PREPARATION OF USEFUL RAW MATERIALS FROM REFINERY SLUDGE AND ITS UTILISATION IN RUBBER PROCESSING

A thesis submitted by

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APRIL, 1998

Dedicated in memory of
my Parents

CERTIFICATE

This is to certify that the thesis entitled "Preparation of useful raw materials from Refinery sludge and its utilisation in rubber processing " is an authentic record of the research work carried out by Mr.Kochu Baby Manjooran.S under my supervision and guidance. No part of the work reported in this thesis has been presented for any other degree or diploma earlier.

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DECLARATION

I hereby declare that the thesis entitled "Preparation of useful raw materials from Refinery sludge and its utilisation in rubber processing " is an authentic record of the research work carried out by me under the supervision of Prof. (Dr.) A.P. Kuriakose, Head of the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology and no part of the work reported in this thesis has been presented for any other degree or diploma earlier.

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CHAPTER 1

INTRODUCTION

Petroleum, a mixture of organic compounds, comes from underground rock formations ranging in age from ten to several hundred million years. The process by which it is formed and developed is not yet completely known. Studies indicate that petroleum is formed mainly from microscopic-sized marine animals and plants. When these organisms died in water of low oxygen content, they did not decompose. Thus their remains sank to the bottom to be buried under accumulations of sediment. Their conversion to petroleum remains a subject of research even today. The theory held generally is that bacteria converted the fats of the marine life into fatty acids. These in turn were changed, by mechanisms still unknown, to the asphaltic material called kerogen. Then, over millions of years, heat and pressure, plus probably catalytic agents in the rock, changed the kerogen to crude oil and gas. Petroleum has been known and used by man for centuries. Explorers have found evidence of asphalt in buildings constructed more than 6,000 years ago in what today is Iraq Historical records indicate the use of mineral oil in various forms down through the ages. However it is only a little over 100 years since the beginning of the oil industry as it is known today, with the 1857 discovery of crude oil in Western Ontario and the boom which followed the discovery in Pennsylvania 2 years later. As the present study deals with the use of some petroleum byproducts, it will be appropriate to discuss petroleum and its refining in some detail at this stage.

1.1 Crude Oil

Crude petroleum is primarily[1] a liquid of widely varying physical and chemical properties. Common colours are green, brown and black and occasionally almost white or straw colour Specific gravity can range from 0.73 to 1 02, however most crudes are between 0.80 and 0.95 Data for a large number of crudes indicate kinematic viscosities from 0 007 to 13 stokes at 100° F, though most of them range from 0.023 to 0.23

Principal elements in crude petroleum are carbon and hydrogen, usually in a carbon-hydrogen ratio between 6 and 8. The hydrocarbons are mainly liquids and gases, with some solids in dispersion or solution. Among the many other materials usually present are small amounts of sulphur, nitrogen and oxygen in the form of hydrocarbon derivatives; traces of such metals as nickel, vanadium and iron and water (emulsified in the oil). Natural gas, the gaseous component of crude petroleum, may also be found some distance away from an oil pool, in separate wells, having been separated from the liquid by natural processes underground. It is composed mainly of light paraffins methane, ethane, propane, butane etc. plus some higher boiling paraffins, nitrogen, carbon dioxide and hydrogen sulphide.

A significant controlling factor in the process to be selected for refining is the type of crude oil to be run. Crudes are commonly classified according to the residue from their distillation which in turn depends on the relative contents of three basic hydrocarbons paraffins, naphthenes and aromatics. Depending upon the variations in hydrocarbon fractions of different crude oils, there are several differences in general properties as indicated in the table below

Property	Paraffin base	Asphalt base
API gravity	High	Low
Naphtha content	High	Low
Naphtha octane number	Low	High
Naphtha odour	Sweet	Sour
Kerosene smoking tendency	Low	High
Diesel-fuel knocking tendency	Low	High
Lube-oil pour point	High	Low
Lube-oil content	High	Low
Lube-oil viscosity index	High	Low

About 85 per cent of all crude oils fall into the following three classifications:

1 Asphalt-base: containing very little paraffin wax and a residue primarily asphaltic (predominantly condensed aromatics). Sulphur, oxygen and nitrogen contents are often relatively high. Light and intermediate fractions have high percentages of naphthenes. These crude oils are particularly suitable for making high-quality gasoline, machine lubricating oils and asphalt.

2. Paraffin base, containing little or no asphaltic materials are good sources of paraffin wax, quality motor lube oils and high grade kerosene. They usually have lower nonhydrocarbon content than do the asphalt-base crudes.

3 Mixed base, containing considerable amounts of both wax and asphalt. Virtually all products can be obtained, although at lower yields than from the other two classes.

1.2 Refining

Refining starts with crude oil distillation. Before crude oil is subjected to refining, it is passed under pressure into cylindrical tanks to remove gas, oil and sand particles. It is then washed with acid and alkali solutions one after the other to remove basic and acidic impurities respectively. The crude oil is then heated to 675 K in coiled pipes in a gas heated furnace and the vapours thus obtained are introduced into the fractionating tower. The fractionating tower is made of steel and is also called bubble tower. The tower is divided into number of compartments by means of shelves having openings. Each shelf is provided with an overflow pipe which keeps the liquid to a certain level and allows the rest to trickle down to the lower shelf.

The bottom of the fractionating column is at a much higher temperature than the top. As the vapours of the oil rise up the fractionating tower, they become cooler and condense in different shelves to form different fractions which are continuously drawn out[2]. The uncondensed vapours pass out of the tower at the top. The fractions, thus obtained consist of mixture of hydrocarbons having close ranges of boiling points. The actual number of fractions and their boiling point ranges depend upon their commercial uses and the source of the crude.

1.3 Sludge accumulation

A petroleum refinery is an organized and co-ordinated arrangement of manufacturing processes designed to provide both physical and chemical change of crude petroleum into salable products with the qualities required and in the volumes demanded by the market. A complete refining installation will include all necessary non-processing facilities: adequate tankage for storing crude oil, intermediates and finished products, a dependable source of electric power; waste disposal and water treating equipment and product blending facilities.

As of today, refineries encounter the problem of accumulation of oily sludge[3] due to pump failures, desalter malfunctioning, frequent oil draining from tankages and units, seepages due to failure of storage tanks and or pipe line ruptures below ground. Thus primary sources of oily sludge in an oil refinery are

a) Cleaning of crude, product and intermediate storage tanks
b) Cleaning of oil separators
c) Cleaning of surge ponds in waste water treatment plant
d) Cleaning of oil water sewer system
e) Cleaning of oil spills

As and when the sludge quantity increases and accumulates in various collection systems, surge ponds, pits etc., the sludge is removed and transferred to a lagoon or quarry This can be a potential hazard to the environment.

Oil content from tank bottom sludge can be recovered using conventional series of vats. The sludge is first taken in the vat and heated by steam in the coils to reach liquid state. During this process, high molecular weight oil separates from the sludge as top layer. The bottom most layer contains insolubles and the middle layer is aqueous. The oil flows to the next stage of separation in the same way and ultimately the recovered oil is taken into the crude tank for processing again. This batch process has been found to be very tedious. For high oil content sludge, bioremediation process also may not be suitable in view of the fact that the entire organics are converted into CO_2 and H_2O without any oil recovery.

Generally the sludge stored in the lagoon has three phases. The top layer of the lagoon has mostly free oil and oil-water emulsion with trapped foreign materials. The middle layer contains water and the bottom layer sand, clay etc. Since the oily sludge is composed of hydrocarbons, clay, sand, other inorganic matters, water etc., it cannot be disposed off without pretreatment[4]

As the present study also involves the preparation of industrial grade bitumen, it will be appropriate to discuss industrial grade bitumen and its preparation in some detail at this stage

1.4 Industrial Bitumen manufacture

Industrial bitumen of various grades are manufactured in India[5] from the vacuum residue of some imported crudes like Arab mix, Suez Blend etc. by air blowing in the presence of catalysts at temperatures ranging from 200-275^0 C. It has been shown[6] that dehydrogenation and polymerization are involved in air blowing and that oxygen is not added to the asphalt except in a very minor amount. It is also reported that naphthene aromatics are converted into polar aromatics and then to asphaltenes[7] The following is reported to be the scheme of transformations during air blowing of the raw material[8]

$$RH + O_2 \longrightarrow \dot{R} + HO\dot{O}$$

By the interaction of the radicals formed with new molecule of hydrocarbon, followed by disproportionation stable products are obtained.

$$\dot{R} + \underset{\substack{\text{unsaturated}\\ \text{compound}}}{R'H} \longrightarrow {}^{\bullet}RR'H$$

$$\dot{R}R'H + R''H \longrightarrow {}^{\bullet}RR'HR''H \xrightarrow{\text{disproportionation}} \text{Stable products}$$

As a result of the comparatively low concentration of hydrocarbon radicals, there is less probability of their recombination ($2\dot{R} \rightarrow R\text{-}R$) and the interaction of the radicals with oxygen takesplace to a smaller extent as follows.

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + R'H \longrightarrow ROOH + R'^{\bullet}$$

$$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$R'H + {}^{\cdot}OH \longrightarrow R'^{\cdot} + H_2O$$

$$RH + HOO^{\cdot} \longrightarrow R^{\cdot} + H_2O_2$$

$$H_2O_2 \longrightarrow 2\,{}^{\cdot}OH$$

$$R'H + {}^{\cdot}OH \longrightarrow R'^{\cdot} + H_2O$$

Many catalysts and oxidising agents can be used for augmenting the air blowing process of the vacuum residue. Since the agents used here cannot be recovered as such, technically they might better be termed chemical reactants than as catalysts. In any event, the general effect is to reduce blowing time, as well as to change the softening point-penetration relationship Reduction of blowing time is an economic incentive, whereas the change in the flow properties permits the manufacture to specifications. In his studies Grundermann[9] has shown that metal chlorides act as catalysts at relatively low temperatures; and without air blowing, causing condensation and polymerization reactions similar to those obtained in air blowing. He has shown that the best catalyst is $AlCl_3$ which converted naphthenic aromatic asphalts by treatment at 150° C for 3 hours into asphalts of medium to high hardness.

A survey of the literature on industrial bitumen will be of interest at this stage. It has been recognized for many years that petroleum products become changed in their physical properties by treating with oxidising agents or air. One of the first to report this fact was Abraham Gesner[10] in 1865 In 1876 W.P.Jenney[11] patented the process of treating sludge oil obtained in refining petroleum, with sulphuric acid, with a current of air at a temperature of

250°C He observed that a resinous substance was produced by the absorption of atmospheric oxygen by the oil. Later D.H.Dorsett oxidised coal tar by heating with manganese dioxide and ammonium chloride[12] C.L.Baillard oxidised a mixture of petroleum and oleic acid by means of air at 160°C[13] Heinrich Busse blew air through a heated mixture of asphalt and vegetable oils in the presence of nitric acid, sulphur or sulphur dichloride[14] F.Salathe blew heated air through melted native asphalt, either alone or in the presence of manganese dioxide or litharge[15] Schreiber proposed blowing melted asphalt, coal-tar pitch, fatty-acid pitch, wool-fat pitch etc., with air in the presence of manganese dioxide, with or without the addition of sulphuric acid, and finally adding formaldehyde[16]

Byerley[17] was the first to manufacture blown asphalt on a commercial scale by passing air through petroleum residues at temperatures between 400 and 600°F J W Hayward[18] and also G.C.K.Culmer[19] got patents for a similar process. According to this a mixture of petroleum residue and refined Trinidad asphalt or gilsonite was heated to 193°C and blown for forty hours at the rate of 15 to 30 cu.ft. air per minute per ton asphalt Non asphaltic petroleum will yield a good grade of blown asphalt if first subjected to high temperature and pressure, which helps to transform saturated hydrocarbons into polymerized unsaturated compounds[20] It is also found that blown asphalts of better temperature susceptibility and high penetration for a high fusing point, may be produced from petrolatum from which micro crystalline wax has been separated. This is achieved by dissolving in a mixture of benzol and methyl

ethyl ketone, chilling the solution, filtering, distilling off the solvent and finally blowing the residue[21] In a similar way, blown asphalts may also be produced from naphthenic residual oils or naphthenic derivatives (i.e., non-asphaltic and non-paraffinic in character) got by extracting petroleum with propane, SO_2, aniline, phenol[22] etc.

Several catalysts and oxidising agents can be used for augmenting the air-blowing process[23] They include manganese dioxide[24], finely powdered limestone[25], caustic soda, sodium carbonate[26] etc. Similarly sulphur[27], phosphoric acid[28] phosphorous pentoxide[29], lead oxide[30], chlorides of zinc, aluminium, iron[31] etc. when incorporated in the blowing mixture are found to improve the oxidation effect significantly. Also used are sulphates of Zn, Al, Fe & Cu[32], Chlorides of zinc or Al together with finely divided metals like Fe, Al, Mg[33] etc. Still many other methods reported in the literature are: blowing in the presence of aluminium or zinc stearate[34]; naphthenates or oleates of cobalt, chromium, manganese, iron, nickel, etc. in the presence of an alkali[35] or with lead oxide (PbO) and naphthalene[36] Another method reported is first blowing with air followed by heating with $AlCl_3$ / HCl[37]; blowing with quinone dioxime[38]; basic acetyl acetonate of manganese, cerium, nickel, cobalt, zinc[39] etc. or with copper, iron, manganese or cobalt soaps[40] Any excess catalyst present after the blowing operation must be removed by boiling the product with dilute HCl and washing with hot water[41]

Various gases are also used for blowing through the melted asphalt including air alone, carbon dioxide with or without air[42], ozone[43], a mixture of air or oxygen with NO_2 or SO_2[44], air containing upto 11.5 percent chlorine[45], chlorine followed by carbon dioxide[46] etc. Several mechanical expedients are suggested to facilitate the blowing process like agitating the asphalt during the process of blowing[47] The blowing of different mixtures has been suggested inorder to improve the characteristics of the finished product say imparting rubber like properties, greater toughness, increasing its resistance to temperature changes, increasing its weather resistance etc. It is reported that a product superior to straight blown asphalt can be obtained by heating the asphalt with a substance which releases oxygen, such as hydrogen peroxide, an alkyl peroxide, an aryl peroxide, a tertiary butyl hydro peroxide, benzoyl peroxide, diacetyl peroxide etc[48] The care with which blown asphalts are prepared largely influences their physical characteristics[49] Actually in the blowing operation the constituents are first converted into heavier oils, then into asphaltic resins and finally into asphaltenes the three changes usually occuring simultaneously[50] Also it has been found that the weather resistance of blown asphalts can be improved[51] by incorporating a small percentage of an oxidation inhibitor in the blown mixture such as nitro groups, sulphonic groups, halogen compounds etc.

1.5 Bitumenous paints

Almost half of the industrial bitumen manufactured is utilised for the manufacture of bitumenous paints. In this study we thought it worthwhile to try the bitumen obtained from refinery sludge for the preparation of bitumenous paints also

Bitumenous paints have the advantages of extreme durability and low cost, since bitumenous materials are less expensive than the other resins used for this purpose. The inherent physical and protective properties of industrial bitumen together with their ready availability and low cost makes them very useful as economical paint coatings. Large volumes of such bitumenous paints are used in industries for protective coatings. A limitation to their more extensive use is their dark colour but this is not a deterrent for many industrial coating requirements.

It was in the field of water proofing and protection against corrosion that industrial bitumen first earned recognition and importance even many centuries ago. Even in those days asphalt was used for applications involving continuous contact with fresh water and sea water as for example, the lining of water storages and public baths and the caulking of ships. These uses continued and increased so that today asphalt is accepted invariably and almost without limitations in water proofing, road building, roofing, industrial surface coatings, industrial flooring and long distance oil and water pipeline coatings[52]

Bitumenous lacquers are composed of a bitumenous base, a volatile solvent[53], with or without the addition of vegetable drying oils, resins, mineral fillers and pigments[54] and are intended to dry or set by the spontaneous evaporation of the solvent. If any vegetable drying oil is present it will contribute little, if at all, to the drying of the lacquer, although it will undoubtedly exert a toughening effect on the coating, which will become more pronounced in time[55] These lacquers are known commercially as "solvent paints" The distinguishing characteristic between a bitumenous lacquer and a bitumenous varnish is that the former will set to a firm coat upon the evaporation of the solvent, whereas the hardening of the latter is contributed largely by the oxidation of the vegetable drying oil, which is present in the base in substantial proportions. The bitumenous base may include native asphalts, asphaltic petroleums, blown petroleum asphalt[56], residual asphalt, sludge asphalt[57], chlorinated blown asphalt[58] etc. Bases may contain in addition to bitumenous substances, a resin with[59] or without a mineral filler; or a coloured pigment. For instance, asphalt combined with phenol-formaldehyde resin[60] is very compatible.

The solvents[61] ordinarily used for the manufacture of bitumenous paints are petroleum products[62] among which gasoline, naphtha (benzene) and kerosene are the most largely used. Among the naphthas there is a series of products boiling within a small temperature range, termed "close-cut distillates" and sold as mineral spirits[63] The gasolines have the lowest flash and boiling points and the poorest solvent power whereas the kerosenes have a higher flash and boiling point and a correspondingly greater solvent action, the naphthas falling in between the two. The solvent properties of petroleum distillates may be improved by adding 4 percent of butyl alcohol, diacetone alcohol or esterified glycols[64] The weight of solvent in commercial bitumenous solvent compositions ranges from 20 to 80 percent. The smaller percentages are used in heavy bodied paints intended for coating masonry, for sealing the joints of composition roofing and for application to porous surfaces. Light bodied paints containing the larger percentages of solvent are used where it is desired to secure great penetration and rapid drying properties or where the paint is used for dipping purposes.

1.6 Rubber Compounding and Vulcanization

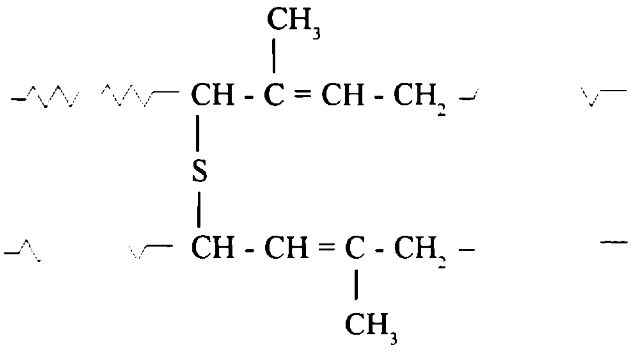
As the following some chapters of the thesis discuss the use of refinery sludge in rubber, an introduction on rubber and rubber vulcanization will be useful here.

Vulcanization is the technique of transforming rubber, by some treatment, from a plastic substance of very low strength and breaking elongation, to a resilient highly elastic material of considerable strength. From the chemical view point, vulcanization can be defined as a process where the flexible, discrete rubber chains are linked together by crosslinking reactions to give a three dimensional network.

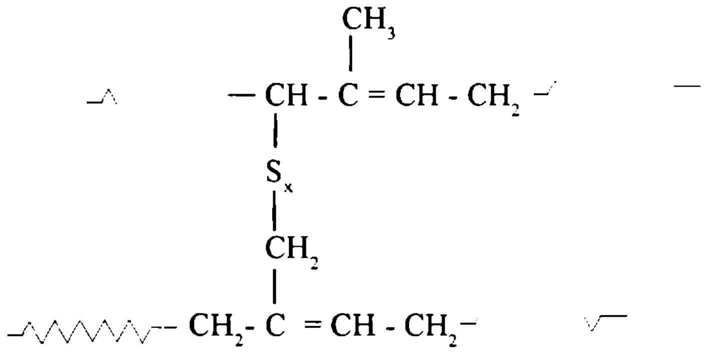
Sulphur vulcanization, the main method used, was discovered by GoodYear, in the USA, in 1844 and by Hancock, in the UK[65], at about the same time Vulcanization of rubber with sulphur alone is a very slow process and requires several hours or even days to acquire optimum curing depending on the nature of rubber and the temperature of vulcanization. This gives rise to vulcanizates of only very low physical and mechanical properties. Moreover they have a strong tendency to revert and their resistance to ageing is very poor Sulphur bloom is also a usual phenomenon Hence vulcanization with sulphur alone is of no technological importance at present. Oenslanger has shown that small amounts of aniline, added to a rubber/sulphur formulation can enhance the rate of vulcanization significantly and can also improve the final vulcanizate properties. Later discoveries showed that a wide variety of amines can function in the same way[66]

An important step before vulcanization is the mixing of rubber with various ingredients, which is usually referred to as compounding. The major objectives of compounding are to facilitate processing and fabrication, to acquire the required balance in vulcanizate properties and to provide durability, all at the minimum cost. The ingredients, usually added to rubber during compounding are processing aids, accelerators and activators, fillers, antidegradants and other additional ingredients. The compounded stock is then vulcanized under heat and pressure. The way compounding and vulcanization are done varies from rubber to rubber depending on whether it is saturated or unsaturated, natural or synthetic etc For eg., synthetic rubbers are slower curing[67] than natural rubber and hence more accelerators are to be added during the compounding of the former. This is because of the comparatively lower unsaturation levels and lesser active chemical bonds of synthetic rubbers. Moreover scorch problems are comparatively less in synthetic rubbers than in natural rubber stocks. Again natural rubber is more stress crystallizable than synthetic rubbers. Gum vulcanizates of natural rubber have good strength whereas reinforcing fillers are required to give strength to synthetic rubber vulcanizates. Both types of rubbers need mastication prior to compounding but synthetic rubber mastication takes longer time. Generally, for vulcanization synthetic rubbers require higher temperature while a rise in temperature leads to degradation in the case of natural rubber. Compounding ingredients are almost the same for natural and synthetic rubbers but the amounts vary especially that of sulphur and accelerator.

The chemistry of both accelerated and unaccelerated sulphur vulcanization is complex and difficult to investigate, and it is by no means fully understood. The major overall effect is to introduce mono-, di- or polysulphide crosslinks into the polymer at carbon atoms adjacent to the double bonds. eg.,



$$\begin{array}{c} \sim\sim CH - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \sim\sim \\ | \\ S \\ | \\ \sim\sim CH - CH = \underset{CH_3}{\underset{|}{C}} - CH_2 - \sim\sim \end{array}$$



$$\begin{array}{c} \sim — CH - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 - \sim \\ | \\ S_x \\ | \\ CH_2 \\ | \\ \sim\sim CH_2 - C = CH - CH_2 - \sim \end{array}$$

The accelerator sulphur ratio determines the efficiency by which sulphur is converted into crosslinks, the nature of crosslinks and the extent of main chain modification. Depending upon the sulphur accelerator ratio the sulphur vulcanizing systems can be categorised as[68].

a) the conventional or high sulphur vulcanization system where sulphur is added in the range of 2.0-3.5 phr (parts per hundred rubber) and the accelerator is added in the range of 1.0 0.4 phr.

b) the efficient vulcanizing (EV) system where sulphur is added in the range of 0.3 0.8 phr and accelerator in the range of 6.0 2.5 phr.

c) the semi EV system where sulphur is added in the range 1 0 1.8 phr and accelerator in the range 2.5 1 0 phr.

Apart from sulphur vulcanization, other vulcanization systems in use are[69].

Sulphurless vulcanization: Here vulcanization is effected without elemental sulphur, by the use of thiuram disulphide compounds (accelerators) or with selenium or tellurium. This produces products which are more resistant to heat ageing. With the thiuram disulphides, efficient crosslinks containing only I or 2 sulphur atoms are formed, and in addition the accelerator fragments act as antioxidants.

Peroxide vulcanization: The saturated rubbers cannot be crosslinked by sulphur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers. When the peroxides decompose, free radicals are formed which gives rise to crosslinks. This type of crosslinks only involve carbon carbon bonds and are quite stable. They are also formed by gamma and X radiations.

Other systems: Some elastomers can be vulcanized by the use of certain non-sulphur bifunctional compounds which form bridge type crosslinks. For eg., neoprene with metal oxides or butyl rubber with dinitrosobenzene.

1.7 Process Aids

One of the important components of compounding is the process aid. As the present work also involve the use of refinery sludge as a processing aid in rubber a brief summary of process aids is given below

The function of the processing oil in rubber compounding is to provide better processability during the addition of fillers. They act as lubricants between the rubber chain molecules and improve the processing properties. Generally processing oils are rubber soluble at the processing temperature. However, they readily exude at relatively low levels and thereby reduce the tackiness of the rubber compound. The efficiency of the processing oil depends on their chemical structure and physical properties as well as on the type of rubber used. The physical properties of the processing oils are important for practical applications in high processing and application temperatures. High boiling point, low vapour pressure and chemical stability are necessary. The gel point is important for the elastic properties of the vulcanizate at low temperature while viscosity influences the hardness.

Use of vegetable oils in rubber compounding has also been reported[70] Certain unsaturated oils such as linseed, rapeseed and safflower oils were used in neoprene rubber to improve properties like low temperature flexibility and tear resistance. Vegetable oils are also used for producing factice by treating with sulphur. Since the composition of the oil[71] has an effect on the property of the rubber compound in which it is included, various identification methods have been developed, of which the major two are (1) the molecular type analysis and (2) the carbon type analysis.

In the molecular type analysis (ASTM D 2007) the oil is absorbed in a chromatographic column containing clay and activated silica gel and eluted with pentane. Material insoluble in pentane is considered to be asphaltene. This method cannot clearly distinguish the amount of aromaticity and naphthenicity

In carbon type analysis, the viscosity gravity constant (VGC) and the refractivity intercept of the oil are measured[72]

$$VGC = \frac{10G - 0.0752 \log (V-38)}{10 - \log (V-38)}$$

where G is the specific gravity of the oil at 60^0 F and V is the Saybolt viscosity at 100^0 F

Refractivity intercept = n_D^{20} $0.5d_4^{20}$,
where n_D^{20} is the refractive index at 20°C for D line of sodium and d_4^{20} is the density at 20° C

These constants are plotted on a unique triangular graph. From their points of interception, the percentage of carbon that is naphthenic, aromatic and paraffinic can be calculated. High value of VGC represents high aromaticity

Another identification method is the aniline point. It is the temperature at which the oil is miscible with aniline. A low aniline point shows high aromaticity and it is inversely proportional to VGC. The rate at which mixing together of ingredients is accomplished, what can be called oil take up time, increases with increase in aromaticity in an oil. Also the dispersion of carbon black is better Naphthenic oils are second and paraffenic oils are last. At least in the early stages higher aromatic oil give faster cure rate. This is attributed to the heterocyclic sulphur and nitrogen compounds they contain. Tensile and tear strength increases with aromatic content and this may be due to better dispersion of 'C' black. But stain and discolouring problems are more in aromatic oil due to the presence of heterocyclic compounds. Highly naphthenic oils have excellent colour and heat stability Paraffenic oils have excellent resistance to discolouration by UV light and have good low temperature flexibility

Processing oils are added together with fillers for their easy incorporation and as a processing aid. They have no chemical reaction with rubber but function by modifying the physical properties of either the compounded rubber or the vulcanizate. The molecules of such additives distribute themselves between and solvate the polymer molecules, thus reducing the attractive forces between them. The consequent increase in mobility of the polymer molecules lead to, for example, a reduction in the glass transition temperature, increased flexibility and reduced melt viscosity. The material used as processing aid usually at 2 10 phr level must be completely compatible with the rubber and the compounding ingredients. Incompatibility will result in poor processing characteristics and or bleeding in the final product. Processing aids can also increase elongation, reduce hardness, improve tack etc. depending on the amount and type used and the rubber involved. Mineral oils like aromatic and naphthenic are the most common processing oils in rubber industry Petroleum bitumen commonly known as mineral rubber are also used as low cost low gravity extenders and process aids[73]

1.8 Scope and Objectives of the Present Work

In petroleum refineries, a lot of sludge gets accumulated at the bottom of the tanks where crude oil is stored. This is taken out during periodical cleaning of tanks and dumped separately in ponds. Also the bottom portion left behind in furnace oil tanks, LSHS (Low Sulphur Heavy Stock) tanks, asphalt tanks etc. is also taken out at the time of their periodical cleaning and dumped at the above mentioned ponds. Together, whatever heavy oil spillages occuring during the operation of a petroleum refinery is also dumped at the above places. Thus thousands of tonnes of oily sludge is accumulated in the quarry ponds of different refineries. This sludge is kept exposed to the atmosphere in all the seasons and creates serious disposal problems also.

A study on the constituents of this sludge has shown[74] that it contains approximately 25% water, 5% inorganic solids and the rest about 70% hydrocarbons. Also the hydrocarbon part is reported to contain 7.8% by weight of asphaltenes and has a gross calorific value, of the order of 10,300Kcal/Kg. The ash content is 4.8% and percentage weight of the different elements in the ash is Fe=23 49; Al=10.57; Ca=1.64, Na=0.57; K=0 46, Ni=0.12; V=0 23, Mg=0.65, Zn=0.21, Ti=0.53 and Mn=0.10. The different methods for the disposal of the sludge recommended in earlier studies are (1) burning in rotary incinerator, (2) burning in step furnace type incinerator (3) microbial treatment to convert hydrocarbons to combustible gases (4) use of refinery sludge in delayed coker and (5) separation of water and sediments at elevated temperature by the use of diluent and emulsifier and subsequent burning of hydrocarbon sludge in furnaces. The above methods help mainly for the disposal of the sludge and not for its effective utilisation. So it was thought worthwhile to see whether this sludge can be utilised in some useful manner. In view of the fact that the refinery sludge mentioned earlier contains many useful hydrocarbons and that it accumulates in large quantities in the refinery creating a disposal problem; it was thought useful to study the possibility of converting this sludge into some useful raw materials like industrial bitumen avoiding the conventional air blowing process. In the present study attempt was also made to separate out the lighter oil fractions from the sludge, characterise them to see whether they are suitable to be blended with the appropriate refinery streams. Keeping this view in mind the sludge obtained was first purified and dehydrated. This was further subjected to vacuum distillation to separate out the light oils. About 17% of the dehydrated sludge was recovered as lighter oil. The residue left was treated with varying amounts of different catalysts like sulphur, $FeCl_3$, P_2O_5 and $AlCl_3$ at different temperatures ranging from 200 to 275°C, for time periods varying from one to 3 hours, The products obtained were tested for different parameters like softening point, penetration, ductility etc. and the results compared with different grades of industrial bitumen. The use of the industrial bitumen so prepared was also tried in the production of bitumenous paints.

As a second part of the study, the purified sludge which contains a good amount of bitumen, wax and lighter oils, was tried as a substitute for processing oil in natural rubber compounding. The study becomes all the more important because petroleum oils used as processing aids are becoming prohibitively costly whereas refinery sludge is a dumped waste. A viscous petroleum extender or plasticizer of low diffusibility and low volatility will be highly beneficial in rubber compounding because of the considerable extent of oil migration during service life[75] and due to the possibility of loss of oil through evaporation under high temperature operating conditions if low volatile oils are used[76] It has been reported that petroleum pitch 170 and 240 [in accordance with their softening points in ^{0}F as measured by the ASTM "Ring and Ball" method (D-36)] offers promise as compatible replacements[77] for aromatic extender oil in different rubbers. Both pitches imparted to the vulcanizates pronounced physical property changes not encountered with the usual extender oils or plasticizers. Although these pitches are solid at normal temperatures, they are readily incorporated into rubber systems under usual mixing conditions.

Since a lot of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis synthetic rubbers, refinery sludge was used as a processing aid in a synthetic rubber viz. SBR (styrene butadiene rubber) also Compared to natural rubber, synthetic rubbers lack tack and green strength and this has consequence in tyre building, particularly with radial tyres. Whilst natural rubber is more or less crystalline with a Tm of about 50^{0}C, synthetic rubbers are highly amorphous. Although crystallinity in natural rubber is reduced by the presence of crosslinks and of fillers and other additives, it still crystallises on extension giving a rubber of good tensile strength, even with gum stocks. On the otherhand gum vulcanizates of the synthetic rubbers are generally weak and it is essential to use reinforcing fillers such as fine carbon black to obtain products of high tensile strength. Again, since SBR is slower curing than natural rubber, more amount of accelerator is required compared to NR.

Known elastomers do not exhibit all the properties desired, and so, are often blended with a second elastomer during processing[78] About 75% of all elastomers are used as blends rather than alone. For eg: SBR has better crack resistance, wet grip and weather resistance than natural rubber and NR has better strength, lower heat build up and shows better performance at low temperature compared to SBR. Hence blends of NR and SBR are used extensively in rubber product manufacture[79] In the present study, we also made an attempt to study the properties of NR SBR blends when refinery sludge is used as a processing aid.

We used sulphur accelerated systems of vulcanization for the present study Different mixes were prepared using this sludge and also control mixes using aromatic oil. Processability of the various mixes was studied in a Brabander Plasticorder. The mixes obtained from these formulations were evaluated for their different cure characteristics and the vulcanizates were evaluated for tensile and other physical properties. The properties of the experimental mixes were compared with those of the control mixes. Heat ageing characteristics and chemical crosslink density of the different vulcanizates were also evaluated.

Chapterwise description of the above study is as given below

Chapter I Gives a general introduction about crude petroleum oil, its refining, refinery sludge, industrial bitumen manufacture, bitumenous paints, vulcanization systems of rubber, and use of process aids in rubber vulcanization.

Chapter II	Explains the various experimental procedures adopted in the present study.
Chapter III	**Part I** This part of the chapter deals with the utilisation of refinery sludge for lighter oils and industrial bitumen. **Part II** Application of industrial bitumen prepared from refinery sludge for the production of bitumenous paints.
Chapter IV	Detailed description on the use of purified refinery sludge as processing aid in sulphur vulcanization of natural rubber This involves the study on compounding, cure characteristics and vulcanizate properties of the experimental and control mixes.
Chapter V	Refinery sludge as a processing aid in the compounding and vulcanization studies of styrene butadiene rubber.
Chapter VI	This chapter explains the use of purified refinery sludge in sulphur vulcanization of NR SBR blends.
Chapter VII	An overall summary and conclusions of the present study

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

A detailed description of the materials used and the experimental procedures adopted are given in this chapter

2.1 MATERIALS USED

2.1.1 Refinery Sludge

The oily sludge accumulated in the sludge pond of Cochin Refineries Ltd. was obtained by the courtesy of Cochin Refineries Ltd., Ambalamugal, Kerala.

2.1.2 Natural Rubber (NR)

Natural Rubber used in the present study was solid block rubber conforming to ISNR 5, of Mooney Viscosity (M_L 1+4, 100°C) equal to 85, obtained from Rubber Research Institute of India, Kottayam. It had the following specifications.

Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, P_0, min.	30.00
Plasticity retention index (PRI) min.	60.00

2.1.3 Styrenebutadiene Rubber (SBR)

Styrenebutadiene rubber used was synaprene 1502, obtained from Synthetics and Chemicals Ltd Bareilly, U P India. The Mooney

Viscosity (M_L 1+4, 100°C) was 52.0 It had the following specifications.

Volatile matter, % by mass	0.23
Ash, % by mass	0.24
Organic acid, %	5 53
Soap	Traces
Bound Styrene	24.30

2.2 OTHER INGREDIENTS

2.2.1 Zinc oxide (activator)

Zinc oxide supplied by M/s Meta Zinc Ltd. Bombay of the following specifications was used.

Specific gravity (g/cm^3)	5.5
Zinc oxide content, % by mass	98.0
Acidity (%)	0.4
Loss on heating (2 hrs at 100°C, %)	0 5

2.2.2 Stearic acid (Coactivator)

Stearic acid supplied by Godrej Soaps (Pvt) Ltd., Bombay of the following specifications was used.

Melting point	65°C
Acid number	200
Iodine number	9 05
Specific gravity (g/cm^3)	0.85
Ash (%)	0 10

2.2.3 Tetramethyl thiuram disulphide (accelerator)

Tetramethyl thiuram disulphide (TMTD) supplied by Polyolefins Industries Ltd., Bombay of the following specifications was used.

Melting point	138°C
Specific gravity (g/cm^3)	1.3
Ash, % by mass, max.	0.5
Moisture, % by mass, max.	1.0

2.2.4 Mercaptobenzthiazyl disulphide (accelerator)

Mercaptobenzthiazyl disulphide (MBTS) supplied by Bayer Chemicals, Bombay of the following specifications was used.

Specific gravity (g/cm^3)	1 51
Melting point	165°C

2.2.5 Sulphur (Crosslinking agent)

Sulphur supplied by M/s Standard Chemicals Co. Pvt. Ltd., Madras of the following specifications was used.

Specific gravity (g/cm^3)	2.05
Ash %	0 10
Solubility in CS_2	98%

2.2.6 Aromatic oil (Process oil)

Aromatic oil supplied by Hindustan Organic Chemicals, Cochin of the following specifications was used

Specific gravity (g/cm^3)	0.98
Aniline point (^{0}C)	43.00
Ash content, % by mass	0.01
Viscosity gravity constant	0 96

2.2.7 High abrasion furnace black (N330)

High abrasion furnace black (N330) supplied by M/s Carbon and Chemicals India, Ltd. Cochin of the following specifications was used.

Appearance	Black granules
DBP absorption	102±5cc/100g
Pour density	376 0 Kg/m^3
Iodine number	82
Loss on heating (per hour at 25^{0}C) max.	2.5%

2.2.8 Ferric chloride Laboratory Reagent grade from Nessler's Laboratories was used.

2.2.9 Aluminium chloride (anhydrous) Supplied by E.Merck (India) Ltd., Bombay was used

2.2.10 Carbon disulphide Laboratory Reagent grade of S D Fine chemicals private Ltd was used.

2.2.11 Phosphorous pentoxide Obtained from E.Merck (India) Ltd., Bombay was used.

2.2.12 Asbestos Laboratory reagent grade from Qualigens Fine chemicals was used.

2.2.13 Toluene Laboratory reagent grade of Ranbaxy Laboratories was used

2.2.14 Mineral turpentine Obtained by the courtesy of Cochin Refineries Ltd. Ambalamugal.

2.2.15 Cashew nut shell liquid (CNSL) Obtained from Resins India, Palai.

2.2.16 Formaldehyde Formaldehyde solution of B.D.H (37%) was used for the investigation.

2.2.17 Hexamethylenetetramine Hexamethylenetetramine from Riedel was used for the investigation.

2.2.18 Petroleum heavy naphtha Obtained by the courtesy of Cochin Refineries Ltd., Ambalamugal.

2.3 EXPERIMENTAL PROCEDURE

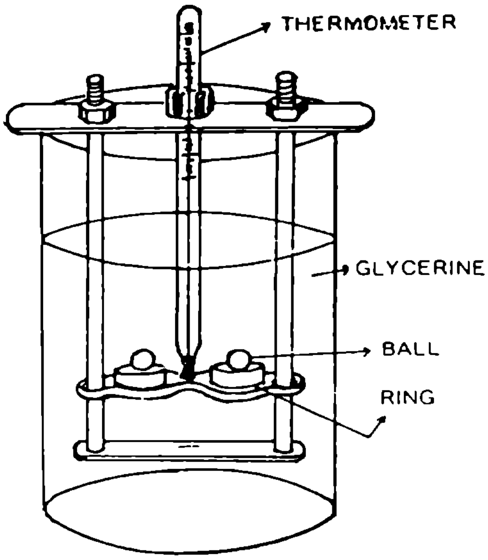
2.3.1 Purification of refinery sludge

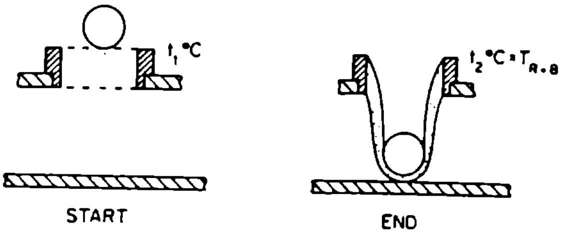
To remove water, inorganic materials etc. the sludge (150 Kg) taken from different portions of the quarry pond was heat treated in a barrel of 200 litres capacity fitted inside with steam coils. It was maintained at 110±10°C for 12 hours when the sludge was fully dehydrated The remaining hot oil was then passed through strainers (60 and 40 mesh) to remove solid impurities. The purified sludge thus obtained was highly viscous at room temperature.

2.3.2 Determination of Softening Point (IP 58/82)

The softening point is the temperature at which the substance acquires a particular degree of softening under specified conditions of the test.

The material is heated to a temperature 75 to 100°C above its expected softening point. It is stirred until it is completely fluid and free from air bubbles and water and filtered through IS sieve 30. The rings, previously heated to a temperature approximately to that of the molten material, were kept on a metal plate coated with a mixture of equal parts of glycerine and dextrose The ring was then filled with sufficient melt to give an excess above the level of the ring when cooled After cooling for 30 minutes in air, the material is levelled in the ring by removing the excess with a warmed sharp knife.



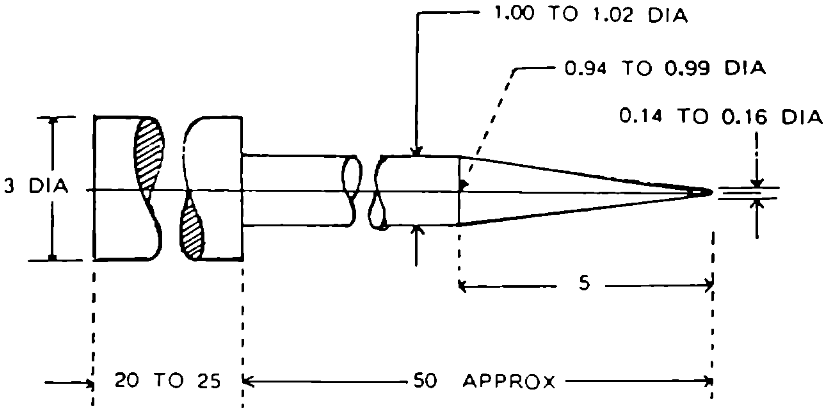


The apparatus is assembled with the rings, thermometer and ball guides in position The bath was then filled with distilled water (For materials having softening point below 80°C) to a height of 50 mm above the upper surface of the rings The bath is then brought to a temperature of 5°C and maintained at that temperature for 15 minutes. Then the ball previously cooled to a temperature of 5°C is kept by means of forceps, in each ball guide. Now heat is applied to the liquid with stirring so that the temperature rises at a uniform rate of 5 0±0 5°C per minute till the material softens and allows the ball to pass through the ring For materials of softening point above 80°C glycerine is used in place of water in the bath and the starting temperature of the test is 35°C. For each ring and ball the temperature shown by the thermometer is recorded at the instant the sample surrounding the ball touches the bottom plate of the support. This temperature is reported as softening point.

