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Electrically conductive silicone rubber

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ELECTRICALLY CONDUCTIVE SILICONE RUBBER

by

JAMES DADA AJAYI, MSc, GradPRI

A Doctoral Thesis submitted as partial fulfilment
of the requirements for the award of
Doctor of Philosophy of the
Loughborough University of Technology

November 1982

Supervisor: C Hepburn, BSc, MSc, ANCRT, FRSC, FPRI
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ABSTRACT

Research work has been carried out to critically study parameters affecting peroxide cured conductive silicone rubbers, using various carbon blacks as the conducting phase.

The following parameters were studied:

Crosslinking Agents: Of the five types of peroxides studied, dicumyl peroxide was found the most suitable crosslinking agent.

Processing (milling) conditions: The volume resistivity was found to pass through a 'minimum' as milling time and dispersion efficiency increases.

Moulding and vulcanisation conditions: The volume resistivity was found to increase with increased flow and the moulding pressure during vulcanisation. The storage time of the uncured rubber and the state of cure were also found to have a marked influence on the volume resistivity.

Carbon black concentration: Results showed the existence of a critical concentration range of carbon black at which silicone rubber was transformed from a 'resistive' to a 'conductive' material. The 'transformation range' was dependent on the type of carbon black, non-conducting filler content and processing history.

Flexing: Results obtained from 0-10,000 deformation cycles showed a significant resistivity increase from 0-250 deformation cycles, followed by the attainment of a constant volume resistivity. The final volume resistivity obtained was dependent on the time lapse before measurement, and the type and proportion of carbon black.

Graphitized carbon black: Comparative results of this with ungraphitized carbon black showed better conductivity at the same loading but lower mechanical properties.

Highly conductive silicone rubbers were found to be little or not affected by the above variables.

A theory based on the probability of conductive chain formation in a filler/rubber composite has been developed.

Results from theoretical calculations agreed with typical carbon black filled silicone rubber experimental values.

Calculations based on equivalent surface areas of different carbon blacks were found to give similar conductivity levels.

An equation for calculating the average 'interparticulate distance' of carbon black in a silicone rubber/carbon black composite has been derived from the Dark Field Reflected Light Microscopy (DFRLM) data. Results from theoretical calculations agreed with typical carbon black filled silicone rubber experimental values and supportedthe electron tunneling phenomena. They also agreed with the concept of build-up of carbon black pseudo-fibre chain formation confirmed as existing by Scanning Electron Microscopy (SEM) observations: vulcanisates with increasing conductive carbon black proportionsshowedthe progressive formation of pseudo-fibre chains.

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DEDICATION

To God, my family and friends

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1 LITERATURE SURVEY

1.1. CONDUCTIVE POLYMERS

1.1.1 HISTORICAL BACKGROUND AND PRINCIPAL USES

Polymers are usually electrically insulating, providing a high proportion of the domestic and insulating materials used today. However, extensive work has been carried out [1] to make these materials conductive by incorporating particulate composites, especially carbon black, with certain types producing considerable conductivity at low, e.g 7.00 phr, proportion.[2]

Patents describing the use of conductive compounds for prevention of corona discharge in cables have been registered as early as 1930, but only put into practical use for antistatic purposes in late 1930s to help prevent frequent explosions in surgical operating theatres due to static electricity generation in the presence of volatile analgesics. However, effective development of antistatic rubber hospital goods did not take place until after 1945. Antistatic materials are now used in many situations where explosive or flammable vapours, liquids or powders are being handled, and for vehicles and aircraft tyres where static charges generated by tyres or acquired in flight are conducted to earth through the tyres. Antistatic and conductive plastics have become prominent recently, (e.g in production of PVC used in colliery conveyor belting, antistatic films and containers), and they have undergone a very rapid expansion.

The use of conducting materials for heating purposes has been the subject of numerous patents [3-5] since about 1940. But there are considerable dificulties associated with the inherent variability of these materials to change in electrical resistance on flexing or when subjected to

various distortions from either compressive or extension forces. In the literature, however, it is assumed that silicone polymers give less variability.[6,7]

Apart from the obvious advantage of flexibility and ability to absorb mechanical shock, polymers, as soft and/or rigid materials, have some advantages over metals in ease of shaping, low density, wide range of 'induced' electrical conductivities and corrosion resistance; although with lower mechanical strength, limited temperature resistance and intermediate electrical conductivities.

Apart from carbon black, metal powders, flakes and oxides especially nickel, silver, iron and platinum have been employed to impart conductivity into polymers but usually with loss of flexibility and with some added expense.

Conductive polymers have been employed in various fields with recent developments[8] in high voltage cable splice housings, rubber toroids, and stress relief terminals.

The class of conductivity in a material is dictated by the magnitude of its resistance. Antistatic products have resistances below 5×10^4 ohms.[9] Polymers employed in the field range from Natural Rubber to Polytetrafluoroethylene. The level of conductivities is dependent on the type of polymer, and also type and amount of conductive composite included.

1.1.2 THEORY OF CONDUCTIVE POLYMERS

Electrical conductivity of materials is a property spanning a very wide range from $>10^{26}$ to $<10^{-18}$ $ohm^{-1}m^{-1}$ (fig. 1.1) and of which the polymeric subgroup falls at the

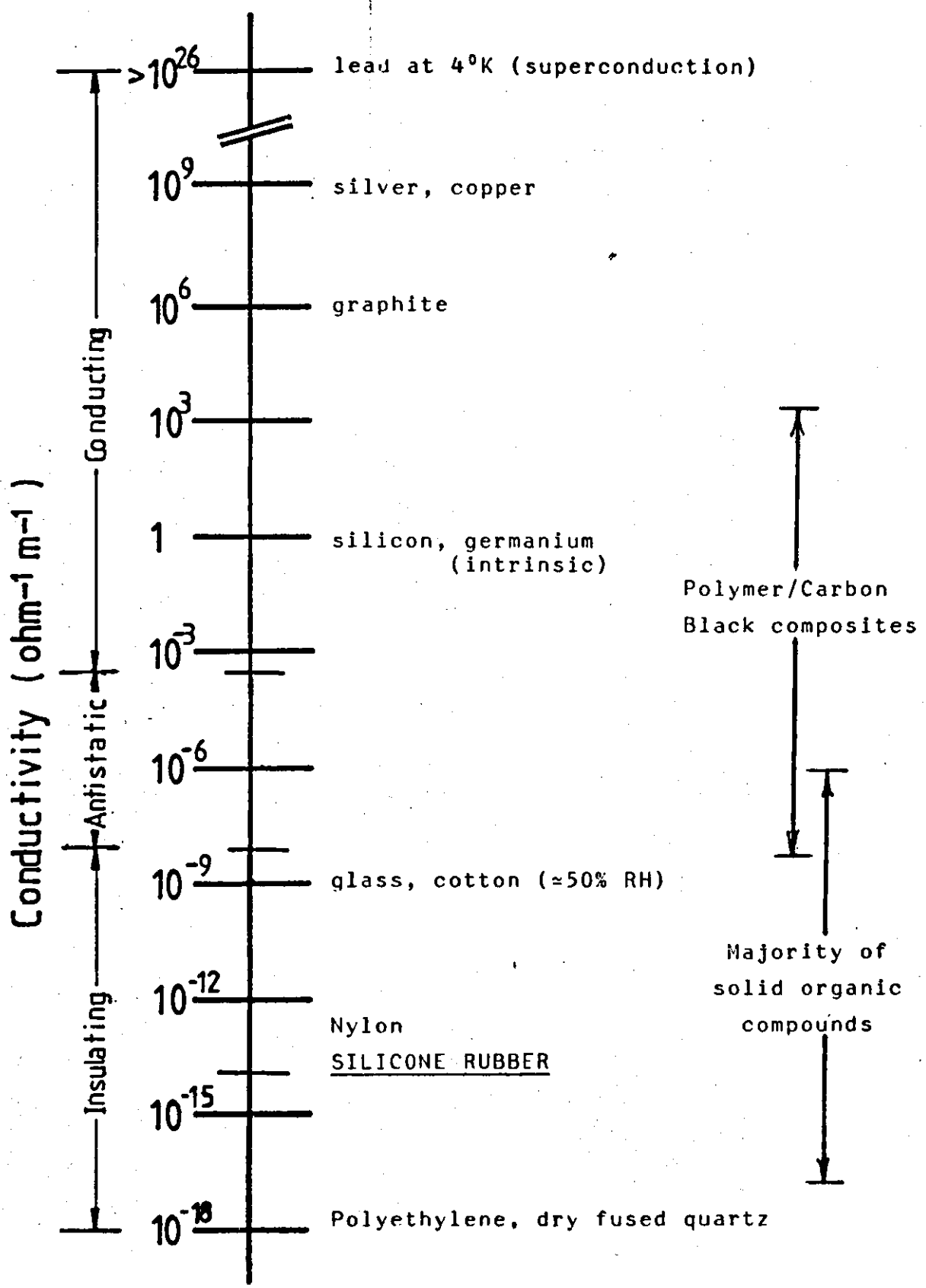


Fig. 1.1 Chart of typical material conductivities.[9,10]

low conductivity end with polyethylene (PE), polytetrafluoroethylene (PTFE), and polystyrene (PS) among the best known insulators. Silicone polymer conductivity is in the range of (2 - 10) X 10^{-14} $ohm^{-1}m^{-1}$. [11]

Electrical conduction in materials is considered to occur through the movement of either electrons (electronic conduction) or ions (ionic conduction), where band theory and hopping conduction [12] are featured. These processes are, however, more common to metals than to polymeric materials. It is very difficult to observe ionic conductivity in polymeric materials as they are designed to contain very low concentrations of ionic impurities from catalyst residues, oxidative products and dissociated groups. Such ionic impurities are not present in sufficient quantity to promote a measurable amount of positive electrical conduction within the material.

1.1.2.1 Intramolecular Conduction Theory

In organic molecular solids the groups of atoms are chemically bonded together in discrete molecules, which in turn are held together by relatively weak Van der Waals forces. In a system of long polymeric molecules, relatively few intermolecular electron transfers are required for electronic conduction to occur. Hence, we could assert, with some justification, that intermolecular conduction problem is much less important as such transfer occurs naturally.

To obtain high intramolecular conduction, we can regard each molecule in a system of long polymeric chain as a part of a miniature lattice and hence one will have the following:

a. A finitely spaced series of atoms with rigidly fixed distances between neighbours. (This is only true for metallic or highly crystalline polymers. Considerable twisting about bonds does occur in the amorphous phase, resulting in changing distances between neighbours).

b. Small separation between individual atoms giving an overlap between atomic orbitals.
c. A full valence shell analogous to a full valence band.
d. For intrinsic conduction to occur, a very large excitation energy will be needed to promote electrons across the wide band gap to the lowest excited electronic state (conduction band) which corresponds to strong chemical binding between chains (fig. 1.2).

On this basis McCubbin and Gurney[13] applied 'band theory' to a single, long polyethylene molecule on its zigzag conformation (represented in fig. 1.3) as found in the crystalline phase. Although such calculations predict a very wide band gap (>5eV) corresponding to the strong chemical bonds between carbon atoms in the polymeric molecule, the estimated carrier mobility is about $5X10^{-3} m^2 V^{-1} s^{-1}$ (for holes), which is comparable to that in metals. The experimental detection is quite difficult due to the very high energy electrons involved and the high degree of chain regularity required to preserve the band structure and avoid a trap formation; this gives rise to a mismatch between theory and practice.
However, excited state energies, of the right order of magnitude, have been found by scattered electron spectroscopy techniques.[14] Hence long saturated polymers like polyethylene will normally have no significant intramolecular conductivity.

Let us now consider a polyalkene conjugated polymer as shown in fig. 1.4. The uniformly overlapping π-orbitals extend throughout its very long chains with the expected discrete set of molecular electronic states merging into a half-full valence band, thereby, giving metallic-like conduction within the molecular chain when excitation causes transfer of an electron from its highest occupied orbit to its lowest unoccupied one. Using a very simple one-dimensional particle-in-a-box model (fig. 1.5), the energy

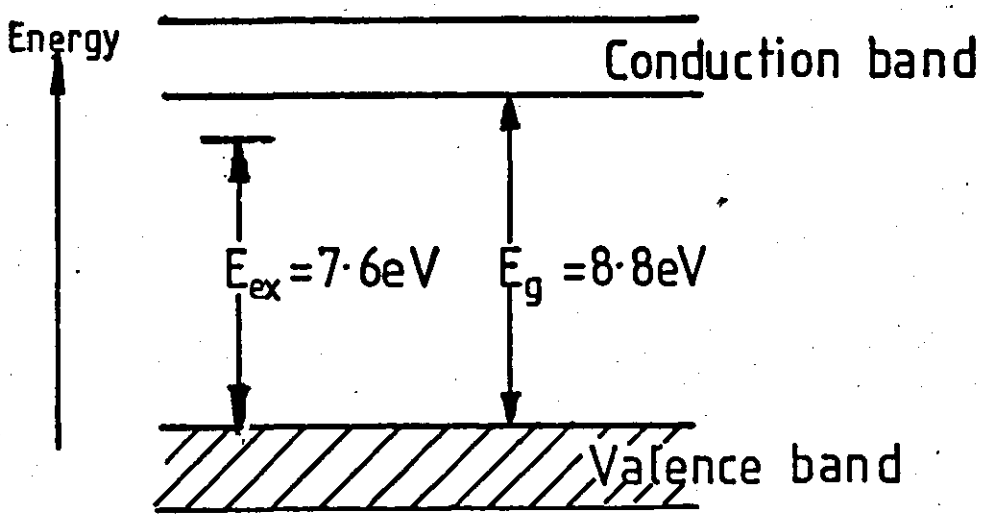


Fig. 1.2 Schematic excitation energies required for electron transfer to the lowest electronic conduction band from valence band in Polyethylene.

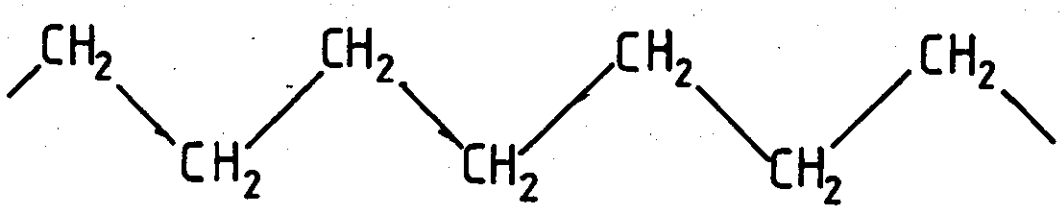


Fig. 1.3 Polyethylene in planar zigzag conformation.

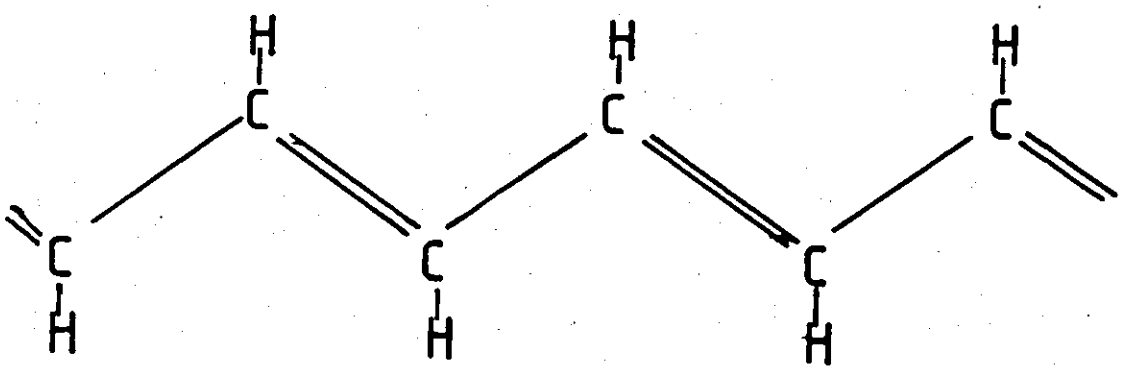


Fig. 1.4 Conjugated Polyalkene.

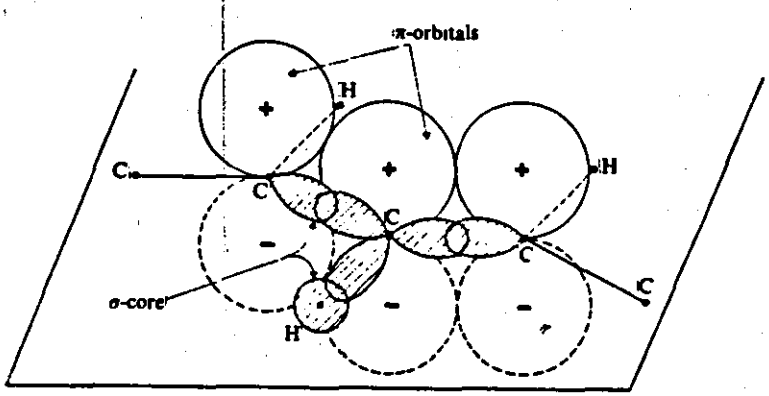


Fig. 1.5 Schematic representation of the bonding electronic orbitals of a conjugated carbon chain.

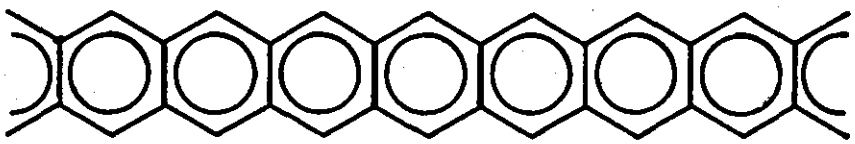
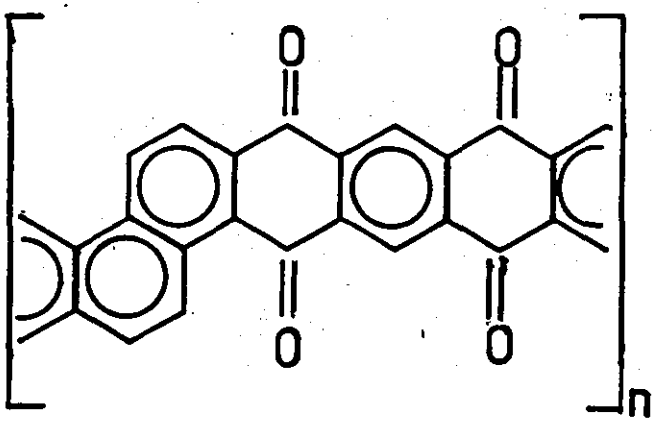


Fig. 1.6 Locking molecules of ladder type polymer.



Length = 50nm

Conductivity = 1-10 $^{7}\Omega^{-1}m^{-1}$

Dielectric constant = 20-50,000

rigid, infusible, insoluble in all solvents, and characterisation is very difficult.

Fig. 1.7 Poly(acene quinone radical) PAQR

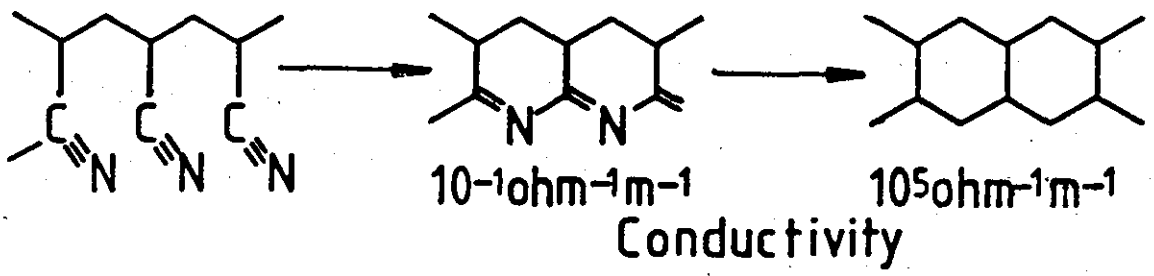


Fig. 1.8 Black Orlon from drawn polyacrilonitrile fibres.

levels for a finite conjugated chain may be calculated by the use of 'Elementary Quantum Mechanics' [14] thus:-

$$\Delta E = 19(N + 1/N^2) \qquad 1.1$$

where ΔE = excitation energy

N = number of atoms 0.14nm apart and uniformly spaced.

Now:

1. For long chain molecules, *e.g* polymers ($N \simeq 10^3$) ΔE is very small (say 0.025eV). Hence a higher equilibrium concentration of carriers is expected.
2. Since the π-orbitals involve a good overlap of component atomic p_z-orbitals, the mobility along the chain will be high.

From the above, therefore, high intramolecular conductivity and modest macroscopic conductivity in *e.g* the Polyacetylene family is expected. In reality, only highly crystalline stereoregular polyacetylenes show appreciable conductivity giving $10^{-1} ohm^{-1} m^{-1}$. [15]

The electrical conductivity of most conjugated polymers is only a little better than that of normal, long saturated polymers due to:-

1. Intermolecular conduction difficulties.
2. Long chains alternation *i.e* long and short bond occurences create self-limiting delocalization, hence the existence of non-linear excitation energy (ΔE).
3. Broken conjugation from bond rotation: for conjugation to be fully maintained, the molecules <u>must remain planar</u>.
4. Steric hinderance from large side groups *e.g* phenyl group in polyphenylacetylene.
5. Entropy considerations: chain mobility due to entropy forms out-of-plane conformations in long chain polymers.

Processes adopted to achieve conductivity in conjugated chains are, therefore:

1. Locking molecules into the required configuration as in a ladder type polymer (fig. 1.6).
   An example of this, poly(acene quinone radical) (PAQR) has been produced (fig. 1.7).[16,17]
2. Graphite-like structures formed by pyrolysis of organic polymers, *e.g* Black Orlon from drawn polyacrylonitrile fibres (fig. 1.8)

1.1.2.2 Theories of conducting composites

Incorporation of conducting additives in polymers is the general trend to convert insulating materials into electrical conductors. Conducting composites, however, require some minimum quantity of the conductive component to achieve the required degree of electrical performance. Hence one requires a knowledge of factors controlling conductive network formation for a given concentration of conducting components, *viz*:-

1. The quality of interparticulate contacts: Particulate additives must be able to make good electrical contacts when close to or touching each other.
2. Shape and size of conductive particles: Analogous to Holm's expression,[18] the resistivity of a compacted carbon powder has been successfully explained on a simple model where constrictions at interparticulate contacts are assumed to have a dominating influence.[19]

The order of preference of factors contributing to electrical conductivity with respect to additive particle shape is: (i) elongated *e.g* fibres, (ii) flakes, (iii) ellipsoidal (non-spherical), and (iv) spherical. The greater the surface to volume ratio of the shapes, the more likely are interparticulate contacts.

Examples of conducting additives employed are:

1. Fine metal powders, with the following limitations:

(a) high proportions of metal powders are required to give effective conductivity.
(b) poor physical and/or chemical properties result from their use.
(c) unnecessarily high conductivity may be induced.
(d) interfacial oxidation formation between particles; *e.g* a copper-filled polymer will not conduct unless the composite is compressed.

However, use is made of noble metals to omit this surface oxidation problem, *e.g* copper-coated with silver or gold.

2. Fibres: fine metal wires, carbon fibres, and metal-coated fibres, *e.g* silver-coated glass where the metal is present as thin-walled tubes.
3. Carbon blacks: these are initially employed as reinforcing agents because of their cheapness and compatibility, with only relatively small density changes in the polymer compared with metals. Reasonably high concentrations are needed for electrical conductivity purposes. The conductivity for a given concentration is generally governed by the carbon black type. Highly conductive carbon blacks are characterised by:
   (a) small particle size,
   (b) a propensity to agglomerate into chains to give a pseudo-fibre arrangement with structure persisting even when mixed into the polymer.

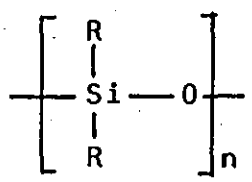
   Exceptionally, acetylene black imparts conductivity into the polymer matrix by forming a continuously conductive path inherent from its bulkiness or greater volume and its high surface porosity; it is not considered to form pseudo-fibre type chains.

Many theories of conductive composites have been postulated, and to some extent investigated in other fields. These are discussed in the section on conductivity theory.

1.2. CHEMISTRY OF SILICONE RUBBERS

1.2.1 HISTORICAL BACKGROUND AND USES

Silicones or siloxanes may be defined as structures which contain a silicon-oxygen polymeric backbone with one or two organic groups (similar or dissimilar) attached to the residual silicone valencies. The simple linear polymer structure is:



where R = is an organic radical such as CH_3

n = 10,000 - 30,000.

The name silicone was postulated and established by Wöhler[20] in 1857, to describe compounds having the emperical formula $-R_2SiO-$ by analogy to organic ketone $-R_2C=O$. Although the latter cannot exist in practice, the established name, 'silicone', has constantly been used and applied to all organosiloxanes.

F S Kipping *et al*[21] of the University College, Nottingham, contributed considerably to the knowledge of organosilicone chemistry. Kipping, however, in his published papers on the chemistry of the silicone intermediates[22] concerned himself with the preparation and characterisation of organosilicone compounds while overlooking the resinous, oily and gelatinous by-product continuously encountered. This high molecular weight polymeric by-product is the focus of silicone chemistry today.

There was a stirring of interest in the industrial potential for silicones in the 1930s. J F Hyde[23] of Corning Glass and W J Patnode of General Electric initiated work

on silicone compounds containing organic groups, while B N Dolgov and K A Andrianov [24] were also working in the field of organosilicone chemistry. E G Rochow [25] discovered the direct process for manufacturing the chlorosilanes. This important process coupled with other development of the basic rubber technology for - silicone rubber by Agens,[26] the curing of rubber by Wright and Oliver,[27] the incorporation of vinyl units by Masden,[28] and reinforcement with fine particle silica by Warrick,[29] - formed the basis for the commercial silicone rubber of today, and led to the use of silicones in various fields (fig. 1.9).

The rubbery silicone is the main interest in this thesis.

1.2.2 PROPERTIES

1.2.2.1 Basic Structure

The special properties of silicones are completely dependent on their molecular structure and they are unique in possessing some of the structural features both of silica and the silicate minerals and of organic compounds. The most common organosilicone materials are those composed largely of dimethyl- or phenyl- and methyl-substituted polysiloxanes. These polymers appear in many forms: fluids, resins and elastomers, dictated by their molecular weight, but all have the same basic silicon-oxygen-silicon backbone.

Fig. 1.10 illustrates the simplified structure of a typical silicone polymer - polydimethylsiloxane(PDMS). Where 'n' is small, we have fluids of varying viscosities. If 'n' is very large say >10,000 we have polymers on which silicone rubbers are based. Fig 1.11 illustrates the relationship between the molecular weight and viscosity of a

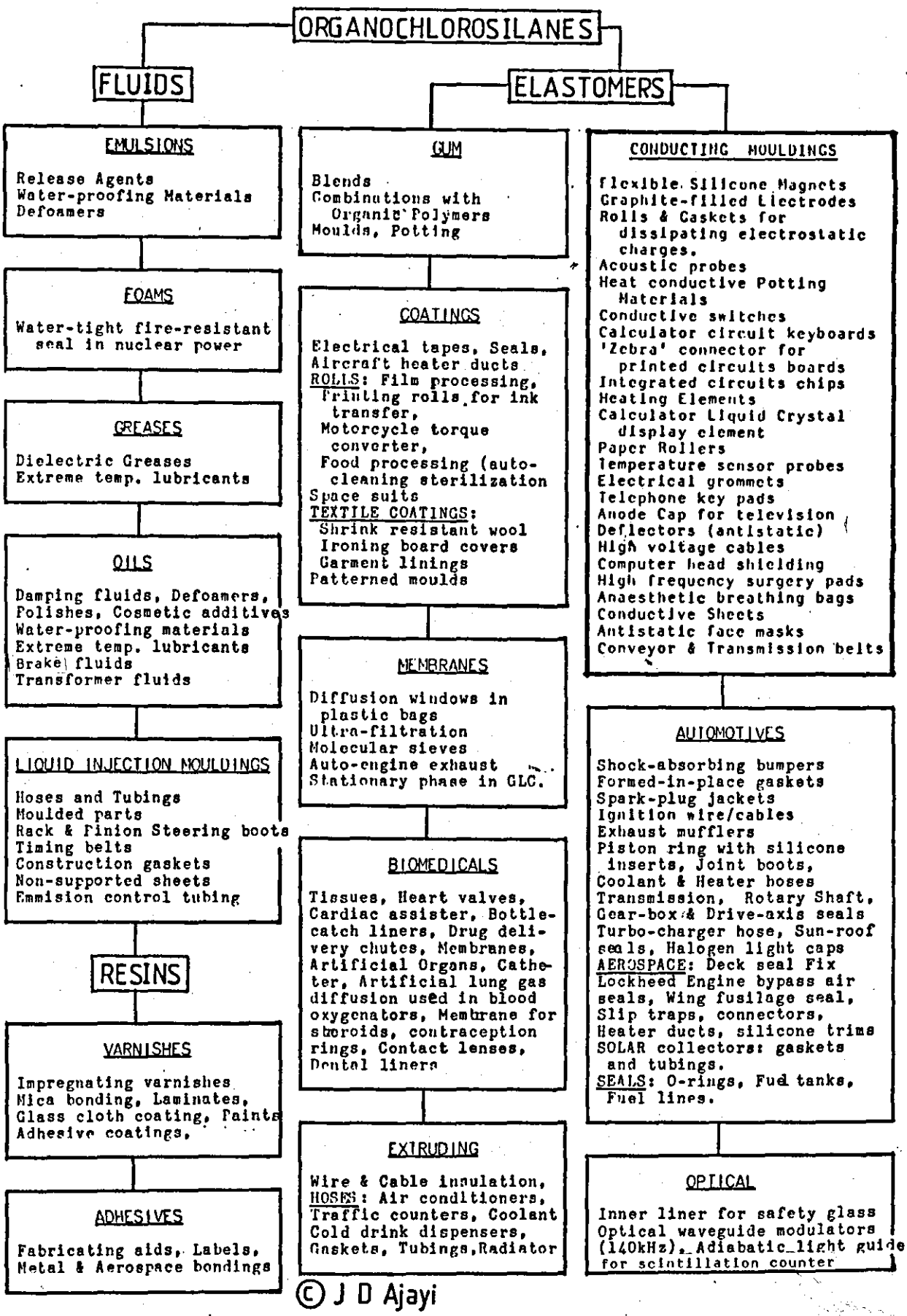


Fig. 1.9 Types of Silicone Products [30, 177, 218]

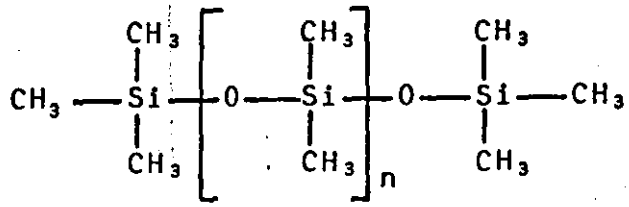


Fig. 1.10 Typical structure of silicone polymers.

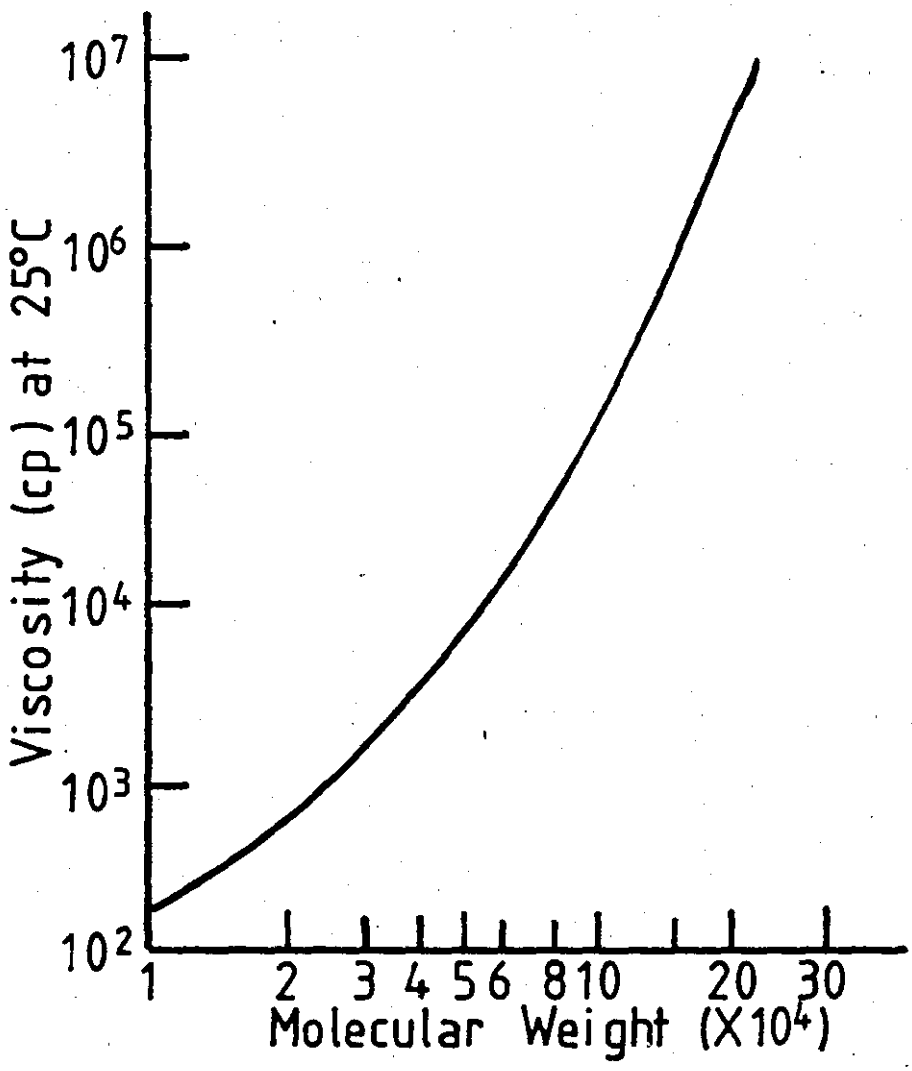


Fig. 1.11 The relationship between viscosity and molecular weight for polydimethylsiloxanes (PDMS).[31]

polydimethylsiloxane(PDMS).[31] It is interesting to note that the silicone polymer will still flow as a high viscosity fluid at a molecular weight of 500,000 whereas most organic polymers would be very hard and tough. When compared with known organic polymers, silicones are more thermally stable, and of the known inorganic polymers silicones are the most useful.

The natural mineral polysiloxane skeletons are usually crosslinked by metalloxy groups while the corresponding chains in silicones are isolated by substitution of organic groups on the silicone atoms. Also the siliceous materials are insoluble and infusible and very stable thermally due to their highly crosslinked structure(fig. 1.12), while silicone chains, owing to the lateral blocking, only interact weakly with one another by weak Van der Waals forces. They, therefore, swell in solvents and have poorer thermal stability than their inorganic counterparts.

1.2.2.2 Thermal Stability

The above unique properties are not surprising since the inherent stability of a polymer to temperature is limited by its bond dissociation energy, disregarding all other factors. It is possible to estimate the temperature at which thermal degradation of any particular bond will occur at some appreciable rate from the Arrhenius equation:

$$k = A_{exp}^{(-E/RT)} \qquad 1.2$$

where R = gas constant
A = a constant that can be estimated
E = Activation energy for dissociation
≡ bond energy or bond dissociation energy
T = Absolute Temperature
k = rate constant

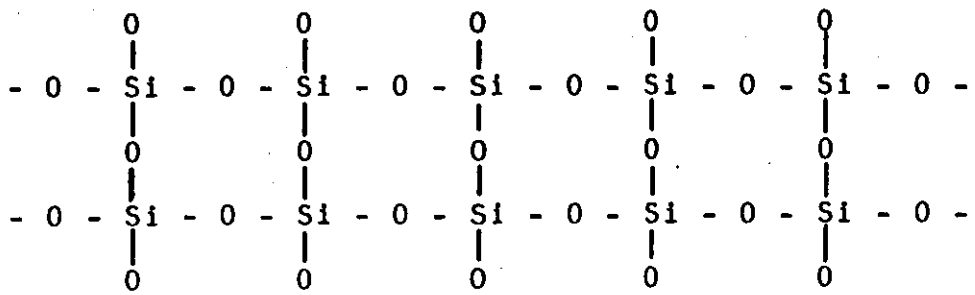


Fig. 1.12 Schematic representation of Quartz.

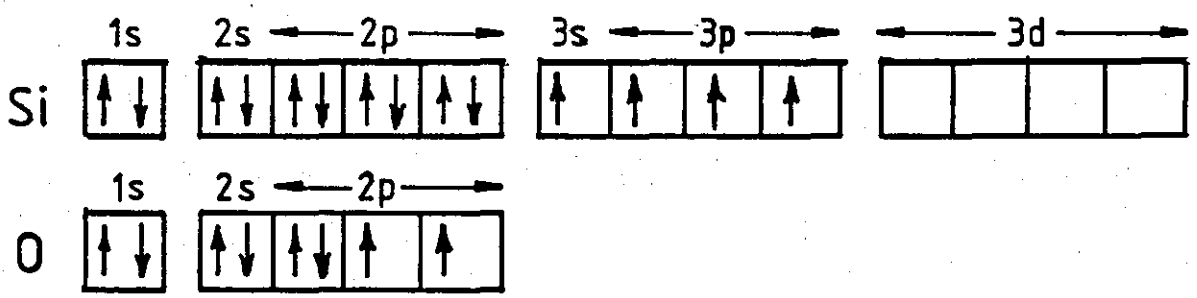


Fig. 1.13 Schematic representation of the orbital arrangement (valence state) of Silicon (Si) and Oxygen (O)

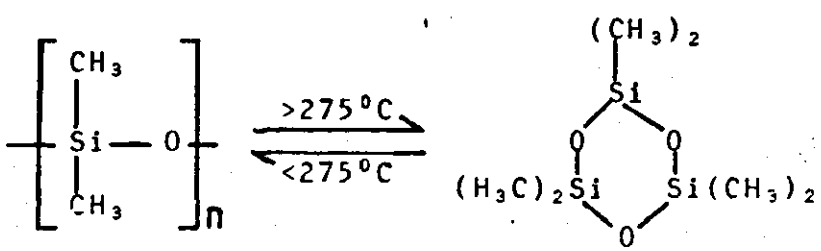


Fig. 1.14 Equilibrium depolymerization of Polydimethylsiloxane (PDMS)

Bond energies[32-34] for several atoms attached to silicon are compared with those attached to Carbon (Table 1.1). Hence a silicone's unique thermal stability is partly a consequence of the very strong Si-O bond. The specific bond energy is, however, dependent on the organic radical attached to the silicon atom and the silicone backbone is susceptible to chemical attack by processes requiring a relatively low activation energy of about 96.30 $kJmole^{-1}$ if other reagents such as air and moisture are present. Hence the expected thermal stability is relatively low compared to the one suggested by the bond energy.

The molar heat of oxidation of silicon is more than twice that of carbon. Hence, in the presence of an oxygen source and the necessary lower activation energy, the Si-C linkage is destroyed in favour of Si-O.

The ability of silicon to use its vacant 3d orbitals to form favourable transition states, as shown in the schematic representation of orbital arrangement (valence state) (fig. 1.13) opens the way to a low energy reaction path for decompositions, impossible with carbon which has no vacant low energy orbitals for bond attacking reagents.[35,41]

It is, therefore, evident that the thermal stability of silicones is thus determined, to some extent, by the kinetics of possible degradation reactions which can occur in the presence of other compounds or reagents such as oxygen and moisture.

The stability of silicones is affected by the tendency for long chain to depolymerise to small rings at elevated temperatures.[36] Many chain-like polymers, for example, on heating above 275°C are partially converted to cyclic siloxanes, usually trimers, tetramers, through to hexamers or some mixture of these (fig. 1.14). Conversely under other conditions, for example using a

TABLE 1.1 BOND ENERGIES ($kJmole^{-1}$)			
BOND	BOND ENERGY	BOND	BOND ENERGY
Si-Si	222	C-Si	318
Si-C	318	C-C	345
Si-H	318	C-H	413
Si-O	451	C-O	357
Si-N	324	C-N	304
Si-F	564	C-F	485
Si-Cl	380	C-Cl	339
Si-Br	309	C-Br	284
Si-I	234	C-I	213

TABLE 1.2 ELECTRONEGATIVITIES AND IONIC CHARACTER OF Si-X BONDS.			
ELEMENT	ELECTRONEGATIVITY (El)	ΔEl	IONIC CHARACTER IN Si-X (%)
Si	1.8	-	-
O	3.5	1.7	50
C	2.5	0.7	12
H	2.1	0.3	2
F	4.0	2.2	70
Cl	3.0	1.2	30
Br	2.8	1.0	22
I	2.4	0.6	8

TABLE 1.3 BOND LENGTHS AND BOND ANGLES		
BOND	LENGTH (nm)	ANGLE (°)
Si-O	164	-
Si-C	188	-
Si-O-Si	-	≈145°(104°- 180°)
O-Si-O	-	≈110°(108°- 112°)
C-Si-C	-	≈110°(106°- 118°)

catalyst NaOH (see fig. 1.17), the cyclic siloxanes can be changed to high polymers emphasizing the ready displacement of the ring/chain equilibrium (fig. 1.14), a property common to many systems. Like many chemical reactions, polymerization involves an equilibrium between reactants (monomers, dimers, trimers *etc.*) and the products (macromolecules in the form of chains, networks *etc.*). Hence cyclic group removal at elevated temperature results in the chemical process being directed in favour of depolymerization.

1.2.2.2.1 *Ionic Character*

The Ionic Character of the siloxane bond is as equally important as that of the availability of silicon's d-orbitals for chemical bonding. It can be seen (Table 1.2) that silicon is decidedly more electropositive than carbon, hydrogen and oxygen. Thus Si-C bond breaks in the direction of $Si^{+}C^{-}$ under electrophilic attack at the carbon or under nucleophilic attack at the silicon; indeed cleavage of bonds always occur in this manner. Hence while the Si-H bond usually breaks in the $Si^{+}H^{-}$ direction ($\Delta El=0.3$), the C-H bond breaks in the opposite direction $C^{-}H^{+}$ ($\Delta El=0.4$). Similarly the Si-O and C-O bonds break in the direction of $Si^{+}O^{-}$ ($\Delta El=1.7$) and $C^{+}O^{-}$ ($\Delta El=1.0$) respectively. The large fraction of ionic character Si-O $\simeq$ 37-51% and C-O $\simeq$ 20-30%[34,37] has been suggested as the source of many polysiloxane properties, such as thermal stability, ease of acid-base catalysed re-arrangements, and optical properties.[38-40]

Silicon, being a second - row element, has d-orbitals available for chemical bonding. While five d-orbitals are avalaible for bonding not more than <u>two</u>, the $d_{x^2-y^2}$ and the d_{z^2} orbitals, are used, since these give the best overlap with the p-orbitals of the oxygen. The co-ordination number never exceeds six. The d_{π}-p_{π} bonding influences the bond angles and the bond distances of Si-O-Si. The average values

for bond angles[42-47] and bond lengths[41,48,49] as determined by X-ray diffraction, Infra-red, Raman Spectra and dipole measurements are as in Table 1.3. These bond angles and bond lengths also play an important role in the chemistry of silicon and are particularly involved in the mechanisms of reactions with silicon, apart from influencing chain conformation.

1.2.2.3 Hydrolytic and Chemical Stability

The bond energies of some Organic Siloxane functional groups are given in Table 1.1 as the energy required to break the bonds homolytically, and these indicate relative high thermal stability. A better guide to reactivity is perhaps given by Ionic Bond Energies[50,51] as in Table 1.4, *i.e* the energy required for the process, *e.g*

$$\equiv Si\text{-}X \longrightarrow \equiv Si^{+} + X^{-} \qquad 1.3$$

to occur. This is a calculated sum of the bond energy, the ionization potential energy of Si, and the electron affinity energy of X (where X is any other substituent atom).
The Ionic Bond Energy is an index of heterolytic fission which is the prevailing mode in reactivity and agrees more closely with the observed chemical and hydrolytic stability.

1.2.2.4 Dielectric Properties

The dielectric properties of polydimethylsiloxane[11] together with their other desirable properties have led to their widespread use as electrical insulators(Table 1.5).[53] These properties are usually dependent on thickness of the sample, nature of the rubber formulation and the type of

TABLE 1.4 IONIC BOND ENERGIES ($kJmole^{-1}$)

BOND	IONIC BOND ENERGY	BOND	IONIC BOND ENERGY
Si-C	932	Si-Cl	795
Si-H	1044	Si-Br	748
Si-O	1013	Si-I	700
Si-F	992	Si-S	805

TABLE 1.5 PROPERTIES OF A HIGH QUALITY SILICONE RUBBER VULCANIZATE SUITABLE FOR ELECTRICAL INSULATION

PROPERTIES (UNITS)	TEST SPECIFICATION	TEST SPECIMEN	VALUE
Dielectric Strength ($kVcm^{-1}$)	DIN 53481	1.2mm thick 95.0mm dia.	250
Surface Resistance (ohms)	DIN 53482	Standard rod	3.0×10^{14}
Resistance between plugs(ohms)	DIN 53482	Standard rod	4.5×10^{14}
Specific Volume Resistance (ohm-cm)	DIN 53482	95mm dia.	2.1×10^{16}
Dielectric constant, ε, dry at 50cps/50V 800cps/50V 10^6cps/50V	DIN 53483	95mm and 30mm dia.	3.1 3.0 2.9
Dielectric loss factor, tan δ, dry at 50cps/50V 800cps/50V 10^6cps/50V	DIN 53484	95mm and 30mm dia.	0.0005 0.0008 0.0040

vulcanisation. The polydimethylsiloxane dielectric constant, ε, a measure of the recoverable energy stored within the polymer, is quoted as 2.74 at 25°C and 1,000 centipoises (cps).[54]

1.2.2.4.1 *Silicones as insulating materials*

An electrical machine must not only withstand the mechanical and thermal stresses but must also satisfy the stringent requirements resulting from the existence of electrical and magnetic fields. The insulation must stand up to variations in humidity, corrosion, glow discharges and voltages of about 30,000 volts. Also, the effect of temperature rise had to be taken into account.[55] This led to drawing up specifications for the use of insulating materials by electrical engineering associations. The electrical insulation classes were established based on time and temperature limits. By using the Arrhenius relation to predict long-term operating life of 25 to 30yrs, an exponential relationship was discovered by Motsinger[56] and from this the expected operating characteristics for electrical insulation of Class A (105°C), B (130°C), E (140°C), F (155°C) and H (180°C) was derived[57] and internationally recognized.[58] Fig. 1.15 shows the life as a function of the temperature determined on the basis of above relationship for insulation systems of Classes A, B, and H.[59,30] Silicone is considered to be Class H insulating material.

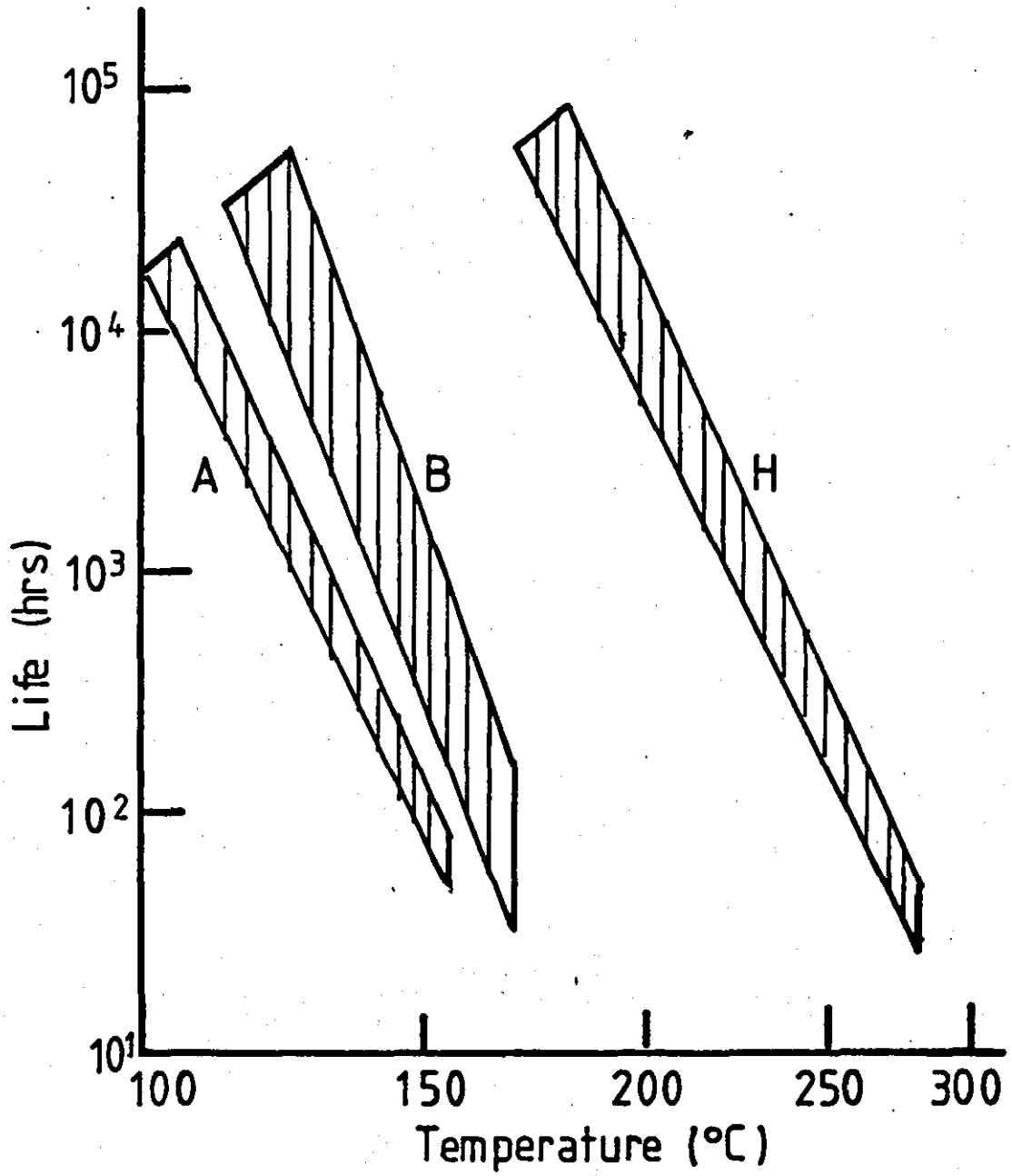


Fig. 1.15 Life of Classes A, B, and H insulation systems.

1.3 COMMERCIAL SILICONES

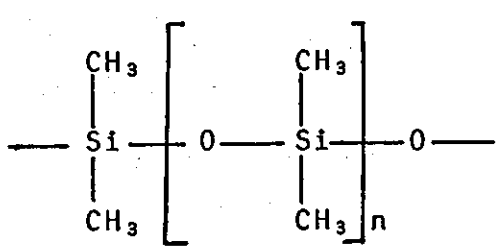
The formulation of a commercial silicone elastomer generally consists of:-

1. Base Gumstock
2. A reinforcing filler
3. An antistructure additive
4. A heat stabilising additive
5. A crosslinking agent.

1.3.1 BASE GUMSTOCK

Depending on their chemical and physical structure, it is possible to produce silicone rubbers which have similar basic properties (such as, for example, heat stability, low temperature flexibility, electrical insulation properties and adhesive properties) but which differ from one another in certain special characteristics.

The basic general purpose chemical skeleton of silicone rubber is the polydimethylsiloxane chain, generally modified by special substituents. The heat vulcanisable types are characterized by extremely high molecular weights (300,000 - 1,000,000).[60] The optimum molecular weight has, however, been given as 600,000.[61]
The formula of polydimethylsiloxane is given below:



where $n = 10{,}000 - 30{,}000$

$\overline{M}n \simeq 600{,}000$

1.3.1.1 Synthesis

There are basically two general methods used to synthesize polydimethylsiloxane:

1. ring opening mechanism - opening of cyclic low molecular weight tetramer siloxanes.
2. condensation of linear polymers with hydroxyl or hydrolyzable terminal groups.

Different routes and processes to synthesize polydimethylsiloxane have been reported.[62] One of these routes is now described:-
Starting from the basic raw materials (coke, quartz and chlorine), polydimethylsiloxane can be produced(fig. 1.16).[63]

Cyclic siloxane intermediates are formed by dimethyl siloxane hydrolysis. High molecular weight polydimethylsiloxane is prepared from cyclic intermediates via a ring opening reaction. A wide variety of catalysts[64],which can be used,have been reported. These include Lewis acids e.g Ferric Chloride, Boron trifluoride, Stannic Chloride[65], proton acids[66] ; acid clays; and many bases e.g tetramethylammonium hydroxide.[67,68] However, the principal route uses a cyclic siloxane to prepare the polymers which is the tetramer that may be polymerized by ring opening using an alkaline catalyst (fig. 1.17).[64]

The polymerization process is an equilibrium reaction in which a certain ratio between cyclic and linear species is maintained. When the desired molecular weight is reached, the reaction is stopped with solid CO_2 which neutralizes the NaOH catalyst. Typical conditions are: heat silicone liquid tetramer at 150°C under vacuum for 23hrs, then add 1% NaOH and polymerize to desired viscosity. The reaction is terminated by adding solid CO_2 which converts the NaOH into the inactive Na_2CO_3.

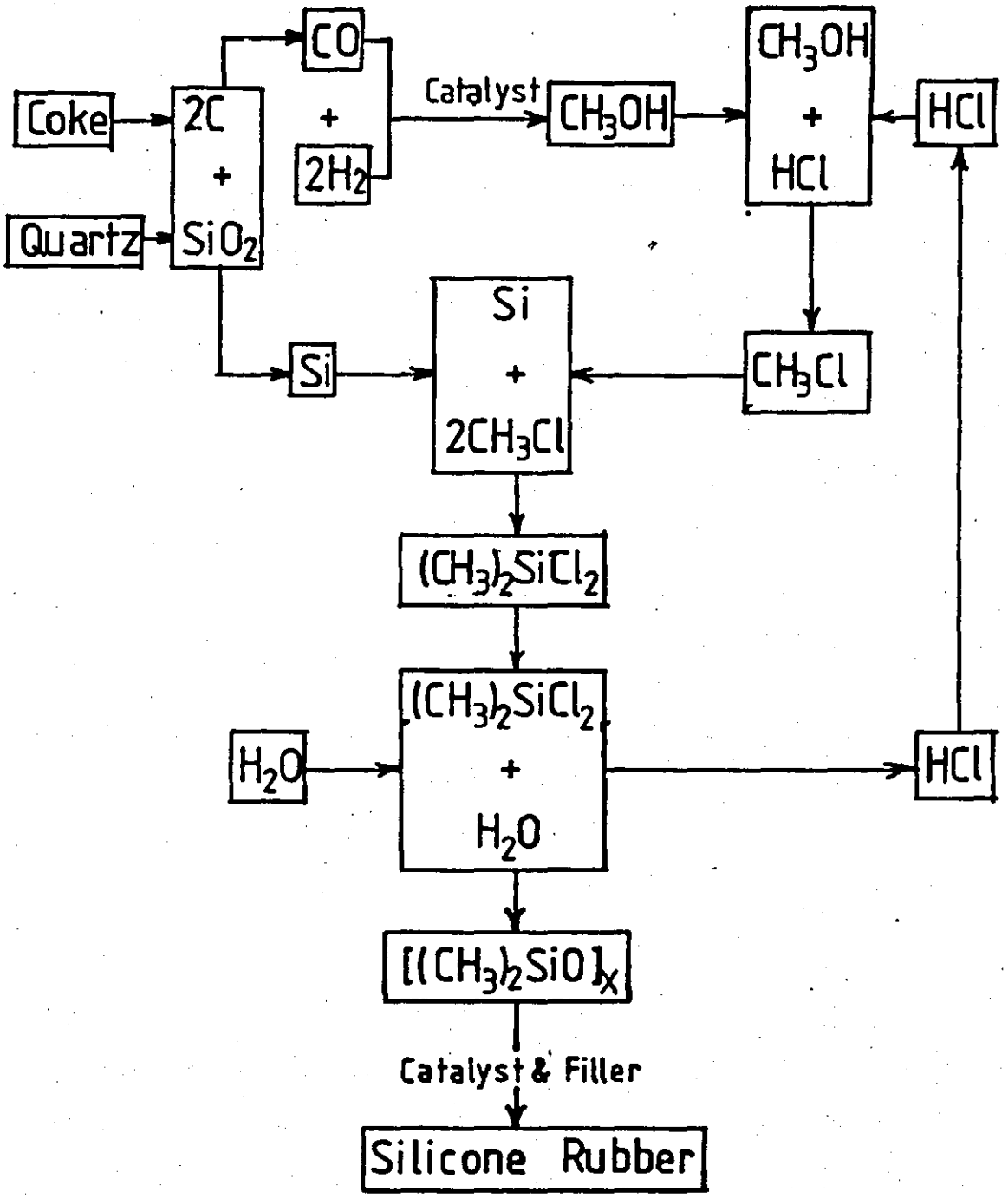


Fig. 1.16 Schematic flow diagram for the preparation of polydimethylsiloxane.

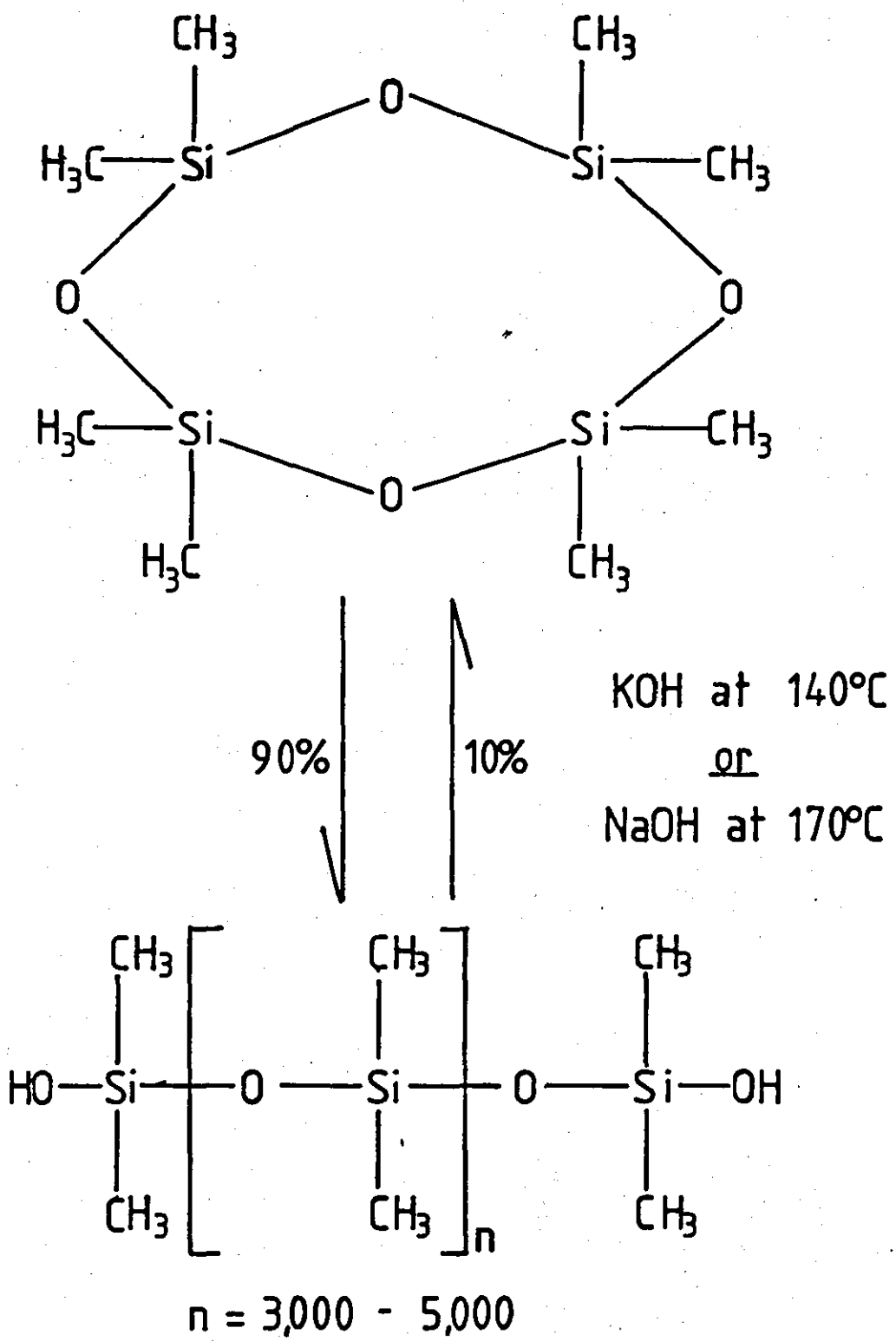


Fig. 1.17 Typical polymerization system of polydimethylsiloxane.

At equilibrium, with ease of polymerization of polydimethylsiloxane, there are 12.5% to 14% cyclics[64] present including species through to A_{11}, where $A = (CH_3)_2SiO$. These have to be removed by devolatilisation through the use of vacuum at 150°C.

The nature of the organic radical attached to the silicon atom has a significant effect on the overall properties of the elastomer. It is, therefore, advantageous to combine several types of organic radicals in the same polymer in order to achieve a particular combination of properties. Examples of these are inclusion of:

a. 4 to 11 mole% of methyl-phenyl or diphenyl groups which break up the regularity of the polydimethylsiloxane chain and impede crystallization. This results in improved lower temperature flexibility, lower 2nd order transition temperature (the lowest known is at 7.5 mole%),[69] and improved heat and radiation resistance.
b. 0.02 to 0.5 mole% of methyl vinyl siloxy units to facilitate a marked increase in the efficiency of the peroxide vulcanisation process.[70] This also improves the compression set. Dimethylsiloxanes containing up to 10 mole% of methyl vinyl siloxy units can be cured with conventional sulphur recipes[71-73], thus providing a method of curing blended silicone and organic rubbers including natural rubber.[73] This is not, however, usually practised industrially.
c. 1.0 to 2.0 mole% of trifluoropropyl methyl siloxy and cyanoalkyl containing units[74-76] which provides some resistance to non-polar solvents, fuels and oils with heat resistance, hydrolytic stability and flexibility. The simpler dimethylsiloxanes have poor resistance to solvent swelling and attack.

Patents have been registered and other works carried out covering a wide range of routes both on ring opening[77-88]

and condensation.[89-93] Copolymers are usually prepared by copolymerization of mixtures of desired cyclics in the presence of suitable catalyst and conditions.

1.3.2 STRENGTH AND REINFORCEMENT

This is one of the most important aspects of silicone rubber technology, both practically and theoretically. Unreinforced, cured silicone gum is too weak to be of much practical use (tensile strength is about 0.35 MNm^{-2}) and very different in strength when compared with other organic rubbers. But in the filled and reinforced state its tensile strength increases by up to a factor of 40. It is therefore necessary to reinforce silicone rubber with fillers in order to improve the vulcanisate mechanical properties.

Silicone polymers possess characteristics that favour their choice as model materials to examine theories describing rubber behaviour. These are:

a. The chains assume a random configuration and exhibit the presence of chain entanglements in a manner consistent with organic polymers
b. The polymers and elastomers are non-glassy, amorphous, and rubbery at room temperature (low T_g and T_c).
c. They do not strain-crystallize except at very low temperatures.
d. They exhibit excellent thermal stability.
e. They are soluble in a variety of convenient solvents which facilitates characterization and studies by a variety of experimental methods.
f. Polymerization chemistry allows functional groups (*e.g* vinyl) to be either incorporated at random or selectively located such that crosslinking sites can be conveniently controlled.
g. A wide range of molecular weights can be easily prepared.

h. Silicone polymers possess significant inorganic characteristics for comparison with organic analogs.
i. Chemical analysis is readily accomplished.
j. Multiphase systems exhibit good contrast in electron microscopy without the need for staining.
k. The polymers respond to reinforcement by silica fillers in a very dramatic manner.

Hence, silicone polymers and elastomers have frequently been selected to test theories for equations of state(PVT), rubber elasticity, Mooney-Rivlin constants($2C_1$ and $2C_2$), network structure effects on properties, thermo-elastic parameters, stress-optical coefficients, *etc.*[94-106]

Commercially available silicone rubbers have tensile strength values from $5.52 MNm^{-2}$ to $10.34 MNm^{-2}$.

1.3.2.1 Types of Fillers

Only thermally stable fillers are used in silicone rubbers as reinforcing and/or extending fillers. [illegible] required as reinforcing fillers and/or extending fillers. A large number of fillers have been evaluated[107-109] in reinforced silicone compounds and the effects observed parallel to those that are found in other elastomer reinforcement. Fillers which have strong acidic (*e.g* acid clay) or basic characteristics must be avoided to prevent depolymerization of polydimethylsiloxane (PDMS).[110]

Amorphous silica, particularly fumed silica, is the primary reinforcing filler used in silicone rubbers.
The secondary reinforcing fillers are:

a. Fibrous materials (*e.g* fibres of organic polymers, inorganic materials and metals): grafted methacrylic acid polymer,[111] blends of emulsion grade PVC,[112] *in situ* formation of polypropylene (PP) fibres,[113] blends of (1mm. dia.) PTFE particles,[114] and electro-conductive

ferromagnetic fibre-reinforced silicone rubbers.

b. Variety of block copolymers: pendant unsaturated groups,[115] aromatic rings in alternating dimethylsiloxane and methylphenylsiloxane.[116]

c. Metal oxides, of a fairly wide variety, are classified as extending fillers in addition to their very important heat stability role.

d. Other extending fillers are quartz, diatomaceous earth, zinc oxide, titanium dioxide, calcium carbonate, alumina zirconium silicate, and carbon black.

However, the most important extending fillers commercially are carbon black, calcined diatomaceous silicas (1-5μ), ground silicas and zirconium silicate (Table 1.6)

1.3.2.1.1 Polymer-filler interaction

This plays a paramount role in the reinforcement of silicone with silica. Hence, the surface chemistry of the silica and the polymer chemical make-up become involved in the details of polymer-filler interaction. The interaction between silicone elastomeric polymers (*e.g* polydimethylsiloxane) and the high surface area (*e.g* 150 to 400m^2g^{-1}) pyrogenic (fumed) silica occurs to a major extent leading to high levels of bound polymer and long mill-softening times. This is often referred to as crepe hardening, and it is a very undesirable processing phenomenon.

The amorphous silicas have three identified[117] types of surface hydroxyls [isolated, vicinal (on adjacent silicon atoms, hydrogen-bonded to one another), and geminal (two hydroxyls on the same silicon atom)] (Table 1.7 and fig.1.18). Also silanol groups plus strained Si-O-Si bonds (formed by heating isolated and vicinal hydroxyls above 110°C).[118] These are available for interaction with silicone polymers.

TABLE 1.6 EXTENDING FILLERS AND THEIR APPLICATIONS

FILLERS	APPLICATIONS
Carbon blacks	1. Colouring, 2. Conducting composites e.g acetylene
Calcined Kaolins	Electrical properties (excellent)
Calcined Ferric Oxide	improves thermal stability, compression set, and/or electrical conductivity
Calcined diatomaceous Silicas (1-5μ)	impart low compression set, and low water absorption
Calcium Carbonate, Zinc Oxide	imparts tack and adhesiveness
Ground silicas	reduce compound volume cost
Titanium dioxide	pigmentation white/grey
Chromium oxide	" green
Iron Oxide	" red
Mapico Tan	" orange
Cadmolith Yellow	" yellow
Cobalt Aluminium	" blue
Copper Oxide, and Low Melting Glass Frit	Flame Retardancy
Barium Sulphate (approx 20phr)	Medical implant
PTFE (low loading)	improves tear resistance
Zirconium silicate	used in liquid RTV systems

NOTE: The normal reinforcing silica used for Silicone Rubber are the pyrogenic (fumed) silicas such as Aerosil (De Gussa) and Cab-O-Sil (Cabot Carbon)

TABLE 1.7 SILANOL INFRARED ABSORPTION ASSIGNMENTS

TYPE	STRUCTURE	INFRARED BAND (cm^{-1})
ISOLATED SILANOL		
Surface, not H-bonded	1	3,750
Surface, H-bonded	2	3,740 3,550
Internal	1	3,650
VICINAL SILANOL		
Pairs H-bonded	3	3,660 3,550
Water H-bonded	4	3,607 3,540
GEMINAL SILANOL	5	3,500 1,604
ADSORBED WATER		
H-bonded to single silanol	6	3,456 1,640
H-bonded to paired silanol	7	3,480 3,400 3,370

N.B For structure see fig. 1.18

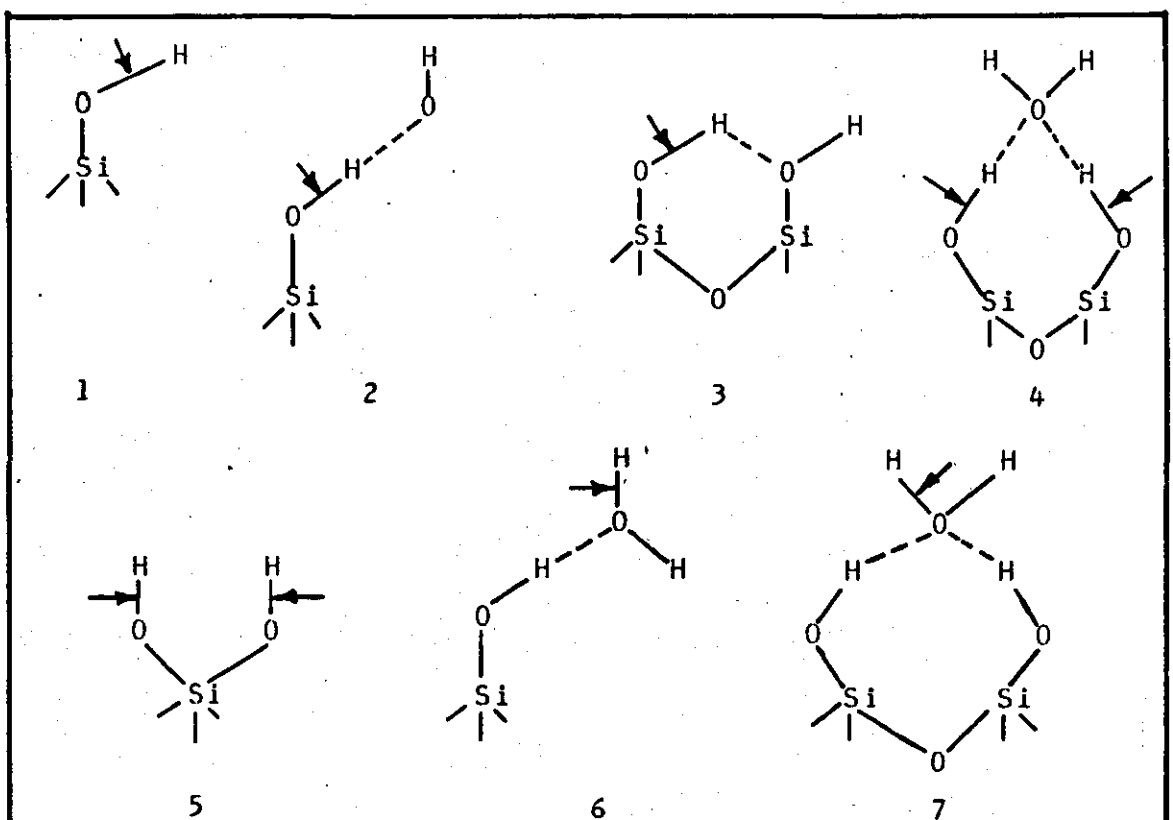


Fig. 1.18 Types of hydroxyl groups present on silicas.

The primary sites within the silicone polymer that interact with the silica are also considered to be terminal chain silanol groups and the $-Me_2Si-O-SiMe_2-$ segments of the polymer chain. Investigators [119-122] concluded that physical adsorption, giving rise to hydrogen bonds and Van der Waals forces, was the major source of polymer-filler interaction in polydimethylsiloxane-silica compositions; in addition to which covalent bonding of the polymer to the filler surface was a possibility, especially upon vulcanisation. However, regardless of whether the interaction (or polymer-filler bonding) is chemical, physical or some combination thereof, it is apparent that the level of interaction is sufficient to increase the effective network chains in the vulcanised elastomer providing sufficient strength for commercial use.

1.3.2.1.2 *Polymer-filler Interaction reduction and control*

To inhibit, retard or completely eliminate crepe hardening, it requires the use of:

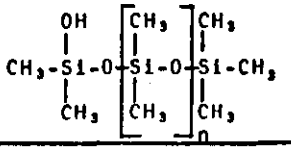
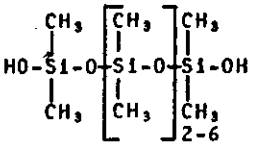
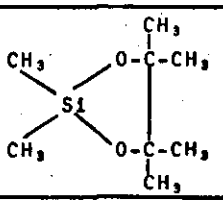
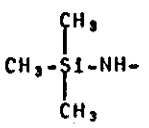
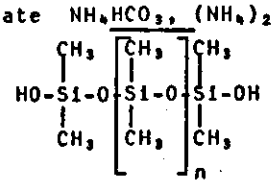
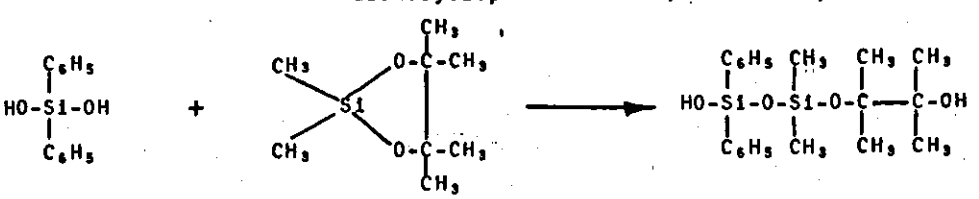
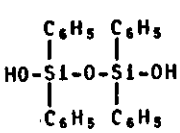
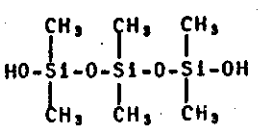
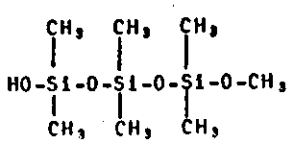
a. Special anti-creping plasticizers *e.g* low molecular weight methyl- and phenyl-substituted linear silanols which may be end-blocked, liquid siloxane diols (I);[124] cyclic ethers of silicon, polyhydric alcohols,[123] and silylamines or silazanes.[125]

b. Antistructural additives: (also see Table 1.8)

1. combination of ammonium carbonate or bicarbonate with hydroxylated siloxanes.[126]
2. diphenylsilanediol[127] + dimethylcyclopinacoxysilane
   ↓
   1,1,2,2,4,4-hexamethyl-6,6-diphenyl-3,5-dioxa-4,6-disila-1,6-hexane diol [128]
3. tetraphenyldisilanediol.[129]
4. hexamethyltrisiloxanediol.[130]
5. methoxyhexamethyltrisiloxanol.[131]

c. Preheated silica *e.g* silsesquioxanes[132], fumed silica[133], hydrophobic aerosils, surface-treated silicas[134], modified aerosils and special silicas[135].

TABLE 1.8 ANTI-CREPING AND ANTISTRUCTURAL ADDITIVES

ANTICREPING ADDITIVES Methyl- or Phenyl- substituted linear silanols (end-blocked)	
Liquid silane diols (I)	
Cyclic ethers of silicon (e.g silyl ethers of pinacols)	
Polyhydric alcohol (e.g ethylene glycol, phenyl ethylene glycol)	$HOCH_2CH_2OH$ Ethylene glycol $HOC_6H_5CH_2OH$ Phenyl ethylene glycol
Silylamines or Silazanes (e.g triphenyl silylamine)	
ANTISTRUCTURAL ADDITIVES Combination of : Ammonium Carbonate or Bicarbonate and Hydroxylated siloxanes	NH_4HCO_3, $(NH_4)_2CO_3$ 
Diphenylsilanediol + Dimethylcyclopinacoxysilane 1,1-dimethyl-1-sila-2,5-dioxacyclopentane → 1,1,2,2,4,4-hexamethyl-6,6-diphenyl-3,5-dioxa-4,6-disila-1,6-hexanediol	
Tetraphenyldisilane diol	
Hexamethyltrisiloxane diol	
Methoxyhexamethyltrisiloxanol	
Vinylsilsesquioxane	$CH_2{=}CHSiO_{3/2}$

1.3.3 VULCANISATION CHEMISTRY

For a stable polymer to exist, a three-dimensional network of the polymer molecules is required. This involves chemically crosslinking (apart from physical crosslinks formed by chain entanglements) the polymer molecules together. This is generally achieved by two main routes:

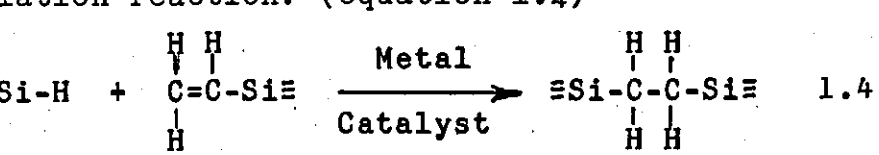
1. Room temperature vulcanisation (RTV)
2. Elevated Temperature/Radiation activated cures

1.3.3.1 Room Temperature Vulcanisation (RTV)

This is normally used with low viscosity or liquid silicone elastomers. The material can, therefore, be easily extruded from a tube and cured by reactions involving a functional chain end and a polyfunctional compound in the presence of a catalyst. RTV can be a dual- or single-component system.

1.3.3.1.1 Dual-component system

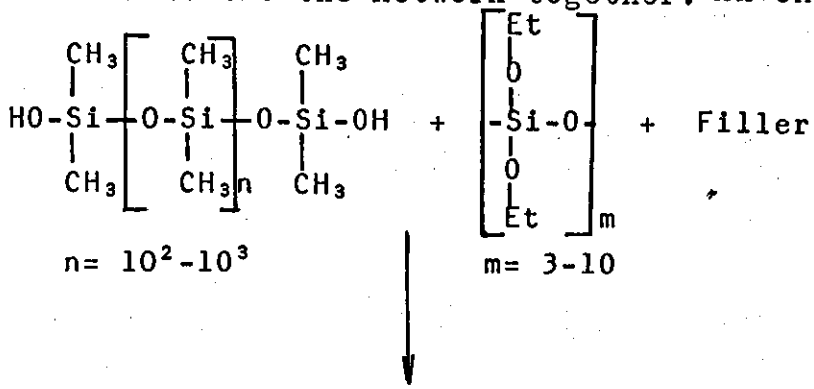
This requires mixing specified amounts of the two components at the time of fabrication. One component could contain a polyfunctional silicone hydride (a crosslinker) and a catalyst, while the other contains an unsaturated (vinyl group) polymer and filler. This usually results in hydrosilation reaction: (equation 1.4)



1.4

Another example is one involving a functional chain end and a polyfunctional compound *e.g* silanol chain end with a silicate.[223] This involves a simple condensation reaction (equation 1.5) catalysed with fatty acid salts of tin, lead, cobalt *etc.* giving a siloxane linkage and ethanol. Thus,

the silicate being polyfunctional can react with several chain ends to tie the network together. An example of the



Crosslinked Rubber + Ethanol 1.5

silicate used is tetraethyl-orthosilicate (TEOS) + Stannous Octoate.

Other examples are:

a. aminoxysilanes (crosslinker) (component 1)
   + polydimethylsiloxane and diatomaceous earth (component 2)
b. organotriacyloxysilanes (crosslinker) (component 1)
   + polydimethylsiloxane and silica (component 2)

1.3.3.1.2 *Single Component system*

The single component system usually contains an excess of multifunctional hydrolizable organosilicon (as a crosslink initiator in the presence of moisture) and silanol end groups packaged under anhydrous conditions into a water impermeable container. On exposure, the atmospheric water reacts with the hydrolyzable groups attached to the silicon:

$$\equiv SiOA + HOH \longrightarrow \equiv SiOH + HOA \qquad 1.6$$

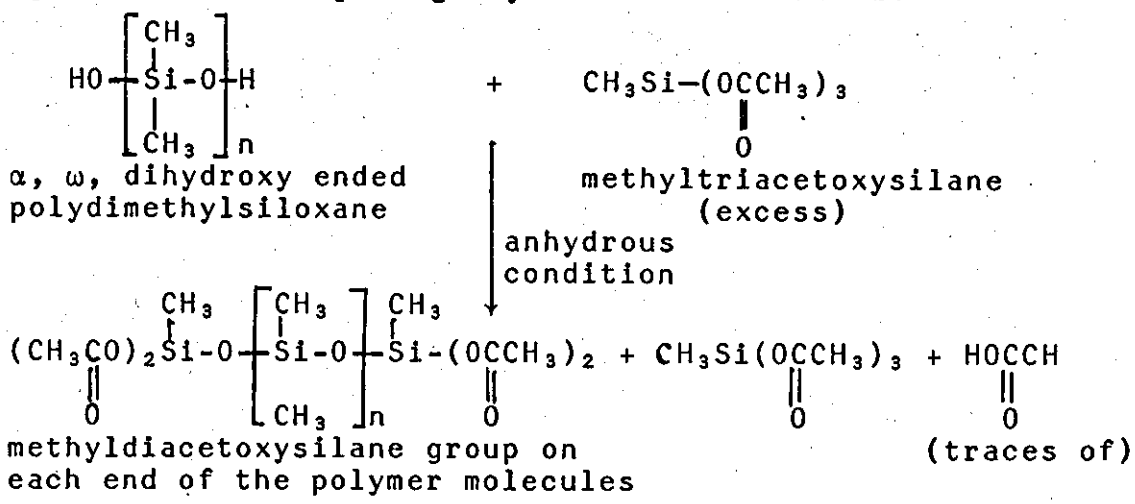
where OA = hydrolyzable groups

Once hydrolysis begins, the silanol formed can either condense with another silanol group or a hydrolyzable group on silicon, thus forming a Si-O-Si linkage and a condensation by-product (equation 1.7)

$$\equiv SiOH + \begin{matrix} HOSi\equiv \\ \underline{or} \\ AOSi\equiv \end{matrix} \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + \begin{matrix} HOH \\ \underline{or} \\ HOA \end{matrix} \qquad 1.7$$

(Condensation reaction)

Example of the one package system manufacture is:

1. 

2. Add Filler $\xrightarrow[\text{Anhydrous condition}]{\text{Package}}$ RTV Compound (packaged)

3. RTV Compound + HOH (Atmospheric water)

   ↓

   Crosslinked Elastomer + $CH_3\underset{\underset{O}{\|}}{C}OH$ ↑

Other examples of one-package systems are:

a. A mixture of grafts of ethyl-polysilicate to silanol-terminated polydimethylsiloxane with dibutyltin-dilurate and hexylamine as catalysts.[138]

b. A mixture of excess tetra-alkoxysilane or alkyltrialkoxysilane with silanol-terminated polydimethylsiloxane and titanate as a catalyst.[136,137]

In excess of fifty patents have been registered on both dual- and single- component systems, a few of which is cited.[139-151]

1.3.3.2 Heat and Radiation activated cures

These require the application of energy in the form of:

1. heat (elevated temperature) *e.g* in the presence of free radical initiators,
2. heat-induced with catalytic initiation *e.g* hydrosilation,
3. radiation-induced *e.g* high energy irradiation,

to the formed mass of polydimethylsiloxane and silica.

1.3.3.2.1 Free radical initiators

The most commonly used heat-activated cure involves free-radical generation to induce abstraction, coupling, and addition reactions with methyl and small amounts of vinyl groups in the polymer chain.

Initiation is usually with peroxides and heat, generally at temperatures in the range of 115-150°C. Peroxides are reported to undergo homolytic cleavage in the presence of various silicone polymers, *via* a second order reaction sensitive to inhibition by oxygen.[152,153] It is generally accepted that the peroxide, when heated to its decomposition temperature, generates free radicals. Hydrogen is abstracted in the free radical reaction with methyl groups while free radicals add on [70] in the vinyl-free radical reaction. The ensuing silylmethyl radicals form crosslinks by coupling or by addition to small amounts of pendant vinyl groups deliberately included in the polymer for improved crosslink efficiency. In addition to vinylsiloxy units, co-monomeric methyltolylsiloxy units are reported to facilitate heat-activated cures with or without peroxides present.[153]

1.3.3.2.1.1 RECOGNISED CROSSLINKING MECHANISMS OF ORGANOPOLYSILOXANES BY PEROXIDES

An essential function of any peroxide in curing a rubber is the production of free radicals. The common method in the rubber industry of causing this free radical formation is by heating the peroxide molecule, in a non-acidic atmosphere. The peroxide then decomposes into two alkoxy radicals (equation 1.8). These free radicals thus produced then react with the rubber chain leading eventually to a chemically crosslinked network.

Early papers [52,63,70] on peroxide crosslinking show two important routes in which polysiloxanes and free radicals may react: by hydrogen abstraction from a methyl group [63] (equation 1.9) and by addition to the vinyl group [63,70] (equation 1.10):

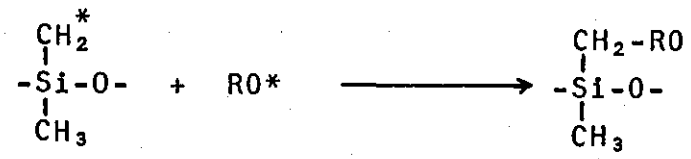
$$ROOR \xrightarrow{\Delta} 2RO^{*} \qquad 1.8$$

$$\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + RO^{*} \xrightarrow[\text{abstraction}]{\text{hydrogen}} \begin{array}{c} CH_2^{*} \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + ROH \qquad 1.9$$

$$\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH{=}CH_2 \end{array} + RO^{*} \xrightarrow{\text{addition}} \begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ {}^{*}CH \\ | \\ CH_2-OR \end{array} \qquad 1.10$$

In the case of reaction (equation 1.9), the polymeric radicals formed may then react by several paths leading to crosslinking (equation 1.11) or radical wastage/chain termination (equation 1.12):

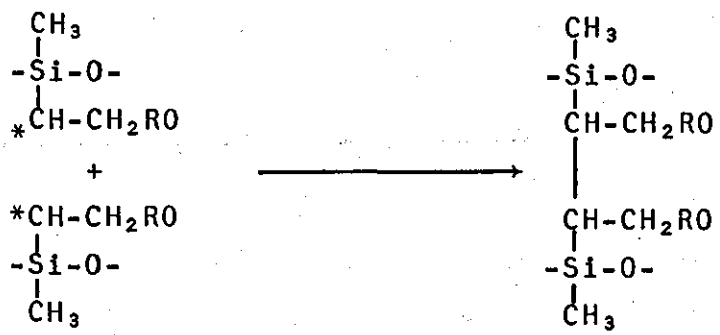
$$2\left[\begin{array}{c} CH_2^{*} \\ | \\ -Si-O- \\ | \\ CH_3 \end{array}\right] \longrightarrow \begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} \qquad 1.11$$



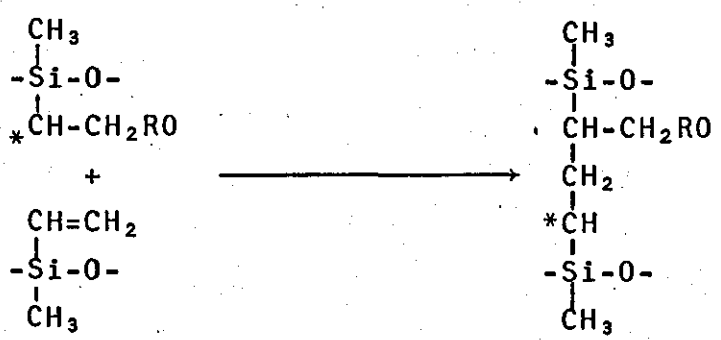
1.12

For an efficient use of peroxide (of structure ROOR) in crosslinking, the reaction(equation 1.12) must occur to only a small extent.

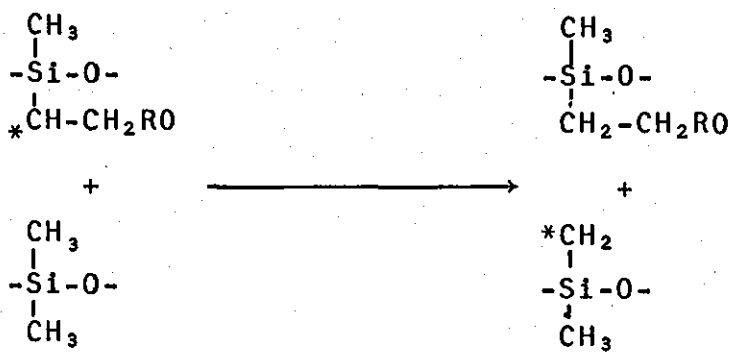
In case of reaction (equation 1.10), the polymeric radicals formed may then crosslink by pairwise combination (equation 1.13), addition to further vinyl groups (equation 1.14), hydrogen abstraction (equation 1.15), or a chain reaction (equation 1.16):



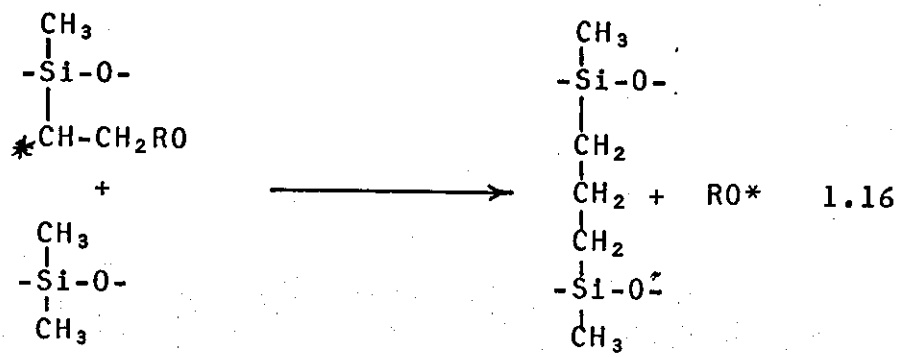
1.13



1.14



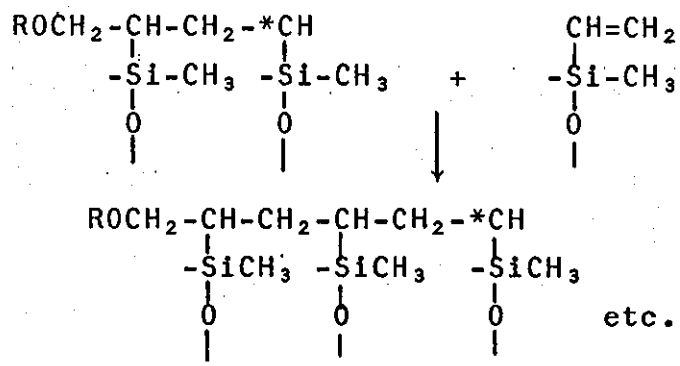
1.15



1.16

Scheme (equation) 1.13 requires the reaction of two vinyl groups for each crosslink unless the addition step occurs in which case at least at the extreme limit only one vinyl group is required.

Scheme (equation) 1.14 appears to be favoured in a continuous chain addition (equation 1.17):



1.17

However, with the observed crosslinking efficiency of $\leqslant 1.0$ [55] at realistic peroxide concentrations, a chain addition can probably be discounted. Also this scheme requires continuous vinyl group addition which is impossible in the presence of predominant dimethyl groups in the chain with relatively few vinyl groups present.

For scheme (equation) 1.16 to apply, a substantial concentration of vinyl groups is needed, otherwise the higher crosslinking demanded is impossible to achieve.

Hence for a realistic efficient crosslinking reaction equation 1.13 is favoured.

1.3.3.2.1.2 CLASSES OF PEROXIDES[154]

Different peroxides are used to vulcanise silicone elastomers. They differ both in their reactivity towards organic radicals substituted on the polymer chain and also their decomposition products.

Structural differences which affect peroxide activities are related to three main factors:

a. the relative stability of radicals formed *i.e* the more stable the radicals formed, the less stable is the peroxide molecule.

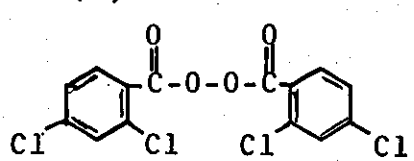
b. steric factors: *i.e* the more highly strained peroxides will be less stable since decomposition relieves steric strain.

c. electronic effects where electron donating functions *e.g* CH_3-, CH_3O- *etc.* destabilize and electron withdrawing functions *e.g* CF_3, NO_2, F, Cl *etc*, stabilize peroxides.

These peroxides suitable for vulcanisation silicone rubbers can be divided into three main classes: diacyl, peroxyesters and dialkyl peroxides:

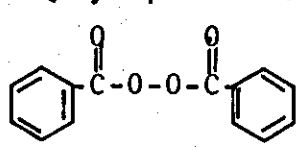
1. Diacyl Peroxides

a. Bis(2,4-dichlorobenzoyl)peroxide.



54°C

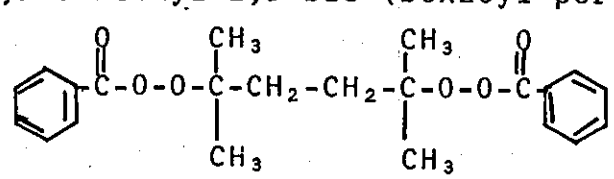
b. Dibenzoyl peroxide.



73°C

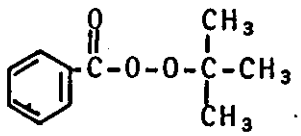
2. Peroxyesters

a. 2,5-dimethyl-2,5-bis (benzoyl peroxy) hexane



100°C

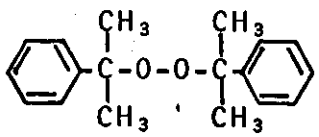
b. Tertiary butyl perbenzoate



105°C

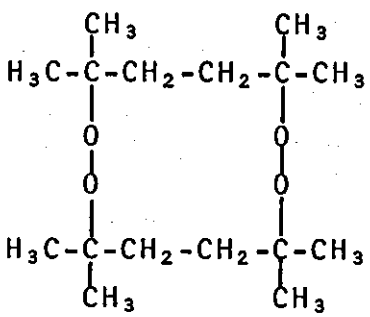
3. Dialkyl Peroxides

a. Dicumyl peroxide



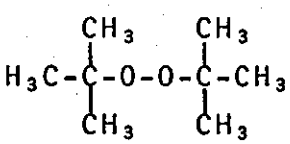
115°C

b. 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane



119°C

c. Di-t-butyl peroxide



126°C

**Figures in ☐ represent the temperature at which the peroxide is 50% decomposed in 10hrs i.e TEN-HOUR HALF LIFE ($t_{\frac{1}{2}}$) TEMPERATURES.*

Diacyl peroxides [155] and peroxyesters [156,157] are all sufficiently reactive to react with both methyl and vinyl groups, but their decomposition products, which include organic acids, are detrimental to the elastomer. While the dialkyl peroxides [156] are 'vinyl-specific' peroxides and are more selective in their reactivities, they do not decompose to form organic acids but tend to form ketones which are less detrimental and easy to remove. They were also claimed to be effective as curatives for carbon black filled silicone

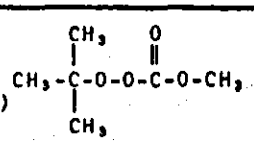
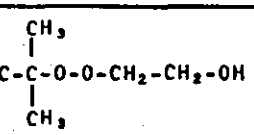
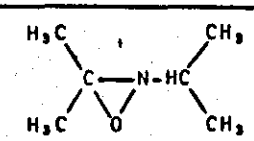
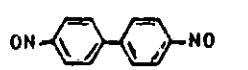
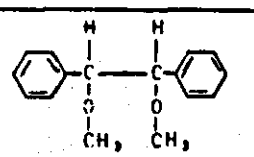
rubbers, though in increased quantities [156]. Acidic carbon blacks CANNOT be used in conjunction with peroxide cures.[110]

1.3.3.2.1.3 NEW FREE RADICAL INITIATORS (Table 1.9)

Free radical initiators newly introduced to silicone rubber vulcanisation include:

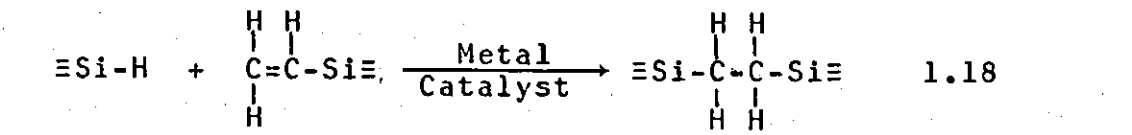
1. t-alkyl peroxyalkyl carbonates [158,159]
2. t-butyl-2-hydroxyethyl peroxide [152,160]
3. oxaziridines [161]
4. dinitroso aromatic compounds [162]
5. 1,2-diphenyl-1,2-dimethoxy ethane [163]

TABLE 1.9 NEW FREE RADICAL INITIATORS

NAME	CHEMICAL STRUCTURE	FUNCTIONS
t-alkyl peroxyalkyl carbonates (e.g t-butyl peroxymethyl carbonate)		This is a very effective initiator both at vulcanisation temperatures higher and lower than those required for the commonly used dicumyl peroxide. It requires no anaerobic conditions or confinement under pressure to effect good end product Its moulded products have superior toughness, heat stability and compression set.
t-butyl-2-hydroxyethyl peroxide		This gives higher rates and degrees of cure in polydimethylsiloxane filled with 'aerosil' than di-t-butyl peroxide. It also gives silicone elastomers with relatively higher elongation at break.
oxaziridines (e.g dimethyl-N-isopropyl-oxaziridine)		This gives storage-stable compositions that cures above 125°C. Its product gives higher elongation at break and tear strengths than similar compositions cured with conventional peroxides.
dinitroso aromatic compounds (e.g p-nitroso benzene)		Dinitroso aromatic compounds are claimed to be effective in heat activated cures
1,2-diphenyl-1,2-methoxy ethane		This initiates cures at higher than normal temperatures without premature cure.

1.3.3.2.2. *Hydrosilation*

Crosslinking can also be achieved by a hydrosilation reaction (equation 1.18) whereby a polyfunctional silicone hydride (Si-H) will add on to an unsaturated (vinyl) group in a polydimethylsiloxane chain in the presence of a metal catalyst.



1.18

Metal carbonyls (*e.g* Dicobalt octacarbonyl)[164], soluble platinum complexes (*e.g* Chloroplatinic acid)[222] with vinyl silanes[165] and alkyl titanates[166] are more common effective catalysts. These give a high degree of crosslinking either at room or elevated temperature, relatively free of side reactions and volatiles. Hence, these have been used as a model system in studies of effects of crosslink placements,[167] in cure kinetics[168-170] and confirmation of theories in network topology.[171]

1.3.3.2.3 *Radiation induced cures*

High energy γ-radiation sources (*e.g* Cobalt-60) have received attention as a useful method of crosslinking silicone rubber (polydimethylsiloxane). Extruded silica-filled formulations[172] and even carbon black filled formulations[173] were reported to exhibit better mechanical and heat ageing properties when cured with Cobalt-60 than with dicumyl peroxide. Crosslinking was suggested to proceed principally *via* free radicals,[174] but, unlike peroxides, radicals are directly formed on the polymer during the irradiation process and by the fracture of the Si-C and C-H bonds.[175] The crosslink density of the polymer is determined by radiation dose and no further reaction takes place once the radiation has ceased. Usually very pure, highly homogenous, clearer and better product results as there exists no catalyst or reaction residues from the vulcanisates. Hence, it is useful for optical or ultrasonic experiments.

Other methods useful to crosslink silicone rubbers are Ultra Violet (U.V) light, and microwaves.[176,177]

1.4 CONDUCTIVE SILICONE RUBBERS

Like other elastomers, conductive silicone rubbers have been employed in various fields both as antistatic and conductive products.

In heating applications, conductive polymers are used as heating elements possessing inherent flexibility, a non-localised heat source, lower maximum temperature for a given heat output, and simpler fabrication. But coupled with these are the disadvantages of: lack of performance reproducibility, negative electrical conductivity changes with temperature, increase in resistivity on flexing, and difficulty of making reliable contacts with the conductive rubber.

It is difficult from the data available to assess the importance of these materials as a source of heat. In most cases, if patents relating to a particular use are followed by any further information, this takes the form of either obvious, transient or subtle advertising matter. This suggests that most of the proposed uses rapidly fall short of expectation, showing lack of initial resistivity control and the change in resistivity during flexing.

However, in recent years, it has been shown that some silicone rubbers loaded with conductive carbon black are not significantly affected by or sensitive to mixing conditions during processing,[6] or to strain of the vulcanisate.[7] These appear suitable for some heating applications.

Conductive silicone rubber has received considerable attention and claims[178] made on its behalf are:

a. its stable current-time characteristics
b. controlled thermal coefficients of resistivity
c. higher thermal limits
d. capability of being fabricated by the conventional techniques.

A typical formulation consists of silica for reinforcement, an appropriate level of acetylene black to impart conductivity, and the usual peroxide additives for cure.[179-181] Resistivity was reported to increase when semi-conductive formulations were strained to 17-18% elongation. However, at further higher strains resistivity then started to decrease and eventually at 90% elongation reached that of the unstrained material. Lighter crosslinking tended to give greater changes in resistivity when samples were strained.[182]

Composite systems based on silver or nickel have been described,[183-185] whose electrical characteristics change with composition and applied compressive force.

Many patents concerned with making silicone rubber conductive for a variety of purposes have been issued.[186-197] Encapsulation of electronic devices was the aim of some.[198] Flexible silicone rubber magnets were prepared by incorporating ferric oxide in di-alkyldisilanols and heating to produce rubber. Graphite-filled silicone rubber electrodes have been used as a titration ion-selective electrode[199-202] to measure flow rate as well as concentration,[203,205] drug determinations in organic solvents and in blood-living organisms.[204,206]

Conductive silicone rubber sealant has been used to provide radio frequency and microwave shielding for electronic systems,[207] on seals, rolls and gaskets to dissipate electrostatic charges,[208] as a replacement for a calculator metal contact circuit keyboards,[209] to reduce dendritic growth and galvanic corrosion by encapsulating metallized circuits with conductive silicone rubber, to provide interference suppression in motor car ignition leads, for the electrical stress relief in cable terminations and splice housings[219]. It is also used as a ribbon conductor (consisting of a moulded-together strips of insulating and conductive silicone rubbers) in 'zebra' connector for printed circuits,[220] in switching applications (where resistance varies reproducibly with stress). Conductive

silicone rubbers have also been used as contact pads in some commercial keyboard switches for calculators and other similar products. The resiliency of the rubber causes the pushbutton to move away without causing contact bounce.[221]

Heating applications also included heating pads in aircraft cameras,[7] clothing and underfloor heating,[210] fabrics coated with conductive silicone rubber as heating elements,[211] glass fabric strips coated with conductive silicone rubber for ceiling heating,[212] vulcanising rubber valve bases to inner tubes.[213]

Base metals coated with silver (possibly with an internal coat of gold to prevent silver migration) have been incorporated in silicone rubber to produce very highly conductive materials with a volume resistivity less than 1 ohm-cm.[214] Also flakes of silver, nickel, zinc or stainless steel have been employed.[215]

A widely advertised and evaluated conductive silicone rubber is Silastic* Q4-1602.[156] This is a flame resistant and electrically conductive silicone rubber extensively used in producing heating tapes. This is usually cured with a platinum catalyst Q4-1602B, although other peroxides *e.g* 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane and dicumyl peroxide are also recommended. It is claimed to have a volume resistivity of 2.50 ohm-cm.

Products from the above example suffer some setbacks in reproducibility and lack of maintaining constant resistivity when flexed or used above certain voltage levels. Thomas French and Sons (Cables) Ltd.,CORBY,[216] manufacturers of conductive heating tapes and using Dow Corning silicone rubber, Silastic Q4-1602 compounds, has experienced development problems of: scorching during processing and short compound life; irreproducibility and inconsistency in maintaining constant resistivity when their products are flexed or used above 250volts; their products having a non-constant self-limiting effect *i.e* the productcheating effect varies over a wide range of voltage (50-250V)

**Silastic is a trade name of Dow Corning Ltd for silicone rubbers*

disproportionately. In addition, other development work on conductive silicone rubber undertaken on behalf of Thomas French by Siltech of Cowbridge, Glamorgan [217] revealed that when carbon black was used as a conducting filler in silicone rubber, it interfered with cure to such an extent to be impractical for the industrial use.

