# STUDIES IN RUBBER CHEMICALS

A THESIS
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THE UNIVERSITY OF POONA

FOR THE DEGREE OF
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IN CHEMISTRY

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# GENERAL INTRODUCTION

India is one of the major cashewnut (Anacardium occidentale) producing countries of the world. India meets about 90% of the total world demand for cashew kernels, which are produced from the cashewnuts. Home production not being sufficient at present, raw cashewnuts are imported from Mozambique and other countries and processed in India to give the kernel. About 75% of the total kernels produced are exported to various countries.[1]

The cashew kernel is present in the kidney shaped nut or shell, which is attached to the cashew apple. The nut which is hard, smooth, shining, thick and cellular carries in it the cashew kernel, the prized commodity of commerce. The nut shell contains an acrid oily juice which is powerfully vesicant.

For the production of kernels the cashewnuts are carefully roasted with constant stirring in shallow iron pans or perforated earthen-ware pans which are heated by direct fire. Under these conditions about 50% of the cashewnut shell liquid is lost. Some of the large processing concerns are using perforated cylindrical rotary roasters, whereby a large portion of the shell liquid is recovered. Current trend, however is to pass the nuts held in wire trays, through a cashewnut shell liquid bath maintained at 188-193°C, at a uniform speed of fifteen feet in eighty to ninety seconds. Owing to the high temperature and the presence of little moisture (7-8%) in the nuts the honey combed cells of the shell burst and the exuded liquid flows into the bath, at the same time roasting the kernels to the desired degree. The recovery of cashewnut shell liquid (CNSL) by this process is much higher and only 10-15% residual oil is left in the broken shells.[2] This can also be extracted by using superheated steam.[3] After the roasting operation, the nuts are carefully broken and shelled manually, to obtain the unbroken kernels. Latest trends are to open the nut mechanically and remove the kernel which is roasted to the required degree. The empty shell is then expressed in expellers to give a red coloured liquid. There is at least one factory in India which is employing this method. The higher cost of expression is well compensated by the higher returns for the better quality of kernels and shell liquid.

The kernel weighs about 30% of the weight of the cashewnut and the proportion of the shell liquid to kernel is approximately 1:1.

The export figures for the last ten years of the cashewnut shell liquid from India to other foreign countries, in the world are given in the Table I.[4]

Cashewnut shell liquid is black, viscous and highly corrosive.

The chemistry of cashewnut shell liquid has been the subject of several investigators. Stadler[5] investigating the ether extract of cashew nuts reported that 90% of it consisted of an acid which he called anacardic acid, the

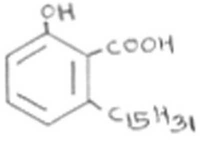
TABLE I

| Year | Quantity exported in Metric Tons | Year | Quantity exported in Metric Tons |
|---|---|---|---|
| 1958 | 5,851 | 1964 | 9,429 |
| 1959 | 3,863 | 1965 | 14,353 |
| 1960 | 5,903 | 1966 | 12,221 |
| 1961 | 5,833 | 1967 | 11,758 |
| 1962 | 6,230 | 1968 | 9,444 |
| 1963 | 7,448 | | |

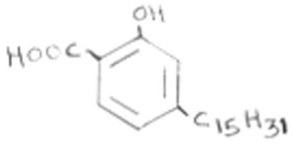
rest being a dihydroxy phenol called cardol. Later on, Ruhemann and Skinner[6] gave anacardic acid its present formula $C_{22}H_{32}O_3$ and observed that it is an hydroxy-carboxylic acid. Smit[7] also working on the ether extract of cashewnuts isolated the acid and hydrogenated both the acid and its decarboxylated product. From the results of oxidative degradation, as well as destructive distillation over zinc chloride, he concluded that anacardic acid was a homologue of salicylic acid having a normal unsaturated fifteen carbon side chain attached somewhere on the nucleus.

The hydrogenated anacardic acid gave violet colour with alcoholic ferric chloride and its methyl ether - methyl ester derivatives on oxidation with chromic acid gave palmitic acid and by analogy of this acid with Pelandjauic acid, Romburgh _et al._[8] suggested that anacardic acid might be $C_6H_3(OH)(COOH)(C_{15}H_{27})$. Later on, Pillay[9] studying the behaviour on oxidation of anacardic acid, anacardol and their hydrogenated derivatives came to the conclusion that anacardic acid is an ortho-hydroxybenzoic acid with an unsaturated side chain $C_{15}H_{27}$.

The facts that anacardic acid and tetrahydroanacardic acid get decarboxylated to anacardol and tetrahydroanacardol respectively and that the phenol-pentadecylate on Fries migration and subsequent reduction of the carbonyl group gives ortho- and para-pentadecyl-phenols, none of which is identical to tetrahydroanacardol led Gokhale, Patel and Shah[10] to conclude that tetrahydroanacardol is metapentadecylphenol. They further substantiated it by showing that tetrahydroanacardol gave a tribromo derivative whereas the o- and p-pentadecyl phenols gave only the dibromo derivatives, and also that the methyl ether of anacardol on oxidation yielded m-methoxy benzoic acid. Hence tetrahydro anacardic acid could have either of the following structure

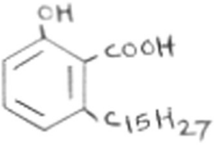


I. m.p. 91-91.5°C

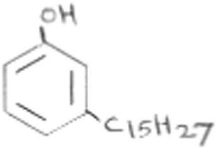


II. m.p. 98.5-99°C

Backer and Haack[11] prepared an acid from tetrahydroanacardol by Kolbe's synthesis. On steric considerations the acid formed was believed to be 2-hydroxy-4-pentadecyl benzoic acid (II) (M.P. 98.5-99°C). Its mixed melting point with tetrahydroanacardic acid showed depression. Thus the structure of tetrahydroanacardic acid was finalised as 2-hydroxy-6-pentadecyl-benzoic acid (I). Hence anacardic acid and its decarboxylated product anacardol would be (III) and (IV) respectively.



(III) Anacardic Acid



(IV) Anacardol

Ittyerah *et al.*[12] studied the properties of the oils obtained from cashewnut shells by solvent extraction and by roasting and observed that they are different. This is because of some decarboxylation or polymerisation or both taking place during the roasting.[13]

Harvey and Caplan[14] distilled the commercial CNSL under vacuum, 70% of the total distillate was single phenolic component with an unsaturated side chain in the meta position. This substance they termed as cardanol and is presumably formed by the decarboxylation of anacardic acid.

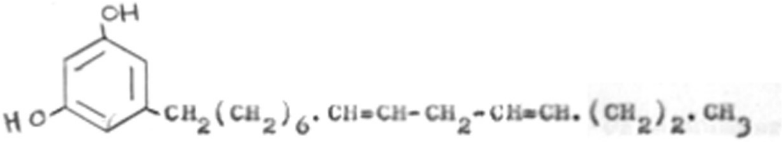
Wasserman and Dawson[15] hydrogenated the monophenols obtained either by heat or by solvent extraction. The hydrogenated product was the same in both cases, thus proving that the heat treatment did not alter the carbon skeleton. Later on, Dawson and co-workers also showed that both anacardic acid and its decarboxylated product anacardol were mixtures of several olefinic components having on an average unsaturation equivalent to about two double bonds.[16]

Symes and Dawson[17] obtained four pure components from the methyl ether of anacardol by chromatography. Their structures were elucidated by studying the products of ozonalysis and oxidative degradations. They reported the following compositions

(1) 3-pentadecyl anisole, 4.3%
(2) 3-(pentadecenyl-8′)-anisole, 45.1%
(3) 3-(pentadecadienyl-8′,11′)-anisole, 19.4%
(4) 3-(pentadecatrienyl-8′,11′,14′)-anisole, 31.2%.

Similarly, Paul and Yeddnappali[18] showed the hetero-olefinic nature of anacardic acid by subjecting it to fractional crystallization at temperatures 0° to -80°. The composition reported by them is - Saturated component, 4%; Monoolefinic, 15%; Diolefinic, 44%; Triolefinic, 37%.

The diphenolic component present in CNSL and responsible for the vesicant nature of it, is cardol, first isolated by Stadler and assigned the molecular formula $C_{21}H_{32}O_2$ by Backer and Haack.[11] Paul and Yeddnapalli[19] also distilled Indian commercial cashewnut shell liquid under vacuum and subjected the total distillate to molecular distillation at $10^{-4}$ mm. They separated the diphenolic component (cardol) from the monophenolic (anacardol) and studied the former's constitution by subjecting it to acetone potassium permanganate oxidation. They observed that cardol is 1,3,dihydroxy-3(pentadecadienyl-8′,11′)-benzene V.



V Cardol

The synthesis of 5-pentadecyl resorcinol by Dawson and Wassermann[15] confirms the above structure of cardol.

The positions of the olefinic linkages in the side chain of cardol were found to be similar to that in cardanol except that only diolefin and triolefin components have been isolated so far.

Thus commercial cashewnut shell liquid is a mixture of a salicylic acid derivative and mono and dihydroxy phenols all having a long unsaturated side chain. To make it a commercially useful commodity, it is necessary to take advantage of these structural features.

Amongst the various uses proposed for CNSL, anacardol and its derivatives are -- for the manufacture of insulating varnishes, typewriter rolls, oil and acid proof cold setting cements, automobile break linings, plasticizers, mosquito larvicides,[20] detergents[21] etc. Many patents have been taken out for using CNSL for lacquers, baking enamels,[22] water proof materials, insulating and plastic compositions etc. Tetrahydroanacardol has been converted to 4- and 6-amino-pentadecyl phenols which are recommended as oil soluble antioxidants and gasoline gum inhibitors.[23] Tetrahydro anacardol has been used for the preparation of azo dyes.[23,24,25,27]

Kudwa[25] patented the preparation of azodyes from the cashewnut shell liquid, but the presence of a number of components in the oil made it difficult to isolate dyes of the required standard of purity.

Sethi[26] made heat exchange media (dowtherm substitutes) surface active agents and detergents, and pesticides from tetrahydroanacardol. Gulati[27] further prepared T.H.A. derivatives such as quaternary ammonium compounds as industrial sanitizing agents or germicides; azo dyes and some special chemicals potentially useful in the pharmaceutical field.

The self polymerisation of CNSL, resulted into the interaction between the phenolic groups and the olefinic double bonds of the alkyl chain to form a polymerised mass, which after suitable curing operation, was used for the production of ion exchange resins.[28]

A comprehensive compilation of the U.S., U.K., Japan and Indian patents taken on the different applications of the cashewnut shell liquid and its products and their uses in different industries, has been made.[29]

The growth of Rubber Industry in India in the years of recent past, is collosal. The present annual rubber consumption is round 120,000 metric tons, which is likely to cross the mark of 200,000 metric tons by 1971-72. The progress of an industry can be also seen from the percentage growth as compared to that prevailing in advanced countries like U.S.A. and those in Europe. The average growth of the tyre industry in this country, in near future, is likely to be of the order of 12-15% as against the anticipated growth of 3-5% in the countries mentioned above.

The rubber chemicals industry also has to keep pace with this growth of the Rubber industry. The present manufacturing capacity for rubber chemicals in this country is in the vicinity of about 5000 metric tons, whereas the demand has already crossed this. Several rubber chemicals, therefore, are already on the list of short supplies. With the growth of the petro-chemical industry in India the synthetic rubber, is contemplated to be in production by round about 1971-72 to 30,000-40,000 metric tons. The nature of this polymer will obviously play a very important role in the requirements of rubber chemicals. If polybutadiene becomes the selective polymer for future economics of India, antidegradant levels are bound to go up.

The present rubber chemicals manufacturing industry submits heavy import bills as practically all rubber chemicals manufactured in India, are dependent on imported raw materials. The need to develop rubber chemicals from indigenous raw materials needs therefore, no stress.[30]

The rubber industry consumes large quantities of materials other than rubber which are called general compounding ingredients. The ingredients may be grouped as

(1) Rubber chemicals
    (a) Antioxidants
    (b) Accelerators
    (c) Auxiliaries such as retarders, blowing agents and peptizing agents
    (d) Activators such as zinc oxide and stearic acid etc.
(2) Fillers
    (a) Carbon blacks
    (b) Silica fillers
    (c) China clays, whiting and other mineral fillers etc.
(3) Plasticisers and Processing Aids
    (a) Pine tars
    (b) Mineral oils, waxes, and jellys, etc.
(4) Colours and pigments

Rubber chemicals are defined as substances, principally organic, used in the compounding of rubber for the purposes of effecting vulcanization, regulating the rate of vulcanization, facilitating the fabrication of the product, and improving its quality and its stability in service.[31] The distinction between rubber chemicals and other compounding ingredients is not sharp and is somewhat arbitrary. In general, however, rubber chemicals are distinguished by being compounded in rubber in relatively small proportions.

Due to the versatile and varied applications of the cashewnut shell liquid, in different industries, Indian Cashew Export Promotion Council is finding no difficulty in exporting whatever quantity of CNSL that has been produced in India. Nearly 10,000 tons/annum of CNSL is exported from India, to various countries in the world.

But due to recent development of cashew kernel processing industries in some of the East African countries like Mozambiq, Tanzania, and other countries like Brazil in Latin America, India will have to face a serious competition from these countries, in near future. To overcome these difficulties it would be desirable to create a potential market for this valuable commodity in this country only.

With this view in mind, the present investigation was undertaken to systematically exploring the possibilities of obtaining some useful new rubber chemicals from cashewnut shell liquid, and to evaluate their activity in natural rubber.

They were mainly -

(1) Antioxidants and

(2) Accelerators

In a study of this nature it is essential to start with pure components, so that the identity and the purity of the final products are beyond doubt. Hence, the tetrahydroanacardol (T.H.A.), a pure hydrogenated component from cashewnut shell liquid, was used as a starting material in the syntheses of new compounds obtained during the course of the present investigation rather than crude CNSL or anacardol, each has been proved to be a mixture of two-three products.

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# PART I - ANTIOXIDANTS

# THE HISTORICAL DEVELOPMENT OF ANTIOXIDANTS

Atmospheric oxygen is the most universally prevalent as well as economically important oxidising agent for fats and fatty acids, for petroleum and its components, and for many other classes of organic compounds. Its action may be beneficial or deleterious depending on the conditions and circumstances under which it occurs. It is advantageously employed in the production of blown oils and in various oxidation and polymerization products in the drying oil industry. Large quantities of organic chemicals are produced by the controlled oxidation of petroleum hydrocarbons. The process of film formation in applied protective coatings is essentially an oxidative process. The ultimate failure of these protective coatings, however, is a result of prolonged and excessive oxidation. Rancidification and other forms of oxidative deterioration of many fats and fat containing materials are like wise due to autoxidation. Other important groups of organic compounds such as rubber, plastics, gasoline, and fuel oil, also undergo autoxidative deterioration, unless precautions are taken to control it. These reactions are highly undesirable and result in serious economic losses. Because of spontaneous nature of the reaction between atmospheric oxygen and many types of organic compounds, the process is frequently referred to as "Autoxidation". The large increase in activity in autoxidation has resulted in a flood of publications. Some excellent books[1-10] and reviews[11-22] have been published recently on various phases of the autoxidation process and antioxidant action in high polymers, especially elastomers. Underlying all investigations of autoxidation is a desire not only to learn the nature of the products formed but also to understand the primary mechanisms involved since only by control of these mechanisms can the desired products be produced or the undesirable products be avoided.

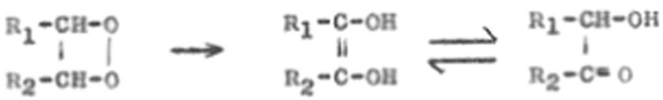
## Development of the concepts of Autoxidation

The phenomenon of autoxidation is mainly concerned with the unsaturated olefinic compounds which are more prone to the attack of atmospheric oxygen. Any explanation of the process of autoxidation must begin, as in all related oxidation reactions, with an understanding of the nature of the first reaction of oxygen with the double bond system. Until this initial step is known with certainty the subsequent steps of the process must remain more or less speculative. Many theories on the autoxidation, have been postulated from time to time.

### (1) Cyclic Peroxide Theory

The early work of Bach[23] and of Engler and co-workers[24] who investigated the role of organic peroxides in slow oxidation processes and introduced the term "Activated oxygen". Bach and Engler, however, believed that autoxidation by atmospheric oxygen was molecular and not atomic in nature, that is, a molecule of oxygen added at the double bond to form a peroxidised compound corresponding to the formula $R_1$-O-O-$R_2$ and that this compound like hydrogen peroxide, could in turn oxidize another oxidizable substance.

In an attempt to explain the action of driers in the formation of linseed oil films Fahrion[25] and later Ellis[26] assumed that an autoxidation occurred in the fatty acid part to form a cyclic peroxide which underwent rearrangement to a dihydroxy ethylenic or a hydroxyketo configuration, as follows

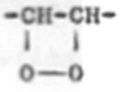


$$\begin{array}{l} R_1\text{-CH-O} \\ \quad | \quad\ \ | \\ R_2\text{-CH-O} \end{array} \longrightarrow \begin{array}{l} R_1\text{-C-OH} \\ \quad \| \\ R_2\text{-C-OH} \end{array} \rightleftharpoons \begin{array}{l} R_1\text{-CH-OH} \\ \quad | \\ R_2\text{-C=O} \end{array}$$

Standinger[27] proposed a theory of autoxidation based on the assumption that the oxidation reaction originally proposed by Bach and Engler was probably not the first but the second step in the autoxidation of ethylenic compounds. He assumed that a molecule of oxygen added at the ethylene bond to form a moloxide, corresponding to formula (I), which subsequently underwent a rearrangement to form a cyclic peroxide (II).

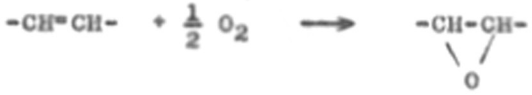
$$\begin{array}{c} R_1\text{—CH—CH—}R_2 \\ \backslash \ / \\ O \\ \| \\ O \end{array} \longrightarrow \begin{array}{c} R_1\text{—CH—CH—}R_2 \\ | \quad\ | \\ O\text{—}O \end{array}$$

(I) (II)

Although the majority of workers in the field accepted at least until very recently, the theory of the formation of a heterocyclic peroxide of the formula  $\begin{array}{c}\text{-CH-CH-}\\ | \quad | \\ O\text{—}O\end{array}$ as a primary step in the autoxidation process, all the evidence for the existence of such peroxides was indirect, and no product containing this grouping had ever been isolated or identified. The existance of cyclic peroxide was assumed on the basis of certain analytical data which were interpreted as substantiating the existance of such structures in olefinic autoxidation systems. These analytical methods were not entirely quantitative, nor specific in their application, especially in the presence of the considerable number of oxidation and degradation products.

(2) Ethylene oxide theory

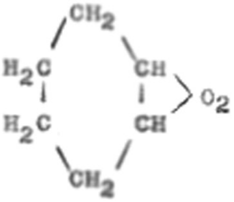
In 1909, Fokin,[27] proposed a theory in which the first step in the autoxidation of an ethylenic bond was the formation of an ethylene oxide ring.



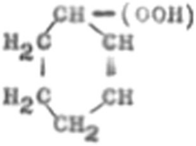
compounds containing the ethylene oxide ring have also been called epoxides. This structure is now known to be formed during epoxidation of unsaturated compounds with perbenzoic, performic, peracetic and other per acids and many of these epoxy derivatives have been isolated and characterized.[28] Although epoxy compounds have been isolated from autoxidation mixtures,[26] it is doubtful that they are primary products. Experimental work in support of the ethylene oxide theory is the least extensive of any of the proposals, and it is no longer seriously considered by investigators in the field of autoxidation.

### (3) Hydroperoxide theory

Much information regarding the mechanism of autoxidation of olefinic compounds derived from fats and other mixtures has been obtained by studying the oxidation of simple monounsaturated compounds such as cyclohexene, which can be readily purified. In 1928, Stephens[29] reported the isolation of a peroxide of cyclohexene, $C_6H_{10}O_2$, which he obtained by treating cyclohexene with oxygen in daylight. He assumed on the basis of the theories of oxidation at that time, that the product was saturated.

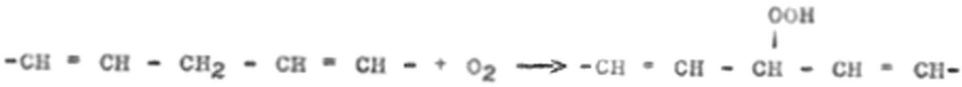


Further research, however, by Crieghee,[30] Hock[31] and notably by Farmer and co-workers[32] established the fact that Stephen's product was a hydroperoxide and that a double bond was present.



It was also determined by Farmer's group that 1-methyl-1-cyclohexene and 1,2-dimethyl-1-cyclohexene behaved similarly when autoxidised.

The isolation of purified hydroperoxides from these and many other autoxidised olefins was a tremendous step forward, and it cast much doubt on the validity of the older concepts of olefin oxidation. Rieche postulated that unsaturated fats and oils probably behaved similarly. He suggested that the autoxidation of mono or poly-unsaturated substances may occur through the formation of oxygen-activated methylene groups.



$$-CH = CH - CH_2 - CH = CH - + O_2 \longrightarrow -CH = CH - \overset{\overset{OOH}{|}}{CH} - CH = CH-$$

Thus, the autoxidation of practically all unconjugated olefinic compounds proceeds by a chain reaction involving addition of a molecule of oxygen to the carbon atom adjacent to the double bond to form a hydroperoxide having an intact double bond. It is now well established that this oxidative process proceeds through a free radical chain reaction, involving three stages, namely the initiation, propagation and termination stages.

Initiation takes place through activation of the unsaturated olefin by heat, ultraviolet light or traces of pro-oxidants, resulting in the formation of free radicals, presumably by abstraction of a hydrogen atom from the active methylene group adjacent to the double bond. The free radical so formed, could undergo 1-3 shifts to form new free radicals. All of them react, with oxygen giving rise to peroxy radicals which subsequently abstract another proton from nearby olefinic hydrocarbon moiety to form the hydroperoxides and another free radical. This is the propogation stage. Termination of the chain reaction is probably effected by mutual destruction of chain carriers to give dimeric products and inert substances which no longer contribute to the free radical chain reaction.

A reasonable mechanism for oxidation in presence of an anti-oxidant (inhibitor) can be given by the following steps.

**Initiation**

$$RH \longrightarrow R\cdot + H\cdot \qquad (1)$$

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (2)$$

$$AH + O_2 \longrightarrow A\cdot + HO_2\cdot \qquad (3)$$

$$ROOH \longrightarrow RO\cdot, RO_2, HO\cdot \qquad (4)$$

$$2\ ROOH \longrightarrow RO\cdot + RO_2\cdot + H_2O \qquad (5)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \qquad (6)$$

$$HO\cdot + RH \longrightarrow R\cdot + H_2O \qquad (7)$$

**Propagation**

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (8)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (9)$$

**Chain Transfer**

$$RO_2\cdot + AH \longrightarrow ROOH + A\cdot \qquad (10)$$

$$A\cdot + RH \longrightarrow AH + R\cdot \qquad (11)$$

**Termination**

$$\left.\begin{array}{l} A\cdot + RO_2\cdot \longrightarrow \\ 2A\cdot \longrightarrow \\ 2\ RO_2\cdot \longrightarrow \end{array}\right\} \text{Non radical stable products} \qquad (12)$$

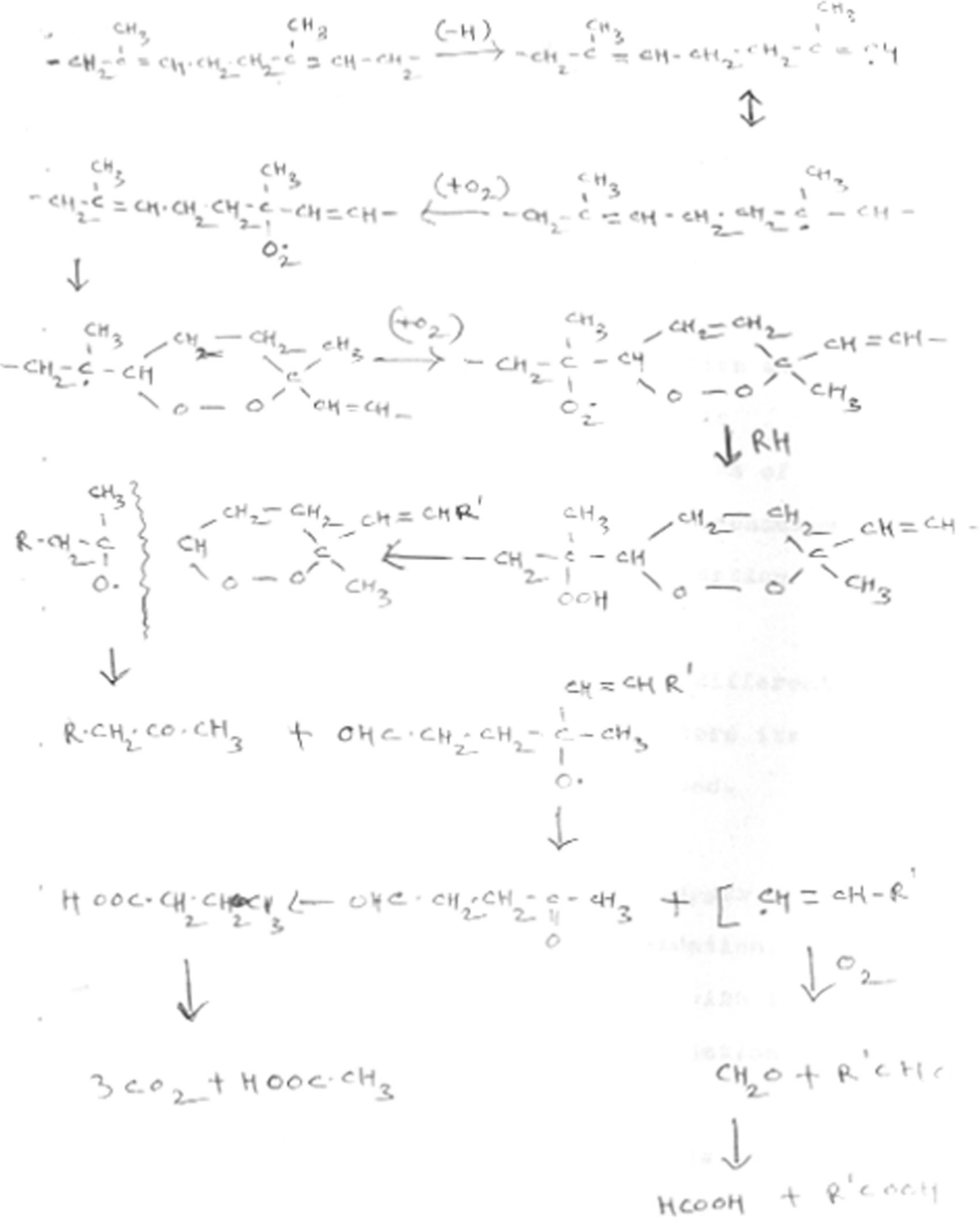
The natural rubber, being 1,-4-cis-polyisoprene is also susceptible for antoxidative degradation. Hoffman[33] for the first time showed that the perishing of rubber involved the absorption of oxygen. Miller[34] and Spiller[35] a few years later demonstrated the accelerating effect of light on the oxidation of rubber. The drastic effect of contacting metallic copper with rubber was noticed by Thomson.[36] The autoxidation of natural rubber, is given on page 25.

## Mechanism of Antioxidation Action and Retardation of Autoxidation

The peroxide decomposition theory of antioxidant action was expounded by Moureu and Dufraisse.[37] They first employed the term 'antioxygens' to define those substances which prevent the oxidation of unsaturated glycerides until they themselves have been destroyed. Moureau suggested the following mechanism of antioxidant action.

The oxidant 'A' unites with oxygen to form a peroxide $AO_2^{\cdot}$. The next stage involves the simultaneous oxidation of the antioxidant B by the peroxide and the transformation of the oxidised oxidant to a lower oxide, AO according to the scheme $AO_2 + B \rightarrow AO + BO$. It is presumed that these two oxides are mutually antagonistic hence they react with each other to regenerate the three original molecules in the following manner : $AO + BO \rightarrow A + B + O_2$. The chain reaction is thus broken.

This theory was criticised by several workers.


(-H)
(+O₂)
(+O₂)
RH
R·CH₂·CO·CH₃
OHC·CH₂·CH₂·C·CH₃
HOOC·CH₂·CH₂·CH₃
O₂
3 CO₂ + HOOC·CH₃
CH₂O + R'CHO
HCOOH + R'COOH

Particularly valid criticism was that contrary to their contention all antioxidants are not readily oxidisable substances. It was also pointed out that peroxides did not normally destroy one another and the addition of organic peroxide to a substrate undergoing autoxidation in fact accelerated the reaction.

Reviews devoted to the mechanism of inhibition of autoxidation have appeared recently.[17,18] There is evidence for at least five different classifications of oxidation inhibitors based on differences in the mechanism by which they appear to inhibit or retard the oxidation reaction.[18]

A given antioxidant is capable to react in different ways in different sets of conditions and thus alters its mode of action in the substrate in which it is used.

### (1) Metal Deactivators

Soluble compounds of many metals such as copper, iron, nickel, cobalt, manganese etc. promote oxidation, presumably by speeding up peroxide decomposition with the formation of free radicals which initiate the oxidation reaction.

Ferrous iron which is typical of those metals which oxidise by one electron transfer, reacts as follows:

$$Fe^{++} + ROOH \longrightarrow RO\cdot + Fe^{+++} + OH^{-}$$

Any substance which can combine with the metal ion to form an insoluble product or a stable chelated complex will slow down the process and thus should be classed as an oxidation inhibitor. Ethylene diamine tetracetic acid (EDTA) is a good example belonging to this group. Both copper stearate and copper dimethyl dithiocarbamate are pro-oxidants, but copper stearate reacts with tetramethylthiuram disulphide (TMT) or with zinc dimethyl dithiocarbamate to form a complex which is an effective inhibitor.[38,39]

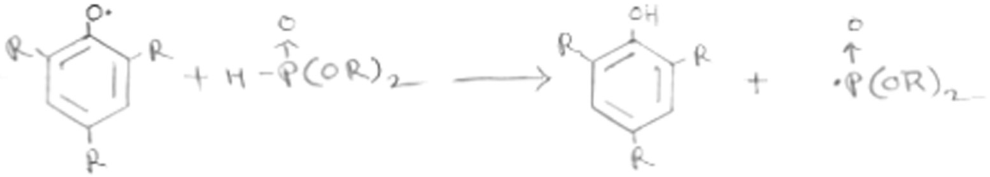
## (2) Light Absorbers

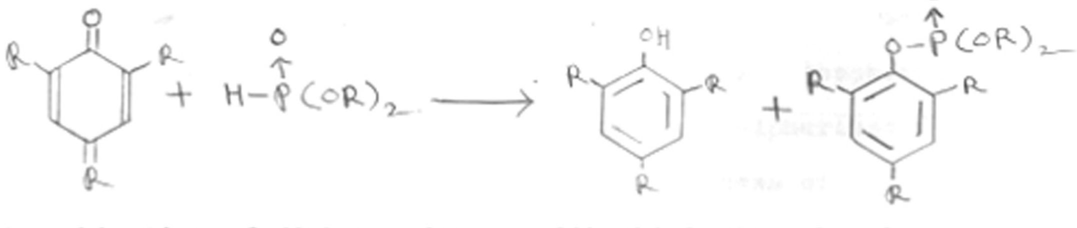
Photo oxidation is difficult to inhibit by conventional antioxidants. Indeed many good inhibitors of thermal oxidation such as the phenyl naphthyl amines, act as photosensitizers for oxidative degradation.[40] Carbon black is an effective light screen when colour is not a problem. It is used for example, in polythene to protect it from outdoor exposure.

A light absorber may be either a photosensitizer or an inhibitor depending upon its activity to dispose of the energy absorbed. Thus, benzophenone is a photosensitizer[41] which either breaks up into free radicals or transmits the activating energy to the substrate. Many derivatives of benzophenone with phenolic hydroxy groups in the ortho position are effective inhibitors of photooxidation.[42,43] Chelation through hydrogen bonding energy apparently permits dissipation of the absorbed radient energy as vibrational energy distributed through the chelated system. Metal chelates with appropriate ultraviolet absorption may also help to dissipate the absorbed energy by distributing it over a more extensive resonance system e.g. Ni and Cr isopropoxy xanthates are effective inhibitors for photooxidation.[40] Hydroxybenzophenone, N-o-hydroxy phenyl benzotriazoles are examples of good light absorbers.

### (3) Inhibitor regenerators

A material which is not an oxidation inhibitor alone may function by reacting with an oxidised form of the inhibitor so as to regenerate it and thus prolongs its effectiveness. The synergistic combination of dialkyl phosphonates with hindered phenols appears to function in part by this mechanism.[44]





A combination of diphenoquinones with thiols may also involve a regeneration mechanism along with radical complexing and transfer reactions which have also been suggested to explain the observed synergistic effect.[45]

## (4) Peroxide Decomposers

Kennerly and Patterson[46] in studies of petroleum antioxidants have called attention to a group of compounds which they call peroxide decomposers. These materials destroy peroxides presumably by a polar mechanism to give stable non radical products, thus reducing the overall rate of oxidation. These materials included phenols, mercaptans, sulphides, sulphonic acids and salts of zinc dialkyl dithiophosphates and dithiocarbamates. While making a careful study of the effects of sulphides as antioxidants in purified hydrocarbon oils, it was concluded earlier by Denison and Condit[47] that the sulphides were oxidized by hydroperoxide to the corresponding sulphoxide and sulphone.

$$R_2S + ROOH \longrightarrow R_2SO + ROH$$

$$R_2SO + ROOH \longrightarrow R_2SO_2 + ROH$$

A second mechanism of hydroperoxide destruction by various sulphur compounds has been advanced based on the research of Murphy,[48] Oberright,[49] Kennerly and Patterson.[46] Their investigations showed that phenothiazine, phosphorus pentasulphide-olefin reaction products, and sulphurized olefins, decomposed hydroperoxides far in excess of amounts that could be accounted for by oxidation of the inhibitors. It was also observed that some of the products of hydroperoxide decomposition were those to be expected from an acid-catalyzed ionic rearrangement of the hydroperoxide.

## (5) Chain Stoppers

The most obvious method of inhibiting a free radical chain reaction is to convert the chain-propagating free radicals to inactive products. This is brought about by five different ways. They are:-

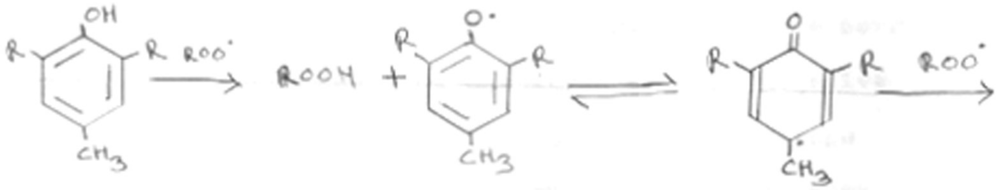
(i) Free radical traps
(ii) Hydrogen donation
(iii) Electron donation
(iv) Addition to aromatic ring
(v) Charge-transfer complex

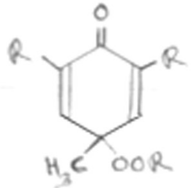
Examples of materials which can trap free radicals by direct combination include various types of quinones which can add free radicals on either O or C with subsequent dimerisation, disproportionation or reaction with a second free radical to form stable products. Electron donation has been suggested to account for the weak antioxidant activity of tertiary amines. Bolland and Ten Have[50] and later Bickel and Kooyman[51] concluded that phenolic and certain aromatic amine inhibitors function by donation of labile hydrogens (O-H or N-H) to free radicals. The initial reaction is as follows

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

where AH is the inhibitor and $A\cdot$ is the inhibitor radical. In the case of a good inhibitor the inhibitor radical $A\cdot$ is stabilized by resonance and does not readily react with the hydrocarbon and start another oxidation chain.

Overall one mole of inhibitor has thus destroyed two peroxy radicals and broken two oxidation chains. The reaction proceeds stepwise -





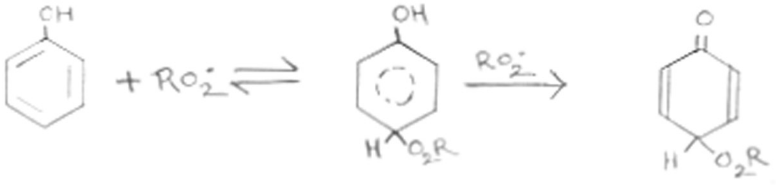
R = tert-butyl.

Thus hydrogen abstraction occurs from phenols and arylamines as an overall result of the inhibition reaction.

If this assumption is correct, it is reasonable to expect that substitution of the labile hydrogen by deuterium should give rise to a kinetic isotope effect. The rate of chain termination should be slower with deuterium than with hydrogen and thus the rate of oxidation of the substrate should be increased by the substitution.

Support for this expectation is found in a study of the reaction of acyl peroxides with phenols in which O-H was replaced by O-D. Several peroxide-phenol-solvent systems showed a small but constant isotope effect, indicating that O-H cleavage is a rate-controlling step in that reaction.[32]

Hammond Boozer and co-workers[33] studied the oxidation of cumene and tetralin in chlorobenzene in the presence of N-methyl aniline and diphenyl amine. The rate of oxidation observed in the presence of the N-deuteroamines was not significantly different from the rate with the corresponding NH compounds. On the basis of this negative evidence due to their failure to observe any isotope effect, they rejected the hydrogen donation mechanism, as an initial step in the inhibition mechanism. They further suggested that addition to the aromatic ring occurs first, followed by loss of the labile hydrogen.



(I)

‡

Thus the intermediate (I) is assumed to be a charge transfer complex rather than a true addition compound. The idea of complex formation between free radicals and the pi-electrons of the aromatic ring is a reasonable expectation.

In contrast to the above negative results, Shelton and coworkers[54] have recently demonstrated a significant deuterium isotope effect in the oxidation of styrene-butadiene copolymer in the presence of both phenol and amine inhibitors. They pointed out that failure to detect a kinetic isotope effect may be due to several factors including loss of deuterium through interchange with water which is formed continuously in the reaction, temperature of the reaction, and concentration of the stabilizer. By carefully controlling these variables, they observed isotope effects as large as 1.8 with 60% deuteration. These results are in accord with the generally accepted mechanism for stabilization with phenols and amines in which hydrogen abstraction is the initial step.

Ingold,[17] has also observed isotope effects which were originally reconciled with Hammond's mechanism.

Ingold and Howard[55] have recently obtained quite large isotope effects by adding $D_2O$ to the oxidation mixture to maintain the inhibitor in a completely deuterated condition. They concluded that the inhibition mechanism is a normal hydrogen abstraction process, and the failure of other workers to observe the expected isotope effect is probably due to a very rapid exchange with traces of $H_2O$ or hydroperoxide in the reaction mixture, thus supporting the observations previously made by Shelton and co-workers.

## Classification of Commercial Antioxidants

Developments in the field of antioxidants for rubber upto 1937 were summarized by Semon.[1] He listed 18 classes of substances which had been found to improve ageing. Recent summaries of commercially important antioxidants used in rubber industry, are described in the literature.[3,56,57]

The antioxidants used in rubber industry are broadly classified into two main classes.

(1) Amines and their derivatives

(2) Phenols and their derivatives

Amine type antioxidants give a better protection to rubber goods than phenolic type, but they cause more discolouration than the latter ones. On the other hand phenolic antioxidants are somewhat weaker in antioxidant action than amine type, but show a distinct nondiscolouring tendency. Their main application is in the fabrication of white rubber articles, where nondiscolouration is a stringent condition. The amines are further subdivided into the following groups:

I. Secondary diarylamines
    A. Phenyl-naphthylamines
    B. Substituted diphenylamines
    C. Para-phenylenediamines
II. Ketone-amine condensates
III. Aldehyde-amine condensates
IV. Alkyl aryl secondary amines
V. Primary arylamines.

