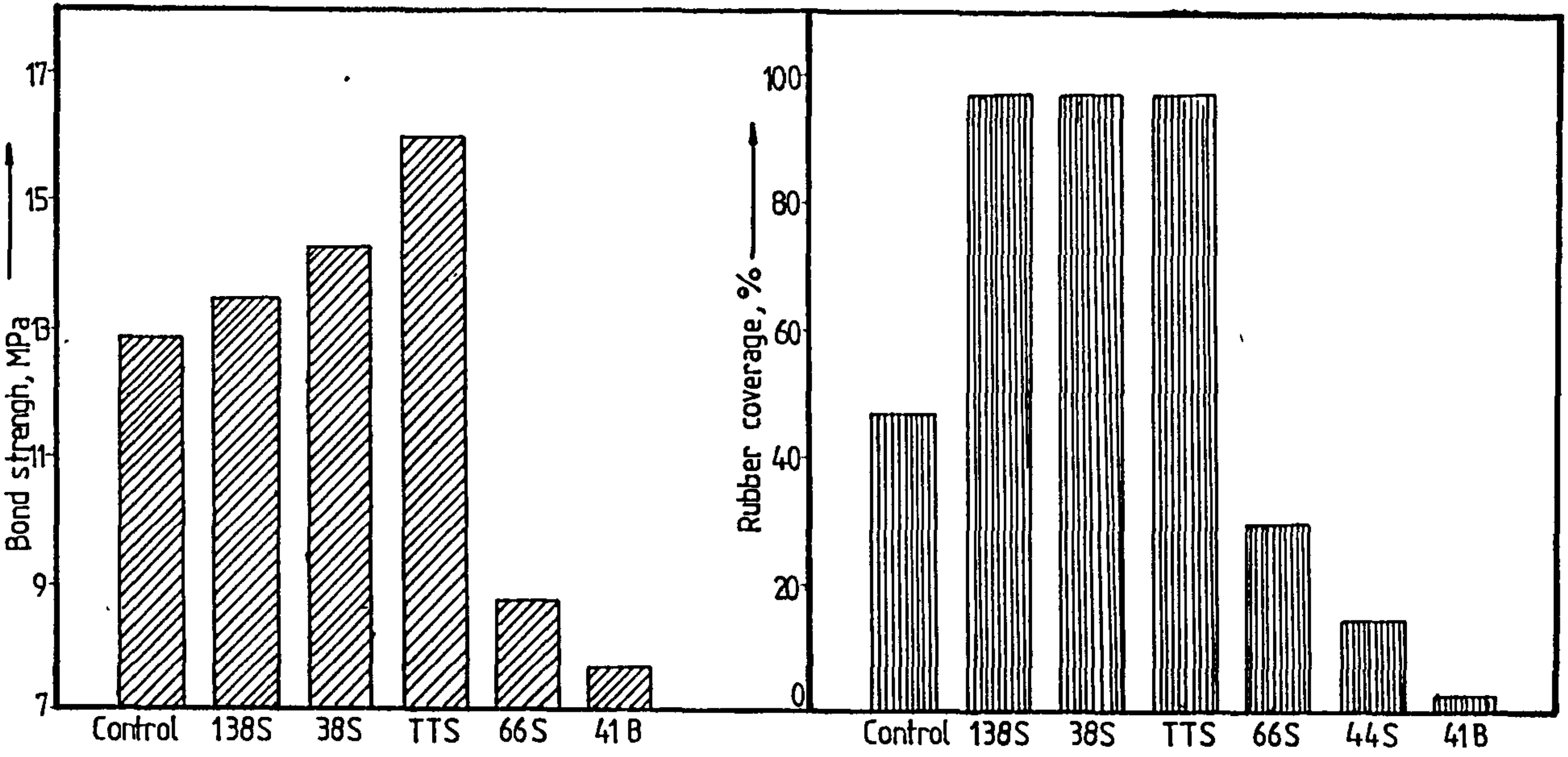


FIGURE 5.2: Effect of Different Types of Titanate on Bond Strength and Rubber Coverage

Deterioration of adhesion may perhaps be due to the effect of KR-66S and KR-44S on the scorch time. Scorch time reduced from the control's 10 minutes to 2 minutes as shown in Figure 5.3. Other effects such as decomposition (KR-44S and KR-41B undergo a change of state below the vulcanization temperature of 170°C) or effect on the rate of sulphidisation between sulphur and copper should be considered. An important point is that KR-41B bloomed heavily to the rubber surface and the low bond strength observed might be due to this effect as well as its relatively low decomposition temperature.

Positive or increased bond strength resulted when KR-38S, KR-138S and KR-TTS were mixed into the rubber. In all cases the rubber coverage increased from 45% in control to 100% (i.e.failure occurred within the rubber). It can be considered that these titanates can be used as bonding promoters in carbon black filled SBR (the mechanism will be discussed in Chapter 7).

The effect of these titanates on physical properties is now discussed. As mentioned earlier, KR-44 and KR-66S reduced the scorch time and accelerated the cure time. This may be due to the amino and mercapto groups in KR-44S and KR-66S respectively which may function as accelerators. KR-138S and KR-38S increased the scorch and cure time (see Figure 5.3). KR-TTS has a cure time closer to that of the control value than the other titanates examined. Mooney viscosity and hardness were reduced with all titanates except in the case of KR-44 (Mooney viscosity of 70 and hardness of 61 IRHD obtained for SBR/carbon black/KR-44 mix in comparison with Mooney viscosity of 63 and hardness of 58 IRHD for the control). A signi-

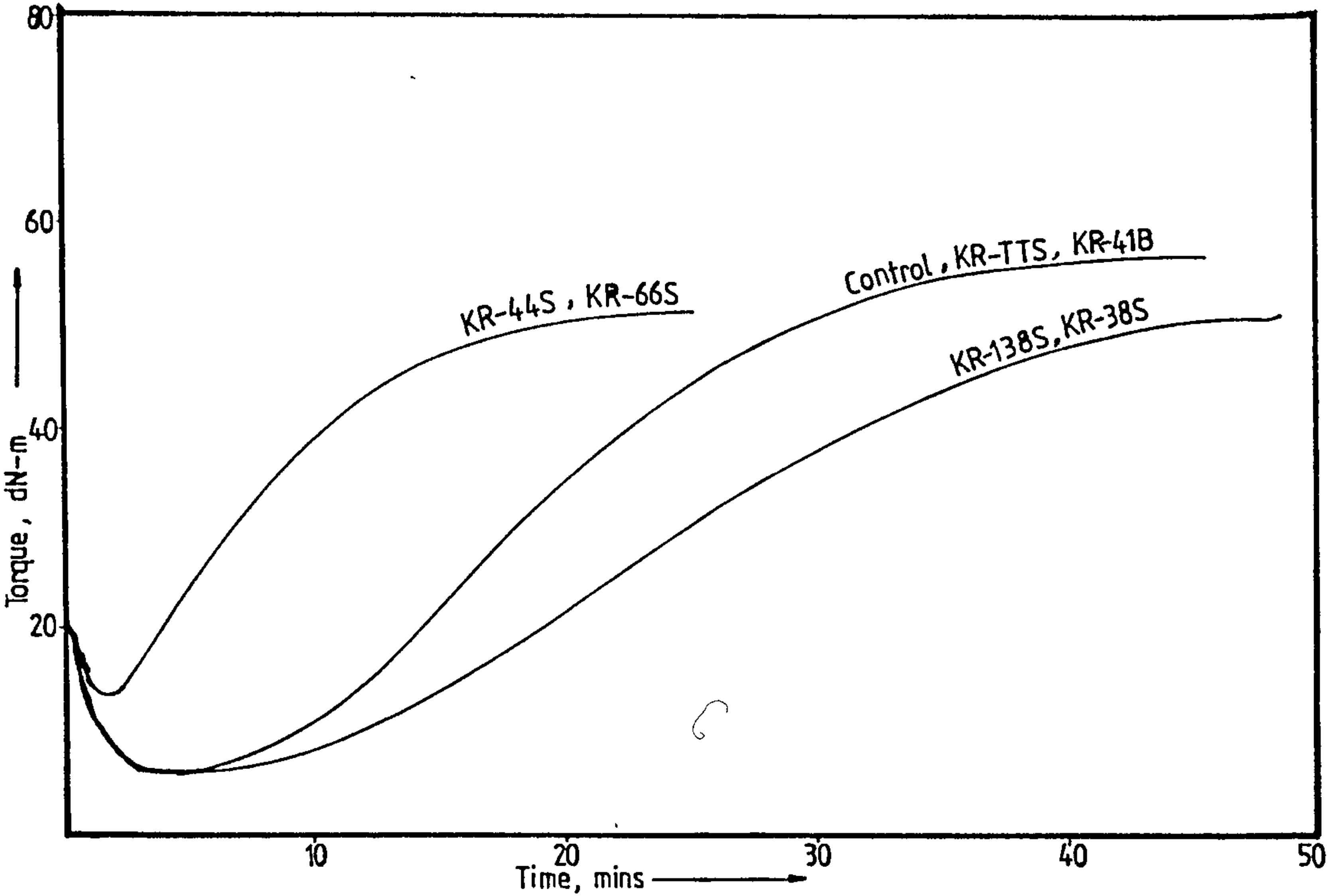


FIGURE 5.3: Effect of Titanates on Cure Rate Properties of Carbon Black Filled SBR at 170°C

ficant increase was observed in the tear strength of SBR/carbon black mix with KR-44S and KR-66S. Tensile strength was observed to increase with KR-38S and KR-41B. However tensile strength substantially decreased with KR-44. High elongations were obtained with all titanates (the above effects on bond strength and physical properties of carbon black filled SBR will be discussed in Chapter 7).

The effect of titanates KR-TTS, KR-138S and KR-38S on the physical properties of silica filled SBR and its adhesion to wire was investigated, (see Table 5.7). In all cases, the bond strength reduced from 9.5 MPa to between 2.2-3.7 MPa and rubber coverage from 45% to 0-5%. No significant effects were observed in physical properties.

TABLE 5.7: Effect of Different Types of Titanateson Physical Properties of Silica Filled SBR and its Adhesion to Brass-Plated Wire

Titanate	Cure rate properties at 170^{o}C		Hardness (IRHD)	Tear Strength kN m^{-1}	Tensile Strength (MPa)	Elongation at break (%)	Bond Strength (MPa)	Rubber Coverage (%)	Comments on bond strength and rubber coverage
	Scorch time t_2 (mins)	Cure time t_{95} (mins)							
Control	5.5	34	70	50	9.2	280	9.5	40-50	-
KR-TTS	5	38	68	50.6	8.6	300	3.7	0- 5	Poorer
KR-138S	5.5	41	67	48.1	9	260	2.4	0- 5	Poorer
KR-38S	6	41	67	48.8	8.3	220	2.2	0- 5	Poorer

CHAPTER 6

ANALYSIS OF BRASS-PLATED WIRE SURFACE AND THE WIRE-RUBBER INTERFACE BY MEANS OF ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)

6.1 Introduction

Information (compositional, chemical state and molecular bonding information) about the topmost atomic layers of solid specimens (metals, organic and inorganic chemicals, polymers) is crucial in order to gain a knowledge and understanding of the manner in which those specimens will behave when placed in any particular environment.

A number of techniques are now available to acquire this type of knowledge. There are three major techniques, viz. Auger Electron Spectroscopy (AES), X-Ray Photo-Electron Spectroscopy (ESCA) and Secondary Ion Mass Spectroscopy (SIMS). Each of these techniques has the ability to measure the composition of the outermost atomic layers, but each technique has advantages and disadvantages and some judgement is necessary when choosing the appropriate technique for a particular problem, Table 6.1. This is possible only through familiarity with the techniques, their fields of application, and the complementary nature of the information that they supply. XPS has been used in the investigation of rubber-to-brass adhesion(39)(66) since it permits quantitative analysis of oxide composition. XPS has also a considerable advantage in comparison to AES in composition depth-profiling since depth information can be obtained not only by angular variation, but also by varying the kinetic energy of the photoelectrons by using different excitation sources. In general, for all depths, the major

TABLE 6.1: Methods of Surface Analysis

	X-ray Photoelectron Spectroscopy (ESCA)	Auger Electron Spectroscopy (AES)	Secondary low mass Spectroscopy (SIMS)
Incident particle	X-ray (1254 eV and 1487 eV)	Electrons (1-10) KeV	Ions (100 eV - 5 KeV)
Emitted particle	Photoelectron (20 - 2000) eV	Auger electrons (20 - 2000) eV	Sputtered ions
Element range	> He (Z = 2)	> Li (Z = 3)	> H (Z = 1)
Detection limit	0.5 atom %	0.1 atom %	$> 10^{-4}$ atom %
Depth of analysis	$\sim$ 2 nm	$\sim$ 2 nm	$\sim$ 1 nm
Lateral resolution	> 1 mm	> 0.5 μm	> 1μ m

advantages of XPS over AES is that it provides chemical information and it can be used with delicate materials, hence XPS was chosen as the primary investigation method in this research.

6.2 Principle of ESCA

Each atom present in the surface (except hydrogen) possesses core electrons not involved in the bonding. The so-called "binding energy" of each core electron (conceptually equivalent to the ionisation energy of that electron) is characteristic of the individual atom. Core electron binding energies vary with atomic number. For any given electron shell, the K shell for instance, the electron binding energy increases with increasing atomic number. Thus, information of the binding energies of electrons within a sample allows qualitative elemental analysis.

In the basic ESCA experiment, the sample surface is irradiated by a source of low-energy X-ray (generally $Al_{K\alpha}$ or $Mg_{K\alpha}$) under ultra-high vacuum (UHV, 10^{-8} - 10^{-11} torr of Hg) conditions which eject core electrons, directly from the surface atoms. These core electrons, originally with a binding energy E_b which are then emitted with a kinetic energy E_K given by:

$$E_K = h\nu - E_b + \phi \qquad (6.1)$$

where: $h\nu$ = X-ray photon energy

E_b = binding energy of electrons

ϕ = work function of solid containing the atom.

Since the value of hν and E_K (measured from spectrum) are known, the binding energy E_b can be calculated using equation 6.1. Figure 6.1 schematically represents the principle of XPS.

6.3 Experimental

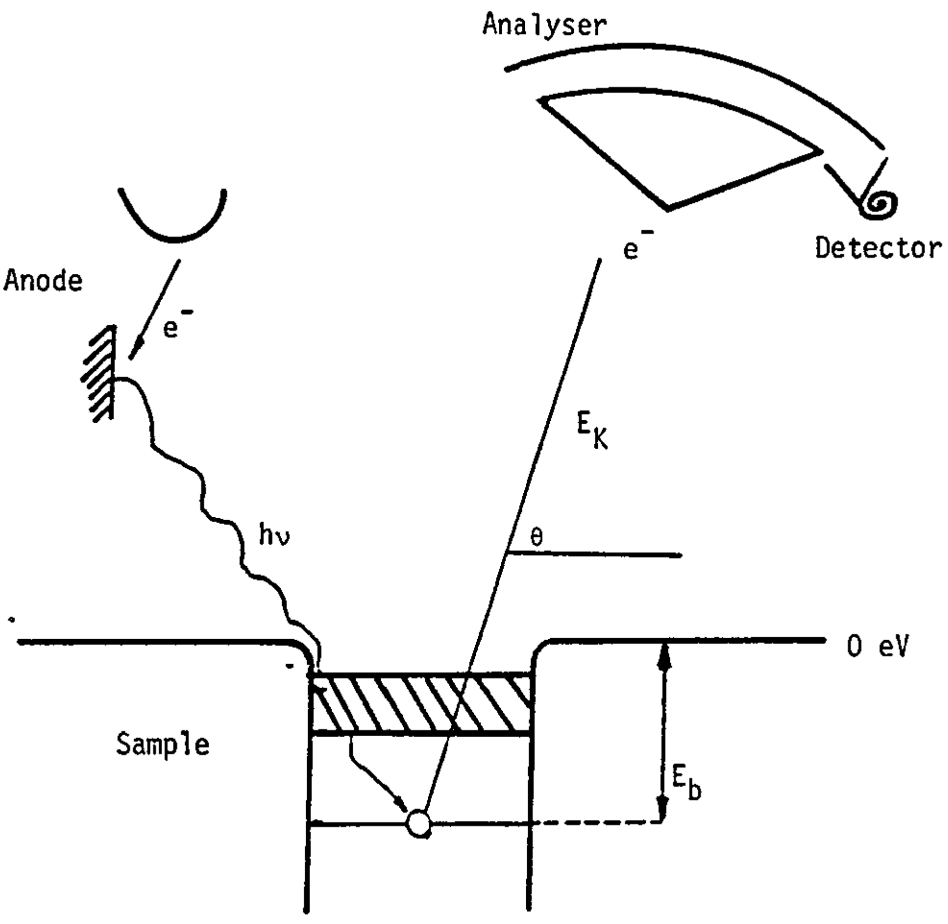
It is the purpose of this work to present the results of a preliminary study of the bonding mechanism and of a search for the various parameters which have an effect on adhesion. This study can be broken down into three parts:

i) Surface composition of brass-plated wire (used in this project).

ii) Identification of the chemical compounds which are formed at the rubber-wire interface during vulcanization.

iii) Effect of rubber compound (carbon black and silica) on the chemical compositions which are formed between rubber and wire.

During this study the X-ray Photoelectron Spectroscopy (XPS or ESCA) analysis were performed on a Vacuum Generator Model VG SCALAB spectrometer using $Al_{K\alpha 1,2}$ radiation and pressure of 10^{-8} torr. Sputter-depth profiling of wire and rubber surface were performed with beams of Ar^+ ions of 10^{-5} torr pressure and 3 KeV energy and 12 $\mu A/cm^2$. The surface of wire and rubber sputtered at the rate of approximately 20 nm/min (i.e. a layer of 20 nm was removed from the surface after one minute). Quantitative evaluation of spectra will be described in Section 6.3.2.



$$E_K = h\nu - E_b + \phi$$

FIGURE 6.1: X-Ray Photoelectron Spectroscopy (XPS)

6.3.1 Sample Preparation

In order to provide a specimen suitable for ESCA analysis, it was necessary to prepare a sample with at least one cm^2 surface area. The single wire "H-test" adhesion type sample used earlier in this project was found to be not suitable for ESCA analysis due to its small surface area (0.3 mm diameter x 8 mm length). It was decided to develop a sample that could give a large surface area (see Figure 6.2). Wire was wound around a frame with strands touching to each other and kept in tension, the band of wires were cleaned with toluene for several times to remove the lubricant residue as much as possible concluding with the wire surface being finally wiped off with acetone to remove any toluene residue. The cleaned wire was then sandwiched between two pieces of rubber and the whole vulcanized. The moulding procedure was the same as mentioned in Section 2.4.2. Then the vulcanized was frozen in nitrogen liquid to separate the rubber from the wire. A small piece of the wire bond (about one cm^{-2} was cut from the wire and rubber and using double sided Sellotape mounted on the specimen probe ready for analysis by ESCA.

6.3.2 Measurement of Binding Energy and Concentration of Elements (Atom %)

As stated earlier, the binding energy is a characteristic of individual atoms, so the binding energy of an electron on the surface of a substrate indicates the elements present.

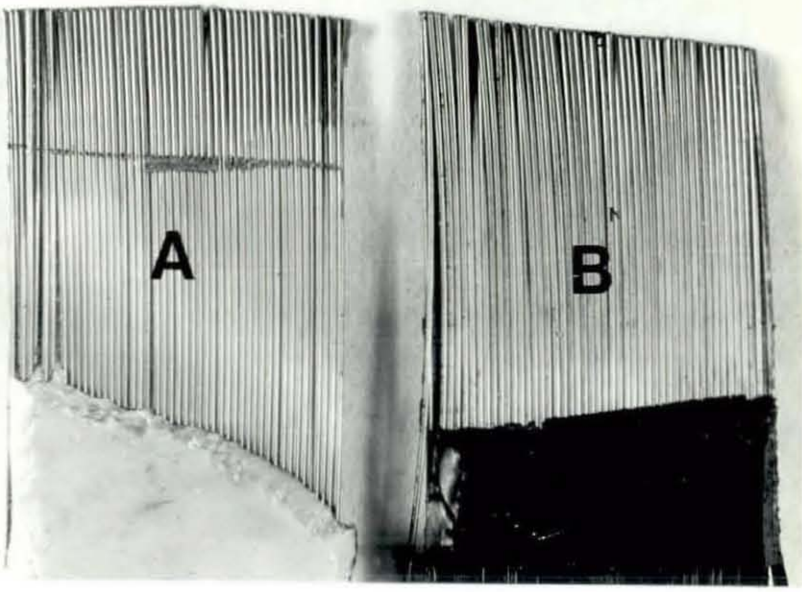


FIGURE 6.2: A Sample Used in ESCA Technique:

A. Wire Side
B. Rubber Side

Measurement of Binding Energy

The binding energy of each peak in the XPS spectrum (see Figure 6.3) was obtained from the literature which gives the reference peak of namely carbon 1s which has a binding energy of 284.7 eV. However in practice the use of an internal reference is also necessary as then the carbon 1s photoelectron peak automatically takes account of the charge build-up at the surface which occurs as a result of the ejection of photoelectrons from the sample. Due to this factor the binding energy of the so-called 284.7 eV for carbon 1s obtained experimentally is inaccurate. Hence to measure an accurate binding energy for reference purposes, high resolution of the reference peak is necessary. In this investigation such high resolution of this reference peak did not prove possible due to experimental problems hence a ± 5 eV error can exist in the results. After measuring its binding energy each peak was identified by reference to the phi handbook. (See Appendix II).