2.3.3 Determination of Penetration (IP 49/79)

The penetrometer of Precision Scientific Co (USA) was used for the purpose. Penetration of a bituminous material is the distance in tenths of a millimetre that a standard needle will penetrate vertically into a sample of the material under standard conditions of temperature (25°C), load (100 g) and time (5 s)

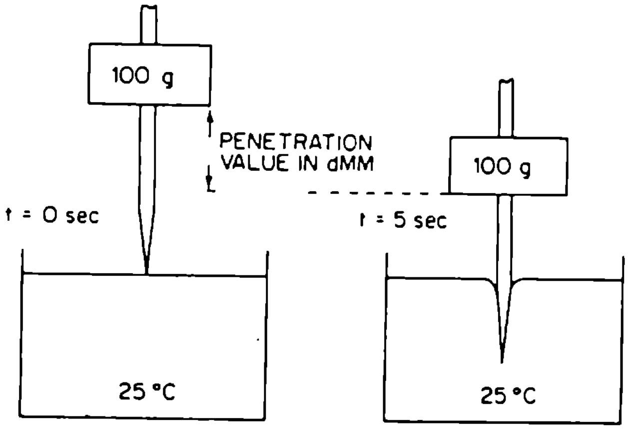
The penetration needle is a highly polished, cylindrical hard steel rod, coaxial, having the following shape, dimensions and tolerances as shown in the figure below



All dimensions in millimetres

The needle is provided with a shank about 3 mm in diameter into which it is fixed immovably The taper shall be symmetrical and the point shall be 'blunted' by grinding to a truncated cone

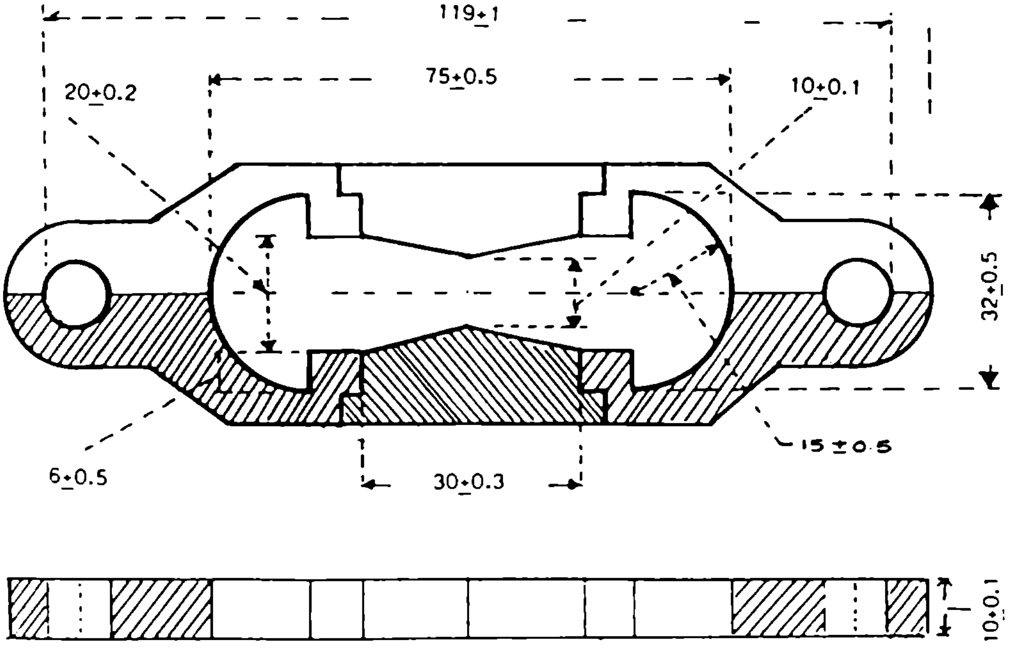
Preparation of sample The material was softened to a pouring consistency between 75°C and 100°C above the approximate softening point and stirred thoroughly till it was homogeneous and was free from air bubbles and water The melt was then poured into the container to a depth 10 mm in excess of the expected penetration. The sample was protected from dust and allowed to cool at a temperature between 15 to 30°C for 1 to 1½ hours. It was then placed along with the transfer dish in the water bath at 25 ± 0 1°C and allowed to remain for another 1½ hour The sample was then placed on the base of the penetrometer and the needle point was kept in contact with the surface of the sample. The needle was then loaded with the weight required to make a total moving weight (i e the sum of the weights of the needle, carrier and superimposed weights) of 100 + 0 25 g



The pointer in the dial was brought to zero Little water at 25°C was poured on the surface of the sample and released the needle for exactly five seconds. The distance in tenths of a millimetre vertically penetrated the sample is reported as the penetration. Two more determinations are made at points on the surface of the sample not less than 10 mm apart and not less than 10 mm from the side of the dish. The mean value of these three determinations is reported as penetration.

2.3.4 Determination of ductility (IP 32/55)

The ductility meter of Humboldt Manufacturing Company, (USA) was used for the purpose. The ductility of a bituminous material is the distance in centimetres to which it will elongate before breaking when the ends of a briquette specimen of the material of the specified form is pulled apart at a specified speed and at a specified temperature. The test was conducted at a temperature of 27 ± 0.5°C and at a rate of pull of 50 ± 2.5 mm per minute. The bituminous material was heated to a temperature about 75 to 100°C above the approximate softening point, till it became thoroughly fluid. It was then filtered through IS sieve 30 and then poured to the mould of the type (total length = 75 mm,



All dimensions in millimetres

distance between the clips = 30 mm, width at mouth of clip = 20 mm, and width at minimum cross section = 10 mm) as shown above.

The mould was assembled on a brass plate and inorder to prevent the material under test from sticking, the surface of the plate as well as interior surface of the sides of the mould were coated with a mixture of equal parts of glycerine and dextrin. The material was poured as a thin stream back and forth from end to end of the mould until it was more than level full The mould containing the sample was then allowed to cool at room temperature for 30 to 40 minutes and then placed in a water bath maintained at the specified temperature for 30 minutes. The excess bitumen was then cut off by means of a hot, straight edged knife, so that the mould was just level full.

The brass plate and mould with briquette specimen was placed in the waterbath at 27 ± 0.5^{0}C for about 85 to 95 minutes. The briquette was then removed from the plate, the side pieces were detached and the rings at each end of the clips were attached to the pins in the testing machine. The two rings are then pulled apart horizontally at a uniform speed of 50 ± 2.5 mm per minute until the specimen ruptures. The density of water in the bath was adjusted by the addition of sodium chloride so that the bituminous thread formed during the test does not touch the bottom of the bath at any time during the test. The distance in centimetres through which the standard briquette elongated before the bituminous thread formed breaks is reported as ductility

2.3.5 Determination of flash point of bitumen (IP 34/85)

The flash point of a material is the lowest temperature at which the vapour of a substance momentarily takes fire in the form of a flash under the specified conditions of the test.

Pensky Martens Closed Method was used for the determination of the flash point of bitumen in this study The flash cup was filled with the material to be tested upto the level indicated by the filling mark. The flash cup was then kept on the heater with the lid carrying the thermometer in position. The test flame was adjusted in such a way so that it is of the size of a bead of 4 mm in diameter The heating rate was adjusted in such a way that the temperature recorded by the thermometer increases not less than 5°C and not more than 6°C per minute. The stirrer was turned at a rate of approximately 60 revolutions per minute The test flame is applied at each temperature reading which is a multiple of 1°C upto 104°C For the temperature range above 104°C the test flame is applied at each temperature reading which is a multiple of 3°C, the first application of the test flame being made at a temperature approximately 17°C below the actual flash point. The test flame is applied by operating the device controlling the shutter and test flame burner so that the test flame is lowered in 0 5 seconds, left in its lowered position for one second and quickly raised to its high position. The stirring has to be discontinued during the application of the test flame. The duplicate results should not differ by more than 3°C of the mean.

2.3.6 Determination of solubility in Carbondisulphide (1P 47/74)

About 2 g of the material is weighed correct to the nearest 0.001 g into a 200 ml conical flask and 100 ml of carbondisulphide is added to it. Stirred the contents of the flask and then allowed to stand for a period of 1 hour. The contents of the flask are then filtered through a gooch crucible which has been weighed to the nearest 0 001 g. Moistened the asbestos pad with carbon disulphide before filtration and filtered at a rate of not more than 2 drops per second. The insoluble matter remaining in the flask is transferred to crucible by washing out the flask with a stream of carbondisulphide from a wash bottle. Washed the material retained in the crucible with successive small amounts of carbon disulphide until a filtrate is obtained which is not discoloured. Allowed the crucible to dry in air for 30 minutes, after which it is placed in an air oven at 100°C for 1 hour Allowed the crucible to cool in a desiccator and weighed.

$$\text{Matter soluble in } CS_2\ \% = \frac{W_1 \qquad W_2}{W_1} \times 100$$

Where W_1 is the weight in grams of dry sample taken for test and W_2 is the weight in grams of insoluble material retained in gooch crucible.

2.3.7 Determination of loss on heating (IP 45/58)

Loss on heating was determined in a stabiltherm oven (Blue M Electric Co USA) 50 g of the sample in the sample container is placed near the circumference of the revolving shelf which is made to rotate at a rate of 5 to 6 revolutions per minute; the temperature being maintained at 163 ± 1°C for 5 hours after the sample has been introduced. At the end of the specified heating period, removed the containers, cooled to room temperature and weighed correct upto 0.01 g. The mean percentage loss in weight for duplicate determinations was reported to the nearest 0.05% as loss on heating.

2.3.8 Determination of Recovery (IP 123/82)

Measured 100 ml of the sample in the graduated cylinder and transfered it completely to the distillation flask, taking care that none of the liquid flows into the vapour tube Fitted the thermometer tightly into the neck of the flask so that the bulb is centred in the neck and the lower end of the capillary is level with the highest point on the bottom of the inner wall of the vapour tube. Adjust the flask so that it is in a vertical position and that the vapour tube extends into the condenser tube for a distance of 1 to 2 inches. Place the graduated cylinder under the lower end of the condenser tube so that the end of the condenser tube extends therein for a distance of atleast 1 inch but not below the 100 ml mark. Applied heat to the distillation flask and recorded the total volume of the distillate collected in the receiver at 366°C as the recovery

2.3.9 Determination of Kinematic Viscosity (IP 71/84)

Kinematic viscosity of a fluid is the quotient of the dynamic viscosity and the density of the fluid at the temperature of the test. The time was measured for a fixed volume of oil to flow through the capillary of a calibrated glass viscometer at the specified temperature. The kinematic viscosity of the oil was then calculated from the measured flow time and the calibration constant of the viscometer obtained using freshly distilled water as the primary standard.

2.3.10 Determination of Diesel Index (IP 21/75)

Diesel index was calculated using the formula GA/100 where G is the API gravity and A is the aniline point in ^{0}F The aniline point was determined as per IP 2/84

Aniline point is the minimum equilibrium solution temperature for equal volumes of aniline and sample.

5 ml each of pure aniline and sample were placed in a tube and mixed mechanically The mixture was heated at a controlled rate until the two phases became miscible. The mixture was then cooled at a controlled rate and the temperature at which the two phases separate was recorded as the aniline point.

2.3.11 Determination of Ramsbottom Carbon Residue (IP 14/82)

5 gm of the sample was introduced into the coking bulb by means of a hypodermic syringe and the bulb was reweighed. The coking bulb was then placed in the furnace at 550^{0}C for 20 minutes. It was then taken out and placed in a desiccator over $CaCl_2$ for 20 minutes and weighed again The percentage weight

of carbon residue was then calculated and reported as Ramsbottom carbon residue.

2.3.12 Determination of total Sulphur (IP 61/84)

0.6 gm of the sample was subjected to combustion using a firing wire of length 100 mm in a bomb of capacity 300 ml containing oxygen at 35 atm pressure. The interior of the bomb and the cup were then washed with distilled water and the washings were collected. The washings were then heated to boiling and 10 ml of barium chloride solution was then added dropwise. Boiling was continued for further 5 minutes and cooled. The supernatent liquid was then filtered through a filter paper (whatman No.40) and the precipitate was washed until free from chloride. The paper and the precipitate was then transferred into a weighed crucible and ignited until the residue was white in colour The crucible was then allowed to cool to room temperature and weighed The percentage weight of total sulphur was then calculated using the formula 13 73 x A/B where A is the weight in grams of barium sulphate and B is weight in grams of the sample taken for test.

2.3.13 Determination of Pour Point (IP 15/86)

Pour point is the lowest temperature, expressed as a multiple of 3^0C at which the oil is observed not to flow when cooled and examined under prescribed conditions.

Pour the oil into the test jar to the level mark Adjust the positions of the cork and the thermometer so that the cork fits tightly, the thermometer and the jar are coaxial and the thermometer bulb is immersed so that the beginning of the capillary is 3 mm below the surface of the oil. The test was started at a temperature 8°C above the expected pour point for oils having pour points above 32°C and for other oils at a temperature 11°C above the expected pour point. At each test thermometer reading that is a multiple of 3°C, removed the test jar from the jacket carefully and tilted it just enough to ascertain whether there is a movement of the oil in the test jar The complete operation of removal and replacement should require not more that 3 seconds. Continued the test in this manner until a point is reached at which the oil in the test jar showed no movement when the test jar is held in a horizontal position for exactly 5 seconds. Recorded the observed reading of the test thermometer. Added 3°C to the temperature recorded and reported the result as pour point.

2.4 Characteristics of Bituminous paints

2.4.1 Determination of drying time (IS: 101-1964 Cl No.7.2)

The material is brushed on a 150 x 150 mm mild steel panel and allowed to air dry under specified drying conditions.

Air drying was conducted at room temperature and at a relative humidity of 65± 5% in a well ventilated chamber, free from dust and the film exposed to diffused day light for atleast six hours in each 24 hours of drying period, taking care to protect it from direct sunlight. The material is examined after definite intervals for the following conditions.

(a) Surface dry shall be such a condition of the paint film that clean, dry, silver sand graded so as to pass 250 micron

IS sieve but to be retained on 125 micron IS sieve, sprinkled on to the surface of the film and allowed to remain for about 10 seconds, can be removed, without injury to the film, by means of a camel hair brush.

(b) Hard dry shall be such a condition of the paint film that a second coat of the material may be applied satisfactorily on it after slight rubbing down.

(c) Tack free A condition of the paint film such that it will pass the test prescribed below.

Placed the panel in one of the pans of a balance and counterpoised it with weights. Placed a further weight of 2 25 Kg and pressed on the dried film surface of the panel with the thumb until the two pans were balanced. Held for one minute and then slowly released. No sign of stickiness to the thumb should be apparent and the thumb impression, if produced, should be such as can be wiped away with dry cotton wool.

2.4.2 Determination of Consistency (1S: 101-1964 Cl.No.7.4)

Inserted a clean metal rod into the original container and examined the nature of settling. The material should not take hard inside the container and should be in such a condition that stirring easily produces a smooth uniform paint suitable for application.

2.4.3 Determination of Finish (1S: 101-1964, Cl. No. 7.5)

The material was applied on a mild steel panel (150 x 150 mm) by brushing to give a dry film so that the weight of the dry fim of a single coat of the material comes in between 17 to 25 5 g/m^2 The panel when allowed to dry in a vertical position under the specified conditions, shall dry to a hard, firmly adherent, flexible and smooth film free from sagging and wrinkling with a matt, semi-glossy or glossy surface in accordance with the requirements of the material specification. The film so produced shall be of normal opacity and in no way inferior to a film prepared in the same manner and at the same time from the approved sample, when examined not earlier than 48 hours and not later than 100 hours after application.

2.4.4 Determination of colour (IS 101-1964, Cl. No.11)

The material is brushed on a 150 x 150 mm mild steel plate in two normal coats. The second coat should be applied after the first coat has become hard dry The colour of the paint film was then compared in diffused daylight with the specified colour 24 hours after the application of the second coat. The colour of the paint film should be a close match to the specified colour.

2.4.5 Determination of Flash Point of Bitumenous Paints (IP 170/75)

Abel Flash Point apparatus is used for the determination of flash point of bituminous paints. The water bath is filled to overflow with warm water, inserted the water bath thermometer, and adjusted the bath temperature to 54^{0}C at the beginning of the test. No heat is applied to the water bath during the course of the test The sample was cooled to a temperature of 10^{0}C and it was then filled in the flash cup upto the filling mark The cup containing the sample was placed in the water bath, lit the test flame and adjusted its size to a bead of 4 mm diameter. When the temperature of the sample reached 18°C, applied the test flame by slowly opening the slide in the cover. Application of the test flame was continued for every 0 5°C rise in temperature until a distinct flash occured in the interior of the cup. The temperature of the sample at which the flash occured is reported as flash point.

2.4.6 Stripping test (IS: 101-1964 Cl. No.17)

Applied a coat of the material by brushing to a 150 x 50 x 0.315 mm tinned plate to give a dry film weight as described in 2.4.3 Allowed the panel to air dry in a horizontal position for 48 hours under the specified drying conditions. Tested the dried film in the apparatus under such a load that scratch is produced showing the bare metal surface. The scratch so produced should be free from jagged edges.

2.4.7 Determination of Flexibility and Adhesion (IS: 101-1964, Cl. No.16)

Applied a coat of material by brushing to a 100 x 50 x 0.315 mm tinned plate, to give a dry film weight as described in 2.4.3 Allowed the panel to air dry in a horizontal position for 48 hours under the specified drying conditions. After air drying, bent the panel double 75 mm from the upper edge over a 6.25 mm diameter rod with the paint film outside Closed the hinge in a regular manner without jerking in not less than 1 second and not more than $1^1/2$ seconds. Removed the panel carefully from the hinge. The paint film should not show any damage, detachment or cracking when examined under magnification.

2.4.8 Keeping properties of paints (IS: 101-1964 Cl. No.31)

When stored under cover in a dry place in original sealed container under normal temperature conditions the material shall retain the properties prescribed in the material specifications for one year after the date of manufacture.

2.4.9 Determination of water resistance of paints (IS:158-1968 Appendix A)

Applied a coat of the material, by brushing to the inside surface of a clean tin container, with a level lid, 125 mm high and 90 mm in diameter, to give a dry film. Allowed the paint film to air dry for seven days. At the end of this period, stored water in the container for 24 hours and then rinsed the container thoroughly with water. Then filled the container with water Allowed the water to remain in contact with the paint film for 3 days with lid closed Examined the water for odour and taste at the end of this period. The water from the container was then taken out to a beaker, heated to boiling, cooled and again examined for odour and taste. The material shall be deemed to have passed the test if the paint film remains firmly adherent and imparts no unpleasant odour or taste to water

2.4.10 Determination of resistance to acid (IS:158-1968 Appendix B)

Applied a coat of the material by brushing, to a 150 x 50 mm clean glass panel to give a dry film. Allowed the panel to air dry in a horizontal position for 24 hours under standard conditions. Immersed the panel partially in dilute sulphuric acid (1:20 v/v) for 24 hours. The panel was taken out, washed carefully and examined the immersed portion of the film after drying for one hour. The material shall be deemed to have passed the test if the paint film on the panel shows no signs of softening, blistering, cracking, dulling or change of colour.

2.4.11 Determination of resistance to alkali (IS: 158-1968 Appendix C)

Immersed partially a panel, prepared as before (for testing acid resistance) in an aqueous solution of sodium carbonate (5% anhydrous sodium carbonate in water w/v) for four hours. The panel was then taken out, washed and examined the immersed portion of the film after drying for one hour The material should be deemed to have passed the test if the paint film on the panel showed no signs of softening, blistering, cracking, dulling or change of colour

2.4.12 Resistance to chlorine (IS 158-1968 Appendix D)

Immersed three quarters of a glass panel prepared as before (for testing acid resistance), in chlorine water (0 05% w/v) in a suitable glass container, which was either covered with black paper or painted outside with black paint and kept in a dark place for 72 hours. After this period the panel was taken out, washed and examined the immersed portion of the film after drying for 24 hours. The material shall be deemed to have passed the test if the paint on the panel showed no blistering and cracking.

2.4.13 Determination of resistance to heat (IS: 158-1968 Appendix E)

Applied a coat of the material by brushing, to a 150 x 100 x 0.800 mm clean mild steel panel to give a dry film. The panel was allowed to air dry in a horizontal position for 24 hours. This was heated in a vertical position in an electrical furnace, the temperature of which was gradually raised from room temperature upto a temperature of 300°C in one and a half hours. Maintained the panel at the maximum temperature of 300°C for half an hour. Removed, the panel from the furnace, cooled to room temperature and immersed in water at room temperature for 24 hours. Taken out the panel and examined it after air drying for one hour The material shall be deemed to have passed the test if the film remained firmly adherent and showed no signs of cracking, blistering or flaking. Formation of hairlines should not be a cause of rejection.

2.4.14 Water content of bitumenous Emulsions

Water content was determined as per IP 291/73.

50 gm of the bitumenous emulsion was weighed into the distillation

flask. 100 ml of toluene was then added as the carrier liquid and the sample heated under reflux. The heating rate is adjusted in such a way that the condensate falls from the end of the condenser at a rate of 2 to 5 drops per second. The carrier liquid distils into a graduated receiver carrying with it the water which then separates to form the lower layer. The excess liquid overflows from the trap and returns to the still. The volume of the water layer thus collected is measured.

$$\text{Water content, \%} = \frac{100 \times \text{Vol. of water in trap (ml)}}{\text{wt. of emulsion sample taken in gm}}$$

2.5 Rubber processability study using Brabender Plasticorder

Brabender Plasticorder (PL 3S) was used for studying processing characteristics. This torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under preselected conditions of shear and temperature. Mixing and shearing of the material in the mixing chamber is done by the two horizontal rotors with protrusions. The resistance put up by the test material against rotating rotors in the mixing chamber is indicated with the help of a dynameter balance. A DC thyristor controlled drive is used for speed control of the rotors. Stock temperature thermocouple with a recorder is used for temperature measurements. The materials were charged into the mixing chamber after setting the test conditions to obtain a torque time curve or a plastogram.

In the present study, the processability of natural rubber/ styrene butadiene rubber using refinery sludge was compared with that of the conventional process aid viz., aromatic oil. The rubber was first passed six times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small strips before feeding into the Brabender Plasticorder. The total mixing time was 16 minutes with the following break-up. The rubber was masticated within 4 minutes followed by adding activator and accelerator within three minutes. Carbon black mixed with purified refinery sludge was then added within 8 minutes and finally sulphur within 1 minute. For the control mixes the same procedure was repeated by replacing sludge with aromatic oil. Inorder to optimise the quantity of oil required, sludge/aromatic oil was added at different phr levels and based on the torque values, the oil quantity required was optimised.

2.6 Mixing and Homogenisation of the Rubber Compounds

Mixes were prepared on a laboratory size two roll mixing mill (15 x 33 cm) as per the procedure given in ASTM designation D 3182 89 The friction ratio during mixing was 1 1 25 for natural rubber and 1 1 1 for styrene butadiene rubber. The mill opening was adjusted at 0.2 mm and the elastomer was given two passes through the rolls without banding. This was then banded on the slow roll mill with opening at 1 4 mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at 60 ± 5^{0}C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per the sequence given in ASTM D 3184 89 and ASTM D 3182 89 in the following order activator, filler, accelerator and curing agents. The batch was thoroughly cooled before the addition of accelerator and sulphur

After complete mixing, the stock was sheeted out and passed six times endwise through tight nip of 0.8 mm and finally sheeted out at a nip gap of 3 mm by passing the stock through the rolls four times folding it back on itself each time.

2.7 Determination of cure characteristics of rubber compounds

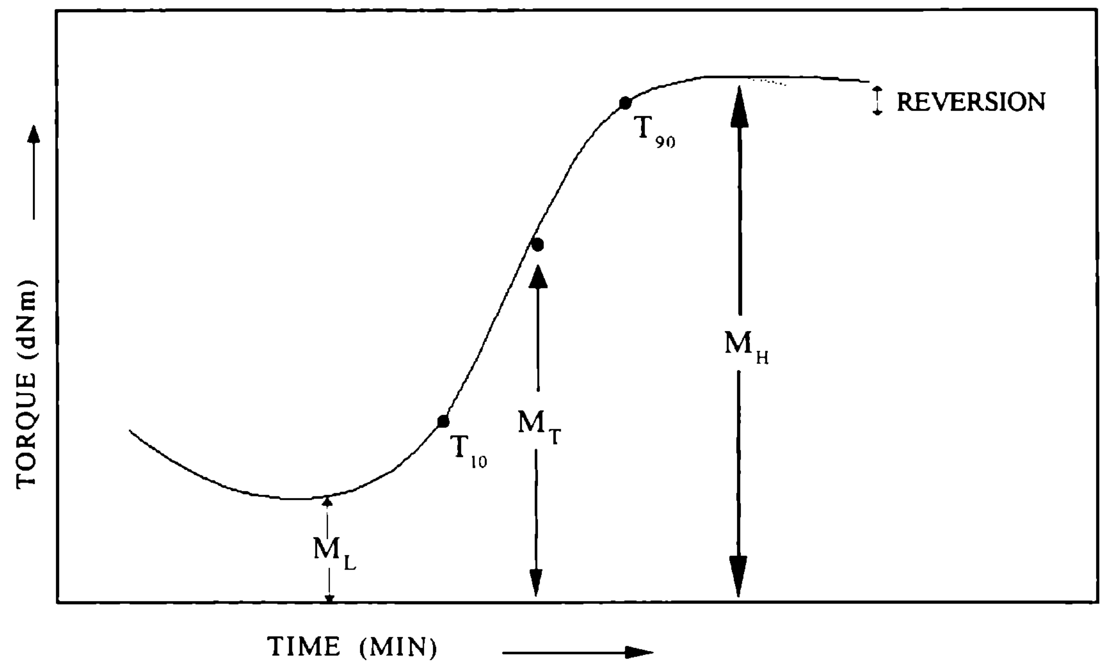
The cure characteristics of the mixes were determined using the Geottfert elastograph, model 67.85 This instrument is a rotorless shear curometer and consists of an upper movable die and a lower immovable die. The lower die half generates a sine shaped oscillation by a step motor at a frequency of 50 oscillations per minute. The rubber compound is cut into round axially symmetrical shape with radical grooves of volume 4.2 cm^3 This rubber is placed on the lower die which is heated by a jacket heater to 150^0C for 30 minutes. The torque transducer on the upper die senses the force being transmitted through rubber The torque envelope curve and cure curve is displayed on the screen. This is attached to a printer which prints the graphs and the test conditions. The relevant data that could be taken from the curing curve are:

i) Minimum torque M_L Torque obtained after homogenising at the test temperature and before the onset of cure

ii) Maximum torque, M_H This is the maximum torque after the curing of the mix is completed.

iii) Torque, M_T This is the torque at any time T

iv) Optimum cure time, T_{90} This is the time taken for obtaining 90% of the maximum torque.



v) Scorch time, T_{10} This is the time taken for 10% vulcanization.

vi) Induction time, T_5 This is the time taken for one unit rise above the minimum torque (i.e., about 5% vulcanization)

vii) Cure rate index This is calculated as $100/(T_{90}\ \ T_{10})$ where T_{90} and T_{10} are the times corresponding to optimum cure and scorch respectively

The elastograph microprocessor evaluates the vulcanization curve and prints out the data after each measurement.

2.8 Moulding of test specimen

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on an electrically heated press having 30 x 30 cm platens at a pressure of 140 Kg cm^{-2} on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150^{0}C. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.,) additional curing times based on the sample thickness was given to obtain satisfactory mouldings.

2.9 Physical Test Methods

At least three specimens per sample were tested for each property and the mean values are reported.

2.9.1 Tensile properties

Modulus, Tensile strength and Elongation at break

The tensile properties of the vulcanizates were determined as per ASTM D 412 -87 (method A). The tests were done in 'Zwick' Universal Testing Machine, model 1445, at 28 ± 2^{0}C at a cross head speed of 500 mm min^{-1} Dumbell specimens for the test were punched out from vulcanized sheets along the mill grain direction, using a dumbell die (C type). Thickness of the narrow portion was measured by a bench thickness gauge. The sample was held tight between two grips, the upper grip of which is being fixed. The rate of separation of power actuated lower grip was 50 cm per minute. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor

The tensile strength and modulus are reported in MPa (Conversion factor 1 Kg/cm^2 = 0.098 MPa)

2.9.2 Tear Resistance

Angular test specimens were used to measure the tear resistance on a Zwick Universal Testing Machine model 1445, in accordance with ASTM D 624 86. The samples were cut from the moulded sheets parallel to the mill grain direction. The speed of extension was 500 mm min^{-1} and the test temperature was 28 ± 2^0C.

2.9.3 Hardness

The hardness (shore A) of the moulded sample was tested using Zwick 3114 hardness tester as per ASTM D 2240 86. The tests were carried out on mechanically unstressed sample of 12 mm diameter and minimum 6 mm thickness. A load of 12.5N was applied and the readings were taken after 10 seconds of identation after firm contact had been established with the specimen.

2.9.4 Compression Set

Compression set was determined in accordance with ASTM D 395-86 (method B). Samples (6 25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in air oven at 70^0C After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows.

$$\text{Compression set (\%)} = \frac{t_0 \quad t_1}{t_0 - t_5} \times 100$$

where t_0 and t_1 are the initial and final thickness of the specimen respectively and t_5 the thickness of the spacer bar used.

2.9.5 Abrasion resistance

The abrasion resistance of the samples were determined using a DIN abrader (DIN 53516). Cylindrical samples having diameter 15 mm and length 20 mm was kept on a rotating sample holder and 10 N load was applied. Initially a pre run was given for the sample and its weight was taken. The sample is then given a complete run and the final weight noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded by its travel through 42 m on a standard abradent surface. The abrasion loss was calculated as follows:

$$V = \frac{\Delta m}{\rho}$$

where V = abrasion loss, Δm = mass loss, ρ = density of the sample.

2.9.6 Heat build-up

The heat build up was determined using the Goodrich flexometer according to ASTM D 623 78 (Method A). Cylindrical samples of height 25 mm and 19 mm diameter were used for the test The oven temperature was maintained at 50°C The stroke was adjusted to 4 45 mm and the load to 10 9 Kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT^0C) at the end of 20 minutes was taken as the heat build-up

2.9.7 Rebound resilience

Dunlop tripsometer (BS 903, part 1 A8) was used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the identor six times. The temperature of the specimen holder and sample was kept constant at 35^0C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience (\%)} = \frac{1 \quad \cos\ \theta_2}{1 \quad \cos\ \theta_1} \text{ x } 100$$

where θ_1 and θ_2 are the initial and final rebound angles respectively θ_1 was 45^0 in all tests.

2.9.8 Ageing Studies

Ageing studies were carried out in an air oven as per ASTM D 573 88 Dumbell specimens were punched out from the vulcanized sheets and kept in the air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc were measured before and after ageing. The percentage retention of these properties were evaluated for assessing the effect of ageing.

2.10 Chemical Test Methods

2.10.1 Determination of concentration of crosslinks of the vulcanizates

The concentration of crosslinks (crosslink density) of the vulcanizates was determined from the equilibrium swelling data as follows:

Samples of approximately 0.3 g weight were cut from the central portion of the vulcanizate and allowed to swell in solvent (toluene) for 24 hours. The outer portion of the swollen samples were dried using a filter paper and weighed. The swollen sample was placed inside the oven at 60°C for 24 hours to remove toluene. The deswollen weight was determined. The volume fraction of rubber, V_r in the swollen network was then calculated by the following equation[1,2]

$$V_r = \frac{(D \quad FT)\rho_r^{-1}}{(D \quad FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where, T = the weight of the test specimen

D = the weight of the deswollen test specimen

F = the weight fraction of insoluble components

A_0 = theweight of the absorbed solvent corrected for the swelling increment

ρ_r = density of the test specimen

ρ_s = density of the solvent

Knowing the value of Vr, the total chemical crosslink density 1/2 Mc was calculated using Flory Rehner equation[3,4]

$$[\ln(1-V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (Vr)^{1\ 3}}{M_c}$$

where, V_s = molar volume of solvent

χ = the parameter characteristic of the interaction between rubber and solvent

M_c = the number average molecular weight of the rubber chains between crosslinks.

The values of the parameter χ taken for calculation were the following[5]

For NR toluene, χ = 0 42

SBR toluene, χ = 0.32

Although natural rubber gum vulcanizates have received much attention, only less details are available on network structure of filled vulcanizates. This is because of the uncertainties introduced by the filler rubber interactions. The volume fraction of rubber (V_r) in filled vulcanizates is calculated assuming that the filler does not swell. It is then converted to V_{r0} (the value V_r would have had in the absence of filler) according to Cunneen and Russel[6]

$$\frac{V_{r0}}{V_r} = ae^{-z} + b$$

where a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black filled systems are; a=0.56 and b = 0 44. The values of V_{r0} were then substituted in the Flory-Rehner equation in place of V_r to obtain the crosslink density 1/2Mc.

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CHAPTER 3

PART I

UTILIZATION OF REFINERY SLUDGE FOR LIGHTER OILS AND INDUSTRIAL BITUMEN

3.1.1 INTRODUCTION

Sludge materials contaminated with oil originate[1] from various sources in refineries and other oil installations. Oily sludge definitely pose problems for handling, treatment and disposal. The experience of the refiners in this field has been varying and at times contradictory. Local environmental factors also play a role in adopting specific measures. Hence environmental factors, apart from techno economic considerations, form part of effective oily sludge management.

Various sources of oil sludge generation are as follows:

1. **Gravity separator sludge:** Oil contaminated water from various sources are routed to gravity oil water separators for separation of free oil as well as suspended solids. The sources include tank bottom water drainings, desalter and other process equipment water draw off, surface water run off from oil contaminated areas etc. Any solids associated with these streams settle out in the form of oily sludge at the bottom of separators requiring periodic removal.

2. **Desalter Sludge:** Sludge and interface emulsions consisting of oil and water usually stabilised by the presence of finely divided solid matter build up in desalters and require periodic removal.

3. Tank bottom Sludge: Sludge accumulates at the bottom of crude oil storage tank and has to be periodically removed. Contaminants in the sludge vary with the characteristics of crude oil stored. The waste sludge, in general, consists of a mixture of water, sediment, oil, wax and rust.

4. Oil Spills: Accidental spills of oil on to the ground require clean up. After the removal of oil to the extend possible, the left over material containing oil, solids, and water require disposal.

Thus refining industry is bogged down with the problem of handling substantial quantity of sludge in some form or the other depending on the type of configuration, crude processing capacity and down stream capacities, design of effluent treatment and pollution abatement measures and the efficiency cum effectiveness of these plants. The information given below refers[2] to the sludge generation details of a typical refining industry having a crude processing capacity of 7 to 8 million metric ton per annum with matching fluid catalytic cracking unit, aromatics and asphalt blowing units.

a) Crude tankages during receipt operations 3750 tons/Yr
b) Catalyst fines in the slurry 270 tons/Yr
c) Product tank bottom sludge from LSHS, F0 and asphalt tankages 22.50 tons/Yr.
d) API separator sludge 600 tons/Yr.
e) Chemical sludge from treatment sections 212 tons/Yr
f) Others: 1060 tons/Yr.

Total quantity of sludge generation 5914.50 tons/Yr

Usually pretreatment of sludge is undertaken to separate oil and water from solid materials to the extent possible. Pretreatment of sludge helps to concentrate the sludge to a much lower volume thereby disposal of the same becomes easier In addition, a part of the valuable oil is also recovered.

The different methods employed for disposal of sludge are:

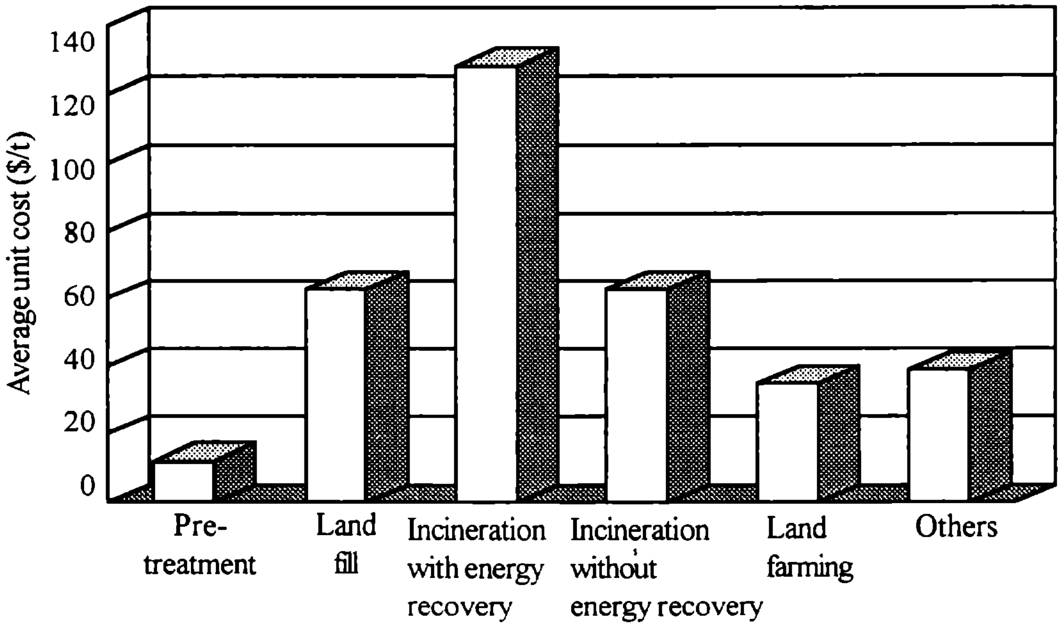
1. **Land fill:** The method of landfilling consists in depositing wastes either in specially excavated or pre existing depressions in the ground. After deposition, the wastes are covered with soil. It is a common practice abroad, before filling, to line the bottom of the depression with an impervious layer of either contacted clay or polymer or both. This serves to stop contaminants leaking out of landfill. A similar impervious layer is also often used to cover the wastes before covering with soil to prevent the ingress of rain water.

2. **Land farming:** Landfarming consists of spreading oily sludge on the ground and cultivating to provide contact with soil microorganisms and air. Natural bacteria in the soil degrade the organic matter, if adequate nutrients, water and air are present. Great care is required to avoid ground water contamination and possible odour problems.

3. **Incineration:** Incineration is high temperature oxidation which converts wastes into gaseous products and solid residues which are less voluminous than the original materials. Less combustible or more hazardous materials may require the use of support fuel and/or the installation of expensive flue gas scrubbing/solids removal equipment

to meet air pollution regulations. It is reported that the economics of incineration are unfavourable and the technique is not always in the best interests of energy conservation.

The figure below gives the average[3] unit cost ($/ton) of waste disposal methods adopted in European refineries.



As understood from the figure; of the various disposal techniques, landfarming is the cheapest with the cost for the majority of wastes land farmed is less than $ 50/ton. But sludge farming of oily wastes although practised for many years is not technically well defined with respect to short or long term environmental effects. Such data is required to convince regulatory agencies about the environmental soundness of the practice.

As the above mentioned methods help only for the disposal of the sludge and that also at a high expense and from the fact that this sludge contains about 70% hydrocarbons in which 7.8% by weight is asphaltenes, we thought it worthwhile to see whether this sludge can be converted into some useful raw material like industrial bitumen avoiding the conventional air blowing process Industrial bitumen of various grades are now manufactured in India by heating the petroleum residuums (after removing volatile and distillable portions) of imported Persian Gulf Crudes like Arab mix, Suez blend, Light Iranian etc. at temperatures of 220 to 280^{0}C for a number of hours and blowing a current of air through the mass continuously Air blowing is usually done in a cylindrical vertical vessel of capacity varying from 40 to 1000 barrels. Compressed air is forced into the mass through a perforated pipe located inside and near the bottom of the vessel. In the actual process, the asphaltic residuum is brought to the necessary temperature in an external heater, charged into the vessel and air is admitted immediately through the perforated pipe near the bottom. Studies by Rescorla, Forney, Blakey and Frino[4] has shown ,that mechanical agitation of liquid-air mixture reduces the time required to airblow an asphalt to a particular consistency The air blowing of asphalt is an exothermic process. As the oxidation proceeds and the asphalt becomes harder, the exothermic reactions decrease and disappears.

Many different materials like CuO, Al_2O_3 V_2O_5, P_2O_5, $AlCl_3$, MoO_3, Zn powder etc., were tried for accelerating the rate of oxidation[5,6] Some of these agents decreased the time required for blowing but had little effect on the properties of the asphalt. Some had a deleterious effect. As later developments, Shearon and Hoiberg[7] described in detail the use of P_2O_5 as a modifier in the air blowing process. Illmann and Sommer[8] patented the use of mono, di or hexafluoro phosphoric acid as an aid in producing air blown asphalts. Fick, Greger and Alsberg[9] proposed the heating of 80 to 90 parts of asphaltic residuum with 2 to 20 parts petrolatum followed by air blowing in the presence of 0.2 to 2.0 percent by weight ferric chloride.

Chlorine has been investigated[10] as an agent for the dehydrogenation and hardening of asphalt but the process has not been used commercially. Large volumes of hydrogen chloride are formed by the combination of chlorine with hydrogen from the asphaltic compounds. The same is true of the use of sulphur which, when heated at a high temperature with asphalt, removes hydrogen to from harder compounds and to liberate hydrogen sulphide. Bencowitz and Boe[11] developed a procedure for incorporating finely powdered sulphur into asphalt without the generation of much hydrogen sulphide. During the air blowing operation, water and volatile highly oxidized products are formed from the residuum. The disposal of this noxious fumes is a big problem associated with the air blowing operation.