## I. Secondary diaryl amines

A. Phenyl-naphthylamines : Phenyl-α-naphthyl amine and Phenyl-β-naphthyl-amine are among the oldest and most widely used antioxidants. They are good general purpose antioxidants.

B. Substituted diphenylamines : Diphenylamine itself has antioxidant properties, but due to its volatile nature, it is of less practical use. However, alkylated diphenyl amines have moderate antioxidant activity.[58] The octylated and nonylated derivatives are commercially available.

C. Para-phenylene diamines : N,N′-Diphenyl-p-phenylenediamine (DPPD) has been used for many years in combination with other amine antioxidants as flex cracking inhibitors. N,N′-dinaphthyl derivative is lower in activity but is more soluble and considerably less staining. A mixed diaryl-p-phenylene diamine is very effective in inhibiting oxidation and flex cracking and has a solubility in rubber several times that of DPPD.[59] They are also effective antiozonants and possess good antioxidant[60] and antiflexcracking[61,62] activity.

### II. Ketone-amine condensates

A study by Sibley[63] indicates that the highest activity among members of this class is provided by the reaction products of acetone with aniline, parasubstituted anilines, and secondary diarylamines. The acetone-primary amine reaction products have been identified as 2,2,4-trimethyl-1,2-dihydroquinolines. These materials are particularly good in providing resistance to degradation at higher temperatures. Products of commercial interest are those prepared by the reaction of acetone with aniline, p-phenetidine, p-dodecyl aniline, diphenyl amine and N-phenyl-2-naphthyl amine.

III. Aldehyde-amine condensates

Members of this class, which are among the oldest of the commercial antioxidants, have moderate antioxidant activity with good heat resistance. Products still in use are condensates of acetaldehyde and butyraldehyde with aniline and of aldol with 1-naphthylamine. Classes IV and V are relatively small and have been little developed in recent years.

Interest in non-staining antioxidants increased greatly with the development of synthetic rubber. Since the synthetics do not contain naturally occurring antioxidants as does natural rubber, it is necessary to add a stabilizing material at the time of manufacture to preserve the rubber until it is compounded and cured.

Phenolic antioxidants may be classified as follows:

VI. Hindered Phenols
VII. Hindered thiobisphenols
VIII. Hindered bisphenols
IX. Polyhydroxy phenols

VI. Hindered Phenols

The commercial products of this class have a fair amount of antioxidant activity and have the best non-staining characteristics of any class. A study by Kitchen and others[64] have shown that in general 2,4,6-trialkyl phenols are more active antioxidants than either less highly substituted phenols or 3,4,6-trialkyl phenols.

### VII. Hindered thiobisphenols

These antioxidants, which are prepared by reaction of two moles of sulphur mono or dichloride, are slightly more active than the substituted phenols but have more tendency to stain. Members of this class currently available are those prepared from di-sec-amylphenol,[65] 6-tert-butyl-3-methyl phenol,[66] and 6-tert-butyl-2-methyl phenol.[67]

### VIII. Alkylidene bisphenols

Antioxidants of this class are prepared by condensing one mole of aldehyde or ketone with two moles of a phenol. Some of the known commercial products are obtained by condensation of 6-tert-butyl-2-methyl phenol with formaldehyde,[68] 2-tert-butyl-4-methyl-(or-ethyl-)phenol and formaldehyde.[69]

### IX. Polyhydroxy phenols

Of the hydroquinone derivatives, butylated hydroxy anisole is one of the few antioxidants acceptable in rubber goods used in contact with food. It is 2-tert-butyl-4-methoxy phenol. 2,5-Ditert-amyl-hydroquinone also belongs to this group.[70]

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## SECTION (A) - SYNTHESIS OF PHENOLIC SULPHIDE TYPE ANTIOXIDANT FROM CNSL AND ITS EVALUATION IN NATURAL RUBBER

## (i) Introduction

White or brightly coloured rubber stocks tend to stain or discolour to a greater or lesser extent when exposed to heat, light, oxygen and ozone and it is generally agreed that this staining or discolouration is largely due to the chemical ingredients especially, antioxidants added to the rubber mix during compounding. Chemically these rubber antioxidants are divided into two classes, (a) Amine type antioxidants, and (b) Phenolic type antioxidants. Literature has shown that these two classes, contain amongst them, most of the antioxidants used in the rubber industry. The first category is classified as staining type antioxidants while the phenolic antioxidants are classed as non-staining antioxidants.

It has been shown that amine type antioxidants, though discolouring in nature have stronger antioxidant action than the corresponding non-discolouring phenolic antioxidants which have weaker antioxidant activity.

Many of the well tried amine antioxidants used are themselves the worst offenders, and although considerable progress has been made in compounding technique, there has long been a demand from the rubber industry for an efficient "non-discolouring" antioxidant.

Considerable amount of progress has been reported in recent times, to develop non-staining phenolic antioxidants, having increased antioxidant power. The increased inhibiting activity of such phenolic antioxidants is mainly attributed to the structural modifications made in phenolic nucleus.

This is generally achieved by making more hindered phenols by inserting bulky substituents such as tertiary butyl groups, or methyl groups ortho and para to the phenolic hydroxyl group in the phenolic moiety. Another way of getting an increased activity in the phenolic antioxidant is to join two such phenolic nuclei to each other through some bridging by methylene groups ($-CH_2-$) or through sulphur ($-S-$) atoms. The commercially available hindered phenols are generally 2,4,6 trisubstituted phenols, such as 2,6-ditertiery butyl-4-methyl phenol. On the other hand, if phenols are reacted with styrene they give the so-called "Styrenated phenols". They are used in stabilization of synthetic rubber litices such as GR-S litice. As a class substituted hindered phenols are characterised by excellent non-staining characteristics.

Bis phenols are prepared by condensing one mole of an aldehyde or a ketone with two moles of hindered phenols. Such condition results into formation of a methylene link in between two phenolic nuclei. These products are fully comparable in antioxidant power with many of the secondary diaryl amines. The fact that non-staining antioxidants, comparable in power to the classical staining amine type antioxidants, are now available to the rubber industry, is a most encouraging sign of progress.

Phenolic sulphides, which are obtained by condensing two moles of substituted phenols with one mole of sulphur halide, are more active than the substituted hindered phenols but have more tendency to stain. However, phenolic sulphides have better heat aging and antimetal aging properties than hindered phenols.[1]

Recently, much attention has been drawn to a number of sulphur containing compounds, which have been classified as "peroxy decomposers".[2-5] Such compounds decompose the peroxides formed during the autoxidation of the polymeric chains to stable, nonradical products, which do not further initiate new peroxy radicals.

$$ROO^{\cdot} + \text{Peroxide Decomposer} \longrightarrow \text{Inert products}$$
$$ROOH + \text{Peroxide Decomposer} \longrightarrow \text{Inert products}$$

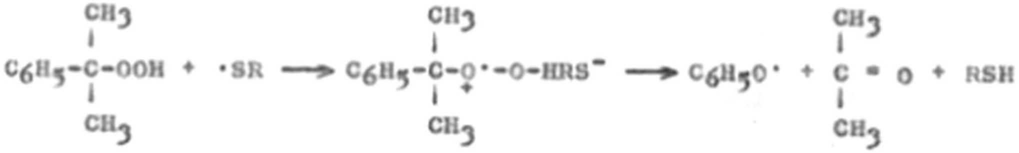
Denison and Condit[2] have made a careful study of the effects of sulphides as antioxidants in purified hydrocarbon oils. They showed that the antioxidant active sulphides had the power to destroy hydroperoxides and were themselves converted to sulphoxides and sulphones in the process. The reaction appeared to be the stoichiometric formation of sulphone based on the hydroperoxide destroyed.

$$R_2S + ROOH \longrightarrow R_2SO + ROH$$
$$R_2SO + ROOH \longrightarrow R_2SO_2 + ROH$$

Kennerly and Patterson[3] have tested a variety of sulphur containing compounds as decomposers of peroxides for peroxidised mineral oil and for cumenehydroperoxide in mineral oil. The rates of decomposition of cumenehydroperoxide at 150°C in (liter)$(\text{mole})^{-1}(\text{min})^{-1}$ obtained with following diphenyl sulphides were for the unsubstituted sulphide, 0.6; for the 4-hydroxy sulphide, 6.0; for the 4,4′-dihydroxy sulphide, 60; and for 4,4′-dimethoxy sulphide, 0.00.

The mechanism by which these materials convert peroxides to stable products has not been established, but a polar reaction would provide a reasonable explanation of the observed behaviour.

High yields of phenol were obtained in the reaction, which suggested the occurrence of an ionic rearrangement process of the type catalyzed by sulphonic acids. It was concluded that the sulphides were only precursors of the active decomposers, and that a mercaptyl radical or a phenoxy radical is the active species,



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-OOH + \cdot SR \longrightarrow C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-\underset{+}{O}^{\cdot}-O-HRS^- \longrightarrow C_6H_5O\cdot + \underset{CH_3}{\overset{CH_3}{C}}=O + RSH$$

$$C_6H_5O^{\cdot} + RSH \longrightarrow C_6H_5OH + RS^{\cdot}$$

In conclusion, sulphur-containing antioxidants react with hydroperoxides by a molecular process at low temperatures but perhaps by an ionic process at higher temperatures. The antioxidants are themselves oxidised to acids, which promote a concurrent catalytic decomposition.

A rather similar mechanism has been proposed by Murphy _et al_[6] to account for the antioxidant activity of phenothiazine and its derivatives. They demonstrated that the phenothiazines caused a catalytic decomposition of tetralin hydroperoxide very similar to other sulphur containing oil antioxidants. They proposed that the resonance stabilised free radical derived from phenothiazine by light activated electron loss is involved in the inhibition process by acting as a catalyst for peroxide decomposition.

Oberright[7] _et al_. have clarified that the nature of the cumenehydroperoxide transformation product formed by reaction of a $P_2S_5$-olefin condensation product is markedly dependent upon the ratio of hydroperoxide to peroxide decomposer. At an equimolar ratio, the major product was found to be dimethyl benzyl alcohol or derived products with minor amounts of phenol, but in the presence of excess cumenehydroperoxide (molar ratio 300:1) a catalytic decomposition occurred which gave phenol as the only identified product.

The same mechanism has been suggested for the antioxidant action of dithiophosphates[8] and dithiocarbamates.[9]

Bateman and coworkers[10] have recently found that a variety of simple sulphoxides and thio sulphinates are effective antioxidants and have a generally higher order of activity than the sulphides from which they are derived.

The initial process is the oxidation of the sulphide to a sulphoxide, which may then catalytically decompose hydroperoxides without the production of free radicals.

## Chemistry of Thiobisphenols and their Applications

Airan and Shah[11] have reported the following equations for the different sulphur halides:-

$$\text{(a)}\quad 2\,S_2Cl_2 \;=\; SCl_2 + S_3Cl_2$$

$$\text{(b)}\quad 2\,SCl_2 \;=\; S_2Cl_2 + Cl_2$$

$$\text{(c)}\quad 4\,SCl_2 \;=\; S_3Cl_4 + SCl_4$$

Because of the interconversion of these compounds "in situ" many workers have reported the formation of different types of compounds in varying yields even in similar experiments.

Thus sulphur dichloride is in equilibrium with sulphur monochloride and chlorine. The product from this compound may contain disulphides, as well as some chlorinated compounds. Sulphurmonochloride is in equilibrium with sulphurdichloride and $S_3Cl_2$ and the reaction product from it may contain monosulphide and trisulphide along with the expected disulphides.

Phenol reacts readily with sulphur halides, even without a catalyst, as shown in the equations below,[11,12]

$$\text{(d)}\quad 2\,C_6H_5OH + SCl_2 \rightarrow HO{-}C_6H_4{-}S{-}C_6H_4{-}OH + 2\,HCl \uparrow$$

$$\text{(e)}\quad 2\,C_6H_5OH + S_2Cl_2 \rightarrow HO{-}C_6H_4{-}S{-}S{-}C_6H_4{-}OH + 2\,HCl \uparrow$$

$$\text{(f)}\quad 2\,C_6H_5OH + S_3Cl_2 \rightarrow HO{-}C_6H_4{-}S{-}S{-}S{-}C_6H_4{-}OH + 2\,HCl \uparrow$$

As phenol monosulphide crystallizes well, it can be isolated in pure condition. The isolation of the pure disulphide is much more difficult. In a recent experiment, 52% of the monosulphide was obtained by the reaction of 1 mol of phenol with 0.5 mol of sulphur dichloride in 1 liter of carbon tetrachloride at -15°C. When sulphur monochloride was used under the same conditions, 37% of the monosulphide was isolated from the product.[13] It is much the same with alkylated[14] and with halogenated phenols.

Sulphur mono chloride and p-chlorophenol give a mixture of mono- and trisulphide.[15] Certain groups may hinder the reaction. Thus methyl salicylate requires a catalyst.[16]

In some cases, thionyl chloride gives the same results as sulphur dichloride.[17]

For the reactions of sulphur chlorides with phenols, carbon tetrachloride is a favourite medium. Elimination of the hydrogen chloride as it is formed is considered beneficial.[14a]

This may be facilitated by carrying out the reaction in a refluxing organic halide.[18,14c]

Various phenolic sulphides have different applications in many industries. In rubber industry they are used as antioxidants and stabilizers.[19]

Some alkyl-phenol sulphides impart desirable characteristics to rubber,[20] and some, particularly those containing more than one atom of sulphur, can supply the sulphur necessary for vulcanization.[20,21] Those suitably alkylated may serve as reclaiming agents for natural or synthetic rubber.[22] Other applications include their use as corrosion inhibitors, stabilizers for lubricants, polymerization inhibitors for vinyl compounds, extreme pressure lubricants, nonionic surface active agents, oil additives, germicides and pesticides.

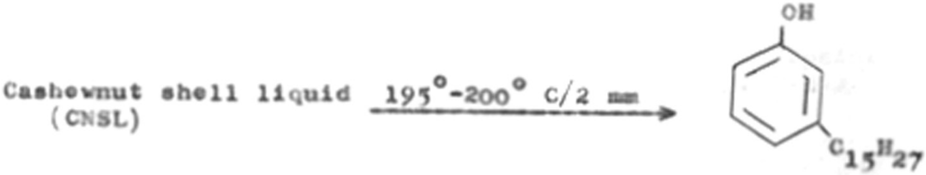
Cashewnut shell liquid (CNSL) and its fractions have been used for various applications[23] in paint, plastics and rubber industry. The main constituent of CNSL anacardol is phenolic in nature. It was therefore decided to use this CNSL phenol, which is abundantly available in India for the preparation of the phenolic type antioxidant.

## (ii) Present Investigation and Results

### Synthesis of Phenolic sulphide type antioxidant from CNSL

### 3-Pentadecadienyl phenol (Anacardol) (I)

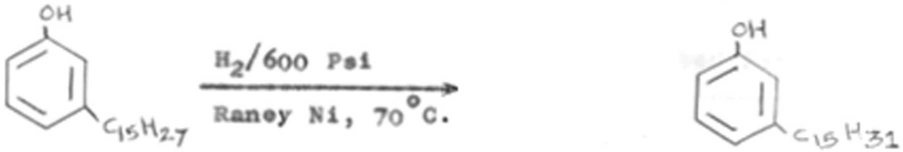
When commercial cashewnut shell liquid is distilled under reduced pressure, 3-pentadecadienyl phenol (anacardol) is obtained as a pale yellowish liquid in 50% yield.



Anacardol (I)

### 3-Pentadecyl phenol (Tetrahydroanacardol)(II)

Anacardol when catalytically reduced over Raney nickel catalyst at 600 lbs/sq.in. hydrogen pressure and at 70°C, in a Parr-autoclave, gave 90% yield of 3-pentadecylphenol (II) (Tetrahydroanacardol). The crude product after crystallizing from petroleum ether (40°-60°) gave a white waxy product. m.p. 50°C.

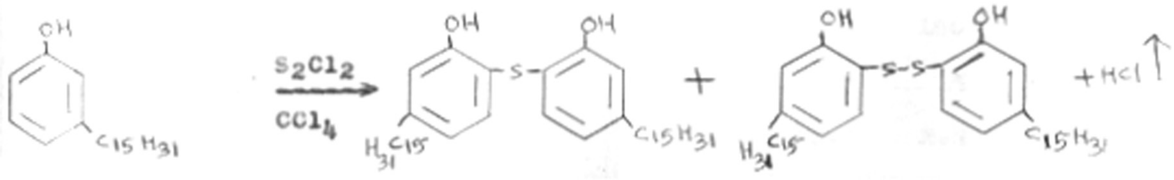


Anacardol

3-Pentadecylphenol(II)
(Tetrahydroanacardol)

### Tetrahydroanacardol-sulphur monochloride reaction product (III)

Tetrahydroanacardol (T.H.A.) was reacted with sulphur mono chloride in an inert solvent like carbontetrachloride, and the resinous mass was obtained, containing the mixture of mono- and disulphides of T.H.A.



Tetrahydro-anacardol

Monosulphide of T.H.A.

Disulphide of T.H.A.

Evaluation of antioxidant in Natural Rubber

The semisolid resinous THA-$S_2Cl_2$ reaction product containing the mixture of mono and disulphide was used as such for evaluation in natural rubber gum and channel black compound according to A.S.T.M. procedure, (A.S.T.M. D-15-59T (1961), p. 5). A similar commercial product santowhite MK of Monsanto chemicals, which is also a mixture of phenolic sulphides, was taken as a commercial antioxidant for comparison.

Table I describes the compounding recipe of natural rubber gum compound (ASTM-2A), prepared on a laboratory type 6" x 12" mixing mill. Optimum cures were selected for the respective mixes, A, B, C.

"A" was blank, containing no antioxidant, while "B" and "C" were containing THA-$S_2Cl_2$ reaction product and Santowhite MK respectively. The changes in the physical properties in the compound A, B and C before and after ageing in an air circulated Geer-ageing oven at $70^\circ \pm 1^\circ C$, are described in Table II.

TABLE I. COMPOUNDING RECIPE FOR THE ANTIOXIDANTS

| Ingredients | A | B | C |
|---|---|---|---|
| (1) Smoked sheet RMA-1 | 100 | 100 | 100 |
| (2) Zinc oxide | 5 | 5 | 5 |
| (3) Sulphur | 2.5 | 2.5 | 2.5 |
| (4) Stearic Acid | 2.0 | 2.0 | 2.0 |
| (5) MBTS | 1 | 1 | 1 |
| (6) THA-$S_2Cl_2$ reaction product | - | 1 | - |
| (7) Santowhite - MK | - | - | 1 |

Cure time: 40' optimum at 140°C/2000 P.S.i.

## Synergistic effects of Antioxidants

By using two or more different types of antioxidants the resistance to oxidation of an organic substrate can frequently be improved to an extent greater than would be predicted on the basis of strict additivity. The two antioxidants are then said to show a "Synergistic" effect towards one another and the compound which is least active, or even inactive, by itself is called synergist for the second component.

Probably the most generally effective synergistic mixtures of antioxidants are those in which one compound functions as decomposer of peroxides and the other as an inhibitor of free radicals. The latter prevents the formation of long reaction chains but some hydroperoxide is neverthe-

TABLE II. ANTIOXIDANTS STUDY IN NATURAL RUBBER PURE GUM COMPOUND

| Abeing | | Blank (No antioxidant) Compound A | | | THA-$S_2Cl_2$ reaction product compound B | | | Santowhite-MK Compound C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Time | Tens. psi | Modu. 300% psi | Elong. at break % | Tens. psi | Modu. 300% psi | Elong. at break % | Tens. psi | Modu. 300% psi | Elong. at break % |
| .. | Original | 2770 | 167.1 | 900 | 2625 | 150 | 950 | 2215 | 135 | 900 |
| 70°C | 2nd day | 2739 | 242.4 | 750 | 2099 | 174 | 800 | 2150 | 125 | 900 |
| " | 4th day | 1723 | 246.1 | 700 | 2036 | 230.3 | 700 | 1945 | 148 | 850 |
| " | 7th day | 1546 | 253.3 | 650 | 1958 | 179.1 | 700 | 1452 | 148 | 750 |
| " | 14th day | 861.6 | 295.4 | 600 | 1012 | 188.2 | 650 | 1259 | 157 | 700 |

less formed. If this hydroperoxide then reacts with a decomposer of peroxides rather than by decomposing into free radicals, the two antioxidants act together to complement one another.

Aliphatic sulphides like Dilauryl thio dipropionate (DLTDP, $S[CH_2.CH_2.CO_2C_{12}H_{25}]_2$) has been shown[24] to be particularly effective as a synergist with a hindered phenol in polypropylene at 150°C.

Bell et al.[25] showed that when the polyisoprene, squalene, is autoxidized at 75°C in the presence of DLTDP, a considerable amount of oxygen is absorbed before any antioxidant action is observed, thus indicating the formation of a more active antioxidant from the DLTDP. The corresponding sulphoxide (DLTDP, $SO[CH_2.CH_2.CO_2C_{12}H_{25}]_2$) retards the autoxidation immediately and is undoubtedly responsible for the antioxidant action. Its ability to destroy hydroperoxide is demonstrated by the rapid reaction with tert-butyl hydroperoxide in benzene at 75°C under vacuum, no hydroperoxide being detected after 8 hours.

A combination of 2.mercaptobenzimidazole (MBI) with both phenolic and amine antioxidants, has been observed to give a synergistic protective effect in the presence of either copper or iron in both vulcanized rubber and the raw polymer.[26]

Carbon black has been reported to have profound effect on the activities of the phenolic and amine type of antioxidants. Hawkins and co-workers[27,28] at the Bell Telephone

Laboratories, discovered that phenol and amine antioxidants which were deactivated by carbon black, become more effective antioxidants when a sulphur atom was included in the phenolic nucleus. It is reported that the presence of the thiobridge in the phenolic nucleus, modifies its behaviour towards carbon black, giving a synergistic effect.

Thus bis-(2-hydroxy-3-tertbutyl-5-methyl-phenyl) methane has oxygen absorption in polyolefin, with 3% carbon black and without carbon black of 50 ml. and 60 ml. in 110 hours and 320 hours respectively. Bis-(2 hydroxy-3-tertbutyl-5-methyl-phenyl) sulphide has oxygen absorption in polyolefin, with 3% carbon black and without carbon black of 10 ml. and 60 ml. in 900 hours and 700 hours respectively. It is significant that the thiobis compound is almost twice as effective as its methylene bishomologue. Several similar thiobis phenols are used as commercial antioxidants.

In the present investigation, it was therefore, decided to compare the effectiveness of the phenolic sulphide type antioxidants THA-$S_2Cl_2$ reaction product and Santowhite-MK in synergistic activities with phenyl-β-naphthylamine in natural rubber channel black compound. In these synergistic mixtures of antioxidants, THA-$S_2Cl_2$-reaction product and Santowhite-MK act as peroxide decomposers while phenyl-β-naphthylamine acts as a chain breaking agent. The compounding recipe used for these experiments, is shown in Table III.

## TABLE III. COMPOUNDING RECIPE FOR THE SYNERGISTIC EVALUATION

| Ingredients | D | E | F | G | H |
|---|---|---|---|---|---|
| (1) Smoked sheet RMA-1 | 100 | 100 | 100 | 100 | 100 |
| (2) Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| (3) Sulphur | 3 | 3 | 3 | 3 | 3 |
| (4) Stearic acid | 3 | 3 | 3 | 3 | 3 |
| (5) M.B.T.S. | 1 | 1 | 1 | 1 | 1 |
| (6) Channel black (EPC) | 50 | 50 | 50 | 50 | 50 |
| (7) Santowhite-MK | 1 | - | - | - | - |
| (8) THA-$S_2Cl_2$ reaction product | - | 1 | - | - | - |
| (9) PBN | - | - | 1 | - | - |
| (10) Santowhite MK (0.5)+PBN(0.5) | - | - | - | 1 | - |
| (11) THA-$S_2Cl_2$ reaction product (0.5) + PBN (0.5) | - | - | - | - | 1 |

Cure time: 40' optimum at 140°C/2000 p.s.i.

The physical properties of the original and the aged specimens at $70^\circ + 1^\circ C$ in air circulated ageing oven of the mixes D, E, F and that of G and H are described in Tables IV and V respectively.

TABLE IV. ANTIOXIDANT STUDY IN NATURAL RUBBER CHANNEL BLACK COMPOUND

| Ageing | | Santowhite-MK (D) | | | THA-$S_2Cl_2$ reaction product (E) | | | Phenyl β-naphthyl amine (F) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Time | Tens. psi | Modu. 300% psi | Elong. at break % | Tens. psi | Modu. 300% psi | Elong. at break % | Tens. psi | Modu. 300% psi | Elong. at break % |
| | Original | 3510 | 1777 | 500 | 3543 | 1691 | 500 | 2659 | 1924 | 500 |
| 70°C | 2nd day | 3459 | 2339 | 400 | 3245 | 2231 | 400 | 2805 | 2232 | 400 |
| " | 4th day | 3314 | 2296 | 400 | 2948 | 2080 | 400 | 1969 | 1959 | 300 |
| " | 7th day | 3200 | 2194 | 400 | 1623 | 1623 | 300 | 1758 | 1758 | 300 |
| " | 14th day | 3176 | 1672 | 400 | 1239 | - | 200 | 1146 | 1146 | 200 |

TABLE V. ANTIOXIDANT STUDY IN NATURAL RUBBER CHANNEL BLACK COMPOUND

| Ageing | | Santowhite-MK + PBN (G) | | | THA-$S_2Cl_2$ reaction product + PBN (H) | | |
|---|---|---|---|---|---|---|---|
| Temp. | Time | Tens. psi | Modu. 300 % psi | Elong. at break % | Tens. psi | Modu. 300% psi | Elong. at break % |
| | Original | 2857 | 2331 | 400 | 3109 | 1966 | 400 |
| 70°C | 2nd day | 2629 | 2286 | 330 | 2836 | 2473 | 350 |
| " | 4th day | 2484 | 2484 | 300 | 2491 | 2491 | 300 |
| " | 7th day | 1965 | 1965 | 250 | 1600 | 1600 | 200 |
| " | 14th day | 1723 | 1723 | 250 | 1391 | 1391 | 200 |

## (iii) Discussion

Most of the organic polymers suffer characteristic deterioration when in use. Generally more the amount of unsaturation in the polymer, more it is susceptible to deterioration. These deteriorations result in the loss of many of the physical properties of the polymers. These polymers can be protected to some extent against deterioration by the use of organic additives such as secondary amines or phenolic compounds.

In the present study, indigenously available phenolic compound has been utilized to prepare a phenolic sulphide type antioxidant which has the polymer (rubber) protecting properties. This THA-$S_2Cl_2$ reaction product and the commercially available phenolic sulphide Santowhite-MK are evaluated in natural rubber gum compound and the changes in the tensile strengths observed before ageing and during 14 days ageing are recorded in Fig. 1.

In the case of the blank (gum-compound with no antioxidant) the rate of deterioration in tensile strength for the first 2 days is nearly steady and then goes on falling till 14th day, while in case of THA-$S_2Cl_2$ reaction product there is a decrease in tensile strength in the first two days. From the 2nd day till 7th day, the THA-$S_2Cl_2$ reaction product shows very little change in tensile strength on ageing, and then again goes on slowly deteriorating till the 14th day. In case of Santowhite-MK, the observed rate of deterioration in tensile strength throughout the 14 days is characteristically slow. In general, it could be said that Santowhite-MK has overall better retention properties.

This phenomenon may be attributed to the more hindered nature of the phenolic molecule in Santowhite MK. It has been reported that Santowhite MK is a reaction product of 3-methyl,6-tert-butyl phenol and sulphur dichloride.[29]

Nixon,[30] Yabroff,[31] Rosenwald,[32] and Wasson[33] have described in detail the effect of substitution of different alkyl groups on phenolic nucleus, upon the antioxidant activity of the resultant alkyl phenols in oxidation studies of gasoline.

All the data show that a single group substituted in the phenol nucleus has little effect in conveying inhibiting power to phenol. The introduction of two alkyl groups has a greater effect. The nature and the position of the substituted groups are very important; of the three positions investigated (2, 4 and 6) the greatest efficiency results if the 4 position is occupied by a methyl group. The maximum effect with two alkyl groups is produced if the group in 2 position is tert-butyl and the group in 4 position is methyl; the least effect results if the groups are interchanged. Leaving the para position unsubstituted and substituting both the ortho positions, with bulky groups such as two isopropyl groups, a tert-butyl and an isopropyl, or two tert-butyl groups, the antioxidant efficiency is reduced.

The substitution of three alkyl groups on the ring makes a further improvement possible in the inhibiting powers of the compound, but again the position and type of the groups substituted are important. Unfortunately not all possible combinations of any three groups around the ring have been investigated. The greater ease of preparation has favoured the use of 2,4,6 substituted compounds. The one example of comparison with a 2,3,6 trisubstituted compound suggests that leaving the 4 position open, the antioxidant effectiveness is reduced. The group substituted in the 4 position should have at least one hydrogen attached to the carbon that is attached to the ring, i.e. tert-butyl reduces effectiveness, whereas isopropyl is as effective as methyl. This is probably the best generalization that can be made, for in no case does a compound having a p-tert-butyl group in 4 position show good inhibiting properties.

In the 2,6-di-tert-butyl-4-alkyl structure, methyl, ethyl and isopropyl groups were found to be equivalent in activities in gasoline. These data also emphasize the importance of the ortho and para positions, but it is also reported that in the tri and tetrasubstituted phenols the meta position can also be more important than one ortho, if the other ortho and the para positions are filled.

In general, it is understandable that the massing of hindering groups in the ortho position and the blocking of the para position will improve inhibiting power. However, it is difficult to understand why substituting a methyl for an o-tert-butyl will improve performance and substituting an octyl group for the o-tert-butyl will decrease it.

In the present investigation, in Santowhite MK, one of the ortho positions of the phenol is blocked by a tert-butyl group while the para position is having a sulphur linkage. On the other hand, in case of THA-$S_2Cl_2$ reaction product, the ortho position is occupied by a sulphur link (structures confirmed by infra red spectroscopy) leaving the para position unoccupied. The sulphur linkages, which may be either mono, di or even mixtures of these in case of THA-$S_2Cl_2$ reaction product,[34] and may be mono- or disulphide in case of Santowhite MK. Both monosulphide and disulphide[35] phenolic compounds have been utilized as antioxidants. It, therefore, appears that the introduction of a bulky group like tert-butyl in Santowhite MK had played a predominant part in better heat ageing retention properties, whereas the comparative low activity of the THA-$S_2Cl_2$ reaction product may probably be due to the vacant para position.

Figures 2 and 3 show the changes in the valuesof moduli and elongations respectively on ageing in natural rubber gum compound. Moduli in cases of both the sulphides increase initially, the maximum on the 4th day and then go on falling. Here again it has been observed that Santowhite MK has better retention properties than THA-$S_2Cl_2$ reaction product. This same phenomenon is also observed while studying the elongation curves (Fig. 3). Santowhite MK and THA-$S_2Cl_2$ reaction product have been separately evaluated in natural rubber channel black compound and the tensile, modulus and elongation results after ageing have been described in Figs. 4, 5 and 6.

## Effect of carbon black loading on synergism

The effect of carbon black upon the oxidation and ageing behaviour of elastomers is clearly quite complex and involves a number of competing effects and is of particular importance due to the common use of reinforcing carbon blacks in many commercial applications including tyres. At low carbon black loadings an inhibiting antioxidant effect has been observed by several workers.[36-39]

The inhibiting effect may be attributed to several factors including the activity of the carbon surface as a free radical acceptor,[40] interaction of the carbon with iron and certain other metal ions with a mutual reduction in the normal catalytic effect of both,[41] and the effect of carbon black upon the decomposition of peroxides to stable products in the presence of certain types of inhibitors.[42]

Other workers[43-45] have reported that at high carbon black loadings the rate of oxidation of polymer is increased. The accelerating effect may be attributed to a number of factors including a direct catalytic effect upon the oxidation reaction and a catalysis of peroxide decomposition to free radicals.

The carbon black, thus also interferes with the antioxidant action of the usual phenolic and amine antioxidants.

Hawkins and co-workers[27,28,46,47] made extensive studies upon the use of carbon blacks as antioxidants for polyolefins. They have shown carbon blacks to act as thermal antioxidants and have demonstrated the existence of synergistic effect of carbon blacks with certain organo-sulphur compounds.

It has been observed, that carbon black and organo-sulphur compounds containing no labile hydrogen effectively inhibit oxidation. Benzyl thiobenzene, though it does not inhibit oxidation of clear polythene at 140°C, is synergistic with carbon black. Disulphides and thiols form synergistic stabilizer combinations with carbon black, 2-naphthalene thiol and its corresponding disulphide being particularly effective.

The mechanism by which carbon black reacts with organo-sulphur compounds to inhibit polyolefin oxidation has not been established. However Hawkins and Worthington[48] have recently suggested that antioxidants which are capable of generating thiyl radicals either by electron transfer reactions with carbon black or by thermal dissociation, can complex with $\pi$ bond of conjugated polycyclic systems (carbon-black) similar to that suggested by Boozer and Hammond.[49] Exactly how this complex interferes with the autoxidation process is not yet clear. Hawkins has suggested that it may act as chain terminator but it is equally possible that the thiyl radical is more readily converted in its complexed form to an oxygenated sulphur compound which acts as a hydroperoxide decomposer. Gruver[50] while studying the antioxidant properties of carbon blacks at low loadings in unsaturated elastomer like cis-polybutadiene, came to the conclusion that carbon blacks distinctly showed mild thermal antioxidant properties. However this antioxidant behaviour varied considerably from black to black and was dependent on the surface chemistry of the carbon blacks.

In the present investigation the tensile studies relating to the synergistic activities of the two phenolic sulphides in combination with phenyl-$\beta$-naphthyl amine are shown in Fig. 7. Here again, the retention properties in case of Santowhite MK-PBN mixture is better than the retention properties of THA-$S_2Cl_2$ reaction product- PBN mixture and only PBN respectively. Similar observation is made in studying the curves relating to moduli and elongation of these two sulphides (Figs. 8 and 9). A positive synergistic effect was shown by THA-$S_2Cl_2$ reaction product - PBN mixture, when the carbon black loading in the natural rubber was as high as 30%.

A more hindered phenolic sulphide such as Santowhite MK is more effective as an antioxidant and as an additive in a synergistic effect than a less hindered phenol sulphide such as THA-$S_2Cl_2$ reaction product.

## Conclusion

THA-$S_2Cl_2$ reaction product shows antioxidant properties in both natural rubber gum and channel black compounds. In combination with PBN it shows better retention properties, than when PBN is used alone, indicating a good synergistic effect.

## (iv) Experimental

The commercial cashewnut shell liquid used throughout the work of present investigation, was having the following specification.

Specification for cashewnut shell liquid (CNSL) of Export variety (Kerala State Govt., India)

(1) Specific gravity ............. 0.983

(2) Viscosity .................... 434.1 C.P.

(3) Moisture ...................... 1.17%

(4) Matter insoluble in Toluene.... 0.29%

(5) Volatiles ...... .............. 3.2%

(6) Iodine values ................. 234

(7) Polymerization tests

    (a) Gel time ............... 10 min. and 6 sec.

    (b) Oven test (viscosity) .. 10.21 C.P.

### 3-Pentadecadienyl phenol (Anacardol) (I)

Raw commercial cashewnut shell liquid (heat extracted) (900 gms) was distilled from a 2-litre round bottom flask, under vacuum. The flask was heated slowly till the initial frothing had subsided. 450 gms. of brown coloured distillate (yield 50%) was collected between 190°-240°C/2-4 mm. Hg. pressure.[51] This was redistilled to give pale yellow anacardol $n_D^{30}$ 1.5080. (410 gms, b.p. 195-200°C/2 mm.). Analysis: Found C, 83.80; H, 10.56%.

$C_{21}H_{32}O$ requires C, 83.94; H, 10.76%.

### 3-Pentadecyl phenol (Tetrahydro anacardol) (II)

Anacardol (300 gms) was hydrogenated at 70°C in a Parr autoclave under 600 lbs/sq. in. pressure of hydrogen after the addition of 3-5 gms. of Raney nickel catalyst. When no more hydrogen absorption was noticed the hydrogenation was stopped and the product filtered and crystallized from petrol ether (40°-60°). 3-Pentadecyl phenol (tetrahydroanacardol) (270 gms.) 90% yield was obtained as white waxy solid, m.p. 50°-51°C.[51] b.p. 215°-220°C/4 mm.

Analysis: Found C, 83.16; H, 11.41%

$C_{21}H_{36}O$ requires C, 82.83; H, 11.92%.

Preparation of tetrahydroanacardol - Sulphurmonochloride reaction product (THA-$S_2Cl_2$ reaction product) (III)

Tetrahydroanacardol 6 gms. (2 mole) dissolved in 30 ml. of carbon tetrachloride was taken in a 100 ml. round bottom flask. Sulphur monochloride 0.84 ml. (1 mol) in 6 ml. of carbontetrachloride, was added to the above solution, under constant stirring, keeping the reaction temperature below 30°C. The mixture was then kept at room temperature for 1/2 hour and further refluxed on waterbath for 3 hrs. The solvent was then removed under reduced pressure. A dark brown black soft mass was obtained. This was taken in ether and then washed with 1% aqueous $NaHCO_3$ and finally with water. The ether dried and removed. The resultant brown soft mass was taken for evaluation.

Compounding of the rubber mixes

All the compounding ingredients were commercial rubber grade chemicals.

Mixing:- All the mixes given in Tables 1 and 3 were prepared on a conventional laboratory size 6" x 12" two roll rubber mixing mill. Rubber was masticated on a cold mill, immediately a band was formed. All the ingredients were then added according to the compounding recipes given in Tables 1 and 3. Sulphur and accelerator were added at the end. The mix was cut thrice from either side and rolled six times through tight mill and sheeted out. The sheets of the mixes were rested overnight. (ASTM D15-59T (1961), P. 5).

<u>Vulcanization</u>:- The rubber sheets 6" x 6" x 0.075" were vulcanized in a laboratory type carver hydraulic press, with a temperature of 140° ± 1°C, and under 2000 lbs/sq.in. pressure for the specified time. Optimum cures were selected for the respective mixes.

## Determination of Physical Properties

From the vulcanized sheets dumb-bell shaped specimens were cut with dumb-bell type C".

The physical properties such as tensile strength elongation at break and modulus at elongation of the vulcanizates were determined on a Scott-tensile testing machine according to A.S.T.M. designation D412-61T (1961), P.142. The rate of the power actuated grip was 40 inches per minute and was kept uniform at all times.

Ageing of the Dumbell shaped test specimens was carried out in an air circulated Emmersion-Ageing oven at 70°± 1°C, according to A.S.T.M. Designation D573-53(1961), P.246. Tensile strength modulus and elongation at break were observed before ageing and after 2nd, 4th, 7th and 14th days ageing of the samples in oven.