Calculation of the Concentration (Atom %) of Each Element

The atom % which gives the concentration of each element on the sample surface either is outer layer or in depth can be calculated as follows:

$$\text{Number of atoms of each element } (N) \propto \frac{h^*}{S} \qquad (6.2)$$

where h = the height of the peak in the XPS

S = sensitivity factor

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* Equation 6.2 is given in greater detail in Appendix III.

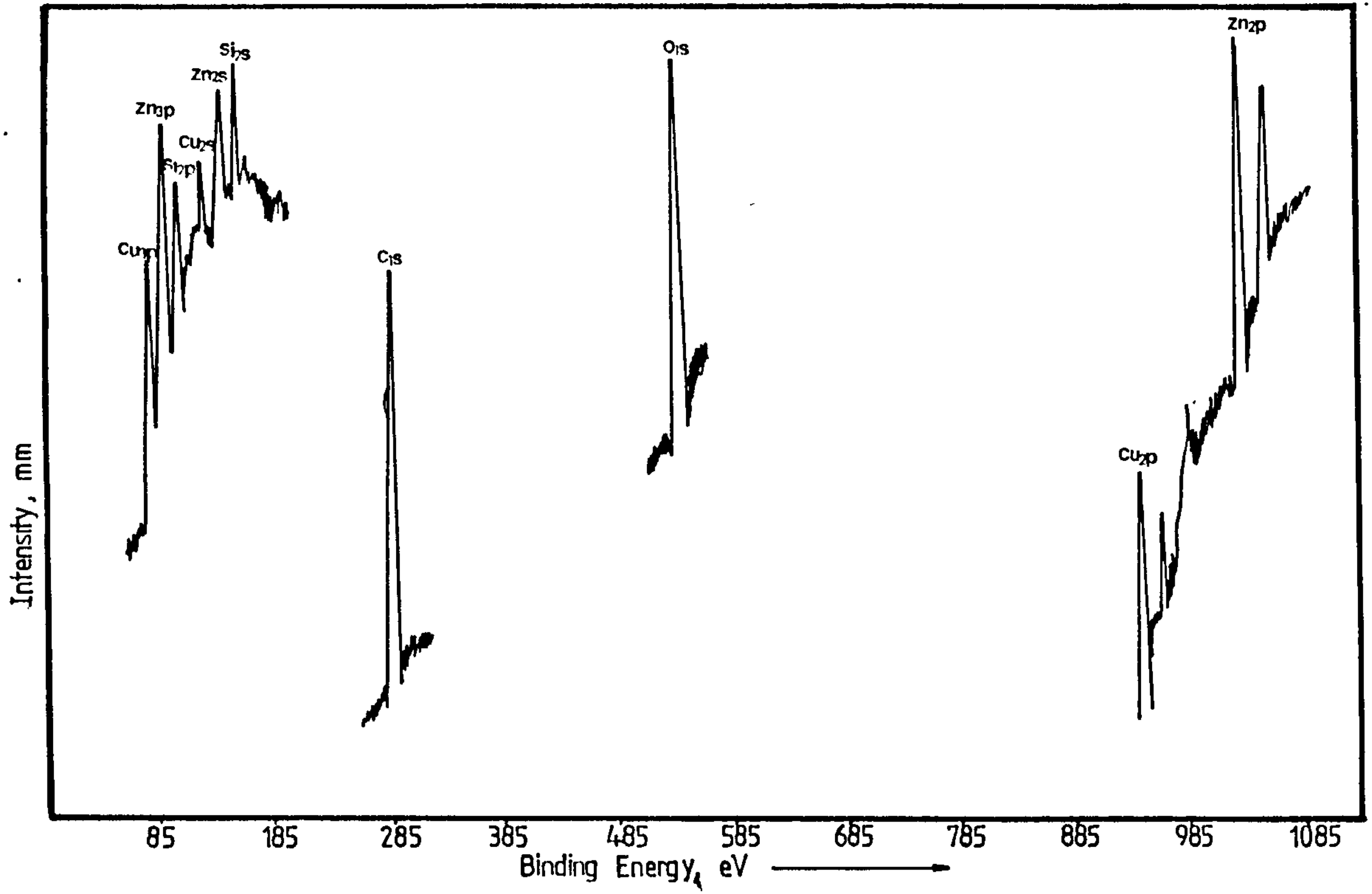


FIGURE 6.3(a): Wide-Scan XPS Spectrum of Brass-Plated Wire Surface (70/30) Using Al $K_{\alpha 1,2}$ Excitation

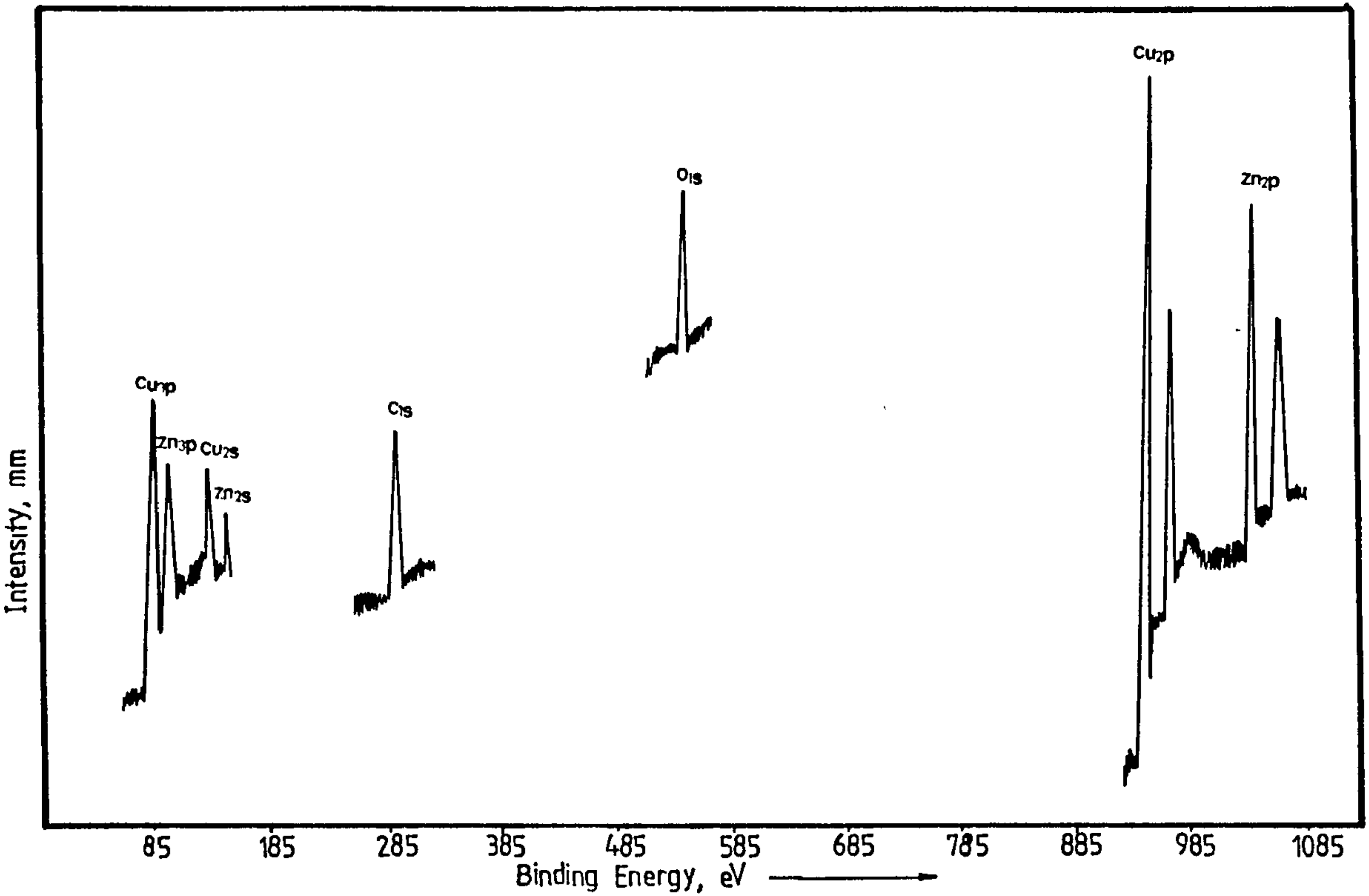


FIGURE 6.3(b): Wide-Scan XPS Spectrum of Brass-Plated Wire (70/30) Using Al $K_{\alpha 1,2}$ Excitation Following 3 Minutes of Argon Ion Bombardment

The sensitivity factor obtained from the chemical standard for detected elements are given in Table 6.2.

TABLE 6.2: Sensitivity Factors for Some Elements

Element	C	O	Cu	Zn	S	Si
S	0.34	1	2.3	3	0.65	0.33

The atom % can be obtained from the equation below:

$$\text{Atom \% of each element} = \frac{N}{\sum_{i=1}^{n} Ni} \times 100 \qquad (6.3)$$

where N represents the number of elements on the surface of the substrate.

6.3.3 Problems Associated with the ESCA Technique Used

1. For a satisfactory analysis the test specimen was required to be flat and large in area. Especially for sputter-depth profiling, for good depth resolution, it required a uniform surface. If a single wire was used then due to its round surface and small radius this was found to be inadequate to obtain an accurate depth scale.

2. The ESCA technique was observed to be sensitive to surface contamination (e.g. high carbon intensity) and especially in the case when strong rubber-wire adhesion occurred, then it was found difficult

to remove the rubber completely from the wire and then the carbon present in the rubber interfered with the ESCA analysis of the wire surface. This disadvantage could lead to inaccurate experimental observations.

3. As the ESCA technique is expensive and not easily accessible, only a limited examination of the sample was possible.

6.4 Results and Discussion

6.4.1 Surface, Composition of Brass-Plated Steel Wire

It has long been recognised that the bonding of Cu/Zn alloys to sulphur-vulcanizable rubber compounds is the result of a reaction between copper and sulphur(35)(42). The quality of the rubber-to-wire bond is therefore likely to depend on the rate of attack of the brass surface by the sulphur. Consequently, the brass oxide thickness and composition play an important role in determining the adhesion behaviour of a given type of brass. For this purpose the elements on the wire (used in the whole of this project) surface were identified and their concentration (atom %) on the outer layer and in-depth profile were measured and given in Table 6.3 and Figure 6.4.

The only detectable elements are seen to be Cu, Zn, O and C. Carbon is the main contaminant and shows the higher concentration, and as mentioned ealier, this is one of the disadvantages of XPS. It is difficult to state whether Zn or Cu is in the form of metal or oxide since their binding energies are close to each other (Table 6.4). The oxidation state of Cu or Zn can be established from the shifts of their photo lines, auger transitions or other details (shake

TABLE 6.3

Evaluation of Atom % of Elements on the Brass-Plated Wire Surface (0.3 Diameter)

Sputter time = 0					
	C	O	Si	Cu	Zn
h	21.9	20.4	7.8	14.4	19.2
N	64.4	20.4	23.6	6.3	6.4
Atom %	53.2	16.8	19.4	5.2	5.3
Sputter time = 3 (mins)					
h	2.8	2.5	-	32.	18
N	7.4	2.5	-	13.9	6
Atom %	24.8	8.4	-	46.6	20
Sputter time = 6 (mins)					
h	2	1	-	45	13.8
N	5.9	1	-	19.6	4.6
Atom %	19.6	3.3	-	65.1	15.3

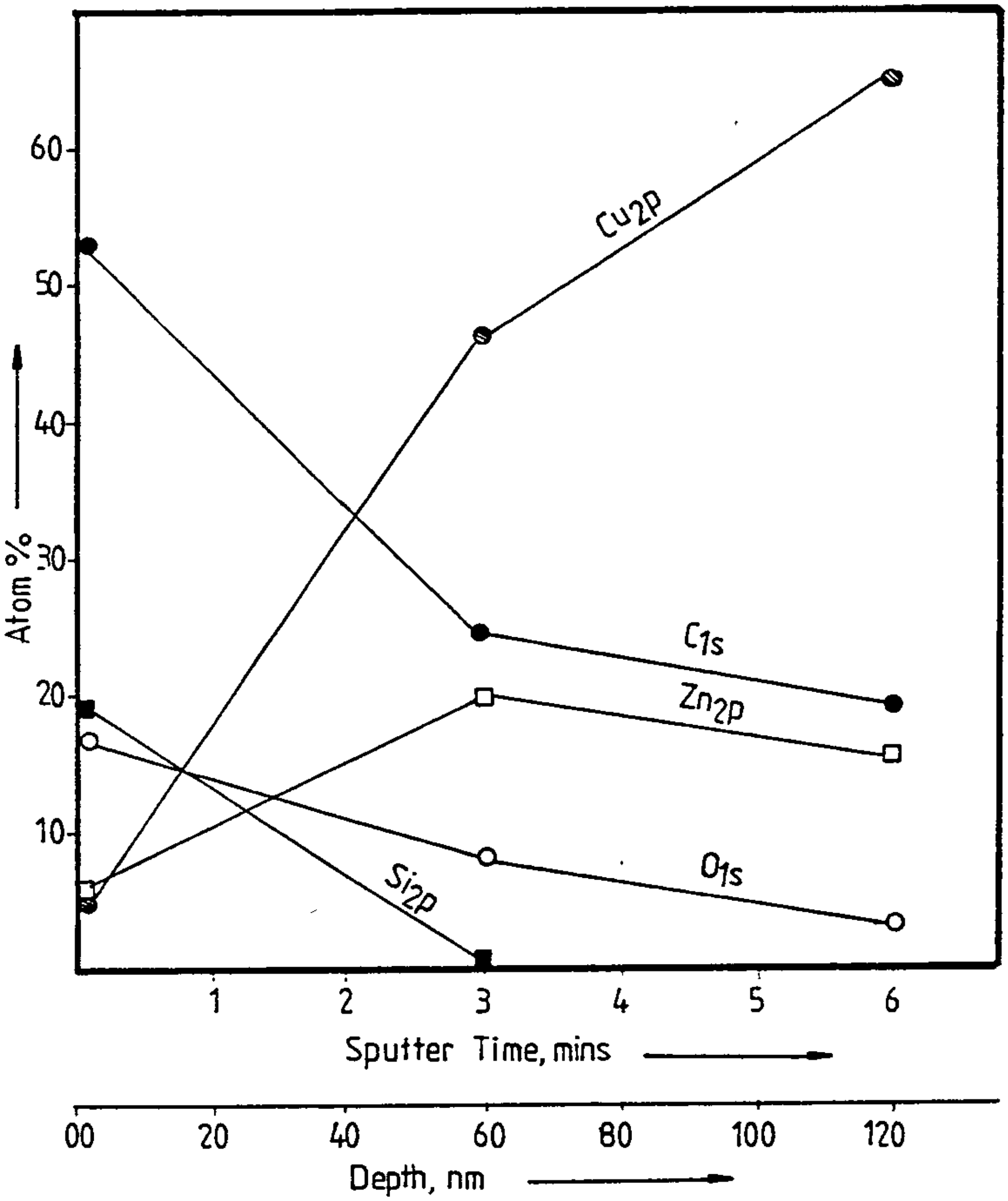


FIGURE 6.4: XPS and Argon Ion Depth Profiling Analysis of Brass-Plated Wire (0.3 mm Diameter) Surface, 70/30 Composition

TABLE 6.4

Binding Energies of Detected Elements on the Brass-Plated Wire Surface and Rubber-Wire Interface

Element	Binding energy[(a)] (eV)	Binding energy[(b)] (eV)
C_{1S}	284.7	284.7
O_{1S}	534.7	531.6
Si_{2P}	104.3	103.4
S_8	164.7	163-164
Cu_{2P}	934.7	932-933
CuO		933-934
Cu_2O		932-934
Cu_2S		932-933
Zn_{2P}	1029.7	1021-1022
ZnO		1021-1023
ZnS		1022-1023

(a) Using C_{1S} = 284.7 eV as reference, estimated accuracy ± 5 eV.

(b) phi handbook.

up phenomena)(80). In this analysis the Auger transition was not examined due to experimental problems and the results are explained by referring to the observations of other researchers. Haemer(66) examined the surface composition of a 0.22 mm diameter brass-plated wire by ESCA. He detected Cu, Zn, O and etc. and stated that oxygen is bonded to the zinc (i.e.zinc is present as ZnO in the outermost layer). Ooij(81) also observed that the surface composition of freshly polished cold-worked brass (64/36) showed the formation of a thin rich zinc oxide layer. This oxide film on brass, interpreted as a defect structure of ZnO, contains Cu and Zn atoms which can diffuse to the surface, where the zinc atoms are preferentially present in the form of oxide. According to the above observation and the presence of oxygen at high concentration (see Figure 6.4), it can be deduced that Zn is in the form of zinc oxide and probably copper in the form of copper oxide at the outer layer. He also stated that the thickness of the zinc oxide film increases as temperature rises. It is probable that a thick zinc oxide layer forms during the vulcanization process when brass wire bonds to rubber.

6.4.2 Interfacial Analysis of Unfilled and Filled SBR to Brass-Plated Wire Samples

The results of the interface analysis and depth profiling of unfilled and filled (carbon black HAF and silica VN3) SBR-wire are given in Tables 6.5a - 6.7b and Figures 6.5a - 6.7b.

In all cases on the wire side, sulphur was detected indicating the migration of sulphur from the rubber to the interface between rubber and wire. On the rubber side of the sample a considerable amount of zinc and copper are detected originating from the brass.

In the carbon black filled SBR wire interface, the relative concentration of Cu, Zn, O and S is found to be low relative to the high concentration of carbon 1s that is observed both on the rubber and wire sides. The high C_{1s} concentration on the rubber side is expected; however it is unexpected on the wire side and considered to be due to the results from good adhesion between carbon black filled SBR and wire as it is very difficult to remove all the rubber from the wire surface even using the liquid nitrogen fracture technique.

By inspection of the ESCA spectrum oxygen is obviously present at the interface.

Again, as was stated in Section 6.4.1, to distinguish between the (1) metal, (2) oxide and (3) the sulphide forms of Zn and Cu, the Auger transition should be examined. This is because Cu with copper oxide and copper sulphide, and Zn with zinc oxide and zinc sulphide, have close binding energies (see Table 6.4). It was not possible to carry out an Auger examination due to experimental problems.

The interpretation of the results uses the observations of other researchers. Ooij(40) has analysed the interfacial composition of rubber bonded to wire by ESCA and confirms that an interfacial layer is present between rubber and wire. On the basis of the observed electron binding energies and relative concentration this layer has been identified as a mixture of ZnO, ZnS and cuprous sulphide (Cu_2S). By reference to the experimentally found in-depth concentration of Cu, Zn, S, and O by ESCA and referring to the observations of Ooij it can be implied that the reaction of wire with rubber had led to the formation of an interfacial zone consisting of sulphide and oxide forms of Cu and Zn.

Comparison of a carbon black filled SBR-wire interface with the unfilled SBR - wire interface indicates that rubber compounding additives have an influence on the concentration of chemical composition in the outer layer and in-depth (see Figures 6.5(a) - 6.6(b)). The results shown in Tables 6.5(a), 6.5(b) and Figures 6.5(a), 6.5(b) are typical of a sample with a very low adhesion level (interfacial failure). The results shown in Tables 6.6(a), 6.6(b) and Figures 6.6(a), 6.6(b) are typical of a sample, which if tested at room temperature, the bond strength would exceed the rubber strength (failure within rubber). As can be.seen there are big differences in chemical composition at the interface between these two types of failure. The results of silica filled SBR-wire interface were found to be similar to the results for unfilled SBR-wire interface (Tables 6.7(a), 6.7(b) and Figures 6.7(a), 6.7(b)). The role of each detected element on the adhesion of rubber to wire will be discussed in chapter 7.