Attempts are also made to separate out the lighter oil fractions from the sludge and to characterise them to see whether they are suitable for blending with other refinery streams.

3.1.2 EXPERIMENTAL

Sludge was collected from the quarry pond of Cochin Refineries Ltd., Ambalamugal, Kerala, India. Sulphur, Ferric Chloride, Phosphorous Pentoxide, Aluminium Chloride (anhydrous) and Carbon disulphide used in the study are all of L.R. Grade. The purification of the sludge was done as described in Chapter 2 by maintaining the sludge at 110 ± 10^{0}C in a barrel fitted inside with steam coils. The highly viscous oil so obtained was then passed through strainers of sizes 60 and 40 mesh to remove solid impurities. The characteristics of this purified sludge are given in Table 3 1 163 gm of this dehydrated sludge was taken in a round bottomed flask and subjected to vacuum distillation. Hot water was circulated round the condenser and the receiver so that the waxy distillate coming out as vapour didn't stick to the sides of the condenser. The temperature at which the first drop of the distillate appears at the lower end of the condenser tube is taken as the initial boiling point. Thereafter, for every 5 ml of the distillate collected, the corresponding temperature at the reduced pressure is measured. From this, the corresponding temperature at atmospheric pressure is determined graphically. (See Table 3.2 for data of vacuum distillation). The lighter oil fraction thus recovered from the sludge was estimated quantitatively and tested for its different characteristics. The residue obtained after vacuum distillation was tested for different parameters. These results are also given in Table 3 1

According to Bureau of Indian Standards (IS 702 1961) there are 10 different grades of industrial bitumen depending upon the softening point penetration relationship. They are 65/25, 75/15, 75/30, 85/25, 85/40, 90/15, 105/20, 115/15, 135/10 and 155/6. The First figure represents the softening point and the second one penetration. A grade 65/25 should have the softening point between 63 5 and 66.5 and penetration between 24 and 26. Attempts to convert the vacuum residue of the sludge to some of the above grades of industrial bitumen were carried out as follows.

Table 3.1 Characteristics of Dehydrated Sludge and Vacuum residue of Sludge

Characteristic	Test Method	Dehydrated Sludge	Vacuum Residue of sludge
Specific gravity at 27^{0}C	BS 2000/82	1.014	1.017
Softening point (^{0}C)	IP 58/82	46	52
Penetration (1/10 mm)	IP 49/79	230	41
Ductility (cm)	IP 32/55	32.5	48
Flash point (^{0}C)	IP 34/85	> 200	> 200
Solublity in CS_2 (wt %)	IP 47/74	99.81	99.78
Loss on heating (wt %)	IP 45/58	0.93	0.1
Total Sulphur (wt %)	IP 61/65	3.43	2.1

Table 3.2 Data of Vacuum Distillation

Recovery in Volume (%)	Temperature (^{0}C)	Pressure (mm)	Temperature on conversion to atmospheric pressure (760 mm) (C) ^{0} [a]
5	149	0.6	347
10	193	0.9	397
15	216	0.8	430
20	235	0.8	455
25	249	0.8	474
30	270	1.75	481 (cracking starts)

[a] Initial boiling point = 295 ^{0}C

A 250 g portion of this vacuum residue was heated without any catalyst in a cylindrical can (16 5 cm height and 9 cm dia) at 250°C for 3 hours with periodical stirring. The sample was then taken out and tested for the different parameters (Table 3 5). The above experiment was repeated adding 2% each of sulphur, ferric chloride, phosphorous pentoxide, and aluminium chloride. From the results (Table 3 5) it is seen that aluminium chloride can bring about appreciable variation in the softening point penetration ratio while the other catalysts used were not able to bring about such a significant variation. To determine the optimum concentration of aluminium chloride and the optimum time and temperature required, the experiment was further repeated with different percentages of $AlCl_3$ ranging from 1 2.75 % and temperatures ranging from 200 to 275°C for periods varying from 1-3 hours (see figures 3·1-3·8).The samples were taken out at definite intervals and tested.

The softening point was determined by the ring and ball method according to IP 58/82. To determine softening point below 80°C, a water bath was used for heating while for those above 80°C, a glycerine bath was used. Penetration was determined as per IP 49/79 A penetrometer (Precision Scientific Co., USA), was used for the purpose. The experiment was conducted at 25°C for 5 seconds with a total moving weight of 100 gm. Ductility was determined as per IP 32/55 at 27°C and at a rate of pull of 50 mm/min. A ductility meter (Humboldt manufacturing Co., USA), was used. Flash point was determined by the Pensky Martens closed method as per IP 34/85, at a heating rate of 5°C/min and with a stirrer speed of 60 rpm.

Solubility in carbon disulphide was determined as per IP 47/74 using 2g of the dry material and 100 ml of carbon disulphide. Loss on heating was determined as per IP 45/58 in a stabiltherm oven (BLUE M Electric Co., USA) Density of the samples was determined as per IP 160/68 using a hydrometer of range 0 85-0.90 g/ml. Recovery was determined as per IP 123/82 using a 100 ml volume of the sample. The total volume of the distillate collected in the receiver at 366°C is taken as recovery. Kinematic viscosity was determined as per IP 71/84 by noting the time taken for a fixed volume of the oil to flow through the capillary of a calibrated glass viscometer at 38°C The diesel index was determined as per IP 21/75 and calculated using the formula GA/100 where G is the API Gravity and A is the aniline point in °F The aniline point was determined as per IP 2/78. Ramsbottom carbon residue was determined as per IP 14/82 by introducing a 5 g portion of the sample into the coking bulb using a hypodermic syringe. Total sulphur was determined as per IP 61/84. Pour point was determined as per IP 15/86. Details of all the above experiments are as given in Chapter 2.

3.1.3 RESULTS AND DISCUSSION

Initial part of the study demonstrates that about 17% (w/w) of lighter oils can be isolated from this refinery sludge. Characteristics of the recovered oil (see table 3.3) viz; disel index and flash point meet the specifications of high speed disel (HSD) fuel while the other characteristics viz., recovery, kinematic viscosity, carbon residue, pour point, total sulphur etc on evaluation, show that it cannot be used as such as HSD fuel But since these characteristics are only slightly away from the specifications of HSD, it can easily be brought within the specifications by blending with appropriate streams of petroleum refineries. The important specifications of HSD are given in Table 3 4.

The catalytic effect on the heat treatment of the vacuum residue of the sludge was investigated. The results of the action of sulphur, ferric chloride, phosphorous pentoxide and aluminium chloride on the heat treatment at 250°C and at a catalyst ratio of 2% for 3 hours are shown in Table 3.5. It is seen that heat treatment without any catalyst gave no notable change in the softening point while some reduction in penetration was observed. Heat treatment with P_2O_5 also gave a similar result. Heat treatment with sulphur/ $FeCl_3$ gave some increase in softening point and a good reduction in penetration. But heat treatment with $AlCl_3$ gave not only a heavy increase in softening point but also a sharp reduction in penetration. Thus sulphur, ferric chloride and phosphorous pentoxide are successful in bringing down the penetration sharply but fail to bring up the softening point which is a requirement for the different grades of industrial bitumen. But aluminium chloride not only brought down the penetration sharply but was also able to bring up the softening point to the required level. (see Fig. 3 5). This observation is also in accordance with the finding of Grundermann[12] that metal chlorides especially aluminium chloride can act as catalysts at relatively

Table 3.3 Characteristics of recovered lighter oil

Density at 15^{0}C (gm/ml) (IP 160/82)	0.8923
Recovery at 366^{0}C (vol % ml) (IP 123/82)	73
Flash point (PMC) (^{0}C) (IP 34/75)	>80
Kinematic viscosity at 38^{0}C (CS) (IP 71/84)	10.6
Diesel index (IP 21/75)	45
Carbon residue (Ramsbottom) (wt %) (IP 14/65)	0.29
Aniline point (^{0}C) (IP 2/78)	86.6
Total sulphur (Wt %) (IP 61/84)	1.3
Pour point (^{0}C) (IP 15/86)	+21

Table 3.4 Specifications of High Speed Diesel Oil

Density @ 15^{0}C (gm/ml)	0.82-0.88
Distillation, Recovery @ 366^{0}C % vol	Min 90
Flash point ^{0}C	Min 32
Kinematic viscosity @ 38^{0}C CS	2 to 7.5
Diesel index	Min 45
Carbon residue (Ramsbottom) %wt	Max 0.2
Total sulphur % wt	Max 1.0
Pour point ^{0}C	+18

Table 3.5 Data on heat treatment of vaccuum residue at 250^{0}C with differentcatalyst for 3 hours

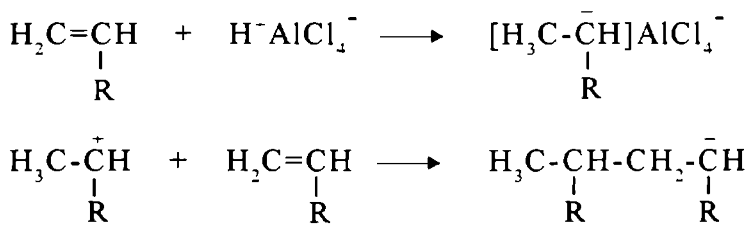
Catalyst (2%)	Specific Gravity	Softening Point (^{0}C)	Penetration (1/10 mm)	Ductility (cm)	Flash point (^{0}C)	Matter soluble in carbon disulphide (wt%)	Loss on heating (wt%)
Nil	1.02	55	31	20.5	>300	99.76	0.07
Sulphur	1.028	58.5	23	13	>300	99.70	0.05
Ferric Chloride	1.024	58	26	17.5	>300	99.72	0.05
Phosphorous pentoxide	1.021	56	29	19	>300	99.74	0.06
Aluminium chloride	1.03	83	20	5	>300	99.64	0.04

low temperatures, and without air blowing causing condensation and polymerisation reactions similar to those obtained in air blowing.

Bitumens are complex mixtures of very many different compounds of high molecular weight. They are generally regarded as colloidal systems[13,14,15] consisting of asphaltene miscelles dispersed in a lower molecular weight medium termed maltenes. The miscelles are considered to be asphaltenes together with an adsorbed covering sheeth of high molecular weight aromatic resins and such layers extend outwards into the less aromatic oily dispersion medium. As the number of miscelles dispersed in the maltenes increases, the behaviour of the colloid changes from a sol-gel to gel[16]

It is reported that[17] when a petroleum fraction is heated, hydrocarbons with a long chain at first split up, and since the C-H bonds are stronger than the C-C bonds, the paraffinic hydrocarbons are cracked predominantly at C-C bonds with the formation of new molecules of paraffins and olefin hydrocarbons. Also the naphthenic hydrocarbons undergo dehydrogenation to form aromatic hydrocarbons which have relatively high thermal stability It is also reported[18] that dehydrogenation and polymerisation are the main reactions involved during the air blowing process for industrial bitumen manufacture and that oxygen is not added to the bitumenous substance except in a very minor amount.

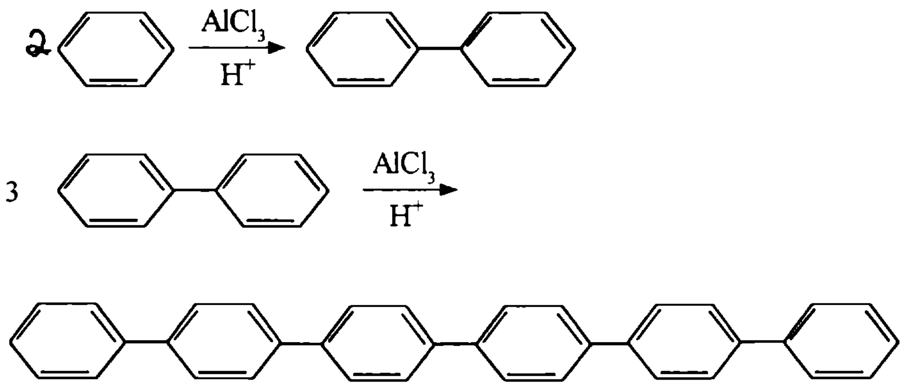
The pronounced catalytic effect of aluminium chloride in such polymerisation reactions involving olefins can be explained by means of the following ionic mechanism. Since aluminium chloride has an incomplete octet, it when added to the olefin polarise it to such an extent that it is capable of adding further monomers[19]



$$H_2C=\underset{R}{CH} + H^-AlCl_4^- \longrightarrow [H_3C-\overset{-}{\underset{R}{C}}H]AlCl_4^-$$

$$H_3C-\overset{+}{\underset{R}{C}}H + H_2C=\underset{R}{CH} \longrightarrow H_3C-\underset{R}{CH}-CH_2-\overset{-}{\underset{R}{C}}H$$

At high temperatures, aluminium chloride can also bring about Friedel Crafts arylation (Sholl reaction[20])



Intramolecular Sholl reaction can also take place as follows.

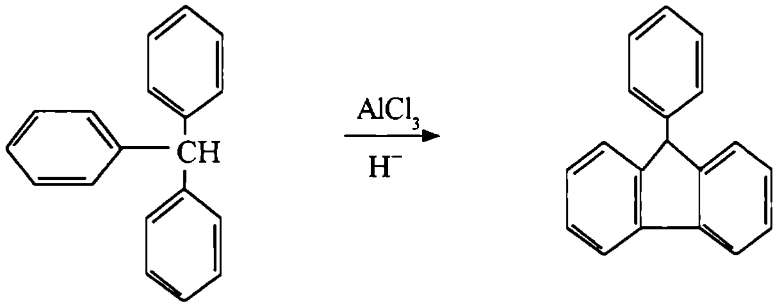


Table 3 6 gives the effect of different percentages (ranging from 1-2.75%) of $AlCl_3$ at 250°C on the heat treatment of the vacuum residue of sludge for periods ranging from 1 3 hours (Figs. 3.1 and 3.6). The results show considerable improvement in the softening point penetration relationship upto a catalyst level

Table 3.6 Data on heat treatment of vacuum residue at 250^{0}C with different percentages of $AlCl_3$ for varying durations

Amount of Aluminium Chloride (%)	Duration of heat treatment (h)	Specific gravity	Softening point (^{0}C)	Penetration (1/10 mm)	Ductility (cm)	Flash Point (^{0}C)	Matter soluble in CS_2 (wt%)	Loss on heating (wt%)
1	1	1.023	56	30	11	> 300	99.76	0.08
	1.5	1.023	59	29	9	> 300	99.72	0.06
	2	1.024	62.5	27	6.5	> 300	99.7	0.05
	2.5	1.026	64	25	6.3	> 300	99.68	0.03
	3	1.026	65	25	6.25	> 300	99.65	0.03
2	1	1.025	69	25	6	> 300	99.74	0.06
	1.5	1.026	75	23	5.75	> 300	99.72	0.06
	2	1.028	78	22	5.5	> 300	99.7	0.05
	2.5	1.03	81	21	5	> 300	99.67	0.05
	3	1.03	83	20	5	> 300	99.64	0.04
2.5	1	1.028	76	24	5.3	> 300	99.72	0.05
	1.5	1.028	81	22	5	> 300	99.69	0.04
	2	1.029	84	20	4.5	> 300	99.64	0.04
	2.5	1.032	88	17	3.75	> 300	99.6	0.03
	3	1.034	89	16	3.5	> 300	99.59	0.03
2.75	1	1.028	80	22	5.1	> 300	99.68	0.04
	1.5	1.03	84	21	4.5	> 300	99.65	0.04
	2	1.031	86	20	4.25	> 300	99.62	0.03
	2.5	1.032	88	18	4	> 300	99.6	0.03
	3	1.033	89	17	4	> 300	99.6	0.03

of 2.5% and duration of 2.5 hours. With higher percentages, the improvement is not significant. Table 3 7 reports the data obtained when the heat treatment was carried out at other different temperatures ranging from 200 275°C for varying periods keeping the catalyst level at 2.5% (Figs. 3.2 and 3 7). The results show that a high temperature of 275°C as well as a lower temperature of 200°C did not give a better softening point penetration relationship. The best result was obtained at the temperature of 225°C and duration of 2.5 hours (Fig. 3.8). This can be taken to be the optimum conditions for preparing grades of industrial bitumen of lower penetration and higher softening point like 90/15

The results show that only four of the 10 different grades of industrial bitumen can be prepared by the methods used in the present study. Heat treatment of the vacuum residue at 250°C for 2.5 hours with 1% $AlCl_3$ is sufficient for preparing the 65/25 grade. 75/30 and 85/25 grades can be obtained by heat treatment at 200°C with 2.5% $AlCl_3$ for one and three hours respectively. Similarly 90/15 grade can be prepared by heat treatment at 225°C for 2.5 hours with 2.5% $AlCl_3$. For the remaining grades, the softening point penetration specifications were found difficult to be met by the methods used in this study, probably due to the low asphaltene content in the vacuum residue of sludge used. It is notable here that a sample of asphalt usually taken for industrial bitumen manufacture contains asphaltenes to a level of 20 to 30% while the sludge contains asphaltenes only to a level of 7.8%.

Table 3.7 Data on heat treatment with 2.5% $AlCl_3$ at varying temperature and durations

Temperature (°C)	Duration of heat treatment (h)	Specific gravity	Softening point (°C)	Penetration (1/10 mm)	Ductility (cm)	Flash Point (°C)	Matter soluble in CS_2 (wt%)	Loss on heating (wt%)
275	1	1.025	78	25	6.00	> 300	99.74	0.06
	1.5	1.026	80	23	5.75	> 300	99.72	0.06
	2	1.028	83	21	5.50	> 300	99.70	0.05
	2.5	1.03	86	19	5.00	> 300	99.64	0.04
	3	1.032	87	18	4.00	> 300	99.61	0.04
225	1	1.026	76	25	5.40	> 300	99.70	0.05
	1.5	1.028	83	22	4.75	> 300	99.67	0.04
	2	1.029	86	18	4.25	> 300	99.65	0.03
	2.5	1.034	89.5	15	3.50	> 300	99.59	0.02
	3	1.036	90	14	3.00	> 300	99.56	0.02
200	1	1.025	75	29	6.00	> 300	99.72	0.06
	1.5	1.026	79	27	5.80	> 300	99.70	0.06
	2	1.026	81	26	5.75	> 300	99.67	0.05
	2.5	1.028	83.5	25	5.00	> 300	99.64	0.05
	3	1.028	84.5	25	5.00	> 300	99.63	0.05

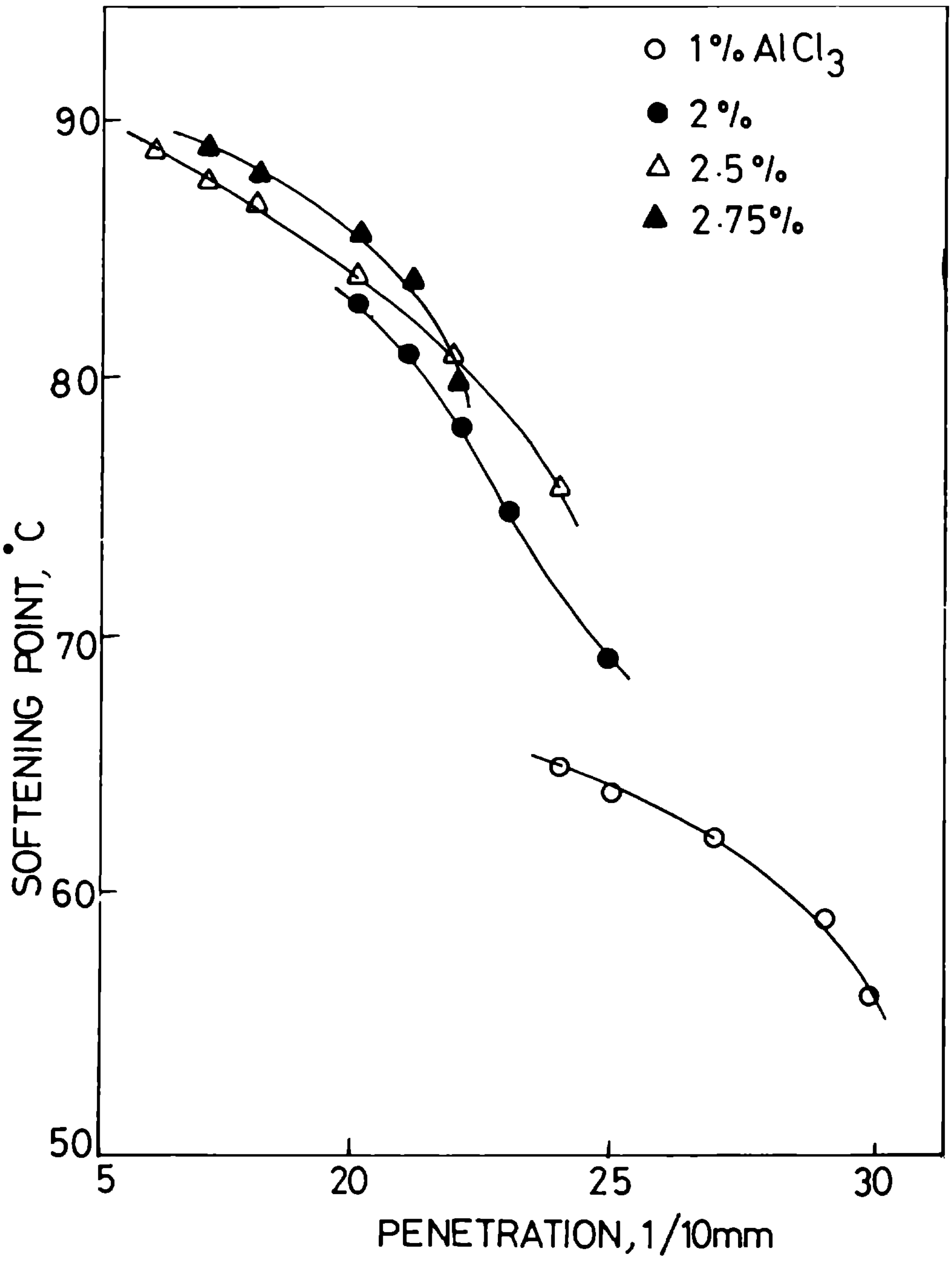


Fig. 3.1 Effect of different percentages of $AlCl_3$ on the properties of vacuum residue of sludge

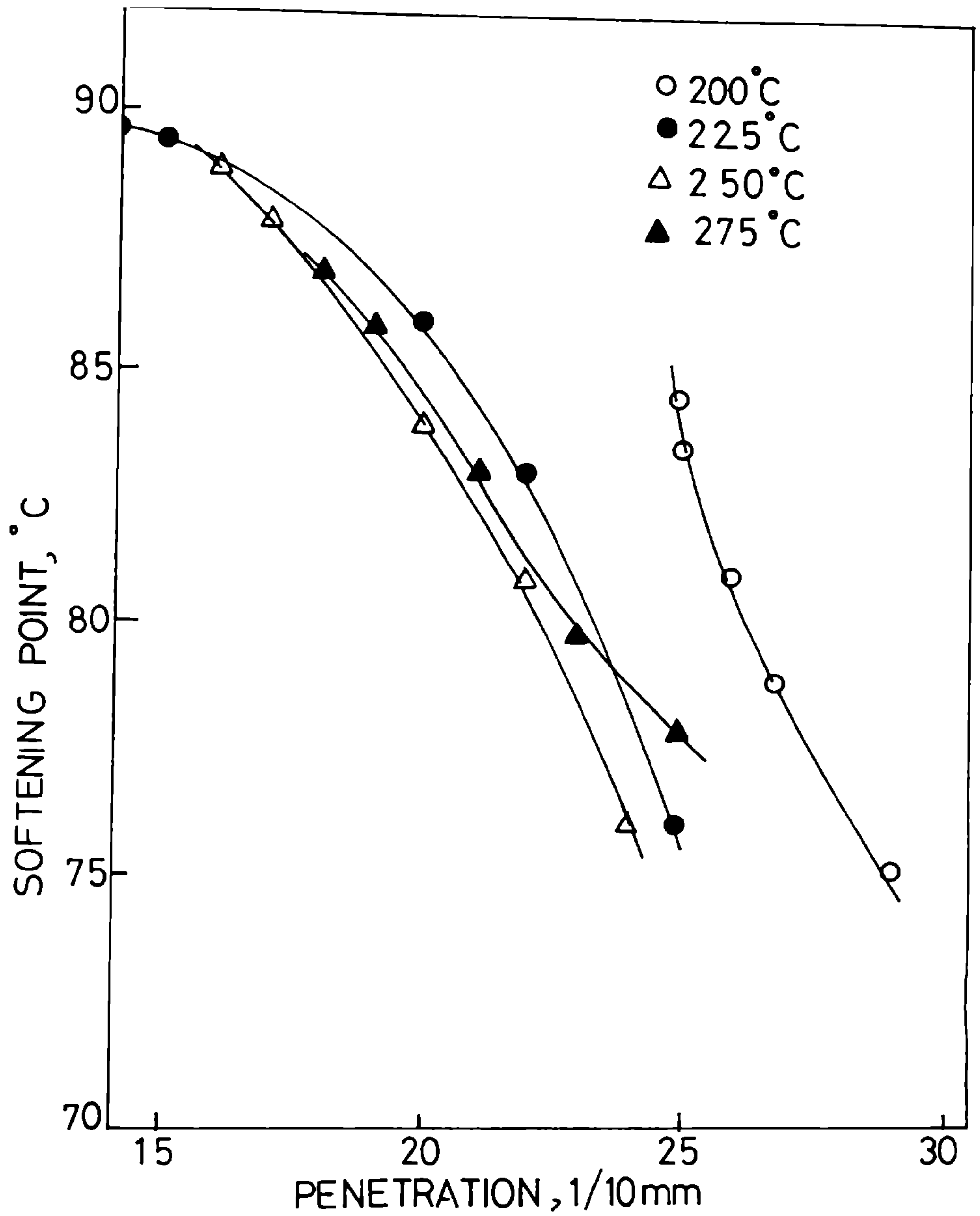


Fig 3.2 Effect of temperature on the properties of vacuum residue of sludge containing 2.5% $AlCl_3$

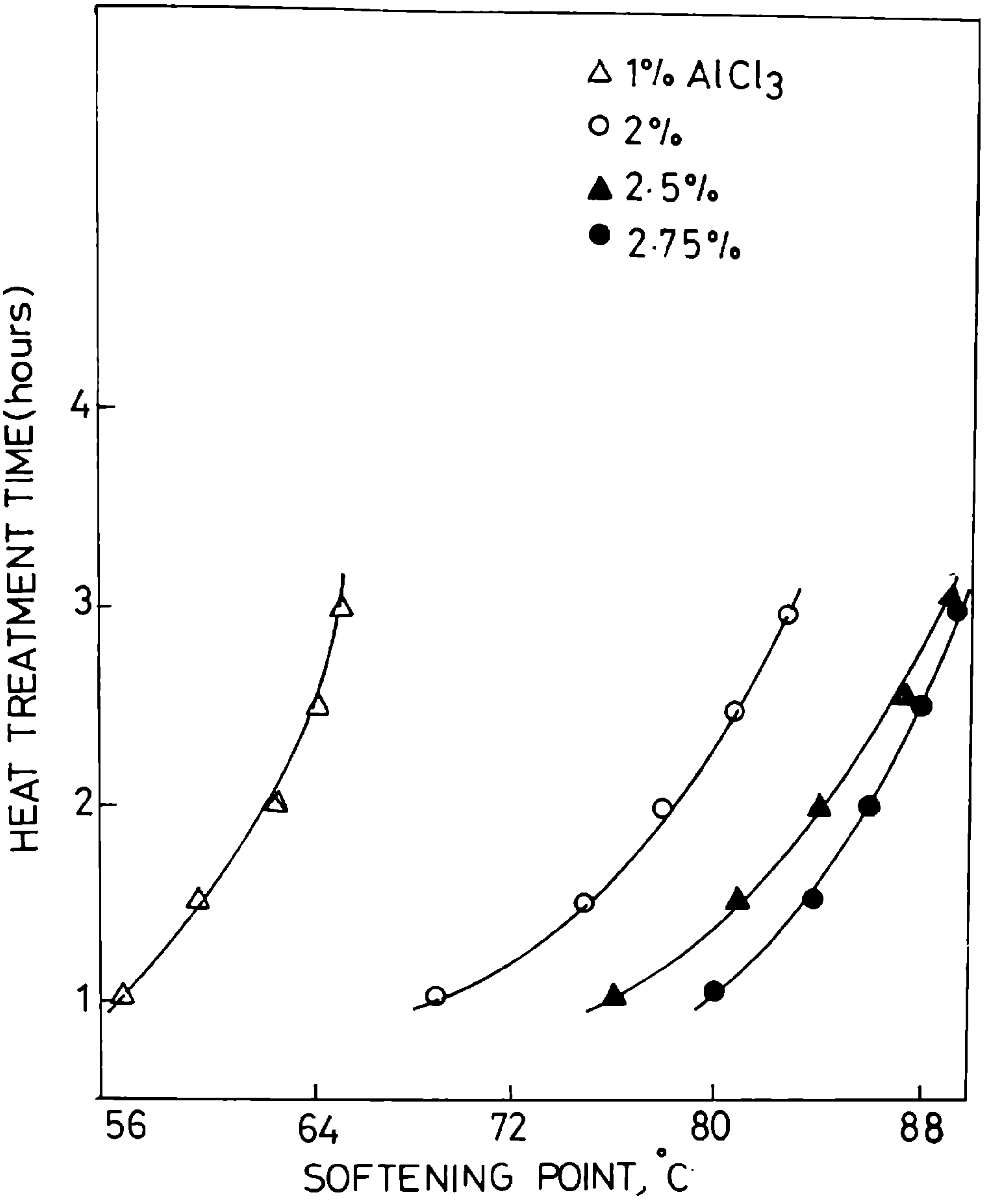


Fig 3.3 Effect of duration of heat treatment with varying percentages of $AlCl_3$

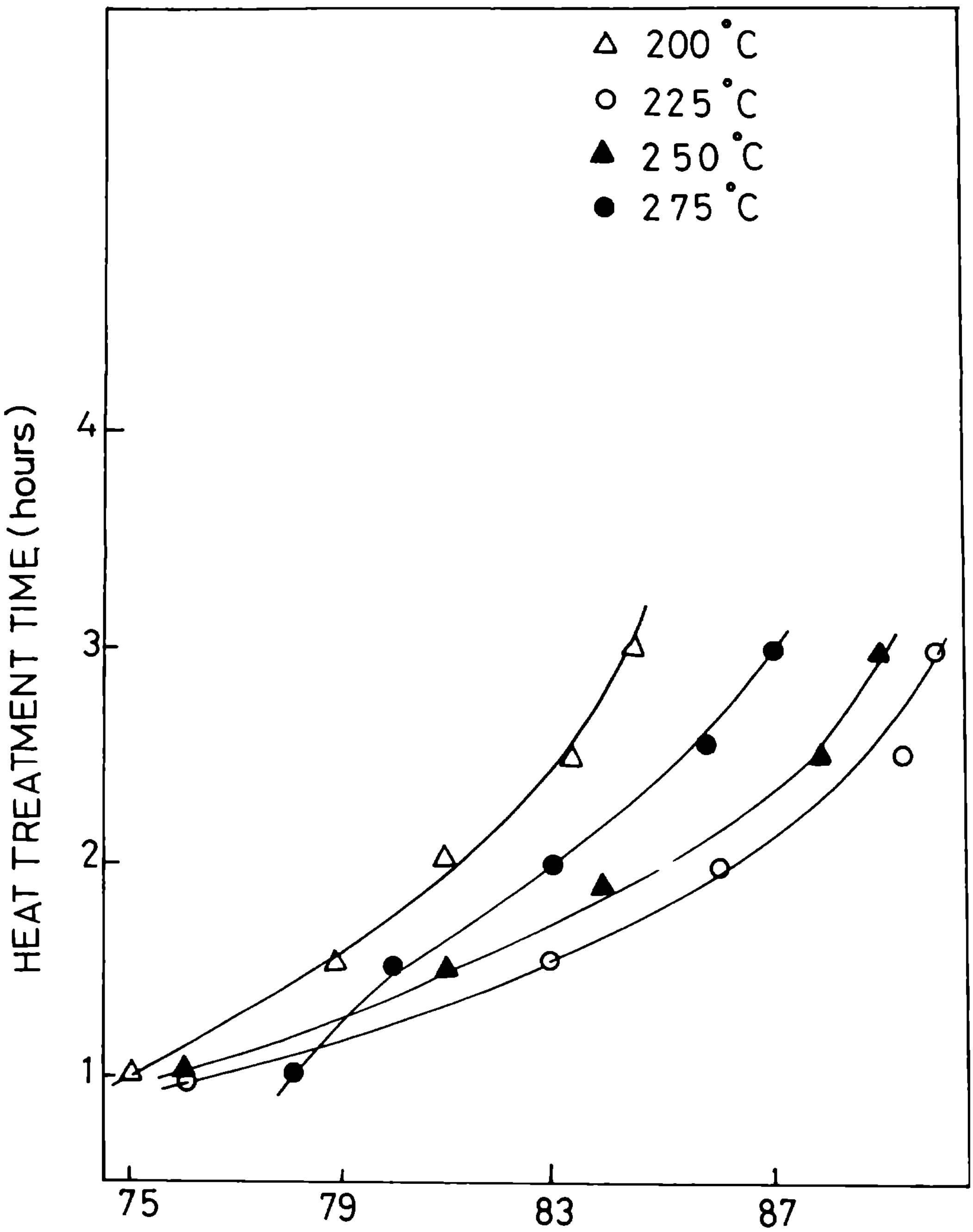


Fig 3.4 Effect of duration of heat treatment at varying temperatures with 2.5% $AlCl_3$

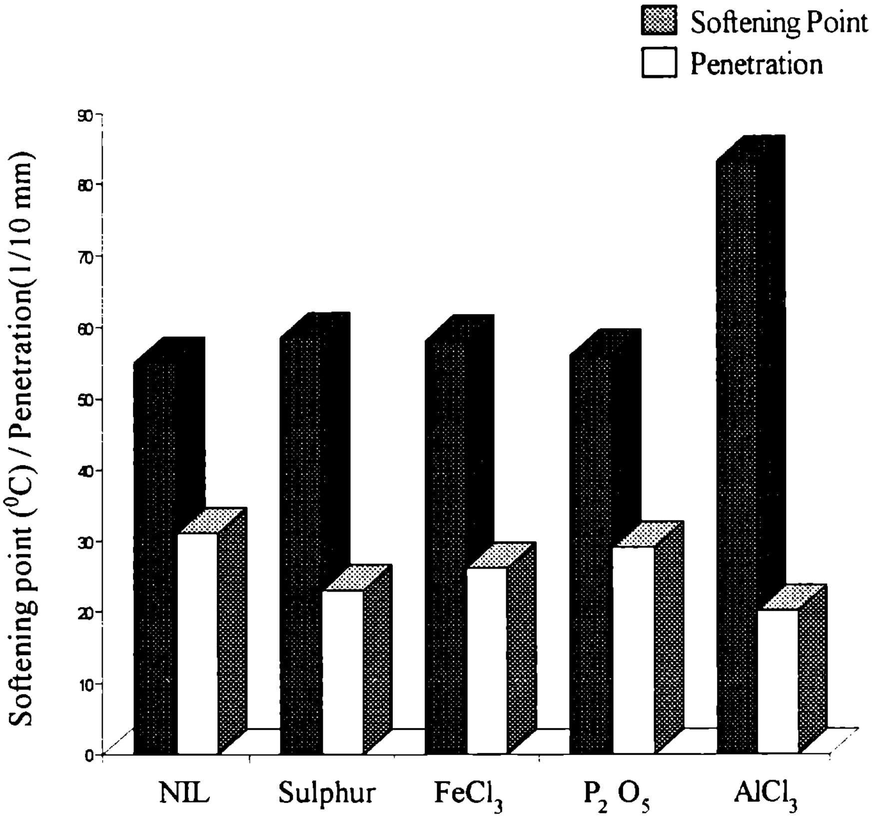


Fig. 3.5 Heat Treatment without and with different catalysts (250^{0}C, 3 hrs.)

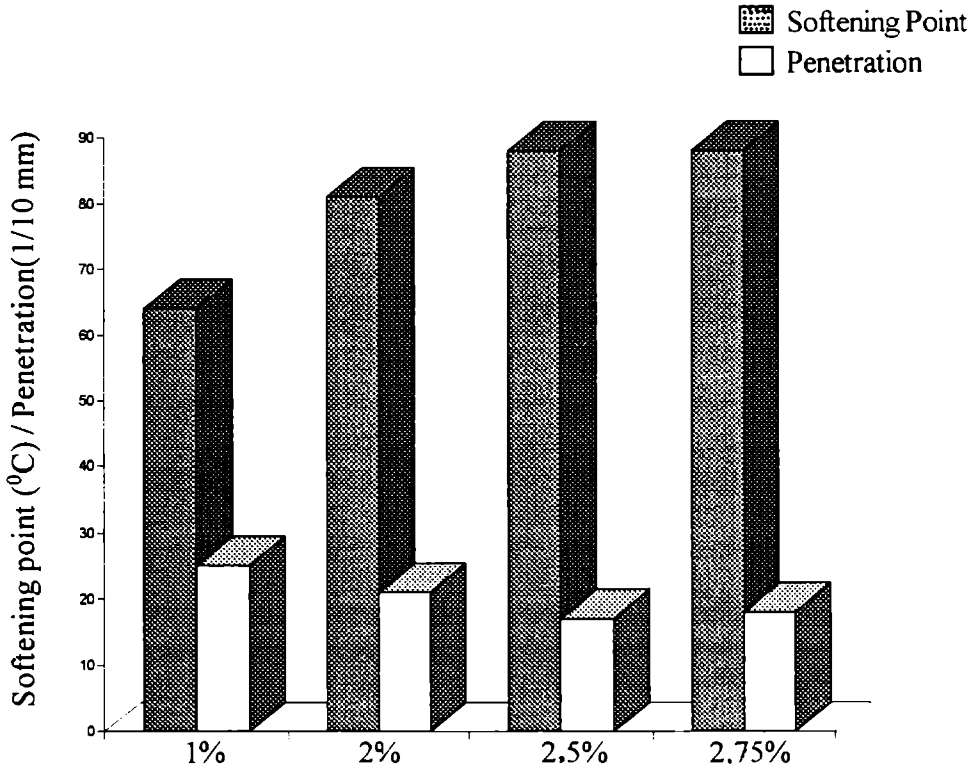


Fig. 3.6 Effect of different percentages of $AlCl_3$ on heat treatment (2.5 hrs., 250^{0}C)

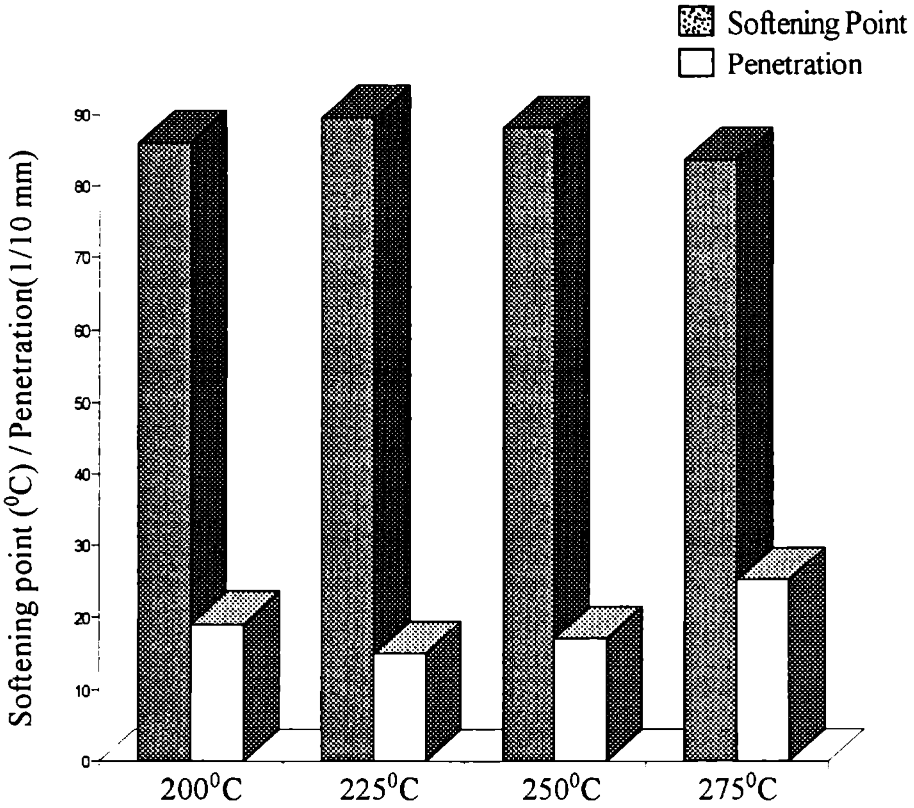


Fig. 3.7 Effect of temperature on heat treatment (2.5 hrs., 2.5% $AlCl_3$)

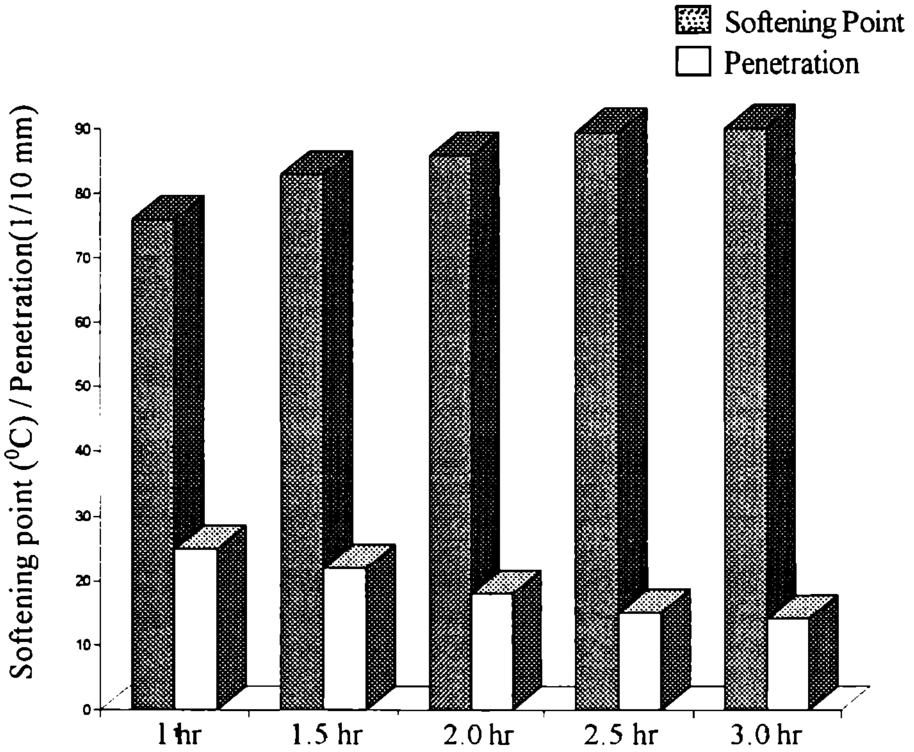


Fig. 3.8 Effect of duration of heat treatment (225⁰C, 2.5% $AlCl_3$)

3.1.4 CONCLUSIONS

The study shows that the sludge which is a dumped waste, can be converted into a reasonably rich source of lighter oils and some specific grades of industrial bitumen. It is found that about 17% of lighter oil fraction can be recovered from this sludge and the characteristics of this light oil indicate that it can meet the specifications of high speed diesel by blending with appropriate streams of petroleum refineries. It is also found that the vacuum residue obtained from the sludge can be heat treated with catalysts to obtain few grades of industrial bitumen viz; 65/25, 75/30, 85/25 and 90/15. Out of the different catalysts tried $AlCl_3$ is the best in bringing condensation and polymerisation reactions in the vacuum residue of the sludge thereby bringing the softening point penetration ratio to a satisfactory level. The products are similar to those obtained by air blowing for industrial bitumen manufacture but at relatively low temperatures and without air blowing. A possible reaction mechanism is also suggested for the catalytic reactivity. Optimum conditions viz. duration of heating, temperature to be employed and percentage of catalyst required are also derived. This method of conversion to industrial bitumen has also the advantage that no noxious fumes are evolved as in the air blowing process.