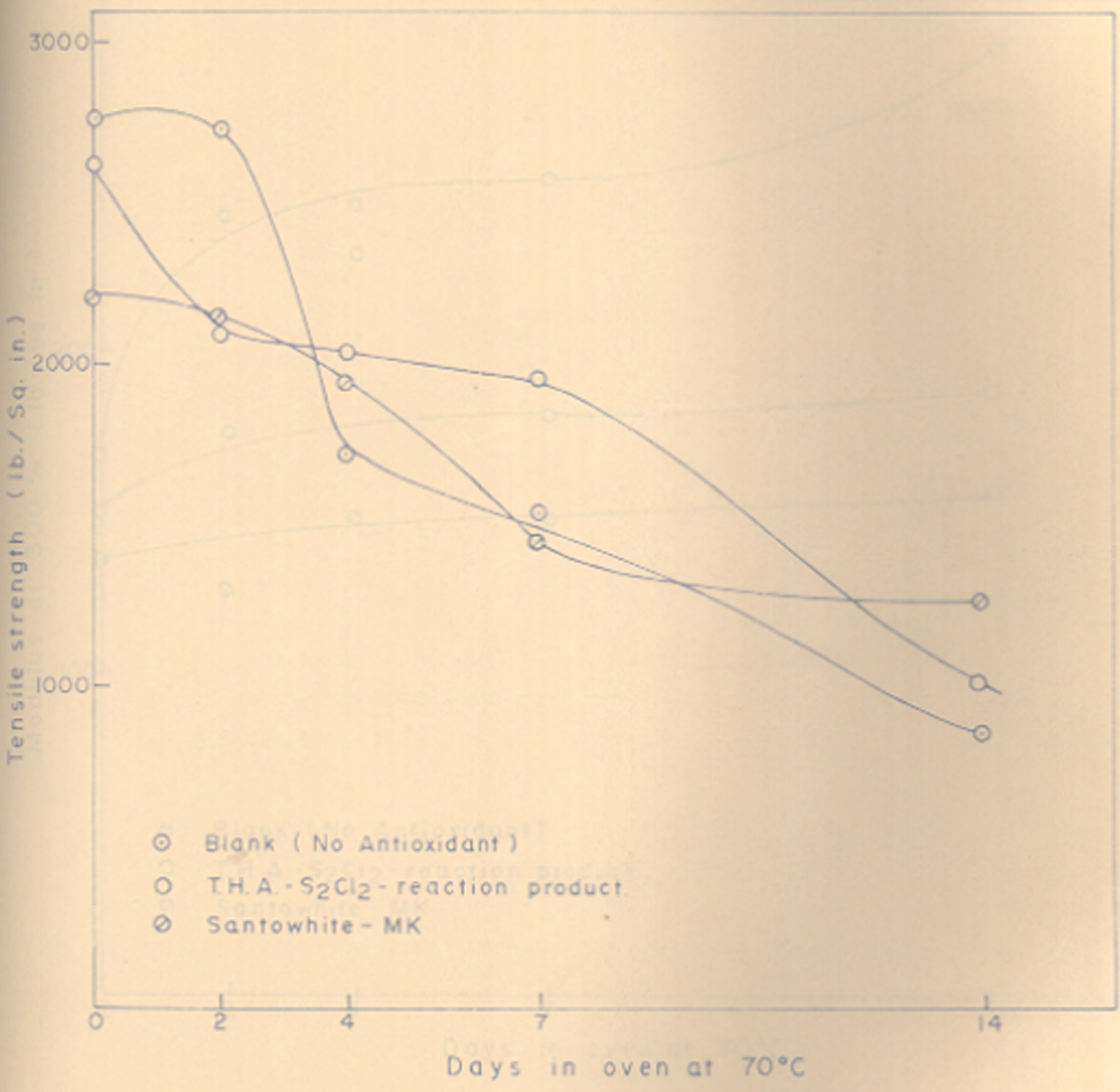


Fig.: 1 TENSILE STUDIES OF THE GUM COMPOUND WITH THE ANTIOXIDANTS

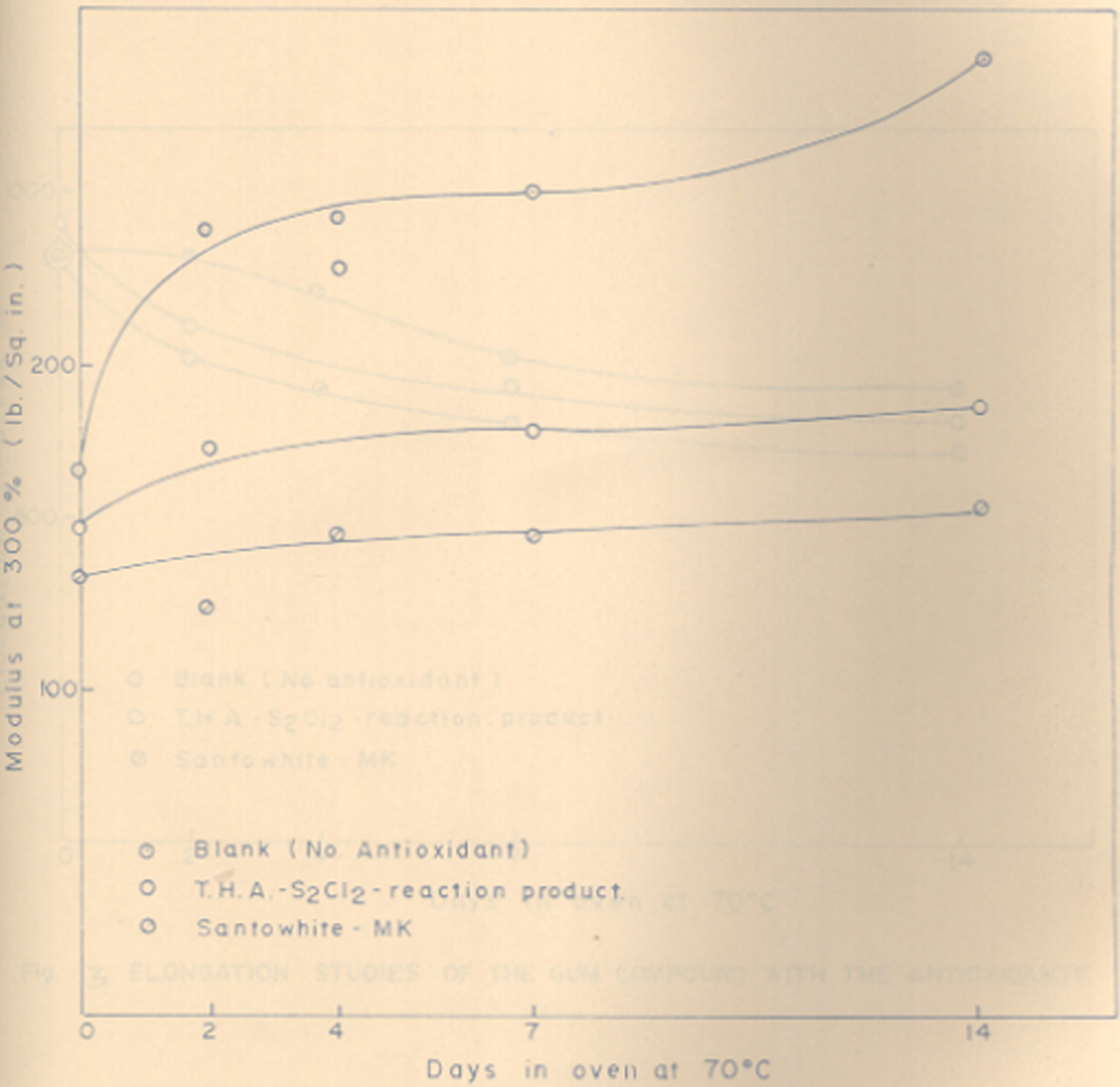


Fig.: **2** MODULUS STUDIES OF THE GUM COMPOUND WITH THE ANTIOXIDANTS.

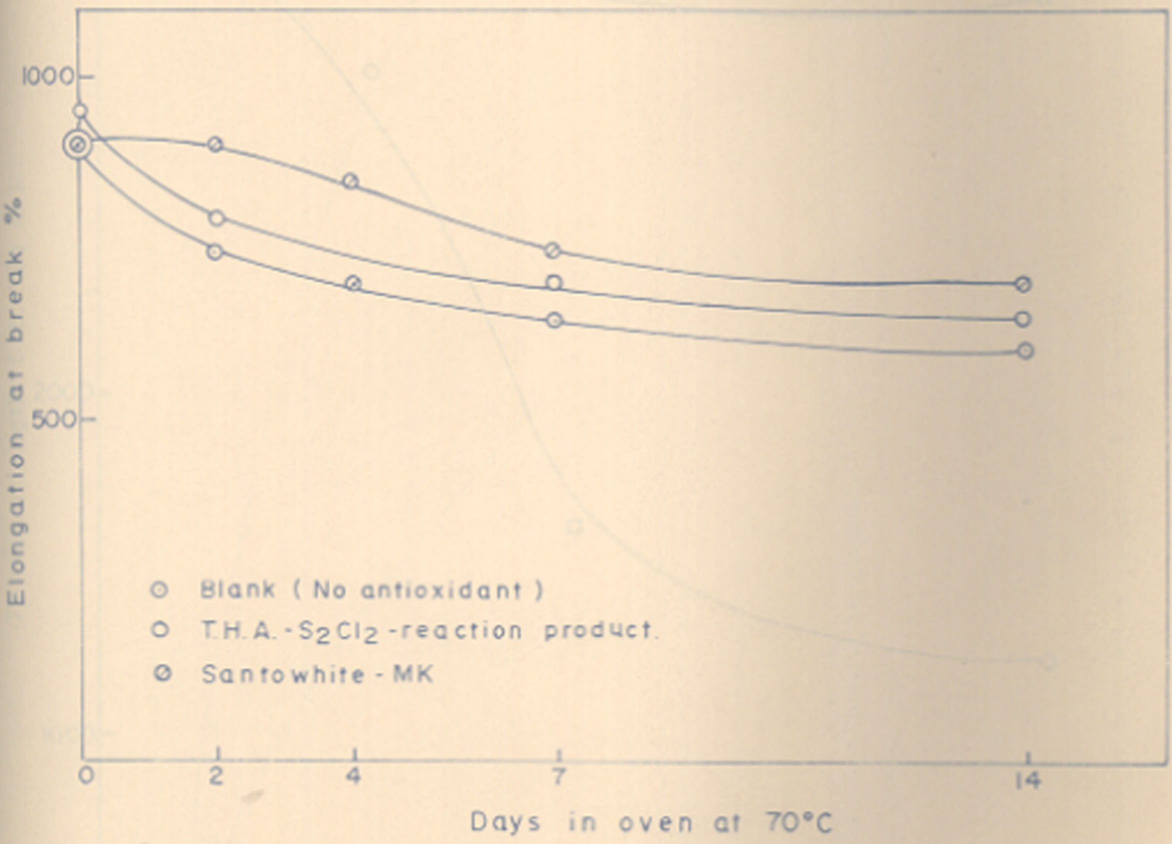


Fig. : 3 ELONGATION STUDIES OF THE GUM COMPOUND WITH THE ANTIOXIDANTS

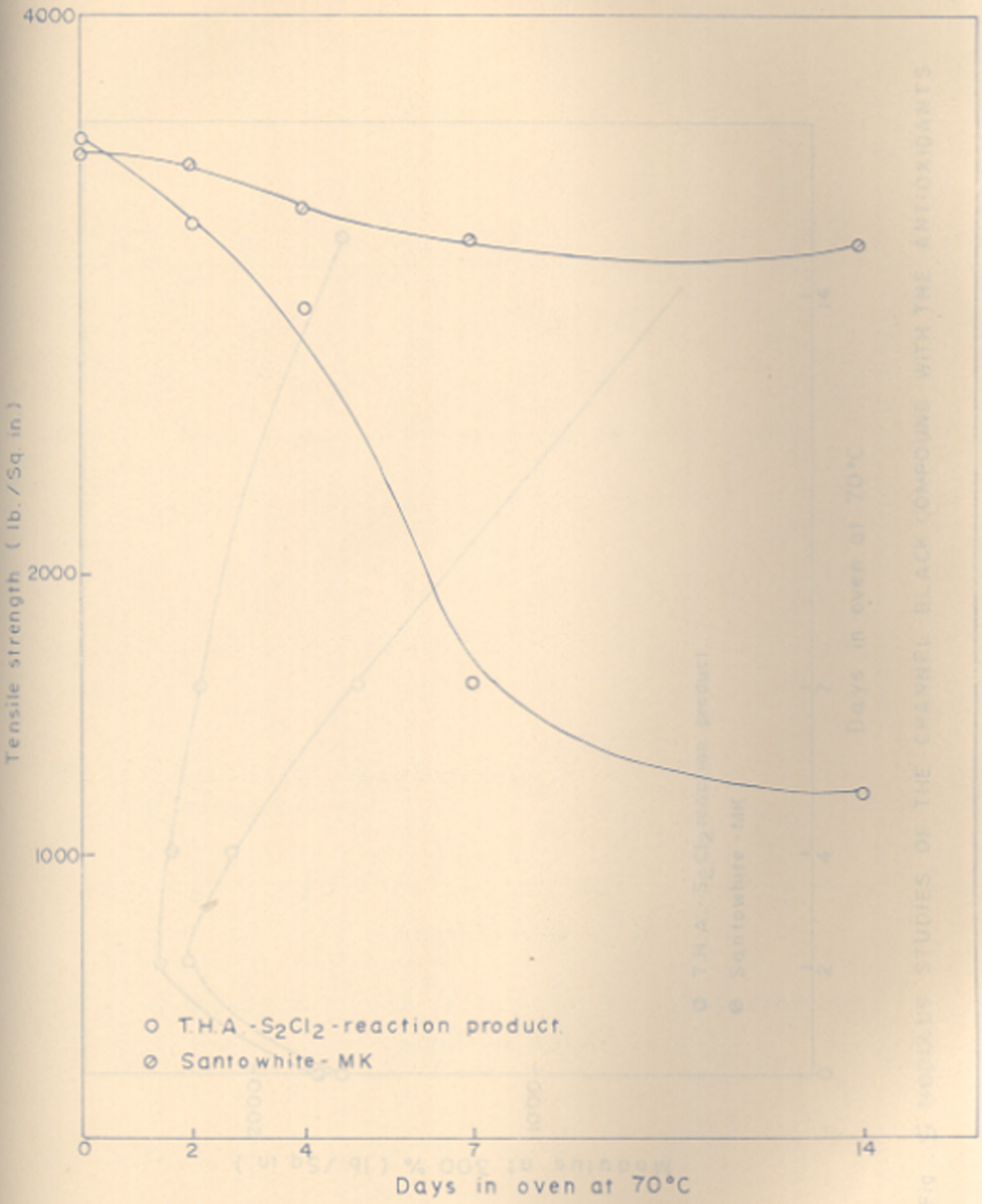


Fig. 4 TENSILE STUDIES OF THE CHANNAL BLACK COMPOUND WITH THE ANTIOXIDANT

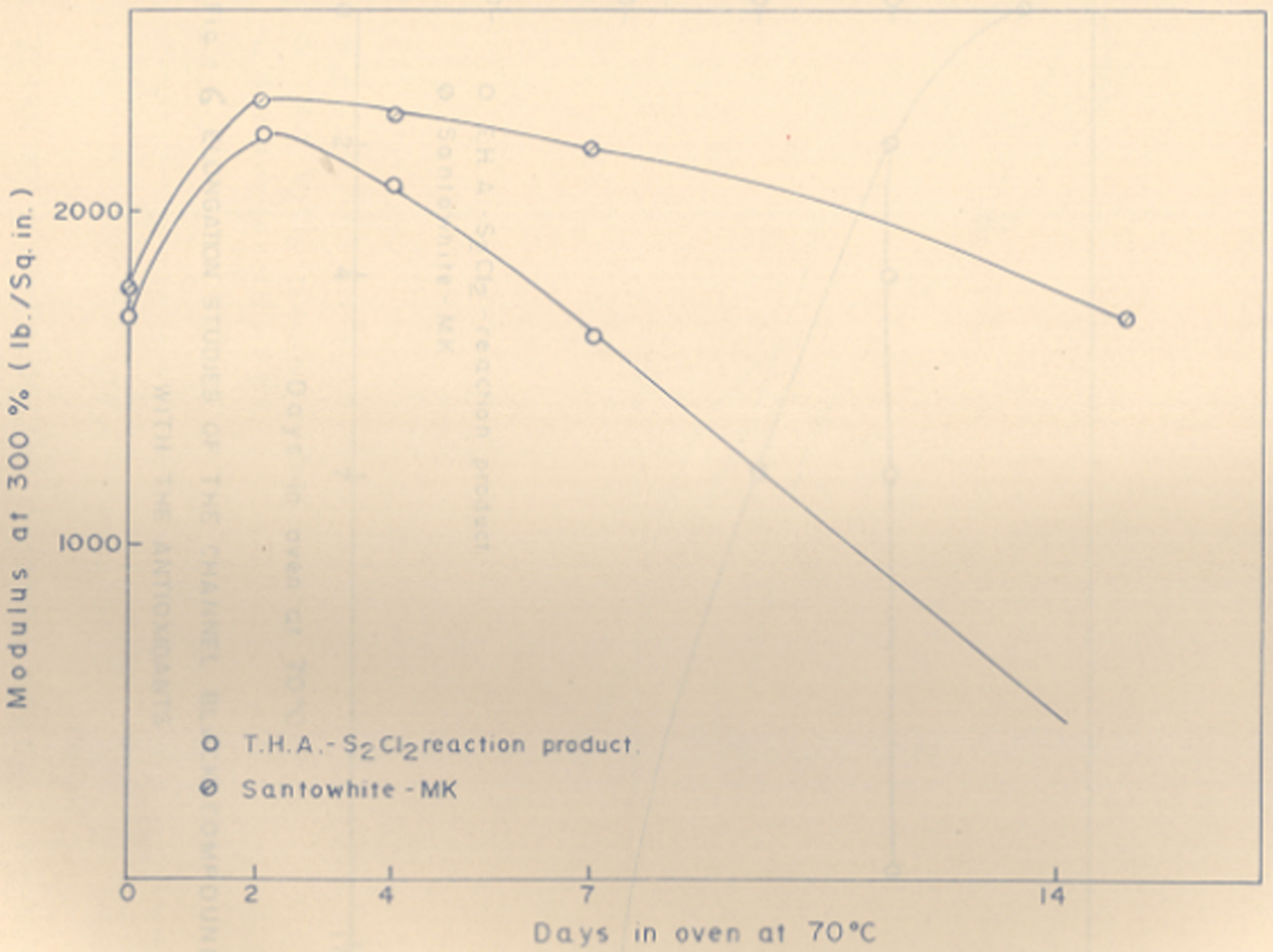


Fig. : 5 MODULUS STUDIES OF THE CHANNEL BLACK COMPOUND WITH THE ANTIOXIDANTS

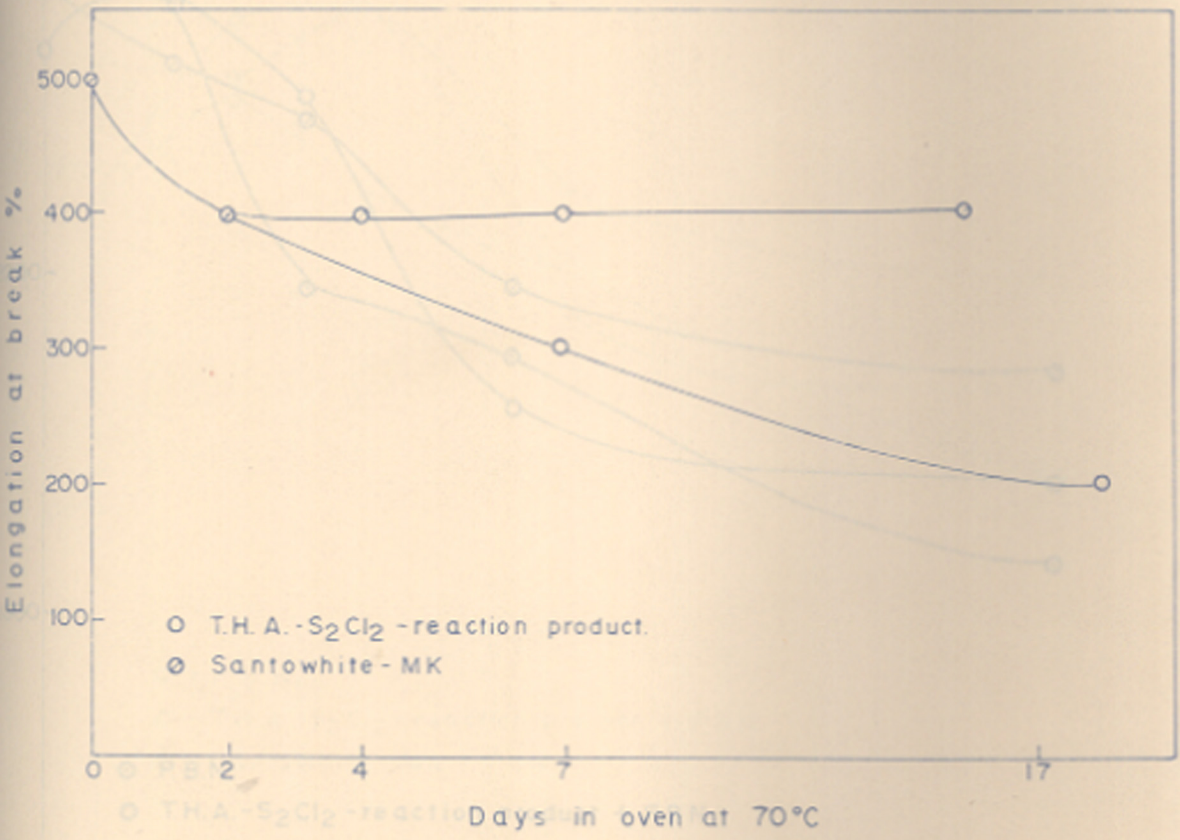


Fig. : 6 ELONGATION STUDIES OF THE CHANNEL BLACK COMPOUND WITH THE ANTIOXIDANTS

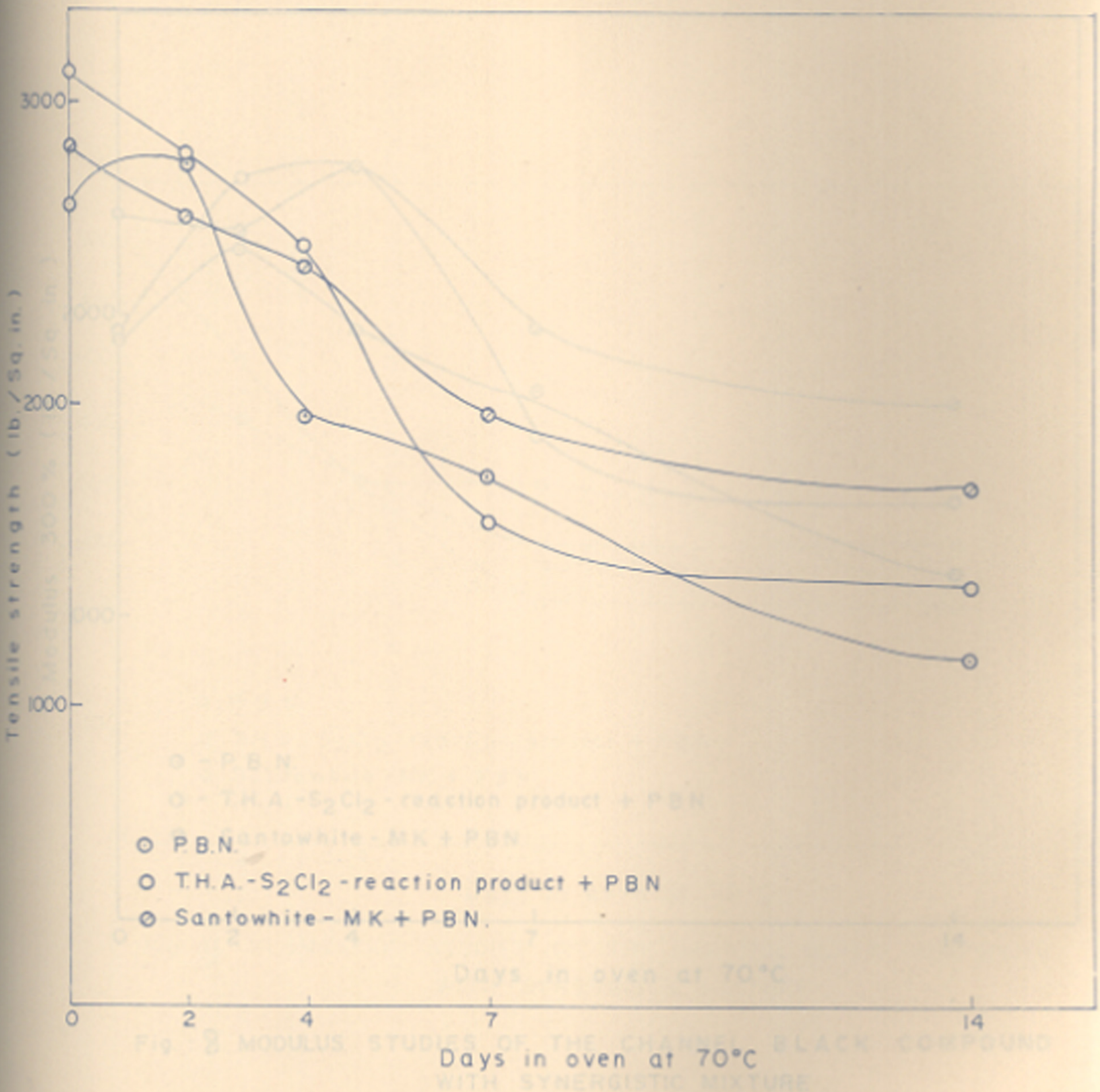


Fig. : 7 TENSILE STUDIES OF THE CHANNEL BLACK COMPOUND WITH SYNERGISTIC MIXTURE

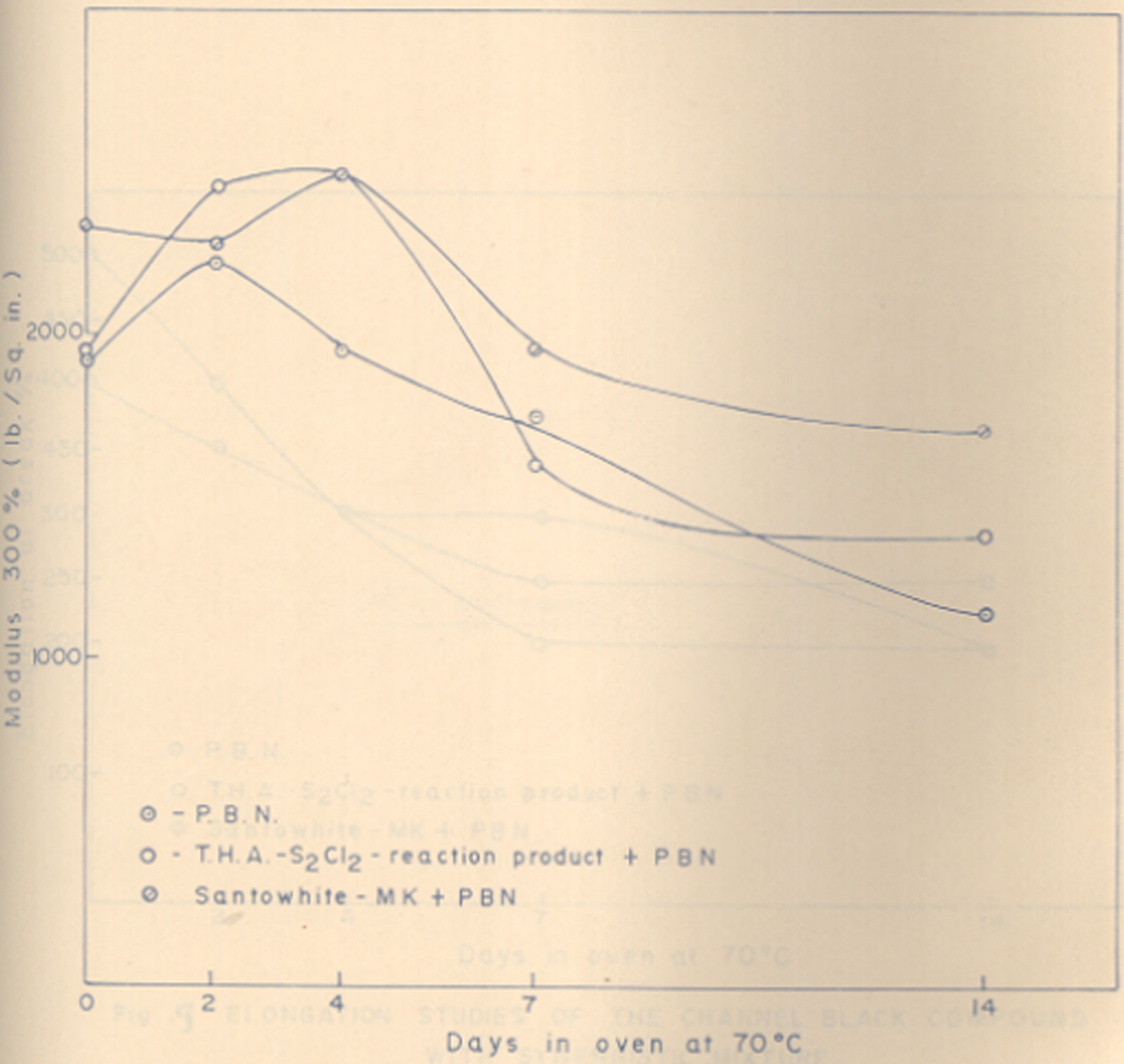


Fig. : 8 MODULUS STUDIES OF THE CHANNEL BLACK COMPOUND WITH SYNERGISTIC MIXTURE

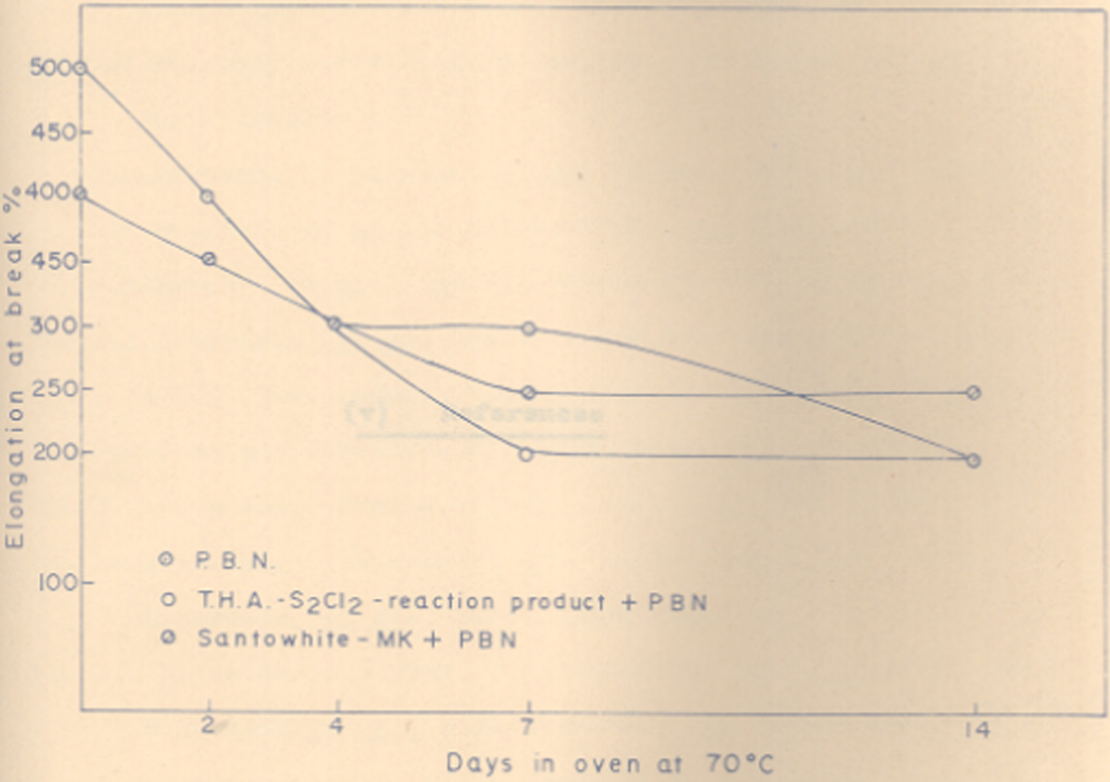


Fig. 9 ELONGATION STUDIES OF THE CHANNEL BLACK COMPOUND WITH SYNERGISTIC MIXTURE

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## SECTION (B) - CONSTITUTION OF DISULPHIDE OF 3-PENTADECYL PHENOL BY INFRA-RED SPECTROSCOPY

## (i) Introduction

The advanced instrumentation techniques developed during the last two decades, has led to creation of new devices for analytical methods for identification of organic compounds.

The application of infrared spectroscopy to the identification of polymers and polymer-auxiliary chemicals, has become a common practice in industrial laboratories.

A comprehensive study made by Mann,[1] deals with the examination of accelerators and antioxidants in rubber vulcanizates by infra red spectroscopy. Infrared spectral investigations have been made use of, in the structural elucidation of large number of hydroxy and dihydroxy compounds.[2] Binder[3] et al. have found characteristic differences in the hydroxy absorptions of O,O′-dihydroxy diphenyl sulphides and p,p′-dihydroxy diphenyl sulphides in the solid state and in carbontetrachloride solutions. Thus while the parahydroxy derivatives showed only a single band in dilute carbontetrachloride solution, they exhibited two bands in the solid, which are ascribed to intermolecular O-H....O and O-H....S hydrogen bonds. In the case of ortho hydroxy derivatives there was very little difference in the hydroxy absorptions in the solid and in solution (both giving rise to at least two bands) which have been interpreted as arising from intra molecular O-H....O and O-H....S hydrogen bonds. In the case of the orthohydroxy disulphide, there was a single band in both solid and solution. In the present study, we have made use of the behaviour of the hydroxy absorption in the solid state and in solution to establish the positions of the hydroxy group relative to the sulphide link.

## (ii) Present Investigation and Results

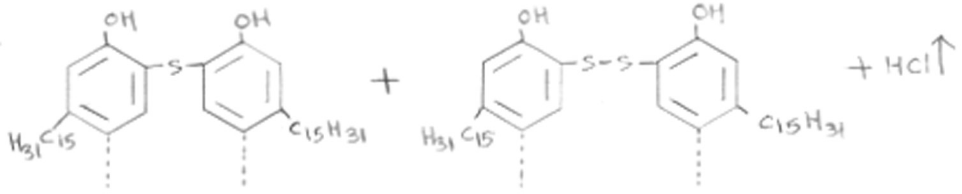
3-Pentadecyl phenol, a hydrogenated derivative from cashewnut shell liquid, was condensed with sulphur monochloride, in an inert solvent such as carbontetrachloride, to give a resinous reaction product (THA-$S_2Cl_2$ reaction product). This resinous mass containing a mixture of phenolic sulphides was evaluated as an antioxidant in natural rubber gum and channel black compounds.[4] The resinous THA-$S_2Cl_2$ reaction product, after fractional distillation under reduced pressure, yielded a monosulphide and a disulphide of 3-pentadecyl phenol (T.H.A.).

The present investigation was undertaken to establish the nature and the position of the sulphide linkage with respect to the position of phenolic hydroxy group, in the disulphide of 3-pentadecyl phenol, by infrared spectroscopy.

The reaction of the sulphide formation in the present study is given below.

3-pentadecyl phenol
(tetrahydroanacardol)

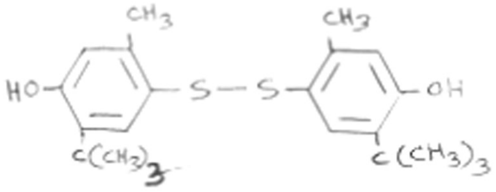
Sulphur monochloride



Monosulphide of 3-pentadecylphenol

Disulphide of 3-pentadecyl phenol (compound taken for spectral study)

The dotted lines indicate the other possible reactive positions for the attachment of sulphide linkage, ~~either ortho or~~ para with respect to the phenolic hydroxy group. The model compound taken for comparison is Monsanto's antioxidant "Santowhite crystals" which has been shown to have the following structure.[5]



Santowhite crystals
Di (2-methyl-4-hydroxy-5-tertbutyl phenyl)disulphide

The sulphide link in this compound as can be seen, is para to the phenolic hydroxy group.

## Infrared spectra

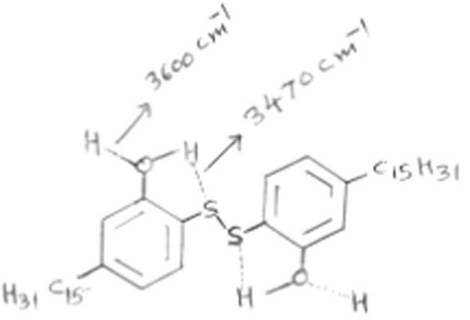
All spectra were recorded on a Perkin-Elmer Model 221 double beam spectrophotometer equipped with a NaCl prism-grating assembly in 4000-650 cm$^{-1}$ region. Solids were studied as Nujol Mull and solution spectra were recorded in 0.05 M, and 0.0005 M carbontetrachloride solution using 0.1 Mm and 1 cm. (Path length) cells at 25 c.

## (iii) Discussion

The infrared spectrum of disulphide of 3-pentadecyl phenol, in Nujol is shown in Fig. 1. The hydroxy and aromatic absorptions have been found in the usual regions and are therefore not discussed. The C-S and S-S stretching modes are observed usually below 700 $cm^{-1}$[6] and cannot therefore be studied. The hydroxy stretching absorptions were however studied in detail in solution to decide the nature of substitution in the aromatic ring and are discussed below.

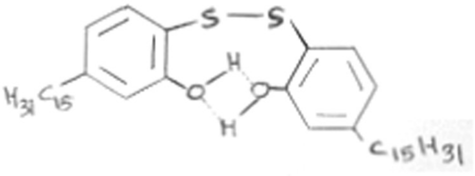
The spectra of antioxidants Santowhite crystals (Monsanto) and the disulphide of 3-pentadecyl phenol in the solid and in solution, in the hydroxy stretching region, are shown in figures 2 and 3 respectively. The Santowhite crystals as can be seen has a single band at 3600 $cm^{-1}$ in solution, while there are two bands at 3300 $cm^{-1}$ and 3315 $cm^{-1}$ in the solid in the hydroxy stretching region. The disulphide link in this compound is located para to the hydroxy group. The doublet in the solid may represent the two hydroxy groups with different strengths of intermolecular hydrogen bonding. In solution, the 3600 $cm^{-1}$ would come from the free hydroxy groups.

In the disulphide of 3-pentadecyl phenol, on the other hand, there are two bands each at 3375 $cm^{-1}$, 3270 $cm^{-1}$ and 3600 $cm^{-1}$, 3470 $cm^{-1}$ in the solid and dilute $CCl_4$ solutions (0.05 M) respectively. There was no change in the position and relative intensities of the bands even after 100 fold dilution (0.0005 M, $CCl_4$). The two bands observed in solution at 3600 $cm^{-1}$ and 3470 $cm^{-1}$ are best explained as arising out of two possible positions the OH groups can take by virtue of the rotations around the C-O band shown below (I), as in the case of orthochlorophenol.



(I)

In dilute solutions of ortho chloro phenol there are two bands observed which are ascribed to the free and intramolecularly bonded OH groups.[7] In the present compound there would be thus an intramolecularly bonded O-H....S band (3470 $cm^{-1}$) and a free hydroxy band (3600 $cm^{-1}$). An alternate assignment for the 3470 $cm^{-1}$ band could be an intramolecular hydrogen bond with O-H....O groups as shown below (II).



(II)

The single band found by Binder[3] for Di(2-hydroxy-3,5-ditertbutyl, 6-methyl phenyl) disulphide at 3472 $cm^{-1}$ in 0.05 M carbontetrachloride solution is ascribed to the intramolecularly bonded (O-H....S) hydroxy group. The absence of free rotation of the OH group in the above compound is probably due to bulky tertiery butyl group substituted in the position 3 (ortho to hydroxy) which makes the formation of the other isomer impossible. The intra molecularly bonded O-H....S frequency at 3472 $cm^{-1}$ is close to that observed in the present compound (Disulphide of 3-pentadecyl phenol) at 3470 $cm^{-1}$.