TABLE 6.5(a): Wire Side

ESCA Evaluation of Atom % of Elements at the Interface Between Unfilled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	3.5	5.3	10	9.3	56.5
N	5.4	15.6	10	4.0	18.9
Atom %	10	28.9	18.5	7.4	35
Sputter time=2 (mins)					
h	3.6	2.5	12	17	93.3
N	5.5	7.3	12	7.4	31.1
Atom %	8.7	11.5	18.9	11.7	49.1
Sputter time=4 (mins)					
h	3	2.4	11.7	21	96
N	4.6	7.1	11.7	9.1	32
Atom %	7.1	11	18.1	14.1	49.6
Sputter time=6 (mins)					
h	2.2	2	10	42.7	83.3
N	3.4	5.9	10	18.6	27.8
Atom %	5.2	8.9	15.2	28.3	42.3

TABLE 6.5(b): Rubber Side

ESCA Evaluation of Atom % of Elements at the Interface Between Unfilled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	4.1	4.7	4.3	11	33.3
N	6.3	13.8	4.3	4.8	11.1
Atom %	15.6	34.2	10.7	11.9	27.5
Sputter time = 2 (mins)					
h	5	3.8	3.7	22.3	39.3
N	7.7	11.2	3.7	9.7	13.1
Atom %	17	24.7	8.1	21.4	28.8
Sputter time = 4 (mins)					
h	5.1	3.6	2.3	35	26.7
N	7.8	10.6	2.3	15.2	8.9
Atom %	17.4	23.7	5.1	33.9	19.9
Sputter time = 6 (mins)					
h	5.1	4	2.1	33.3	26.7
N	7.8	11.8	2.1	14.5	8.9
Atom %	17.3	26.2	4.6	32.1	19.7

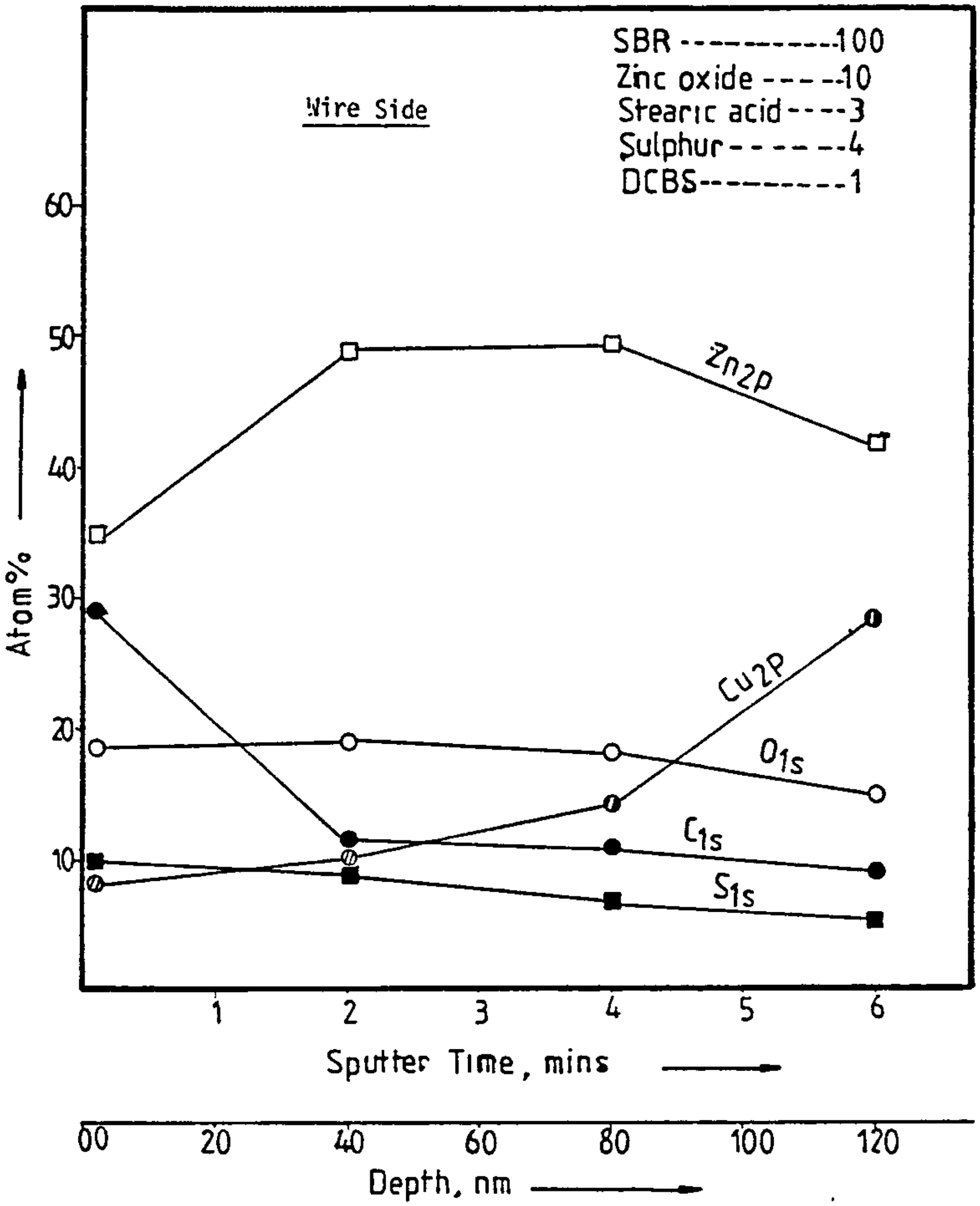


FIGURE 6.5(a): XPS and Argon Ion Depth Profiling Analysis of Interface between Unfilled SBR and Wire, Compound as Indicated

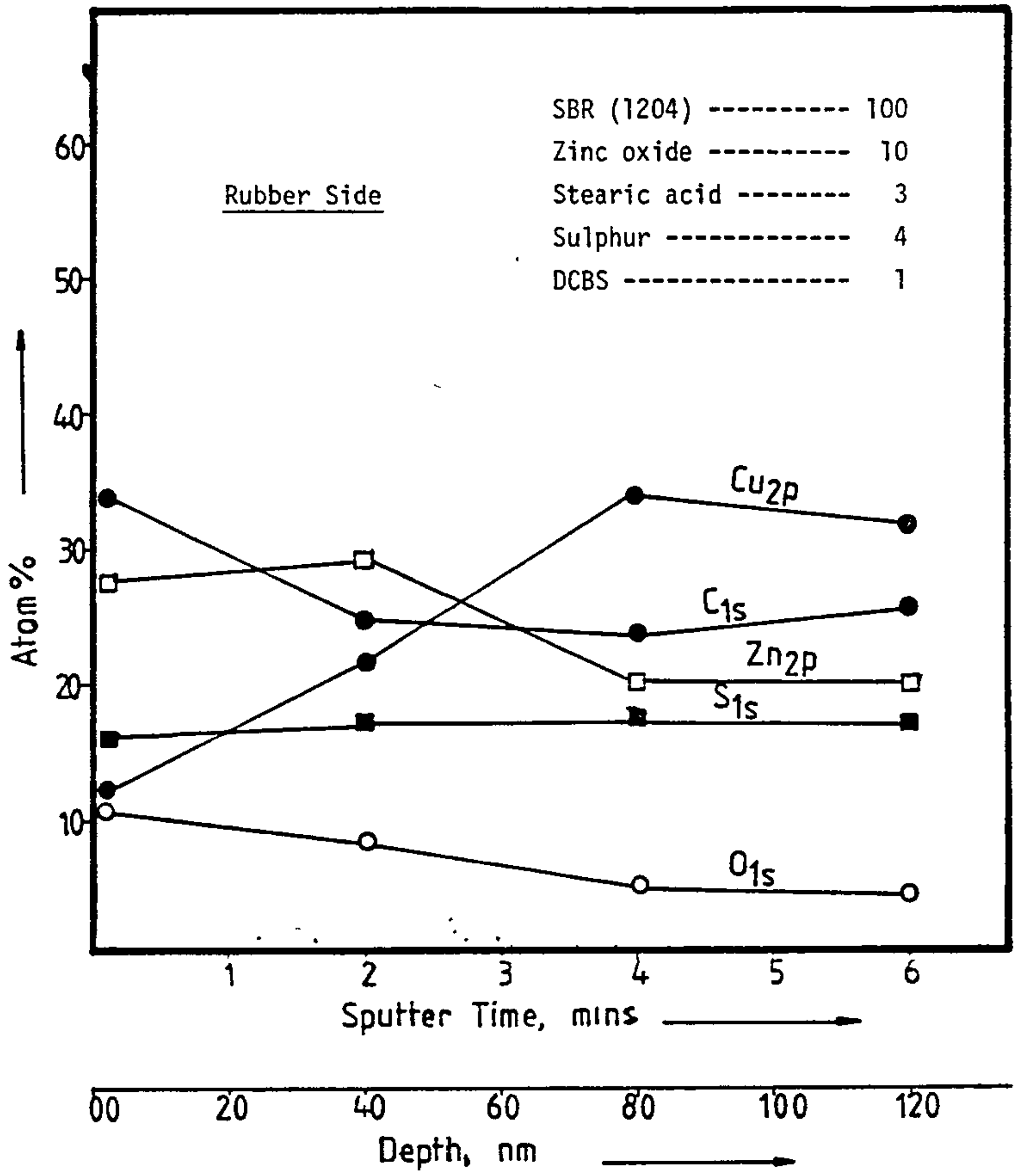


FIGURE 6.5(b) XPS and Argon Ion Depth Profiling Analysis of Interface between Unfilled SBR and Wire, Compound as Indicated

TABLE 6.6(a): <u>Wire Side</u>

ESCA Evaluation of Atom % of Elements at the Interface Between Carbon Black Filled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	2	16.7	11.7	31	19.7
N	3.1	49.1	11.7	13.5	6.6
Atom %	3.7	58.5	13.9	16.1	7.8
Sputter time = 2 (mins)					
h	2.8	18.3	6	42.7	28.7
N	4.3	53.8	6	18.7	9.6
Atom %	4.7	58.3	6.5	20.2	10.4
Sputter time = 4 (mins)					
h	2.6	15.7	5.7	42	28.7
N	4	46.2	5.7	18.3	9.6
Atom %	4.8	55.1	6.8	21.8	11.5
Sputter time = 6 (mins)					
h	2.4	19	8.3	72.7	44.7
N	3.7	55.9	8.3	31.6	14.9
Atom %	3.2	48.9	7.3	27.6	13

TABLE 6.6(b): Rubber Side

ESCA Evaluation of Atom % of Elements at the Interface Between Carbon Black Filled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	1.2	20	10	18.3	3
N	1.8	58.8	10	6.1	1.3
Atom %	2.3	75.4	12.8	7.8	1.7
Sputter time = 2 (mins)					
h	2.5	23.3	8.7	34.3	4
N	3.8	68.5	8.7	11.4	1.7
Atom %	4	72.8	9.2	12	1.8
Sputter time = 4 (mins)					
h	2.7	24.3	6.7	32	3
N	4.1	71.5	6.7	10.7	1.3
Atom %	4.3	75.8	7.1	11.3	1.4
Sputter time = 6 (mins)					
h	2.9	23.3	5	28	4.3
N	4.5	68.5	5	9.3	1.9
Atom %	5.0	76.8	5.6	10.4	2.1

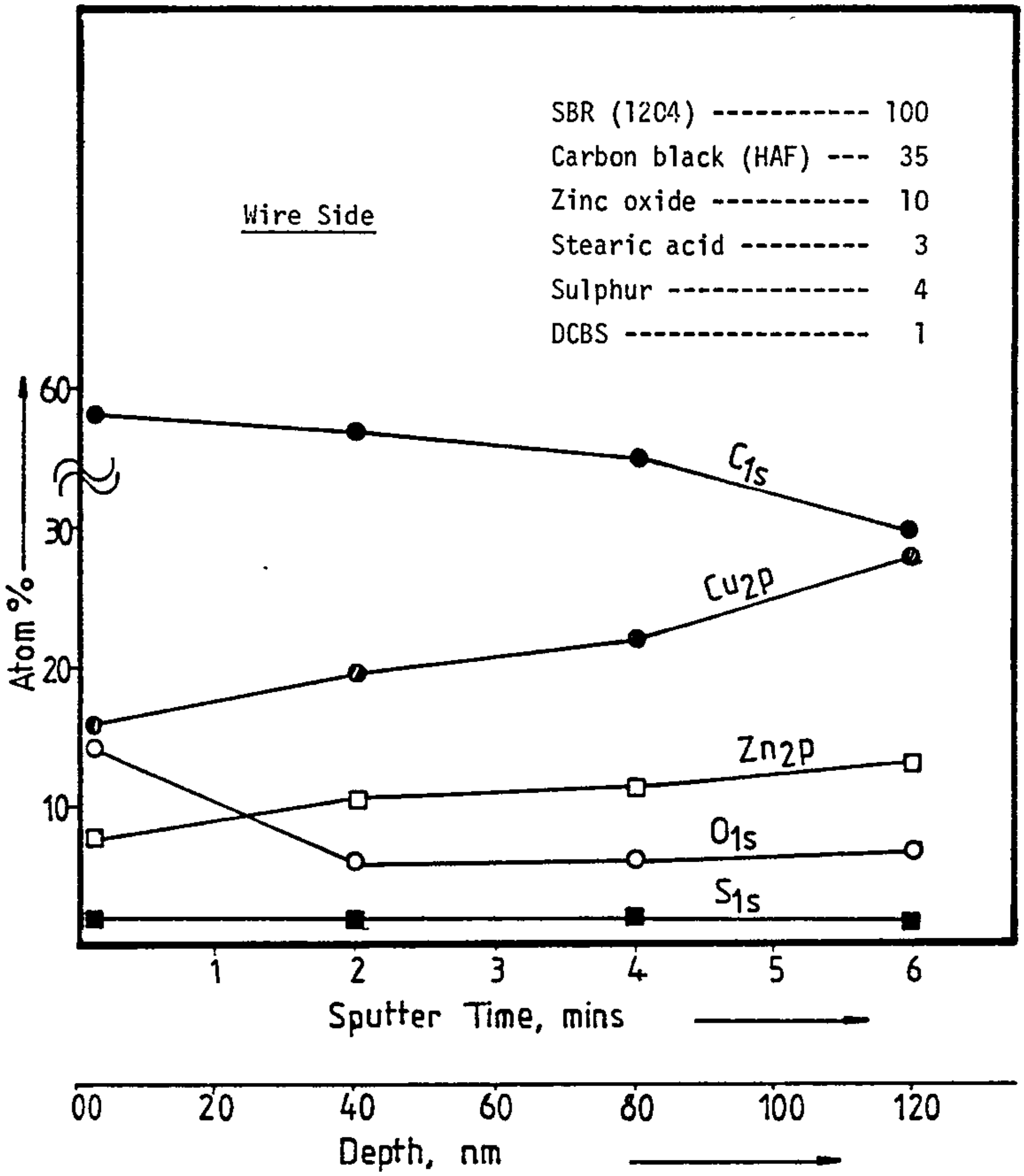


FIGURE 6.6(a) XPS and Argon Ion Depth Profiling Analysis of Interface between Carbon Black Filled SBR and Wire, Compound as Indicated

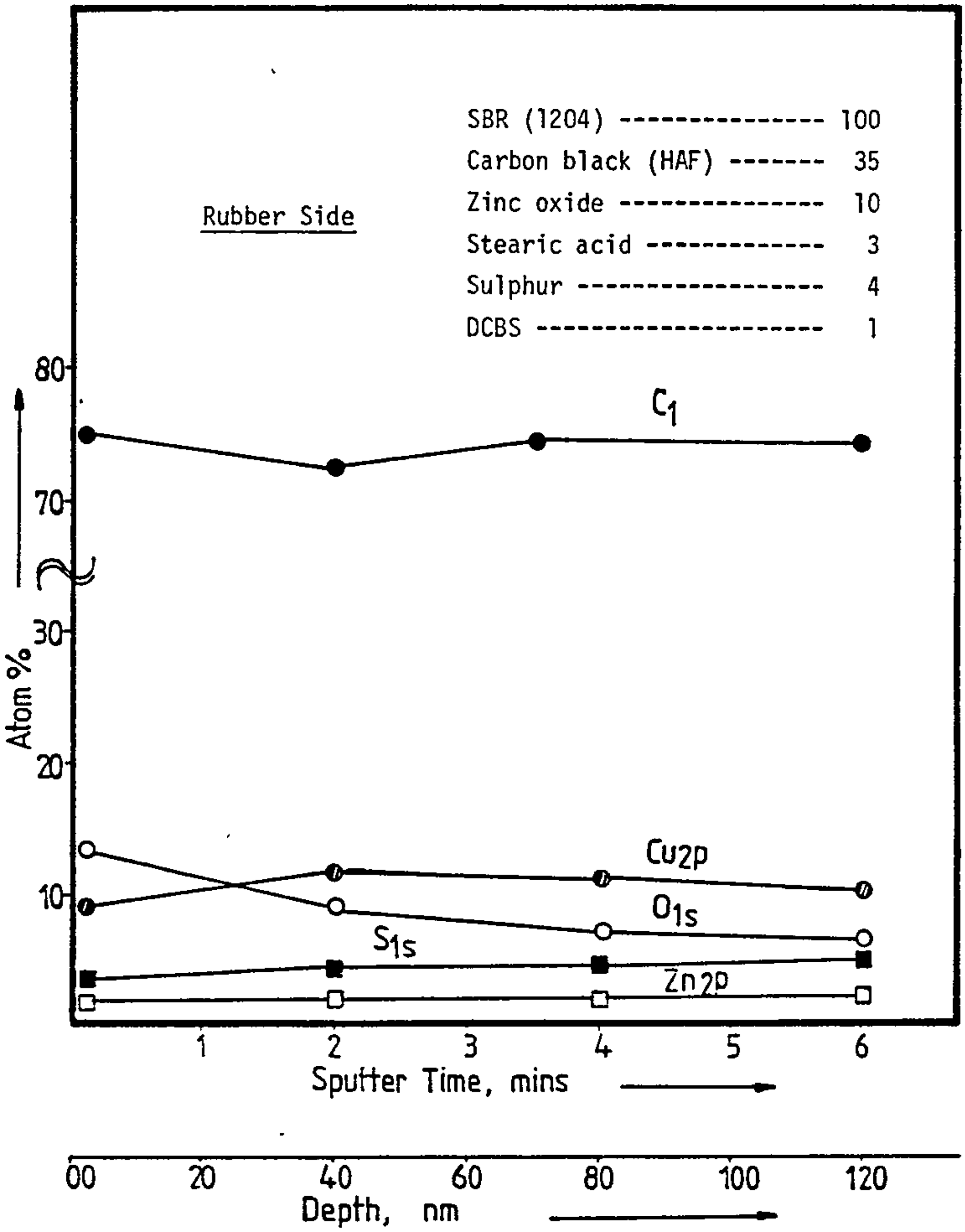


FIGURE 6.6(b): XPS and Argon Ion Depth Profiling Analysis of Interface Between Carbon Black Filled SBR and Wire, Compound as Indicated.

TABLE 6.7(a): Wire Side

ESCA Evaluation of Atom % of Elements at the Interface Between Silica Filled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	7.7	12.3	15	24.7	73.3
N	11.8	36.2	15	10.7	24.4
Atom %	12	36.9	15.3	10.9	24.9
Sputter time = 2 (mins)					
h	8.7	7.3	15.5	42.7	134.7
N	13.4	21.5	15.5	18.6	44.9
Atom %	11.8	18.9	13.6	16.3	39.4
Sputter time = 4 (mins)					
h	8	6.7	20	45.3	134.7
N	12.3	19.7	20	19.7	44.9
Atom %	10.5	16.9	17.2	16.8	38.5
Sputter time = 6 (mins)					
h	6.7	6.7	14.3	77.3	129.3
N	10.3	19.7	14.3	33.6	43.1
Atom %	8.5	16.3	11.8	27.8	35.6

TABLE 6.7(b): Rubber Side

ESCA Evaluation of Atom % of Elements at the Interface Between Silica Filled SBR and the Wire

Sputter time = 0					
	S	C	O	Cu	Zn
h	3.9	8	5.2	10	24
N	6	23.5	5.2	4.3	8
Atom %	12.8	50	11.1	9.1	17
Sputter time = 2 (mins)					
h	6.2	5.7	7.3	12	29
N	9.5	16.8	7.3	5.2	9.7
Atom %	19.6	34.6	15	10.7	20
Sputter time = 6 (mins)					
h	6.2	6.4	2	45	22.3
N	9.5	18.8	2	19.6	7.4
Atom %	16.6	32.8	3.5	34.2	12.9

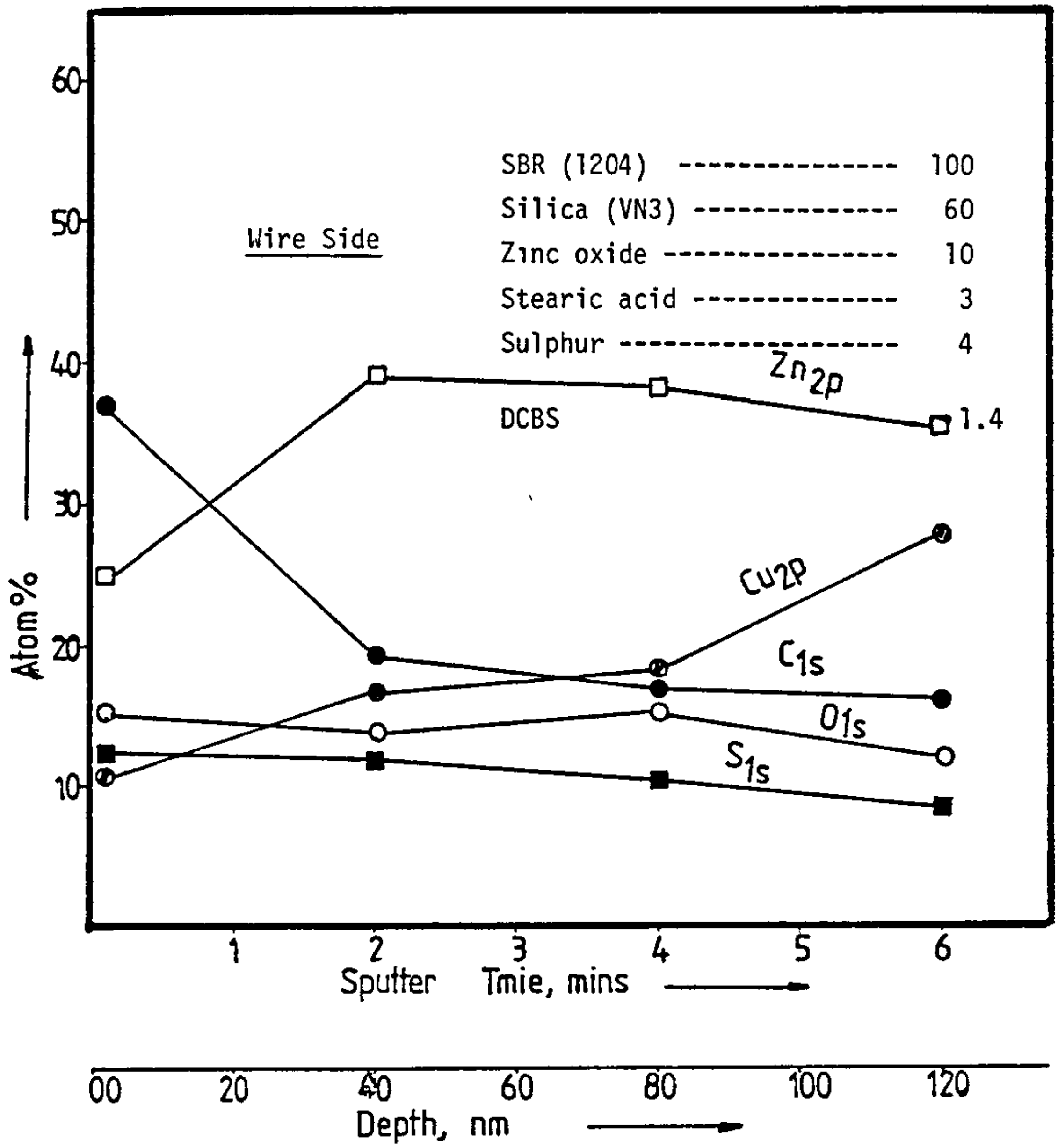


FIGURE 6.7(a): XPS and Argon Ion Depth Profiling Analysis of Interface between Silica Filled SBR and Wire, Compound as Indicated.