The above is a known example challenging the claimed less variability in resistivity due to processing and insensitivity to strain when flexed in carbon black filled conductive silicone rubber.[6,7]

1.5 OBJECTIVES OF THE RESEARCH

Conductive compounds developed and used in the previously identified examples fell short of acclaimed less variability in resistivity due to processing and insensitivity to strain when flexed in carbon black filled silicone rubbers.

The objectives of this research, therefore, are:

1. to carry out a detailed investigation of the variables which affects electrical property reproducibility, and
2. to develop an understanding of the compounding factors which control electrical conductivity in carbon black filled silicone rubber.

II MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 MATERIALS

The major materials used in this research work are as outlined in tables 2.1, 2.2 and 2.3 below:

TABLE 2.1 CURING AGENTS AND MISCELLANEOUS

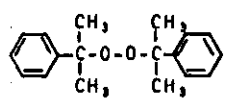
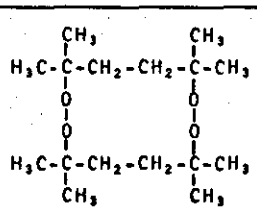
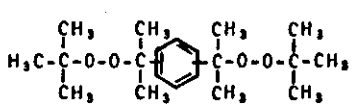
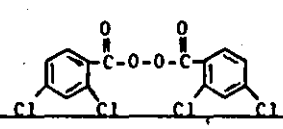
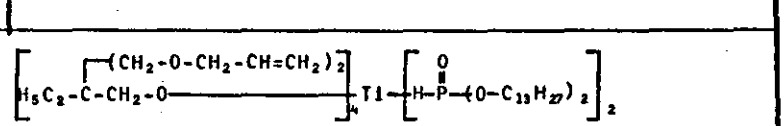
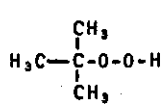
NAME (Supplier)	DESCRIPTION
Dicumyl Peroxide: Perkadox SB (Akzo Chemie)	 95% active; S.G=1.018 Molecular Weight =270 Vulcanising Temp.=150°C+ =16.50g contain 0.01g mole of peroxide group.
2,5-dimethyl-2,5-di(t-butyl peroxy) hexane: Varox (R T Vanderbilt)	 50% active; S.G=1.50±0.3 Molecular Weight =290.45 Vulcanising Temp.=150°C+ =2.90g contain 0.01g mole of peroxide group.
a,a'-bis (t-butyl peroxy) di-isopropyl benzene: Vulcup 14R (Hercules Powder Co. Ltd)	 100% active; S.G=1.030 Molecular Weight=338 It contains a mixture of meta and para isomers in the ratio 1.5:1 to 2:1
2,4-dichlorobenzoyl peroxide: Perkadox PDS 50 (Akzo Chemie)	 50% active; Vulcanising Temp Vulcanising Temperature 116°C
Q4-1602 Catalyst B (Dow Corning Ltd)	a platinum-based cure catalyst for Silatic Q4-1602
Alkyl titanate KR-55 (Hubron Sales Ltd)	 tetra(2,2-diallyloxymethyl-1-butoxy)-titanium-di(ditridecyl)phosphite
Chloroplatinic Acid (Aldrich Chem. Co. Ltd)	$H_2PtCl_6.4H_2O$ Hydrogen hexachloroplatinate (IV) hydrate
Tertiary butyl hydroperoxide (Kochlight Lab. Ltd)	 70% solution in water. The hydroperoxide was extracted by petroleum ether 30/40°C in a seperating funnel. Petroleum ether was removed under reduced pressure and the hydroperoxide obtained was dried with anhydrous Magnesium Sulphate ($MgSO_4$)
Silane Z-6082 (K & K Greef Chem. Ltd)	$[H_3CO(CH_2)_2O]_3SiCH{=}CH_2$ Vinyl tris(β-Methoxyethoxy)silane

TABLE 2.2 SILICONE POLYMERS

NAME (Supplier)	DESCRIPTION
Silastic GP 30 (Dow Corning Ltd.)	Poly dimethyl siloxane: S.G. 1.09 (at 25°C), Vinyl groups attached, 19% fumed silica and 32 IRHD.
Silastic GP 45 (Dow Corning Ltd.)	Poly dimethyl siloxane: S.G. 1.10 (at 25°C). Vinyl groups attached, 24% fumed silica and 42 IRHD.
Silastic Q4-1602 Compound (Dow Corning Ltd.)	Electrically conductive, carbon black filled, flame-resistant silicone compound. 2.5 ohm-cm volume resistivity attainable when HAV cured with Catalyst B.
Siltech 17 (Siltech Ltd.)	Poly dimethyl siloxane: Vinyl groups attached, 42% silica content, 64 IRHD.
Polymer 1 (Dow Corning Ltd.)	2,000 - 2,500 cps
Polymer 12 (Dow Corning Ltd.)	3,000 - 5,000 cps
	$HO\left[\begin{matrix}CH_3\\ \\ Si-O\\ \\ CH_3\end{matrix}\right]_n\begin{matrix}CH_3\\ \\ Si-OH\\ \\ CH_3\end{matrix}$ Hydroxyl-terminated Polydimethyl-siloxanes
Compound A (Dow Corning Ltd.)	$H_3C-\begin{matrix}CH_3\\ \\ Si\\ \\ CH_3\end{matrix}\left[\begin{matrix}H\\ \\ O-Si\\ \\ CH_3\end{matrix}\right]_{14}O-\begin{matrix}CH_3\\ \\ Si-CH_3\\ \\ CH_3\end{matrix}$
Compound B (Dow Corning Ltd.)	$H_3C-\begin{matrix}CH_3\\ \\ Si\\ \\ CH_3\end{matrix}\left[\begin{matrix}H\\ \\ O-Si\\ \\ CH_3\end{matrix}\right]_2O-\begin{matrix}CH_3\\ \\ Si\\ \\ CH_3\end{matrix}\left[\begin{matrix}H\\ \\ O-Si\\ \\ CH_3\end{matrix}\right]_3O-\begin{matrix}CH_3\\ \\ Si-CH_3\\ \\ CH_3\end{matrix}$ Hydrogen containing Polydimethyl-siloxanes
Polymer 26 (Dow Corning Ltd.)	$H_2C=CH-\begin{matrix}CH_3\\ \\ Si\\ \\ CH_3\end{matrix}\left[\begin{matrix}CH_3\\ \\ O-Si\\ \\ CH_3\end{matrix}\right]_nO-\begin{matrix}CH_3\\ \\ Si-CH=CH_2\\ \\ CH_3\end{matrix}$ Dimethyl vinyl-endblocked polydimethylsiloxane 4.2gms William Plasticity 55-65
Polymer 11 Dow Corning Ltd.)	$H_2C=CH-\begin{matrix}CH_3\\ \\ Si\\ \\ CH_3\end{matrix}\left[\begin{matrix}CH=CH_2\\ \\ O-Si\\ \\ CH_3\end{matrix}\right]_nO\left[\begin{matrix}CH_3\\ \\ Si-O\\ \\ CH_3\end{matrix}\right]_y\begin{matrix}CH_3\\ \\ Si-CH=CH_2\\ \\ CH_3\end{matrix}$ Dimethyl vinyl-endblocked vinyl containing poly-dimethyl siloxane 4.2gms William Plasticity 55-65

TABLE 2.3 ANALYTICAL PROPERTIES OF HIGHLY CONDUCTIVE CARBON BLACKS

Brand	DBP absorption (ml/100g)	Surface Area (m^2g^{-1})				Particle size (nm)	Volatile content (%)	pH		Density (gl^{-1})		Ash content (%)	Moisture pick-up (%)
		BET	EM	CTAB	BET*			Lit	Mes	Helium	Bulk		
Shawinigan[227,228]	145	64.5	70.0	-	65.8	42.0±2.5	0.06	5.0	5.5	1.95	90	0.04	-
Vulcan P[229,231]	116	149	-	115	158	20	1.50	8.5	8.5	-	340	0.15	1.89
Vulcan PF[229,231]	116	149	-	115	157	20	0.94	8.5	8.6	-	220	0.15	1.80
Vulcan XC72[224,229,231]	178	254	111	134	260	30	1.50	5.0	5.0	-	264	-	3.86
Vulcan XC72R[229,231]	185	254	110	134	262	30	0.80	8.5	7.5	-	99	-	3.90
Conductex 900[226]	120	125	-	-	128	25	0.20	6.2	6.2	-	110	0.46	1.55
Conductex SC[225,226,232]	140	240	-	-	242	30	0.80	8.5	8.5	-	180	0.20	4.93
Conductex 975[226]	165	250	110	153	274	30	1.00	7.0	7.0	-	-	0.05	3.85
Ketjenblack EC[2,230]	340	1,000	108	-	1,003	30	1.00	9.5	9.5	2.05	150	0.50	7.58
Philblack XE2[230]	400	1,000	-	620	1,010	-	-	6.0	6.6	-	-	-	-
Conductex 40-220[226]	228	1,075	-	510	1,030	18	1.60	5.1	5.4	-	142	0.45	12.26

N.B. BET=Brunauer, Emmett and Teller N_2 Absorption Method; EM=Electron Microscope Method; CTAB=Cetyltrimethylammonium Absorption Method; BET*=BET N_2 Method carried out by the researcher (Section 2.2.6); Lit=Literature figures; Mes=pH measurement (Section 2.2.5).

2.2 EXPERIMENTAL TECHNIQUES

2.2.1 PROCESSING (MILLING)

2.2.1.1 Apparatus

Laboratory 2-roll mill (300mm X 150mm)
Nylon Scraper

2.2.1.2 Procedure

The standard milling procedure established was as follows: Small batches of each mix formulation were prepared using a water-cooled, chilled, small (300mm X 150mm) laboratory 2-roll mill. Owing to silicone being soft, effective and rapid mixing can only be achieved for all mixings by efficient roll cooling, and using a nip with constant mobile bank, and high roll speed. Use of a high friction ratio speed ratio of 1.4:1.0 (front:back) was maintained throughout since silicone bonds on a faster roll during milling. A nylon roll scraper was used for cross blending, and which, unlike metal roll scraper, does not impart metal-metal wear particles into the mix, readily assumes the rolls contour and is safer, as no sparks are produced by metal to nylon contact.

2.2.2 CURE CHARACTERIZATION

2.2.2.1 Apparatus

Oscillating Disc Monsanto Rheometer.

2.2.2.2 Basic Principles

Monsanto ODR TM100 consists of a die cavity located in a large electrically heated platens as shown in fig. 2.1.

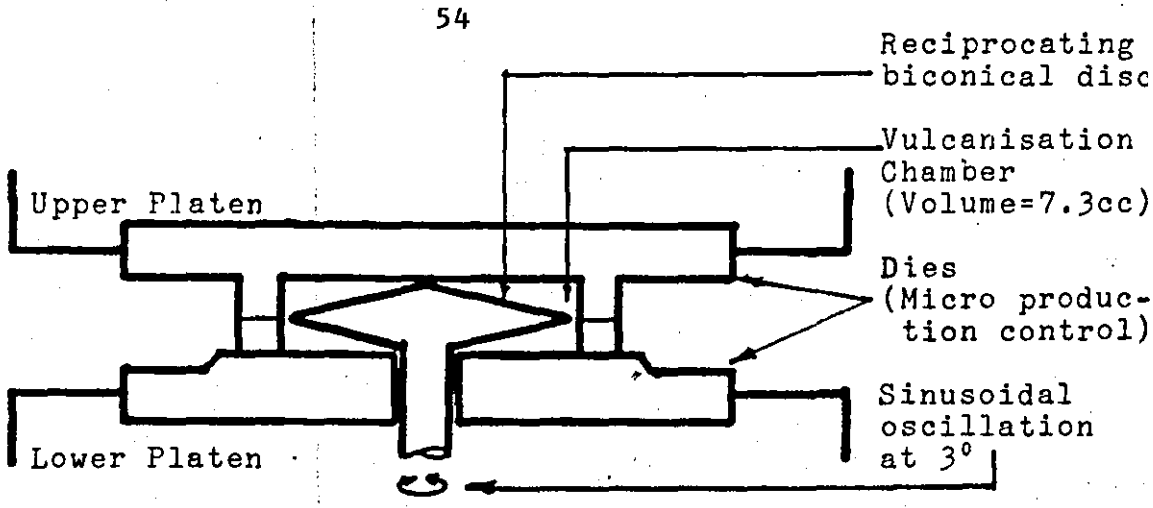


Fig. 2.1 Basic principles of Monsanto ODR.

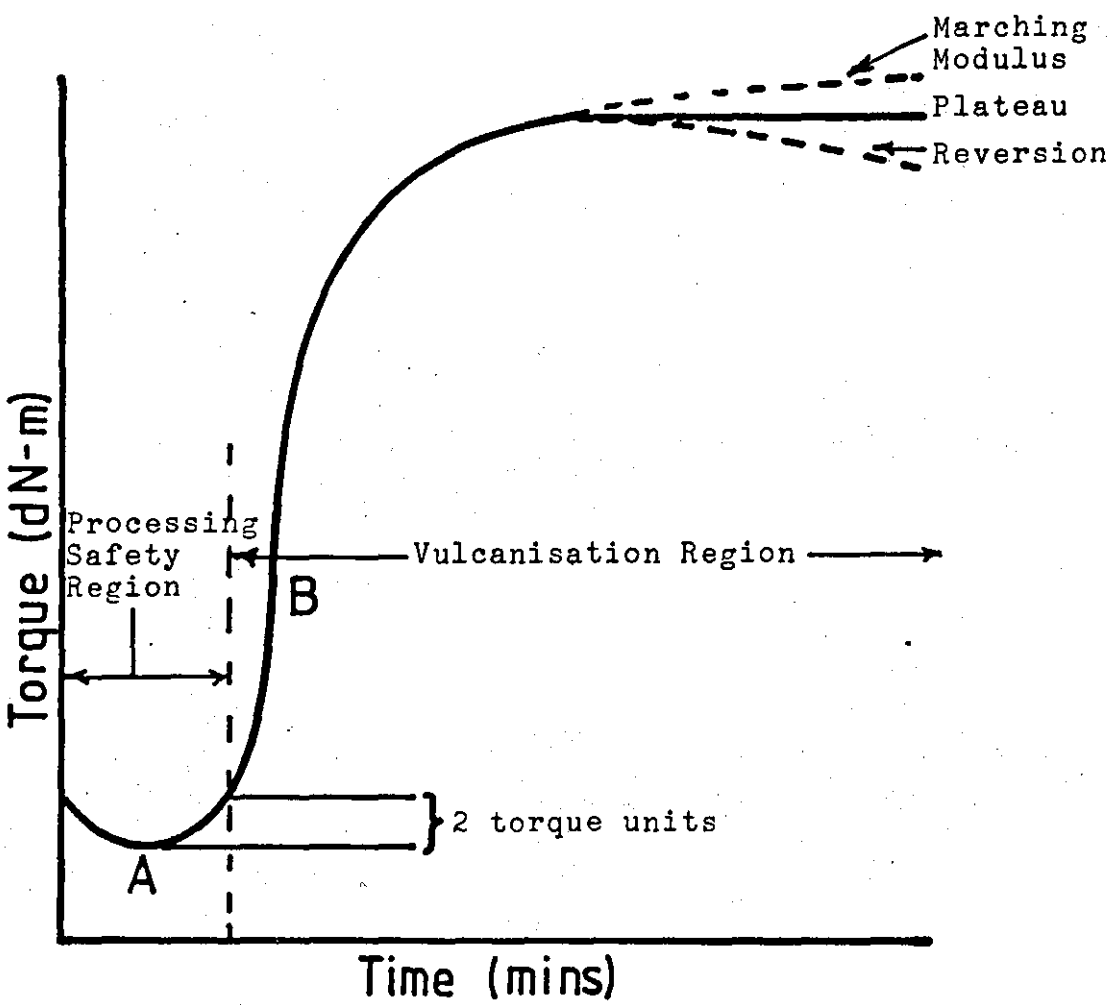


Fig. 2.2 Rubber vulcanisation features as measured by ODR.

The temperatures of the platens and dies are maintained to within ±0.5°C by proportional temperature controllers. A mix is placed within the vulcanisation 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 vulcanisation proceeds, the torque required to shear the mix increases and a curve of torque versus cure time is generated. The torque value is directly related to the shear modulus of the mix.

A typical torque-time curve produced is as shown in fig. 2.2. The initial decrease in the viscosity of the mix occurs (A) due to the increasing rubber temperature. This then troughs until the onset of crosslinking producing a sharp rise in viscosity (B), and, therefore, in the torque exerted by the oscillating rotor embedded in the specimen. This torque increases until the crosslinking is complete. The cure may then either show a decrease in torque with time if chain scission takes place on extended heating (reversion), <u>or</u> remain steady in a plateau form (non reversion and constant properties maintained at extended heating), <u>or</u> have a continual increase if a slow crosslinking reaction takes place (marching modulus).

2.2.2.3 <u>Experimental</u>

The temperature of the platens and dies was maintained at the required cure temperature and the biconical disc was kept in the engaged or driven position. A mix of 9g. was placed within the vulcanisation chamber and the high pressure was applied so that the biconical disc was embedded in the mix. The motor which oscillates the disc was immediately switched on and the characteristic cure trace was recorded on the chart.

2.2.2.4 Evaluation of cure rates and cure times from the Kinetic interpretation of the ODR Rheographs.

2.2.2.4.1 *Theory* (fig. 2.3)

Assuming that the crosslink formation is a first order reaction after an induction period of t_1

then $$\frac{dv}{dt} = k(V_\infty - V_t) \qquad 2.1$$

where k = overall first order rate constant
V_t = crosslink density at time, t
V_∞ = maximum crosslink density
t = time (mins)
t_1 = the induction time (mins)

on integration:

$$\int_{V_0}^{V_t} \frac{dv}{V_\infty - V_t} = k\int_{t_1}^{t} dt \qquad 2.2$$

therefore $$\ln\left[(V_\infty - V_t)\right]_{V_0}^{V_t} = k\left[t\right]_{t_1}^{t} \qquad 2.3$$

therefore $$\ln\frac{V_\infty - V_t}{V_\infty - V_0} = k(t - t_1) \qquad 2.4$$

Since $V_t \propto R_t$

where R_t = the developed torque at time, t

therefore

$$V_t = kR_t \qquad 2.5$$

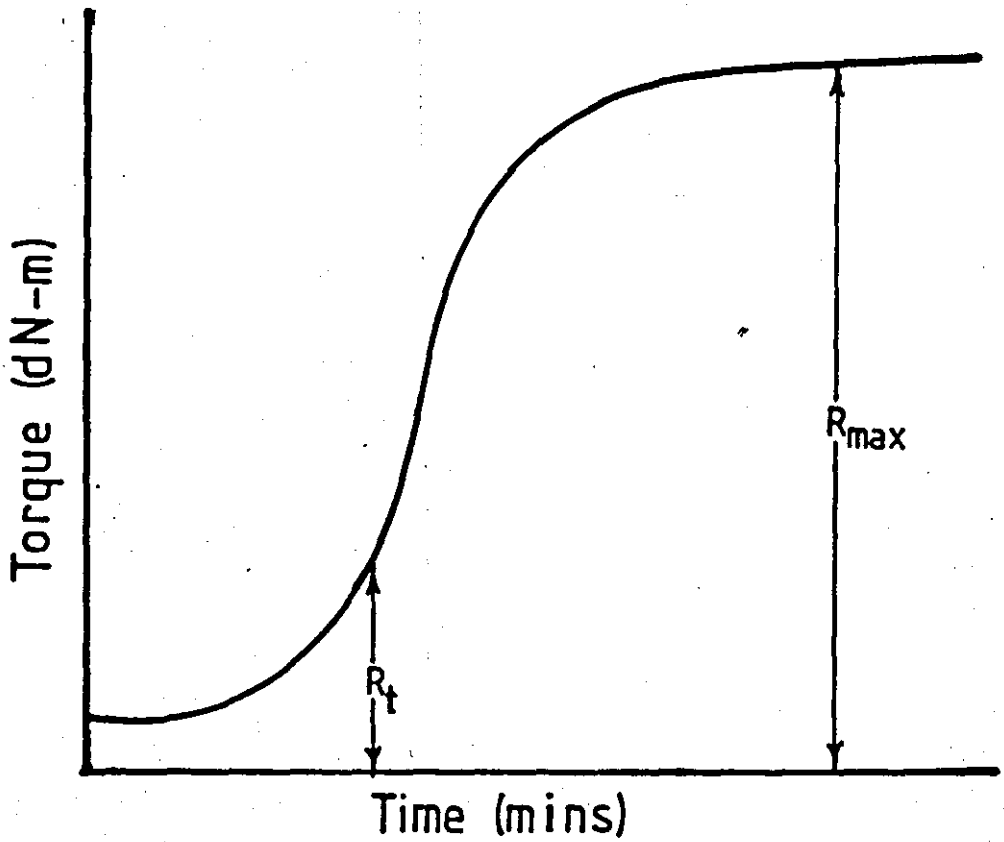


Fig. 2.3 A typical ODR graph showing defined points on the time axis for theoretical cure time calculation.

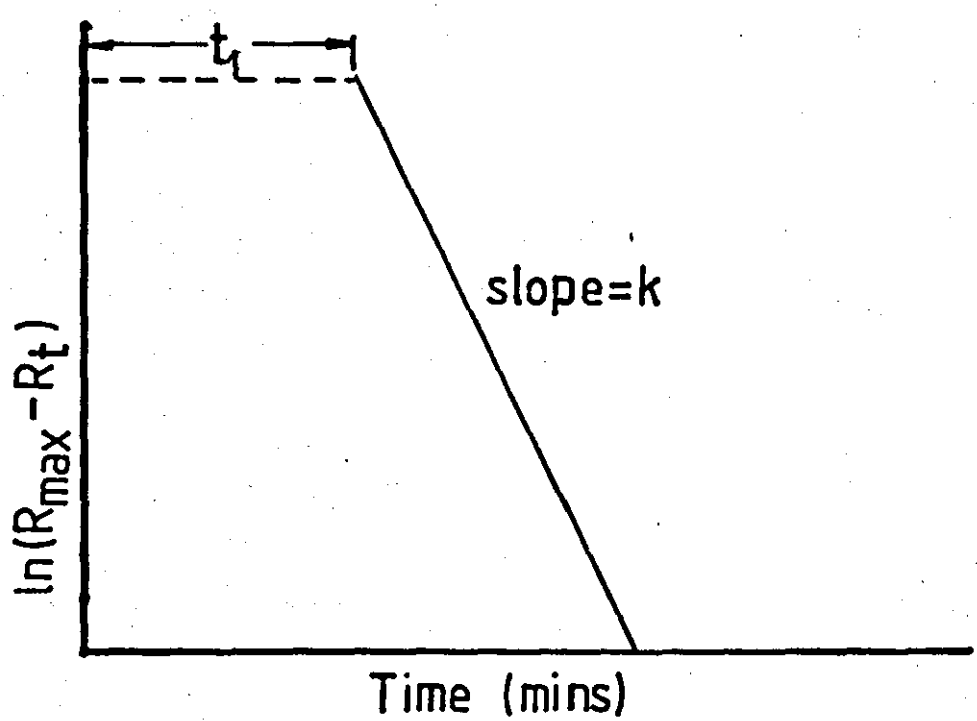


Fig. 2.4 $\ln(R_{max}-R_t)$ vs. time graph to calculate the theoretical cure rate and cure time.

similarly

$$V_\infty \propto R_{max}$$

therefore

$$V_\infty = kR_{max} \qquad 2.6$$

where R_{max} = maximum torque developed and this is taken as a direct reading from the rheograph.

By substituting the values in equation 2.4

$$\ln\left[\frac{R_{max}-R_t}{R_{max}}\right] = k(t-t_1) \qquad 2.7$$

therefore

$$\ln(R_{max}-R_t) = \ln R_{max} + k(t-t_1) \qquad 2.8$$

R_t and R_{max} can be read directly from the rheographs (fig. 2.3)

To obtain the cure rate, k, value of $\ln(R_{max}-R_t)$ can be plotted against time in minutes (fig. 2.4).
From the graph, the slope is equivalent to the cure rate, k, and this can be measured.

Therefore

k = slope (min^{-1}) cure rate

t_1 = the time necessary for the reaction to become the first order.

Each rheograph obtained was analysed to obtain the cure rates and times for each mix. A typical example of the kinetic analysis of a rheograph is as shown in figs. 2.5 and 2.6 and also table 2.4.

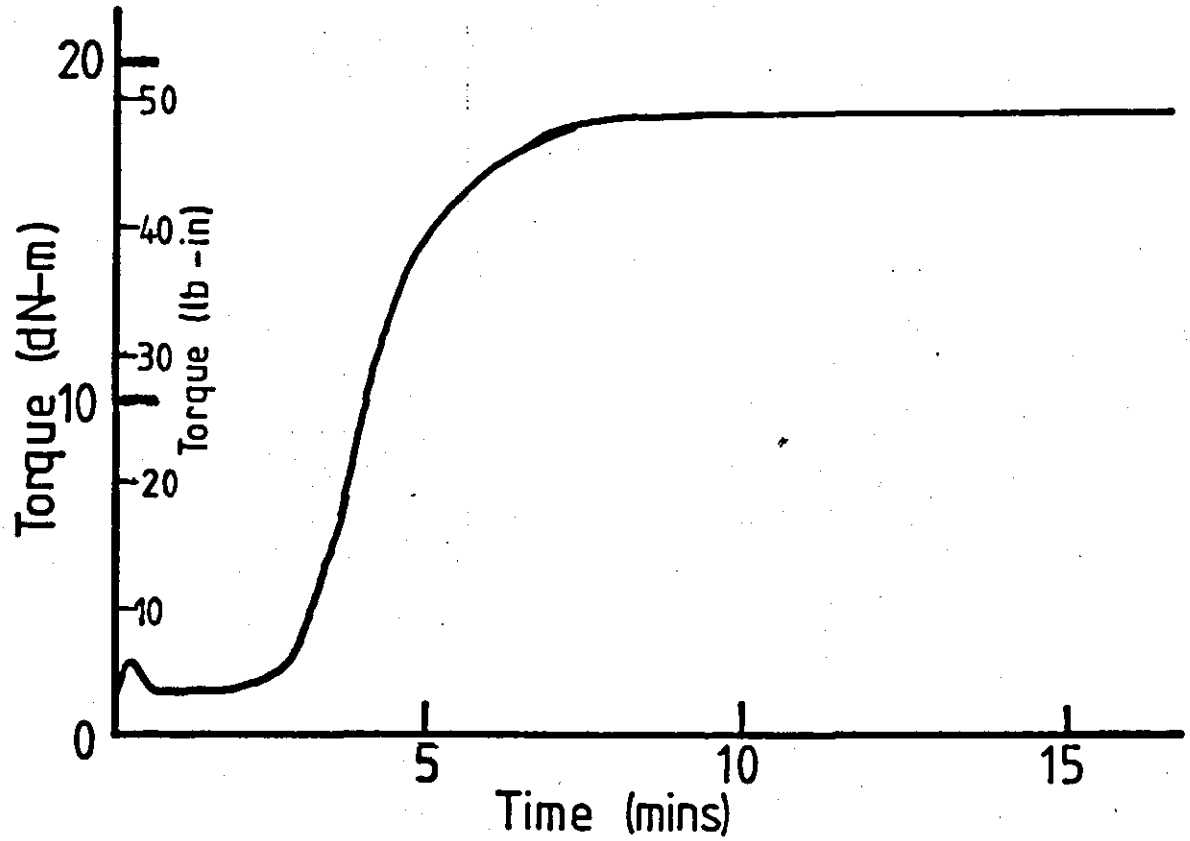


Fig. 2.5 Curing characteristics of Dicumyl Peroxide cured Silastic Q4-1602 compound at 170°C

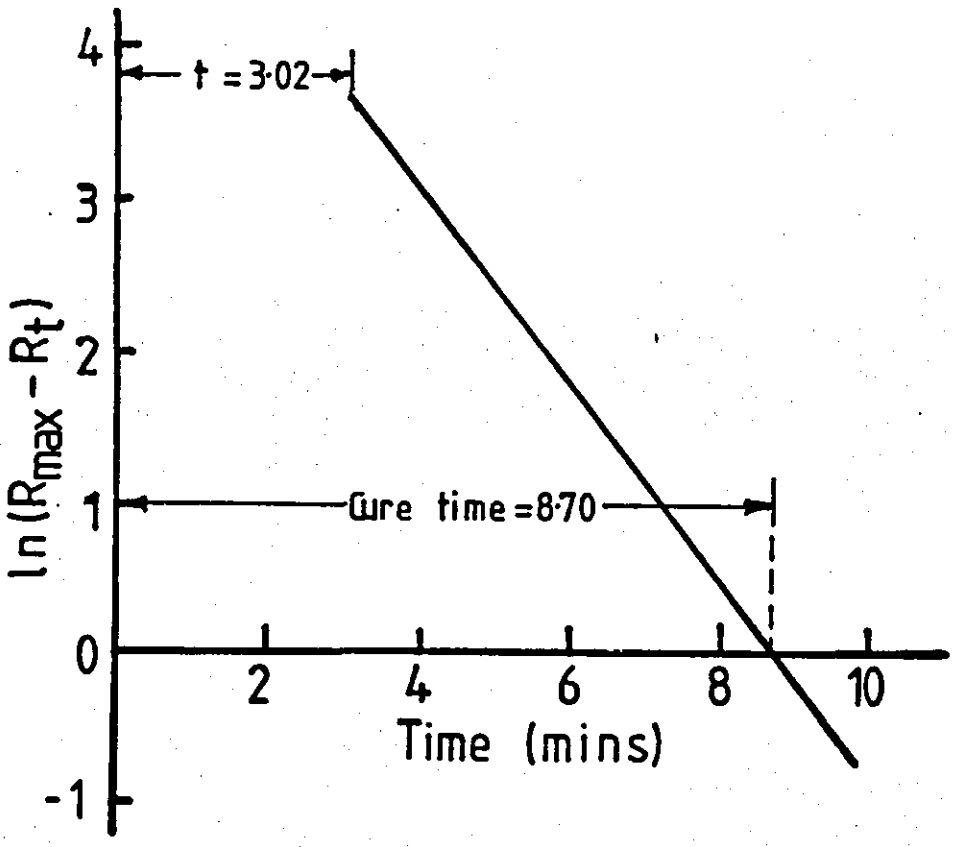


Fig. 2.6 Cure rate characterisation of Dicumyl Peroxide cured Silastic Q4-1602 compound at 170°C

TABLE 2.4 KINETIC ANALYSIS OF RHEOGRAPHS FOR DICUMYL PEROXIDE CURED SILASTIC Q4-1602 COMPOUND.

t (mins)	3.0	3.5	4.0	5.0	6.0	8.0	10.0
R_t	8.00	18.00	28.00	40.00	44.50	47.00	48.00
$R_{max} - R_t$	40.00	30.00	19.50	8.00	3.50	0.50	--
$\ln(R_{max} - R_t)$	3.69	3.40	2.97	2.08	1.25	-0.69	-

R_{max} from the Rheograph = 48.00units

From the graph $\ln(R_{max} - R_t)$ versus time, cure time = 8.70 mins

$k = 0.86\ min^{-1}$

$t_1 = 3.02$ mins.

2.2.3 VULCANISATION

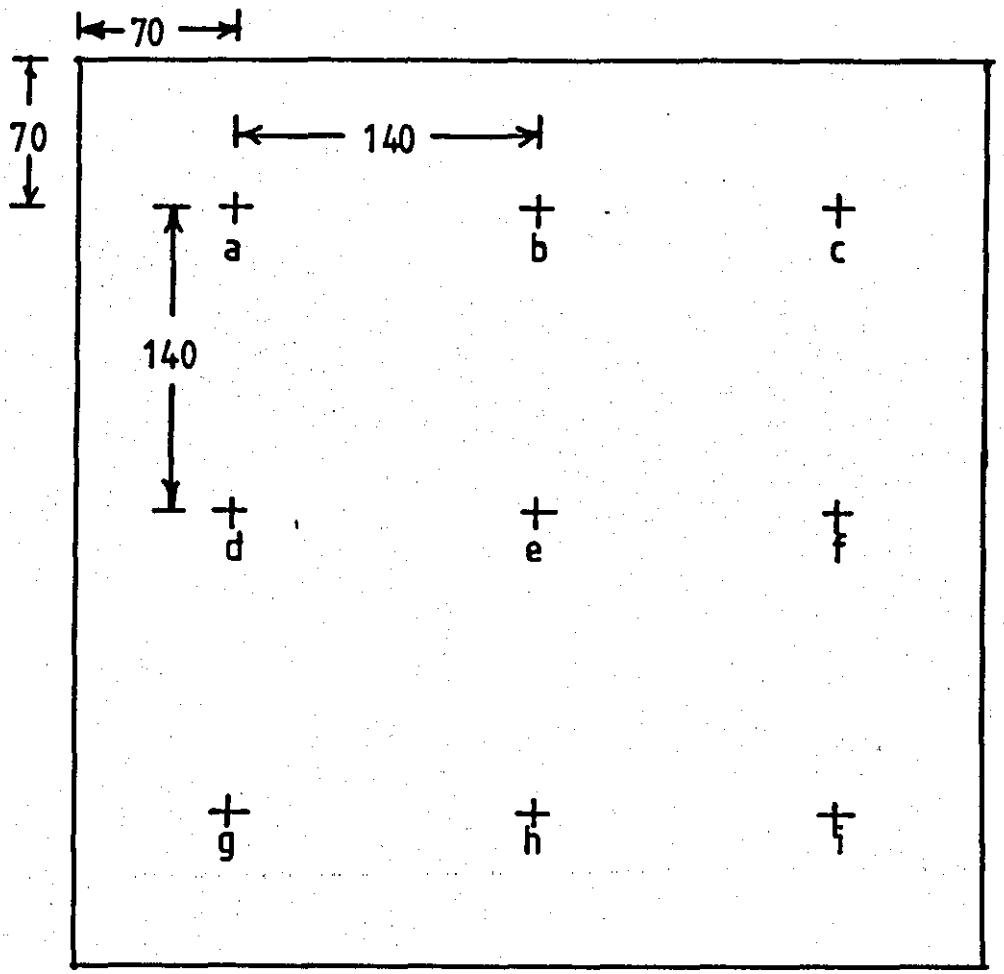
All mouldings were carried out using a single daylight press with electrically heated platens set at the required cure temperature (usually 170°C).

Prior to any moulding exercise, the moulds together with their top and bottom plates were always prewarmed at moulding temperature under pressure for at least 30 mins. The press platen was also checked, and/or calibrated to the correct temperature uniformity in accordance with BS 1674: 1976 Appendix C [234] (fig. 2.7 and Table 2.5).

2.2.3.1 Test pieces

These were moulded rectangular plaques 70mm X 60mm X2.0mm. Milled compounds are carefully sheeted out to be uniform and calculated thickness; such that rectangular blanks were cut out in size to exactly fit the mould cavity and of reproducible weight. This procedure was performed to minimise mould flow which was known to affect the electrical resistivity of the vulcanisate.

It was found by experiment best to mould the rubber test pieces between two sheets of polyester films 'melinex'. This technique allow the test specimen to be easily removed without strain. The melinex was then usually left on the test piece and only removed immediately prior to testing. By this means the test piece surfaces were kept clean and actually giving better electrode contact and thus minimising contact resistance, probably known to be a major obstacle in obtaining accurate and/or reproducible measurement of the volume resistivity of conductive rubbers. The cure times obtained from the Kinetic Analysis of each of the rheographs of the Monsanto (ODR) Rheometer were used.



* All dimensions in mm

Fig.2.7 Check points for Temperature Uniformity calibration of Press Platen.

TABLE 2.5 MEASUREMENT OF PRESS PLATEN TEMPERATURE UNIFORMITY

SET TEMP °C	PLATEN	AVERAGE TEMP. READINGS(°C)								
		a	b	c	d	e	f	g	h	i
170	UPPER	162	162	163	164	165	165	163	164	163
170	LOWER	161	162	162	163	164	164	164	163	162
175	UPPER	170	169	169	170	171	170	170	169	169
175	LOWER	168	168	167	168	168	168	167	168	167
175	UPPER	170	170	170	170	171	170	170	169	169
177	LOWER	170	169	169	170	170	170	170	169	170

*Measuring Instrument: Comark Temperature Testing Device

*The temperature control gauges were, therefore, set on 175°C for the upper platen and 177°C for the lower platen for the average uniform vulcanisation temp. of 170°C

2.2.4 ELECTRICAL (VOLUME) RESISTIVITY MEASUREMENT AND EQUIPMENTS

In assessing the conductive nature of materials the most important property to be measured is their resistance in ohms. Suitable equipment for the measurement of resistance depends on the magnitude of the resistance to be measured. Quick and convenient methods include the use of the Ohmmeter, the Digital Multimeter and the Four Point Probe for the measurement of high and low resistances. The description and operating instructions for these instruments are given in Appendix A.

2.2.4.1 Test Method

Electrical volume resistivity measurement was carried out basically in accordance with BS2044: Method 3 1978 [235]. This method is only suitable for measuring resistivities up to 10^9 Ωcm. The method as described in BS903: Part C2 1956 [236] should be used to measure resistivities greater than 10^9 Ωcm.

The method used here is based on BS2044: Method 3: 1978 [235] 'modified' to allow resistivities up to 10^{12}Ωcm to be measured.

2.2.4.2 Contact Electrodes (fig. 2.8)

These consist of 4 brass strips of the shown dimensions (fig. 2.8a) and assembled in place with the test piece (fig. 2.8b and c). It was found by experiment that they are best gold-plated for better electrical contacts during measurement. Constant electrode cleaning with carbon tetrachloride (CCl_4) solution was maintained. Fig. 2.9 shows the simple circuit diagram.

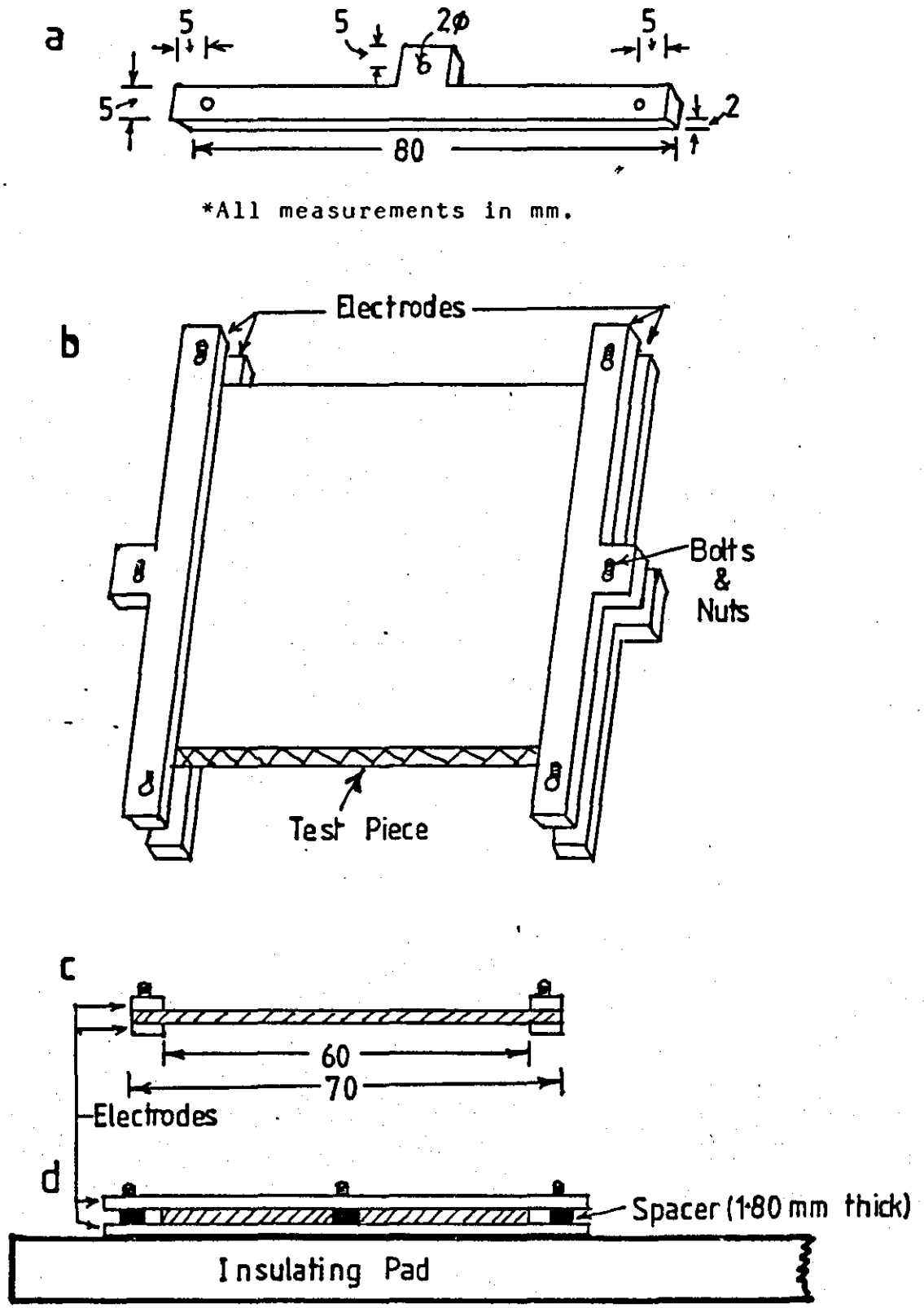


Fig 2.8 Diagrams showing: a. A single electrode
b. Test Piece and Electrodes Assembly
c. Side view of (b)
d. End view of (b)

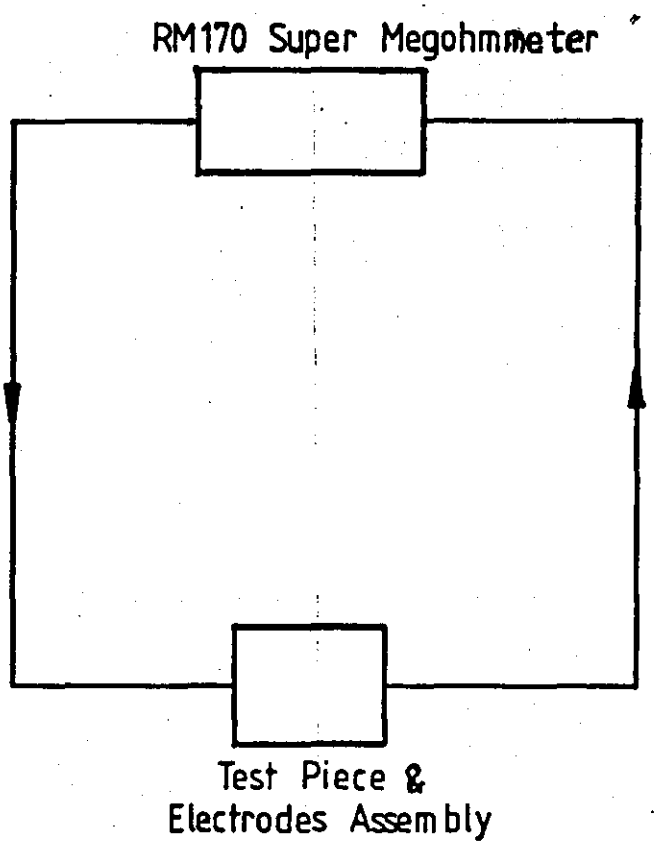


Fig. 2.9 Circuit Diagram of the Electrical Volume Resistivity Measurement.

2.2.4.3 Insulating Pads

These were moulded polystyrene (for lower temperatures) and asbestos plates (for higher temperatures) to serve as base pads for conditioning and keeping the test piece in place during measurement. The dimensions are 200mmX200mmX10mm.

2.2.4.4 Test Piece

2.2.4.4.1 *Dimensions*

Moulded rectangle 70mm X 60mm X 2mm. It was found by experiment to mould the test specimens between two sheets of polyester film 'melinex' and which were kept in place until testing. These kept the surfaces fresh for better electrode contact, facilitated strainless and easy moulding removal, and minimised any contact resistance which is a major obstacle to accurate and/or reproducible measurements of the volume resistivity of conductive rubbers.

2.2.4.4.2 *Conditioning*

The assembled test pieces are then firmly placed on the insulating pad and heated for two hours at 70±3°C to remove any strain and allowed to cool and stand for not less than 16hrs at the environmental test conditions. On the average 24hrs storage time after moulding was maintained for all experiments (unless otherwise stated) before carrying out the volume resistivity measurement.

2.2.4.4.3 *Measurement*

After conditioning, volume resistivity measurement was carried out as in Section 2.2.4.2, using the Super Mégohmmeter to measure the resistance of the two test samples. All measurements are carried out at 23±2°C and 50±5% Relative Humidity.

2.2.4.4.4 *Expression of Results*

The volume resistivity of each test piece was calculated using the formula:

$$\frac{R \times A}{d} \times 10^{-1} \quad \text{ohm-cm} \qquad 2.9$$

where

R = Resistance (ohms)

A = the cross sectional area (mm^2)

d = the distance between the inner edges of the electrodes.

The average of the resistivity results for the two test pieces are then recorded as the volume resistivity of the material.

Example of volume resistivity calculation

From the test piece dimensions,

A = 60mm X 2mm

d = 60mm

Therefore

$$\text{Volume Resistivity} = \frac{R \times 60 \times 2}{60} \times 10^{-1} \text{ ohm-cm}$$

$$= 2R \times 10^{-1} \text{ ohm-cm}$$

From the Super Megohmmeter,

Range selection = kΩ = 1,000 Ω

Multiplier = 10

Test Voltage = 100

Reading = 20

Resistance, R

$$= \frac{\text{Test Voltage}}{100} \times \text{Range Selection} \times \text{Multiplier} \times \text{Reading}$$

$$= \frac{100 \times 1{,}000 \times 10 \times 20}{100} \text{ ohms}$$

$$= 2 \times 10^5 \text{ ohms}$$

Substituting for R

$$\text{Volume Resistivity} = 2R \times 10^{-1} \text{ ohm-cm}$$

$$= 2 \times 2 \times 10^5 \times 10^{-1} \text{ ohm-cm.}$$

$$= \underline{4 \times 10^4} \text{ ohm-cm}$$

Table 2.6 shows an example of Data Sheet of calculated results.

TABLE 2.6 Shawinigan filled Silastic GP30: Calculated Volume Resistivity and Hardness

Mix No. (CB%)	Voltage V	Range Ω	Multiplier	Meter Readings 1	2	3	Average	Resistance Ω	Volume Resistivity Ω cm	Hardness IRHD
7 (5)	500	10^6	10^3	90.0	90.0	89.0	90.0	45.0×10^{10}	9.00×10^{10}	44
	500	10^6	10^3	91.0	91.0	92.0	91.0	45.5×10^{10}	9.10×10^{10}	44
8 (10)	500	10^6	10^3	62.0	62.0	60.0	62.0	31.0×10^{10}	6.20×10^{10}	45
	500	10^6	10^3	60.0	61.0	60.0	60.0	30.0×10^{10}	6.00×10^{10}	45
9 (15)	500	10^6	10^3	19.5	19.0	19.0	19.0	9.5×10^{10}	1.90×10^{10}	45
	500	10^6	10^3	20.0	20.0	20.0	20.0	10.0×10^{10}	2.00×10^{10}	46
10 (20)	100	10^3	10^2	15.0	15.0	16.0	15.0	15.0×10^5	3.00×10^5	46
	100	10^3	10^2	16.0	16.0	16.0	16.0	16.0×10^5	3.20×10^5	46
11 (25)	10	10^3	1	12.0	11.0	11.0	11.5	11.5×10^2	2.30×10^2	47
	10	10^3	1	12.0	13.0	11.0	12.0	12.0×10^2	2.40×10^2	47
12 (30)	10	1	10	16.0	16.0	16.0	16.0	16.0	3.20	49
	10	1	10	16.0	16.0	16.0	16.0	16.0	3.20	48
13 (35)	10	1	10	14.0	14.0	14.0	14.0	14.0	2.80	50
	10	1	10	14.0	14.0	14.0	14.0	14.0	2.80	50

2.2.4.5. Assembly and standardisation of equipment

The testing and standardisation of the Super Megohmmeter was carried out as outlined below:

2.2.4.5.1 *Avometer Standard Resistance Tester*

A range of resistances selected in the Super Megohmmeter was checked against that of the Avometer. Steady and accurate readings were got on the Avometer corresponding to the ranges selected on the Super Megohmmeter (see Table 2.7). ter (see Table 2.7).

2.2.4.5.2 *Standard Resistors*

Two standard resistors each 10^6 ohms were measured seperately, connected in series, and in parallel, with and without the electrodes. Steady and accurate readings were got corresponding to the expected theoretical calculations (see Table 2.8).

2.2.4.5.3 *Comparable test results with standard test pieces*

The volume resistivity of standard test pieces were measured with different equipment and standard methods: the Super Megohmmeter, the Digital Multimeter, the Four Point Probe, and BS903: Part C2 1956 [236]. Calculated results from these comparable methods were observed to be similar (see Table 2.9).

TABLE 2.7 SUPER MEGOHMMETER CALIBRATION WITH AVO-METER

Voltage V	Range Ω	Multiplier	Resistance Ω	Avo-Meter Reading Ω
100	10^3	10^3 10^2 10	10^6 10^5 10^4	10^6 10^5 10^4
100	10^6	10^3 10^2 10	10^9 10^8 10^7	10^9 10^8 10^7
100	10^9	10^3 10^2 10	10^{12} 10^{11} 10^{10}	10^{12} 10^{11} 10^{10}

TABLE 2.8 SUPER MEGOHMMETER CALIBRATION WITH STANDARD RESISTORS

Standard Resistors $10^6\Omega$	Voltage V	Range Ω	Multiplier	Reading Ω		Calculated Resistance Ω	
				without electrodes	with electrodes	without electrodes	with electrodes
Single	50 100 100	10^3	10^3 10^2 10	2.0 10.0 100.0	2.0 10.0 100.0	10^6	10^6
Series	50 20 10	10^9	10^3	2.0 5.0 10.0	2.0 5.0 10.0	10^{12}	10^{12}
Parallel	10 100 100	10^3	10^3 10^2 10	5.0 5.0 50.0	5.0 5.0 50.0	$5X10^5$	$5X10^5$

TABLE 2.9 COMPARABLE VOLUME RESISTIVITY RESULTS OF SHAWINIGAN FILLED SILASTIC GP30 USING DIFFERENT EQUIPMENT AND METHODS

Mix No. (CB%)	Super Megohmmeter	Digital Multimeter	Four Point Probe	BS 903 Part C2 :1956 Method
7 (5)	$9.00X10^{10}$	-	-	$(9.20\pm0.70)X10^{10}$
8 (10)	$6.20X10^{10}$	-	-	$(6.00\pm1.40)X10^{10}$
9 (15)	$2.00X10^{10}$	-	-	$(2.00\pm0.40)X10^{10}$
10 (20)	$3.20X10^5$	$3.00X10^5$	-	-
11 (25)	$2.40X10^2$	$2.40X10^2$	$2.40X10^2$	-
12 (30)	3.20	3.30	3.20	-
13 (35)	2.80	2.90	2.80	-

2.2.5. METHOD OF pH MEASUREMENT OF CARBON BLACK

This was carried out in accordance with ASTM D 1512-75 [237] and as outlined below:

2.2.5.1 Apparatus

1. pH Meter: A Pye Unican PW9418 pH Meter equipped with glass and calomel electrodes having an accuracy of ±0.05pH and conforming to the requirements of ASTM Method E70: Test for pH of aqueous solutions with glass electrodes was used. (see Appendices B1 and B2 for the pH Meter specification, glass electrodes, and the calibration procedure for the pH Meter).

2. Stainless Steel Beakers and covers: 50ml. stainless beakers were used to accomodate the samples to eliminate any contamination during boiling.

3. Hot Plate: Electrically heated and thermostatically controlled hot plate was used.

4. Mortar and Pestle.

5. Stainless Steel container: A 500ml stainless steel beaker was used to boil distilled water.

2.2.5.2 Procedure

1. Carbon blacks pellets and lumps were first ground to very fine powder, using the mortar and pestle.

2. A 2.00g portion of carbon black was adopted as the standard sampling for comparison purposes. 20cm^3 of boiling distilled water was added to the 2.00g of carbon black weighed into the 50ml stainless steel beaker. 5 drops of ethanol were added to the contents to facilitate rapid wetting of the carbon black.

The mixture was boiled for 15mins and allowed to cool to room temperature in a clean atmosphere. The supernatant liquid was decanted off.

3. After calibrating the pH meter in two standard buffer solutions (see Appendix B2) the electrodes and Pt100 were inserted in the sample sludge. The beaker was gently rotated in alternate directions until a constant pH value was obtained and read.

4. The procedure was repeated in the second sample and the pH recorded.

2.2.5.3 Results

An average of two samples results was taken (Table 2.10).

TABLE 2.10 THE pH VALUES OF CONDUCTIVE CARBON BLACKS

		pH VALUES		
	°C	SAMPLE 1	SAMPLE 2	AVERAGE
Vulcan P	0	8.50	8.50	8.50
	1200	10.40	10.40	10.40
	1300	10.35	10.45	10.40
	1450	10.40	10.20	10.30
	2800	9.70	9.70	9.70
Vulcan PF	0	8.70	8.50	8.60
	1200	10.20	10.40	10.30
	1300	10.25	10.35	10.30
	1450	10.20	10.20	10.20
	2800	9.80	9.80	9.80
Vulcan XC72	0	5.10	4.90	5.00
	1200	6.80	7.00	6.90
	1300	6.90	6.90	6.90
	1450	7.20	7.00	7.10
	2800	7.10	7.10	7.10
Vulcan XC72R	0	7.50	7.50	7.50
	1200	9.30	9.10	9.20
	1300	9.10	9.10	9.10
	1450	9.05	9.15	9.10
	2800	8.50	8.50	8.50
Shawinigan	0	5.50	5.50	5.50
	1200	7.50	7.70	7.60
	1300	7.45	7.55	7.50
	1450	7.50	7.50	7.50
	2800	7.10	7.10	7.10
Ketjenblack EC	0	9.50	9.50	9.50
	1200	10.70	10.70	10.70
	1300	10.50	10.70	10.60
	1450	10.50	10.50	10.50
	2800	10.00	10.00	10.00
Conductex 900		6.15	6.25	6.20
Conductex SC		8.40	8.60	8.50
Conductex 975		7.00	7.00	7.00
Conductex 40-220		5.50	5.30	5.40
Philblack XE-2		6.60	6.60	6.60

2.2.6 CARBON BLACK SURFACE AREA MEASUREMENT BY BET METHOD

The Brunauer, Emmett and Teller (BET) Method was used to measure the surface area of conductive carbon blacks used in this research work.

This was carried out in accordance with ASTM D3037-78 Method D [238]. The detailed Method of operating the BET equipment and the individual readings are given in Appendix C. However, an example of a data sheet (fig. 2.10) and a sheet of calculation by computer analysis (fig. 2.11) is hereby given.

Table 2.11 shows a summary of the results of the surface area of the various conductive carbon blacks used.

Fig. 2.10 Data Sheet for Carbon black surface area measurement by BET Method.

DATA SHEET

SAMPLE: Vulcan P

SAMPLE WEIGHT: 0.143 g

GRAPHITIZATION PROCESS:*

a. Temperature: - °C

b. Time: - Hrs

VOLUME CALIBRATION WITH HELIUM

H-mark	Original Mercury Height	Helium Pressure Height
1	89.2	87.1
2	78.8	74.2
3	72.2	63.5
4	66.3	48.3
5	61.2	11.8
6	58.0	-

TAP T8 OPEN TO HELIUM

H-mark	Original Mercury Height	Helium Pressure Height
1	89.2	87.5
2	78.8	75.6
3	72.2	67.3
4	66.3	59.4
5	61.2	52.2
6	58.0	47.6

VOLUME CALIBRATION WITH NITROGEN

H-mark	Original Mercury Height	Original Nitrogen Height
1	89.2	81.7

TAP T8 OPEN TO HELIUM

H-mark	Original Mercury Height	New Pressure Height
1	89.2	83.9
2	78.8	69.4
3	72.2	58.6
4	66.3	48.8
5	61.2	38.4
6	58.0	32.6

N.B. All heights in CMS

JACKET TEMPERATURE: 298 °K

LABORATORY ATMOSPHERIC PRESSURE: 79 cm.Hg

NITROGEN DIFFUSION PRESSURE: 79 cm.Hg

B.E.T. RESULT: 158 m^2g^{-1}

pH READING: 8.5

*Graphitization process are accomplished at:

1. Institute of Polymer Technology, LUT.

2. Stockpole Carbon Company, USA.

A

Fig. 2.11 Calculation of Carbon black Surface Area by the Computer Analysis.

```
                    VULCAN P
                    --------                    ? S 1000

          IF SOMETHING GOES WRONG AND YOU WISH TO QUIT
          . PUSH THE PANIC BUTTON LABELLED 'BREAK'
              AND HOLD IT DOWN UNTIL PRIME RESPONDS 'QUIT,'
                THEN TYPE 'S 1000' TO REPEAT PROGRAM
                  OR 'LOGOUT' TO FINISH.

WHEN TYPING IN DATA, SEPARATE EACH NUMBER OF A SET WITH A COMMA,
AND AT THE END OF EACH SET PRESS 'RETURN'.

YOU MAY DELETE A SINGLE DIGIT BY TYPING '"'
OR A WHOLE LINE BY TYPING '?'
OR A WHOLE SERIES BY TYPING 'ERASE' AT ANY TIME BEFORE
    THE FINAL 'RETURN'.

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

IN  ALL SUBSEQUENT BURETTE READING ENTRIES DESIGNATE:-
    LOWEST ETCH MARK ON BURETTE '1',
    SECOND ETCH MARK ON BURETTE '2',
         AND SO ON UP TO
    UPPER ETCH MARK ON BURETTE '6'.

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

DO YOU WISH TO CALCULATE THE VOLUME OF THE TUBING
     BETWEEN THE TOP BURETTE ETCH MARK AND THE SAMPLE TAP ?
TYPE IN   '1'    IF YES    OR   '0'  IF NO.

1

                    CALCULATION OF THE TUBING VOLUME.

TYPE IN CODE NUMBER OF ETCH MARK,
SCALE READING OF ETCH MARK, CMS.,
SCALE READING OF THE MERCURY LEVEL IN MANOMETER TUBE, CMS.
FOR EACH SET OF THE SERIES.

 AT THE END OF THE SERIES TYPE '9,9,9' AND PRESS 'RETURN'.

1, 89.2, 87.1
2, 78.8, 74.2
3, 72.2, 63.5
4, 66.3, 48.3
5, 61.2, 11.8
6, 58.0, 0
9,9,9
```

B

TUBING VOLUME CALIBRATION.

TUBING VOLUME= 5.71CCS.
CORRELATION COEF. = 0.999856

PRESSURE(CMS. HG)	1/PRESSURE	BURETTE VOL.
2.10	0.4762	210.90
4.60	0.2174	92.40
8.70	0.1149	46.30
18.00	0.5556E-01	20.50
49.40	0.2024E-01	5.30
58.00	0.1724E-01	0.00

WHEN PLOTTING DATA WITH '1/PRESSURE' ON THE X-AXIS,
AND 'BURETTE VOLUME' ON THE Y-AXIS USE THE FOLLOWING POINTS
TO DEFINE THE LEAST SQUARES LINE:-

BURETTE VOLUME	1/PRESSURE
-5.71	0.00
39.73	0.10

DO YOU WISH TO CALCULATE THE DEAD SPACE VOLUME ?
TYPE IN '1' IF YES OR '0' IF NO.

1

CALCULATION OF THE 'DEAD SPACE' ABOVE THE SAMPLE.

TYPE IN CODE NUMBER OF ETCH MARK,
SCALE READING OF ETCH MARK, CMS.,
SCALE READING OF MERCURY LEVEL IN MANOMETER TUBE, CMS.,
FOR EACH SET OF THE SERIES.

AT END OF EACH SERIES TYPE '9,9,9' AND PRESS 'RETURN'.

1.? 1, 89.2, 87.5
2, 79.8, 75.6
3, 72.2, 67.3
4,66.3, 59.4
5, 61.2, 52.2
6, 58.0, 47.6
9,9,9

TYPE IN:-
ROOM TEMPERATURE (DEGREES KELVIN) AT TIME OF DEAD SPACE DETERM

298.0

C

DEAD SPACE CALIBRATION.

DEAD SPACE VOLUME= 36.03CCS.
CORRELATION COEF. = 0.999987
ROOM TEMPERATURE= 298.00K

PRESSURE(CMS. HG)	1/PRESSURE	BURETTE VOL.
1.70	0.5882	215.60
3.20	0.3125	98.10
4.90	0.2041	52.00
6.90	0.1449	26.21
9.00	0.1111	11.01
10.40	0.9615E-01	5.71

WHEN PLOTTING DATA WITH '1/PRESSURE' ON THE X-AXIS,
AND 'BURETTE VOLUME' ON THE Y-AXIS USE THE FOLLOWING POINTS
TO DEFINE THE LEAST SQUARES LINE:-

BURETTE VOLUME	1/PRESSURE
-36.03	0.00
6.92	0.10

CALCULATION OF THE ADSORPTION ISOTHERM.

TYPE IN SAMPLE WEIGHT, GRAMS, AND
ROOM TEMPERATURE (DEGREES KELVIN) DURING THE ADSORPTION RUN. AND
SATURATION VAPOUR PRESSURE OF NITROGEN (CMS. OF MERCURY).

0.143, 298.0, 79.0

ENTER PARAMETERS DEFINING THE INITIAL DOSE. TYPE IN :-
CODE NUMBER OF ETCH MARK,
SCALE READING OF ETCH MARK, CMS.,
READING OF THE MERCURY LEVEL IN MANOMETER TUBE, CMS.

1, 89.2, 81.7

ENTER SERIES OF ADSORPTION RUN PARAMETERS AT EQUILIBRIUM.
TYPE IN:-
CODE NUMBER OF ETCH MARK,
SCALE READING OF ETCH MARK, CMS.,
SCALE READING OF THE MERCURY LEVEL IN MANOMETER TUBE, CMS.,
FOR EACH EQUILIBRIUM POINT ON ONE LINE THEN PRESS 'RETURN'..
AT END OF SERIES TYPE IN '9,9,9' AND PRESS 'RETURN'.

1, 89.2, 83.9
2, 78.8, 69.4
3, 72.2, 58.6
4, 66.3, 48.8
6? 5, 61.2, 38.4
6, 58.0, 32.6
9,9,9

D

ADSORPTION ISOTHERM DATA.

SAMPLE WT. = 0.1430GRAMS
ROOM TEMPERATURE= 298.00K
SATURATION VAPOUR PRESSURE OF NITROGEN= 79.000CMS.HG

VOLUME ADSORBED, CCS. AT STP.	RELATIVE PRESSURE, P/P0.
3.444	0.6709E-01
4.386	0.1190
5.153	0.1722
6.458	0.2215
6.659	0.2886
6.808	0.3215

DO YOU WISH TO DO BET PLOT ?
TYPE IN '1' IF YES OR '0' IF NO.

1

BET PLOT CALCULATION.

LEAST SQUARES LINE THROUGH THE POINTS LISTED BELOW GIVES:-
VOLUME ADSORBED IN COMPLETE MONOLAYER (CCS.(STP)PER GRAM), VM= 36.38
SPECIFIC SURFACE AREA (SQ.M. PER GRAM)= 158.
BET CONSTANT, C=-0.175 FROM THE SLOPE,
= 3.49 FROM THE INTERCEPT
CORRELATION COEF. =0.991062

BET PLOT DATA.
INDIVIDUAL POINT ERRORS IN X/V(1-X).

X=P/P0	X/V(1-X)	POINT ERROR	POINT N
0.6709E-01	0.2088E-01	0.6343E-03	1
0.1190	0.3079E-01	0.9791E-03	2
0.1722	0.4035E-01	0.7407E-03	3
0.2215	0.4406E-01	-0.4650E-02	4
0.2886	0.6092E-01	-0.1608E-03	5
0.3215	0.6961E-01	0.2457E-02	6

WHEN PLOTTING DATA WITH 'P/P0' ON THE X-AXIS
AND 'X/V(1-X)' ON THE Y-AXIS
USE THE FOLLOWING POINTS TO DEFINE THE LEAST SQUARES LINE:-

X/V(1-X)	X
0.7877E-02	0.00
0.4475E-01	0.20

E

ROUGH PLOT OF THE POINTS LISTED ABOVE.
GRAPH OF INSUFFICIENT PRECISION TO BE USED IN YOUR LAB. BOOK
REDRAW THE GRAPH TO BE PRESENTED USING DATA PREVIOUSLY LISTED.
O = EXPERIMENTAL BET POINTS.
* = POINTS DEFINING THE LEAST SQUARES LINE.

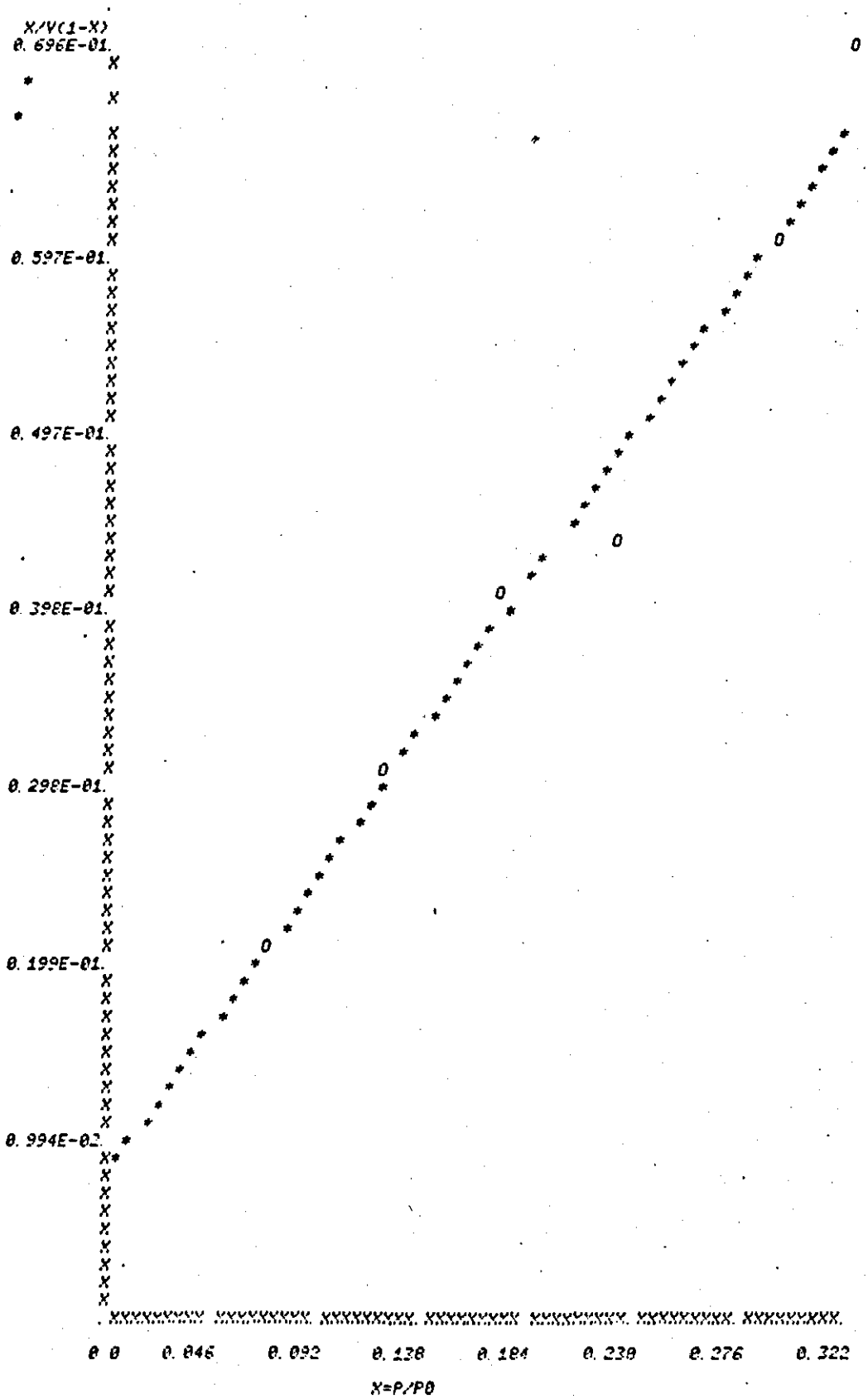


TABLE 2.11 THE SURFACE AREA AND pH VALUES OF CONDUCTIVE CARBON BLACKS

	°C	B E T Surface Area (m^2g^{-1})	% Difference from original Carbon black(±)	pH Value
Vulcan P	0	158.00	-	8.5
	1200	158.70	+ 0.456	10.4
	1300	157.20	- 0.506	10.4
	1450	156.40	- 1.013	10.3
	2800	140.80	- 10.886	9.7
Vulcan PF	0	157.00	-	8.6
	1200	157.50	+ 0.338	10.3
	1300	156.20	- 0.510	10.3
	1450	155.40	- 1.019	10.2
	2800	139.90	- 10.892	9.8
Vulcan XC72	0	260.00	-	5.0
	1200	261.30	+ 0.500	6.9
	1300	257.40	- 1.000	6.9
	1450	256.00	- 1.538	7.1
	2800	232.00	- 10.796	7.1
Vulcan XC72R	0	262.00	-	7.5
	1200	263.30	+ 0.496	9.2
	1300	259.60	- 0.902	9.1
	1450	258.20	- 1.450	9.1
	2800	233.40	- 10.916	8.5
Shawinigan	0	65.80	-	5.5
	1200	66.60	+ 1.216	7.6
	1300	62.50	- 5.015	7.5
	1450	60.10	- 8.663	7.5
	2800	46.60	- 29.179	7.1
Ketjenblack EC	0	1,003.00	-	9.5
	1200	1,005.00	+ 0.199	10.7
	1300	998.00	- 0.499	10.6
	1450	984.00	- 1.894	10.5
	2800	960.00	- 4.287	10.0
Conductex 900		128.00	-	6.2
Conductex SC		242.00	-	8.5
Conductex 975		274.00	-	7.0
Conductex 40-220		1,030.00	-	5.4
Philblack XE-2		1,010.00	-	6.6

2.2.7 ASSESSMENT OF CARBON BLACK DISPERSION IN SILICONE COMPOUNDS USING THE DARK FIELD REFLECTED LIGHT MICROSCOPY (DFRLM)[239-24]

2.2.7.1 Principle

The principle of dark field reflected light microscopy (DFRLM) is that a hollow beam of light is produced by a stop situated in front of the illuminating source. This beam is directed on to the sample by a system of reflected mirrors, such that it does not pass through the objective lens (fig. 2.12). If the incident light falls on a flat, even surface, no diffraction of the light beam occurs. If, on the other hand, the viewed surface bears irregularities such as steps, hollows or craters, these act as diffracting centres for the incident light beam (fig. 2.13). Thus, on reflection from the sample, the non-diffracted light is returned outside the objective lens. The diffracted fraction passes through the objective lens and is admitted into the optical system, where an image is perceived at the eyepiece. Thus the diffracting centres will appear as light boundaries on a dark background.

2.2.7.2 Equipment (fig. 2.14 & 2.23)

The heart of the equipment was a Reichert Microscope with a trinocular head set-up for reflected light work in the dark field mode using white light. (A magnification of X350 is derived from a X10 eyepiece, X28 Epi objective of NA=0.55 and X1.25 tube factor).

The image obtained from the DFRL microscope is relayed through a standard television system (camera and control unit) into a TV monitor. The analogue signal from the television system is fed into an oscilloscope (Tektronix Type 529 waveform monitor) with a single line strobing facility. That is, the instrument has the capability of scanning any one line of a multiline television signal and of displaying a trace of intensity distribution across that image line on its screen.

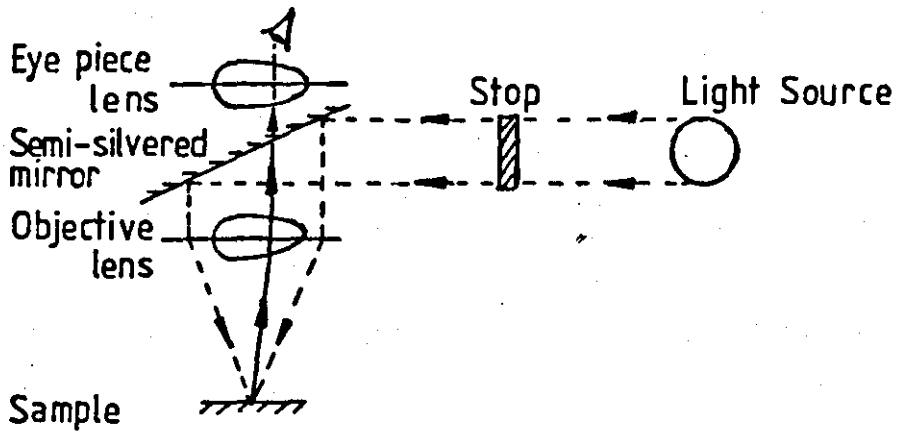


Fig. 2.12 Dark Field Reflected Light Microscopy.

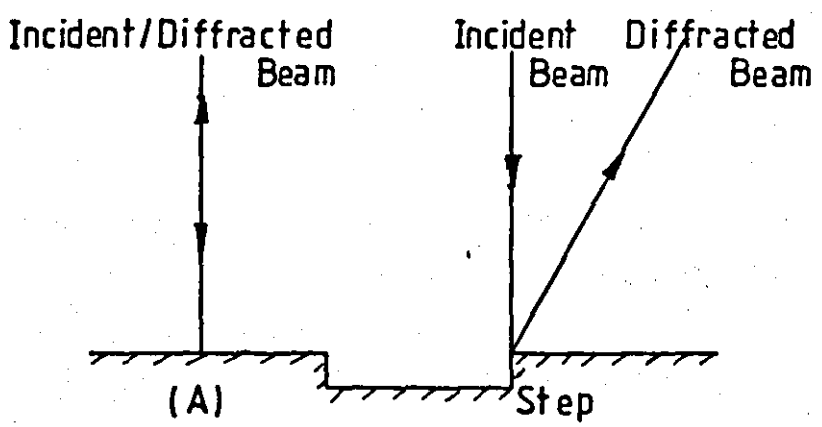


Fig. 2.13 Diffraction at a step.

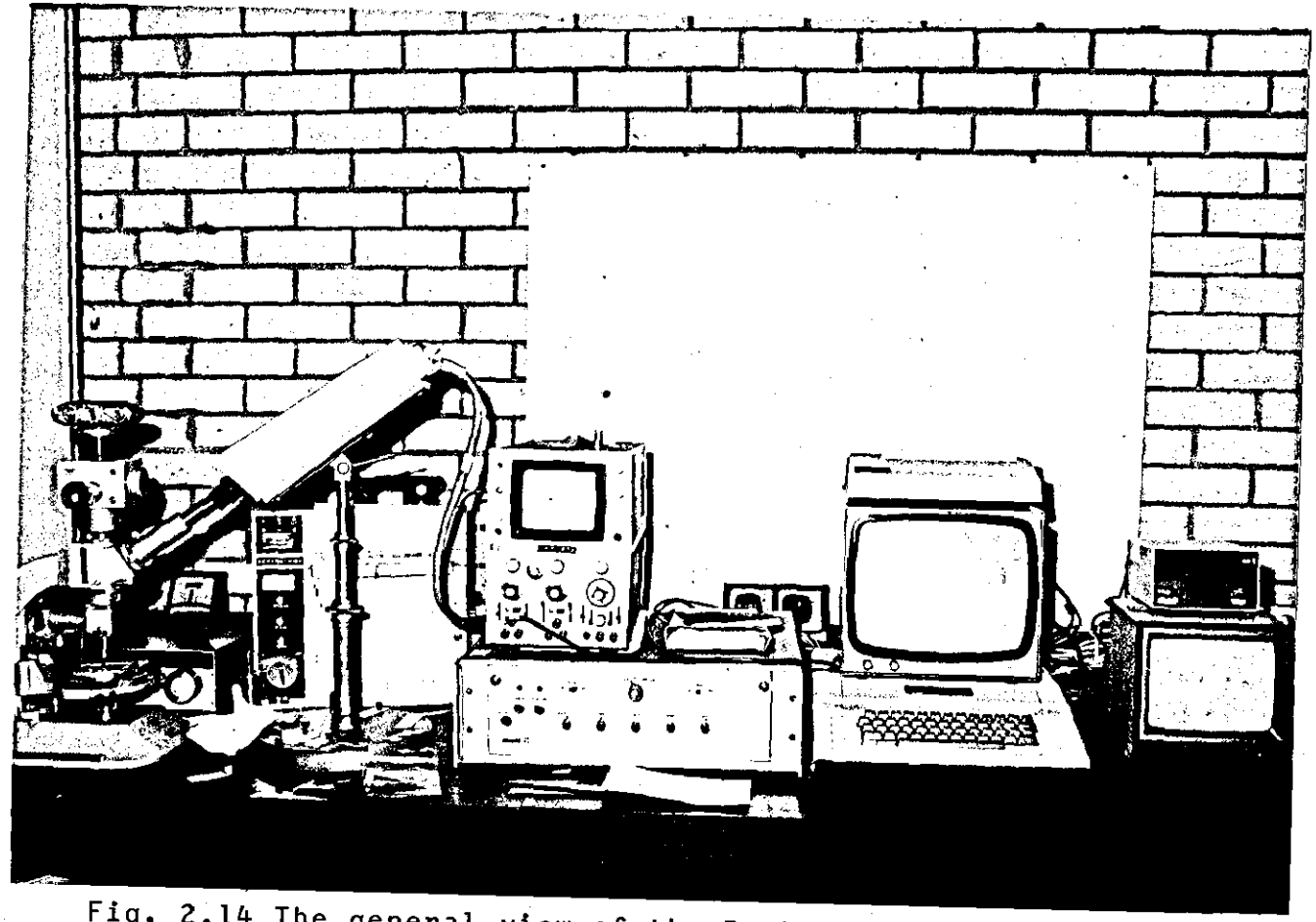


Fig. 2.14 The general view of the Dark Field Reflected Light Microscopy/Oscilloscope Analysis System.

When used manually without the computer attachment, the television line selected for scanning analysis by the oscilloscope appears as a bright-up pulse (fig. 2.15) on the TV monitor. The image signal from the television monitor is accepted by a micro computer via an interfacing board. The signal is digitised and stored in the memory of the computer. At the line of sampling a bar is superimposed on the television image (fig. 2.16). A vertical, and not a horizontal line as used in the manual operation above, is utilized here, due to the type of analogue to digital converter (ADC) contained in the video interface board (Appendix D). Several microseconds are required to digitise the analogue signal, thus horizontal signal is impractical. Effective magnification was found to be X1,000 to X10,000 on the television monitor, equivalent to scanning a linear dimension of 300μm of sample.

The software (held presently on diskette) manipulates these digitised signals and gives a choice of several user selected processing functions for interactive operation which result ultimately in the computation of the dispersion related parameters.

The micro computer takes several samples (usually 20) automatically or manually across the surface of the test piece. The output, in the form of graphics/text, is via a second television monitor. This is in the form of:

a. a graphical display of the reflected light intensity from the sample.
b. an analysis of the peak height and the number of peaks above a threshold level.

The oscilloscope traces (figs. 2.17 and 2.18) and hard copy traces (figs. 2.19 and 2.20) from bad and good dispersions are appended. Also hard copy of results (fig. 2.21) obtained from the analysis is obtained from a thermal printer. Block diagrams of operational sequence (fig.2.22) and DFRLM/ Oscilloscope (fig. 2.23) are appended.

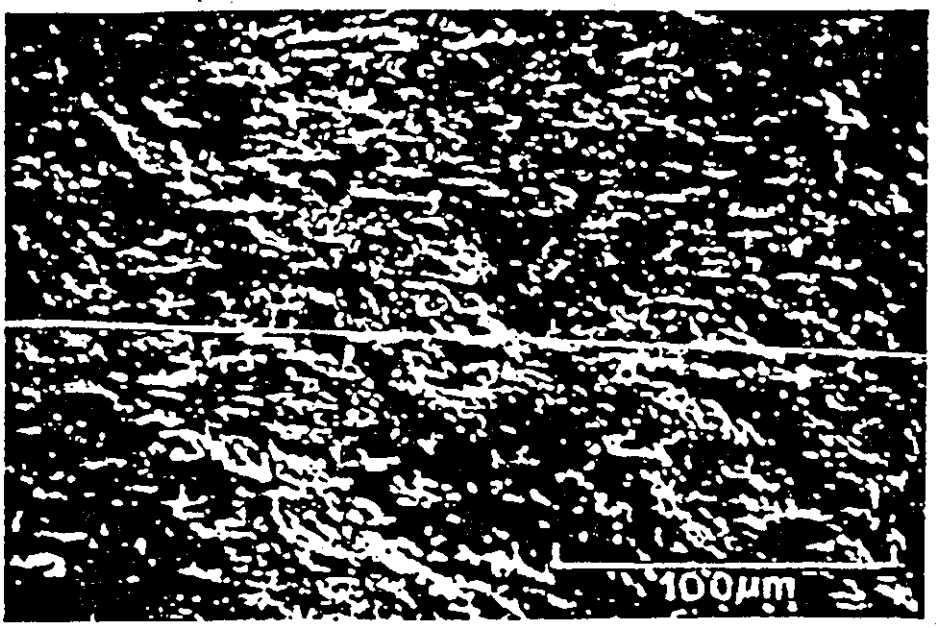


Fig. 2.15 Television Monitor of DFRLM image of rubber surface showing bright-up pulse (manual).

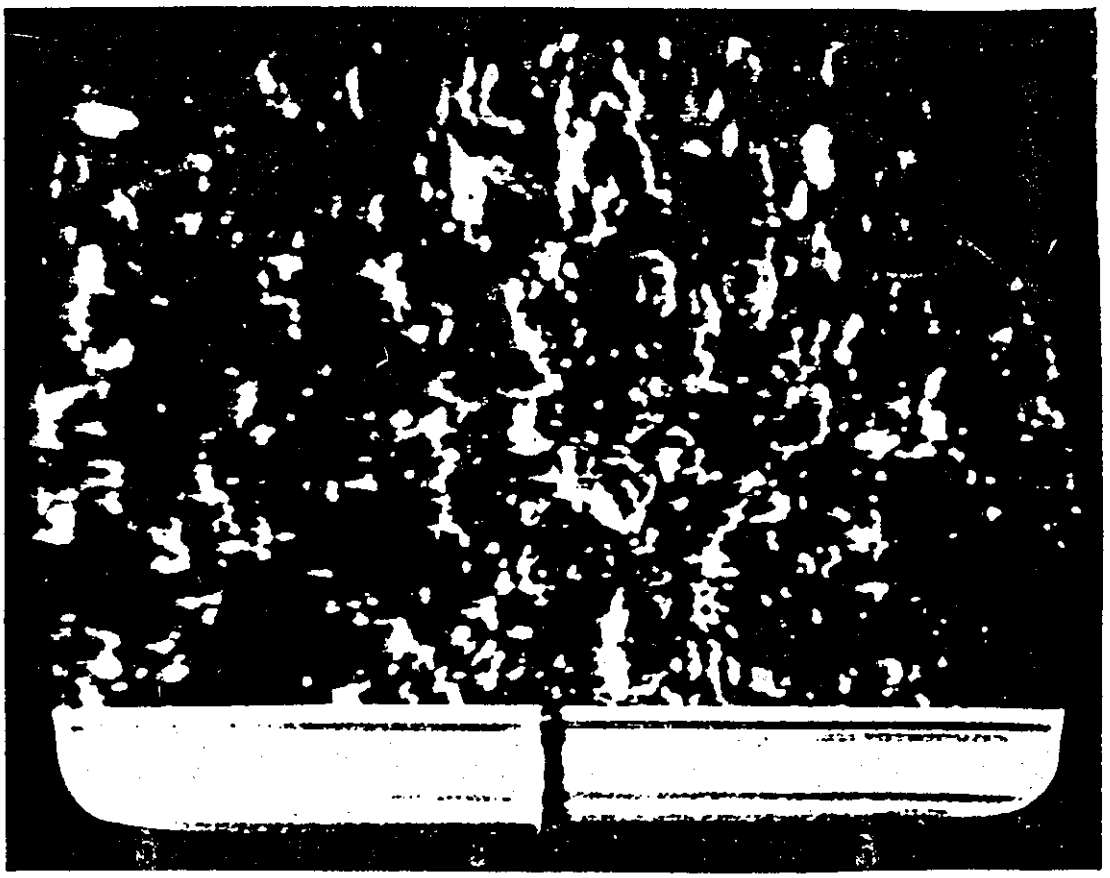


Fig. 2.16 Television Monitor of DFRLM image of rubber surface showing sampling bar (automatic)

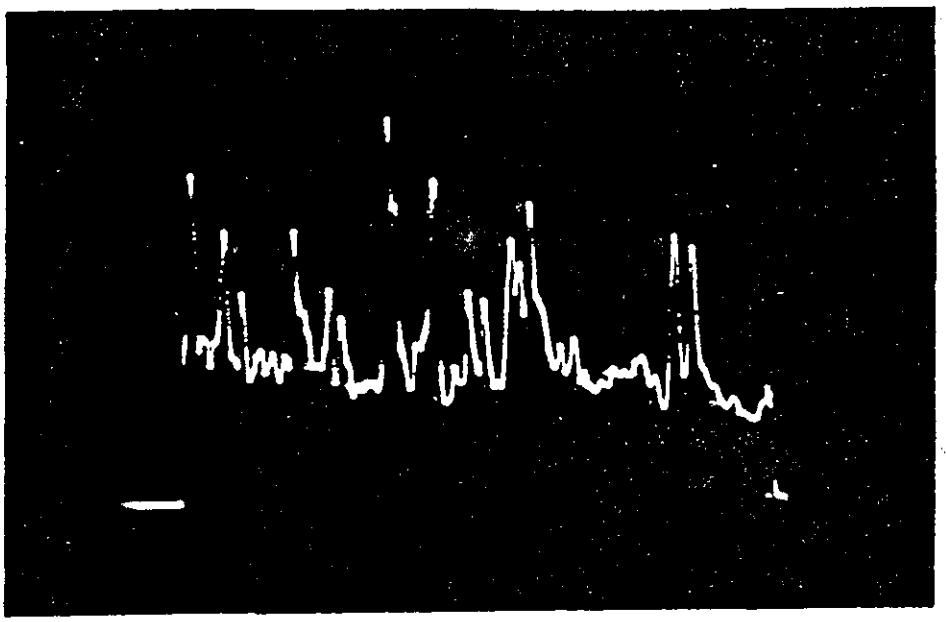


Fig. 2.17 Oscilloscope Trace from a bad dispersion.

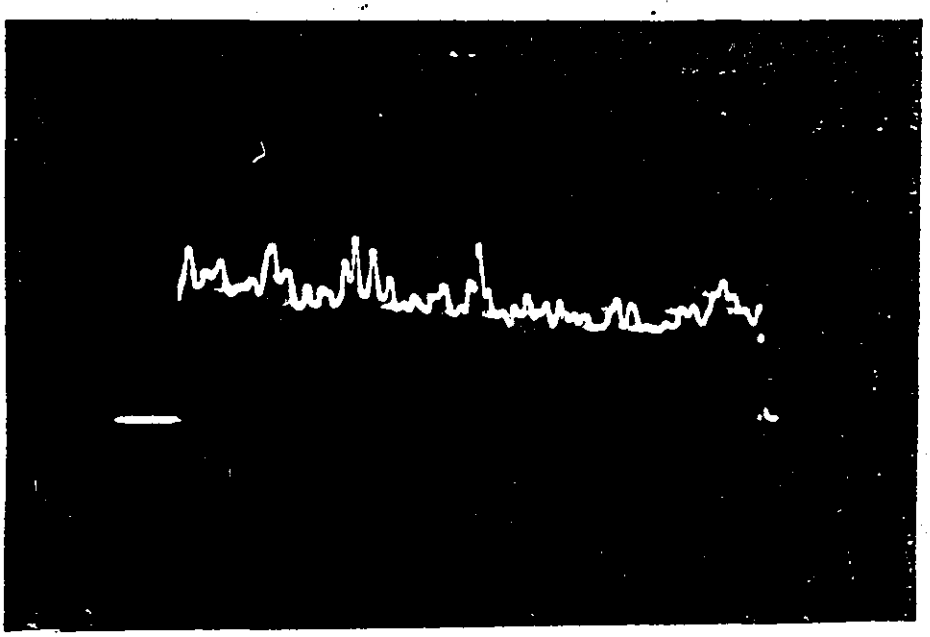
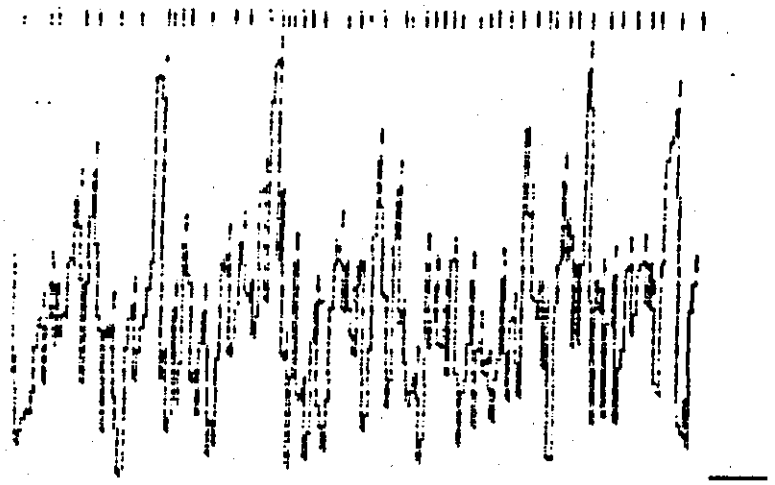


Fig. 2.18 Oscilloscope Trace from a good dispersion.

TEST NUMBER GP4525P

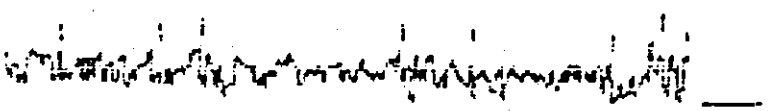


TEST NUMBER GP4525P

THRESHOLD.	NO'OF PEAKS.	MEAN HEIGHT.	VARIANCE.	STD DEVIATION.
3	50	121.987	2158.402	46.68

Fig. 2.19 Hard copy trace from a bad dispersion.

TEST NUMBER 4524SH2



TEST NUMBER 4524SH2

THRESHOLD.	NO'OF PEAKS.	MEAN HEIGHT.	VARIANCE.	STD DEVIATION.
36	9	30.931	14.987	3.89

Fig. 2.20 Hard copy trace from a good dispersion.

TEST NUMBER 4524SHI

THRESHOLD.	NO'OF PEAKS.	MEAN HEIGHT.	VARIANCE.	STD DEVIATION.
31	9	36.696	51.004	7.177
35	12	33.161	84.074	9.214
37	11	29.014	66.678	8.206
33	9	35.125	33.273	5.797
31	10	33.33	50.051	7.109
31	10	34.34	20.684	4.566
36	13	28.124	19.669	4.457
35	8	31.183	19.171	4.4
31	10	32.42	25.453	5.071
30	11	33.88	24.111	4.934
35	6	31.141	21.984	4.712
38	11	28.004	55.77	7.505
35	11	31.952	12.983	3.921
34	12	29.037	36.199	6.046
31	10	31.916	7.227	2.701
31	9	31.197	49.602	7.078
29	11	30.116	28.243	5.34
29	10	31.31	37.482	6.152
33	7	25.25	25.286	5.083
29	10	30.097	23.521	4.874
MEAN VALUES				
32.7	10	31.365	35.125	5.925

Fig. 2.21 Hard copy print-out of result.

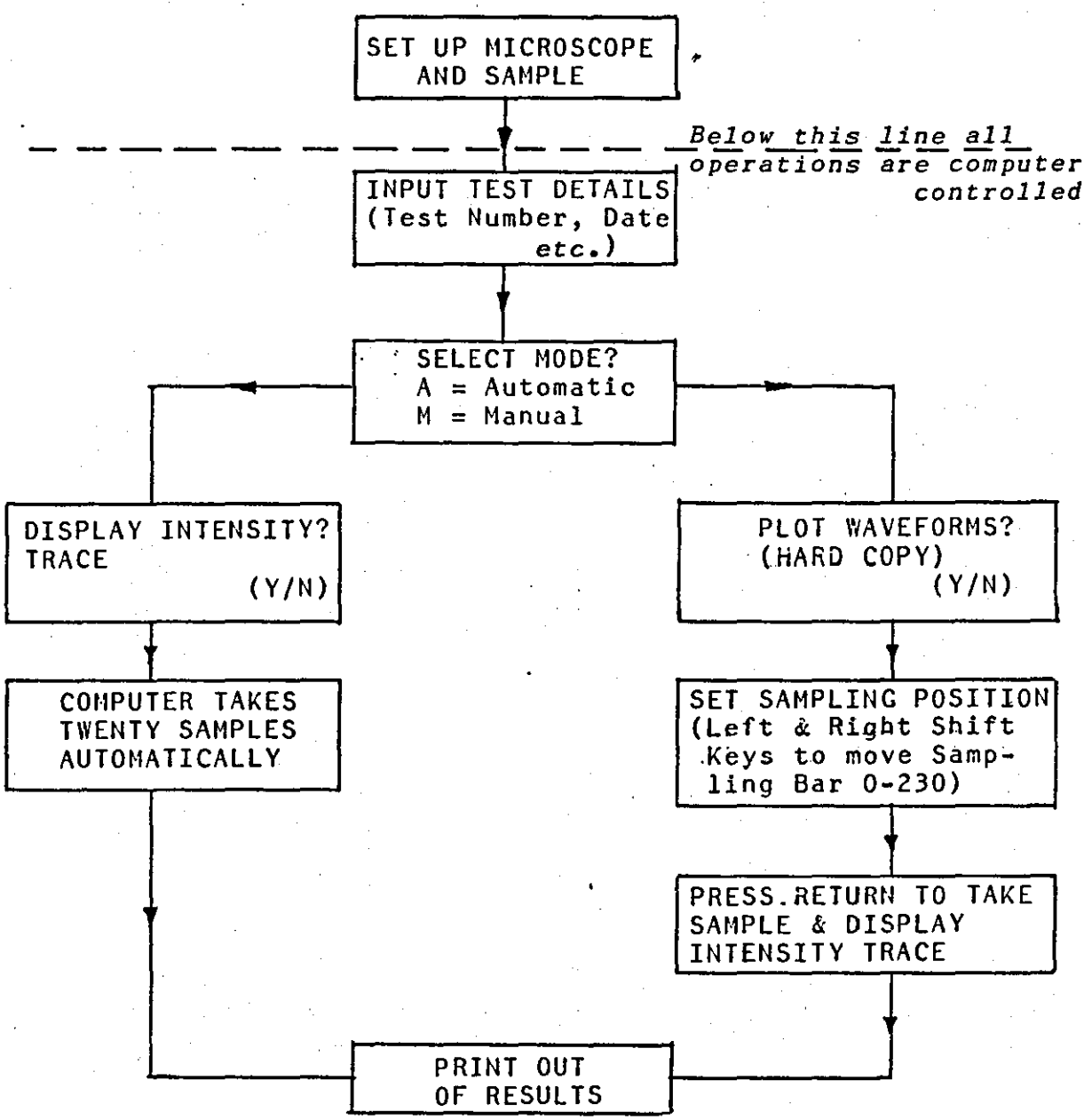


Fig. 2.22 Operational sequence of Dark Field Reflected Light Microscopy/Oscilloscope.

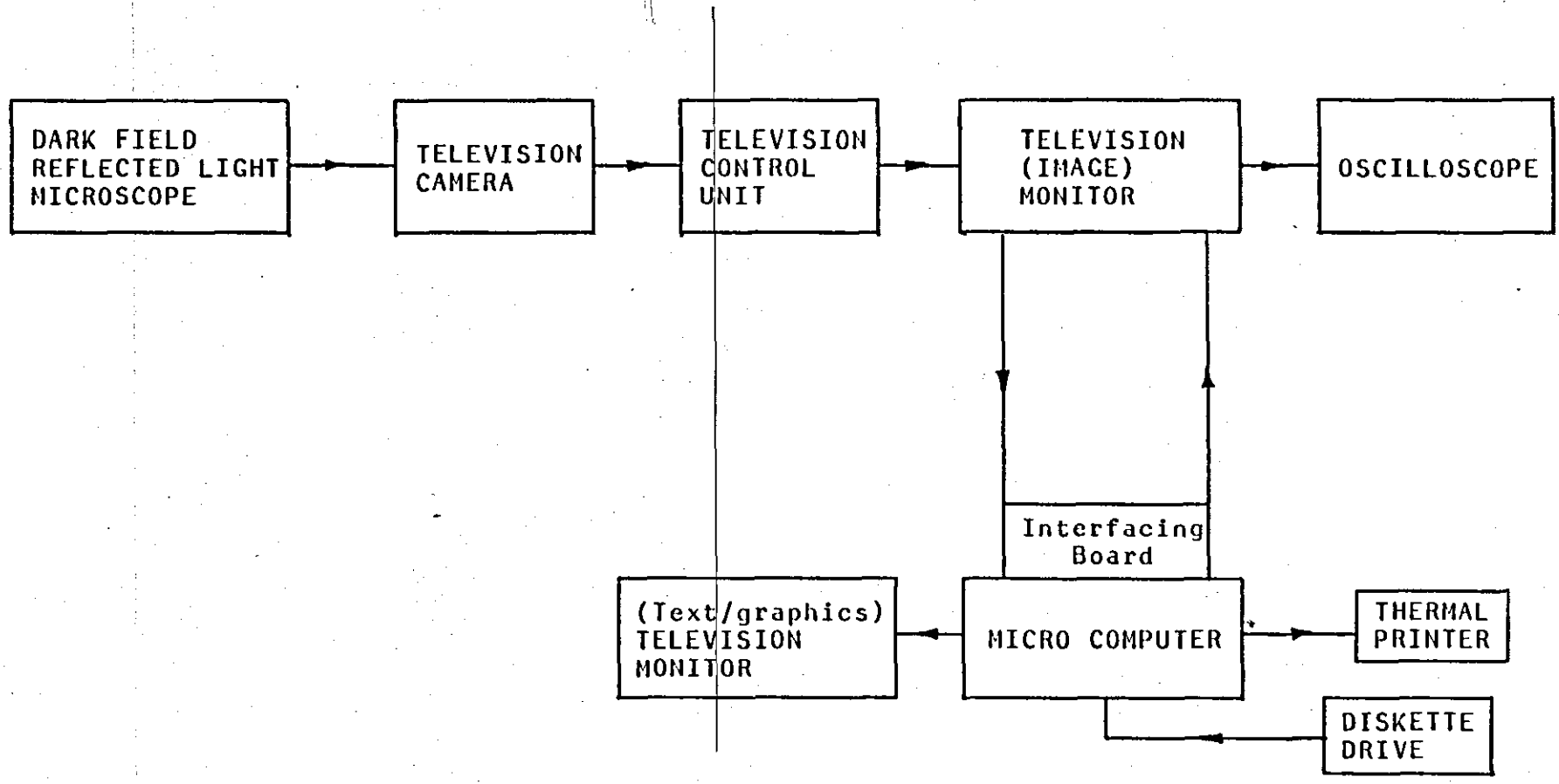


Fig. 2.23 Block Diagram of Dark Field Reflected Light Microscopy/Oscilloscope.

2.2.7.3 Sample Preparation

A new, degreased, single edged razor blade was attached to a holder which in turn was accomodated in the rubber sample cutting equipment. Using a new blade for each cut, good surfaces, free of knife marks and other artifacts, were produced on a 20mm X 10mm X 2mm rubber strips. A second cut, about 4mm from, and parallel to the first cut surface leaves a 10mm X 4mm X 2mm 'first cut side' sample for examination.

The unvulcanised rubber was first sandwiched between 'melinex' sheet, inserted in a mould, and pressed in an hydraulic rubber moulding press at $5kgcm^{-2}$ pressure, $100^{0}C$, for 5 minutes to rid the bulk of porosity that exists when the stock is offloaded from a batch off mill. Then the same cutting operation followed using a wooden base, and lubricating the razor blade with a drop of water for a better, undistorted cut.

2.2.7.4 Experimental Procedure

The microscope was set-up paying particular attention to the centering of the lamp to obtain an evenly intense field. A horizontal line on the oscilloscope screen indicated even light distribution. The lamp was set to a constant intensity, and the microscope switched to dark field operation.

The slide bearing the sample was focused on using the free ocular of the microscope. Samples with knife marks or dust were rejected. Sample blocks with unparallel surfaces were mounted on plasticine on the glass slide and made parallel by pressing lightly with a grease-free glass slide.

The image was then transferred to the Television (image) Monitor. Other operations follow manually or automatically using the micro computer (fig. 2.23).

2.2.7.5 Standardisation

Before starting any experimental work and in order to to make sure that comparative study of different surfaces was achieved, a Stepped Diffracting Grating (fig. 2.24) is first used. The image in the form of horizontal lines are adjusted to 15 lines per inch on the TV Monitor. The intensity is observed and adjusted with a graded tester. The horizontal line on the oscilloscope, an indication of even light distribution, is noted.

A 'standard' test piece - a well-dispersed carbon black compound with a reproducible composite parameter consistency within 2% on repeat tests on different areas - is then viewed and a hard copy (fig. 2.25) taken after a balanced adjustment, if necessary.

2.2.7.6 Sampling

Two samples, and three different areas per sample, of each compound is viewed with automatic (20 lines) scanning on each area for the cured samples. Hard copy of the mean values is then obtained for calculations.

Only limited number of unvulcanised stocks were monitored as above for comparative purposes.

2.2.7.7 Calculations

From the mean values in the hard copy, an empirical composite parameter has been derived[241] which is a medium of expressing the dispersion index of carbon black in rubber compounds:

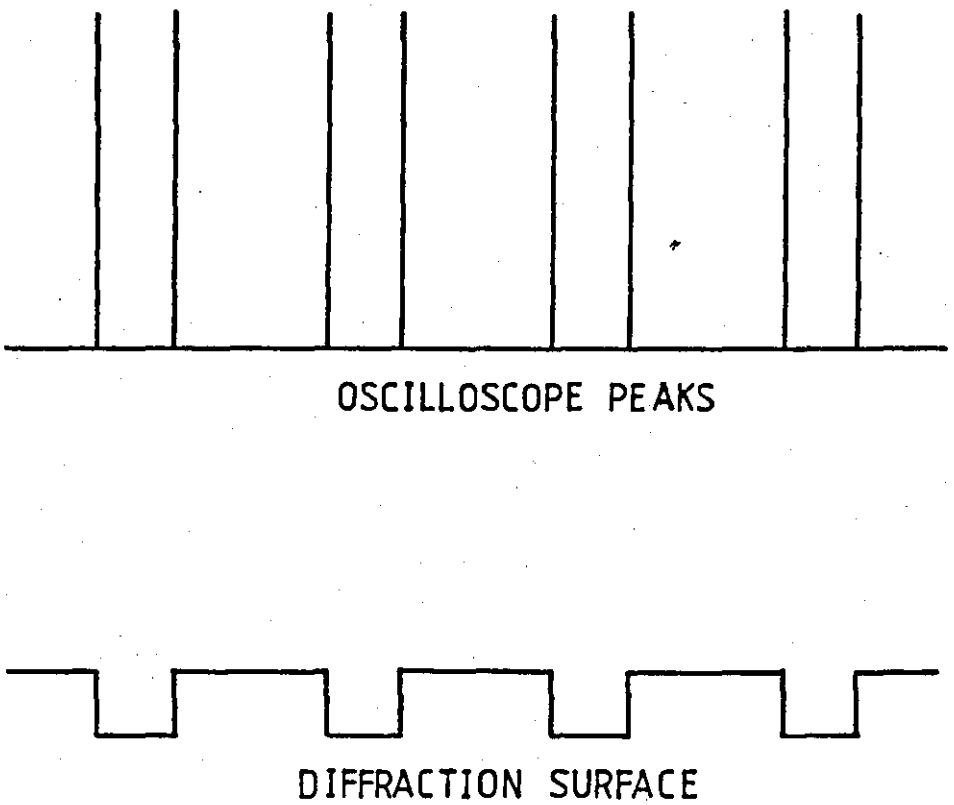
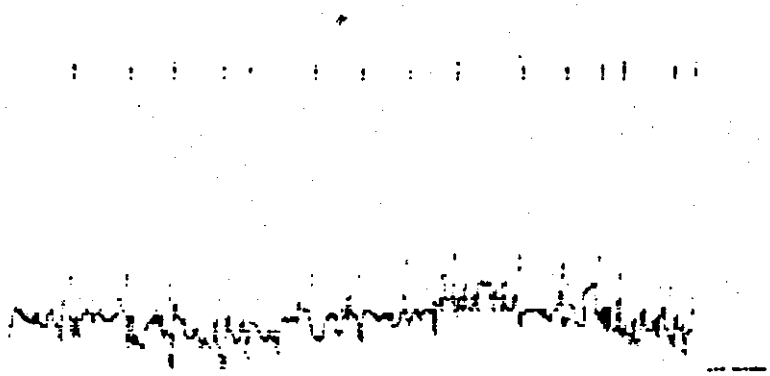


Fig. 2.24 Oscilloscope peaks from a diffraction grating.