## Conclusion

The above infrared study in the hydroxy absorption region thus indicates that the sulphide link in the disulphide of 3-pentadecyl phenol is situated in the ortho position with respect to the two phenolic hydroxy groups which can form intramolecular hydrogen bonds with the sulphur atoms.

## (iv) Experimental

The preparation of THA-$S_2Cl_2$ reaction product is described previously.

Distillation of THA-$S_2Cl_2$ reaction product

THA-$S_2Cl_2$ reaction product (5 gms) was distilled under vacuum and the following fractions were collected.

1st fraction ... 220°C/1.5 mm (0.200 gms) - unreacted tetrahydroanacardol.

2nd fraction ... 225-240°C/1.5 mm (1.8 gms) - THA contaminated with sulphides.

3rd fraction ... 250-260°C/1.5 mm (3 gms) - Mixture of sulphides.

3rd fraction on redistillation under vacuum gave two fractions. Fraction boiling at 185°C/0.4 mm. resulted into solid (2 gms). This was recrystallized five times from petroleum ether (60°-80°) to give white crystalline solid. m.p. 89°-90°C. This was analysed for disulphide of 3-pentadecylphenol (THA).

Analysis: Found, C, 75.44; H, 10.96; S, 9.91%.

$C_{42}H_{70}O_2S_2$ requires C, 75.21; H, 10.45; S, 9.55%.

Fraction boiling at 270°C/0.4 mm., pale yellowish liquid which solidified on cooling to a low melting (30°-32°C) sticky solid, about 0.8 gms. This was analysed for monosulphide of 3-pentadecyl phenol.

Analysis: Found, C, 79.29; H, 11.27; S, 5.47%.

$C_{42}H_{70}O_2S$ requires C, 79.00; H, 10.97; S, 5.01%

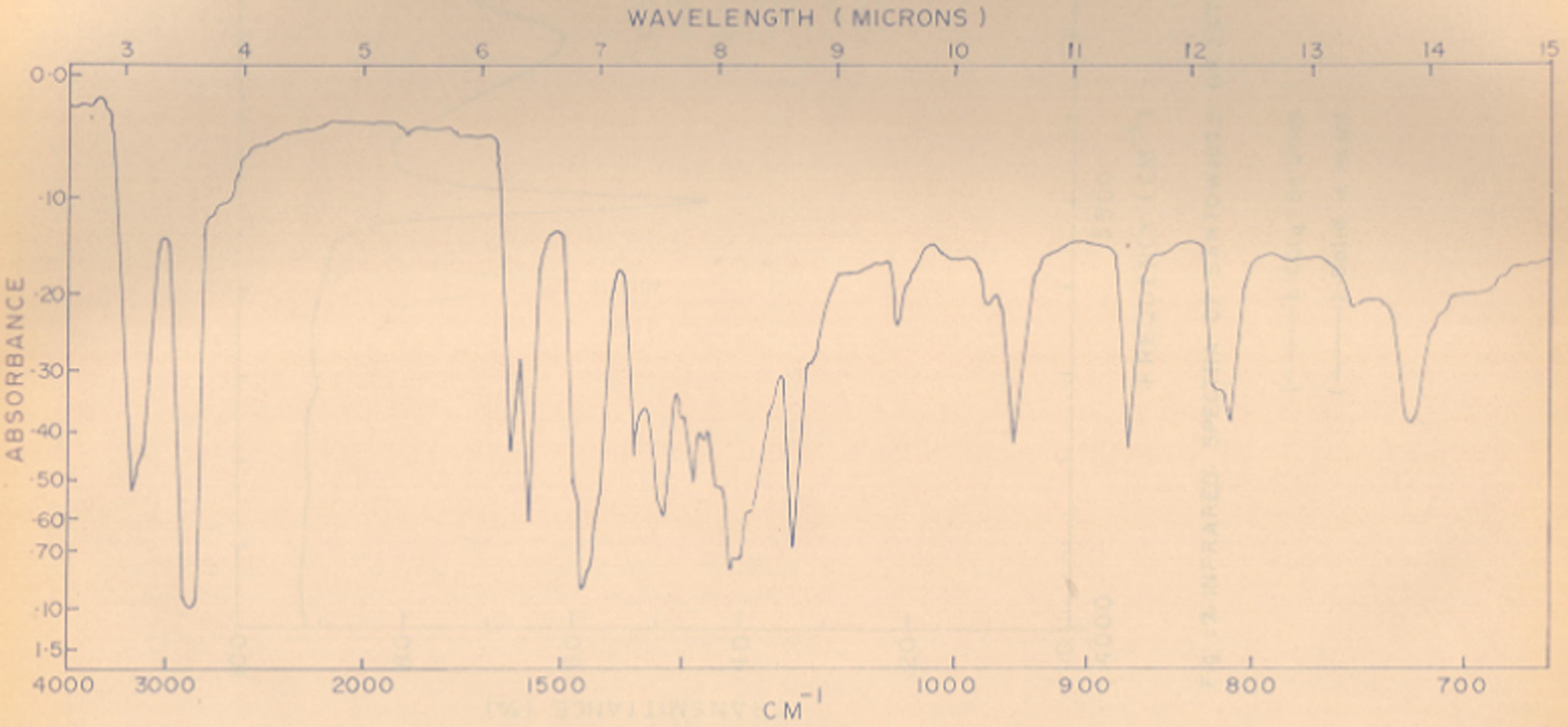


Fig. : 1 INFRARED SPECTRUM OF DISULPHIDE OF 3-PENTADECYLPHENOL IN NUJOL

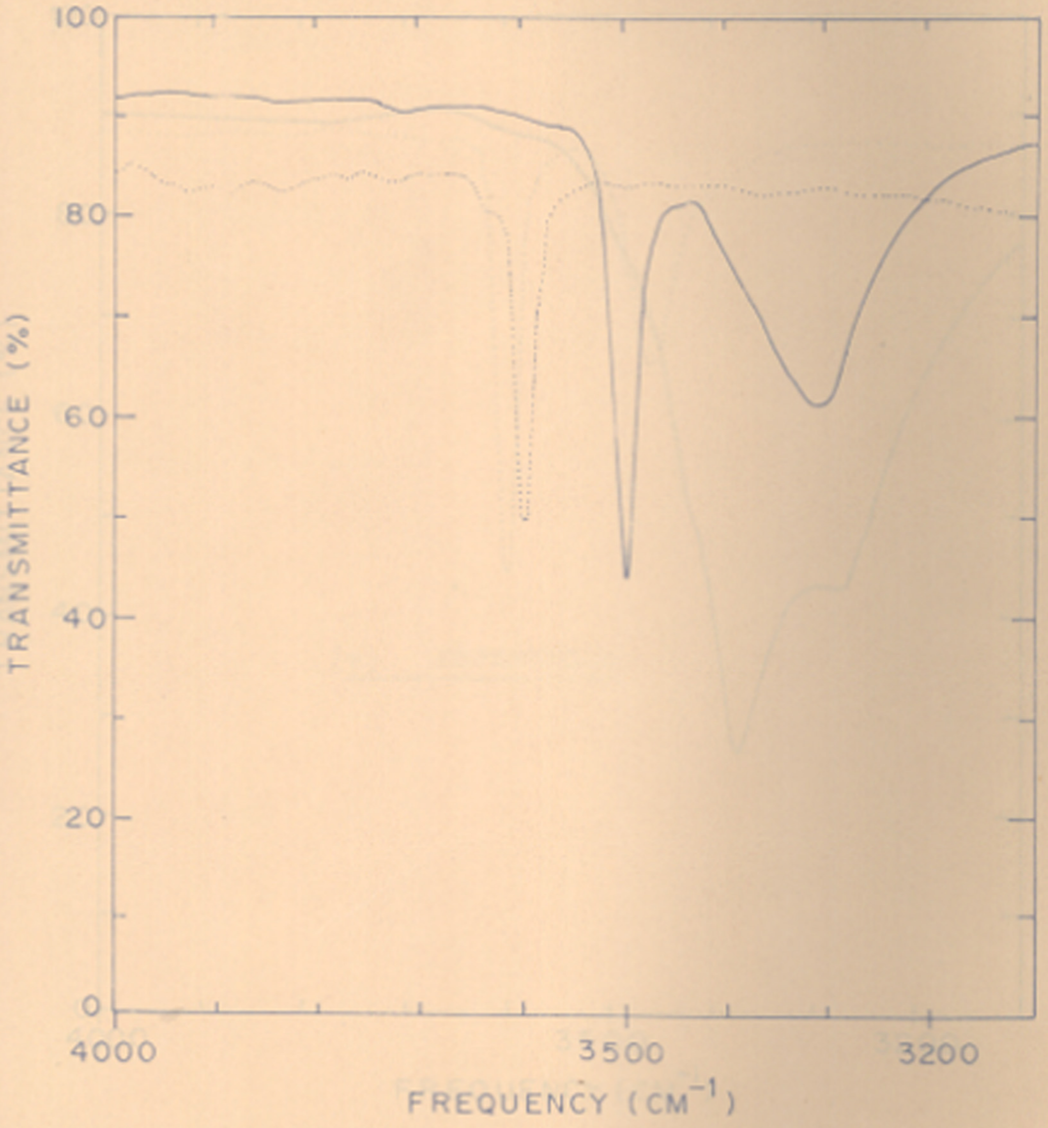


Fig. :2 INFRARED SPECTRA OF SANTOWHITE CRYSTALS

(..........) $CCl_4$ Solution.

(————) Solid in nujol.

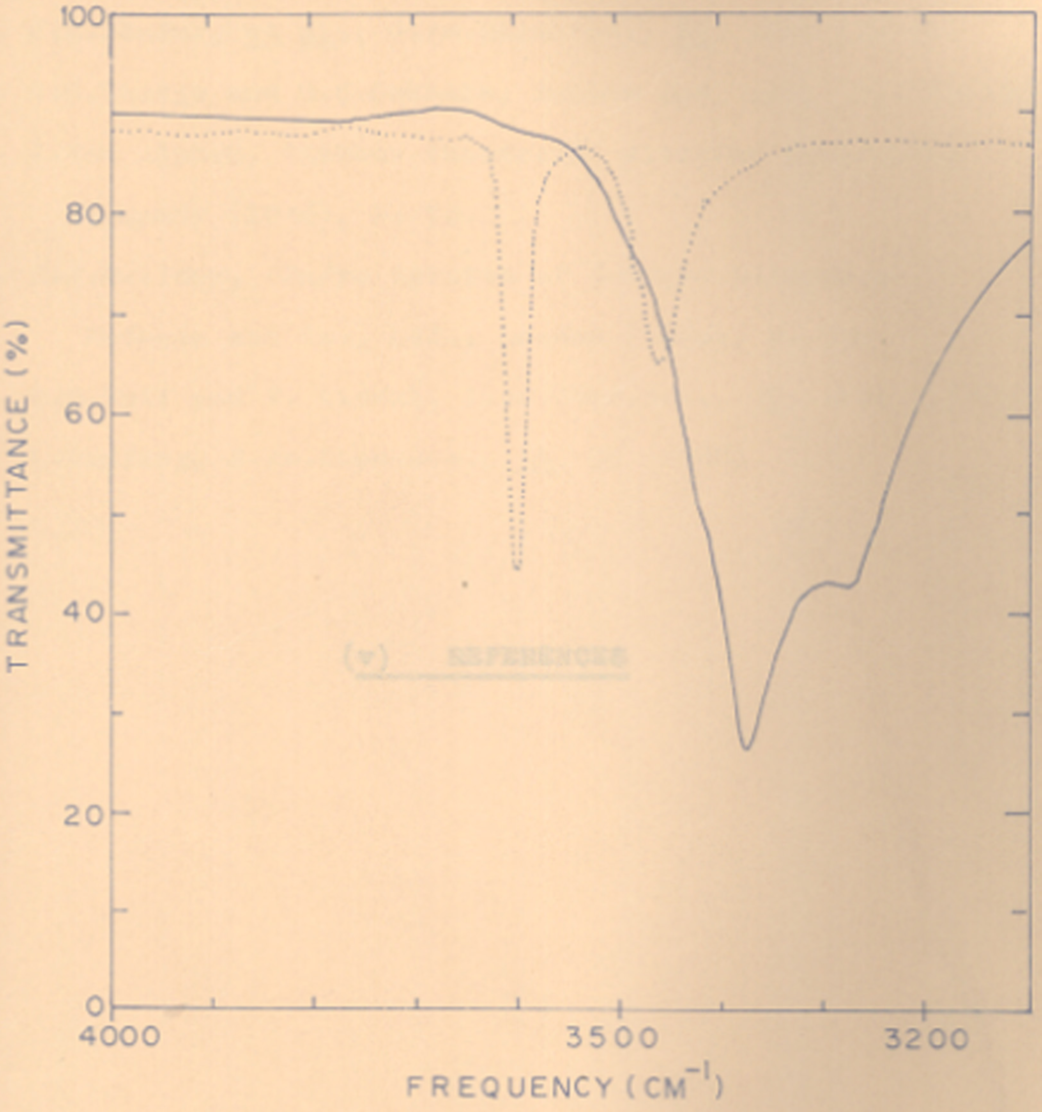


Fig. : 3 INFRARED SPECTRA OF DISULPHIDE OF 3-PENTADECYLPHENOL

(··········) $CCl_4$ Solution.

(———) Solid in nujol .

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## SECTION (C) - SYNTHESES OF SUBSTITUTED PHENYL-β-NAPHTHYL AMINES AND ARYL UREAS FROM 4-AMINO-3-PENTADECYL PHENOL AND EVALUATION OF THEIR ANTIOXIDANT ACTIVITY IN NATURAL RUBBER

## (i) Introduction

One of the main causes of irreversible changes in the structure of polymer molecules is the oxidation of the latter by molecular oxygen. The result of this process is the ageing of raw and vulcanized rubber, thereby loosing its important physical properties during storage and use.

It is therefore quite obvious how important is the study of the problem of inhibited oxidation and of the mechanism of antioxidant action in creating effective protection of raw and vulcanized rubber against thermal ageing.

During the last two decades voluminous research work has been done on the autoxidative degradation of natural rubber. Most of the work is connected on the mechanism of autoxidation and the antioxidant action of various amine and phenolic type antioxidants on natural rubber.[1-5]

A mechanism, in which the antioxidant has a possible fourfold action, is described below:-

Initiation

(Peroxide decomposition) $x\ ROOH \rightarrow nR\ (RO\cdot,\ RO_2\cdot)$

(Direct $O_2$ attack on hydrocarbon) $RH + O_2 \rightarrow R\cdot$

(Direct $O_2$ attack on antioxidant) $AH + O_2 \rightarrow A\cdot$

Propogation

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot$$

Chain transfer
(with antioxidant)

$$RO_2\cdot + AH \rightarrow RO_2H + A\cdot$$

$$A\cdot + RH \rightarrow AH + R\cdot$$

Termination

$$2\ RO_2^{\cdot} \longrightarrow \text{Stable products}$$

((Chain stopping by antioxidant radical)

$$2\ A^{\cdot} \longrightarrow \text{Stable products}$$

$$A^{\cdot} + RO_2^{\cdot} \longrightarrow \text{Stable products}$$

(Peroxide destruction-Anti-oxidant induced decomposition)

$$x\ ROOH \xrightarrow[AH]{} \text{Stable products}$$

The four ways in which an antioxidant might act would then be :

(1) Initiation of oxidation by direct oxygen attack on the antioxidant.

(2) Chain transfer involving the antioxidant, but without termination.

(3) Termination in which an antioxidant radical reacts with another radical to give stable products and thus ends the oxidation chain.

(4) Direction of peroxide decomposition to stable products, rather than to free radicals which could initiate further oxidation.

Various theories have been postulated for the mechanism of antioxidant action on rubber.[6]

The generally accepted (but not established) mechanism in the case of aromatic amines and phenols involves the removal of a labile hydrogen by a peroxy radical as a controlling step of the reaction.[7]

$$ArOH + RO_2^{\cdot} \longrightarrow ArO\cdot + RO_2H$$

$$R_2NH + RO_2^{\cdot} \longrightarrow R_2N\cdot + RO_2H$$

If hydrogen abstraction is a controlling step in chain termination, it is reasonable to expect that substitution of a labile hydrogen by deuterium should give rise to a kinetic isotope effect. The rate of chain termination should be decreased by deuterium substitution, thereby lowering the antioxidant efficiency and increasing the rate of oxidation of the substrate.

The existence of a kinetic isotope effect in some oxidation reactions and related steps have been previously established. In the reaction of acyl peroxides with phenols when O-H was replaced by O-D, several peroxide-phenol-solvent system showed a small but constant isotope effect, indicating that O-H cleavage is a rate controlling step in the reaction.[8]

Kinetic studies by Bickel and Kooyman[9] on both amine and phenolic antioxidants support the theory of hydrogen abstraction as a controlling step. Kinetic studies of inhibited oxidation of rubber made by Shelton,[10] were consistent with a mechanism based on donation of hydrogen to $RO_2^{\cdot}$ by the antioxidant.

However, literature reports have also demonstrated a failure to observe an isotope effect with aromatic amine antioxidants. Hammond, Boozer and coworkers[7,11] have reported no effect upon the rate of oxidation when they compared diphenyl amine with N-deuterio-diphenyl amine, and N-methylaniline with N-deuterio-N-methyl aniline, in the oxidation of cumene and tetralin. Pedersen[12] has reported no difference in the effect of N,N'-diphenyl-p-phenylene diamine and N,N'-dideuterio-N,N'-diphenyl-p-phenylenediamine on the induction period of gasoline oxidation.

These authors, because of their failure to find an isotope effect, have concluded that hydrogen abstraction is not the controlling step. They propose instead that π-complex formation with the peroxy radical,[11] or electron abstraction by the peroxy radical,[12] is the rate-controlling reaction.

To support the hydrogen abstraction theory, Shelton and McDonel[13] using both a hindered phenol and an aromatic amine as antioxidants, found a definite kinetic isotope effect in the rate of oxidation of butadiene-styrene rubber. In this study, 2,6-di-tert butyl-4-methyl phenol and N-phenyl-2-naphthylamine were each compared with their corresponding deuterated derivatives with regard to their inhibitory properties. They observed isotope effects as large as 1.8 with 60% deuteration. They further pointed out that failure to detect a kinetic isotope effect by others may be due to several factors including loss of deuterium through interchange with water which is formed continuously in the reaction, temperature of the reaction, and concentration of the stabilizer.

Ingold and Howard[14] have recently obtained quite large isotope effects by adding $D_2O$ to the oxidation mixtures to maintain the inhibitor in a completely deuterated condition. They concluded that the inhibition mechanism is a normal hydrogen abstraction process, and the failure of other workers to observe the expected isotope effect is probably due to a very rapid exchange with traces of water or hydroperoxide in the reaction mixture, thus supporting the observations previously made by Shelton and co-workers.

Pedersen[12] has reported that tertiary amine like tetramethyl-p-phenylenediamine is 36% as efficient as the powerful antioxidant N,N′-di(sec-butyl)-p-phenylenediamine and since it has no labile hydrogen atom, the deactivating mechanism, if it is kinetic chain breaking, can only involve electron transfer from the nitrogen, forming an ion radical (like that of a Wurster cation). $RO_2\cdot + Ar\ddot{N}R_2 \rightarrow RO_2{:}^{(-)} + Ar\dot{N}R_2^{(+)}$. The ion-radical is not stable and like most phenol and amine antioxidants, it terminates two kinetic chains.

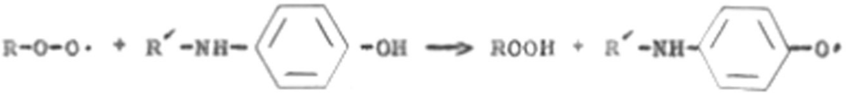
It is well known that the antioxidants for rubber have been classified into two main classes, (1) amine type and (2) phenolic type. The former class included substituted aryl naphthylamines, aryldiamines, etc. This class is more powerful than the phenolic type in antioxidant action. However, the amine type indicated more discolouration in the white stock whereas the phenolic type indicated no discolouration. It was therefore decided to synthesise new compounds which have in their molecules characteristics similar to both these classes and it was felt that these compounds may prove more efficient in their antioxidant properties than the compounds belonging to the two separate classes.

Semon[15] in his elaborate article on rubber antioxidants, has described the application of various amino phenols and derivatives, as useful antioxidants for rubber. The following are patented compounds having mixed functional groups[16]- p-aminophenol, p-aminophenol on inert base, p-hydroxybenzyl aniline, p-hydroxy-N-phenyl morpholine, hydroxydimethyl aniline, 2 hydroxynaphthyl phenylaminomethane, p-hydroxy phenyl-$\beta$-naphthyl amine, $\alpha$-amino-$\beta$-naphthol, hydroxyaminobiphenyl, p-phenyl amino-p-hydroxy diphenyl amine, p-amino-m-cresol.

Although both amines and phenols are generally antioxidants, it has been found that, more effective results can be obtained when the two are used together as salts, or as compounds having both amino and hydroxy functional groups.

In the benzene series, para orientation of the two groups seems to increase the activity more than does either ortho or meta. Aminophenols, usually combine the effects of both phenol and amine in an intensified form. In general, combinations take share of the staining properties of the ingredients.

Pedersen,[12] while studying the antioxidant activity of some antioxidants in gasoline, has shown that the effects of the substituents on the antioxidant efficiency of p-aminophenol are less active than for p-phenylenediamine. This suggests that something common to these compounds has become dominent, probably the hydroxyl group. However alkyl ethers of p-aminophenols are at most extremely feeble antioxidants, hence, N-substituted p-aminophenols must terminate chains by reaction with ROO. at the hydroxyl group as shown below.

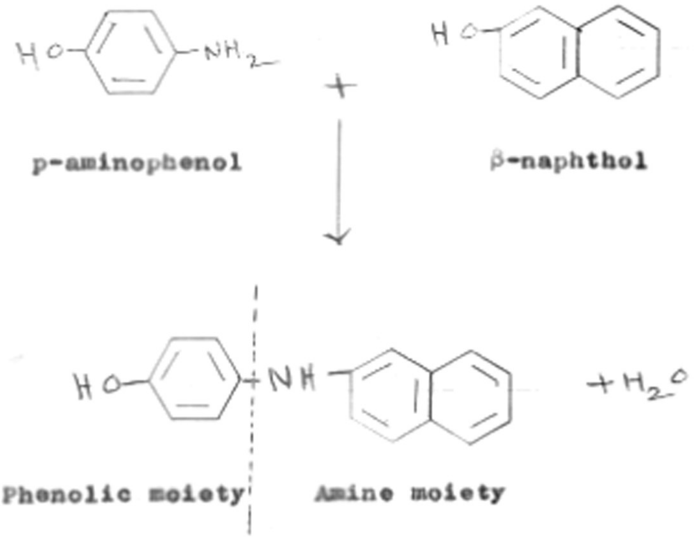


The fate of p-amino free radical is not yet known but it probably involves chemical rearrangement which does not initiate, either directly or indirectly, an oxidative chain reaction.

## (ii) Present investigation and results

For getting the maximum benefit of both phenolic as well as amine moieties in one and the same nucleus of an antioxidant it is obvious to join the two moieties together through effective functional groups such as amino, or urea linkage, without loosing the benefits of conjugation.

For example the antioxidant capacity of an amino phenol, can be conveniently increased by substitution of the hydrogen of the amino group with a naphthalene moiety. Thus the resulting compound gets the combined antioxidant activity of both phenol and amine type antioxidant.

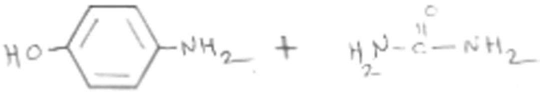


P-hydroxy-phenyl-β-naphthyl amine

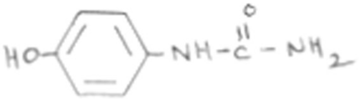
Thus p-aminophenol when reacted with β-naphthol in presence of catalytic amount of sulphuric acid (as dehydrating catalyst), p-hydroxy phenyl-β-naphthylamine is formed.

Due to the presence of both phenolic hydroxyl and a secondary amine groups in this compound, a very powerful antioxidant is made. Such antioxidant gives a better performance than the simple phenyl-β-naphthyl amine, which contains no hydroxyl group on the phenyl ring.

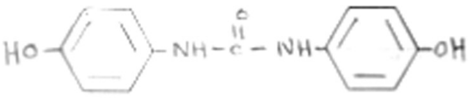
The amino group in the aminophenol may also be substituted by urea linkage giving the corresponding monoaryl or diaryl ureas.



Amino phenol Urea



p-hydroxy phenylurea



NN'-bis(p-hydroxyphenyl),
urea

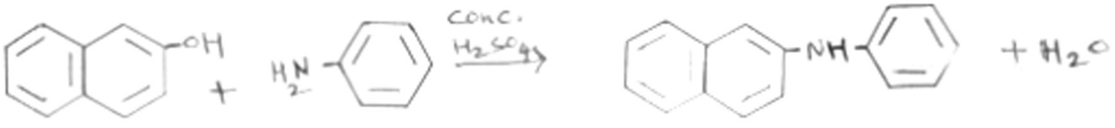
The combined effect of phenolic hydroxyl and urea linkage in such compounds makes these compounds as good antioxidants in rubber.

Many symmetrical and unsymmetrical aryl ureas have been patented as antioxidants for rubber.[17] It is also reported that the unsymmetrical aryl ureas are more effective antioxidants than the symmetrical aryl ureas.[18]

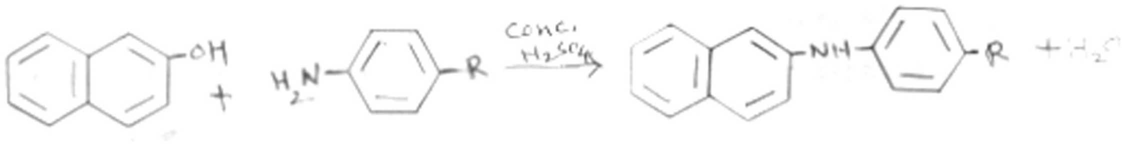
## General methods of the preparation of aryl-naphthyl amines and symmetrical and unsymmetrical arylureas

Phenyl-β-naphthylamine (PBN) and other substituted phenyl-β-naphthylamines are generally prepared by the following methods -

(1) By heating β-naphthol with aniline[19] or substituted aniline[20] in the presence of a small quantity of concentrated sulphuric acid at 200°-250°C.



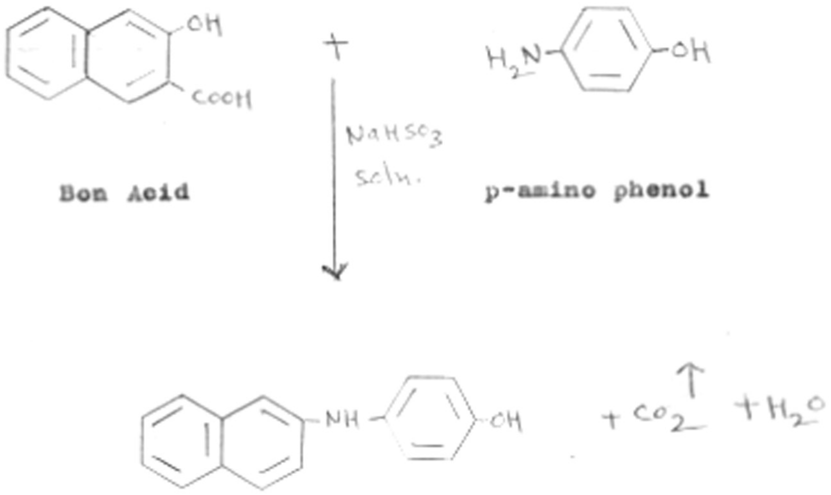
β-naphthol aniline phenyl β-naphthylamine



β-naphthol substituted aniline Substituted Phenyl β-naphthylamine

R = $CH_3$, isopropyl,
t-butyl and OH

(2) p-Hydroxy-phenyl-β-naphthylamine may also be prepared conveniently by treating 3-hydroxy-2-naphtholic acid (Bon acid) with p-aminophenol in presence of sodium bisulphite solution.[21]



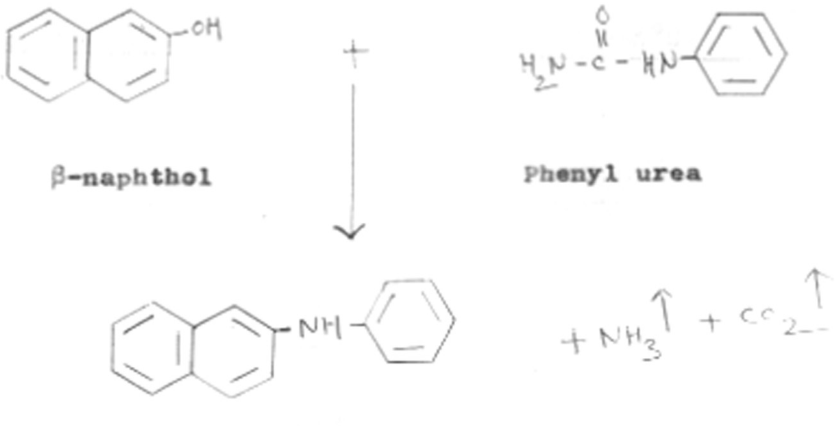
**Bon Acid**

**p-amino phenol**

**p-hydroxy-phenyl-β-naphthylamine**

(3) **Arylation made by β-naphthol on monoaryl ureas, gives aryl naphthyl amines.**[22]

**β-Naphthol and phenyl urea were gradually heated to 245°C and kept there for 6 hours. The reaction mass, after treating with 10% NaOH and then crystallizing from ethanol yielded phenyl-β-naphthyl amine.**

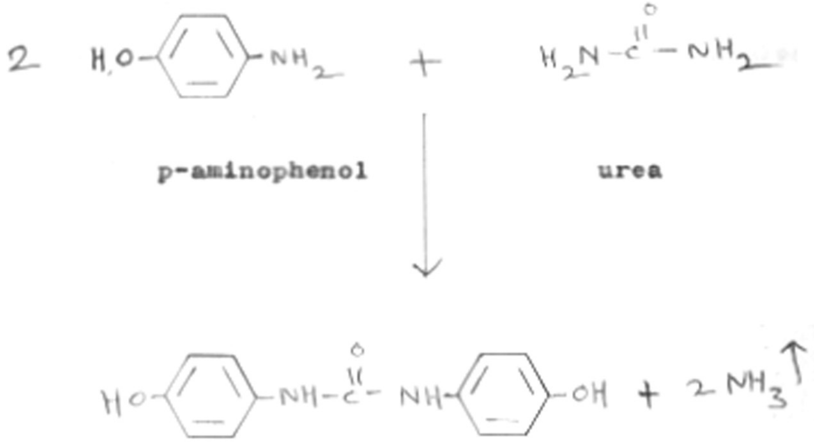


**β-naphthol**

**Phenyl urea**

**Phenyl-β-naphthylamine**

The substituted aryl urea derivatives can be readily prepared by the following known procedures.[23] Thus the symmetrical hydroxy phenyl urea can be prepared by condensation of 1 mol of urea with 2 moles of p-aminophenol in amyl alcohol.[24]

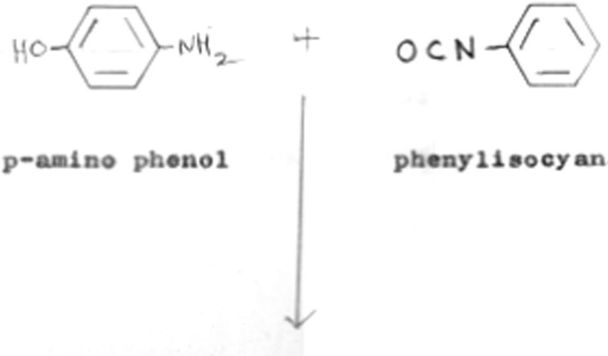


p-aminophenol

urea

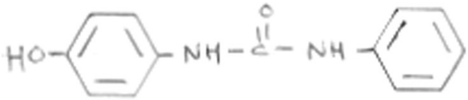
N,N´-di(p-hydroxy phenyl) urea

The unsymmetrical hydroxy phenyl urea can be prepared by dropwise addition of an appropriate amount of phenyl isocyanate to a stirred suspension of an appropriate amino phenol in dry benzene at a temperature of 70-80°C.



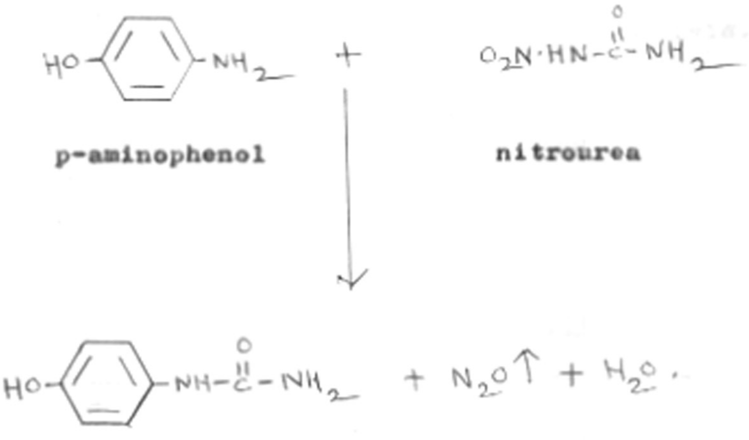
p-amino phenol

phenylisocyanate



N-(p-hydroxyphenyl),N′-phenyl urea

The hydroxy phenyl urea can be prepared by reaction of amino phenol with nitrourea in presence of an aqueous alcohol.[25]



p-aminophenol

nitrourea

p-hydroxyphenyl urea

The present investigation deals with the development of suitable substituted phenyl-β-naphthyl amine and symmetrical and unsymmetrical aryl ureas by adopting the above general methods of syntheses.

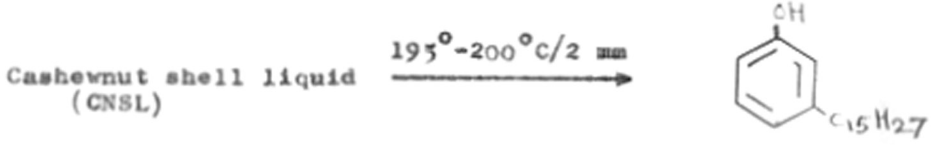
The new compounds were synthesized from 4-amino-3-pentadecyl phenol as a starting material, and their antioxident properties were studied in A.S.T.M. standard recipes such as natural rubber gum compound and channel black compound.

## Methods of syntheses of substituted phenyl-β-naphthyl amine and symmetrical and unsymmetrical aryl urea type antioxidants from CNSL

The several steps involved in the syntheses of above new compounds are shown diagrammatically in Fig. 1.

### 3-pentadecadienyl phenol (Anacardol) (I)

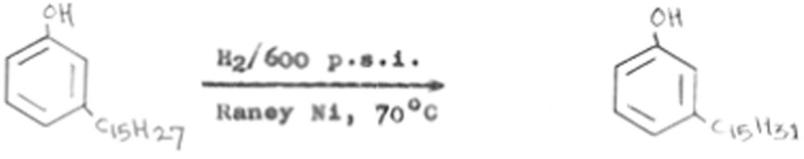
When commercial cashewnut shell liquid is distilled under reduced pressure, 3-pentadecadienyl phenol (anacardol) is obtained as a pale yellowish liquid in 50% yield.



Anacardol (I)

### 3-pentadecyl phenol (tetrahydroanacardol)(II)

Anacardol when catalytically reduced over Raney nickel catalyst at 600 pounds hydrogen pressure and at 70°C, in a Parr-autoclave, gave a 90% yield of 3-pentadecyl phenol (II). The crude product after crystallizing from petroleum ether (40°-60°) gave a white waxy product m.p. 50°C.

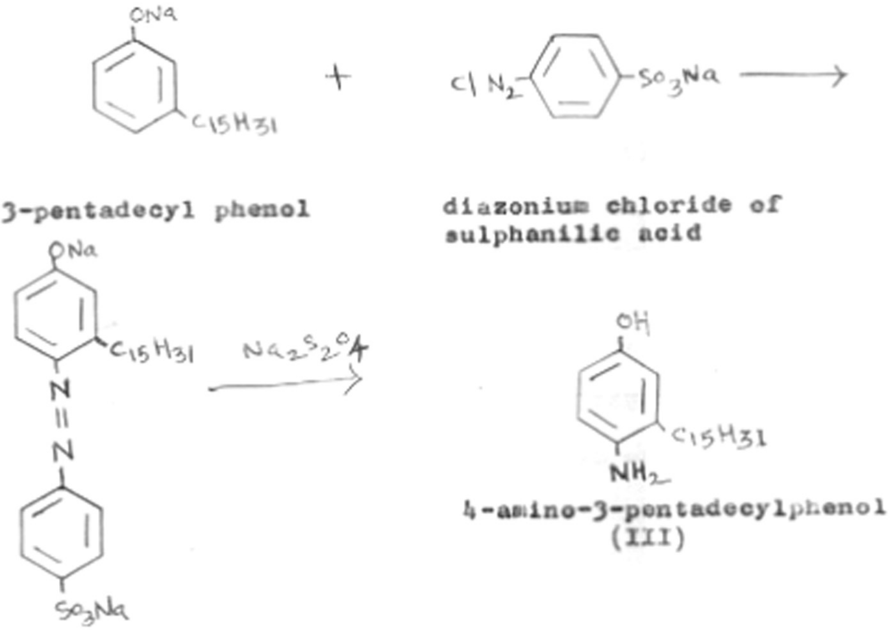


Anacardol

3-pentadecyl phenol
(II)

## 4-Amino-3-pentadecyl phenol (III)

A suspended solution of diazotized sulphanilic acid in ethanol was slowly added to the alcoholic solution of sodium salt of 3-pentadecyl phenol cooled at 0°C, whereupon coupling of the diazotized sulphanilic acid with 3-pentadecyl phenol took place resulting in the formation of a red azo dye solution. The red dye solution was further reduced with a saturated sodium dithionite solution at about 75°C, when the red colour was changed to pale tan colour. This solution was cooled to 0°C when crude 4-amino-3-pentadecyl phenol was obtained, it was crystallized from ethanol. It had a m.p. 105°-106°C.



3-pentadecyl phenol

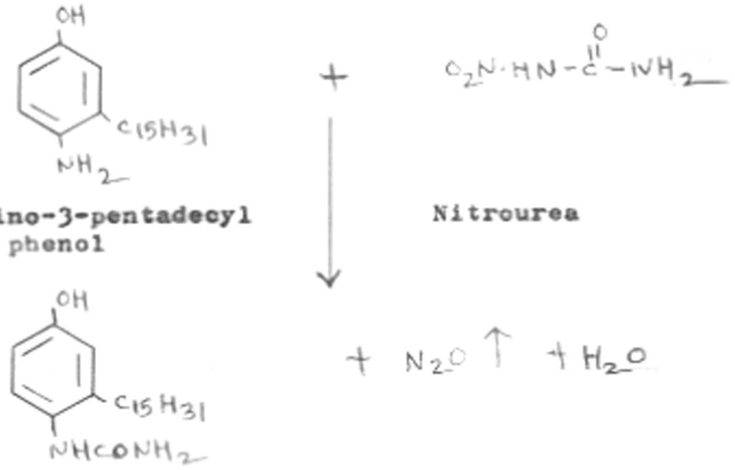
diazonium chloride of sulphanilic acid

4-amino-3-pentadecylphenol (III)

Monoazo dye

## 4-hydroxy-2-pentadecyl-1-phenyl urea (IV)

4-Amino-3-pentadecyl phenol was reacted with nitrourea in 50% aqueous ethanol, when the crude monoaryl urea was obtained. After crystallizing from ethanol, a white crystalline powder was obtained. m.p. 142°-143°C.