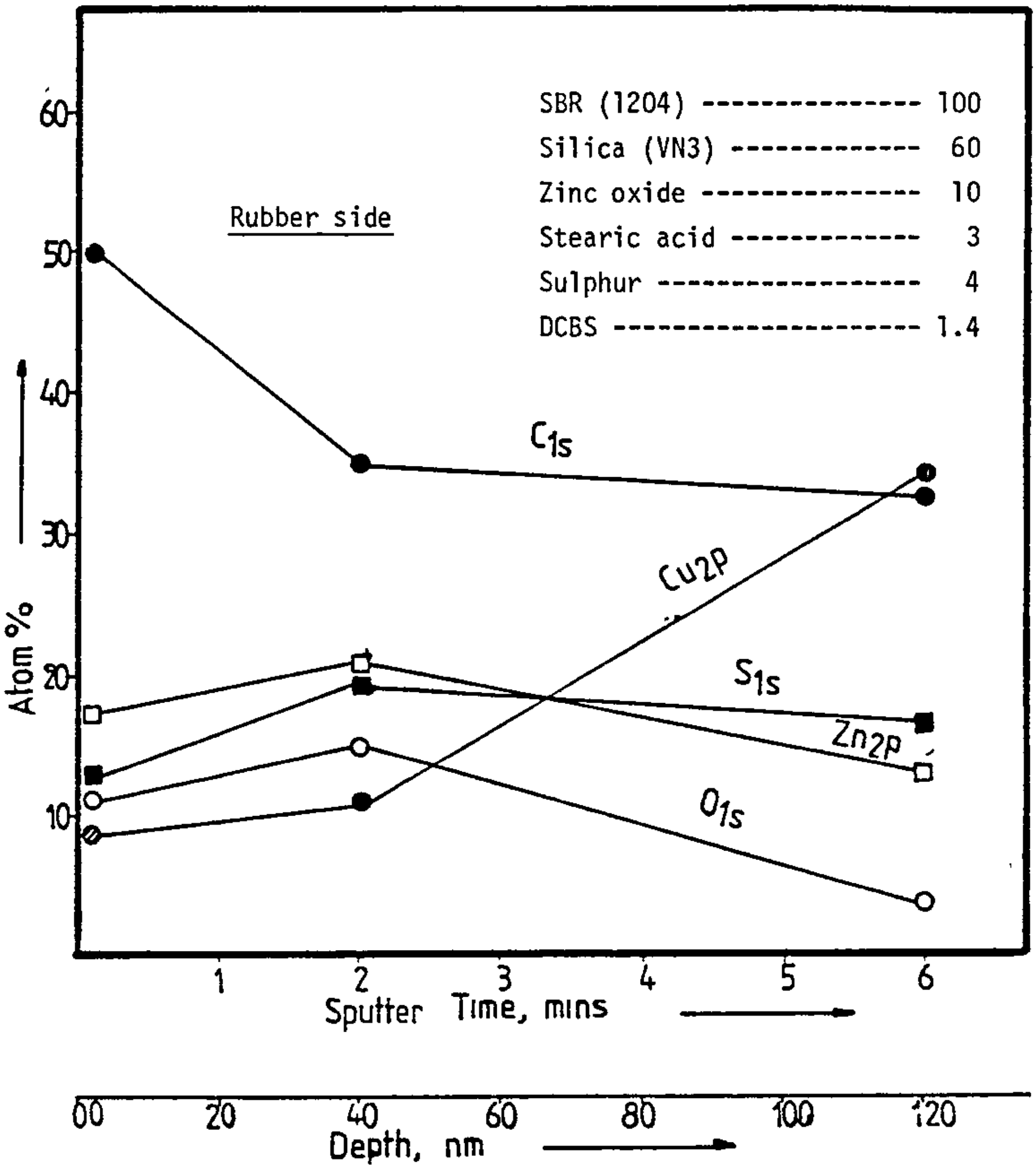


FIGURE 6.7(b): XPS and Argon Ion Depth Profiling Analysis of Interface between Silica Filled SBR and Wire, Compound as Indicated.

CHAPTER 7

GENERAL DISCUSSION

7.1 Introduction

In any bonding investigation, it is important to identify the two primary criteria that together constitute the total adhesion forces. These criteria are the chemical reaction and physical chemistry wetting forces that apply at the interface of the two adherents. Bonding, due to the formation of chemical valency, must always be stronger than that of surface wetting energy and such valency bonds can only fail by internal rupture of one of the adherents. Wetting energy adhesion failure can be recognised by interfacial separation of its adherents such that a clear adherent surface is visible. Therefore in any evaluation of rubber-wire bonding it is necessary to consider the following:

a) The total force required to break the bond is the sum of both chemical valency and surface energy forces.

b) The proportion of the weaker adherent, in this instance the rubber, adhering to the strong adherent substrate, the brass, and giving a separate and independent measure of the chemical valence adhesion force.

Percentage rubber coverage of the brass-plated wire after a bond strength test can be regarded as a method through which the contribution made by valency forces can be quantised.

There are a number of factors which directly influence the adhesion between brass-plated wire and rubber. In the present work the effect of the following parameters on the adhesion of rubber to brass-plated steel wire were investigated and are discussed below on the basis of results obtained in the preceding chapters.

1. Effect of wire drawing lubricant residue on bonding.
2. Effect of compounding additives (carbon black (HAF), Silica (VN3), sulphur) proportions on bonding and physical properties of rubber.
3. Effect of various organic titanates on the bonding and physical properties of SBR rubber.

7.2 Effect of the Brass-Plated Steel Wire Surface Factors on Bonding

7.2.1 Effect of Wire Drawing Lubricant Residue

While the drawing of brass-plated wire lubricant is usually required to reduce the tension, this lubrication was found to have an effect on rubber-wire adhesion which can be due to:

1. Chemical and Physical changes in the brass (heat dissipation) as a result of lubricant-brass interaction.
2. The effect which residual lubricants on the wire surface exert on the wire adhesion.

If case one happens, i.e. the lubricant reacts chemically with the brass, which is very reactive chemically during the drawing process, this chemical reaction causes staining of the wire surface. Such wire, if bonded to rubber, results in the deterioration of the adhesion because the rubber cannot wet the stained area(28) which thus causes a reduction in bond strength. This usually happens when the drawing temperature is high. The other effect of high temperature drawing is to increase the formation of zinc oxide on the brass-plated wire surface and, as will be discussed later, the zinc oxide film, due to the individual properties, retards the formation of Cu_xS, therefore the loss of adhesion.

In case two there is no chemical reaction between the drawing lubricant and the wire and the effect which the residual lubricants at the wire surface exert on the rubber adhesion of the wire and the reduction is low and also inconsistent results are usually obtained. McConnel and Richards(38) who studied the effect of commonly used lubricants found them to adversely affect adhesion.

In the present investigation solvent cleaning of the surface of brass-plated steel wire is considered to increase the rubber-wire bond strength by 10%: this increase is considered statistically significant, being based on the averaging of a minimum of 10 specimens and supported by consistently higher rubber coverage percentages. Perhaps of more importance is that increases in the percentage rubber coverage exhibited by a solvent-cleaned specimen is as much as 25%. However, the coefficient of variation, i.e. bond irreproducibility remains high despite such surface cleaning. This higher bond irreproducibility is considered to be due to the wire drawing lubricant, identified in part as a siloxane, being only partially adsorbed simultaneously into the rubber and the brass surface during vulcanization, as shown by the ESCA technique (Figure 3.4).

Despite the use of extraction or physical washing techniques, as SEM studies reveal, a minor, but significant, proportion of residue always remains behind on the surface of the cleaned wire. It is considered that this tenacious residue has an adverse effect on the consistency of the rubber-wire bond strength. It is also thought that it is this small residue that accounts for the element of bond strength irreproducibility and that this is due to the presence of wire drawing lubricant.

It is difficult to explain how an organic wire drawing lubricant mixture can so tenaciously adhere to a wire surface such that its removal by strong solvents is either impossible or can be only partially successful. A hypothesis is that possibly some reaction occurs between drawing lubricant and the copper and/or zinc in the brass during operation as then, for a short instant of time (microseconds), a very high temperature is generated between wire and drawing die. Zinc and copper are known to react readily with many organic compounds forming organo-metallic complexes and possibly this occurs in a typical wire drawing operation. This implication is that the rubber would not bond well to wire in areas containing such patches of organo-metallic complex.

Some evidence in support of the above hypothesis is offered by IR studies which showed the lubricant to contain in its composition a rubber active siloxane which DSC examination established as being chemically active during the normal vulcanization temperature range (Figure 3.5). Commercial wire drawing lubricants (as mentioned earlier) are known to be mixtures and probably in addition to the siloxane there may be present a metallic stearate (Zn or Ca) and possibly a fatty acid amine (e.g. triethanolamine). If these additives were present on this particular wire they were not extracted by solvent and hence not detectable by IR spectroscopy and may have remained behind on the wire surface in conjunction with some of the siloxane.

7.2.2 Composition of the Brass-Plated Wire Surface

After the steel wire is brass-plated (coating of Cu-Zn alloy) it undergoes various thermal and chemical (lubricant) treatments which allow physical and chemical changes to occur on the brass surface. As has already been discussed, the wire drawing lubricant might react with the brass surface (Section 7.2.1); the other apparent changes are the drawing marks and the formation of ZnO on the brass surface which are believed to affect adhesion. The effect of drawing marks on bond strength is outside the scope of this discussion. Only the composition of brass surface is discussed here.

An in-depth profile composition of the brass-plated wire surface detected the elements Zn, Cu and O (Figure 6.4). The presence of oxygen implies that Zn and Cu are in the form of oxide up to a certain depth. The affinity of Zn to O is higher than Cu to oxygen, thus it can be considered that there is a thin layer of ZnO on the top of CuO or Cu. The thickness of this layer is a function of temperature and increased proportionally with temperature(81). If this ZnO layer exceeds a critical thickness, it will prevent the rubber-brass reaction, and consequently adhesion formation due to its n-type semiconductor properties (and these will be discussed in Section 7.3.1). This is in agreement with the results of ESCA analysis of this investigation which showed that the concentration of Zn, in the form of ZnO or ZnS increases during the vulcanization process (Figure 6.5(a)). This increase can be due to two factors; one is the presence of zinc oxide in the vulcanization process and the second, as mentioned above, is that the concentration of ZnO at the bond interface increases with temperature, so that at the vulcanization temperature (170°C) the ZnO layer is relatively high thus adversely affecting bonding.

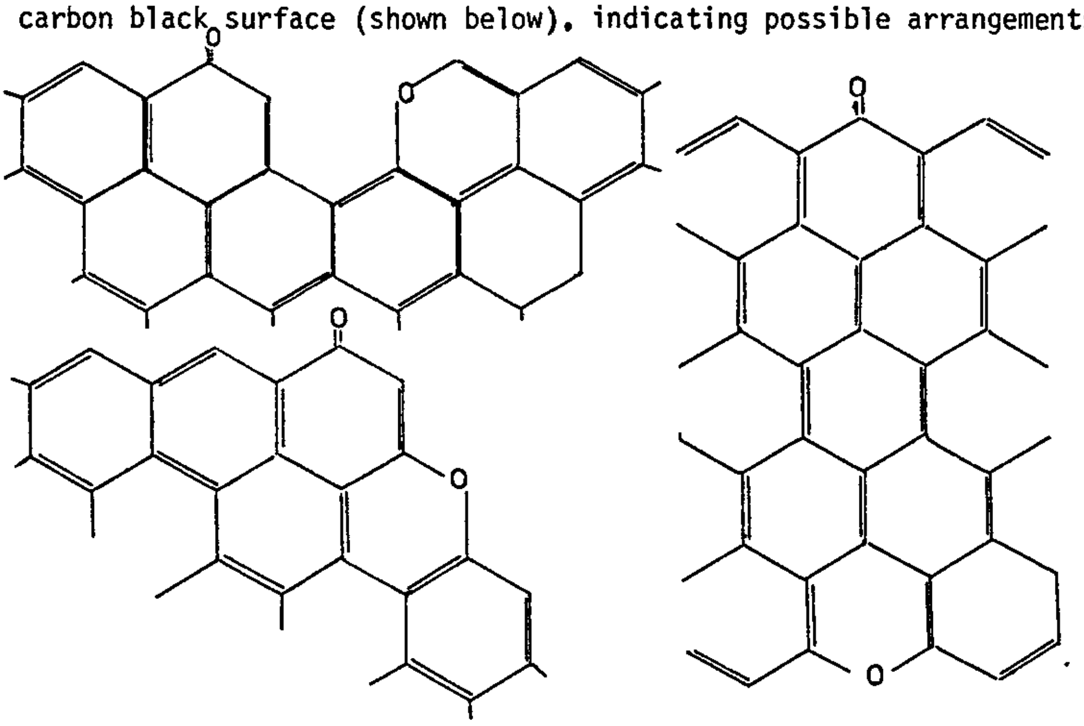
7.3 Effect of Compounding Additives

In addition to the factors described earlier, and associated with brass-plated wire that influence rubber-wire adhesion, some commonly used rubber ingredients are also known to affect bonding. These ingredients, such as fillers, sulphur and bonding promoters, have been found to have a marked influence on both the mechanical properties of rubber and its adhesion to brass-plated wire. The aim of the present work was to investigate the influence of these ingredients in order to achieve a good combination of bonding and rubber physical properties. The compounding ingredients selected were various proportions of sulphur in unfilled and filled rubber, carbon black (HAF), silica (VN3) and organic titanate coupling agents (bonding promoters). Each of these were separately studied, keeping all other variables constant.

7.3.1 Effect of Carbon Black (HAF)

As carbon black is one of the most important ingredients commonly used in the rubber industry for both reducing the total cost and to improve service life of the rubber articles, its influence on rubber properties (physical and bonding to brass-plated wire) was investigated and it was found that carbon black had a marked effect. It may now be useful to give a brief discussion of the properties of carbon black, such as O and H containing functional groups, and then its effect on the physical properties of the rubber and its adhesion to brass-plated wire.

The presence of carbon-hydrogen bonds on the surface of carbon black, and even inside the mass of the particle, has been found by using bromine and chlorine substitution at room temperature(82.83). Similarly the existence of oxygen in the form of oxides has been found by several workers(84,85) and their characteristics studied (86,87). Boehm and Voll proposed a model for oxides present on the carbon black surface (shown below), indicating possible arrangements



of pyrone-like structures on the carbon black surface. Sulphur has also been detected by various workers(88,89) where the existence of sulphurous surface complexes(90) and other sulphides(91) were found. Sykes and White(92) postulated the presence of surface sulphides and proposed the following structure:

Lewis et al(93) showed by means of an isotope technique with sulphur 35, that the sulphur present in carbon blacks is highly reactive and that about 20% of the total sulphur content is located on the particle surface in the form of polysulphide complexes. In the present investigation the carbon black used with its particle size and ultimate composition is given in Table 7.1.

Carbon Black	Classification	Particle Diameter (nm)	Ultimate Composition-Dry Basis %				
			H	C	Ash	S	O
HAF(Vulcan 3)	N330	26-30	0.3	97.57	0.24	0.56	1.33

TABLE 7.1: Particle Size and Composition of HAF Carbon Black

It is apparent from the Table 7.1 that this black essentially contains about 96% carbon plus significant traces of other reactive functional groups containing H, S, O and Ash. These functional groups are considered to have some influence on the physical and bonding properties of rubber(94,95).

It is known that carbon black, due to its properties, is always used as a reinforcing filler in the rubber industry. The term 'reinforcement' is used to indicate an improvement of strength in the properties of the rubber. In reinforced rubber, strong carbon-polymer bonds are formed with the result that the filler particles are actually a part of the elastomer network. The net result is improved tensile strength, tear strength, modulus and abrasion resistance. It is notable that the strong polymer-black association which results in reinforcement involves chemical interaction between polymer and black (H, O and S functional groups). It should be mentioned that there is a severe limitation on the quantity of black which can associate closely with the rubber, and so be active in reinforcement. Gessler(96), using a butyl-black system containing a series of carbon black concentrations, found (as shown in Figure 7.1) that for an appreciable tensile strength to be obtained chemical oxidation of the carbon black surface is necessary. No chemical oxidation leads to no improvement in tensile strength.

In this research an HAF carbon black was used and the results of this work are given in Chapter 4, Section 4.3.2.3 and can be summarised as follows:

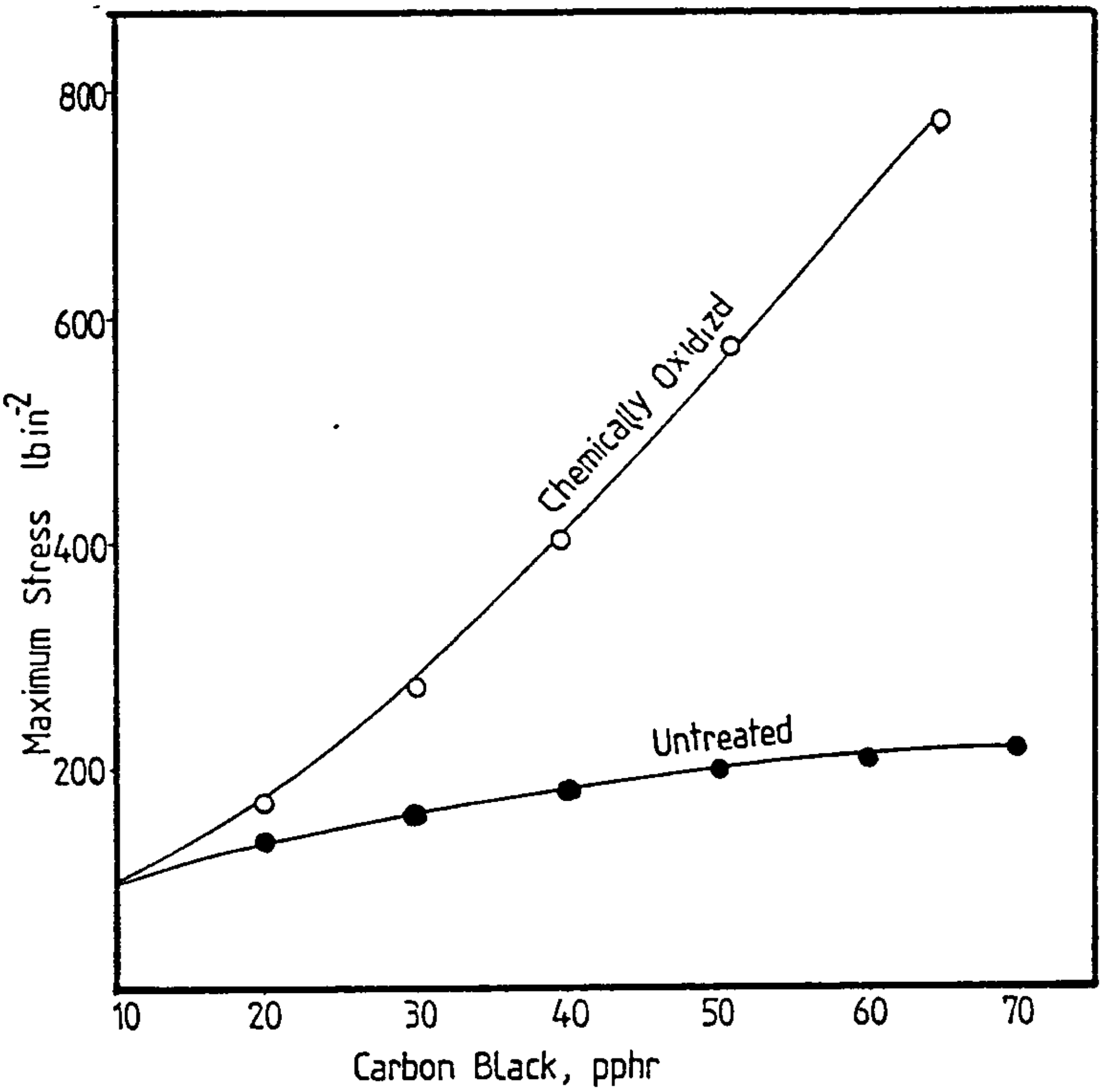


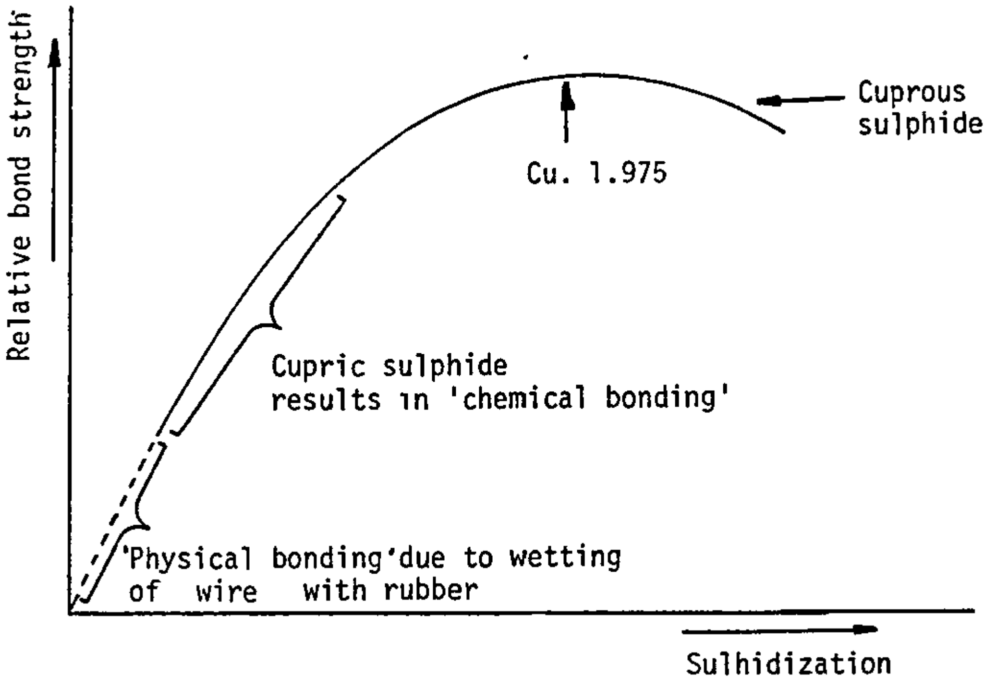
FIGURE 7.1: Tensile Strength of Butyl Systems, Heat Treated with Untreated and Chemically Oxidized Black