TEST NUMBER SE2



TEST NUMBER SE2

THRESHOLD.	NO'OF PEAKS.	MEAN HEIGHT.	VARIANCE.	STD DEVIATION.
93	15	40.602	77.51	8.847

Fig. 2.25 Hard copy trace of the Standard Sample

$$C = \frac{n \times \bar{h} \times s}{t \times 100} \qquad 2.10$$

where

C = composite parameter
n = number of peaks
$\bar{h}$ = mean height of the peaks
s = standard deviation
t = threshold

Results from these are used to express the dispersion index of the carbon black in silicone compounds, and an example of which is as shown in table 2.12.

TABLE 2.12 DFRLM/OSCILLOSCOPE DATA OF CONDUCTIVE SILICONE RUBBERS

TEST NUMBER	THRES-HOLD (t)	NUMBER OF PEAKS (n)	MEAN HEIGHT (h)	VARIANCE (v)	STANDARD DEVIATION (s)	DISPERSION INDEX $C = \frac{nhs}{t \times 100}$
Vulcan P						
5	31.00	17.00	33.202	244.853	18.492	3.33
10	39.40	20.10	25.157	219.52[illegible]	18.715	2.38
15	44.00	24.90	22.924	194.694	14.107	1.83
20	47.25	28.20	23.221	109.097	13.996	1.94
25	49.85	32.40	20.[illegible]	86.233	10.600	1.46
30	50.25	34.60	24.[illegible]	55.006	7.[illegible]	1.20
Shawinigan						
5	28.90	16.00	53.066	299.047	14.966	4.43
10	32.80	17.70	46.067	233.618	16.372	4.07
15	48.40	19.50	43.551	252.5[illegible]	20.928	3.70
20	56.60	21.00	34.497	174.835	21.017	2.69
25	57.90	22.10	34.897	142.446	16.594	2.21
30	62.40	23.40	34.550	76.223	11.1[illegible]	1.45
35	62.95	24.70	34.606	71.032	10.22[illegible]	1.39
Ketjenblack EC						
4	23.00	19.60	24.227	31.196	7.603	1.57
6	25.60	22.30	24.200	26.960	6.522	1.38
8	28.10	24.90	24.340	22.582	5.756	1.25
10	28.80	25.80	23.800	20.915	5.625	1.18
12	29.05	27.80	22.320	19.02[illegible]	5.290	1.13
14	31.40	28.60	22.334	16.7[illegible]	5.216	1.06
16	33.80	29.90	22.506	14.52[illegible]	4.948	0.98
18	35.40	31.10	21.917	12.59[illegible]	4.635	0.89
20	37.00	32.20	21.352	10.282	4.255	0.78

III PEROXIDE CURE SYSTEMS FOR ORGANOPOLYSILOXANES

3.1 INTRODUCTION

The use of organic peroxide as a crosslinking agent for an elastomer was first reported by Ostromyslenski[242] in 1915. In his work, benzoyl peroxide was used to cure Natural Rubber (NR). Later, additional peroxides, *e.g* dicumyl peroxide, were used to cure Natural Rubber.[243-245] The vulcanisate produced, however, had inferior mechanical properties, but superior ageing and lower compression set. Hence, the commercial use of peroxides was small and employed only where the presence of sulphur would be deleterious.

Introduction of saturated polymers, for which the usual accelerated sulphur systems are unsuitable, generated interest in the use of peroxides as crosslinking agents. These saturated rubbers, *e.g* Polydimethylsiloxane (PDMS), are generally more resistant to ageing, more thermally stable and useful in more severe operational conditions. Hence, an extensively detailed study of peroxides has been carried out [52] and several books published.[246-249]

Before looking into the efficiency and basic mechanisms of crosslinking PDMS by peroxides, a scrutiny of the classification of peroxides will be an advantage.

3.1.1 CLASSES OF PEROXIDES [154]

The organic peroxides generally decompose by initial oxygen-oxygen bond cleavage to produce two free radicals:

$$ROOR' \xrightarrow{\Delta} RO^* + {}^*OR' \qquad 3.1$$

However, structural differences affect peroxide activities and these are related to three main factors:

a. the relative stability of radicals formed, *i.e* the more stable the radicals formed, the less stable is the peroxide.
b. steric factors, *i.e* higher strained peroxides will be less stable, since decomposition relieves steric strain.
c. electronic effects:where electron withdrawing functions *e.g* CF_3, NO_2, F, Cl,*etc* stabilize peroxides, and the electron donating functions *e.g* CH_3-, CH_3O-, *etc* destabilize peroxides.

These factors manifest themselves in the E and A factors in the Arrhenius first order equation:

$$k = A_{exp}^{(-E/RT)} \qquad 3.2$$

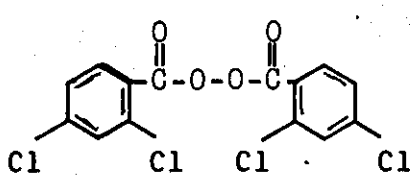
where

k = velocity constant dependent on the rate constant
R = Gas constant
A = (velocity coefficient) can be estimated
E = activation energy
T = Temperature in ^0K

The peroxide commonly available and superficially suitable for crosslinking polymers generally and silicone rubber specifically can be divided into three main classes: diacyl, peroxyesters and dialkyl peroxides.

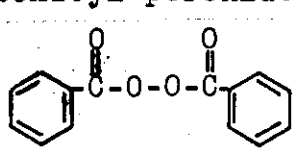
3.1.1.1 Diacyl peroxides: Examples of these are:

a. Bis(2,4-dichlorobenzoyl)peroxide.



54°C

b. Dibenzoyl peroxide



73°C

**Figures in ☐ represent the temperature at which the peroxide is 50% decomposed in 10hrs i.e TEN-HOUR HALF LIFE ($t_{\frac{1}{2}}$) TEMPERATURES.*

The benzoyl peroxide derivative without ortho-substituents are more stable than its ortho-substituted analogue benzoyl peroxide, *e.g* bis(2,4-dichloro benzoyl)peroxide. This is due to the so-called "ortho-effect" possibly involving both electronic and steric effect.

The activity relationship with structure can best be correlated with the relative stability of the radicals generated from the peroxide. Although peroxides cleave at the oxygen-oxygen bond, other bond cleavages can and do occur either simultaneously with (or sequentially to) the oxygen-oxygen bond breaking.

With diacyl peroxides, oxygen-oxygen bond breaking alone would produce two acyloxy radicals

$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O^* + {}^*O-\overset{O}{\overset{\|}{C}}-R' \qquad 3.3$$

The acyloxy radicals formed can undergo decarboxylation:

$$R-\overset{O}{\overset{\|}{C}}-O^* \longrightarrow R^* + CO_2 \qquad 3.4$$

The decarboxylation rate depends primarily upon three factors: temperature, pressure, and the relative stability of the R* radical formed. The more stable the radical R* the faster the decarboxylation and also the less stable is the diacyl peroxide.

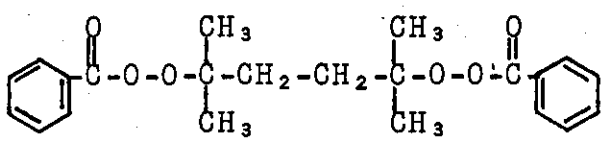
The relative stability of the radicals can be correlated to the hydrogen bond dissociation energies [250] of the parent compound (table 3.1). The higher the bond dissociation energy the less stable (*i.e* the more reactive) is the corresponding radical formed by removing the hydrogen atom. The stability of the alkyl radicals are in the order of Phenolic > benzylic > allylic > tertiary > secondary > primary

TABLE 3.1 BOND DISSOCIATION ENERGIES [250]	
PARENT COMPOUND	BOND DISSOCIATION ENERGY ($kJmole^{-1}$)
R_3C - - - - - H	381.00
R_2CH - - - - - H	397.75
RCH_2 - - - - - H	410.31
CH_3 - - - - - - H	435.43
C_6H_5 - - - - - H	468.92

Decarboxylation of dibenzoyl peroxide can occur subsequently to peroxy bond breaking depending on the environment. Works carried out [251,252] proved decarboxylation occuring at 30°C and 80°C respectively, if the acyloxy radicals formed are not quickly scavenged. This type of reaction is referred to as ionic cleavage of the radicals [245] resulting in self-destruction of the peroxide without the free radical formation being sufficiently stable to produce crosslinking. Hence (up to 10phr) a higher percentage than the theory of peroxide proportions is required to produce enough undecarboxylated radical for effective crosslinking.

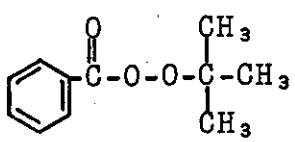
3.1.1.2 <u>Peroxyesters</u>: Examples of these are:

a. 2,5-dimethyl-2,5-bis(benzoyl peroxy)hexane



100°C

b. Tertiary butyl perbenzoate



105°C

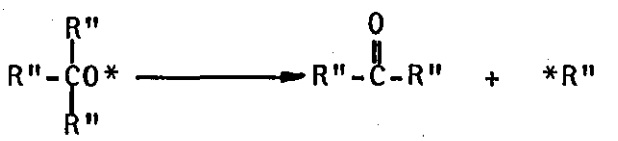
Peroxyesters can form acyloxy radicals upon cleavage of the peroxy bond:

$$R-\overset{O}{\overset{\|}{C}}-O-O-R' \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O^{*} + {}^{*}OR' \qquad 3.5$$

Again, the stability of the radical formed on decarboxylation of the acyloxy radical correlates with the activity of the radical. Peroxyesters are significantly more stable than the diacyl peroxides derived from the same carboxylic acids, and of which peroxybenzoates are most stable, due to the high activity of the phenyl radical. Also as important is the electronic effects. Peroxyesters also generate tertiary-alkoxy radicals (R'O*) upon cleavage of the peroxy bond. The nature of the tertiary R' group plays a secondary role in determining the activity of the peroxyesters. The order of stability is t-butyl > t-amyl > t-octyl > t-cumyl.

Diperoxyesters derived from 2,5-dimethyl-2,5-dihydroperoxy hexane are more reactive than the corresponding t-butyl peroxyesters primarily due to combined electronic and radical stability effects.

Alkoxy radicals undergo a subsequent reaction known as a beta scission reaction:



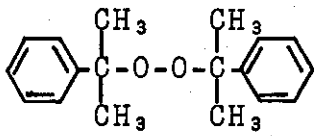
3.6

The production of a more stable *R" radical boosts the scission reaction, sometimes occuring simultaneously with peroxy bond breaking. This may partially account for the fact that the higher tertiary alkyls are less stable than the t-butyl peroxyesters because of the methyl radical (from beta scission of the tertiary butoxy radical) is more reactive than other primary-alkyl radicals (see Table 3.1).

Since the methyl radical is about as reactive as the alkoxy radical, beta scission is probably not involved in the transition state of t-butyl and t-cumyl peroxyester decompositions. Cumyloxy radicals undergo beta-scission exclusively to acetophenone and methyl radical. The low thermal stability of cumyl peroxyesters is, therefore, attributed to other factors, primarily electronic. The beta scission reaction is also temperature dependent *i.e* more scission occurs if the alkoxy radical is generated at a higher temperature.

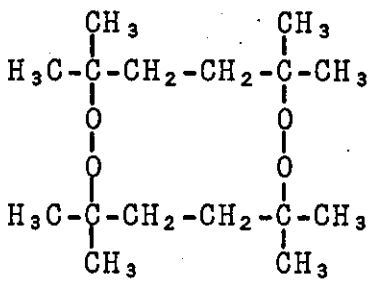
3.1.1.3 <u>Dialkyl peroxides</u>: Examples of these are:

a. Dicumyl peroxide



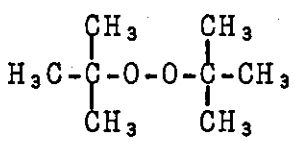
115°C

b. 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane



119°C

c. Di-t-butyl peroxide



126°C

Dialkyl peroxides generate two alkoxy radicals upon cleavage of the peroxy bond:

$$ROOR' \longrightarrow RO^* + {}^*OR' \qquad 3.1$$

These are the most stable of the organic peroxides. The activity of the dialkyl peroxides, is affected by the nature of the 'R' groups and correlates somewhat with their electron donating (or withdrawing) ability.

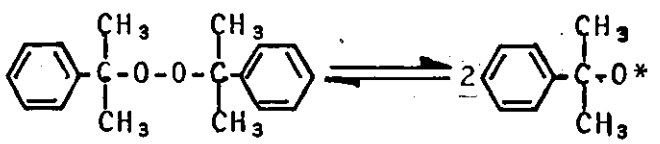
Other new free radical initiators recently employed in vulcanising silicone elastomers include: (cf. Table 1.9 of Chapter 1, section 1.3.3.2.1.3)

a. hexylene glycol-benzoate perbenzoate [253]
b. t-alkyl peroxyalkyl carbonates [158,159]
c. hydroxymethyl t-butyl [152]
d. oxazidrines [161]
e. dinitroso aromatic compounds [162]
f. 1,2-diphenyl-1,2-dimethoxy ethane [163]
g. t-butyl-2-hydroxyethyl peroxide [160]

3.1.2 PEROXIDE CROSSLINK EFFICIENCY

Dialkyl peroxides and t-butyl perbenzoate give high crosslink efficiency in gum rubbers. But only t-butyl and dicumyl peroxides are capable of curing compounds containing reinforcing carbon black fillers. The dicumyl peroxide, a non-volatile solid compound, is, however, most generally used.

The decomposition as studied in a wide variety of solvents, has been shown to occur by a first order mechanism, the rate of which is essentially independent of the solvent.[245,254-256] Its decomposition in the rubber has also been quite extensively studied[257,258] and again a first order reaction is observed over a wide range of concentration and temperature. An example is the decomposition mechanism of dicumyl peroxide in a neutral or basic medium yielding free radicals[259]:

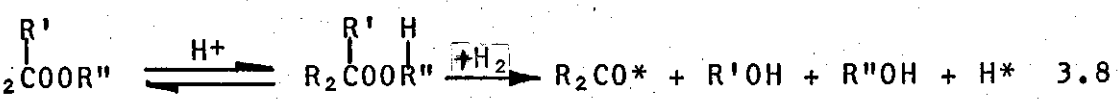


3.7

dicumyl peroxide cumyloxy radical

Failure of some peroxides to obtain a satisfactory cure in the presence of certain fillers, notably some blacks and silica, are claimed to result in part from the:

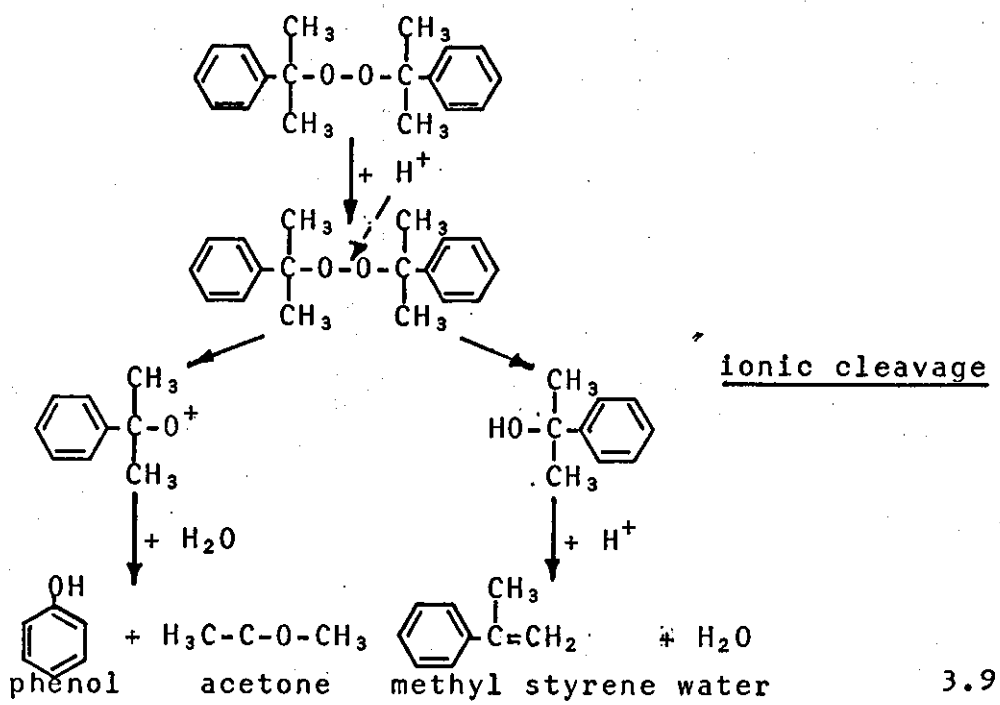
a. catalysed, non-radical breakdown of the peroxide by a mechanism[260] such as:



3.8

which readily occurs in hydroperoxides and diacyl peroxides

b. induced decomposition of peroxide radicals in the presence of acidic radicals from e.g channel blacks. An example of this is the decomposition mechanism of dicumyl peroxide in an acidic media[259]:



3.9

c. adsorption of peroxides unto filler surfaces.

d. radical wastage reactions [261] :

$$ROOR' \xrightarrow{\Delta} RO^* + {}^*OR'$$

$$RO^* + PH \longrightarrow P^* + ROH \quad (1)$$

$$RO^* + R^* \longrightarrow ROR \quad (2)$$

$$RO^* + P^* \longrightarrow ROP \quad (3)$$

$$RO^* + {}^*OR \longrightarrow ROOR \quad (4)$$

$$P^* + {}^*P \longrightarrow PP \quad (5)$$

Reactions 1,2,3, and 4 are radical wastage reactions. While reaction 3 is an example of chain scission, chain termination or short chain, reaction 5 is an example of crosslinking of two polymer radicals.

e. combination of primary peroxide radicals

f. decarboxylation.

The methyl group forms the weak spot in PDMS structure under oxidative conditions. The methyl groups are, therefore, replaced with more reactive groups, *e.g* pendant vinyl, to improve curing and other groups, *e.g* phenyl, fluoropropyl, cyanomethyl *etc*, to improve ageing and solvent resistance.

PDMS are normally cured with diacyl peroxides, but, with a low crosslink efficiency. This is due to their inability to

abstract hydrogen rapidly enough from the methyl side group of silicone polymer. However, the most commonly used diacyl peroxides are bis(2,4-dichloro benzoyl)peroxide, and benzoyl peroxide. Post cure in circulating air oven is required to remove accumulated acidic material of polymerization and cure which can act as a degradant during use. Their action is presumably accelerating hydrolytic breakdown of the polymer backbone. This can, however, be offset by the polymer purification, and use of peroxides giving nonacidic products.[262] Crosslinking reaction results from hydrogen abstraction from the methyl group of the polymer, followed by the combination of the polymeric radicals in suitable conditions.

The above difficulties of low crosslinking efficiency and acidic decomposition products, where acyl peroxides are obviously considerable, prompted preparing polysiloxanes containing small concentrations of vinyl groups (<1.0 mole%) which have better curing characteristics. The methylvinyl polysiloxanes are curable by all the usual peroxides[30,52,70,263] with identical degree of efficiencies in several cases.[157] Crosslink efficiencies of benzoyl peroxide[264,265] and t-butyl perbenzoate [52] are shown in tables 3.2 and 3.3 respectively.

TABLE 3.2 CROSSLINKING EFFICIENCIES OF BENZOYL PEROXIDES IN SILICONE RUBBERS

Weight % Peroxide	0.0 mole % methylvinyl		0.1 mole % methylvinyl		0.2 mole % methylvinyl	
	A	B	A	B	A	B
0.472	-	0.150	-	0.318	1.360	0.528
0.750	0.138	-	0.333	-	0.492	-
1.000	-	0.068	-	0.155	0.462, 0.810	0.305
1.500	0.085	-	0.202	0.139	0.354, 0.580	-
2.000	-	0.051	0.167	-	0.420	-
3.000	0.053	-	-	-	-	-

A = Bis(2,4-dichloro benzoyl)peroxide; B = Benzoyl peroxide

TABLE 3.3 CROSSLINKING EFFICIENCIES OF t-BUTYL PERBENZOATE IN SILICONE RUBBERS: (Shown here as moles of crosslinks per mole of peroxide).

Peroxide Concentration (%)	Vinyl concentration (mole %)			
	0	0.0714	0.1428	0.3330
0.05	0.592	5.6420	7.8660	10.1800
0.50	0.460	1.0180	1.6120	2.4040

3.1.3 SUGGESTED BASIC MECHANISMS OF CROSSLINKING POLYDIMETHYL SILOXANES (PDMS) BY PEROXIDES

An essential function of any peroxide in curing a rubber is the production of free radicals. The common method in the rubber industry of causing this free radical formation is by heating the peroxide molecule, in a non-acidic atmosphere. The peroxide then decomposes into two alkoxy radicals (equation 3.1). These free radicals thus produced then react with the rubber chain leading eventually to a chemically crosslinked network.

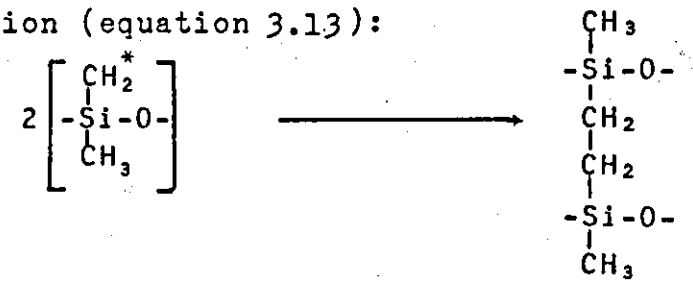
Early papers [52,63,70] on peroxide crosslinking show two important routes in which polysiloxanes and free radicals may react: by hydrogen abstraction from a methyl group [63] (equation 3.10) and by addition to the vinyl group [63,70] (equation 3.11):

$$ROOR \xrightarrow{\Delta} 2RO^* \qquad 3.1$$

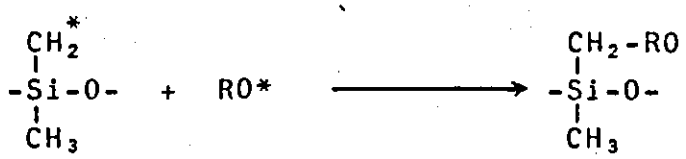
$$\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + RO^* \xrightarrow[\text{abstraction}]{\text{hydrogen}} \begin{array}{c} CH_2^* \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + ROH \qquad 3.10$$

$$\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH{=}CH_2 \end{array} + RO^* \xrightarrow{\text{addition}} \begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ {}^*CH \\ | \\ CH_2\text{-}OR \end{array} \qquad 3.11$$

In the case of reaction (equation 3.10), the polymeric radicals formed may then react by several paths leading to crosslinking (equation 3.12) or radical wastage/chain termination (equation 3.13):



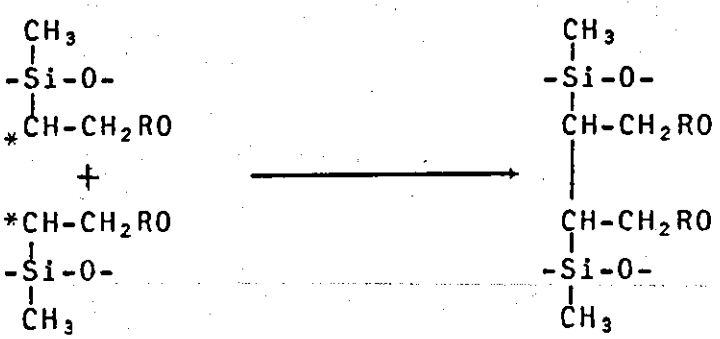
3.12



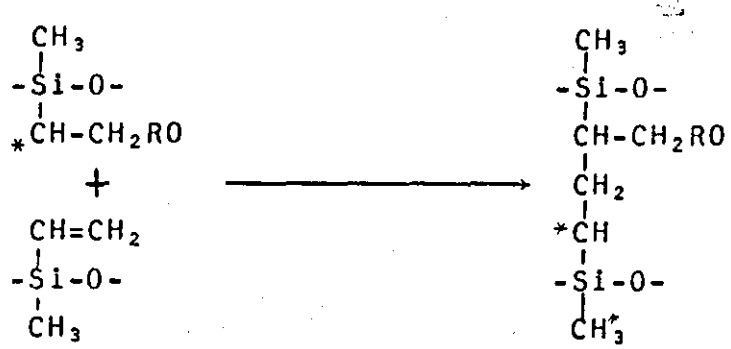
3.13

For an efficient use of peroxide (of structure ROOR) in crosslinking, the reaction(equation 3.13) must occur to only a small extent.

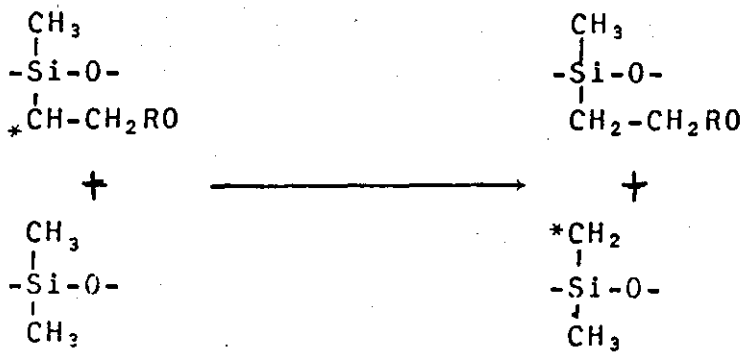
In case of reaction (equation 3.11), the polymeric radicals formed may then crosslink by pairwise combination (equation 3.14), addition to further vinyl groups (equation 3.15), hydrogen abstraction (equation 3.16), or a chain reaction (equation 3.17):



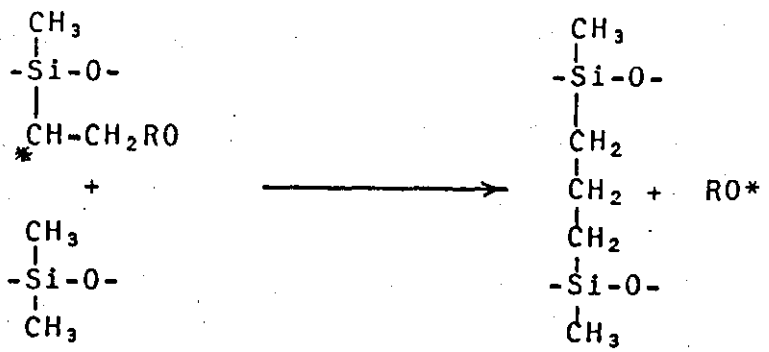
3.14



3.15



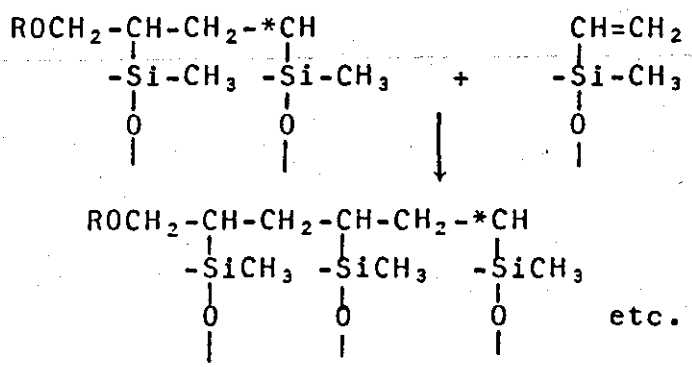
3.16



3.17

Scheme (equation) 3.14 requires the reaction of two vinyl groups for each crosslink unless the addition step occurs in which case at least at the extreme limit only one vinyl group is required.

Scheme (equation) 3.15 appears to be favoured in a continuous chain addition (equation 3.18):



3.18

However, with the observed crosslinking efficiency of $\leqslant 1.0$ % at realistic peroxide concentrations, a chain addition can probably be discounted. Also this scheme requires continuous vinyl group addition which is impossible in the presence of predominant dimethyl groups in the chain with fewer vinyl groups present.

For scheme (equation) 3.17 to apply, a substantial concentration of vinyl groups is needed, otherwise the higher crosslinking demanded is impossible to achieve.

Hence for a realistic efficient crosslinking reaction equation 3.14 is favoured.

3.2 OBJECTIVES

a. To carry out a preliminary investigation on the degree of vulcanisation, volume resistivity and hardness using different peroxides; and also to assess the maximum degree of vulcanisation obtained from different peroxide loading, in highly carbon black loaded silicone rubber. The commercial conductive Silastic Q4-1602 (see table 2.2) compound is to be used as a control mix.

b. To assess the effect of increasing carbon black loading on the crosslink efficiency of the peroxide cure.

c. To improve the peroxide crosslinking efficiency, if necessary, by compound modification; and also assess the effect of this compound modification on the volume resistivity of the modified compounds.

3.3 EXPERIMENTAL

3.3.1 MATERIALS (see also Ch.2, Section 2.1)

a. Polymers

Silastic GP30, and Silastic Q4-1602

b. Curing Agents (Peroxides)

Dicumyl Peroxide: 95% active Perkadox SB: 1.05pbw≡1.0phr

2,5-dimethyl-2,5-di(t-butyl peroxy) hexane: 50% active Varox: 2.0pbw≡1.0phr

a,a-bis t-peroxy diisopropyl benzene: 100% active Vulcup 14R: 1.0pbw≡1.0phr

2,4-dichloro benzoyl peroxide: 50% active Perkadox PDS50: 2.0pbw≡1.0phr

Catalyst B

c. Representative Conductive Carbon blacks

Furnace	Vulcan P
Acetylene	Shawinigan
Special Furnace blacks	Ketjenblack EC

3.3.2 MIX FORMULATION

Table 3.4 shows the detailed mix formulation.

TABLE 3.4 MIX FORMULATIONS

Mix Number	1	2	3	4	5
Silastic Q4-1602	← 100.0 →				
Catalyst B	4.0	-	-	-	-
Perkadox SB	-	1.0	-	-	-
Perkadox PDS	-	-	1.0	-	-
Varox	-	-	-	1.0	-
Vulcup 14R	-	-	-	-	1.0

Mix Number	6	7	8	9	10	11	12	13	14	15	16	17
Silastic GP30	← 100.0 →											
Vulcan P	← 30.0 →				-				-			
Shawinigan	-				← 30.0 →				-			
Ketjenblack EC	-				-				← 20.0 →			
Perkadox SB	1.0	-	-	-	1.0	-	-	-	1.0	-	-	-
Perkadox PDS	-	1.0	-	-	-	1.0	-	-	-	1.0	-	-
Varox	-	-	1.0	-	-	-	1.0	-	-	-	1.0	-
Vulcup 14R	-	-	-	1.0	-	-	-	1.0	-	-	-	1.0

Mix Number	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Silastic GP30	← 100.0 →														
Vulcan P	← 30.0 →					-					-				
Shawinigan	-					← 30.0 →					-				
Ketjenblack EC	-					-					← 20.0 →				
Perkadox SB	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	2.5	3.0

Mix Number	33	34	35	36	37	38	39	40	41	42	43	44
Silastic GP30	← 100.0 →											
Vulcan P	← 30.0 →											
Perkadox SB	← 2.5 →											
Triallyl Cyanurate	0.5	1.0	1.5	2.0	-	-	-	-	-	-	-	-
Ethylene Glycol	-	-	-	-	1.0	2.0	3.0	4.0	-	-	-	-
Titanate KR44	-	-	-	-	-	-	-	-	0.5	1.0	1.5	2.0

3.3.3 MIXING

This was carried out as described in Ch.2, Section 2.2.1.

3.3.4 VULCANIZATION

This was carried out as described in Ch.2, Section 2.2.2

3.3.5 EVALUATION OF VULCANISATE PROPERTIES

3.3.5.1 Electrical Volume Resistivity Measurement

This was carried out as described in Ch.2, Section 2.2.4

3.3.5.2 Hardness (IRHD) measurement

This was carried out in accordance with BS 903 Part A26: 1969.

3.4 RESULTS AND DISCUSSIONS

A summary of the vulcanisate properties of Silastic Q4-1602 and Silastic GP30 based compounds is shown in Table 3.5 (The results are based on 4 samples of each mix).

3.4.1 EFFECT OF PEROXIDE TYPE ON SILICONE BASED COMPOUNDS

3.4.1.1 Silastic Q4-1602 (Control Compounds)

Fig. 3.1 gives a comparison of volume resistivity and hardness obtained from different types of catalyst/peroxides used in the investigation. Mix Nos. 1-5 of Table 3.5 give a comparable summary of the results when 4phr of Catalyst B (recommended) and 1.0phr of the other peroxides are used.

Significantly higher cure rate and less cure time, suitable for rapid cures and Hot Air Vulcanisation (HAV), was shown by Catalyst B over other peroxide cures. But coupled with this was the reversion phenomenon, fig.3.2, possessed by Catalyst B which was a disadvantage when compared with the peroxide plateau type cures. This might offer an explanation for the reversion experienced with Silastic Q4-1602 cured with Catalyst B as apparently a rapid deterioration in the

TABLE 3.5 VULCANISATE PROPERTIES OF CONDUCTIVE SILICONE RUBBERS

Mix No	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
Silastic Q4-1602 mixes				
1	5.00	1.75	2.49 ± 0.40	61
2	0.86	8.70	2.20 ± 0.30	62
3	-	-	-	-
4.	0.49	11.65	2.70 ± 0.40	58
5	0.61	10.70	2.50 ± 0.50	60
Silastic GP30 mixes				
6	0.52	11.40	2.65 ± 0.30	56
7	-	-	-	-
8	0.27	16.20	3.00 ± 0.40	52
9	0.40	12.40	3.10 ± 0.50	58
10	0.98	7.75	2.40 ± 0.30	50
11	-	-	-	-
12	0.48	11.70	2.90 ± 0.50	48
13	0.62	10.60	3.00 ± 0.50	52
14	0.72	9.80	2.40 ± 0.20	55
15	-	-	-	-
16	0.42	12.20	3.50 ± 0.40	54
17	0.54	11.25	4.20 ± 0.40	56
18	0.50	11.55	2.70 ± 0.30	52
19	0.63	10.50	2.50 ± 0.30	53
20	0.78	9.35	2.46 ± 0.40	55
21	1.06	7.10	2.44 ± 0.20	57
22	1.40	5.00	2.42 ± 0.20	62
23	0.97	7.90	2.60 ± 0.30	48
24	1.01	7.50	2.56 ± 0.30	50
25	1.05	7.20	2.55 ± 0.20	53
26	1.21	5.90	2.48 ± 0.20	55
27	1.22	5.85	2.46 ± 0.20	60
28	0.78	9.75	2.42 ± 0.20	56
29	0.76	9.50	2.40 ± 0.20	58
30	0.80	9.20	2.40 ± 0.20	59
31	0.83	8.95	2.36 ± 0.20	62
32	0.83	8.95	2.36 ± 0.20	74
33	1.43	5.00	2.80 ± 0.50	58
34	1.84	4.50	2.45 ± 0.40	63
35	1.86	4.50	2.40 ± 0.20	68
36	1.92	4.50	2.40 ± 0.20	72
37	1.24	5.70	3.46 ± 0.40	56
38	1.40	5.00	4.20 ± 0.40	54
39	1.56	4.70	4.60 ± 0.50	50
40	1.60	4.70	5.40 ± 0.60	48
41	1.06	7.10	3.50 ± 0.40	54
42	1.12	6.65	3.30 ± 0.40	56
43	1.24	5.70	3.30 ± 0.30	60
44	1.40	5.00	2.80 ± 0.20	64

Fig. 3.1 Comparison of Volume Resistivity and Hardness of Silastic Q4-1602 silicone rubber. (Ref. Mix numbers 1-5 of Table 3.5)

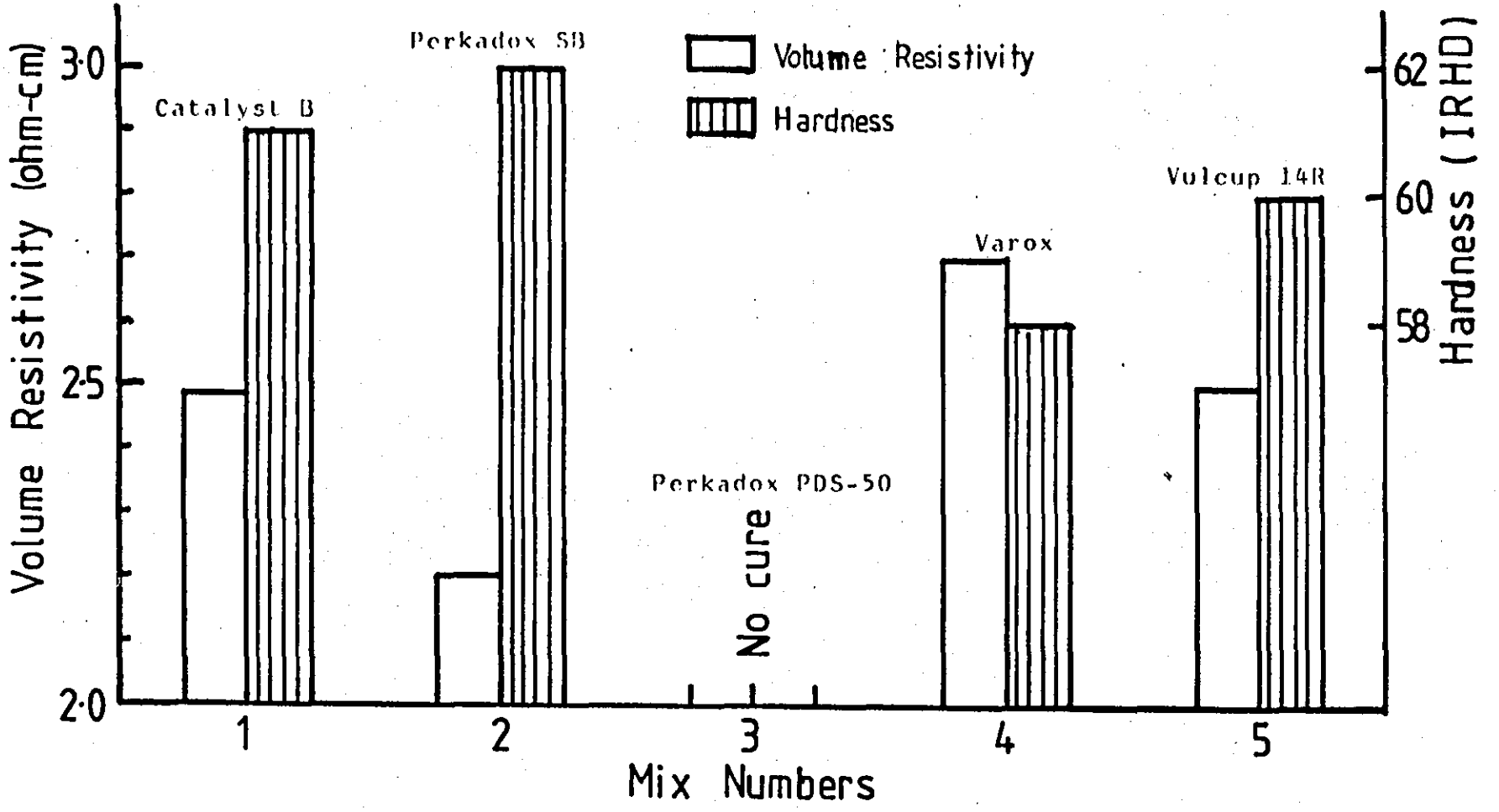
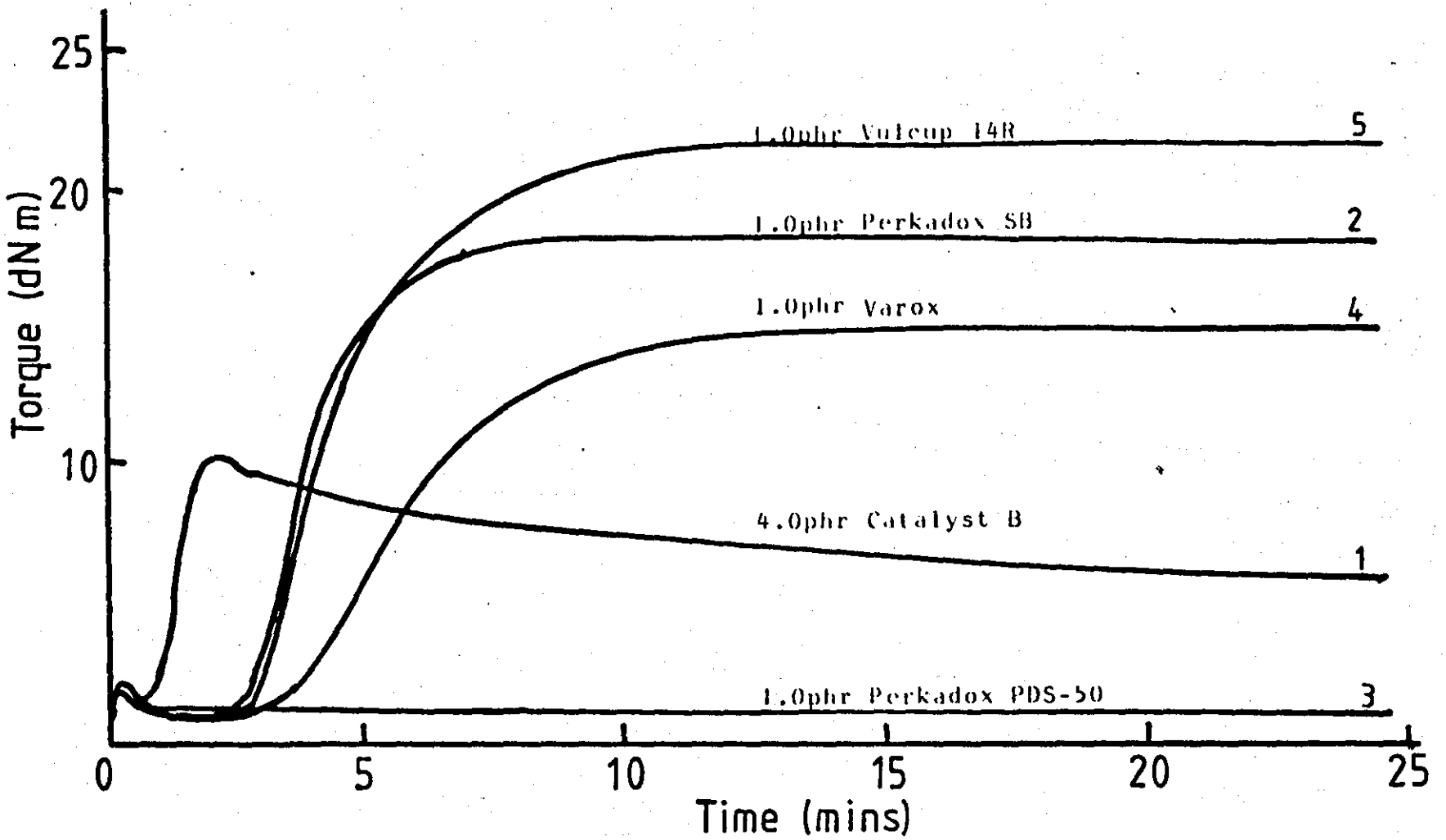


Fig. 3.2 Curing characteristics of Silastic Q4-1602 compounds @ 170°C. (Ref. Mixes 1-5 of Table 3.5)



vulcanisate properties occurs due to deterioration when the temperature of the mix during cure reaches a critical temperature that accelerates deterioration in the vulcanisate. Even when cured at temperatures as low as 130°C, the reversion reaction was still evident, and the surface deterioration of the vulcanised test pieces at 30 seconds over the calculated cure time was noticed and recognised by excessive surface stickiness. Use of lower concentrations of Catalyst B resulted in severe undercure.

The vulcanisate hardnesses, a measure of flexibility, were all in the range of 58-62 IRHD.

It is interesting to note that Catalyst B cured vulcanisate gave a 2.49 ± 0.40 ohm-cm volume resistivity compared with the standard 2.50 ohm-cm given in the Silastic Q4-1602 Catalyst B cured specification. The Dicumyl peroxide cured vulcanisate gave the lowest volume resistivity of 2.20 ± 0.30 ohm-cm. In fact, Dicumyl peroxide featured predominantly in all other different silicone based vulcanisates, and hence, its choice as the standard catalyst for all the highly black-loaded compounds investigated.

Bis(2,4-dichloro benzoyl)peroxide, in carbon black filled silicones, even with as high as 10.00phr loading results in unvulcanised compound. This phenomenon also featured in all carbon black loaded compounds (cf. Mix Nos 7, 11, and 15) suggesting that it is unsuitable for such cures. Other steps that were used experimentally to try and remedy this problem are now listed:

a. lower (120°C) vulcanisation temperature to lessen the decarboxylation rate of the peroxide free radical common to diacyl peroxides.
b. lower (5%) carbon black concentration, coupled with a lower (120°C) vulcanisation temperature and a 10.00phr of peroxide.

c. carbon free radical scavengers (antioxidant diphenylamine) thoroughly blended with the carbon black before mixing with peroxide containing PDMS.
d. more basic environment: addition of zinc oxide and ethylene glycol to counteract any acidic reaction product.
f. graphitized carbon black.

No successful vulcanised rubbers were obtained with any of these techniques.

All compounds were hot-air-oven cured at 200°C. Visual inspection showed porosity due to entrapped air. Surface deterioration features predominated with the Catalyst B-cured vulcanisates.

3.4.1.2 Silastic GP30 based compounds

To investigate the effect of peroxide type on PDMS, Silastic GP30 was chosen as the base polymer. Three representative conductive blacks (furnace, acetylene, and 'special' furnace black) were chosen to cover the range. Compounds highly filled with conductive carbon blacks were used in this exercise for comparative purposes. Peroxide concentration was limited to 1.0phr in all compounds.

Mix Nos 6-17 of Table 3.5 and fig. 3.3 are considered in this exercise. The pre-eminence of dicumyl peroxide in giving the lowest volume resistivity when compared with the other peroxide cures was demonstrated. It also gave the fastest cure rate and the shortest cure time. Hence dicumyl peroxide was chosen for all the subsequent investigations. The hardness investigated was 48-56 IRHD.

Comparing some of the various Perkadox SB (dicumyl peroxide) vulcanisates of Table 3.5, there was found to be a variation in the volume resistivity and hardness due to the carbon black type, although this was comparatively small as shown in Table 3.6.

Fig. 3.3 Comparison of Volume Resistivity and Hardness of Silastic GP30 vulcanizates. (Ref. Mix Nos 6-17 of Tables 3.4 & 3.5)

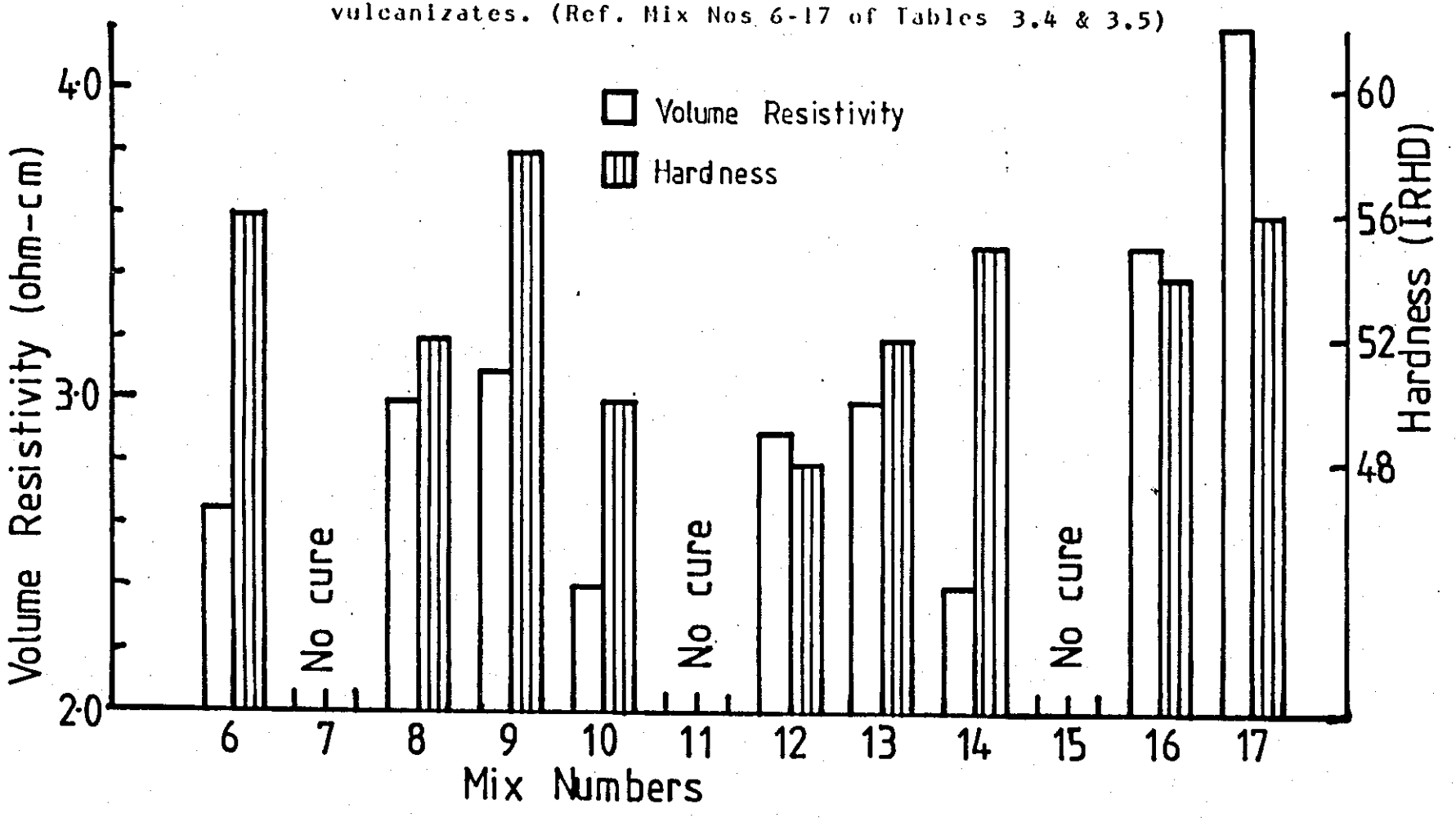


TABLE 3.6 COMPARISON OF PERKADOX SB CURED CARBON BLACK FILLED VULCANISATES

Mix No	Carbon black Type	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
6	Vulcan P	0.52	11.40	2.65 ± 0.30	52
10	Shawinigan	0.98	7.75	2.40 ± 0.30	50
14	Ketjenblack EC	0.72	9.80	2.40 ± 0.20	55

It is interesting to note that an equal volume resistivity is obtained with comparatively less Ketjenblack EC (20.0phr) than Shawinigan (30.0phr).

3.4.1.3 Perkadox SB cured Silastic GP30 based compounds

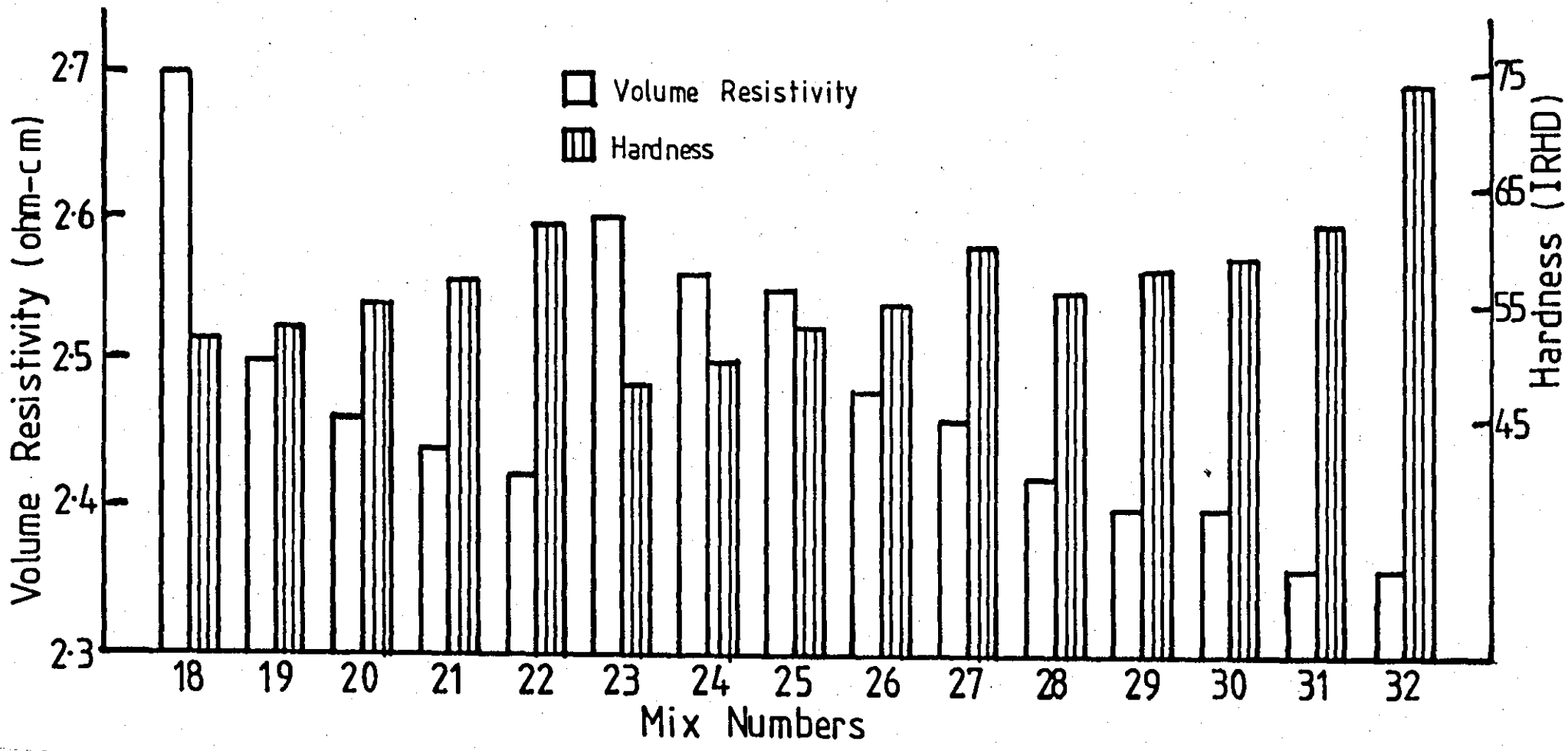
Fig. 3.4 gives a comparison of volume resistivity and hardness obtained from investigating the concentration of Perkadox SB required to give the maximum degree of vulcanisation. Mix Nos 18-32 of Table 3.5 give a comparative summary of the results.

The 2.5phr and 3.0phr gave the highest and nearly the same rate of, and optimum, cure (Table 3.7). But the Ketjenblack EC vulcanisate containing 3.0phr of Perkadox SB were very hard and brittle, while, those containing 2.5phr remained flexible. The volume resistivities of both were the same and with similar volume resistivity variation. Hence the choice of 2.5phr Perkadox SB for use in subsequent mixes.

TABLE 3.7 COMPARISON OF OPTIMUM EFFICIENCY OF PERKADOX SB IN CONDUCTIVE CARBON BLACK FILLED VULCANISATES.

Mix No	Carbon black Type	Cure rate (min^{-1})	Cure time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
21	Vulcan P	1.06	7.10	2.44 ± 0.20	57
22	"	1.40	5.00	2.42 ± 0.20	62
26	Shawinigan	1.21	5.90	2.48 ± 0.20	55
27	"	1.22	5.85	2.46 ± 0.20	60
31	Ketjenblack EC	0.83	8.95	2.36 ± 0.20	62
32	"	0.83	8.95	2.36 ± 0.20	78

Fig. 3.4 Comparison of Volume Resistivity and Hardness of Perkadox SB cured Silastic GP30 vulcanizates. (Ref. Mixes 18-32 of Tables 3.4 & 3.5)



3.4.1.4 Peroxide Hot Air Vulcanisable cures

One of the objectives of this research programme is to investigate the possibility of obtaining modified peroxide-cured, carbon black filled, suitable compounds for Hot Air Vulcanisation (HAV). Hence, some compound modifications to improve the crosslinking efficiency of the established Perkadox SB cured compounds, suitable for HAV cures were adopted.

Mix Nos 33-44 and fig.3.5 are considered in this exercise. Three types of modifiers are employed:

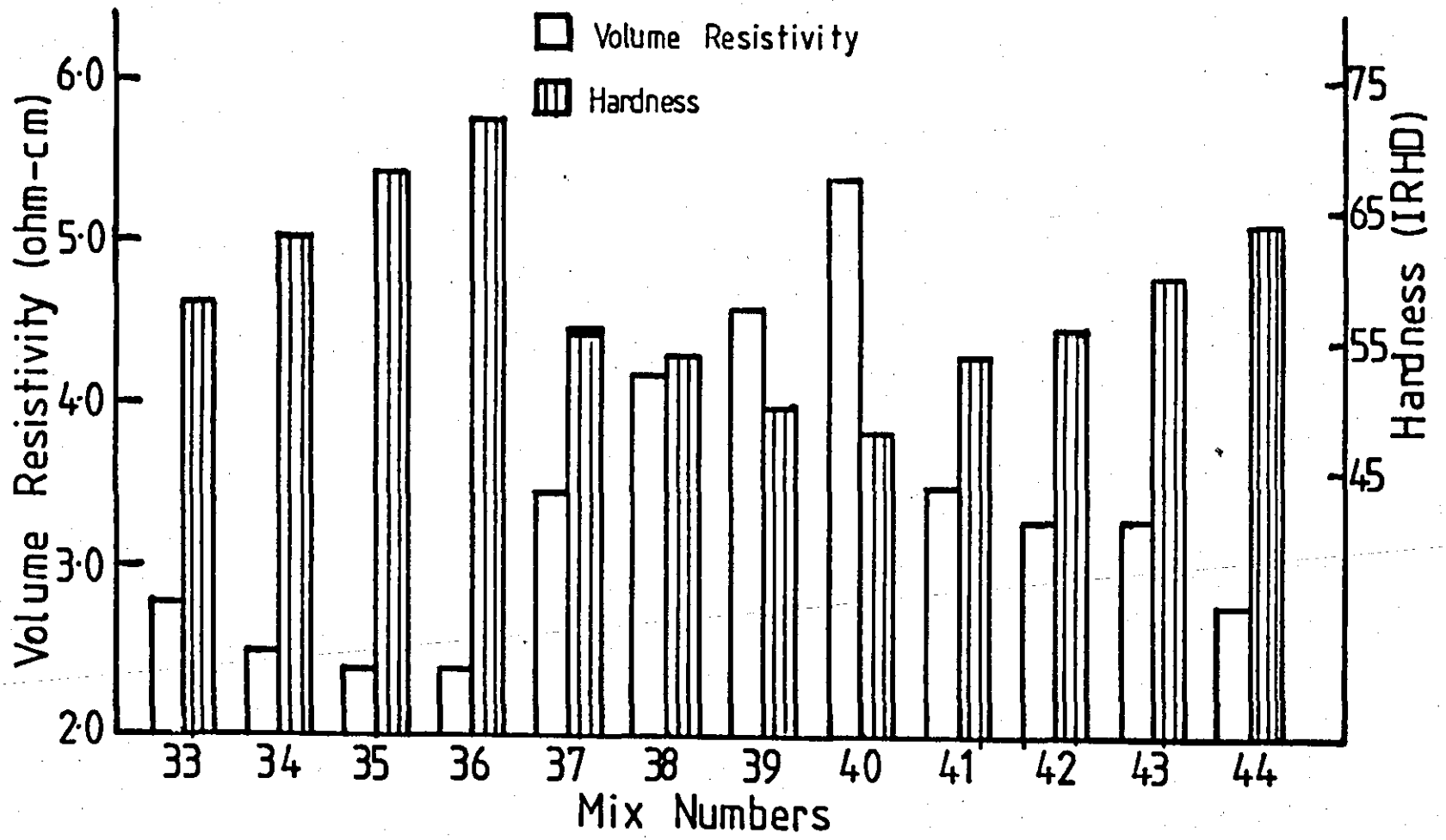
a. Triallyl Cyanurate - a bifunctional alkenyl compound - to serve as both a carbon black wetting agent and a vulcanisate properties improver. TAC is used as a coagent.
b. Ethylene Glycol - this is used as a carbon black wetting agent and a basic compound to counteract any acidic reaction product generated during vulcanisation.
c. Alkyl titanate KR44 - this is a compound recommended as a polymer-filler compound bridge, a carbon black wetting agent, and a material for improving the vulcanisate properties of compounds.

Coupling agent

From the results obtained the three 'modifiers' were observed to give increased cure rate coupled with decreased cure time compared with the non-modified compounds. However, none were good enough for HAV cures. The hardness and the volume resistivity improved with increased concentration of triallyl cyanurate and KR44, but for the ethylene glycol containing compounds, volume resistivity increased with increasing glycol concentration.

All compounds were hot air oven cured at 200°C. Visual inspection showed them to possess only a little porosity due to entrapped air; it was considered that no porosity was caused by the peroxide. It was also observed that there was less surface deterioration of the rubber due to oxidation when modifiers were present than in the non-modifier containing rubbers.

Fig. 3.5 Comparison of Volume Resistivity and Hardness of furnace black (Vulcan P) filled Silastic GP30 vulcanizates (Ref Tables 3.4 & 3.5)



3.5 CONCLUSIONS

Silastic Q4-1602, catalyst B cured, shows reversion properties and surface deterioration. This is considered to be the cause of its lack of consistency in the vulcanisate properties especially the volume resistivity.

Bis(2,4-dichloro benzoyl)peroxide, Perkadox PDS50, was found to be unsuitable for curing carbon black filled silicone rubbers.

Porosity obtained in hot air oven cured silicone rubber at 200°C was considered to be mainly due to entrapped air, and not to peroxide reaction products.

Dicumyl peroxide, Perkadox SB, gave balanced and better cured silicone rubbers, that have good cure state and volume resistivities. However, its cure rate is too slow to prevent the development of porosity inherent from trapped and dissolved air in the compound when HAV cured.

Increase in dicumyl peroxide proportions in carbon black filled silicone base has the following effects:

a. increases cure rate,
b. decreases cure time,
c. decreases volume resistivity, and
d. increases hardness.

IV PROCESSING CHARACTERISTICS OF CARBON BLACK FILLED CONDUCTIVE SILICONE RUBBERS

4.1 INTRODUCTION

Processing conditions, especially those involving a degree of shear of the polymer/filler mixture, have been claimed by many workers to have a considerable effect upon the electrical resistivity of polymers which incorporate conductive fillers, especially carbon blacks.

Morrell[267] in a review of electrical measurements, a measure characterising dispersion, has noted that the d.c resistivity passes through a minimum as dispersion efficiency progresses. This increased conductivity starts to occur at a very early stage (low) of dispersion and has been ascribed to the presence of the large carbon black aggregates being in close proximity to each other at this stage and thus possibly forming conductive paths. Penetration of voids in the carbon black by rubber also evidently increases conductivity and this is one of the phenomena claimed to be exhibited by the highly hollow shelled/porous type of carbon black e.g Ketjenblack EC, Conductex 40-220, and Philblack XE-2. As mixing progresses, some of the aggregates are broken up and gradually separated from each other and the corresponding electrical volume resistivity rises.

Several workers[268-271] have noted this phenomenon while yet others, without noting this 'minimum criterion' have noted an increase in electrical resistivity with dispersion[272-282]. While the majority of this experimental work has been carried out in the cured state, Boonstra,[283] Ford,[284] and Wan Idris [285] tested uncured samples with the same general findings but without any exponential increase being noted by the last worker for SBR; indeed this relationship was found to be linear in nature. Boonstra,[283] in addition, applied the statistics of variation to his resistivity observations and found, as with physical properties, the variation to fall progressively with mixing.

Usachev, *et al* [286] measured resistivity continuously by inserting two needle probes (the contacts) into the chamber of an internal mixer and found the differences in resistance between the two selected microareas fell to a low constant value as mixing approached completion.

A.C resistivity was measured on a series of mixes having different dispersions by Woods and Krosky.[287] Zaitseva, *et al* [288] and Fedyukin, *et al* [289] used the variability of attenuation of microwaves and ultra high frequency radio signals respectively, while Havenhill, *et al* [290] measured the electrostatic contact potential developed during processing in an internal mixer.

van Beek and van Pul [291] showed a decrease in resistivity with increasing dispersion. This is possibly associated with the breakdown of the large separated aggregates shown in their electron micrographs of the poorly dispersed blacks, while Ladd and Wiegand [292] showed the variation in residual degree of carbon black structure as dependent on the type of black. Gul' and Zhuravlev [266] showed that a low carbon conductive rubber can easily be produced from the 'relatively low vicosity' latex, as the carbon black structures are more easily formed in the absence of the structure destroying effect of milling/mixing procedure. Pil'menshtein, *et al* [293] recorded similar effects in films produced from polychloroprene latex containing acetylene black. It was claimed that for such latexes a conductivity was obtained of 3 to 4 orders of magnitude higher than from vulcanisates prepared from solid rubbers/polymers with the same carbon black content.

Kirschbaum [231] carried out a series of experiments on different polymers filled with various carbon blacks at two different loading levels. He concluded that for such vulcanisates, the deterioration in conductivity resulting from excessive stock working was dependent on the amount of mixing or total shear work applied, grade of carbon black and its loading, and the type of polymer.

Polley and Boonstra [294] noted that highly conductive blacks, e.g Vulcan XC72, possess, to a high degree, the ability to retain a certain amount of structure and to resist the dispersion action of the rubber during milling. This means that the tenacious structure of these blacks enable them to adequately retain their structure with less breakdown during mixing. Shenfil' *et al* [181] noted 'a much smaller extent' of the acetylene black structure breakdown in silicone rubber as compared with NR, resulting in a vulcanisate of higher (approx. 2 orders of magnitude) conductivity with the same acetylene loading. They further stressed that despite the poor dispersion, the conductivity of the vulcanisate is of the same order as that of films of natural rubber latex[293] into which the black is introduced in the form of aqueous dispersion. They further claimed that silicone rubber had the ability to retain a constant value of resistivity whilst undergoing a repeated processing cycle.

Wolfer [295] claimed that certain specific silicone rubber compounds were consistent, but, referring to the sharp transition from resistive to conductive region of the volume resistivity vs carbon black concentration curves obtained, still further stressed that it was necessary to develop accurately reproducible compounds that did not have a strong dependence on the electrical volume resistivity variations in processing conditions.

Pyne [296] noted the presumed lower shear forces associated with lower viscosity rubber during the mixing operation causing less breakdown of the blacks' structure. This is an advantage in the low viscosity nature of silicone rubber.

From the above, it is apparent that distribution of carbon black particles in solid rubber is inevitably accompanied by a reduction in the size of the black aggregates, arising from breaking down the non-persistent structure with increased resistivity,[297] but the extent of breakdown is dependent on the rubber viscosity [296] where silicone rubber is at

an advantage due to its low viscosity. A critical investigation was therefore considered necessary to substantiate the above claims.

4.2 OBJECTIVE

To determine the effect of milling on the electrical volume resistivity of conductive silicone compounds, by:

a. taking samples at preset time intervals during the milling process of each batch and assessing the vulcanisate properties, especially the volume resistivity, and taking into account the following subjective variables: compound viscosity, carbon black types and concentrations, and
b. estimating the degree of carbon black dispersion with increasing milling using the Dark Field Reflected Light Microscopy/Oscilloscope data for confirmation purposes.

4.3 EXPERIMENTAL

4.3.1 MATERIALS (see also Ch. 2, Section 2.1)

a. Polymers
Silastic GP30, Silastic GP45 and Siltech 17

b. Curing Agent
Dicumyl peroxide: Perkadox SB

c. Conductive Carbon blacks
Vulcan P, PF, XC72, and XC72R
Shawinigan
Conductex 900, 975, SC, and 40-220
Ketjenblack EC
Philblack XE-2

4.3.2 MIX FORMULATION

Table 4.1 shows the detailed mix formulation.

TABLE 4.1 MIX FORMULATIONS

Mix Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Silastic GP30	100.0																	
Perkadox SB	2.5																	
Vulcan P	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–
Shawinigan	–	–	–	–	–	–	5	10	15	20	25	30	35	–	–	–	–	–
Ketjenblack EC	–	–	–	–	–	–	–	–	–	–	–	–	–	4	8	12	16	20

Mix Number	19	20	21	22	23	24	25	26
Silastic GP30	100.0							
Perkadox SB	2.5							
Vulcan PF	30	–	–	–	–	–	–	–
" XC72	–	30	–	–	–	–	–	–
" XC72R	–	–	30	–	–	–	–	–
Conductex 900	–	–	–	30	–	–	–	–
" 975	–	–	–	–	30	–	–	–
" SC	–	–	–	–	–	30	–	–
" 40-220	–	–	–	–	–	–	20	–
Philblack XE-2	–	–	–	–	–	–	–	20

Mix Number	27	28	29	30	31	32	33	34	35	36	37
Silastic GP45	100.0										
Perkadox SB	2.5										
Vulcan P	30	–	–	–	–	–	–	–	–	–	–
" PF	–	30	–	–	–	–	–	–	–	–	–
" XC72	–	–	30	–	–	–	–	–	–	–	–
" XC72R	–	–	–	30	–	–	–	–	–	–	–
Shawinigan	–	–	–	–	30	–	–	–	–	–	–
Ketjenblack EC	–	–	–	–	–	20	–	–	–	–	–
Conductex 900	–	–	–	–	–	–	30	–	–	–	–
" 975	–	–	–	–	–	–	–	30	–	–	–
" SC	–	–	–	–	–	–	–	–	30	–	–
" 40-220	–	–	–	–	–	–	–	–	–	20	–
Philblack XE-2	–	–	–	–	–	–	–	–	–	–	20

Mix Number	38	39	40	41	42	43	44	45	46	47	48	49	50
Siltech 17	100.0												
Perkadox SB	2.5												
Vulcan P	5	10	15	20	–	–	–	–	–	–	–	–	–
Shawinigan	–	–	–	–	5	10	15	20	25	–	–	–	–
Ketjenblack EC	–	–	–	–	–	–	–	–	–	4	6	8	10

4.3.3 MIXING

The standard milling procedure, as described in Ch. 2, Section 2.2.1 was closely followed as well as taking samples from each batch at the following milling intervals: 2, 5, 8, 12, and 20 mins.

4.3.4 VULCANISATION

This was carried out as described in Ch.2, Section 2.2.2

4.3.5 EVALUATION OF VULCANISATE PROPERTIES

4.3.5.1 Electrical Volume Resistivity Measurement

This was carried out as described in Ch.2, Section 2.2.4

4.3.5.2 Hardness (IRHD) Measurement

This was carried out in accordance with BS903:PartA26:1969.

4.3.5.3 Dispersion Index Measurement

This was carried out as described in Ch.2, Section 2.2.7

4.4 RESULTS AND DISCUSSIONS

For investigating the effect of representative carbon black proportions on both dispersion and volume resistivity, Silastic GP30 based compounds were used.

High proportions and different types of carbon black filled Silastic GP30 and Silastic GP45 were used to investigate the effect of compound viscosity variables on both dispersion and volume resistivity. Such compounds were considered to represent very conductive rubbers.

One highly filled silica containing rubber compound, Siltech 17, was used to embrace both high compound viscosity and carbon black variation to ascertain the combined effect

of variables on the volume resistivity and dispersion.

4.4.1 Vulcan P loaded Silastic GP30

Fig. 4.1 gives a comparison of volume resistivity versus milling times obtained from increasing Vulcan P proportions. Mix Nos 1-6 of Table 4.2 give a comparable summary of results.

It was observed that with increasing milling time, the cure rate decreases, the cure time increases and the dispersion index decreases. The dispersion index is considered to indicate the degree of carbon black particle deagglomeration and possible aggregate breakdown. Initially volume resistivity decreases to a minimum at between 5 and 8mins milling time and then is increased on further milling. This phenomenon suggests that volume resistivity decreases with carbon black incorporation and this is followed by the carbon black deagglomerating and thus giving improved dispersion such that with increasing milling time dispersion increases as well as increasing breakdown in the carbon black agglomerates and subsequent increased interparticulate distances.

The effects of these variables, however, were found to decrease with increasing carbon black loading. Only marginal resistivity increases were observed with prolonged milling after the initial carbon black incorporation stage. This can be explained by the fact that increasing carbon black concentration increases the number of carbon black aggregates and therefore results in decreasing interparticulate distance and decreased importance of a possible chain breaking and re-formation mechanism which occurs as milling progresses.

4.4.2 Shawinigan loaded Silastic GP30

Mix Nos 7-13 and fig. 4.2 are now considered. Features similar to and comparative with the Vulcan P loaded Silastic GP30 were noted, but with a higher and more rapidly decreasing dipersion index suggesting that a more pronounced milling

TABLE 4.2 VULCANISATE PROPERTIES OF CONDUCTIVE SILICONE RUBBERS

Mix Number	Milling Time (mins)	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C = \frac{n\bar{h}s}{t \times 100}$
1	2	1.10	6.80	-	40	4.44
	5	1.00	7.60	10.28×10^{10}	46	3.33
	8	0.96	7.90	10.40×10^{10}	46	2.36
	12	0.92	8.30	10.60×10^{10}	46	1.45
2	2	0.86	8.70	9.20×10^{10}	45	3.40
	5	0.80	9.20	8.60×10^{10}	47	2.38
	8	0.78	9.40	8.62×10^{10}	48	2.03
	12	0.72	9.80	8.70×10^{10}	48	1.30
3	2	0.76	9.50	6.80×10^{10}	46	3.10
	5	0.72	9.80	5.70×10^{10}	49	2.22
	8	0.70	10.00	5.70×10^{10}	49	1.83
	12	0.68	10.20	6.20×10^{10}	50	1.29
4	2	0.68	10.20	5.40×10^{6}	48	2.99
	5	0.66	10.30	3.20×10^{6}	51	2.09
	8	0.66	10.90	2.80×10^{6}	51	1.93
	12	0.62	10.60	5.10×10^{6}	52	1.27
5	2	0.60	10.80	6.20×10^{2}	50	2.51
	5	0.58	10.90	4.10×10^{2}	53	1.54
	8	0.58	10.90	3.90×10^{2}	53	1.46
	12	0.56	11.10	5.30×10^{2}	53	1.12
6	2	0.58	10.90	6.60	54	2.27
	5	0.52	11.40	2.80	55	1.53
	8	0.52	11.40	2.52	55	1.09
	12	0.52	11.40	2.60	55	0.74
7	2	1.10	6.80	10.40×10^{10}	40	8.47
	5	1.10	6.80	9.00×10^{10}	44	4.43
	8	1.00	7.60	9.60×10^{10}	44	3.53
	12	0.96	8.30	9.80×10^{10}	44	1.27
8	2	1.00	7.60	8.20×10^{10}	42	6.66
	5	1.00	7.60	6.20×10^{10}	45	4.07
	8	0.96	7.90	7.40×10^{10}	45	2.70
	12	0.92	8.30	8.10×10^{10}	45	1.06
9	2	1.00	7.60	6.10×10^{10}	43	8.35
	5	1.00	7.60	1.90×10^{10}	45	3.70
	8	0.96	7.90	2.10×10^{10}	46	3.17
	12	0.90	8.40	4.30×10^{10}	46	1.27
10	2	0.84	8.90	6.20×10^{6}	44	8.54
	5	0.80	9.20	3.10×10^{5}	46	3.44
	8	0.76	9.50	3.00×10^{5}	46	2.69
	12	0.73	9.80	5.40×10^{5}	46	1.33
11	2	0.76	9.50	4.20×10^{2}	45	7.52
	5	0.72	9.80	2.40×10^{2}	47	3.05
	8	0.70	10.00	2.30×10^{2}	47	2.21
	12	0.68	10.20	4.00×10^{2}	47	1.06
12	2	0.66	10.30	5.80	46	5.71
	5	0.62	10.60	3.20	48	2.58
	8	0.62	10.60	3.12	49	1.45
	12	0.60	10.80	4.20	49	0.96
13	2	0.58	10.90	4.20	48	4.63
	5	0.53	11.30	2.88	50	2.53
	8	0.50	11.60	2.80	50	1.39
	12	0.50	11.60	3.20	50	0.82
14	2	1.10	6.80	10.50×10^{10}	47	2.27
	5	1.00	7.60	9.70×10^{10}	48	1.62
	8	0.98	7.80	9.60×10^{10}	48	1.57
	12	0.90	8.40	9.60×10^{10}	48	1.34
	20	0.82	9.00	10.00×10^{10}	48	1.00
15	2	0.96	7.90	9.60×10^{2}	48	2.19
	5	0.92	8.30	9.00×10^{2}	50	1.68
	8	0.88	8.60	9.00×10^{2}	50	1.42
	12	0.80	9.20	9.20×10^{2}	50	1.13
	20	0.70	10.00	9.40×10^{2}	50	0.95

TABLE 4.2 (CONTD)

Mix Number	Milling Time (mins)	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C = \frac{n\bar{h}s}{1 \times 100}$
16	2	0.82	9.00	9.20×10^1	53	1.76
	5	0.80	9.20	8.70×10^1	54	1.25
	8	0.76	9.50	8.70×10^1	54	0.96
	12	0.70	10.00	8.70×10^1	54	0.94
	20	0.62	10.60	9.00×10^1	54	0.88
17	2	0.74	9.70	1.02×10^1	54	1.47
	5	0.70	10.00	6.00	56	1.02
	8	0.66	10.30	6.00	56	0.98
	12	0.58	10.90	6.20	56	0.84
	20	0.48	11.70	6.70	56	0.76
18	2	0.64	10.50	3.20	57	1.01
	5	0.62	10.60	2.80	60	0.92
	8	0.60	10.80	2.60	62	0.78
	12	0.48	11.70	2.80	62	0.64
	20	0.42	12.20	2.80	62	0.40
19	2	0.50	11.60	8.40	50	2.75
	5	0.48	11.70	3.20	54	1.80
	8	0.46	11.90	2.70	54	1.06
	12	0.44	12.00	4.80	54	0.70
20	2	0.50	11.60	6.60	46	1.25
	5	0.50	11.60	2.80	48	1.05
	8	0.48	11.70	2.80	48	0.68
	12	0.48	11.70	3.90	48	0.49
21	2	0.54	11.30	7.20	46	1.29
	5	0.50	11.60	2.92	48	1.03
	8	0.48	11.70	2.90	48	0.69
	12	0.46	11.90	4.30	48	0.60
22	2	0.54	11.30	8.60	45	1.35
	5	0.52	11.40	3.10	47	1.02
	8	0.50	11.60	5.00	47	0.66
	12	0.48	11.70	7.60	47	0.51
23	2	0.52	11.40	9.20	47	1.24
	5	0.52	11.40	2.90	48	1.06
	8	0.50	11.60	2.50	48	0.68
	12	0.50	11.60	6.20	48	0.49
24	2	0.68	10.20	6.60	48	4.52
	5	0.64	10.50	3.20	49	2.49
	8	0.62	10.60	3.20	49	1.33
	12	0.60	10.80	4.80	49	0.87
25	2	0.48	11.70	3.80	57	1.00
	5	0.46	11.90	2.60	58	0.89
	8	0.46	11.90	2.60	58	0.76
	12	0.44	12.00	2.60	58	0.64
	20	0.41	12.30	3.40	58	0.41
26	2	0.58	10.90	5.20	58	1.02
	5	0.56	11.10	2.40	60	0.85
	8	0.54	11.30	2.40	60	0.79
	12	0.50	11.30	2.40	60	0.65
	20	0.46	11.90	2.80	60	0.43
27	2	0.60	10.80	9.40	57	2.10
	5	0.56	11.10	3.60	59	1.37
	8	0.54	11.30	3.40	59	0.98
	12	0.50	11.60	10.60	60	0.71
28	2	0.58	10.90	10.20	58	2.22
	5	0.56	11.10	3.50	60	1.78
	8	0.54	11.30	3.60	60	1.03
	12	0.50	11.60	10.10	60	0.70
29	2	0.62	10.60	5.20	48	1.23
	5	0.54	11.30	2.60	50	1.04
	8	0.52	11.40	2.60	52	0.69
	12	0,50	11.60	8.60	52	0.48
30	2	0.60	10.80	7.80	48	1.24
	5	0.54	11.30	2.60	50	0.97
	8	0.52	11.40	2.80	50	0.66
	12	0.50	11.60	8.80	52	0.56

TABLE 4.2 (CONTD)

Mix Number	Milling Time (mins)	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm- cm)	Hardness (IRHD)	Dispersion Index $C = \frac{\bar{n}hs}{t \times 100}$
31	2	0.66	10.30	6.90	57	5.72
	5	0.62	10.60	3.40	59	2.07
	8	0.60	10.80	3.20	58	1.44
	12	0.58	10.90	4.20	58	0.90
32	2	0.64	10.50	4.80	62	0.97
	5	0.62	10.60	2.90	64	0.89
	8	0.62	10.60	2.80	64	0.79
	12	0.56	11.10	2.80	64	0.65
	20	0.48	11.70	3.20	64	0.38
33	2	0.60	10.80	10.20	46	1.26
	5	0.54	11.30	3.20	49	0.99
	8	0.54	11.30	5.30	49	0.63
	12	0.52	11.40	5.90	55	0.49
34	2	0.58	10.90	9.20	53	1.25
	5	0.54	11.30	3.00	55	1.03
	8	0.54	11.30	2.80	55	0.70
	12	0.52	11.40	5.90	55	0.48
35	2	0.78	9.40	7.80	53	4.50
	5	0.72	9.80	3.40	55	2.58
	8	0.70	10.00	3.40	56	1.37
	12	0.68	10.20	5.60	56	0.87
36	2	0.52	11.40	4.80	64	0.98
	5	0.48	11.70	3.20	66	0.85
	8	0.48	11.70	3.20	66	0.75
	12	0.44	12.00	3.20	66	0.64
	20	0.41	12.30	4.00	66	0.39
37	2	0.58	10.90	6.40	62	1.02
	5	0.56	11.10	2.80	68	0.85
	8	0.56	11.10	2.80	68	0.78
	12	0.52	11.40	2.80	68	0.44
	20	0.48	11.70	4.00	68	0.25
38	2	1.14	6.50	-	70	3.66
	5	1.14	6.50	-	70	2.71
	8	1.14	6.50	-	70	2.28
	12	1.14	6.50	-	70	1.57
39	2	1.10	6.80	-	72	3.70
	5	0.94	8.10	10.60×10^{10}	72	2.71
	8	0.90	8.40	10.40×10^{10}	72	2.02
	12	0.90	8.40	10.00×10^{10}	72	1.46
40	2	0.78	9.30	10.20×10^{10}	74	3.29
	5	0.70	10.00	1.60×10^{10}	76	2.23
	8	0.70	10.00	1.20×10^{10}	76	2.08
	12	0.70	10.00	1.40×10^{10}	76	1.88
41	2	0.52	11.40	3.20×10^{9}	76	2.98
	5	0.48	11.70	1.30×10^{9}	78	1.96
	8	0.48	11.70	8.00×10^{8}	78	1.69
	12	0.46	11.90	9.20×10^{8}	78	1.39
42	2	1.20	6.00	-	70	-
	5	1.12	6.70	-	70	-
	8	1.00	7.60	-	70	-
	12	1.00	7.60	-	70	-
43	2	1.10	6.80	-	70	8.34
	5	1.00	7.60	20.00×10^{10}	72	3.15
	8	1.00	7.60	15.50×10^{10}	72	2.76
	12	1.00	7.60	10.00×10^{10}	72	1.17
44	2	1.00	7.60	3.40×10^{10}	72	7.15
	5	0.96	7.90	1.10×10^{10}	74	3.18
	8	0.92	8.30	1.00×10^{10}	74	2.58
	12	0.88	8.60	9.20×10^{9}	74	1.35
45	2	0.96	7.90	1.10×10^{9}	74	7.89
	5	0.90	8.40	3.50×10^{8}	76	3.19
	8	0.86	8.70	4.00×10^{8}	76	2.34
	12	0.82	9.00	5.40×10^{8}	76	1.87

TABLE 4.2 (CONTD)

Mix Number	Milling Time (mins)	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C = \frac{n\bar{h}s}{t \times 100}$
46	2	0.90	8.40	2.30×10^{7}	76	7.60
	5	0.84	8.90	7.50×10^{6}	78	2.94
	8	0.80	9.20	7.00×10^{6}	78	2.19
	12	0.78	9.40	6.80×10^{6}	78	2.22
47	2	1.00	7.60	10.20×10^{10}	70	2.40
	5	1.00	7.60	9.60×10^{10}	70	2.15
	8	1.00	7.60	9.20×10^{10}	70	1.90
	12	1.00	7.60	9.20×10^{10}	70	1.52
	20	1.00	7.60	9.20×10^{10}	70	1.24
48	2	1.00	7.60	8.40×10^{9}	70	2.15
	5	0.96	7.90	6.40×10^{8}	72	1.52
	8	0.94	8.10	6.60×10^{8}	72	1.46
	12	0.92	8.30	6.60×10^{8}	72	1.13
	20	0.88	8.60	6.60×10^{8}	72	1.00
49	2	1.00	7.60	7.20×10^{6}	73	2.15
	5	0.92	8.30	2.80×10^{6}	74	1.54
	8	0.90	8.40	2.80×10^{6}	74	1.39
	12	0.87	8.60	2.60×10^{6}	74	1.12
	20	0.82	9.00	2.60×10^{6}	74	0.95
50	2	0.90	8.40	10.20×10^{5}	75	2.12
	5	0.84	8.90	7.00×10^{5}	76	1.53
	8	0.80	9.20	6.80×10^{5}	76	1.29
	12	0.76	9.50	6.40×10^{5}	76	1.09
	20	0.70	10.00	6.40×10^{5}	76	0.90

Fig. 4.1 Effect of milling on volume resistivity of furnace black (Vulcan P) filled Silastic GP 30 based compounds.(Ref. Mix Nos. 1-6 of Tables 4.1 & 4.2).

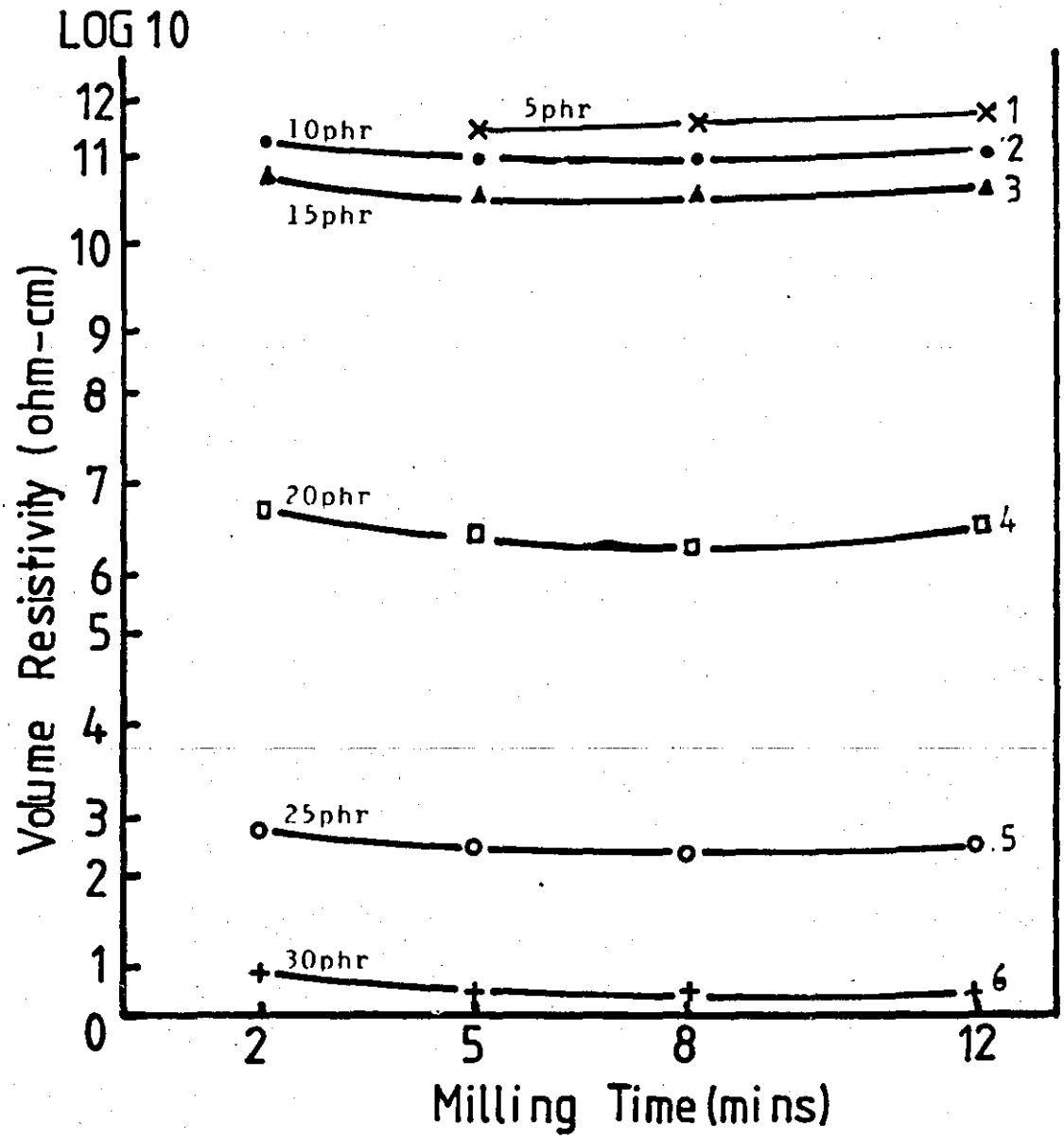
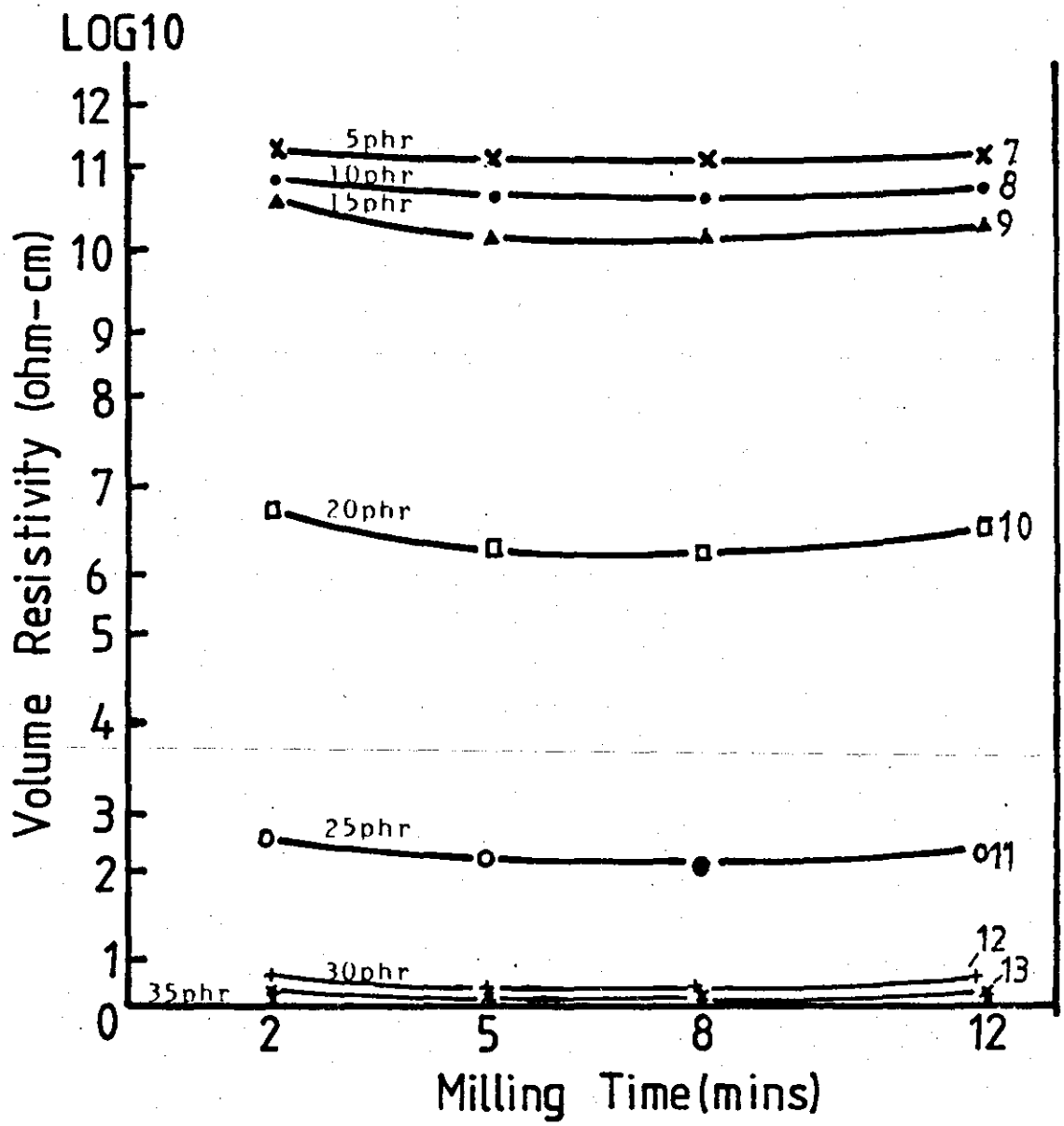


Fig.4.2 Effect of milling on the Volume Resistivity of acetylene black (Shawinigan) filled Silastic GP30 based compounds (Ref. Mix Nos. 7-13 of Tables 4.1 & 4.2).



effect occured with the softer, bulkier acetylene carbon black. As seen in Table 4.2, there was less variation in resistivity with milling time with Vulcan P compared with Shawinigan. Even at 35phr loading there was produced a small, though significant, degree of resistivity increase with long milling time.

4.4.3 Ketjenblack EC loaded Silastic GP30

Mix Nos 14-18 of Table 4.2 and fig. 4.3 are considered in this exercise. As could be seen from the results, lower concentrations of this carbon black were required to give similar/equivalent volume resistivities to those of Vulcan P and Shawinigan. Variations of the volume resistivity and dispersion index were minimal when compared with the Vulcan P and Shawinigan loaded compounds. But for a rapidly decreasing cure rate with increasing milling time especially at maximum black loading, the material would have been 'the perfect electrical conductor' in the polymer/filler composite.

The unique features of the Ketjenblack EC are its porous, hollow shells, light in weight with therefore higher number of aggregates on a weight basis, tough and not easily broken down particles. All these features are a pointer to pseudo-fibre chain formation occuring, and thus encouraging electron tunnelling phenomenon.

4.4.4 Highly(Carbon black)filled Silastic GP30

Figs. 4.4 and 4.5 give a comparison of volume resistivity versus milling times for highly filled Silastic GP30 for the different carbon blacks used in this investigation. Mix Nos 19-26 of Table 4.2 summarise the results of the vulcanisate properties. It could be observed that each mix has at least a period of milling time of between 5-8mins during which volume resistivity remained constant. The exception to this was the Conductex 900 black filled vulcanisate. In addition to the above, both Conductex 40-220 and Philblack

Fig. 4.3 Effect of milling on the Volume Resistivity of special furnace black (Ketjenblack EC) filled Silastic GP30 based compounds (Ref. Mix Nos. 14-18 of Tables 4.1 & 4.2)

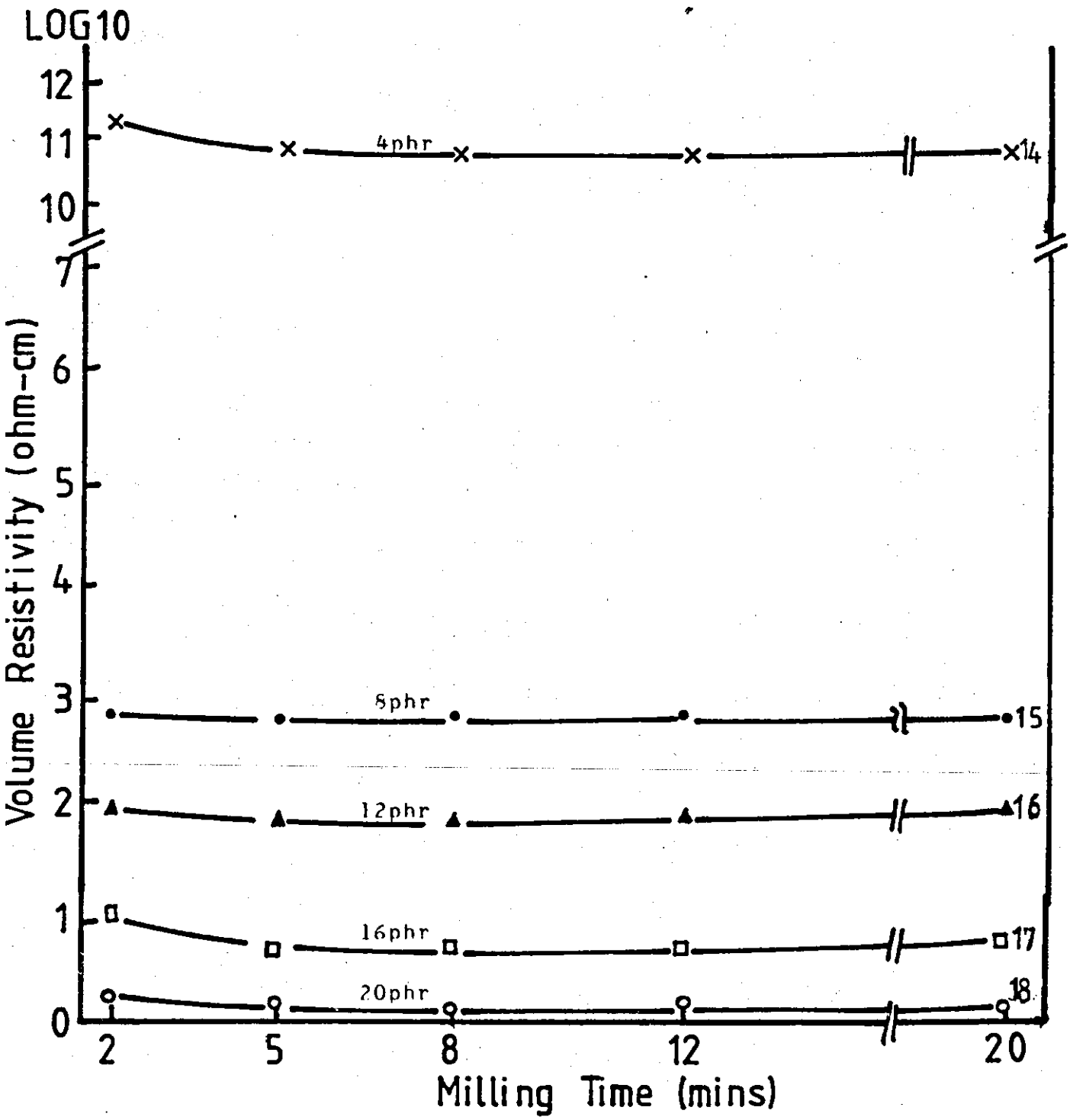


Fig 4.4 Effect of milling on the Volume Resistivity of highly (carbon black) filled Silastic GP30 based compounds I (Ref. Mix Nos. 19-22 of Tables 4.1 & 4.2).