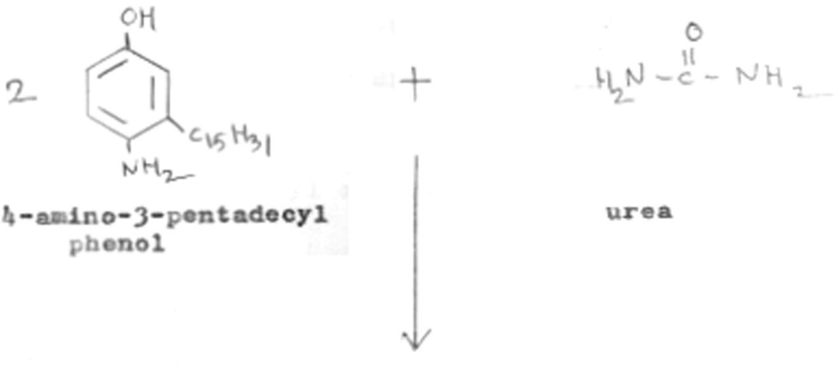
4-amino-3-pentadecyl phenol

Nitrourea

4-hydroxy-2-pentadecyl-1-phenylurea (IV)

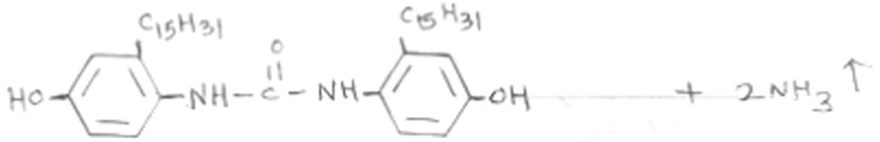
## N,N′-Di(4-hydroxy-2-pentadecyl phenyl) urea (V)

Urea (1 mol) was reacted with 4-amino-3-pentadecyl phenol (2.25 moles) in n-amylalcohol and the mixture was refluxed. On cooling, brownish residual mass resulted. The crude product after crystallizing from ethanol, melted at 174°-175°C.



4-amino-3-pentadecyl phenol

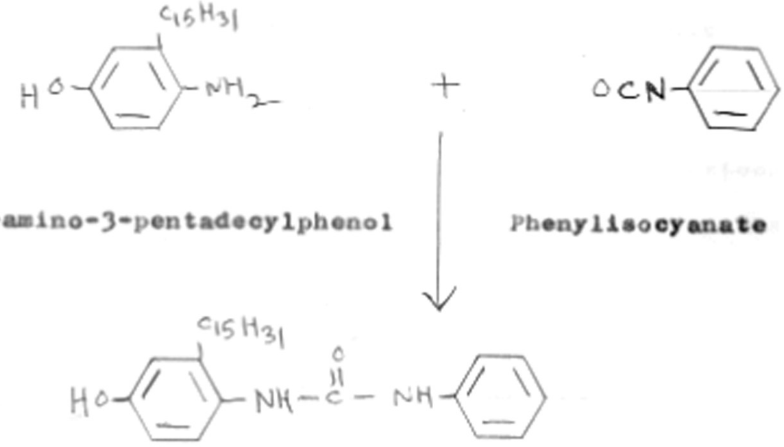
urea



N,N′-Di (4-hydroxy-2-pentadecyl phenyl) urea (V)

N-(2-pentadecyl-4-hydroxyphenyl) N′-phenyl urea (VI)

Phenyl isocyanate and 4-amino-3-pentadecyl phenol were reacted in dry benzene. After refluxion and cooling, a white powdery mass separated. It was crystallized from ethanol, yielding white crystals. m.p. 162°-163°C.



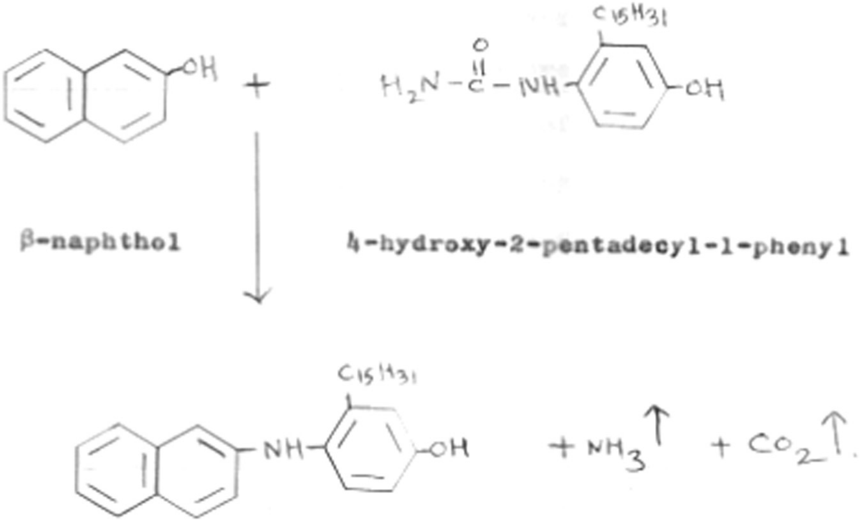
4-amino-3-pentadecylphenol

Phenylisocyanate

N-(2-pentadecyl-4-hydroxyphenyl)N' phenyl urea (VI)

2-pentadecyl-4-hydroxyphenyl-β-naphthyl amine (VII)

4-Hydroxy-2-pentadecyl-1-phenyl urea (IV) and β-naphthol were condensed at 250°-260°C for 8 hours. After removing the unreacted β-naphthol, and distilling the condensation product under vacuum, gave a semisolid mass of 2-pentadecyl-4-hydroxy phenyl-β-naphthyl amine.



β-naphthol

4-hydroxy-2-pentadecyl-1-phenyl urea

2-pentadecyl-4-hydroxyphenyl-β-naphthyl amine (VII)

## Evaluation of antioxidants in Natural Rubber

The evaluation of antioxidants for use in elastomers and other polymers is complicated by many factors. The best inhibitor for one polymer is often ineffective in others, and a good antioxidant for polymer stabilization may be of little value in a vulcanizate. Problems of solubility, and volatility limit the use of some materials at higher temperatures.

In the last two decades, voluminous research work has been done all over the world for the testing of accelerated ageing of rubber by the introduction of new physical methods. In particular the determination of penetrating oxidation has suffered until now because of the normal methods of testing, i.e.

(1) Oxidation in oxygen bomb after Bierer-Davis
oxygen at 21 atm. gauge, 60 or 70°C.

(2) Oxidation in hot air without pressure at 70°C.

These two methods require a great deal of time for the assessment of the antioxidants in rubber stocks. Oxygen absorption measurements offer a useful and quick method for comparing antioxidants in a given material under controlled conditions. This method is based on the fact that the ageing of rubber is always associated with the absorption of oxygen. If finely milled vulcanizates are exposed to oxygen at an appropriate temperature there occurs a rapid consumption of oxygen by the rubber, whose course can be accurately measured. Rubber stocks, inhibited with antioxidants absorb oxygen slowly, while very rapid absorption is observed in unprotected stocks. Hence the amount of oxygen absorbed in a given time, is a measure of the ageing properties.

Duffraisse[26] was the first to describe an apparatus in which oxygen absorption is determined by manometric measurement of the amount of gas consumed. Technically speaking the apparatus is satisfactory but the relatively complicated conversion from the pressure change to the volume decrease is unfavourable, apart from not being absolutely accurate.

A volumetric process has been described by Kohman,[27] Amerongen,[28] and particularly by Shelton and coworkers,[29] and in a technical service bulletin.[30]

## Fabrication of the oxygen absorption apparatus for oxidation studies

The apparatus initially assembled for volumetric oxygen absorption was adapted from Kohman[27] and has been fully described by Shelton and Winn.[29a] This unit was significantly improved by substituting an aluminium block for the oil bath as a source of heat at constant temperature as described in detail by Blum, Shelton and Winn.[29c] A recent adaptation of a commercially produced aluminium ageing block has resulted in a volumetric gas absorption unit with performance superior to that of previous units.[29e] In the present investigation, a quantitative oxygen absorption apparatus similar to that developed by Shelton and co-workers[29e] of Case Institute of Technology, Cleveland, Ohio, U.S.A., was fabricated in this laboratory. A photograph of the complete assembly of the oxygen absorption apparatus is shown in Fig. 2.

The constant temperature section consists of a modification of a Scott Tester's standard model LG aluminium ageing block heating bath, 15 inches high, 23 inches in diameter, and weighing about 400 pounds. The block contains 28 holes, approximately 12 inches deep (including insulation) and 1 1/2 inches in diameter, for inserting sample tubes. Fourteen holes are located on a 5 1/2 inch radius from the centre and fourteen holes are located on a 7 1/2 inch radius. The unit was modified to hold sample tubes with ground glass joints by counter boring the outer row of fourteen holes 1 3/8 inches into the aluminium block (3 3/8 inches including insulation) and two inches in diameter. Four 1000-watt strip heaters on the circumference of the block and a Fenwal thermo-regulator provide maximum temperatures in the range of 290°C and control within ± 0.25°C.

The commercial ageing block, after modification as described above,was mounted within an octagonal-shaped carriage with the control panel utilizing one side of the octagon, as may be seen in Fig. 2. On each of the seven remaining sides are mounted two water-jacketed burettes and two steel rode as runners for the levelling bulb clamps. The burettes are held to the frame by ordinary broom clamps to facilitate easy dismantling for cleaning. The burettes are connected to the sample tubes through three-way stopcocks which also join to a manifold on the top of the unit for evacuating and filling the sample tubes. Short sections of Tygon tubing (transparent P.V.C. tubing) are used to seal these connections.

The frame is constructed of 1 1/2 x 1 1/2 x 1/4 inch angle iron and is mounted on four truck casters for easy moving. Funnel support arms are mounted on the lower part of the frame for holding the levelling bulbs when not in use or when evacuating the sample tubes. The overall height of 30 inches makes the unit low enough for easy loading from the top.

The sample tubes are ten inches long and the upper ends are made from 40/50 ground glass joints. Selected nominal 38 mm. o.d. Pyrex tubing is used to make the sample tube walls. This diameter gives a snug fit in the ageing block holes. The caps are made from 40/50 inner members with drip tips. A 2 mm. capillary tubing is sealed through the center of the cap. The space surrounding the capillary tubing is evacuated and permanently sealed. This vacuum seal reduces convection cooling from the top and gives much better temperature distribution within the sample tube than does the ordinary open cap. In the whole assembly, there are in all fourteen units of absorption tubes and fourteen gas burettes.

The assembled absorption tubes (containing the appropriate weight of dumbbell shaped rubber sample suspended from the hooks and a small lump of calcium oxide to absorb water vapour and carbon dioxide generated during oxidation) are placed in the constant-temperature aluminium block and connected to the gas burettes. Throughout the present investigation the operating temperature of the block was kept at 90° ± 0.25°C.

All tubes are then evacuated simultaneously through the manifold to remove the air from the system and as much as possible of the dissolved and adsorbed gases from the samples. Oxygen is then admitted, and the alternate evacuation and admission of oxygen repeated three times. The three-way stop-cocks at the top of each burette are then turned so as to disconnect the manifold while allowing the absorption tube and gas burette of each independent unit to remain connected. The levelling bulbs are set to give the proper differential of mercury so that the total pressure in each tube is 760 mm. The initial volume is read and recorded, together with the barometric pressure and jacket temperatures. After appropriate time intervals, the pressure is adjusted to 760 mm. by setting the levelling bulb at the proper differential before the next set of readings is taken. All volume changes are calculated to a reference temperature of 25°C, and are reported as ml. of oxygen absorbed per gm. of polymer in the sample. For this purpose the observed volume of oxygen in each burette as measured at water jacket temperature is correct to 25°C. The rest of the system remains at constant volume and temperature except for the upper portion of the absorption tubes and the capillary connecting tubes, which are exposed to the temperature of the room. Small variations due to such factors are adjusted by the use of control tubes. Any change in the corrected volumes of the control tubes can then be applied directly to the corrected volumes of each sample tube, and the difference between the resulting volume for two successive readings represents the volume absorbed.

All samples are run in duplicate tubes and the results averaged. The readings were taken for 5 days at regular time intervals of 24, 48, 72, 96 and 120 hours respectively.

N,N$'$-Di(4-hydroxy-2-pentadecyl phenyl) urea (sym. urea of 4 APP), N-(2-pentadecyl-4-hydroxy phenyl) N$'$-phenyl urea (unsym. urea of 4 APP) and (2-pentadecyl 4-hydroxy phenyl β-naphthylamine (substituted PBN from 4 APP), all the three newly synthesized compounds were evaluated in natural rubber gum compound ASTM-2A, and channel black compound ASTM-3A. [A.S.T.M. D15-64T(1965), P.1]. A blank was run which contained no antioxidant. Tables I and II describe the recipes of these compounds. The mixes were made on a laboratory type 6" x 12" mixing mill.

The vulcanizate sheets cured under optimum conditions were taken and dumbbells were cut out from them. Duplicate samples of the dumbbells were taken for oxidation study, and the rate of oxygen absorbed by the dumb-bells was determined in an oxygen absorption apparatus described above. The ageing studies were carried out in pure oxygen at atmospheric pressure and at a temperature of 90°C. The samples were withdrawn in duplicate after a definite interval of time (24, 48, 72, 96 and 120 hrs respectively) and the oxygen absorbed per gm. of polymer along with the corresponding physical properties of the different antioxidant containing samples were noted. These results along with the corresponding physical properties, are given in Tables III and IV.

## TABLE I. NATURAL RUBBER GUM COMPOUND RECIPE

| | Blank (no anti-oxidant) | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Smoked sheet RMA-1-X | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 |
| Sulphur | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| MBTS | 1 | 1 | 1 | 1 | 1 |
| Antioxidant | | | | | |
| Sym. urea from 4 APP | - | 1 | - | - | - |
| Unsym. urea from 4 APP | - | - | 1 | - | - |
| Nonox D(ICI) | - | - | - | 1 | - |
| Substituted PBN from 4 APP | - | - | - | - | 1 |

Cure time: 40' optimum at 140°C/2000 p.s.i.

## TABLE II. NATURAL RUBBER CHANNEL BLACK COMPOUND RECIPE

| | Blank (no anti-oxidant) | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Smoked sheet RMA 1-X | 100 | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 3 | 3 | 3 | 3 | 3 |
| Sulphur | 3 | 3 | 3 | 3 | 3 |
| M.B.T.S. | 1 | 1 | 1 | 1 | 1 |
| Carbon black E.P.C. (Spheron 9) | 50 | 50 | 50 | 50 | 50 |
| Antioxidant | | | | | |
| Sym. urea from 4 APP | - | 1 | - | - | - |
| Unsym. urea from 4 APP | - | - | 1 | - | - |
| Nonox D (ICI) | - | - | - | 1 | - |
| Substituted PBN from 4 APP | - | - | - | - | 1 |

Cure time: 40' optimum at 140°C/2000 p.s.i.

### TABLE III. AGEING DATA FOR NATURAL RUBBER GUM COMPOUND IN OXYGEN AT 90°C, 760 mm.

| Antioxidant concentration P.h.r. | Ageing period in hrs. | $O_2$ absorbed ml/gm polymer (25°C) | Tensile strength psi | Modulus M200 psi | Elongation at break % |
|---|---|---|---|---|---|
| A. Blank (No added antioxidant) | | | | | |
| 0.0 | 0.00 | 0.0 ml | 2593 | 143 | 800 |
| | 24 | 6.9 | 703 | 96 | 600 |
| | 48 | 12.1 | 163 | 58 | 500 |
| | 72 | 30.4 | 72 | 48 | 400 |
| | 96 | 42.1 | 46 | 35 | 300 |
| | 120 | 55.7 | 24 | 24 | 200 |
| B. Phenyl-β-naphthylamine (Nonox D ICI) | | | | | |
| 1.0 | 0.0 | 0.0 | 2905 | 145 | 850 |
| | 24 | 2.9 | 2704 | 143 | 750 |
| | 48 | 3.5 | 2541 | 160 | 675 |
| | 72 | 5.0 | 2554 | 186 | 650 |
| | 96 | 6.0 | 2577 | 167 | 650 |
| | 120 | 6.9 | 1709 | 158 | 600 |
| C. Substituted PBN from 4-amino-3-pentadecyl phenol | | | | | |
| 1.0 | 0.0 | 0.0 | 2802 | 169 | 825 |
| | 24 | 1.3 | 3272 | 169 | 750 |
| | 48 | 2.5 | 2665 | 167 | 700 |
| | 72 | 3.5 | 3115 | 196 | 650 |
| | 96 | 4.4 | 2957 | 193 | 650 |
| | 120 | 5.1 | 2393 | 191 | 650 |
| D. Symmetrical urea from 4 amino-3-pentadecyl phenol | | | | | |
| 1·0 | 0.0 | 0.0 | 2770 | 142 | 800 |
| | 24 | 3.1 | 3103 | 169 | 750 |
| | 48 | 4.8 | 2306 | 176 | 700 |
| | 72 | 8.3 | 1885 | 172 | 650 |
| | 96 | 11.1 | 1115 | 145 | 600 |
| | 120 | 13.2 | 1021 | 134 | 500 |
| E. Unsymmetrical urea from 4 amino-3-pentadecyl phenol | | | | | |
| 1.0 | 0.0 | 0.0 | 2627 | 144 | 800 |
| | 24 | 0.6 | 2916 | 183 | 750 |
| | 48 | 3.0 | 2465 | 174 | 700 |
| | 72 | 5.5 | 2208 | 192 | 650 |
| | 96 | 5.8 | 1733 | 174 | 600 |
| | 120 | 9.4 | 1103 | 157 | 500 |

TABLE IV. AGEING DATA FOR NATURAL RUBBER CHANNEL BLACK COMPOUND IN OXYGEN AT 90°C, 760 mm.

| Antioxidant concentration P.h.r. | Ageing period in hrs. | $O_2$ absorbed ml/gm polymer (25°C) | Tensile strength psi | Modulus M200 psi | Elongation at break % |
|---|---|---|---|---|---|
| | A. Blank (no added antioxidant) | | | | |
| 0.0 | 0.0 | 0.0 | 2857 | 865 | 400 |
| | 24 | 14.6 | 831 | 562 | 300 |
| | 48 | 23.4 | 496 | 496 | 200 |
| | 72 | 37.4 | 434 | 434 | 200 |
| | 96 | 48.8 | 384 | 384 | 200 |
| | 120 | 69.3 | 373 | 373 | 200 |
| | B. Phenyl-β-naphthylamine (Nonox D ICI) | | | | |
| 1.0 | 0.0 | 0.0 | 3124 | 999 | 500 |
| | 24 | 7.6 | 2852 | 1105 | 450 |
| | 48 | 8.6 | 2088 | 1071 | 400 |
| | 72 | 16.8 | 1559 | 944 | 300 |
| | 96 | 22.7 | 1002 | 831 | 250 |
| | 120 | 33.8 | 640 | 640 | 200 |
| | C. Substituted PBN from 4-amino 3-pentadecyl phenol | | | | |
| 1.0 | 0.0 | 0.0 | 3320 | 1314 | 500 |
| | 24 | 6.4 | 3282 | 1272 | 450 |
| | 48 | 6.3 | 2721 | 1089 | 400 |
| | 72 | 15.3 | 1802 | 1030 | 300 |
| | 96 | 20.1 | 993 | 886 | 250 |
| | 120 | 27.8 | 865 | 865 | 200 |
| | D. Symmetrical urea from 4-amino 3-pentadecyl phenol | | | | |
| 1.0 | 0.0 | 0.0 | 3158 | 907 | 450 |
| | 24 | 7.5 | 1769 | 917 | 350 |
| | 48 | 13.8 | 1059 | 800 | 300 |
| | 72 | 16.2 | 717 | 717 | 200 |
| | 96 | 27.1 | 591 | 591 | 200 |
| | 120 | 41.1 | 632 | 632 | 200 |
| | E. Unsymmetrical urea from 4-amino 3-pentadecyl phenol | | | | |
| 1.0 | 0.0 | 0.0 | 3213 | 940 | 450 |
| | 24 | 8.6 | 1893 | 897 | 350 |
| | 48 | 11.0 | 967 | 805 | 300 |
| | 72 | 14.3 | 617 | 617 | 200 |
| | 96 | 29.4 | 612 | 612 | 200 |
| | 120 | 45.4 | 424 | 424 | 200 |

### (iii) Discussion

The one important chemical test of an antioxidant is its effect on the rate of oxygen absorption. Buist[31] published a critique of oxygen absorption tests in 1956. Oxygen absorption is a meaningful test only in so far as it can be related to changes in physical properties of the rubber. Shelton and co-workers[32] related volume of oxygen absorbed to the tensile properties of SBR and natural rubber. The relation between degradation and oxygen absorption is discussed in Shelton's review.[33] Shelton pointed out that modulus is much more sensitive than tensile strength to changes in relative amounts of chain scission and cross-linking. Shelton made use of oxygen absorption method for the evaluation of staining and non-staining type of antioxidants.[34,1,35,10] Spacht et al.[36] in comparing antioxidants, related oxygen absorption to creep and air-bomb ageing at 120°C.

## Relation between antioxidant activity and structure

There is a good deal of information now available on the relationship between the antioxidant activity of phenol and amine type antioxidants and their structure. In case of phenols, (a) Electron releasing groups (e.g. methyl, methoxy, etc.) in the ortho and para positions markedly increase the antioxidant activity. (b) Electron attracting groups (e.g. nitro, carboxy, halogen etc.) decrease activity. (c) α-Branched ortho alkyl groups (e.g. tert-butyl) considerably increase antioxidant activity, whereas such groups in the para position decrease it.

The mechanism of amine antioxidant action under autoxidation conditions is basically similar to that of phenols. As with the amine type antioxidants, three structural factors need to be satisfied for the highest activity. They are - (a) effective delocalisation of the unpaired electron formally resident on the nitrogen, (b) high electron density on the nitrogen to facilitate electron transfer to the alkyl peroxy radical, and (c) sufficient steric protection of the nitrogen atom to reduce chain transfer by the arylamino radical. In contrast to the phenols, this is achieved better by substitution on the nitrogen than in the ortho positions of the aromatic ring. N-Aryl substituents also have a powerful augmenting effect upon the antioxidant activity, and some of the most important industrial antioxidants are diarylamines. Electron releasing groups in the para position of the benzene ring and particularly dialkylamino and alkoxy have even more pronounced effect which has been studied extensively by Kuzminskii and Angert[37-39] and Doede[40] in rubber.

On the basis of the fundamental concepts of organic chemistry, the inhibiting action of amines is usually related to abstraction of the hydrogen atom of the NH group.

Kuzminskii and Angert[39] studied the mobility of the hydrogen atom in the NH group of the antioxidant Phenyl-β-naphthyl amine and the corresponding N-methyl derivative. It is evident that the absence of hydrogen of the NH group leads to practically full suppression of the amine inhibition power, i.e. primarily the N-H bond is responsible for chain termination. Some decrease in the inhibitor effectiveness is also observedin case of substitution of hydrogen atom in $\alpha$-position of the naphthalene nucleus (e.g. Phenyl-$\alpha$-methyl-$\beta$-naphthyl amine).

It is known that secondary amines do not inhibit polymerization and also do not influence the process of thermal crosslinking of polymers if oxygen is absent from the system. On the basis of these facts it can be stated with a high degree of certainty that abstraction of hydrogen from the amine occurs as a result of the interaction of the latter with the oxygen containing radical of the polymer chain. On abstraction of the hydrogen atom from the amino group, a phenyl-naphthyl radical is formed, which combines with the polymer chain. Inhibition of an oxidation process by secondary amines is connected with rupture of the N-H bond and formation of a radical with free valance at nitrogen atom, the effectiveness of such inhibitors must increase with decreasing activity of the radical formed and correspondingly decreasing N-H bond energy. From the relationship between the reactivity ofmolecules and their structure, it follows that the relative activity of radical $A^\cdot$ and the energy of A-H bond which is a function of activity, decreases with an increase in the conjugation energy of the radical "free" electron.

To throw light on the relationship between the effectiveness of inhibitors of the secondary amine type antioxidants, Kuzminskii and co-workers investigated the inhibiting action of series of amines having different numbers of aromatic nuclei. This series consisted of the following compounds: diphenyl amine, Phenyl-β-naphthylamine and di-β-naphthylamine. The evaluation of the relative relativity of these amines in reactions connected with N-H bond rupture was by the speed of their interaction with α,α-diphenyl-β-picrylhydrazyl, a low activity radical.

According to literature data this radical reacts with amines and on abstracting the hydrogen atom from the amino group, is transformed into α,α-diphenyl-β-picrylhydrazine. The kinetics of such reaction can be followed easily by measuring the gradual decrease in the intensity of the violet colour of the benzene solutions of both components, which is connected with the disappearance of hydrazyl.

Inhibiting effect of amines on rubber oxidation showed that an increase in the effect of conjugation does contribute to the growth of inhibiting power of amine. This leads to the fact that there is a direct relationship between the reactivity and the inhibiting power of the compounds investigated.

The N-H bond energy must also change if various substituents are introduced in the p-position to the benzene nucleus. The effect of this structural factor of the mobility of the hydrogen of the NH group and on the inhibiting power of the amine was investigated in the following compounds: Phenyl-β-naphthylamine, p-tolyl-β-naphthyl-amine, p-chloro-phenyl-β-naphthylamine, p-methoxy phenyl-β-naphthylamine, p-hydroxy-phenyl-β-naphthylamine and O,O,p-trinitrophenyl-α-naphthylamine.

Evaluation of the mobility of the hydrogen atom of the amino group on the basis of the reaction with hydrazyl, showed that the reaction rate constant values were gradually increased in the order phenyl-β-naphthyl amine, p-tolyl-β-naphthyl amine and p-methoxy phenyl-β-naphthylamine. The reaction with p-hydroxyphenyl-β-naphthylamine took place instantaneously. Thus the substituents can be arranged in the following order, according to their influence on the increase in the reactivity of molecule in the reactions connected with rupture of the N-H bond:

$$OH > OCH_3 > CH_3 > H$$

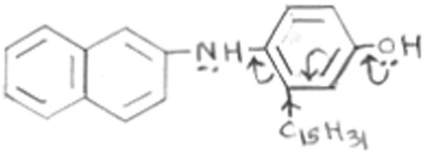
It was further shown while studying the kinetics of rubber oxidation in the presence of amines that the rate of oxidation as well as the length of induction period differed greatly in the presence of various amines. A conclusion drawn from the above results is that the inhibiting action of amines depends on the nature of the p-substituents in the benzene nucleus, the positive influence following the order:

$$OH > OCH_3 > CH_3 > H > Cl > NO_2$$

The position of the substituents in this series coincides with their positions if arranged according to their effect on the reactivity of amines and also according to the electron doner properties of the radicals with respect to the benzene nucleus. It follows, then, that an increase in the electron density at the carbon atom joined to the nitrogen atom leads to the weakening of the N-H bond, and thus to an increase in the inhibiting power of the amine.

The rubber oxidation inhibiting property of a number of amines was also studied with respect to the structural changes occurring in the rubber network. The kinetics of change in the number of crosslinks, present in a unit volume of a heat vulcanizate undergoing oxidation in the presence of various inhibitors, showed rate of reactivity in the same order as found previously.

In the present investigation, substituted phenyl-β-naphthyl amine prepared from 4-amino-3-pentadecyl phenol showed better ageing properties than the conventional PBN, in both natural rubber pure gum compound and channel black compound. The structure and the mechanism of the antioxidant action of this compound is given below.



$$AH + ROO^{\cdot} \longrightarrow ROOH + A^{\cdot}$$

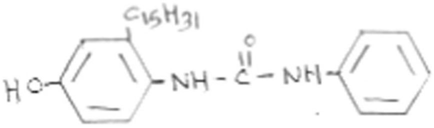
The combined electronic effect of the phenolic hydroxyl group in the para position and the long alkyl chain $C_{15}H_{31}$ in the ortho position helps in quick release of the hydrogen atom for termination of the peroxy radical. It may be mentioned here that "Paraoksineozon", the Russian commercial rubber antioxidant is 4-hydroxy phenyl-β-naphthyl amine, which has been used in preference to Phenyl-β-naphthyl amine (PBN) for its superior antioxidant properties.[41]

Oxygen Absorption

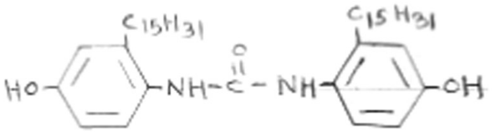
Fig. 3 shows the rate of oxygen absorbed by natural rubber gum compound having PBN and substituted PBN as antioxidants and having no antioxidant (blank). This figure clearly shows the better protection of the rubber in ageing, by substituted PBN. Similar are the observations noted when the tensile strength, 200% modulus properties of the aged gum compound are plotted against the oxygen absorbed (Figs. 4 and 5).

In natural rubber channel black compound (Fig. 6) the rate of oxygen absorption is uniform upto 48 hours in both the substituted PBN and the PBN. After this period, PBN sample gradually absorbs more oxygen than the substituted PBN sample. There is a marked rapid oxygen absorption where there is no antioxidant (blank). The changes in the physical properties, tensile strength, 200% modulus, with respect to the volume of oxygen absorbed are shown in Figs. 7 and 8 respectively.

The oxygen absorption values with respect to time of a natural rubber gum compound containing the two aryl ureas are given in Fig. 9. It is observed here that the rubber samples containing unsymmetrical aryl urea absorb less of oxygen, confirming the views noted earlier. The corresponding tensile strength and 200% modulus values with respect to oxygen absorption are given in Figs. 10 and 11. In natural rubber channel black compound, it is also observed that the unsymmetrical urea has a property of absorbing less oxygen than the symmetrical urea (Fig. 12). The tensile strength and 200% modulus values with respect to oxygen absorption in a channel black compound are given in Figs. 13 and 14. The pronounced behaviour shown by (I) can perhaps be explained as follows:

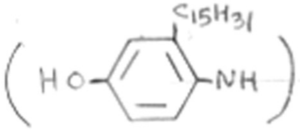


(I)



(II)

In the symmetrical urea (II), the balance of electrons round >C = O group is nearly equal because of the presence of two similar groups.



But in case of unsymmetrical urea (I), because of the presence of the phenolic hydroxyl group in para position and the long alkyl chain in ortho position to N-H, an imbalance of electron density around the >C=O is created. This facilitates the abstraction of hydrogen atom from the -NH group for reaction with a peroxy radical in rubber and thus becoming a more effective antioxidant than (II).

## Conclusion

More effective antioxidants have been prepared from a naturally occurring alkyl phenol. It is shown experimentally that the antioxidant action of one of these new compounds (substituted PBN from 4 amino 3-pentadecyl phenol) was better than the conventional antioxidant used commercially (PBN). The activity of these compounds was correlated to their structure on the electronic theory.

## (iv) Experimental

### 3-Pentadecadienyl phenol (Anacardol) (I)

Raw commercial cashewnut shell liquid (heat extracted) (900 gm) was distilled from a 2-litre round bottom flask, under vacuum. The flask was heated slowly till the initial frothing had subsided. 450 gms of brown coloured distillate (yield 50%) was collected between 190°-240°C/2-4 mm. Hg Pressure.[42] This was redistilled to give pale yellow anacardol $n_D^{30}$ 1.5080 (410 gms b.p. 195°-200° C/2 mm.).

Analysis: Found, C, 83.80; H, 10.56%.

$C_{21}H_{32}O$ requires C, 83.94; H, 10.76%.

### 3-Pentadecyl phenol (Tetrahydroanacardol) (II)

Anacardol (300 gms) was hydrogenated at 70°C in a Parr autoclave under 600 lbs/sq.in. pressure of hydrogen after the addition of 3-5 gms of Raney nickel catalyst. When no more hydrogen absorption was noticed the hydrogenation was stopped and the product filtered and crystallized from petrol ether (40°-60°). 3-Pentadecyl phenol (tetrahydroanacardol) (270 gms.) 90% yield was obtained as white waxy solid, m.p. 50°-51°C.[42] b.p. 215°-220°C/4 mm.

Analysis: Found, C, 83.16; H, 11.41%

$C_{21}H_{36}O$ requires C, 82.83, H, 11.92%.

### 4-Amino-3-pentadecyl phenol (III)

7.5 gms. (0.025 mole) of 3-pentadecyl phenol dissolved in 3.9 gms(0.0687 mole) of potassium hydroxide in 50 ml. of 95% ethanol was placed in 1 litre, 3 necked flask fitted with a stirrer, and was cooled to 0-5°C. To this was added diazonium chloride prepared from 5.25 gms. of sulphanilic acid dihydrate suspended in 25 ml. of ethanol. The resulting red dye solution was stirred for 2 hours and was reduced by saturated solution of 11.25 gms. of sodium dithionite at 75°C on a water bath. A solution of 4 gms of acetic acid in 30 ml. of water was added to it. It was refluxed for 1 hour when the red colour of the dye changed to pale tan colour. The reduced solution was poured in a beaker and was cooled to 0°C when crude 4-amino-3-pentadecyl phenol separated. It was filtered off and was crystallized from petrol ether. (100-120°). The resulting amino phenol had a m.p. 105°-106°C,[43] (75% yield).

Analysis: Found, C, 79.09; H, 11.28; N, 4.02%

$C_{21}H_{37}ON$ requires C, 78.94; H, 11.67; N, 4.3%.

<u>4-Hydroxy-2-pentadecyl-1-phenyl urea</u> (IV)

3.2 gms. (1 mol.) of 4-amino-3-pentadecylphenol was taken in 20 ml. of 50% ethanol in a 100 ml. round bottom flask, fitted with a condenser. 1.2 gm. (1.5 mole) of nitrourea was added to it. The mixture was then refluxed on the water bath for 3 hours and cooled, when crude aryl urea separated. It was recrystallised from ethanol to give a white crystalline powder. m.p. 142°-143°C. Yield 2.5 gms. (78%).

Analysis: Found, C, 73.10; H, 10.54; N, 7.41%

$C_{22}H_{38}N_2O_2$ requires C, 72.93; H, 10.50; N, 7.73%

### N,N′-Di(4-hydroxy-2-pentadecyl phenyl) urea (V)

0.2 gms urea (1 mol), 2.4 gms. 4-amino-3-pentadecyl phenol (2.25 moles), and 20 ml. of n-amyl alcohol were taken in a 100 ml. round bottom flask fitted with a long air condenser. The mixture was refluxed on a wire gauge with an open flame burner. Initially a brisk evolution of ammonia took place. The mixture was refluxed for further 10 hours. At the end of this period, amyl alcohol was removed under vacuum when a brownish residual mass resulted. It was washed with petroleum ether (40°-60°) and was further crystallized from ethanol. Faint brown crystals weighed 1.2 gms. (50%). m.p. 174°-175°C.

Analysis: Found, C, 77.13; H, 11.19; N, 4.05%.

$C_{43}H_{72}N_2O_3$ requires C, 77.69; H, 10.84; N, 4.21%.

### N-(2-pentadecyl-4-hydroxy phenyl), N′-Phenyl urea (VI)

1.09 ml. of phenyl isocyanate (1 mol) and 20 ml. of pure dry benzene were taken in 100 ml. round bottom flask. 3.20 gms of 4-amino-3-pentadecyl phenol (1 mol) dissolved in 10 ml. of dry benzene was added to the first solution with constant stirring. The mixture was initially maintained initially between 40°-70°C. when a jelly like consistency of the reaction mixture was observed. The temperature was further raised and the mixture was refluxed on the water bath for 2 hours. After cooling a white solid powdery mass separated. It was filtered and was crystallized from ethanol, yielding white crystals. 2 gms. (62.5%) m.p.162°-163°C.

Analysis: Found C, 76.26; H, 9.19; N, 7.07%

$C_{28}H_{42}N_2O_2$ requires C, 76.70; H, 9.58; N, 6.39%

2-Pentadecyl-4-hydroxy phenyl-β-naphthyl amine (VII)

4-hydroxy-2-pentadecyl-1-phenyl urea (IV) 2 gms. (1 mol) and 1.2 gms β-naphthol (1.5 moles) were intimately mixed and were taken into 50 ml. round bottom flask, fitted with a long air condenser. The mixture was heated in a heating mantle to 250°-260°C for 8 hours. The molten mass was intermittently shaken and the sublimed β-naphthol deposited on the condenser wall was again added back to the flask. After completion of the heating period, the mass was cooled and was taken up with ether. It was washed with 5% NaOH solution to remove, unreacted β-naphthol. It was then washed with water till neutral and the ether extract dried over anhydrous sodium sulphate and filtered. After evaporating the ether a dark brown sticky viscous material was obtained. It was distilled under reduced pressure and 3 different fractions were collected.

| | |
|---|---|
| Ist fraction | - unreacted β-naphthol (about 0.2 gm). |
| IInd fraction | - B.P. 260°-270°C/1 mm. product contaminated with traces of β-naphthol. |
| IIIrd fraction | - B.P. 300°C/1 mm. (0.800 gms) a brown viscous semisolid which gave the correct analysis for the desired substituted naphthylamine. |

Analysis: Found, C, 82.99; H, 9.01; N, 3.38%.

$C_{31}H_{43}ON$ requires C, 83.58; H, 9.66; N, 3.1%

## Compounding of the rubber mixes

All the compounding ingredients were commercial rubber grade chemicals.

Mixing:- All the mixes given in Tables I and II were prepared on a conventional laboratory size 6" x 12" two roll rubber mixing mill. Rubber was masticated on a cold mill, immediately a band was formed. All the ingredients were then added according to the compounding recipes given in Tables I and II. Sulphur and accelerator were added at the end. The mix was cut thrice from either side and rolled six times through tight mill and sheeted out. The sheets of the mixes were rested overnight. (A.S.T.M. D15-64T (1965), P. 1).

Vulcanization:- The rubber sheets 6" x 6" x 0.075" were vulcanized in a laboratory type carver hydraulic press, with a temperature of $140^{\circ} \pm 1^{\circ}C$, and under 2000 lbs/sq.in. pressure for the specified time. Optimum cures were selected for the respective mixes.

## Determination of physical properties

From the vulcanized sheets dumb-bell shaped specimens were cut with "dumb-bell type C". The physical properties such as tensile strength elongation at break and modulus at 200% elongation of the vulcanizates were determined on a Scott-tensile testing machine, according to ASTM designation D412-64T(1965), p. 198. The rate of power actuated grip was 40 inches per minute and was kept uniform at all times.

Ageing of the dumb-bell shaped test specimens was carried out in the oxygen absorption apparatus as described previously. Oxidation of the samples was carried out in pure oxygen and at 90°C temperature, and 760 mm. pressure. The rate of oxidation was studied against the time (in hours) and the rate of degradation in physical properties (such as tensile strength, modulus at 200% elongation was studied as a function of oxygen absorbed per gm. of polymer. The samples were withdrawn for testing on 24, 48, 72, 96 and 120 hours respectively.