- The carbon black increased the tensile strength and tear strength of the IR rubber and in particular the non-crystallizable SBR whose tensile strength increased from 2 MPa to 22 MPa at optimum filler levels. The bond strength also increased together with the tensile strength up to a maximum level which depended on the proportion of carbon black present. The maximum values for bond strengths were obtained for SBR/carbon black and IR/carbon black respectively as 15.5 MPa and 15.9 MPa over the carbon black ranges 35-65 and 25-45 pphr respectively. Rubber coverage was 100% in these ranges (i.e. failure was within the rubber).

From the above results, one effect of using carbon black to improve bond strength is by its ability to increase the strength of the rubber as a stronger rubber will require progressively more energy to deform at the rubber-wire interface than is possessed by a weaker rubber thus leading to a higher pull-out force. Hence it can be considered that the bond between rubber and wire is partially physical in nature. Hicks and co-workers(50) have published a comprehensive study of carbon black proportions and properties on the adhesion of rubber to brass cord. Black properties such as dispersion, structure, porosity, activity, sulphur content, and concentration of volatiles were all found to affectadhesion quite noticeably and he explained these observations on the basis of the well known effect of black properties on compound stiffness and, insofar as the volatiles were concerned, on the pH of the mix.

Another effect of carbon black which was found in this investigation to be important was the relative concentration of the elements e.g. Zn, Cu, S, O, C at the rubber-wire interface. These results are given in Chapter 6, Section 6.4.2. Comparison of elements concentration between the interfacial layers of respectively unfilled SBR (Figure 6.5) with carbon black filled SBR-wire (Figure 6.6) shows that carbon black has an influence in elemental concentration at the interfacial films and consequently on the adhesion of SBR to wire.

According to the results of the ESCA analysis, the in-depth concentration of Cu, Zn, S and O found on both rubber and wire surfaces implies that the reaction of brass with rubber led to the formation of an interfacial zone consisting of zinc oxide, zinc sulphide, copper oxide, and copper sulphide. The copper sulphide film present has been identified(40) but was imprecisely defined in terms of a non-stoichiometric structure and in the form of Cu_xS which formed during vulcanization; it is this Cu_xS which is considered the real adhesive between rubber and brass wire. Levels of adhesion depend on the amount of Cu_xS present but should not exceed specific maximum and minimum values at the end of the vulcanization process, because it was observed(40) that too little or too much Cu_xS adversely affects wire-rubber adhesion, as shown in the schematic diagram overleaf.



The rate of film growth has been considered to be determined by cationic diffusion(41) i.e. transport of metal ions and free electrons through the sulphide layer; at the sulphur-sulphide interface where the reaction 7.1 occurs:

$$S + 2e^- \rightarrow S^{--} \qquad (7.1)$$

while at the sulphide-metal interface the reaction 7.2. takes place:

$$2\ Cu \rightarrow 2Cu^+ + 2e^- \qquad (7.2)$$

If any of these steps are omitted or accelerated by the presence of certain chemical compounds at the sulphide surface then sulphide film growth may be retarded or accelerated. One of these chemical compounds is the ZnO film. Haemers(66) stressed the importance of the ZnO on the brass surface. He explained its importance in terms of its partial transformation into ZnS which, due to its n-type semiconductor properties, will reduce the Cu_xS formation.

However, this seems doubtful as the reaction

$$ZnO + S \rightarrow ZnS + \frac{1}{2} O_2 \qquad (7.3)$$

is thermodynamically impossible under the conditions of cure(97). It is well documented that ZnS is formed during the rubber vulcanization process and that this reaction takes place via the formation of soluble zinc stearate which itself is produced in the rubber by reaction between the ZnO and stearic acid(98). Further, it has been shown that ZnS is also formed on brasses initially devoid of any ZnO(39, 99) film. It can also be argued that ZnO has n-type characteristics with a growth mechanism via interstitial Zn^{2+} ion diffusion, so the ZnO will control Cu^+ ion diffusion in its own right. Such a mechanism has been demonstrated by other researchers using sulphidization experiments on brass surfaces which were initially enriched with copper or zinc(40). In contrast to the above CuO and Cu_2S have p-type semiconductor properties and increase the Cu_xS formation. It seems that CuO reacts very rapidly with elemental sulphur, probably according to the following equation:

$$8\ CuO + S_8 \rightarrow 4\ Cu_2S + 4\ SO_2 \qquad (7.4)$$

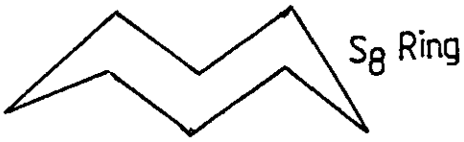
ESCA analysis of the unfilled SBR-wire interface (see Table 6.5 and Figure 6.5, rubber and wire side) shows that the concentration of the ZnO/ZnS layer is higher than the concentration of CuO/Cu_xS. Due to the n-type semiconductor characteristics of ZnO/ZnS the diffusion of Cu^+ is very slow in a gum stock and forms not enough

Cu_xS to give good adhesion. By contrast the concentration of ZnO/ZnS is relatively lower than the concentration of CuO/Cu_xS at the carbon black filled SBR-wire interface (see Table 6.6 and Figure 6.6, rubber and wire side) and due to p-type properties of CuO/Cu_xS, the accelerated diffusion rate of Cu^+ leads to the formation of a film of Cu_xS, which gives very good adhesion.

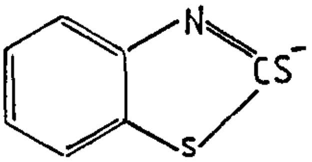
When a sulphide film is formed during bonding a colour change is observed on the wire surface which can be explained on the basis of copper sulphide properties. The colour of the surface of the wire debonded from unfilled SBR is observed to be yellow (see Figure 4.7(b)) indicating that copper sulphide is not formed (the colour of copper sulphide is blue) and here no adhesion is obtained. However the surface colour of the wire debonded from carbon black filled SBR was seen to be greenish-blue (see Figure 4.7(a)) indicating the formation of copper sulphide, where high adhesion is obtained. This observation is in agreement with other recent observations(100) that:

1. There is much more ZnO in the yellow film.
2. There is an enrichment of Zn and O (ZnO) on top of the Cu_xS layer of the yellow film.
3. The concentration of Zn in the Cu_xS film is higher in the yellow film than in the blue one.

The high growth of the Cu_xS film at the interface of carbon black filled SBR-wire can be presumed to be the result of involvement carbon black in activating the sulphur thus; sulphur is in the form of the S_8 ring:



This is opened during the vulcanization process for example S_8 is normally opened by negative ions (anions)

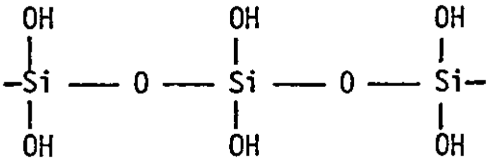


which may come from accelerators. It is also known that carbon black can promote the opening of the S_8 ring(101). Some of the activated sulphur is involved in the cross-linking of rubber and some migrates to the interface between rubber and wire and reacts with Cu^+ by the adsorption-desorption process (see Figure 1.13) which leads to the growth of Cu_xS.

In summary an increase in the bond strength of SBR to wire in the presence of carbon black can be interpreted as a combination of two effects: first, increase in the bond strength of rubber leads to high mechanical bond strength (physical type); secondly, promotion of the formation of copper sulphide results in good adhesion of a chemical type (see through the percentage rubber coverage values).

7.3.2 Effect of Silica (Ultrasil VN3)

Of the many inorganic fillers which have been used in rubber compounding the finely divided silicas are the most highly reinforcing. Besides the unique physical properties (tensile, tear strength) imparted to rubber by silica, it is now possible to add adhesion promotion. The reinforcing and adhesion promotion characteristics of silica are assumed to be due to the presence of reactive oxygen in the silica structure. The following is a schematic concept of the silica structure showing oxygen atom distribution



$$-\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}-O-\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}-O-\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}-$$

In this investigation, it was found that the silica filled SBR vulcanizate gave poor physical properties (tensile and tear strength) and consequently poor bond strength (see Table 4.2). This was considered to be due to the lack of interaction between silica and rubber in that it is thought SBR does not wet the silica particle adequately thus the unwetted particles of silica are assumed to cause a drop in the mechanical strength characteristics of the vulcanizate(70). These physical properties were found to be improved by the use of a mercapto type silane coupling agent (Bis-(3-[triethoxisilyl]-propyl)-tetrasulphane). It seems that the silane's functionality was capable of chemical reactivity with both the silica and the rubber network.

The alkoxysilanes are known to readily bond to surface silanols of silica via stable siloxane linkage and their organic functionality can participate in reactions that lead to a linkage with the rubber.

Although the use of the mercapto silane coupling agent (Si 69) improved the tensile strength and bond strength of the SBR/silica mix such values were still lower than the best values obtained with SBR/carbon black mix (see Table 7.2). The tensile strength value of the SBR/silica mix was expected to be at least similar to the tensile strength value of the SBR/carbon black mix since the particle size of silica (19 nm) is smaller than carbon black (29 nm) and its surface area (170 g/m^2) is larger than carbon black (88 g/m^2). The lower tensile strength can be considered to be due to the inadequate physico-chemical interaction between silica particles and SBR rubber. The low bond strength and rubber coverage can be explained by considering two effects:

i) the low strength of the silica filled rubber, and

ii) the ESCA analysis results of the silica filled SBR-wire interface.

These results indicate that the ZnO/ZnS concentrations are higher than the Cu_xS/CuO concentration (see Table 6.7 and Figure 6.7, rubber and wire sides) for silica filled SBR; thus according to the bonding mechanism proposed in Section 7.3.1, there is not enough Cu_xS formed to produce a satisfactory film, thus leading to poor adhesion. It was also observed that the colour of the wire surface debonded from the silica filled SBR is similar to the wire surface colour debonded from unfilled SBR (see Figure 4.7(b)).

Mix	Tensile Strength MPa	Tear Strength kN m^{-1}	Bond Strength MPa	Rubber Coverage %
SBR/Carbon black	20.5	53	15.5	100
SBR/ Silica	11.0	60.1	9.9	40

TABLE 7.2: A Comparison of the Physical Properties of SBR/Carbon Black and SBR/Silica Mixes

This is further evidence that during the cure silica prevents the formation of Cu_xS, therefore poor adhesion results. The 3-fold increase in bond strength between silica filled SBR and wire is due to an increase in SBR rubber strength as a result of filler reinforcement. Hence this bond is considered more of a physical type rather than a chemical type.

The reason that the presence of silica in SBR prevents the formation of enough Cu_xS at the rubber-wire interface can be explained by a similar route to that given in Section 7.3.1: during the vulcanization and bonding processes, which occur at the same time, sulphur (S_8) must be activated into forming an S ion by the presence of an amine type accelerator. It is known that silica can absorb such an accelerator thus retarding such activation of sulphur. Due to this silica absorption effect cure time is delayed and probably retards the diffusion of activated sulphur to the bond interface.

Carbon black is often preferred to silica because:

a) Carbon black has better reinforced properties and bond strength.

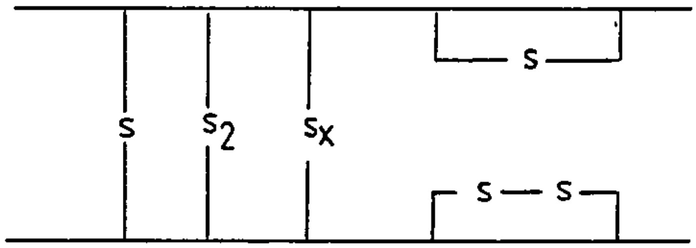
b) The processing of carbon black is easier than silica as the latter increases rubber viscosity and consequently sticks to the mill during mixing.

c) The use of a coupling agent in silica filled SBR is necessary.

7.3.3 Effect of Sulphur

Sulphur is the key reactant during the bonding reaction. Rubber mixes containing no sulphur give no adhesion to brass wire because sulphur takes place with the formation of copper sulphide which is real adhesive for bonding of rubber to wire.

The existence of sulphur found at both the wire interface and rubber interface by ESCA analysis, can be interpreted in that, during the vulcanization of the rubber, ZnO reacts with the vulcanization accelerator and with sulphur (S_8) which, in a very complex reaction scheme, results in the formation of active sulphur atoms. Some of the active sulphur reacts with the rubber molecules to form sulphur cross-links, (rubber side) and some diffuse to the rubber-wire interface (see Figure 1.13) and react with Cu^+ to form copper sulphide. Ooij(39) observed that the sulphur at the rubber-wire interface is in the form of activated sulphur and rubber-sulphur cross-links ($-C\ S_xC\ -$), which are mixtures of various bonds of the following types:



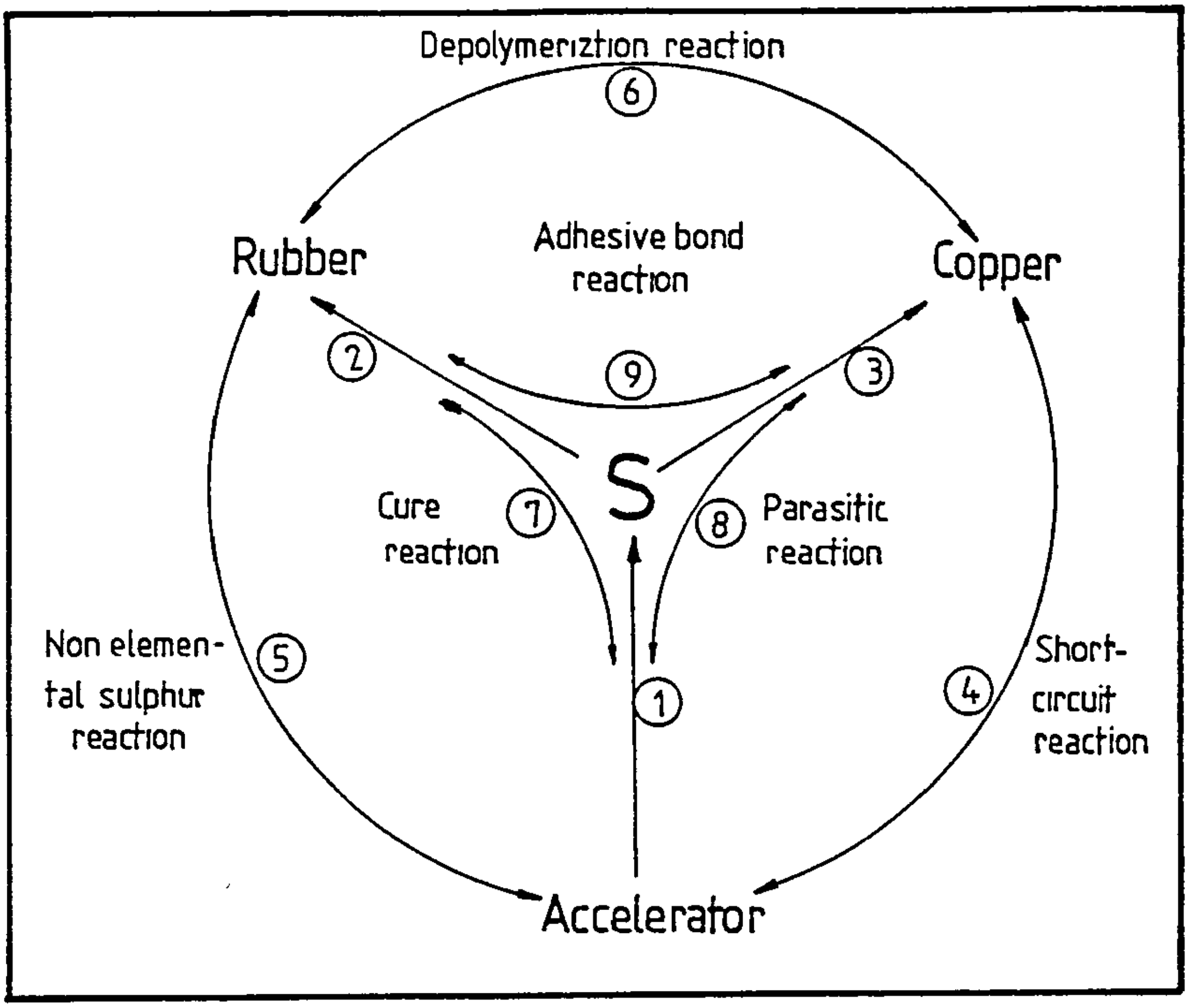
Also another hypothetical scheme of the reactions occurring during the cure of brass in rubber is postulated by Heamer(102) (see Figure 7.2).

In this study, it was found that a relatively high level of sulphur is needed to give optimum bond strength (maximum bond strengths were obtained for SBR/carbon black and SBR/silica at levels of 3-4 pphr of sulphur and for IR/carbon black at 4-6 pphr of sulphur). These results were supported by the Weening postulation(73) that the presence of polysulphide cross-links in the vulcanizate network is required for bonding to wire. This postulation argues that as the bonding of rubber to wire is partially physical in type therefore polysulphide cross-links increase the modulus of rubber in the region close to the brass surface hence high energy is required to pull out the rubber from the bond interface thus leading to high pull out forces.

7.3.4 Relationship Between Bond Strength and Mechanical Failure of a Vulcanizate

In principle when bonding rubber to metal there are three types of failure:

1. 'Rubber failure' means that the rubber is ruptured and the wire is completely covered by rubber (cohesive).



Main Reactions:

① Accelerator Activates Sulphur (S_8) Ring

② Some Activated Sulphur is Involved in Cross-linking with Rubber and Cure Reaction Occurs ⑦

③ Some Activated Sulphur Migrates to the Rubber-wire Interface and makes Possible the Formation of Cu_xS Layer ⑨

Side Reactions:

④ Short-circuit Reaction

⑤ Non-elemental Sulphur Reaction

⑥ Depolymerisation Reaction

FIGURE 7.2: General Reaction Scheme of Possible Interaction During the Vulcanization of Rubber in Contact with Brass

2. 'Bond failure' is failure between rubber and wire at adhesive layer (interfacial).
3. Partial rubber failure and partial bond failure.

In a well bonded rubber-brass specimen adhesion failure should be within the rubber itself and not at the interface of the brass substrate and rubber adherent, hence ideal bond strength values can be considered as those of the mechanical failure properties of the rubber. Figure 2.8 illustrates practical examples of these phenomena. In Figure 2.8(a) 'within rubber' failure has occurred and this is regarded as the ideal situation in which rupture is within the weaker adherent. Figure 2.8(b) represents interfacial failure between rubber and brass substrate which is an undesirable state to occur in the engineering design of bonds. Figure 2.8(c) represents a failure that is partially interfacial and partially within the rubber.