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BITUMENOUS PAINTS FROM INDUSTRIAL BITUMEN OBTAINED FROM REFINERY SLUDGE

3.2.1 INTRODUCTION

Coatings generally meant to resist[1] corrosion must fundamentally resist the corrosive atmosphere and must prevent it from reaching the basic structure. Thus, there are as many variations in the types of coatings as there are in the forms of corrosion. The design of an effective anticorrosive coating is a complex task which requires an extensive knowledge of not only corrosion principles, but of the science and chemistry of coating formation as well. The basic formation of a coating is a highly technical reaction, and the type of reaction is extremely important to the effectiveness of the coating in its particular use. Inorder to produce a film which will perform practically and satisfactorily in a given environment, the coating, after its application, must convert to a very dense, solid membrane which is resistant to that particular environment. This conversion from the liquid resin to the solid resin film is the most important reaction that takes place in the formation of a coating.

Molecular size, weight and complexity of the coating resin often determine the type of coating film which forms. Generally, for corrosion resistant applications, a very dense, tight, chemical resistant film is desired. Resins which form this type of film by evaporation are of very high molecular weight, and are reacted into their finished form prior to being formulated into a coating. For the high molecular weight film to form on the surface, it is only necessary for the solvents to evaporate from the resin solution. Because of the high molecular weight of these resins, they are often difficult to put into solution, requiring strong solvents with the total coating formulation having relatively low solids. On the other hand, resins, which are of relatively low molecular weight may be liquids in themselves. These require, reaction in place, either by catalytic action, reacting with other resins or by reaction with oxygen or moisture from the air to form films. These materials which are of lower molecular weight to begin with, have the advantage of building a higher solid combination into the coating so that there can be less volatile material or in some cases, no volatile material in the coating. The polymerisation or condensation, creates the high molecular weight coating resin in place. In this case, the conditions during application are critical for the film forming reaction to take place.

There are several different types of binders, or film formers, which are used to formulate protective coatings for corrosion resistant applications. Each of these have their own characteristics and requirements for film formation. The types of binders are those formed by solvent evaporation, oxidation, polymerisation, condensation, reaction with moisture from the air, coalescence and the formation of inorganic coatings. Materials which form a film may generally be classified under two categories; thermoplastic and convertible. A thermoplastic material is one that becomes soft or fluid when heated. On cooling it regains its original physical and chemical properties. Convertible film formers undergo a chemical change or conversion. This results in a definite alteration of their physical properties. The resins which dry by solvent evaporation are all thermoplastic film formers. Film formation by solvent evaporation, which appears to be of the simplest type is actually far from simple. The film formation does not commence until the evaporation of the solvent has reached an advanced stage which brings the molecules of the resin into such close contact that their mutual chemical attraction draws them together. Film properties are influenced by the molecular arrangement or structure within the film. A homogeneous, dense structure is promoted by a solvent that maintains maximum dispersion and mobility of the polymers during film formation.

Industrial bitumen along with solvents are also extensively used as corrosion resistant coatings. Bitumenous coatings[2] give better results out-of-doors on metal than on wooden surfaces, although most manufacturers recommend them indiscriminately for both types of construction. However, it should be noted that any resinous constituents in the wood will act deleteriously on the coating after a time, due to their solvent action on the bitumenous constituents present. If manufactured according to correct principles, bitumenous lacquers will give fair service on exposed metal work, including metal roofs, corrugated iron, farm implements etc. They are at the same time considerably less expensive. Pigmented bitumenous lacquers[3] have been used to protect the bottom of ships against the corrosive influences of sea water and the growth of barnacles and sea weed. Bitumenous coatings have given excellent service for many years on ships and docks, steel structures and underground tanks and pipelines. A typical example is the performance of the bitumenous paints on the dry dock of "The Dewey" which was built at Sparrows point in 1915 and towed to the Philipines. Upon inspection before the fall of Manila in world war II, when the dock was 35 years old, the enamel was reported to be in excellent condition[4] An asphalt wax[5] composition has been proposed for coating the interior of beer cans.

Bitumenous coatings provide good chemical and corrosion resistant films, but can only be applied where appearance is not a factor. Since bitumenous coatings do not impart any bad taste to water, they are often used for painting steel water tanks and concrete reservoirs for storing drinking water. These coatings also are combined with higher polymer petroleum resins which increase the strength and provide more flexibility to the coatings. Bitumenous coatings are also made with inert fillers which add to the thickness of the coating and in many cases, to its impervious characteristics. Some of these coatings have excellent resistance to industrial fumes, moisture and exterior weather exposure. They do tend to lose gloss and to chalk when exposed to the weather. On the other hand, this apparently does not detract from their other good characteristics or reduce their overall weather resistance.

Bitumenous coatings have the disadvantage of being black, and while, some very dark iron oxide colours can be obtained from the bitumenous type coatings, they must generally be used where a black coating with generally poor appearance is adequate. Bitumenous coatings can be pigmented with leafing aluminium and provide a bright aluminium colour in this manner. This, however is the limit to which bitumenous coatings can be pigmented for decorative purposes.

It may be noted that almost 50% of the industrial bitumen manufactured is used for the production of bitumenous paints. In this study, the usefulness of the industrial bitumen obtained from refinery sludge is tried in the preparation of bitumenous paints. Bitumenous paints usually contain an asphaltic base in a volatile solvent with or without drying oils, resins, fillers and pigments. Inorder to obtain a smooth continuous resin film, it is usually necessary to use a combination of solvents which are classed as active solvents, latent solvents and diluents. The active solvents are those which easily dissolve the resin and are the primary ones for putting it into solution. The latent solvents are less active, but still act as solvents while the diluents are materials which will tend to soften the resin, but will not actively dissolve it. The combination of these three types working together often provides a better and stronger film than a single solvent alone. Mineral spirit is often called Painter's naphtha. It is a relatively high boiling petroleum product used for dissolving asphalts. Other solvents used are benzene, toluene, xylene, high flash naphtha etc. Red lead is an ingredient sometimes incorporated in the formulation as a rust inhibitive pigment. Chlorinated rubber can be used in coatings to get hard, inert films showing high resistance towards acids, alkalies, oxidising agents etc. Carbon black occupy a special position among the pigments and fillers owing to their chemical nature and their colloidal structure. Among pigments they are the strongest absorbers of light over the entire visible spectrum and are preferably used for jet black colours[6] or for darkening of colour developed by other pigment compositions. CNSL resin can be used in protective coatings, paints etc. because they are internally plasticized, making them flexible and more compatible with drying oils and solvents[7] Hexamethylene tetramine functions as a catalyst to help the crosslinking of the linear polymer of CNSL in a way to improve the overall appearance of the paint film. This study also investigates the incorporation of cashew nut shell liquid formaldehyde resin, chlorinated rubber etc., to the bitumenous paints thus obtained to modify their properties.

3.2.2 EXPERIMENTAL

The 90/15 grade industrial bitumen is used for the preparation of bitumenous paints. It is prepared as follows. The purified sludge is subjected to vacuum distillation and thus the lighter oils are removed. The vacuum residue of sludge so obtained was then subjected to heat treatment at 225°C for 2.5 hours with 2.5% $AlCl_3$ (Details are given in Chapter 3, Part I). Its characteristics are given in Table 3.5, Part I of this chapter.

Three different formulations were tried using the industrial bitumen (Grade 90/15) derived from refinery sludge.

Formulation I is prepared by mixing the ingredients as shown in Table 3 7

Mineral turpentine is first fluxed with industrial bitumen at 150 200°C until the mass became stringy It is then cooled to 100°C and red lead, litharge and the drier mixture were incorporated. Finally it is thinned with petroleum heavy naphtha.

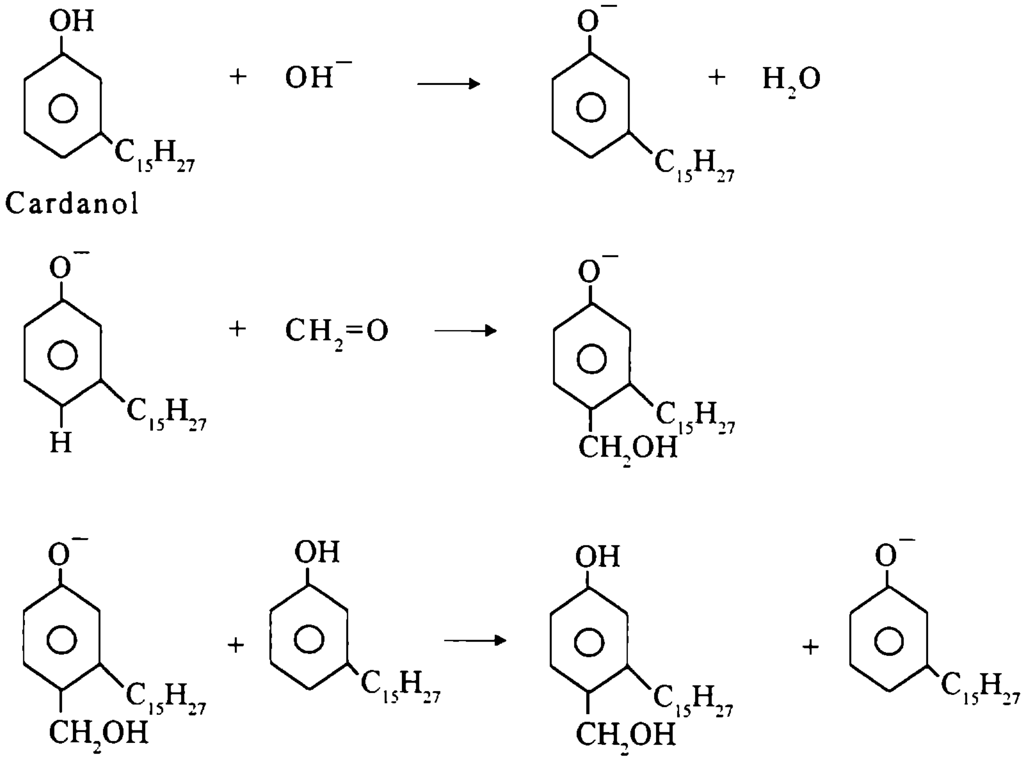
Formulation II

Preparation of CNSL Formaldehyde resin

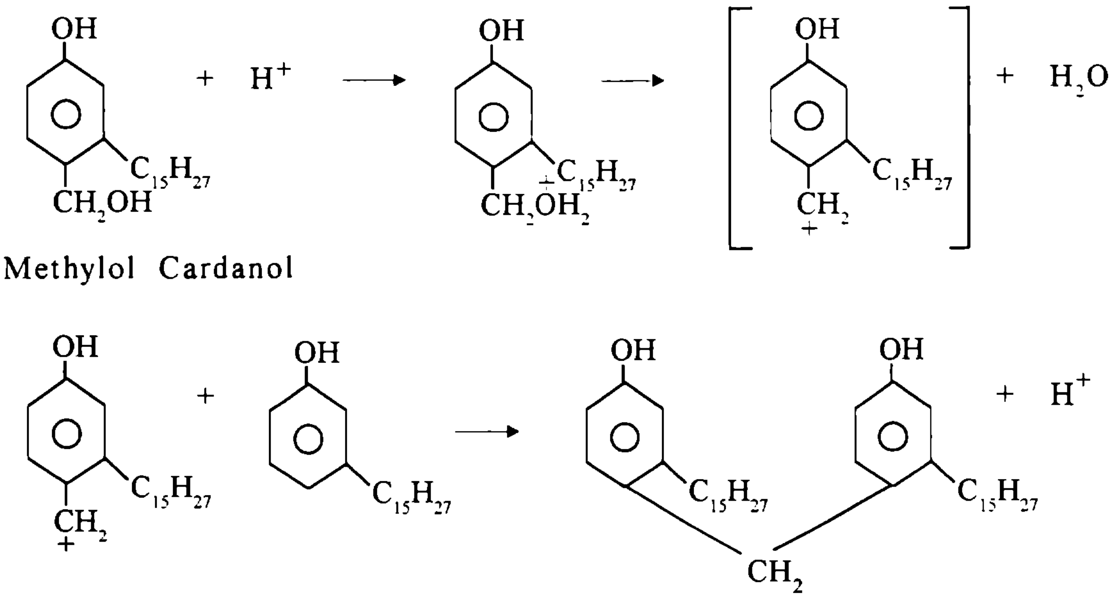
The resin is prepared by carrying out the condensation; taking formaldehyde and cashew nut shell liquid in the ratio 1 4 by weight. 7.5 ml of 25% ammonia was added as the catalyst per 100 ml of CNSL. The mixture is shaken well and kept overnight for the reaction to take place to the required extend. The resin so obtained is then vacuum distilled to remove the water of condensation.

The probable course of reaction[8] is illustrated here (cardanol, being the major constituent of CNSL).

(a) Formation of Methylol Cardanol



(b) Formation of Polymer



Methylol Cardanol

Dimer

The polymerisation so continues to form higher polymers to form a network.

In formulation II Pot A and B are prepared by mixing the ingredients as described in Table 3.8

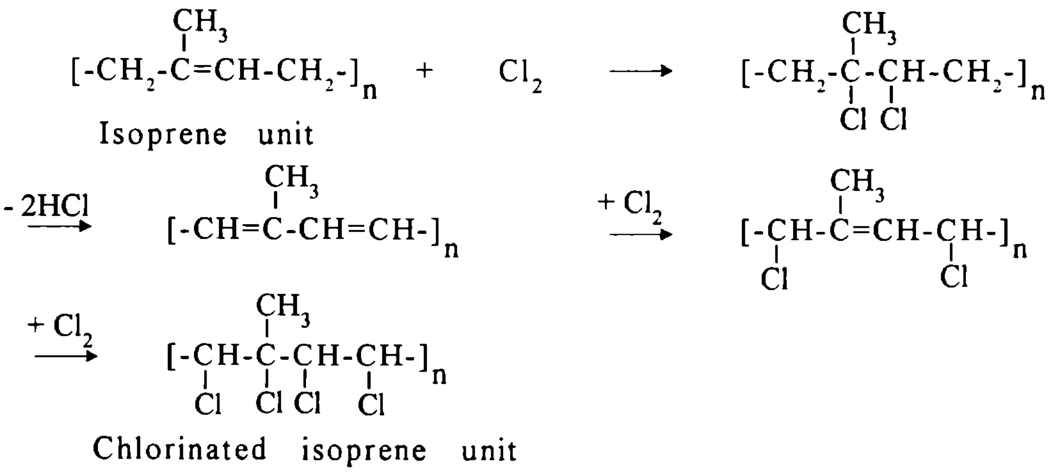
Equal quantities of Pot A and B are mixed together prior to application. Hot air is then supplied to cause the thermosetting reactions of the CNSL formaldehyde resin.

Formulation No. III

Preparation of Chlorinated rubber

NR is masticated for half an hour at tight nip in a two roll mill. It is then dissolved in carbon tetra chloride to get a 3% solution. The solution is stirred to make it uniform and chlorine gas is passed through it continuously for 5-6 hours until a thick rubbery layer is formed on the surface. Chlorine gas is passed for another one hour The chlorinated rubber is poured into hot water (90°C) slowly so that it becomes a white solid mass which is taken out and dried.

In the chlorination process, rubber reacts with chlorine in an amount sufficient to yield a product of approximately 64 to 65% chlorine. Isoprene units of NR undergo a complex chlorination reaction with both addition and substitution of chlorine. The chlorination process is brought to an end when the double bonds have disappeared and the chlorine content is high enough to assure optimum stability, compatibility and resistance to fire. The chlorine atoms get scattered along the available carbon atoms with little tendency for more than one chlorine atom to be on a single carbon atom. The isoprene chlorine reaction takesplace as follows:



$$[\text{-CH}_2\text{-}\overset{CH_3}{\overset{|}{C}}\text{=CH-CH}_2\text{-}]_n + Cl_2 \longrightarrow [\text{-CH}_2\text{-}\underset{Cl}{\overset{CH_3}{C}}\text{-}\underset{Cl}{CH}\text{-CH}_2\text{-}]_n$$

$$\xrightarrow{-2HCl} [\text{-CH=}\overset{CH_3}{C}\text{-CH=CH-}]_n \xrightarrow{+Cl_2} [\text{-}\underset{Cl}{CH}\text{-}\overset{CH_3}{C}\text{=CH-}\underset{Cl}{CH}\text{-}]_n$$

$$\xrightarrow{+Cl_2} [\text{-}\underset{Cl}{CH}\text{-}\underset{Cl}{\overset{CH_3}{C}}\text{-}\underset{Cl}{CH}\text{-}\underset{Cl}{CH}\text{-}]_n$$

Formulation III with chlorinated rubber is prepared by mixing the ingredients as given in Table 3 9 All the three different formulations were applied by brushing and were tested for the various parameters. Drying time with respect to surface dry, hard dry and tack free was determined as per IS:101-1964 Cl. No. 7.2 using a mild steel panel of size 150 x 150 mm at room temperature and at a relative humidity of 65±5% in a well ventilated chamber. Consistency, colour and finish were determined as per IS:101-1964 Cl. Nos. 7.4, 7.5 and 11 respectively. Flexibility, adhesion, stripping etc. were determined according to IS:101 1964 Cl. Nos. 16 and 17 respectively. Keeping property was determined as per IS:101 1964 Cl. No. 31 by storing the material under cover in a dry place for a period of one year after the date of manufacture. Water resistance was determined as per IS 158-1968, appendix A, by allowing water to remain in contact with the paint film for 3 days with the lid of the metal container closed whose inside surface is coated with the material. Acid resistance was determined as per IS.158-1968, appendix B, by immersing a panel coated with the material for 24 hours in 1.20 V/V H_2SO_4. Alkali resistance was found according to IS:158-1968 appendix C, by dipping a panel coated with the material in 5% anhydrous sodium carbonate in water W/V for four hours. Chlorine resistance was determined as per IS.158-1968 appendix D by immersing three quarters of a glass panel coated with the material in 0 05% w/v chlorine water kept in a dark place for 72 hours. Heat resistance was determined as per IS 158-1968 appendix E, by keeping the coated panel in an electrical furnace whose temperature is raised from room temperature to 300^{0}C in one and a half hours time. Flash point was determined as per IP 170/75 using the Abel apparatus keeping the bath temperature at 54^{0}C and applying the test flame for every 0.5^{0}C rise in temperature of the sample until a distinct flash occured in th interior of the cup. Water content was determined according to IP 291/73

3.2.4 RESULTS AND DISCUSSION

All the three formulations prepared were found to be homogeneous. They show no separation of solvent or coagulation of the asphalt base, nor settling or packing in the container that cannot be overcome by stirring for a short time. Also the emulsion formed was consistent and it does not take hard inside the container and is in such a condition that stirring easily produces a smooth uniform paint suitable for application. They were found very easy to apply. Recoatability of these formulations was found to be very good.

It can be seen from table 3.10 and 3 11 that bitumenous paints made using formulation I, II and III are meeting the requirements of drying time, consistency, finish, stripping, flexibility and adhesion, keeping properties etc. as required by IS 101 1964 Formulation I exhibited good resistance towards water, chlorine, acid and alkali. But its heat resistance was found to be very poor as indicated by the softening of the coated film when the temperature of the furnace was raised from room temperature to 300°C. This indicated that formulation I cannot be used for high temperature application as for industrial chimneys, boilers etc. where the paint coatings should be resistant to heat. It can also be seen from table 1 that incorporation of CNSL formaldehyde resin in formulation II boosted the heat resistance retaining the other properties including resistance towards water, chlorine and alkali. The hexamethylene tetramine incorporated as catalyst in this formulation act in a way as to crosslink the linear polymer of CNSL to a three dimensional network

Table 3.7 Ingredients of Formulation I

Industrial bitumen (Grade 90/15)	=	50%
Red lead	=	1.5%
Litharge (PbO)	=	1.5%
Mineral Turpentine	=	21.5%
Petroleum heavy naphtha	=	25%
Drier mixture (cobalt naphthenate + manganese naphthenate + lead naphthenate)	=	0.5%

Table 3.8 Ingredients of Formulation II

Pot A			
	CNSL - Formaldehyde resin	=	40%
	Carbon black (ground)	=	20%
	Toluene	=	40%
Pot B			
	Industrial bitumen (Grade 90/15)	=	47%
	Hexamethylene tetramine	=	3%
	Mineral Turpentine	=	20%
	Petroleum heavy naphtha	=	30%

Table 3.9 Ingredients of Formulation III

Industrial bitumen (Grade 90/15) = 35%

CNSL - Formaldehyde resin = 20%

Chlorinated rubber in solution = 5%

Toluene = 10%

Mineral Turpentine = 10%

Petroleum heavy naphtha = 20%

Table 3.10 Different Characteristics of the Paint film from various Formulations

	Characteristic	Formulation I	Formulation II	Formulation III
1.	Drying Time			
	a) Surface dry	8 hrs	6 hrs	7 hrs
	b) Hard dry	20 hrs	18 hrs	18 hrs
	c) Tack free	30 hrs	24 hrs	24 hrs
2.	Consistency	Smooth & Uniform	Smooth & Uniform	Smooth & Uniform
3.	Finish	Smooth & Semi glossy	Smooth & Glossy	Smooth & Glossy
4.	Colour	Black	Shining black	Shining black
5.	Flash point °C	36	38	39
6.	Water content % wt.	0.2	0.2	0.2
7	Stripping test	...............Scratches free from jagged edges.....................		

Table 3.11 Other characteristics of the Paint film from different formulations

Characteristic	Formulation I	Formulation II	Formulation III
1. Flexibility & adhesion	No visible change or detachment of the film		
2. Keeping properties	More than one year		
3. Resistance to water	Paint film is firmly adherent, no signs of re-emulsification, loss of adhesion and imparts no undesirable odour or taste to water		
4. Resistance to alkali	Paint film shows no sign of softening, dulling, blistering or cracking or changes of colour		
5. Resistance to chlorine	Paint film shows no sign of softening, dulling, blistering or cracking or changes of colour......................		
6. Heat resistance	Paint film softens	Paint film firmly adherent and shows no signs of sag, blistering or slippage from metal	
7 Acid resistance	Paint film remains firmly adherent and and shows no sign of dulling	Paint film gets detached from the metal	Paint film remains firmly adherent and shows no sign of dulling

But its acid resistance was found to be very poor as indicated by the detachment of the paint film from the panel when it is dipped in 1:20 v/v sulphuric acid for a period of 24 hours. Acid resistance is essential to protect the coating from the destructive action of mineral acids, acid salts and other corrosive chemicals. Hence this formulation can be applied only for those surfaces where contact with acids/acid salts is unlikely.

Table 3 10 & 3 11 also show that formulation III containing both CNSL formaldehyde resin and chlorinated rubber exhibits good heat resistance as well as acid resistance besides retaining all the other properties exhibited by the formulations I and II. As can be seen from the formula of chlorinated rubber, the amount of chlorine in the molecule is substantial. Chlorine containing organic radicals generally have very good chemical resistant properties. It is this, as well as the saturated carbon bonds, that give it good chemical resistance. The enhanced heat resistance exhibited by this formulation as in the case of formulation II can be attributed to the presence of CNSL formaldehyde resin in the formulation. The high chlorine content is also responsible for the observed heat resistance.

3.2.4 CONCLUSIONS

This part of the study shows that industrial bitumen derived from refinery sludge can be utilised to prepare acid, alkali, heat and water resistant bitumenous paints. It is also seen that the heat resistance of bitumenous paints can be increased considerably by including cashew nut shell liquid formaldehyde resin in the formulation. Cashew nut shell liquid is a cheap by-product of the cashew industry and its utilisation can also help to bring down the cost of production of bitumenous paints. This study also shows that incorporation of chlorinated rubber in the formulation will enhance the acid resistance considerably without affecting the heat resistance and other desirable properties.

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CHAPTER 4

PURIFIED REFINERY SLUDGE AS PROCESS AID IN SULPHUR VULCANIZATION OF NATURAL RUBBER

4.1 INTRODUCTION

Natural rubber is the preferred polymer in many areas of rubber use. This is because of its superior building tack, green stock strength, better processing, high resilience and excellenct dynamic properties. Purified natural rubber hydrocarbon is a long chain polymer made up of cis-1,4-poly isoprenoid units arranged in a highly stereoregular manner. The molecular weight of the polymer ranges from 10^5 to 10^6 and it varies widely[1] Due to the high structural regularity, natural rubber tends to crystallize on stretching. This strain induced crystallization gives it the unique high tensile strength in gum and non-reinforcing filler vulcanizates.

In rubber industry, it is compounding and vulcanization that transforms raw rubber into useful products. During vulcanization, the long chain rubber molecules become crosslinked by reaction with the vulcanizing agents to form three dimensional structures. The reaction transforms the weak plastic like material to a strong elastic product. The properties of the latter, in particular, the modulus, hardness, elastic properties, resistance to swelling etc are greatly influenced by the course of vulcanization[2] The extent of changes in properties is governed by the choice of vulcanization agents added to the rubber to bring about the vulcanization process and also by the vulcanization conditions. Hence inorder to get the rubber products with better properties, it is necessary to use the correct combination of vulcanization agents and vulcanization conditions. The vulcanization of natural rubber may be effected with the aid of sulphur, peroxides, resins, ionizing radiation, metal oxides etc[3] Sulphur vulcanization of natural rubber forms the subject of numerous publications[2-7] Compounding of rubber is usually done by mixing raw rubber with other ingredients like processing aids, vulcanizing agents, accelerators, activators, age resistors, fillers, colouring agents, etc. Processing aids are used to facilitate easy mixing or to aid in a specific manner during extrusion, calendering or moulding operations. Vulcanizing agents are the chemicals which crosslink the rubber chains so as to get the desired physical properties to the final product. Accelerators together with the vulcanizing agents reduce the vulcanization time by increasing the rate of vulcanization. Accelerator activators form chemical complexes which increase the efficiency of the accelerator Zinc oxide is the most common accelerator activator and it is usually used together with a fatty acid (like stearic acid) to form a rubber soluble soap in the rubber matrix. Fatty acid acts as a coactivator. The mechanism by which this complex speeds up the cure has not been well understood even now. It is presumed that zinc oxide reacts with stearic acid to form zinc stearate which is soluble in the rubber and in this form facilitate the crosslinking process. It is essential to have the zinc ions in soluble form. Stearic acid or other fatty acids used also serve as lubricants between the polymer chains and allow easier flow of the compound in shear Both ends of the stearic acid molecule help processing. The paraffenic end provides the lubricating effect while the acid group along with other functions absorbs the pigments on the surface. Although stearic acid is by far the most common fatty acid used, others like oleic acid may also be used.

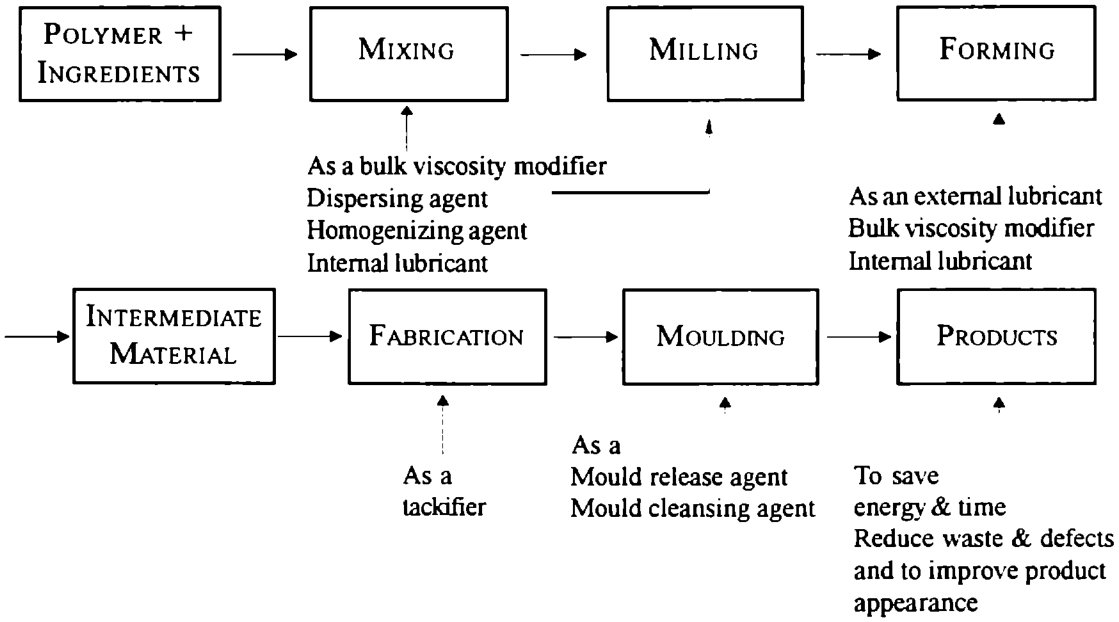
Fillers are generally incorporated for improved processability, reinforcement or for cost reduction. The effect of a filler on rubber vulcanizates depends on its physical properties, such as particle size, surface area, surface reactivity, electrical charge on the particles and chemical properties such as pH and reactivity with accelerators. Fillers may be classified as reinforcing and non-reinforcing. A reinforcing filler is one that improves modulus and failure properties such as tensile strength, tear resistance, abrasion resistance of the final vulcanizate. On the other hand a non reinforcing filler is used to cheapen and/or stiffen the final product. In general the best reinforcing fillers are those that have the smallest particle size The basic aspect of polymer filler interaction has been studied in detail in a number of polymers[8-11] Studies on filled systems have also been reviewed by Kraus[12] and Voet[13]

Carbon blacks are the most effective reinforcing fillers. They are essentially elemental carbon and are composed of aggregated particles. Depending on the process adopted for the preparation, carbon blacks are named as furnace black, thermal black, channel black, lamp black etc. with general purpose elastomers like NR, high abrasion furnace (HAF) blacks with average particle size in the range of 24-28 nm are most widely used It is known that carbon black contain active functional groups such as phenolic, ketonic and carboxylic, together with lactones[14] During vulcanization, carbon black enters into chemical reaction with sulphur, accelerator etc., participating in the formation of vulcanized network. Carbon black interacts strongly with unsaturated hydrocarbon rubbers during milling and the rubber is adsorbed on the filler. This altes the stress strain properties and reduces the extent of swelling in a solvent[15] Two of the most important effects of reinforcing fillers on the properties of vulcanized rubber are a substantial increase in modulus and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. Thus the filler may influence the degree of crosslinking.

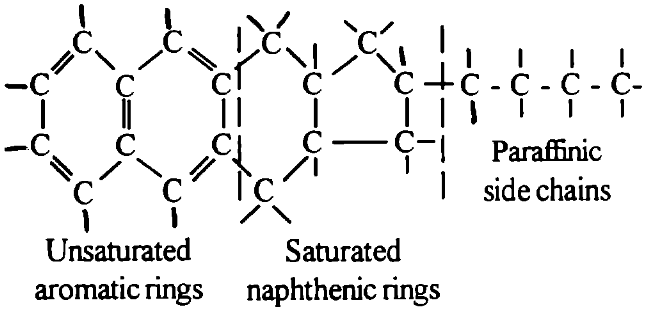
Age resistors are used in rubber compounding to reduce ageing processes in the vulcanizates. Ageing is normally caused by chain scission, crosslinking or some form of chemical alteration of the polymer chains. Consequently, the age resistors used must be capable of reacting with the agents causing ageing, prevent or slow the polymer breakdown to improve the anti-ageing qualities and to extend the service life of the product involved. Amines and phenols are generally used as age resistors to slow down the oxidative degradation of rubber products.

The present study deals with the use of purified refinery sludge as a process aid in natural rubber compounding. The study becomes all the more important because petroleum oils used as process aids are becoming prohibitively costly whereas refinery sludge is available as a dumped waste and it is found to contain a lot of bitumen, wax and lighter oils.

Presence of process aids are absolutely essential to help the dispersion of fillers and to achieve a considerable improvement in physical properties. At the same time building tack and other processing characteristics are also improved. The material used as processing aid should not chemically react with the rubber but instead it should act as an internal lubricant favouring slippage between the flow units of the compound. The function of processing aids at different stages of rubber processing can be shown as below[16]



It is important to know the composition of a particular grade of oil to determine its properties, its effects on physical properties of rubber and its compatibility with different types of rubbers. Process oils are generally classified into three based on the relative content of aromatic, naphthenic and paraffinic hydrocarbons[17,18]



The various properties required for a plasticizer are good plasticizing efficiency, low volatility, good stability to heat, light and oxidation and low cost. A viscous petroleum extender or plasticizer of low diffusibility and low volatility will be highly beneficial in rubber compounding because of the considerable extent of oil migration during service life[19] and due to the possibility of loss of oil through evaporation under high temperature operating conditions if more volatile oils are used[20] It has been reported that[21] petroleum pitch 170 and 240 [in accordance with their softening points in °F as measured by the ASTM "Ring and Ball" method (D-36)] offers promise as compatible replacements for aromatic extender oil in styrene butadiene and polybutadiene rubber. Both pitches imparted to the vulcanizates pronounced physical property changes not encountered with the usual extender oils or plasticizers. Although these pitches are solid at normal temperatures, they are readily incorporated into rubber systems under usual mixing conditions.

In the present study, an attempt is made to utilize the oily sludge obtained from the refinery as a compounding ingredient in the sulphur vulcanization of natural rubber Different mixes were prepared using this sludge and also control mixes using aromatic oil. Processability of the various mixes containing aromatic oil/refinery sludge was studied in a Brabender Plasticorder. Processability in this context can be defined as any compounding step commencing with mixing and ending at vulcanization. The addition of oil at the mixing stage serves to reduce the overall viscosity of the mix to a workable level, reduce power consumption at high filler loading, keep heat generation down and ease the dispersion of pigments[22] The mixes obtained from these formulations were evaluated for their different cure characteristics and the vulcanizates were also evaluated for tensile and other physical properties. The properties of the experimental mixes were compared with those of the control mixes. Heat ageing characteristics of the vulcanizates were evaluated and compared with those of the control mixes. Chemical crosslink density of the different vulcanizates was also estimated to evaluate the variation in the tensile properties of the different vulcanizates.

4.2 EXPERIMENTAL

Natural rubber conforming to ISNR 5 having the specifications as given in Chapter 2 was used in the present study Zinc oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF N 330) and aromatic oil used are all of rubber grade. Refinery sludge obtained from Cochin Refineries Ltd., Kochi (India) was used after purification. The purification of the sludge was done as described in Chapter 2 by maintaining the sludge at a temperature of 110 ± 10°C for 12 hours until it is fully dehydrated. The remaining hot oil was then passed through strainers of different sizes to remove solid impurities. The conventional system of rubber vulcanization which contains a much higher concentration of sulphur than accelerator was followed in the present study In the mixes under review the accelerator (MBTS + TMTD) level was maintained at 1 phr while sulphur level was maintained at 2.5 phr. Table 4.2 shows the composition of the various mixes used. In all these mixes 5 phr zinc oxide, 2 phr stearic acid and 1 phr Accinox HFN are added as activator, co-activator and antioxidant respectively for hundred parts of rubber (phr). All mixes contain 50 phr carbon black (HAF N330) as filler Mix A contain 5 phr of aromatic oil and it is taken as the control. Mix B contains 4 phr of aromatic oil and 1 phr sludge. Mix C contains 3 phr aromatic oil with 2 phr sludge and mix D contains 2 phr aromatic oil with 3 phr sludge. Mix E contains 1 phr aromatic oil and 4 phr sludge while mix F contains 5 phr sludge alone. The characteristics of the purified sludge used are as given in Table 4 1

Brabender Plasticorder (PL 3S) was used for studying the processing characteristics of the mixes. This torque rheometer is a device for measuring the torque generated due to the resistance of a material to mastication under the preselected conditions of shear and temperature. The processability of natural rubber using purified sludge was compared with that of conventional aromatic oil. The materials are charged into the mixing chamber after setting

Table 4.1 Characteristics Of Purified Refinery Sludge

Density @ 15°C g/ml	0.9573
Pour Point °C	+42
Wax %Wt.	6.0
Asphaltenes %Wt.	7.8
Acidity mg KOH/g	4.3
Flash Point °C	>200
Kinematic Viscosity CS @ 100°C	30.33
Total Sulphur %Wt.	3.43
Ash Content %Wt.	4.8

Table 4.2 Formulation of mixes containing aromatic Oil/Sludge

Ingredients	A	B	C	D	E	F
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Mercapto benzthiazyl disulphide (MBTS)	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide (TMTD)	0.2	0.2	0.2	0.2	0.2	0.2
N-1,3-dimethyl-N'-phenyl paraphenylene diamine (Accinox HFN)	1	1	1	1	1	1
Carbon black (HAF N330)	50	50	50	50	50	50
Aromatic Oil	5	4	3	2	1	0
Sludge	0	1	2	3	4	5
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

the roller mixing heads at 30 rpm and at room temperature (30^{0}C) to obtain a torque time curve or a plastogram. NR was passed six times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small strips before feeding into the plasticorder. The total mixing time was 16 minutes with the following break-up. NR was masticated within 4 minutes followed by adding activator and accelerator within 3 minutes. Carbon black mixed with purified refinery sludge was then added within 8 minutes and finally sulphur within 1 minute. The formulations of the different mixes are as given in Table 4.2 except for the fact that the oil levels are varied. For the control mixes the same procedure was repeated by replacing refinery sludge with aromatic oil. Inorder to optimise the quantity of oil required, aromatic oil/sludge was added at 4, 5 and 6 phr levels. The addition of 4 phr of aromatic oil/sludge was found insufficient for proper mixing of the filler whereas 5 phr of aromatic oil/sludge resulted in proper mixing of the filler with maximum reduction in torque. There was not significant reduction in torque even when 6 phr of aromatic oil/sludge was used compared to the mix containing 5 phr. So 5 phr of aromatic oil/sludge can be taken as the optimum quantity (Figs. 4 1 & 4 2) for carbon black filled (50 phr) NR compounds used in the present study

After the processability studies in the plasticorder the mixes for vulcanization were prepared on a laboratory size two roll mixing mill (15 x 33 cm) at a friction ratio of 1 1.25 according to the procedure given in ASTM D 3182 89 NR required four passes to make a band in the mill. After the nerve had disappeared, the compounding ingredients were added as per sequence given in ASTM D 3182 89. The composition of the different mixes are as given in Table 4.2. Goettfert Elastograph model 67.85 was used for determining the cure characteristics of the different mixes at 150^{0}C. The relevant cure data reported are the following. Optimum cure time (t_{90}) is the time taken for attaining 90% of the maximum torque. Elastographic scorch is calculated as the time for 10% vulcanization. Induction time(t_5) is the time taken for one unit (0.1 Nm) rise above the minimum torque (about 5% vulcanization). Cure rate index was determined from the cure curve of the respective mixes as $100/(t_{90}\ \ t_{10})$ where t_{90} and t_{10} are times corresponding to the optimum cure and ten percent vulcanization respectively All the above cure characteristics obtained for the various mixes are reported in Table 4.3 and the corresponding cure curves are given in Figs. 4.3 and 4.4 The compounds were vulcanized upto their optimum cure time in an electrically heated laboratory type hydraulic press at 150^{0}C at a pressure of 140 Kg/cm^2 The tensile properties of the vulcanizates were determined on a Zwick Universal Testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM designation D 412 87 (method A). Dumbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat ageing was studied as per ASTM designation D 573, at 100^{0}C for 24 hours in an air oven.