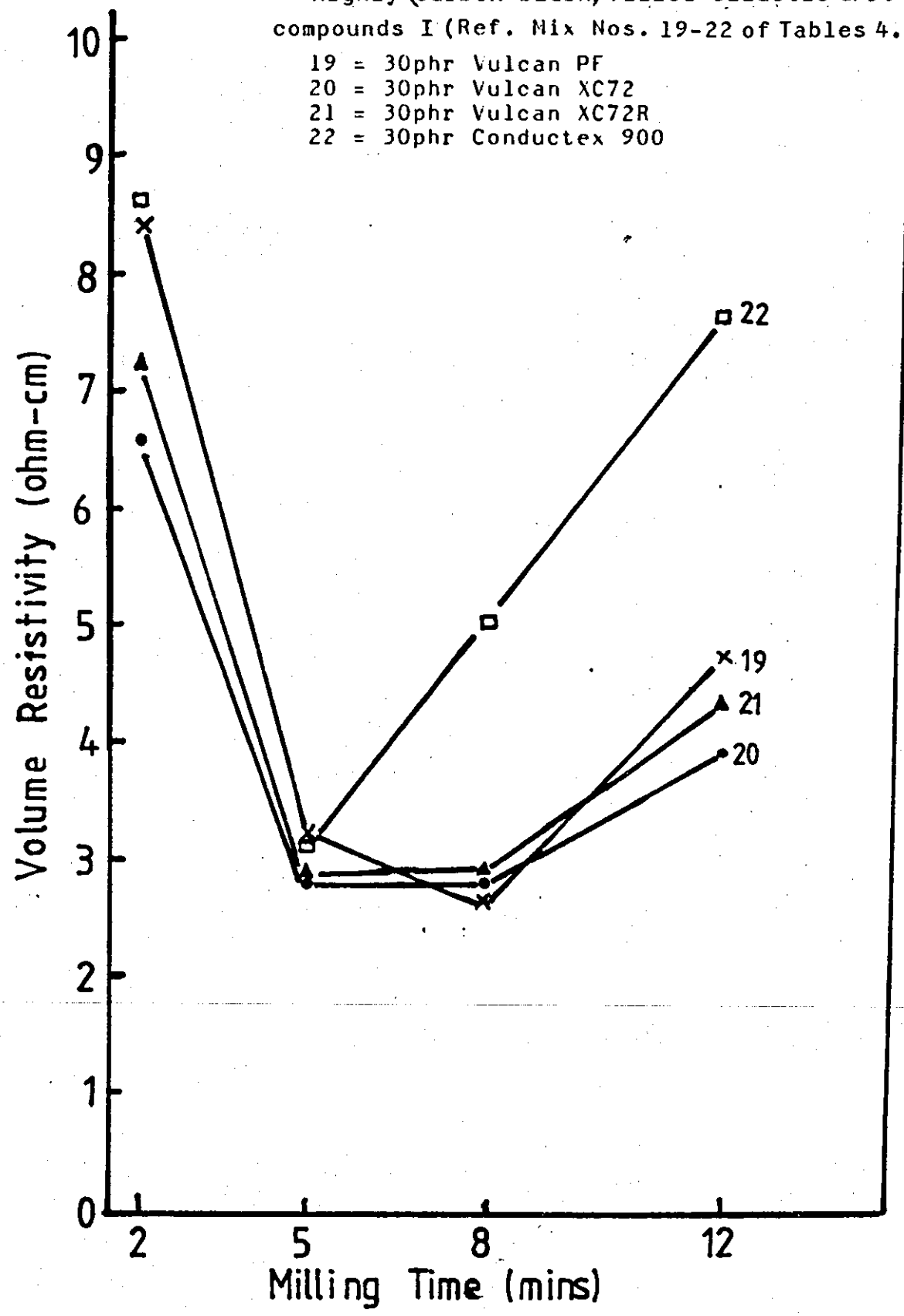
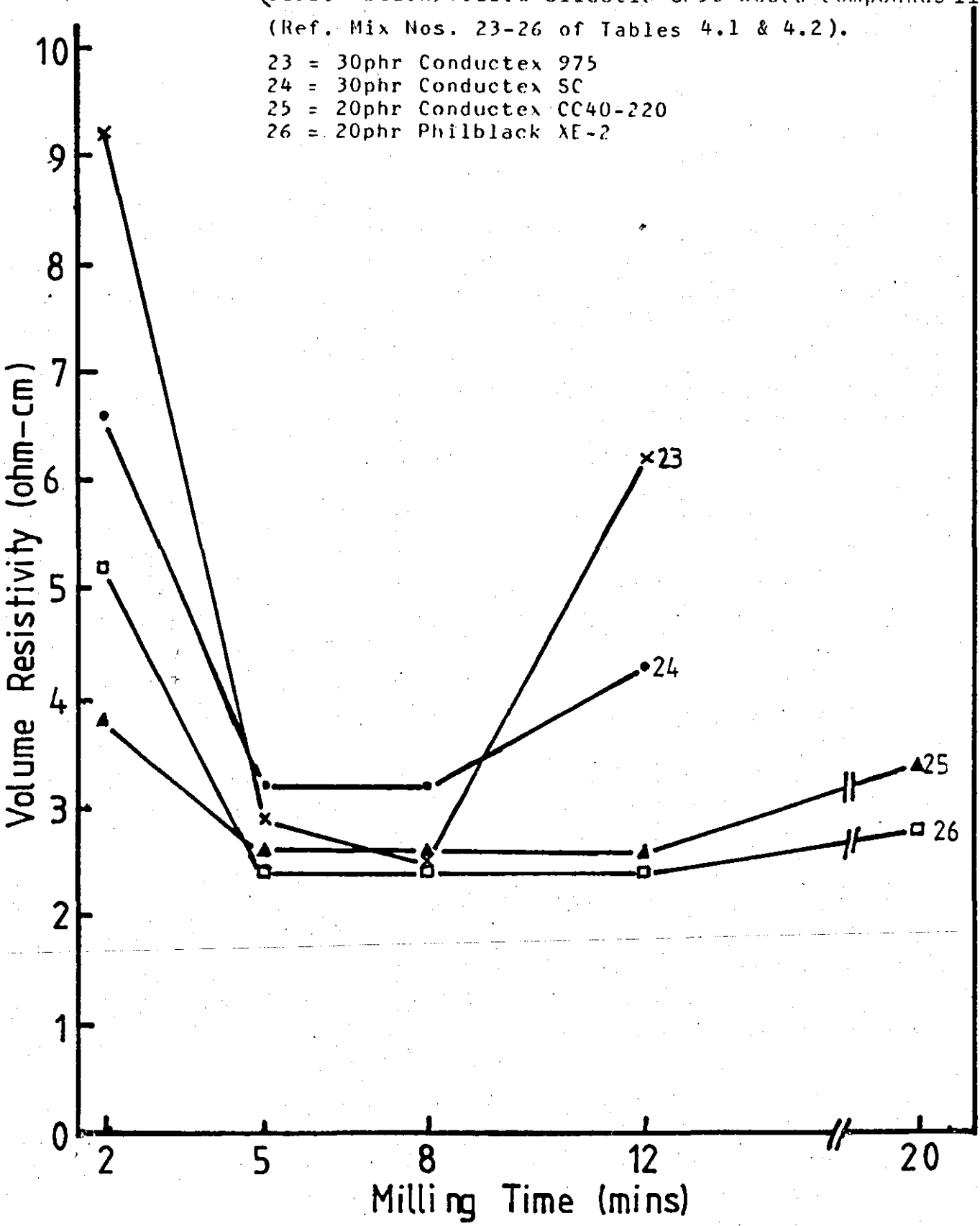


Fig. 4.5 Effect of milling on the Volume Resistivity of highly (carbon black) filled Silastic GP30 based compounds II (Ref. Mix Nos. 23-26 of Tables 4.1 & 4.2).



XE-2 filled vulcanisates had similar (unique) characteristics to Ketjenblack EC and thus stood out as a class which was found less variable.

4.4.5 Highly(carbon black)filled Silastic GP45

Mix Nos 27-36 of Table 4.2 and figs. 4.6 and 4.7 are considered in this exercise. The features of these compounds were found similar to the highly filled Silastic GP30 compounds, but they possessed higher volume resistivity values.

It is interesting to note that Furnace, Acetylene, and 'Furnace Special blacks' can be separated in a volume resistivity 'cluster' range. Within the furnace range alone the Vulcan P and PF and Conductex SC group together; the Vulcan XC72 and 72R and Conductex 975 group together, but Conductex 900 appears to stand out in a class of its own being generally less conductive. The acetylene black has a volume resistivity range between that of Vulcan 72 and P clusters and that of the special blacks. The special blacks Mix Nos 32, 36 and 37 show similar 'no change in resistivity' with processing time of 5-12mins but a small significant variation to longer milling times.

4.4.6 Vulcan P filled Siltech 17

Limited proportions of Vulcan P loadings were incorporated into this highly filled (with silica) silicone rubber, which, due to its difficult to process features, could only accept 20phr maximum of Vulcan P whilst remaining processable. Mix Nos 39-41 and fig. 4.8 are now considered.

It was observed that the response of these compounds to increased milling times was little different when compared with their Vulcan P filled Silastic GP30 cousins. An initial sharp drop in volume resistivity between 0-5mins milling time is usually followed by a characteristic slight increase in volume resistivity with increasing milling times. This

Fig.4.6 Effect of milling on the Volume Resistivity of highly(carbon black)filled Silastic GP45 based compds I (Ref. Mix Nos. 27-31 of Tables 4.1 & 4.2)

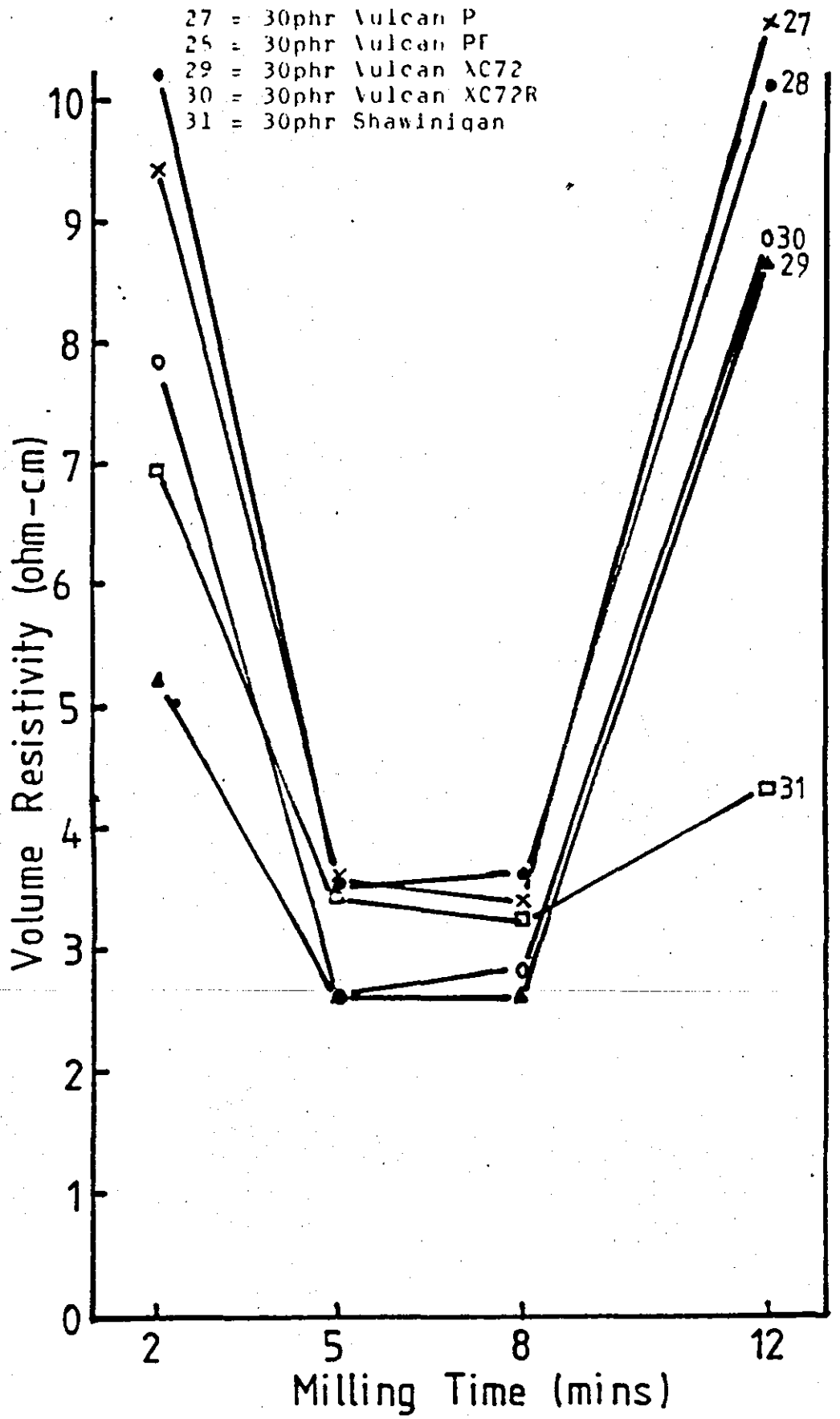


Fig. 4.7 Effect of milling on the volume resistivity of highly (carbon black) filled Silastic GP45 based compounds II (Ref. Mix Nos 32-37 of Tables 4.1 & 4.2)

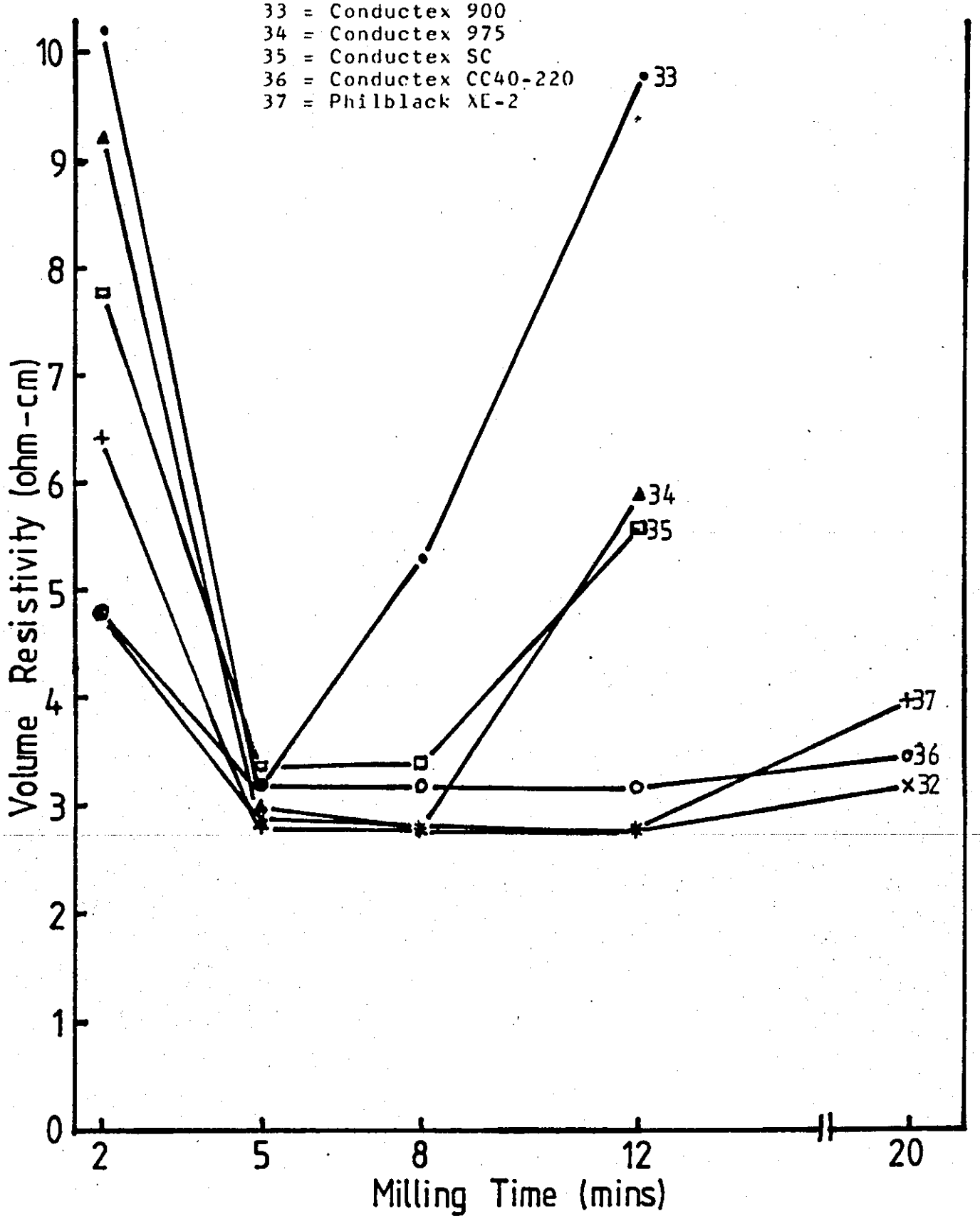
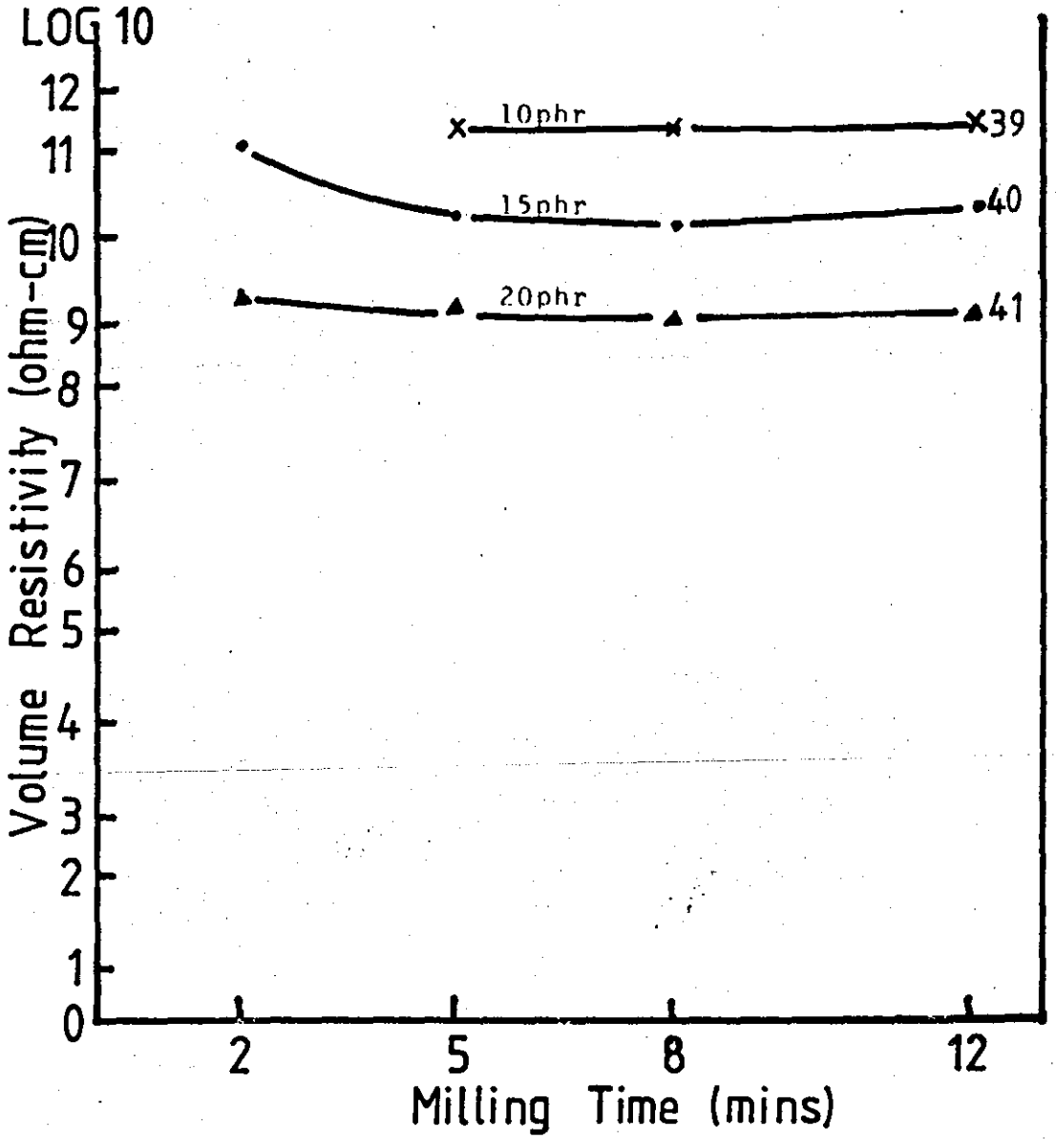


Fig.4.8 Effect of milling on the Volume Resistivity of furnace black (Vulcan P) filled Siltech 17 based compounds (Ref Nos 39-41 of Tables 4.1 & 4.2)



suggests an initial rapid incorporation and deagglomeration of the carbon black aggregates followed by a steadily and increasingly effective dispersion of carbon black. The dispersion index was observed to decrease almost linearly with increasing milling times (after the initial rapid drop). Thus this confirmed the previously suggested pattern in which increasing carbon black dispersion occurs with increased milling times, after the initially rapid incorporation of aggregates and the subsequent deagglomeration.

4.4.7 Shawinigan filled Siltech 17

These were Mix Nos 43-46 and fig. 4.9. Initially the volume resistivity decreased to a minimum after 5mins of the milling time and then on further milling the resistivity started to increase but at a slower rate than that obtained with Silastic GP30. It was also observed that there was an initial rapid decrease in the dispersion index between 0-5 mins milling time, and then on further milling the dispersion index continued to decrease linearly. This observation is similar to that of Vulcan P filled Siltech 17.

4.4.8 Ketjenblack EC filled Siltech 17

Mix Nos 47-50 of Table 4.2 and fig. 4.10. As can be seen from the results, features similar to and comparable with Ketjenblack EC filled Silastic GP30 were noted. But with Siltech 17, initially there was a more rapid volume resistivity decrease between 0-5mins milling time than that obtained with its analogue Ketjenblack EC filled Silastic GP30. This again suggests that initially rapid carbon black incorporation occurs followed by deagglomeration of the carbon black. On further milling, the volume resistivity initially decreased marginally and then became completely constant. This was in contrast to Ketjenblack EC in Silastic GP30 where resistivity increased with increasing milling time.

Fig.4.9 Effect of milling on the Volume Resistivity of acetylene black (Shawinigan) filled Siltech 17 based compounds (Ref Nos 43-46 of Tables 4.1 & 4.2)

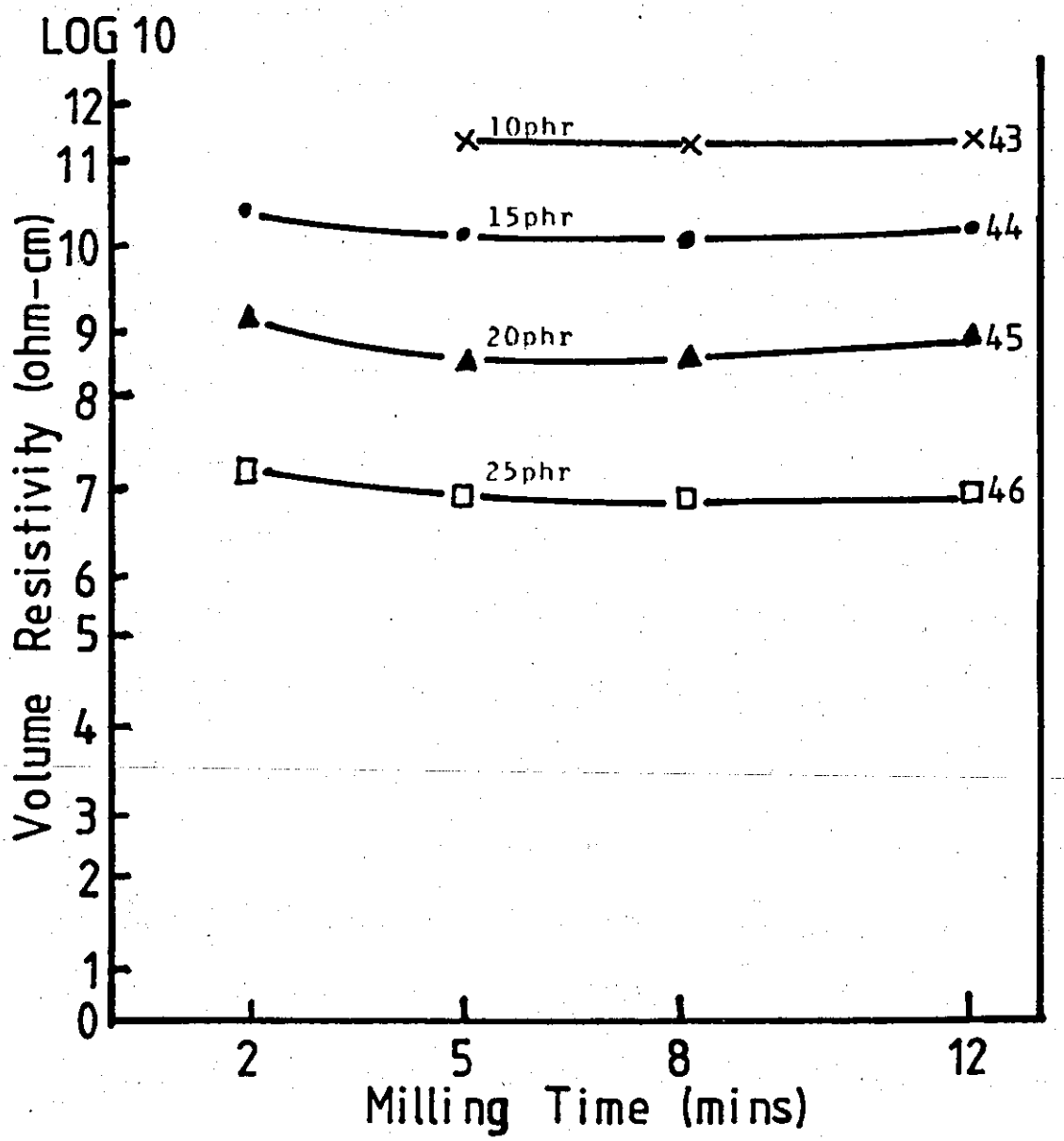
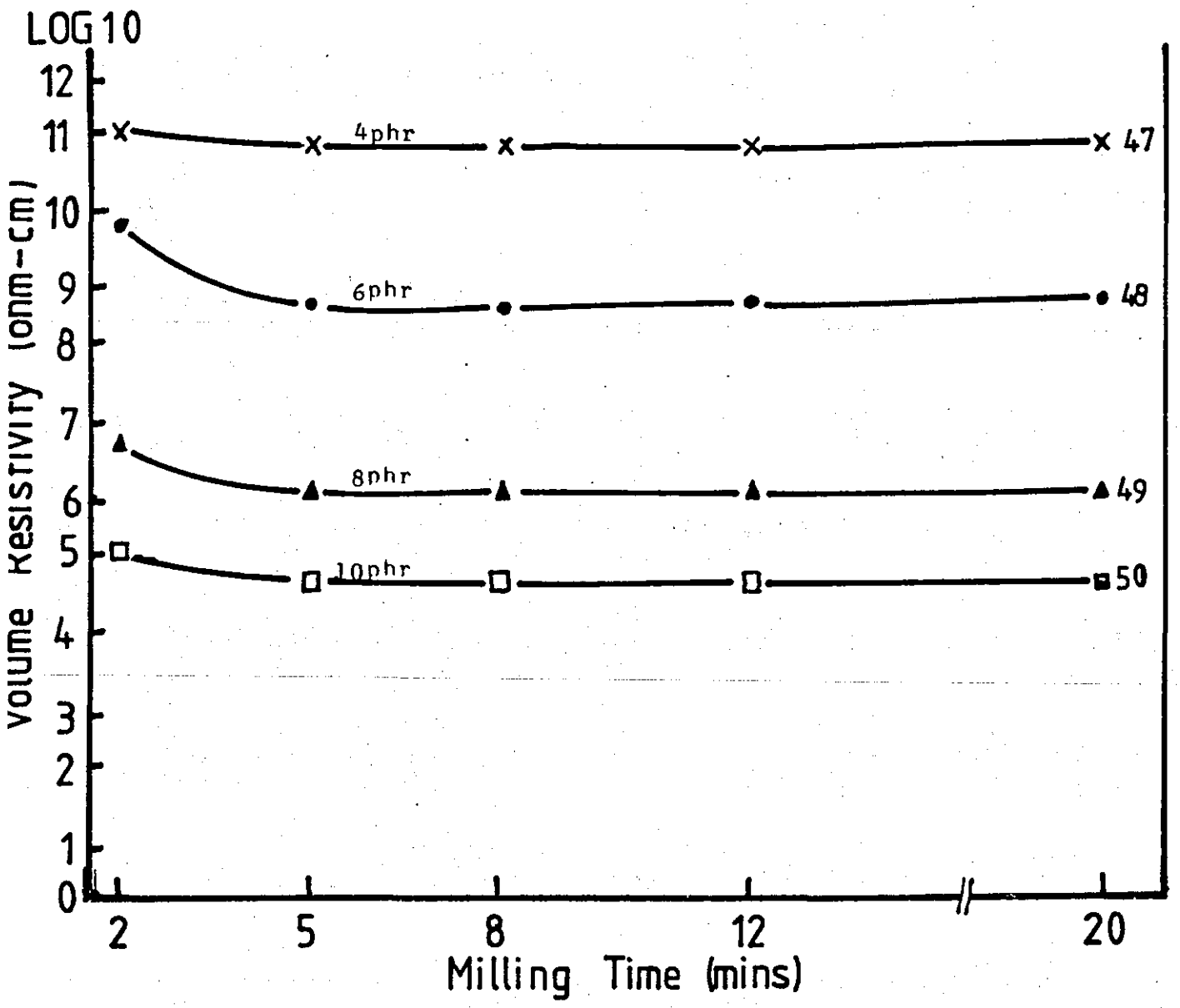


Fig. 4.10 Effect of milling on the Volume Resistivity of furnace special black (Ketjenblack EC) filled Siltech 17 based compounds (Ref Mix Nos 47-50 of Tables 4.1 & 4.2)



It was also observed that the dispersion index decreases approximately linearly with increasing milling time. This suggests a slow but constantly improving carbon black dispersion occurs as milling progresses. It is, therefore, considered that no carbon black particle breakdown and/or substantial increase in interparticulate distance occured to affect the compound volume resistivity since this remained constant with further milling.

4.5 CONCLUSIONS

Generally, the milling process is found to affect the volume resistivity of carbon black filled silicone rubber. The degree of this milling effect is dictated by the type and concentration of the carbon black, the viscosity of the compound and the milling time.

Nearly all low viscosity compounds exhibit an initial volume resistivity decrease to a minimum at between 5 and 8 mins milling time and then this increases on further milling. A suggested explanation of this phenomenon is that volume resistivity decreases with the simple incorporation of the carbon black aggregates and that this is then followed by the carbon black deagglomerating into its elementary particles thus giving improved dispersion such that with increasing milling time dispersion efficiency increases as well as the increasing breakdown of the carbon black aggregates into particles and the subsequent creation of an increased number of interparticulate distances and hence increased electrical volume resistivity.

With increasing silica content (higher viscosity), the initial rate of volume resistivity decreases in the 0-5 mins milling time interval; it goes through a minimum and then increases as milling progresses. The change in volume resistivity with milling time is observed to either reach

a steadily increasing volume resistivity as in the Silastic GP45 vulcanisates or to become almost constant as in the Siltech 17 vulcanisates.

As the carbon black content increases the rate of the initially rapid volume resistivity drop (from 0-5 mins milling times) becomes less. The volume resistivity, which slowly increases on further milling in low carbon black filled compounds, becomes almost constant as the carbon black content increases irrespective of the milling time. However, the rate at which the latter change occurs is dependent on the type of carbon black e.g Ketjenblack EC>Vulcan P>Shawinigan.

A reproducible low resistive compound state existed between the 3-8mins processing region for furnace blacks e.g Vulcan P, 3-7mins for acetylene blacks e.g Shawinigan, and 3-12mins for special furnace blacks, e.g Ketjenblack EC. It should thus be noted that milling within the above time belt can be used to offset an undercure experienced due to the presence of Ketjenblack EC. Excessive milling of conductive rubber compounds, especially those highly filled with Ketjenblack EC, gives silicone rubber compounds which are undercured.

V MOULDING AND VULCANISING CONDITIONS

5.1 INTRODUCTION

Vulcanisation is usually essential before electrical resistivity can be measured, and the process of vulcanisation affects the electrical resistivity within a particular mix. Hence the effect of vulcanisation conditions on electrical resistivity was investigated.

Bulgin[271] using different moulding and vulcanising conditions, *viz:-*

a. moulding and vulcanising in a press,
b. lapping and vulcanising in open steam,
c. sheeting and vulcanising (free from constrictions) in open steam,

showed that the relative effects of each process on the electrical resistivity varied with the type (and probably with the concentration) of carbon black. He further stressed that in nearly all the compounds, the resistivity of the press-cured samples generally increases with increasing moulding pressure due to the increased expansion of the sample when removed from the mould. He also noted that the electrical resistivity is substantially independent of the vulcanisation process in a highly conductive compound. He concluded that the final resistivity is dependent on the total curative content of the mixes.

Newton[298] in his work established that most of the change in resistivity occured during the first 8mins, long before the rubber reached its optimum cure time of, in this case, 30mins. This phenomenon was confirmed by other workers[280,299-301]. It was suggested that a slight undercure or considerable overcure of soft rubbers has relatively little effect on the electrical resistivity of the vulcanisate.

Lane and Gardner[299] allowed a conductive compound (NR + 60phr Acetylene black), with an increasing mixing times of 45-120mins, to stand for 0, 24, and 72hrs before vulcanising. They recorded a marginal, though important, increasing electrical resistivity, with increasing shelf ageing period.

McKinney and Roth[302] confirmed Bulgin's deduction of the electrical resistivity dependency on the total curative content of the mixes. Boonstra and Dannenberg[278] in their findings concluded that electrical resistivity increased with increasing moulding pressure, thus confirming Bulgin's deduction. They further suggested that mould flow greatly affects (increases) the electrical resistivity.

A singular observation was recorded by Berry and [illegible]. They observed that at the beginning of [illegible], [illegible] causes some of the carbon black structure, already broken down [illegible] to reform due to the increased mobility of conductive elements [illegible] structure reforming process, therefore, decreases the electrical resistivity.

5.2 OBJECTIVE

The above examples noted the dependency of the product's final resistivity on the moulding and vulcanising conditions. The objective of this chapter, therefore, is to critically investigate the effect of the following:

a. mould flow,
b. moulding pressure,
c. storage periods of 24hrs, 72hrs and 7days after milling, and
d. moulding time: a slight undercure (≈10%) and a considerable overcure (≈50%),

on the vulcanisate properties and especially that of the electrical volume resistivity.

5.3 EXPERIMENTAL

5.3.1 MATERIALS (see also Ch.2, Section 2.1)

a. Polymer

Silastic GP45 (chosen for having a reasonable amount of silica content)

b. Curing Agent

Perkadox SB

c. Representative conductive carbon blacks

Furnace black - Vulcan P

Acetylene black - Shawinigan

Special Furnace black - Ketjenblack EC

5.3.2 MIX FORMULATION

Table 5.1 shows the detailed mix formulations.

TABLE 5.1 MIX FORMULATIONS

Mix Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Silatic GP45	100.0																	
Perkadox SB	2.5																	
Vulcan P	5	10	15	20	25	30	-	-	-	-	-	-	-	-	-	-	-	-
Shawinigan	-	-	-	-	-	-	5	10	15	20	25	30	35	-	-	-	-	-
Ketjenblack EC	-	-	-	-	-	-	-	-	-	-	-	-	-	4	8	12	16	20

5.3.3 MIXING

The standard milling procedure as described in Ch.2, Section 2.2.1 was closely followed. The milling time was controlled to within the 'safety time belt' as observed in Ch.4.

5.3.4 VULCANISATION

This was carried out as described in Ch.2, Section 2.2.2 coupled with the variations as outlined in the folowing sub-sections:

5.3.4.1 Mould Flow

Different shapes and sizes of moulding blanks with almost equal weights (Table 5.2) were carefully prepared for a controlled mould flow during vulcanisation.

TABLE 5.2 TYPE OF MOULDING BLANKS

Number	Length (mm)	Width (mm)	Thickness (mm)	Volume (mm^3)	Weight (g)	Mould Flow
a	70	60	2.2	9,240	12.00	None
b	50	60	3.1	9,300	12.07	Unidirectional
c	50	40	4.6	9,260	12.03	Bidirectional

5.3.4.2 Moulding Pressure

Three different moulding pressures, $0.98MNm^{-2}$ (standard), $1.96MNm^{-2}$, and $2.94MNm^{-2}$ were used to assess the effect of moulding pressure on the volume resistivity of the vulcanisates. The standard moulding blank 'a' was used in this exercise.

5.3.4.3 Storage Time

Three different storage times after milling, 24hrs (standard), 72hrs, and 7days, were used in this exercise.

5.3.4.4 Moulding Time

The following three different moulding times:

a. Standard calculated moulding times,

b. Slightly undercure: 10% below calculated cure times,

c. Considerable overcure: 50% above calculated cure times,

were used in this exercise.

5.3.5 EVALUATION OF VULCANISATE PROPERTIES

5.3.5.1 Hardness (IRHD) Measurement

This was carried out in accordance with BS903:PartA26:1969

5.3.5.2 Electrical Volume Resistivity Measurement

This was carried out as described in Ch.2, Section 2.2.4

5.4 RESULTS AND DISCUSSIONS

5.4.1 MOULD FLOW

To evaluate the effect of mould flow, three different shapes (sizes) of moulding blanks were carefully prepared (Table 5.2) and blank 'a' was considered as the standard moulding blank. These blanks were shaped to control the mould flow direction during vulcanisation, with most of the mould flow being unidirectional (⟷) for blank 'b' and bidirectional (✚) for blank 'c'. All other moulding conditions were kept constant for comparative purpose.

The summary of the assessed vulcanisate properties is as in Table 5.3. Figs. 5.1 to 5.3 are the volume resistivity % increase vs carbon black concentration curves. The volume resistivity % increase was calculated from the difference (increase) in measured volume resistivity between 'a' (the standard moulding blank) and 'b' and 'c'.

It was observed that the volume resistivity % increase is generally:

a. higher in the bidirectional mould flow ('c' test samples) than in the unidirectional mould flow ('b' test samples).
b. decreasing with increased carbon black concentration. The value and rate of this decrease, however, is dependent on the type of carbon black (see Table 5.4).

TABLE 5.3 VULCANISATE PROPERTIES OF CONDUCTIVE SILASTIC GP45 BASED COMPOUNDS: EFFECT OF MOULD FLOW

Mix Number		Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Percentage Increase	Hardness (IRHD)
1	a	1.20	6.00	10.20×10^{10}	–	49.0
	b			–	–	
	c			–	–	
2	a	1.01	7.50	9.50×10^{10}	–	51.0
	b			10.00×10^{10}	5.26	
	c			10.10×10^{10}	6.32	
3	a	0.83	8.90	8.70×10^{10}	–	54.0
	b			9.10×10^{10}	4.60	
	c			9.20×10^{10}	5.75	
4	a	0.70	10.00	3.80×10^{6}	–	55.0
	b			3.93×10^{6}	3.50	
	c			3.97×10^{6}	4.50	
5	a	0.63	10.50	6.50×10^{2}	–	58.0
	b			6.65×10^{2}	2.31	
	c			6.70×10^{2}	3.08	
6	a	0.52	11.40	3.80	–	60.0
	b			3.87	1.64	
	c			3.88	2.11	
7	a	1.10	6.80	10.00×10^{10}	–	50.0
	b			–	–	
	c			–	–	
8	a	1.00	7.60	7.00×10^{10}	–	52.0
	b			7.40×10^{10}	5.13	
	c			7.55×10^{10}	7.86	
9	a	0.92	8.30	1.40×10^{10}	–	54.0
	b			1.46×10^{10}	4.29	
	c			1.48×10^{10}	5.71	
10	a	0.78	9.40	4.00×10^{5}	–	55.5
	b			4.15×10^{5}	3.75	
	c			4.20×10^{5}	5.00	
11	a	0.73	9.80	3.26×10^{2}	–	57.5
	b			3.36×10^{2}	3.07	
	c			3.38×10^{2}	5.00	
12	a	0.62	10.60	3.38	–	59.0
	b			3.46	2.11	
	c			3.47	2.66	
13	a	0.54	11.30	2.82	–	60.0
	b			2.86	1.42	
	c			2.87	1.77	
14	a	1.00	7.60	9.40×10^{10}	–	48.0
	b			9.85×10^{10}	4.79	
	c			9.90×10^{10}	5.32	
15	a	0.88	8.60	2.60×10^{5}	–	52.0
	b			2.68×10^{5}	3.08	
	c			2.69×10^{5}	3.46	
16	a	0.82	9.00	4.80×10^{1}	–	55.0
	b			4.89×10^{1}	1.88	
	c			4.91×10^{1}	2.29	
17	a	0.70	10.00	4.60	–	60.0
	b			4.65	1.09	
	c			4.66	1.30	
18	a	0.62	10.60	2.20	–	64.0
	b			2.20	–	
	c			2.21	0.91	

*The above results are an average of results from six samples.

Fig. 5.1 Effect of mould flow on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP45 based compounds (Ref Tables 5.1, 5.2 and 5.3)

b = compound with unidirectional mould flow
c = compound with bi-directional mould flow

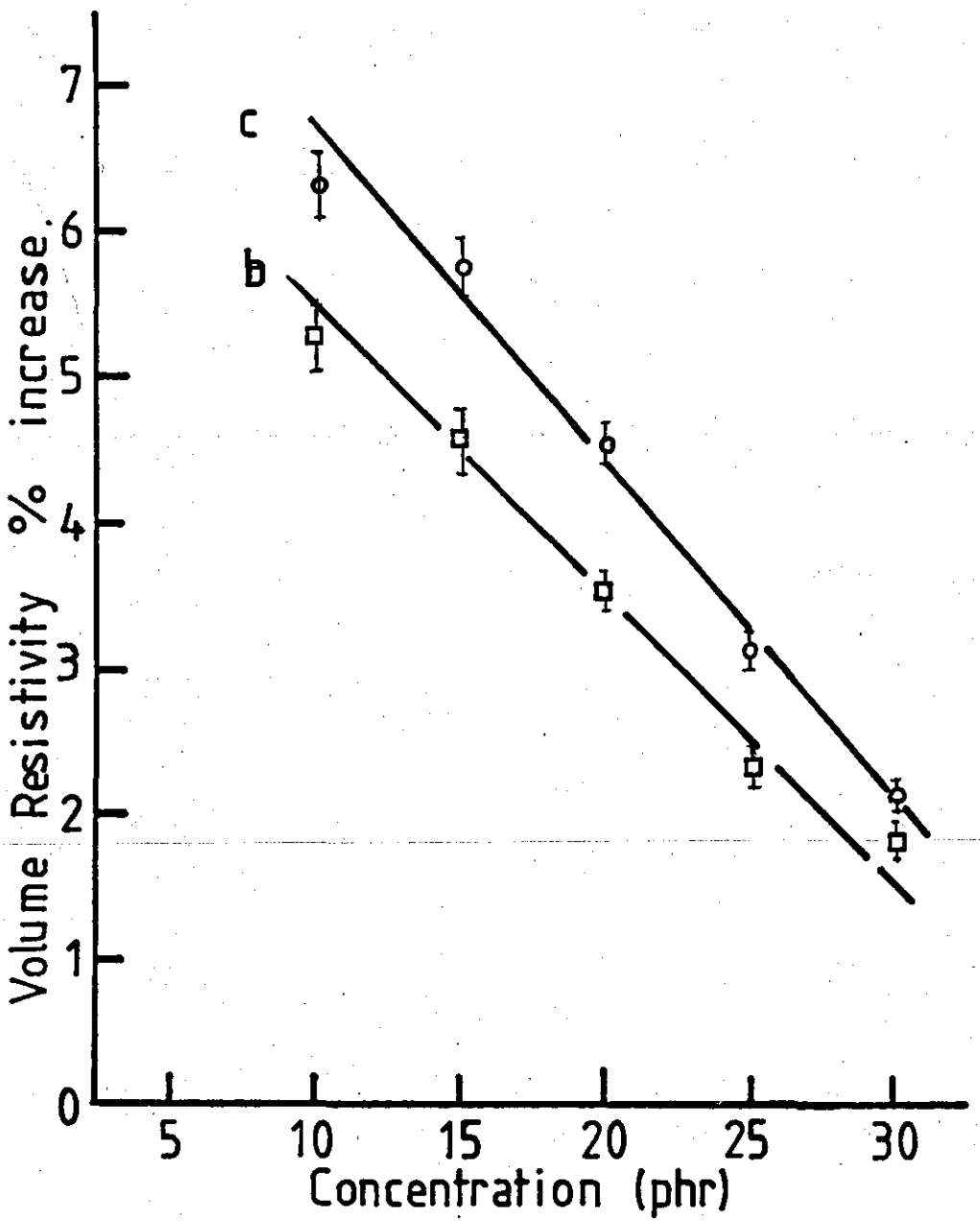


Fig 5.2 Effect of mould flow on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Tables 5.1, 5.2 and 5.3)

b = compound with unidirectional mould flow
c = compound with bi-directional mould flow

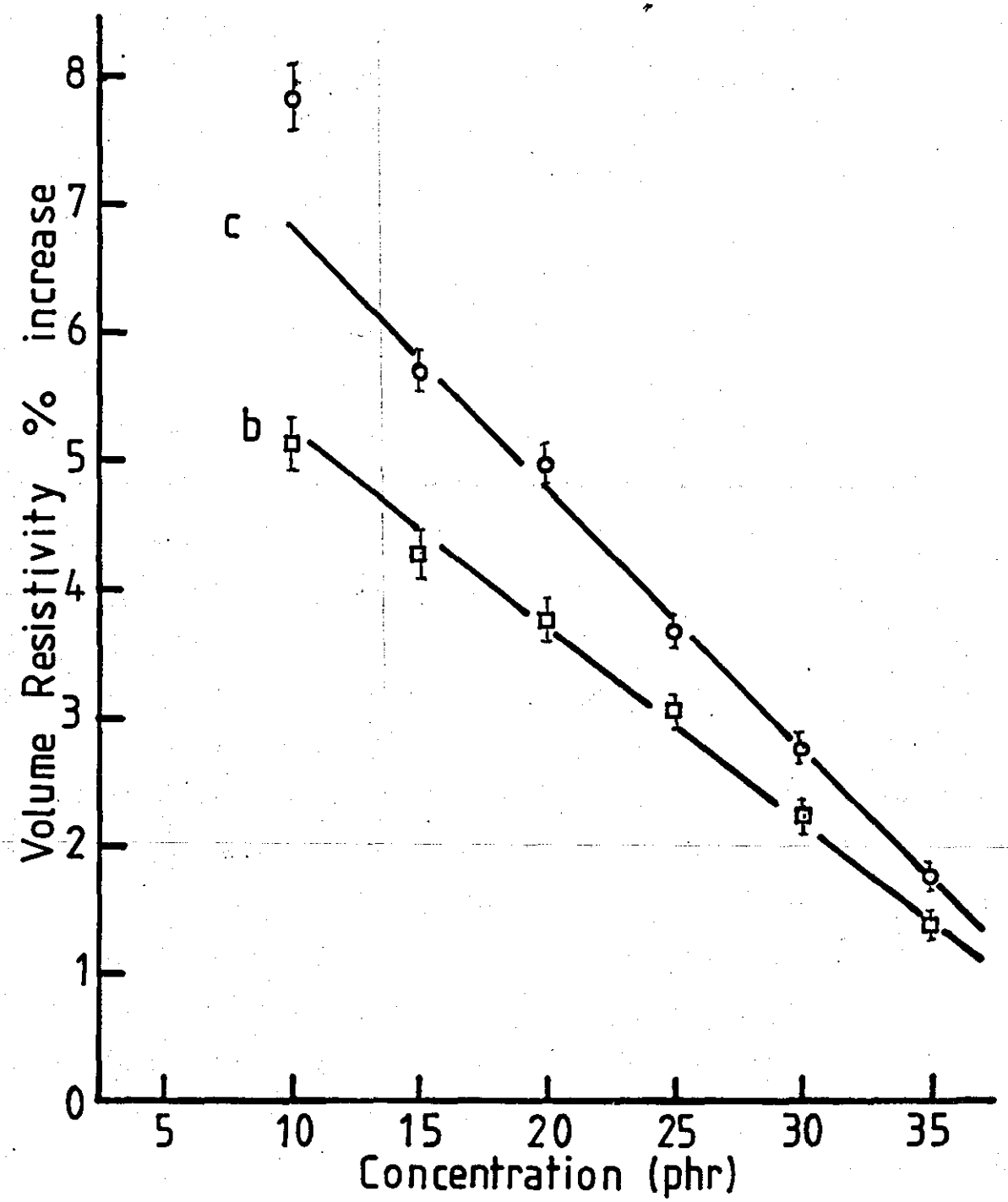


Fig. 5.3 Effect of mould flow on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Tables 5.1, 5.2, and 5.3).
b = compound with unidirectional mould flow
c = compound with bi-directional mould flow

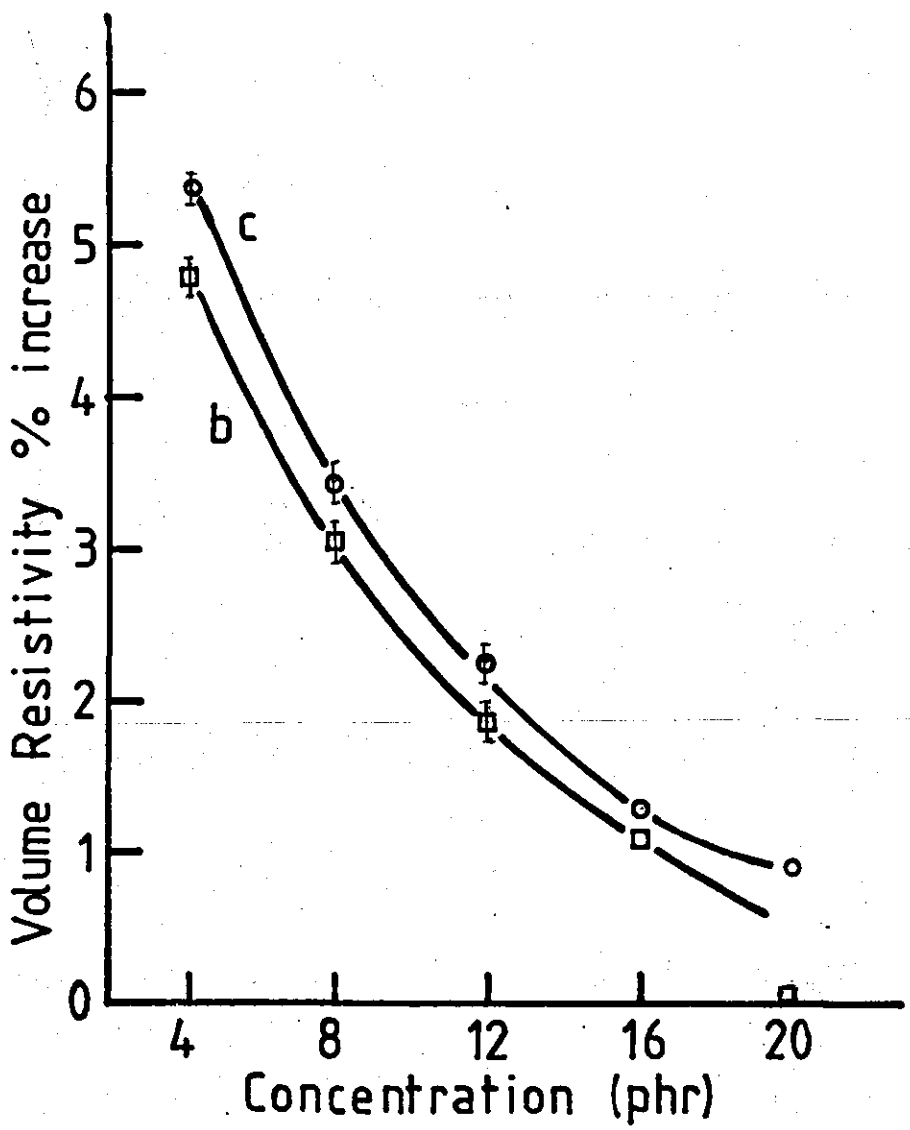


TABLE 5.4 VOLUME RESISTIVITY PERCENTAGE INCREASE RANGE (MOULD FLOW)			
	Vulcan P	Shawinigan	Ketjenblack EC
CB concentration	10 - 30	10 - 35	4 - 20
Unidirectional 'b'	5.30 - 1.80	5.10 - 1.40	4.80 - 0
Bi-directional 'c'	6.30 - 2.10	7.90 - 1.80	5.30 - 0.90

Also from the slope of the graphs, it was observed that the rate of decrease (of the volume resistivity % decrease), with increasing carbon black concentration is of the order Ketjenblack EC>Shawinigan>Vulcan P. Additionally, in the Ketjenblack EC graph, the rapid decrease of the volume resistivity could be attributed to its unique features of its light, hollow-shelled and porous particles, which encourages a more stable conducting networks.

This observed volume resistivity % increase due to mould flow can be attributed to the fact that a break of some of the already formed conducting chains within the moulding blanks,does occur during the mould flow. The higher the mould flow, the greater the number of chains broken. Also the higher the carbon black concentration the higher the number of particles, and the higher the probability of interparticulate contacts forming conducting chains, and therefore the smaller the relative number of broken chains.

5.4.2 MOULDING PRESSURE

Table 5.5 and figs. 5.4-5.6 are now considered. The summary of the assessed vulcanisate properties is as in Table 5.5. Figs. 5.4-5.6 are graphs of the volume resistivity % increase vs carbon black concentration. Similar to Section 5.4.1, the volume resistivity % was calculated from the difference (increase) in measured volume resistivity of increased moulding pressure (b and c) from the standard (a).

It was observed that the volume resistivity % increase

TABLE 5.5 VULCANISATE PROPERTIES OF CONDUCTIVE SILASTIC CP45 BASED COMPOUNDS: EFFECT OF MOULDING PRESSURE

Mix Number		Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Percentage Increase	Hardness (IRHD)
1	a	1.20	6.00	10.00×10^{10}	–	46.0
	b			–	–	
	c			–	–	
2	a	1.01	7.50	8.00×10^{10}	–	48.0
	b			8.30×10^{10}	3.75	
	c			8.60×10^{10}	7.50	
3	a	0.83	8.90	5.50×10^{10}	–	49.0
	b			5.65×10^{10}	2.73	
	c			5.75×10^{10}	4.55	
4	a	0.70	10.00	2.60×10^{6}	–	51.0
	b			2.66×10^{6}	2.31	
	c			2.70×10^{6}	3.85	
5	a	0.63	10.50	3.90×10^{2}	–	53.0
	b			3.95×10^{2}	1.28	
	c			3.98×10^{2}	2.05	
6	a	0.52	11.40	2.52	–	55.0
	b			2.54	0.79	
	c			2.55	1.19	
7	a	1.10	6.80	9.00×10^{10}	–	44.0
	b			9.30×10^{10}	3.33	
	c			9.60×10^{10}	6.67	
8	a	1.00	7.60	5.80×10^{10}	–	45
	b			5.95×10^{10}	2.59	
	c			6.05×10^{10}	4.31	
9	a	0.92	8.30	1.90×10^{10}	–	45
	b			1.94×10^{10}	2.11	
	c			1.97×10^{10}	3.68	
10	a	0.78	9.40	2.60×10^{5}	–	46
	b			2.64×10^{5}	1.54	
	c			2.66×10^{5}	2.31	
11	a	0.73	9.80	2.20×10^{2}	–	47.0
	b			2.22×10^{2}	0.91	
	c			2.23×10^{2}	1.36	
12	a	0.62	10.60	3.12	–	49.0
	b			3.14	0.64	
	c			3.15	0.96	
13	a	0.54	11.30	2.80	–	51.0
	b			2.81	0.36	
	c			2.82	0.71	
14	a	1.00	7.60	8.90×10^{10}	–	48
	b			9.20×10^{10}	3.37	
	c			9.40×10^{10}	5.62	
15	a	0.88	8.60	9.00×10^{2}	–	50.0
	b			9.20×10^{2}	2.22	
	c			9.30×10^{2}	3.33	
16	a	0.82	9.00	8.52×10^{1}	–	54.0
	b			8.62×10^{1}	1.24	
	c			8.63×10^{1}	1.30	
17	a	0.70	10.00	6.20	–	58.0
	b			6.24	0.65	
	c			6.25	0.81	
18	a	0.62	10.60	2.80	–	62.0
	b			2.80	–	
	c			2.80	–	

*The above results are an average of results from six samples.

Fig.. 5.4 Effect of moulding pressure on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP45 based compounds (Ref Tables 5.1 and 5.5)

b.= 1.96MNm^{-2} and c = 2.94MNm^{-2}

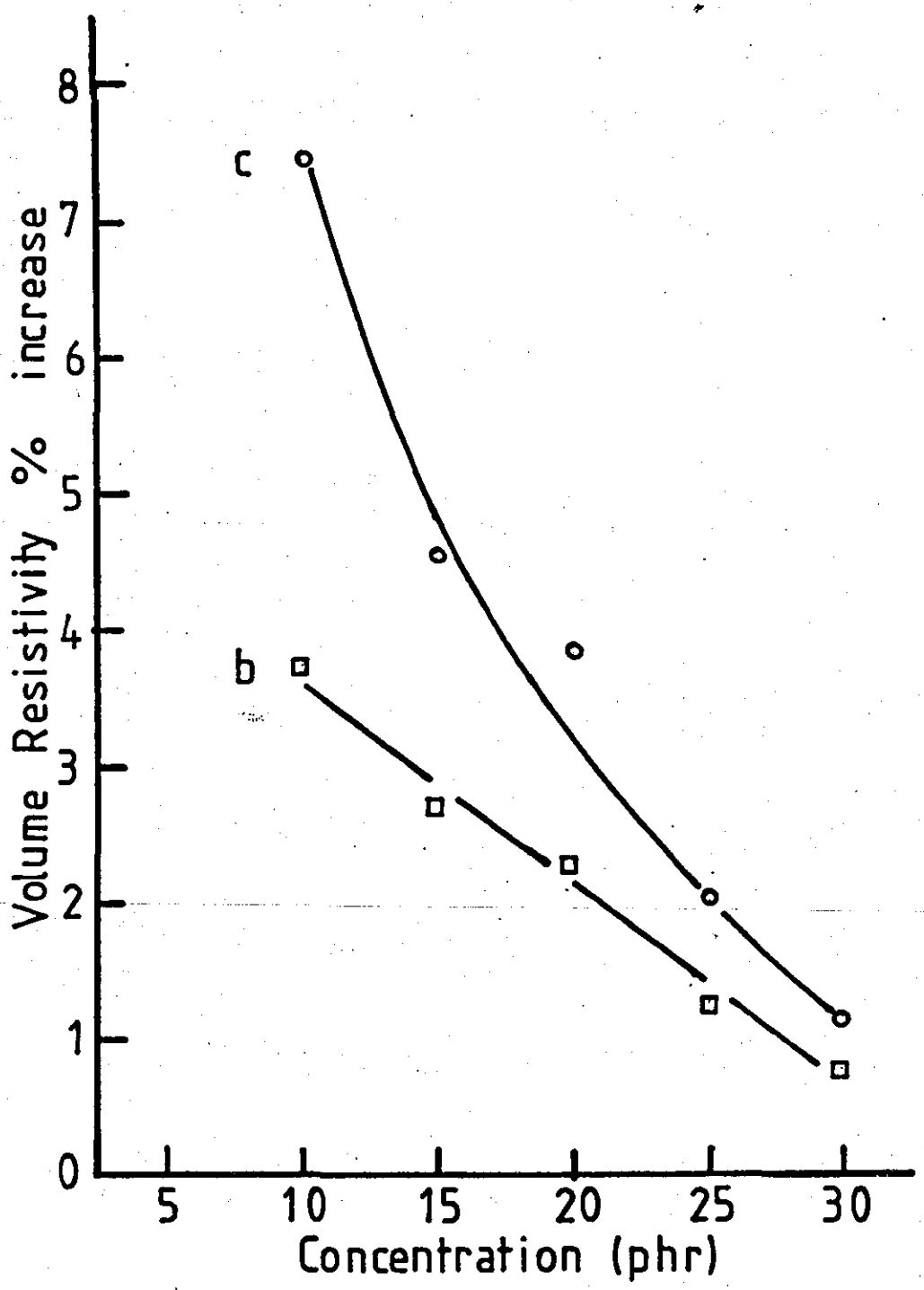


Fig. 5.5 Effect of moulding pressure on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.5)
b = 1.96MNm^{-2} and c = 2.94MNm^{-2}

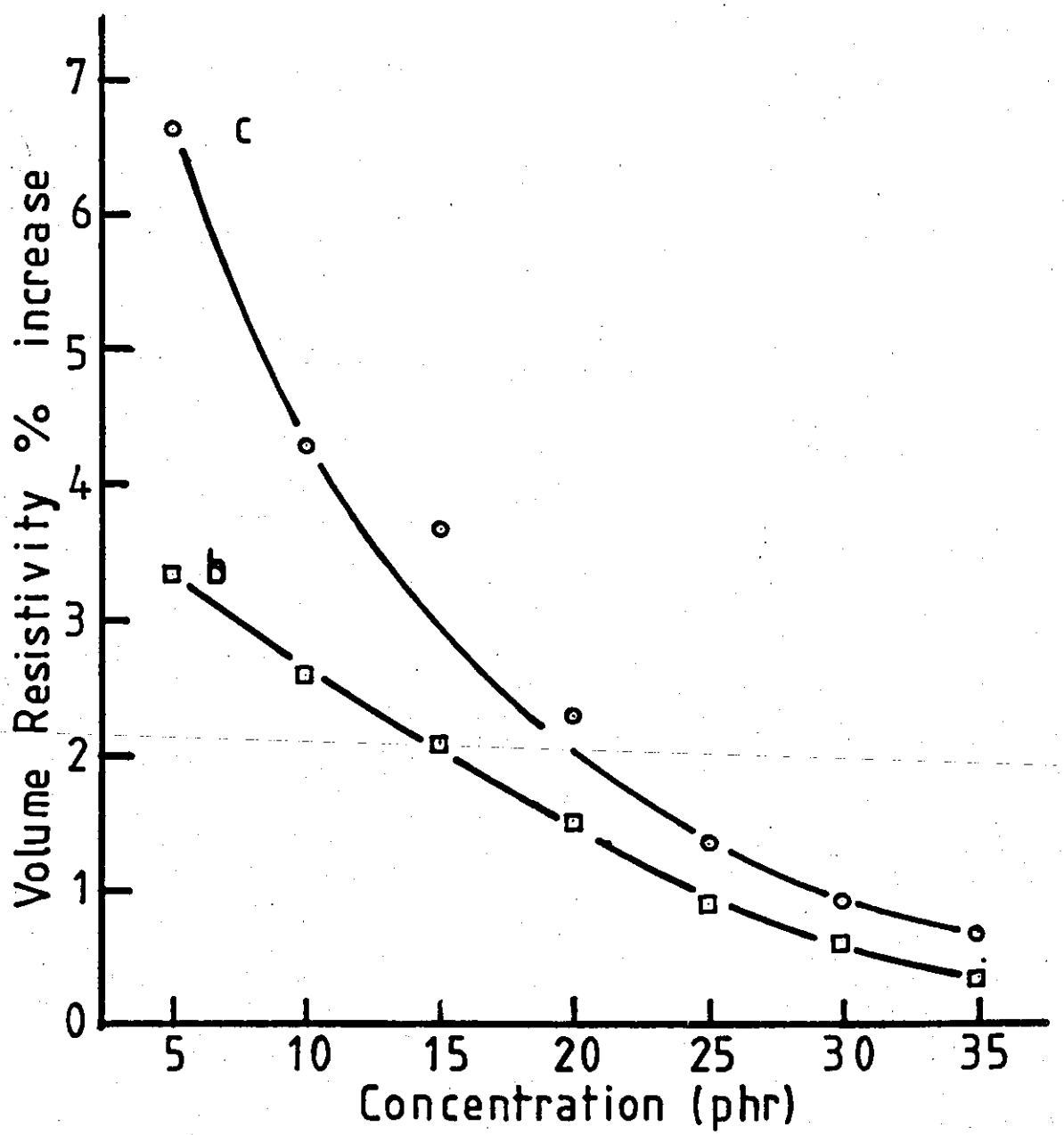
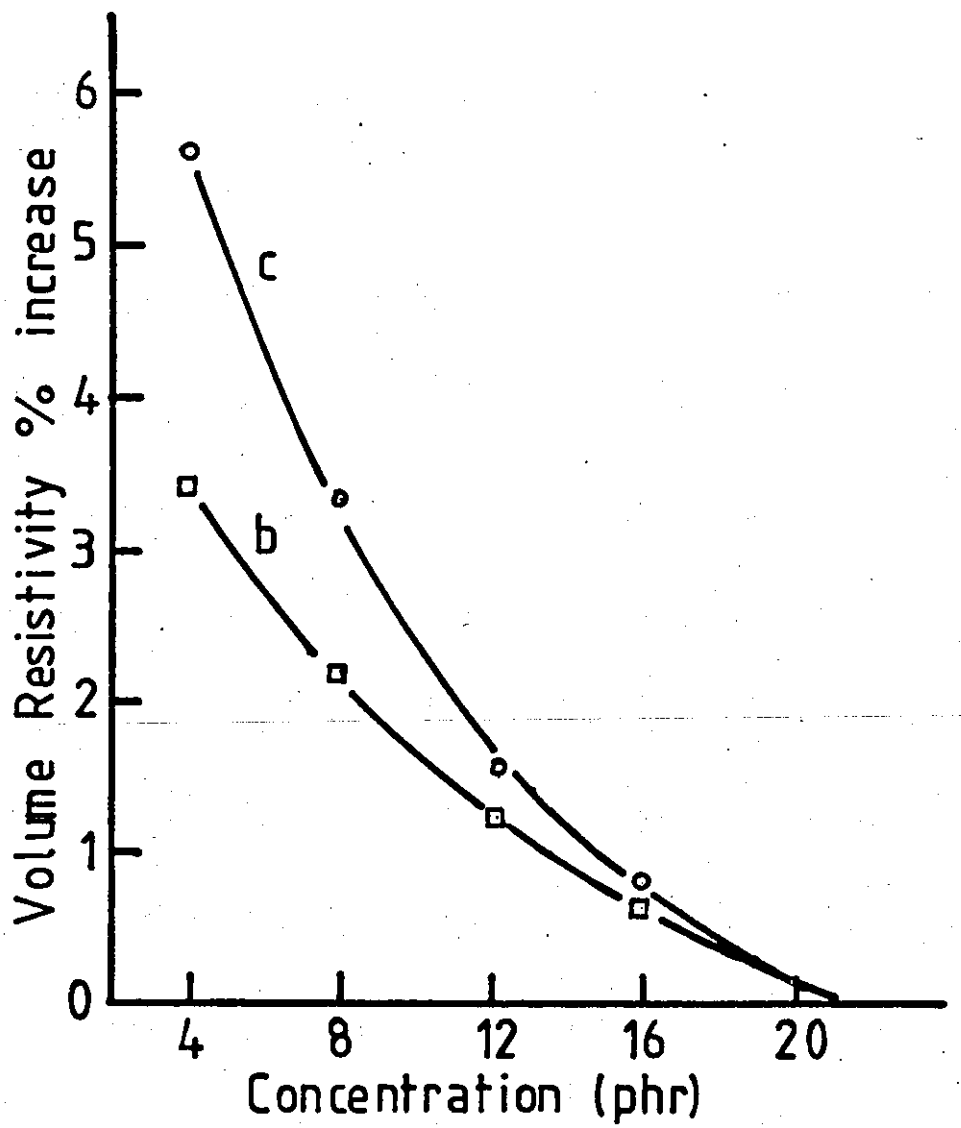


Fig. 5.6 Effect of moulding pressure on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.5)
b = 1.96MNm^{-2} and c = 2.94MNm^{-2}



a. increases with increased moulding pressure,
b. decreases with increased carbon black concentration. However, the magnitude and rate of decrease is dependent on the type of carbon black as shown in Table 5.6.

TABLE 5.6 VOLUME RESISTIVITY PERCENTAGE INCREASE RANGE (MOULDING PRESSURE)

	Vulcan P	Shawinigan	Ketjenblack EC
CB concentration	10 - 30	10 - 35	4 - 20
1.96 MNm^{-2} 'b'	3.80 - 0.80	3.30 - 0.40	3.40 - 0.70
2.94 MNm^{-2} 'c'	7.50 - 1.20	6.70 - 0.70	5.60 - 0.80

Similarly, the volume resistivity % increase increases 'rapidly' with increasing carbon black concentration. This was observed to occur in all vulcanisates (figs 5.4-5.6).

5.4.3 STORAGE TIME

A summary of the vulcanisate properties is given in Table 5.7. Figs. 5.7-5.9 are graphs of the volume resistivity % decrease vs carbon black concentration. The volume resistivity % decrease was calculated from the difference (decrease) in measured volume resistivity of increased storage time (b and c) from the standard storage time (a).

It was observed that the cure rate decreased and cure time increased by a small amount with increased storage time. Similarly a decrease in hardness was observed to occur as storage time increased.

The volume resistivity % decrease was observed to occur with increased storage time. [illegible] Different carbon blacks responded to this phenomenon, figs. 5.7-5.9, in surprisingly different ways. The storage-softening phenomenon, common to nearly all

TABLE 5.7 VULCANISATE PROPERTIES OF CONDUCTIVE SILASTIC GP45 BASED COMPOUNDS: EFFECT OF STORAGE TIME

Mix Number		Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Percentage Decrease	Hardness (IRHD)
1	a	1.20	6.00	10.20×10^{10}	—	46.0
	b	1.20	6.00	10.20×10^{10}	—	46.0
	c	1.10	6.80	10.00×10^{10}	2.00	45.0
2	a	1.01	7.50	8.60×10^{10}	—	48.0
	b	1.01	7.50	8.50×10^{10}	1.16	47.0
	c	0.96	7.90	8.30×10^{10}	3.49	43.0
3	a	0.83	8.90	5.80×10^{10}	—	49.0
	b	0.80	9.20	5.70×10^{10}	1.73	48.0
	c	0.76	9.50	5.60×10^{10}	3.45	43.0
4	a	0.70	10.00	2.70×10^{6}	—	51.0
	b	0.66	10.30	2.65×10^{6}	1.85	50.0
	c	0.61	10.70	2.60×10^{6}	3.70	46.0
5	a	0.63	10.50	4.00×10^{2}	—	53.0
	b	0.58	10.90	3.92×10^{2}	2.00	52.0
	c	0.52	11.40	3.85×10^{2}	3.75	50.0
6	a	0.52	11.40	2.50	—	55.0
	b	0.46	11.90	2.47	1.20	53.0
	c	0.38	12.50	2.42	3.20	51.0
7	a	1.10	6.80	9.60×10^{10}	—	44.0
	b	1.10	6.80	9.60×10^{10}	—	44.0
	c	1.08	7.00	9.50×10^{10}	1.04	43.0
8	a	1.00	7.60	6.20×10^{10}	—	45.0
	b	1.00	7.60	6.12×10^{10}	1.29	45.0
	c	0.97	7.90	6.00×10^{10}	3.23	43.0
9	a	0.92	8.30	2.00×10^{10}	—	46.0
	b	0.89	8.50	1.97×10^{10}	1.50	45.0
	c	0.86	8.70	1.96×10^{10}	3.20	43.0
10	a	0.78	9.40	2.70×10^{5}	—	47.0
	b	0.74	9.70	2.66×10^{5}	1.48	47.0
	c	0.70	10.00	2.61×10^{5}	3.33	45.0
11	a	0.73	9.80	2.30×10^{2}	—	48.0
	b	0.68	10.20	2.26×10^{2}	1.74	48.0
	c	0.64	10.50	2.22×10^{2}	3.48	45.0
12	a	0.62	10.60	3.20	—	49.0
	b	0.56	11.10	3.14	1.88	47.0
	c	0.51	11.50	3.08	3.75	44.0
13	a	0.54	11.30	2.80	—	51.0
	b	0.47	11.80	2.74	2.14	50.0
	c	0.42	12.20	2.69	3.93	47.0
14	a	1.00	7.60	9.60×10^{10}	—	48.0
	b	1.00	7.60	9.60×10^{10}	—	48.0
	c	0.98	7.80	9.60×10^{10}	—	46.0
15	a	0.88	8.60	9.20×10^{2}	—	50.0
	b	0.86	8.70	9.12×10^{2}	0.87	49.0
	c	0.86	8.70	9.02×10^{2}	1.96	46.0
16	a	0.82	9.00	8.70×10^{1}	—	54.0
	b	0.79	9.30	8.62×10^{1}	0.92	52.0
	c	0.78	9.40	8.53×10^{1}	1.95	50.0
17	a	0.70	10.00	6.20	—	58.0
	b	0.67	10.20	6.14	0.97	58.0
	c	0.66	10.30	6.07	2.10	56.0
18	a	0.62	10.60	2.40	—	60.0
	b	0.58	10.90	2.37	1.25	60.0
	c	0.56	11.10	2.32	3.33	56.0

The above results are an average of results from six samples

Fig. 5.7 Effect of storage time on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.7)
b = 72hrs & c = 7 days of storage times

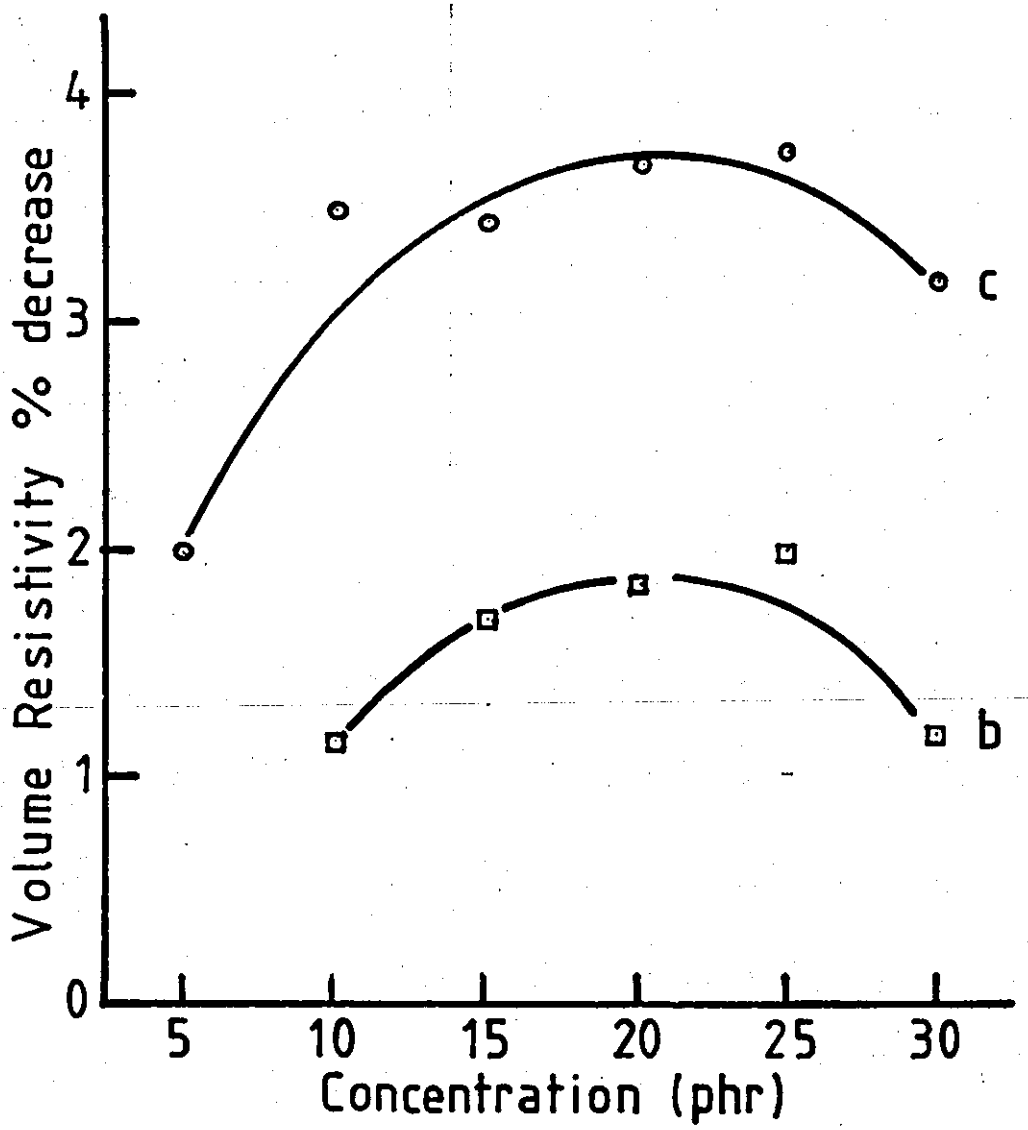


Fig. 5.8 Effect of storage time on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.7).
b = 72 hrs & c = 7 days of storage times

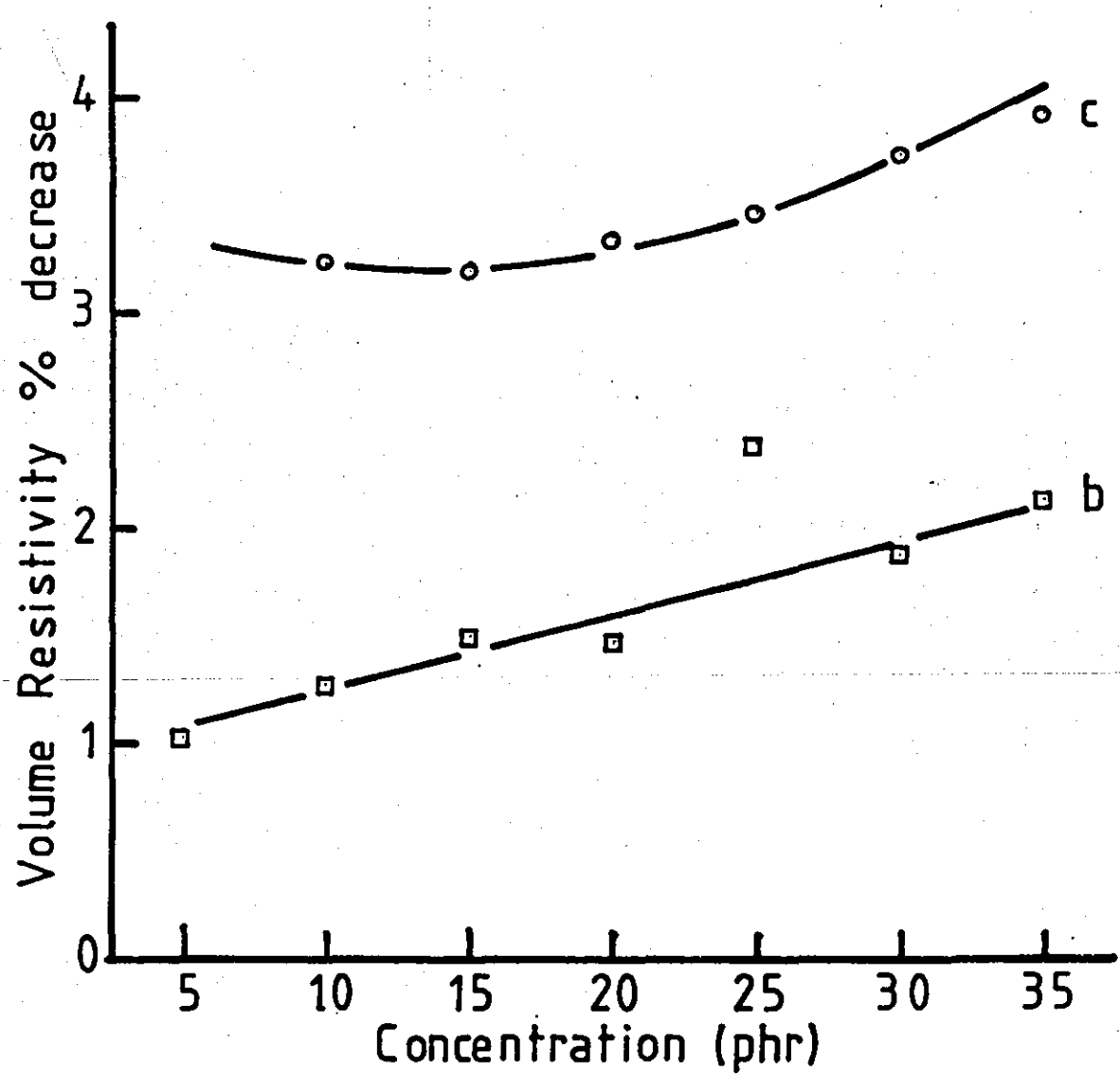
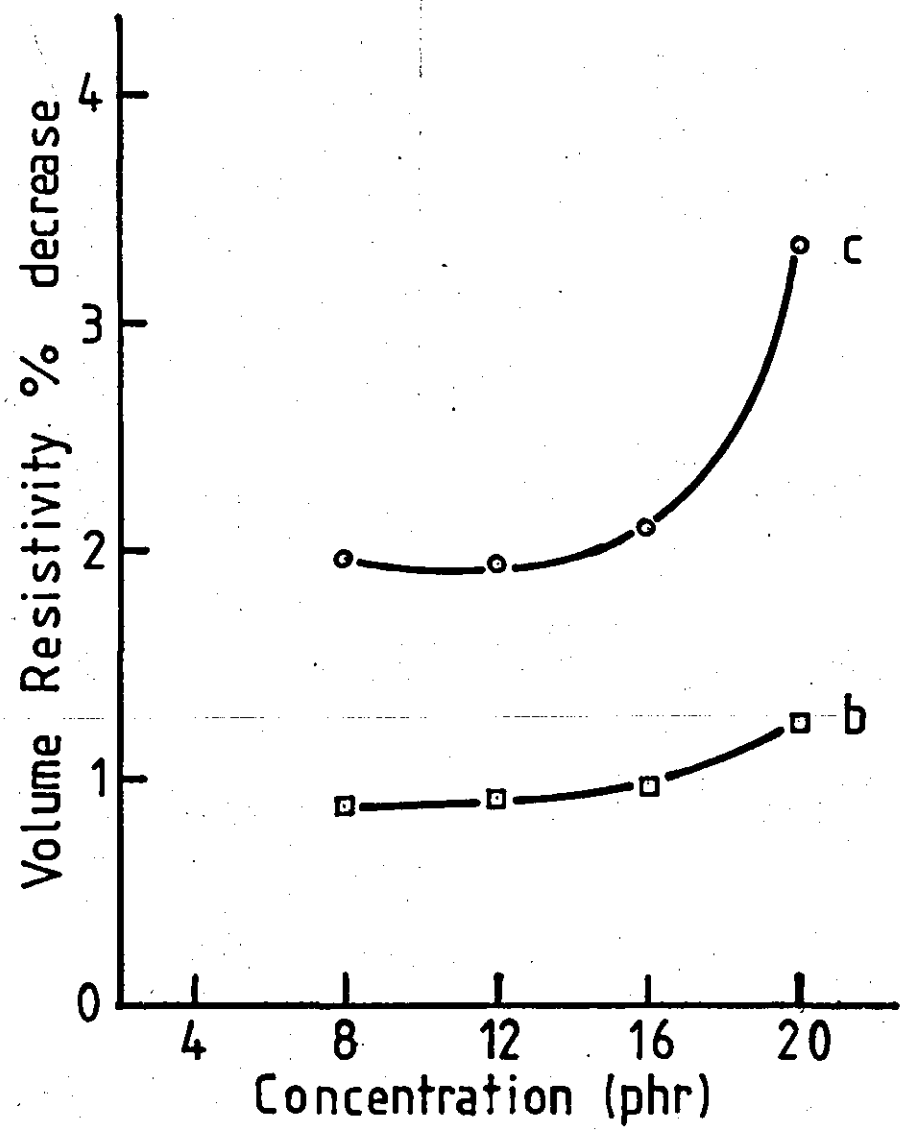


Fig. 5.9 Effect of storage time on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.7).
b = 72 hrs & c = 7 days of storage times



carbon black filled silicone-based compounds, is offered as an explanation for the lower hardness and increased cure time which were observed to occur in the vulcanisates. It is also suggested that the 'softening' may have encouraged carbon black migration and 'alignment' during storage and therefore encouraged chain formation. Hence the decrease in volume resistivity that ensued.

5.4.4 CURE TIME

Table 5.8 gives a summary of the vulcanisate properties and figs. 5.10-5.12 are now considered. The volume resistivity % difference was based on the difference in the measured resistivity of decreased (b) and increased (c) cure time from the standard (a) cure time.

It was observed that the hardness decreased with decreased cure time and slightly increased with overcure. An increase in volume resistivity with decreased cure time and decrease in volume resistivity with increased cure time was observed to occur. The volume resistivity % difference was also observed to decrease with increased carbon black content. The different carbon blacks responded to this unexpected phenomenon (figs 5.10-5.12) varied from one to another.

5.5 CONCLUSIONS

The effects of mould flow, moulding pressure, storage period, and moulding time on the volume resistivity are as outlined above. The volume resistivity was found to increase with increasing mould flow and mould pressure; and decrease with increased storage time. When vulcanised at lower (10%) than calculated curing time, the volume resistivity of the vulcanisate was found to increase by a very small percentage, but decrease when considerably (50%) overcured.

TABLE 5.8 VULCANISATE PROPERTIES OF CONDUCTIVE SILASTIC GP45 BASED COMPOUNDS: EFFECT OF CURE TIME VARIATION

Mix Number		Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Percentage Difference (±)	Hardness (IRHD)
1	a	1.20	6.00	10.20×10^{10}	—	46.0
	b		5.40	10.35×10^{10}	+ 1.47	42.0
	c		9.00	10.12×10^{10}	- 0.78	48.0
2	a	1.01	7.50	8.60×10^{10}	—	48.0
	b		6.80	8.68×10^{10}	+ 0.93	44.0
	c		11.20	8.54×10^{10}	- 0.70	50.0
3	a	0.83	8.90	5.80×10^{10}	—	49.0
	b		8.00	5.85×10^{10}	+ 0.86	46.0
	c		13.40	5.76×10^{10}	- 0.69	52.0
4	a	0.70	10.00	2.70×10^{6}	—	51.0
	b		9.00	2.72×10^{6}	+ 0.74	46.0
	c		15.00	2.69×10^{6}	- 0.40	52.0
5.	a	0.63	10.50	4.00×10^{2}	—	53.0
	b		9.50	4.02×10^{2}	+ 0.50	47.0
	c		15.80	3.99×10^{2}	- 0.25	55.0
6	a	0.52	11.40	2.50	—	55.0
	b		10.30	2.50	—	47.0
	c		17.10	2.50	—	56.0
7	a	1.10	6.80	9.60×10^{10}	—	44.0
	b		6.10	9.74×10^{10}	+ 1.46	41.0
	c		10.20	9.52×10^{10}	- 0.83	45.0
8	a	1.00	7.60	6.20×10^{10}	—	45.0
	b		6.80	6.27×10^{10}	+ 1.13	40.0
	c		11.40	6.16×10^{10}	- 0.65	46.0
9	a	0.92	8.30	2.00×10^{10}	—	46.0
	b		7.50	2.02×10^{10}	+ 1.00	42.0
	c		12.50	1.99×10^{10}	- 0.50	48.0
10	a	0.78	9.40	2.70×10^{5}	—	47.0
	b		8.50	2.72×10^{5}	+ 0.74	42.0
	c		14.10	2.69×10^{5}	- 0.37	49.0
11	a	0.73	9.80	2.30×10^{2}	—	48.0
	b		8.80	2.31×10^{2}	+ 0.43	43.0
	c		14.70	2.29×10^{2}	- 0.43	50.0
12	a	0.62	10.60	3.20	—	49.0
	b		9.50	3.21	+ 0.31	43.0
	c		15.90	3.19	- 0.31	50.0
13	a	0.54	11.30	2.80	—	51.0
	b		10.20	2.80	—	47.0
	c		17.00	2.80	—	53.0
14	a	1.00	7.60	9.60×10^{10}	—	48.0
	b		6.80	9.68×10^{10}	+ 0.83	42.0
	c		11.40	9.53×10^{10}	- 0.73	50.0
15	a	0.88	8.60	9.20×10^{2}	—	50.0
	b		7.70	9.24×10^{2}	+ 0.43	46.0
	c		12.90	9.17×10^{2}	- 0.33	51.0
16	a	0.82	9.00	8.70×10^{1}	—	54.0
	b		9.90	8.72×10^{1}	+ 0.23	46.0
	c		13.50	8.69×10^{1}	- 0.11	54.0
17	a	0.70	10.00	6.20	—	58.0
	b		9.00	6.21	+ 0.16	52.0
	c		15.00	6.20	—	58.0
18	a	0.62	10.60	2.80	—	60.0
	b		9.50	2.80	—	52.0
	c		15.90	2.80	—	61.0

*The above results are an average of results from six samples.

Fig. 5.10 Effect of cure time on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.8).
b = 10% less than calculated cure time,
c = 50% more than calculated cure time

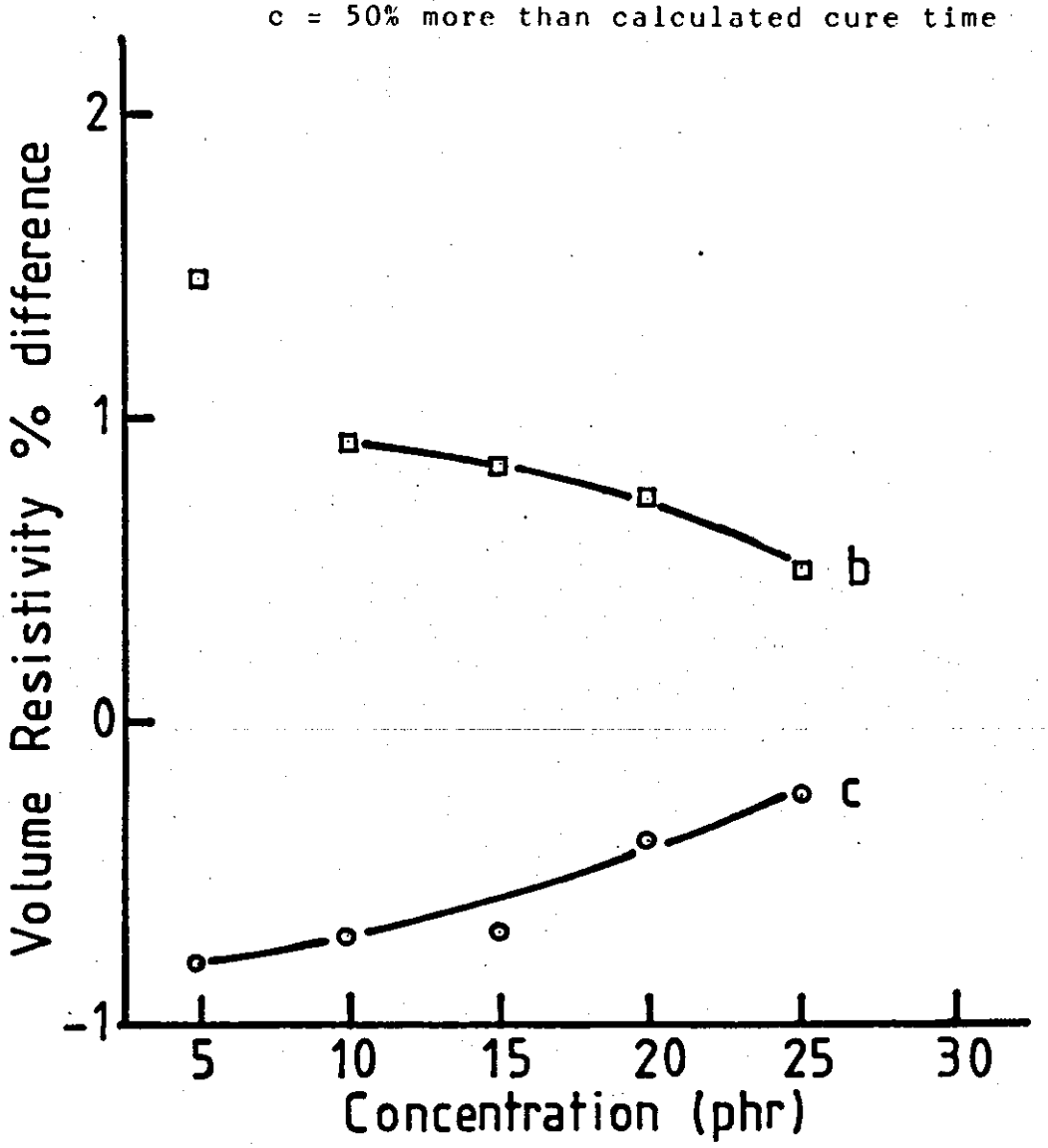


Fig.5.11 Effect of cure time on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Tables5.1 & 5.8).

b = 10% less than calculated cure time
c = 50% more than calculated cure time

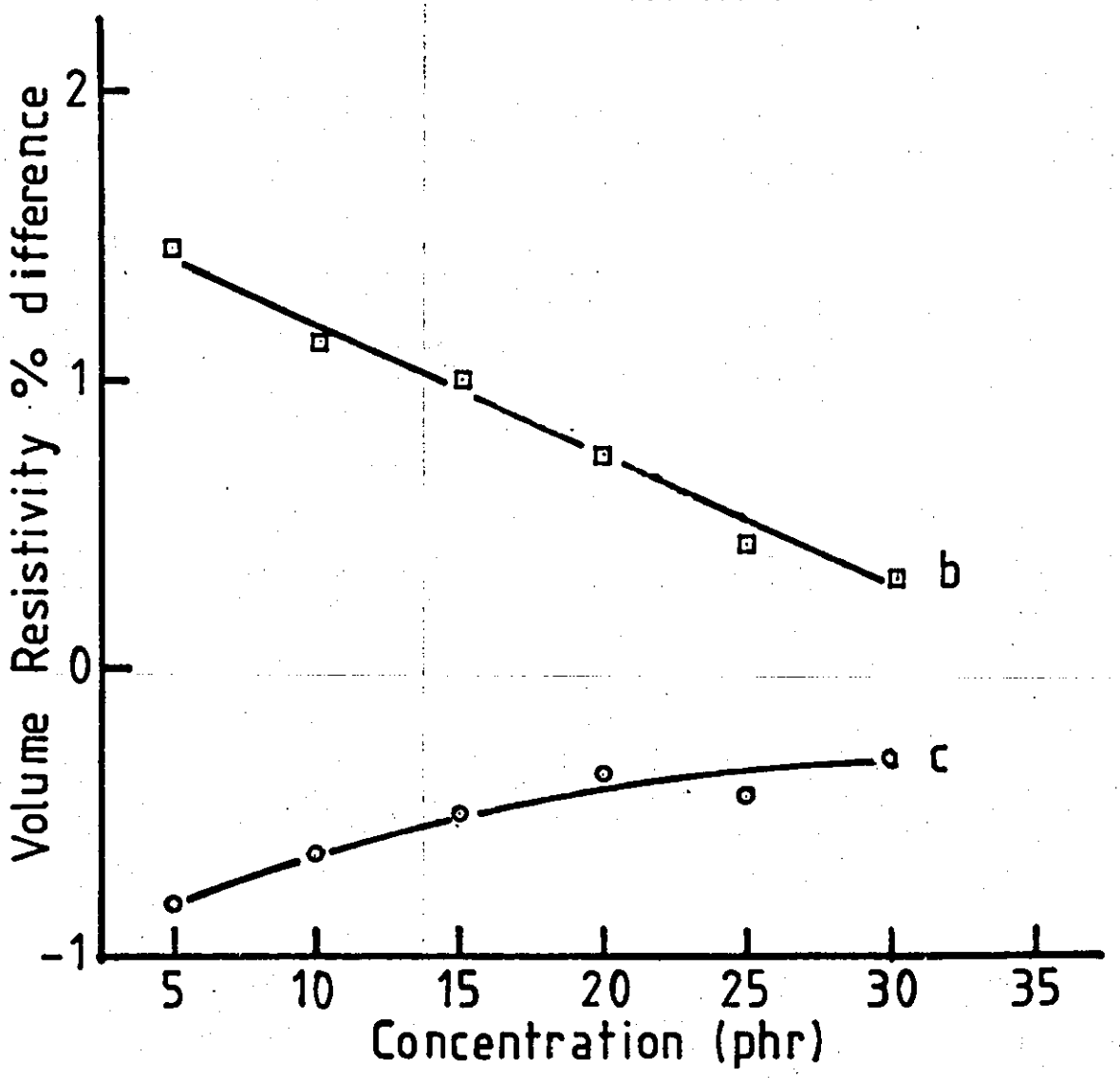
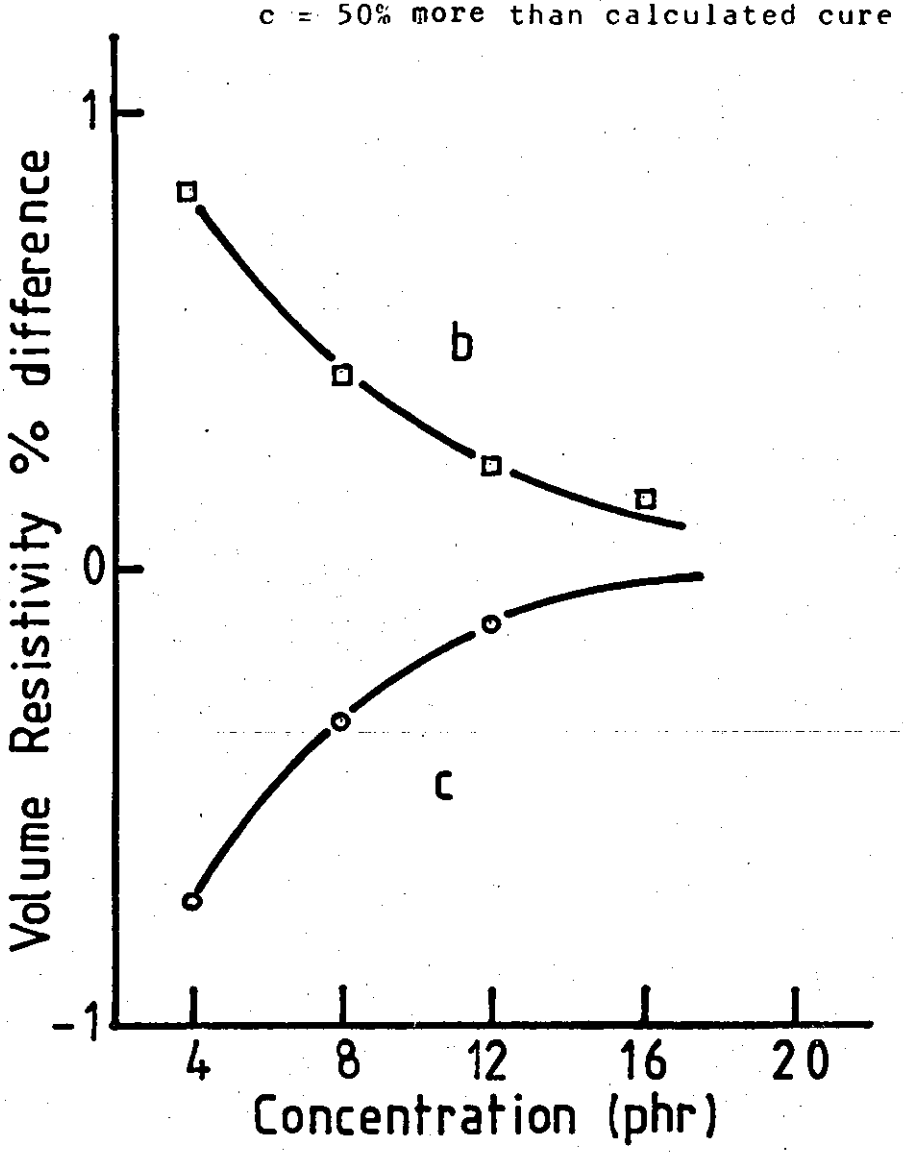


Fig.5.12 Effect of cure time on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Tables 5.1 & 5.8).
b = 10% less than calculated cure time
c = 50% more than calculated cure time



The extent to which the above criteria affected the volume resistivity is, however dependent on the type and concentration of the carbon black in the compound. The volume resistivity % difference in all compounds reduced as the carbon black concentration decreased. It is, therefore, suggested that conductive vulcanisates containing high concentrations of carbon black are less (or not) affected by the vulcanisation factors mentioned above. But when less conductive compounds are vulcanised, critical control of these factors are required in order to obtain mouldings with reproducible electrical properties.

VI CARBON BLACK CONCENTRATION IN CONDUCTIVE SILICONE RUBBERS

6.1 INTRODUCTION

Rubbers are usually electrically insulating with a resistivity usually between 10^{13} and 10^{15} ohm-cm (conductivity between 10^{-13} and 10^{-15} mho-cm^{-1}). Extensive work has been carried out[304] to convert these electrically insulating materials, especially Natural Rubber (NR), into conductors by incorporating particulate fillers.

These fillers include antistatic agents, metal particles and carbon blacks. Antistatic agents, such as quaternary ammonium compounds, are used for moderate reduction in resistivities. Very low resistive rubbers (0.02 ohm-cm or even lower if the rubber is used to stick the metal particles together) can be produced using metal powders, but with a disadvantage of an expensive and stiff product. Hence, to produce reasonably low cost material with a combination of flexibility and low resistivity, carbon blacks are usually employed. The addition of carbon black can provide low resistive (1.0ohm-cm) rubbers at very low proportions[2].

The most important factors determining the resistivity of the rubber are the concentration and type of carbon black. Graphite is rarely used commercially, presumably, because of the poor reinforcement provided. High loadings of lamp blacks were known to confer some conductivity while acetylene (e.g Shawinigan) black, termed a 'conductive black', gave a combination of high degree of conductivity and low hardness at moderate loadings. A range of conductive furnace blacks and conductive channel blacks have also been used[305]. Both acetylene and lamp blacks are differentiated from the others by a more pronounced tendency for their ultimate particles to be grouped together in three-dimensional networks; these blacks are said to have higher structures than others.

In fact, high structure is a characteristic common to more recently developed highly conductive carbon blacks, but it is worth noting that the conductivity imparted by a carbon black appears to depend on a balance of several factors: high degree of structure, high particle surface area, low volatile matter content and fine particle size.
Before going further, an understanding of the analytical properties of conductive carbon blacks will be an advantage.

6.1.1 ANALYTICAL PROPERTIES OF CONDUCTIVE CARBON BLACKS

Carbon black is described as crystallographically related to graphite and as such is an intrinsic semiconductor with a very small energy barrier between its full aromatic band and the conduction band[306]. Carbon blacks are thus employed as a conductive media in insulating polymers. The degree of conductivity contributed by these carbon blacks is dependent on the magnitude of the 'smaller energy barrier' and which is lower in the carbon blacks classified as the 'conductive carbon blacks'.

To conduct effectively, current must flow through a system. In order for this to happen, in especially a conductive polymer product, electrons must travel via the carbon black since the polymer phase is an insulator[294].
To achieve this continuous electron flow, the carbon black aggregates must be in contact or separated by very small distances[294]. Hence those factors which increases aggregate to aggregate contact or reduce the distance between aggregates tend to increase conductivity. Various researchers have theorized that various distances between aggregates must exist - with typical values being <1.0nm,[341] <10-18nm,[294] ≪2.0-2.5μm[291] - in order to achieve electron flow across the insulating polymer barrier. It is felt that these electrons penetrate through these barriers *via* the mechanism known as 'electron tunnelling'.[291,294,307,341]
Basic carbon black properties affecting the inter-aggregate distance for a given carbon black loading in polymer systems are as follows:

6.1.1.1 Nodule or primary particle size [294,307].

Since compounding ingredients are added on a weight basis, the smaller the particle size the higher the number of aggregates in contact and the smaller the interparticulate distance, hence the higher the conductivity. Surface area as measured by nitrogen absorption using the Brunauner, Emmett and Teller (BET) method [308] gives an indication of the particle size and shape. The effective surface area of a porous carbon (as some conductive carbon blacks are) can be considered to be composed of the sum of the geometric surface area, given by the particle size of the carbon, the open internal surface area (the surface pores) and the closed internal surface area (the surface roughness) [309]. Electron microscope gives the geometrical surface area calculated from the particle size distribution whereas the BET gives both the geometrical and the open internal surface area.

6.1.1.2 Aggregate shape or structure [294,307].

The high structure carbon blacks are irregular in shape and therefore have less packing together capability. In contrast to this, they tend to produce a larger number of aggregates (*i.e* particles that are strongly attached to one another) in contact as well as smaller interparticulate distance, hence higher conductivity.

The oil [Dibutylphthalate (DBP)] absorption figure gives information on the combined effects of void volume (volume between) of particles, void volume of aggregates, and void volume of agglomerates (volume between weakly attached aggregates) *i.e* a measure of carbon black 'structure' and defined as the degree of particle aggregation. The higher the DBP absorption, the higher is the structure and the bulkier the formed unit aggregates.

6.1.1.3 Porosity or roughness [294,307]

The more porous, the lighter. Since compounding ingredients are added on a weight basis, the more porous a black is, in effect, the more particles or aggregates being added to the compound as well as interaggregate/interparticulate distance decrease, hence higher conductivity.

Very high DBP absorption is not only due to the large interstice volume (*i.e* structure) as described above, but also because of penetration of hollow (porous) particles by DBP molecules through gaps in the shells. This existing porosity in the very highly conductive carbon blacks is easily penetrated by the rubber molecules. Rubber compounds containing Ketjenblack EC (S.G=2.05), therefore, have a higher density than those containing other carbon blacks (S.G≈1.8).

6.1.1.4 Surface chemistry (Chemisorbed oxygen complexes)

Carbon black surface chemical constituents are mainly carbon-bound hydrogen, hydroquinones, quinones, lactones and carboxylic acids [310]. This is high in channel blacks (5-15%) and low in furnace blacks (<2%). The chemisorbed oxygen groups affect both the availability and mobility of free electrons [307]. This electron damping effect of the surface chemistry is very important in the choice of carbon black. However, the effect of these chemisorbed and electron damping oxygen complexes is a minor one in case of low volatile content conductive carbon blacks but becomes very significant where free radical mechanism curing systems are involved such as silicone-peroxide cures.

The pH values give information on only the carbon-oxygen complexes and a possibility of carbon reacting with the polymer or compounding ingredients to form non-conducting bonds, whereas the volatile content value is an indication of overall impurity content which can be determined by its removal. For conductivity, high purity carbon black is required to offset either chemisorption effect or immobilization of the impure atoms.

Published data[2,225-233,311] on the highly conductive carbon blacks used in this exercise are given in Table 6.1.