The relationship between bond strength and vulcanizate properties was examined by progressively increasing the reinforcing filler content (carbon black (HAF) and precipitated silica (VN3)) and sulphur content in a rubber (SBR, IR) to wire bonding formulation known to give 'within rubber' bond failure until the optimum filler or sulphur content for various mechanical properties was exceeded. The results obtained when carbon black, silica and sulphur levels in SBR and IR were increased, have shown that physical properties (tensile and tear strength) along the bond strength increases to achieve an optimum level then reduces as optimum proportions are exceeded. Highest bond strengths were obtained at low levels of filler content than those required to give maximum tensile strength (see Figures 4.4(a), 4.5(a) and 4.10(a)). Also maximum bond strengths were achieved at levels of sulphur greater than those giving maximum tensile strength (see Figures 4.8(a), 4.9(a) and 4.11(a)).

Comparison of vulcanizate properties, tensile strength and rupture energy showed a good relationship to bond strength.

7.4 Effect of Organic Titanate Coupling Agents (Bonding Promoters) on the Physical Properties of SBR and its Adhesion to Brass-Plated Wire

The terms 'bonding promoters' and 'adhesion systems' are in fact misleading. These terms stem from the use of these materials in textile cord adhesion which cannot be bonded directly and requires the use of an adhesive between cord and rubber.

In steel-cord to rubber adhesion the actual adhesive is the brass coating on the steel. Excellent bonds, both initial and aged, can be obtained. Therefore in discussing the effect of the various adhesion promoters we have to evaluate how they affect the strength or durability of the bond which would have been formed in their absence. It is of special interest if one could conclude whether the observed effects of adhesion promoters were due to modification of the interfacial film of reaction products or changes in the rubber properties. As mentioned earlier, the adhesion between rubber and wire depends on copper sulphide formation and also the many rubber properties.

The study of the effect of titanates on the interfacial film (copper sulphide layer) was not carried out because for such an investigation a model similar to the Ooij model is needed. He used a paraffin (bath) as a model hydrocarbon instead of rubber at 180°C, and then investigated the effect of compounding additives on the rate of sulphidisation between sulphur and copper. Here the results are discussed on the basis of the effect of titanates on the physical properties of rubber. Many of these physical properties are related to bond strength.

However in this study some of the organic titanate coupling agents which can be used as bonding promoters were investigated. They were KR-TTS, KR-138S, KR-38S, KR-66S, KR-44S and KR-41B (the chemical descriptions and structures are given in Table 5.1). These titanates were used in two different methods:

i) A solution of each titanate was directly applied to the wire surface.

ii) Each titanate was incorporated by mixing it into the rubber.

7.4.1 Titanate Applied to the Wire Surface

The mechanism of these organic titanates coupling agents is complicated but some general rules apply. The general formulation of titanates is as follows:

$$(\mathrm{RO})_{M}{}^{1} \;\text{—}\; \mathrm{Ti}\text{—}{}^{2}(\mathrm{OX}^{3}\text{—}\mathrm{R}^{4}\text{—}\mathrm{Y}^{5})\mathrm{N}^{6}$$

The function 1 reacts with free protons at the inorganic (filler, substrate) interface. This results in the formation of organo-functional monomolecular layers on the inorganic surface. The other functions react with organic or (polymer) components. It is supposed that when a solution of selected titanate is applied to the wire surface, function 1 reacts with free protons of the wire and the other functions react with SBR rubber.

However results show that all five titanates reduced the bond strength and rubber coverage between rubber and wire in comparison with the control. Two of these (KR-44S and KR-41B) severely reduce bond strength, and KR-TTS, KR-138S and KR-38S slightly, decreased bond strength (see Table 5.5). Deterioration of bond strength when KR-44S and KR-41B are used is considered to be due to changes in their structure which occur during heat to the vulcanization temperature of 170°C. Apparently they are decomposed on the wire surface during the vulcanization process (see Figure 5.1), so no surface activity can occur between the wire and the rubber and therefore KR-44S and KR-41B seem only to act as lubricants.

In the case of KR-138S, KR-38S, the bond strength values are slightly lower than the control value. It is considered that these two exhibit some surface activity towards wire and rubber and it is known that KR-38S and KR-138S contain phosphato and phosphito groups respectively (Table 5.1): hence this offers the possibility of some complexing between the metal and the phosphato or phosphito radicals. Some slight deterioration due to the presence of water at the wire-titanate interface may also occur as it was observed by Cotton and Wilkinson(79) that titanium alkoxides can be hydrolysed by small traces of water and all rubbers and their compounding ingredients contain a little water.

KR-TTS has shown equal adhesion results to the control indicating some reaction of KR-TTS between wire and rubber.

Electron Spectroscopy for Chemical Analysis (ESCA) was employed to try and detect the presence of titanium or phosphorous on the wire surface, but none was detected.

In general, it is concluded that the titanates which were studied exhibited some surface activity though this resulted in adverse bond strength values.

7.4.2 Titanate Incorporated into the Rubber

It has already been discussed that the adhesion between rubber and brass-plated wire is based on the formation of copper sulphide (Cu_xS) and also the strength of rubber. Any compounding additives which have an influence on these two parameters may have an effect on adhesion. For example the improvement in adhesion of sulphenamide-accelerated systems to brass of low copper content was explained by postulating that the accelerator-sulphur complex reacts with the cobalt leading to the formation of the following complex:

$$A_{cc} - S_x - CoX_2 \rightarrow Co - S_y - X_2 + A_{cc} - S_{x-y}$$

This cobalt complex was assumed to promote the Cu_xS formation of the brass with low copper content(60). Rutz(51) also showed that in the presence of cobalt stearate, sulphur is used more efficiently for bonding the NR to brass of low copper content: it also increases the cross-link density. These two factors combined to lead to a higher adhesion level.

As mentioned earlier the effect of titanate on the formation of Cu_xS was not examined. The effect of these titanates on bond strength is now discussed in relation to its effect on physical properties.

Negative bond strengths were obtained with the titanates KR-44S, KR-41B and KR-66S. The reduction in bond strength with KR-66S and KR-44S can be explained on the basis of the effect of these two on the scorch time (see Figure 5.3). It is well known in bonding technology that poor adhesion results when the scorch time is very short. In the case of KR-44S and KR-66S perhaps there was not enough time for the rubber to wet the wire surface during the vulcanization. The effect of these two titanates on scorch time is considered due to the presence of amino and mercapto groups which can function as accelerators. KR-41B was observed to bloom heavily to the rubber surface and thus gave low bond strength.

The effect of KR-38S, KR-138S and KR-TTS on bond strength were to give beneficial results though quantitatively the increase in bond strength was (4-20%). However the rubber coverage increased from 45% in the control to 100% when all these titanates were incorporated. This increase in bond strength might also be due to some increase in tensile strength (4-16%) when KR-TTS and KR-38S are used (see Table 5.6). It is noted that in the case of KR-138S no tensile strength increase is found. As has already been discussed, bond strength can be related to tensile strength.

The ESCA technique was employed to trace the presence of any titanium on the wire surface but no titanium was detected and this was assumed to be due to the high molecular weight of titanates which thus contained very low amounts of titanium.

An important observation was that those titanates (KR-138S, KR-38S and KR-TTS) which showed beneficial results of bond strength when applied directly to the wire surface, also showed positive results when they were incorporated by mixing into the rubber.

CONCLUSIONS

The following conclusions are drawn on the basis of the experimental results and discussion:

A. Wire Effect:

1. It is considered that an important factor contributing to bond strength irreproducibility in the adhesion of rubber to brass-plated wire is the presence of a wire drawing lubricant. A further consideration is that such a lubricant cannot be removed effectively by conventional solvent washing or extract techniques. It is hypothesised that possibly some reaction occurs between drawing lubricant and the copper or zinc in the brass during the drawing operation and forms complexes rendering the surface inactive to adhesion.

   In normal industrial use, such as tyre manufacture, no attempts are usually made to remove this lubricant. It is interesting to speculate whether the present amount of lubricant applied during the wire drawing process is necessary. Ideally none should be used; this is probably impractical for industry but its presence does seem to adversely affect rubber-wire bond strength criteria and hence by inference must lead to poor adhesion values between the plies of a wire reinforced tyre.

2. It was observed that the concentration (atom%) of copper which is probably in the form of CuO is relatively higher than the concentration of Zn/ZnO on the surface of unbonded brass-plated

wire. When this wire was bonded to unfilled rubber the Zn/ZnO concentration increased. This increase was thought to be due to the presence of ZnO in the vulcanization process and also due to the vulcanization temperature. A relatively high ZnO concentration has adverse effects on bond strength.

B. Rubber Ingredient Effects:

1. Carbon black (HAF) was found to have a significant effect on bond strength. This effect was considered to be due to an increase in strength of rubber which occurs when the rubber is reinforced with filler so stronger rubber will require more energy to deform it at the rubber-wire interface than is possessed by a weaker rubber thus leading to a higher pull-out force (physical type of adhesion). Also the carbon black has an effect on the concentration of various elements (Zn, Cu, S) at the rubber-wire interface. It is thought that carbon black (HAF) promotes the activation of sulphur by formation of S* from its normal stable S_8 state, thus accelerating the formation of Cu_xS at the rubber-wire interface (chemical type of adhesion).

2. Silica filled SBR vulcanizates showed relatively poor physical properties (tensile and tear strength). This was thought to be due to the lack of physico-chemical interaction between silica and rubber, hence the use of a mercapto type silane was necessary to bond the silica filler to the rubber.

Relatively poor bond strength was observed between silica filled SBR and wire in comparison to carbon black filled SBR. This low bond strength was considered due to the combination of the relatively low tensile strength of silica filled SBR vulcanizate and the relatively neutral effect of silica on the concentration of elements at the rubber-wire interface.

3. Sulphur detected on the wire surface by ESCA analysis indicated that the migration of sulphur occurred from the rubber to the wire-rubber interface and reacted with Cu to form Cu_xS which forms the actual bond between rubber and wire.

   It was observed that a relatively high level of sulphur is needed to give optimum bond strength.

C. Effect of Organic Titanates as Bonding Agents:

It was found that the various titanates used had effects on the physical properties of SBR and its adhesion to brass-plated wire. Titanates KR-TTS, KR-138S and KR-38S have shown beneficial results in the bonding of SBR to wire when they were either applied directly to the wire surface in the form of solution, or were incorporated by mixing into the rubber.

RECOMMENDATIONS FOR FURTHER WORK

1. Further investigation of the different lubricating oils that affect rubber-wire adhesion is required to try to obtain a selective oil that shows the least interference in adhesion mechanism.

2. A detailed study of the effects of different functional groups present on carbon black on rubber-wire adhesion could be rewarding. Consideration of black particle size may provide a useful relationship between the physical properties and adhesion of rubber to wire.

3. The influence of different particle size silicas due to their varying reinforcement properties could provide useful information regarding physical properties and adhesion of rubber to wire.

4. The investigation of the effects of different types of antioxidant can provide useful information in relation to the adhesion between rubber and wire.

5. A detailed study of the effects of different types of organic titanate coupling agents on the rubber-wire adhesion could be rewarding. It would be convenient to use squaline as a model that represents rubber employing the same vulcanizing systems and conditions. Hence it would be possible to study the effect of each titanate on the rate of sulphidisation between sulphur and copper by employing X-ray fluorescence analysis.

6. Investigation of sulphur migration from rubber, and the migration of copper and zinc from the brass-plated wire surface, to the interface between the rubber and wire to form Cu_xS at the interface during vulcanization would be useful by employing ESCA and AES techniques.

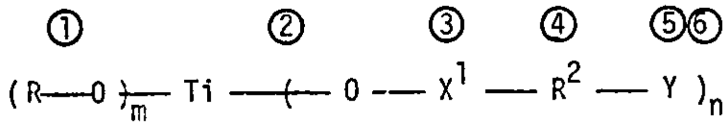
APPENDIX I

MECHANISM OF ORGANIC TITANATE COUPLING AGENTS

APPENDIX I

Titanate coupling agents can provide a chemical bridge between the inorganic (substrate, filler) and organic polymer. The chemical mechanism of titanate coupling may be linked to pregnancy wherein the head of the spermatozoan is similar to the alkoxy group (function 1) of the titanate coupling agent and the tail of the spermatozoan is similar to the organo-functional ligands (functions 2 to 6) of the titanate coupling agent. The "egg" is the inorganic filler, fibre, metal, or wood substrate, or proton bearing species. Pregnancy or filler coupling is achieved when the alkoxy group of the titanate reacts with the protons of the inorganic (see Figure I). Further success of the titanate coupled filler now depends upon the compatibility and interaction of functions 2 to 5 of the titanate coupler's organic ligand in the organic phase.

The titanate molecule has six basic areas of functionality as shown below:



$$\overset{\textcircled{1}}{(R-O)_m}-Ti-\overset{\textcircled{2}}{(}-O-\overset{\textcircled{3}}{X^1}-\overset{\textcircled{4}}{R^2}-\overset{\textcircled{5}\textcircled{6}}{Y})_n$$

They are identified as follows:

Function ① $(R-O-)_m$ concerns itself with the attachment of the coupling agent molecule to the surface of the inorganic. Water and free protons (H+) on the filler interface are the reaction sites for coupling agents.

Function② $-(-$ relates to the ability of the titanate molecule to transesterify. This phenomenon results in crosslinking between the titanate and carboxyl-bearing polymers and permits titanates, filler and polymer to cross-link.

Function③ $-O-X^1$. The portion of the titanate molecule immediately adjacent to the titanium centre - the titanium centre binding group - affects performance as determined by the chemistry of alkylate, carboxyl, sulphonyl, phenolic, phosphato, pyrophosphato and phosphito groups.

Function④ $-R^2-$ The long carbon chain entanglement group provides Van der Waals entanglement for thermoplastic impact improvement, internal lubricity for improved processing and a superior plasticizing effect.

Function⑤ $--Y$ when a functional group such as a methacrylate is attached to the titanate organic backbone, a reaction site for a curative is provided. The filler or inorganic substrate becomes chemically bound to the polymer.

Function⑥ $-)_n$ The difunctionality and trifunctionality, or presence of two to three pendant groups, allows all functionality to be controlled to first, second, or third degree levels.

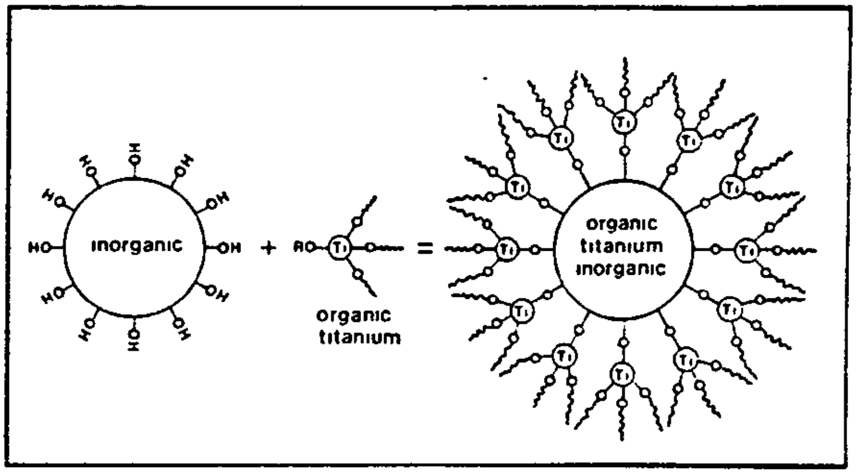
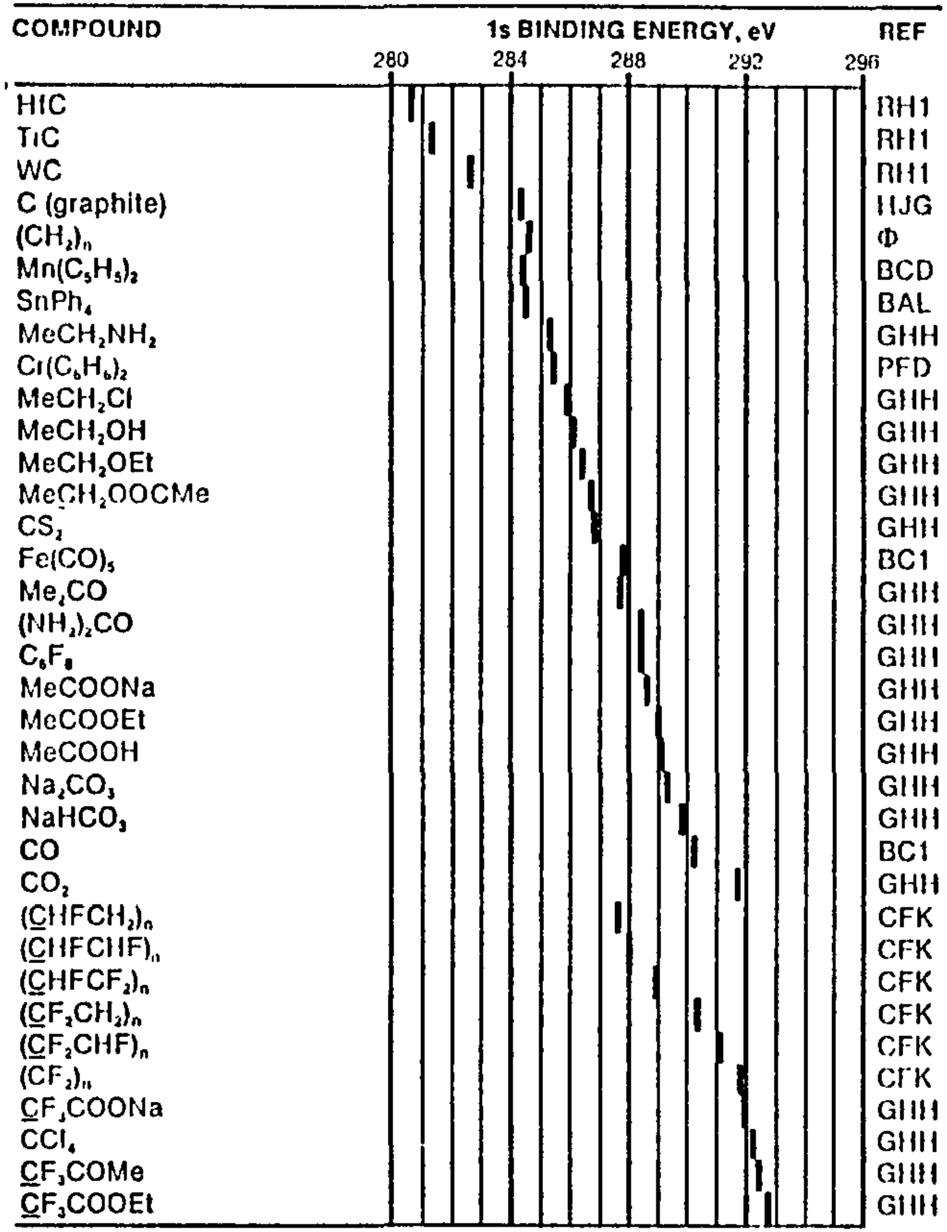


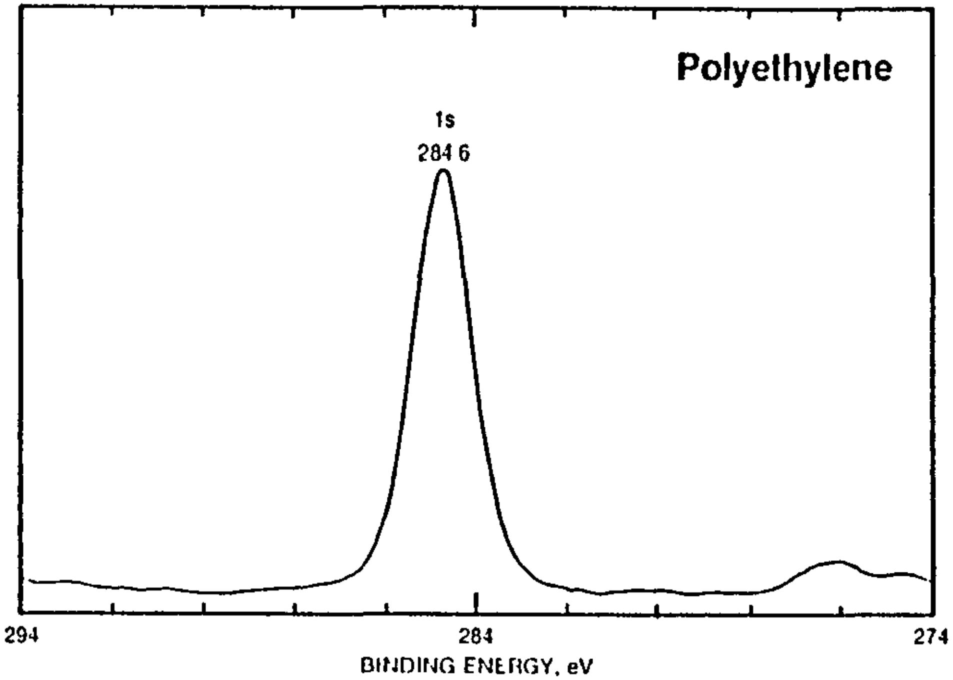
FIGURE I: The Reaction of a Monoalkoxy, Triorganofunctional Titanate Coupling Agent with the Surface of a Proton Bearing Inorganic Resulting in the Formation of an Organic Titanium Monomolecular Layer on the Inorganic Surface