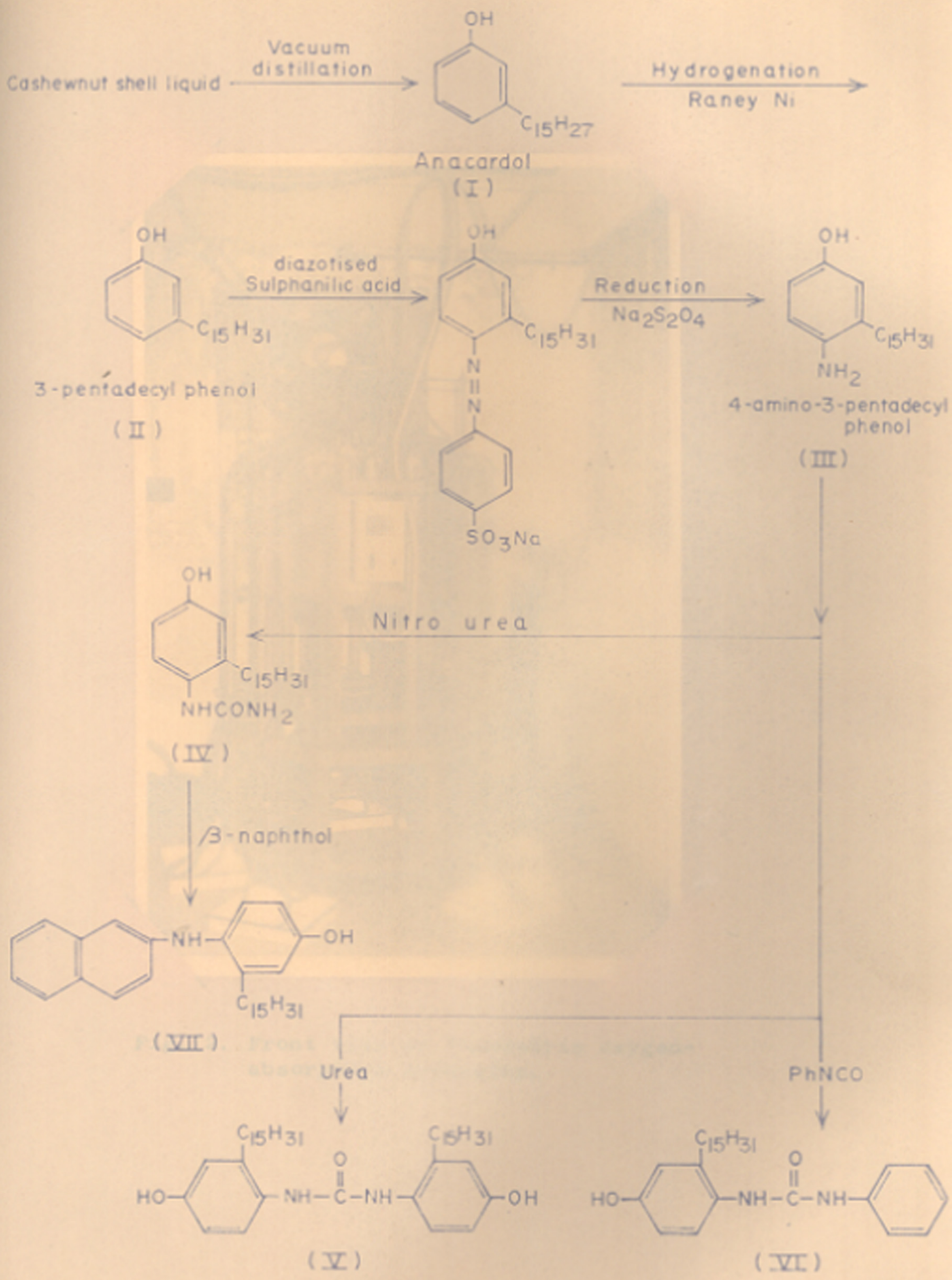

Cashewnut shell liquid
Vacuum distillation
OH
$C_{15}H_{27}$
Anacardol
(I)
Hydrogenation
Raney Ni
OH
$C_{15}H_{31}$
3-pentadecyl phenol
(II)
diazotised Sulphanilic acid
OH
$C_{15}H_{31}$
N
N
$SO_3Na$
Reduction
$Na_2S_2O_4$
OH
$C_{15}H_{31}$
$NH_2$
4-amino-3-pentadecyl phenol
(III)
Nitro urea
OH
$C_{15}H_{31}$
$NHCONH_2$
(IV)
β-naphthol
NH
OH
$C_{15}H_{31}$
(VII)
Urea
PhNCO
$C_{15}H_{31}$
HO
NH–C–NH
O
$C_{15}H_{31}$
OH
(V)
$C_{15}H_{31}$
HO
NH–C–NH
O
(VI)

Fig. 1

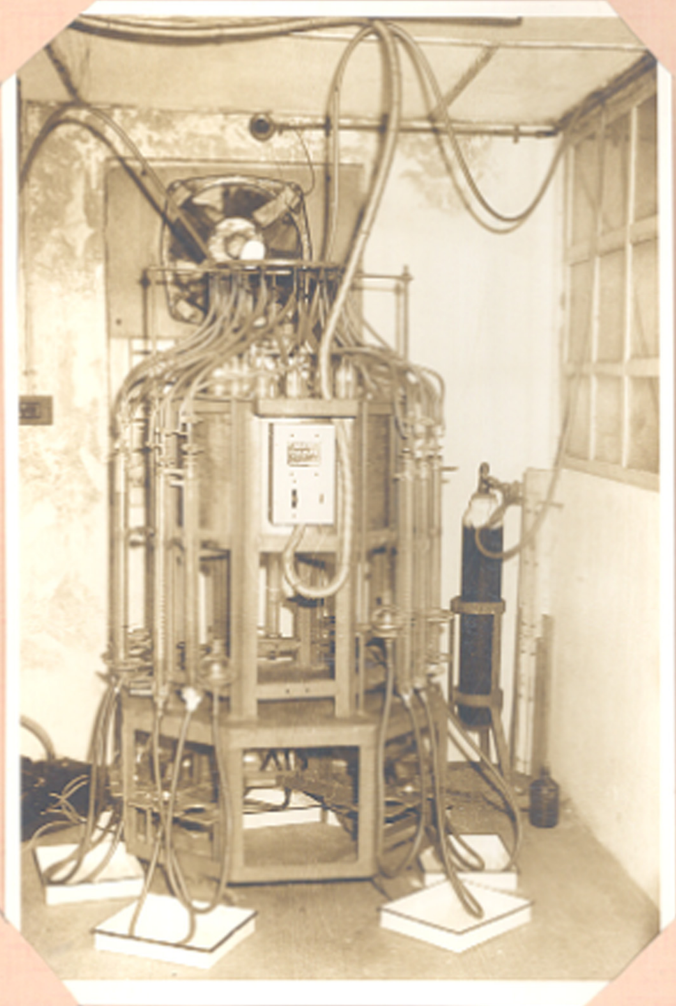


Fig. 2. Front view of Volumetric oxygen-absorption apparatus.

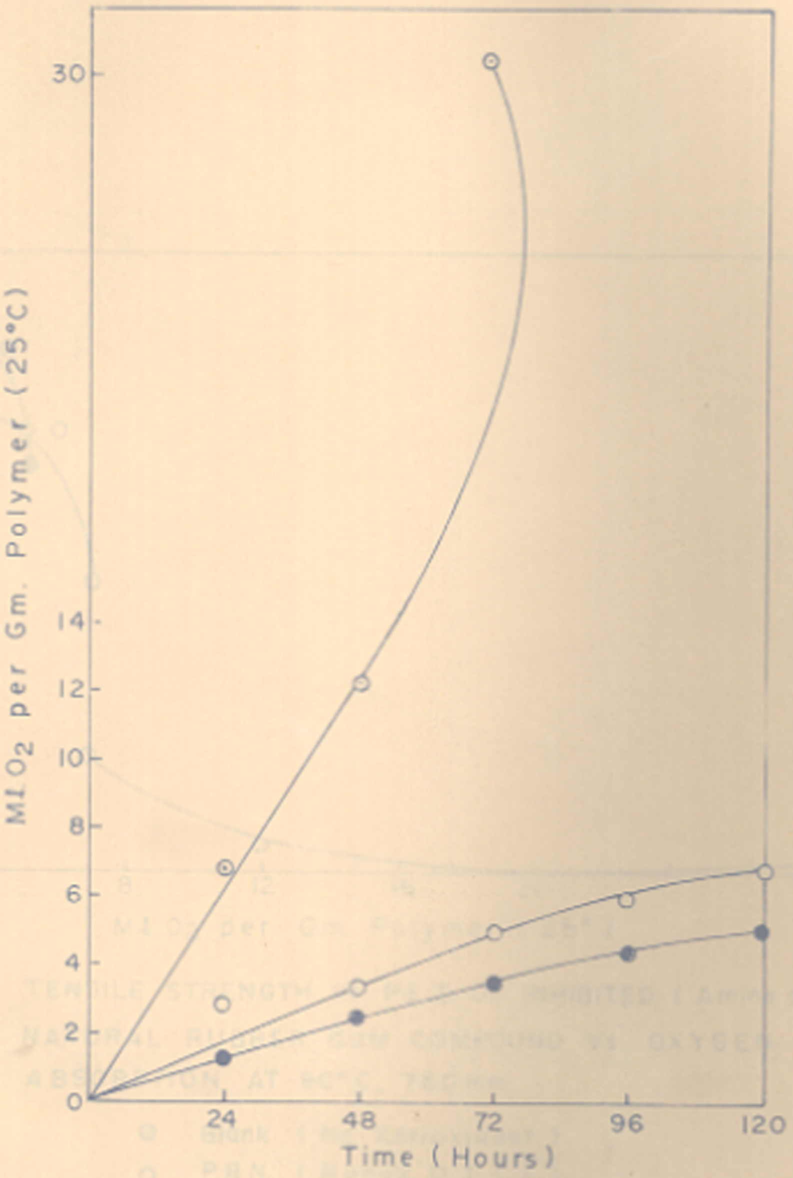


Fig.: 3 OXYGEN ABSORPTION OF INHIBITED ( Amine type ) NATURAL RUBBER GUM COMPOUND AT 90°C AND 760 mm.

⊙ Blank ( No Antioxidant )
○ P.B.N. ( Nonox D, I.C.I. )
● Substituted PBN of 4A.P.P.

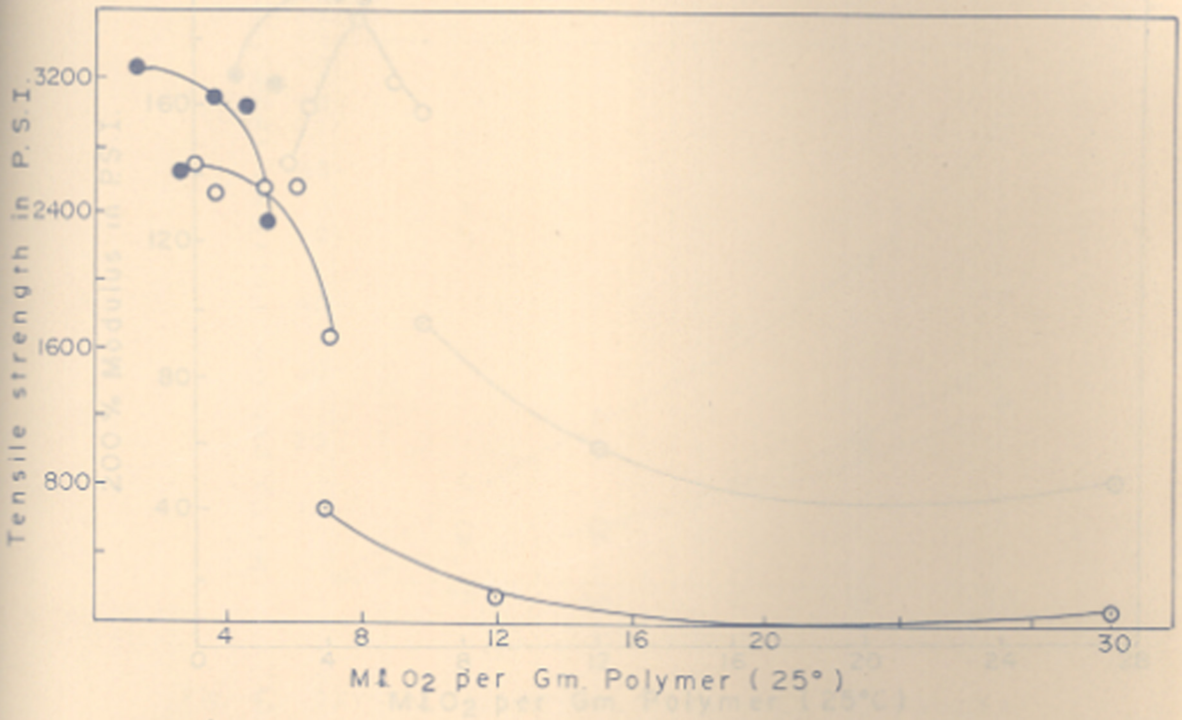


Fig. 4 TENSILE STRENGTH IN P.S.I. OF INHIBITED ( Amine type ) NATURAL RUBBER GUM COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank ( No Antioxidant )
○ PBN ( Nonox D, I. C. I. )
● Substituted PBN of 4 APP.

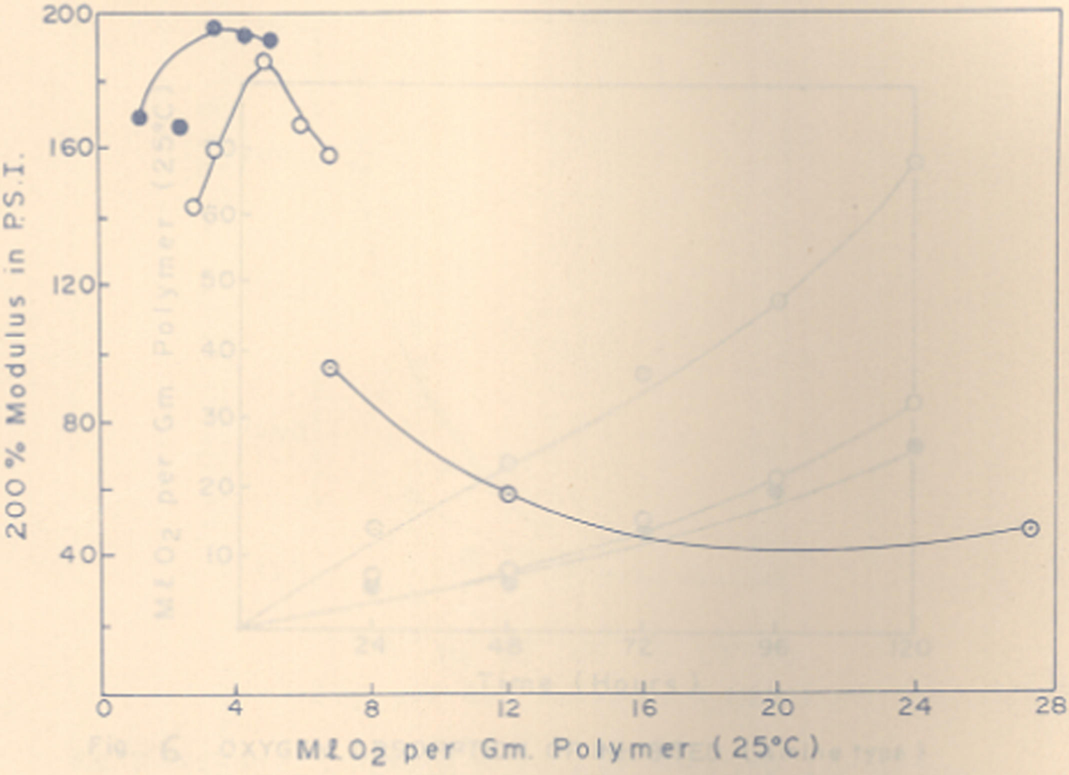


Fig. 5 200% MODULI IN P.S.I. OF INHIBITED (Amine type) NATURAL RUBBER GUM COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ PBN (Nonox D, I.C.I.)
● Substituted PBN of 4 A.P.P.

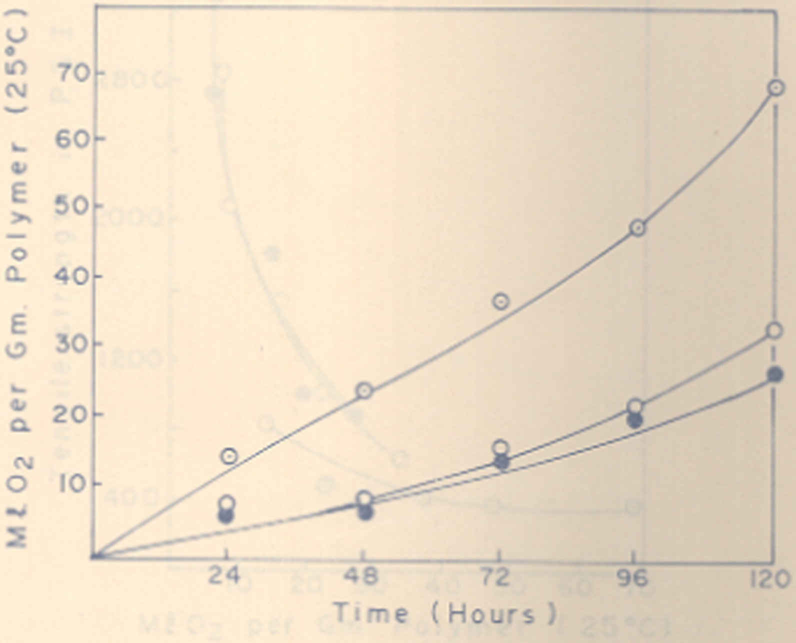


Fig. 6 OXYGEN ABSORPTION OF INHIBITED (Amine type) NATURAL RUBBER CHANNEL BLACK COMPOUND AT 90°C & 760 mm.

⊙ Blank (No Antioxidant)
○ P.B.N. (Nonox D, I.C.I.)
● Substituted PBN of 4 A.P.P.

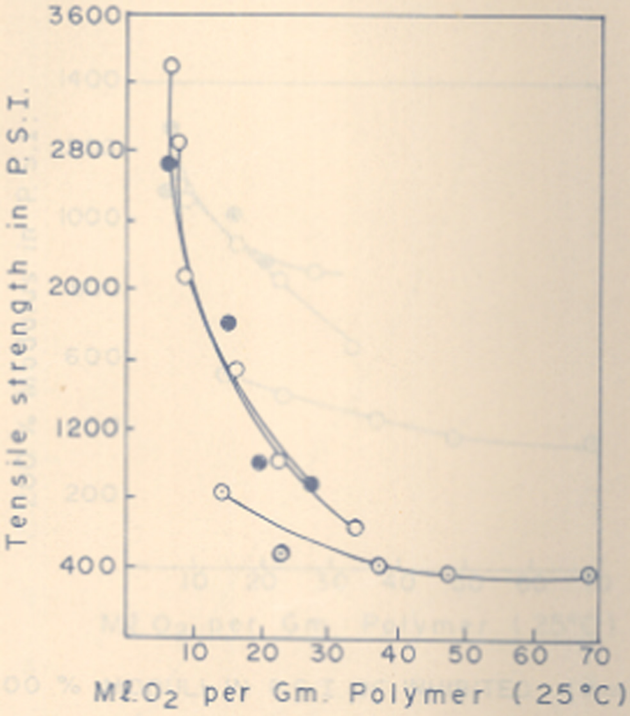


Fig. 7 TENSILE STRENGTH IN P.S.I. OF INHIBITED (Amine type) NATURAL RUBBER CHANNEL BLACK COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ PBN (Nonox D, I.C.I.)
● Substituted PBN of 4 A.P.P.

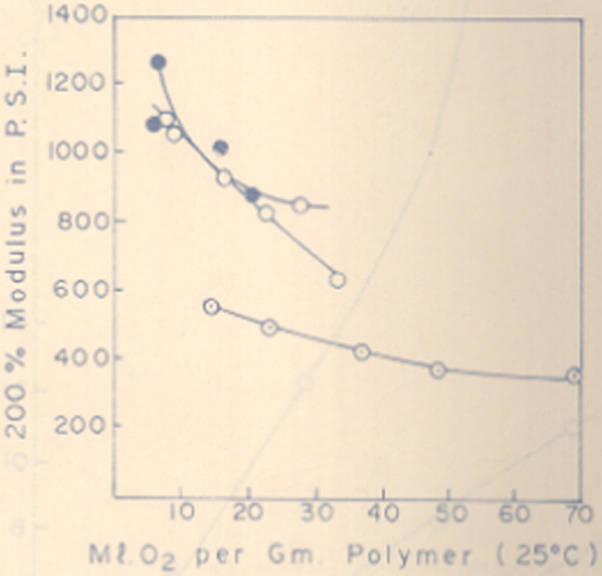


Fig. 8 200 % MODULI IN P.S.I. OF INHIBITED (Amine type) NATURAL RUBBER CHANNEL BLACK COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

- ⊙ Blank ( No Antioxidant )
- ○ PBN ( Nonox D, I.C.I. )
- ● Substituted PBN of 4 A.P.P.

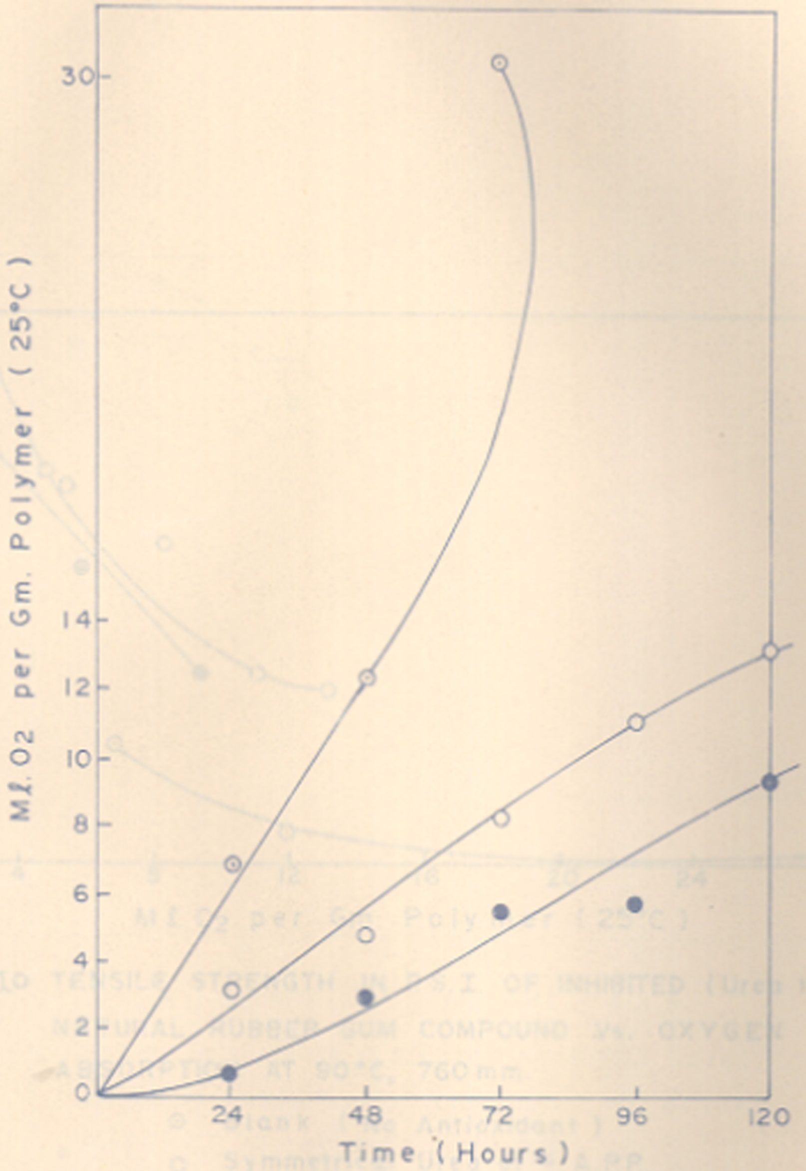


Fig. 9 OXYGEN ABSORPTION OF INHIBITED (Urea type) NATURAL RUBBER GUM COMPOUND AT 90°C AND 760 mm.

⊙ Blank ( No Antioxidant )
○ Symmetrical Urea of 4 A.P.P.
● Unsymmetrical Urea of 4 A.P.P.

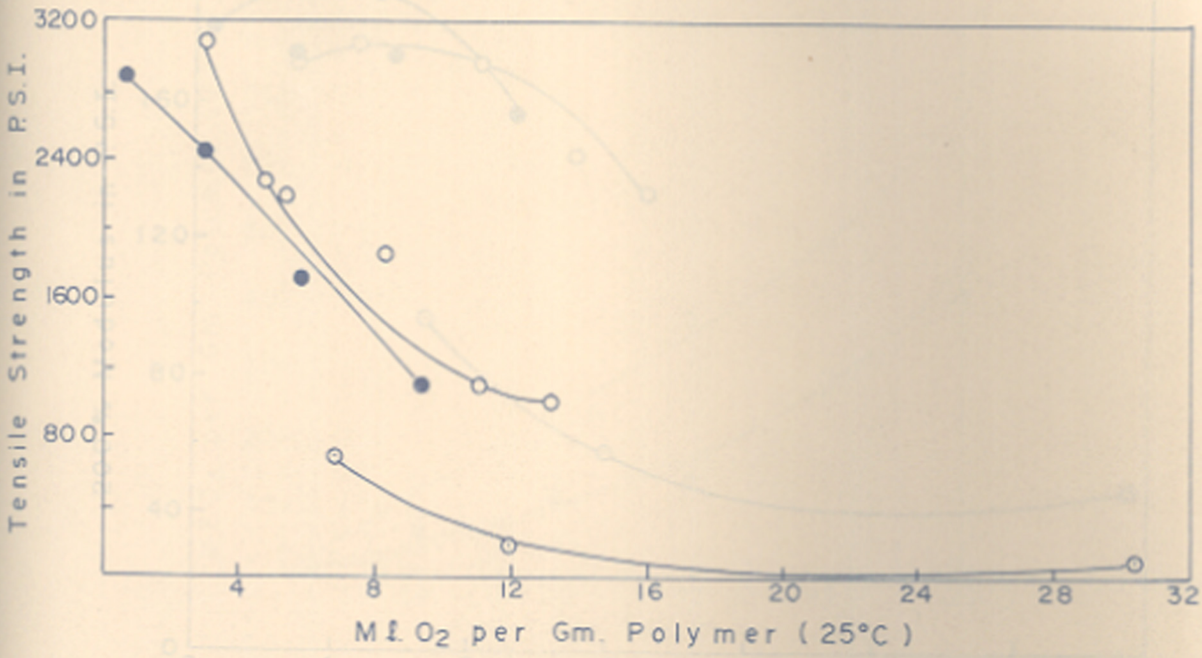


Fig. 10 TENSILE STRENGTH IN P.S.I. OF INHIBITED (Urea type) NATURAL RUBBER GUM COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ Symmetrical Urea of 4 A.P.P.
● Unsymmetrical Urea of 4 A.P.P.

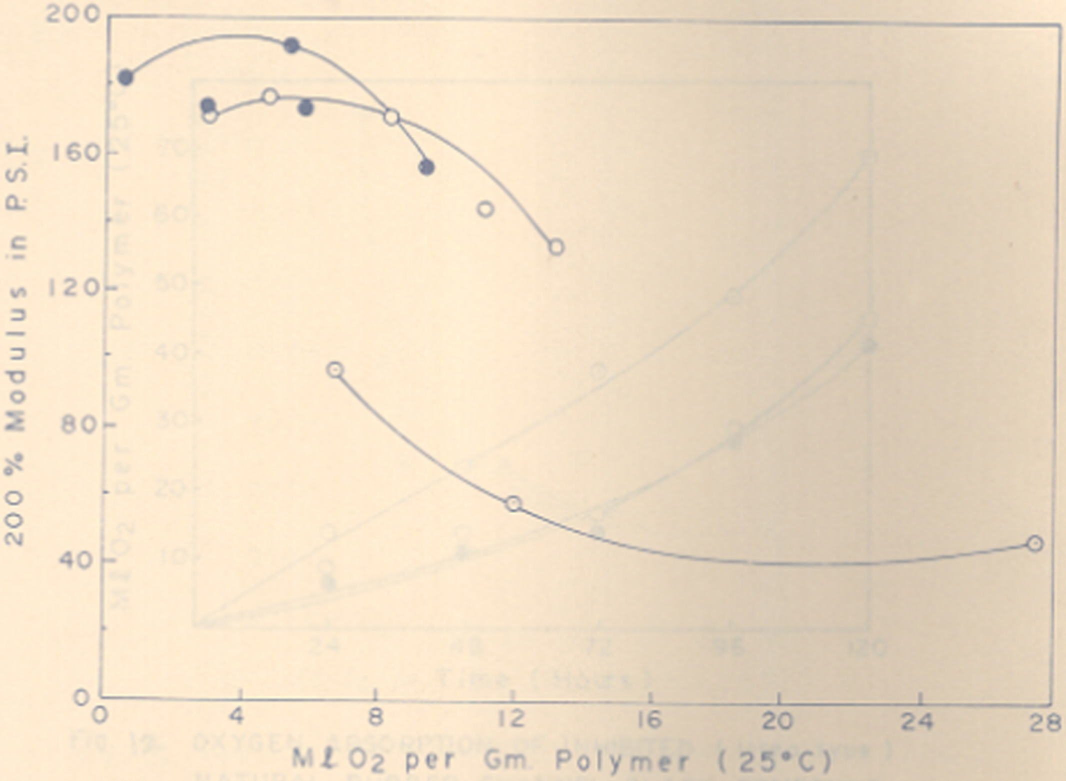


Fig. 11 200 % MODULI IN P.S.I. OF INHIBITED (Urea type) NATURAL RUBBER GUM COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ Symmetrical Urea of 4 A.P.P.
● Unsymmetrical Urea of 4 A.P.P.

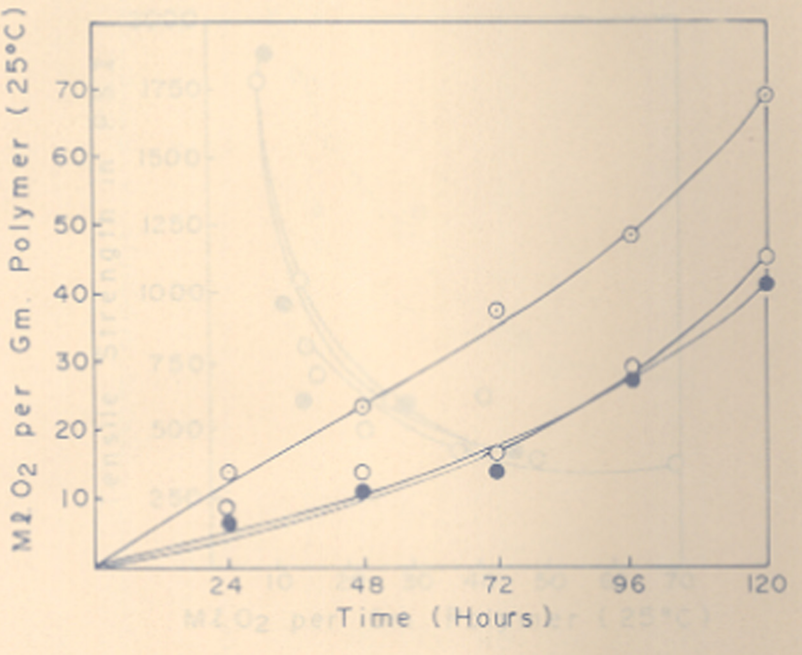


Fig. 12 OXYGEN ABSORPTION OF INHIBITED ( Urea type ) NATURAL RUBBER CHANNEL BLACK COMPOUND AT 90°C & 760 mm.

⊙ Blank ( No Antioxidant )
○ Symmetrical urea of 4 A.P.P.
● Unsymmetrical urea of 4 A.P.P.

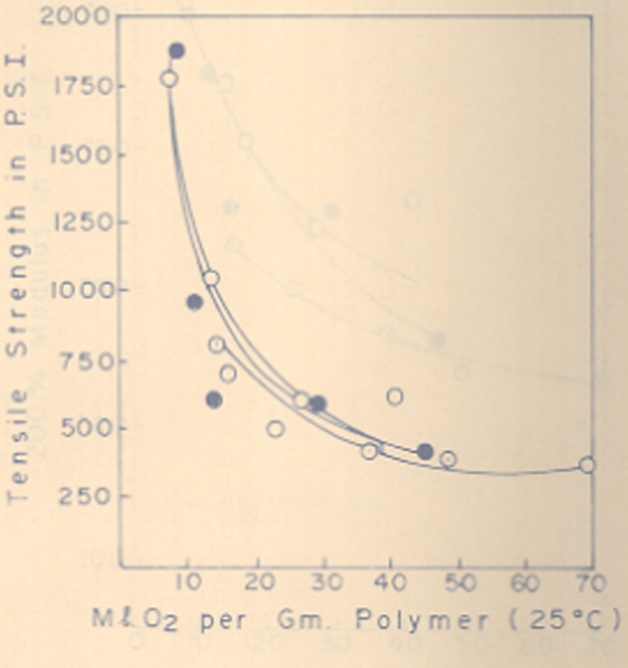


Fig. 13 TENSILE STRENGTH IN P.S.I. OF INHIBITED (Urea type) NATURAL RUBBER CHANNEL BLACK COMPOUND Vs OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ Symmetrical urea of 4 A.P.P.
● Unsymmetrical urea of 4 A.P.P.

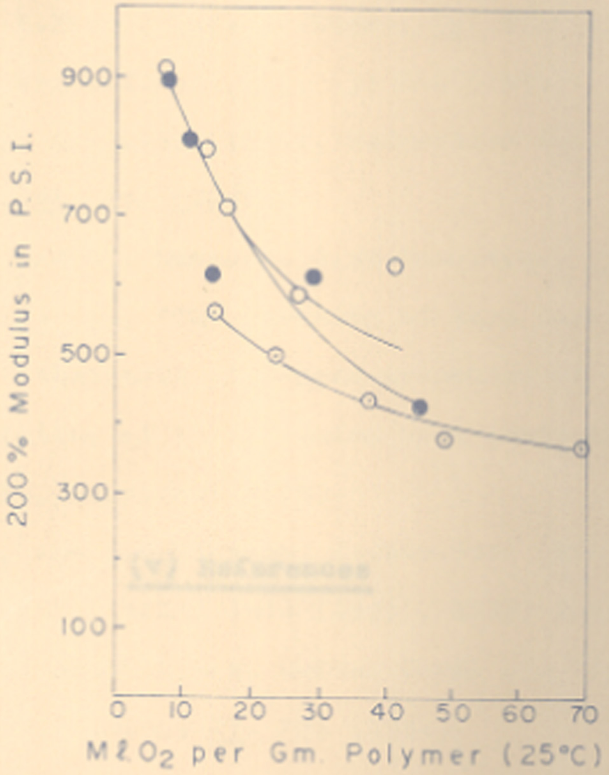


Fig. 14 200 % MODULI IN P.S.I. OF INHIBITED (Urea type) NATURAL RUBBER CHANNEL BLACK COMPOUND Vs. OXYGEN ABSORPTION AT 90°C, 760 mm.

⊙ Blank (No Antioxidant)
○ Symmetrical urea of 4 A.P.P.
● Unsymmetrical urea of 4 A.P.P.

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# PART II - ACCELERATORS

# THE HISTORICAL DEVELOPMENT OF ACCELERATORS

Rubber is extensively used in various fields of the national economy owing to its high elasticity, strength, resistance to abrasion, and impermeability to air, gases and water. Moreover, rubber can be made resistant to heat, frost, corrosion, oils and lubricants. Rubber is an almost ideal constructional material. Crude rubber mixture can be easily given any desired shape by forming, calendering, profiling, pressure-molding, etc. Various articles of different shapes intended for various purposes can be manufactured by employing different production techniques. Vulcanization, which is the last stage in the processing of the rubber mixture, fixes the mixture in the desired shape by converting it from viscous to a highly elastic state. The process of vulcanization produces complex chemical changes in raw rubber molecules. The linear or branched molecular structure of the rubber is converted into a tridimentional, spatial network (vulcanized product).

Small amounts of substances known as vulcanization accelerators are added to the rubber stock during compounding, and have a great effect on the physical, mechanical and service properties of the finished articles. In modern rubber technology, the most important accelerators are organic compounds.* They act in many ways : not only is the vulcanization process accelerated, but also many properties of the finished rubber products are altered. This is because the presence of accelerators greatly affects the formation of the spatial structure of the rubber molecules which in turn determines the physical, mechanical, chemical and service properties of the finished articles.

The first substances used to shorten the uneconomically long vulcanization times were inorganic ones, mainly oxides of the metals calcium, magnesium, and lead. It so happens that the earliest accelerator, which was used by Charles Goodyear, though without him understanding the relationship, was basic lead carbonate.[1] These inorganic accelerators have now been almost entirely ousted by organic compounds.

During the first work on synthetic rubber, which took place at Farben Fabriken Varm. Friedr. Bayer and Co.[2] during the years 1906 to 1909, Fritz Hofmann and his colleagues observed that it vulcanized poorly, or hardly at all, and that it was easily destroyed by oxidation. In the light of research by Wolfgang and Walter Oswald[3] who attempted to protect rubber against oxidation by adding organic bases, scientists at Elberfeld tested a whole series of organic bases with a view to making synthetic rubber more resistant to oxidation. They found that specimens containing piperidine oxidized less easily and vulcanized surprisingly well.[4,5] The significance of this observation was realized and experiments were then carried out on natural rubber. It was found that here again small additions of strong organic bases greatly accelerated the vulcanization. These discoveries were pursued and their scope was enlarged. They resulted in the first patents in the field of organic acceleration.[5-7] The claims of the patents covered aliphatic, cycloaliphatic, and heterocyclic amines, such as dibutyl amine, ethylene cyclohexyl amine, piperidine, the reaction products of aliphatic and aromatic bases with carbondisulphide, the ammonium salts of disubstituted dithiocarbamic acids, such as N-pentamethylene-ammonium dithiocarbamate, and condensation products of aliphatic aldehydes with ammonia, e.g. acetaldehyde ammonia and hexamathylene tetramine, of which some are still being used in the rubber industry. Although Hofmann and Gottlob were the first to use dithiocarbamates, they failed to observe the influence of zinc oxide on vulcanization with these compounds. Not until later was it found that zinc oxide influence and reinforces the action of many accelerators.[8] This effect is of great importance and now-a-days hardly any accelerator is used without zinc oxide, except in exceptional circumstances. This also applies to the zinc dithiocarbamates,[9] which were not discovered until 1919.

Independently of German chemists, Oenslager,[10] working with the Diamond Rubber Co., had already discovered and used organic accelerators in 1906. He first succeeded in using aniline as an accelerator for rubber. Later because of the toxicity of aniline, he used thiocarbanilide and other compounds instead. Oenslager's findings were not published in Europe and not known until after the First World War.

Among early developments in the field of accelerators were the researches of Peachey in England. Peachey took out a patent covering the use of p-nitrosodimethyl aniline[11] and of condensation products of aromatic amines with formaldehyde.[12] D. Spence[13] claimed to have used organic bases and other compounds as accelerators even earlier.

Although the first accelerators became available before the First World War, it was not until about 1920 that they succeeded in establishing themselves and were recognised at their true value. Within a short time feverish inventive activity began throughout the world; innumerable patents and studies were published and one accelerator after the other was offered for sale. The first of them were dithiocarbamates, aldehyde ammonia, hexamethylenetetramine and diaryl thiourea.[14]

A further class of accelerators was formed by the conversion products of alkali alcoholates with carbon disulphide, the alkyl xanthogenates,[15] and their metal salts, the alkyl xanthogen-mono- and disulphides.[16,17] These products were less successful. The series of aldehyde amine condensation products was soon extended by more effective compounds. They were the condensation products of saturated and unsaturated aliphatic aldehydes with ammonia and aromatic amines. Just a few typical representatives of these numerous compounds are tricrotonylidene tetramine,[18] ethylidene aniline, butylidene aniline, heptylidene aniline,[19,20] crotonylidene aniline, and methyl propyl acroleine aniline.[21,22]

Some of them have proved highly suitable and are still being used today.

About 1922 a new class of accelerators, the diaryl guanidines,[23-26] appeared, which were soon followed by aryl biguanides,[27] e.g. o-tolyl biguanide. For a fairly long time they were the most widely used accelerators, except for o-tolyl-biguanide, they are now used in most cases only as secondary accelerators in conjunction with derivatives of the mercapto arylene thiazole series.

The year 1921 brought considerable progress in the development of organic accelerators. C.W.Bedford and L.B. Sebrell[28-30] in America and G. Bruni and E. Romani[31] in Italy discovered independently that 2-mercapto benzothiazole, its homologues, its disulphides,[32,33] and its metal salts are very effective accelerators with particularly valuable properties. Later it was found that thiazole derivatives e.g. 2-mercaptothiazole and its homologues,[29] and 2-mercapto-thiazoline,[30] also belong to this class.