The tensile properties obtained are reported in Table 4 4

Tear resistance is tested as per ASTM designation D 624 86 using angular test pieces. Compression set and hardness were tested as per ASTM D 395-86 (Method B) and D 2240-86 respectively Abrasion resistance was evaluated using DIN abrader (DIN 53516). These test data obtained are reported in table 4.5 Rebound resilience was evaluated using Dunlop tripsometer (BS 903,part A8). The crosslink density of the vulcanizates was determined by swelling the sample in toluene. Heat build-up was determined as per ASTM D 623-78 (method A). All these experiments are described in detail in Chapter 2.

4.3 RESULTS AND DISCUSSION

4.3.1 Processability

The optimum quantity of refinery sludge/aromatic oil required for the mixes was found out by using different dosages in a Brabender Plasticorder. Both aromatic oil and sludge were tried in the mixes at 4,5 and 6 phr levels. Both these oils when tried at 4 phr levels gave higher torque values and were found insufficient for proper mixing in the carbon black filled systems tried in this study But both aromatic oil and sludge when tried at 5 phr levels gave acceptable torque values and were found sufficient for proper mixing of the ingredients. There was not any significant reduction in torque even when aromatic oil/sludge were used at 6 phr levels. Hence 5 phr may be taken as the optimum requirement of aromatic oil/ sludge in the carbon black filled systems in the present study (Figs. 4 1 and 4.2). Based on these processing characteristics, cure characteristics, vulcanizate properties etc reported in the subsequent

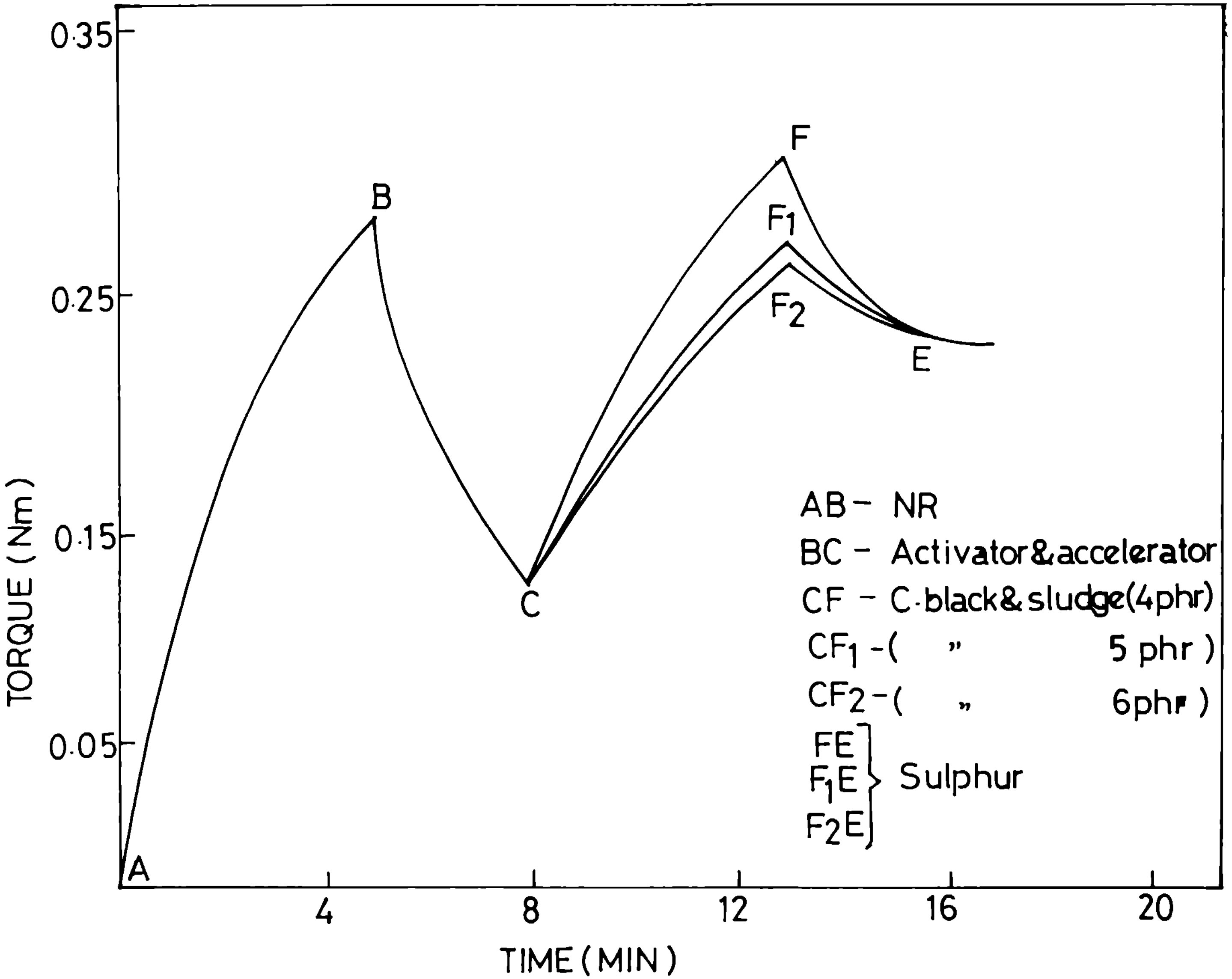


Fig. 4.1 Brabender torque curves of mixes containing sludge

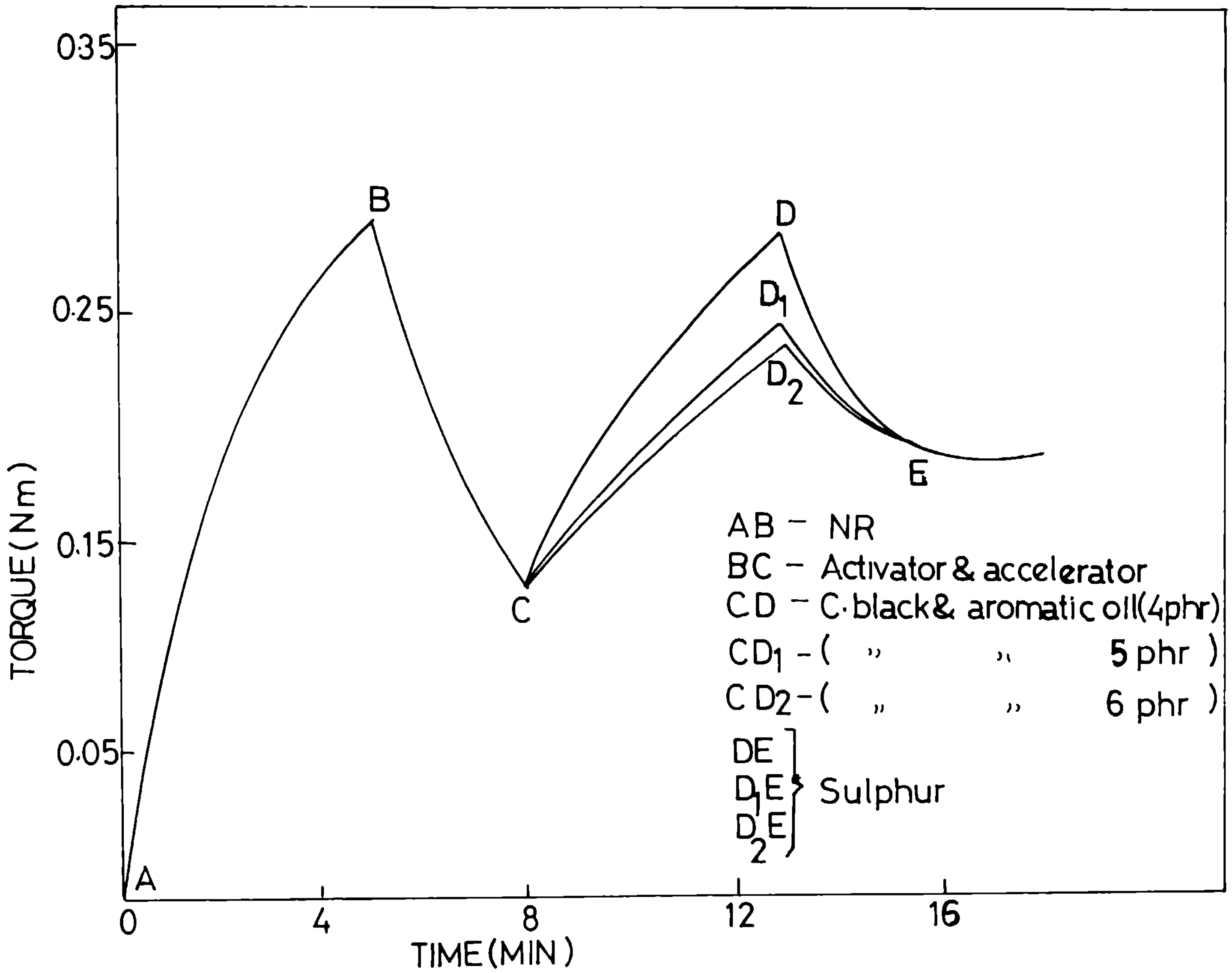


Fig 4.2 Brabender torque curves of mixes containing aromatic oil

sections, it is evident that refinery sludge can be effectively used as a processing aid in the different natural rubber systems included in the present study.

4.3.2 Cure characteristics

The cure characteristics of the various mixes (at 150°C) were evaluated using Goettfert Elastograph and are given in Table 4.3 The cure curves are shown in Figs. 4.3 and 4 4 It is evident from the cure curves that the compounds show reversion tendency. From the cure curves it is seen that the maximum torque develope
is more in mixes containing purified sludge compared to those containi
aromatic oil. There is not much variation in the induction ti
and scorch time when sludge is used in place of aromatic
It can be seen that there is substantial reduction in the opt
cure time when aromatic oil is replaced by refinery sludge
mixes. Compared to the mix A containing aromatic oil alon
mixes B-F containing increasing concentration of purified slu
gradual reduction in the optimum cure time and the re
found to be proportional to the amount of sludge u
mixes. Mix F containing 5 phr sludge gave the leas
the optimum cure time showing that the incorporatio
sludge as process aid in the compounding of natural
can reduce the optimum cure time significantly
cure rate index also increases with the increase
of sludge. The reduction in cure time and the in
index observed when aromatic oil was substituted

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Table 4.3 Cure characteristics of the mixes (cured at 150^0C)

Mix No.	A	B	C	D	E	F
Minimum torque ((Nm)	0.0200	0.0200	0.0269	0.0239	0.0283	0.0317
Maximum torque (Nm)	0.3687	0.4180	0.4849	0.4394	0.4673	0.5064
Optimum cure time t_{90} (min)	4.6	4.3	4.2	4.1	3.9	3.8
Scorch time [a] t_{10} (min)	2.1	2.0	1.9	1.8	1.7	1.7
Induction time t_5 (min)	1.1	1.0	1.0	0.9	0.9	0.9
Cure rate index	40.0	43.5	43.5	43.5	45.5	47.6

[a] Elastographic Scorch time (t_{10})

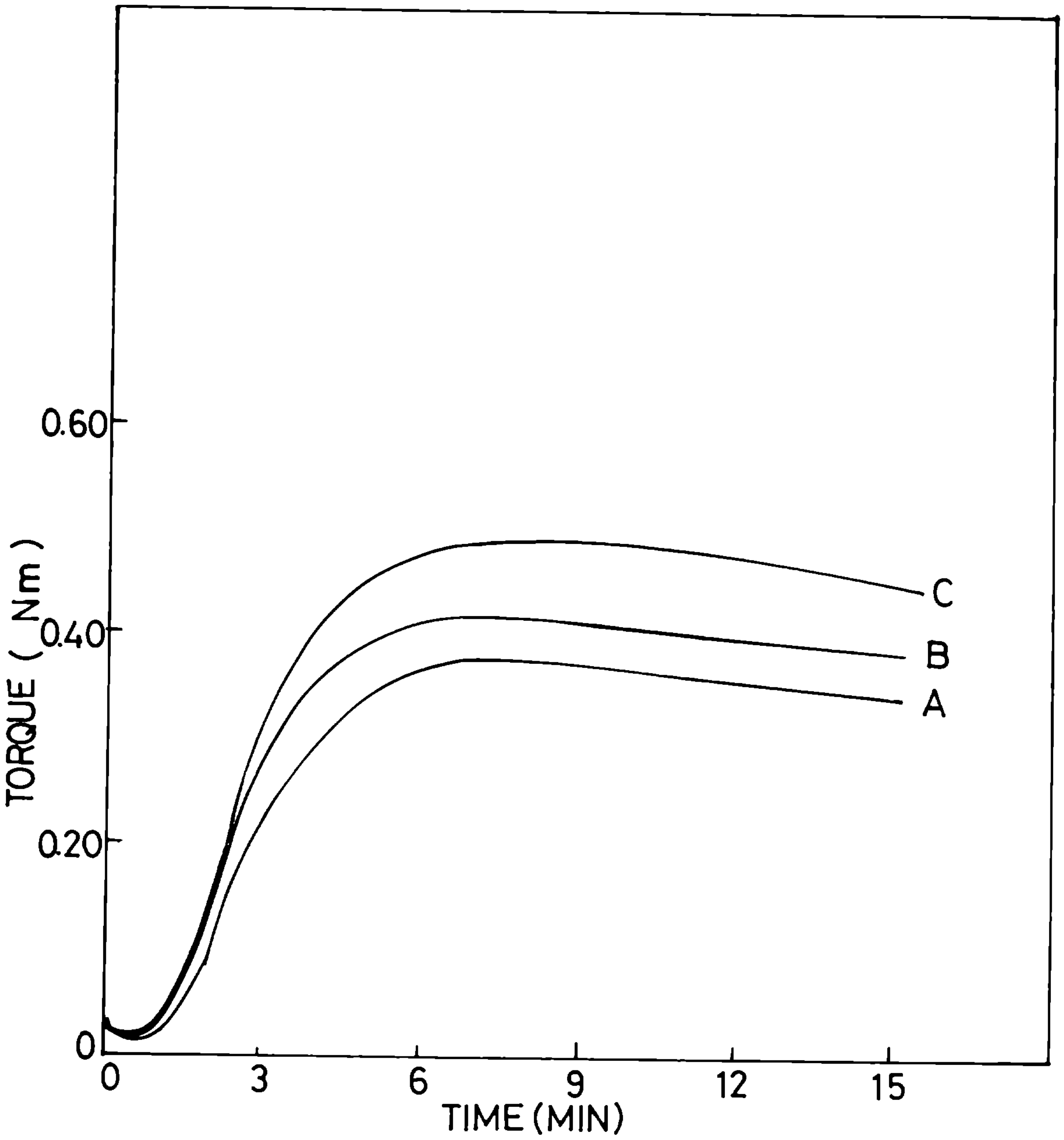

Fig 4.3 Cure curves of the various mixes

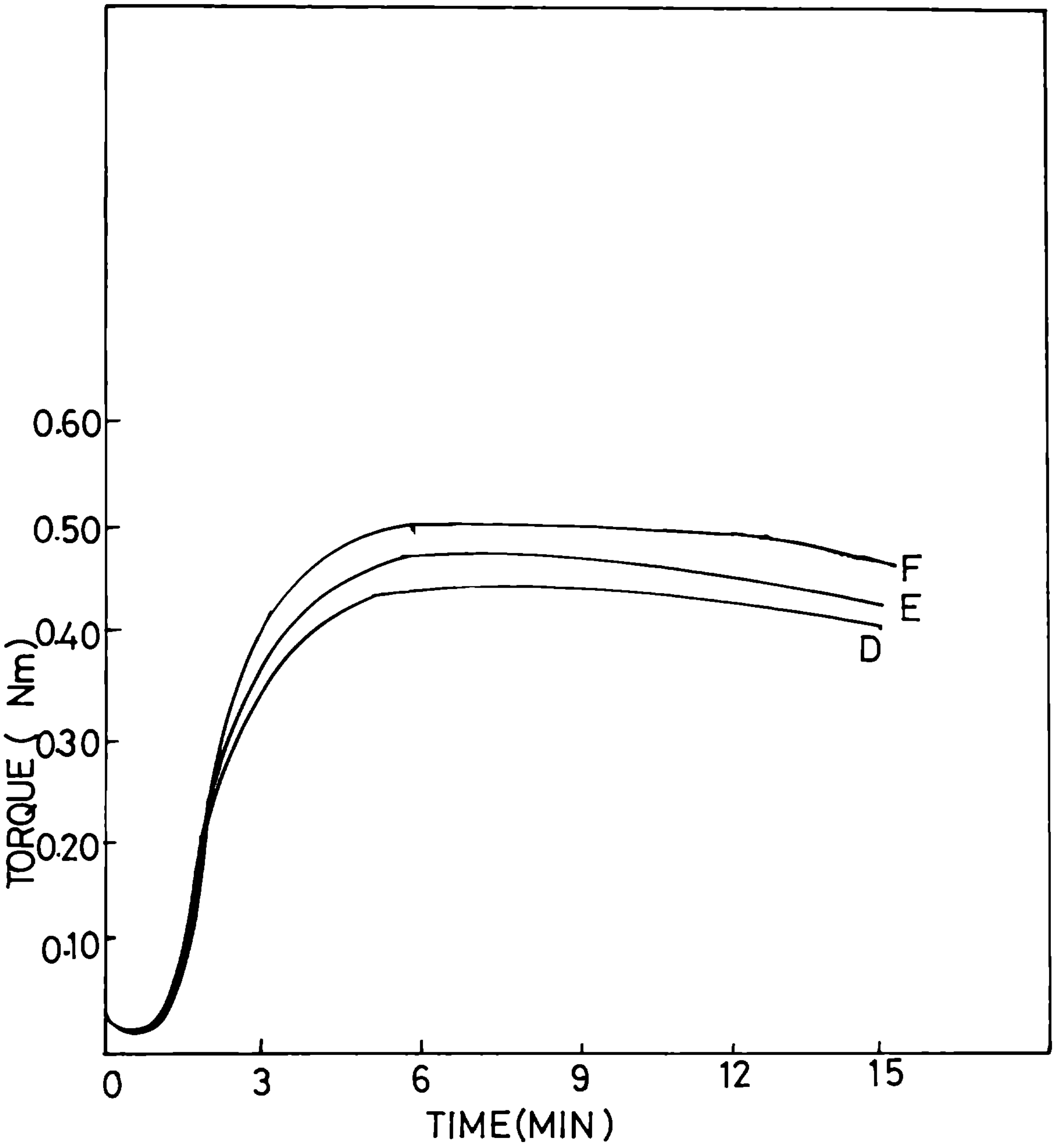

Fig 4.4 Cure curves of the other mixes

may be explained to be due to the presence of accelerating compounds in the purified sludge which might have activated the process of vulcanization. In order to compare the cure properties with that of the reference mix, bar graphs are used. Figs. 4.5 and 4 6 represent the bargraphical representation of the cure properties.

4.3.3 Crosslink density

The most important single factor upon which the physical properties of the vulcanizates depend is the degree of crosslinking[23] All network properties depend to some extent on this variable, although not always in a straight forward way. For this reason, there is usually no single degree of crosslinking at which each property is at its optimum for a given application. The total chemical crosslink density of the different vulcanizates were evaluated and the results are given in Table 4 5 It is found that the crosslink density values show a regular increase with increase in the concentration of sludge. Mixes B-F containing increasing amounts of sludge gave higher crosslink density values compared to the reference mix A. The highest crosslink density value was exhibited by the mix F which contain 5 phr of sludge. This is also evidenced by the increase in tensile strength and significant increase in tear strength exhibited by the mixes B-F containing increasing concentrations of sludge. The higher crosslink density values obtained may be attributed[24] to the better interaction between rubber and filler interface in the case of mixes containing refinery sludge. Refinery sludge seems to have a positive effect in this interaction.

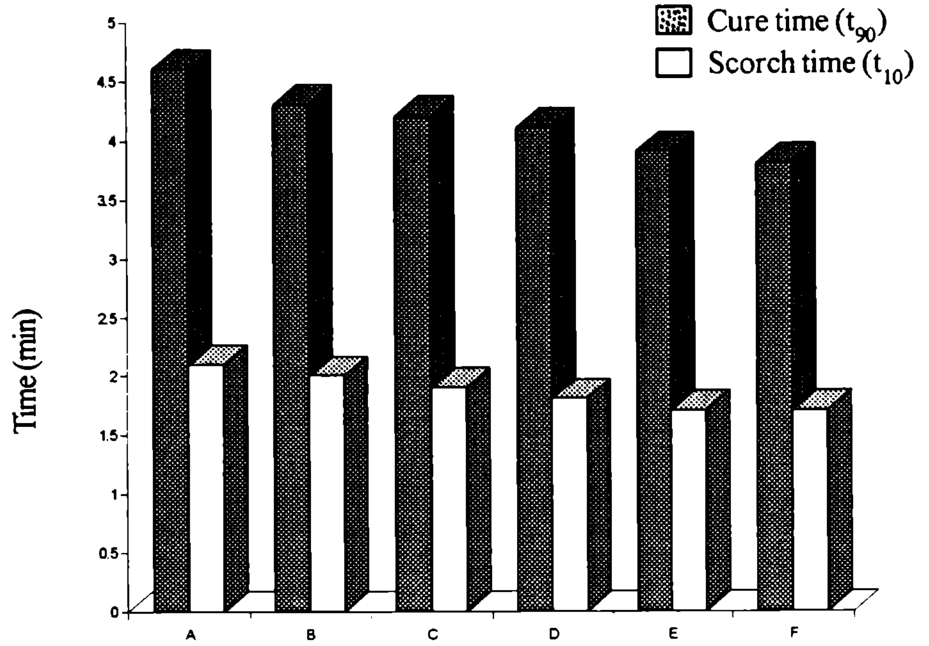

Fig. 4.5 A comparative study of optimum cure time (t_{90}) and scorch time (t_{10}) of the different mixes

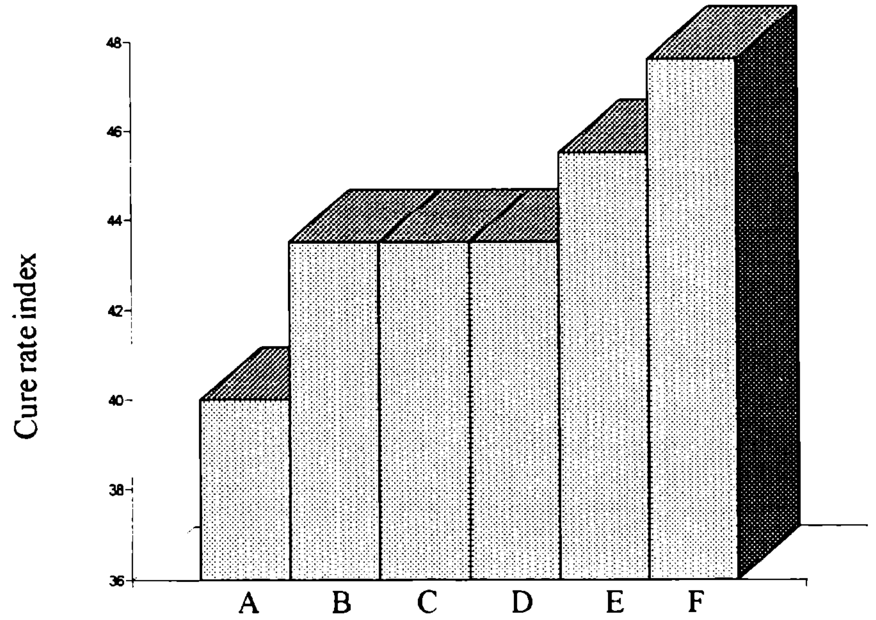

Fig. 4.6 Comparison of cure rate index of vulcanizates

4.3.4 Tensile Properties

The variation in tensile properties of the vulcanizates with concentration of refinery sludge both before and after ageing is shown in Table 4.4. It is seen that the initial tensile strength of mixes B-F shows a marginal increase when compared to that of the reference mix A. This is in conformity with the higher values of crosslink density obtained for the former mixes which in turn, as suggested earlier, may be due to the better black dispersion brought about by sludge. Elongation at break values show a decreasing trend in the case of mixes B to F when compared to that of the reference mix A. As expected the modulus values show a marginal increase from B to F compared to that of A.

Heat ageing resistance of the vulcanizates from mixes B to F are found to be better as compared to that of the control mix A. This is evidenced by the higher tensile values after ageing and accordingly higher percentage retention given by the former mixes. Strong ageing resistance is exhibited by the mix F It is presumed that the phenols present in purified sludge might have supplemented the antioxidant activity. The activity of the phenols as antioxidants is a consequence of the ease with which the phenolic hydrogen may be abstracted, to give a resonance stabilised phenoxy radical. In an oxidising polymer, abstraction of phenolic hydrogen by intermediate radicals, usually polymer peroxy radicals occurs. For the phenol to be effective as a chain breaking antioxidant, it should

Table 4.4 Tensile propeties of the various vulcanizates

Mix No.	Tensile Strength (Mpa)			Elongation at break (%)			Modulus at 100% (Mpa)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
A	25.18	19.41	77.08	483.02	281.45	58.26	4.21	5.04	119.71
B	25.27	19.70	77.95	482.88	280.89	58.16	4.28	5.13	119.86
C	25.36	19.98	78.78	482.02	279.81	58.05	4.33	5.20	120.09
D	25.38	20.62	81.24	481.64	276.87	57.48	4.39	5.27	120.05
E	25.49	21.24	83.33	481.44	276.07	57.34	4.70	5.68	120.85
F	25.69	21.74	84.65	480.98	275.57	57.29	4.79	5.80	121.08

react readily with polymer peroxy radicals and the phenoxy radicals formed should undergo reactions leading to inactive products.

The tensile properties obtained in this study are shown bar graphically in Figs 4 7 and 4.8. The modulus values of the vulcanizates before and after ageing are also shown in Fig. 4.9 The variation of tensile properties with the concentration of sludge are shown in Figs. 4 10 & 4.11

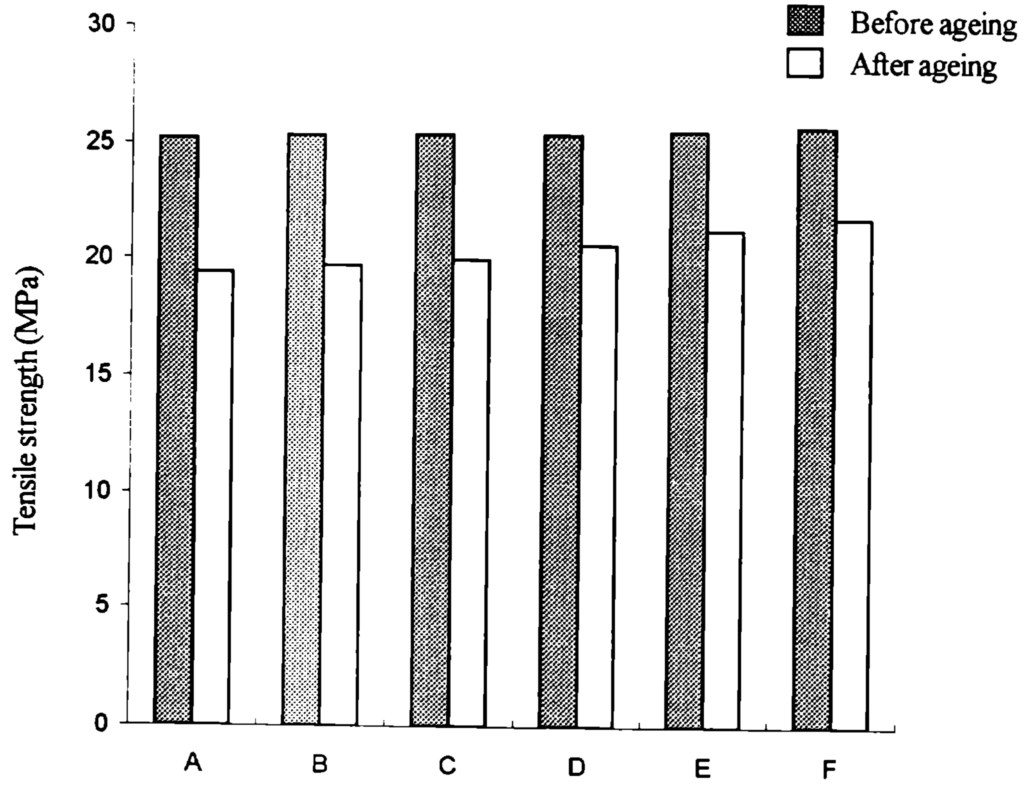

Fig. 4.7 Tensile strength of vulcanizates

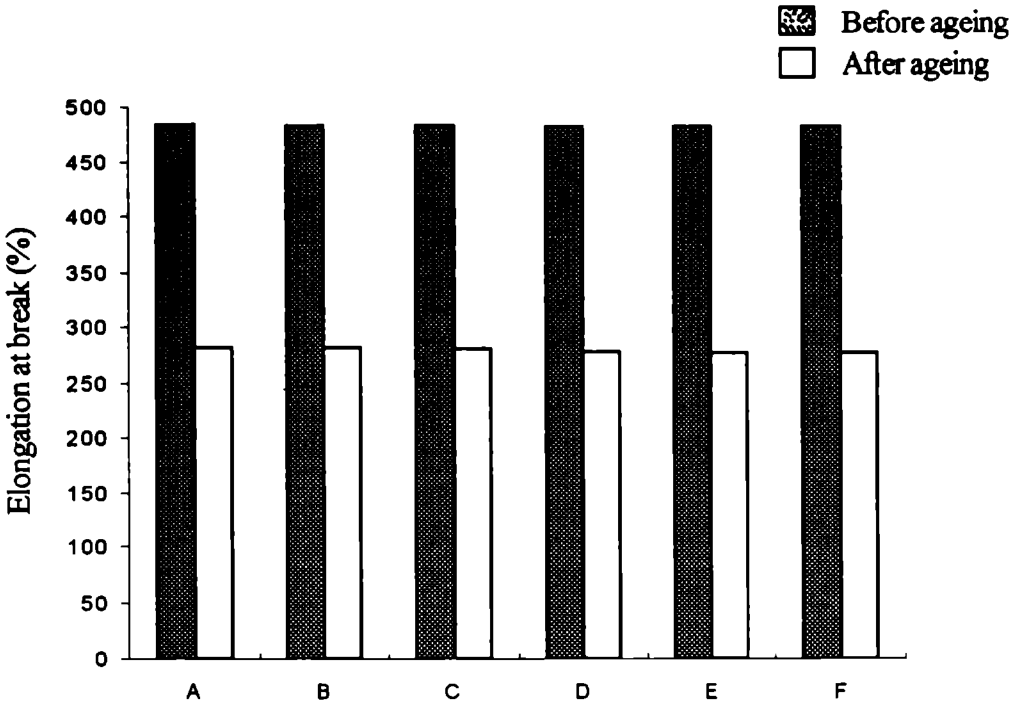

Fig. 4.8 Elongation at break of vulcanizates

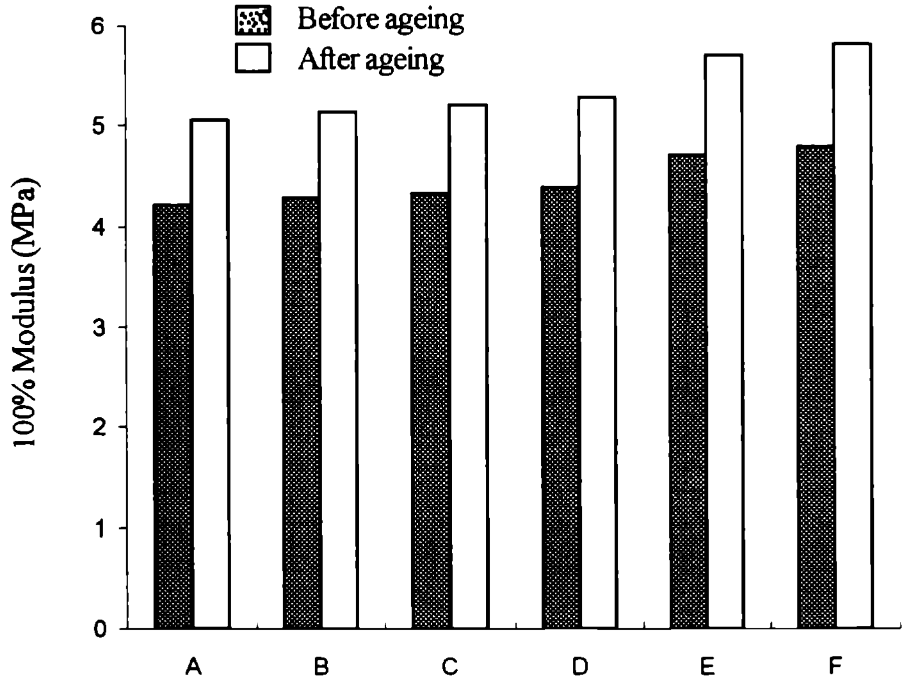

Fig. 4.9 Modulus (100%) of the vulcanizates

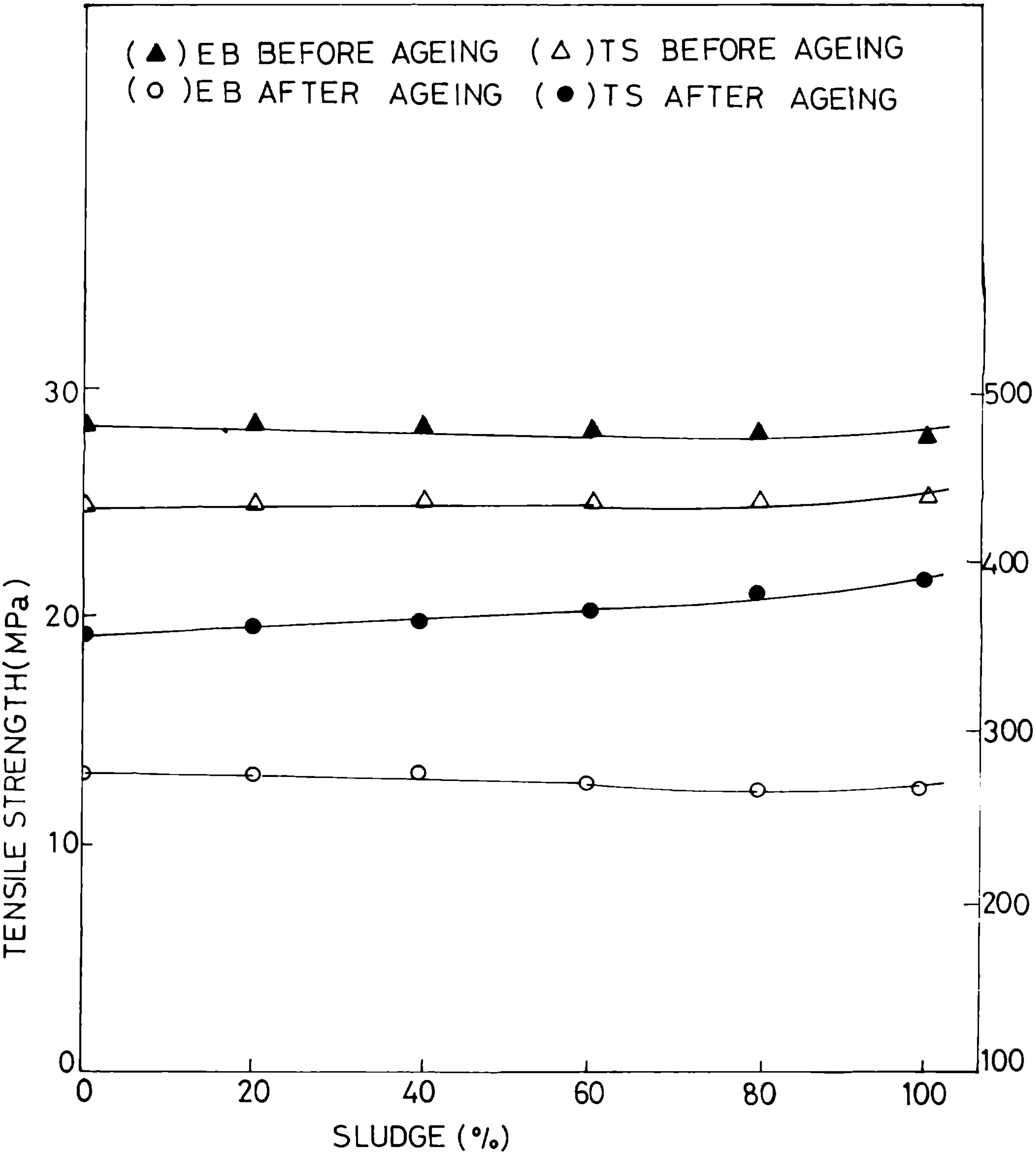

Fig 4.10 Effect of concentration of sludge on tensile strength/elongation at break

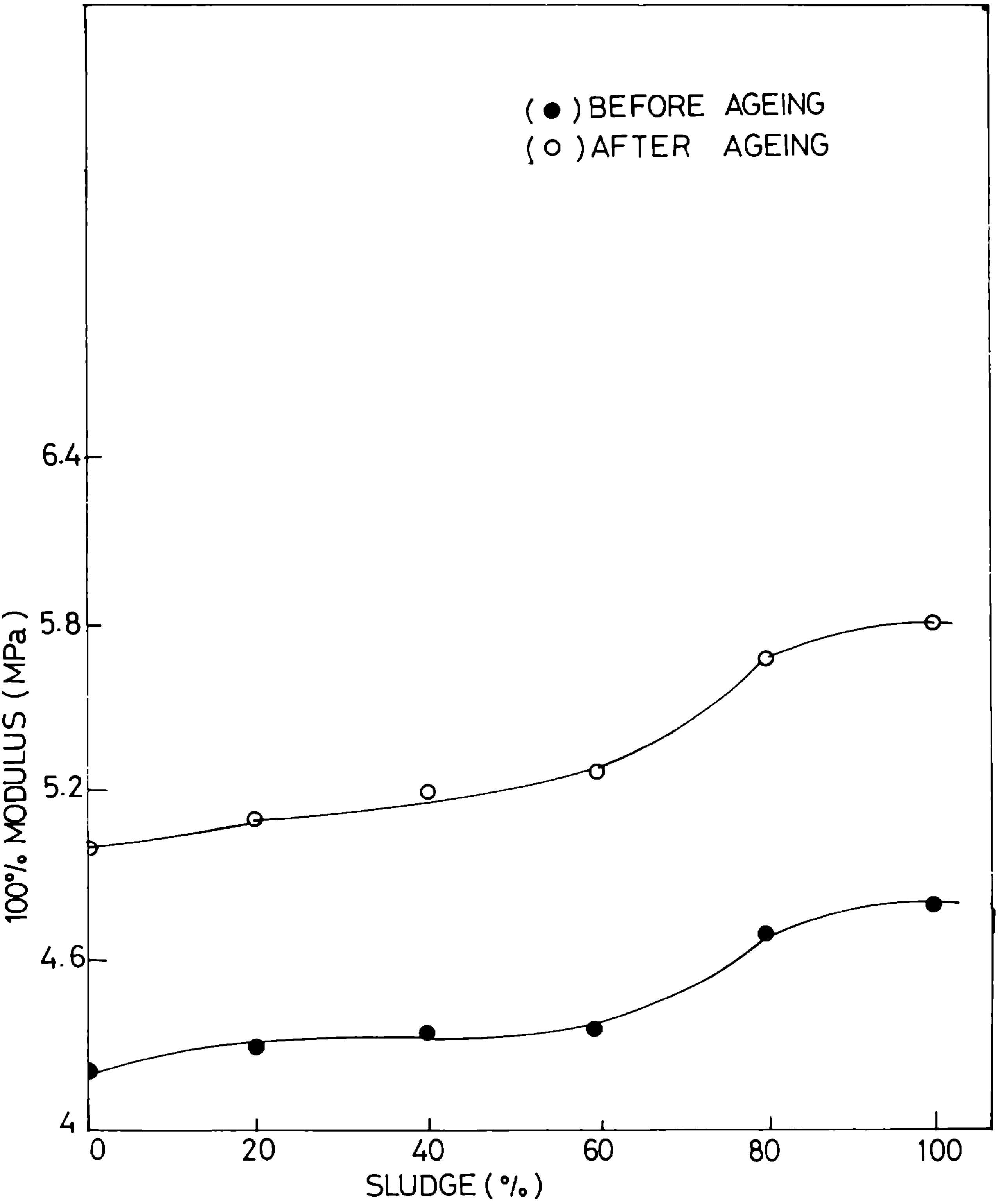

Fig 4.11 Effect of concentration of sludge on 100% modulus

4.3.5 Other Properties

Other physical properties studied for the systems under review are tear strength, hardness (Shore A), compression set, heat build-up, resilience and abrasion resistance. These are given in Table 4.5. The tear strength values exhibit a substantial, regular increase from B to F compared to the reference mix A (Fig. 4.12). The increase is found to be proportional to the concentration of sludge in the mix. This is also in accordance with the higher crosslink density values obtained for these mixes. The abrasion resistance also showed an increasing trend from mix B to F compared to the control vulcanizate. In this case also the increase is proportional

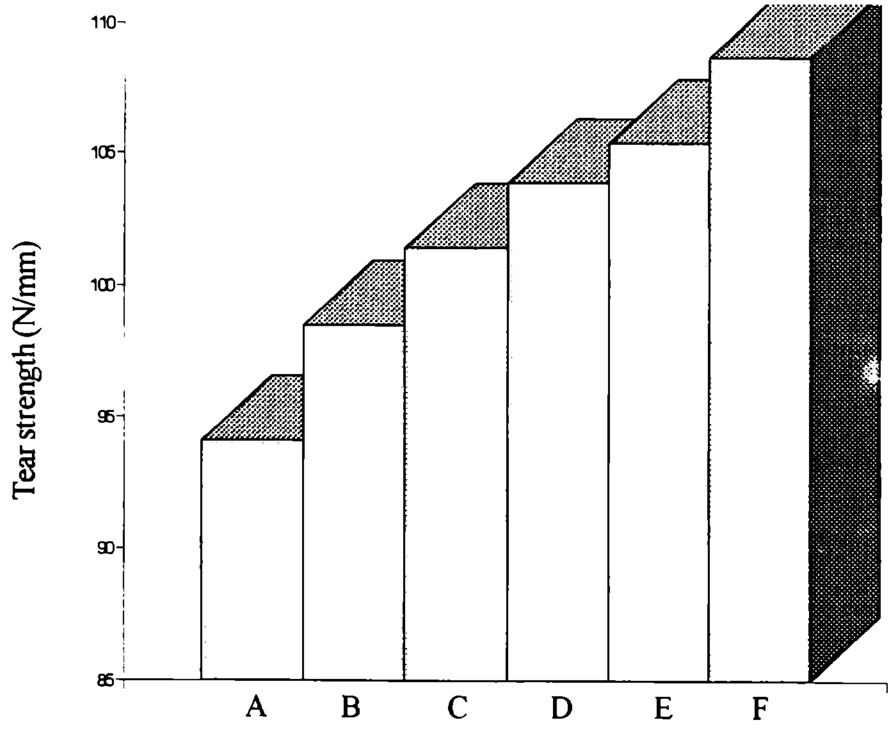

Fig. 4.12 Tear strength of the vulcanizates

Table 4.5 Other physical properties evaluated

Mix No.	Hardness (Shore A)	Compression set (%)	Abrassion loss (cm^3/hr)	Heat buildup (ΔT^0C)	Resilience (%)	Tear Strength N/mm	Total crosslink density $x10^5 gmol/cm^3$
A	63.00	33.98	5.30	31.20	37.75	94.05	5.40
B	63.00	33.86	5.25	31.20	37.81	98.46	5.48
C	63.00	33.72	5.20	31.60	37.78	101.42	5.58
D	63.00	33.64	5.15	31.40	38.68	103.91	5.89
E	63.00	33.58	5.09	31.30	36.72	105.41	5.93
F	63.00	33.52	5.05	31.50	37.76	108.65	6.04

to the increased concentration of sludge in the former mixes. Hardness, compression set, resilience and heat build-up values are found to be more or less same for the mixes A to F Details of these results are also as given in Table 4.5

4.4 CONCLUSIONS

The results of this study indicate that sludge obtained from petroleum refineries can be used, after purification, in natural rubber compounding as a processing aid when sulphur accelerator system is used. Studies of the processing characteristics suggest that NR compounds can be processed with sludge similar to other conventional process oils. The use of sludge does not adversely affect the cure characteristics of the mixes or the physical properties of the vulcanizates. Some improvement is noticed in properties like tensile strength, ageing resistance and abrasion resistance in the mixes where sludge is used. Significant improvement in tear strength and substantial decrease in the optimum cure time are added advantages. The only disadvantage with sludge seems to be its black colour due to which it can be used only for black coloured products. It may be noted that the conventional process oils used at present in rubber are becoming prohibitively costly while the sludge is a dumped waste of the refinery.