6.2 OBJECTIVE

The objective of this exercise is to investigate the effect of carbon black type and proportion on the vulcanisate properties, especially the electrical volume resistivity and hardness of the conductive silicone rubbers

6.3 EXPERIMENTAL

6.3.1 MATERIALS (see also Ch.2, Section 2.1)

a. Polymers

Silastic GP30, Silastic GP45 and Siltech 17

b. Curing Agent

Perkadox SB

c. Conductive Carbon blacks

Vulcan P, PF, XC72, and XC72R

Shawinigan, Ketjenblack EC and Philblack XE-2

Conductex 900, SC, 975 and 40-220.

6.3.2 MIX FORMULATIONS

Table 6.2 shows the detailed mix formulations.

6.3.3 MIXING

This was carried out as described in Ch.2, Section 2.2.1. The milling times were controlled to within the 'safety time belt' as observed in Ch.4.

6.3.4 VULCANISATION

This was carried out as described in Ch.2, Section 2.2.2.

6.3.5 EVALUATION OF VULCANISATE PROPERTIES

6.3.5.1 Electrical Volume Resistivity Measurement

This was carried out as described in Ch.2, Section 2.2.4

TABLE 6.1 ANALYTICAL PROPERTIES OF HIGHLY CONDUCTIVE CARBON BLACKS

Brand	DBP absorption (ml/100g)	Surface Area (m^2g^{-1})				Particle size (nm)	Volatile content (%)	pH		Density (gl^{-1})		Ash content (%)	Moisture pick-up (%)
		BET	EM	CTAB	BET*			Lit	Mes	Helium	Bulk		
Shawinigan [227,228]	145	64.5	70.0	-	65.8	42.0±2.5	0.06	5.0	5.5	1.95	90	0.04	-
Vulcan P [229,231]	116	149	-	115	158	20	1.50	8.5	8.5	-	340	0.15	1.89
Vulcan PF [229,231]	116	149	-	115	157	20	0.94	8.5	8.6	-	220	0.15	1.80
Vulcan XC72 [224,229,231]	178	254	111	134	260	30	1.50	5.0	5.0	-	264	-	3.86
Vulcan XC72R [229,231]	185	254	110	134	262	30	0.80	8.5	7.5	-	99	-	3.90
Conductex 900 [226]	120	125	-	-	128	25	0.20	6.2	6.2	-	110	0.46	1.55
Conductex SC [225,226]	140	240	-	-	242	30	0.80	8.5	8.5	-	180	0.20	4.93
Conductex 975 [226]	165	250	110	153	274	30	1.00	7.0	7.0	-	-	0.05	3.85
Ketjenblack EC [2,230]	340	1,000	108	-	1,003	30	1.00	9.5	9.5	2.05	150	0.50	7.58
Philblack XE2 [233]	400	1,000	-	620	1,010	-	-	6.0	6.6	-	-	-	-
Conductex 40-220 [226]	228	1,075	-	510	1,030	18	1.60	5.1	5.4	-	142	0.45	12.26

N.B. BET=Brunauer, Emmett and Teller N_2 Absorption Method; EM=Electron Microscope Method; CTAB=Cetyltrimethylammonium Absorption Method; BET*=BET N_2 Method carried out by the researcher (Section 2.2.6) Lit=Literature figures; Mes=pH measurement carried out by the researcher (Section 2.2.5)

TABLE 6.2 MIX FORMULATIONS

Mix Number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Silastic GP30		100.0																		
Perkadox SB		2.5																		
	A																			
Vulcan P	I	5	10	15	20	25	30	20	22	24	26	28	30							
Vulcan PF	II	5	10	15	20	25	30	20	22	24	26	28	30							
Vulcan XC72	III	5	10	15	20	25	30	18	20	22	24	26	28							
Vulcan XC72R	IV	5	10	15	20	25	30	18	20	22	24	26	28							
Shawinigan	V	5	10	15	20	25	30	35	20	22	24	26	28	30						
Ketjenblack EC	VI	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16
Conductex 900	VII	5	10	15	20	25	30	18	20	22	24	26	28							
Conductex SC	VIII	5	10	15	20	25	30	35	20	22	24	26	28	30						
Conductex 975	IX	5	10	15	20	25	30	18	20	22	24	26	28							
Conductex 40-220	X	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16
Philblack XE-2	XI	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16

Mix Number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Silastic GP45		100.0																		
Perkadox SB		2.5																		
	B																			
Vulcan P	I	5	10	15	20	25	30	20	22	24	26	28	30							
Vulcan PF	II	5	10	15	20	25	30	20	22	24	26	28	30							
Vulcan XC72	III	5	10	15	20	25	30	18	20	22	24	26	28							
Vulcan XC72R	IV	5	10	15	20	25	30	18	20	22	24	26	28							
Shawinigan	V	5	10	15	20	25	30	35	20	22	24	26	28	30						
Ketjenblack EC	VI	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16
Conductex 900	VII	5	10	15	20	25	30	18	20	22	24	26	28							
Conductex SC	VIII	5	10	15	20	25	30	35	20	22	24	26	28	30						
Conductex 975	IX	5	10	15	20	25	30	18	20	22	24	26	28							
Conductex 40-220	X	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16
Philblack XE-2	XI	2	4	6	8	10	12	14	16	18	20	8	9	10	11	12	13	14	15	16

Mix Number		1	2	3	4	5
Siltech 17		100.0				
Perkadox SB		2.5				
	C					
Vulcan P	I	5	10	15	20	
Vulcan PF	II	5	10	15	20	
Vulcan XC72	III	5	10	15	20	
Vulcan XC72R	IV	5	10	15	20	
Shawinigan	V	5	10	15	20	25
Ketjenblack EC	VI	2	4	6	8	10
Conductex 900	VII	5	10	15	20	
Conductex SC	VIII	5	10	15	20	25
Conductex 975	IX	5	10	15	20	
Conductex 40-220	X	2	4	6	8	10
Philblack XE-2	XI	2	4	6	8	10

6.3.5.2 Hardness (IRHD) Measurement

This was carried out in accordance with BS903:Part A26:1969

6.4 RESULTS AND DISCUSSIONS

A summary of the vulcanisate properties of Silastic GP30-, Silastic GP45-, and Siltech 17- based compounds is shown in Tables 6.3-6.5

6.4.1 SILASTIC GP30 BASED COMPOUNDS

Mix Numbers AI to AXI of Table 6.3 and figs. 6.1-6.5 are considered in this exercise.

Observation of the log resistivity versus concentration graphs figs 6.1-6.3 generally shows a little change in volume resistivity initially (5-15phr loading for the furnace blacks and acetylene blacks; and 2-4phr loading for the special furnace blacks). This is usually followed by a sudden drop, giving rise to a very steep curve of volume resistivity and a very sharp transition from resistivity to conductivity at a concentration dependent on the carbon type. This established that the 'transitional' critical range from transforming an 'insulating' Silastic GP30 to a 'conductive' Silastic GP30 compound is usually between 15-26parts of furnace black and acetylene black loading and 4-14parts of 'special furnace blacks'. Hence within these ranges of black loadings, the compounded polymer will become a semi- to fully-conducting material suitable for various applications; for example as a heating material for use as an electric element.

Figs. 6.4 and 6.5 show graphs from a more detailed investigation into the effect of this critical 'transition' range. These gave logarithmic curves and ones with a different gradient to those in figs. 6.1-6.3. These 'narrow' steep bands explain why very small variations in either black concentration or processing variables give a greatly amplified increase or decrease in volume resistivity. The steeper the

TABLE 6.3 VULCANISATE PROPERTIES OF SILASTIC GP30 BASED COMPOUNDS

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
AI Vulcan P					
1	5	1.12	6.60	10.53×10^{10}	46
2	10	0.80	9.20	8.75×10^{10}	47
3	15	0.72	9.80	5.73×10^{10}	49
4	20	0.61	10.70	3.24×10^{6}	52
5	25	0.53	11.30	4.12×10^{2}	53
6	30	0.48	11.70	2.51	54
7	20	0.62	10.60	8.20×10^{6}	52
8	22	0.60	10.80	5.03×10^{5}	53
9	24	0.56	11.10	5.00×10^{3}	54
10	26	0.54	11.30	3.72×10^{2}	54
11	28	0.52	11.40	8.30	55
12	30	0.48	11.70	2.60	55
AII Vulcan PF					
1	5	1.12	6.60	10.53×10^{10}	48
2	10	0.80	9.20	8.88×10^{10}	49
3	15	0.72	9.80	6.13×10^{10}	50
4	20	0.61	10.70	3.42×10^{6}	51
5	25	0.53	11.30	4.19×10^{2}	53
6	30	0.48	11.70	2.68	54
7	20	0.62	10.60	8.40×10^{6}	51
8	22	0.60	10.80	6.00×10^{5}	52
9	24	0.57	11.00	7.15×10^{3}	53
10	26	0.54	11.30	4.88×10^{2}	55
11	28	0.51	11.50	2.50×10^{1}	56
12	30	0.47	11.80	2.70	56
AIII Vulcan XC72					
1	5	1.00	7.60	10.03×10^{10}	40
2	10	0.80	9.20	8.05×10^{10}	42
3	15	0.70	10.00	5.41×10^{10}	43
4	20	0.60	10.80	3.40×10^{6}	44
5	25	0.53	11.30	3.72×10^{2}	46
6	30	0.50	11.60	2.54	48
7	18	0.62	10.60	8.24×10^{6}	43
8	20	0.60	10.00	2.77×10^{5}	44
9	22	0.59	10.90	5.00×10^{3}	44
10	24	0.58	10.90	2.48×10^{2}	45
11	26	0.54	11.30	1.06×10^{1}	46
12	28	0.51	11.50	2.52	48
AIV Vulcan XC72R					
1	5	1.00	7.60	10.12×10^{10}	40
2	10	0.80	9.20	7.90×10^{10}	41
3	15	0.72	9.80	5.10×10^{10}	42
4	20	0.64	10.50	2.90×10^{6}	44
5	25	0.54	11.30	3.34×10^{2}	45
6	30	0.50	11.60	2.44	48
7	18	0.64	10.50	8.20×10^{6}	43
8	20	0.62	10.60	2.72×10^{5}	44
9	22	0.58	10.90	3.40×10^{3}	45
10	24	0.54	11.30	1.50×10^{2}	46
11	26	0.50	11.60	9.64×10^{1}	48
12	28	0.50	11.60	2.48	48
AV Shawinigan					
1	5	1.10	6.80	9.10×10^{10}	44
2	10	1.00	7.60	6.20×10^{10}	45
3	15	1.00	7.60	2.00×10^{10}	46
4	20	0.80	9.20	3.14×10^{5}	46
5	25	0.72	9.80	2.40×10^{2}	48
6	30	0.62	10.60	2.81	49
7	35	0.53	11.30	2.38	50
8	20	0.80	9.20	8.41×10^{6}	46
9	22	0.76	9.50	6.04×10^{5}	46
10	24	0.74	9.70	1.14×10^{4}	47
11	26	0.70	10.00	8.40×10^{2}	47
12	28	0.62	10.60	5.08×10^{1}	48
13	30	0.54	11.30	2.80	49

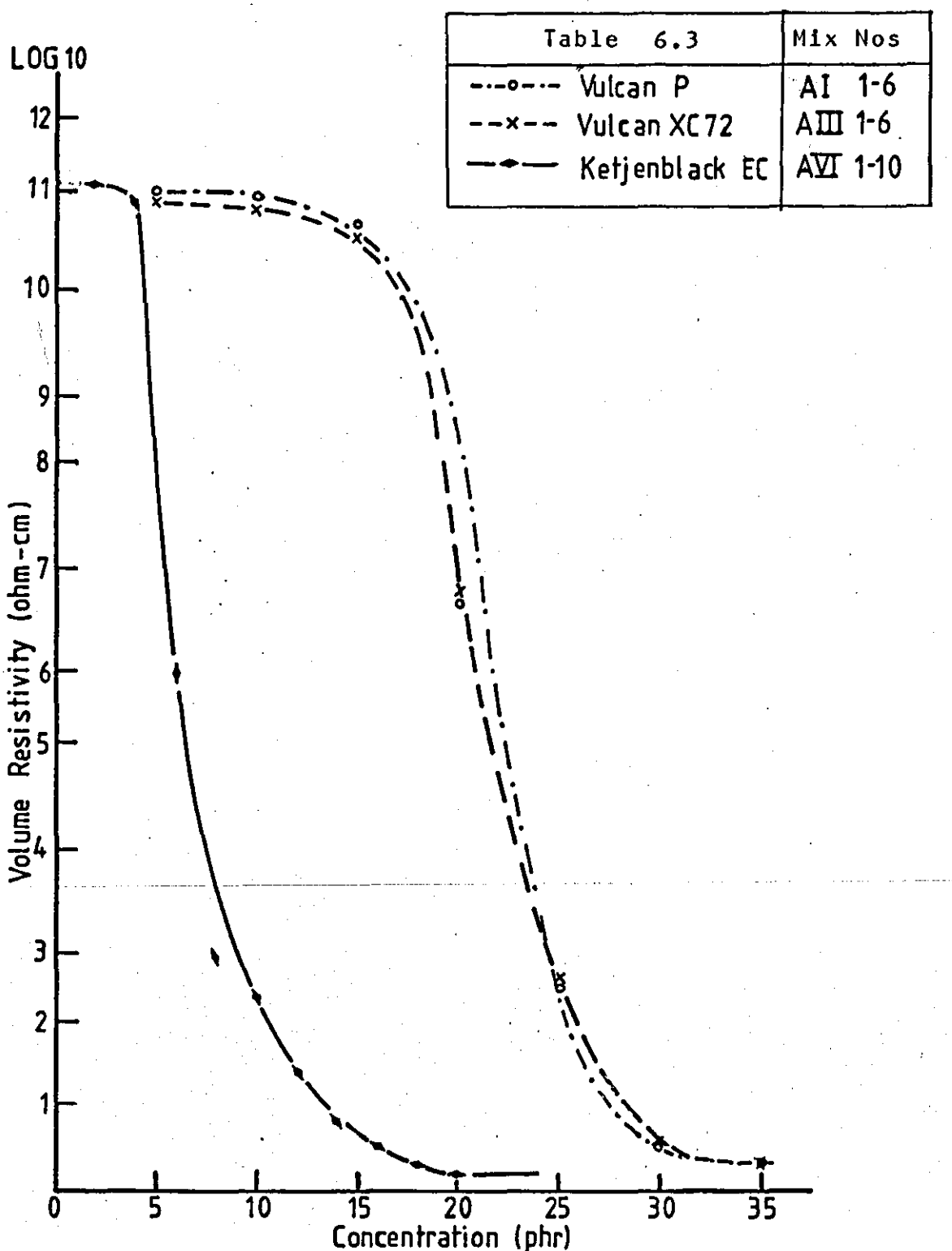
TABLE 6.3 CONTINUED

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
AVI Ketjenblack EC					
1	2	1.12	6.60	10.50×10^{10}	47
2	4	1.00	7.60	9.70×10^{10}	48
3	6	0.90	8.40	9.40×10^{5}	49
4	8	0.90	8.40	9.00×10^{2}	50
5	10	0.84	8.90	2.50×10^{2}	53
6	12	0.80	9.20	8.70×10^{1}	54
7	14	0.76	9.50	8.30	55
8	16	0.70	10.00	5.10	56
9	18	0.64	10.50	2.55	58
10	20	0.62	10.60	2.20	60
11	8	0.90	8.40	9.00×10^{2}	50
12	9	0.90	8.40	6.50×10^{2}	51
13	10	0.84	8.90	1.00×10^{2}	52
14	11	0.82	9.00	8.90×10^{1}	53
15	12	0.80	9.20	4.80×10^{1}	54
16	13	0.79	9.30	2.30×10^{1}	54
17	14	0.76	9.50	8.20	55
18	15	0.72	9.80	4.00	56
19	16	0.70	10.00	2.80	56
AVII Conductex 900					
1	5	1.00	7.60	10.10×10^{10}	40
2	10	0.80	9.20	7.80×10^{10}	41
3	15	0,72	9.80	5.00×10^{10}	42
4	20	0.64	10.50	4.20×10^{6}	43
5	25	0.54	11.30	1.00×10^{3}	45
6	30	0.50	11.60	3.60	47
7	18	0.64	10.50	9.40×10^{6}	42
8	20	0.62	10.60	3.20×10^{5}	43
9	22	0.58	10.90	9.40×10^{3}	44
10	24	0.54	11.30	9.80×10^{2}	45
11	26	0.50	11.60	2.00×10^{1}	46
12	28	0.50	11.60	4.20	47
AVIII Conductex SC					
1	5	1.00	7.60	9.10×10^{10}	44
2	10	1.00	7.60	5.40×10^{10}	45
3	15	0.80	9.20	1.20×10^{10}	46
4	20	0.76	9.50	7.40×10^{4}	47
5	25	0.72	9.80	8.00×10^{1}	48
6	30	0.62	10.60	2.80	49
7	35	0.53	11.30	2.38	50
8	20	0.80	9.20	8.20×10^{6}	46
9	22	0.76	9.50	3.00×10^{5}	46
10	24	0.74	9.70	7.20×10^{3}	47
11	26	0.70	10.00	4.80×10^{2}	48
12	28	0.62	10.60	1.02×10^{1}	49
13	30	0.54	11.30	2.80	50
AIX Conductex 975					
1	5	1.00	7.60	10.00×10^{10}	40
2	10	0.80	9.20	8.00×10^{10}	42
3	15	0.70	10.00	4.20×10^{10}	43
4	20	0.60	10.80	2.00×10^{6}	45
5	25	0.53	11.30	7.20×10^{2}	46
6	30	0.50	11.60	2.50	48
7	18	0.62	10.60	8.00×10^{6}	43
8	20	0.60	10.80	1.10×10^{5}	44
9	22	0.58	10.90	3.20×10^{3}	45
10	24	0.56	11.10	1.08×10^{2}	46
11	26	0.54	11.30	1.04×10^{1}	47
12	28	0.48	11.70	2.80	48
AX Conductex 40-220					
1	2	0.84	8.90	9.80×10^{10}	47
2	4	0.76	9.50	9.40×10^{10}	48
3	6	0.70	10.00	2.20×10^{6}	49
4	8	0.66	10.30	2.00×10^{3}	51
5	10	0.61	10.70	5.20×10^{2}	53
6	12	0.60	10.80	5.00×10^{1}	54
7	14	0.56	11.10	1.20×10^{1}	56
8	16	0.54	11.30	8.60	56
9	18	0.50	11.60	6.80	57
10	20	0.46	11.90	2.80	58

TABLE 6.3 CONTINUED

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
AX Conductex 40-220 (cntd)					
11	8	0.64	10.50	1.20×10^{3}	50
12	9	0.62	10.60	9.50×10^{2}	51
13	10	0.60	10.80	3.40×10^{2}	52
14	11	0.60	10.80	10.20×10^{1}	53
15	12	0.58	10.90	7.00×10^{1}	53
16	13	0.58	10.90	3.30×10^{1}	54
17	14	0.56	11.10	1.60×10^{1}	55
18	15	0.56	11.10	6.20	55
19	16	0.54	11.30	3.20	56
AXI Philblack XF-2					
1	2	0.98	7.80	10.50×10^{10}	47
2	4	0.96	7.90	9.70×10^{10}	48
3	6	0.90	8.40	9.40×10^{5}	49
4	8	0.86	8.70	9.00×10^{2}	50
5	10	0.82	9.00	6.40×10^{1}	52
6	12	0.76	9.50	2.50×10^{1}	53
7	14	0.70	10.00	8.30	54
8	16	0.64	10.50	5.10	56
9	18	0.62	10.60	2.55	58
10	20	0.56	11.10	2.20	60
11	8	0.86	8.70	9.52×10^{2}	51
12	9	0.84	8.90	6.00×10^{2}	51
13	10	0.82	9.00	2.60×10^{2}	52
14	11	0.78	9.40	8.20×10^{1}	53
15	12	0.76	9.50	5.20×10^{1}	53
16	13	0.72	9.80	2.60×10^{1}	54
17	14	0.70	10.00	8.40	55
18	15	0.68	10.20	5.80	55
19	16	0.64	10.50	2.60	56

Fig. 6.1 Effect of carbon black concentration on the volume resistivity of Silastic GP30 based compounds I.



N.B. The highest resistivity obtained in these measurements is 10^{11} ohmc because the base compound used in the programme already containe 5phr of carbon black. The volume resistivity of silicone rubber containing 0phr carbon black is not measured, but its value fron literature is known to be 10^{14} ohmcm.

Fig. 6.2 Effect of carbon black concentration on the volume resistivity of Silastic GP30 based compounds II.

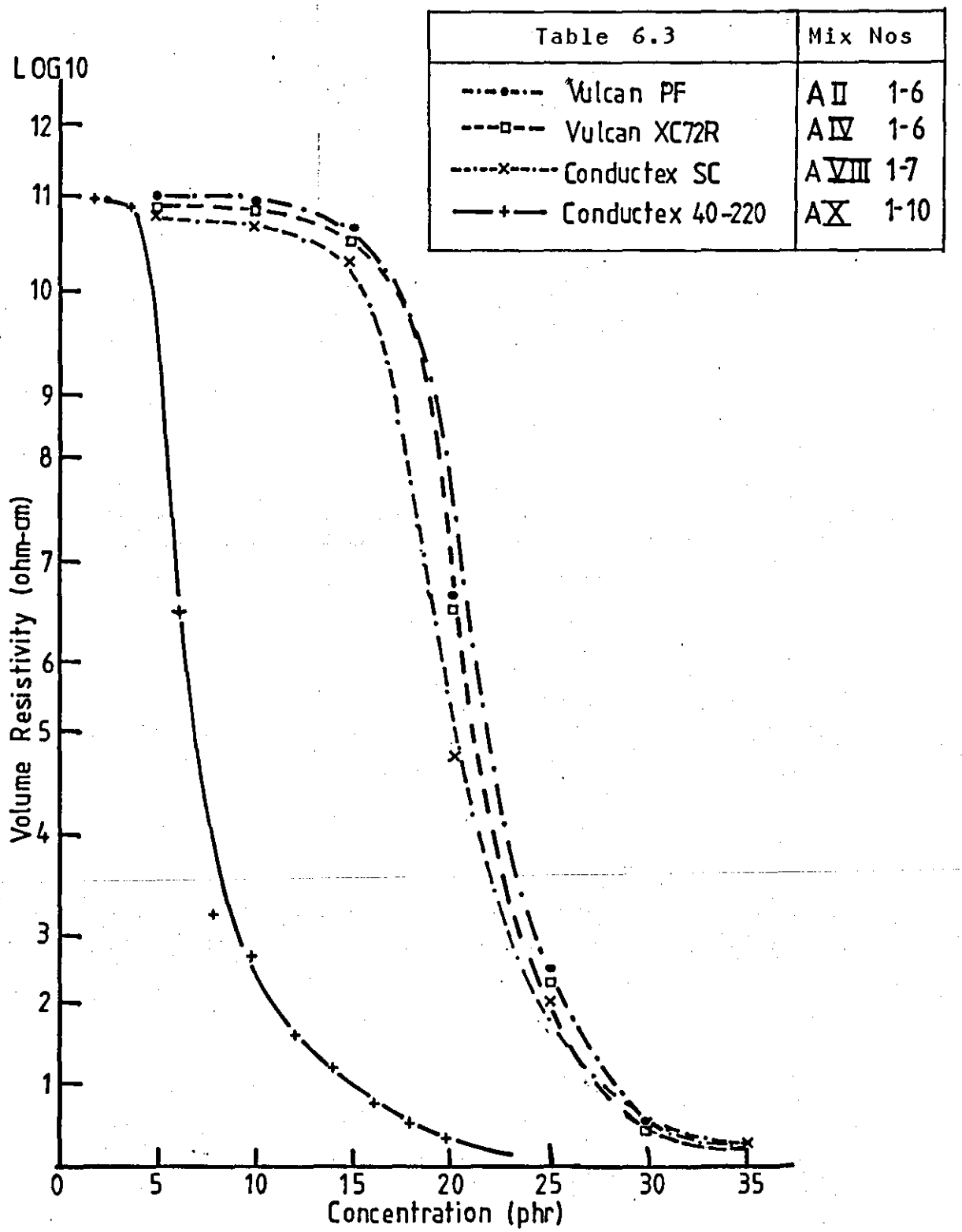


Fig. 6.3 Effect of carbon black concentration on the volume resistivity of Silastic GP30 based compounds III.

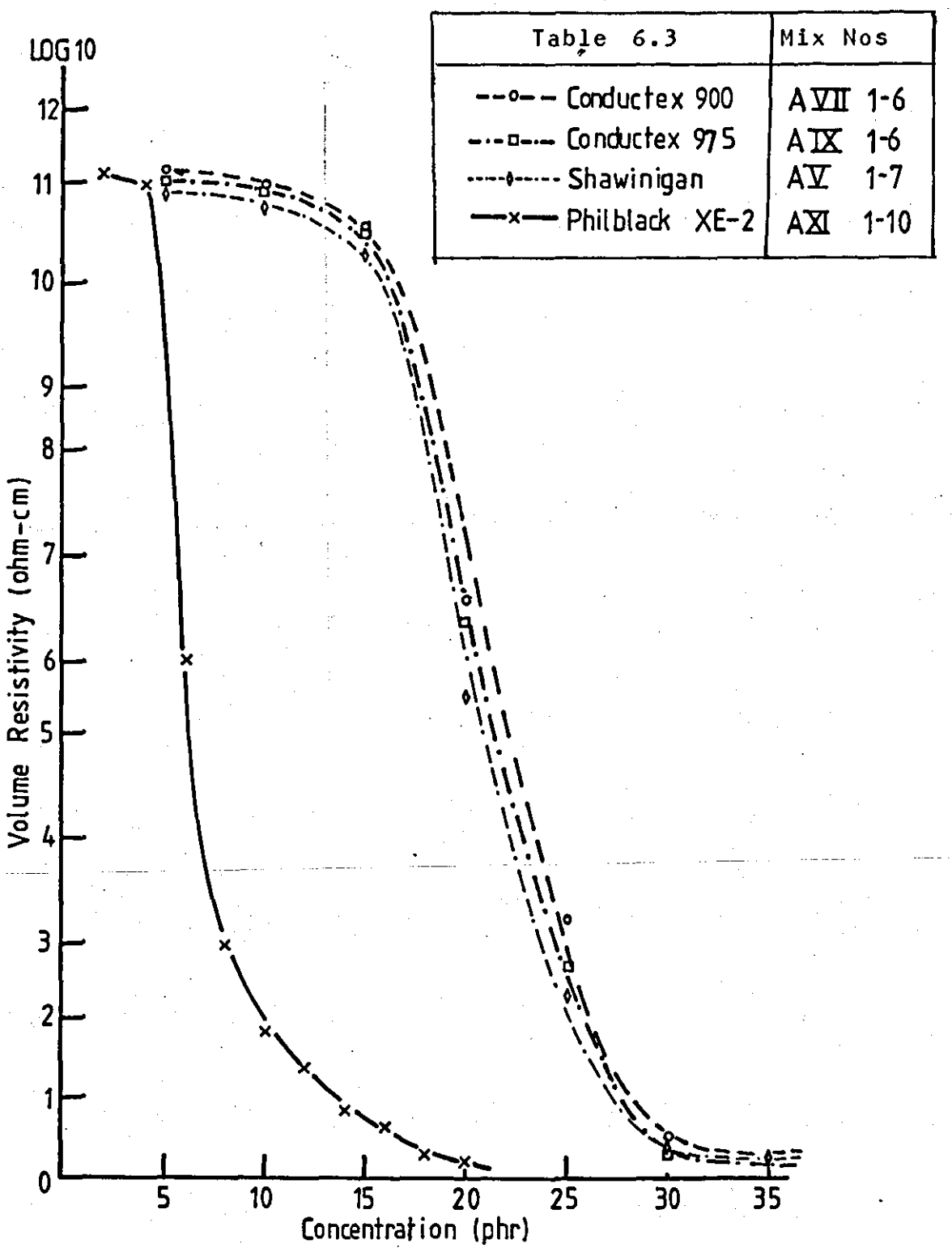


Fig. 6.4 Effect of carbon black concentration on the volume resistivity of Silastic GP30 based compounds IV.

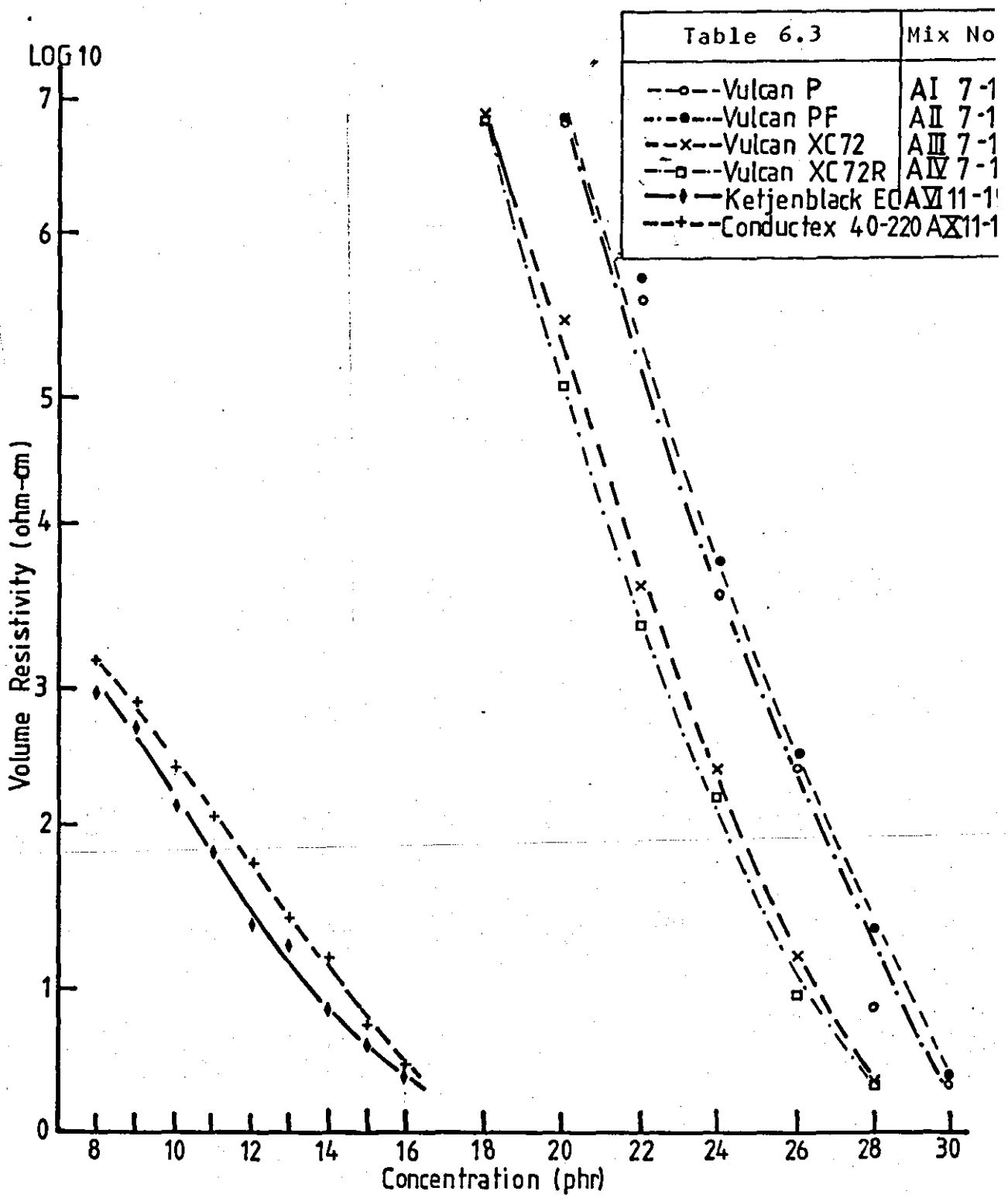
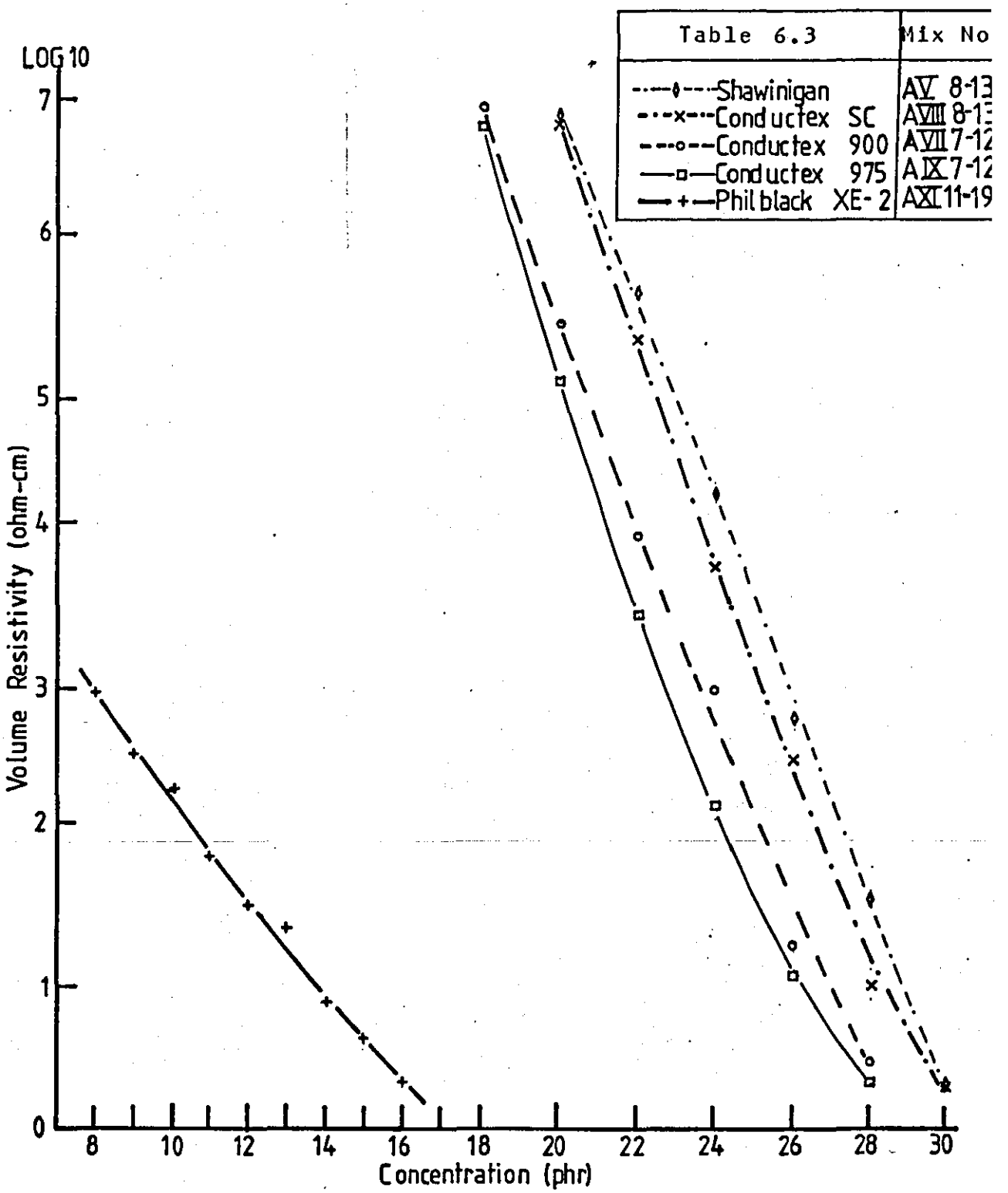


Fig.6.5 Effect of carbon black concentration on the volume resistivity of Silastic GP30 based compounds V.



resistivity-conductivity curve, the more sensitive the variation becomes.

The 'special furnace blacks' (Ketjenblack EC, Philblack XE-2 and Conductex 40-220) are observed to be outstanding in this respect. It can be seen that apart from being in a class of their own, their narrow transition is less steep compared to their furnace and acetylene counterparts and therefore suggesting a better and possibly less variable volume resistivity at this region.

This 'narrow' steep band can also be used as a guide towards predicting the effect . a particular carbon black proportion will exert on the volume resistivity and even the rubber hardness.

The hardness range is as shown in Column 5 of Table 6.3, and which, of course, increases with increasing carbon black concentration.

6.4.2 SILASTIC GP45 BASED COMPOUNDS

Figs. 6.6-6.10 and table 6.4 are hereby referred to.

It was observed in figs 6.6-6.8 that features similar to Silastic GP30-based vulcanisates predominate in these, with a similar sharp transition in the volume resistivity/carbon black proportions curve which is in the corresponding critical carbon black range that occurs between 15 and 30parts of black loading for the furnace and acetylene blacks; and 4-16parts of special furnace blacks.

Figs 6.9 and 6.10 detailed the further investigation of the critical transition area. It was observed that these yield almost linear and very slightly, but importantly, reduced rate of change with respect to volume resistivity versus carbon loading. This reduced rate of change identifies that the increased fumed silica content known to be present in GP45 had, to some limited extent, desensitised the latter's electrical conductivity response to the carbon black content. This phenomenon is considered to be an important observation, as one of the major problems associated with the manufacture of conductive rubber is its extreme sensitivity to small

TABLE 6.4 VULCANISATE PROPERTIES OF SILASTIC GP45 BASED COMPOUNDS

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min).	Volume Resistivity (ohm-cm)	Hardness (IRHD)
BI Vulcan P					
1	5	1.20	6.00	19.80×10^{10}	49
2	10	1.01	7.50	12.50×10^{10}	51
3	15	0.83	8.90	8.80×10^{10}	54
4	20	0.70	10.00	3.62×10^{6}	55
5	25	0.63	10.50	6.50×10^{2}	58
6	30	0.54	11.30	3.60	60
7	20	0.70	10.00	8.70×10^{6}	54
8	22	0.68	10.20	1.02×10^{5}	56
9	24	0.67	10.20	6.54×10^{3}	57
10	26	0.63	10.50	1.04×10^{2}	58
11	28	0.54	11.30	1.90×10^{1}	58
12	30	0.52	11.40	3.60	60
BII Vulcan PF					
1	5	1.20	6.00	20.50×10^{10}	49
2	10	1.00	7.60	14.00×10^{10}	52
3	15	0.83	8.90	9.80×10^{10}	54
4	20	0.70	10.00	3.90×10^{6}	56
5	25	0.63	10.50	8.40×10^{2}	58
6	30	0.54	11.30	3.50	60
7	20	0.70	10.00	8.89×10^{6}	56
8	22	0.68	10.20	2.38×10^{5}	57
9	24	0.67	10.20	6.97×10^{3}	58
10	26	0.63	10.50	1.28×10^{2}	58
11	28	0.54	11.30	2.60×10^{1}	59
12	30	0.52	11.40	3.80	60
BIII Vulcan XC72					
1	5	1.08	6.90	10.20×10^{10}	42
2	10	1.00	7.60	8.60×10^{10}	43
3	15	0.82	9.00	5.90×10^{10}	44
4	20	0.68	10.20	3.22×10^{6}	46
5	25	0.63	10.50	4.10×10^{2}	48
6	30	0.54	11.30	2.60	50
7	18	0.68	10.20	8.36×10^{6}	44
8	20	0.64	10.50	1.84×10^{5}	45
9	22	0.61	10.70	5.52×10^{3}	46
10	24	0.58	10.90	2.80×10^{2}	48
11	26	0.54	11.30	2.60×10^{1}	50
12	28	0.48	11.70	2.68	50
BIV Vulcan XC72R					
1	5	1.08	6.90	10.50×10^{10}	43
2	10	1.00	7.60	8.30×10^{10}	44
3	15	0.84	8.90	5.20×10^{10}	45
4	20	0.70	10.00	3.16×10^{6}	46
5	25	0.66	10.30	4.00×10^{2}	48
6	30	0.54	11.30	2.58	50
7	18	0.70	10.00	8.30×10^{6}	44
8	20	0.68	10.20	1.78×10^{5}	46
9	22	0.66	10.30	4.80×10^{3}	47
10	24	0.64	10.50	1.90×10^{2}	48
11	26	0.60	10.80	1.92×10^{1}	50
12	28	0.56	11.10	2.63	50
BV Shawinigan					
1	5	1.10	6.80	10.20×10^{10}	50
2	10	1.00	7.60	7.10×10^{10}	52
3	15	1.00	7.60	1.40×10^{10}	54
4	20	0.80	9.20	4.00×10^{5}	56
5	25	0.72	9.80	1.26×10^{2}	58
6	30	0.62	10.60	3.38	59
7	35	0.53	11.30	2.82	60
8	20	0.80	9.20	9.76×10^{6}	56
9	22	0.76	9.50	2.40×10^{5}	57
10	24	0.74	9.70	1.02×10^{4}	58
11	26	0.70	10.00	4.06×10^{2}	58
12	28	0.62	10.60	4.80×10^{1}	59
13	30	0.54	11.30	3.40	60

TABLE 6.4 CONTINUED

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
BVI Ketjenblack EC					
1	2	1.12	6.70	10.10×10^{10}	47
2	4	1.00	7.60	9.40×10^{10}	48
3	6	0.90	8.40	9.10×10^{5}	50
4	8	0.88	8.60	8.45×10^{2}	52
5	10	0.84	8.90	2.10×10^{2}	54
6	12	0.80	9.20	8.10×10^{1}	56
7	14	0.76	9.50	6.40	58
8	16	0.70	10.00	4.30	60
9	18	0.66	10.30	2.37	62
10	20	0.62	10.60	2.20	64
11	8	0.88	8.60	9.14×10^{2}	54
12	9	0.88	8.60	5.30×10^{2}	55
13	10	0.84	8.90	9.90×10^{1}	56
14	11	0.84	8.90	6.60×10^{1}	57
15	12	0.82	9.00	5.00×10^{1}	57
16	13	0.80	9.20	2.61×10^{1}	58
17	14	0.76	9.50	9.20	58
18	15	0.74	9.70	5.80	59
19	16	0.70	10.00	2.30	60
BVII Conductex 900					
1	5	1.00	7.60	10.48×10^{10}	43
2	10	0.90	8.40	8.60×10^{10}	43
3	15	0.80	9.20	5.70×10^{10}	45
4	20	0.70	10.00	4.22×10^{6}	47
5	25	0.64	10.50	7.60×10^{2}	48
6	30	0.54	11.30	2.82	49
7	18	0.70	10.00	9.50×10^{6}	45
8	20	0.66	10.30	1.10×10^{5}	46
9	22	0.64	10.50	6.42×10^{3}	47
10	24	0.62	10.60	3.80×10^{2}	48
11	26	0.60	10.80	4.06×10^{1}	49
12	28	0.56	11.10	4.40	50
BVIII Conductex SC					
1	5	1.00	7.60	10.20×10^{10}	50
2	10	1.00	7.60	6.30×10^{10}	51
3	15	0.90	8.40	1.80×10^{10}	52
4	20	0.80	9.20	8.20×10^{4}	52
5	25	0.76	9.50	8.86×10^{1}	54
6	30	0.72	9.80	3.37	55
7	35	0.62	10.60	2.78	56
8	20	0.80	9.20	9.55×10^{6}	52
9	22	0.76	9.50	9.60×10^{4}	53
10	24	0.74	9.70	2.90×10^{3}	54
11	26	0.70	10.00	1.10×10^{2}	54
12	28	0.62	10.60	1.70×10^{1}	55
13	30	0.60	10.80	3.36	56
BIX Conductex 975					
1	5	1.08	6.90	10.20×10^{10}	46
2	10	1.00	7.60	8.20×10^{10}	48
3	15	0.82	9.00	5.10×10^{10}	49
5	20	0.68	10.20	1.80×10^{6}	52
6	25	0.63	10.50	4.64×10^{2}	53
7	30	0.54	11.30	2.56	55
8	18	0.68	10.20	8.12×10^{6}	50
9	20	0.64	10.50	7.00×10^{4}	52
10	22	0.64	10.50	1.30×10^{3}	53
11	24	0.63	10.60	9.90×10^{1}	54
12	26	0.54	11.30	1.02×10^{1}	54
13	28	0.52	11.40	3.10	55
BX Conductex 40-220					
1	2	0.82	9.00	10.20×10^{10}	48
2	4	0.76	9.50	9.60×10^{10}	50
3	6	0.72	9.80	3.20×10^{6}	52
4	8	0.68	10.20	4.00×10^{3}	54
5	10	0.62	10.60	6.00×10^{2}	55
6	12	0.60	10.80	6.80×10^{1}	57
7	14	0.58	10.90	1.60×10^{1}	58
8	16	0.54	11.30	8.80	60
9	18	0.50	11.60	6.80	64
10	20	0.48	11.70	3.20	66

TABLE 6.4 CONTINUED

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
BX Conductex 40-220 (continued)					
11	8	0.66	10.30	4.20×10^{3}	52
12	9	0.64	10.50	9.50×10^{2}	53
13	10	0.62	10.60	5.20×10^{2}	54
14	11	0.62	10.60	2.12×10^{2}	55
15	12	0.60	10.80	7.80×10^{1}	56
16	13	0.58	10.90	5.00×10^{1}	56
17	14	0.58	10.90	1.30×10^{1}	57
18	15	0.56	11.10	7.20	60
19	16	0.54	11.30	4.60	62
BXI Philblack XF-2					
1	2	0.96	7.90	10.10×10^{10}	48
2	4	0.94	8.00	8.70×10^{10}	50
3	6	0.90	8.40	8.40×10^{5}	52
4	8	0.86	8.70	9.80×10^{2}	54
5	10	0.82	9.00	9.60×10^{1}	55
6	12	0.76	9.50	3.20×10^{1}	57
7	14	0.70	10.00	9.80	58
8	16	0.64	10.50	5.20	59
9	18	0.62	10.60	3.25	64
10	20	0.56	11.10	2.80	68
11	8	0.86	8.70	9.42×10^{2}	54
12	9	0.84	8.90	6.80×10^{2}	54
13	10	0.82	9.00	9.20×10^{1}	55
14	11	0.80	9.20	7.30×10^{1}	56
15	12	0.76	9.50	3.20×10^{1}	56
16	13	0.74	9.70	2.00×10^{1}	57
17	14	0.70	10.00	9.60	59
18	15	0.68	10.20	5.20	59
19	16	0.64	10.50	3.60	60

Fig. 6.6 Effect of carbon black concentration on the volume resistivity of Silastic GP45 based compounds I.

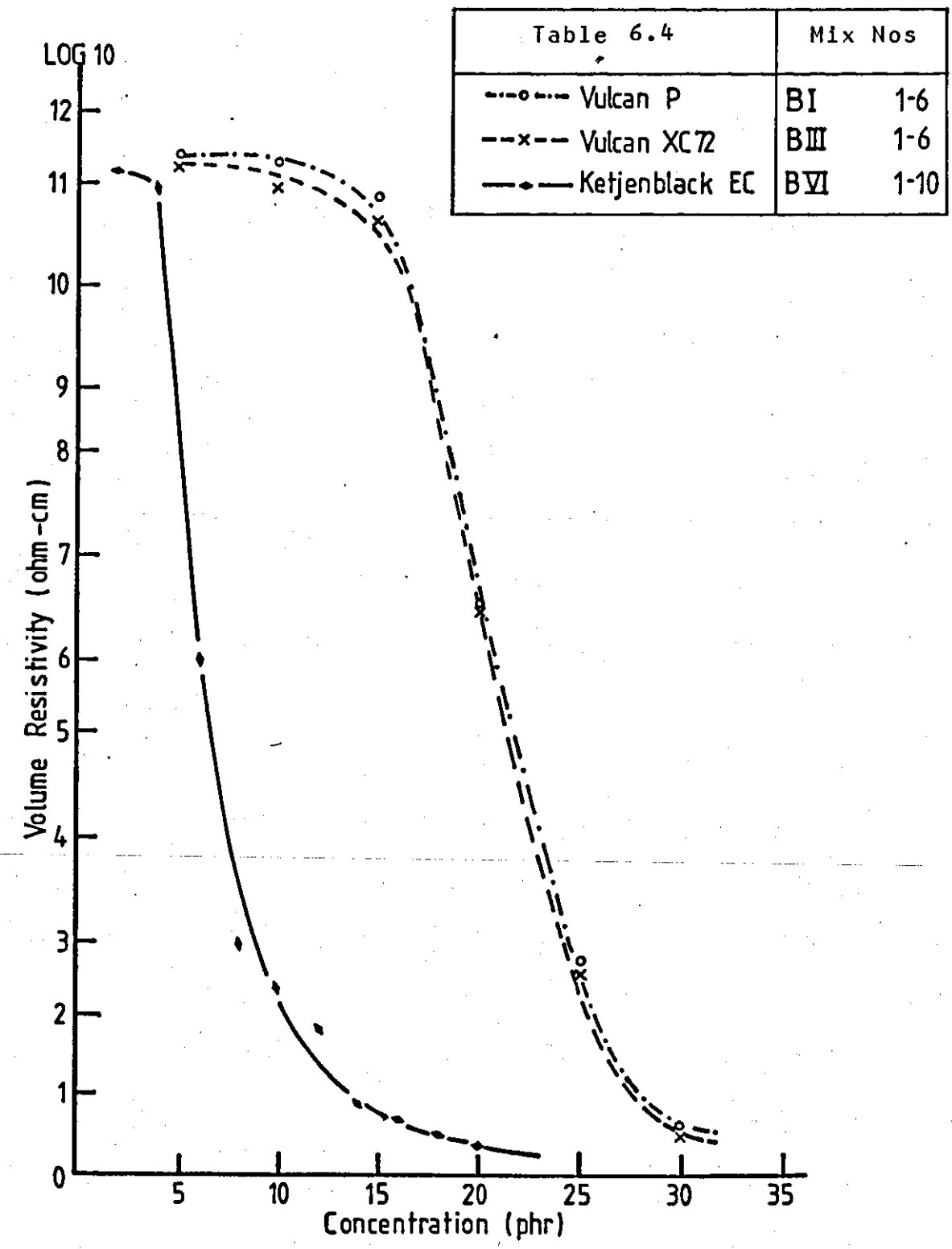


Fig. 6.7 Effect of carbon black concentration on the volume resistivity of Silastic GP45 based compounds II.

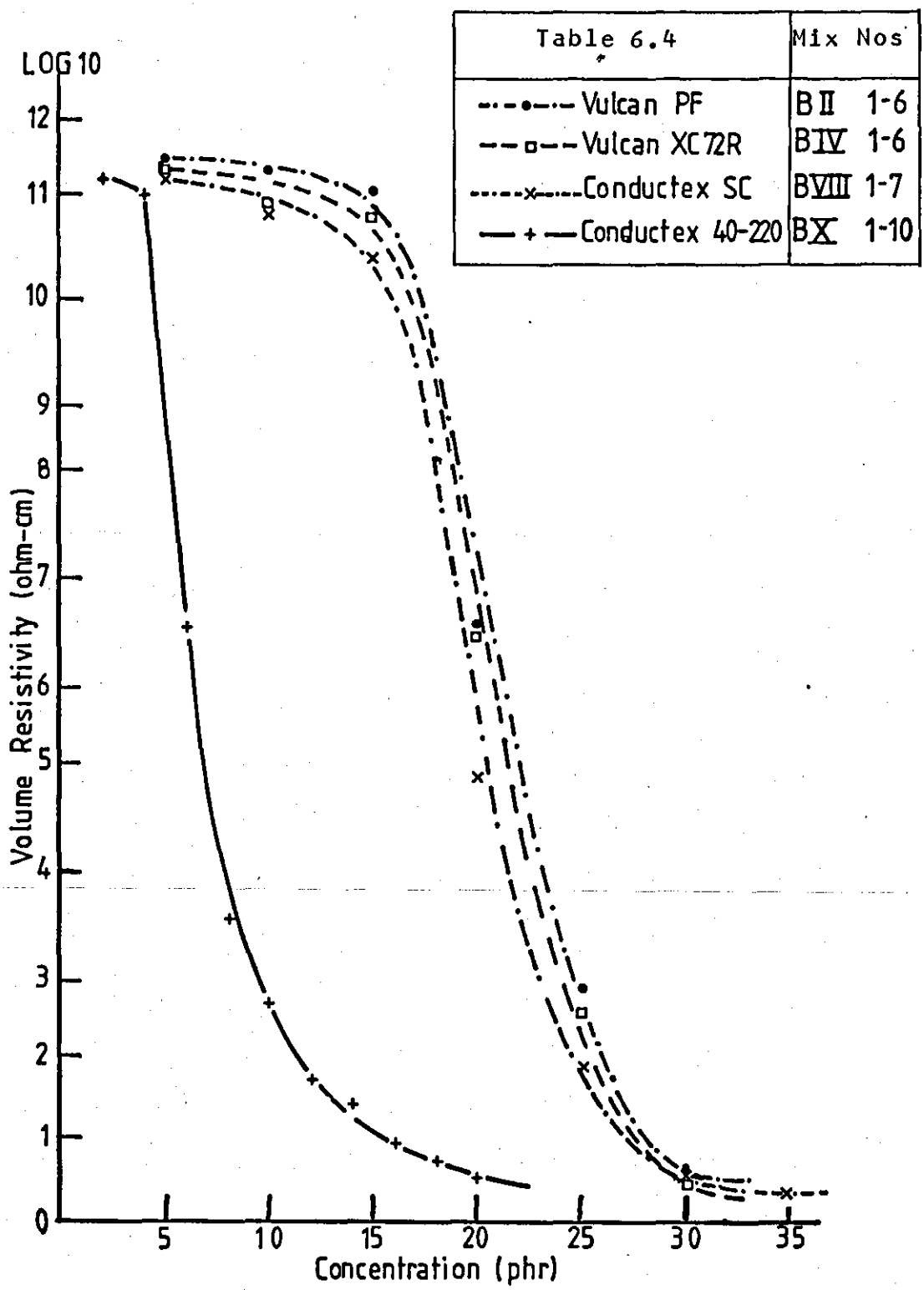


Fig. 6.8 Effect of carbon black concentration on the volume resistivity of Silastic GP45 based compounds III.

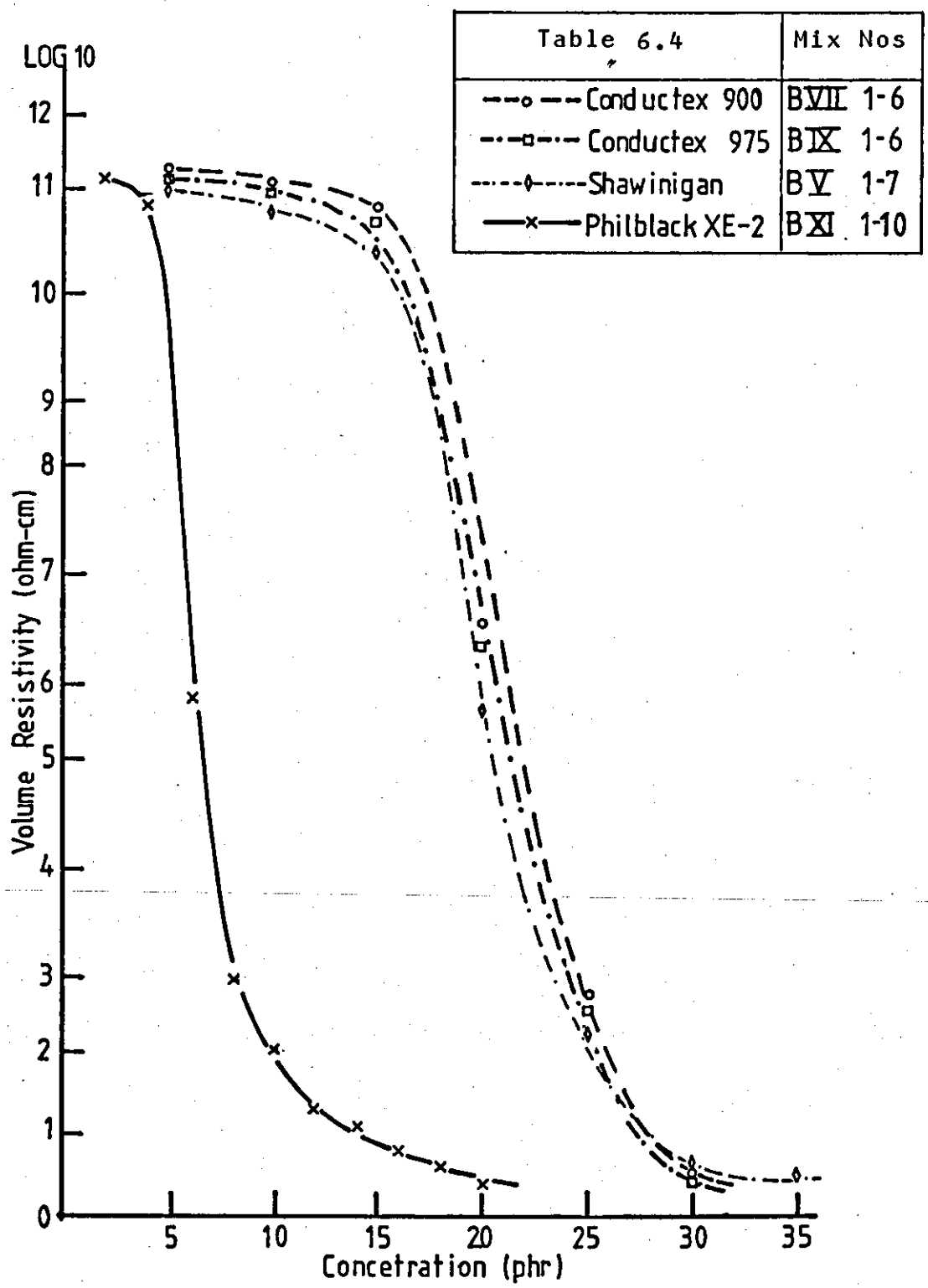


Fig. 6.9 Effect of carbon black concentration on the volume resistivity of Silastic GP45 based compounds IV.

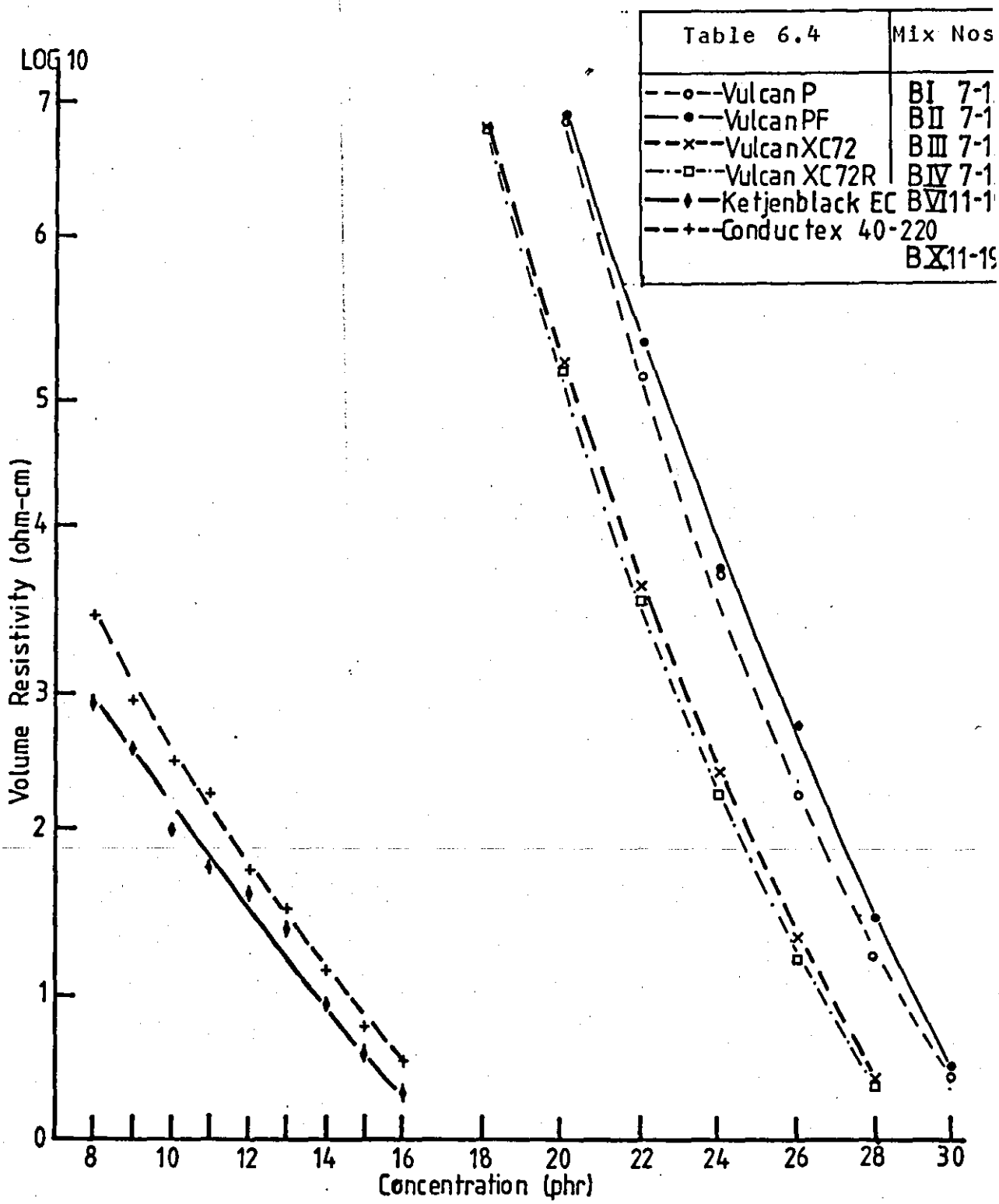
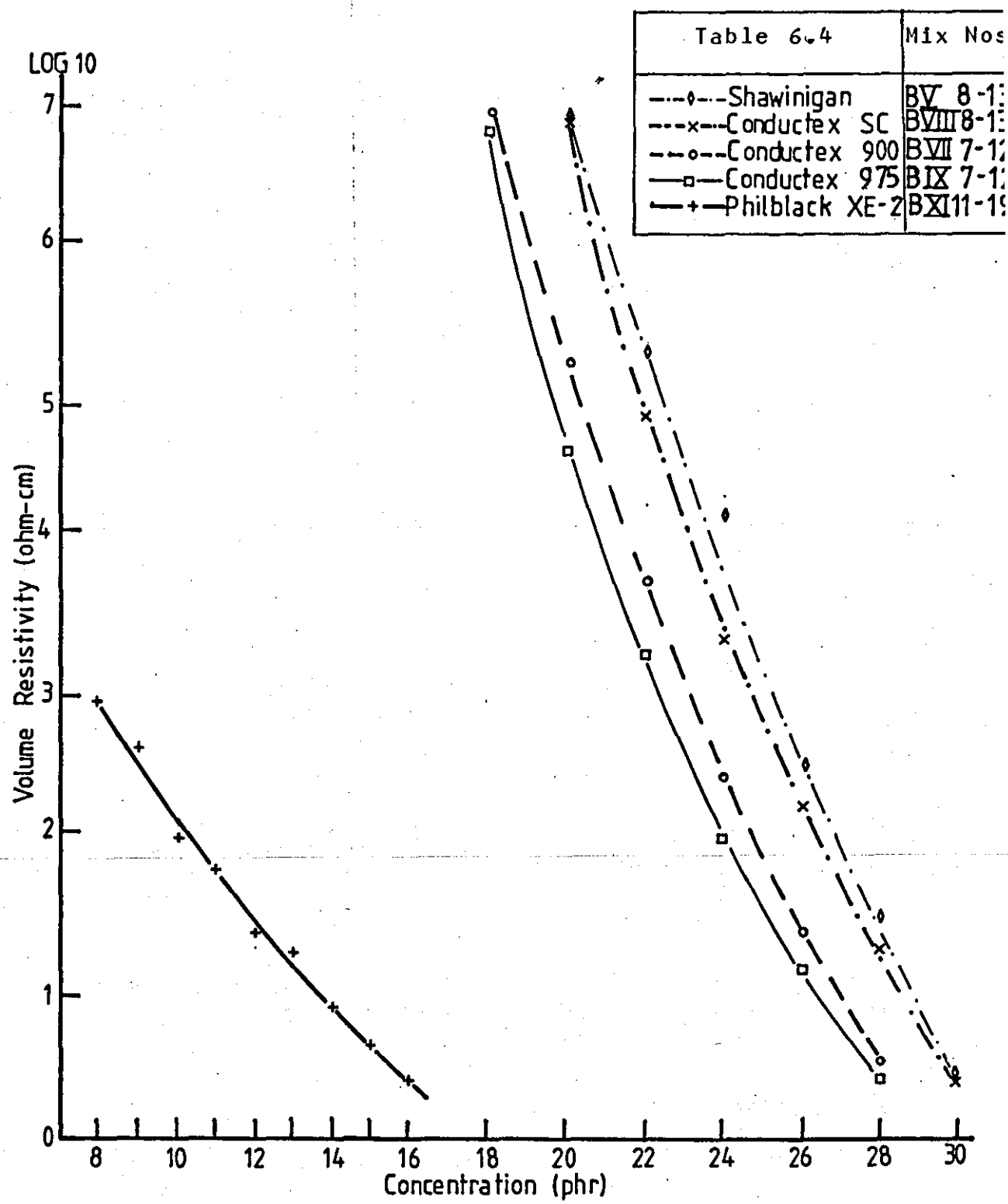


Fig. 6.10 Effect of carbon black concentration on the volume resistivity of Silastic GP45 based compounds V.



variations in carbon content and dispersion.

Like the GP30 based vulcanisates, the reduced proportion of the rate of change is dependent on the carbon black type. For example, an insignificantly reduced rate of change with respect to volume resistivity versus carbon black loading was observed to occur with the special furnace blacks. This also suggests the less variability of these blacks at these transition region.

The hardness range is as shown in Column 5 of table 6.4.

6.4.3 SILTECH 17 BASED COMPOUNDS

Table 6.5 and figs 6.11-6.13 are now considered. Only limited carbon black proportions were found practical due to difficult processing features at higher carbon black proportions.

It was observed that these vulcanisates give very unexpected features; no abrupt resistivity change with carbon black loading *i.e* there was no sudden transformation from resistivity to conductivity as experienced in the low silica GP30 and GP45 mixes, but only a steady logarithmic reduction in volume resistivity with increasing black loading. This is ascribed to the large quantity of insulating ground silica filler present in Siltech 17 which dilutes the carbon black conductivity effect and therefore the electrical resistivity response. This observation suggests that suitable insulating fillers, such as ground and fumed silica, can be used,(in controlled proportions), to desensitise, (with a calculated effect), the otherwise extremely sensitive effect of carbon black on electrical conductivity region of a conductive silicone rubber.

Possibly this would also result in a rubber mix which, when used as an electrical heating medium, would demonstrate a relatively calculated (smaller) response to volume resistivity changes (decrease) as its temperature rises.

Table 6.6 shows the analytical properties of representative conductive carbon blacks (from Table 6.1) for comparative purposes.

TABLE 6.5 VULCANISATE PROPERTIES OF SILTECH 17 BASED COMPOUNDS

Mix Number	CB%	Cure Rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
CI Vulcan P					
1	5	1.14	6.50	-	70
2	10	0.90	8.40	10.00×10^{10}	72
3	15	0.70	10.00	9.90×10^{9}	76
4	20	0.48	11.70	8.00×10^{8}	78
CII Vulcan PF					
1	5	1.10	6.80	-	70
2	10	0.90	8.40	9.80×10^{10}	70
3	15	0.78	9.40	10.00×10^{9}	72
4	20	0.54	11.30	9.60×10^{8}	76
CIII Vulcan XC72					
1	5	1.00	7.60	-	70
2	10	1.00	7.80	9.70×10^{10}	72
3	15	0.92	8.30	9.00×10^{9}	74
4	20	0.62	10.60	4.20×10^{8}	76
CIV Vulcan XC72R					
1	5	1.00	7.60	-	70
2	10	0.96	7.90	9.60×10^{10}	71
3	15	0.90	8.40	9.20×10^{9}	73
4	20	0.62	10.60	6.40×10^{8}	76
CV Shawinigan					
1	5	1.00	7.60	-	70
2	10	1.00	7.60	9.90×10^{10}	72
3	15	0.92	8.30	8.40×10^{9}	74
4	20	0.90	8.40	9.80×10^{7}	76
5	25	0.78	9.40	8.20×10^{6}	78
CVI Ketjenblack EC					
1	2	1.00	7.60	-	70
2	4	1.00	7.60	9.20×10^{10}	70
3	6	0.94	8.10	6.60×10^{9}	72
4	8	0.87	8.60	4.80×10^{8}	74
5	10	0.80	9.20	7.40×10^{4}	76
CVII Conductex 900					
1	5	1.10	6.80	-	70
2	10	0.92	8.30	10.00×10^{10}	72
3	15	0.78	9.40	10.20×10^{9}	74
4	20	0.68	10.20	9.90×10^{8}	76
CVIII Conductex SC					
1	5	1.00	7.60	-	68
2	10	0.96	7.90	8.80×10^{10}	71
3	15	0.90	8.40	8.40×10^{9}	73
4	20	0.84	8.90	4.80×10^{8}	74
5	25	0.76	9.50	9.20×10^{6}	76
CIX Conductex 975					
1	5	1.00	7.60	-	70
2	10	0.96	7.90	9.80×10^{10}	71
3	15	0.92	8.30	8.90×10^{9}	73
4	20	0.80	9.20	3.80×10^{8}	76
CX Conductex 40-220					
1	2	1.00	7.60	-	70
2	4	0.94	8.10	9.92×10^{10}	70
3	6	0.86	8.70	9.90×10^{9}	72
4	8	0.80	9.20	7.20×10^{6}	74
5	10	0.70	10.00	1.02×10^{5}	76
CXI Philblack XE-2					
1	2	1.00	7.60	-	70
2	4	0.96	7.90	9.00×10^{10}	71
3	6	0.90	8.40	6.20×10^{8}	72
4	8	0.84	8.90	3.90×10^{6}	74
5	10	0.76	9.50	1.80×10^{4}	78

Fig.6.11 Effect of carbon black concentration on the volume resistivity of Siltech 17 based compounds I.

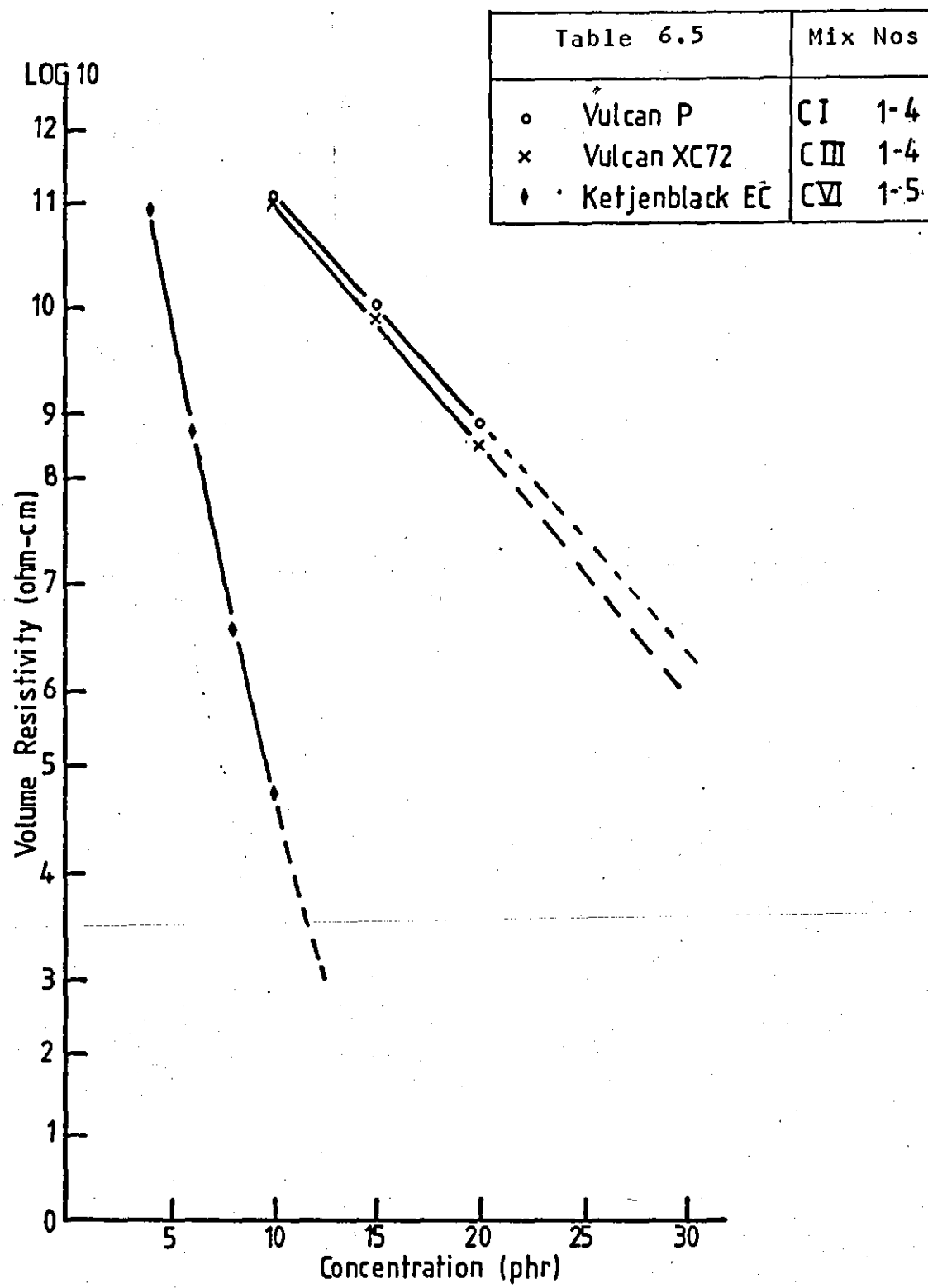


Fig. 6.12 Effect of carbon black concentration on the volume resistivity of Siltech 17 based compounds II.

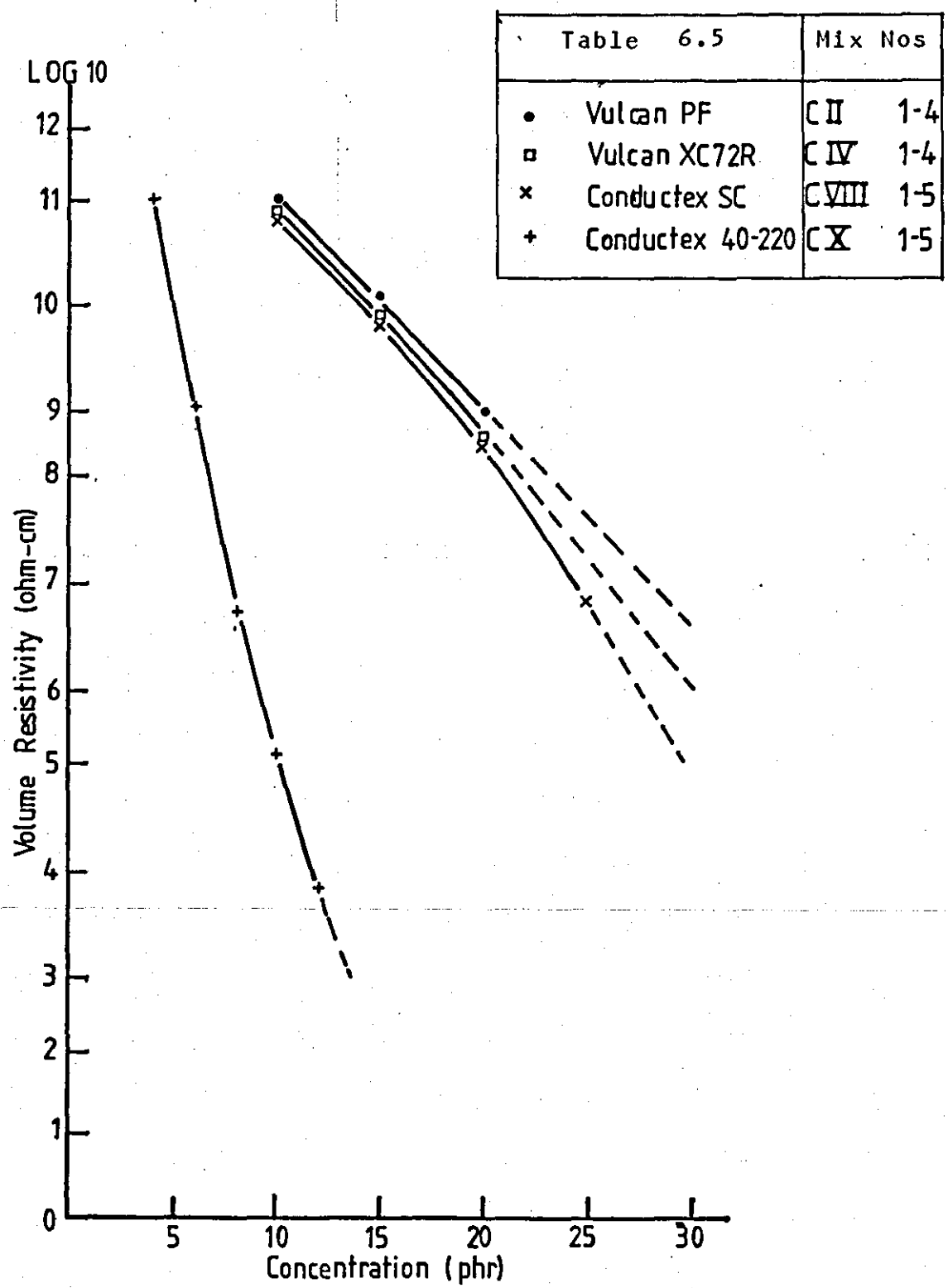


Fig. 6.13 Effect of carbon black concentration on the volume resistivity of Siltech 17 based compounds III.

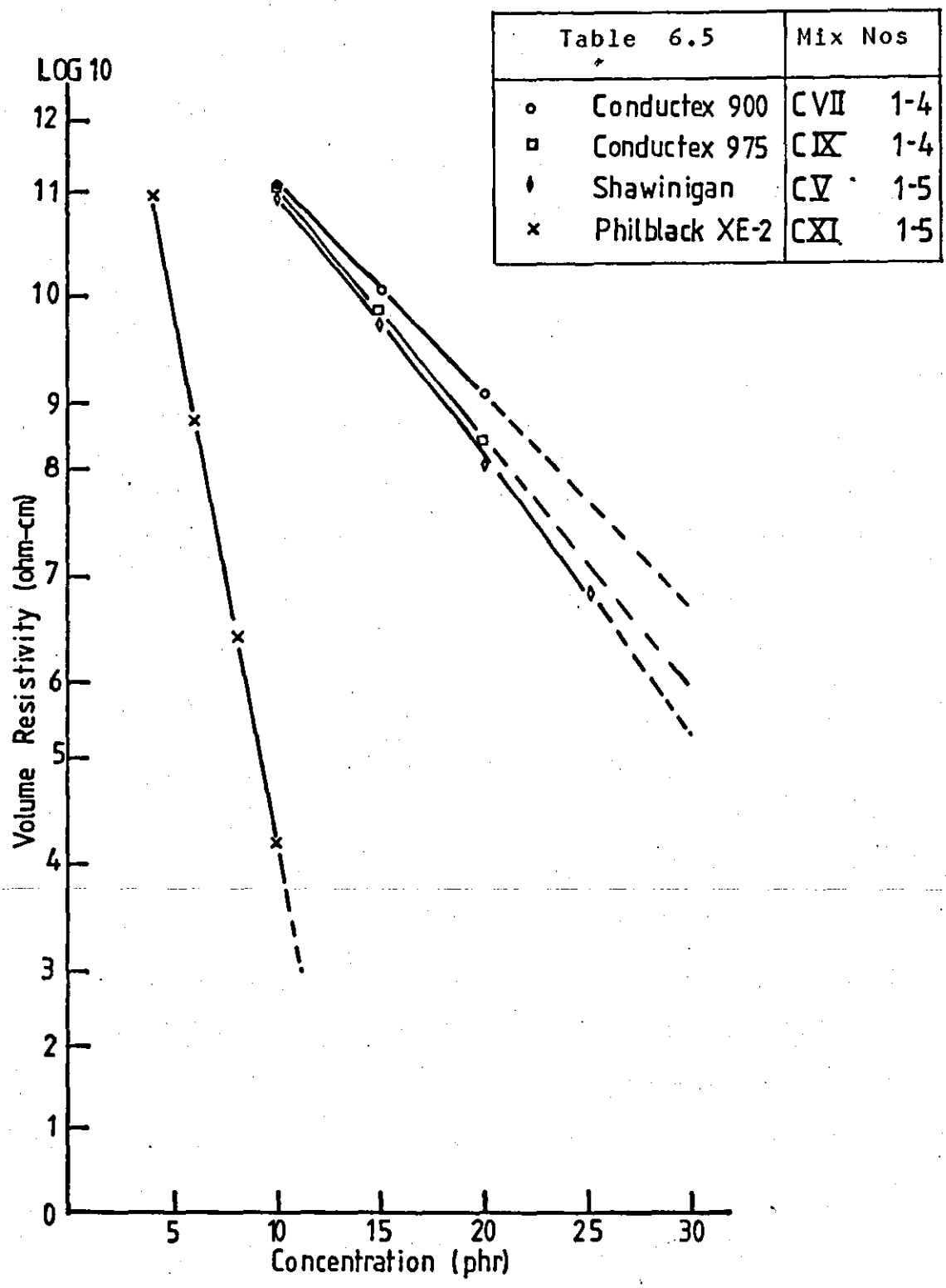


TABLE 6.6 ANALYTICAL PROPERTIES OF CONDUCTIVE CARBON BLACKS				
Carbon black Type	Particle size (nm)	Surface area (m^2g^{-1})	DBP Absorption (ml/100g)	Volatile content (%pbw)
Shawinigan	42.0±2.5	64.5	145	0.06
Vulcan P	20.0	149	116	1.50
Ketjenblack EC	30.0	1,000	340	1.00

From table 6.6, it could be observed that the comparative carbon blacks could impart conductivity into the rubber compound *via* different mechanisms. Conventionally, compounding ingredients are added on weight basis to rubber. Hence, addition of smaller particle size compounding ingredient Vulcan P, would, in effect, add more particles to the mix than the larger particle size, Shawinigan carbon black. With Vulcan P, particles are conceivably separated from each other by smaller distances than will, in theory, apply to Shawinigan black. This gives rise to their propensity to agglomerate into chains which results in a pseudo-fibre forming arrangement or structure, whereas, Shawinigan black, with its larger diameter particles, forms a continuous path inherent in its bulkiness and higher porosity. The Ketjenblack EC, though with an average particle size intermediate between Vulcan P and Shawinigan, has the highest DBP Absorption figure (a measure of porosity), and the highest surface area. This suggests a hollow and very light particle, and which, on weight basis, contains a higher number of particles per same concentration and hence higher interparticulate contact when compared to Vulcan P. The higher porosity will suggestively not only allow a pseudo-fibre formation but also encourage electron flow resulting in higher conductivity when compared to the other blacks.

From the above comparison, it could also be suggested that the degree of variability in the critical region is also dependent on the conductivity mechanism and in which Ketjenblack EC is reasonably least variable.

6.5 CONCLUSIONS

In general, increasing the carbon black proportions in low silica filled silicone rubber decreases the cure rate, increases the cure time, gives an initially low volume resistivity change followed by a 'critical and sharp' transition from an insulating to a 'conductive' polymer and then an insignificant and slow change. The range and gradient of transformation is dependent on the carbon black type and properties, and the proportion of insulating filler present.

The Siltech 17, containing a large amount of insulating ground silica gives logarithmic volume resistivity reduction with increasing carbon black proportion. A pointer to the dilution effect of the contained insulating ground silica. It is therefore, suggested that suitable insulating fillers can be effectively used in controlled proportion to obtain a precise volume resistivity control.

The mechanism by which the individual carbon black imparts conductivity into the rubber compound is suggested to influence the rate of change occuring at the transition region. Ketjenblack EC is observed to possess a combination of properties: light and highly porous particles. This means a higher number of particles and aggregates per gram when compared with other blacks. Hence there is a possibility of an increased aggregate-aggregate and particle-particle contact, and reduced distances between particles and aggregates. While the former (*i.e* aggregate to aggregate contact) is a pointer to carbon black pseudo fibre chain formation, the latter (*i.e* reduced inter-aggregate distance) is a pointer to electron tunneling mechanism. The above unusual properties, coupled with a combination of possible conductivity mechanism is hereby suggested as responsible for the unusually higher conductivity of compounds containing comparatively low loadings of Ketjenblack EC.

VII STRAIN (FLEXING) EFFECT ON THE VOLUME RESISTIVITY OF CARBON BLACK FILLED CONDUCTIVE SILICONE RUBBERS

7.1 INTRODUCTION

Applications of rubber products can be classified into two categories: static and dynamic applications. As such, the required properties of each class of products differ. Since stress and strain are an added effect to that of the environment, products for dynamic applications are usually subjected to more severe tests than those for static applications.

Strain and time of application had been claimed[312] to have the greatest effect on the electrical resistivity of particulate filler-containing conductive rubbers. Sensitivity of conductive compounds to strain is also said to vary with the following criteria:

a. range of conductive filler concentration: the resistivity-filler concentration curves usually show an initial slow change in resistivity with increasing filler concentration (see Ch.6). This is followed by a steep narrow band of transition from resistive to conductive compound and then a much slower resistivity change. Materials in this 'transition region' are said to be more sensitive to strain than are the more conductive region at higher loadings.
b. different carbon black filled rubbers: cis polybutadiene[313] and polypropylene oxide[314] polymers are said to be less sensitive to strain, while conductive silicone rubbers[7] are claimed to be relatively insensitive to strain and that recovery is said to be completed within 24hours.

It has also been shown[315-320] by dynamic modulus measurement, that the greatest change in resistivity with strain occurs at strain less than 10% and this is associated with carbon black structure breakdown effects. It is also claimed that structure breakdown is substantially dependent on the polymer, the carbon black type and concentration, the attrition of the carbon black, heat treatment of the mixing, other mixing details or even the rubber replacement by liquid media.

Other workers[231,278,321-324] recorded a thirteen to twenty-nine times resistivity increase when conductive rubber test-pieces are flexed. However the recorded resistivity increase is dependent on the recovery time after flexing. A non-linearity of the current-voltage relationship was observed by some[278] and theorized that this could be indicative of the relative rubber/rubber and rubber/carbon black bonds breakdown.

7.2 OBJECTIVE

From the foregoing, it could be concluded that deformation (flexing) has a pronounced effect on the electrical resistivity of carbon black filled conductive rubbers. The objective of this section, therefore, is to scrutinize the conductive stability of carbon black filled conductive silicone rubbers by measuring the extent by which their conductivity is affected by flexing conditions.

7.3 EXPERIMENTAL

7.3.1 MATERIALS (see also Ch.2, Section 2.1)

a. Polymers
   Silastic GP30, Silastic GP45, and Siltech 17
b. Curing Agent
   Perkadox SB
c. Conductive Carbon blacks
   Vulcan P, PF, XC72, and XC72R
   Shawinigan, Ketjenblack EC and Philblack XE-2
   Conductex 900, SC, 975 and 40-220
d. Coupling agent
   Silane Z6082

7.3.2 MIX FORMULATIONS

Table 7.1 shows the detailed mix formulations.

TABLE 7.1 MIX FORMULATIONS

Mix Number	1	2	3	4	5	6	7	8	9	10	11
Silastic GP30	100.0										
Perkadox SB	2.5										
Silane Z6082	1.5										
Vulcan P	20	25	30	–	–	–	–	–	–	–	–
Shawinigan	–	–	–	20	25	30	35	–	–	–	–
Ketjenblack EC	–	–	–	–	–	–	–	8	12	16	20

Mix Number	12	13	14	15	16	17	18	19	20	21	22
Silastic GP45	100.0										
Perkadox SB	2.5										
Silane Z6082	1.5										
Vulcan P	20	25	30	–	–	–	–	–	–	–	–
Shawinigan	–	–	–	20	25	30	35	–	–	–	–
Ketjenblack EC	–	–	–	–	–	–	–	8	12	16	20

Mix Number	23	24	25	26	27	28	29	30
Silastic GP30	100.0							
Perkadox SB	2.5							
Silane Z 6082	1.5							
Vulcan PF	30	–	–	–	–	–	–	–
Vulcan XC72	–	30	–	–	–	–	–	–
Vulcan XC72R	–	–	30	–	–	–	–	–
Conductex 900	–	–	–	30	–	–	–	–
Conductex 975	–	–	–	–	30	–	–	–
Conductex SC	–	–	–	–	–	30	–	–
Conductex 40-220	–	–	–	–	–	–	20	–
Philblack XE-2	–	–	–	–	–	–	–	20

Mix Number	31	32	33	34	35	36	37	38
Silastic GP 45	100.0							
Perkadox SB	2.5							
Silane Z6082	1.5							
Vulcan PF	30	–	–	–	–	–	–	–
Vulcan XC72	–	30	–	–	–	–	–	–
Vulcan XC72R	–	–	30	–	–	–	–	–
Conductex 900	–	–	–	30	–	–	–	–
Conductex 975	–	–	–	–	30	–	–	–
Conductex SC	–	–	–	–	–	30	–	–
Conductex 40-220	–	–	–	–	–	–	20	–
Philblack XE-2	–	–	–	–	–	–	–	20

7.3.3 MIXING

This was carried out as described in Ch.2, Section 2.2.1. The milling times were controlled to within the 'safety time belt' as observed in Ch.4.

The sheets of rubber were taken off the mill approximately the same predetermined thickness.

7.3.4 VULCANISATION

7.3.4.1 Test Specimen

The Test Specimens (70mm X 10mm X 2mm) with brass-bonded electrodes (10mm X 5mm X 2mm) were used.

The brass plates were first sand blasted; surfaces to be in contact with the rubber were roughened with coarse sand paper and degreased in Carbon tetrachloride (CCl_4). Prior to to use, the brass plates were dried in air circulating oven at 70°C for 4hrs, allowed to cool and carefully placed in the moulding cavity. Blanks, cut to a predetermined weight and size, such as to give little or no mould flow, were then placed carefully between the end brass electrodes and moulded.

7.3.4.2 Moulding

This was carried out as described in Ch.2, Section 2.2.2

7.3.5 EVALUATION OF VULCANISATE PROPERTIES

7.3.5.1 Low strain (flexing) and Volume Resistivity Measurement

Flexing was at 25% extension on a De Mattia Flexometer with a speed of approximately 300cycles per minute.

The volume resistivity measurement was carried out in accordance with BS2044:Method I:1978 using the Avo Super Megohmmeter and DM131 Digital Multimeter (cf. Ch.2, Sec.2.2.4). To measure the volume resistivity immediately after flexing, measuring leads are attached to the end electrodes of test samples mounted on the Flexometer. The volume resistivity of the individual test sample prior to flexing is as recorded in Table 7.2, and at the specified recovery time after 10^4 flexes, are as recorded in Table 7.3.

TABLE 7.2 VULCANISATE PROPERTIES OF CONDUCTIVE SILICONE RUBBERS

Mix No.		Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
1	A B	0.62	10.60	3.24×10^6 3.20×10^6	48
2	A B	0.58	10.90	4.12×10^2 4.12×10^2	50
3	A B	0.52	11.40	2.60 2.60	54
4	A B	0.76	9.50	3.14×10^5 3.20×10^5	44
5	A B	0.70	10.00	2.40×10^2 2.40×10^2	45
6	A B	0.62	10.60	2.81 2.80	46
7	A B	0.50	11.60	2.38 2.38	48
8	A B	0.80	9.20	9.00×10^2 9.00×10^2	48
9	A B	0.70	10.00	7.80×10^1 7.80×10^1	52
10	A B	0.58	10.90	5.10 5.00	54
11	A B	0.50	11.60	2.20 2.20	57
12	A B	0.70	10.00	8.70×10^6 8.60×10^6	53
13	A B	0.63	10.50	2.40×10^3 2.60×10^3	55
14	A B	0.52	11.40	3.80 3.80	57
15	A B	0.78	9.40	4.00×10^5 4.00×10^5	55
16	A B	0.73	9.80	3.26×10^2 3.30×10^2	57
17	A B	0.62	10.60	3.38 3.40	59
18	A B	0.54	11.30	2.82 2.80	60
19	A B	0.88	8.60	8.45×10^2 8.40×10^2	52
20	A B	0.82	9.00	8.10×10^1 8.00×10^1	55

TABLE 7.2(ctn) VULCANISATE PROPERTIES OF CONDUCTIVE SILICONE RUBBERS

Mix No.		Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
21	A B	0.70	10.00	4.30 4.30	60
22	A B	0.62	10.60	2.20 2.20	64
23	A B	0.46	11.90	2.70 2.70	50
24	A B	0.48	11.70	2.80 2.80	46
25	A B	0.50	11.60	2.90 2.90	46
26	A B	0.52	11.40	3.10 3.20	45
27	A B	0.50	11.60	2.90 3.00	47
28	A B	0.62	10.60	3.20 3.20	49
29	A B	0.40	11.90	2.60 2.60	57
30	A B	0.50	11.60	2.40 2.40	58
31	A B	0.54	11.30	3.50 3.50	57
32	A B	0.52	11.40	2.60 2.60	50
33	A B	0.52	11.40	2.80 2.60	48
34	A B	0.54	11.20	3.40 3.60	46
35	A B	0.54	11.20	2.90 2.90	53
36	A B	0.70	10.00	3.40 3.40	54
37	A B	0.48	11.70	3.20 3.20	64
38	A B	0.56	11.10	2.80 2.80	65

TABLE 7.3 VOLUME RESISTIVITY OF FLEXED CONDUCTIVE SILICONE RUBBERS

Mix No.		NUMBER OF FLEXES									RECOVERY TIME					
											Minutes				Days	
		1	10	100	200	500	10^3	2000	5000	10^4	15	30	45	60	1	7
1	A	7.2×10^6	8.2×10^6	9.0×10^6	9.8×10^6			9.80×10^6			9.6×10^6	9.0×10^6	8.4×10^6	8.0×10^6	4.6×10^6	3.3×10^6
	B	7.4×10^6	8.4×10^6	9.0×10^6	9.6×10^6			9.80×10^6			9.6×10^6	9.1×10^6	8.2×10^6	8.1×10^6	4.6×10^6	3.3×10^6
2	A	5.2×10^2	7.0×10^2	8.1×10^2	9.0×10^2			9.00×10^2			8.2×10^2	7.0×10^2	6.0×10^2	5.4×10^2	4.2×10^2	4.2×10^2
	B	5.2×10^2	7.0×10^2	8.0×10^2	9.0×10^2			9.00×10^2			8.0×10^2	7.2×10^2	6.0×10^2	5.2×10^2	4.1×10^2	4.1×10^2
3	A	3.00	3.20	3.50	3.68			3.68			3.30	3.10	2.90	2.60	2.60	2.58
	B	3.10	3.24	3.50	3.70			3.70			3.30	3.10	2.90	2.60	2.60	2.58
4	A	5.2×10^5	7.4×10^5	7.8×10^5	8.1×10^5			8.30×10^5			7.8×10^5	6.4×10^5	5.2×10^5	4.4×10^5	3.7×10^5	3.3×10^5
	B	4.8×10^5	7.0×10^5	7.6×10^5	8.2×10^5			8.20×10^5			7.6×10^5	6.0×10^5	5.0×10^5	4.0×10^5	3.7×10^5	3.4×10^5
5	A	2.8×10^2	4.2×10^2	5.3×10^2	5.5×10^2			5.60×10^2			5.2×10^2	4.0×10^2	3.2×10^2	2.8×10^2	2.6×10^2	2.4×10^2
	B	2.9×10^2	4.0×10^2	5.0×10^2	5.6×10^2			5.80×10^2			5.4×10^2	4.0×10^2	3.0×10^2	2.6×10^2	2.5×10^2	2.4×10^2
6	A	3.20	4.40	4.80	4.80			4.80			3.80	3.20	3.00	2.80	2.80	2.80
	B	3.30	4.60	4.80	4.80			4.80			3.60	3.20	3.00	2.80	2.80	2.76
7	A	2.50	2.60	2.80	2.80			2.80			2.60	2.50	2.42	2.40	2.40	2.36
	B	2.50	2.60	2.80	2.80			2.80			2.60	2.50	2.42	2.40	2.40	2.34
8	A	1.4×10^3	1.8×10^3	2.4×10^3	2.4×10^3			2.4×10^3			1.2×10^3	1.0×10^3	9.6×10^2	9.4×10^2	9.2×10^2	9.2×10^2
	B	1.2×10^3	1.5×10^3	1.8×10^3	1.8×10^3			1.8×10^3			1.5×10^3	1.0×10^3	9.4×10^2	9.3×10^2	9.2×10^2	9.2×10^2
9	A	80.00	84.00	90.00	90.00			90.00			84.00	82.00	81.40	80.00	79.00	78.50
	B	80.00	85.00	90.00	90.00			90.00			84.00	82.00	81.40	79.80	78.60	78.30
10	A	5.12	5.18	5.19	5.20			5.20			5.16	5.12	5.10	5.10	5.10	5.00
	B	5.10	5.16	5.18	5.20			5.20			5.16	5.12	5.10	5.10	5.06	5.00
11	A	2.20	2.24	2.24	2.24			2.24			2.22	2.20	2.20	2.20	2.20	2.16
	B	2.22	2.26	2.26	2.26			2.26			2.23	2.20	2.20	2.20	2.20	2.16
12	A	9.0×10^6	9.8×10^6	1.4×10^7	1.8×10^7			1.8×10^7			1.3×10^7	9.9×10^6	9.6×10^6	9.4×10^6	9.0×10^6	8.9×10^6
	B	9.0×10^6	9.7×10^6	1.2×10^7	1.7×10^7			1.7×10^7			1.3×10^7	9.8×10^6	9.5×10^6	9.3×10^6	9.0×10^6	8.9×10^6
13	A	2.9×10^3	3.8×10^3	4.2×10^3	4.4×10^3			4.5×10^3			4.2×10^3	4.0×10^3	2.9×10^3	2.6×10^3	2.5×10^3	2.5×10^3
	B	3.0×10^3	3.8×10^3	4.0×10^3	4.4×10^3			4.5×10^3			4.4×10^3	4.0×10^3	3.0×10^3	2.8×10^3	2.6×10^3	2.6×10^3
14	A	4.20	4.80	5.20	5.20			5.20			4.80	4.20	4.00	3.80	3.80	3.78
	B	4.10	4.70	5.10	5.20			5.20			4.80	4.20	4.00	3.80	3.80	3.56
15	A	4.4×10^5	5.8×10^5	7.0×10^5	8.2×10^5			8.2×10^5			7.4×10^5	6.2×10^5	5.4×10^5	4.8×10^5	4.2×10^5	4.1×10^5
	B	4.3×10^5	5.8×10^5	7.7×10^5	8.2×10^5			8.2×10^5			7.3×10^5	6.0×10^5	5.3×10^5	4.8×10^5	4.3×10^5	4.1×10^5
16	A	3.6×10^2	4.0×10^2	5.2×10^2	6.0×10^2			6.2×10^2			5.1×10^2	4.2×10^2	3.8×10^2	3.6×10^2	3.5×10^2	3.4×10^2
	B	3.6×10^2	4.0×10^2	5.1×10^2	6.0×10^2			6.0×10^2			5.0×10^2	4.2×10^2	3.8×10^2	3.6×10^2	3.4×10^2	3.3×10^2
17	A	3.70	4.20	4.48	4.60			4.60			4.10	3.90	3.60	3.40	3.40	3.38
	B	3.70	4.20	4.46	4.60			4.60			4.10	3.80	3.60	3.40	3.40	3.36
18	A	2.92	3.04	3.20	3.20			3.20			3.00	2.89	2.83	2.80	2.80	2.78
	B	2.88	2.92	3.10	3.10			3.10			2.90	2.85	2.82	2.80	2.80	2.78
19	A	9.6×10^2	1.0×10^3	1.4×10^3	1.4×10^3			1.4×10^3			9.7×10^2	9.1×10^2	8.8×10^2	8.7×10^2	8.6×10^2	8.6×10^2
	B	9.7×10^2	1.1×10^3	1.5×10^3	1.5×10^3			1.5×10^3			9.7×10^2	9.1×10^2	8.8×10^2	8.7×10^2	8.6×10^2	8.6×10^2
20	A	83.00	87.00	92.00	92.00			92.00			86.00	84.00	82.50	81.30	80.60	80.40
	B	83.00	86.00	90.00	90.00			90.00			84.00	82.00	82.00	81.30	80.60	80.40

NOTE: BOND STRENGTH: Each flexed sample was pulled to break after recording the final volume resistivity. Only results of samples which broke in the middle were retained.

TABLE 7.3 VOLUME RESISTIVITY OF FLEXED CONDUCTIVE SILICONE RUBBERS (contd)

Mix No.	NUMBER OF FLEXES									RECOVERY TIME					
										Minutes				Days	
	1	10	100	200	500	10^3	2000	5000	10^4	15	30	45	60	1	7
21A	4.30	4.30	4.42	4.42	4.42					4.30	4.30	4.30	4.30	4.30	4.26
21B	4.30	4.30	4.42	4.42	4.42					4.30	4.30	4.30	4.30	4.30	4.30
22A	2.20	2.22	2.26	2.26	2.26					2.22	2.20	2.20	2.20	2.20	2.16
22B	2.20	2.24	2.24	2.24	2.24					2.22	2.20	2.20	2.20	2.20	2.16
23A	2.80	2.90	3.20	3.40	3.50					3.40	3.10	2.90	2.80	2.70	2.68
23B	2.80	2.90	3.20	2.40	3.50					3.40	3.10	2.90	2.80	2.70	2.68
24A	2.80	2.85	2.88	2.90	2.94					2.86	2.83	2.81	2.80	2.80	2.77
24B	2.80	2.85	2.87	2.90	2.94					2.86	2.83	2.81	2.80	2.80	2.77
25A	2.90	2.95	2.98	3.04	3.04					2.96	2.93	2.91	2.90	2.90	2.87
25B	2.90	2.94	2.96	3.02	3.02					2.96	2.94	2.90	2.90	2.90	2.87
26A	3.10	3.20	3.50	3.90	4.00					3.50	3.50	3.30	3.20	3.14	3.10
26B	3.20	3.20	3.60	3.90	4.00					3.70	3.50	3.30	3.20	3.20	3.16
27A	3.00	3.00	3.10	3.10	3.10					3.06	3.02	3.00	2.90	2.90	2.90
27B	3.00	3.00	3.00	3.10	3.10					3.04	3.00	3.00	3.00	3.00	2.94
28A	3.20	3.40	3.80	4.00	4.20					4.00	3.60	3.30	3.20	3.20	3.18
28B	3.20	3.30	3.80	4.00	4.20					4.00	3.70	3.30	3.20	3.20	3.18
29A	2.63	2.64	2.66	2.66	2.66					2.66	2.63	2.62	2.60	2.60	2.56
29B	2.63	2.64	2.66	2.66	2.66					2.66	2.64	2.62	2.60	2.58	2.54
30A	2.42	2.43	2.46	2.46	2.46					2.44	2.42	2.40	2.40	2.38	2.36
30B	2.42	2.44	2.46	2.46	2.46					2.46	2.43	2.41	2.40	2.38	2.36
31A	3.62	3.90	4.20	4.34	4.42					4.30	3.84	3.66	3.56	3.50	3.46
31B	3.68	3.96	4.24	4.40	4.48					4.36	3.90	3.70	3.56	3.50	3.50
32A	2.60	2.64	2.70	2.74	2.74					2.70	2.66	2.64	2.60	2.60	2.56
32B	2.60	2.64	2.68	2.72	2.72					2.70	2.65	2.64	2.60	2.60	2.58
33A	2.70	2.74	2.76	2.76	2.80					2.76	2.72	2.70	2.70	2.70	2.68
33B	2.70	2.74	2.78	2.78	2.80					2.76	2.72	2.70	2.70	2.70	2.66
34A	3.60	3.90	4.20	4.40	4.50					4.20	3.80	3.50	3.40	3.40	3.40
34B	3.70	3.90	4.16	4.40	4.50					4.20	3.90	3.70	3.60	3.60	3.56
35A	2.94	3.00	3.04	3.04	3.04					3.00	2.96	2.92	2.90	2.90	2.86
35B	2.94	3.00	3.04	3.04	3.04					3.00	2.96	2.92	2.90	2.90	2.86
36A	3.40	3.60	3.90	4.10	4.20					3.90	3.70	3.50	3.40	3.40	3.38
36B	3.40	3.60	3.80	4.00	4.20					3.80	3.60	3.50	3.40	3.40	3.38
37A	3.20	3.22	3.26	3.26	3.26					3.24	3.22	3.22	3.20	3.20	3.14
37B	3.20	3.24	3.28	3.28	3.28					3.26	3.24	3.22	3.20	3.20	3.14
38A	2.80	2.82	2.86	2.88	2.88					2.86	2.84	2.82	2.80	2.80	2.76
38B	2.80	2.82	2.84	2.86	2.86					2.86	2.84	2.84	2.82	2.80	2.74

NOTE: *BOND STRENGTH: Each flexed sample was pulled to break after recording the final volume resistivity. Only the results of samples which broke in the middle were retained.*

7.3.5.2 Hardness (IRHD) Measurement

This was carried out in accordance with BS903:PartA26:1969

7.4 RESULTS AND DISCUSSIONS

For investigating the effect of flexing (low strain) on the volume resistivity of conductive silicone rubbers, both Silastic GP30- and GP45- based compounds were used (Table 7.1). Also compounds with high carbon black loadings were used, since compounds with low loadings, when flexed, gave recorded resistances higher than that measurable by the equipment used. A summary of the vulcanisate properties are as shown in Tables 7.2 and 7.3.