Further development in the field of organic accelerators was based on these discovered. Efforts were directed at slowing down the over-rapid vulcanizing materials, e.g. converting them into ones with a delayed onset of vulcanization, with a view to obtaining better processing, Safety and a longer flow period than were possible with dithiocarbamate accelerators and mercapto arylene thiazoles. It was found that this could be done by substituting the groups actually responsible for the vulcanizing action. The mercaptan sulphur, for example, was substituted in the case of derivatives of dialkyl alkylcycloalkyl and alkylaryl dithiocarbamic acids and in the case of the mercapto arylene thiazoles.

Attempts to modify the extraordinary fast ammonium dithiocarbamates resulted in the zinc dialkyl dithio carbamates;[31] thus products with a considerably slower cure were already arrived at. Further efforts to substitute the mercaptan sulphur in dithiocarbamate resulted in tetraalkyl thiuram disulphide,[32,33] (e.g. tetramethyl thiuram disulphide) and 'tetra-alkyl thiuram monosulphides,[34,35] (e.g. tetramethyl thiuram monosulphide), and thiuram tetrasulphide.[36] All of these products are still being used on a large scale as ultra-accelerators. Further conversion products from the sodium salts of the dithiocarbamic acids with 2,4-dinitrochlorobenzene and with benzal chloride, the relatively safe product 2,4-dinitrophenyl-N-dialkyl-dithiourethane[37] and the similar product benzalbis-N-dialkyl-dithio-urethane[38] have acquired no technical importance.

Unlike the last two products mentioned, a series of derivatives of 2-mercapto benzothiazole has become outstandingly important. A particularly important representative of these first modified products was dibenzothiazyl disulphide which had already been discovered by C.W.Bedford and L.B.Sebrell[28,39-40] and by G.Bruni and E.Romani.[42]

Further work revealed that the sodium salts of the mercapto arylene thiazoles can be beneficially reacted with organic compounds which contain labile halogen atoms. In this way a large number of compounds was synthesized of which only a few typical examples will be given. All of these compounds have a common structural principle, the mercaptan sulphur of 2-mercapto benzothiazole being substituted in each of them by an organic residue. Because of the substitution the onset of vulcanization is retarded, because the organic residue has to be split off before the vulcanization can begin.

Serviceable accelerators of this type have been obtained by for example, reacting 2,4-dinitrochlorobenzene with the sodium salt of 2-mercapto-benzothiazole. The resulting substances were 2-benzothiazyl-S-2,4-dinitrophenyl thioether.[42,43] Benzoyl chloride and the sodium salt of 2-mercaptobenzothiazole gave s-benzoyl-2-mercaptobenzethiazole.[44]

These derivatives of mercapto arylene thiazoles are actually rather weak accelerators, they are therefore used almost exclusively in conjunction with a secondary accelerator, e.g. a diaryl guanidine. Serviceable products, many of which are still used today, were also obtained by combining dibenzothiazyl disulphide, a very safe, yet weak, accelerator, with diaryl guanidine.

Further development in this field led to a new class of accelerators, the sulphenamides of mercapto arylene thiazoles, especially 2-mercapto-benzothiazole, which was introduced in 1932 by Farben Fabriken Bayer A.G. of Leverkusen, Germany (at that time IG Farbenindustrie A.G., Leverkusen Factory). They proved to be particularly valuable substances with a delayed onset of vulcanization and it is probably true to say that they are still the most widely used accelerators. They are formed, for example, by the action of N-chloramines on the sodium salts of the mercaptothiazoles[45-47] or by co-oxidation of a mercaptothiazole with a primary or secondary aliphatic or heterocyclic amine.[48-50] Mention should be made of the sulphenamides from 2-mercaptobenzothiazole with diethylamine,[45-47] piperidine,[45-47] morpholine,[51-53] 2,6-dimethylmorpholine,[54,55] cyclohexylamine,[56-58] dicyclohexylamine,[59-60] diisopropylamine,[61,62] butylamine[63,64] and tertoctylamine.[65,66]

## Classification of organic Accelerators

According to the chemical nature, the industrially important organic accelerators are divided into the following groups.

### Acidic Accelerators

(1) Dithiocarbamates.

(2) Xanthates.

(3) Thiuram sulphides.

 (a) Thiuram monosulphides.

 (b) Thiuram disulphides.

(4) Thiazole accelerators.

 (a) Mercapto accelerators.

 (b) Sulphenamide accelerators.

Basic Accelerators

(5) Aldehyde amine accelerators.

(6) Guanidine accelerators.

(7) Thiourea derivatives.

(1) Dithiocarbamates

Zinc diethyl dithiocarbamate (ZDC). When diethyl amine, carbondisulphide and sodium hydroxide are mixed at 20°-30°C, the sodium salt of diethyl dithiocarbamate is formed. On addition of a solution of zinc chloride to this mixture, ZDC precipitates out. Dithiocarbamate accelerators are ultra-accelerators and are widely employed in rubber and wire insulation industries.

(2) Xanthates

Zinc isopropyl xanthate (ZIX). Isopropyl alcohol, carbondisulphide and sodium hydroxide are reacted together to form sodium isopropyl xanthate. On addition of zinc chloride to this mixture, ZIX is precipitated. The xanthate accelerators belong to the extremely fast-acting ultra accelerators. They are even faster curing than dithiocarbamates and hence are very scorchy. Therefore, they have only limited application, and are generally used in latex formulations.

(3) Thiuram sulphides

Tetramethyl thiuram disulphide (TMT). This is obtained by gradually adding dilute sulphuric acid to an aqueous solution of sodium dimethyl dithiocarbamate in presence of hydrogen peroxide below 30°C. Tetramethyl thiuram monosulphide (TMTM). This is obtained by treating TMT with sodium cyanide. Thiuram sulphide accelerators are ultra-accelerators, widely employed in rubber and cable industry. They are always used in small dosages with other accelerators, to boost up the rate of cure.

(4) Thiazole accelerators

Mercaptobenzothiazole (M.B.T.):- This is prepared by reacting aniline, carbondisulphide and sulphur in an autoclave at a pressure of 150 atms. at about 300°C. Alternatively, o-nitro-chlorobenzene, carbondisulphide, sulphur and aqueous sodium sulphide are heated to about 95°C. The mixture is cooled and filtered, M.B.T. is precipitated by acidification of the filtrate.

The sodium salt of MBT exchanges zinc from zinc chloride to form zinc salt of mercaptobenzothiazole (Z.M.B.T.).

Benzothiazolyl disulphide (M.B.T.S.):- This is obtained by oxidising M.B.T. with nitrous acid or chlorine with air.

Sulphenamide derivatives of mercaptobenzothiazoles, e.g. N-cyclohexyl-2-benzothiazole sulphenamide is obtained by oxidative condensation of mercaptobenzothiazole with cyclohexylamine.

Morpholine gives N-Morpholine derv. of 2-M.B.T.

The products of the thiazole class, 2-mercaptobenzothiazole and its derivatives, are among the most popular accelerators. They are frequently used on a large-scale than any other class, and they offer the high level of good physical properties to the vulcanizates.

Sulphenamide derivatives are popularly known as delayed action accelerators as they give maximum scorch delaying action and occupy the topmost position in the present day tyre manufacturing industry.

(5) Aldehyde-amine Accelerators:-

These types of accelerators are obtained by condensing aliphatic aldehydes with aromatic amines. Butyraldehyde and heptaldehyde reaction products with aniline and o-toluidine are mostly used in commerce. These accelerators are extremely slow in their reaction. They are generally used in the manufacture of ebonite articles.

(6) Guanidine Accelerators

Diphenyl Guanidine (D.P.G.). It is prepared by the reaction of cyanogen chloride with aniline or desulphuration of thiocarbanilide followed by reaction with ammonia. Diorthotolyl guanidine is also prepared similarly from o-toluidine. Accelerators belonging to this class are distinctly basic in nature and are classed as 'slow' accelerators. They are, therefore, always used in conjunction with acidic thiazoles to get the 'activating effect' in vulcanization.

(7) Thiourea derivatives

Thiourea derivatives and their mixtures with other accelerators are used as accelerators in a number of rubber articles, examples are diphenyl thiourea i.e. thiocarbanilide and sym-Di-o-tolyl thiourea.

## The Mechanism of activation of Accelerators

In general, accelerators are relatively stable products. Hence they cannot by themselves exert much influence on the curing process. This is to be seen from the fact that they rarely develop their optimum effect in rubber compounds which contain sulphur and accelerators only. The rate of cure of such compounds is low and the mechanical properties of the cured goods are absolutely inadequate. Hence apart from accelerators it is necessary to add activators[67,68] such as zinc oxide, which at curing temperature make the accelerators capable of reaction. In this way the rate of cure is adequately increased and the mechanical properties of the vulcanizates are improved. With many types of accelerators, fatty acids such as stearic acid can be used as additional activators. They are usually added together with zinc oxide and their activating effect on the accelerator is often synergistic and in spite of a delay in the onset of cure caused by the fatty acid, the resulting vulcanizates have good mechanical properties.

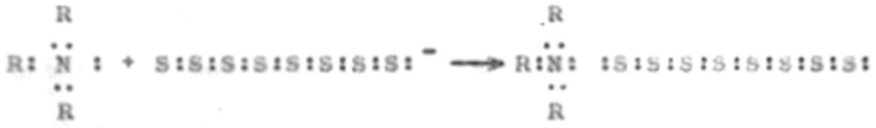
The elemental sulphur invariably used in almost all rubber compounding recipes as a primary cross-linking agent exists as a stable S8 ring. According to Krebs[69] the sulphur ring can generally be split up in two ways. After splitting up of the ring one pair of electrons can remain attached to one sulphur atom, as electron gap being formed at the other end of the resulting S8 chain. Secondly each of the terminal sulphur atoms may take up a single electron.

In the first case the fission is ionic and in the second it is radical.

If substances capable of forming radical, e.g. tetramethylthiuram (TMT) disulphide, dibenzothiazuldisulphide (MBTS) or others, act on sulphur, they can cause radical fission according to above equation, the radicals so formed can react with the S8 biradicals.

$$R\cdot + \cdot S{:}S{:}S{:}S{:}S{:}S{:}S{:}S\cdot \longrightarrow R{:}S{:}S{:}S{:}S{:}S{:}S{:}S{:}S \uparrow$$

Such an intermediatory reaction product formed with accelerator, is unstable and splits up into smaller sulphur biradicals, which are capable of taking part in the vulcanization process on their own account. If, on the contrary, substances possessing a free pair of electrons, e.g. amines are present, the sulphur can be split up according to ionic fission given in above equation. The lone pair of electrons present on the basic nitrogen atom can easily be donated to the electron deficient sulphur atom in the S8 chain, forming the polysulphide



$$R{:}\overset{\overset{R}{\cdot\cdot}}{\underset{\underset{R}{\cdot\cdot}}{N}}{:} + S{:}S{:}S{:}S{:}S{:}S{:}S{:}S{:}^{-} \longrightarrow R{:}\overset{\overset{R}{\cdot\cdot}}{\underset{\underset{R}{\cdot\cdot}}{N}}{:}\;{:}S{:}S{:}S{:}S{:}S{:}S{:}S{:}S{:}$$

The polysulphide of this type has little stability and very shortly after its formation it separates off reactive $S_2$ fragments, and because of their pairs of free electrons these can again have an activating effect on the sulphur.

On the basis of kinetic studies, of the reaction of sulphur and accelerators with natural rubber and other elastomers, Scheele[70] proposes that intermediate compounds are formed by reaction of sulphur and accelerators, and that these intermediates then transfer sulphur to the rubber chain.

Shelton and McDonel[71] on the basis of their study of the effect of free radical scavengers (benzoquinone, hydroquinone, 1,1-diphenyl-2.picrylhydrazyl) on various curing systems, concluded that the accelerators were activated by polar, free radical and mixed polar and free radical mechanisms.

Dogadkin and co-workers[72] in their extensive review on the mechanism of vulcanization and the action of accelerators, have shown that in the complicated phenomenon of vulcanization both polar and free radical mechanisms are operative, depending on types of accelerators and activators and the type of rubber used.

The activated biradicals of sulphur generated from the dissociation of the accelerator-polysulphide complex, further crosslink the polymeric chains, thus resulting in a three dimentional network structure, comprehensive reviews[70,72-74] and books[75-78] have recently been available on the mechanism of vulcanization of rubbers and the action of accelerators during vulcanization.

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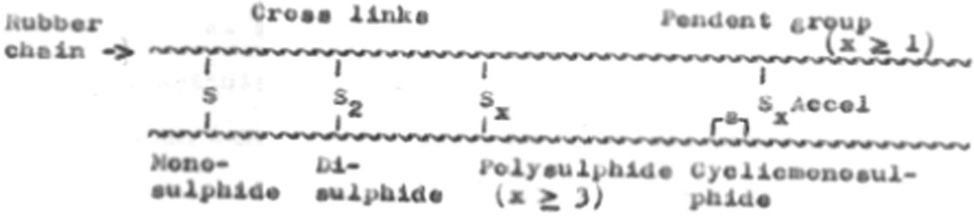
# DEVELOPMENT OF NEW ACCELERATOR SYSTEMS IN 'EFFICIENT VULCANISATION' OF NATURAL RUBBER

## (i) Introduction

The vulcanization of natural rubber is generally carried out by mechanically processing it with compounding ingredients and heating at a temperature of about 140°C and a pressure of about 1000-2000 lbs/sq.in. The resulting cured vulcanizate consists of a spatial network structure formed by the covalent bonds between the sulphur atoms and the reactive sites present on the macromolecular chains of rubber.

A vulcanizate can thus be represented schematically as in fig. 1.



The conventional sulphur vulcanized natural rubber polymer matrix, generally consists of a mixture of mono-, di-, and poly-sulphidic crosslinks, along with some additional net work of cyclic sulphides and pendent sulphur-Accelerator residues.

These different sulphide crosslinks have different bond energies. The following table[1] describes the bond energies of different sulphur-sulphur and carbon-carbon linkages.

TABLE I. BOND ENERGIES OF SULPHUR-SULPHUR AND CARBON-CARBON- LINKAGES

| Type of link | Bond energy (Kcal/Mol.) |
|---|---|
| $- C - S_x - C$ | $< 64$ |
| $- C - S_2 - C -$ | 64 |
| $- C - S - C -$ | 68 |
| $- C - C -$ | 84 |

As the bond energy of sulphur-sulphur link is smaller than that of the carbon-carbon link, it is expected that during thermal splitting, the sulphur-sulphur link will be more susceptible towards dissociation than the carbon-carbon link. It is also expected that the polysulphide link will be more susceptible towards heat than the mono or disulphide link.

It is now established that there is a definite relationship between the physical and chemical properties of the vulcanized rubber to the vulcanizate net-work structure. Thus properties of natural rubber vulcanizates can change by varying the choice of vulcanization ingredients.

By the use of peroxide curing system protected with antioxidants,[2] carbon-carbon crosslinks are formed which are resistant to heat. The peroxide curing systems have drawbacks such as poor scorch characteristics, sticky spew, odor and poor initial vulcanization properties.

Unaccelerated sulphur or DPG-accelerated sulphur cured natural rubber vulcanizates have long polysulphidic cross links. Vulcanization of natural rubber using 2.5 PPhr sulphur and 0.5 PPhr sulphenamide type accelerator has a network structure having mainly polysulphidic cross-links and some cyclic monosulphide crosslinks. TMTD- zinc oxide cured vulcanizates of natural rubber have a network of relatively simple monosulphide crosslinks.

Unaccelerated sulphur or DPG-accelerated sulphur vulcanizates of natural rubber age badly due to the presence of polysulphide linkages. TMTD-zinc oxide cured vulcanizates have better ageing properties but have the disadvantage of being somewhat scorchy and bloom very badly.[3] The vulcanizates obtained by low sulphenamide/high sulphur accelerated systems have ageing characteristics in between the two systems mentioned above. However, this system is not stable to 'Reversion' when subjected to high curing temperature condition (between 180°-200°C).

In order to overcome this problem of 'Reversion' of conventional accelerator systems at elevated temperatures and scorchiness and blooming tendency of TMT-sulphurless curing systems, recently, attention has been drawn to so-called 'E.V. Systems' - E.V. standing for 'Efficient vulcanization'. Much literature, now has been published on 'E.V. Systems'.[3-11]

In such systems, a high dosage of accelerator like sulphenamide or MBTS (3-5%) is generally used with a very small amount (0.1-0.3%) of sulphur, resulting into vulcanizates which give a preponderance (often 90%) of mono- or disulphidic crosslinks in the cured stocks. These stocks can be further protected by conventional antioxidants. Conventional curing systems yield 70% or more of polysulphidic crosslinkages with remainder being the more thermally stable mono or disulphide linkages. Studies have shown that sulphur vulcanizates with no accelerator give polysulphidic linkages with as high as 50 sulphur atoms per cross link. A conventional sulphur-accelerator system with a long cure time at low temperatures will give large amounts of mono or disulphidic linkages. However, at normal cure conditions (140°C) polysulphidic linkages are formed.

A system which produces the desired mono and disulphidic linkages in normal times and cure temperatures is more effective and therefore called an 'Efficient vulcanization System'.

Vulcanizates of sulphur-cure elastomers with mainly monosulphidic or disulphidic crosslinkages have different properties from vulcanizates containing mainly polysulphidic crosslinkages. These differences are shown in Table 11.[7]

E.V.Compounds are also more resistant to set under both static and dynamic loads. However, their fatigue and cut growth properties are inferior to those of vulcanizates with polysulphide crosslinks. Such systems should be valuable in applications where diamentional stability is important - such as in engine mountings - particularly when the components

TABLE II. COMPARISON OF VULCANIZATES WITH DIFFERENT CROSS-LINK STRUCTURES

| Vulcanizate/cross-link structure | Advantages | Disadvantages |
|---|---|---|
| Conventional | | |
| Polysulphide 70% or ><br>Di-sulphide 15% or ≯ <<br>Mono-sulphide 15% or < | 1. Cure systems available to suit all normal processing requirements.<br>2. Excellent static physical properties.<br>3. Excellent dynamic physical properties. | 1. Rapid reversion in natural rubber at high curing temperature(e.g. 180 °C)<br>2. Poor retention of properties during ageing/service. |
| Efficient | | |
| Polysulphide 10% or <<br>Di-sulphide 40% or ><br>Mono-sulphide 50% > | 1. No reversion at high curing temperature.<br>2. Excellent static physical properties.<br>3. Excellent retention of properties during ageing/service. | 1. No systematic information on cure systems which allow easy control of curing and processing conditions.<br>2. Reduced resistance to fatigue when flexed through zero strain. |

is required to operate at elevated temperatures. They are however more expensive but intermediate ratios of accelerator to sulphur may be used to achieve intermediate properties. Another compromise approach is to use a sandwich of E.V. and conventional compounds, for example in the carcass and tread section of a tyre, thus using each type of compound to best advantage. The use of 'E.V.compounds' has recently been made in the injection moulding of natural rubber.[6,10]

Further progress was made by choosing an E.V. system using sulphur donor such as 4,4′-dithiodimorpholine in place of sulphur and with a sulphenamide or thiazole accelerator.[7] This combination gave a long scorch time, which is not normally required.

Adjustment of processing safety and rate of cure was made by using tetramethyl thiuramdisulphide (TMT) as a booster accelerator.

It has recently been shown that thiourea and certain of its N-substituted derivatives, accelerate TMT-zinc oxide natural rubber vulcanization,[12,14] and sulphenamide-zinc oxide natural rubber vulcanization,[13] to such an extent that excellent vulcanizates can be produced at 100°C or even at lower temperatures.

N-substituted mono aryl thioureas[15] are effective secondary accelerators when used together with MBTS, giving effective protection for vulcanizates from various types of ageing. A complex resulting from the reaction of hexachloroethane with thiourea[16] was found to be an effective accelerator and gave good thermally resistant vulcanizates.

At the same time further development made in Germany,[11] revealed the use of thiourea with disulphides and sulphenamides - in vulcanization. It was found that thiourea itself was not a vulcanizing agent but in combination with disulphides or sulphenamides showed vulcanization to take place to quite an appreciable extent. Similarly MBTS, Morpholine disulphide, morpholine- monosulphide, N-oxydiethylene-benzothiazyl sulphenamide (Moz) and di-isopropyl-thiophosphoryl disulphide were all found to give characteristic vulcanization in combination with thiourea. The degree of vulcanization did not reach the same level as with sulphur vulcanization and the compounds were scorchy, but nevertheless the ageing and resistance to reversion were good, and it was evident that other disulphides or sulphenamides might quite well give a better combination of properties. If, however, thiourea was used in conjunction with a sulphur donor such as TMT or 2-benzothiazylmorpholine-disulphide, a rapid reaction was found to take place, resulting in a normal level of crosslinking. Not only could natural rubber be vulcanized in this way, but also SBR and Butyl rubber. Furthermore, the progress was particularly useful in continuous vulcanization, injection moulding and salt-bath vulcanization, where a rapid cure was desirable.

A further development of this idea suggested that a sulphenamide and thiourea should be combined with a small addition of sulphur. A very high rate of crosslinking was provided by this means. An example of this was the combination of 3 PPhr of CBS, 0.5 PPhr of sulphur and 1.0 PPhr of thiourea with natural rubber, which gave full vulcanization within 10 minutes at 112°C.

When thiourea was added to a conventional sulphur/

accelerator system in natural rubber the rate of vulcanization was increased considerably, and physical properties were improved, although the ageing resistance was not noticeably better.

The experiments upto this stage had only used thiourea at a level of 1 PPhr. Further work showed that this was indeed a limiting value and that there was no advantage in decreasing it. Below this level, however, it was possible to obtain relatively scorch-resistant compounds. Finely crystalline sample of thiourea was used in these experiments.

Similar experiments with substituted thioureas showed that better scorch resistance was obtained, without reduction in the rate of cure. Ethylene thiourea showed good acceleration of cure, even at high temperatures with good mechanical properties and good age resistance, but the heat build-up was inclined to be high in dynamic tests. Diphenyl thiourea was found to be more suitable for SBR and NBR, as it was rather scorchy when used with natural rubber.

Finally the authors described the properties of six natural rubber compounds containing 45 parts HAF black. A compound with 2.3 PPhr sulphur and 0.15 PPhr CBS was chosen as control; this had a relatively long scorch time at curing temperatures (27% of optimum cure) with good mechanical properties but poor age resistance and compression set at 100°C. The second compound had 0.2 pphr sulphur and 2.5 pphr TMT. It was more scorchy and had a short optimum cure, as well as good mechanical properties. It had good ageing and compression set with little tendency to reversion. On the other hand there was a danger of bloom formation from TMT or the dithiocarbamates formed from it. The third compound had 0.6 pphr sulphur and 3.0 pphr Moz : here the scorch time was much longer than in the first compound and this would be preferred for the moulding of complex articles. The fourth compound contained 0.5 pphr sulphur, 0.5 pphr TMT and 2.0 pphr of Moz; ageing resistance and reversion stability were good, and the compression set was better than in the first and third compounds, whilst only a small amount of blooming occurred. The fifth compound was similar to the third compound, with the addition of 1.0 pphr of ethylenethiourea; this resulted in a better ratio between the scorch and cure time, better ageing behaviour and greater reversion stability together with good compression set. In the last compound, the 1 pphr of ethylenethiourea was replaced by 0.2 pphr of thiourea, giving a saving of cost without deterioration of properties.

## (ii) Present investigation and results

Introduction of automation in industries is ~~has~~ becoming a very common practice throughout advanced countries. Rubber compression moulding processes, which are normally slow in operation and which produce large flash waste products, are now being replaced by the efficient and fast processes such as injection moulding.

Injection moulding of natural rubber is generally done at a temperature of $180^\circ$-$200^\circ$C. This has created a need for developing such formulations which will not show any 'reversion', in the moulding operation. Utilization of 'efficient vulcanization systems' in such injection mouldings, has practically overcome this problem of reversion of natural rubber.

However, sufficient information on the easy control of the curing and processing conditions in E.V. systems is lacking, which evidently is dependent on the proper selection of the accelerator system. Such accelerator system should give thermally stable net work structure, preventing the reversion. It should have an adequate balance between scorch delaying action and maximum crosslinking.

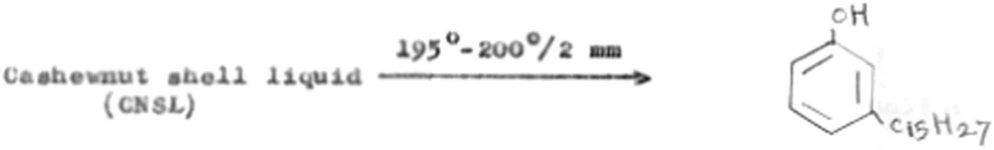
The present investigation deals with the development of suitable E.V. systems based on accelerators developed from indigenous raw materials, (1) which produce superior vulcanizates at temperature of $140^\circ$C. to the vulcanizates produced by the conventional system and (2) which produce superior vulcanizates at $180^\circ$C without reversion, which may be very suitable for injection moulding of natural rubber stocks.

### Methods of syntheses of Aryl thioureas from CNSL

The several steps involved in the syntheses of aryl thioureas are shown diagrammatically in Fig. 2.

### 3-pentadecadienyl phenol (Anacardol) (I)

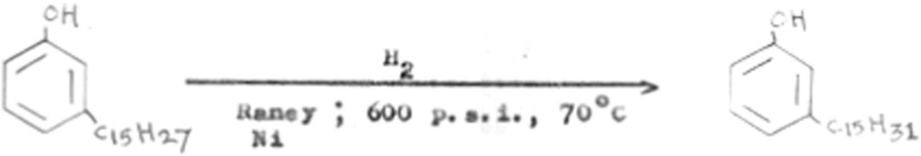
When commercial cashew nut shell liquid is distilled under reduced pressure, 3-pentadecadienyl phenol (anacardol) is obtained as a pale yellowish liquid in 30% yield.



Anacardol (I)

### 3-pentadecyl phenol (Tetrahydroanacardol (II)

Anacardol when catalytically reduced over Raney nickel catalyst at 600 pounds hydrogen pressure and at 70°C, in a Parr-autoclave, gave 90% yield of 3-pentadecyl phenol (II). The crude product after crystallizing from petroleum ether (40°-60°) gave a white waxy product. M.P. 30°C.



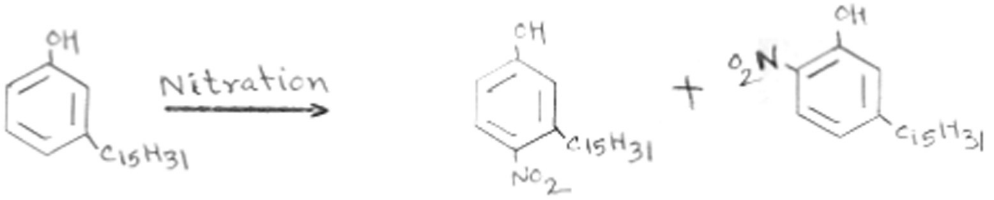
Anacardol

3-pentadecyl phenol (II)

### 4-Nitro-3-pentadecyl phenol (III) and 6-Nitro-3-pentadecyl phenol (IV)

3-Pentadecyl phenol was nitrated with fuming nitric acid (sp. gr. 1.5) below $10^{\circ}$C, in chloroform, when mixed mononitro isomers 4-nitro-3-pentadecyl phenol (III) and 6-nitro-3-pentadecyl phenol (IV) were obtained. 4-Nitro-isomer was separated from the 6-nitroisomer by selective solubility of the latter in petroleum ether ($60^{\circ}$-$80^{\circ}$) at freezing temperature. Crude 4-nitro-3-penta-decyl phenol after recrystallizing from petroleum ether ($60^{\circ}$-$80^{\circ}$) melted at $70^{\circ}$-$71^{\circ}$C. 6-Nitro-3-pentadecyl phenol after removing petroleum ether, was recrystallized from ethanol. M.P. $39^{\circ}$C.

The melting points of these compounds were same as those reported by Dawson.[23]



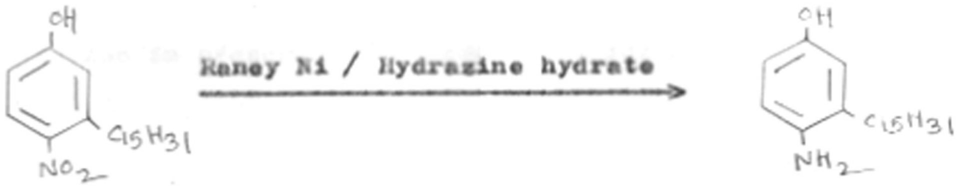
3-pentadecyl phenol

4-Nitro-3-pentadecyl phenol (III)

6-Nitro-3-pentadecyl phenol(IV)

### 4-Amino-3-pentadecyl Phenol (V)

Following the reduction method of Furst,[24] 4-Nitro-3-pentadecyl phenol was reduced to the corresponding aminophenol, by using Raney nickel and hydrazine hydrate. Crude 4-amino-3-pentadecyl phenol was crystallized from ethanol and had a M.P. $105^{\circ}$-$106^{\circ}$. The same compound previously obtained by Dawson[23] by a different route, melted at $105^{\circ}$-$106^{\circ}$C.



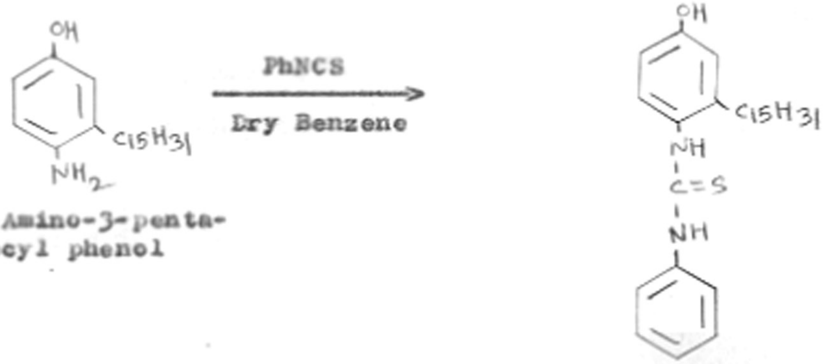
4-Nitro-3-pentadecyl phenol

4-Amino-3-pentadecyl phenol (V)

### N-(2-pentadecyl-4-hydroxyphenyl), N′-phenyl thiourea (VI)

4-Amino-3-pentadecyl phenol was further reacted with phenylisothiocyanate in dry benzene to give the unsymmetrical thiourea,

N-(2-pentadecyl-4-hydroxyphenyl), N′-phenyl thiourea (VI) m.p. 134°C

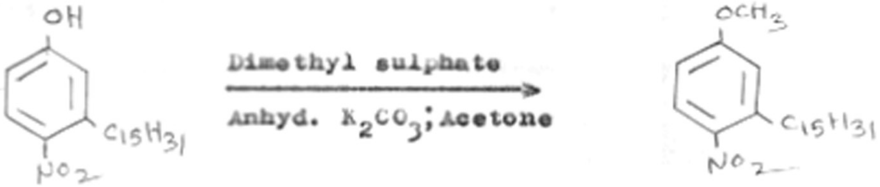


4-Amino-3-pentadecyl phenol

N-(2-pentadecyl-4-hydroxyphenyl), N′-phenyl thiourea (VI)

### 4-Nitro-3-pentadecyl anisole (VII)

4-Nitro-3-pentadecyl phenol was methylated in dry acetone using anhydrous potassium carbonate and dimethyl sulphate. White crystals of 4-Nitro-3-pentadecyl anisole (VII) melting at 49°-50°C (98% yield) were obtained. The same compound was previously obtained by Dawson[23] who carried out the methylation in presence of sodium hydroxide and dimethyl sulphate.



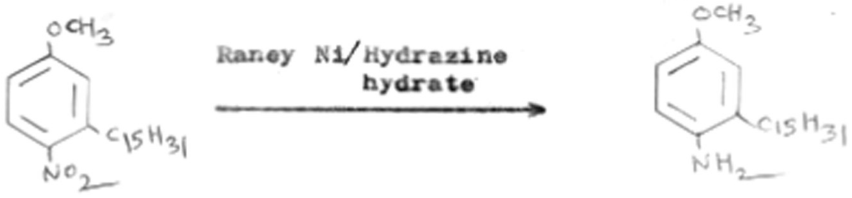
4-Nitro-3-pentadecyl phenol

4-Nitro-3-pentadecyl anisole (VII)

4-Amino-3-pentadecyl anisole (VIII)

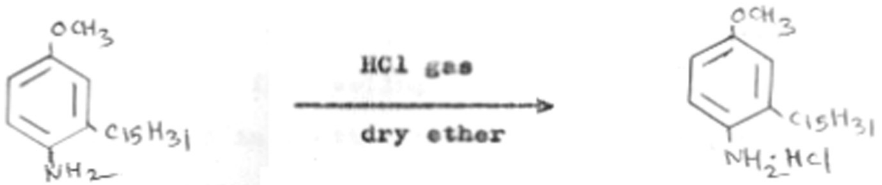
4-Nitro-3-pentadecyl anisole after reducing with Raney nickel and hydrazine hydrate gave 4-amino-3-pentadecyl anisole (VIII) M.P. 45°C.

The hydrochloride of the 4-amino-3-pentadecyl anisole was prepared by passing hydrochloric acid gas through the solution of amino compound in dry ether. The insoluble white hydrochloride was separated washed and dried. The hydrochloride had a M.P. 114°-115°C.



4-Nitro-3-pentadecyl anisole

4-Amino-3-pentadecyl anisole (VIII)

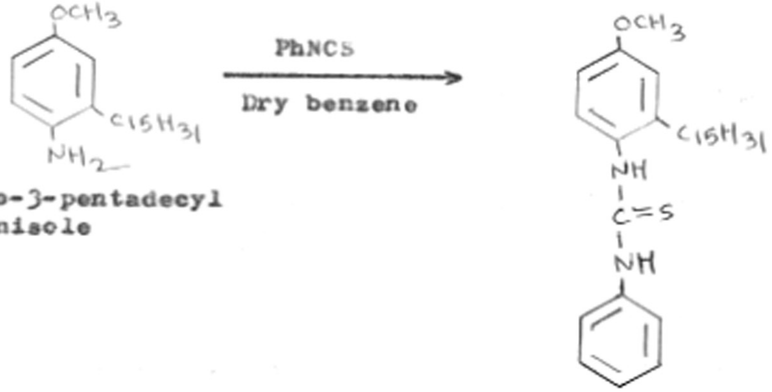


4-Amino-3-pentadecyl anisole

Hydrochloride of (VIII)

### N-(2-pentadecyl-4-methoxy phenyl), N′-phenyl thiourea (IX)

4-Amino-3-pentadecyl anisole after reacting with phenyl isothiocyanate in dry benzene, yielded the methylated unsymmetrical thiourea, N-(2-pentadecyl-4-methoxy phenyl), N′-phenyl thiourea (IX) m.p. 87°C.



4-Amino-3-pentadecyl anisole

N-(2-pentadecyl-4-methoxy-phenyl),N′-phenyl thiourea (IX)

### Monsanto Rheometer and Evaluation of Accelerators

The Monsanto oscillating Disc Rheometer is a valuable tool for rubber compounding, quality control and research applications. Model MP is a versatile model which quickly and precisely determines the curing and processing characteristics of elastomers during the entire cycle of curing. It is completely automated. The specification about the use of this valuable apparatus has recently been published by American Society for Testing and Materials (A.S.T.M.),[25] and also described in another technical bulletin.[17]

A brief summary of the method is given below.

In this test a specimen of rubber is contained in a sealed test cavity under a positive pressure and maintained at an elevated temperature. A biconical disc is embedded in the test specimen and is oscillated through a small arc. The sinusoidal oscillation of the disc exerts a shear strain on the test specimen and the force (torque) required to oscillate the disc is proportional to the stiffness (shear modulus) of the rubber. The torque is recorded autographically as a function of time.

The stiffness of the rubber specimen increases as cure begins. A complete cure curve is obtained when the recorder torque either rises to an equilibrium value or to a maximum value. The time required to obtain a cure curve is a function of the test temperature and the curing characteristics of the rubber compound. The following measurements may be taken from a cure curve:-

(a) Minimum torque,

(b) Time to incipient cure (Scorch time),

(c) Time to optimum cure or a percentage of full cure and

(d) Maximum, equilibrium or highest torque attained by a particular cure curve.

The minimum torque is proportional to the stiffness or low shear rate viscosity of the uncured compound. The scorch time is a measure of processing safety. The time to optimum or some percentage of full cure is an inverse measure of cure rate while the fully cured torque is a measure of cured shear modulus or stiffness at the test temperature.

The cure rate index is the average slope of the rising cure curves.

## Evaluation of Accelerators

The two new unsymmetrical aromatic thioureas (VI) and (IX), in combination with thiourea, were evaluated as secondary booster accelerators in a low sulphur/high sulphenamide accelerated natural rubber tyre tread type 'E.V.' compound.

It has been previously reported that the limiting value for use of thiourea in rubber stocks is 1 pphr. Hence thiourea and the two aromatic thioureas were used in quantities of 1 pphr. The proportion of the thioureas in the mixtures was varied from 75:25, 50:50, and 25:75 of thiourea:aromatic thiourea, keeping the limiting value of the mixture 1 pphr.

Table III describes the seven tyre tread compounds prepared on a laboratory type 6" x 12" mixing mill. Compound 1 is based on the conventional system, while compounds 2 to 7 are based on the E.V. system. The compounds 1 to 7 were cured using the Monsanto Oscillating Disc Rheometer Model MP, at different temperatures of 140°, 160° and 180°C. with a proper range selection and suitable chart motor. The curing behaviours of the different stocks were recorded graphically on a flat bed recorder attached to the Rheometer.[17]

The parameters 1 to 10 with a clear meaning of each in Rheometric studies of rubber compounds are given in Table IV.

In the initial step, the temperature of vulcanization

**TABLE III.** NR TYRE TREAD COMPOUND HAVING DIFFERENT PROPORTIONS OF THE THIOUREA SECONDARY ACCELERATORS

**Base stock**

| | |
|---|---|
| Smoked sheet RMA-1X | 100 |
| HAF Black (Philblack O) | 50 |
| Zinc oxide | 5 |
| Stearic acid | 1 |
| Dutrex R | 3 |
| Santoflex IP | 1 |

| | Conventional | E.V. System | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Sulphur | 2.5 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 | 0.33 |
| Santocure NS | 0.5 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 | 5.00 |
| Thiourea | - | 1.00 | 0.75 | 0.50 | 0.25 | - | - |
| Compound VI | - | - | 0.25 | 0.50 | 0.75 | 1.00 | - |
| Compound IX | - | - | - | - | - | - | 1.00 |

TABLE IV. THE PARAMETERS WITH THEIR MEANING IN RHEOMETER STUDIES

| Parameter | Meaning |
|---|---|
| 1. Initial viscosity - Lo (in/lb) | Effect of mastication - time and procedure of milling. Effect of peptizers. |
| 2. Minimum viscosity - Li (in/lb) | Joint effect of acc. and processing characteristics flow properties in moulding. |
| 3. Thermoplasticity - Tp (Lo-Li)(in/lb) | Plastic effect before chemical reaction starts. |
| 4. Induction time - t1-time for one unit rise above Li (min). | Time when the chemical reaction starts. |
| 5. Scorch time - t2-time for two units rise above Li (min) | Characterises processing safety. |
| 6. Maximum cure - Lf (in/lb) | Highest crosslinking reached. |
| 7. Optimum cure - 0.9 (Lf-Li) + Li(in/lb) | Level of cure at which most properties would be satisfactory. |
| 8. Optimum cure time - t90 (min) | Time to reach optimum cure level. |
| 9. Cure rate - CR 100/(t90-t2)(min) | Comparative value of cure activity. |
| 10. Reversion time - RT-time to reach 98% LF after passing Lf(min) | Time to reach notable fall in maximum vulcanization level chain scission. |

was chosen to be 140°C which is usually the conventional temperature of vulcanization. The Rheometric results - parameters of the compounds 1 to 6, at 140°C are described in Table V.