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CHAPTER 5

REFINERY SLUDGE AS PROCESSING AID IN THE COMPOUNDING AND VULCANISATION STUDIES OF STYRENE BUTADIENE RUBBER

5.1 INTRODUCTION

In view of the fact that the purified sludge contains a good amount of bitumen, wax and lighter oils; and based on the encouraging results obtained on the use of purified refinery sludge in the compounding of natural rubber[1], we thought it worthwhile to try this oil in the compounding and vulcanization studies on a synthetic rubber also. This is mainly because a lot of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis synthetic rubbers[2] When compared to natural rubber, synthetic rubbers are more uniform in quality and the compounds are more consistent in both processing and product properties. They are also available at viscosity ranges which facilitate better dispersion of ingredients and ease of flow in extrusion, calendering and moulding. This helps to save both energy consumption and time and hence cost reduction. But it should be noted that mill mixing of synthetic rubbers is more difficult when compared to natural rubber.

We selected styrene butadiene rubber (SBR 1502) for the present study. It is a general purpose synthetic rubber of large tonnage use. It is a copolymer of styrene and butadiene and is manufactured by polymerising them under controlled conditions of reaction using different techniques of polymerisation such as by emulsion or solution method[3] Both cold and hot polymerised styrene butadiene rubbers are available and they are marketed under various trade names. These brands differ from one another in the relative proportions of butadiene and styrene, content of different initiating agents, emulsifiers, oils, fillers etc. and temperature of polymerisation. The degree of unsaturation in SBR is less than that of natural rubber and the double bonds are less active chemically than the double bond of the isoprenoid unit in NR. Hence styrene butadiene rubbers are slower curing than NR and require either more accelerator or a more active accelerator system[4] Also scorch problems are less with SBR than with natural rubber stocks.

SBR possesses lower green strength and gum tensile strength. This can be attributed to its molecular irregularity and the presence of large pendent groups which prevent crystallisation on stretching. To avoid this type of behaviour of SBR, usually fine reinforcing fillers are incorporated. Addition of fillers increases tensile strength several times to that of gum vulcanizates[5] Among the commonly used fillers and reinforcing agents, carbon black offers the most potential reinforcement[6] Carbon black contribute much to increase the desirable properties of vulcanized rubber and it is a universal compounding ingredient for quality stocks[7] The mechanism of reinforcement by carbon black has been studied by several authors[7-11] The modification of an elastomer by carbon black reinforcement generates a unique three dimensional visco-elastic network that transfer the soft elastomer into a strong elastic product[12] The most important factor on which the processability of SBR depends is on its viscosity. Grades of lower viscosity band more easily on mills, incorporate fillers and oils more readily. Also they show less heat generation during mixing and are more easily calendered. The lower viscosity grades are also found to give higher extrusion rate compared to the higher viscosity grades. On the other hand higher viscosity grades have better green strength. They tend to give porosity in the vulcanizate and at the same time accept higher filler and oil loading which is attractive pricewise. The higher the molecular weight of SBR, the higher the resilience of the vulcanizate and there is generally an improvement in the mechanical properties, particularly tensile strength and compression set. But most of the differences in the vulcanizate properties of high and low molecular weight SBR's can be eliminated through the choice of active fillers in the rubber compound.

The compounding of styrene butadiene rubber is done in a way more or less similar to that of natural rubber and other unsaturated hydrocarbon rubbers. SBR like NR require mastication prior to compounding. The increase of temperature during mastication leads to degradation of NR to same extent while SBR is not much degraded. Zinc oxide and stearic acid are the most common activators used with SBR. The amount of activator used is same for both NR and SBR whereas the concentration of accelerator and sulphur used are varied for both rubbers. Again SBR require higher temperature for vulcanization compared to NR.

The reinforcing carbon blacks give more or less same level of mechanical properties for SBRs as for NR vulcanizates. The relative order of activity of fillers is the same in SBR as in NR, but the degree of reinforcement of the fillers is higher in SBR compared to NR. Tear resistance, elastic properties etc.

of SBR are poorer than NR. The compression set values depends very much on the compound formulation, the cure condition and the specific test method. By means of proper compounding and use of optimum cure times it is possible to obtain very low values of compression set. The dynamic fatigue resistance and heat ageing resistance of SBR vulcanizates surpass NR vulcanizates. The abrasion resistance of SBR is also better when compared to that of NR.

As in the case of natural rubber, sulphur vulcanization of SBR involves heating it with accelerator, activator, co-activator, anti-oxidant, filler, processing oil etc., to get products of required properties. Accelerators help to reduce the vulcanization time considerably. Zinc oxide is the common activator used in rubber vulcanization to promote the action of accelerators. Stearic acid is the usual co-activator used along with zinc oxide. Substituted amines and phenols are the usual antioxidants added to reduce the ageing processes in the vulcanizates. Fillers are included inorder to improve the physical properties and/or to reduce the cost of the final product. Processing aids are materials which when added to a rubber compound at relatively low loading will improve processability without adversely affecting physical properties. It is found that the incorporation of the correct process aid can improve compound's physical properties like tensile strength, tear, hardness, modulas, abrasion resistance, resistance to ageing etc. Processing aids can perform multifunctions during the different stages of rubber compound mixing and processing. It is claimed that the process aids can bring improved filler dispersion, reduce mixing time and energy, better mill handling, faster extrusion, easier fabrication, improved product appearance etc. The factors involved in selecting processing aids are compatibility, cost, efficiency, staining and low temperature properties. If the oil used as processing aid is not compatible with the polymer, it will bleed out and cause poor physical properties, a sticky surface and poor adhesion in uses where it should adhere to materials like cord or metal. It is emphasised that the processing aids synergise with the elastomer compounding ingredients[13] producing noticeable improvements in mixing, processing and flow property. Aromatic and naphthenic oils are the most common processing oils used in rubber industry. Petroleum bitumens, sold as mineral rubber[14] are also used as low cost low gravity extenders and process aids.

SBR used in the present study is synaprene 1502. It is a non staining cold rubber and gives good physical properties in either black or light coloured products. It has a high loading capacity and is used in the manufacture of tyres, moulded and extruded articles, footwears, coated fabrics etc. In our studies with SBR we used sulphur accelerated system for the vulcanization using purified refinery sludge in place of aromatic oil. The results obtained from these mixes were compared with the control formulation containing aromatic oil. The variation in processing characteristics brought about by the incorporation of refinery sludge was studied with the help of a Brabender plasticorder. The optimum quantity of sludge required in the different formulation's has also been derived. The mixes were evaluated for their cure characteristics and the vulcanizate samples were evaluated for their tensile and other physical properties. Since definite relationship exist between chemical structure of the vulcanizates and their physical and mechanical properties, the total chemical crosslink density of the vulcanizates was also estimated using the equilibrium swelling method to understand the variation in tensile properties among the different mixes. The heat ageing resistance of the vulcanizates of both control and the experimental samples were also evaluated and compared.

5.2 EXPERIMENTAL

For SBR, Synaprene 1502 supplied by Synthetics and Chemicals Ltd., Bareilly, U.P having specifications reported in Chapter II was used. The other additives used viz., zinc oxide, stearic acid, mercaptobenzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, aromatic oil, carbon black (HAF N-330) were all of rubber grade. Refinery sludge obtained from Cochin Refineries Ltd., Kochi was used after purification. The purification of the sludge was done as described in Chapter 2 by maintaining the sludge at a temperature of 110±10°C for a period of 12 hours and then passing the viscous oil so obtained through strainers of 60 and 40 mesh size.

Table 5.1 gives the composition of the various mixes used. The sulphur level was maintained at 2 phr and the accelerator (MBTS + TMTD) level was maintained at 1.5 phr in the mixes. All these mixes contain 5 phr zinc oxide, 2 phr stearic acid and 1 phr accinox HFN as activator, co-activator and anti-oxidant respectively for hundred parts of rubber (phr). These mixes contain 50 phr carbon black (HAF N 330) as filler Mix A is the control mix containing 5 phr aromatic oil Mix B contains 4 phr aromatic oil

Table 5.1 Formulation of mixes containing aromatic oil/sludge

Ingredients	A	B	C	D	E	F
SBR	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
MBTS	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5
Accinox HFN	1	1	1	1	1	1
Carbon Black (HAF N330)	50	50	50	50	50	50
Aromatic Oil	5	4	3	2	1	0
Sludge	0	1	2	3	4	5
Sulphur	2	2	2	2	2	2

and 1 phr sludge. Mix C contains 3 phr aromatic oil and 2 phr sludge. Mix D contains 2 phr aromatic oil and 3 phr sludge. Mix E contains 1 phr aromatic oil and 4 phr sludge. Mix F contains 5 phr sludge alone. The characteristics of the purified sludge used are given in Table 4.1 under chapter 4.

Brabender Plasticorder (PL 3S) was used for studying the processing characteristics of the mixes. The processability of styrene butadiene rubber using purified sludge was compared with that of the conventional aromatic oil. The ingredients were added into the mixing chamber after setting the test conditions to obtain a torque time curve (plastogram). In our studies, the speed of the roller mixing heads in the plasticorder was kept at 30 rpm and at 30°C. First SBR was passed 6 times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small pieces and fed into the Brabender Plasticorder. The mixing time was 16 minutes in total with the following break-up. SBR was masticated within 4 minutes followed by adding activator and accelerator within three minutes. Carbon black mixed with purified refinery sludge was then added within 8 minutes and finally sulphur within 1 minute. The formulation of the different mixes are as given in Table 5.1 except for the fact that the oil levels were varied. In order to optimise the quantity of sludge required, experiment was repeated using 4,5,6,7 and 8 phr of refinery sludge. The addition of 4,5 and 6 phr of refinery sludge was found insufficient for proper mixing with the filler whereas 7 phr of the sludge was found sufficient for proper mixing and that too with a significant reduction in the torque. There was no significant reduction in the torque even when 8 phr of sludge was used compared to the mix containing 7 phr. So 7 phr of sludge may be taken as the optimum level required (Fig. 5.1) for carbon black filled SBR compounds. For the control mixes, the same procedure was repeated by replacing refinery sludge with aromatic oil. To determine the optimum level of aromatic oil required, it was added at 4,5,6 and 7 phr levels. The addition of 4 and 5 phr of aromatic oil was found insufficient for proper mixing of the filler with rubber whereas 6 phr of aromatic oil resulted in proper mixing of the filler with maximum reduction in torque. There was no significant reduction in torque even when 7 phr of aromatic oil was used compared to the mix containing 6 phr. So 6 phr of aromatic oil can be taken as the optimum quantity (Fig 5.2) for carbon black filled SBR compounds.

After the processability studies in the plasticorder, the mixes for vulcanization were prepared on a laboratory size two roll mixing mill (15x33 cm) at a friction ratio of 1 1 1 according to the procedure given ASTM D 3182-89 SBR required 6 passes to make a band in the two roll mill. The formulation of the mixes were designed in such a way as to study the effect of refinery sludge as a processing aid in the sulphur vulcanization of SBR. Due to the higher shearing force in the mill compared to the plasticorder only lower dosage of oil was found sufficient for mill mixing during the addition of fillers. Hence 5 phr of both sludge and aromatic oil were found sufficient when compounding was done in the mixing mill. The composition of the different mixes are as given in Table 5 1

The cure characteristics of the various mixes were evaluated at 150°C using Goettfert elastograph model 67.85. Details of the procedure are as given in chapter 2. The cure characteristics of the mixes are as given in Table 5.2. Maximum and minimum torque, cure rate index, induction time, optimum cure time and elastographic scorch time etc. are all reported therein. The cure curves obtained are given in Figs 5 3 and 5.4. The compounds were vulcanized upto the optimum cure time in an electrically heated laboratory type hydraulic press at 150°C at a pressure of 140 Kgcm^{-2} The tensile properties of the vulcanizates were determined on a Zwick Universal testing machine model 1445 using a cross head speed of 500 mm/min. (ASTM designation D 412-87 method A). Dumbell specimens for the test were punched out of the moulded sheets along the mill grain direction. Heat ageing was studied as per ASTM designation D 573-88, at 100°C for 48 hrs in an air oven. The tensile properties are reported in Table 5.3 Tear resistance was tested as per ASTM designation D 624-86 using angular test pieces. Compression set and hardness were tested as per ASTM D 395-86 (method B) and D 2240-86 respectively Abrasion resistance was evaluated using DIN abrader (DIN 53516). These test data obtained are reported in Table 5 4 The concentration of the chemical crosslinks (crosslink density) of the vulcanizates was determined from the equilibrium swelling data. Swelling was done in toluene for 24 hours using samples of 0.2 cm thickness, 1 cm diameter and 0.3 g weight.

5.3 RESULTS AND DISCUSSION

5.3.1. Processability

Variation in the processing characteristics brought about by using purified refinery sludge instead of the usual conventional aromatic oil in this synthetic rubber compounding was studied by using a Brabender Plasticorder The optimum quantity of refinery sludge/aromatic oil required in the mixes was found out by the use of various dosages in the plasticorder. 6phr of aromatic oil and 7 phr of refinery sludge were found to be the optimum requirements in the carbon black filled systems used in this present study The maximum torque obtained in the mixes containing refinery sludge was found to be slightly higher than those of the mixes containing aromatic oil (Figures 5 1 and 5.2) But in actual practice, the compounds were prepared in a two roll mill and it is found that lower dosages of oil i.e., 5 phr each of sludge and aromatic oil are found sufficient for processing in the two roll mill. This is due to the higher shearing force of the mixing mill compared to plasticorder. The processing characteristics obtained in the plasticorder as well as in the mixing mill and other results reported in the subsequent sections indicate that this refinery sludge can replace aromatic oil as a processing aid in the vulcanization systems of SBR under review

5.3.2 Cure Characteristics

The cure curves obtained for the different mixes are given in Figs. 5.3 and 5 4. It can be seen from the cure curves

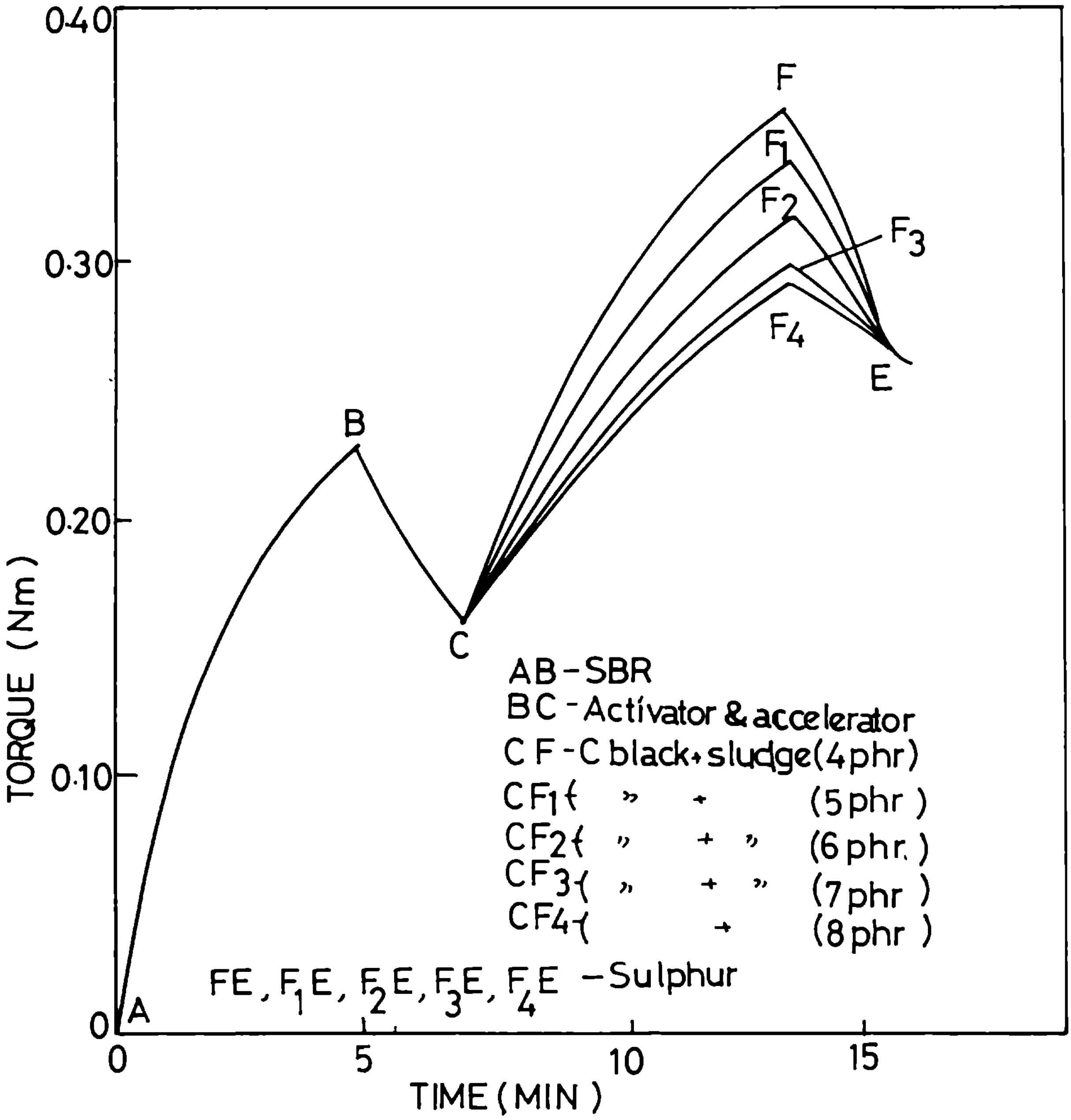

Fig. 5.1 Brabender torque curves of the mixes with sludge

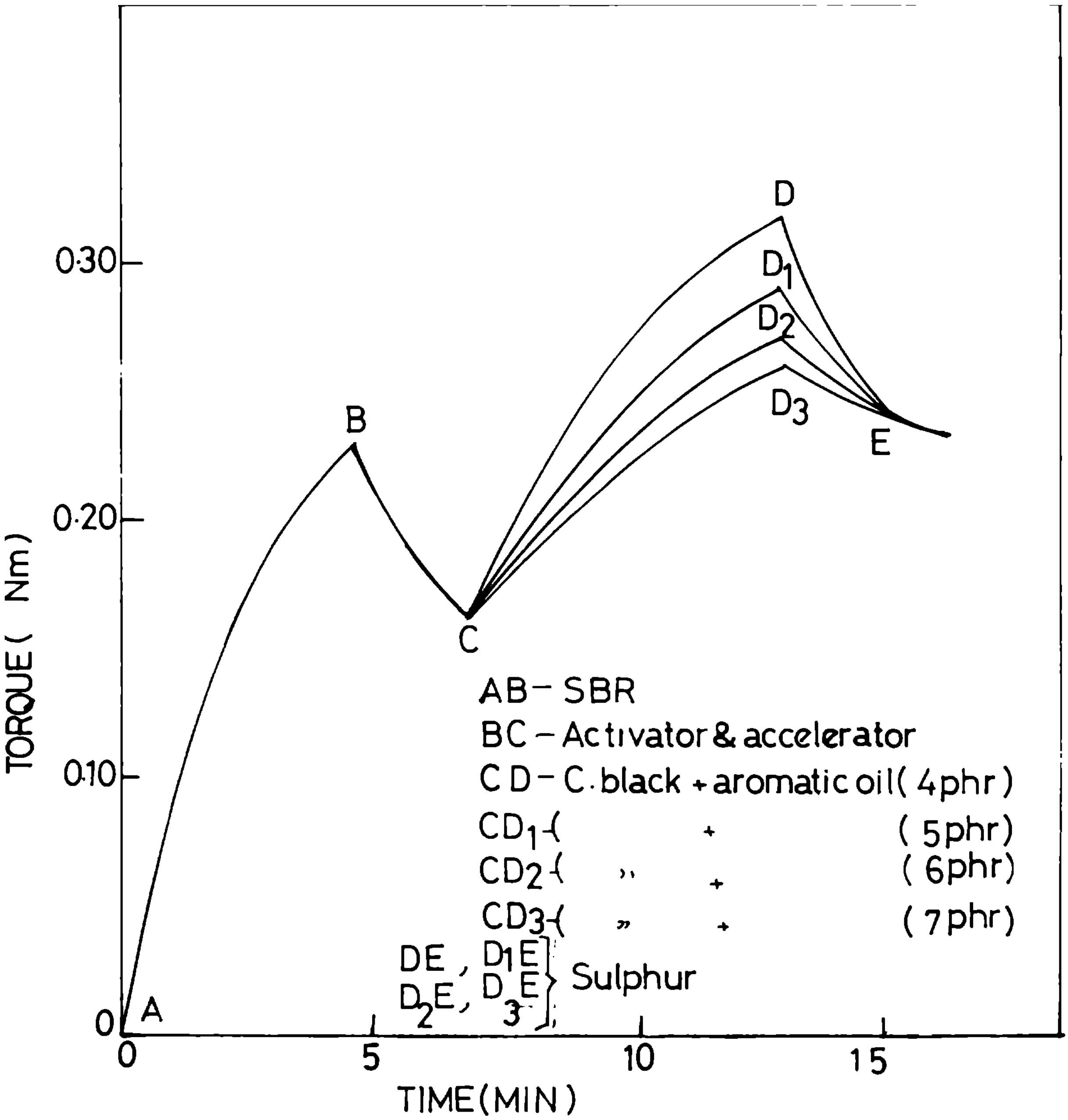

Fig 5.2 Brabender torque curves of the mixes with aromatic oil

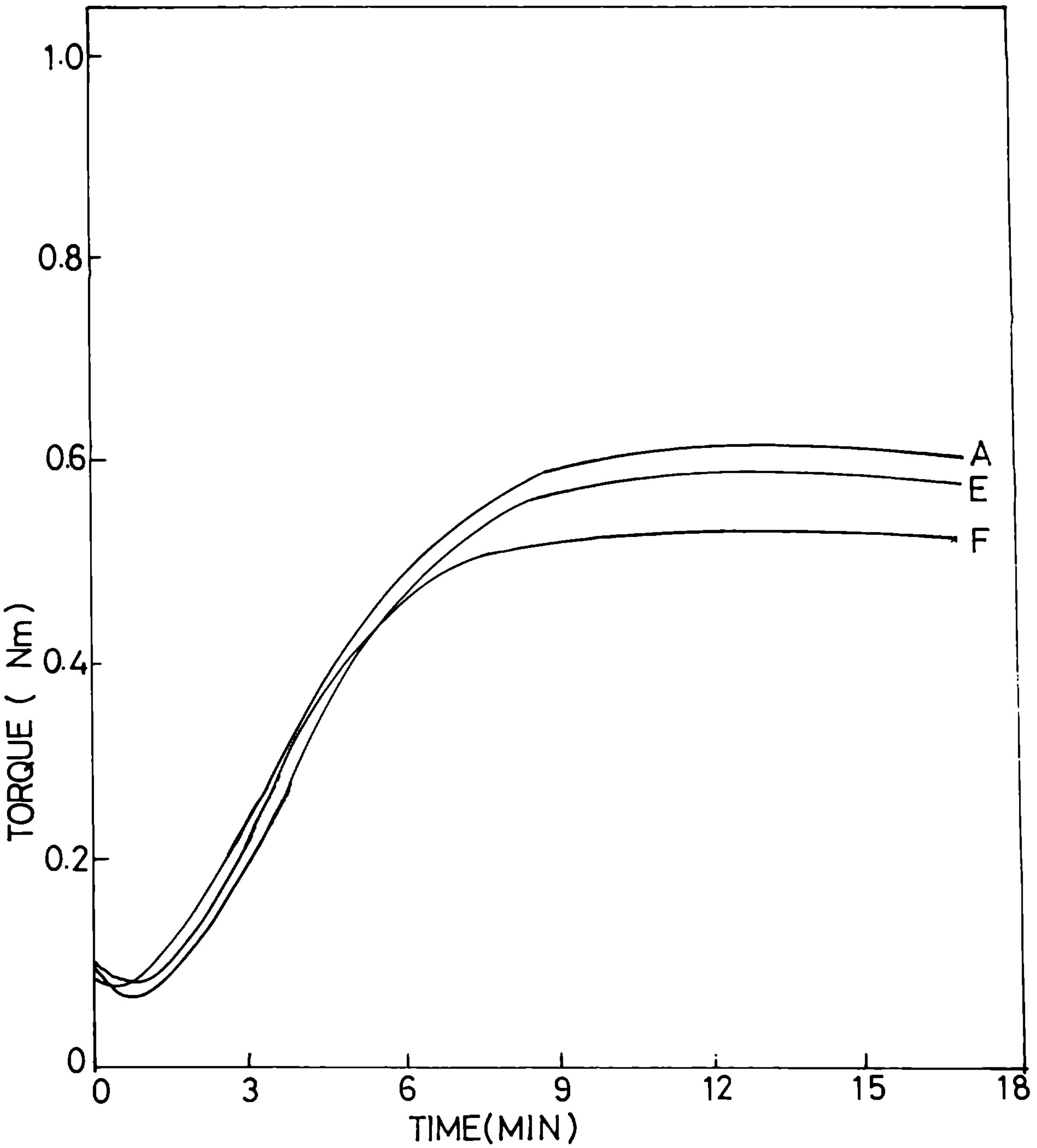

Fig 5.3 Cure curves of the various mixes

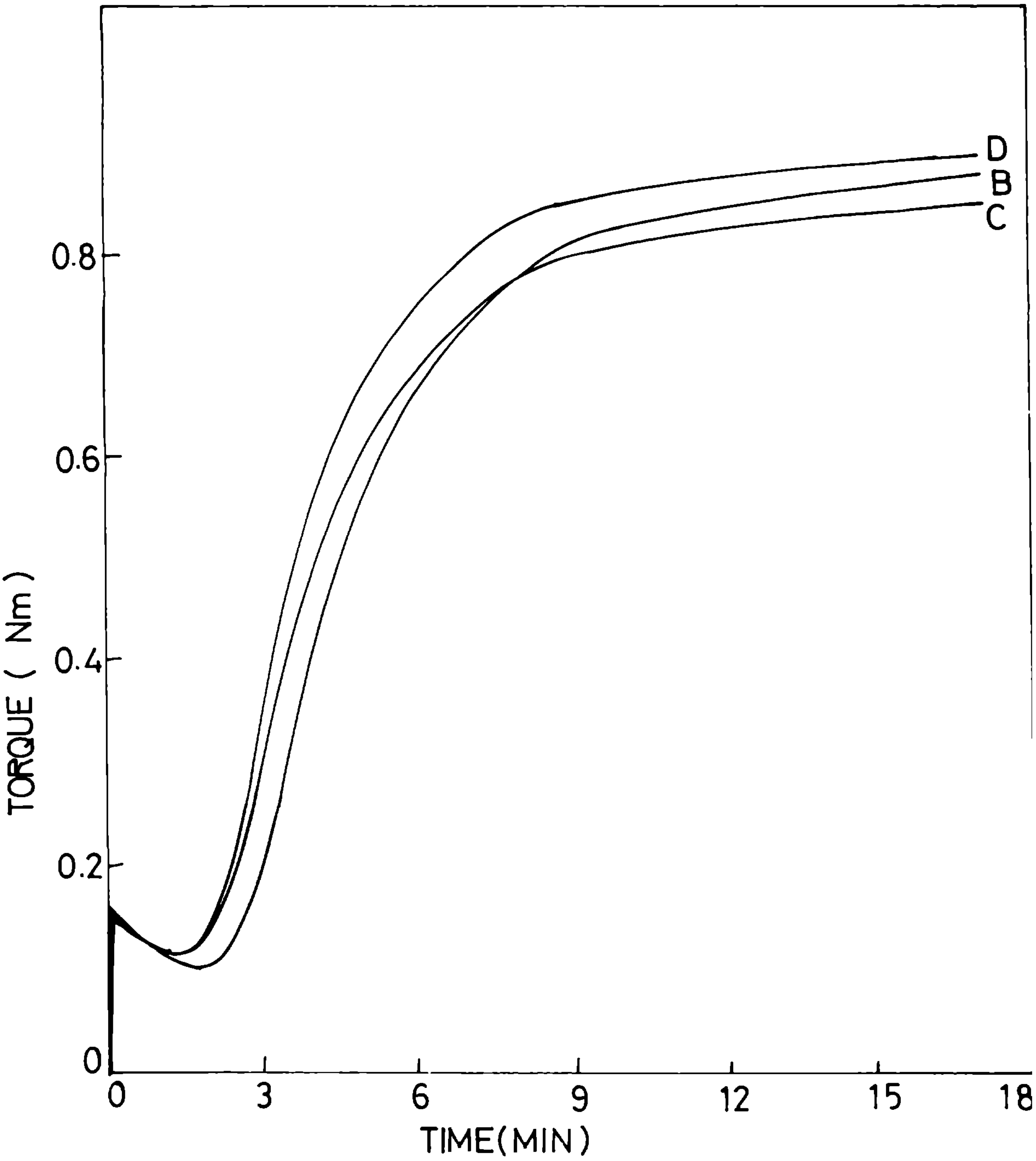

Fig 5.4 Cure curves of the other mixes

Table 5.2 Cure characteristics of the mixes (cured st 150^{0}C)

Mix No.	Optimum cure time (t_{90}) min.	Scorch[a] time (t_{10}) min.	Induction time (t_5) min	Cure rate index	Maximum torque (Nm)	Minimum torque (Nm)
A	7.2	2.2	1.3	20.00	0.6304	0.0689
B	8.7	3	1.4	17.54	0.8799	0.0947
C	9.4	2.6	1.1	14.70	0.8691	0.1304
D	8	2.6	1.1	18.50	0.915	0.1318
E	7.6	2.5	1.4	19.60	0.5795	0.0386
F	6	2.3	1.2	27.00	0.5337	0.0591

[a] Elastographic Scorch time

that none of the mixes show any tendency for reversion. The relevant cure characteristics are given in Table 5 2. From these results it is seen that the maximum torque developed is more or less same for the mixes containing 100% aromatic oil and 80% and 100% sludge. But the mixes B, C, and D containing 20%, 40% and 60% sludge with aromatic oil show higher torque values compared to the former mixes. There is also not much variation in the scorch time and induction time when refinery sludge is used in place of aromatic oil. It is noted that the optimum cure time is reduced significantly when aromatic oil is replaced completely with refinery sludge (Fig. 5 5). Accordingly the cure rate index also increases with increase of sludge (Fig. 5 6). It is assumed that the presence some accelerating chemicals in the dehydrated sludge might have helped in activating the process of vulcanization. Thus it is evident that purified refinery sludge can be advantageously used as a processing aid in place of the other conventional processing oils and that the cure characteristics of the system is not affected by this change. This observation is further supported by the evaluation of tensile and other physical properties (before and after ageing) reported in the subsequent sections.

5.3.3 Crosslink density

The total chemical crosslink density of the different vulcanizates were evaluated and the results are given in Table 5.4 Mixes C and D gave higher crosslink density values compared to the others. Mix B containing 20% sludge with aromatic oil showed the minimum value This is also evidenced by the slight increase in tensile strength

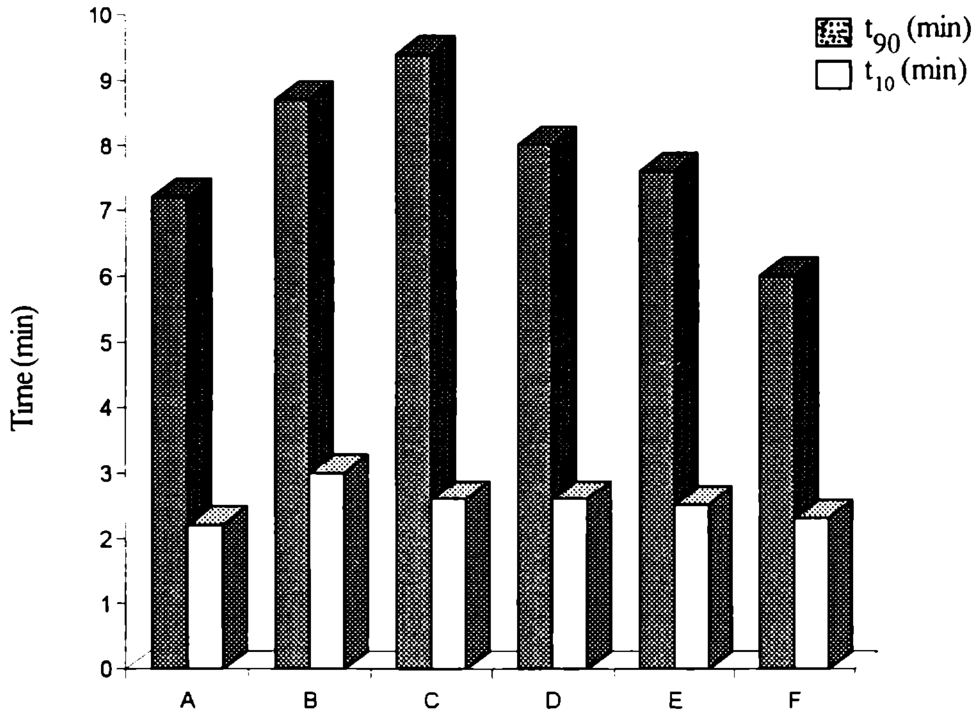

Fig. 5.5 A comparative study of optimum cure time (t_{90}) and scorch time (t_{10}) of different mixes

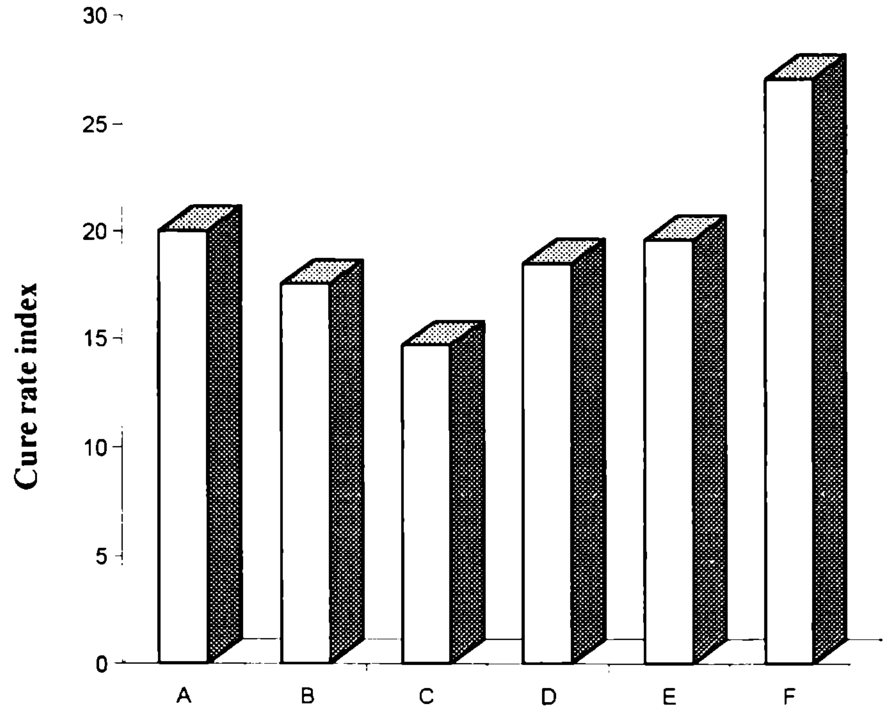

Fig. 5.6 Cure rate index of vulcanizates

and tear strength values of the vulcanizates containing refinery sludge. The higher crosslink density values obtained may be attributed[15] to the better interaction between rubber and filler interface in the case of mixes containing refinery sludge

5.3.4. Tensile and other physical properties

The variation in tensile properties of the vulcanizates with concentration of refinery sludge both before and after ageing is shown in Table 5.3 It is seen that the initial tensile strength is slightly higher for the mixes C and D containing 40% and 60% sludge compared to the other mixes (Fig. 5 7). Regarding the initial tensile strength, mix A containing aromatic oil alone and mix F containing refinery sludge alone gave identical value. Elongation at break is more or less same for the mixes containing purified refinery sludge and those containing aromatic oil (Fig. 5 8). Regarding the modulus values, mixes C and D containing 40% and 60% sludge gave higher values compared to the other mixes. The modulus values of the other mixes A, B, E and F containing 100% aromatic oil, 20%, 80% and 100% sludge respectively were found to be more or less the same (Fig. 5 9).