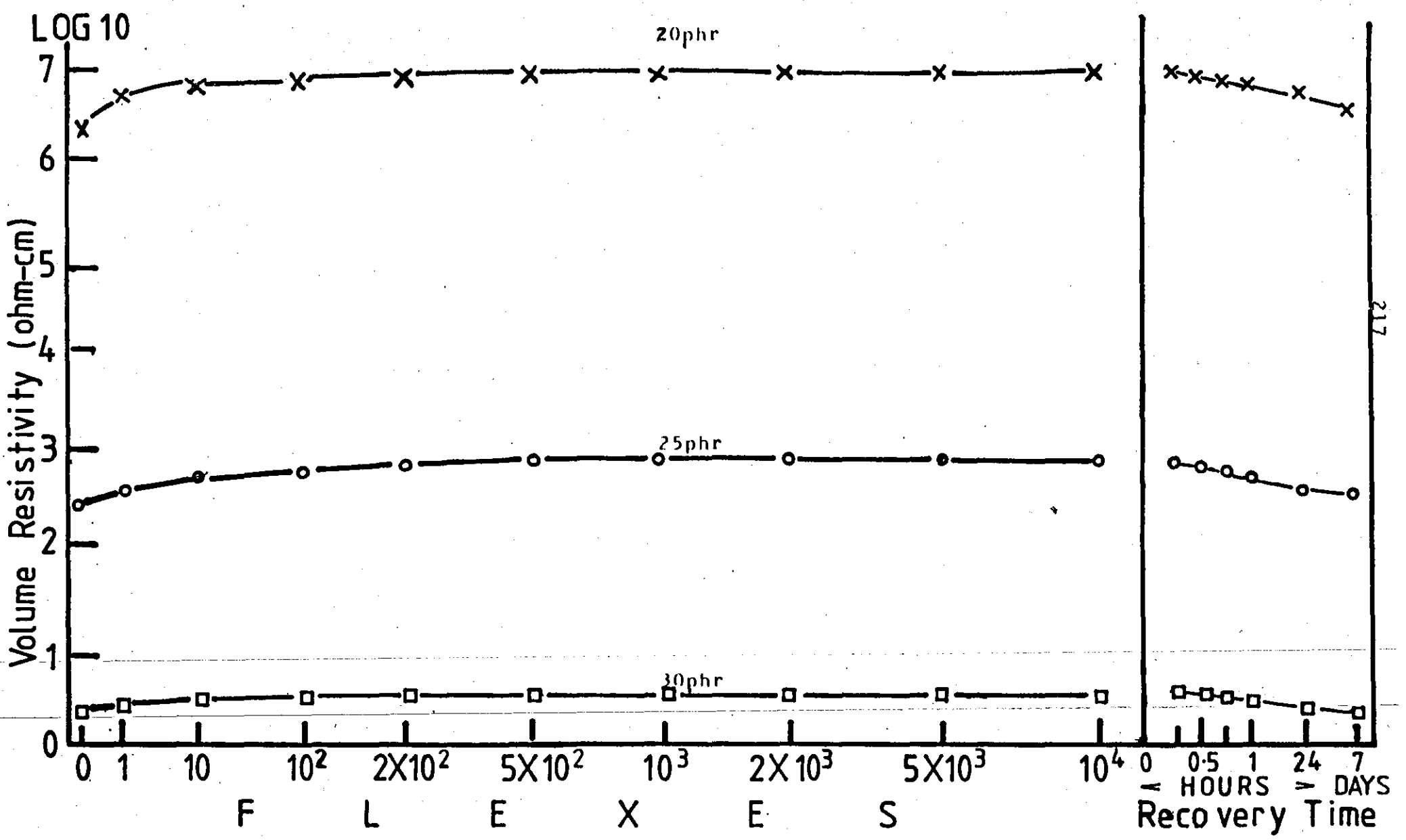
7.4.1 VULCAN P FILLED SILASTIC GP30 VULCANISATES

Mix Nos 1-3 of Tables 7.2 and 7.3 and fig. 7.1 are now discussed. It was observed that an initial sharp increase in volume resistivity occurs after only a low number of flexes and reached a maximum after about 200 flexes. No further volume resistivity increase was observed, but, a reasonably constant peak volume resistivity was maintained till 10,000 flexes. This initial sharp increase in volume resistivity could be attributed to increasing breakage in the conducting path formed through the pseudo-fibre chain formation of the carbon black in the conductive compound. The increase in volume resistivity reached a constant peak, when/where, it could be assumed, that dynamic equilibrium of breakdown and reformation of conductive path occured.

However, with increasing carbon black content, it was observed that the initial sharp increase in volume resistivity declined, with little or no increase at very high carbon black loading. It is suggested that as the carbon black increases, the more probable will be the increased number of pseudo-fibre chain formation and therefore the more likely the residual unbroken chains and thus the lower the resistivity.

A vulcanisate's final volume resistivity and the rate at which this is obtained was noted to depend on the time

Fig. 7.1 Effect of Flexing (Low Strain) on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP 30 based compounds (Ref Mix Nos 1-3 of Tables 7.2 & 7.3).



allowed to lapse before measurement and on the carbon black content. A further analysis of the results (Table 7.4:Mix Nos 1-3) showed peak volume resistivity with very high percentage increase which rapidly declined with increasing carbon black content. Similarly the final volume resistivity percentage difference decreased with increasing carbon black content.

It was noted that vulcanisates containing the 20phr and 25phr Vulcan P gave an increase in the measured final volume resistivity, but a decrease in that containing 30phr Vulcan P. The unusual observation in the latter was further investigated and a similar result obtained. The above observations suggested a temporary chain breakage which was responsible for the increased volume resistivity during flexing. The broken carbon black chains might have reformed during the recovery (or storage) time, but with a degree of permanent damage in some, giving rise to increased final volume resistivity (Mix Nos 1 & 2) and a possible carbon chain realignment by an unknown mechanism which resulted in 'decreased' final volume resistivity in the latter case.

7.4.2 SHAWINIGAN FILLED SILASTIC GP30 VULCANISATES

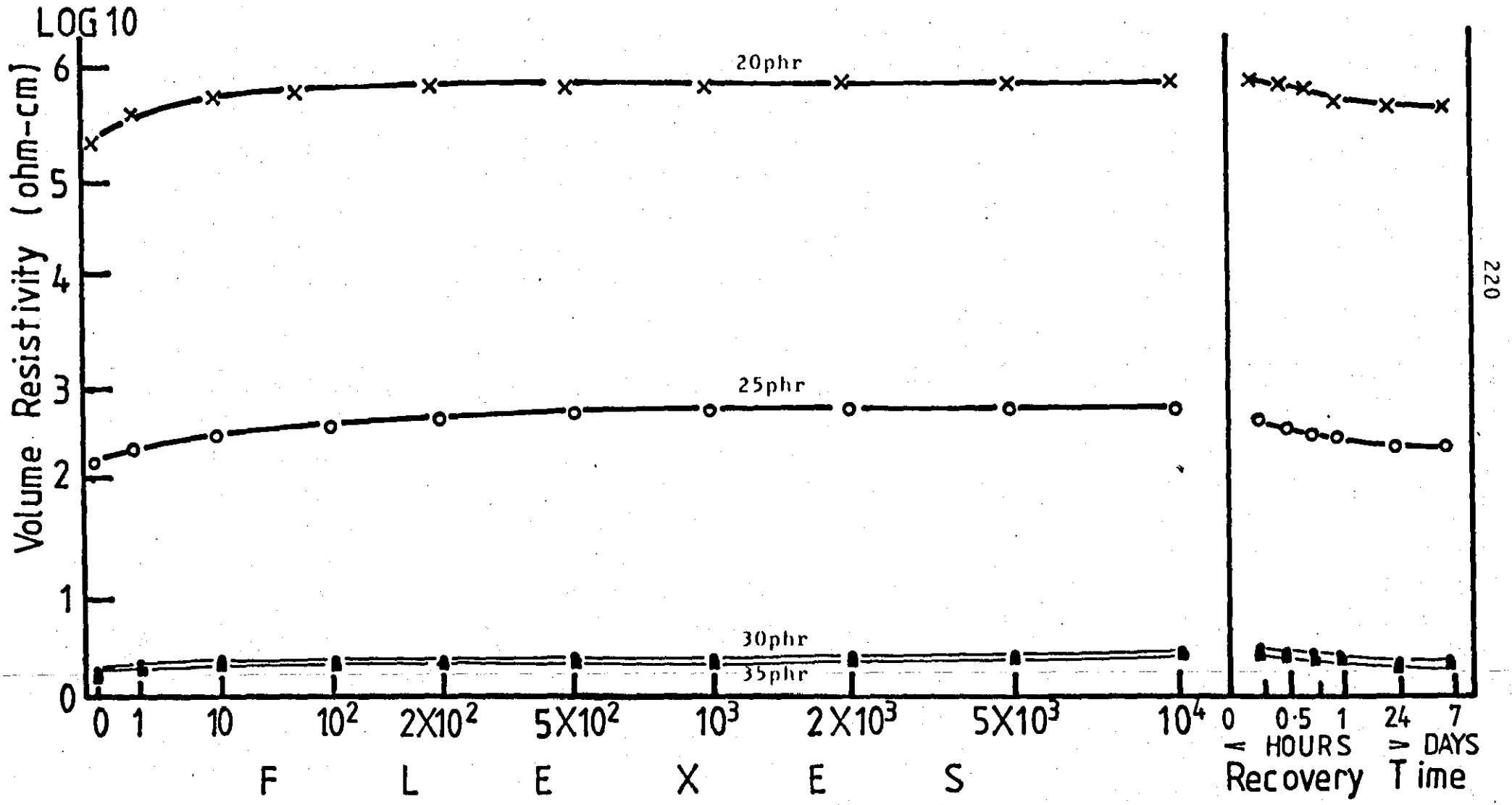
Mix Nos 4-7 of Tables 7.2, 7.3 & 7.4 and fig. 7.2 are now considered. Features similar to Vulcan P filled Silastic GP30 were observed to occur here. The results of the vulcanisates, however, show a decrease in the peak volume resistivity percentage increase during flexing, and also the final volume resistivity obtained after recovery (Table 7.4).

It had been suggested that the electrical conduction through vulcanisates containing acetylene (e.g Shawinigan) carbon black do not occur by a pseudo-fibre chain formation but by virtue of the aggregate bulkiness and overlap in the compound. It is suggested that its superior volume resistivity change during flexing when compared with Vulcan P vulcanisates could be attributed to the carbon black aggregates' 'softer' and 'bulkier' nature, with, therefore, an added flexibility. Hence, during flexing, the particles and agglomerates distort and stretch without breaking down to smaller particles. Also the webs of overlapped carbon particles may

TABLE 7.4 EFFECT OF FLEXING ON THE VOLUME RESISTIVITY OF CONDUCTIVE SILICONE RUBBERS: FINAL ANALYSIS.

Mix No.	Volume Resistivity (ohm-cm)		Percentage Increase	Final Volume Resistivity after recovery (ohm-cm)	Percentage Difference (±)
	Initial	Peak			
1	$3.22X10^6$	$9.80X10^6$	204.40	$3.30X10^6$	+ 2.90
2	$4.11X10^2$	$8.95X10^2$	117.80	$4.15X10^2$	+ 1.00
3	2.60	3.69	42.30	2.58	- 0.80
4	$3.17X10^5$	$8.25X10^5$	160.30	$3.35X10^5$	+ 2.40
5	$2.40X10^2$	$5.70X10^2$	107.50	$2.42X10^2$	+ 0.50
6	2.80	4.80	71.40	2.78	- 0.70
7	2.38	2.80	17.70	2.35	- 1.20
8	$9.00X10^2$	$2.20X10^3$	144.40	$9.20X10^3$	+ 2.20
9	$7.80X10^1$	$9.00X10^1$	15.40	$7.84X10^1$	+ 0.50
10	5.05	5.20	3.00	5.00	- 0.90
11	2.20	2.25	2.30	2.16	- 1.60
12	$8.65X10^6$	$1.76X10^7$	103.50	$8.92X10^6$	+ 3.10
13	$2.50X10^3$	$4.50X10^3$	72.00	$2.54X10^3$	+ 1.60
14	3.70	5.20	36.80	3.67	- 0.80
15	$4.00X10^5$	$8.20X10^5$	105.00	$4.10X10^5$	+ 2.50
16	$3.28X10^2$	$6.10X10^2$	86.00	$3.32X10^2$	+ 1.20
17	3.39	4.60	35.70	3.37	- 0.60
18	2.81	3.15	12.10	2.78	- 1.10
19	$8.42X10^2$	$1.45X10^3$	72.20	$8.60X10^2$	+ 2.10
20	$8.00X10^1$	$9.10X10^1$	13.80	$8.04X10^1$	+ 0.50
21	4.30	4.42	2.80	4.26	- 0.90
22	2.20	2.25	2.10	2.16	- 1.80
23	2.70	3.50	29.60	2.68	- 0.70
24	2.80	2.94	5.00	2.77	- 1.10
25	2.90	3.03	4.50	2.87	- 1.00
26	3.15	4.00	27.00	3.13	- 0.60
27	2.95	3.10	5.10	2.92	- 1.00
28	3.20	4.20	31.25	3.18	- 0.60
29	2.60	2.66	2.20	2.55	- 1.90
30	2.40	2.46	2.46	2.36	- 1.70
31	3.50	4.45	27.10	3.47	- 0.90
32	2.60	2.73	5.00	2.57	- 1.20
33	2.70	2.80	3.70	2.67	- 1.10
34	3.50	4.50	28.60	3.48	- 0.60
35	2.90	3.04	4.90	2.86	- 1.40
36	3.40	4.20	23.50	3.38	- 0.60
37	3.20	3.27	2.30	3.14	- 1.90
38	2.80	2.87	2.50	2.75	- 1.80

Fig. 7.2 Effect of Flexing (Low Strain) on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP 30 based compounds (Ref Mix Nos 4-7 of Tables 7.2, 7.3 & 7.4).



slide past each other without an end to end tail separation. The possibility of the above phenomena occuring increases with increasing carbon black content. Hence the peak resistivity obtained during flexing as well as the final volume resistivity after recovery declines with increasing carbon black content. The 30phr and 35phr containing carbon black vulcanisate shows a final volume resistivity slightly lower than the original volume resistivity as observed in the Vulcan P vulcanisate.

7.4.3 KETJENBLACK EC FILLED SILASTIC GP30 VULCANISATES

Mix Nos 8-11 of Tables 7.2, 7.3 & 7.4 and fig. 7.3 are considered in this exercise. As can be seen from the results, the effect of flexing on this carbon black containing vulcanisates is minimal when compared to vulcanisates containing Vulcan P and Shawinigan. The rate of recovery after flexing is also higher and gives the lowest percentage difference of the final volume resistivity obtained. This outstanding properties could be attributed to the unique features of the Ketjenblack EC - porous, hollow shell and light weight - particles, namely a unique criteria of better conduction and retention of the volume resistivity.

7.4.4 HIGHLY (CARBON BLACK FILLED) SILASTIC GP30 VULCANISATES

Fig. 7.4 gives a comparison of the effect of flexing on the volume resistivity of highly filled Silastic GP30 for the different carbon blacks used in this investigation. Mix Nos 23-30 of Tables 7.2, 7.3 & 7.4 summarise the results of the vulcanisate properties.

It could be observed that features similar to those described above occur in these mixes. Summarily the effect of flexing on the highly filled conductive silicone rubber is minimal and recovery is very rapid. In addition to the above, both Conductex 40-220 and Philblack XE-2 filled vulcanisates possess similar unique characteristics to Ketjenblack EC.

Fig. 7.3 Fffect of Flexing (Low Strain) on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP 30 based compounds (Ref Mix Nos 8-11 of Tables 7.2,7.3&7.4)

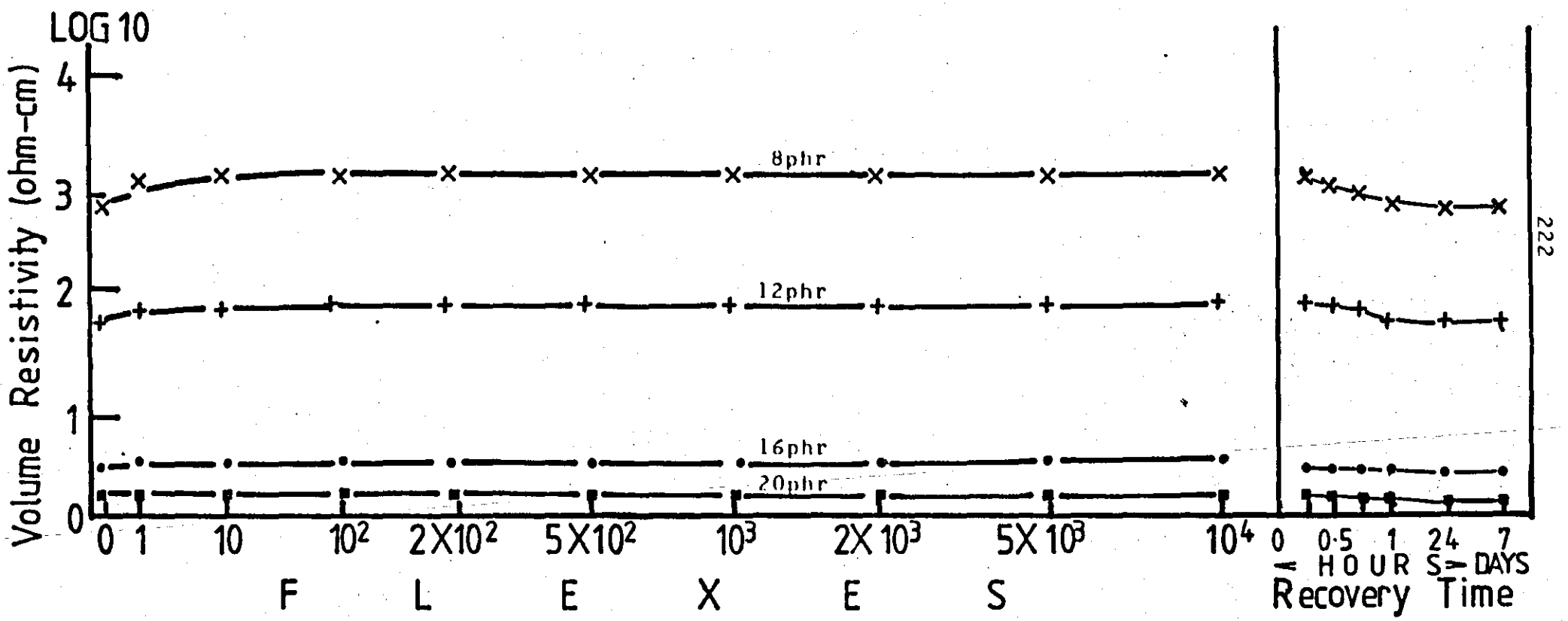
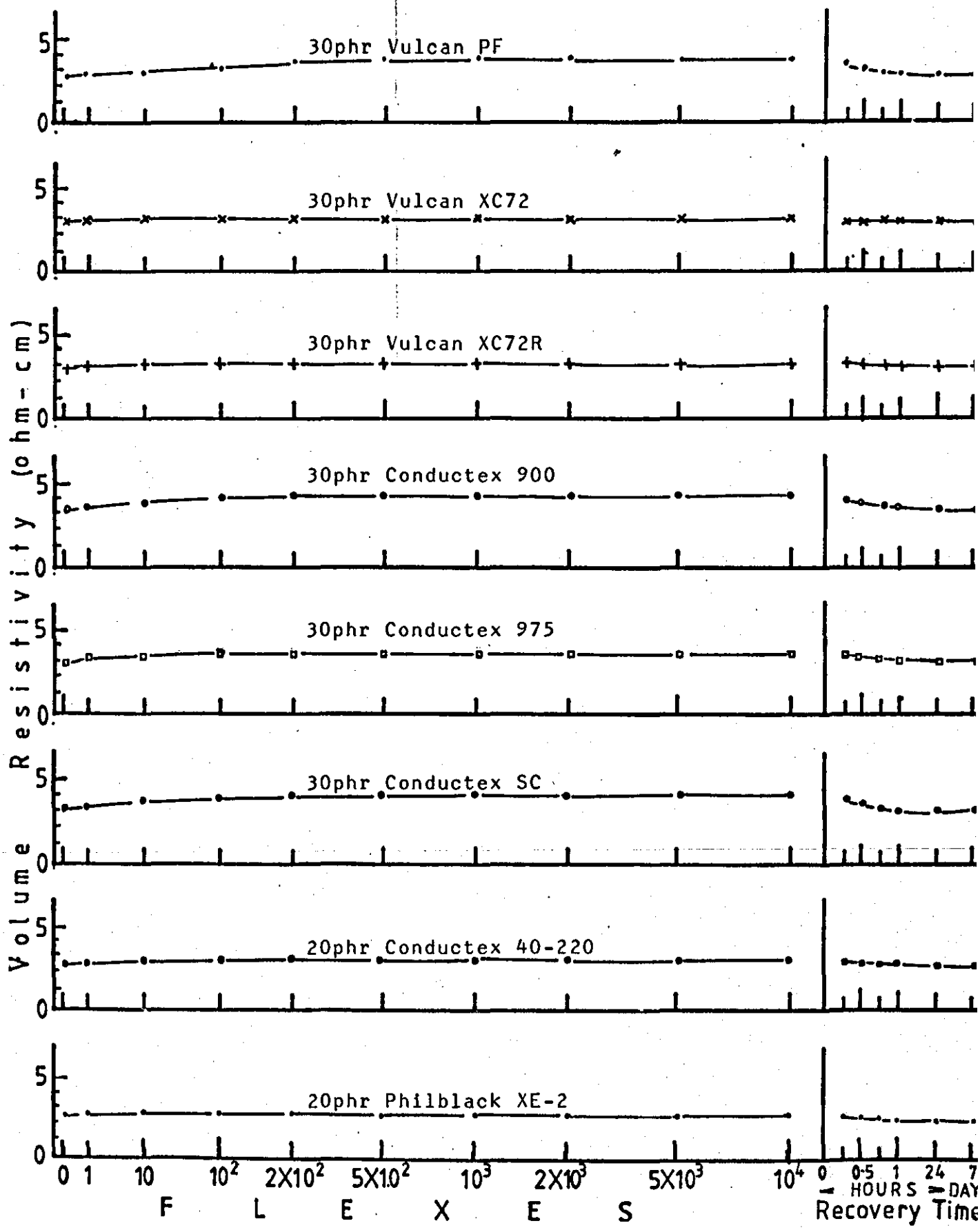


Fig. 7.4 Effect of Flexing (Low Strain) on the volume resistivity of carbon black filled Silastic GP 30 based compounds (Ref Mix Nos 23-30 of Tables 7.2, 7.3 & 7.4).



7.4.5 VULCAN P FILLED SILASTIC GP45 VULCANISATES

Mix Nos 12-14 of Tables 7.2, 7.3 & 7.4 and fig. 7.5 are now considered. Features similar to their Silastic GP30 vulcanisate cousins were observed to be prominent here. It is interesting to note that there is a lower value of maximum volume resistivity percentage increase during flexing. In the final volume resistivity after recovery, the 20phr and 25phr containing carbon black vulcanisates were observed to have a higher percentage difference, while the 30phr showed a percentage difference similar to the GP30 based vulcanisates. It is suggested that while the former(reduced value of maximum volume resistivity percentage increase during flexing) could be attributed to the damping effect of the higher silica content, the latter (higher final volume resistivity percentage difference) shows a comparatively more permanent carbon-carbon chain breakage in the 20phr and 25phr containing carbon black vulcanisate while the higher 30phr containing carbon black vulcanisate is not significantly affected by the silica content.

7.4.6 SHAWINIGAN FILLED SILASTIC GP45 VULCANISATES

Mix Nos 15-18 of Tables 7.2, 7.3 & 7.4 and fig. 7.6 show the effect of flexing on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP45 based compounds.

Features similar to their Silastic GP30 counterparts were observed to occur here. As with Vulcan P filled Silastic GP45 vulcanisates, a reduced peak volume resistivity percentage increase during flexing was observed. However, the 20phr and 25phr carbon black containing vulcanisates have a higher percentage increase in the final volume resistivity after recovery, whereas vulcanisates containing 30phr and 35phr carbon black had a reduced percentage.

7.4.7 KETJENBLACK EC FILLED SILASTIC GP45 VULCANISATES

Mix Nos 19-22 of Tables 7.2, 7.3 & 7.4 and fig. 7.7 are now considered.

Fig. 7.5 Effect of Flexing (Low Strain) on the volume resistivity of the furnace black (Vulcan P) filled Silastic GP 45 based compounds (Ref Mix Nos 12-14 of Tables 7.2, 7.3 & 7.4).

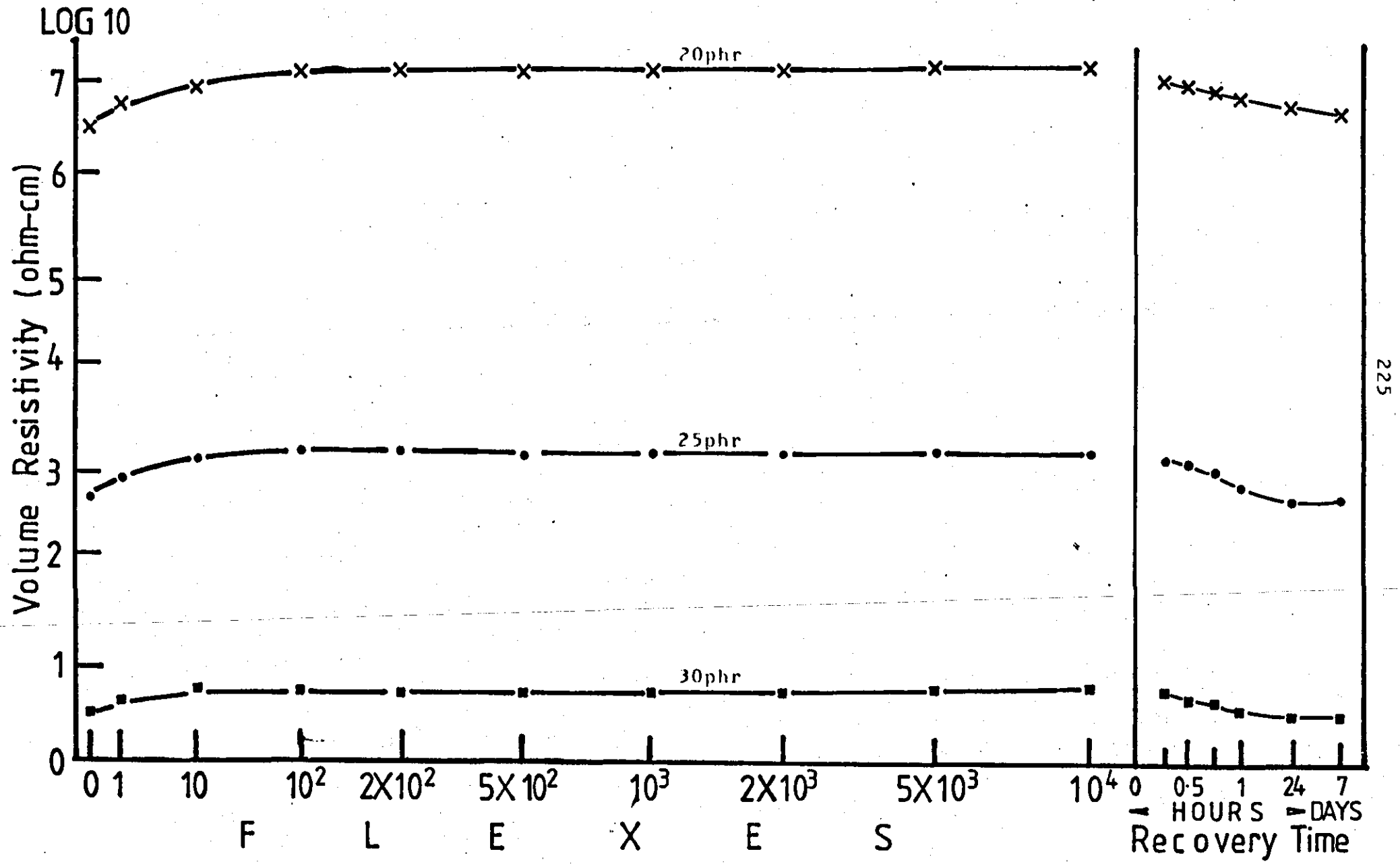


Fig. 7.6 Effect of Flexing (Low Strain) on the volume resistivity of the acetylene black (Shawinigan) filled Silastic GP 45 based compounds (Ref Mix Nos 15-18 of Tables 7.2, 7.3 & 7.4).

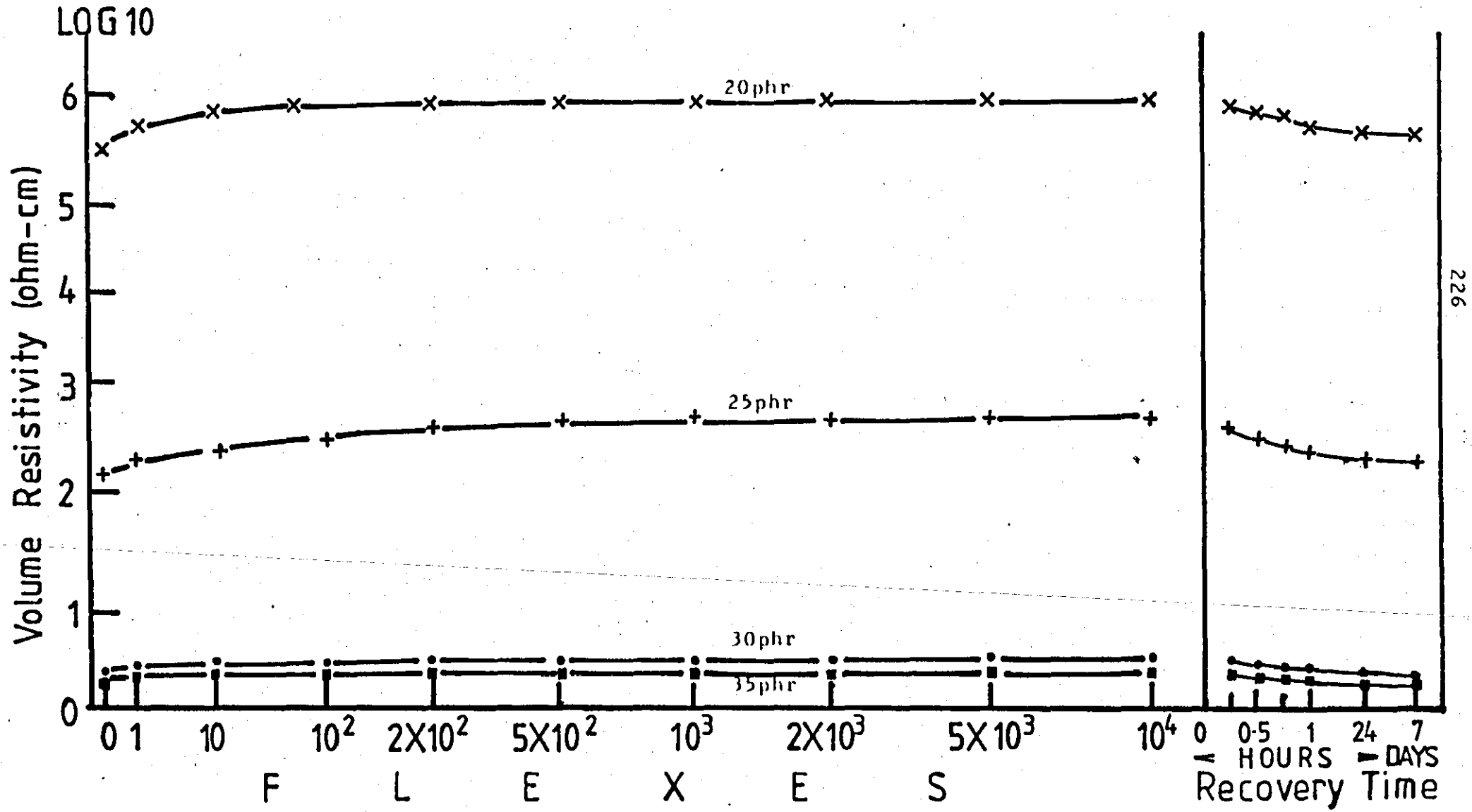
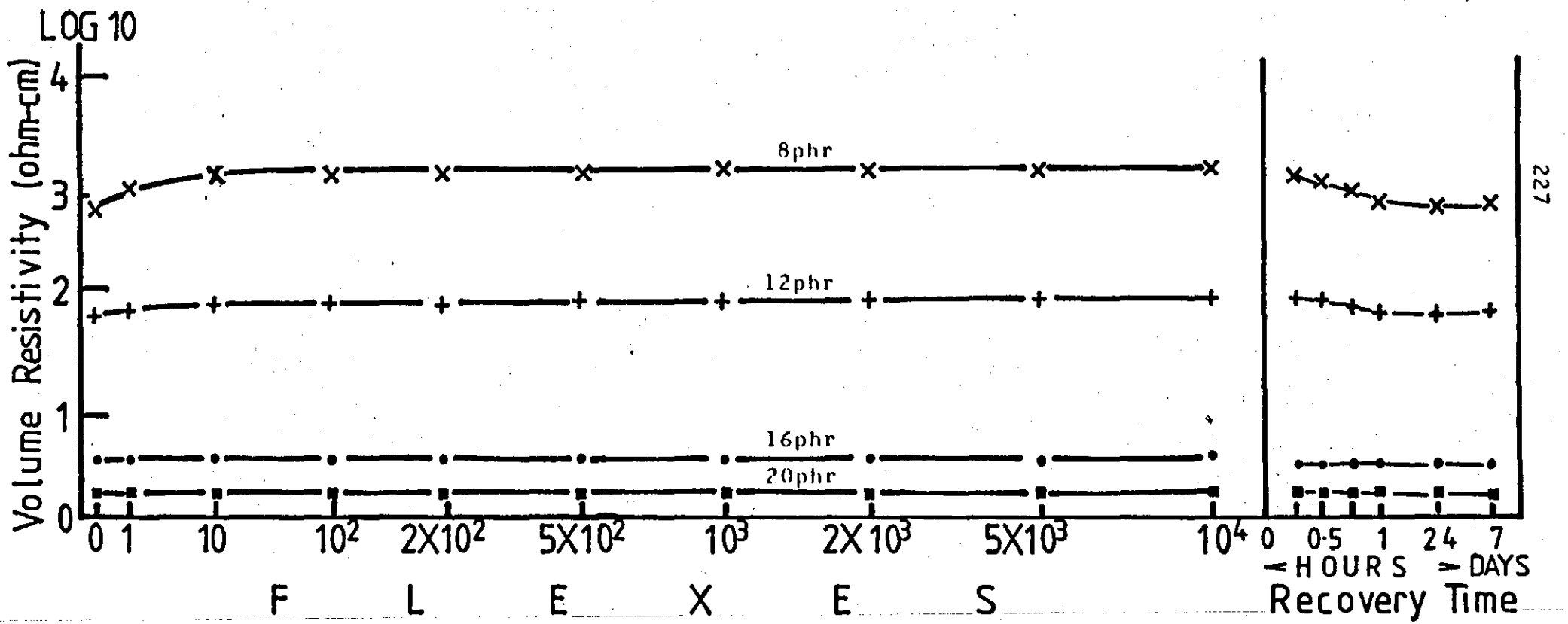


Fig. 7.7 Effect of Flexing (Low Strain) on the volume resistivity of the special furnace black (Ketjenblack EC) filled Silastic GP 45 based compounds (Ref Mix Nos 19-22 of Tables 7.2, 7.3 & 7.4).



Features similar to their Silastic GP30 vulcanisate cousins were observed to be also prominent. As with the above Vulcan P and Shawinigan vulcanisates, there was an observed much reduced peak resistivity during flexing. An almost similar mixture of higher and reduced volume resistivity after recovery as with their Silastic GP30 counterparts was observed. Reasons similar to those given above could be attributed to these phenomena.

7.4.8 HIGHLY (CARBON BLACK) FILLED SILASTIC GP45 VULCANISATES

Fig. 7.8 gives a comparison of the effect of flexing on the volume resistivity of highly filled Silastic GP30 for the different carbon black used in this investigation. Mix Nos 31-38 of Tables 7.2, 7.3 & 7.4 give a summary of the results.

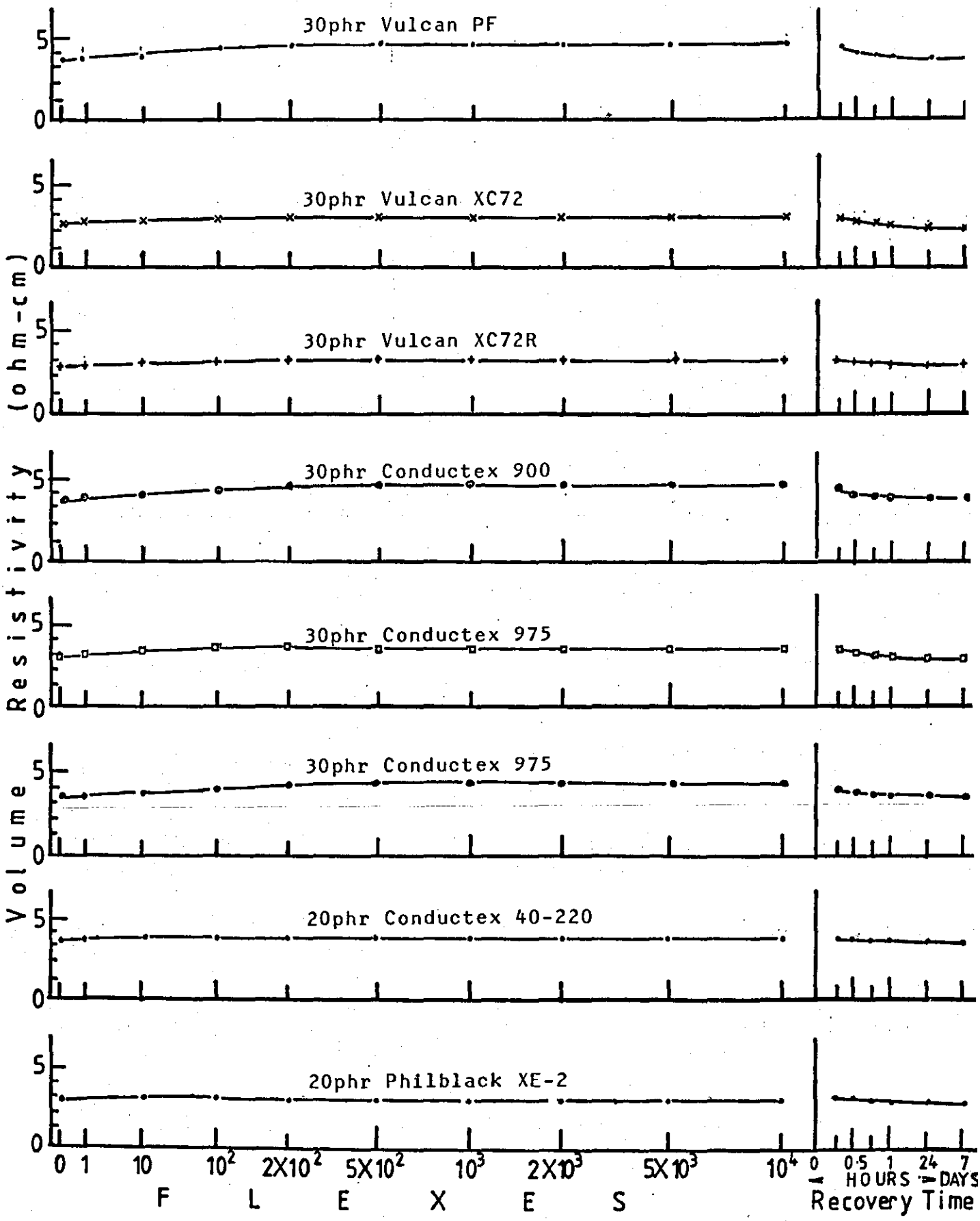
As with highly filled Silastic GP30, it was observed that the effect of flexing on highly filled conductive silicone rubbers is small and recovery is very rapid. Conductex 40-220 and Philblack XE-2 filled vulcanisates show similar characteristics to Ketjenblack EC.

7.5 CONCLUSIONS

Generally, a repeated deformation (low strain flexing) is found to affect the volume resistivity of carbon black filled conductive silicone rubbers. The degree of this low strain effect is dictated by the type and concentration of the carbon black, the percentage of the silica content, and the time lapse after recovery.

Nearly all vulcanisates exhibited a sharp increase in volume resistivity after the onset of flexing and reaching a constant value at around 200cycles. A suggested explanation of this phenomenon is that volume resistivity increased due to either the formation of an increase in the number of temporary breakages in the number of conducting paths formed by pseudo-fibre chain formation (of the furnace carbon black particles); or, the webs of overlapped carbon black particles in the soft and bulkier acetylene blacks slide past each

Fig. 7.8 Effect of Flexing (Low Strain) on the volume resistivity of carbon black filled Silastic GP 45 based compounds (Ref Mix Nos 31-38 of Tables 7.2, 7.3 & 7.4)



other and stretch. Also coupled with this movement is increased interparticulate distance.

As carbon black content increases the initial sharp increase in volume resistivity rapidly reduces with little or no increase at very high carbon black loadings. It is suggested that as the carbon black particles are added, the interparticulate distances tend towards zero and hence the more probable is the increasing pseudo-fibre chain formation with furnace blacks and the bulky carbon chain overlap with acetylene black. Hence, when flexed, a comparatively lower percentage of 'chain' breakage is likely to occur with increasing carbon black content.

Vulcanisates with an increased silica content (Silastic GP45) exhibit lower peak volume resistivity percentage increases when compared with those of Silastic GP30. It is suggested that this reduced criteria could be attributed to the viscoelastic damping effect of the increased silica content.

The final volume resistivity of all vucanisates depends mainly on the time lapse after recovery. The rate of recovery increases with increasing carbon black content. An interesting phenomenon is the final volume resistivity percentage difference observed with all vulcanisates. The vulcanisates containing the comparatively lower percentage of the carbon black content (e.g 20, 25phr and 8, 12phr) had an increased percentage difference of volume resistivity while those with higher percentage of carbon blacks (30, 35 and 16, 20) had a decreased percentage difference of volume resistivity when compared with initial volume resistivity figures..It is, therefore, suggested that the two possible mechanisms responsible for electrical conduction in conductive carbon blacks are:

a. pseudo-fibre carbon black formation with the furnace blacks and carbon black particle overlap with the bulky acetylene blacks.
b. electron tunnelling dictated by the interparticulate distance of the carbon blacks.

From the above, it is suggested that a combination of the two mechanisms is possible to exist in all conductive compounds. However, with increasing carbon black content, the increasing proportion of 'a' will probably be more than that of 'b'. Hence the proportionate increase in ratio a:b will tend towards 'a'.

Let us assume that the ratio a:b at 20phr, 25phr, 30phr and 35phr loading of Shawinigan are 30:70, 45:55, 55:45 and 70:30 respectively. The tendency for a compound to suffer a more permanent damage will be an increase in the particulate or inter-aggregate distance which is more prominent in 'b'. Hence our assumption suggests a declining permanent damage with increasing carbon black content. This may, therefore, be responsible for the increased final volume resistivity after recovery as recorded in the 20phr and 25phr loadings respectively.

The decrease in the final volume resistivity after recovery of the vulcanisates containing 30phr and 35phr carbon black content may be attributed to the above assumption *i.e* the fact that they contained a higher percentage of 'touching' pseudo-fibre carbon black chains which are easier to reform than the 'electron-tunneling-based' rubber-carbon black conformation (which may create a more permanent increased interparticulate distance). Coupled with this is the possibility of a 're-arrangement' and a 're-alignment' of the isolated carbon black particles during flexing and which remained trapped in their new positions where they are forced to participate in the pseudo-fibre chain formation thereby decreasing the resultant volume resistivity.

The unique properties of the 'special furnace blacks' (Ketjenblack EC, Philblack XE-2, and Conductex 40-220) are exhibited in all their vulcanisates. These are porous, hollow-shelled and light weight, smaller particles. These unique criteria encourage a high pseudo-fibre chain formation inherent from the light weight, smaller particles with, therefore, a higher number of aggregates on a weight basis. Also the porous and hollow shells encourage electron tunnelling. It is therefore not surprising to observe the resultant lower final volume resistivity of their vulcanisates at equivalent carbon black volume proportions.

VIII GRAPHITIZED CARBON BLACK

8.1 INTRODUCTION

Carbon blacks, depending on the manufacturing process, i.e channel or furnace, on analyses are found to contain 95-99% carbon, the remainder consisting chiefly of combined oxygen or hydrogen. Hence, carbon blacks can chemically be considered as a series of imperfect polycyclic aromatic hydrocarbons in various states of oxidation. The presence of oxygen and hydrogen atoms in quantities up to 5% of the weight of carbon cause it to be very reactive.

Apart from the above chemistry, carbon black particles contain pores facilitating migration and/or difussion of additives, in small quantities, into the carbon black particles.

This combination of structure and surface chemistry of carbon black, therefore, have a strongly profound absorption effect, besides other chemical and physical effects on curing agents especially where an effective degree of curing is dependent on the free radical generation e.g in peroxide cures. This is, therefore, thought of as the cause for the common observation of the decreasing effect of the state of cure obtained with peroxides when in the presence of increasing carbon black content in silicone rubber vulcanisates.

Other workers have observed that heat treatment of carbon black at various temperatures in inert atmosphere produces both physical and chemical changes in its surface activities. These changes occur in stages beginning with the evolution of carbon dioxide just below 200°C[325] (fig.8.1) and ending with the product graphitized carbon black at a temperature approaching 3,000°C.

The surface oxygen complexes are apparently removed as carbon dioxide and carbon monoxide at temperatures between 200°C and 1,200°C[325]. The carbon black surface area increases due to the development of pores coinciding with the loss of oxygen groups. Hydrogen evolution starts at about 600°C

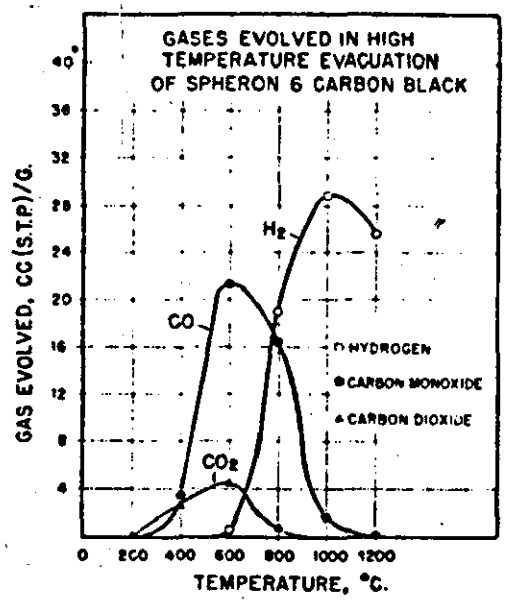


Fig. 8.1 Gases evolved in high temperature evacuation of Spheron 6 carbon black[325].

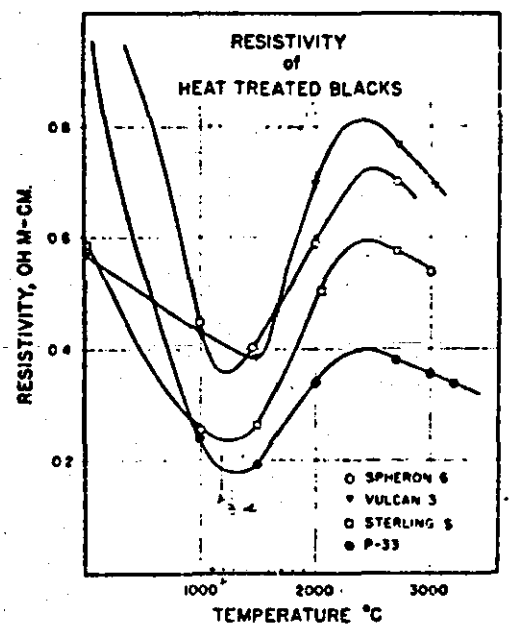


Fig. 8.2 The electrical volume resistivity of heat treated carbon blacks[325].

and continues to about 1600°C.[310,325,327,334] The surface area starts to decrease with hydrogen evolution coupled with carbon black surface annealing (hardening) and reorganisation of the surface layers.[310]

Significant changes take place in the surface, which affects the electrical volume resistivity[325] (fig 8.2) and the rubber reinforcing properties of carbon blacks in the temperature ranges of 800°C to 1,500°C. There is decrease in the:

a. concentration of unpaired spins[328] (fig.8.3),
b. modulus and percentage of the bound rubber[326] (fig.8.4),
c. immersional heats in alcohols[329] (fig.8.5),
d. rupture resistance of rubbers[336],
e. surface physical adsorption activity[326,327] - reduction in moisture adsorption (fig.8.4),
f. concentration of acid groups[310] (fig.8.6), and
g. chemisorption capacity[310,336] (fig.8.7).

At higher temperatures, other changes take place, such as, loss of chemically combined sulphur, and ordering of the layer planes and increases in the crystallite dimensions[326] (fig.8.8). Eventually, the highly ordered, graphitized carbon is formed. Relative to the original blacks, graphitized carbon blacks have decreased structure[330] (fig.8.9), lower surface energy[331], less bound rubber[332] and a lower level of adhesion to rubber[333]. These changes are reflected in a low modulus[326,330], a high abrasion loss, and a 70% loss in retained strain energy[334]. Elongation and tensile strength, however, change by relatively minor amounts[335].

Hence, the change in surface activity is both physical and chemical in nature. The chemical nature of the surface is changed to a greater extent below 1,000°C than at higher temperatures with a minimum effect on the rubber performance, whereas the physical nature of the surface changes to a greater extent at 1,000°C-1,500°C (and above) with a maximum effect on the rubber performance.

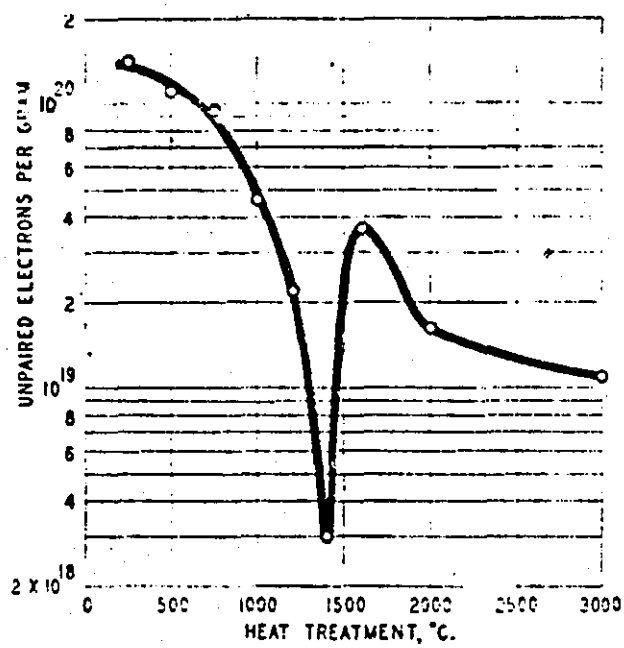


Fig. 8.3 Unpaired electron concentration in heat treated channel black (degassed at 250°C).[328]

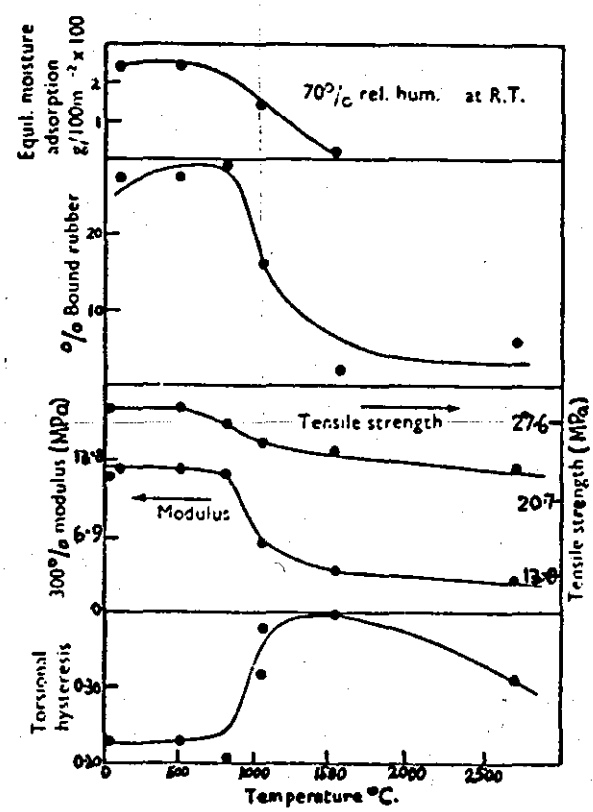


Fig. 8.4 Properties of ISAF versus heat treatment temperature (50phr in SBR 1500)[326]

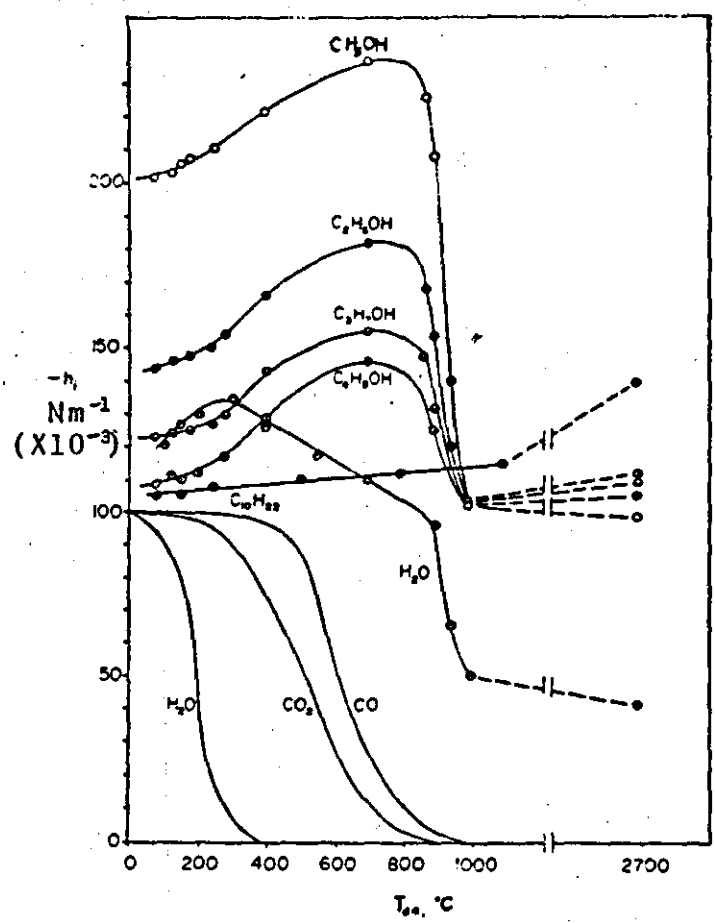


Fig. 8.5 The immersion heats $[Nm^{-1}(X10^{-3})]$ plotted versus outgassing pretreatment along with the percentage of H_2O, CO and CO_2 thermally degraded[329].

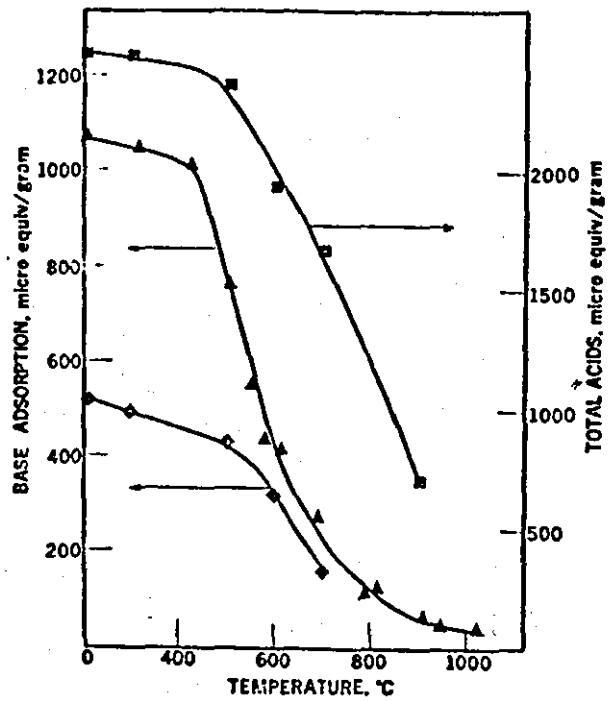


Fig. 8.6 Concentration of acid groups on Black Pearls 2 as a function of High Thermal Temperature (HTT).[310] *Total acids from $LiAlH_4$ ■; Strong acids from 0.03N NaOH ▲; Strong acids from $NaHCO_3$ ◆.*

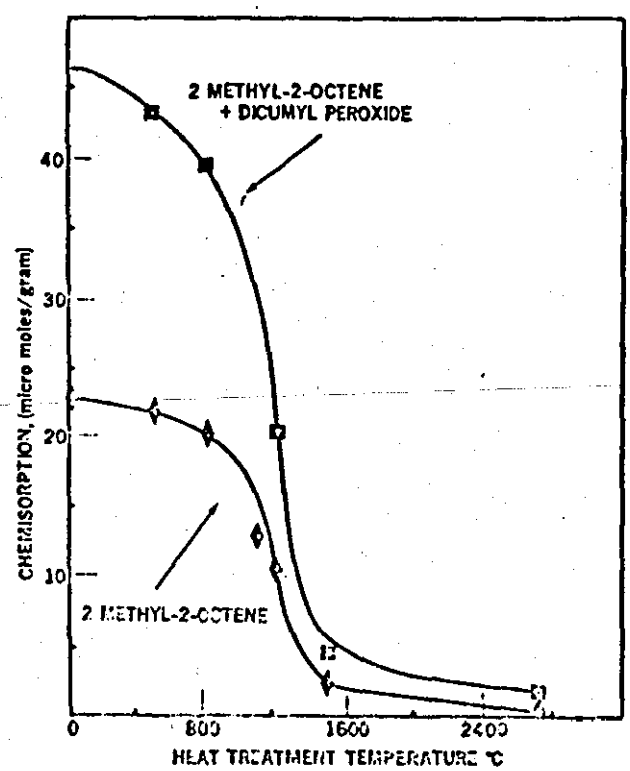


Fig. 8.7 Chemisorption capacity of ISAF black as a function of High Thermal Temperature (HTT).[310]

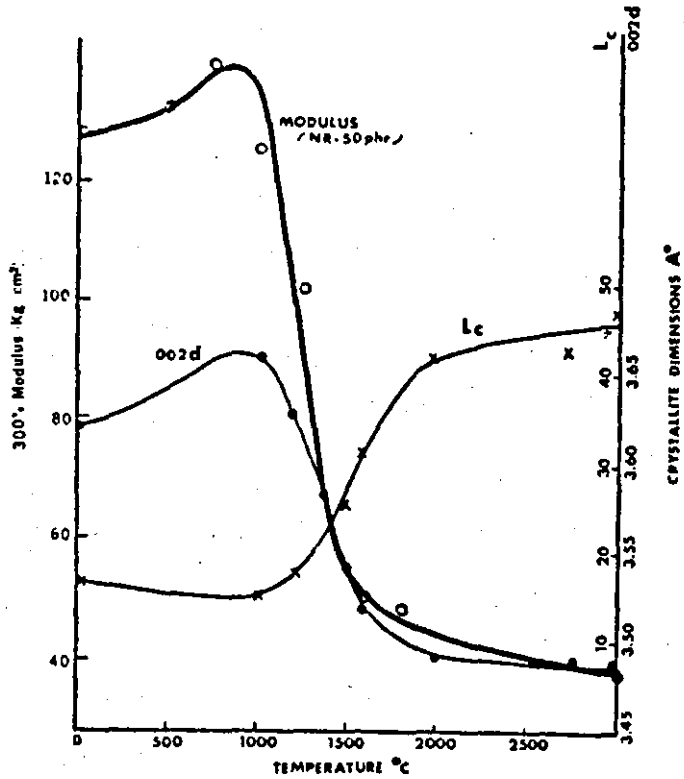


Fig. 8.8 Effect of heat treatment temperature on the crystallite dimensions (as determined by X-ray diffraction) of MPC black and on the vulcanisate modulus.[326]

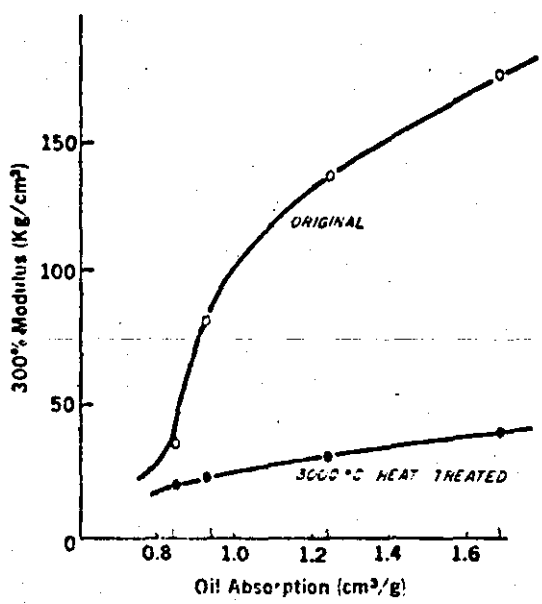


Fig. 8.9 Modulus-structure relationship with original and heat-treated ISAF-type carbon blacks (50phr in SBR 1500)[330]

8.2 OBJECTIVE

In summary, it can be seen from the above that some useful criteria can be concluded about graphitizing carbon blacks:

a. elimination/decrease in the reactive surface chemistry, volatiles and pores,

b. depending on the type of carbon black, a resultant lower resistive carbon black could perhaps be attained, giving rise to lesser chemisorption capacity, better and cleaner surfaces with lower electrical contact resistances where chain formation might occur.

The objective of this section, therefore, is to investigate this proposed criteria by assessing the vulcanisate properties especially the electrical volume resistivity of graphitized carbon black filled silicone compounds; and making a comparative study with the ungraphitized carbon black filled compounds.

8.3 GRAPHITIZATION PROCESS

8.3.1 EQUIPMENT

The main equipment is an electrically heated K45B Type Horizontal Tube Furnace (fig.8.10) with a maximum continuous and short term operating temperature of 1,500°C and 1,600°C respectively. Other auxilliary items were as specified in fig. 8.10.

8.3.2 CALIBRATION

The furnace was first calibrated using constructed Alumel/Chromel thermocouple insulated with ceramic beads and connected to Wheatstone Resistance box from which the millivolts-equivalent temperatures were read off (Table 8.1, fig. 8.11).

8.3.3 PROCEDURE

Well blended samples of carbon black were put into small ceramic boats and spread at the bottom of the tube inside the furnace (fig. 8.10).

Fig. 8.10 Diagramatic representation of the Apparatus set-up for graphitizing conductive carbon blacks.

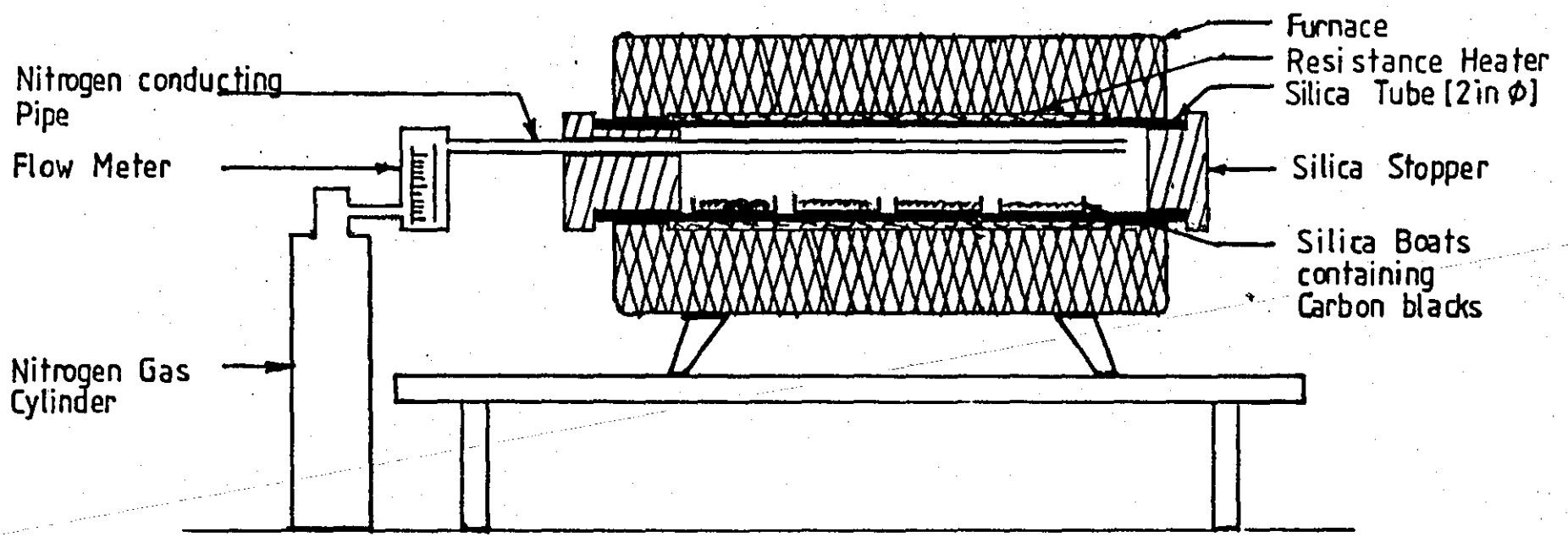


TABLE 8.1 FURNACE CALIBRATION

Set Temperature (°C)	Average Reading (millivolts)	Real Temperature (°C)
20	0.80	20
100	4.00	100
200	8.10	199
300	12.20	300
400	16.28	398
500	20.46	496
600	24.80	598
700	29.00	697
800	33.30	800
900	37.24	896
1,000	41.20	997
1,100	45.00	1,096
1,200	48.64	1,195
1,300	51.00	1,260
1,350	52.50	1,303
1,400	54.00	1,346
1,450	55.24	1,380
1,500	56.30	1,410
1,550	57.20	1,440
1,600	58.70	1,480

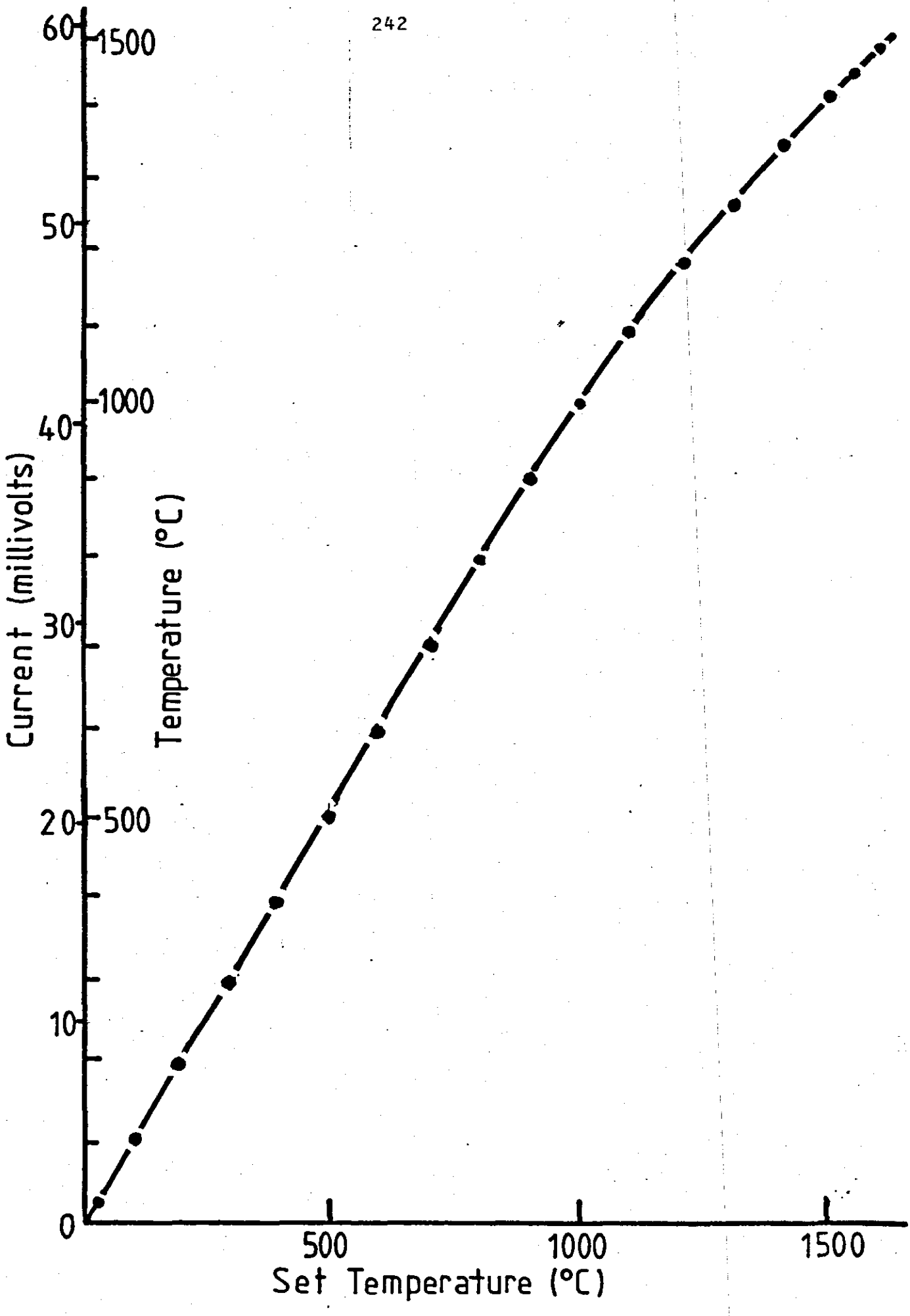


Fig. 8.11 Calibration Chart for the Horizontal Tube Furnace

Oxygen was carefully removed from the sample bed and replaced with a flush of nitrogen for 10minutes at $10cm^3min^{-1}$ before heating and a continuous $5cm^3min^{-1}$ flow of dry nitrogen surrounded the sample during the required heat treatment.

A gradually stepped up, carefully controlled heating process was adopted(as recommended by the manufacturer):

0-10mins ——— 0°C-200°C; and 10-30mins ——— 200°C-700°C

The furnace was then allowed to rise to a preset temperature at full power.

Carbon black samples were treated at 1200°C, 1300°C, and 1450°C for three hours each. The carbon blacks graphitized at 2800°C for 3hrs were prepared by the Stackpole Carbon Corp. USA[337].

The following conductive carbon blacks were heat treated as representing commercial chemical classes available:

a. Furnace blacks: Vulcan P and Vulcan XC72
b. Acetylene black: Shawinigan
c. Special furnace black: Ketjenblack EC

Only about 90-100g of graphitized carbon black can be obtained per run. Hence, only a limited number of experiments was carried out.

8.4 EXPERIMENTAL

8.4.1 MATERIALS (see also Ch.2, Section 2.1)

a. Polymer
Silastic GP45

b. Curing Agent
Perkadox SB

c. Graphitized carbon blacks
Vulcan P and XC72, Shawinigan, and Ketjenblack EC

d. Coupling agents
Silane Z6082 and Titanate KR55

8.4.2 MIX FORMULATIONS

Table 8.2 shows the detailed mix formulations.

TABLE 8.2 MIX FORMULATIONS

Mix Number	A	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Silastic GP45		100.0															
Perkadox SB		2.5															
Vulcan P	1200	30	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1300	–	30	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1450	–	–	30	–	–	–	–	–	–	–	–	–	–	–	–	–
	2800	–	–	–	30	–	–	–	–	–	–	–	–	–	–	–	–
Vulcan XC72	1200	–	–	–	–	30	–	–	–	–	–	–	–	–	–	–	–
	1300	–	–	–	–	–	30	–	–	–	–	–	–	–	–	–	–
	1450	–	–	–	–	–	–	30	–	–	–	–	–	–	–	–	–
	2800	–	–	–	–	–	–	–	30	–	–	–	–	–	–	–	–
Shawinigan	1200	–	–	–	–	–	–	–	–	30	–	–	–	–	–	–	–
	1300	–	–	–	–	–	–	–	–	–	30	–	–	–	–	–	–
	1450	–	–	–	–	–	–	–	–	–	–	30	–	–	–	–	–
	2800	–	–	–	–	–	–	–	–	–	–	–	30	–	–	–	–
Ketjenblack EC	1200	–	–	–	–	–	–	–	–	–	–	–	–	20	–	–	–
	1300	–	–	–	–	–	–	–	–	–	–	–	–	–	20	–	–
	1450	–	–	–	–	–	–	–	–	–	–	–	–	–	–	20	–
	2800	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	20

Mix Number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Silastic GP45		100.0																							
Perkadox SB		2.5																							
Vulcan P	BI																								
	1200	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1300	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–
	1450	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–
	2800	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30
Vulcan XC72	BII																								
	1200	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1300	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–
	1450	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–
	2800	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30
Shawinigan	BIII																								
	1200	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	1300	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–	–	–	–	–	–	–
	1450	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30	–	–	–	–	–	–
	2800	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5	10	15	20	25	30
Ketjenblack EC	BIV	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20				
	1200	4	8	12	16	20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–				
	1300	–	–	–	–	–	4	8	12	16	20	–	–	–	–	–	–	–	–	–	–				
	1450	–	–	–	–	–	–	–	–	–	–	4	8	12	16	20	–	–	–	–	–				
	2800	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	4	8	12	16	20				

Mix Number	C	1	2	3	4	5	6	7	8	9	10
Silastic GP45		100.0									
Perkadox SB		2.5									
Silane Z6082		1.0									
Titanate KR-55		0.5									
Vulcan P	2800	20	30	–	–	–	–	–	–	–	–
Vulcan XC72	2800	–	–	20	30	–	–	–	–	–	–
Shawinigan	2800	–	–	–	–	20	30	–	–	–	–
Ketjenblack EC	2800	–	–	–	–	–	–	8	12	16	20

8.4.3 MIXING

The standard milling time as described in Ch.2, Section 2.2.1 was closely followed. For Sections 8.5.2 and 8.5.3 the milling time was controlled to within the safety time belt, as observed in Section 8.5.1, for each compound.

8.4.4 VULCANISATION

This was carried out as described in Ch.2, Section 2.2.2

8.4.5 EVALUATION OF VULCANISATE PROPERTIES

8.4.5.1 Electrical Volume Resistivity Measurement

This was carried out as described in Ch.2, Sect.2.2.4.

8.4.5.2 Hardness (IRHD) Measurement

This was carried out in accordance with BS903:PartA26:1969

8.4.5.3 Dispersion Index Measurement

This was carried out as described in Ch.2, Sect.2.2.7

8.5 RESULTS AND DISCUSSIONS

8.5.1 PROCESSING (MILLING)

For investigating the effect of processing (milling) on both dispersion and volume resistivity, high proportions of different types of graphitized carbon black filled Silastic GP45 based compounds were used. Such compounds were considered to represent highly conductive rubbers.

8.5.1.1 Graphitized Vulcan P loaded Silastic GP45 vulcanizates

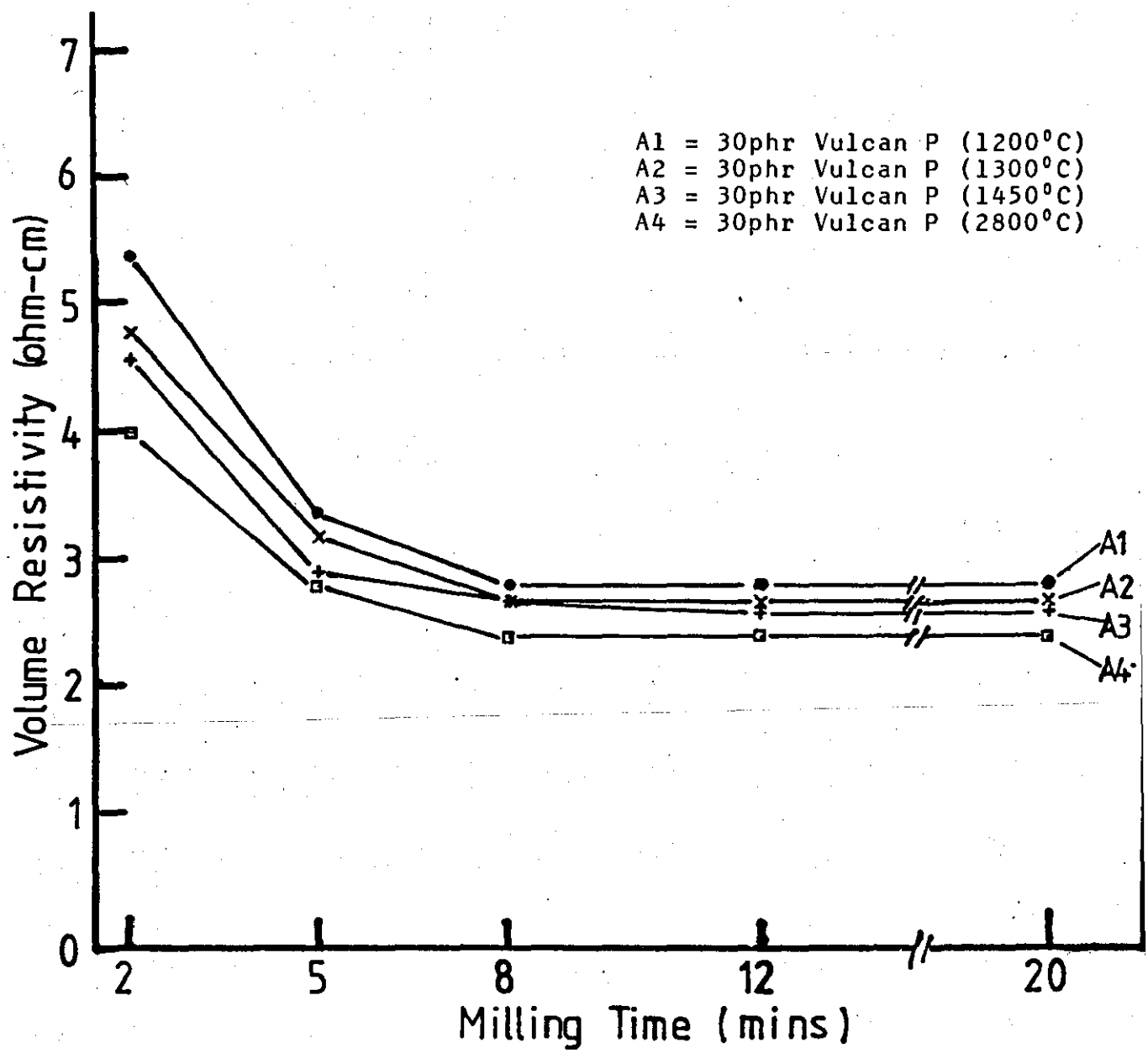
Fig.8.12 gives a comparison of volume resistivity versus milling times obtained from increasing the carbon black graphitization temperature. Mix Nos A1-A4 of Table 8.3 give a comparative summary of results.

It was observed that with increasing milling time, there was a marginal decrease in the cure rate, cure times and the dispersion index. The dispersion index is considered to indicate the degree of carbon black particle de-agglomeration and possibly aggregate breakdown. The volume resistivity of nearly all compounds decreases to a minimum at 8mins milling time and remains constant on further milling. The

TABLE 8.3 VULCANISATE PROPERTIES OF GRAPHITIZED CARBON BLACK FILLED SILASTIC GP45 BASED CONDUCTIVE COMPOUNDS: PROCESSING

Mix Number	Milling Time (mins)	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C=\frac{\mu h s}{t \times 100}$
A1	2	0.52	11.40	5.40	50	1.62
	5	0.52	11.40	3.20	54	1.42
	8	0.50	11.60	2.80	55	1.03
	12	0.50	11.60	2.80	55	0.80
	20	0.48	11.70	2.80	55	0.52
A2	2	0.60	10.70	4.80	50	1.52
	5	0.60	10.70	3.40	56	1.38
	8	0.58	10.90	2.80	56	1.00
	12	0.58	10.90	2.70	56	0.66
	20	0.54	11.20	2.70	56	0.50
A3	2	0.62	10.60	4.60	50	1.33
	5	0.62	10.60	2.90	56	1.14
	8	0.60	10.70	2.70	56	0.92
	12	0.60	10.70	2.60	56	0.52
	20	0.58	10.90	2.60	56	0.46
A4	2	0.66	10.30	4.00	52	1.02
	5	0.64	10.40	2.80	56	0.67
	8	0.62	10.60	2.40	56	0.48
	12	0.62	10.60	2.40	56	0.41
	20	0.60	10.70	2.40	56	0.34
A5	2	0.52	11.40	5.20	54	2.12
	5	0.50	11.60	3.40	58	1.61
	8	0.50	11.60	2.70	58	1.22
	12	0.48	11.70	2.70	58	0.91
	20	0.48	11.70	2.70	58	0.68
A6	2	0.56	11.10	4.90	54	1.98
	5	0.54	11.20	3.60	58	1.49
	8	0.54	11.20	2.80	58	1.16
	12	0.52	11.40	2.60	58	0.83
	20	0.52	11.40	2.60	58	0.66
A7	2	0.58	10.90	4.40	52	1.77
	5	0.56	11.10	3.80	57	1.48
	8	0.56	11.10	2.80	58	2.10
	12	0.54	11.20	2.60	58	0.70
	20	0.54	11.20	2.60	58	0.59
A8	2	0.62	10.60	4.20	56	1.48
	5	0.60	10.70	2.80	58	0.95
	8	0.60	10.70	2.40	58	0.78
	12	0.58	10.90	2.40	58	0.46
A9	2	0.68	10.10	6.60	60	2.60
	5	0.62	10.60	4.40	62	3.60
	8	0.62	10.60	3.60	62	1.41
	12	0.60	10.70	3.60	64	1.02
	20	0.60	10.70	3.60	64	0.84
A10	2	0.70	10.00	5.40	60	2.42
	5	0.66	10.30	4.00	62	1.59
	8	0.66	10.30	3.80	64	1.32
	12	0.62	10.60	3.60	64	0.99
	20	0.62	10.60	3.60	64	0.81
A11	2	0.74	9.60	4.80	61	2.21
	5	0.70	10.00	3.80	63	1.42
	8	0.70	10.00	3.40	64	1.18
	12	0.69	10.00	3.40	64	0.92
	20	0.68	10.10	3.40	64	0.79
A12	2	0.80	9.20	4.20	62	1.95
	5	0.76	9.50	3.40	64	1.23
	8	0.76	9.50	3.00	64	1.09
	12	0.74	9.60	3.00	64	0.82
	20	0.74	9.60	3.00	64	0.60
A13	2	0.72	9.80	6.20	62	0.99
	5	0.62	10.60	3.80	64	0.87
	8	0.60	10.70	3.00	66	0.76
	12	0.56	11.10	2.20	66	0.64
	20	0.48	11.70	2.20	66	0.39
A14	2	0.70	10.00	4.40	62	0.95
	5	0.66	10.30	3.20	64	0.76
	8	0.66	10.30	2.60	66	0.63
	12	0.62	10.60	2.20	66	0.48
	20	0.58	10.90	2.20	66	0.36
A15	2	0.70	10.00	3.80	64	0.92
	5	0.68	10.10	2.80	64	0.72
	8	0.68	10.10	2.40	66	0.60
	12	0.64	10.40	2.20	66	0.38
	20	0.58	10.90	2.20	66	0.28
A16	2	0.76	9.50	3.20	64	0.88
	5	0.72	9.80	2.40	66	0.69
	8	0.72	9.80	2.20	66	0.56
	12	0.68	10.10	2.10	66	0.32
	20	0.64	10.40	2.10	66	0.24

Fig. 8.12 Effect of milling on the volume resistivity of the graphitized furnace black (Vulcan P) filled Silastic GP 45 based compounds (Ref Mix Nos A1-4 of Table 8.3)



dispersion index, however, continuously decreases with increasing milling time. A suggested explanation of the two above phenomena is that the volume resistivity decreases with carbon black incorporation, followed by a continuous improved dispersion without a 'significant' carbon black deagglomeration or aggregate breakdown. It should hereby be noted that the volume resistivity of a similar compound containing ungraphitized carbon black decreases to a minimum at between 5 and 8mins milling time and then is slightly increased on further milling.

It was also observed that the volume resistivity as well as the rate of carbon black incorporation during milling decreases with increasing graphitization temperature.

8.5.1.2 Graphitized Vulcan XC72 loaded Silatic GP45 vulcanizates

Mix Nos A5-A8 and fig.8.13 are now considered. Features similar to and comparable with the Vulcan P loaded Silastic GP45 were noted, but the rate of the initial carbon black incorporation (as well as the volume resistivity decrease) during milling is slower. However, a higher and slightly less rapidly decreasing dispersion index was observed. This suggests a less pronounced milling effect and thus in agreement with the slower initial rate of carbon black incorporation.

With respect to change in volume resistivity with prolonged milling, the compounds containing graphitized carbon black was observed to be better when compared to the ungraphitized carbon black filled compounds.

8.5.1.3 Graphitized Shawinigan loaded Silastic GP45 vulcanizates

Fig. 8.14 and Mix Nos. A9-A12 of Table 8.3 are hereby considered. Features similar to and comparable with the above two were noted, but with a higher and more 'slightly' decreasing dispersion index suggesting a slightly more pronounced milling effect. It was observed that the rate of initial carbon black incorporation, as well as the rate of the volume resistivity decrease, during milling was slightly higher. However, with further milling, unlike its ungraphitized carbon black filled compound, the volume resistivity

Fig. 8.13 Effect of milling on the volume resistivity of the graphitized furnace black (Vulcan XC72) filled Silastic GP45 based compounds (Ref Mix Nos A5-8 of Table 8.3).

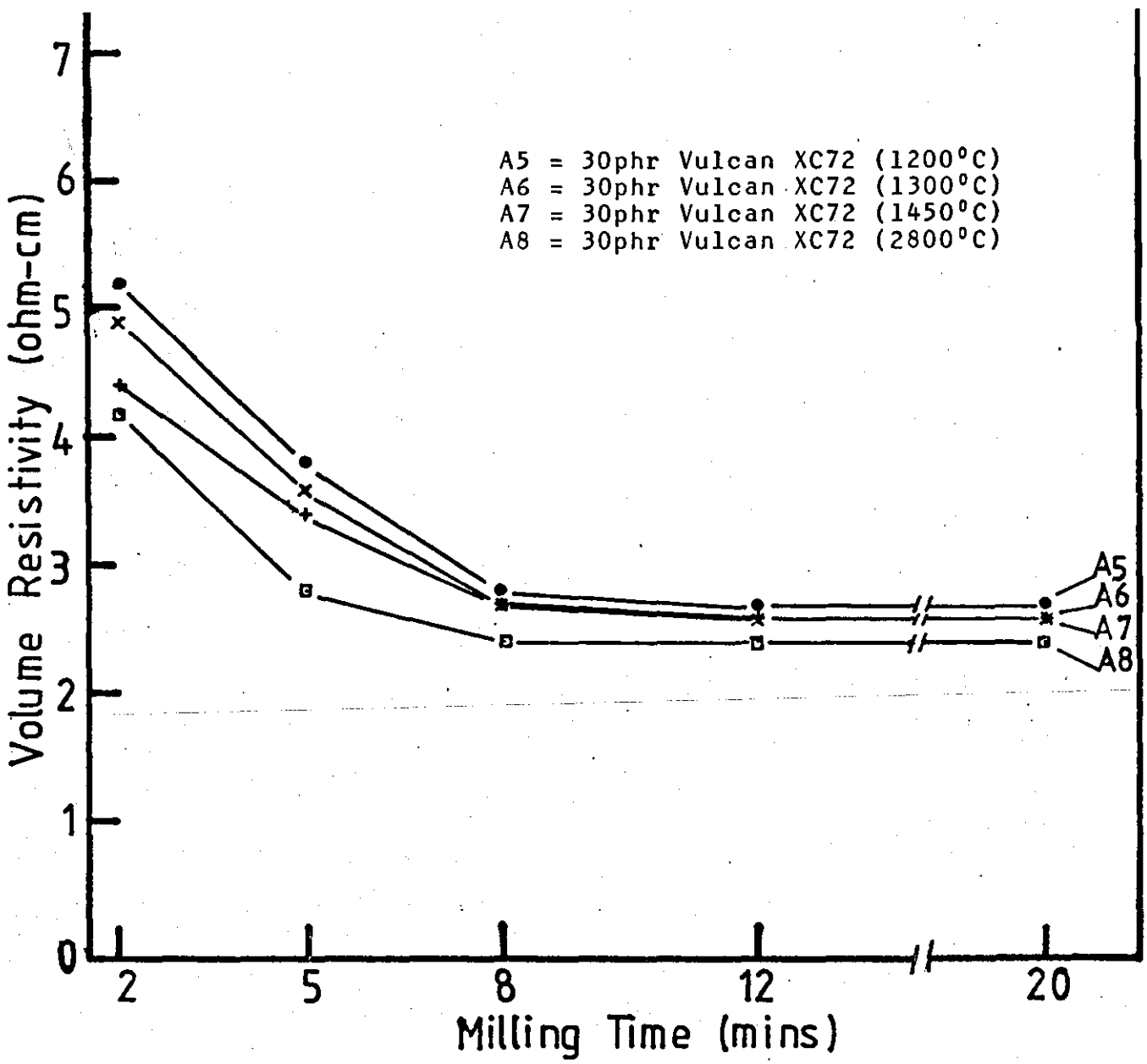
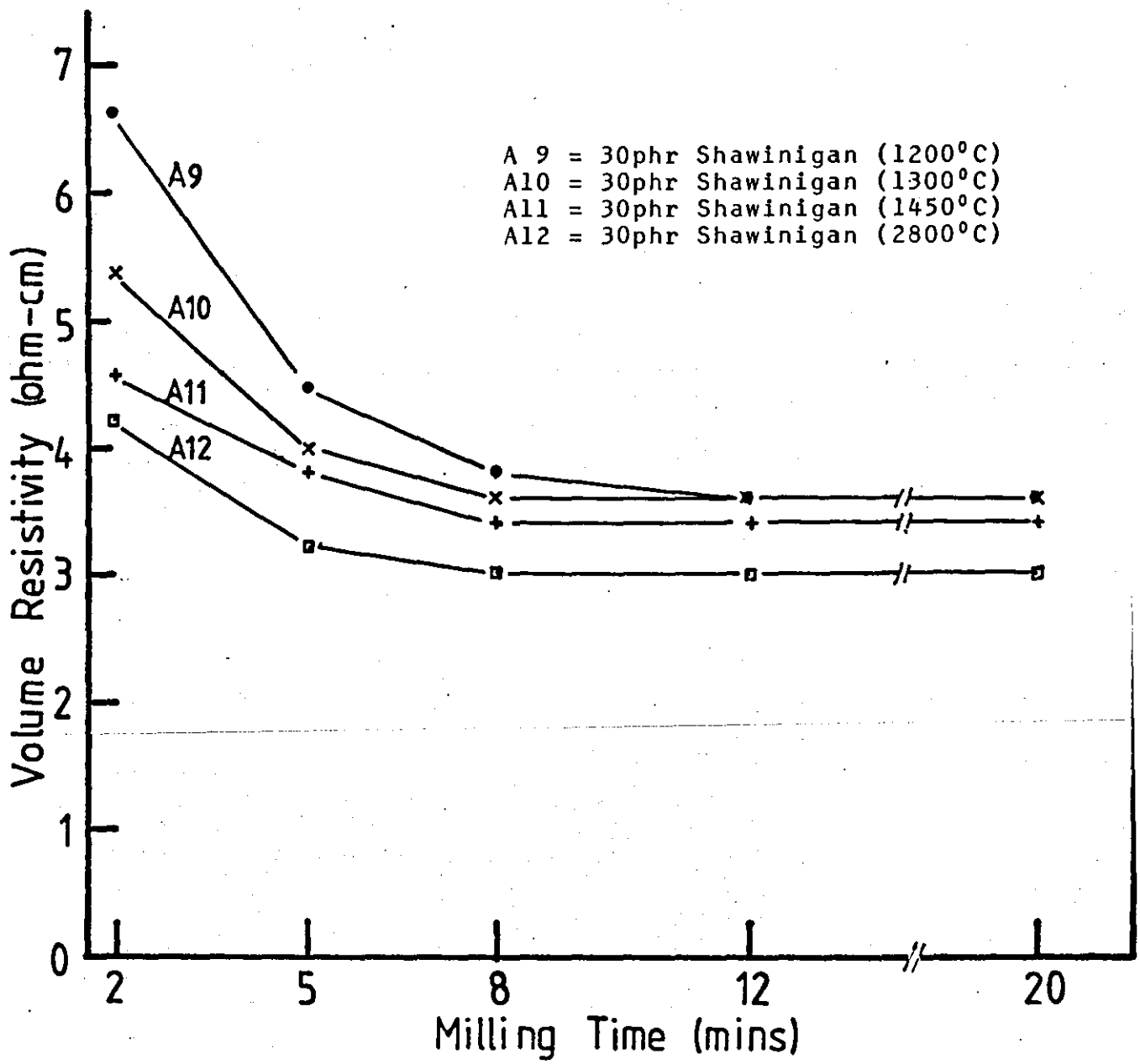


Fig. 8.14 Effect of milling on the volume resistivity of the graphitized acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Mix Nos A9-12 of Table 8.3).



remained constant. This thus suggests improved dispersion without any significant increasing breakdown of the carbon black into its elementary particles and, therefore, a constant volume resistivity.

8.5.1.4 Graphitized Ketjenblack EC loaded Silastic GP45

Mix Nos A13-A16 of Table 8.3 and fig. 8.15 are considered in this exercise. Features similar to and comparable with the above three are observed. However, the dispersion variation (decrease) is small when compared with the Vulcan P, Shawinigan and Vulcan XC72 loaded compounds. This suggests a progressively improved dispersion as observed with the initial continuous decrease in the volume resistivity. Also, the initial carbon black incorporation is slower when compared with similar compounds containing ungraphitized carbon black.

On further milling, however, the volume resistivity remained constant, an improvement over the ungraphitized carbon black filled compound which showed a slight increase in volume resistivity with prolonged milling. It was also observed that the cure rate decreases at a much reduced rate than that of the ungraphitized carbon black filled compounds on prolonged milling.

8.5.2 CARBON BLACK CONCENTRATION

A summary of the vulcanisate properties of Silastic GP45 based compounds on the effect of carbon black concentration is shown in Table 8.4. Mix Nos BI-BIV of Table 8.4 and figs. 8.16-8.19 are considered in this exercise.

Observation of the log-resistivity versus carbon black concentration graphs(figs. 8.16-8.19) generally show a gradual change in volume resistivity initially (5-15phr loading for graphitized furnace and acetylene blacks; not shown in that of Ketjenblack EC). This is followed by a more rapid drop and a very steep curve of volume resistivity, and a sharp 'transition' from resistive to conductive compound at a concentration dependent on the carbon black type. This established that the 'transitional' critical range from transforming an 'insulating' to 'conductive' Silastic GP45

Fig.8.15 Effect of milling on the volume resistivity of the graphitized special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Mix Nos A13-16 of Table 8.3).

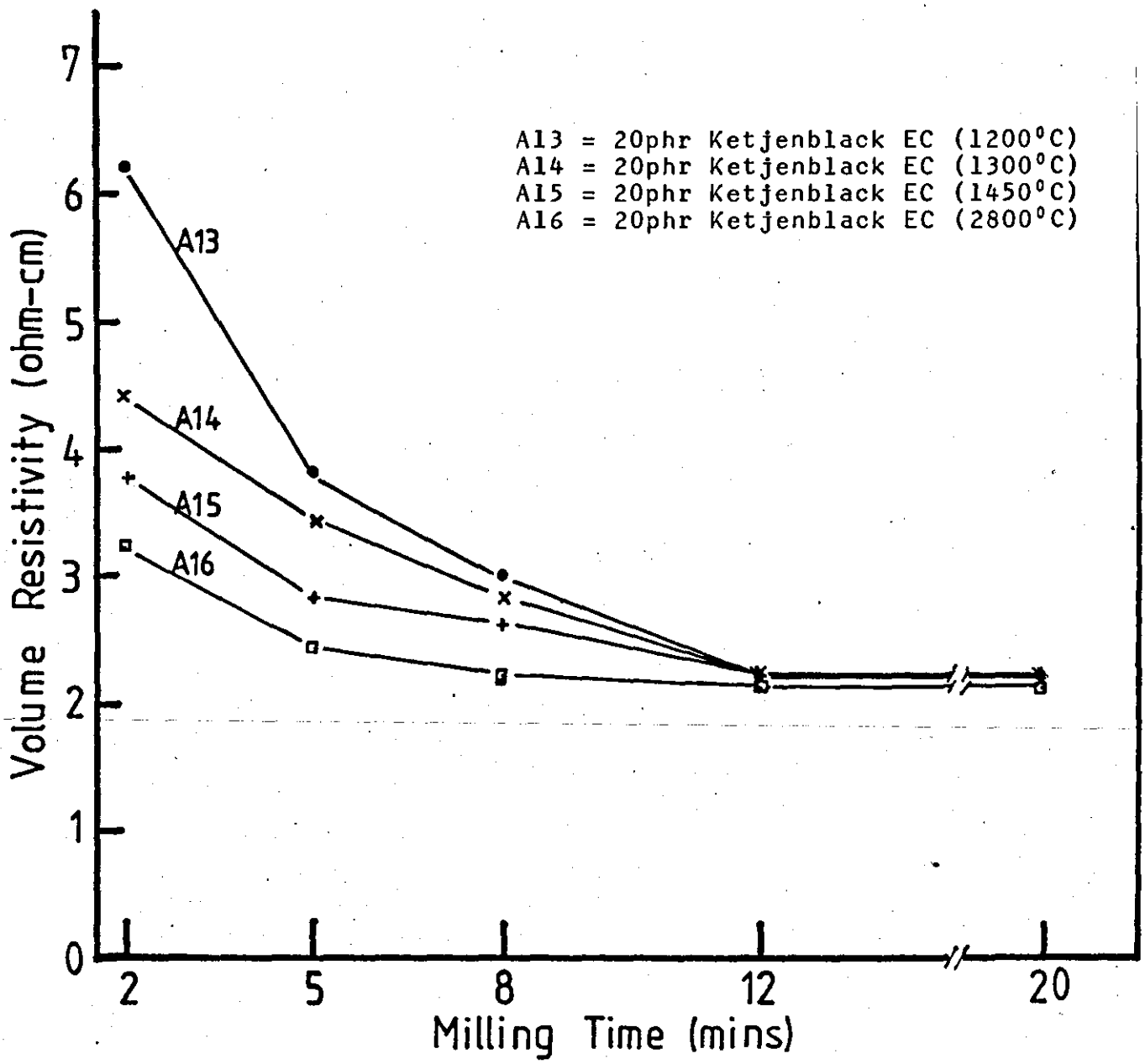
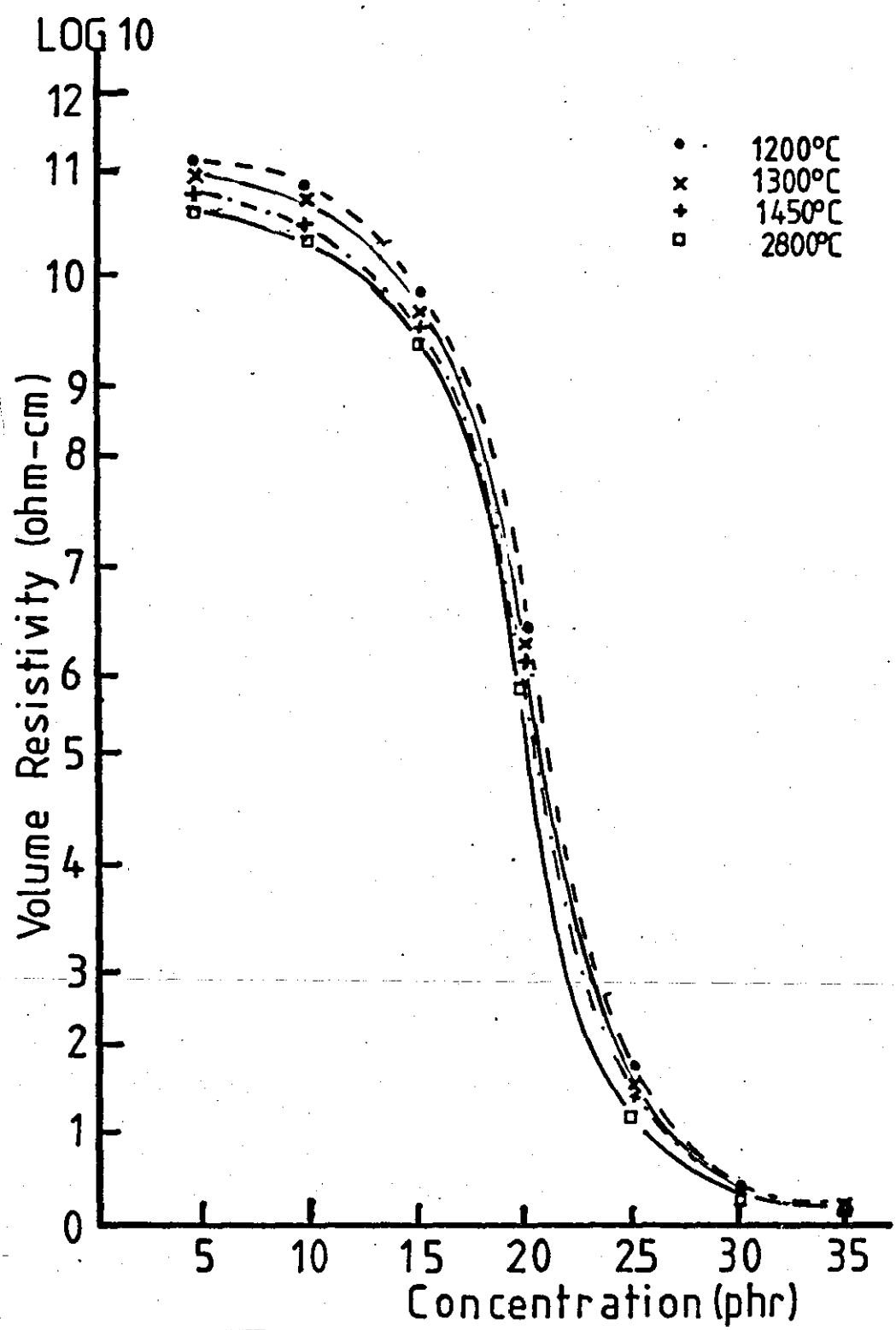


TABLE 8.4 VULCANIZATE PROPERTIES OF GRAPHITIZED CARBON BLACK FILLED SILASTIC GP45 BASED CONDUCTIVE COMPOUNDS: CARBON BLACK CONCENTRATION

Mix Number	Carbon black %	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C=\frac{n\bar{h}s}{t \times 100}$
BI Vulcan P						
1	5	1.20	6.00	11.20×10^{10}	48	
2	10	1.01	7.50	8.80×10^{10}	50	
3	15	0.83	8.90	9.20×10^{9}	51	
4	20	0.66	10.30	2.82×10^{6}	52	
5	25	0.63	10.50	6.20×10^{1}	53	
6	30	0.50	11.60	2.80	55	0.91
7	5	1.20	6.00	9.20×10^{10}	48	
8	10	1.06	7.10	6.40×10^{10}	50	
9	15	0.87	8.60	7.30×10^{9}	52	
10	20	0.70	10.00	1.64×10^{6}	53	
11	25	0.68	10.20	5.00×10^{1}	55	
12	30	0.58	10.90	2.70	56	0.83
13	5	1.22	6.00	6.20×10^{10}	50	
14	10	1.10	6.80	2.30×10^{10}	51	
15	15	0.90	8.40	4.80×10^{9}	52	
16	20	0.76	9.50	8.20×10^{5}	53	
17	25	0.70	10.00	3.24×10^{1}	54	
18	30	0.60	10.70	2.60	56	0.70
19	5	1.24	5.70	3.40×10^{10}	51	
20	10	1.16	6.30	1.04×10^{10}	52	
21	15	0.96	7.90	3.00×10^{9}	53	
22	20	0.81	9.10	4.80×10^{5}	54	
23	25	0.73	9.70	2.00×10^{1}	55	
24	30	0.62	10.60	2.40	56	0.45
BII Vulcan XC72						
1	5	1.12	6.70	9.80×10^{10}	50	
2	10	1.08	6.90	8.40×10^{10}	52	
3	15	0.82	9.00	9.20×10^{9}	53	
4	20	0.68	10.20	3.20×10^{6}	55	
5	25	0.63	10.50	3.20×10^{1}	56	
6	30	0.50	11.60	2.80	58	1.07
7	5	1.16	6.30	8.40×10^{10}	50	
8	10	1.10	6.80	6.40×10^{10}	52	
9	15	0.86	8.60	4.00×10^{9}	53	
10	20	0.74	9.70	2.08×10^{6}	54	
11	25	0.68	10.20	2.90×10^{1}	56	
12	30	0.54	11.20	2.70	58	0.94
13	5	1.20	6.00	5.40×10^{10}	50	
14	10	1.12	6.70	3.20×10^{10}	52	
15	15	0.88	8.60	9.80×10^{8}	54	
16	20	0.78	9.40	9.60×10^{5}	55	
17	25	0.70	10.00	2.20×10^{1}	56	
18	30	0.56	11.10	2.70	58	0.88
19	5	1.24	5.70	3.40×10^{10}	50	
20	10	1.18	6.20	9.80×10^{9}	52	
21	15	0.92	8.30	4.00×10^{8}	54	
22	20	0.84	8.90	3.20×10^{5}	56	
23	25	0.74	9.70	1.70×10^{1}	57	
24	30	0.60	10.70	2.40	58	0.79

N.B Continued on page 256.