APPENDIX II

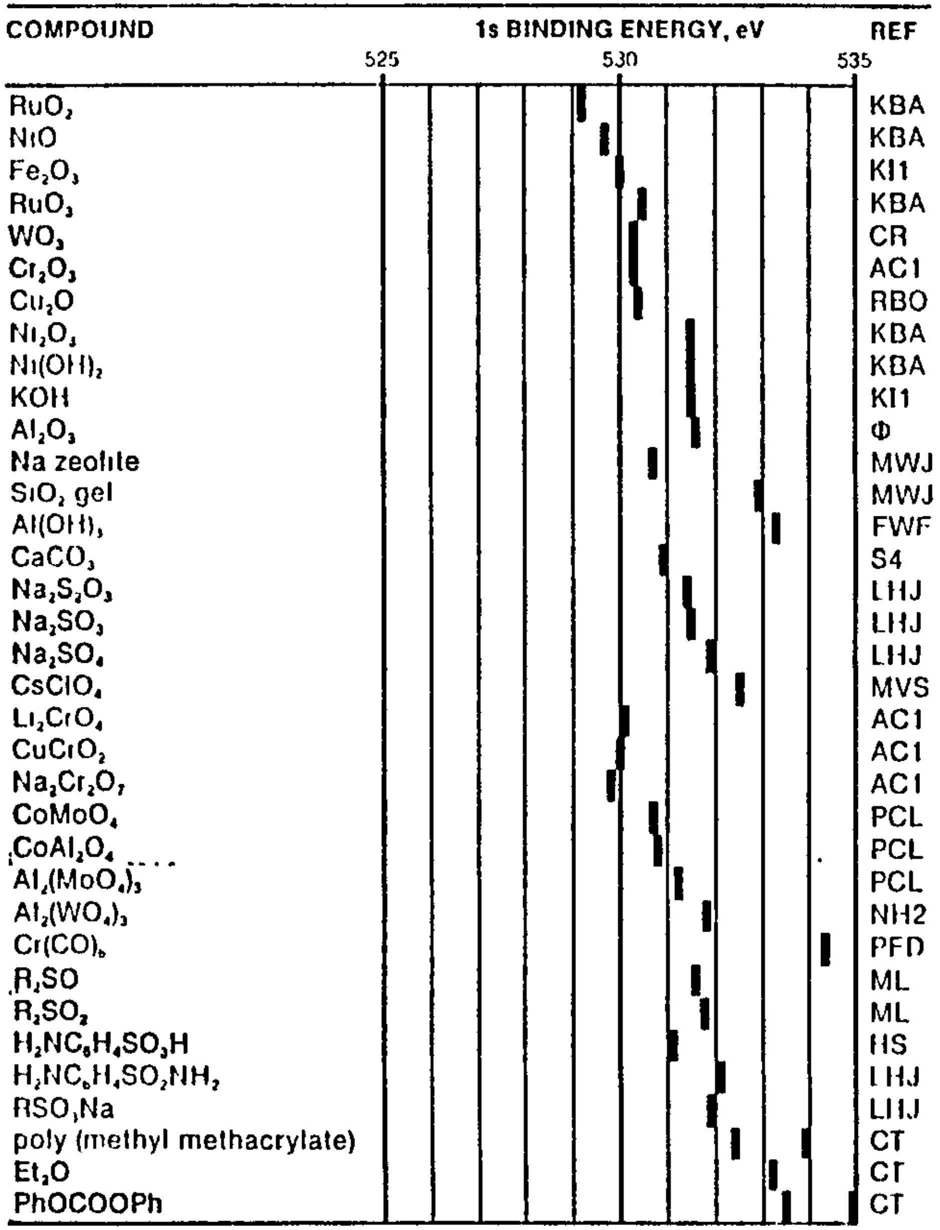
BINDING ENERGIES OF ELECTRONS IN VARIOUS COMPOUNDS

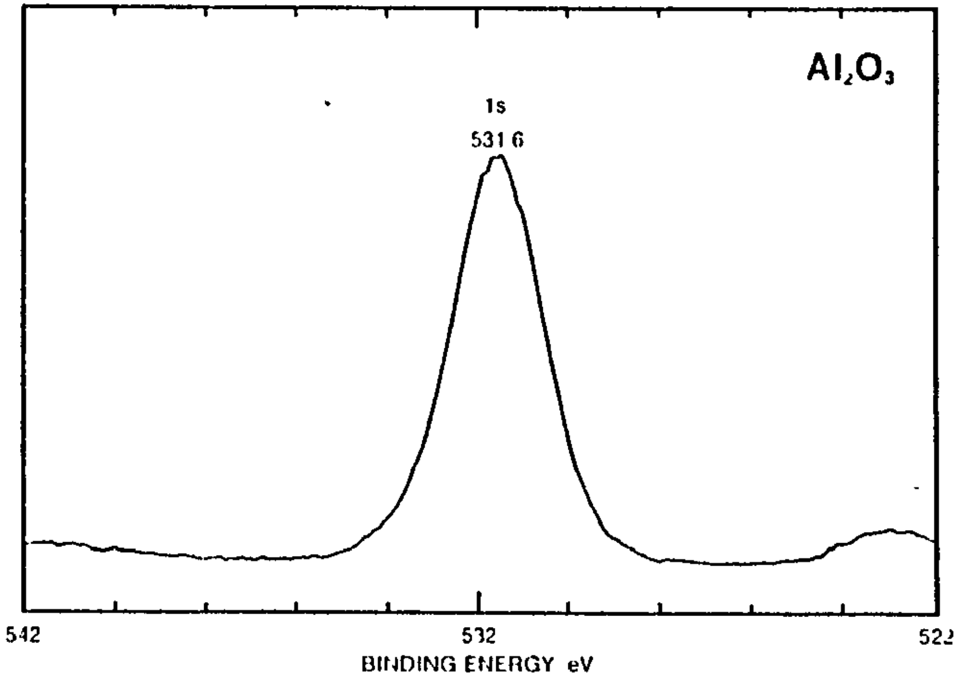
Carbon, C Atomic Number 6





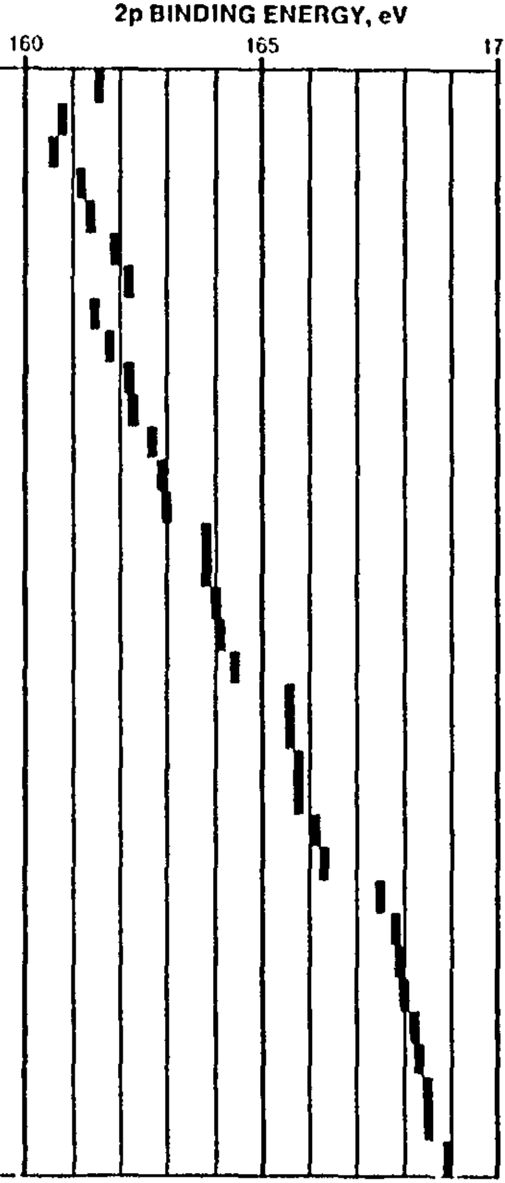
Oxygen, O Atomic Number 8

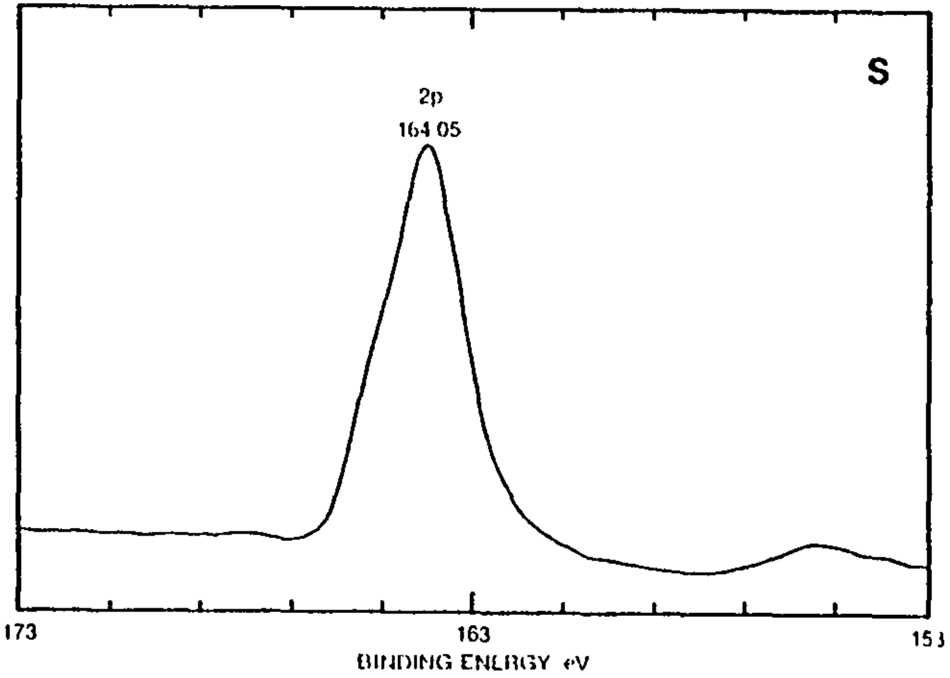




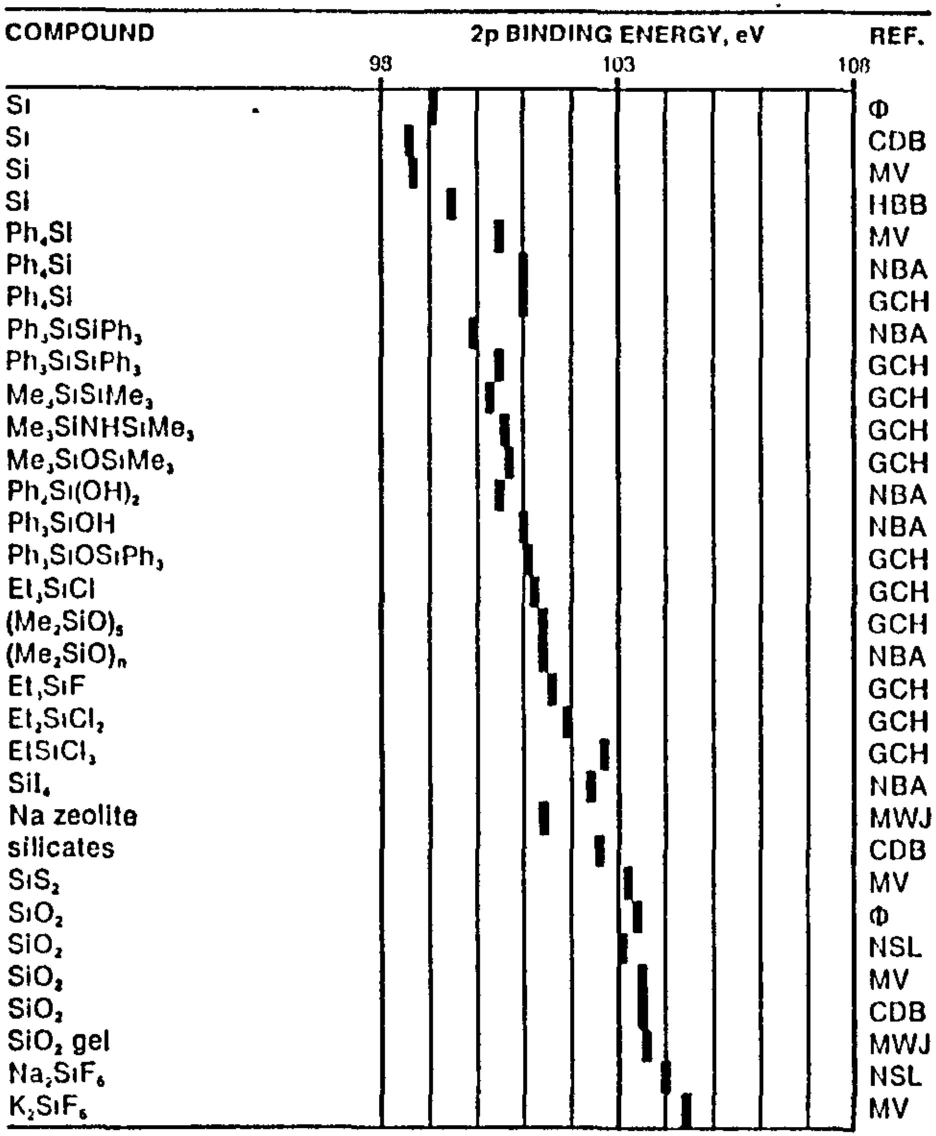
Sulfur, S Atomic Number 16

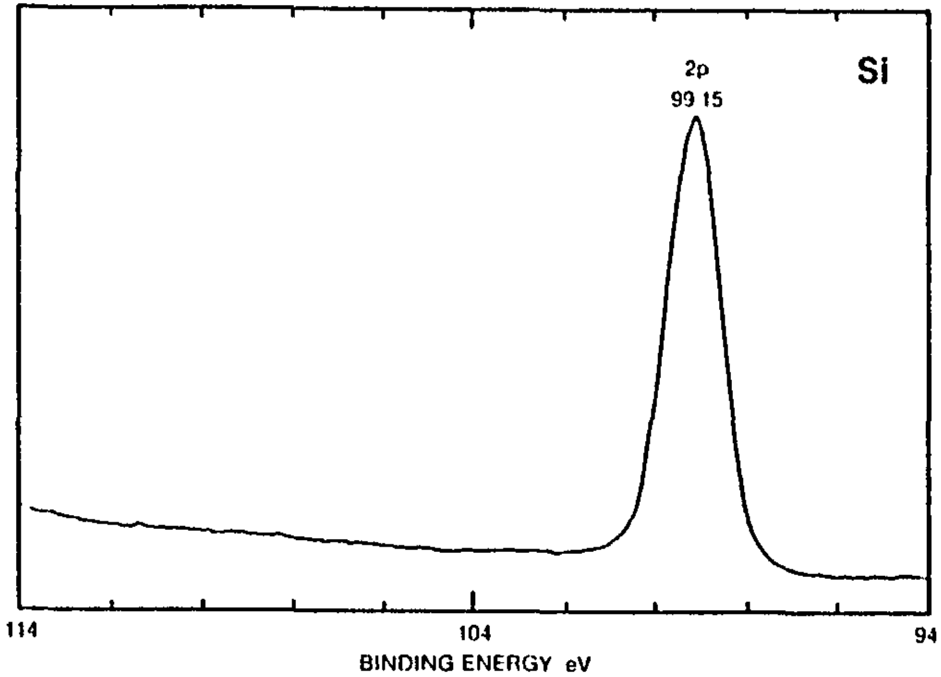
COMPOUND	REF.
Na_2S	LHJ
p-$NaSC_6H_4NO_2$	LHJ
PbS	SFS
FeS	B4
$KFeS_2$	B4
WS_2	NH2
MoS_2	PCL
$Na_2\underline{S}SO_3$	LHJ
PhNHCSNHPh	PNS
$PhSCMe_3$	PLB
Ph_3PS	MSA
tetrahydrothiophene	MMP
PhSH	LHJ
Ph_2S	LHJ
PhSSPh	LHJ
S_8	LHJ
S_n	Φ
thiophene	LHJ
S_4N_4	SDI
Me_3SI	LHJ
$O_2NC_6H_4SO_2Na$	LHJ
Ph_2SO	LHJ
BzMeSO	ML
$PhSO_2Na$	LHJ
Na_2SO_3	LHJ
$Na_2S\underline{S}O_3$	LHJ
$BzMeSO_2$	ML
SO_2	LHJ
$PhSO_3Na$	W1
p-$H_2NC_6H_4SO_2NH_2$	LHJ
$PhSO_2Me$	LHJ
Na_2SO_4	LHJ
$FeSO_4$	LHJ
$Fe_2(SO_4)_3$	LHJ