Heat ageing resistance of the vulcanizates C, D and F containing increased amounts of refinery sludge is found to be better than those containing aromatic oil The percentage retention of tensile strength is found to be higher for those mixes containing higher percentage of refinery sludge. Comparatively poor retention of tensile properties is noticed for the mixes A, B and E containing 100% aromatic oil, 20% and 80% sludge respectively Variations

Table 5.3 Tensile properties of the various vulcanizates

Mix No.	Tensile Strength (MPa)			Elongation at break (%)			Modulus 100% (MPa)		
	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)
A	20.53	15.36	74.81	301.96	174.85	57.90	2.59	4.07	157.14
B	20.22	13.92	68.84	319.03	187.67	58.83	2.31	3.75	162.30
C	20.81	15.82	76.02	296.43	170.83	57.63	2.72	4.26	156.60
D	21.71	16.27	74.94	279.83	157.68	56.35	2.82	4.31	152.83
E	20.19	14.67	72.66	321.18	183.12	57.01	2.30	3.84	166.90
F	20.53	15.47	75.35	301.96	172.96	57.28	2.58	4.10	158.90

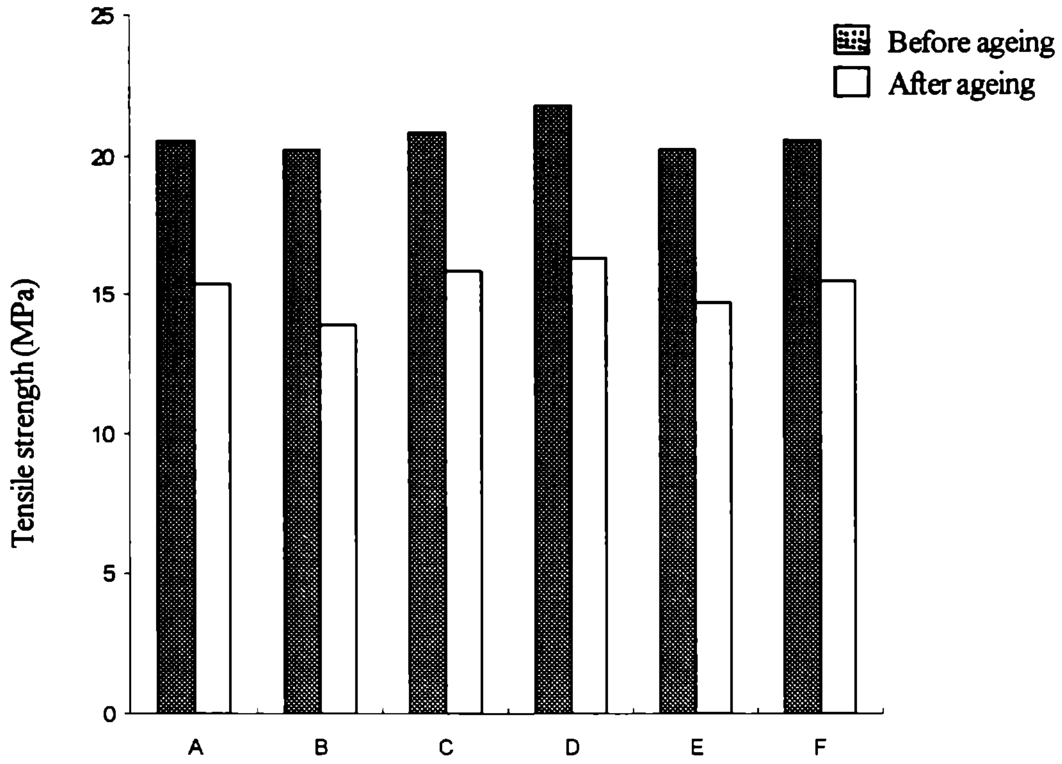

Fig 5.7 Tensile strength of the vulcanizates

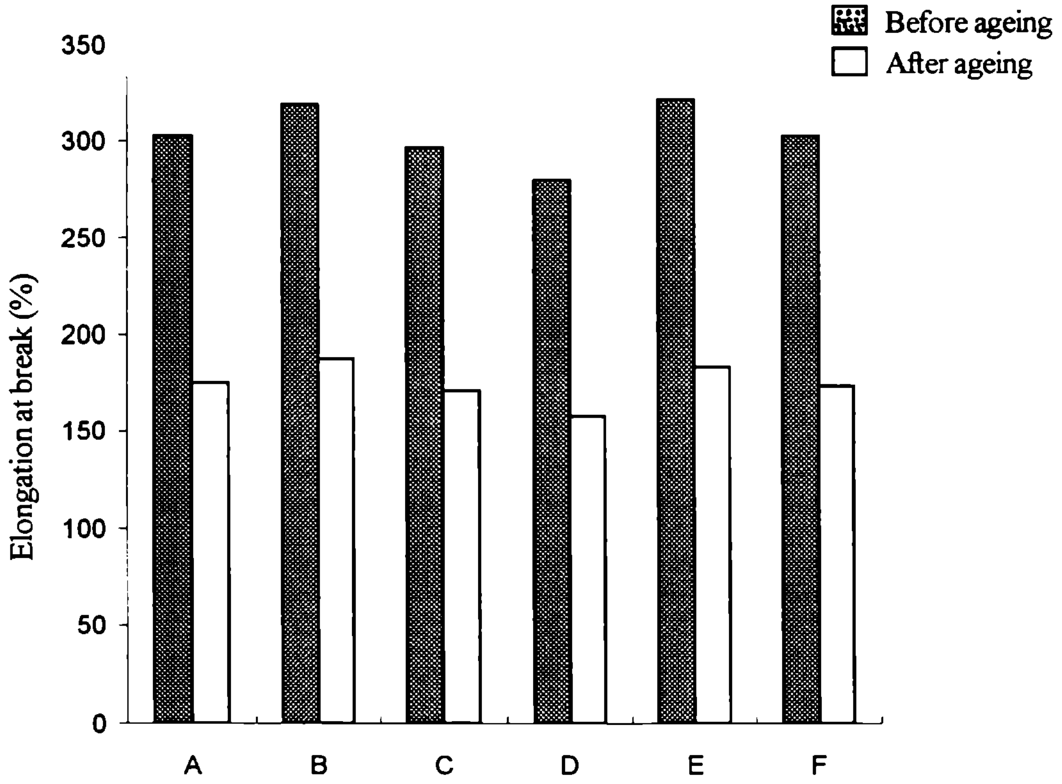

Fig. 5.8 Elongation at break of vulcanizates

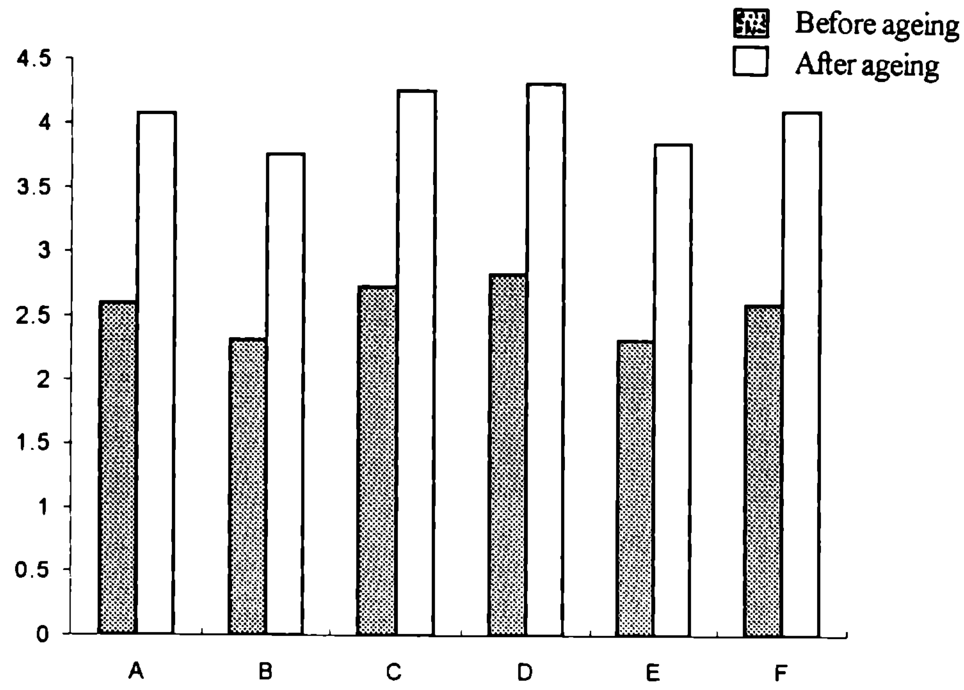

Fig. 5.9 100% Modulus of vulcanizates

in tensile strength, modulus (100%) and elongation at break with concentration of sludge before and after ageing are shown in Figs. 5.10 and 5 11 As suggested earlier, the increased retention of tensile properties exhibited by the mixes C, D and F containing 40%, 60% and 100% sludge respectively can be attributed to the phenols present in purified sludge which might have supplanted the anti-oxidant properties of the vulcanizates containing this oil.

Hardness (shore A), compression set, abrasion loss and tear strength are the other physical properties evaluated for these vulcanizates. These results are given in Table 5.4 The tear strength values of the vulcanizates were seen to increase from the mix A to F, the maximum value exhibited by the mix F containing

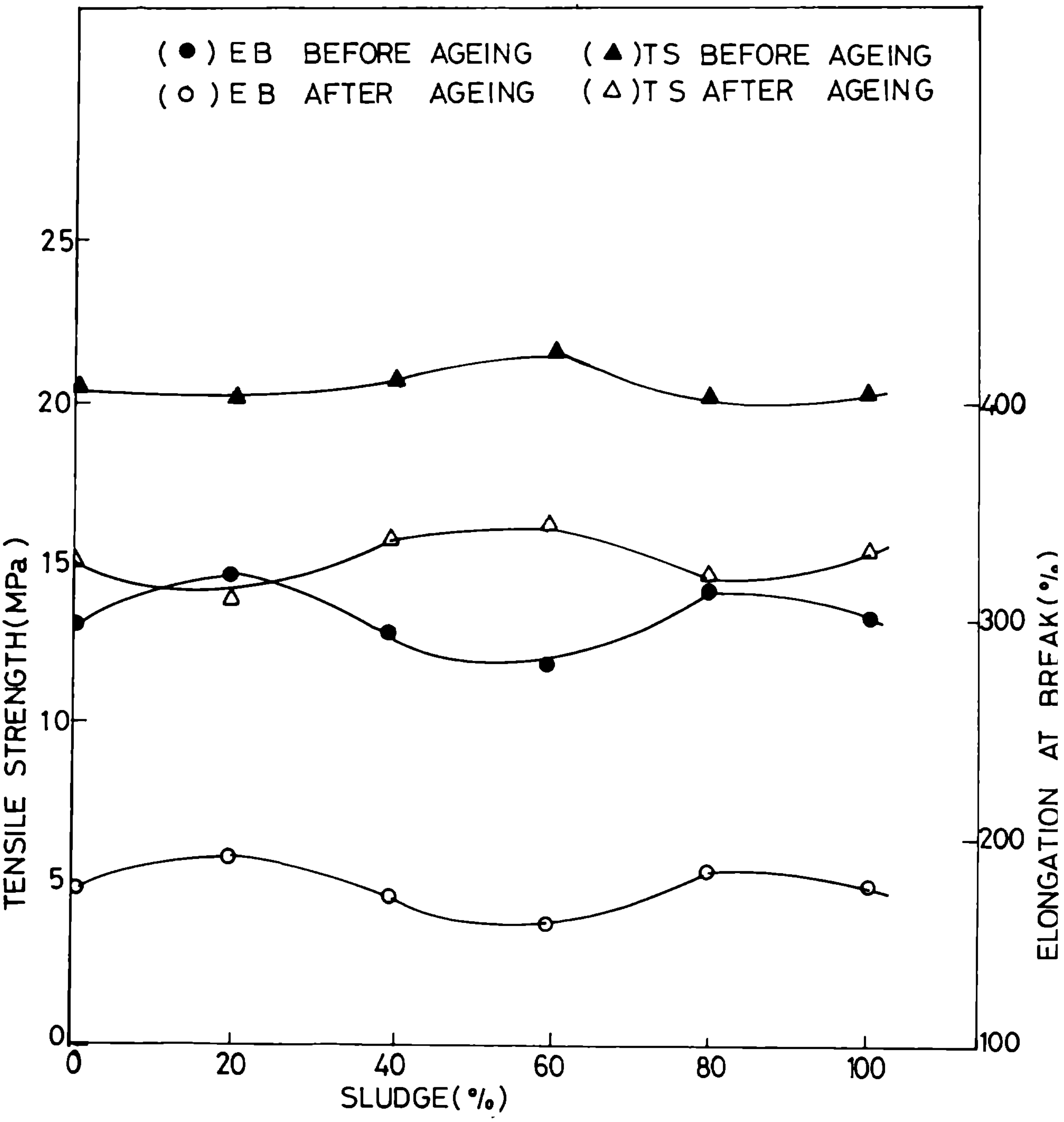

Fig 5.10 Effect of sludge on tensile strength/elongation at break of vulcanizates

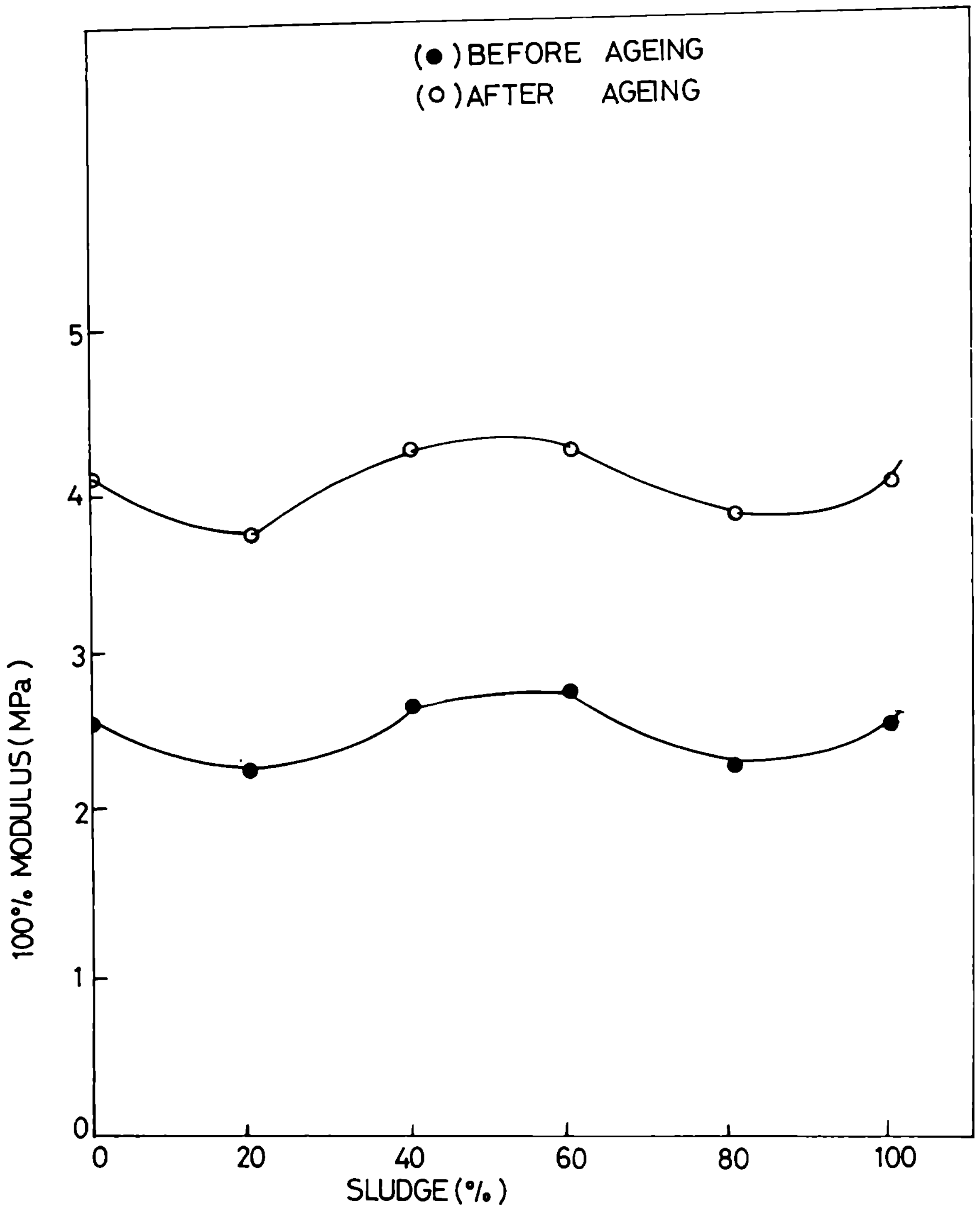

Fig 5.11 Effect of sludge on modulus of vulcanizates

Table 5.4 Other physical properties evaluated

Mix No.	Tear Strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrassion Loss (cm^3 /hr)	Total crosslink density x 10^{5}g mol /cm^3
A	64.18	64	23.60	5.54	8.84
B	66.03	64	23.20	5.60	8.79
C	67.26	64	23.40	5.59	9.12
D	69.87	64	23.80	5.14	9.49
E	71.94	64	23.80	5.34	8.89
F	72.41	64	24.00	5.50	9.012

refinery sludge alone. The increase in above values is found to be proportional to the increase in sludge content of the mixes (Fig. 5 12) Hardness, compression set and abrasion resistance were found to be more or less same for the mixes containing aromatic oil and refinery sludge.

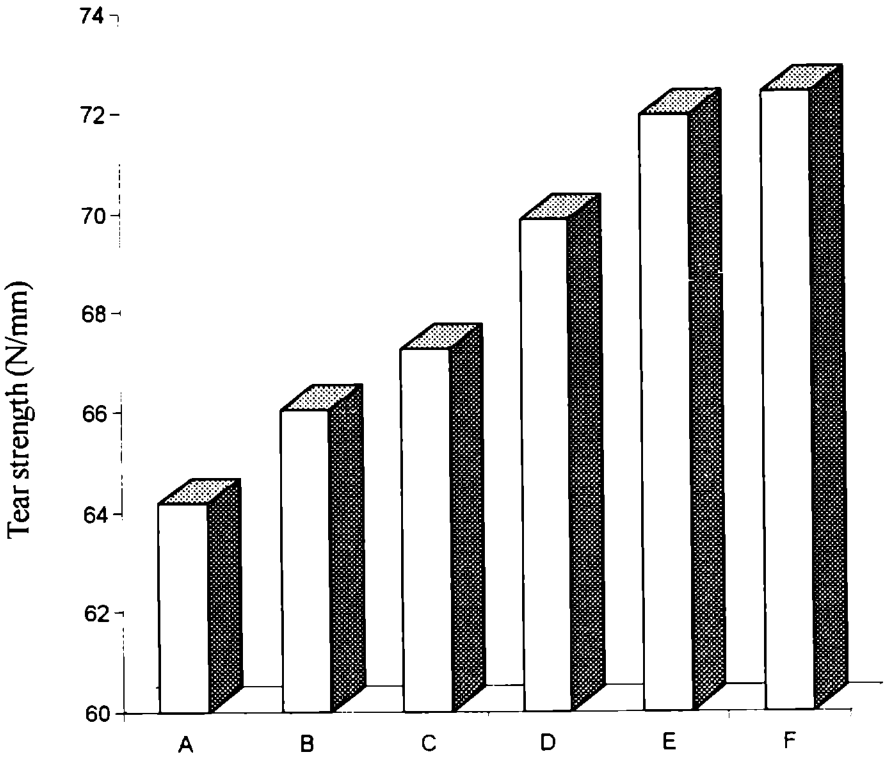

Fig. 5.12 Tear strength of the vulcanizates

5.4 Conclusions

These results show that sludge obtained from petroleum refineries can be used, after purification, as a processing aid. Studies of the processing characteristics suggest that SBR compounds can be processed with sludge similar to other conventional process aid viz., aromatic oil. The use of sludge does not adversely affect the cure characteristics of the mixes or the physical properties of the vulcanizates. Some improvement is noticed in properties like tensile strength and ageing resistance. Significant improvement in tear strength is noticed in the vulcanizates containing refinery sludge. Apart from being very cheap, it can also be a practical method of disposal of this sludge in refineries.

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CHAPTER 6

REFINERY SLUDGE AS A PROCESS AID IN THE COMPOUNDING OF NR/SBR BLENDS

6.1 INTRODUCTION

Since encouraging results were obtained when purified refinery sludge was used in the compounding of natural as well as styrene butadiene rubber, we thought it worthwhile to investigate its utility in a blend of NR and SBR. This study was undertaken mainly because one type of rubber may not possess all the physical properties desired and so it is a usual phenomenon that two or more rubbers are blended together All rubbers have shortcomings in one or more properties. There are therefore technical reasons for blending as it makes possible to obtain the right compromise in properties on blending two rubbers. The difficulties encountered in the processing of some rubbers also emphasize the need for blending. Economic reasons also can be given for blending since appreciable price differences exist between different rubbers. For example[1], the resistance of polychloroprene (CR) to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubbers is normally practiced for applications in white sidewalls. Similarly, in tread compounds, the high abrasion resistance under certain conditions conferred by the use of polybutadiene (BR) is desirable but the poor road holding and rib tearing properties are undesirable. Hence blends of BR with NR and SBR are usually preferred.

Eventhough elastomer blends are in use for several years, a clear understanding of their rheological and physical properties in relation to the properties of constituents and morphology is still limited[2] Physical properties of cured polymer blends are generally inferior to those predicted from the properties of the component polymers. This behaviour is especially seen in the cured blends of dissimilar polymers having large differences in polarity and unsaturation. In polymer blends of similar polarity and unsaturation, the cured blends exhibit additive properties and the socalled covulcanized state is realized[3]

A major cause for the inferior properties exhibited by the cured elastomer blends is that the constituents are incompatible on the molecular scale and exist in the form of two separate phases[4] A heterogenous blend usually results when two chemically dissimilar rubbers are mixed. Many investigators[5-8] have examined this morphology under electron microscopes but little scientific work has been done to establish the factors on which the mechanical properties of such blends depend. It is found that the mechanical properties of elastomers depend very strongly on crosslinks density[9]

When filler is added to a binary elastomer blend, it goes to the less viscous polymer and when the viscosity becomes equal to that of the highly viscous polymer, it would be taken up by both the polymers[10] Hence usually the low viscosity polymer gets highly loaded. The incorporation of carbon black into 50-50 elastomer preblends indicated that black affinity decreased in the order of BR, SBR, CR, NBR, NR, EPDM and IIR[11] The factors that dominate the partitioning of carbon black are the degree of saturation of the polymers, their viscosities, their polarities and the method of mixing[12]

Two component polymer systems in general can be described by the following equation[13,14]

$$P = P_1C_1 + P_2C_2 + IP_1P_2.$$

where P is a certain property value for the blend, P_1 and P_2 are the values of that property for the isolated components and C_1 and C_2 are the respective concentrations of the constituents in the blend. I is a number which indicates the level of synergism created by combining the two constituents. A positive value of I indicates synergistic behaviour and the blend will exhibit improved properties than the arithmetic average of the two components. A negative value of I indicates non synergistic behaviour and the blend has properties that are below the values predicted by an arithmetic averaging. Polymer systems where I is equal to zero (or very close to zero) are additive blends where their properties are essentially arithmetic averages of the properties of their components.

NR and SBR belong to the general purpose rubber group They can be usefully blended if the fundamental differences and similarities between them is recognised. NR and SBR are unsaturated hydrocarbon polymers and hence unvulcanized compounds will dissolve in most hydrocarbon solvents and other liquids of similar solubility parameters, while cured stocks will swell extensively Both rubbers may be reinforced by carbon black and neither can be categorised under heat resistant rubber.

SBR is more uniform in quality than NR. During mastication, SBR retains its plasticity while the plasticity of NR decreases during processing. SBR compounds are found less scorchy than NR compounds and thus allow safer processing. NR possesses good gum tensile strength while SBR requires reinforcing fillers such as carbon black for developing comparable modulus and tensile strength. SBR has better abrasion resistance and tear resistance than NR while hysteresis and resilience characteristics are inferior to those of NR. Making use of these characterisitics, blends of NR and SBR can be prepared which will give better processing, strength, ageing and resilience properties.

Practical information regarding processing and vulcanization of NR SBR blends were reported by Springer[15] Mastication of NR[16] is necessary prior to blending with SBR. Shundo[17] has compared the use of roll mill and Banbury mixer for the preparation of NR SBR blends and found that mill mixing furnish more uniform compounds. In the vulcanization of NR SBR blends, NR phase takes a larger share of curatives leaving the SBR phase slightly under crosslinked[18] This necessitates more active accelerator or binary accelerator system to obtain uniform curing.

In rubber compounding, the process of incorporation of filler requires a lot of power/energy and time. Uniform distribution and dispersion of the incorporated filler and other ingredients are the key factors which determine the quality of the product ultimately. Rubber as such cannot perform these functions So inorder to make the compounding and processing of rubber easy without affecting the desired properties of the product, processing aids are incorporated. Because of the easy availability and good compatibility with most of the general purpose rubbers, aromatic oil is the most commonly used processing aid. Based on the encouraging results obtained on the use of purified refinery sludge as processing aid in both NR and SBR systems, we thought it appropriate to try this sludge as process aid in a 50-50 NR/SBR blend using carbon black as filler. Different formulations are employed by varying the amounts of sludge and the results are compared with those obtained for the control mix containing aromatic oil. The variation in processing characteristics brought about by sludge was compared with that of aromatic oil using a Brabender Plasticorder. The mixes were then cured upto their optimum cure times and the cure characterisitics and vulcanizate properties were compared. The crosslink density values were also assessed to correlate them with the vulcanizate properties.

6.2 EXPERIMENTAL

Natural rubber conforming the ISNR 5 and Synaprene 1502 having specifications as given in chapter 2 were used for the present study Rest of the ingredients viz. zinc oxide, stearic acid, mercapto benzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), carbon black (HAF N330), aromatic oil, sulphur etc. used were all of rubber grade. The sludge used for the present study was obtained from Cochin Refineries Ltd. Kochi., India. The purification of the sludge was effected by keeping the sludge at a temperature of 110±10°C for an interval of 12 hours until it is dehydrated The viscous hot oil left behind was then passed through strainers of various sizes to get rid of solid contaminants. Details are as given in chapter 2

The formulation of the different mixes used are given in table 6.1. All these mixes contain 5 phr zinc oxide as activator, 2 phr stearic acid as coacitvator, 1 phr accinox HFN as antioxidant and 2 phr sulphur as vulcanizing agent per hundred parts of rubber [NR + SBR (50-50)]. All mixes contain 50 phr carbon black as filler and accelerator (MBTS + TMTD) to a level of 1.5 phr. Mix A contain 5 phr aromatic oil and it is taken as the control mix. Mix B contains 4 phr aromatic oil and 1 phr sludge. Mix C contains 3 phr aromatic oil and 2 phr sludge. Mix D contains 2 phr aromatic oil and 3 phr sludge. Mix E contains 1 phr aromatic oil and 4 phr sludge. Mix F contain only 5 phr sludge. The characteristics of the sludge used for this study are as given in Table 4.1 under chapter 4.

The processing characteristics of the mixes employed were compared using the Brabender Plasticorder (PL 3S). This torque rheometer gives a torque time curve (plastogram) by measuring the torque generated while mastication. The processability of 50-50 NR/SBR blend with sludge was compared with that of the conventional process aid viz., aromatic oil. The rubber before feeding into the plasticorder was passed six times through a laboratory size two roll mixing mill at an opening of 0.8 mm so as to get a thin sheet. This was then cut into small strips and fed into the mixing chamber of the plasticorder, the mixing heads being set at 30 rpm and at 30^{0}C. The total mixing time of 16 minutes had the following break up. Rubber mastication was completed within the first four minutes, activator + accelerator addition took three minutes, addition of carbon black mixed with sludge took eight minutes and

Table 6.1 Formulation of the mixes

Ingredients	A	B	C	D	E	F
Natural Rubber	50	50	50	50	50	50
SBR	50	50	50	50	50	50
Zinc Oxide	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
MBTS	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5
Accinox HFN	1	1	1	1	1	1
Carbon Black (HAF N330)	50	50	50	50	50	50
Aromatic Oil	5	4	3	2	1	0
Sludge	0	1	2	3	4	5
Sulphur	2	2	2	2	2	2

finally sulphur was added in the last one minute. The ingredients were added as per the formulation given in table 6.1 except for the fact that the amounts of oil were varied. The same procedure was repeated for the control mixes with aromatic oil. The torque curves obtained were recorded. An attempt was made to optimise the oil level by repeating the experiment using both aromatic oil/ sludge at 4,5,6 and 7 phr levels. The Brabender torque curves obtained in each case were recorded. It was found that the addition of aromatic oil/sludge at 4 and 5 phr levels were not sufficient for proper mixing and comparatively higher torque values were obtained. But when aromatic oil/sludge were added at 6 phr levels, proper mixing occured with maximum reduction in torque. There was not much reduction in torque even when aromatic oil/sludge were added at 7 phr levels. Hence 6 phr of aromatic oil/sludge can be taken as the optimum requirement (Figs. 6.1 and 6.2) in these carbon black filled NR/SBR blends.

Compounding was done in a laboratory size two roll mixing mill at a friction ratio of 1:1.1 as per ASTM D 3182-89. NR/SBR blend was made initially and then the other additives followed in the usual order. It was found that aromatic oil/sludge at 5 phr levels was enough for the proper incorporation of the filler during mill mixing. The cure characteristics of the mixes were evaluated using the Goettfert elastograph model 67.85 and the cure curves obtained are given in figs. 6.3 and 6.4. The cure characteristics calculated are given in Table 6.2. The compounds were vulcanized upto the optimum cure time in an electrically heated laboratory type hydraulic press at 150^{0}C at a pressure of 140 Kgcm^{-2}. The tensile properties of the vulcanizates were determined according to ASTM D 412-87 method A using dumb-bell specimens at 25°C at a crosshead speed of 500 mm/min with a Zwick Universal testing machine. Ageing resistance was determined as per ASTM D 573-88 by maintaining the samples at 100°C for 48 hours in an air oven and then measuring the retention in the tensile properties. The tensile properties evaluated are reported in Table 6.3. Tear resistance was evaluated as per ASTM D 624 86 using angular test pieces. Hardness of the vulcanizates were determined according to ASTM D 2240-86 and expressed in shore A units. Compression set was determined as per ASTM D 395-89 (method B). Abrasion resistance was evaluated using DIN abrader (DIN 53516). All these results are reported in table 6.4. The overall crosslink density of the vulcanizates was determined from the swelling data in toluene by the procedures outlined in chapter 2.

6.3 RESULTS AND DISCUSSION

6.3.1. Processability

The processing characteristics of purified refinery sludge was compared with that of the conventional aromatic oil in this 50-50 NR/SBR carbon black filled system using the Brabender Plasticorder From the trials made using different dosages in the plasticorder, it was found that 6 phr of aromatic oil/sludge was the optimum level to be used while mixing. Mixes containing sludge imparted comparatively higher torque than those containing aromatic oil (figs 6.1 and 6.2). But during mill mixing the optimum levels required in both cases was found to be only 5 phr This is attributed

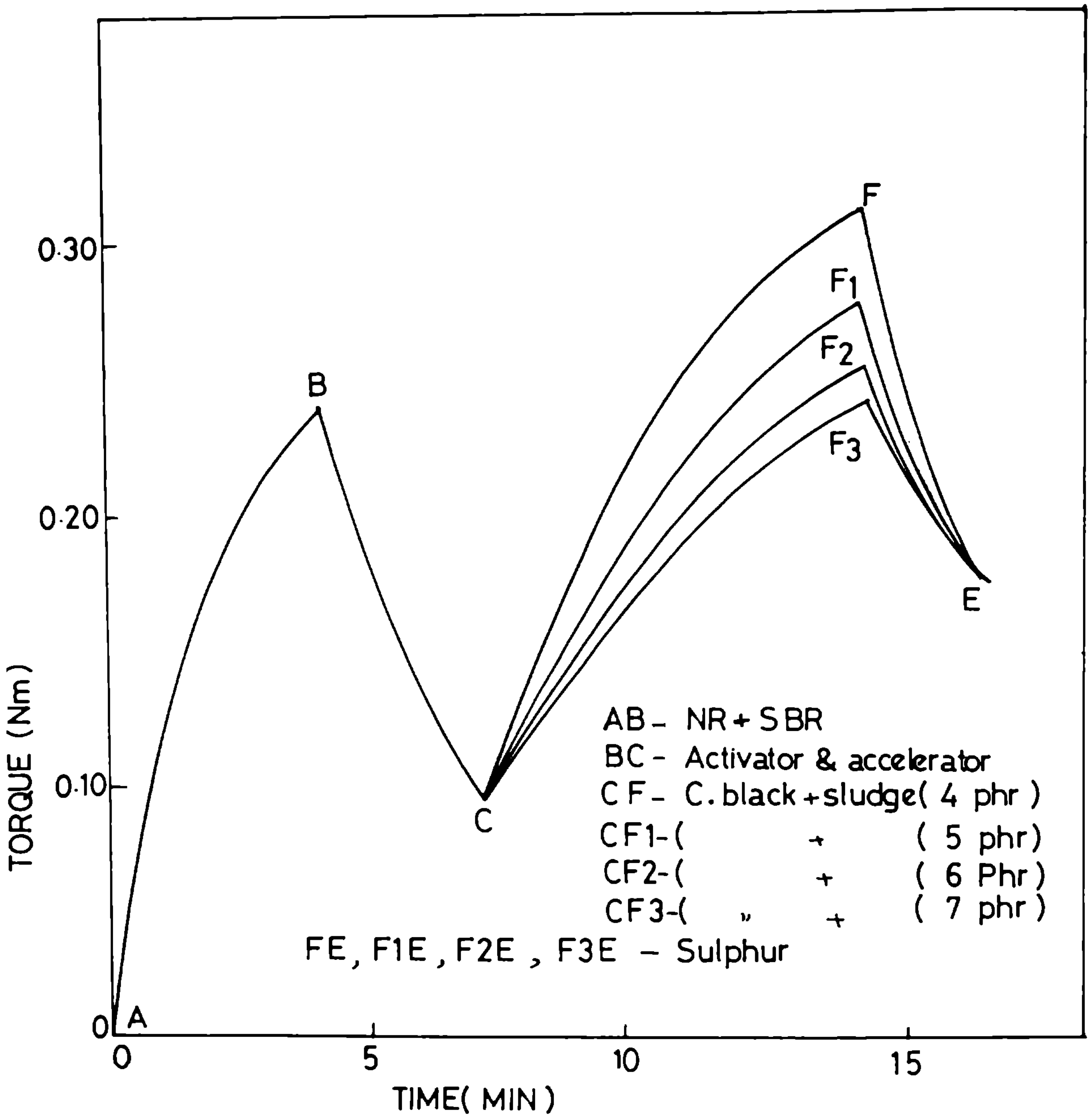

Fig 6.1 **Brabender torque curves of mixes containing sludge**

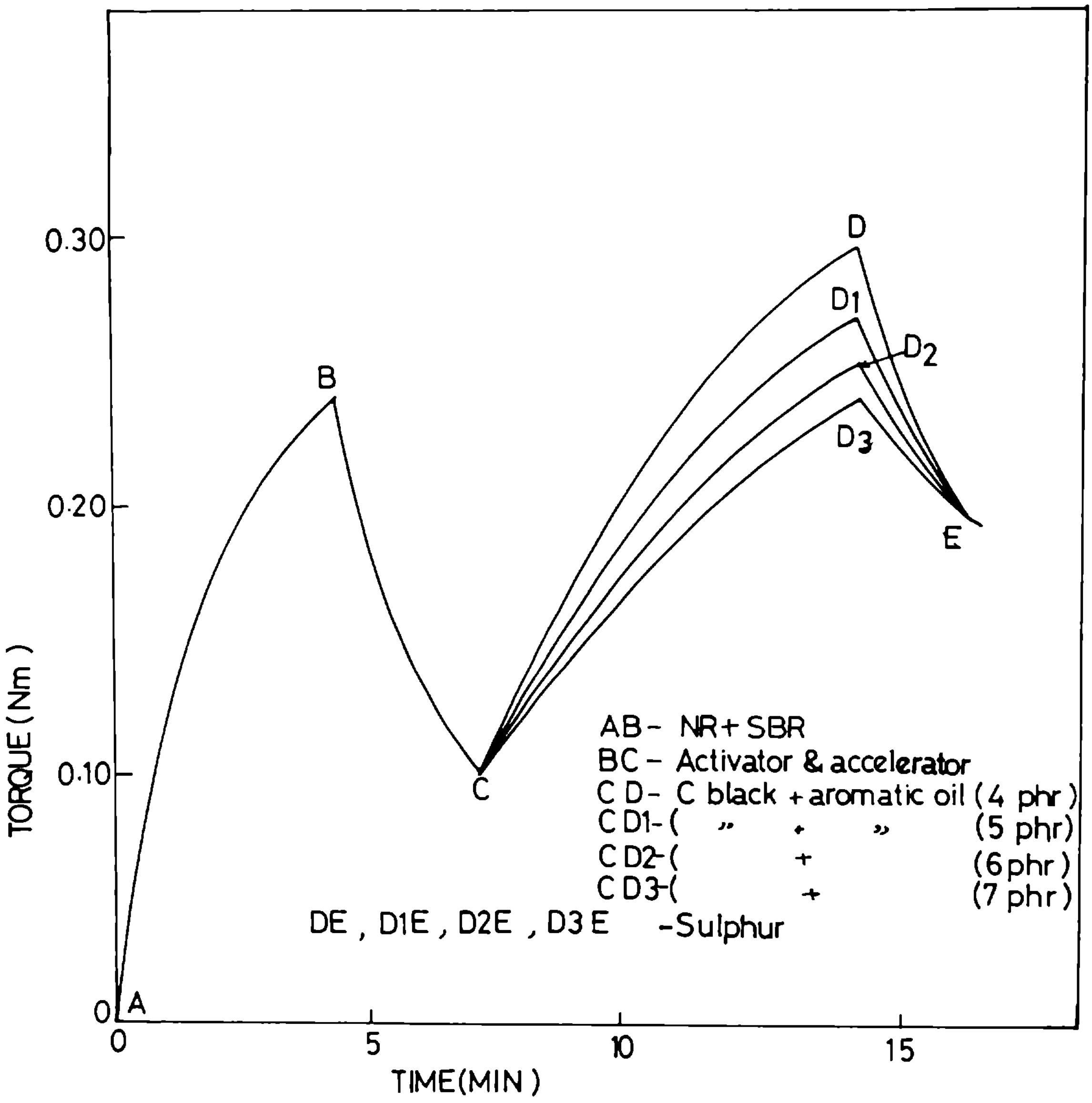

Fig 6.2 Brabender torque curves of mixes containing aromatic oil

to the higher shearing force occurring in the mixing mill compared to the plasticorder. Based on these processing characteristics and also the cure characteristics, vulcanizate properties etc. reported in the subsequent sections, it is evident that refinery sludge can be effectively used as a processing aid in the various NR/SBR carbon black filled blends used in the present study.