Fig.8.16 Fffect of graphitized furnace black (Vulcan P) concentration on the volume resistivity of Silastic GP45 based compounds (Ref Mix Nos BI 1-24 of Table8.4)



N.B. The highest resistivity obtained in these measurements is 10^{11}ohmcm because the base compound used in the programme already contained 5phr some carbon black. The volume resistivity of silicone rubber containing no carbon black is not measured, but its value from literature is known to be 10^{14}ohmcm.

Fig.8.17 Effect of graphitized furnace black (Vulcan XC72) concentration on the volume resistivity of Silastic GP45 based compounds (Ref Mix Nos BII 1-24 of Table8.4)

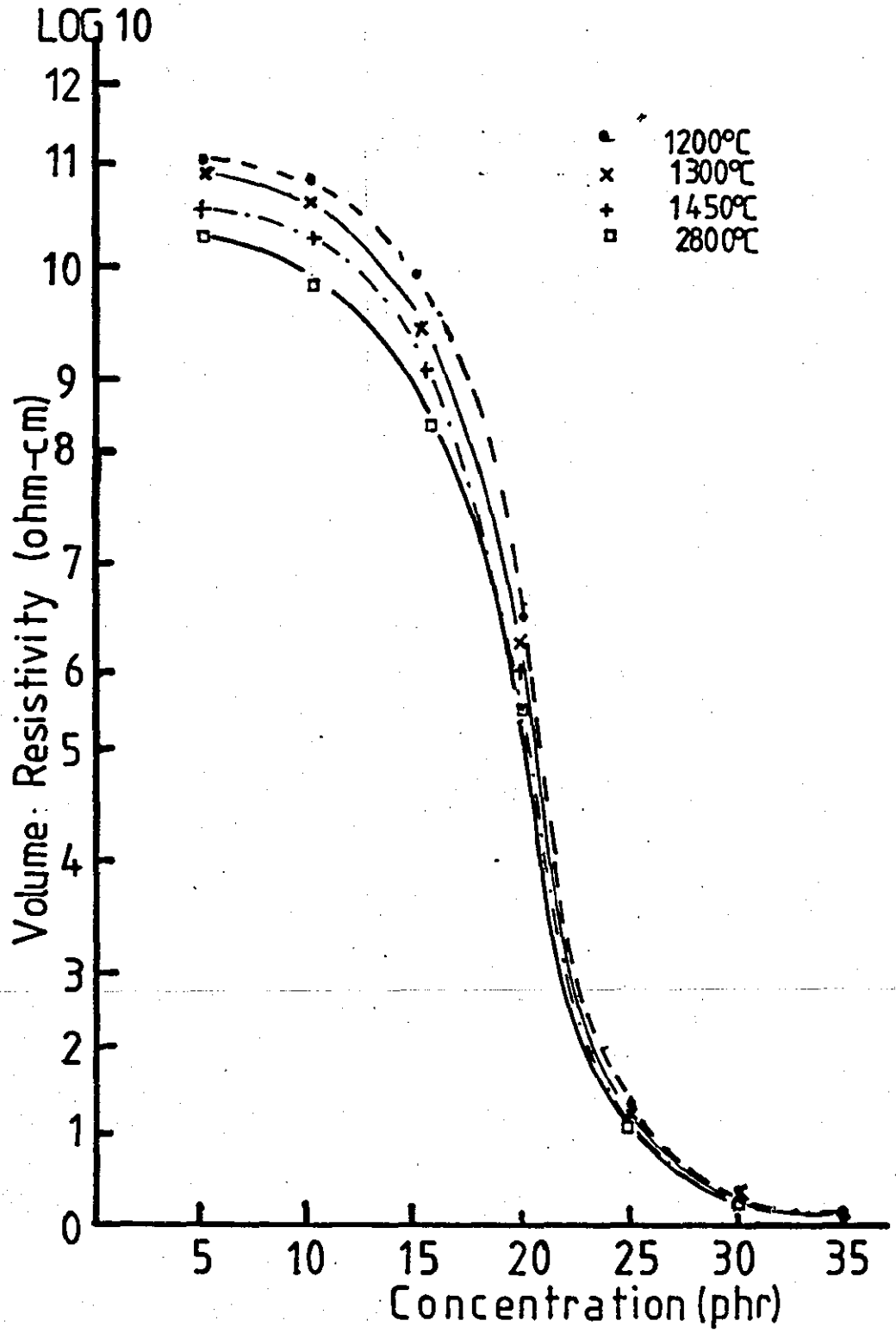


TABLE 8.4 CONTINUED

Mix Number	Carbon black %	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C=\frac{nhs}{tX100}$
BIII Shawinigan						
1	5	1.10	6.80	9.80×10^{10}	50	
2	10	1.00	7.60	7.00×10^{10}	52	
3	15	0.92	8.30	8.90×10^{9}	55	
4	20	0.80	9.20	4.00×10^{5}	57	
5	25	0.72	9.80	3.40×10^{1}	60	
6	30	0.62	10.60	3.60	62	1.22
7	5	1.16	6.30	8.80×10^{10}	50	
8	10	1.04	7.30	6.10×10^{10}	52	
9	15	0.96	7.90	7.40×10^{9}	55	
10	20	0.82	9.00	2.80×10^{5}	58	
11	25	0.74	9.70	3.00×10^{1}	61	
12	30	0.66	10.30	3.60	64	1.16
13	5	1.16	6.30	6.20×10^{10}	50	
14	10	1.10	6.80	5.00×10^{10}	52	
15	15	1.00	7.60	6.00×10^{9}	56	
16	20	0.86	8.70	1.40×10^{5}	58	
17	25	0.78	9.40	2.40×10^{1}	60	
18	30	0.70	10.00	3.40	64	1.05
19	5	1.24	5.70	5.20×10^{10}	50	
20	10	1.18	6.20	2.40×10^{10}	52	
21	15	1.06	7.20	4.80×10^{9}	56	
22	20	0.92	8.30	9.80×10^{4}	58	
23	25	0.82	9.00	1.90×10^{1}	62	
24	30	0.76	9.50	3.00	64	0.96
BIV Ketjenblack EC						
1	4	1.00	7.60	9.00×10^{10}	48	
2	8	0.88	8.60	8.40×10^{5}	54	
3	12	0.80	9.20	8.00×10^{1}	58	
4	16	0.70	10.00	4.30	62	
5	20	0.60	10.70	3.00	66	0.76
6	4	1.03	7.40	9.00×10^{10}	48	
7	8	0.92	8.30	8.20×10^{5}	54	
8	12	0.84	8.90	7.40×10^{1}	57	
9	16	0.76	9.50	4.20	62	
10	20	0.66	10.30	2.60	66	0.63
11	4	1.04	7.30	8.40×10^{10}	48	
12	8	0.92	8.30	8.00×10^{5}	54	
13	12	0.84	8.90	7.00×10^{1}	58	
14	16	0.78	9.40	3.80	62	
15	20	0.68	10.10	2.40	66	0.60
16	4	1.10	6.80	7.20×10^{10}	48	
17	8	0.96	7.90	6.40×10^{2}	54	
18	12	0.90	8.40	6.80×10^{1}	58	
19	16	0.82	9.00	3.60	62	
20	20	0.72	9.80	2.20	66	0.56

Fig. 8.18 Effect of graphitized acetylene black (Shawinigan) concentration on the volume resistivity of Silastic GP45 based compounds (Ref Mix NosBIII 1-24 of Table8.4)

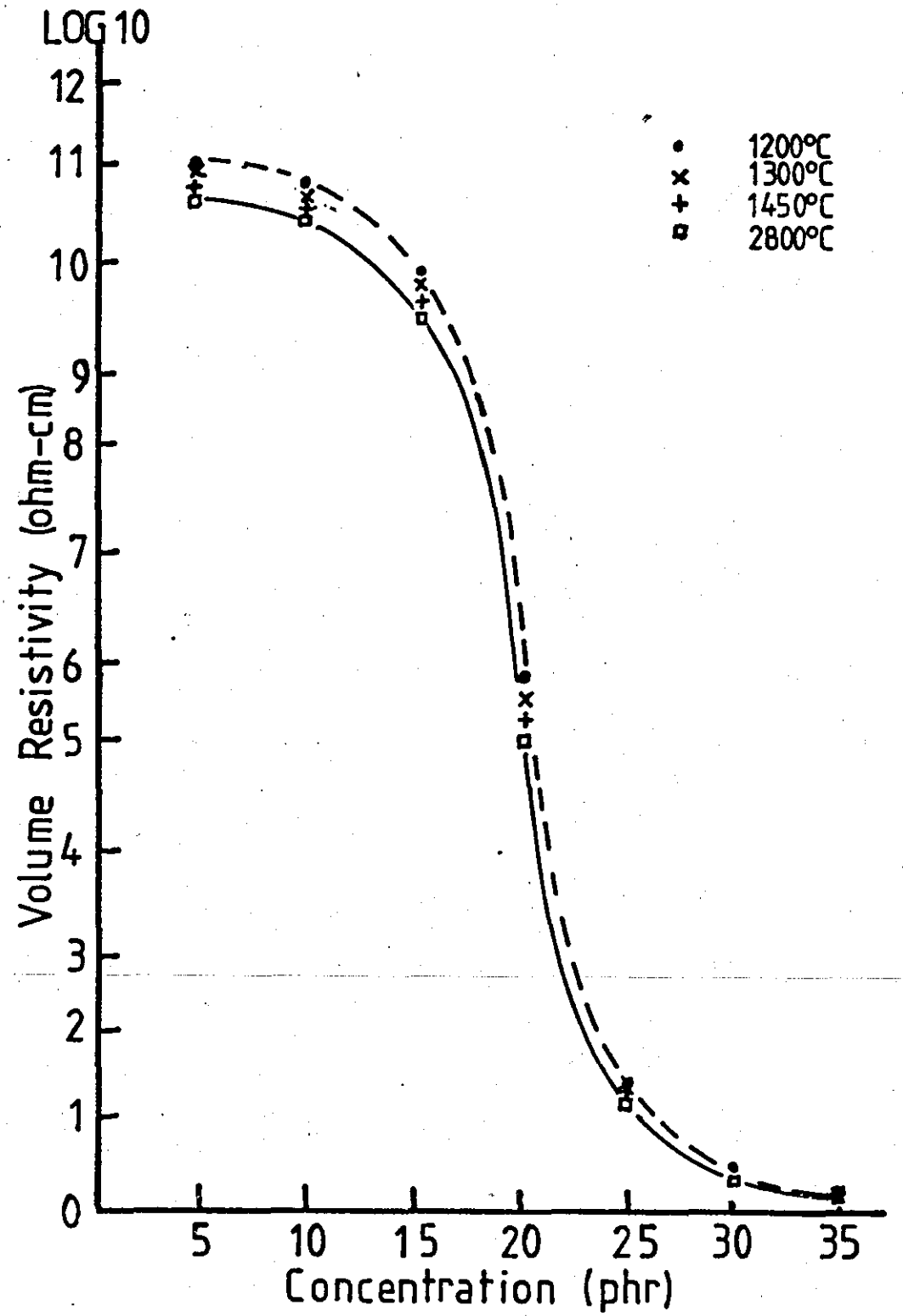
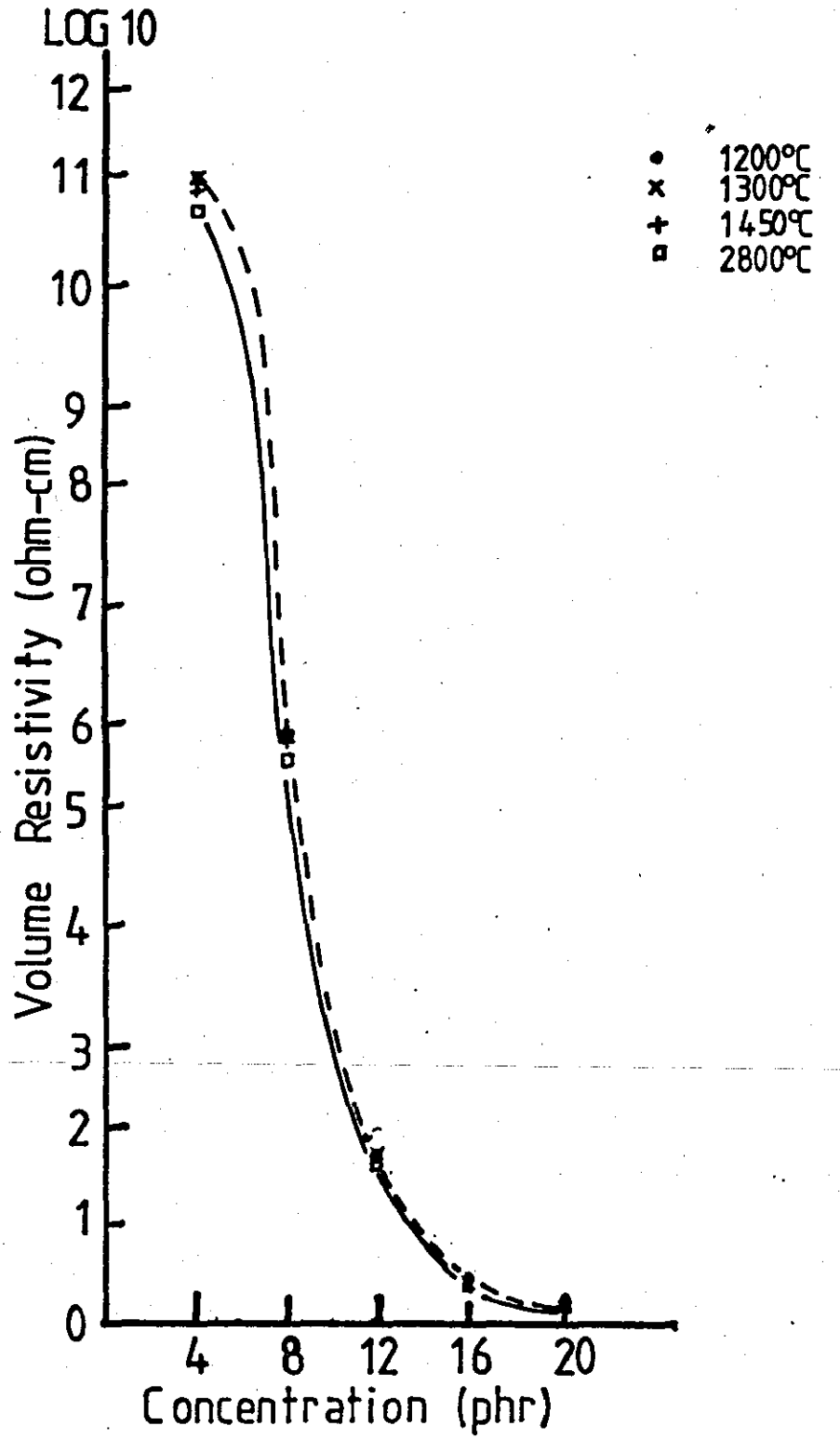


Fig. 8.19 Effect of graphitized special furnace black (Ketjenblack EC) concentration on the volume resistivity of Silastic GP45 based compounds (Ref Mix Nos BIV 1-20 of Table 8.4)



based compound is usually between 15-25phr of graphitized furnace and acetylene blacks and 4-12phr of Ketjenblack EC. Hence, within these ranges of black loadings, the compounded polymer will become a semi- to fully- conducting materials. Only a gradual change in volume resistivity followed the more rapid drop at higher black loadings.

When compared with similar compounds containing ungraphitized carbon blacks, it was observed that the initial volume resistivity change at low loadings is 'gradual' and not 'little to none', coupled with a less steep narrow transition regions. It has been suggested that these 'narrow transition regions' explain why very small variations in either black concentration and/or processing variables give a greatly amplified increase or decrease in volume resistivity. Also the steeper the resistivity to conductivity curve the more sensitive the variation becomes. Since compounds filled with graphitized carbon blacks have less steep curves, a lower sensitivity to other variables is thus expected. This was observed in the volume resistivity measurements.

At equal loadings, it was observed that the volume resistivity decreases with increasing graphitization temperature. The difference is comparatively large at low loadings and small at higher loadings. Also the percentage difference is observed to be dependent on the type of carbon black - Vulcan XC72>VulcanP>Shawinigan>Ketjenblack EC.

8.5.3 FLEXING (LOW STRAIN)

Mix Nos C1-C10 of Tables 8.5 & 8.6 and figs. 8.20-8.23 are hereby considered. It was observed that all compounds show a general trend of initial increase in volume resistivity at the lower number of flexes (200-500). The magnitude of this initial volume resistivity increase was found to be dependent on the type and concentration of the graphitized carbon black. This was generally followed by a constant peak volume resistivity. The final volume resistivity obtainable was observed to depend on the recovery time allowed after flexing.

TABLE 8.5 VULCANISATE PROPERTIES OF GRAPHITIZED CARBON BLACK FILLED SILASTIC GP45 BASED CONDUCTIVE COMPOUNDS: FLEXING EFFECT

Mix Number C	Cure Rate (min^{-1})	Cure Time (mins)	Volume Resistivity (ohm-cm)	Hardness (IRHD)	Dispersion Index $C=\frac{nhs}{tX100}$
1	0.81	9.10	4.80×10^5	54	
2	0.62	10.60	2.40	56	0.45
3	0.84	8.90	3.20×10^5	56	
4	0.60	10.70	2.40	58	0.79
5	0.92	8.30	9.80×10^4	58	
6	0.76	9.50	3.00	64	0.96
7	0.96	7.90	6.40×10^2	54	
8	0.90	8.40	6.80×10^1	58	
9	0.82	9.00	3.60	62	
10	0.72	9.80	2.20	66	0.56

TABLE 8.6 VOLUME RESISTIVITY OF FLEXED GRAPHITIZED CARBON BLACK FILLED SILASTIC GP45 BASED COMPOUNDS

Mix No. C		NUMBER OF FLEXES									RECOVERY TIME					
											Minutes				Days	
		1	10	100	200	500	10^3	2000	5000	10^4	15	30	45	60	1	7
1	A	$6.4X10^5$	$7.6X10^5$	$8.6X10^5$	$9.2X10^5$			9.20×10^5			$9.0X10^5$	$8.4X10^5$	$6.8X10^5$	$6.0X10^5$	$5.6X10^5$	$5.6X10^5$
	B	$6.2X10^5$	$7.6X10^5$	$8.2X10^5$	$9.0X10^5$			9.00×10^5			$9.0X10^5$	$8.4X10^5$	$6.8X10^5$	$6.0X10^5$	$5.6X10^5$	$5.6X10^5$
2	A	3.00	3.20	3.60	3.80			3.80			3.60	3.40	3.20	3.00	2.60	2.60
	B	3.00	3.20	3.60	3.80			3.80			3.60	3.40	3.30	3.00	2.60	2.60
3	A	$5.0X10^5$	$6.6X10^5$	$8.0X10^5$	$8.6X10^5$			9.00×10^5			$8.6X10^5$	$7.9X10^5$	$6.6X10^5$	$5.8X10^5$	$4.6X10^5$	$4.4X10^5$
	B	$4.8X10^5$	$6.0X10^5$	$7.6X10^5$	$8.2X10^5$			8.40×10^5			$8.2X10^5$	$7.6X10^5$	$6.4X10^5$	$5.2X10^5$	$4.0X10^5$	$4.0X10^5$
4	A	2.80	3.20	3.80	4.00			4.00			3.80	3.20	3.00	2.90	2.60	2.60
	B	2.80	3.20	3.80	3.80			4.00			3.80	3.20	3.10	3.00	2.70	2.70
5	A	$1.1X10^5$	$1.7X10^5$	$2.0X10^5$	$2.1X10^5$			2.14×10^5			$1.8X10^5$	$1.6X10^5$	$1.3X10^5$	$1.2X10^5$	$1.1X10^5$	$1.1X10^5$
	B	$1.1X10^5$	$1.8X10^5$	$2.1X10^5$	$2.1X10^5$			2.16×10^5			$1.8X10^5$	$1.6X10^5$	$1.3X10^5$	$1.2X10^5$	$1.1X10^5$	$1.1X10^5$
6	A	3.80	4.30	3.70	3.90			4.90			4.40	4.00	3.60	3.30	3.20	3.20
	B	3.60	4.20	4.60	4.70			4.70			4.30	3.80	3.50	3.20	3.10	3.10
7	A	$7.2X10^2$	$7.8X10^2$	$8.4X10^2$	$9.2X10^2$			9.60×10^2			$9.0X10^2$	$8.2X10^2$	$7.9X10^2$	$7.6X10^2$	$7.4X10^2$	$7.2X10^2$
	B	$7.6X10^2$	$8.0X10^2$	$8.8X10^2$	$9.4X10^2$			9.80×10^2			$9.4X10^2$	$8.6X10^2$	$8.2X10^2$	$7.8X10^2$	$7.6X10^2$	$7.6X10^2$
8	A	$7.4X10^1$	$7.8X10^1$	$8.0X10^1$	$8.2X10^1$			8.40×10^1			$7.8X10^1$	$7.4X10^1$	$7.3X10^1$	$7.0X10^1$	$7.0X10^1$	$7.0X10^1$
	B	$7.6X10^1$	$8.0X10^1$	$8.4X10^1$	$8.6X10^1$			8.80×10^1			$8.4X10^1$	$8.0X10^1$	$7.8X10^1$	$7.6X10^1$	$7.4X10^1$	$7.4X10^1$
9	A	3.70	3.80	4.00	4.00			4.00			3.90	3.80	3.70	3.70	3.70	3.70
	B	3.70	3.80	4.00	4.00			4.00			4.00	3.90	3.80	3.70	3.70	3.70
10	A	2.26	2.28	2.30	2.30			2.30			2.30	2.28	2.26	2.24	2.24	2.24
	B	2.26	2.28	2.30	2.30			2.30			2.30	2.28	2.26	2.24	2.24	2.24

TABLE 8.7 VOLUME RESISTIVITY OF FLEXED GRAPHITIZED CARBON BLACK FILLED SILASTIC GP45 BASED CONDUCTIVE COMPOUNDS: FINAL ANALYSIS

Mix Number C	Volume Resistivity(ohm-cm) Initial	Volume Resistivity(ohm-cm) Peak	Percentage Increase	Final Volume Resistivity after recovery(ohm-cm)	Percentage Increase
1	4.80×10^5	9.10×10^5	89.60	5.60×10^5	16.70
2	2.40	3.80	58.30	2.60	8.30
3	3.20×10^5	8.70×10^5	171.90	4.20×10^5	31.30
4	2.40	4.00	66.70	2.65	10.40
5	9.80×10^4	2.15×10^5	119.40	1.10×10^5	12.20
6	3.00	4.80	60.00	3.15	5.00
7	6.40×10^2	9.70×10^2	51.60	7.40×10^2	15.63
8	6.80×10^1	8.60×10^1	26.50	7.20×10^1	5.80
9	3.60	4.00	11.10	3.70	2.80
10	2.20	2.30	4.60	2.24	1.80

NOTE: BOND STRENGTH: Each flexed sample was pulled to break after recording the final volume resistivity. Only results of samples which broke in the middle were retained.

Fig. 8.20 Effect of flexing (low strain) on the volume resistivity of the graphitized furnace black (Vulcan P) filled Silastic GP45 based compounds (Ref Mix Nos C1 & C2 of Tables 8.5 and 8.6)

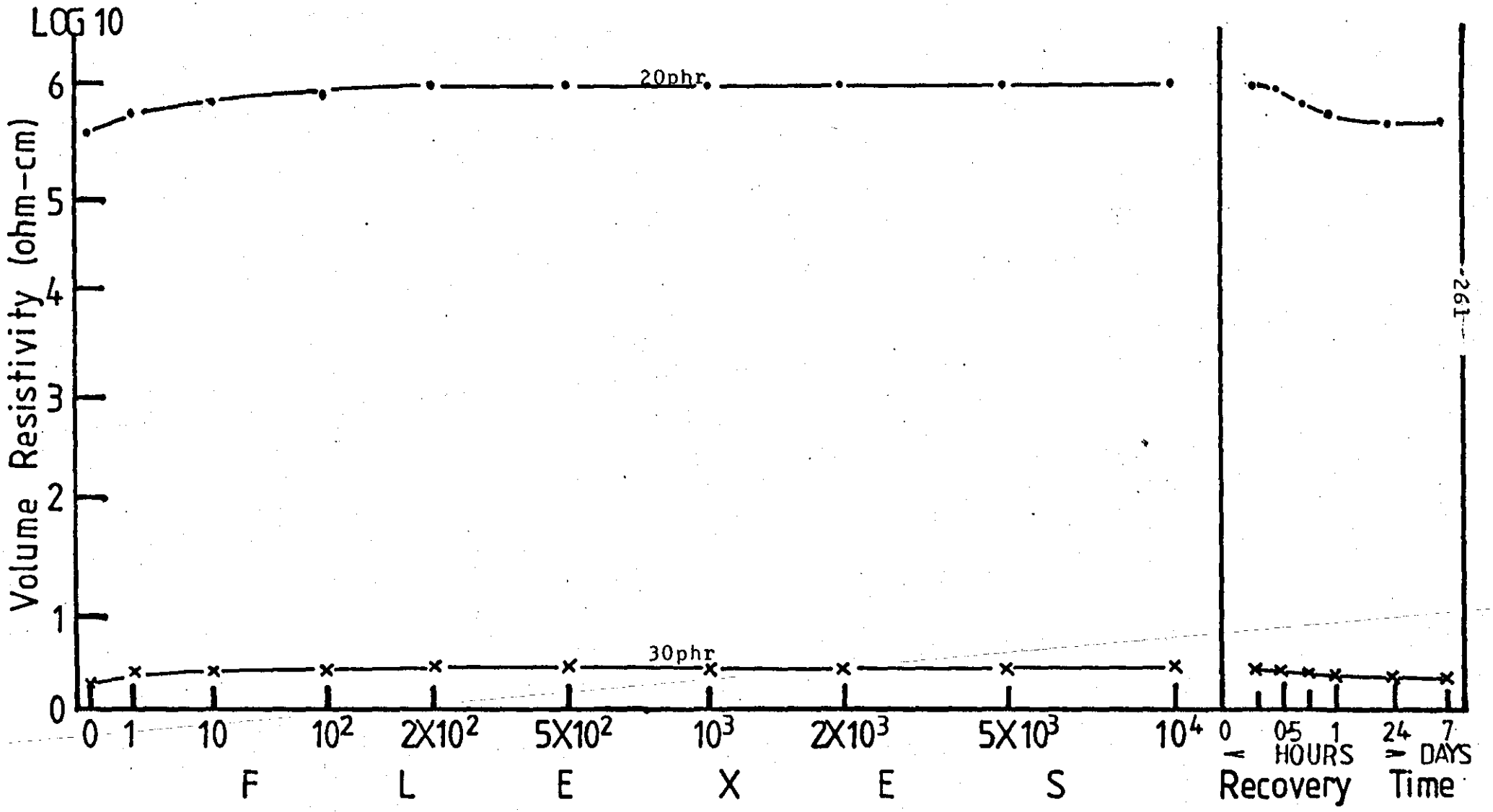


Fig. 8.21 Effect of flexing (low strain) on the volume resistivity of the graphitized furnace black (Vulcan XC72) filled Silastic GP45 based compounds (Ref Mix Nos C3-4 of Tables 8.5 and 8.6)

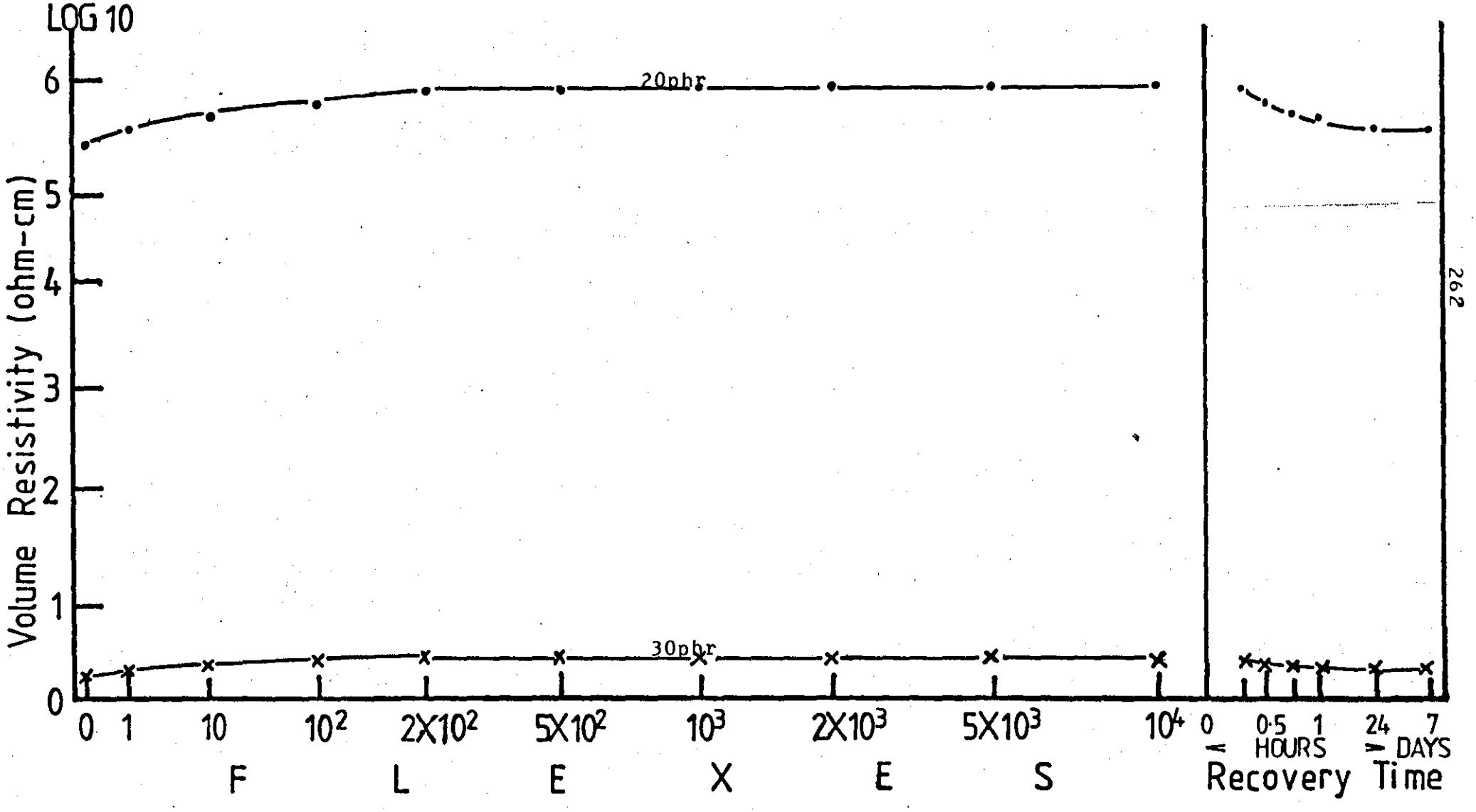


Fig. 8.22 Effect of flexing (low strain) on the volume resistivity of the graphitized acetylene black (Shawinigan) filled Silastic GP45 based compounds (Ref Mix Nos C5-6 of Tables 8.5 and 8.6)

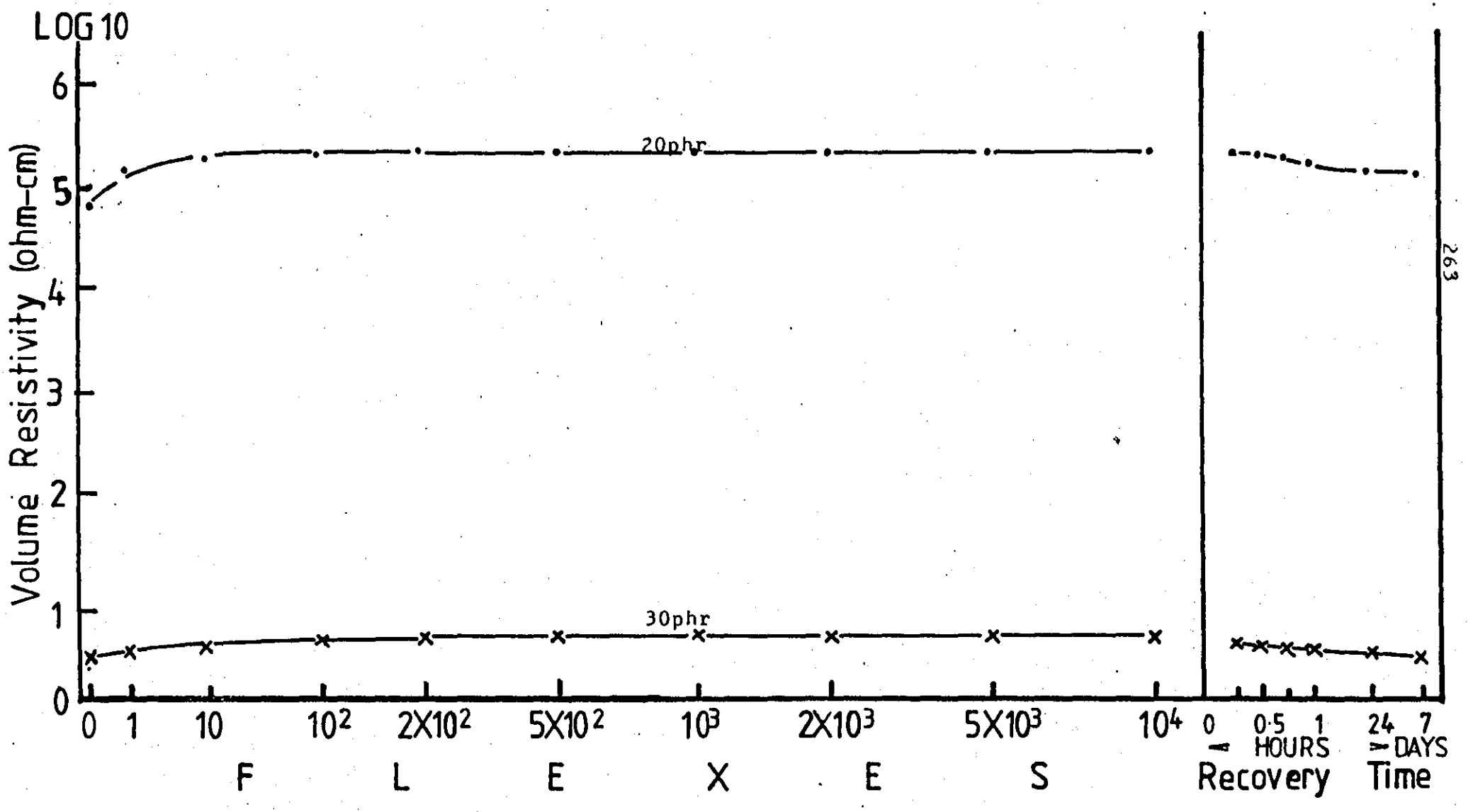


Fig. 8.23 Effect of flexing (low strain) on the volume resistivity of the graphitized special furnace black (Ketjenblack EC) filled Silastic GP45 based compounds (Ref Mix Nos C7-10 of Tables 8.5 and 8.6)

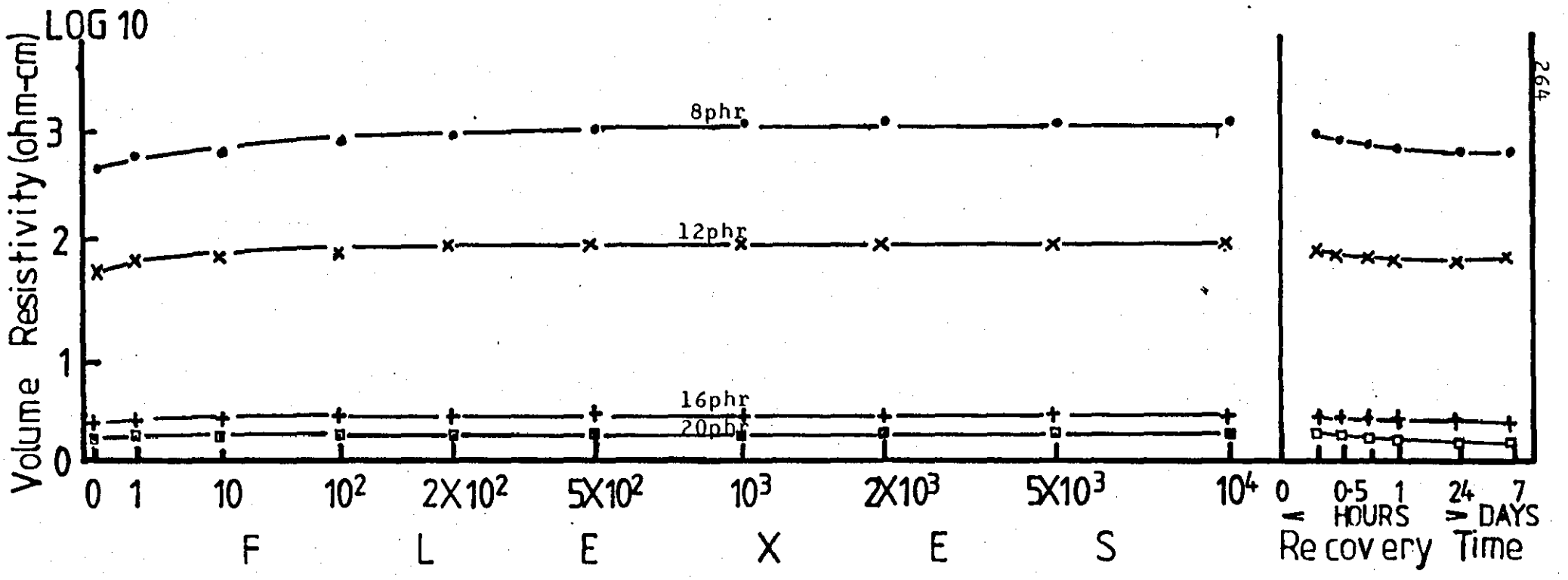


Table 8.7 shows the detailed final analysis of the volume resistivity of the flexed conductive graphitized carbon black filled Silastic GP45 based compounds. It was observed that there was an increase in the final volume resistivity measured after 7days in every compound. This is thought to be an indication of permanent breakage in some of the rubber-carbon and carbon-carbon linkage in the compound after flexing.

When compared with similar compounds containing the ungraphitized carbon black, graphitized carbon black filled compounds were found to have a lower volume resistivity in the unstrained compound but gave higher final volume resistivity after recovery. The initial lower resistivity is thought to be an indication of a lower resistive, cleaner carbon black and, therefore, a better electrical conductor. But, contrary to expectation, the final volume resistivity was comparatively higher. This is, therefore, an indication of permanent breakage in some of the rubber-carbon and the carbon-carbon linkage as earlier suggested, and arising from a compound with a comparatively lower mechanical properties (Table 8.8).

8.6 CONCLUSIONS

Generally, graphitized carbon black filled Silastic GP45 based compounds were found to possess higher rate of cure, lower cure times and lower volume resistivities when compared with similar compounds filled with ungraphitized blacks. In fact an average of 5% less concentration of graphitized(2800°C) carbon black is required to give equivalent conductivity when compared with a non-graphitized carbon black compound.

With increasing graphitization temperatures, graphitized carbon black filled compounds were found to exhibit comparatively decreasing volume resistivity, dispersion index and cure time. A suggested explanation to these phenomena is the increasingly lower chemisorption capacity and better(cleaner) surface. These, therefore, result in lower interparticulate electrical contact resistance in the latter,

TABLE 8.8 MECHANICAL (VULCANISATE) PROPERTIES OF CARBON BLACK FILLED CONDUCTIVE SILICONE RUBBERS

	Silastic GP30 based compounds				Silastic GP45 based compounds							
	Volume Resistivity (ohm-cm)	Tensile Strength (MPa)*	Elongation @ break (%)*	Hardness (IRHD)	Volume Resistivity (ohm-cm)		Tensile(MPa) Strength		Elongation @ break(%)		Hardness (IRHD	
CB%					*1	*2	*1	*2	*1	*2	*1	*2
Vulcan P												
5	10.50×10^{10}	6.80	214	46	19.80×10^{10}	3.40×10^{10}	7.10	7.03	244	240	49	51
10	8.70×10^{10}	6.86	210	47	12.50×10^{10}	1.40×10^{10}	7.26	7.11	236	231	51	52
15	5.70×10^{10}	7.02	204	49	8.80×10^{10}	3.00×10^{10}	7.40	7.18	228	216	54	53
20	3.20×10^{6}	7.08	192	52	3.60×10^{6}	4.80×10^{5}	7.58	7.24	218	206	55	54
25	4.10×10^{2}	7.14	188	53	6.50×10^{2}	2.00×10^{1}	7.72	7.30	210	196	58	55
30	2.50	7.20	180	54	3.60	2.40	7.80	7.27	204	188	60	56
Vulcan XC72												
5	10.00×10^{10}	6.80	210	40	10.20×10^{10}	3.40×10^{10}	7.00	6.90	240	237	42	50
10	8.00×10^{10}	6.90	206	42	8.60×10^{10}	9.80×10^{9}	7.20	7.00	232	227	43	52
15	5.40×10^{10}	7.10	202	43	5.90×10^{10}	4.00×10^{8}	7.40	7.20	222	215	44	54
20	3.40×10^{6}	7.15	194	44	3.20×10^{6}	3.00×10^{5}	7.60	7.24	213	204	46	55
25	3.70×10^{2}	7.20	186	46	4.10×10^{2}	1.70×10^{1}	7.70	7.24	205	194	48	56
30	2.50	7.30	180	48	2.60	2.40	7.80	7.18	198	186	50	58
Shawinigan												
5	9.10×10^{10}	6.60	220	44	10.20×10^{10}	5.20×10^{10}	7.00	6.93	240	235	50	50
10	6.20×10^{10}	6.74	216	45	7.10×10^{10}	2.40×10^{10}	7.12	6.98	224	218	52	52
15	5.40×10^{10}	6.86	213	46	1.40×10^{10}	4.80×10^{9}	7.26	7.04	216	210	54	56
20	3.10×10^{5}	7.10	208	46	4.00×10^{5}	9.80×10^{4}	7.44	7.14	208	200	56	58
25	2.40×10^{2}	7.24	202	48	1.20×10^{2}	1.90×10^{1}	7.62	7.24	202	192	58	62
30	2.81	7.28	198	49	3.38	3.00	7.78	7.24	196	184	59	64
35	2.38	7.40	192	50	2.82	2.80	7.90	7.35	192	178	60	64
Ketjenblack EC												
4	9.70×10^{10}	6.80	210	48	9.40×10^{10}	7.20×10^{10}	7.20	7.13	240	235	48	48
8	9.00×10^{2}	6.88	202	50	8.45×10^{2}	6.40×10^{2}	7.32	7.17	228	221	52	54
12	8.70×10^{1}	7.00	198	54	8.10×10^{1}	6.80×10^{1}	7.43	7.21	212	203	56	58
16	5.10	7.10	194	56	4.30	3.60	7.52	7.22	200	190	60	62
20	2.20	7.20	190	60	2.20	2.20	7.60	7.22	192	180	64	66

*BS 903: Part A2:1956 *1=Ungraphitized carbon black *2=Graphitized carbon black

and less 'mopping' effect on the efficiency of the peroxide radicals in the former; hence a better and relatively more conductive compound ensued.

Nearly all compounds exhibit an initial volume resistivity decrease to a minimum of about 8mins milling time followed by a constant volume resistivity on further milling, but their dispersion indices continuously decrease with increasing milling time. A suggested explanation to the above phenomena is that volume resistivity decreases with the simple incorporation of the carbon black aggregates followed by an improved dispersion as milling progresses. It is, therefore, considered that no carbon black aggregate breakdown and/or substantial increase in interparticulate distance occured to affect the compound volume resistivity since this remained constant with further milling.

Another significant observation with graphitized carbon black compounds is the 'gradual' volume resistivity change at low loading followed by a less steep narrow 'resistive' to 'conductive' transition region when compared with the ungraphitized carbon black filled compounds. The sensitivity to variation in this region is less.

However, when a graphitized carbon black filled vulcanisate is subjected to repeated low strain(flexing), it was observed to have a slower rate of recovery and a higher final volume resistivity, contrary to its ungraphitized carbon black filled vulcanizate. A suggested explanation to these phenomena is some permanent carbon-rubber scission and carbon-carbon chain discontinuity. It is suggested that while the former results in a slightly decreased mechanical properties and therefore a weaker compound, a higher resistive compound ensued in the latter.

Therefore, although with slightly decreased mechanical properties of the investigated compounds, graphitized carbon black filled silicone compounds possess higher cure rates, lower volume resistivities, and can withstand longer processing conditions without showing volume resistivity changes.

IX ELECTRICAL CONDUCTIVITY THEORIES OF COMPOSITES

9.1 INTRODUCTION

Incorporation of conducting additives in dielectric polymers is the conventional method of obtaining controlled resistivity. Conducting composites are usually formulated to have the minimum quantity of conductive component necessary to achieve the required degree of electrical performance. Hence one requires knowledge of factors controlling the formation of conductive networks; for a given concentration of conductive components and a given quality of interparticulate contacts, individual conductive particle must be able to make good electrical contact when close to or touching each other. Shape and size of conductive particles have been examined in an analogue using Holm's expression[18]; in this the resistivity of a compacted carbon powder has been successfully explained by a simple model where the constrictions at the interparticulate contacts are assumed to have a dominating influence[19]. The greater the surface to volume ratio of the shapes the more likely is the interparticulate contact.

Carbon black powders are presently employed as reinforcing agents in organic rubbers (though not in silicone rubber) for their technical properties, cheapness and compatibility. In organic rubber, high concentrations of carbon black are used for electrical conductivity purposes. The conductivity for a given concentration is, of course, governed by the carbon black type. Highly conductive carbon blacks (prepared with clean oil-free surfaces) are characterized by their particle size and a propensity to agglomerate into chains to give a pseudo-fibre arrangement whose structure persists even when mixed into another material *e.g* polymer. Exceptionally, acetylene black imparts conductivity into a polymer matrix by forming a continuously conductive path inherent from its greater volume or bulkiness and its high surface porosity; it is not considered to form pseudo-fibre type chains.

9.1.1 CONCEPT OF ELECTRON TUNNELLING

During the last few decades, much research has been done to relate the electrical properties of mixtures with polymers to three main variables: particle size, surface contamination, and the proportion of conducting component present.[271,304,338-340] By using the electron microscope to study the distribution of carbon black particles in the mixtures, it has been revealed that the very small particles with clean surfaces tend to agglomerate to form chains, and that there gaps between the agglomerates. Conduction by electrons crossing the gaps if they are small enough has been studied.[290,291,294,307]

Frenkel[341] estimated a gap width of 1.0nm (with a mean free path of electrons ≈10.0nm) for electrical conductivity between solid (metallic) conductors to exist *i.e* when the gap between two solid conducting bodies is <1.0nm the electrons have a reasonable chance to jump across the gap and thus conduction results.
Polley and Boonstra[294] concluded from their experiments, using calculated distances of carbon black particle seperation in rubber compounds, that a gap width less than the calculated 10.0-18.0nm is required for conduction to exist.
Van Beek and van Pul[291] found that the non-ohmic (*i.e* non-linear current-voltage) 'characteristics' of compounds with poor black dispersion was due to internal field emission across the insulating gap widths of 2.0μm and 2.5μm. With improved dispersion and gap widths ≪2.0μm, the compounds were observed to exhibit ohmic (*i.e* linear current-voltage) behaviour as if the **black** particles were in contact.

A generally accepted explanation of the above interparticulate distance and the non-ohmic behaviour is known as the 'concept of electron tunnelling' *i.e* the electron transfer mechanism bet-between the black particles. The above concept also implies that each carbon black particle, aggregate or agglomerate must practically touch each other or else a continuous chain will be broken. The number of conducting or through-going paths will be a function of loading and the particle size of the carbon black, and in addition to which intrinsic conductivity of the carbon blacks themselves is very important.

The major disadvantages of the above concept of the through-going paths are:

a. they do not appear on electron micrographs of ultra-thin microtomed sections. This is possibly due to mechanical

disturbance during preparation;

b. carbon black intrinsic conductivity is mainly a contact resistance phenomena;

c. the definition of 'touching' is not clearly defined;

d. resistivity changes with deformation are not accounted for e.g bending, elongation, flexing, compression and shearing;

e. no differences are noticed in the degree of particle chaining in the dry blacks (characteristics of 'high structure blacks) and the number of the through-going paths, as seen by the electron micrographs.

No full explanation presently exists of the increase of conductivity with increased black loading and decreasing particle size.

The total carbon chain length that can be built from a number of carbon particles in a cm^3 should be directly proportional to $\frac{\text{proportion of carbon black present}}{(\text{average particle diameter})^2}$.

The total chain length is proportional to the number of chains that can be stretched from one electrode of the sample to the other and should, therefore, represent a simple function of electrical conductivity. The plot of resistivity versus carbon black loading (fig.9.1) shows clearly that the actual function is far different from simple proportionality.

The interparticulate or interagglomerate or interaggregate gap width is an 'exponential function' and, therefore, a contributory factor to the non-proportionality of the concept. Hence it is assumed that the resistivity of the carbon-polymer dispersions is *not* only governed by the number of through-going 'particle-to-particle' chains but also by the width of the gaps of these chains.

9.1.2 SURFACE AREA AND THE VOLUME OF CONDUCTING PARTICLE

Aharomi[343] considered a model rationalizing the curve of resistivity versus volume percent of a metal powder component in a metal/polymer composite (fig. 9.2). The model defined the point M_1, at which incipient formation of infinitely long chain contacts between conducting particles, at a volume percent V_1[344], ensued; the resultant precipitious

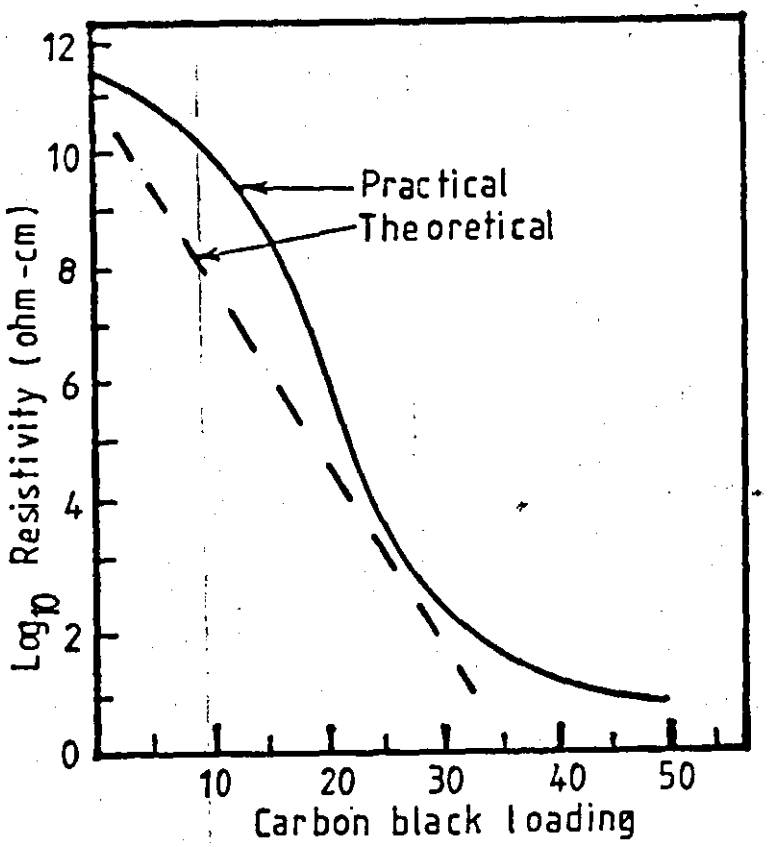


Fig. 9.1 Typical Electrical Resistivity versus Carbon black loading graphs[290].

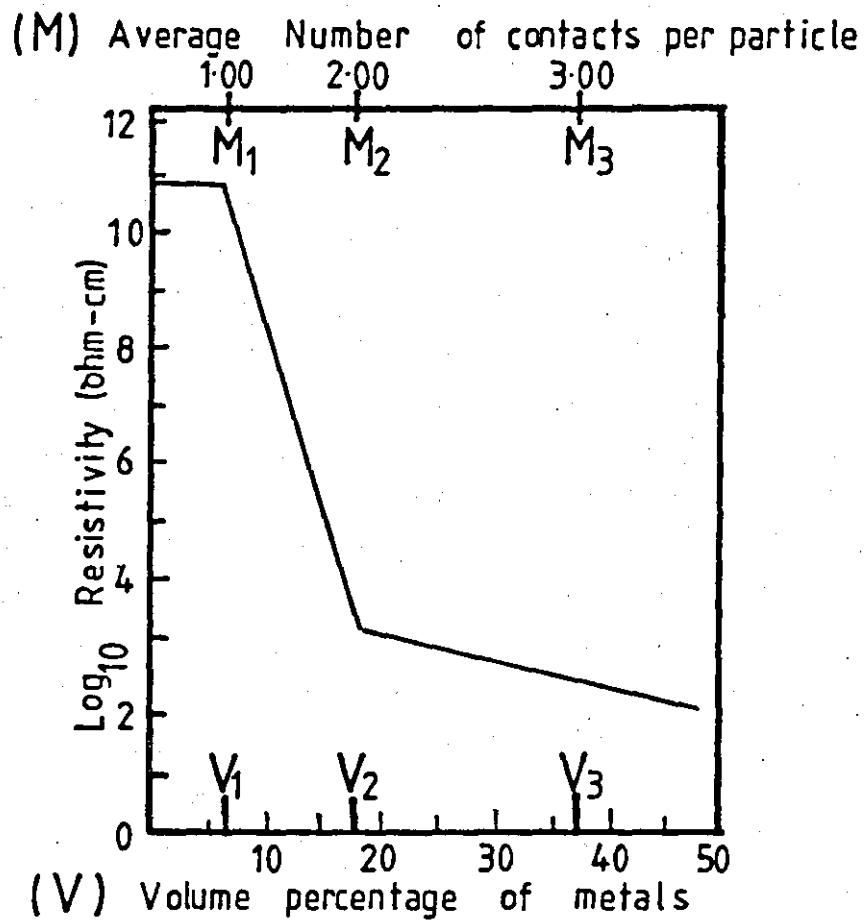


Fig. 9.2 Electrical Resistivity as a function of the volume percentage of metal powder in the composite.[343].

ASSUMPTION: Metal particles are randomly dispersed throughout the composite layer.

drop in resistivity from M_1 to M_2, and where M_1 is defined as the point at which the surface area of the conducting particles is one half of the surface area at the point M_2; and the insignificant drop in resistivity above M_2 due to only increase in average number of contacts per particle without significantly increasing conductivity, since M_2 is the saturated conductivity point.

The model also defined that the average and absolute number of the contacts made between the surfaces of the conducting particles depended on the surfaces available to form the contacts (*i.e* the surface area) and depended only to the two-thirds of the power on the particle volume.

He concluded that dependable continuity of the conducting particulate phase in a conductor/insulator composite critically influences the overall conductivity of the composite, exhibited by sharp breaks in the conductivity curves when the latter are plotted as a function of the volume percent of the conducting phase in the composite[266,345,346]. The same phenomenon holds true, among others, for thermal and electrical conductivities[344] and certain diffusion processes[347]. With small differences in conductivity between two components in a composite, there exists a gradual transition in conduction properties from those of either components, giving rise to smooth and monotomic curves describing these changes as a function of either component[348-350].

9.1.3 ELECTRICALLY CONDUCTING MIXTURES

Scarisbrick[351] considered mixtures consisting of conducting particles dispersed in an insulating medium. He derived a relationship between resistivity and the volume, or proportion of conductive material for a mixture in which the conducting particles are considered to be touching. From this relationship, limiting values of resistivity can be predicted for randomly dispersed particles and also for 'concentrated' systems of particles. He also considered the way in which the relationship can be modified by the shape, size and orientation of the particles. He also carried out measurements from a range of conductive systems which confirmed that the

resistivity of practical mixtures approaches the predicted limiting values.

9.2 OBJECTIVES OF THIS RESEARCHER

The objectives of this exercise are: a. to try and develop a suitable theory relating the electrical volume resistivity to the volume proportion, or concentration, of conductive material in a conducting/insulating composite, then to relate this to the electrical volume resistivity measurements made from the experimentally investigated conductive silicone rubbers;

b. to relate the total surface area of the carbon black in the carbon black/silicone rubber composite to its electrical volume resistivity; and

c. to use a combination of data obtained from the 'hard' copy of Dark Field Reflected Light Microscopy (DFRLM) and the micrographs from the Scanning Electron Microscopy (SEM) to calculate the average distance between carbon black particles and to correlate this with the volume resistivity obtained from the experimentally investigated conductive silicone rubbers.

9.3 THEORY AND CALCULATIONS

9.3.1 CRITICAL RELATIONSHIP BETWEEN RESISTIVITY OF A COMPOSITE AND ITS CARBON BLACK CONTENT.

An earlier theory by other researchers established that the critical relationship between the resistivity of a composite and its carbon black is difficult to obtain. However, the following theory has been postulated[351].

Assumption: Interparticulate contacts are ohmic[18].

Calculation: Probability of conductive chain formation (*cf* Appendix E1).

Suppose composites consist of a random mixture of conducting and non-conducting elements. The probability, p, of obtaining 'n' conducting elements is:

$$f_v^n \qquad (i.e \quad p = f_v^n) \qquad 9.1$$

where: f_v = the volume fraction of conducting element

If the average conducting element is of a sphere of diameter, d, associated with a spherical region of diameter, D, of the composite, then:

$$\frac{D}{d} = \left[f_v^{1/3}\right]^{-1} \qquad 9.2$$

By random walk theory, if the diameter, D, is taken as the mean distance between the ends of a chain of 'n' links of length 'd', then:

$$D = dn^{1/2} \qquad 9.3$$

Combining equations 9.2 and 9.3

$$n = f_v^{-2/3} \qquad 9.4$$

Hence, the probability, p, that the volume associated with one conductive element may be bridged by the chain formation is given by:

$$p = f_v^{f_v^{-2/3}} \qquad 9.5$$

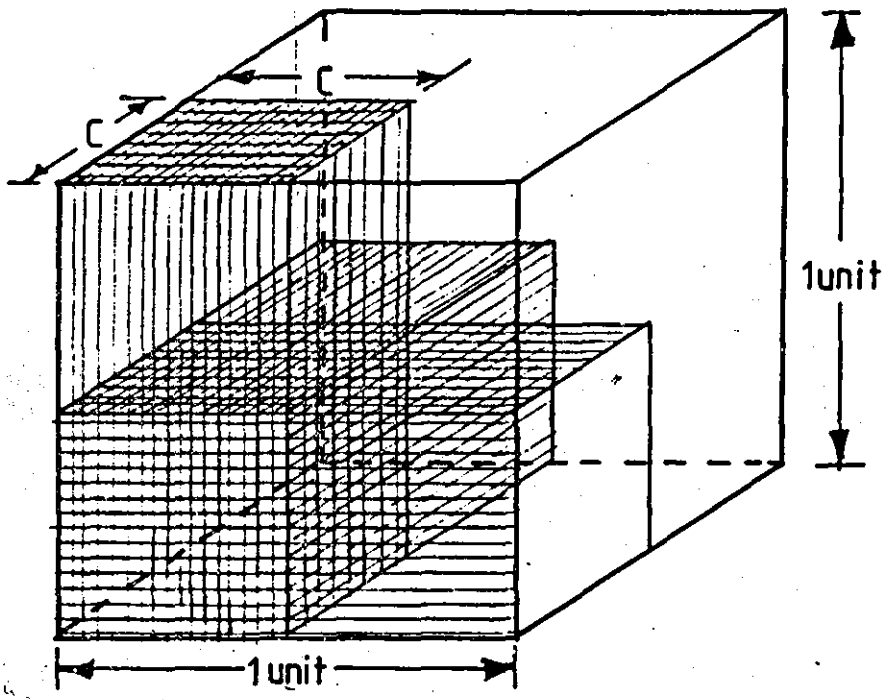
The researcher now assumes that the conductivity of the composite, δ_c, is directly proportional to 'p' *i.e*

$$\delta_c \propto f_v^{f_v^{-2/3}} \qquad 9.6$$

Therefore,

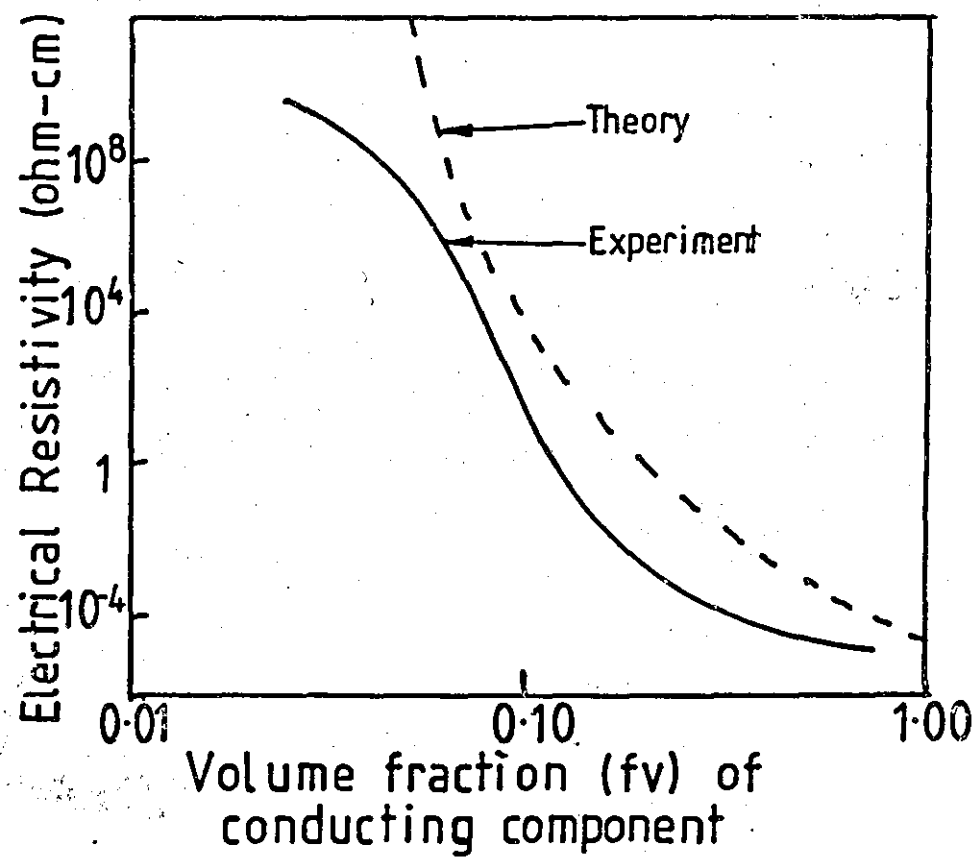
$$\log \delta_c = \log f_v^{f_v^{-2/3}} + C \qquad 9.7$$

where: C = the constant of probability, the value of which could be positive or negative depending on the polymer/filler composite.



Omit

Fig. 9.3 Equivalent distribution of conducting chains along the principal direction of a unit cube of an isotropic conduction mixture, defining the geometrical factor [351].



Omit

Fig 9.4 Dispersion of carbon black in polythene. Theory versus experiment using Holm's expression [351].

In an ideal composite system, we assume that C=0, then:

$$\delta_c = f_v^{f_v^{-2/3}} \qquad 9.8$$

The theoretical calculations based on equation 9.8 (Table 9.1) show that as f_v increases from 0.01 to 1.00, resistivity decreases very rapidly within 0.04 to 0.20 region and then progresively reduces (fig. 9.5).

A comparison of the graph from theoretical calculations (Table 9.1) and typical experimental graphs from volume fraction calculations (Table 9.2) shows a moderate agreement (fig. 9.6).

The difference observed between theory and experiments could be attributed to other factors unaccounted for by the theory, some of which are listed below:

a. assumptions and constants;
b. microstructural aspect of the conducting component either quantitatively or qualitatively - high or low structure and surface chemistry effects;
c. dispersion quality - chain formation, ohmic or non-ohmic phenomena;
d. processing characteristics.

Control of all the above is vital in obtaining a controlled and reproducible conductive rubber product.

TABLE 9.1 THEORETICAL CALCULATIONS BASED ON $\delta_c = f_v^{f_v^{-2/3}}$

f_v	$f_v^{-2/3} = \frac{1}{3\sqrt{f_v^2}}$	Conductivity $f_v^{f_v^{-2/3}}$	Resistivity $\frac{1}{f_v^{f_v^{-2/3}}}$
0.01	21.54	8.15×10^{-44}	1.23×10^{43}
0.02	13.57	8.74×10^{-24}	1.14×10^{23}
0.04	8.55	1.12×10^{-12}	8.96×10^{11}
0.06	6.52	1.07×10^{-8}	9.38×10^{7}
0.08	5.39	1.24×10^{-6}	8.09×10^{6}
0.10	4.64	2.28×10^{-5}	4.38×10^{4}
0.12	4.11	1.64×10^{-4}	6.09×10^{3}
0.14	3.71	6.81×10^{-4}	1.47×10^{3}
0.16	3.39	1.99×10^{-3}	5.01×10^{2}
0.18	3.14	4.61×10^{-3}	2.16×10^{2}
0.20	2.92	9.04×10^{-3}	1.10×10^{2}
0.22	2.74	1.57×10^{-2}	6.37×10^{1}
0.24	2.59	2.48×10^{-2}	4.03×10^{1}
0.26	2.45	3.66×10^{-2}	2.73×10^{1}
0.28	2.34	5.11×10^{-2}	1.96×10^{1}
0.30	2.23	6.81×10^{-2}	1.47×10^{1}
0.32	2.14	8.76×10^{-2}	1.14×10^{1}
0.34	2.05	1.09×10^{-1}	9.16
0.36	1.97	1.33×10^{-1}	7.53
0.38	1.91	1.58×10^{-1}	6.32
0.40	1.84	1.85×10^{-1}	5.41
0.50	1.59	3.33×10^{-1}	3.01
0.60	1.41	4.88×10^{-1}	2.05
0.70	1.26	6.36×10^{-1}	1.57
0.80	1.16	7.72×10^{-1}	1.30
0.90	1.07	8.93×10^{-1}	1.12
1.00	1.00	1.00	1.00

Fig. 9.5 Electrical resistivity versus volume fraction of conducting component based on theory.

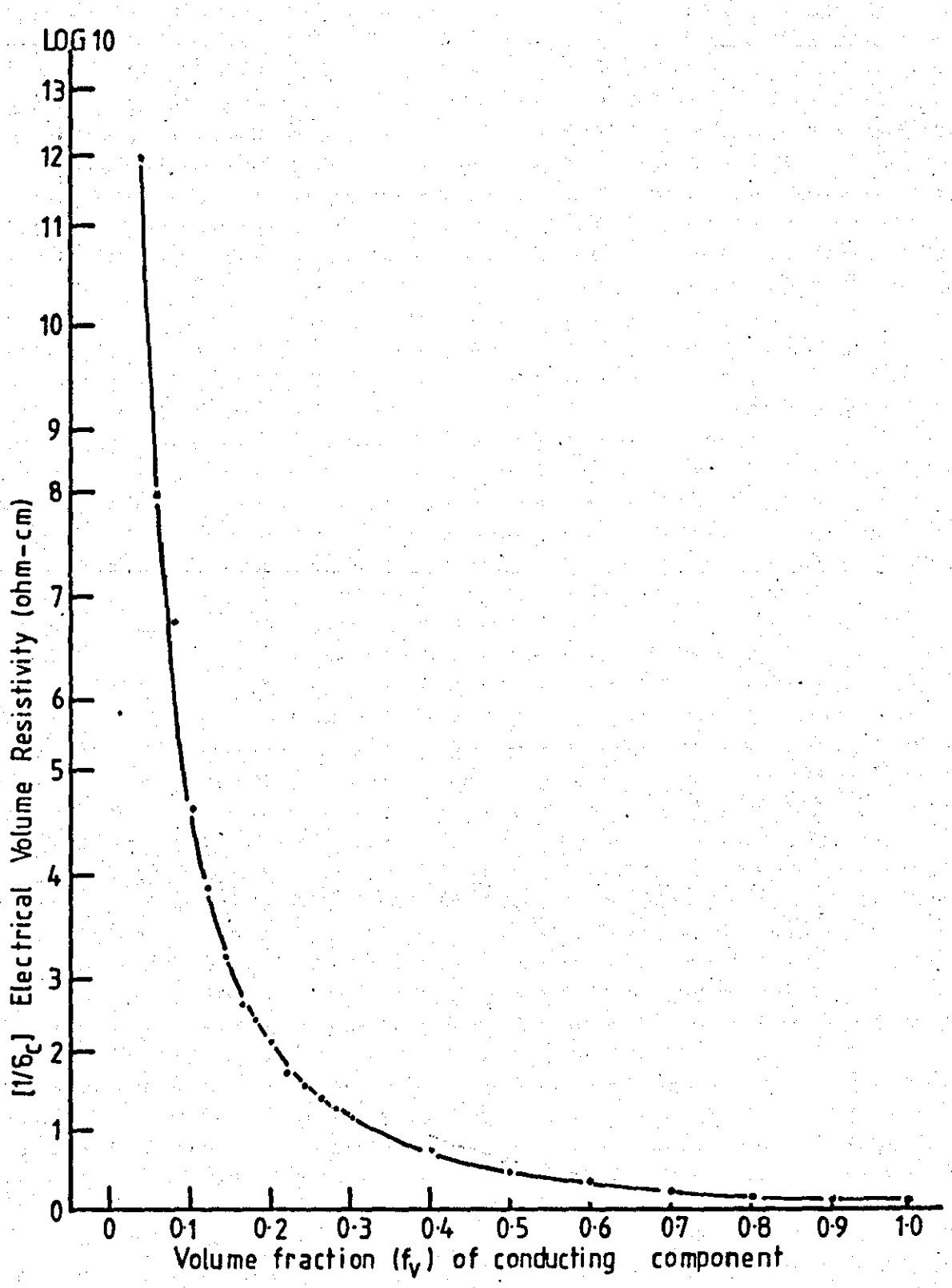
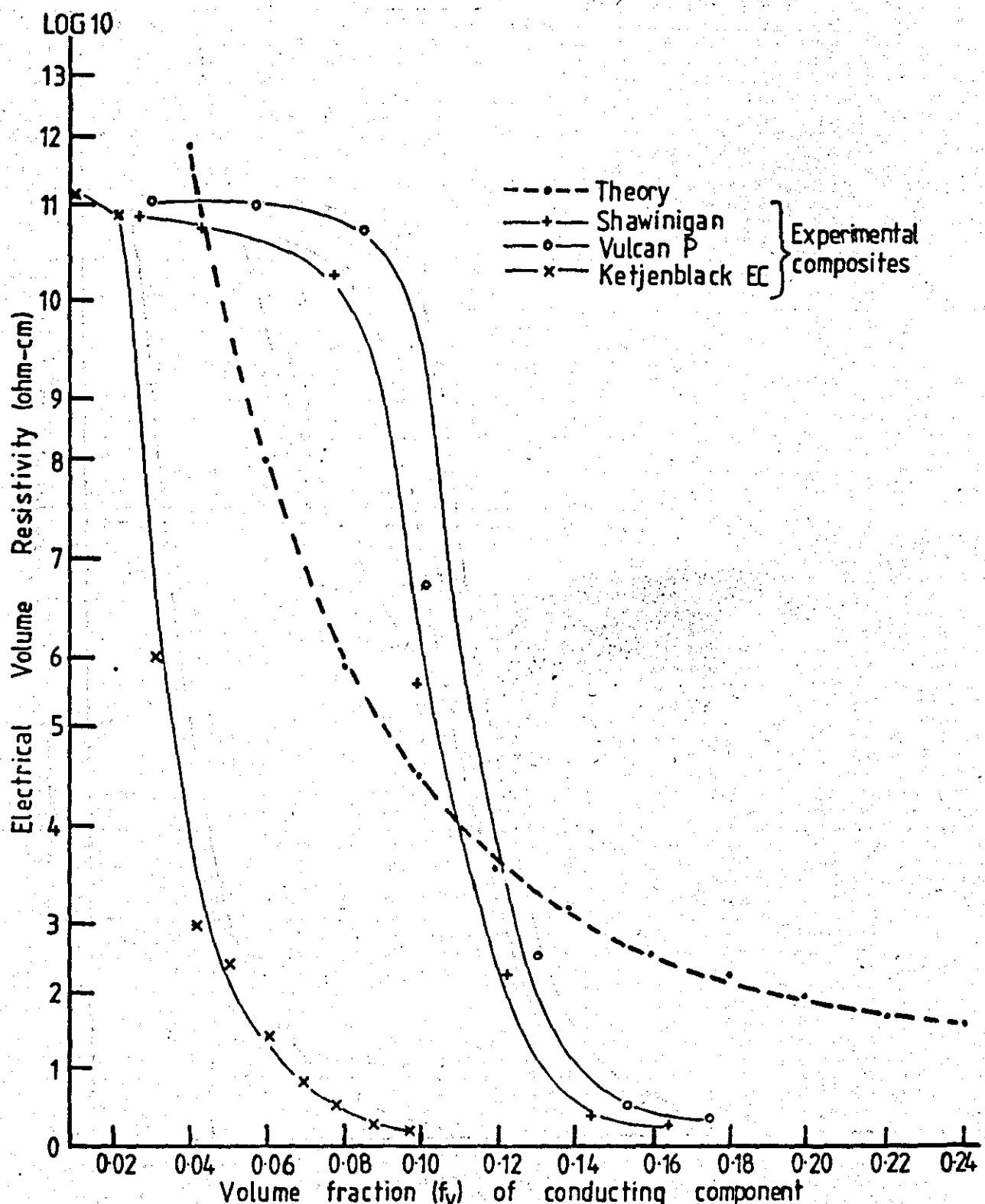


TABLE 9.2 VOLUME FRACTIONS (f_v) OF CONDUCTIVE CARBON BLACKS IN SILASTIC GP30 BASED COMPOUNDS

Carbon black type	Weight (g)	Volume (cm^3)	Composite Total Volume (cm^3) Rubber=91.74 + Carbon black	Volume fraction (f_v)	Volume Resistivity (ohm-cm)
Vulcan P (density =1.8)	5	2.78	94.52	0.029	10.53×10^{10}
	10	5.56	97.30	0.057	8.75×10^{10}
	15	8.33	100.08	0.083	5.73×10^{10}
	20	11.11	102.85	0.011	3.24×10^{6}
	25	13.89	105.63	0.132	4.12×10^{2}
	30	16.67	108.41	0.154	2.51
	35	19.44	111.19	0.175	2.40
Shawinigan (density =1.95)	5	2.56	94.31	0.027	9.10×10^{10}
	10	5.13	96.87	0.053	6.20×10^{10}
	15	7.69	99.44	0.077	2.00×10^{10}
	20	10.26	102.00	0.101	3.14×10^{5}
	25	12.82	104.56	0.123	2.40×10^{2}
	30	15.39	107.13	0.144	2.81
	35	17.95	109.69	0.164	2.38
Ketjenblack EC (density =2.05)	2	0.98	92.72	0.011	10.50×10^{10}
	4	1.95	93.69	0.021	9.70×10^{10}
	6	2.93	94.67	0.031	9.40×10^{5}
	8	3.90	95.65	0.041	9.00×10^{2}
	10	4.89	96.62	0.051	2.50×10^{2}
	12	5.85	97.60	0.060	8.70×10^{1}
	14	6.83	98.57	0.069	8.30
	16	7.81	99.55	0.078	5.10
	18	8.78	100.52	0.087	2.55
	20	9.76	101.50	0.096	2.20

Fig. 9.6 Comparison between experimental values and the theoretical calculation of electrical resistivity versus volume fraction of conducting component.



9.3.2 CONDUCTIVE CARBON BLACK TOTAL SURFACE AREA IN A COMPOSITE

9.3.2.1 Introduction

To relate the surface area of the conductive carbon black in the silicone rubber/carbon black composite to its electrical volume resistivity, different compounds containing 'equal surface areas' of different carbon blacks were used for consistency. Surface area figures from BET measurements carried out by the researcher (Ch.2, Section 2.2.6) were used in this exercise.

This 'equivalent surface area' was based on the ungraphitized Ketjenblack EC surface area $=1{,}003 m^2 g^{-1} \equiv 1.00$, *e.g* Vulcan P BET surface area $= 158.00 m^2 g^{-1}$; the proportion of Vulcan P required to give the same ('equivalent') surface area as 1.0g. of Ketjenblack EC $= \frac{1{,}003.0}{158.0} = 6.348$g. This is regarded as the 'equivalent surface area'. Table 9.3 shows the calculated 'equivalent surface area' for each carbon black type.

9.3.2.2 Experimental

9.3.2.2.1 Materials

a. Polymers

Silastic GP30 and GP45

b. Curing Agent

Perkadox SB

c. Conductive carbon blacks

Vulcan P, PF, XC72, and XC72R

Shawinigan, Ketjenblack EC, and Philblack XE-2

Conductex 900, SC, 975 and 40-220.

9.3.2.2.2 Mix Formulations

Table 9.4 shows the detailed mix formulations

9.3.2.2.3 Mixing

This was carried out as described in Ch.2, Section 2.2.1.

9.3.2.2.4 Vulcanisation

This was carried out as described in Ch.2, Section 2.2.2.

9.3.2.2.5 Electrical Volume Resistivity measurement

This was carried out as described in Ch.2, Section 2.2.4.

TABLE: 9.3 EQUIVALENT SURFACE AREAS OF CONDUCTIVE CARBON BLACKS

	°C	B E T Surface Area (m^2g^{-1})	Equivalent Surface Area
Vulcan P	0	158.00	6.348
	1200	158.70	6.320
	1300	157.20	6.380
	1450	156.40	6.413
	2800	140.80	7.124
Vulcan PF	0	157.00	6.389
	1200	157.50	6.368
	1300	156.20	6.421
	1450	155.40	6.454
	2800	139.90	7.169
Vulcan XC72	0	260.00	3.858
	1200	261.30	3.838
	1300	257.40	3.897
	1450	256.00	3.918
	2800	232.00	4.323
Vulcan XC72R	0	262.00	3.828
	1200	263.30	3.809
	1300	259.60	3.864
	1450	258.20	3.885
	2800	233.40	4.297
Shawinigan	0	65.80	15.243
	1200	66.60	15.060
	1300	62.50	16.048
	1450	60.10	16.689
	2800	46.60	21.524
Ketjenblack EC	0	1,003.00	1.000
	1200	1,005.00	0.998
	1300	998.00	1.005
	1450	984.00	1.019
	2800	960.00	1.045
Conductex 900		128.00	7.836
Conductex SC		242.00	4.145
Conductex 975		274.00	3.661
Conductex 40-220		1,030.00	0.974
Philblack XE-2		1,010.00	0.993

TABLE 9.4 MIX FORMULATIONS

	A	B
Silastic GP30	100.0	-
Silastic GP45	-	100.0
Dicumyl Peroxide	2.50	
1. Vulcan P	50.00*	
2. Vulcan P (2800)	50.00*	
3. Vulcan PF	50.00*	
4. Vulcan PF (2800)	50.00*	
5. Vulcan XC72	38.60	
6. Vulcan XC72 (2800)	43.20	
7. Vulcan XC72R	38.30	
8. Vulcan XC72R (2800)	43.00	
9. Shawinigan	60.00*	
10. Shawinigan (2800)	60.00*	
11. Ketjenblack EC	10.00	
12. Ketjenblack EC	20.00	
13. Ketjenblack EC (2800)	10.50	
14. Conductex 900	50.00	
15. Conductex SC	41.50	
16. Conductex 975	36.60	
17. Conductex 40-220	9.70	
18. Conductex 40-220	19.50	
19. Philblack XE-2	9.90	
20. Philblack XE-2	19.90	

**Maximum easily processable concentration of carbon black*

9.3.2.3 Results, Discussions and Conclusions

The volume resistivity data of the vulcanisates containing equal surface area of different carbon blacks are as shown in Tables 9.5 and 9.6.

It is worth noting that all compounds, except a few, gave similar volume resistivities ranging from 2.20±0.04 to 3.44±0.05. Also vulcanizates containing graphitized carbon black (2800°C) gave volume resistivities up to about 6% less than those for ungraphitized carbon black; a prominent feature already discussed in Chapter 8. It could also be seen that the volume resistivity of a conductive vulcanisate is dependent, to some extent, on the 'total' surface area of the conducting composite.

However, a further analysis of this equivalent carbon black surface area data giving similar conductivities (Table 9.7) reveals some questionable peculiarities. While only 70-79% of Vulcan P and PF, 63.81% of Conductex 900 and 28-40% of Shawinigan equivalent surface areas were used, double that of the special furnace blacks (Ketjenblack EC, Conductex 40-220 and Philblack XE-2) had to be used to give approximately similar, *i.e* a little lower, volume resistivities. It was expected that equal carbon black surface areas should give equal conductivities, but the above observations were contrary to expectation. This warranted further scrutiny of the theoretical criteria.

Since DBP absorption figure is a measure of carbon black structure, which in turn plays an important role in the degree of conductivity imparted to a compound by the carbon black content, the data in Table 9.7 was rearranged to give prominence to the DBP absorption (Table 9.8) method of measuring surface area to see if a relationship between theory and practice could be obtained. It was observed in Table 9.8 that in some cases the percentages of the different carbon black equivalents required to give similar conductivities decreased with increasing black structure. This was observed to be only true for the first three furnace blacks in the table (*i.e* Vulcan P, PF, and Conductex 900). Above

TABLE 9.5 VULCANISATE PROPERTIES OF SILASTIC GP30 BASED HIGHLY CONDUCTIVE SILICONE RUBBERS

Mix No. A	Cure rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
1.	0.43	12.10	2.80 ± 0.60	72
2.	0.56	11.10	2.62 ± 0.50	72
3.	0.42	12.20	2.70 ± 0.40	72
4.	0.54	11.20	2.66 ± 0.40	70
5.	0.44	12.00	2.66 ± 0.40	70
6.	0.58	10.90	2.62 ± 0.30	70
7.	0.44	12.00	2.62 ± 0.30	70
8.	0.60	10.70	2.60 ± 0.30	70
9.	0.48	11.70	2.46 ± 0.20	74
10.	0.60	10.70	2.36 ± 0.10	72
11.	0.84	8.90	170.00 ± 1.20	54
12.	0.62	10.60	2.20 ± 0.05	60
13.	0.93	8.20	142.00 ± 0.80	56
14.	0.43	12.10	2.62 ± 0.50	76
15.	0.60	10.70	2.68 ± 0.50	72
16.	0.44	12.00	2.84 ± 0.40	76
17.	0.62	10.60	230.00 ± 1.40	52
18.	0.47	11.80	2.80 ± 0.05	58
19.	0.83	8.60	140.00 ± 0.60	52
20.	0.57	11.00	2.20 ± 0.04	60

**The results are average results from six samples for each compound*

TABLE 9.6 VULCANISATE PROPERTIES OF SILASTIC GP45 BASED HIGHLY CONDUCTIVE SILICONE RUBBERS

Mix No. B	Cure rate (min^{-1})	Cure Time (min)	Volume Resistivity (ohm-cm)	Hardness (IRHD)
1.	0.44	12.00	3.00 ± 0.60	76
2.	0.56	11.10	2.86 ± 0.60	76
3.	0.43	12.10	3.00 ± 0.50	74
4.	0.55	11.20	2.80 ± 0.50	74
5.	0.46	11.90	2.92 ± 0.40	72
6.	0.58	10.90	2.80 ± 0.40	70
7.	0.46	11.90	2.82 ± 0.40	72
8.	0.60	10.70	2.78 ± 0.30	72
9.	0.48	11.70	2.66 ± 0.30	78
10.	0.62	10.60	2.60 ± 0.20	76
11.	0.84	8.90	180.00 ± 1.60	54
12.	0.62	10.60	2.40 ± 0.05	64
13.	0.94	8.10	150.00 ± 0.80	56
14.	0.43	12.10	3.02 ± 0.60	78
15.	0.60	10.70	2.98 ± 0.50	76
16.	0.46	11.90	3.44 ± 0.50	80
17.	0.62	10.60	270.00 ± 1.80	55
18.	0.50	11.60	2.80 ± 0.05	66
19.	0.82	9.00	160.00 ± 0.80	54
20.	0.57	11.00	2.80 ± 0.04	68

**The results are average results from six samples of samples for each compound*

TABLE 9.7 ANALYSIS OF COMPARATIVE EQUIVALENT SURFACE AREA USED TO GIVE SIMILAR CONDUCTIVITY

Type of Carbon black	Required Amount (EquivalentX10) (g)	Amount used (g)	% used (%)	Volume Resistivity (ohm-cm)	DBP Absorption (ml/100g)	EM Surface Area (m^2g^{-1})	Volatile Content (%)
Vulcan P	63.48	50.00*	78.77	2.80 ± 0.60	116	-	1.50
Vulcan P (2800)	71.24	50.00*	70.19	2.62 ± 0.50			
Vulcan PF	63.89	50.00*	78.26	2.70 ± 0.40	116	-	0.94
Vulcan PF (2800)	71.69	50.00*	69.74	2.66 ± 0.40			
Conductex 900	78.36	50.00*	63.81	2.62 ± 0.50	120	-	0.20
Conductex SC	41.45	41.45	100.00	2.68 ± 0.50	140	-	0.80
Shawinigan	152.43	60.00*	39.36	2.46 ± 0.20	145	70	0.06
Shawinigan (2800)	215.24	60.00*	27.88	2.36 ± 0.10			
Conductex 975	36.61	36.61	100.00	2.84 ± 0.40	165	110	1.00
Vulcan XC72	38.58	38.58	100.00	2.66 ± 0.40	178	111	1.50
Vulcan XC72 (2800)	43.23	43.23	100.00	2.62 ± 0.30			
Vulcan XC72R	38.28	38.28	100.00	2.62 ± 0.30	185	110	0.80
Vulcan XC72R (2800)	42.97	42.97	100.00	2.60 ± 0.30			
Conductex 40-220	9.70	9.70 19.40	100.00 200.00	230.00±1.40 2.80 ± 0.05	228	-	1.60
Ketjenblack EC	10.00	10.00 20.00	100.00 200.00	170.00±1.20 2.20 ± 0.05	340	108	1.00
Ketjenblack EC (2800)	10.45	10.45	100.00	142.00±0.80			
Philblack XE-2	9.93	9.93 19.86	100.00 200.00	140.00±0.60 2.20 ± 0.04	400	-	-

this, the percentage of carbon black required for similar conductivity was observed to increase, e.g 100% to 200% for the remaining furnace blacks and special furnace blacks respectively. The acetylene black, Shawinigan, was observed to be in a class of its own in this respect.

However, by considering the actual amount of carbon black used (Column 4) to give similar conductivities, it was observed that this decreases with increasing structure. Therefore, one can infer, from the above, that the total surface area of, especially the high structure, conductive carbon blacks do not participate 'fully' in promoting conductivity.

Since surface area, as measured by DBP absorption is a composite value of the sum of the geometrical and the open and closed internal surface areas, an attempt to separate these two components was made; the surface area as measured by the Electron Microscope was examined (Table 9.7, column 7) This gives only the geometrical surface area of the carbon blacks.

The SEM surface area figures show that theoretically Ketjenblack EC, Vulcan XC72, XC72R and Conductex 975 should, by proportionation, require the same amount to impart similar conductivity. But this does not concur with experimental observation. However, the theoretical internal surface areas, calculated by subtracting the SEM surface area figures, are 55, 69, 75 and 232 for Conductex 975, Vulcan XC72, XC72R, and Ketjenblack EC respectively. It was observed that the theoretical internal surface area increases with the increased percentage equivalent used for these carbon blacks. It is, therefore, suggested that the effective surface area of carbon black participating in the conductivity is composed of largely the geometrical surface area plus a fraction of the internal surface area.

Now considering the volatile contents of the carbon blacks; the volatile contents may evaporate away at higher processing and curing temperatures and thus affect the relative efficiency of the carbon black content in its ability to provide a surface area able to participate in conducti-

vity. This is, of course, shown in the lower resistivity figures obtained when equal amount of graphitized carbon black are used, compared with the volume resistivity figures of the ungraphitized carbon black(Table 9.7).

It is, therefore, considered that the total available surface area of a conductive carbon black does not participate 'fully' in the conductivity. The electrical conducting efficiency of the conductive carbon black is considered to be fractionally dependent on its volatile content. Also the effective surface area of carbon black participating in the conductivity is thought to be composed of the average geometrical surface area plus a fraction of the internal surface area.

TABLE 9.8 EQUIVALENT SURFACE AREA ARRANGED WITH INCREASING DBP ABSORPTION DATA FOR CONDUCTIVE CARBON BLACKS

Carbon black	DBP Absorption (ml/100g)	Equivalent Carbon black used (%)	Amount of Carbonblack used (g)	Volume Resistivity (ohm-cm)
Vulcan P	116	78.77	50.00	2.80±0.60
Vulcan PF	116	78.26	50.00	2.70±0.40
Conductex 900	120	63.81	50.00	2.62±0.50
Conductex SC	140	100.00	41.45	2.68±0.50
Shawinigan	145	39.36	60.00	2.46±0.30
Conductex 975	165	100.00	36.61	2.84±0.40
Vulcan XC72	178	100.00	38.58	2.66±0.40
Vulcan XC72R	185	100.00	38.28	2.62±0.30
Conductex 40-220	228	200.00	19.40	2.80±0.05
Ketjenblack EC	340	200.00	20.00	2.20±0.05
Philblack XE-2	400	200.00	19.86	2.20±0.04

9.3.3 AVERAGE INTERPARTICULATE DISTANCE OF CONDUCTIVE CARBON BLACK IN A SILICONE RUBBER/CARBON BLACK COMPOSITE

9.3.3.1 Introduction

Calculating the average distance between the conducting carbon black particles in a silicone rubber/carbon black composite is the aim of this section. However, a series of difficulties encountered in the analysis of the figures and micrographs obtained limited the number of the positive results obtained. These problems emanate from the following facts:

a. Conductive carbon black is randomly dispersed in a composite and hence the 'cut' surface scanned and the micrographs obtained can only be taken as an average representation of the whole compound and must be regarded as a relative and not an absolute value.
b. Structure is a phenomenon common to conductive carbon blacks, therefore the particles come in different shapes and sizes. The particle size, as quoted in the literature, used here is an average value.
c. Undispersed carbon black agglomerates in a compound appear as lumps and are, therefore, counted as one single broad peak in the scan. Hence, the number of particles in these clusters cannot be fully analysed. Figures, therefore, are given as the number of peaks, and represent equivalent number of particles, in the DFRLM /Oscilloscope data (Table 9.9), and these include individual particles as well as agglomerates.
d. Conduction in a composite is a 'three dimensional phenomena' (see Section 9.3.1.1). The scanned and micrographed area is two dimensional and, therefore, does not give a true picture of all the contributory factors which control conductivity, since the third projection is not recorded.

9.3.3.2 Experimental

9.3.3.2.1 Dark Field Reflected Light Microscopy Examination

The experimental procedure as described in Chapter 2, Section 2.2.7 was followed.

Magnifications: Magnifications are selected by operating the hand-held keyboard, directly after the instrument measures the surface, but prior to results being shown on the Video Display Unit (VDU). The VDU displays a selection of possible magnification. The largest magnification gives a pen trace very close to the out-of-scale boundary. Obviously, this depends on the roughness of the sample analysed, and arranged from X1,000 (for very rough rubber) to X10,000 (for the smoothest samples). Usually a figure lying between these two extremes is the commonly opted one for magnification. An effective magnification of X3,500 on the VDU, equivalent to scanning a linear dimension of 300μm of sample, was found out by experiment to be most suitable and thus used throughout the experiment. Figures from the DFRLM/Oscilloscope data (Table 9.9) were used to calculate the average distance between the carbon 'particles'.

9.3.3.2.2 Scanning Electron Microscope Examination

The same sample used in the DFRLM/Oscilloscope examination was used in this exercise. These samples were, however, sputter coated with gold to prevent electron charge build-up during electron microscopy and consequent loss of contrast. The gold coating also improves the secondary electron emission from the sample surface. Sputter coater settings were as follows:

Coating Time	- 2X1 minute
Argon gas	- to maintain vacuum of $2X10^{-2}$ torr
Current	- 25 amps
Voltage	- 6volts

The SEM viewing was accomplished under nominal magnifications of X20,000, X50,000 and a few X100,000 magnifications. A 10kV accelerating voltage was used. SEM micrographs (X20,000 magnification) of Vulcan P (5-30phr), Shawinigan (5-35phr) and Ketjenblack EC (4-20phr) conductive silicone compounds are shown in figs. 9.7-9.9 respectively while figs. 9.7A-9.9A shows the corresponding DFRLM traces of same compounds.

TABLE 9.9 DFRLM/OSCILLOSCOPE DATA OF CONDUCTIVE SILICONE RUBBERS

TEST NUMBER	THRES-HOLD (t)	NUMBER OF PEAKS (n)	MEAN HEIGHT (h)	VARIANCE (v)	STANDARD DEVIATION (s)	DISPERSION INDEX $C = \frac{n\bar{h}s}{t \lambda 100}$
Vulcan P						
5	31.00	17.00	33.[illegible]	244.[illegible]	18.[illegible]	3.33
10	39.40	20.10	25.197	219.[illegible]	18.[illegible]	2.38
15	44.00	24.90	22.[illegible]	194.[illegible]	14.[illegible]	1.83
20	47.25	28.20	23.[illegible]	109.[illegible]	13.[illegible]	1.94
25	49.85	32.40	20.[illegible]	86.[illegible]	10.[illegible]	1.46
30	50.25	34.60	24.[illegible]	55.[illegible]	7.[illegible]	1.20
Shawinigan						
5	28.90	16.00	53.[illegible]	299.[illegible]	14.[illegible]	4.43
10	32.80	17.70	46.[illegible]	233.[illegible]	16.[illegible]	4.07
15	48.40	19.50	43.[illegible]	252.[illegible]	20.[illegible]	3.70
20	56.60	21.00	34.[illegible]	174.[illegible]	21.[illegible]	2.69
25	57.90	22.10	34.[illegible]	142.[illegible]	16.[illegible]	2.21
30	62.40	23.40	34.[illegible]	76.[illegible]	11.[illegible]	1.45
35	62.95	24.70	34.[illegible]	71.[illegible]	10.[illegible]	1.39
Ketjenblack EC						
4	23.00	19.60	24.[illegible]	31.[illegible]	7.[illegible]	1.57
6	25.60	22.30	24.[illegible]	26.[illegible]	6.[illegible]	1.38
8	28.10	24.90	24.[illegible]	22.[illegible]	5.[illegible]	1.25
10	28.80	25.80	23.[illegible]	20.[illegible]	5.[illegible]	1.18
12	29.05	27.80	22.[illegible]	19.[illegible]	5.[illegible]	1.13
14	31.40	28.60	22.[illegible]	16.[illegible]	5.[illegible]	1.06
16	33.80	29.90	22.[illegible]	14.[illegible]	4.[illegible]	0.98
18	35.40	31.10	21.[illegible]	12.[illegible]	4.[illegible]	0.89
20	37.00	32.20	21.[illegible]	10.[illegible]	4.[illegible]	0.78

Fig. 9.7 Scanning Electron Micrographs (SEM) of Vulcan P filled Silastic GP30 based compounds (X20,000).

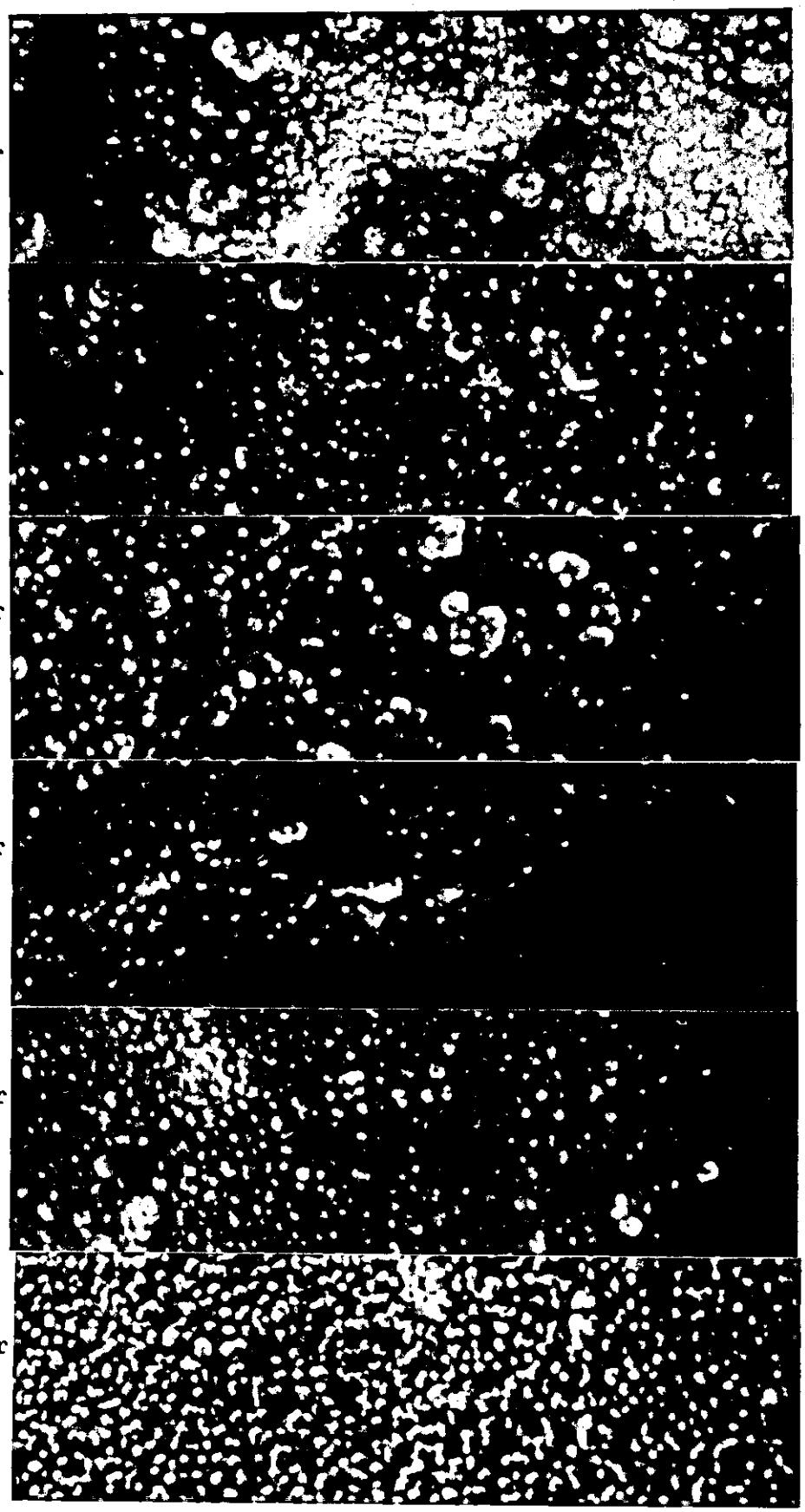


Fig. 9.7A Dark Field Reflected Light Microscope (DFRLM) Hard copy traces of Vulcan P filled Silastic GP30 based compounds (Ref. Table 9.9).