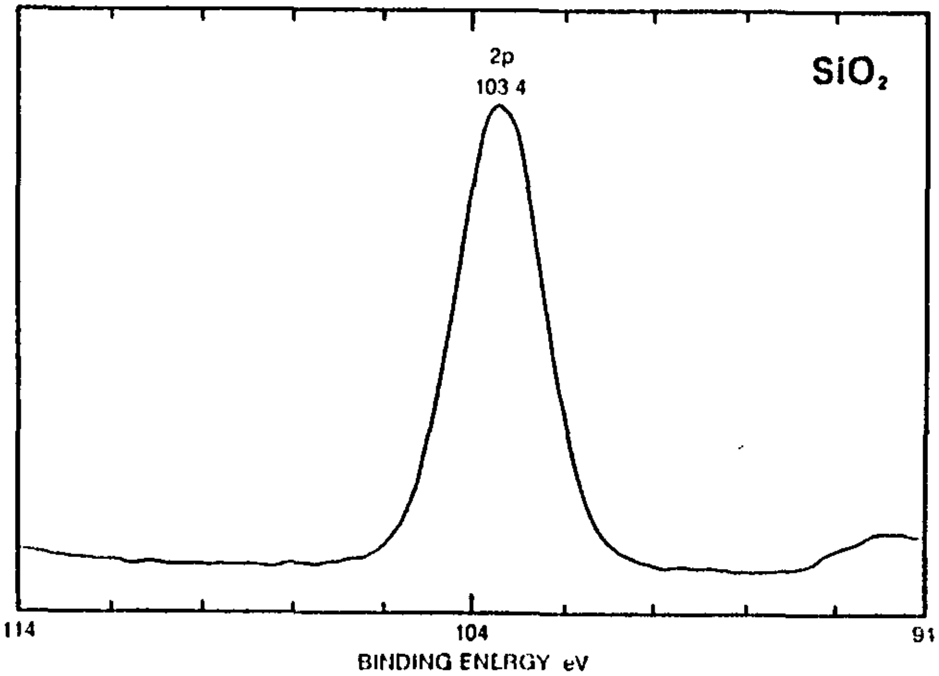




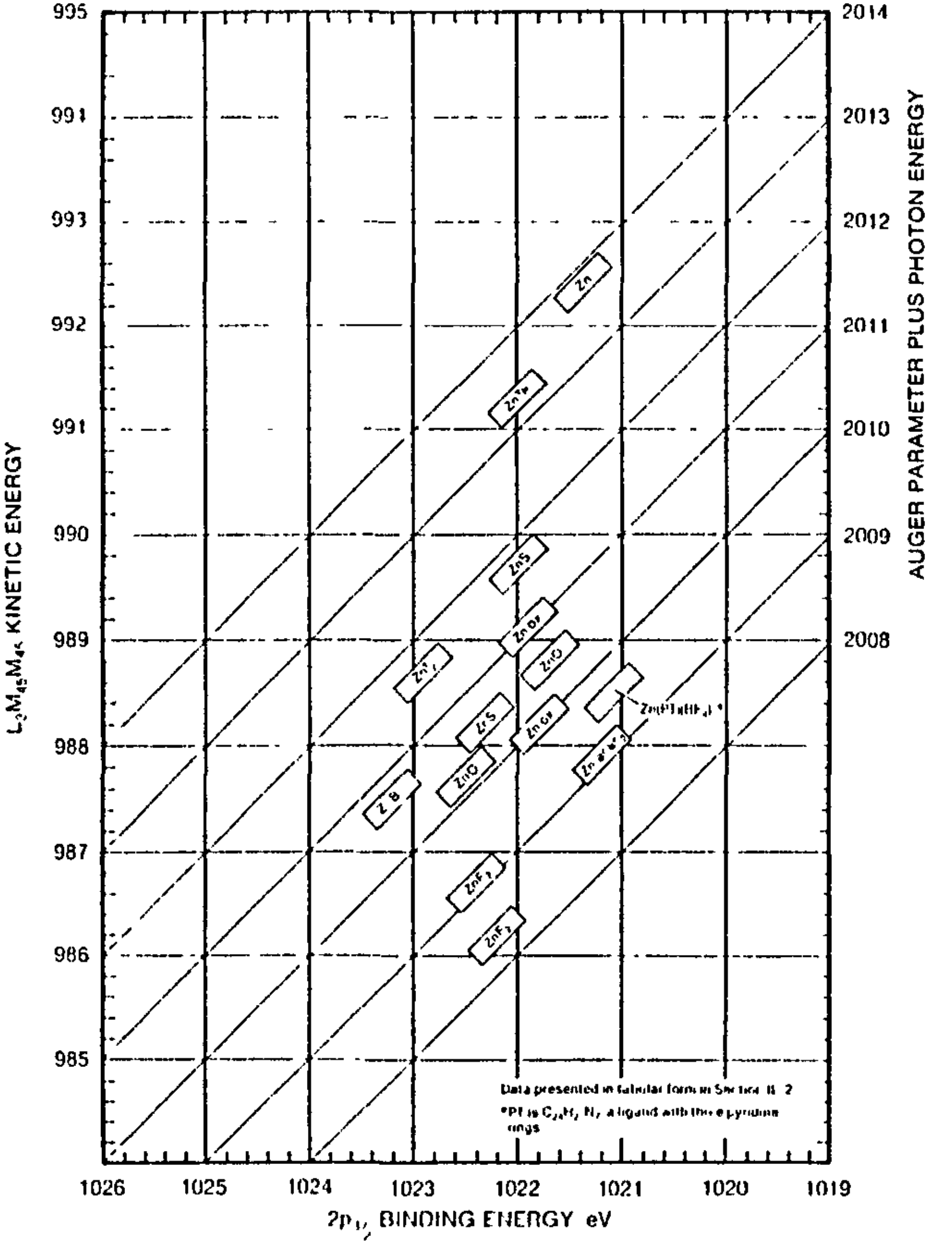
Silicon, Si Atomic Number 14





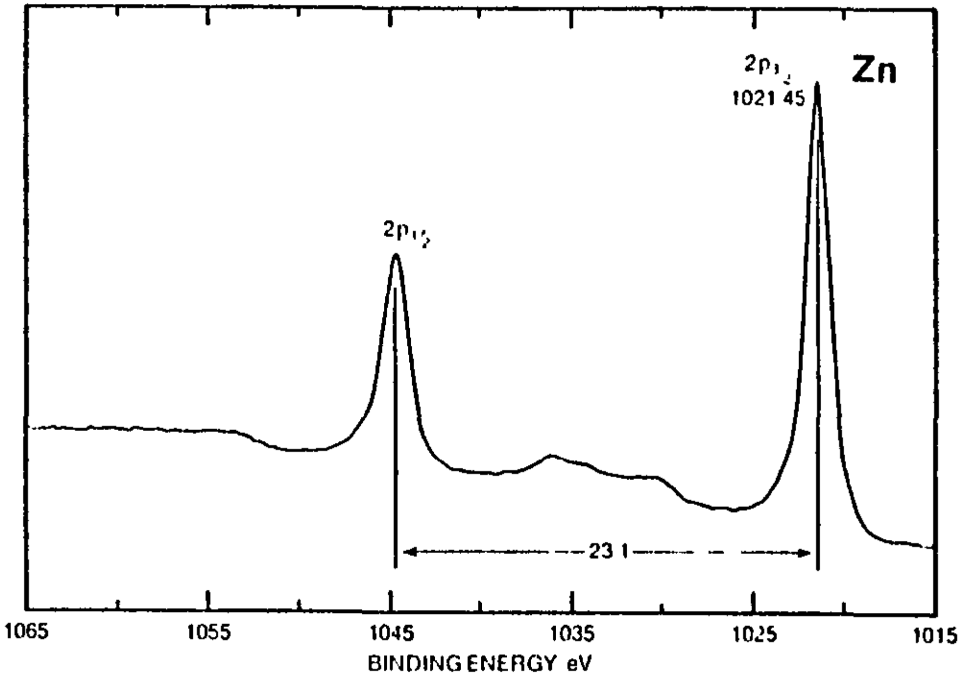


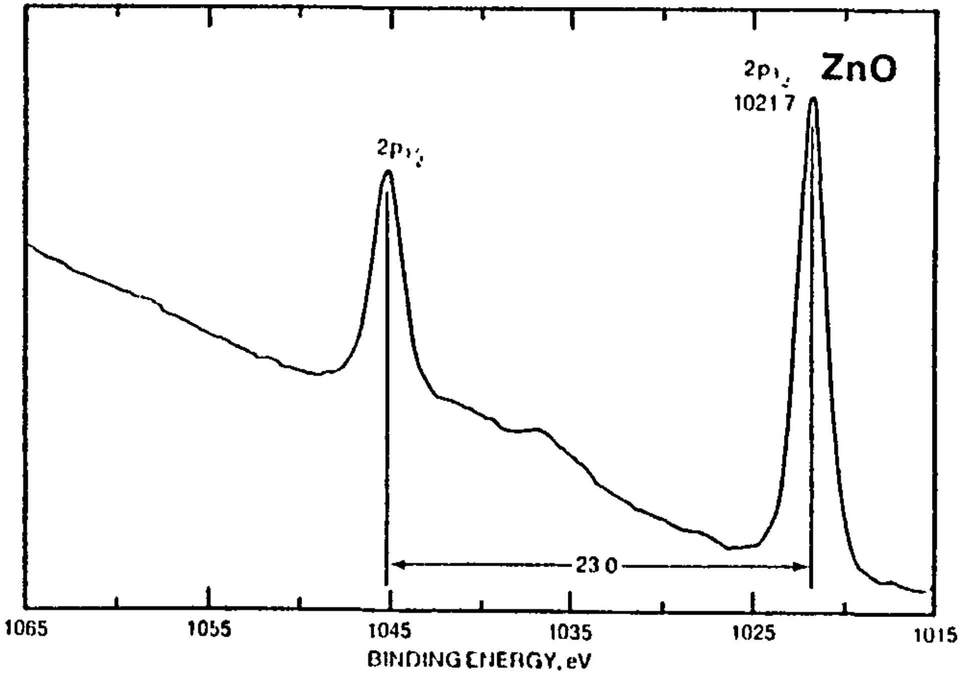
Zinc, Zn Atomic Number 30



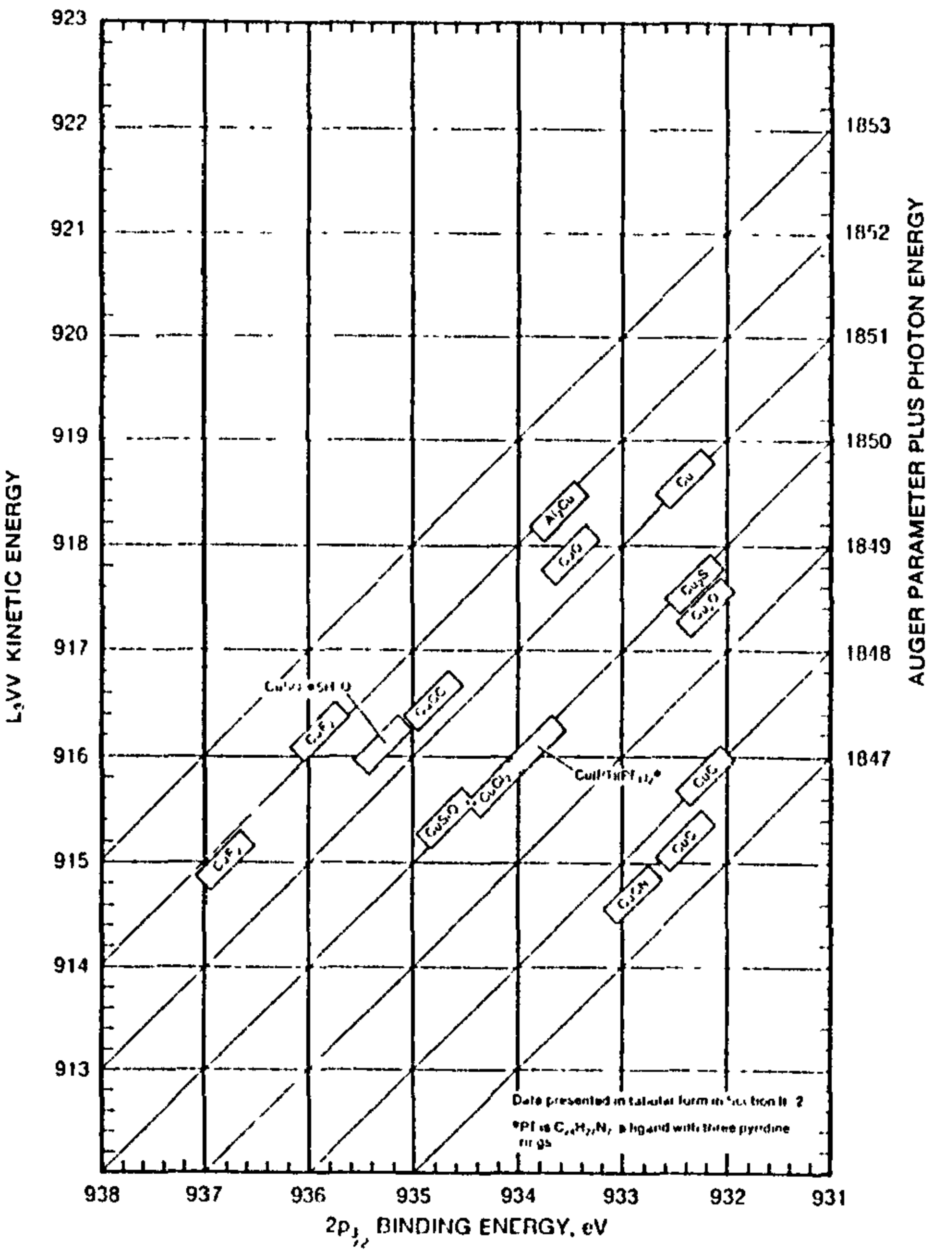
Data presented in tabular form in Section II. 2

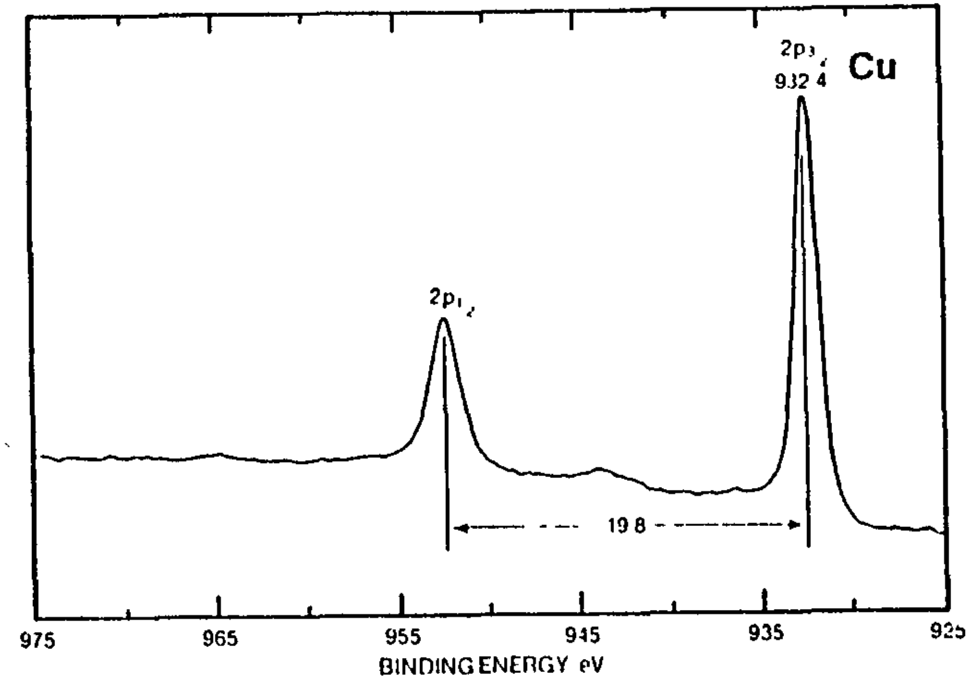
*Pt is C[illegible]H[illegible] N[illegible], a ligand with three pyridine rings

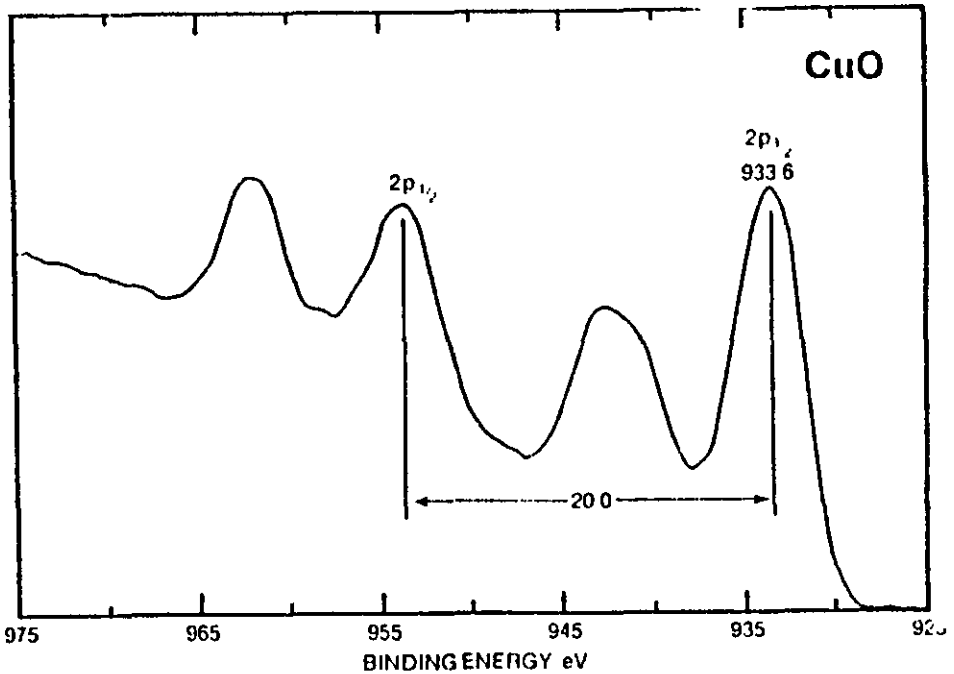




Copper, Cu Atomic Number 29







APPENDIX III

QUANTIFICATION TO GIVE THE CONCENTRATION OF ELEMENTS ON THE SURFACE OF SUBSTRATE

APPENDIX III

The intensity of a photoelectron peak depends on the number of atoms of that element in the surface region and also on a variety of parameters associated with the photoemission process and the instrument used for the analysis. These factors must be taken into account in obtaining a quantitative analysis and, broadly speaking, there are two different approaches. The relevant factors may be calculated from first principles or by using the various empirical relationships that have been proposed. This method has proved successful in some instances (1) but is not often used in routine analysis. The second approach is to calibrate the system using standard samples of known composition. This is the method generally used in routine analysis and gives good results provided suitable well characterised standards can be obtained (2).

Each of the two approaches outlined above will be treated in turn. The former since it conveniently summarises the various factors involved in determining the relative intensity of peaks in the photoelectron spectrum and the latter since it is generally applicable and widely used.

Quantification without reference standards

The area (I_A) under a photoelectron peak due to atoms of type A in a homogeneous sample (S) may be written:

$$I_A = N_A \sigma_A L_A(\gamma)\lambda_S(E_A) \times T(E_p E_A w) D(E_p) \qquad (1)$$

N_A - is the number of atoms of type A per unit volume of the sample

σ_A - is the total photoionisation cross-section for electrons in the appropriate orbital of atom A.

Values of σ have been calculated for X-ray energies commonly used in ESCA (3) and are in broad agreement with those values determined experimentally (4).

$L_A(\gamma)$ is known as the angular asymmetry parameter. $L_A(\gamma)$ takes account of the fact that the probability of observing photoemission from an orbital processing strong angular dependence (i.e. p, d, f ... orbitals) depends on the angle γ between the incoming X-ray photon and the ejected photoelectron. γ is determined by the geometry of the spectrometer used for the analysis:

$$L_A(\gamma) = 1 + \tfrac{1}{2}\beta_A \left(3/2 \sin^2\gamma - 1\right) \qquad (2)$$

and values of β_A have been tabulated (5).

$\lambda_S(E_A)$ is the inelastic mean free path of an electron having kinetic energy E_A in a sample S. A variety of empirical relationships have been proposed for the estimation of λ (5):

$$\lambda(E) = 538\ mE^{-2} + 0.13\ (m^3E)^{0.5}\ [\text{elements}] \qquad (3)$$

$$\lambda(E) = 2170\ mE^{-2} + 0.23\ (m^3E)^{0.5}\ [\text{compounds}] \qquad (4)$$

$$\lambda(E) = DE^{0.75} \qquad (5)$$

$$\lambda(E) = \frac{E}{[a(\ln E + b)]} \qquad (6)$$

where m is the monolayer thickness and D, a and b depend on the electron density in the sample. However, inelastic mean free paths estimated using the above relationships may be in error by as much as 30-40% (5). χ is the X-ray flux at the sample. $T(E_p, E_A, w)$ represents the fraction of electrons transmitted by the lens electron energy analyser system.

$D(E_p)$ is the detector efficiency. This is constant for a hemispherical analyser operating in the CAE mode.

Provided all the above factors may be determined with sufficient accuracy then equation (1) may be used to give a quantitative analysis. However, in view of the possible errors involved, a recent study (6) has concluded that data obtained from standards is still to be preferred for quantification of spectra.

Quantification using reference standards

This is more straightforward than the previous method. The concentration (N_A) of atoms of type A is assumed to be related to the intensity (I_A), of a given photoelectron peak due to that element, by the equation

$$N_A \propto \frac{I_A}{S_A}$$

where S_A is the relative sensitivity factor for photoemission from the appropriate orbital an atom A. Sensitivity factors are determined experimentally using standards of known composition and are often expressed relative to the oxygen or fluorine 1s orbitals. S_A is assumed to take account of the various factors and the concentration (C_A) of element A in a sample of unknown composition may then be determined using the equation

$$C_A = \frac{100 \frac{I_A}{S_A}}{\sum \frac{I_i}{S_i}}$$

where the sum is over all elements present in the sample surface. The accuracy of the concentrations determined by this method will obviously depend on the standards used. Errors of 10% and above have been quoted (2) for routine analyses obtained by this method. However this should be capable of further improvement by choice, where possible, of standards appropriate to the system being studied.

Relative sensitivity factors may be based on the measurement of peak area or peak height. Tables of relative sensitivity factors have been published (7) and may be used in quantification provided possible differences between spectrometers in the angular asymmetry factor and electron energy analyser characteristics are taken into account. This introduces additional sources of error. Provided well characterised standards can be obtained it is preferable to use sensitivity factors determined on the same spectrometer used for the analysis.

The measurement of peak area

Two methods have been adopted for the measurement of area under a photoelectron peak (Figure III, a,b). The first assumes a straight line background drawn from sensible points either side of the peak. The second assumes that each photoelectron is associated with a small constant background to lower energies starting at the photoelectron energy. The choice of background clearly makes little difference for a single symmetric peak (Figure IIIa). However, the presence of satellites to the photoelectron peak will result in different numerical values being obtained by the two methods. Such satellites are fairly common in ESCA spectra and may be due to shake up (where a valence electron is left in an excited state), shake off (where a valence electron is simultaneously ejected from the atom) and plasmon loss (quantised collective oscillations of electrons (8)) processes accompanying photoemission. Provided the choice of background is consistent for the standard and the sample being analysed, errors in the quantification will be kept to a minimum.

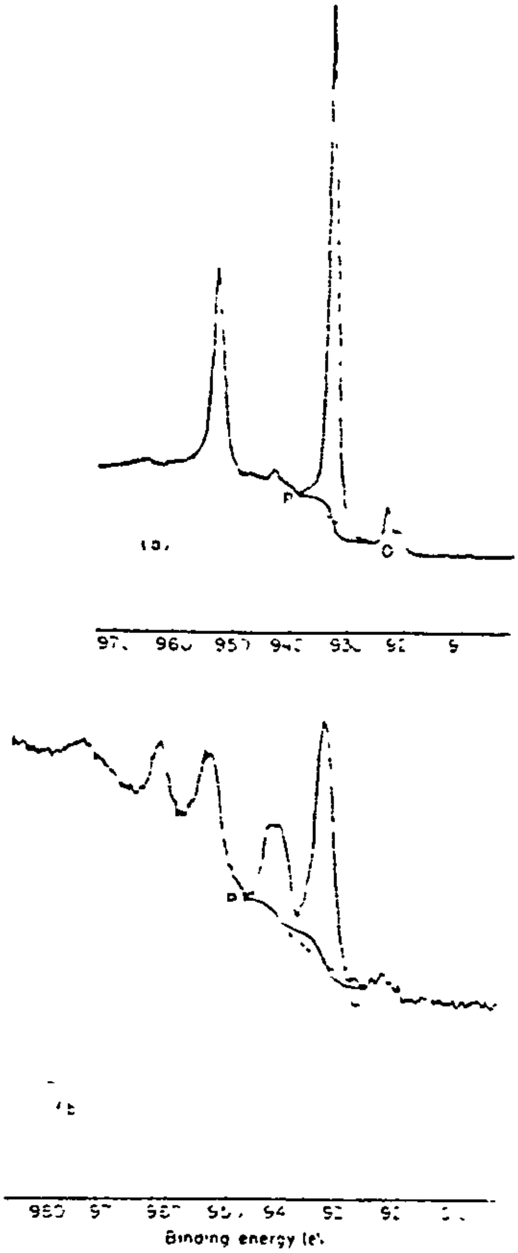


FIGURE III: Copper 2p Photoelectron Peaks from

(a) Metallic Copper
(b) CuO Powder Showing Two Modes of Background Subtraction.

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