6.3.2. Cure characteristics

The cure curves obtained for the different mixes are given in figures 6.3 and 6.4. The relevant cure characteristic are given in table 6.2. It can be seen from the cure characteristics, that as the amount of sludge increases, the vulcanization becomes faster as evidenced by the decrease in the cure times. The maximum torque, a measure of the crosslink density, increases steadily with the increase in concentration of sludge. Mix C containing 40% sludge alone behaves differently from this general trend. The presence of SBR has given good reversion resistance to the blends (Figs. 6.3 and 6.4). Other cure characteristics of the blends show more of NR behaviour than of a synthetic rubber. This might be because a major share of the curatives might have gone to the NR phase. The increased vulcanization rate brought about by sludge may be attributed to the presence of chemical compounds present in the residual portion of petroleum fractions which might have functioned as accelerators. From the results it is evident that purified refinery sludge can be advantageously used as a processing aid in place of other processing oils. There is substantial reduction in cure time while the other cure characteristics of the system is not adversely

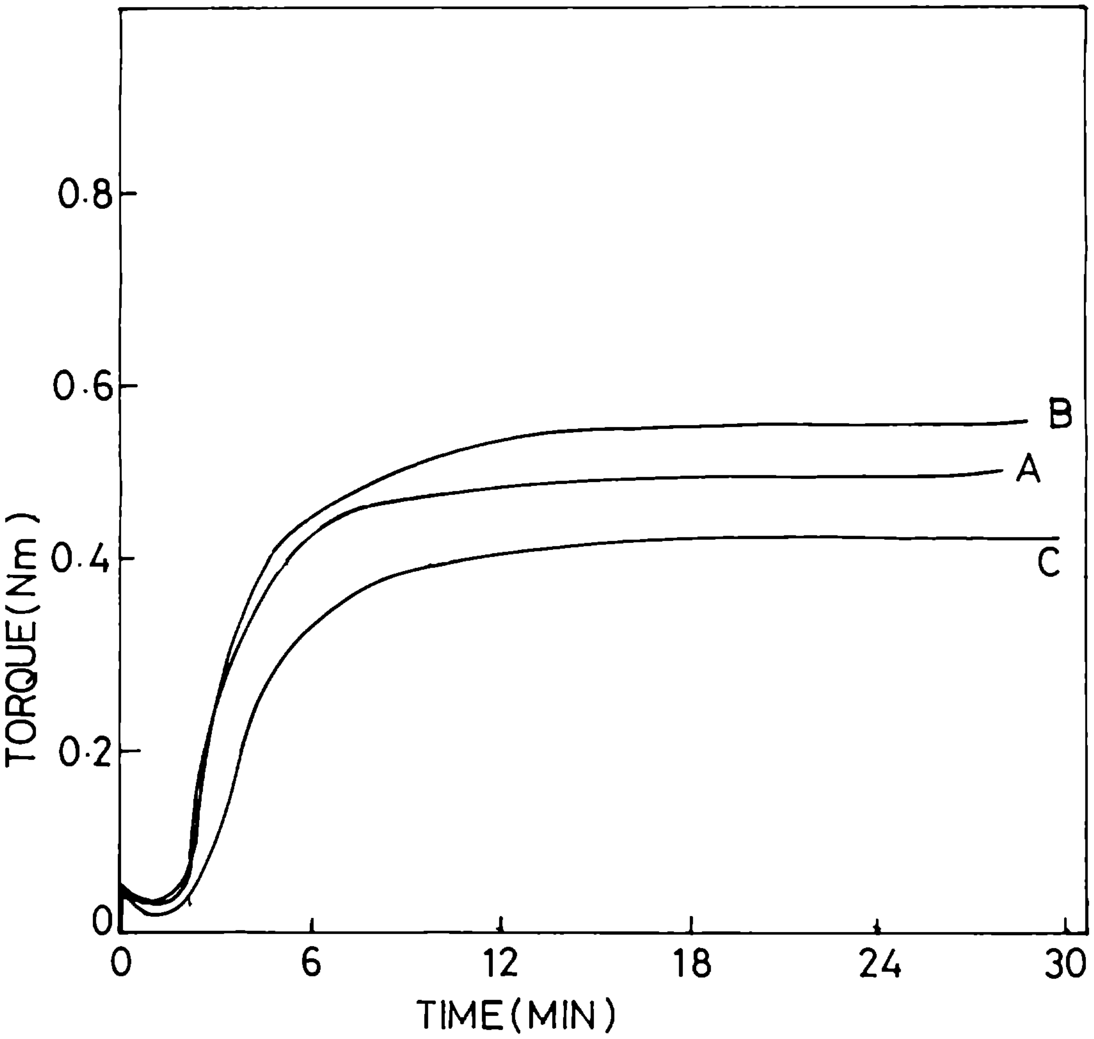

Fig 6.3 Cure curves of the different mixes

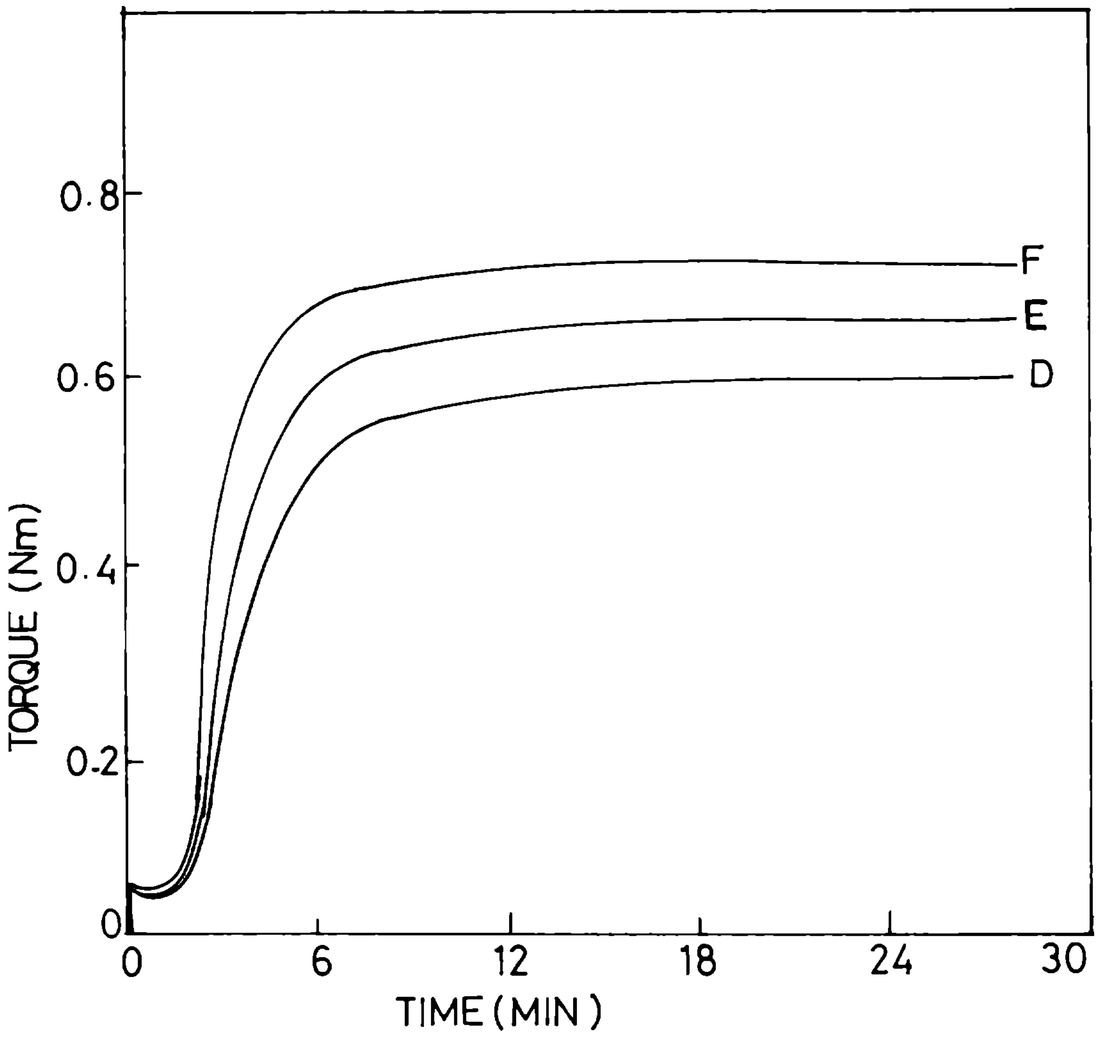

Fig 6.4 Cure curves of the other mixes

Table 6.2 Cure characteristics of the mixes

Mix No.	Optimum cure time (t_{90}) min.	Scorch time (t_{10}) min.	Induction time	Cure rate index	Maximum torque (Nm)	Minimum torque (Nm)
A	7.3	2.3	1.2	20	0.50049	0.02832
B	8.5	2.2	1.6	15.87	0.56103	0.03223
C	8.8	2.6	1.6	16.13	0.42871	0.02197
D	7.8	2.6	1.6	19.2	0.60492	0.04234
E	6.7	2.2	1.8	22.2	0.65967	0.04199
F	5.5	1.9	1.6	27.8	0.72754	0.04932

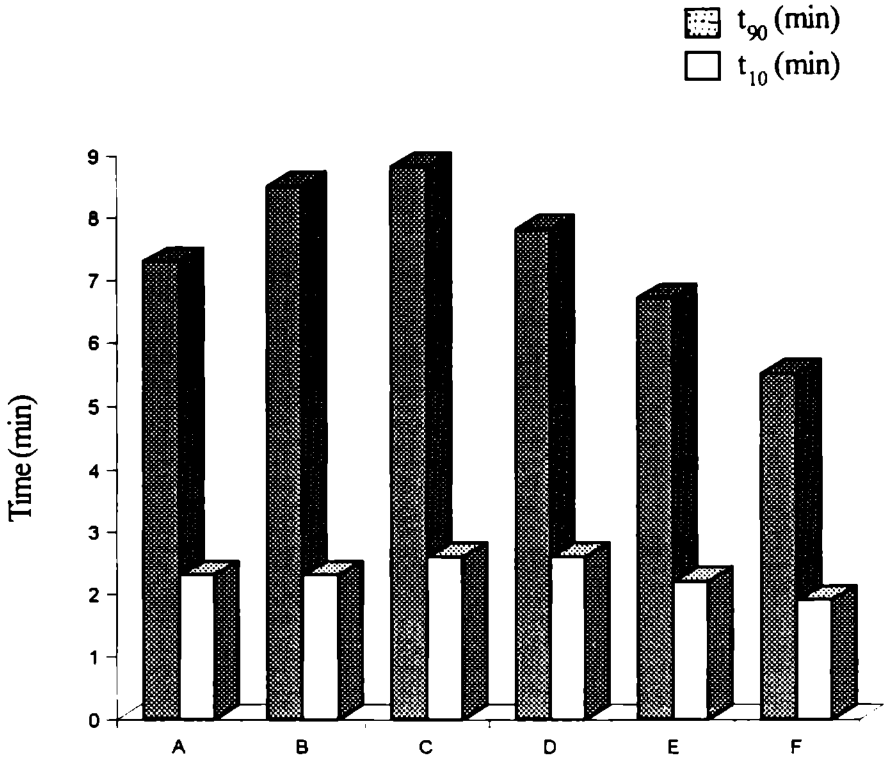

Fig. 6.5 A comparison of t_{90} and t_{10} of the different mixes

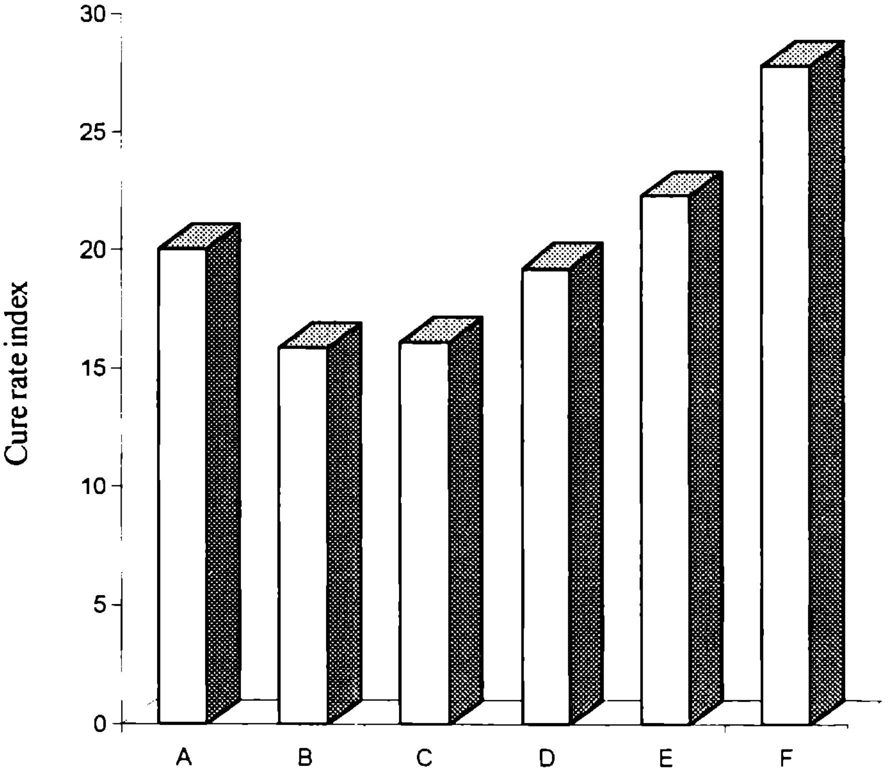

Fig. 6.6 Cure rate index of the various mixes

affected by this change (Figs. 6.5 and 6.6).

6.3.3. Crosslink density

The total crosslink density values of the different blends were evaluated and the results are given in table 6.4 It is found that the crosslink density increases from blend A to E containing 80% sludge, minimum being exhibited by blend A containing 100% aromatic oil. This is also evidenced by the increasing trend in maximum torque value observed during cure. Tensile and tear strength also exhibited an increasing trend when aromatic oil was substituted more and more with purified refinery sludge. As explained in the earlier chapter, this can be due to the better interaction between rubber and filler interface in mixes containing sludge. The mixes E and F containing 80 and 100% sludge respectively gave almost identical values showing that substitution of aromatic oil with sludge beyond 80% brings only very little effect.

6.3.4. Tensile and other physical properties

Table 6.3 gives the tensile properties of the vulcanized samples. In the systems under review it can be seen that there is an increase in modulus and tensile strength and a corresponding decrease in elongation at break from mix A containing 100% aromatic oil to mix E containing 80% sludge. This clearly reflects the definite relationship between these properties and the crosslink density values. Mixes E and F containing 80 and 100% sludge give almost identical values for initial tensile strength. Heat ageing resistance of the vulcanizates give comparable results regarding tensile strength with the control

Table 6.3 Tensile properties of the various vulcanizates

Mix No.	Tensile Strength (MPa)			Elongation at break (%)			Modulus 100% (MPa)		
	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)
A	18.70	11.17	59.73	442.46	198.46	44.85	4.29	7.21	168.07
B	18.78	11.18	59.53	440.24	198.40	45.06	4.48	7.32	163.39
C	18.80	11.28	60.00	431.26	196.04	45.46	4.50	7.50	166.67
D	18.98	11.30	59.54	420.94	195.38	46.42	4.55	7.59	166.81
E	19.06	11.38	59.71	418.90	190.08	45.38	4.62	7.86	170.13
F	19.02	11.36	59.72	418.96	190.25	45.41	4.60	7.82	170.00

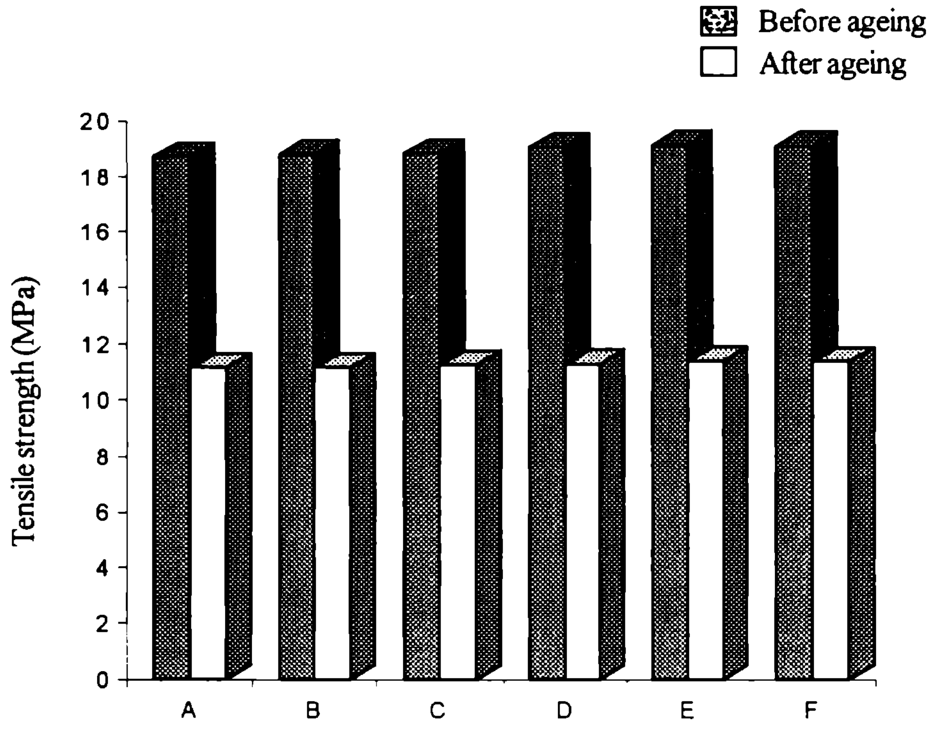

Fig. 6.7 Tensile strength of the different vulcanizates

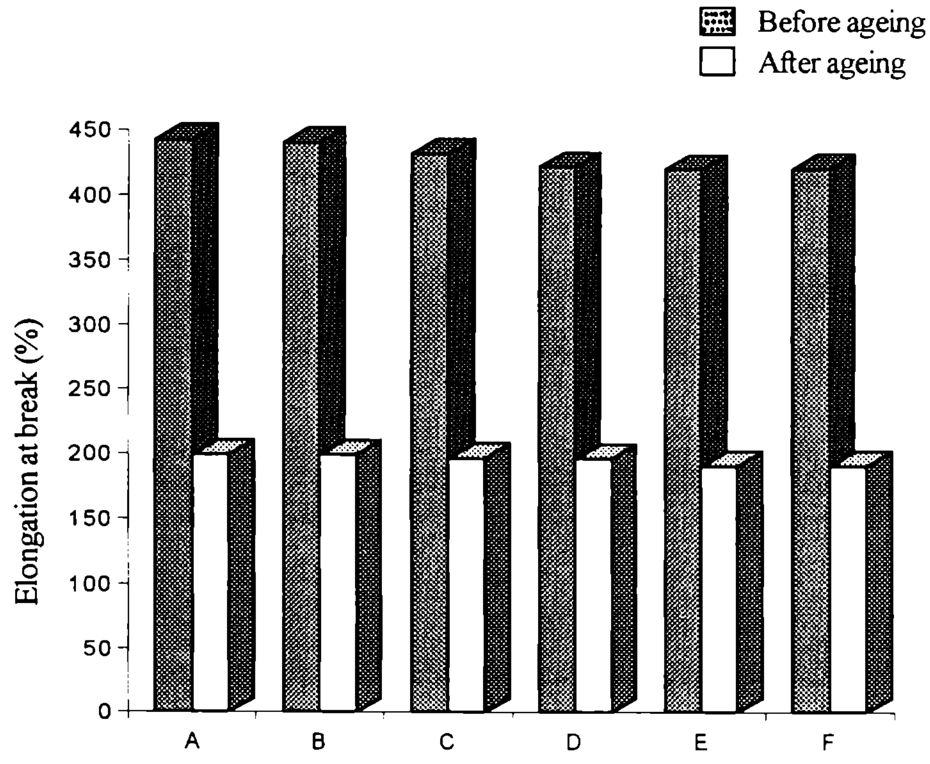

Fig. 6.8 Variation in Elongation at break of the vulcanizates

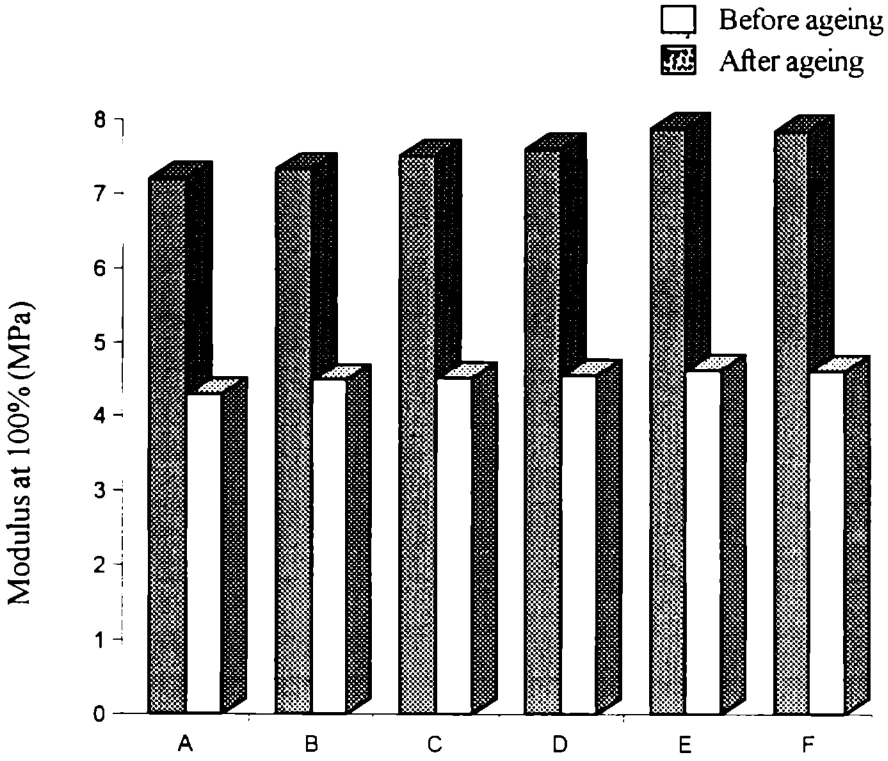

Fig. 6.9 Modulus (at 100%) of the vulcanizates

mix. But the percentage retention of modulus and elongation at break exhibits a positive trend with the increase in concentration of the sludge even though the increase is marginal These data also indicates that substitution of aromatic oil with sludge does not adversely affect the ageing properties of the vulcanizates (Figs 6 7 to 6 11)

The other physical properties evaluated are tear strength, compression set, hardness, abrasion loss etc These results are given in table 6 4 The tear strength values were seen to increase from the blend A to F, the maximum being exhibited by the blend F containing 100% sludge and the minimum by A containing 100% aromatic oil The increase is found to be proportional to the sludge

Table 6.4 Other physical properties evaluated

Mix No.	Tear Strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrassion Loss (cm^3 /hr)	Total crosslink density x 10 ^{5}g mol /cm^3
A	68.2	63	21.40	3.99	8.264
B	68.3	63	21.40	3.90	8.28
C	70.2	64	21.30	3.88	8.362
D	71.1	64	21.20	3.78	8.424
E	71.8	64	21.00	3.76	8.486
F	72	64	21.00	3.78	8.484

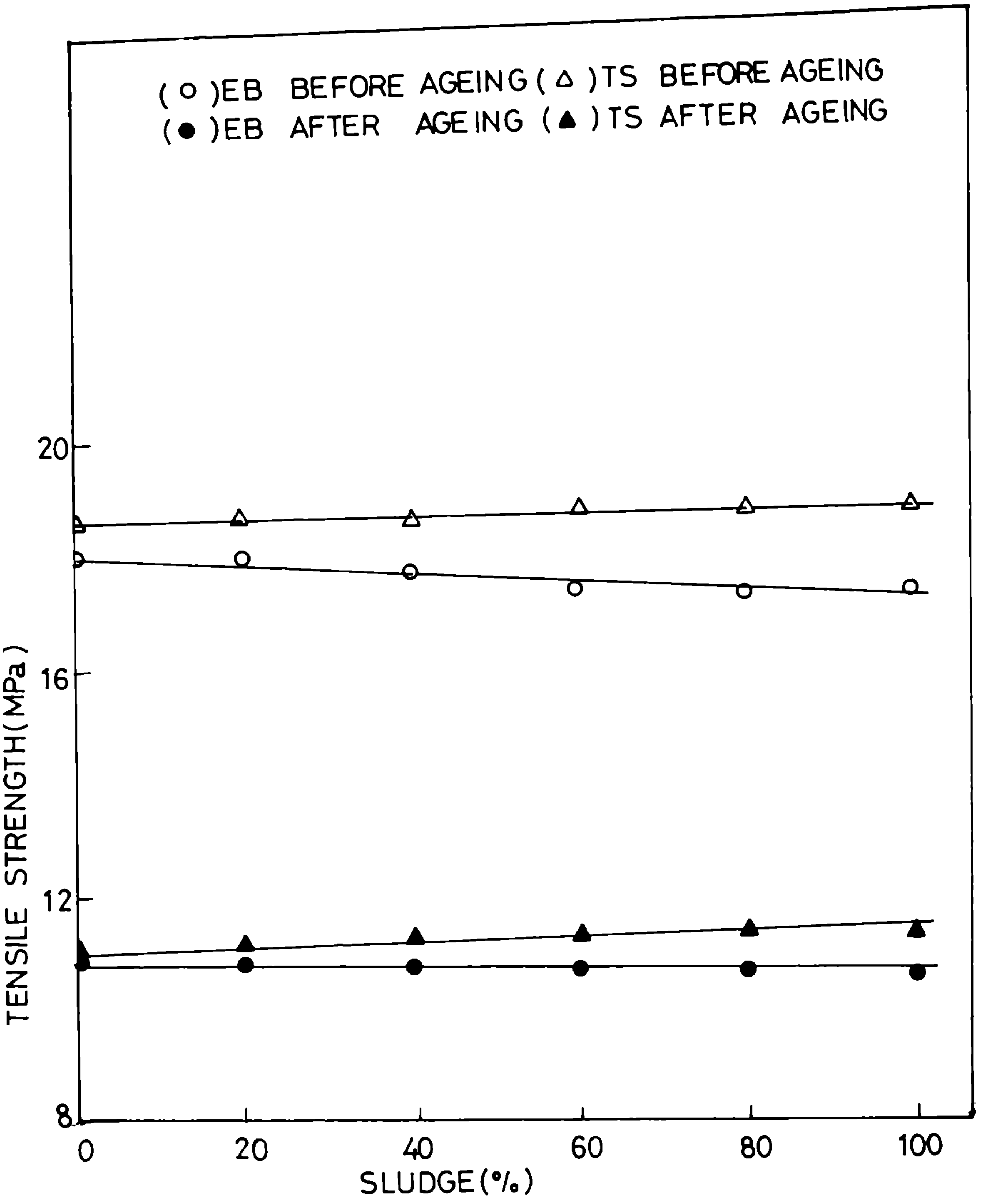

Fig 6.10 Effect of sludge on tensile strength and elongation at break of vulcanizates

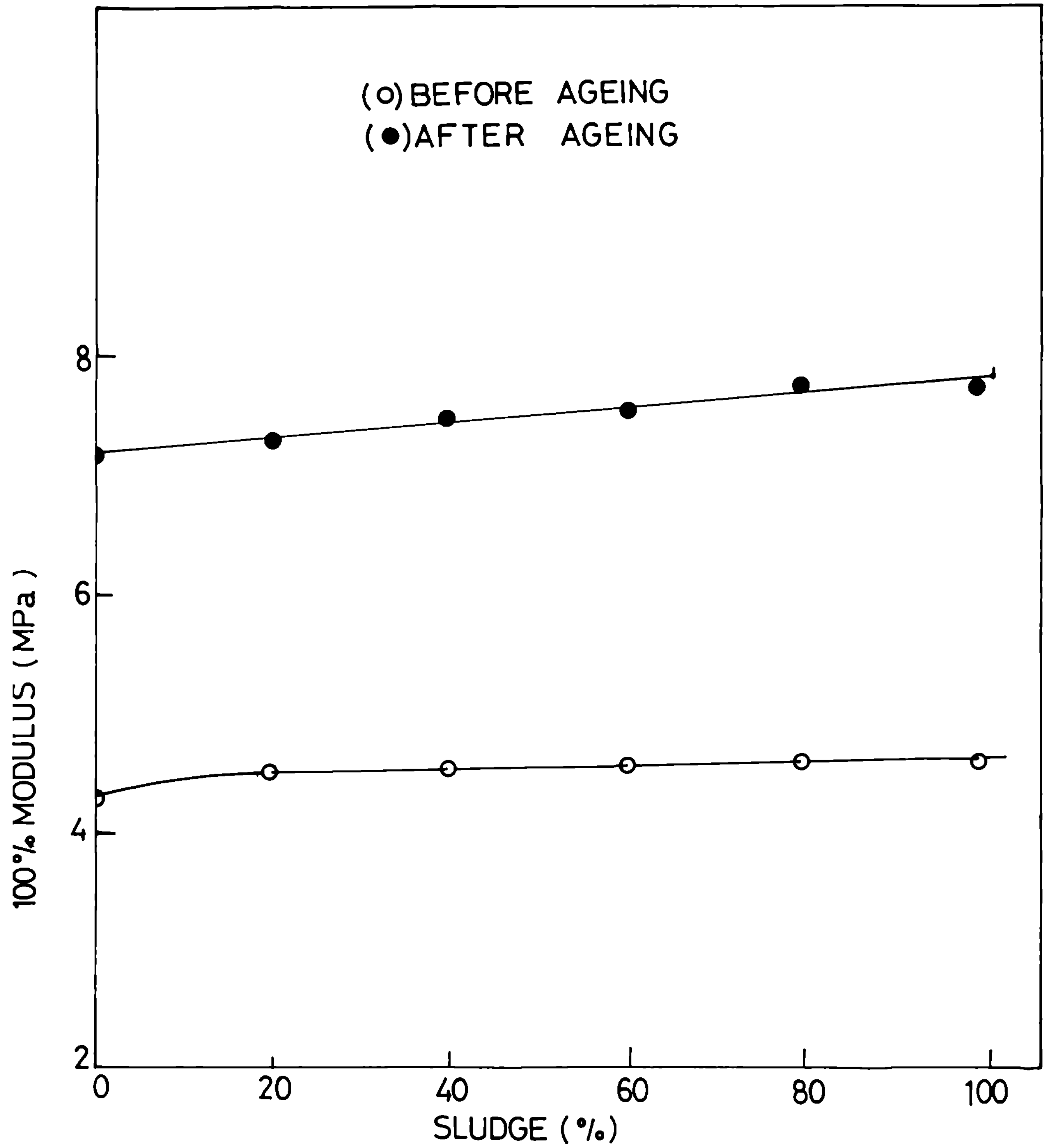

Fig 6.11 Effect of sludge on modulus of vulcanizates

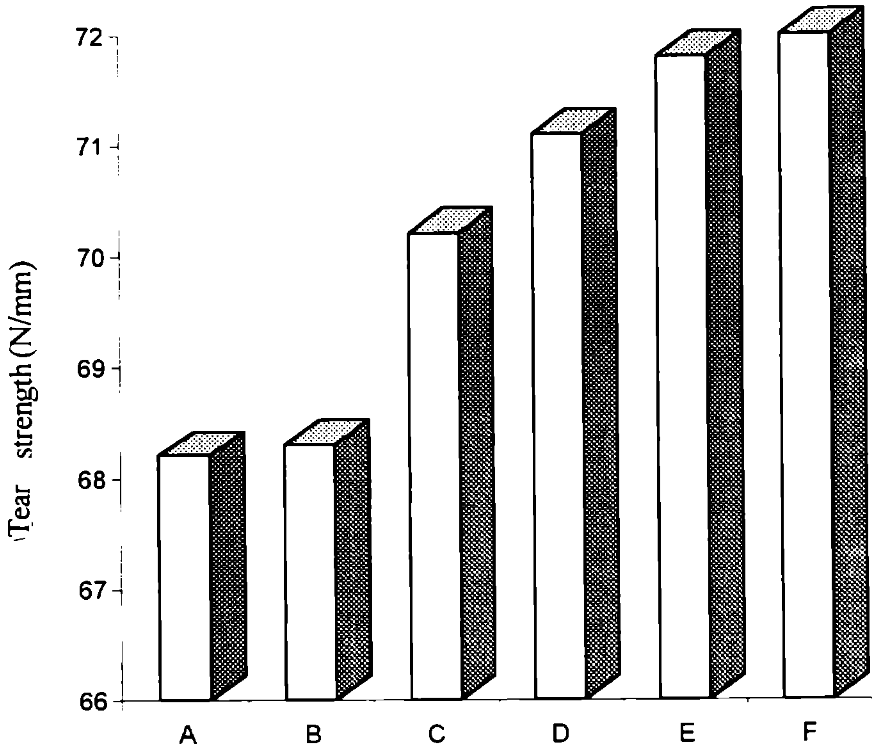

Fig. 6.12 Tear strength of the vulcanizates

content in the blend (Fig. 6 12). Hardness, compression set and abrasion loss were found to be more or less same for blends containing aromatic oil and refinery sludge.

6.4. CONCLUSIONS

The results obtained in the above investigations show that the sludge obtained from petroleum refineries can be effectively used as a process aid in the sulphur vulcanization of NR/SBR blends. Evaluation of the processing characteristics show that NR/ SBR blends can be processed with sludge just like the conventional process oil viz aromatic oil It is found that the use of sludge neither adversely affect either the cure characteristics of the mixes nor the physical properties of the vulcanizates The optimum cure time of the mixes is found to get significantly reduced by the incorporation of sludge Some improvement is also noticed in properties like tensile strength and tear strength in vulcanizates containing sludge compared to that of aromatic oil As suggested earlier since sludge is a waste material in the oil refineries, its utilisation as a process aid can be a simple practical method of disposal in a useful manner One of the disadvantages with sludge is that it can be used only in black or dark coloured rubber products.

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CHAPTER 7

SUMMARY

Petroleum refining industries are bogged down with the problem of handling substantial quantity of sludge in some form or the other depending on the type of configuration, crude processing capacity and down stream capacities, design of effluent treatment and pollution abatement measures and the efficiency cum effectiveness of these plants. Sludge accumulates in refineries due to pump failures, desalter malfunctioning, frequent oil draining from tankages and units, seepages due to failure of storage tanks, pipeline ruptures below ground, periodical cleaning of storage tanks etc. At present, many refineries do not have any established method of disposing this oily sludge. As and when the sludge quantity increases and accumulates in various collection systems, surge ponds, pits etc. the sludge is removed manually in drums and transferred to a lagoon or quarry, which is a potential hazard to the environment. The oily sludge is primarily composed of hydrocarbons, inorganic matters, water etc. and hence cannot be disposed off without pretreatment. The usual methods of disposal of sludge like landfill, landfarming, incineration etc. help only for disposal and not for its effective utilisation. Moreover the methods like landfill and landfarming have problems like groundwater contamination whereas the incineration method is highly expensive as it requires the use of support fuel and/ or the installation of expensive flue gas scrubbing/solids removal equipment to meet air pollution regulations. The present study aims at utilising the refinery sludge in a useful manner and that too without many of the above mentioned problems.

The first chapter of the thesis gives an introduction about crude petroleum, its refining, details of sludge accumulation, industrial bitumen manufacture, bitumenous paints etc. It also gives details about rubber compounding and vulcanization, process aids and their functions in rubber compounding. It also includes the scope and objectives of the present work. A detailed description of the experimental procedure adopted in the present study is given in chapter II. It covers the materials used for this study, their specifications and different experimental procedures adopted. It also includes the procedure adopted for the purification of sludge, details of processability studies using Brabender Plasticorder, methods adopted for compounding, vulcanization and determination of the different physical properties. The method used for the estimation of total crosslink density is also given in this chapter. Also described are the methods of determination of softening point, penetration, ductility, flash point, loss on heating, kinematic viscosity, diesel index,ramsbottom carbon residue etc. Methods of determination of the various characteristics of bitumenous paints like drying time, consistency, finish, flexibility and adhesion, resistance towards acid, alkali, chlorine, heat etc are all reported therein.

In view of the fact that the refinery sludge mentioned earlier contains about 70% hydrocarbons in which 7.8% by weight is asphaltenes and that it accumulates in large quantities in the refinery creating a disposal problem, a study was made to separate out the lighter oils from the sludge and to convert the residue left behind into some useful grades of industrial bitumen without the conventional air blowing process. This forms part I of chapter 3 The purification of the sludge was done as described in chapter 2 by maintaining the sludge at 110±10°C in a barrel fitted inside with steam coils for 12 hours. The viscous oil so obtained was then passed through strainers of different size to remove solid impurities. The purified sludge thus obtained was then subjected to vacuum distillation at a pressure of about 1 mm of mercury and the volume of the distillate collected upto the cracking point was noted. The lighter oil fraction thus recovered from the sludge amounts to 17% (w/w). The lighter oil so recovered was tested for its different characteristics viz. recovery, flash point, kinematic viscosity, diesel index, carbon residue (Ramsbottom), pour point, total sulphur etc. Evaluation of these characteristics showed that the recovered lighter oil meets the basic requirements of diesel fuel like flash point, diesel index etc. But since the other characteristics are away from the specifications of high speed diesel, it cannot be used as such as HSD Since the characteristics which do not meet the specifications of HSD are only slightly away, it can easily be brought within the specifications by blending with appropriate streams of petroleum refineries.

A portion of the residue obtained after vacuum distillation was subjected to heat treatment at 250°C for 3 hours without any catalyst. The sample was then tested for the different parameters like softening point, penetration, ductility, flash point, solubility in carbon disulphide, loss on heating etc. The above experiment was then repeated adding 2% each of sulphur, ferric chloride, phosphorous pentoxide and aluminium chloride. It is seen that heat treatment without any catalyst gave no notable change in the softening point while some reduction in penetration was observed. Heat treatment with P_2O_5 also gave a similar result Heat treatment with sulphur/ $FeCl_3$ gave some increase in softening point and a good reduction in penetration. But heat treatment with $AlCl_3$ gave not only substantial increase in softening point but also a sharp reduction in penetration. Thus out of the different catalysts tried, $AlCl_3$ alone was successful in bringing down the penetration sharply and to bring up the softening point to the required level for the different grades of industrial bitumen. A mechanism is suggested to explain the pronounced catalytic effect of $AlCl_3$.

To determine the optimum concentration of aluminium chloride and the optimum time and temperature required, the experiment was further repeated with different percentages of $AlCl_3$ ranging from 1 2.75% and temperature ranging from 200 to 275^{0}C for periods varying from one to three hours. The results showed that a high temperature of 275^{0}C as well as a lower temperature of 200^{0}C do not give a better softening point penetration relationship. The best result was obtained at the temperature of 225^{0}C and duration of 2.5 hours. This can be taken to be the optimum conditions for preparing grades of industrial bitumen of lower penetration and higher softening point like the 90/15 grade.

The results of this study also show that only four of the 10 different grades of industrial bitumen can be prepared by the methods used by us. Heat treatment of the vacuum residue at 250^{0}C for 2.5 hours with 1% $AlCl_3$ is sufficient for preparing the 65/25 grade. 75/30 and 85/25 grades can be obtained by heat treatment at 200^{0}C with 2.5% $AlCl_3$ for one and three hours respectively Similarly the 90/15 grade can be prepared by heat treatment at 225^{0}C for 2.5 hours with 2 5% $AlCl_3$. For the remaining grades, the softening point-penetration specifications were found difficult to be met by the methods used in this study, probably due to the low asphaltene content in the vacuum residue of sludge used. It may be noted here that a sample of asphalt usually taken for industrial bitumen manufacture contains asphaltenes to a level of 20 to 30% while the sludge contains asphaltenes only to a level of about 7.8%. The method of preparation of industrial bitumen envisaged in this study has the added advantage that no noxious fumes are produced polluting the environment as in the conventional air blowing process.

Since almost 50% of the industrial bitumen manufactured is used for the production of bitumenous paints, a study was made about the applicability of the industrial bitumen obtained from refinery sludge in the preparation of bitumenous paints. This study form part II of this chapter. Bitumenous paints usually contain an asphaltic base in a volatile solvent with or without drying oils, resin, fillers and pigments. The 90/15 grade industrial bitumen obtained from refinery sludge was used for this purpose. CNSL formaldehyde resin and chlorinated rubber were also incorporated in the formulations to modify the properties of the bitumenous paints. Three different formulations were tried using this industrial bitumen (90/15) derived from refinery sludge. Formulation I contained 50% industrial bitumen together with 1.5% red lead as antirust compound, 0.5% naphthenates of manganese, cobalt and lead as drying agent and the rest solvents. In formulation II, two pots A and B were prepared and mixed prior to application. Pot A contained 40% CNSL-formaldehyde resin, 20% carbon black (ground) and the rest solvent. Pot B contained 47% industrial bitumen, 3% hexamethylene tetramine as catalyst and the rest solvents. Formulation III contained industrial bitumen 35%, CNSL-formaldehyde resin 20%, chlorinated rubber (in solution) 5% and the rest solvents. The paint films from these formulations were investigated for the different characteristics.

It was seen that bitumenous paints made using formulation I, II and III are meeting the requirements of drying time, consistency, finish, stripping, flexibility and adhesion, keeping properties etc. Also all the three formulations were found to be homogeneous showing no separation of the solvent phase or coagulation of the asphalt base nor settling or packing in the container that cannot be overcome by stirring for a short time. Formulation I exhibited good resistance towards water, chlorine, acid and alkali. But its heat resistance was found to be very poor indicating that it cannot be used for high temperature applications like in industrial chimneys, boilers etc. It can also be seen that incorporation of CNSL-formaldehyde resin in formulation II boosted the heat resistance retaining the other properties. But its acid resistance was found to be very poor. Hence this formulation can be applied only for those surfaces where contact with acid/acid salts is unlikely Formulation III containing both CNSL-formaldehyde resin and chlorinated rubber exhibits good heat resistance as well as acid resistance besides retaining all the other properties exhibited by formulations I and II. This study also shows that heat resistance of bitumenous paints can be increased considerably by the incorporation of CNSL-formaldehyde resin and that incorporation of chlorinated rubber will help to boost up the acid resistance together with heat resistance.

Chapter IV deals with the use of purified refinery sludge as process aid in sulphur vulcanization of natural rubber where carbon black is used as filler. The processing behaviour of purified sludge was compared with the conventional process aid viz. aromatic oil and the quantity of oil required in each case was optimised with the help of a Brabender Plasticorder. The mixes obtained from different formulations were evaluated for the various cure characteristics like induction time, scorch time, optimum cure time etc. and for the various physical properties like tensile strength, tear strength, ageing resistance, abrasion resistance, compression set etc. The results showed that neither the cure characteristics nor the physical properties of the vulcanizates were adversely affected by the introduction of purified sludge in these carbon black filled systems. Studies of the processing characteristics suggest that NR compounds can be processed with sludge similar to other conventional process oils. Some improvement is noticed in properties like tensile strength, ageing resistance and abrasion resistance in the mixes where sludge is used. Significant improvement in tear strength and substantial decrease in the optimum cure time are added advantages when sludge is used. However one of the disadvantages with sludge is that it can be used only in black coloured rubber products. It may be noted that the conventional process oils used at present in rubber are becoming prohibitively costly while sludge is a dumped waste of the refinery

The fifth chapter describes the use of purified sludge as process aid in carbon black filled sulphur vulcanization of a synthetic rubber viz. styrene butadiene rubber (SBR 1502). This study was undertaken mainly because of the fact that a lot of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis a synthetic rubber. The optimisation of processing characteristics in this rubber using aromatic oil/sludge was carried out in plasticorder. The different cure characteristics of the mixes were evaluated and it was found that the cure values are comparable with the reference mixes where conventional process aid used. Tensile and other physical properties evaluated for the vulcanizates containing sludge indicate only marginal differences between experimental mixes and the control formulations. In the case of chemical crosslink density, the mixes containing sludge exhibit slightly higher values compared with those containing aromatic oil. Ageing resistance of the vulcanizates containing sludge was also found to be comparable with the control formulations. Significant improvement in tear strength is noticed in the vulcanizates containing sludge.

A study on the effect of purified sludge as process aid in the compounding and vulcanization of NR/SBR blends is given in the sixth chapter. This study was undertaken mainly because known elastomers do not exhibit all the properties desired and so, are often blended with a second elastomer during processing. About 75% of all elastomers are used as blends rather than alone. Cure characteristics of the blends were studied at 150°C and in this case also sludge was found to give appreciable reduction in optimum cure time. The cure characteristics of the blends show more of an NR behaviour than that of a synthetic rubber. This might be because a major share of the curatives used in this study might have gone to the NR phase. The optimum dosage of sludge required was derived here also using the processability studies in the plasticorder. Tensile strength, modulus and elongation at break of vulcanizates were also evaluated. In many of these properties studied, vulcanizates containing sludge showed slightly better performance. Comparable values with those of the control mix were obtained in the case of other physical properties such as hardness, compression set and abrasion loss. Regarding tear strength, vulcanizates containing sludge showed better results. Total chemical crosslink density values estimated also support the above conclusions. In these systems mixes containing 80% and 100% sludge gave almost identical values showing that substitution of aromatic oil beyond 80% brings only very little effect. Also noticed is the fact that the presence of SBR in the blend has given good reversion resistance to the stocks.

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
IP	Institute of Petroleum
BS	British Standards
IS	Indian Standards
ISNR	Indian Standard Natural Rubber
SBR	Styrene Butadiene Rubber
IIR	Isoprene - Isobutylene Rubber
EPDM	Ethylene - Propylene - Diene Rubber
NBR	Acrylonitrile Butadiene Rubber
CR	Chloroprene Rubber
BR	Poly butadiene Rubber
CNSL	Cashew Nut Shell Liquid
PMC	Pensky Marteus Closed Method
API	American Petroleum Institute
LSHS	Low Sulphur Heavy Stock
HSD	High Speed Diesel
HAF black	High Abrasion Furnace black
MBTS	Mercapto benzthiazyl disulphide
TMTD	Tetramethyl thiuram disulphide
EV	Efficient Vulcanization
VGC	Viscosity Gravity Constant
PRI	Plasticity Retension Index
CS_2	Carbon disulphide
T_m	Melting temperature

ML(1+4)100^{0}C	Mooney Viscosity determined using large rotor after a dwell time of 1 minute and rotor run of 4 minutes at 100^{0}C.
M mol/Kg RH	Millimole per Kilogram of Rubber Hydrocarbon
N/mm	Newton per millimetre
n_D^{20}	Refractive index at 20^{0}C for D line of Sodium
Nm	Newton metre
Min	Minutes
MPa	Mega Pascal
nm	Nano metre
phr	Parts per hundred rubber
rpm	Revolutions per minute
Mc	Number average molecular weight of rubber chains between crosslinks
V_r	Volume fraction of rubber
V_s	Molar volume of solvent
χ	Polymer - Solvent interaction parameter
ρ_s	Density of solvent
ρ_r	Density of rubber
Z	Weight fraction of filler
t_{90}	Optimum cure time
t_{10}	Scorch time
t_5	Induction time
CS	Centi Stocks
hrs	Hours
w/w	Weight/weight
w/v	Weight/Volume

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3. Refinery Sludge as a Processing Aid in the Compounding of Styrene Butadiene Rubber.

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4. Refinery Sludge as a Process Aid in the Compounding of NR/SBR Blends.

   (Communicated)

5. Utilisation of Refinery Sludge in Bitumenous paints.

   (To be communicated)