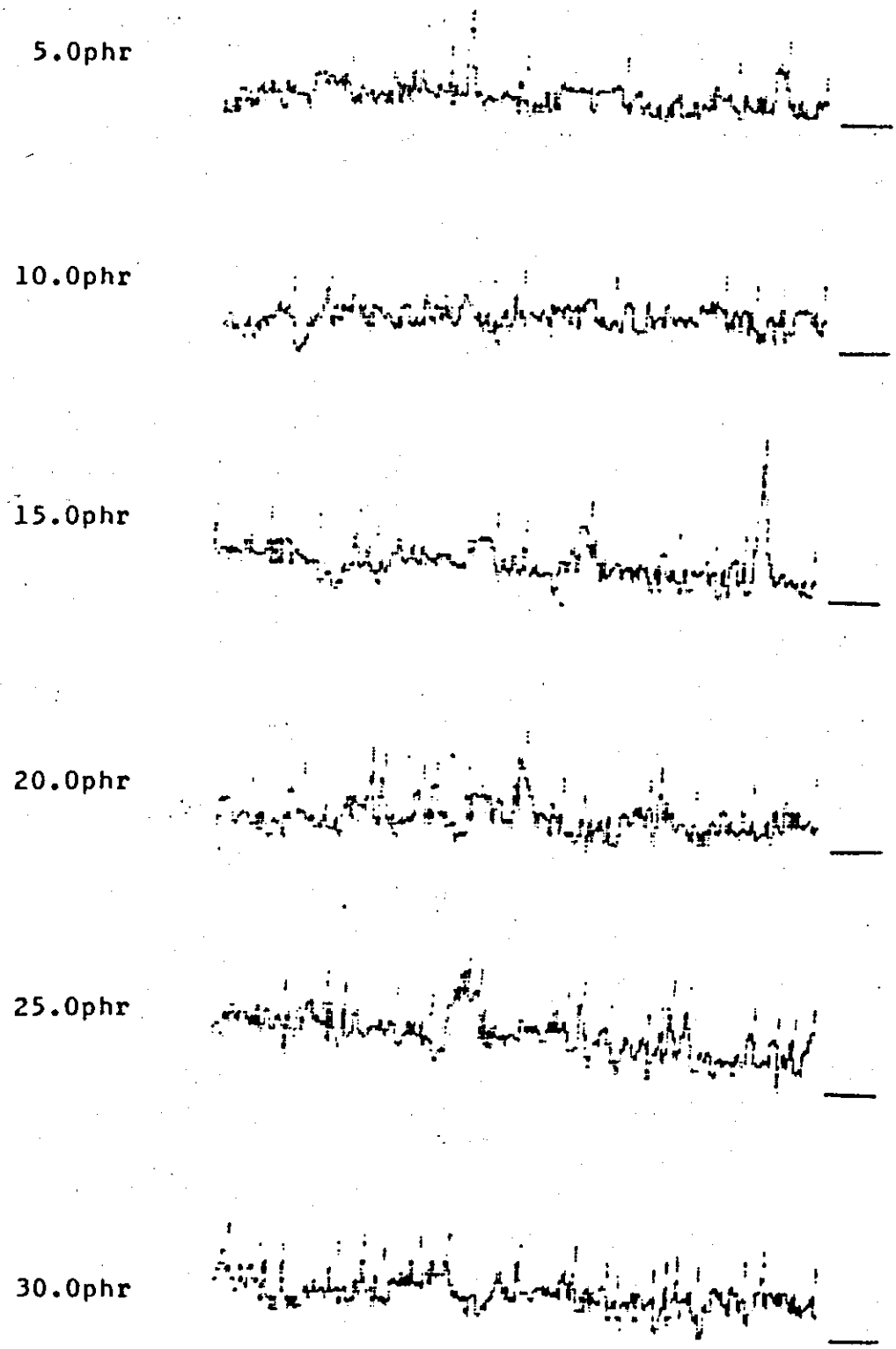


Fig. 9.8 Scanning Electron Micrographs (SEM) of Shawinigan filled Silastic GP30 based compounds (X20,000).

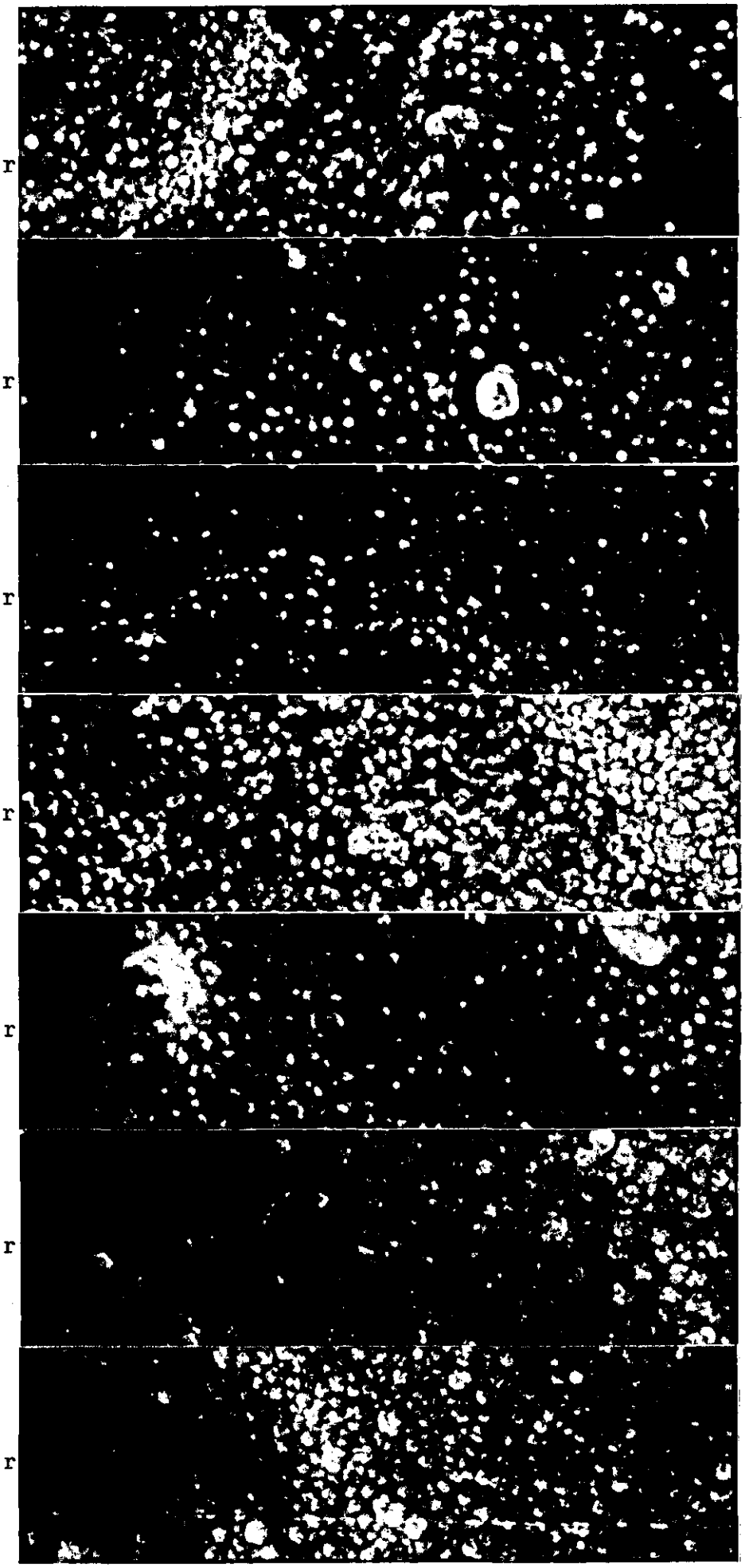
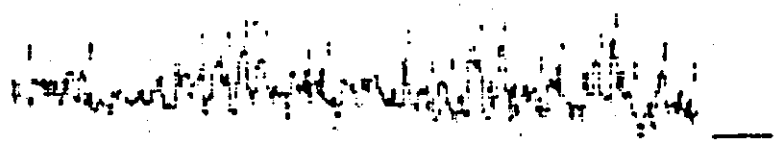
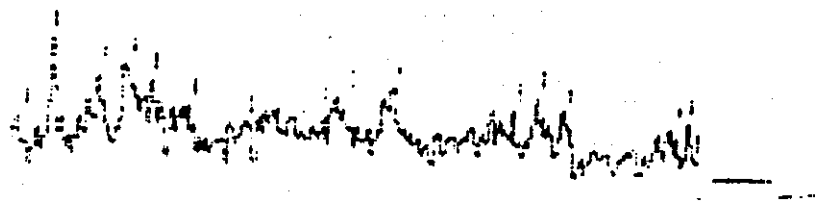


Fig. 9.8A Dark Field Reflected Light Microscope (DFRLM) Hard copy traces of Shawinigan filled Silastic GP30 based compounds (Ref. Table 9.9).

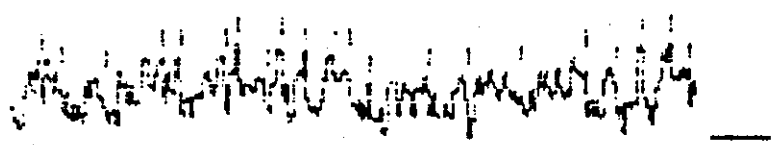
5.0phr



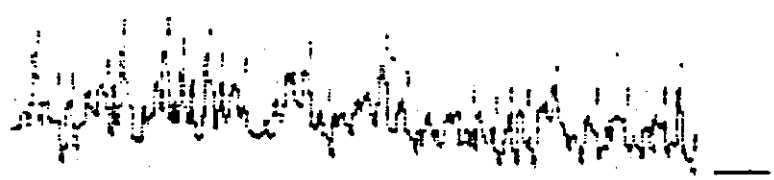
10.0phr



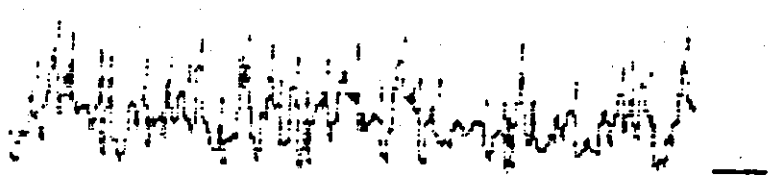
15.0phr



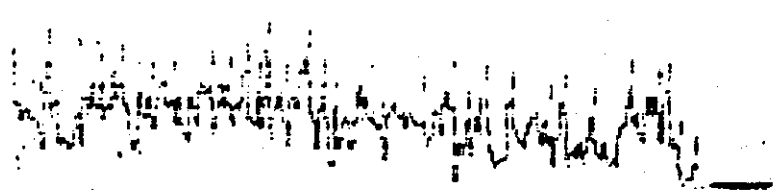
20.0phr



25.0phr



30.0phr



35.0phr

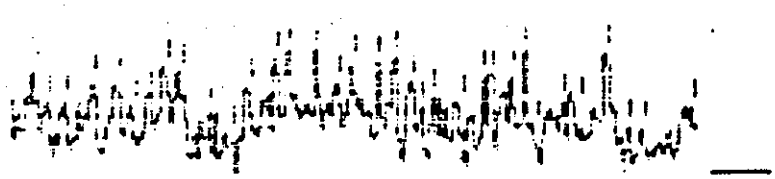
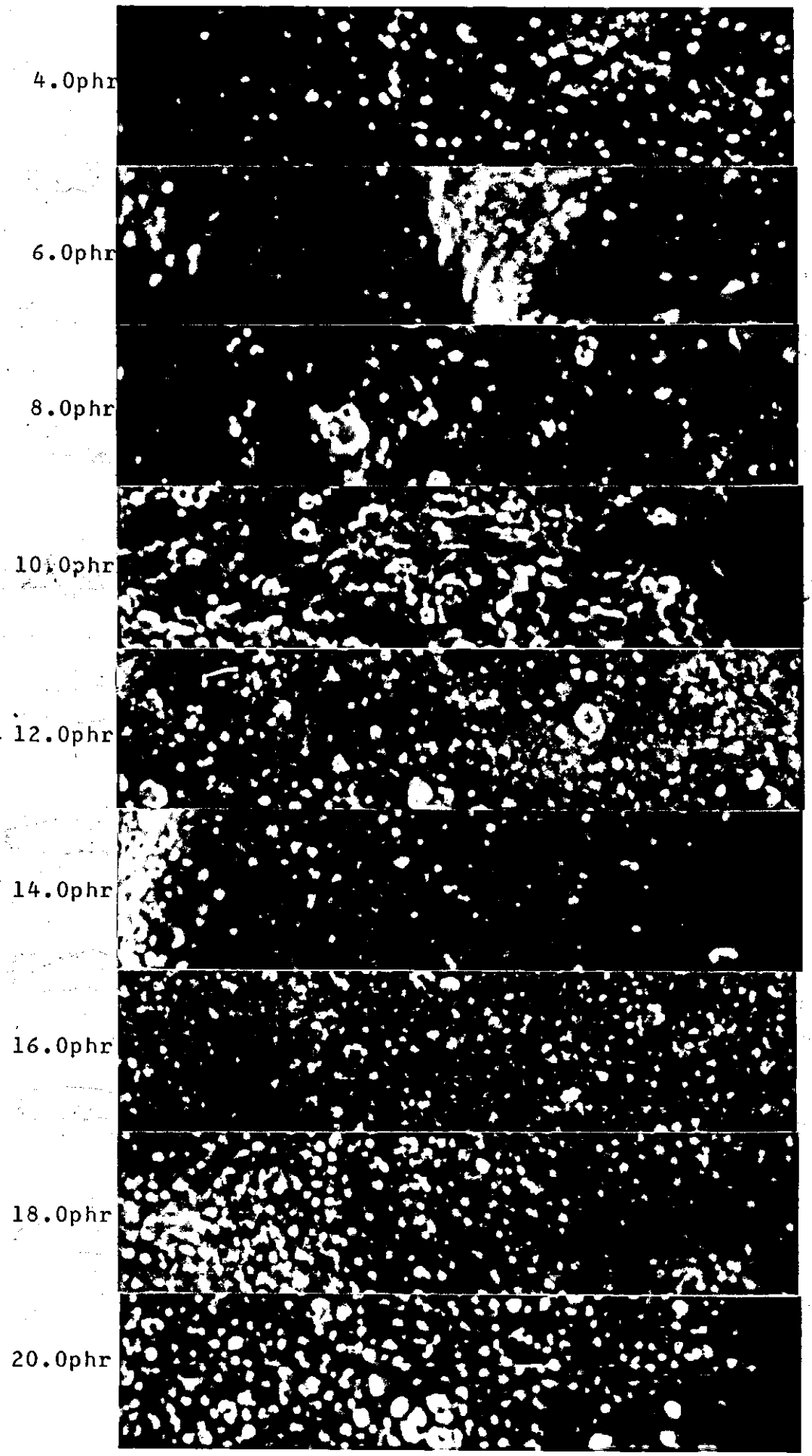
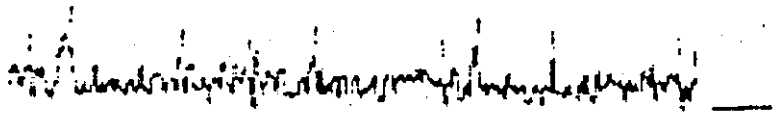


Fig. 9.9 Scanning Electron Micrographs (SEM) of Ketjenblack EC filled Silastic GP30 based compounds (X20,000).

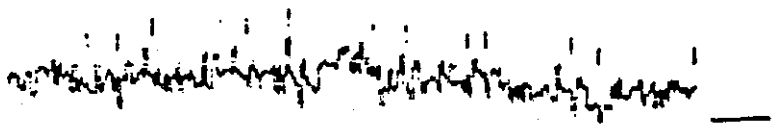


copy traces of Ketjenblack EC filled Silastic GP30 based compounds (Ref. Table 9.9).

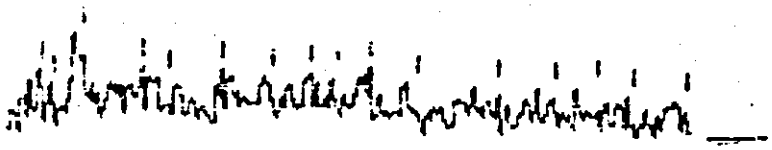
4.0phr



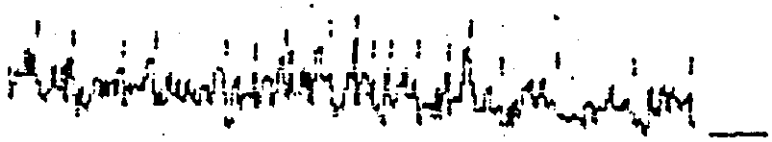
6.0phr



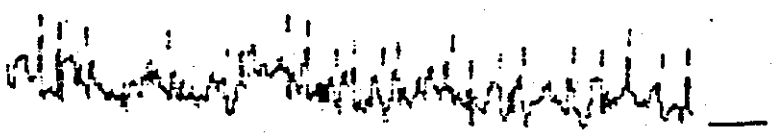
8.0phr



10.0phr

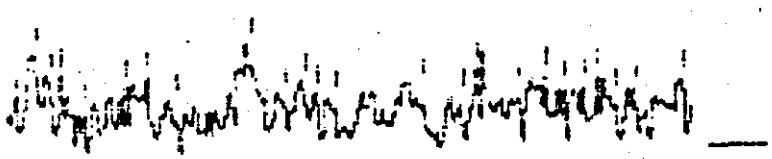


12.0phr

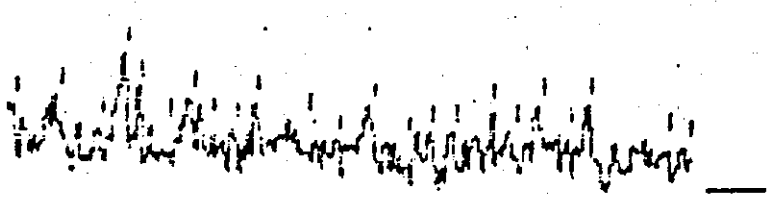


14.0phr

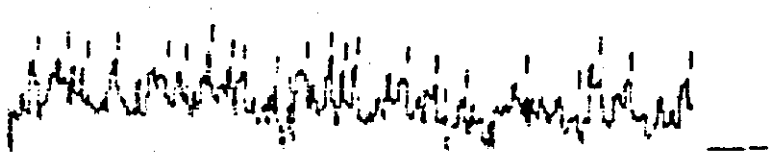
16.0phr



18.0phr



20.0phr



9.3.3.3 Calculations

Table 9.9 shows the DFRLM/Oscilloscope data from the compounds of representative conductive carbon blacks - Vulcan P for furnace blacks, Shawinigan for acetylene blacks and Ketjenblack EC for special furnace blacks.

In a line of scan, the number of peaks, n, is equivalent to the average number of particles. Hence, the number of peaks which is the mean values of 20 lines of scan for each sample is taken as the number of carbon black particles. The scan is, however, made on the effective X3,500 magnification projected on the VDU. Hence, an average lineal dimension of 300μm of sample was magnified 3,500times to give the average number of peaks, n, recorded on the hard copy (Table 9.9).

Assuming that the carbon black maintains the same average particle size,d, as given in the literature; then, this could be used to calculate the total distance, dn, covered by the number of particles, n, in a line of scan of a total 300μm X 3,500(magnification) projected on the VDU. Hence, for each sample, the average distance between each particle is calculated from the following equation:

$$(n-1)y + dn = 300\mu m \times 3{,}500 = 1{,}050nm \qquad 9.9$$

where:

n-1 = average number of spaces between 'n' particles
n = average number of particles
y = average distance between each particle
d = average particle diameter

From equation 9.9

$$(n-1)y = 1{,}050 - dn$$

$$y = \frac{1{,}050 - dn}{n - 1} \qquad 9.10$$

9.3.3.4 Results and discussions

Table 9.10 shows the calculations of the average carbon black interparticulate distances using the equation 9.10. It was observed that the average interparticulate distance from above calculations decreases with increasing carbon black concentration. The rate at which this distance decreases was

TABLE 9.10 AVERAGE CARBON INTER-PARTICULATE DISTANCE DATA

Carbon Black (phr)	Number of particles (n)	Particle size, d, (nm)	nd (nm)	$y = \frac{1,050 - dn}{n - 1}$ (nm)
Vulcan P 5	17.00	30	510.00	33.75
10	20.10	"	603.00	23.40
15	24.90	"	747.00	12.17
20	28.20	"	846.00	7.50
25	32.40	"	960.00	2.90
30	34.60	"	1038.00	0.36
Shawinigan				
5	16.00	42.5	680.00	24.67
10	17.70	"	752.25	17.83
15	19.50	"	828.75	11.96
20	21.00	"	892.50	7.88
25	22.10	"	939.25	5.25
30	23.40	"	994.50	2.84
35	24.70	"	1049.75	0.01
Ketjenblack EC				
4	19.60	30	588.00	24.84
6	22.30	"	669.00	17.89
8	24.90	"	747.00	12.68
10	25.80	"	774.00	11.13
12	27.80	"	834.00	8.06
14	28.60	"	858.00	6.96
16	29.90	"	897.00	5.29
18	31.10	"	933.00	3.89
20	32.20	"	966.00	2.69

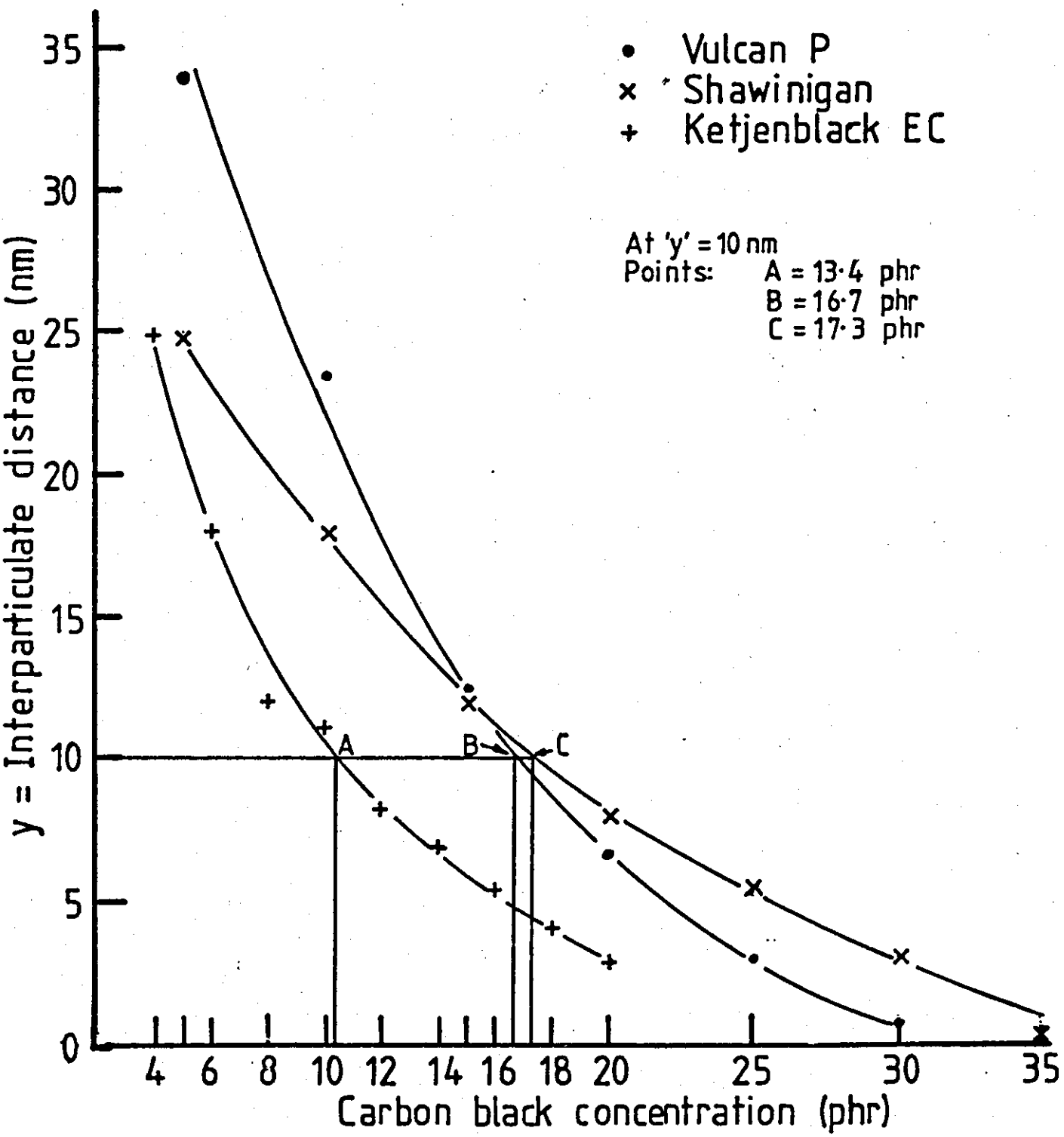
found to be dependent on both the type of carbon black (particle size) and the concentration.

Fig. 9.10 shows a plot of carbon black concentration (phr) versus the interparticulate distance (nm). The graphs obtained were observed to agree with the general nature of the volume resistivity versus carbon black concentration curves. The dependence of the volume resistivity on the distance between particles, agglomerates and aggregates was thus observed and thought to contribute to the general nature of the graphs obtained from the volume resistivity/carbon black concentration curves.

The curves usually obtained from the volume resistivity/carbon black concentration data have an initial slow change, followed by the abrupt 'transition' from resistive to conductive region, between a narrow band of carbon black concentration. The curves obtained here were observed not to have any initial slow change. However, at points A, B, and C (fig. 9.10), where y=10.0nm, the carbon black concentrations are 13.4, 16.7 and 17.3 for Ketjenblack EC, Vulcan P and Shawinigan respectively. These figures averagely correspond to where the abrupt resistive to conductive 'transition' regions in volume resistivity/carbon black concentration curves usually starts in both Vulcan P and Shawinigan filled conductive silicone rubbers. In case of Ketjenblack EC filled compound, the starting point for the abrupt 'transition' occurs at a lower figure (approx. 5.0phr) in the volume resistivity/carbon black concentration curves. Differences in the curves obtained may be attributed to other contributory factors, such as, assumptions, carbon black random distribution within the compound, carbon black structure and processing characteristics.

The above observations tend to agree with the concept of electron tunnelling. [illegible] have a reasonable chance to jump across the gap, resulting in the electron tunnelling phenomena. The above observation tend to agree with this principle. It is, therefore, suggested that the interparticulate distance is one of the strongest factors contributing to the general nature of the volume resistivity/carbon black concentration curves obtained.

Fig. 9.10 The effect of carbon black concentration on the distance between carbon black particles in the Silastic GP30 based compounds.



Another critical observation of the SEM micrographs of Ketjenblack EC filled compounds (fig. 9.9) show a build-up of carbon black pseudo-fibre chain configuration between 6phr and 10phr (see fig. 9.11 for larger micrographs). This pseudo-fibre chain formation is a phenomenon attributed to small particle size conducting furnace blacks and which promotes electron conducting pathways. It was observed that the above described build-up of carbon black pseudo-fibre chain as seen in the SEM micrographs lie in the resistive to conductive 'transition' region of the volume resistivity/carbon black concentration curve. This suggests that the abrupt resistive to conductive 'transition' starts when a progressive build-up of the carbon black pseudo-fibre chain as seen in the micrographs commences.

Figure 9.11 also shows clearly the hollow nature of Ketjenblack EC particles. An important contributory factor to the 'extra conductive' nature of this carbon black.

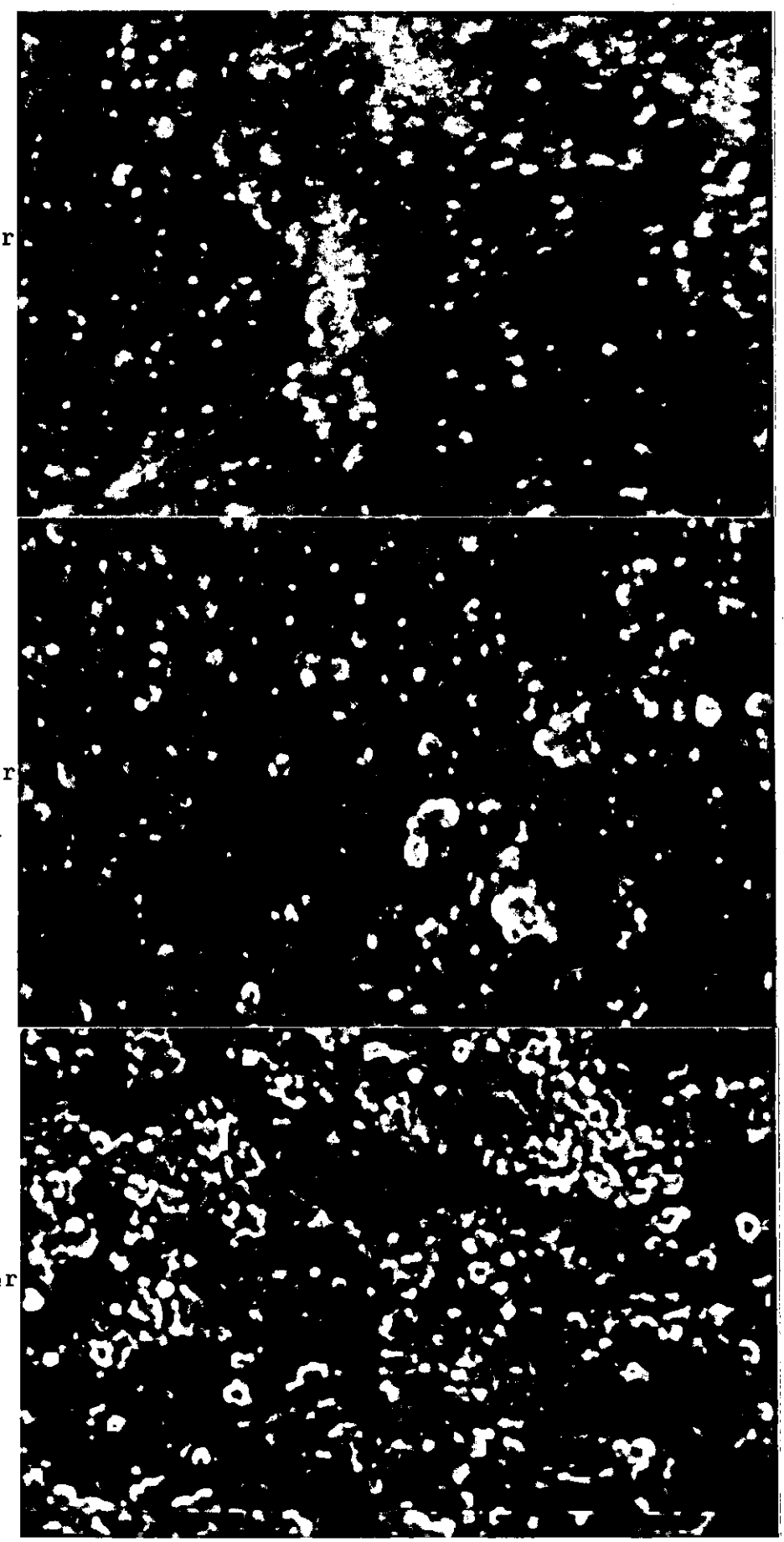
9.3.3.5 Conclusions

Observations of the results from calculated average distances between carbon black 'particles' in carbon black/silicone rubber composites:

a. gave graphs similar to those obtained from the volume resistivity/carbon black concentration curves;
b. supported the electron tunnelling phenomena; and
c. agreed with the concept of build-up of carbon black pseudo-fibre chain formation, as observed in Ketjenblack EC compounds (fig. 9.11).

It could, therefore, be concluded that the average distance between the carbon black particles, agglomerates and aggregates in the silicone rubber/carbon black composites served as a major contributory factor to the electrical conductivity of the composite.

Fig. 9.11 SEM Micrographs of Ketjenblack EC filled Silastic GP30 based compounds (X20,000) showing the gradual build-up of the carbon black pseudo-fibre chain configuration from 6.0phr to 10phr black concentration.



X. GENERAL DISCUSSIONS, CONCLUSIONS AND RECOMMENDATIONS

10.1 GENERAL DISCUSSIONS AND CONCLUSIONS

For the past FOUR decades, the electrotechnical industry has profited in many ways by the rapid development and spreading use of synthetic materials which have replaced classical ones such as natural rubber, mica, ceramics, glass and also various metals in a number of applications.
A material gaining constantly more importance and which from being a speciality is advancing to regular industrial application, is silicone rubber.

On the one hand, high temperature vulcanizable (HTV) silicone rubber has excellent low temperature performance. Due to the silicon-oxygen-silicon backbone of the polymer, a highly flexible chain is formed with segments requiring only small energy input to move. The ease of rotation of the organic groups attached to the silicone atoms plays an integral part in the above characteristics. At the same time it is a highly heat resistant, track resistant insulating material, partly a consequence of the very strong silicon-oxygen bond (451 $kJmole^{-1}$). The corona resistance and the insulation properties of the silicone rubber are nearly equal to mica. On the other hand, by adding electrically conductive pigments, a new material class is formed which in many areas has already replaced metallic conductors or contacts.

Silicone rubber is a highly versatile material. Just as the volume resistivity may be varied from $(2\text{-}10)\times10^{14}$ ohmcm to <2.0ohmcm, the same may be done with other parameters, for example mixing with especially suitable fillers, *e.g* pyrogenic (fumed) silica, increases the tensile strength, compared with the purely crosslinked polymer, by a factor of 40. This is a unique phenomenon, since, in comparable amorphous polymers, *e.g* polybutadiene, a reinforcement factor of only 10 is realized. An important difference from organic elastomers concerns the electrical and mechanical properties of silicone

rubber which are generally less dependent on temperature. Silicone rubbers remain elastic up to 300°C and are less susceptible to thermal decompositon, but decompose primarily by hydrolytic attack.

For HTV systems, the silicone polymer is generally crosslinked by means of organic peroxides; the reactivity of the various types of silicone elastomer differs with respect to the organic radical attached to the silicone backbone; it is also possible to cure silicone rubber with a platinum-catalyzed hydrogenated siloxane (SiH) addition, or condensation or by radiation crosslinking.

Carbon blacks with surface areas between 80 and 1,000m^2g^{-1} are the preferred conductive fillers due to their economical price, low density and chemically inert performance, and thus these avoid corrosive damage or local cell formation upon contact with metals. The use of graphites or metallic fillers or metal-coated ballottini results in materials with extremely poor mechanical properties. Factors operating against metallic fillers are their relatively high cost, high specific weight and also their susceptibility to corrosion, unless precious metals are used alone or as coatings.

Carbon black filled conductive silicone rubbers have been claimed to be insignificantly affected by or insensitive to mixing conditions during processing or to strain in the vulcanisate. In contrast to these claims, many existing products are known to suffer from some setbacks such as poor reproducibility and lack of capability to maintain a constant resistivity when flexed or used above certain voltage levels. This led to the objectives of this research; to carry out a detailed investigation of the variables which affect electrical property reproducibility and develop an understanding of the compounding factors which control electrical conductivity in carbon black filled silicone rubbers.

Three well established commercial silicone rubbers, (Silastic GP30, Silastic GP45 and Siltech 17 containing 19%,

24% and 42% fumed silica respectively), and three major classes of conductive carbon blacks, (furnace, acetylene and 'special' furnace), were investigated.

While no difficulties occurred in measuring the volume resistivities in the range of 1 to 10ohmcm, the contact resistance between rubber and measuring electrode played an ever increasing part as conductivity progressively decreases. However, the simple experimental method used and described in Chapter 2, Section 2.2.4 gave reasonably reproducible volume resistivity measurements. In practice, most conductive silicone rubbers were found not to show unwanted variation or polarization effects until resistivities above 10^9ohmcm, were reached, when measured with this method.

In the preliminary investigation of the effect of peroxide cure on the degree of vulcanisation, volume resistivity and hardness using different peroxides (cf. Ch. 3), dicumyl peroxide, Perkadox SB, with a 2.5phr (best) optimum loading was found to give a balanced cure to silicone rubber in that the vulcanisate had a good cure state.

However, it was observed that the cure rate of silicone rubber containing carbon black in proportions >10-15% was too slow to prevent the development of porosity inherent from the presence of trapped and dissolved air in the compound when HAV cured. The conventional peroxidic crosslinking system is, therefore, recommended for vulcanisation under pressure as in compression, transfer or injection mouldings, while the addition (platinum based) crosslinking system is highly recommended for HAV (pressureless) cures. The latter can, however, also be cured under pressure. Acyl peroxides, e.g bis(2,4-dichloro benzoyl)peroxide, Perkadox PDS50, were found to be unsuitable for curing carbon black filled silicone rubbers, but alkyl or aryl peroxides were found to be satisfactory and in this class dicumyl peroxide gives reasonably fast curing silicones with low volume resistivities and is considered the best system presently available.

In the experiments carried out in this programme, increasing dicumyl proportions were found to increase cure rate and hardness, and to decrease cure time and volume resistivity. It is interesting to note that no difference was observed in volume resistivity between conductive silicone rubber post-cured for 4hrs at 200°C and the non-post-cured samples when the test specimen was 2mm thick. But post-curing was found necessary to develop reproducibility in samples that are >2mm (*i.e* say, 3mm) thick.

In the experiments carried out on the effect of processing(milling)on the electrical volume resistivity of the carbon black filled silicone rubber (*cf.* Ch.4), the degree of the milling effect is found to be dictated by the type, concentration and graphitization temperature (*cf.* Ch.8) of the carbon black, the viscosity of the compound and the milling time. Generally, Silastic GP30 based (low viscosity) compounds exhibit an initial volume resistivity which decreases to a minimum between 5 and 8mins of milling (for furnace and acetylene blacks), and 5 and 12mins (for 'special' furnace blacks) milling time, and, then on further milling, the resistivity starts to increase. With increased silica content (higher viscosity rubber), there is a higher initial rate of volume resistivity decrease from 0-5min milling time, followed by a minimum, as observed in Silastic GP30 based compounds, and then this increases as milling further progresses. The change in volume resistivity with further milling time was observed to exhibit steadily increasing volume resistivity, as in the Silastic GP45 vulcanisates, or to reach an almost constant value as in the highly filled Siltech 17 vulcanisates. However, graphitized carbon black filled Silastic GP45 based compounds show an initial rapid decrease (from 0-5min milling time) to a minimum (between 5 and 8min milling time) resistivity and then this results in a constant volume resistivity on further milling.

The existence of this 'minimum volume resistivity effect' suggests that volume resistivity initially decreases during

the carbon black incorporation phase of the milling process to be followed by the carbon black aggregate deagglomerating to give improved dispersion; this results in no significant change of electrical volume resistivity value between milling times of 5-8mins for furnace and acetylene blacks and 5-12mins for the speciality conductive furnace blacks whose mixes acquire a minimum constant value of resistivity. This phase is followed by increased efficiency of carbon dispersion as well as increased breakdown in the carbon black aggregates and subsequent increased inter-particulate distances, all of which result in a further increase in volume resistivity. An exception is found when the silica content is increased significantly as a constant value of volume resistivity then results.

The sensitivity of resistivity to milling time is found to decrease with increasing carbon black loading for all compounds. Similarly, in graphitized carbon black filled compounds, the effects of other variables are found to decline with increasing graphitization temperature. However, the rate at which these variables decline is found to be in the following order: Ketjenblack EC>Shawinigan>Vulcan P.

The observation of a minimum resistivity value with respect to milling agrees with the findings of other earlier workers[267-271]. By keeping processing time within this 'minimum time belt' a reproducible and controlled low resistive compound can be produced, other conditions being kept constant.

The investigation of the effects of mould flow, moulding pressure, storage time and moulding time on the volume resistivity using three moulding blanks of varying sizes (Table 5.2), and involving the process variables, moulding pressure, storage time, and moulding time respectively (*cf.* Ch.5) demonstrated that volume resistivity increases with increasing mould flow and mould pressure; and decreases

with increased storage time. Also when the rubber is vulcanised for 10% less than the calculated curing time, this results in a slightly higher volume resistivity; 50% overcuring produces a small change. [illegible] The extent to which these factors affect the volume resistivity is found to be dependent on the type and concentration of the particular individual carbon black. Volume resistivity changes due to these processing variables were found to be reduced as the carbon black increased. The resistivity of a highly conductive vulcanisate is less (or not) affected by these processing factors. A more critical control of these processing criteria becomes increasingly necessary with the less conductive compounds if mouldings with reproducible electrical properties are to be obtained.

In assessing the effect of carbon black concentration on the vulcanisate properties of conductive silicone rubbers, eleven types of conductive carbon black in three well established silicone rubber compounds were investigated making a total of 359 individual compounds (*cf.* Ch.6). Additionally, a further 96 graphitized carbon black filled conductive silicone compounds (*cf.* Ch.8) were also examined.

In the experiments carried out in this exercise, increasing the carbon black proportions in the low silica containing silicone rubber was found to decrease the cure rate, increase the cure time, give an initially 'low' volume resistivity change, followed by a 'critical and sharp' transition from a 'resistive' to 'conductive' polymer; and then a region of very slow change in the volume resistivity occured as high conduction was attained. The range and gradient of this transformation is found to be dependent on the carbon black type and properties, and the proportion of insulating filler present. Siltech 17, which contains a large amount of insulating ground silica, is found to produce compounds with logarithmic volume resistivity reduction with increasing carbon black proportion. This is ascribed to the

uniform dilution effect of the insulating filler. It is, therefore, suggested that suitable insulating fillers are effective when used in controlled proportions, to obtain precise and reproducible volume resistivity.

The graphitized carbon black filled Silastic GP45 based compounds are found to give more 'gradual' volume resistivity changes when compared with their ungraphitized carbon black filled counterparts.

The mechanism by which the individual carbon blacks impart conductivity into the rubber compound is considered to influence the rate of change occuring at the transition region. Ketjenblack EC is known to possess an unusual combination of properties due to its light and highly porous particles. Hence, the possibility of an increased number of aggregate-aggregate and particle-particle contacts, and a reduced number of interparticulate and interaggregate distances is favoured. While the former (*i.e* aggregate-aggregate contact) is a pointer to carbon black pseudo-fibre chain formation, the latter (*i.e* reduced interaggregate distance) points to the existence of the electron tunnelling mechanism. Other 'special furnace blacks' (Philblack XE-2 and Conductex 40-220) possess characteristics similar to that of Ketjen black EC. While furnace blacks (*e.g* Vulcan P) are suggested to impart conductivity into their vulcanisates by pseudo-fibre chain formation, acetylene blacks (*e.g* Shawinigan) are suggested to impart conductivity into their vulcanisates by overlap of their bulky particles.

Therefore, the unusual combination of properties which is suggested to encourage the co-existence of both 'pseudo-fibre chain formation' and 'electron tunneling' mechanisms (in vulcanisates containing 'special furnace blacks' *e.g* Ketjenblack EC) is suggested as responsible for their less steep and less variable transition region when compared with the analogous vulcanisates containing furnace and acetylene blacks. The higher conductivity possessed by vulcanisates containing lower proportions of the 'special furnace blacks'

when compared with furnace and acetylene black filled vulcanisates is also attributed to their unusual combination of properties.

The best method found to facilitate the *in situ* measurement of volume resistivity immediately after flexing was to attach leads to the end electrodes of the brass-bonded test specimens mounted on the De Mattia Flexometer (*cf.* Ch.7).

All vulcanisates were found to exhibit a sharp increase in volume resistivity after the onset of flexing and to reach a constant value after 200cycles. This phenomenon is thought to occur as a result of an initially large number of breakages in conducting paths formed from the pseudo-fibre chain formation of the furnace carbon black particles; or, as the webs of overlapped carbon black particles in the soft and bulkier acetylene blacks slide past each other, stretch and break contact as a result of flexing. Also coupled with this movement is an increased interparticulate distance [illegible]

The rate and change in volume resistivity with flexing was observed to reduce with carbon black content, a phenomenon fully explained by increased number of particles and decreased interparticulate distance (*cf.* Ch.7).

The final value of volume resistivity obtained in a conductive vulcanisate also depends on the time difference between the cessation of flexing and measurement.

The cure rate and cure time of peroxide cured carbon black filled conductive silicone rubbers were found to decrease with increased carbon black content. These are thought to occur partly due to a 'mopping effect', i.e the chemisorption capacity of the carbon black on the peroxide free radicals. From the literature survey (*cf.* Ch.8), some useful criteria are discovered to exist when carbon blacks are graphitized. These are elimination of or decrease in the reactive surface

chemistry, volatiles and pores, giving the result of a lower resistive carbon black.

In the experiments carried out, graphitized carbon black filled Silastic GP45 based compounds were found to possess a higher rate of cure, lower cure times and lower volume resistivities, when compared with compounds filled with ungraphitized carbon black. An average of 5% less concentration of graphitized carbon black (at 2800°C) was required to give the equivalent conductivity in a non-graphitized carbon black filled compound. With increasing graphitization temperatures, graphitized carbon black filled compounds were found to exhibit progressively increasing conductivity, [illegible] dispersion (i.e. the [illegible] index [illegible]), and cure time also decreased. These changes were thought to result from the decreasing chemisorptive capacity and better (cleaner) surface of the graphitized carbon black. Hence, graphitization is considered to reduce electrical contact resistance of individual carbon black particle as well as improving curing efficiency.

The volume resistivity/carbon black concentration curves of graphitized carbon black filled vulcanisates were observed to possess more 'gradual' volume resistivity changes when compared with their non-graphitized carbon black filled compounds.

The final volume resistivity of the flexed graphitized carbon black filled vulcanisates was found to be higher than those of the ungraphitized carbon black filled vulcanisates.

The theory describing the critical relationship between volume resistivity of a composite and its carbon black content has been developed (*cf.* Ch.9, Section 9.3.1). A comparison of the theoretical calculations and typical experimental graphs using volume fraction calculation was found to show moderate agreement. The difference observed between theory and experiments are attributed to other factors unaccounted for by the

theory; some of which are listed below:

1. assumptions and constants,
2. microstructural aspect of conductive component,
3. dispersion quality,
4. processing characteristics.

Calculations of the relationship between the total surface area of conductive carbon black in a composite and the varying electrical volume resistivity of the composite (*cf.* Ch.9, Section 9.3.2) showed that the total available surface are of a conductive carbon black does not participate 'fully' in conductivity. The electrical efficiency of the conductive carbon black is considered to be partially dependent on its volatile content. Also the effective surface area of carbon black participating in the conductivity is thought to be composed largely of the average geometrical surface area plus some unknown fraction of the internal surface area.

An equation for calculating the average 'interparticulate distance' of carbon black in a silicone rubber/carbon black composite was derived from the DFRLM/Oscilloscope data obtained from the compounds filled with representative conductive carbon blacks (*cf.* Ch.9, Section 9.3.3).

Results accrueing from the calculations gave graphs similar to those obtained from the volume resistivity/carbon black concentration curves; supported the electron tunnelling phenomena; and agreed with the concept of build-up of carbon black pseudo-fibre chain formation as observed in Scanning Electron micrographs of Ketjenblack EC (fig. 9.11). The average distance between the carbon black particle, agglomerates and aggregates is considered to be a major contributory factor to the general nature of resistivity/carbon black concentration curves of conductive silicone composites.

The above systematic and comprehensive investigation on the factors affecting the volume resistivity of

conductive silicone rubbers shows that highly conductive silicone rubbers are less affected than less conductive types by the variables investigated - type and concentration of peroxides, processing(milling), moulding and vulcanising conditions, type and concentration of carbon black, proportion of bulking filler content, flexing, and type and concentration of graphitized carbon black.

The special properties of 'special conductive furnace' carbon blacks are considered important in providing stability and reproducibility in volume resistivity of vulcanisates containing the comparatively low proportions of these carbon blacks.

At very low carbon black concentrations, and especially in the 'resistive' to 'conductive' transition region (as observed from the volume resistivity/carbon black concentration curves), accurate control of the above variables is required in order to obtain vulcanisates with reproducible conductivity.

10.2 RECOMMENDATIONS

1. In the present research work, three general purpose silicone based rubbers are used. It would be useful to explore other types of silicone based rubbers such as platinum-catalysed SiH addition silicone based compounds, phenyl methyl siloxanes, *etc.*
2. To investigate the effect of other variables such as temperature, large strain (tensile), compression, *etc.*, on the volume resistivity of conductive silicone rubbers.
3. To develop a more detailed study on the 'dilution effect' of the insulating fillers as a 'measured control' on the volume resistivity of conductive silicone rubbers.
4. To explore the use of carbon black blends to produce vulcanisates with reproducible and stable electrical

conductivity.

5. To develop a theoretical relationship for the insulating filler/rubber composite or insulating filler/conducting filler/rubber composite.

APPENDICES

APPENDIX A: EQUIPMENT FOR MEASURING ELECTRICAL PROPERTIES: SPECIFICATIONS AND OPERATING INSTRUCTIONS

1. THE SUPER MEGOHMMETER[352]

The Avo Super Megohmmeter RM170 (fig. A1) measures directly resistances in the range of 10ohms to 10^{15} ohms in accordance with the current Test Methods[235,236,353,354]

1.1 RM170 Specifications.

The following details are taken from the instruction manual supplied with the equipment.

Resistance Measurements:

Basic Ranges	- ohm, kilo-ohm, Mega-ohm, and Giga-ohm.
Multiplier Ranges	- 3, 10, 30, 100, 300 and 1,000
Accuracy	- ±3.5% of the scale length.

Test Voltage Supply:

Range	-	1 to 500 volts dc in 1 volt steps.
Accuracy	-	±1.5% of reading 1 to 9 volts.
		±1.0% of reading 10 to 99 volts.
		±0.5% of reading 100 to 500 volts.

1.2 Operating Instructions (fig. A1).

a. Ensure that the power 'off' button (1) is depressed.
b. Ensure that the lever (2) is in the floating mode and the lever (3) is in the off/discharge position.
c. Connect the measuring leads to the high (4) and low (5) terminal sockets and leave open-circuited for floating mode.
d. Depress the power on switch (6) and allow ten minutes for the equipment to stabilize.
e. With both the set zero (7) and the multiplier 10^3 (8) buttons depressed, adjust the meter reading to zero current on the

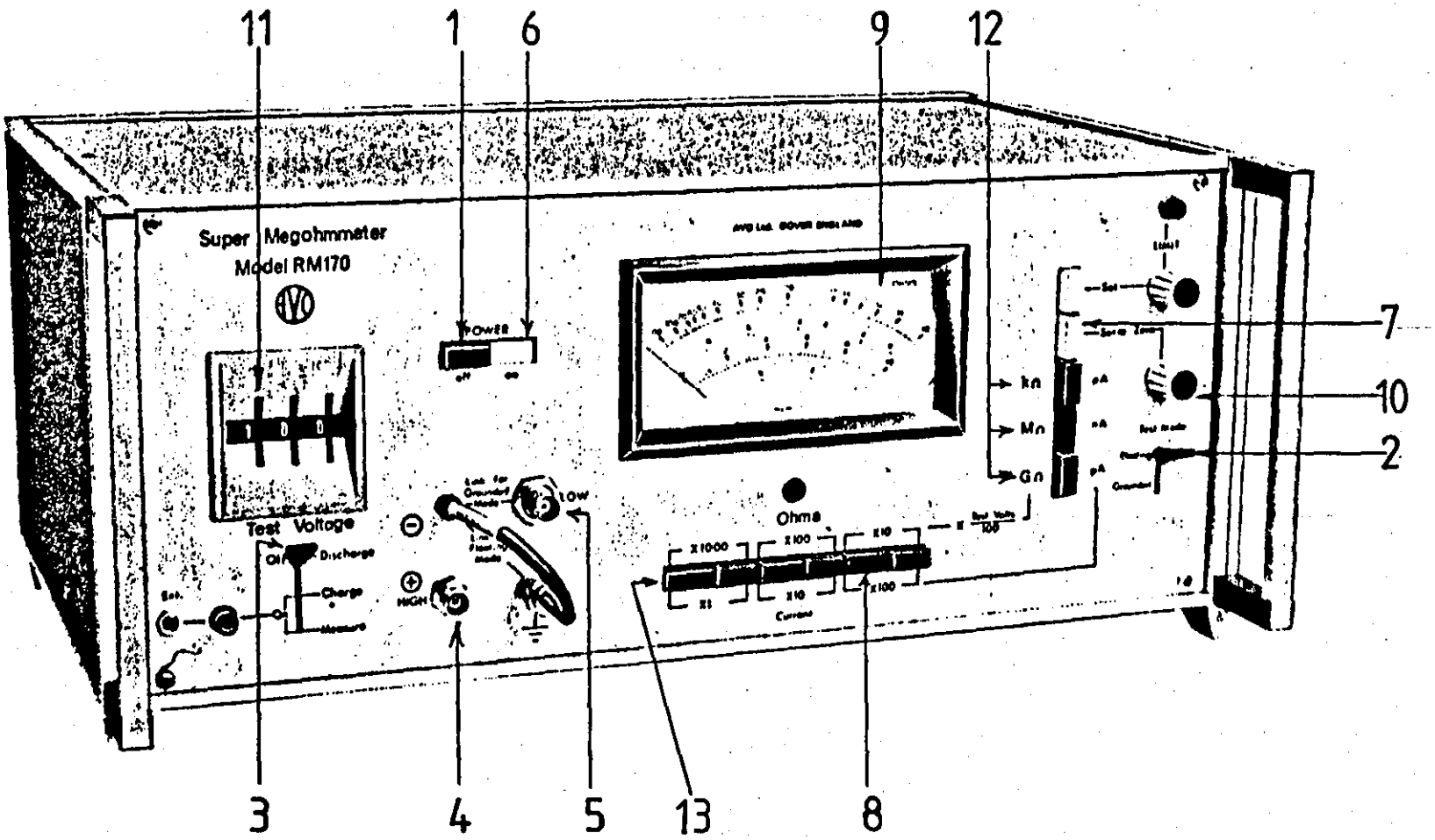


Fig. A1: RM170 SUPER MEGOHMMETER

scale (9) using the set zero control knob (10).

f. Select the required test voltage using the thumb wheel dials (11).

g. For resistances <300 ohms read off from scale. For resistances >300 ohms, select the resistance range (k-ohm, M-ohm, G-ohm) (12) and the resistance multiplier (10, 100 or 1,000) (13) as appropriate if the approximate resistance to be measured is known. Otherwise select the lowest possible range (i.e 10 and k-ohm) by depressing the appropriate buttons.

h. Connect the measuring leads (4,5) to the test rig.

i. Depress the test voltage switch lever (3) to the 'measure' position and read the meter. If no reading is obtained, increase the multiplier and range switches until a reading is obtained.

j. Return the test voltage lever to the off/discharge position before removing the test piece.

k. To obtain the resistance value, multiply the reading by the product of the multiplying factor, the basic range (i.e k-ohm, M-ohm, or G-Ohm), and the test voltage factor (i.e Test Voltage/100.

2. THE DIGITAL MULTIMETER [355]

The Farnell DM131 Digital Multimeter is suitable for the direct measurement of resistances from 0.1 to 20×10^6 ohms.

2.1 DM131 Specifications.

The following details are taken from the instruction booklet supplied with the equipment.

Resistance Measurements:

Basic Ranges:	0	ohm	to 199.9	ohms.
	200	ohms	to 1.999	k-ohms.
	2.0	k-ohms	to 19.99	k-ohms.
	20	k-ohms	to 199.9	k-ohms.
	200	k-ohms	to 1999	k-ohms.
	2.0	M-ohms	to 19.99	M-ohms.

Accuracy: ±(0.25% of reading +0.05% of full scale) except on the 2.0M-ohms to 19.99M-ohms range which is ±(0.5% of reading +0.1% of full scale).

The Test Voltage up to 1999 k-ohms is 200mV (max)

N.B. All ranges are automatically selected except the 2.0M-ohm range which must be selected manually.

2.2 Operating Instructions.

a. Switch on the meter and allow 30minutes for the equipment to stabilize.
b. Switch the selector to the resistance (ohm) range.
c. Connect the measuring leads to the test rig electrodes.
d. Note the resistance reading on the digital display and record.

3. THE MULTIPURPOSE OHMMETER (fig.A2).[356]

The Four Point Probe Model FPP-100, a multipurpose ohmmeter, was designed to simplify measurement of the resistivity of conductive and semi-conductive sheets and films. The equipment digitally computes and directly displays:

a. Surface (sheet) resistivity in ohm/sq (Ωsq^{-1}).
b. Bulk (volume) resistivity in ohm-cm (Ω-cm).
c. Resistance (V/I) in ohms (Ω).
d. Metalization thickness in kilo-angstrom units (KÅ)

It features a single compact package which incorporates both the probe mechanism and the display.

3.1 FPP-100 Specifications.

The following details are taken from the instruction manual supplied with the equipment.

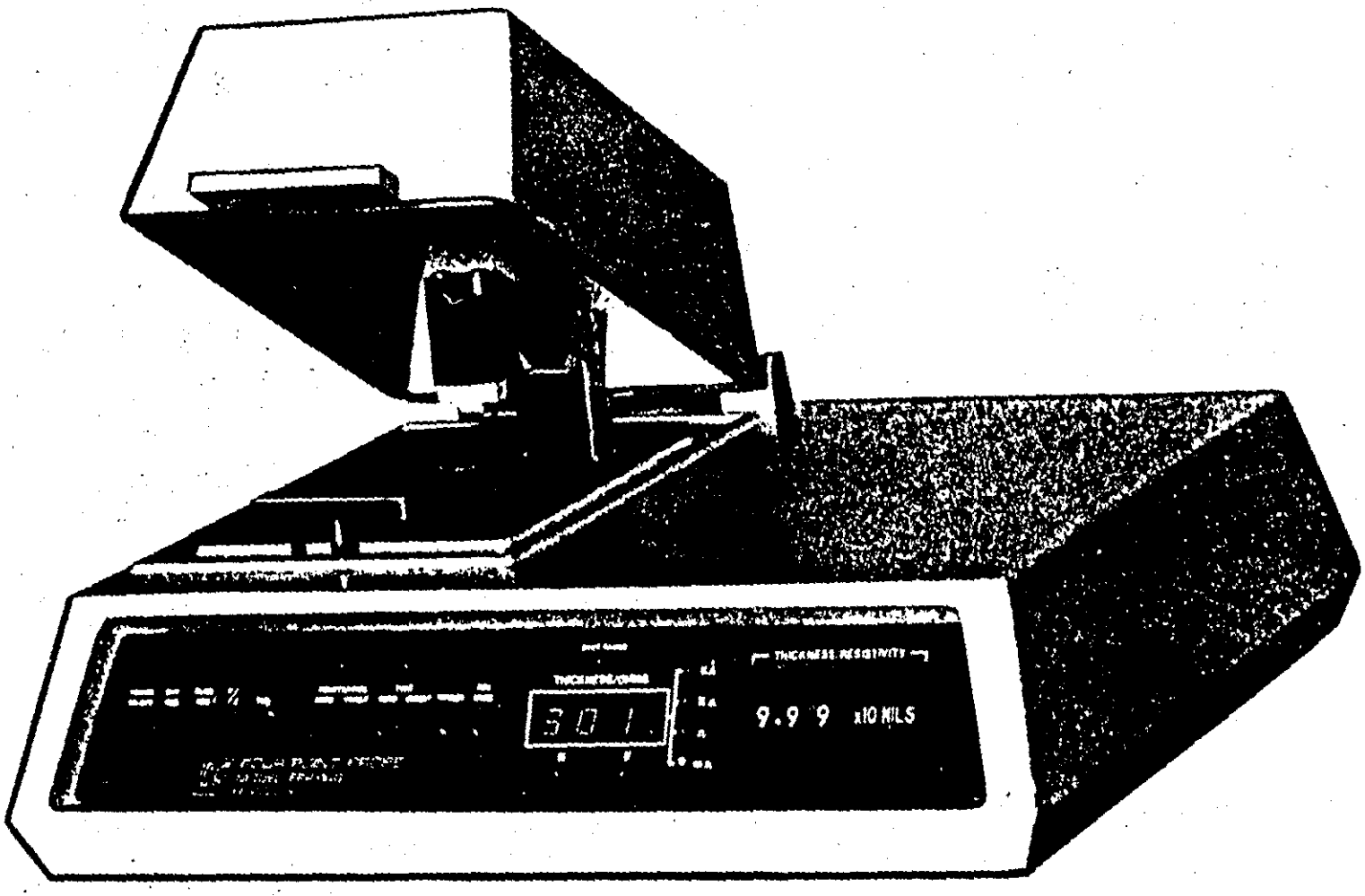


Fig. A2: Model FPP-100 Four Point Probe

MODE	MULTIPLIER	RANGE Minimum	RANGE Maximum
Surface (Sheet) Resistivity.	-	0.00mΩsq^{-1}	99.9 KΩsq^{-1}
Bulk (Slice or Volume) Resistivity	1.0 to 9.99 mil 10 to 99.9 mil 1.0 to 9.99 μ 10 to 99.9 μ 100 to 999. μ	0.000 mΩ cm 0.00 mΩ cm 1.000 to .250 mΩcm 1.000 to .250 mΩcm 0.000 mΩ cm	0.45 to 4.5 KΩ cı 4.5 to 45.0 KΩ cı 99.9 Ω cm 999. Ω cm 9.99 KΩ cm
Thickness	1.0 to 9.99 μΩ cm 10 to 99.9 μΩ cm 100 to 999. μΩ cm	0.250 to 1.000 KÅ 0.250 to 1.000 KÅ 0.250 t0 1.000 KÅ	4.50 to 45.0 KÅ 45.0 to 450. KÅ 450. to 999. KÅ
(V/I) Resistance	-	0.00mΩ	40.0KΩ

Resolution: With the exception of the minimum range the resolution of the display is maintained between 0.5% and 0.05% of reading

Note: 1 mil = 1 thou in. = 0.0254 mm. 2 mm = 78.74 mil.

Accuracy: ± 0.5% of reading in all but extreme resistivity range.

Probe Head Mechanism:

a. Type: Parallel beam with flexural pivots.

b. Force Range: 0-200 g/pin.

c. Force variation with height: <0.2g/mil (average per pin force).

d. Pressure: Unique 'constant force' spring balance system assures repeatable probe pressure.

Conditions of Measurement.

a. Temperature: 15°C-35°C

b. Relative Humidity: <50%

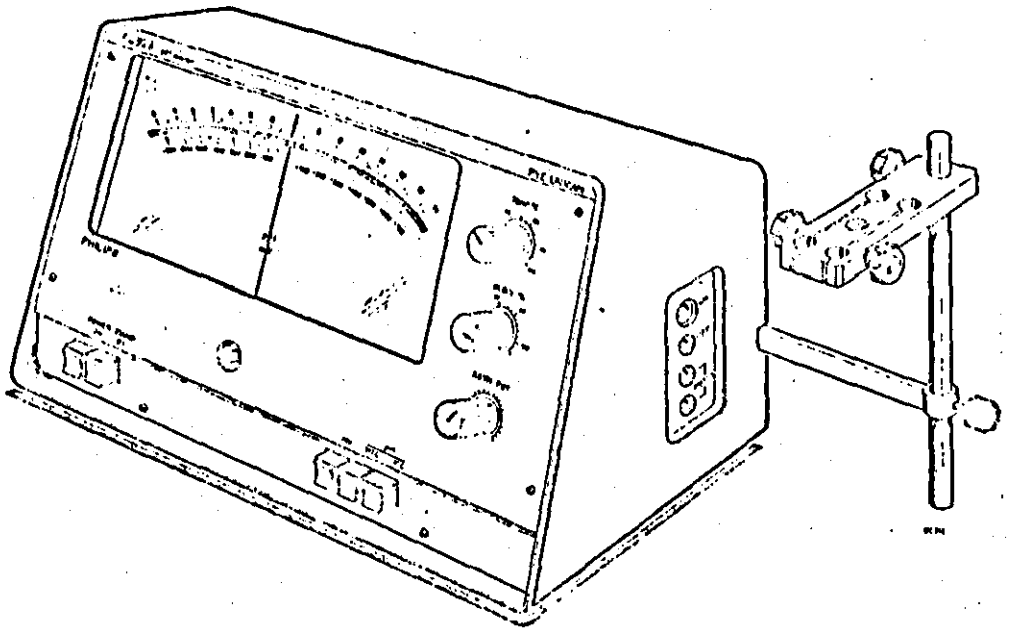
c. Power Requirement: 115/230 V±10%, 50/60Hz. Approx. 10 watts (i.e very low power requirement).

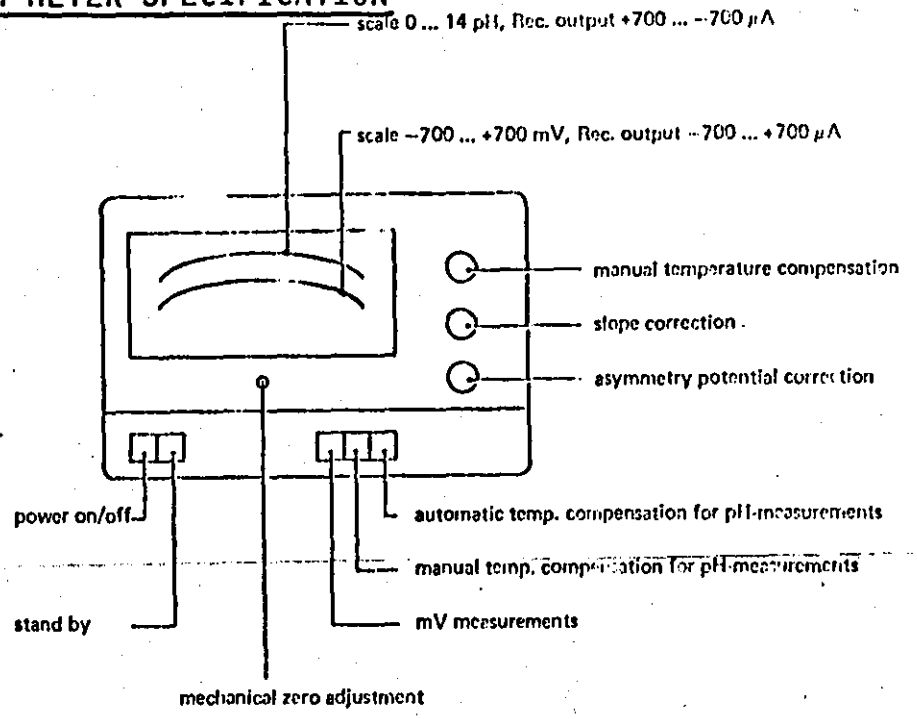
3.2 Operating Instructions

a. Lift the probe head to an upright position to expose the test piece supporting glass disc.
b. Depress the power on switch button.
c. Place the test piece on the supporting glass disc.
d. Select the 'measured' test sample thickness (≯2.00mm) using the thumbwheel dials.
e. Depress the Slice (Bulk) Resistivity switch.
f. Depress the spring balance mechanism in order to lower the probe head unto the test piece and hold until the volume resistivity is automatically displayed.
   A questionable or invalid result is indicated by a flashing display of the over range indicator and type indicator.
g. Read the resistivity on the display.

N.B The last reading automatically holds after the probe is released and until the next measurement is made.

APPENDIX B1: PYE UNICAM PW9418 pH METER SPECIFICATION





SPECIFICATION PW 9418/10

MEASURING RANGES

0 ... 14 pH
−700 ... 0 ... +700 mV

INDICATING METER

Scale length 190 mm
Minimum divisions 0.1 pH or 10 mV

INPUT

Resistance $> 10^{12}$ Ohm
Current $< 10^{-12}$ A (25 °C)

CONTROLS

Asymmetry potential correction

−100 ... 0 ... +100 mV

Slope correction

80 to 103 % of Nernst value

Temperature compensation

Manual: 0 ... 100 °C
Automatic: −10 ... +150 °C with Pt 100 resistance thermometer

STABILITY

Temperature

better than ±0.002 pH/°C

Long term

better than ±0.02 pH/24 hrs or ±1.0 mV/hrs

Mains voltage

better than ±0.01 pH/10 %

OUTPUT

Voltage

100 μA/Δ pH, zero at 7 pH
100 μA/Δ 100 mV, zero at 0 mV

AMBIENT TEMPERATURE

Instrument specifications are valid for temperature variations in between 5 and 40 °C

POWER REQUIREMENTS

200 ... 240 V
100 ... 120 V
50 or 60 Hz
5 VA

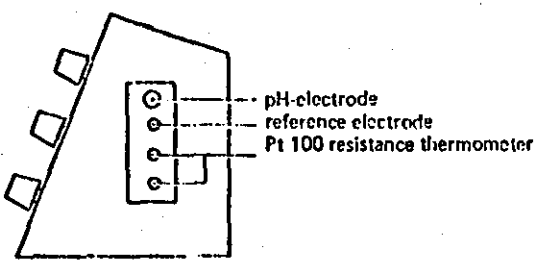
DIMENSIONS AND WEIGHT

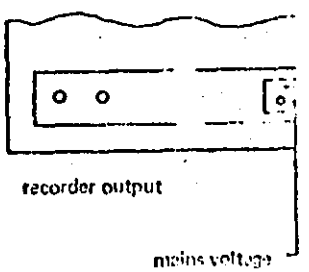
(33 ... 31) x (22 ... 19.5) x 17 cm
3.2 kg.

ACCESSORIES

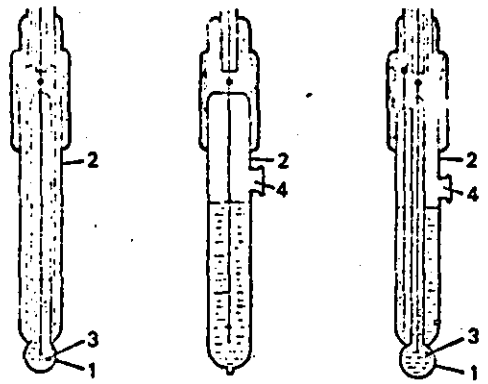
Electrode stand including electrode hol
Mains cable

Full service support available from
PYE UNICAM Ltd
Yorkstreet
Cambridge
tel. 58866





APPENDIX B2: pH ELECTRODES



Glass electrode — Reference electrode — Combined electrode

INSTRUCTIONS FOR USE

1. GLASS ELECTRODES

General

	Membrane Glass	pH Range	Temp. Range
200 series fitted with 1 metre of polythene-insulated coaxial cable	Standard	0-12	0 to 70°C
	L.O.T.	0-11	−10 to +70°C
	H.A.	0-14	+20 to +70°C
260 series fitted with 1 metre of PTFE-insulated coaxial cable	Standard	0-12	0 to 130°C
	H.A.	0-14	+20 to 130°C

Preparation

(a) When unpacking check the electrode for mechanical damage to the membrane (1 on illustration) or body (2).

(b) Check that the Eo value, marked on the identification sleeve and box, is correct for the type of instrument being used. Normally Eo2 or Eo7.

If the Eo value of the instrument is not known, this may be checked by short circuiting the glass and reference electrode input sockets; with the instrument switched to read and the standardise or asymmetry control in the mid position a reading of approximately 2 or 7 pH will be achieved.

(c) Remove protective membrane cap which should contain a liquid. If dry carry out the conditioning procedures as detailed in 1(e).

(d) Eliminate any air bubbles in the membrane space (3) by smoothly swinging the electrode in the vertical plane.

Internal electrolyte solutions are coloured for ease of identification during manufacture. This colouring does not affect the electrode performance and tends to fade completely during use.

Storage

(e) Glass electrodes should not be allowed to dry out but should be stored after use in water acidified with HCl (pH 4 to 5) or distilled water.

An electrode which has been allowed to remain dry for a long period should be conditioned by soaking it in water acidified with HCl (pH 4 to 5) for some hours (e.g. overnight).

In extreme cases the dried out gel layer may be removed by washing the dry membrane for 30 seconds in a 1 to 2% HF—solution prior to soaking for approximately 12 hours in distilled water.

2. REFERENCE ELECTRODES

General

	Half Cell	Electrolyte	Temp. Range
300 series fitted with 1 metre PVC-insulated cable	Calomel	Saturated KCl	0 to 70°C
	Calomel	Saturated NaCl	−5 to +70°C
	Calomel	Friscolyt	−20 to +70°C
360 series fitted with 1 metre PTFE-insulated cable	Silver/ Silver Chloride	3m KCl with AgCl	0 to 130°C
	Silver/ Silver Chloride	Viscolyt 3M KCl + TY + AgCl	0 to 130°C

Preparation

(a) Remove salt crystals from the exterior by washing with water and check body (2) for damage.

(b) Remove or puncture the stopper on the electrolyte filling hole (4) to obtain pressure equality.

(c) The reference electrode must always be filled with the appropriate electrolyte to within approximately 10mm of the filling hole to prevent the galvanic cell from drying out. Refill if necessary with electrolyte as per the above table.

Storage

(d) Reference electrodes should be stored dry with the electrolyte filling hole closed or in a solution identical to the internal electrolyte (e.g. saturated KCl for calomel and 3 molar KCl for Ag/AgCl half cells).

3. COMBINED GLASS AND REFERENCE ELECTRODES

General

	Membrane Glass	pH Range	Temp. Range
400 series fitted with 1 metre of polythene-insulated cable	Standard	0-12	0 to 70°C
	LOT	0-11	−10 to +70°C*
	H.A.	0-14	20 to 70°C
460 series fitted with 1 metre of PTFE-insulated cable	Standard	0-12	0 to 130°C
	H.A.	0-14	+20 to 130°C*

*With appropriate reference electrode electrolyte (see paragraph 2).

Preparation

(a) These electrodes should be treated in accordance with the instructions under paragraphs 1 and 2.

Storage

(b) Combined glass and reference electrodes should be stored in 3 molar KCl solution.

4. PRACTICAL INFORMATION

(a) The instructions of the instrument manufacturer should be observed when using electrodes with any particular type of pH Meter.

(b) Calibration of the measuring system should be carried out daily, weekly or monthly depending upon the measuring accuracy required.

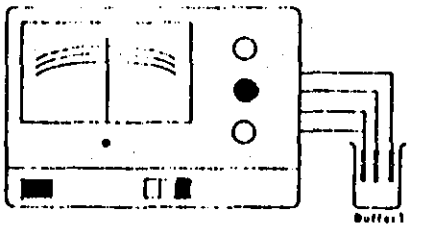
(c) To ensure good measuring results the electrolyte in the reference electrode should be replaced every six months.

(d) A positive outflow of electrolyte is required from the reference electrode. This is particularly important in industrial processes where it may be necessary to apply an overpressure of 2 to 3 psig to the electrolyte.

(e) The interpretation of pH measurements in organic solutions should be handled with care. It is advisable to use a reference electrode with a large surface area liquid junction such as a ground glass sleeve or one with a built in salt bridge. To reduce the liquid junction potential of the latter the outflowing electrolyte should consist of a salt e.g. NH_4NO_3 LiCl or KNO_3 in an organic solvent.

(f) In order to maintain the required insulation resistance of a glass electrode it is essential that the upper part of the electrode, the connecting cable, and any conpector plug or socket are kept dry and clean.

1. CALIBRATION PROCEDURE

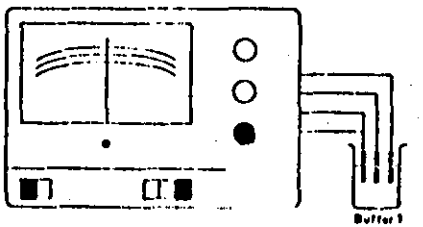


Connect instrument to the mains and plug in electrodes and a Pt 100 resistance thermometer

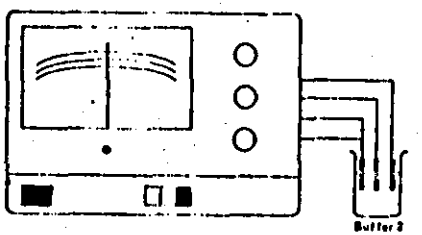
Place electrodes and Pt 100 in buffer 1.

Press buttons: POWER ON
STAND BY
pH/ATC

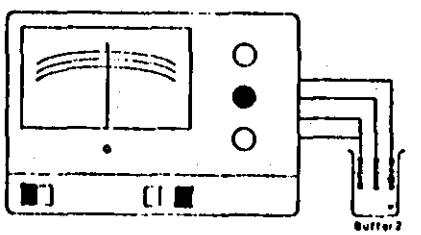
Set SLOPE correction: 100 %. The pH of this buffer must be close pH 7.



Release STAND BY button. Adjust the ASYM POT, until the meter indicates the same pH value as the buffer at this temperature.



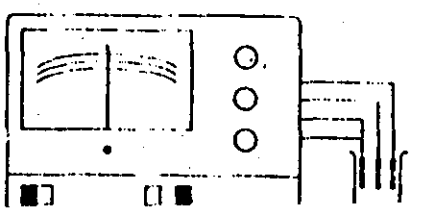
Press STAND BY button. Rinse the electrodes and Pt 100 in distilled water, dry them with a tissue* and insert them in the second buffer whose pH value is close to the expected value of the sample.



Release STAND BY button. Adjust the SLOPE until the meter indicates the same pH value as the second buffer at this temperature.

Press STAND BY button. Remove electrodes and Pt 100 from the second buffer, clean and dry them with a tissue*.

2. MEASURING PROCEDURE



Insert the electrodes and Pt 100 in the sample.
Release STAND BY button.
Read pH-value of the sample.

(* Non greased or non siliconed tissues)

APPENDIX C

THE MEASUREMENT OF SURFACE AREA BY THE BRUNAUER, EMMETT AND TELLER (BET) METHOD.

1. INTRODUCTION

The specific surface area of a powdered sample, i.e. the surface area per gram of material, is a frequently determined parameter during the characterisation of a powder. Of the many methods employed, that due to Brunauer, Emmett and Teller[1,2,3] is one of the most popular.

NOTE: The references are those given at the end of the appendix and not those at the end of the thesis.

2. PRINCIPLE AND THEORY

If the amount of gas required to cover the surface of a particular sample with a complete monolayer of adsorbate can be evaluated, then the surface area can be calculated if the area occupied by a single adsorbate molecule is known.

The BET equation is a theoretical description of the adsorption isotherm of a gas on a solid, and describes how the amount of gas adsorbed, expressed as an equivalent volume at STP, V, varies with the pressure, P. It has the form:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_o} \qquad 1$$

where: P_o = the saturation vapour pressure of the adsorbate
V_m = the equivalent volume of gas at STP in a complete monolayer
C = the constant characteristic of the particular system

A straight line results if $P/V(P_o-P)$ is plotted against P/P_o, the relative pressure. The value of V_m can be calculated from the slope, $C-1/V_mC$, of this graph. Thus $V_m = 1/(\text{slope} + \text{intercept})$. The constant C is related to the heat of adsorption of the first layer, E_1, by:

$$C = \exp\{(E_1 - E_L)/RT\} \qquad 2$$

where: E_L = the heat of liquefaction of the bulk of liquid adsorbate
R = gas constant
T = absolute temperature

N.B. Most experimental systems may be described by the BET equation over the relative pressure range 0.05 to 0.30[4]

The most commonly used adsorbate is nitrogen at liquid nitrogen temperatures, 77.5°K. At this temperature, the area occupied by a single nitrogen molecule in a complete monolayer is 162 nm (16.2 Å)². If pure liquid nitrogen is used as the thermostat liquid surrounding the sample tube, then saturation vapour pressure of nitrogen at the adsorption temperature will be equal to the atmospheric pressure.

3. APPARATUS

The experimental apparatus is based on a design by Krieger[5], but for a larger volume in the gas burette and a reduced "dead" space above the sample (fig. C1) The volumes of the burette bulbs are approximately 5, 15, 25, 40 and 125 ccs and these volumes have been accurately determined before the apparatus was assembled. Tap 9 (T9) is used to fill helium and nitrogen storage vessels from cylinders of the gases.

4. SAMPLING

The amount of sample chosen (carbon black, alumina, silica etc) should have a total surface area of about 20 sq. metres.

5. METHOD

Depending on when the apparatus was last used the system may be full of air at atmospheric pressure or be already evacuated and ready.

5.1 Evacuating the system

1. Close taps T1, T2, T10 and T11 and switch on both mechanical vacuum pumps.
2. Turn on the water supply to the mercury diffusion pump and switch on its heater.
3. Fill the Dewar flask round the vapour trap with liquid nitrogen and top up from time to time as necessary.
4. Close taps T4, T6, T7 and T9, and open taps T3 and T5.
5. Slowly open tap T2.

   **Follow the pressure changes in the system with the Pirani Guage, and do not proceed until the pressure is stable and not less than 10^{-3}mm of mercury, by closing and opening T2 until a steady vacuum reading 10^{-3} is achieved.*
6. Close taps T3, T5 and T8.
7. Very slowly and partially open T7 and raise the level of the mercury to the bottom of the bend in the manometer, then close T7.
8. Very slowly open T10to the vacuum line and lower the mercury level to its original position, then close T10.

   *Repeat steps 7 and 8 until there is no further movement of the mercury level.
9. Open T7 and follow the pressure changes in the system with the Pirani guage until a pressure of 10^{-3}mm is achieved.
10. Place the weighed sample in the sample tube. Replace the filler rod. Grease the joint with vacuum grease and connect to the appropriate socket on the frame.
11. Very, very slowly open T8. Allow the system to pump out until a pressure $<10^{-3}$mm can be held with T2 shut.

    **To attain this rapidly, gently heat the sample tube[6].*
12. Close T8.

5.2 Original Volume Calibration

1. Close T2.
2. Raise the mercury level by means of very careful T10 manipulation and adjust it to each of the top calibration marks (H-marks) of the gas burette in turn and record the pressure in each case. } Original mercury heights
3. Close T7 and very slowly open T10 to the vacuum line to lower the mercury level to its original position. Then close T10.

5.3 Volume calibration with Helium

1. Open T7 and T2 to check pressure which must be $<10^{-3}$mm.
2. Close T2.
3. Open T6 and fill space between T5 and T6 with helium. Then close T6.
4. Open T5 and admit helium to the gas burette and then close T5 again.
5. Repeat the procedure with T6 and T5 until an estimated helium pressure of approx. 20mm Hg. is registered on the manometer attached to the system.
6. Very slowly open T10 to admit air through it, just enough to raise the mercury level below H-mark 1, and above the bend.
7. Open T2 to evacuate the part of the system above the manometer limits of the gas burette until a steady $<10^{-3}$mm vacuum is registered.

   **The pressure of helium is equivalent to the difference in height of the mercury levels in the two limbs of the gas burette.*
8. Close T2.
9. Raise the mercury level by means of very careful T10 manipulation and adjust it to each of the top calibration marks (H-marks) of the gas burette in turn and record the pressure in each case. } Helium Pressure heights

Since the quantity of gas has been kept constant during these measurements, use the ideal gas law and graphically determine the volume between the upper calibration mark and T8.

10. Close T7 and very slowly open T10 to the vacuum line to lower the mercury level to just below H-mark 1, and above the bend.
11. Open T8 and put a Dewar vessel full of liquid nitrogen round the sample tube AT A FIXED AND CONSTANT HEIGHT/LEVEL, and take the readings of new helium pressure heights at the H-marks (see No 9 above)

Physical adsorption only occurs to an appreciable extent at pressures and temperatures close to those required for liquefaction. Therefore helium will not be measurably adsorbed at liquid nitrogen temperatures and consequently may be used for volume calibrations at this low temperature. Graphically determine the equivalent volume of the sample tube which is usually termed "dead space".

12. Close T7 and very slowly open T10 to the vacuum line to lower the mercury level to its original level (i.e. below the bend) to evacuate helium.
13. Open T7 and T2 to evacuate the system to $<10^{-3}$mm vacuum pressure held when T2 is shut.

5.4 Determination of Nitrogen Adsorption

1. Close T8 and T2.
2. Open T4 and fill the space between T3 and T4 with nitrogen. Then close T4.
3. Open T3 and admit nitrogen to the gas burette and then close T3 again.
4. Repeat the procedure with T4 and T3 until an estimated nitrogen pressure of approx. 70mm Hg. is registered on the manometer attached to the system.
5. Very slowly open T10 to admit air through it, just enough to raise the mercury level above the bend and just below the H-mark 1 to trap the nitrogen gas.
6. Open T2 to evacuate the part of the system above the manometer limb of the gas burette until a steady $<10^{-3}$mm vacuum is registered.
7. Close T2 and raise the mercury level to H-mark 1 and record the pressure height.

Thus, knowing the pressure and the volume occupied by the nitrogen in the gas burette enables the quantity of gas present to be calculated by means of ideal gas law.

8. Put a Dewar vessel full of nitrogen round the sample tube at exactly the same FIXED AND CONSTANT LEVEL as in volume calibration with helium.
9. Open T8 and keep the mercury level adjusted to the H-marks, and take the equilibrium pressure readings.

The change in pressure is due to:
a. the increase in volume on opening T8, and
b. the adsorption of some of the nitrogen in the system.

The pressure and volume of the system at equilibrium enable the quantity of nitrogen remaining unadsorbed in the system to be determined, and the difference between the value and the quantity of nitrogen originally trapped in the gas burette represents the amount adsorbed by the sample at the equilibrium pressure. This process is repeated for each of the calibration of H-marks[7].

10. Note the temperature of the air in the jacket around the gas burette, and record the atmospheric pressure.
11. Close T7 and very slowly open T10 to the vacuum line to lower the mercury level below the bend of the burette.
12. Remove the Dewar vessel of liquid nitrogen from around the sample tube and allow it to return to room temperautre.
13. Slowly open T7 and T2 to evacuate the system.

5.5 Closing Down the System

1. Set all taps to a closed position.
2. Switch off the mercury diffusion pump and allow it to cool before turning off the water supply to the pump.
3. Switch off the mechanical vacuum pumps and IMMEDIATELY open T11 and T1.
4. Remove the Dewar vessel of liquid nitrogen from around the vapour trap.

6. CALCULATION OF RESULTS

**The data is at present in the form of pairs of values of the amount adsorbed and the corresponding equilibrium pressure:*

a. Convert the amount adsorbed to an equivalent volume at STP per gram of adsorbent.

b. Apply the BET equation.

c. Calculate the specific surface area and the BET constant C.*

6.1 Calculation of the Volume of the Tubing between the top of H-mark and the Tap, from Helium PV data

ASSUMPTIONS

a. Gas pressure is sufficiently low to apply the ideal gas law.

b. The room temperature is constant.

Applying the Ideal Gas Law:

$$PV = nRT \qquad 3$$

where: P = the total volume occupied by the gas
≡ the known burette volume and unknown tubing volume.

Thus:

$$P(V_{tubing} + V_{burette}) = nRT \qquad 4$$

Rearranging equation 4:

$$V_{burette} = nRT.\frac{1}{P} - V_{tubing} \qquad 5$$

Therefore, if $V_{burette}$ is plotted on the y-axis and 1/P on the x-axis then the slope of the graph will be nRT and the negative intercept, $-V_{tubing}$.

6.2 Calculation of the Dead Space Volume

Similarly, this could be calculated by adding the tubing volume to the burette volume; thus:

$$V_{burette + tubing} = nRT.\frac{1}{P} - V_{dead\ space} \qquad 6$$

Determine dead space from a similar plot used for tubing.

6.3 Calculation of the Amount Adsorbed in the Nitrogen Adsorption Experiment

ASSUMPTIONS

a. Gas pressure is also sufficiently low to apply the ideal gas law.

b. The room temperature is constant.

Hence:

$$\Delta(PV)_{ads,n} = P_1V_{b1} - P_{en}(V_{bn} + V_{dead}) \qquad 7$$

where: $\Delta(PV)_{ads,n}$ = the amount adsorbed at room temperature, T_v, at n

P_1 = initial pressure of nitrogen dose

V_{b1} = initial total burette volume with mercury at H-mark 1

P_{en} = equilibrium nitrogen pressure at n

V_{bn} = burette volume with mercury at H-mark$_n$

V_{dead} = dead space volume

**Using the above equation the subsequent points on the isotherm may be evaluated.*

Convert to the equivalent volume adsorbed at STP, V_{ads}^{STP}, using equation:

$$\frac{\Delta(PV)_{ads,n}}{T_v} = \frac{76 \times V_{ads}^{STP}}{273.15} \qquad 8$$

Let $V_{ads}^{STP} = V$

P_o = saturation (pure) vapour pressure of nitrogen
= (atmospheric pressure from barometer + 4) cm Hg

Using the above data:

$$X = P/P_o$$

where: X = relative pressure which can be calculated for each value of P_{en}

Plot the X values on x-axis and $X_n/(V_n(1-X_n))$ on y-axis

The BET equation has the form

$$\frac{X_n}{V_n(1-X_n)} = \frac{1}{CV_m} + \frac{C-1}{CV_m} \cdot X_n \qquad 9$$

where: C = BET constant
V_m = the volume adsorbed in a complete monolayer at STP

The value of V_m is obtained from

$$V_m = 1/(\text{Slope} + \text{intercept})$$

where slope $= (C-1)/CV_m$

intercept $= 1/CV_m$

The specific surface area can be calculated from V_m using:

$$S = \frac{V_m \times 6.023 \times 10^3 \times \sigma_m}{22414 \times (\text{weight of sample})} \; m^2g^{-1} \qquad 10$$

where: σ_m = the adsorption cross-sectional area for nitrogen
$= 16.2 \times 10^{-20} m^2$

Calculations may be performed using Fortran programme stored in the PRIME computer[9]:

LOGIN.CALC, CMUC, your user number
password
A.CM>LIB
SEG. BET

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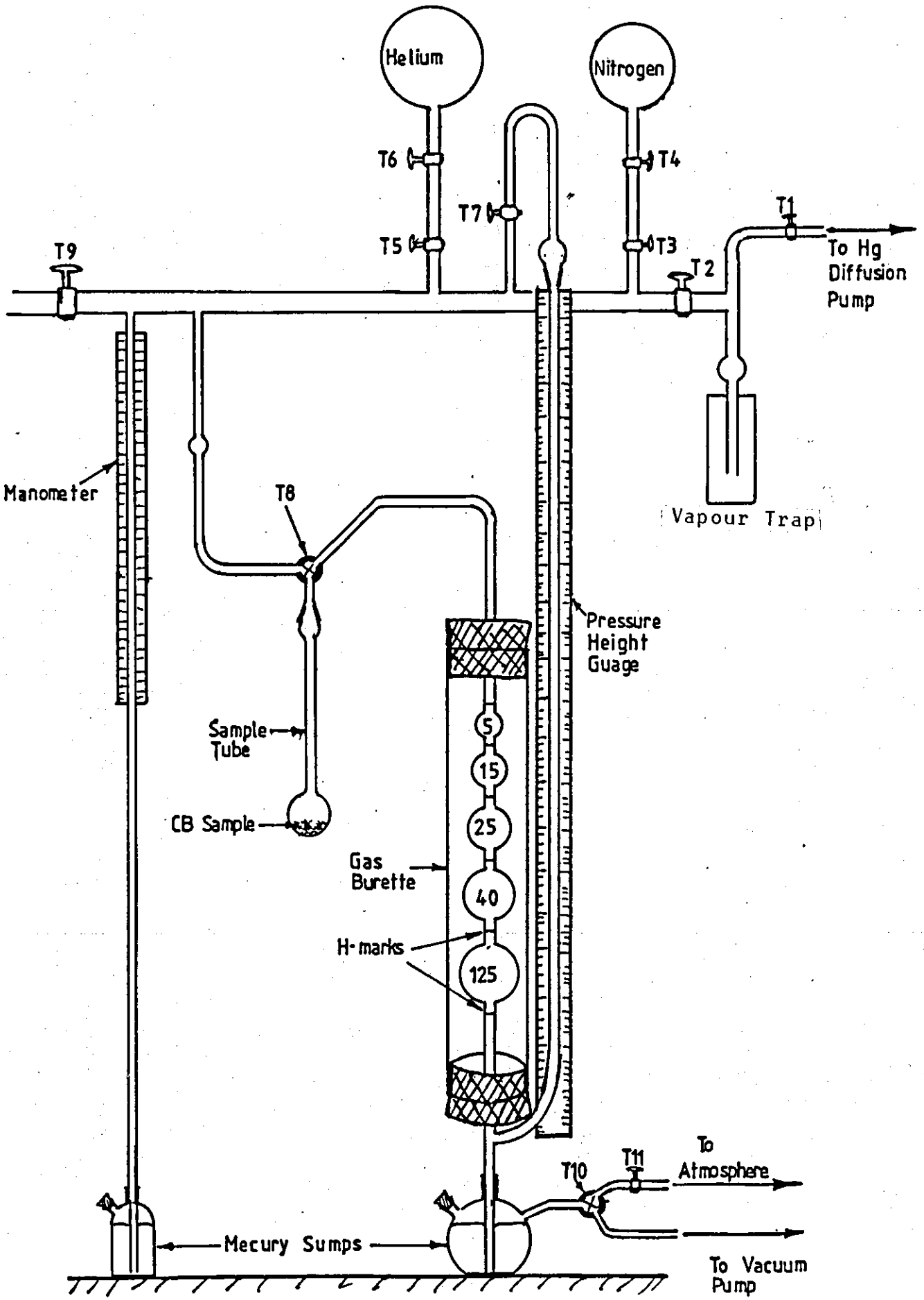
Fig. C1: B.E.T. Apparatus (A diagrammatic illustration)



NB. Not drawn to scale.

APPENDIX D

DESCRIPTION OF THE VIDEO INTERFACE BOARD (Fig. D1)

The interface board consists of FOUR basic units:

a. Analogue to Digital Converter ADC
b. Digital to Analogue Converter DAC
c. Sample and Hold S&H
d. Sync. Separator

The output signal from the television camera consists of three signals, an analogue video signal proportional to the light intensity and a mixed sync signal. The mixed sync signal consists of a series of line and frame sync pulses, the frame pulses occuring once every 20 milliseconds and the line pulses every 64.5 microseconds.

These pulses are separated from the video signal by the sync separator, both the line and frame pulses are interfaced to the data bus of the computer. The line pulses are used to provide a ramp of length 64.5 microseconds, the ramp and an analogue signal from the DAC are then compared by the comparator; if the two signals are equal, then a strobe pulse is produced which is used to enable the sample and hold. The output of the DAC is under the control of the computer program. Therefore, by increasing or decreasing the output voltage of the DAC, it is possible to adjust the delay between the start of the line pulse and the strobe pulse.

When the strobe pulse occurs, the sample hold is enabled, causing it to hold the value of the analogue video signal at its input, the sampled signal is now in a stable form for digitization by the ADC. Once the signal has been digitized, the computer can interrogate the ADC at any point in time before the next strobe pulse. The strobe pulse is recombined with the frame and line sync pulses to produce a visual indication on a TV monitor of the sampling position.

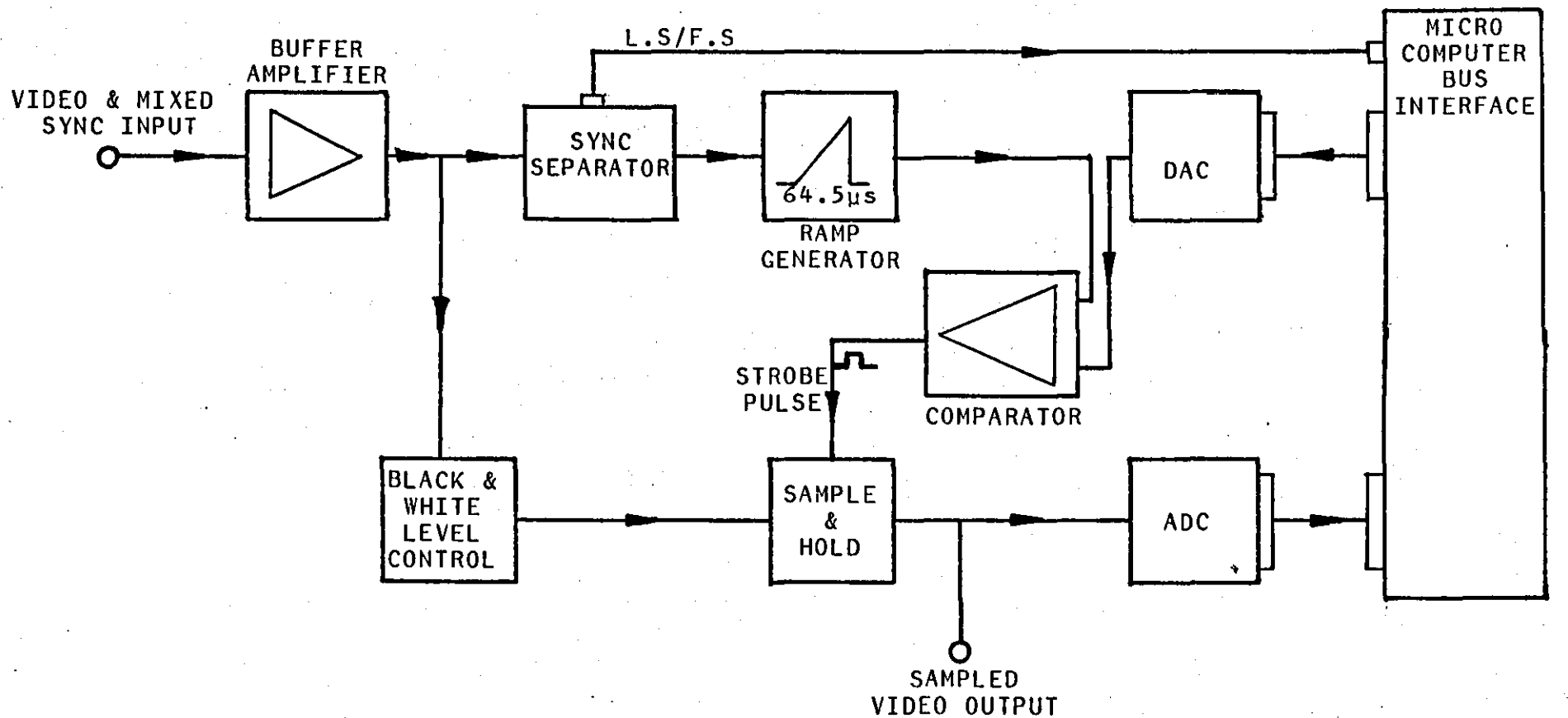


Fig. D1 Block Diagram of Video Interface Board

APPENDIX E

APPENDIX E1: EXPLANATION OF THEORY: Formation of chains of conducting elements

If a bag contains a mixture of black and white balls, and the volume fraction of the black balls is f_v, then, the probability, p, of picking out one black ball is $f_v^1 = f_v$; the probability of picking out two black balls simultaneously is f_v^2; therefore, the probability, p, of picking up 'n' black balls simultaneously will be f_v^n.

To find a value for 'n'. Consider that on a microscale each conducting element is in a very small volume of the mix, so that the volume ratio of the conducting element to the volume of the mix is f_v:1. For the bulk material, the properties are the average of the individual situation and may be obtained by considering the conducting elements as spherical with a mean diameter, d, and associated with the volumes of the mix also considered as spherical and of a mean diameter, D. By relating the mean diameters D and d.

$$\frac{D}{d} = \frac{1}{f_v^{1/3}} = \left[f_v^{1/3}\right]^{-1} \quad \text{or} \quad \left[\frac{D}{d}\right]^2 = f_v^{-2/3}$$

By random walk theory, if the diameter, D, is taken as the mean distance between ends of a chain of 'n' links of length, d, mathematically:

$$D = d(n)^{\frac{1}{2}} \quad \text{or} \quad \frac{D}{d} = n^{\frac{1}{2}}$$

$$n = \left[\frac{D}{d}\right]^2 = f_v^{-2/3}$$

The value of 'n' allows a probability 'p' to be obtained in terms of the single variable f_v

$$p = f_v^n = f_v^{f_v^{-2/3}}$$

It is taken that if a sufficient number of conducting element touch so as to form a chain across the insulation associated with a conducting element, and by employing average values the term 'p' represents the probability of conduction occuring through the bulk material.

APPENDIX E2: SOLUTION TO EQUATION COMBINATION.

$$\frac{D}{d} = \left[f_v^{1/3} \right]^{-1} \qquad 9.2$$

$$D = dn^{\frac{1}{2}} \qquad 9.3$$

From equation 9.3

$$\frac{D}{d} = n^{\frac{1}{2}}$$

By substituting $n^{\frac{1}{2}}$ for $\frac{D}{d}$ in equation 9.2

$$n^{\frac{1}{2}} = \left[f_v^{1/3} \right]^{-1}$$

By squaring both sides of the equation:

$$n^{\frac{1}{2}} = \left\{ \left[f_v^{1/3} \right]^{-1} \right\}^2$$

$$n = \left[f_v^{-1/3} \right]^2$$

$$n = f_v^{2/3} \qquad 9.4$$

Now:

$$p = f_v^{n} \qquad 9.1$$

By substituting for 'n' in equation 9.1

$$p = f_v^{f_v^{-2/3}} \qquad 9.5$$

APPENDIX E3: GEOMETRICAL FACTOR RELATING ELECTRICAL CONDUCTION TO PRACTICAL MEASUREMENT

In the kinetic theory of gases, complex molecular motion are resolved along the three main axes (x, y, z). Similarly, complex conducting chains in a mixture can be resolved to form a three-dimensional structure of equivalent conduction (fig. E1 A).

Consider a unit cube of conducting mixture (fig.E1 A). The value of conduction, measured between two opposite faces of the cube, will depend upon the number of chains terminating at the surface. By collecting together the chains along each axis, the unit cube is replaced by an equivalent network of straight chains set along the axes of the cube (fig. E1 B). The chains along each axis are then considered as being collected together to form the masses of square cross section, C^2, in a unit cube (fig. E1 C).

The volume of chain mass on one axis is C^2. The volume of the three chain masses is $3C^2$. But in the diagram (fig.E1 C) it can be seen that volume C^3 is in all and should only be counted once. Therefore, volume in unit cube is $3C^2-2C^3$. This is f_v, so $f_v = 3C^2 - 2C^3$.

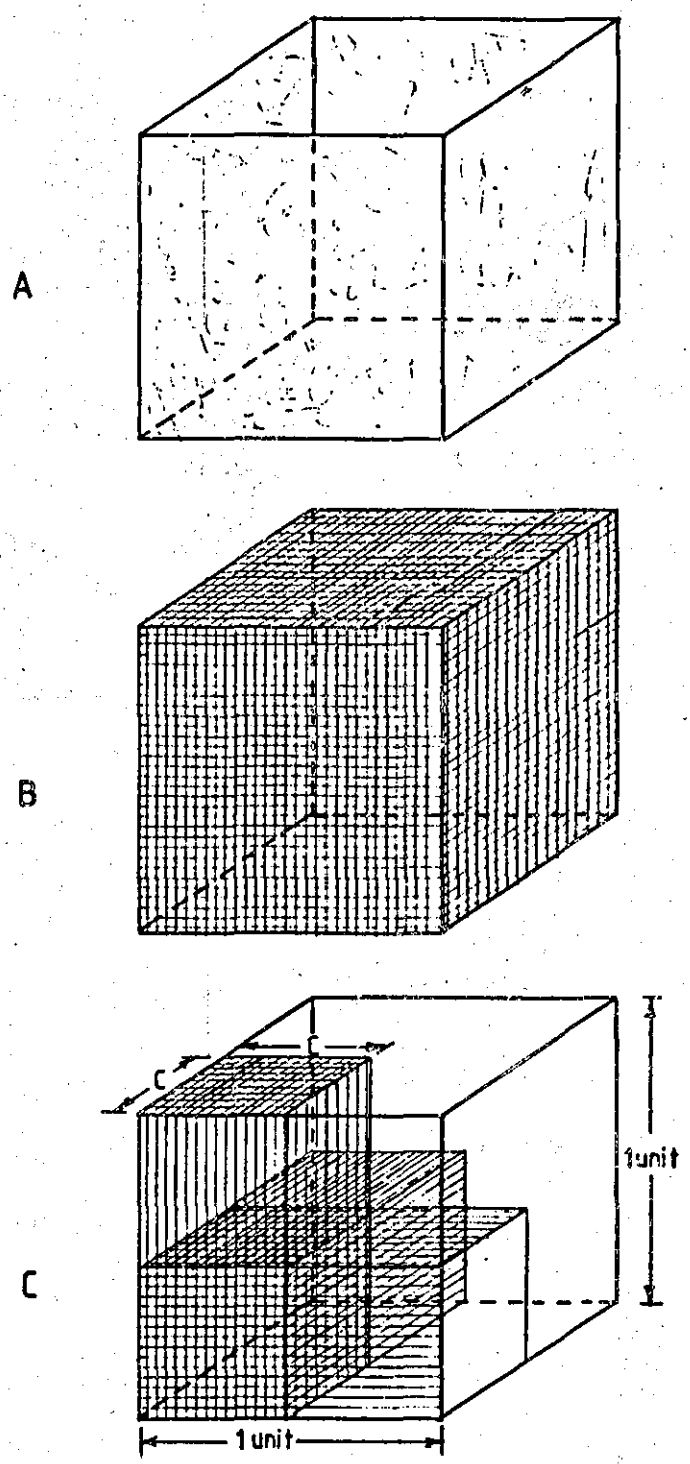


Fig. E1 Structural changes to allow resistance measurement.

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Publication and presentation arising from this Thesis

1. A paper entitled: *"Electrical resistivity in carbon black filled silicone rubber"*, had been published in the **Plastics and Rubber Processing and Applications**, Volume 1, Number 4, 1981.

2. A paper entitled: *"A relationship between practice and theory for electrical conductivity in carbon filled silicone rubber"*, was presented at a conference of the PRI Polymer Properties Group held in London on June 24, 1982.