From the calculated parameters in Table V, it appeared that compounds 2 and 3 have shorter scorch time than the conventiohal compound 1 while compounds 5 and 6 have longer scorch delay whereas c ompound 4 has scorch time nearly equal to the conventional compound 1. It therefore, appeared that the unsymmetrical aromatic thiourea (VI) had an effect of delaying the scorch time. It was also observed that maximum cure levels were higher in compounds 2 and 3 than in compounds 5 and 6.

Compounds 2,3,4 and 5, which are mixtures of thiourea and unsymmetrical thiourea, have maximum cure levels higher than the maximum cure level obtained by the conventional compound 1. However the maximum cure level obtained by unsymmetrical aromatic thiourea i.e. compound 6 is lower than the maximum cure level obtained by the conventional compound 1. The optimum cure time was observed to increase gradually from compound 1 to compound 6.

The compounds were then vulcanized at 160°C in order to assess the influence of temperature on these compounds. The Rheometric results at 160°C are described in Table VI.

The parameters in Table VI show that compounds 2, 3, 4 and 5 have shorter scorch times than the scorch time for the conventional compound 1, while compound 6 has longer scorch

TABLE V. THE PARAMETERS OBTAINED AT 140°C TEMPERATURE OF VULCANISATION

Stock = NR
Temperature = 140°C
Preheat = 20 seconds
Chart motor = 60'
Range Sel. = 100

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1. Initial viscosity - Lo (in/lb) | 28.00 | 19.00 | 19.00 | 18.50 | 19.00 | 19.00 |
| 2. Min. viscosity - Li (in/lb) | 18.40 | 12.00 | 10.50 | 11.40 | 11.00 | 9.00 |
| 3. Thermoplasticity - Tp (Lo-Li)(in/lb) | 9.60 | 7.00 | 8.50 | 7.10 | 8.00 | 10.00 |
| 4. Induction time - t1 - time for one unit rise above Li (min) | 3.5 | 1.50 | 2.60 | 3.65 | 6.40 | 10.50 |
| 5. Scorch time - t2 time for two units rise above Li (min) | 3.75 | 1.60 | 2.75 | 3.90 | 6.50 | 11.90 |
| 6. Maximum cure - Lf (in/lb) | 64.50 | 83.00 | 74.00 | 71.00 | 72.00 | 56.00 |
| 7. Optimum cure - 0.9 (Lf-Li) + Li (in/lb) | 68.90 | 75.90 | 67.65 | 64.14 | 65.90 | 51.30 |
| 8. Optimum cure time - t90 (min) | 10.90 | 13.00 | 18.00 | 19.00 | 32.50 | 42.50 |

TABLE VI. THE PARAMETERS OBTAINED AT 160°C TEMPERATURE OF VULCANISATION

Stock = NR
Preheat = 20 seconds
Temperature = 160°C
Chart Motor = 12′
Range Sel. = 100

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1. Initial viscosity - Lo (in/lb) | 17.80 | 11.00 | 12.50 | 13.20 | 15.00 | 12.00 |
| 2. Minimum viscosity - Li (in/lb) | 9.40 | 9.40 | 9.20 | 9.50 | 9.40 | 6.90 |
| 3. Thermoplasticity - Tp (Lo-Li)(in/lb) | 8.40 | 1.60 | 3.30 | 3.70 | 5.60 | 5.10 |
| 4. Induction time - t1 - time for one unit rise above Li (min) | 3.90 | 1.05 | 1.45 | 1.85 | 2.90 | 4.35 |
| 5. Scorch time - t2 - time for two units rise above Li (min) | 4.05 | 1.15 | 1.58 | 2.00 | 3.06 | 4.70 |
| 6. Maximum cure - Lf (in/lb) | 54.80 | 69.80 | 63.20 | 66.80 | 66.00 | 47.00 |
| 7. Optimum cure - 0.9 (Lf-Li) + Li (lb/in) | 50.26 | 63.76 | 57.80 | 61.07 | 61.24 | 43.00 |
| 8. Optimum cure time - t90 (min) | 9.35 | 4.80 | 5.50 | 6.90 | 8.85 | 10.00 |

delay than compound 1.

Compounds 2, 3, 4 and 5, which are mixtures of thiourea and unsymmetrical thiourea, have maximum cure levels higher than the maximum cure level obtained by the conventional compound 1. The maximum cure level obtained by unsymmetrical aromatic thiourea i.e. compound 6 is lower than the maximum cure level obtained by the conventional compound 1.

The optimum cure time in each of compounds 2, 3, 4, and 5 is lower than the optimum cure time for the conventional compound 1. The optimum cure time for compound 6, is however slightly higher than the optimum cure time for the conventional compound 1. These studies revealed that mixture of thiourea and unsymmetrical aromatic thiourea are affected by rise in temperature of vulcanization.

The use of high temperature for vulcanization of rubber has been considered as an attractive proposition. However, it was observed that high temperature vulcanization of natural rubber, was of inferior quality due to reversion phenomenon. It was therefore thought interesting to further increase the temperature of vulcanization and to see the effects of these thiourea mixtures on reversion.

The compounds were therefore vulcanized at 180°C and that these results are described in Table VII.

The parameters in Table VII indicate that compounds 2, 3, 4 have shorter scorch times than the scorch time for the conventional compound 1, while compound 6 has longer scorch delay than compound 1. Compound 5 has scorch time which may be

TABLE VII. THE PARAMETERS OBTAINED AT 180°C TEMPERATURE VULCANISATION

Stock = NR
Preheat = 20 seconds
Temperature = 180°C
Chart motor = 30'
Range Sel. = 100

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1. Initial viscosity - Lo (in/lb) | 15.00 | 11.50 | 11.50 | 13.50 | 15.00 | 14.00 |
| 2. Minimum viscosity - Li (in/lb) | 10.00 | 10.60 | 10.80 | 12.00 | 11.00 | 8.70 |
| 3. Thermoplasticity - Tp (Lo/Li) (in/lb) | 5.00 | 0.90 | 0.70 | 1.50 | 4.00 | 5.30 |
| 4. Induction time - ti - time for one unit rise above Li (min) | 1.37 | 0.20 | 0.65 | 0.80 | 1.25 | 2.00 |
| 5. Scorch time - t2 - time for two units rise above Li (min) | 1.50 | 0.30 | 0.70 | 0.92 | 1.40 | 2.12 |
| 6. Maximum cure - Lf (in/lb) | 56.80 | 70.30 | 64.80 | 67.40 | 66.00 | 54.80 |
| 7. Optimum cure - 0.9 (Lf-Li) + Li (in/lb) | 52.12 | 64.33 | 59.40 | 61.86 | 60.50 | 50.19 |
| 8. Optimum cure time - t90 (min) | 3.62 | 2.25 | 2.75 | 3.12 | 4.00 | 4.87 |
| 9. Reversion time - RT - time to reach 98% Lf after passing Lf (min) | 6.37 | - | - | - | - | - |

said as nearly equal to scorch time for compound 1.

Compounds 2, 3, 4 and 5 have maximum cure levels, higher than the maximum cure level for compound 1. The maximum cure level for compound 6 may be said to be slightly lower than the maximum cure level for compound 1.

Compounds 2, 3 and 4 have optimum cure times lower than the optimum cure time for compound 1 and compounds 5 and 6 have optimum cure time to be slightly more than the optimum cure time for compound 1.

One promising feature of this study was that compounds 2 to 6 containing mixtures of thioureas were stable towards reversion at 180°C.

The unsymmetrical aromatic thiourea (VI) used in this study has a free phenolic hydroxyl group. It was considered that this free phenolic group may have some advantageous effects in the vulcanization. It was therefore decided to convert the phenolic group into an ether linkage by methylation. The methylated unsymmetrical aromatic thiourea (IX), aromatic unsymmetrical thiourea (VI) and conventional compound 1, were then evaluated in similar Rheometric studies at 180°C. These results are shown in Table VIII.

The parameters in Table VIII indicate that compounds 6 and 7 have slightly higher scorch time than the scorch time for compound 1. The maximum cure levels for compounds 6 and 7 may be said to be slightly lower than the maximum cure level for compound 1. Optimum cure times for compounds 6 and 7 were slightly higher than the optimum cure time for

TABLE VIII. COMPARATIVE PARAMETERS AT 180°C FOR CONVENTIONAL COMPOUND NO. 1 AND THE TWO UNSYMMETRICAL THIOUREAS

Stock = NR
Preheat = 20 seconds
Temperature = 180°C
Chart motor = 12′
Range Sel. = 100

| | 1 | 6 | 7 |
|---|---|---|---|
| 1. Initial viscosity - Lo (in/lb) | 22.00 | 17.00 | 18.00 |
| 2. Minimum viscosity - Li (in/lb) | 18.00 | 13.50 | 14.00 |
| 3. Thermoplasticity - Tp (Lo-Li)(in/lb) | 4.00 | 3.50 | 4.00 |
| 4. Induction time - ti - time for one unit rise above Li(min) | 1.28 | 1.25 | 1.45 |
| 5. Scorch time - t2 - time for two units rise above Li (min) | 1.38 | 1.40 | 1.60 |
| 6. Maximum cure - Lf (in/lb) | 60.80 | 56.00 | 55.80 |
| 7. Optimum cure - 0.9 (Lf-Li) + Li (in/lb) | 56.52 | 57.75 | 51.62 |
| 8. Optimum cure time - t90 (min) | 2.64 | 3.05 | 3.20 |
| 9. Reversion time - RT - time to reach 98% LF after passing Lf(min) | 4.05 | - | - |

compound 1. Compounds 6 and 7 were stable towards reversion at 180°C whereas compound 1 was observed to revert at 180°C. This study indicated that compounds 6 and 7 gave nearly similar results.

Since a 50:50 combination of thiourea and hydroxy-aromatic thiourea (Table III, E.V. system No. 4) gave parameters at 140°C, very close to the conventional tyre tread compound (Table III No. 1), it was decided to study a comparative heat ageing performance of these two compounds at 100°C in ageing oven. The results of the degradation in physical properties, before and after ageing are given in Table IX.

Table IX describes that, before ageing the tensile strength and elongation properties of the two vulcanizates-conventional and E.V. compound are nearly similar. After 100°C air-oven ageing for 7 and 14 days, however, the tensile strength and elongation at break, in case of the conventional compound were retained to 20%, 8%, and 22% and 10% respectively. In case of the E.V. System the tensile strength and elongation at break retained were 74.98%, 70% and 60% and 50% respectively.

## TABLE IX. PHYSICAL PROPERTIES OF THE AGED AND UNAGED VULCANIZATES

| | Conventional (Table III, No. 1) | E.V. System (Table III, No. 4) |
|---|---|---|
| Optimum cure time at 140°C t90 (min) determined on Monsanto Oscillating Disc Rheometer | 10.90 (min) | 19.60 (min) |
| **Physical properties before ageing** | | |
| Tensile strength (p.s.i.) | 3562 | 3457 |
| Elongation at break % | 460 | 450 |
| **Air-oven ageing at 100°C** | | |
| **7 days** | | |
| Tensile strength (p.s.i.) | 712.4 | 2592 |
| % Tensile strength retained | 20% | 74.98% |
| Elongation at break % | 101 | 315 |
| % Elongation retained | 22% | 70% |
| **14 days** | | |
| Tensile strength (p.s.i.) | 284.9 | 2074 |
| % Tensile strength retained | 8% | 60% |
| Elongation at break % | 46 | 225 |
| % Elongation retained | 10% | 50% |

## (iii) Discussion

In modern rubber compounding advantage is frequently taken of combined action of two or more accelerators. If the accelerator combination is properly chosen, not only is pre-vulcanization prevented, but the vulcanized rubbers have better physical and mechanical properties, and the vulcanization requires less time and may be effected at a lower temperature than when either accelerator is used separately. As an example, a 1:1 mixture of mercaptobenzthiazole with hexamethylene-tetramine produces vulcanizates with optimum physical and mechanical properties and with a minimum tendency to scorch. The high activity of this mixture is explained due to the synergistic activity of the combined effect of the two accelerators.

Efficient vulcanization system[3-11] gives vulcanizates which are markedly superior in many respects to those given by the more conventional high sulphur/accelerator systems. The reason for obtaining superior properties by the E.V. system is because the vulcanizate network structure consists predominently of monosulphide and disulphide linkages. Vulcanizates consisting of these linkages are reported to have resistance to influence of heat and fatigue.

The vulcanization system employed in the present investigation is based on an E.V. system high accelerator/low sulphur boosted by thiourea or a mixture of thiourea and an unsymmetrical aromatic thiourea (VI). Initially the vulcanization studies were carried out at 140°C (Fig. 3).

In this study it was found that thiourea alone in the

E.V. System gave short scorch time with maximum crosslinking. The aromatic thiourea when used alone in the same E.V. system gave maximum scorch delay, showing thereby good processing safety. Thus, it was possible to obtain a more balanced level of optimum cure, maximum crosslinking and processing safety in comparison with the conventional system by balancing the proportions of thiourea and aromatic thiourea in the E.V. system.

By increasing the temperature of vulcanization from 140°C to 160°C the same mixtures of thiourea in E.V. system gave faster rate of cure (Fig. 4). This clearly showed that this E.V. system was more sensitive towards higher temperature ranges. In natural rubber compound, a tremendous amount of reversion is experienced, even at very low levels of accelerators of the sulphenamide type by vulcanization at high temperatures.

When the present system was run at 180°C (Fig. 5) it was noted that none of the compounds 2 to 6 showed any reversion, while the standard compound with normal level of sulphur and accelerator had an excessive reversion. It is thus clear that the thiourea based E.V. system produces vulcanizates which are more stable towards the influence of heat, even in natural rubber.

Effect of protection of free phenolic hydroxyl group, in the unsymmetrical aromatic thiourea (VI) by methylation and further evaluating the methylated product (IX) along with the aromatic thiourea (VI) and conventional compound 1, at

180°C, on Monsanto Rheometer, revealed that practically there was no difference in the overall curing performance of the two thioureas. However, the methylated thiourea had a slight delayed action, shown by the slightly longer scorch time than the thiourea containing free hydroxyl group (Fig. 6), (Table VIII).

The resistivity towards high temperature ageing (100°C) of the E.V. system, in study, is clearly indicated by the higher retention figures Table IX (75% and 60%) of the tensile properties, during the entire period of ageing. On the contrary, the conventional compound degrades very rapidly with a sudden fall in tensile properties, Table IX (20% and 8%) showing complete deformation of network structure towards the end of the ageing period. The same rate of degradation, in elongation at break, was shown by the conventional compound. This further confirmed that the E.V. compound in question, was superior to the conventional compound.

The lesser tendency towards the thermal oxidative degradation shown by the E.V. compound, might perhaps be due to the additional inhibiting antioxidant effect of the phenolic hydroxyl group present in the aromatic thiourea. Thus, the dual effect, such as acceleration, as well as antioxident activity shown by the aromatic thiourea, might have been the main cause of the high reactivity of this compound, shown in the present study.

## Conclusions

The following conclusions are derived :-

(1) Thiourea acts as excellent booster to the E.V. systems.

(2) By changing the ratios of thiourea and the unsymmetrical aromatic thiourea, the desired safety of scorch and rate of cure can be achieved to match the standard vulcanization system or any semi or full E.V. systems.

(3) Fastest rate of cure is obtained with thiourea and the lowest with the aromatic thiourea.

(4) The systems employed are sensitive towards temperature and as the temperature is raised, the rate of cure increases very rapidly.

(5) Highest rate of cure, maximum crosslinking and hence better physical properties can be achieved by using thiourea.

(6) A 50:50 combination of thiourea and the aromatic thiourea gives parameters very close to the conventional tyre-tread compound.

(7) The presence or absence of a hydroxyl group in the aromatic thiourea showed no marked effect in the rate of cure of cross-linking (Fig. 6).

(8) Presence of phenolic hydroxyl group in the aromatic thiourea (VI), gives additional protection to the E.V. compound, subjected to oven ageing at 100°C.

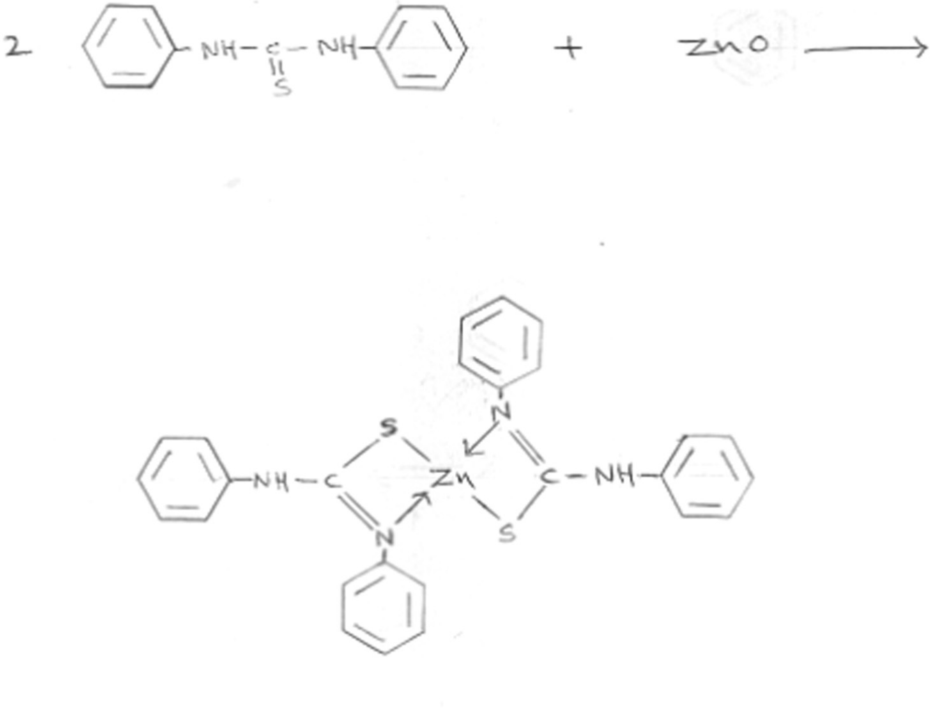
(9) Thiourea-accelerated E.V. system showed a distinct stability towards 'reversion' at 180°C. Thus such a system

will be of very much use in the injection moulding of natural rubber at high curing temperature conditions.

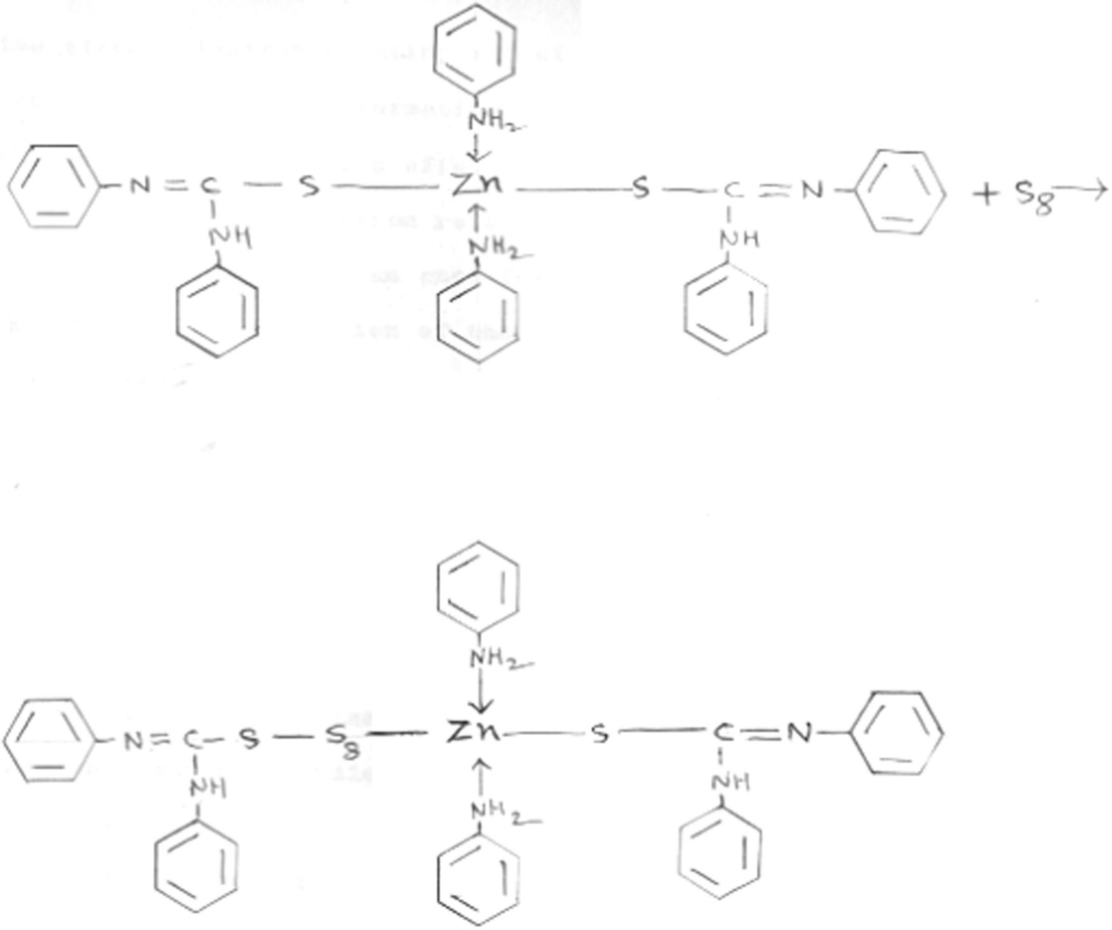
## Mechanism of Vulcanization

It is well known that the thioketo form of the thiocarbonilide is in equilibrium with the ene-thiol form.[18]

In the ene-thiol form the thiocarbonilide is then able to react with zinc oxide, which means that the accelerator is activated.[19,20]

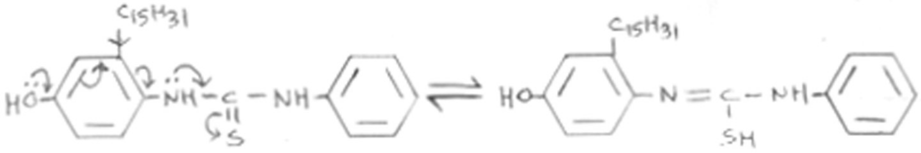


The structure of the zinc complex reminds one of the zinc complexes described in connection with di-thiocarbamate and thiazole accelerators. It is natural to assume that the activation reactions are similar to those in the case of those accelerators. According to Bedford and Sebrell,[21] a zinc complex formed from thiocarbanilide adds amines. Bateman[22] thinks that such an addition compound is able to react with sulphur and to activate it.



from the accelerator molecule, which thus acquires a large proportion of sulphur, some sulphur is then split off, again in a reactive form, and becomes available for cross-linking reactions.

In case of the unsymmetrical aromatic thioureas used in the present investigation,



the strong electron donating effect of the phenolic hydroxyl group facilitates the formation of enol form of the aromatic thiourea. The inductive effect of the long alkyl side chain adds to the electron release in the direction of nitrogen, thus resulting in an enol form. The rest of the mechanism of acceleration of the enol form of the unsymmetrical aromatic thiourea can then be explained as above. Acceleration of simple thiourea may also befit in a similar mechanism.

Even though the reaction mechanisms of the various accelerators cannot be expressed in terms of one universal equation, they still have a common chemical principle. They all accelerate vulcanization by forming active sulphur fragments and free radicals, including polymeric free radicals, as well as reactive intermediate compounds which are unstable and readily decompose.

As a result of the reaction between these free radicals and sulphur fragments with the chain molecules of the rubber or with polymeric free radicals, three-dimensional cross-linking soon occurs at various sites of the chain, this results in far-reaching changes in the physical and mechanical properties of the rubber.

## (iv) Experimental

### 3-Pentadecadienyl phenol (Anacardol) (I)

Raw commercial cashewnut shell liquid (heat extracted) (900 gms) was distilled from a 2-litre round bottom flask, under vacuum. The flask was heated slowly till the initial frothing had subsided. 450 gms. of brown coloured distillated (yield 50%) was callected between 190°-240°/2-4 mm.Hg. pressure.[26] This was redistilled to give pale yellow anacardol $n_D^{30}$ 1.5080 (410 g., b.p. 195-200°C/2 mm).

Analysis: Found C, 83.80; H, 10.56%.

$C_{21}H_{32}O$ Requires C, 83.94; H, 10.76%.

### 3-Pentadecyl phenol (Tetrahydroanacardol)(II)

Anacardol (300 gms) was hydrogenated at 70°C in a Parr autoclav under 600 lbs/sq.in. pressure of hydrogen after the addition of 3-5 gms of Raney nickel catalyst. When no more hydrogen absorption was noticed the hydrogenation was stopped and the product filtered and crystallized from petrol ether (40°-60°). 3-pentadecyl phenol (tetrahydro-anacardol) (270 gms) 90% yield was obtained as white waxy solid, m.p. 50°-51°C.[26] b.p. 215°-20°C/4 mm.

Analysis: Found, C, 83.16, H, 11.41%.

$C_{21}H_{36}O$ requires C, 82.83, H, 11.92%

### 4-Nitro-3-pentadecyl phenol (III) and 6-nitro-3-pentadecyl phenol (IV)

3-Pentadecyl phenol was nitrated with fuming nitric acid (sp.gr. 1.5) below 10°C, in chloroform, according to the method given in literature.[23]

3-Pentadecyl phenol (20 gms), dissolved in 75 ml. of chloroform was taken in a 250 ml. beaker. 5.3 g. (1.2 mol) of fuming nitric acid (Sp.gr. 1.5) was added to it dropwise with stirring and cooling in an ice bath. The temperature was maintained at 5°-10°C during the ten minutes of addition of the acid, and the solution was stirred for another 20 minutes at 10°C. The reaction mixture was poured into water, solvent removed in vacuo and the residue solidified on cooling in freez. After filtration and drying 23 g. of red-orange solid separated. The crude solid mixture of mononitro isomers of 3-pentadecyl phenol was dissolved in 150 ml. of petroleum ether (60°-80°) and cooled overnight. About 8 gms. of light tan powder of 4-nitro-3-pentadecyl phenol separated. This on further two crystallizations from the same solvent gave the product which melted at 70°-71°C.

Analysis: Found: C, 72.01; H, 10.24; N, 4.05%

$C_{21}H_{35}O_3N$ requires C, 72.16; H, 10.10; N, 4.01%

The filtrate was saved for the isolation of the 6-nitro isomer, which was obtained in the form of dark brown oil, after removing the solvent from the filtrate. The oil was taken up in 95% ethyl alcohol, treated with active charcoal and filtered. Upon cooling slowly, 5.0 gms. of 6-nitro-3-pentadecyl phenol separated. It melted at 39°C.

Analysis. Found, C, 72.54; H, 10.13; N, 4.05%

$C_{21}H_{35}O_3N$ requires C, 72.16; H, 10.10; N, 4.01%

### 4-Amino-3-pentadecyl phenol (V)

4-Nitro-3-pentadecyl phenol 1.75 gms (1.mol), was taken in 100 ml. round bottom flask, containing 25 ml. of absolute alcohol. To this, 0.80 ml. (3 mols) of 98% hydrazine hydrate and 0.200 gms. of Raney nickel catalyst were added. Then the whole solution was refluxed on the water bath for 3-4 hours. After this period, the solution was filtered concentrated and cooled to 0°C, when 4-amino-3-pentadecyl phenol separated.

It was crystallised from ethanol. Light brownish coloured crystals (1 gm.) m.p. 105°-106°C.[23]

Analysis: Found, C, 79.09; H, 11.28; N, 4.02%.

$C_{21}H_{37}ON$ requires C, 78.94; H, 11.67; N, 4.3%.

### N-(2-pentadecyl-4-hydroxyphenyl), N′-phenyl thiourea (VI)

4-Amino-3-pentadecyl phenol 4.264 gms. (1 mol) was taken in 100 ml. round bottom flask. 16 ml. of dry benzene and 1.6 ml. (1 mol.) phenyl isothiocyanate were added to the flask. The solution was refluxed on a water bath for 5 hours. On cooling, a solid was crystallised from ethanol. Brown crystals (3 gms.) m.p. 134°C.

Analysis: Found, C, 73.41; H, 9.13; N, 6.67; S, 7.33%.

$C_{28}H_{42}ON_2S$ requires C, 73.99; H, 9.24; N, 6.16; S, 7.04%

### 4-Nitro-3-pentadecyl anisole (VII)

4-Nitro-3-pentadecyl phenol 10 gms. (1 mol), was dissolved in 150 ml. dry acetone in a 1 litre capacity round bottom flask. To the above solution 30 gms. of anhydrous potassium carbonate and 4.15 ml. (1.5 mols) of freshly distilled dimethyl sulphate, were added. The whole mixture was refluxed on a water bath for about 30-35 hours. The acetone was removed by distillation. The dry mass was treated with sufficient amount of warm water in order to decompose unreacted dimethyl sulphate. The solution was cooled and filtered. The crude reaction product was crystallized from ethyl alcohol. The product weighed 9.80 gms. m.p. 49°-50°C.[23]

Analysis: Found, C, 73.40; H, 10.08; N, 3.81%

$C_{22}H_{37}O_3N$ requires C, 72.68; H, 10.26; N, 3.85%.

### 4-Amino-3-pentadecyl anisole (VIII)

4-Nitro-3-pentadecyl anisole 1.80 gms. (1 mol) dissolved in 25 ml. of absolute alcohol, was taken in 100 ml. round bottom flask. 0.2 gm. of Raney nickel catalyst was added, and 0.8 ml. of 98% hydrazine hydrate solution (3 moles) was slowly dropped in, when a brisk reaction was started. The mixture was refluxed on a water bath for 3 hours. By the end of this period, the reaction was subsided. Then the solution was filtered, catalyst removed and the filtrate was concentrated and cooled to 0°C, when crystals of amine separated. The crude product after recrystallizing from ethanol, melted at 45°C.

Analysis: Found, C, 79.20; H, 11.28; N, 4.21%.

$C_{22}H_{39}ON$ requires C, 79.20, H, 11.81, N, 4.20%.

Hydrochloride derivative of amine had a m.p. 114°-115°C.

Analysis: Found, C, 71.74; H, 10.90%.

$C_{22}H_{40}NOCl$ requires C, 71.55; H, 10.84%.

N-(2-pentadecyl-4-methoxyphenyl), N′-phenyl thiourea (IX)

4-Amino-3-pentadecyl anisole 4.44 gms. (1 mol), 1.6 ml. (1 mol) of phenylisothiocyanate and 8 ml. dry benzene were taken in a 100 ml. round bottom flask. The mixture was refluxed on a water bath for 5 hours and cooled, when solid crude thiourea separated. It was filtered and the solid mass was recrystallized twice from methyl alcohol, when white crystals were separated (2 gms.). m.p. 87°C.

Analysis: Found, C, 74.70; H, 9.72; N, 5.66; S, 6.43%.

$C_{29}H_{44}ON_2S$ requires C, 74.37; H, 9.40; N, 5.98; S, 6.83%.

Compounding of the rubber mixes

All the compounding ingredients were commercial rubber grade chemicals.

Mixing: All the mixes given in Table III were prepared on a conventional laboratory size 6" x 12" two roll rubber mixing mill. Rubber was masticated on a cold mill, immediately a band was formed. All the ingredients were then added according to the compounding recipes given in Table III. Sulphur and accelerator were added at the end. The mix was cut thrice from either side and rolled six times through tight mill and sheeted out. The sheets of the mixes were rested overnight.?

Vulcanization: The rubber sheets 6" x 6" x 0.075" were vulcanized in a laboratory type carver hydraulic press, with a temperature of 140° ± 1°C, and under 2000 lbs/sq.in. pressure for the specified time.

Determination of physical properties

From the vulcanized sheets dumb-bell shaped specimens were cut with 'dumb-bell type C'.

The physical properties such as Tensile strength, Elongation at break of the vulcanizates were determined on a Scott-tensile testing machine according to A.S.T.M. designation D 412-64T (1965). The rate of the power actuated grip was 40 inches per minute and was kept uniform at all times.

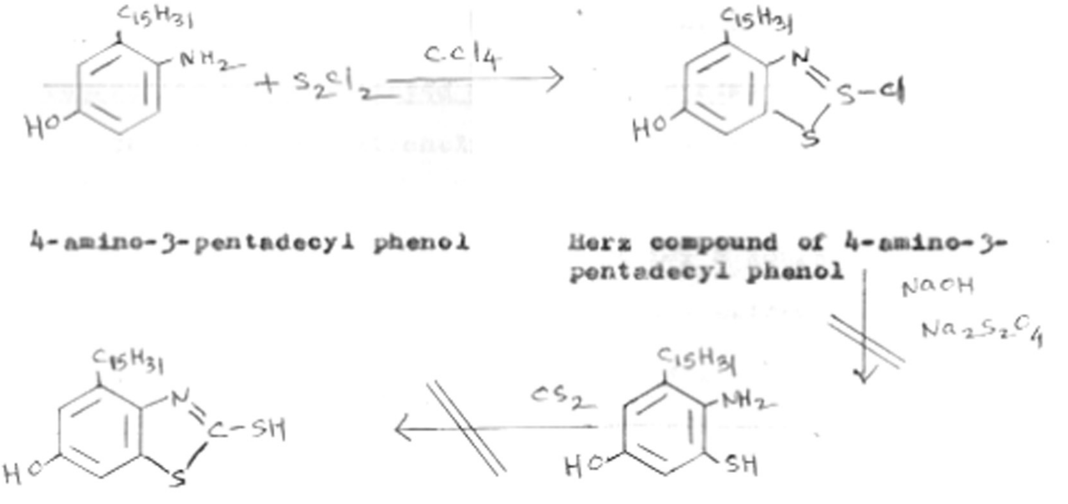
Ageing of the Dumb-bell shaped test specimens was carried out in an air circulated Emmersion-Ageing oven at 100° ± 1°C, according to A.S.T.M. Designation D-573-53. Tensile strength and elongation at break were observed before ageing and after 7th and 14th days ageing of the samples in oven.

Rheometric studies of the mixes in Table III were carried out in Monsanto Oscillating-Disc Rheometer Model MP, according to A.S.T.M. Designation D-2705-68T.

Apart from the syntheses of unsymmetrical arylthioureas from 4-amino-3-pentadecyl phenol and 4-amino-3-pentadecyl anisole, an attempt was made to prepare substituted mercapto-benzothiazole and substituted unsymmetrical diphenyl guanidine type accelerators from 4-amino-3-pentadecyl phenol, but these attempts did not reach upto the successful stage. Though the results in the syntheses of these compounds were negative, the experimental part for the attempted syntheses of these compounds are described below.

Attempted synthesis of substituted mercaptobenzothiazole

4-Amino-3-pentadecyl phenol was condensed with sulphur-monochloride, in presence of carbon tetrachloride. After completion of the reaction a typical reddish-brown 'Herz compound' was obtained. It had a m.p. 210°-215°C (with decomposition). The Herz compound was further subjected to hydrolysis with alkali, in presence of small amount of sodium dithionite, for getting the corresponding substituted ortho-amino-thiol. But a fluffy silky compound with a m.p. 125°-126°C was obtained which surprisingly contained no sulphur. A similar observation made by other workers is given in literature.[27] Hydrolysis of the Herz compound in situ and further cyclization with carbondisulphide for getting the corresponding substituted mercaptobenzothiazole,[27] failed. The steps involved in the attempted synthesis are given below.



4-amino-3-pentadecyl phenol

Herz compound of 4-amino-3-pentadecyl phenol

6-hydroxy-4-pentadecyl-2-mercapto-benzothiazole

2-amino-3-pentadecyl-5-hydroxy-phenyl mercaptan

## Preparation of substituted Herz compound

4-Amino-3-pentadecyl phenol 1.063 gms. (1 mol), sulphur monochloride 0.58 ml. (2.1 moles) and carbontetrachloride 10 ml., were taken in a 25 ml. round bottom flask. The reaction mixture was refluxed on water bath for 10 hours, cooled, filtered and washed with benzene. A reddish brown Herz compound, m.p. 210°-215°C (decomposition) (1.2 gms) was obtained.

## Preparation of substituted O-amino-thiol

To the Herz compound 1.6 gms dissolved in 10 ml. of 30% ethyl alcohol, 1.0 gms. of NaOH and 0.5 gm. of sodium hydrosulphite ($Na_2S_2O_4$) were added and the solution was refluxed on water bath for 5 hours in a 25 ml. round bottom flask. It was further cooled, and acidified with dilute acetic acid, when a solid separated. It was further crystallized several times, from ethyl alcohol when silvery fluffy crystals were separated. m.p. 125°-126°C. (0.8 gms).

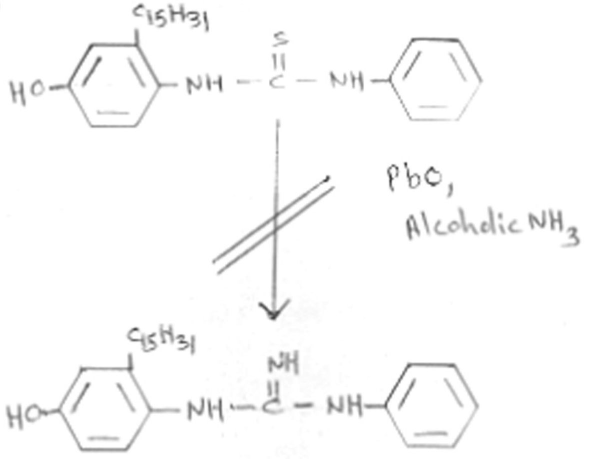
Analysis: Found, C, 71.25; H, 10.24; N, 3.74; S, nil %
$C_{21}H_{37}ONS$ requires C, 71.80; H, 10.54; N, 3.98; S, 9.1%

## Preparation of substituted Mercaptobenzothiazole

To the reduced alcoholic solution of Herz compound, as described above, 5 ml. of carbondisulphide was added and the solution was refluxed on a water bath for 8 hours. It was cooled, acidified with dilute HCl and was extracted with ether. After drying over anhydrous $Na_2SO_4$, it was filtered, and ether was evaporated, the mass was crystallized from ethanol, when a gummy resinous mass was obtained. The microanalytical results for C, H, N, and S did not tally with the expected substituted mercaptobenzothiazole.

### Attempted synthesis of unsymmetrically substituted diphenyl guanidine from N-(2-pentadecyl-4-hydroxy phenyl), N′-phenyl thiourea.

An unsymmetrical aryl thiourea (VI) was subjected to desulphuration and aminolysis in presence of litharge - (yellow lead oxide) and ethanolic ammonia, under pressure in a pressure vessel, according to the procedure given in literature.[28]



N-(2-pentadecyl-4-hydroxyphenyl), N′-phenyl guanidine

### Preparation of substituted unsymmetrical diphenyl guanadine from unsymmetrical aryl thiourea

N-(2-pentadecyl-4-hydroxy phenyl), N′-phenyl thiourea (VI) 1.135 gms. (1 mol), yellow lead oxide 1.115 gms (1. mol) and 5 ml. of strong ethanolic ammonia were heated in a stainless steel pressure vessel on a water bath for 8-10 hours.

Lead sulphide formed in the reaction was removed by filtration, and the excess ammonia was removed by heating the alcoholic solution. The filtrate was concentrated and cooled to 0°C when 0.5 gms of a white compound m.p. = 163°-165°C was obtained. It unexpectedly contained sulphur and there was no indication of D.P.G. formation. The micro-analytical results for C, H, and N did not tally with the expected unsymmetrically substituted diphenyl guanidine.

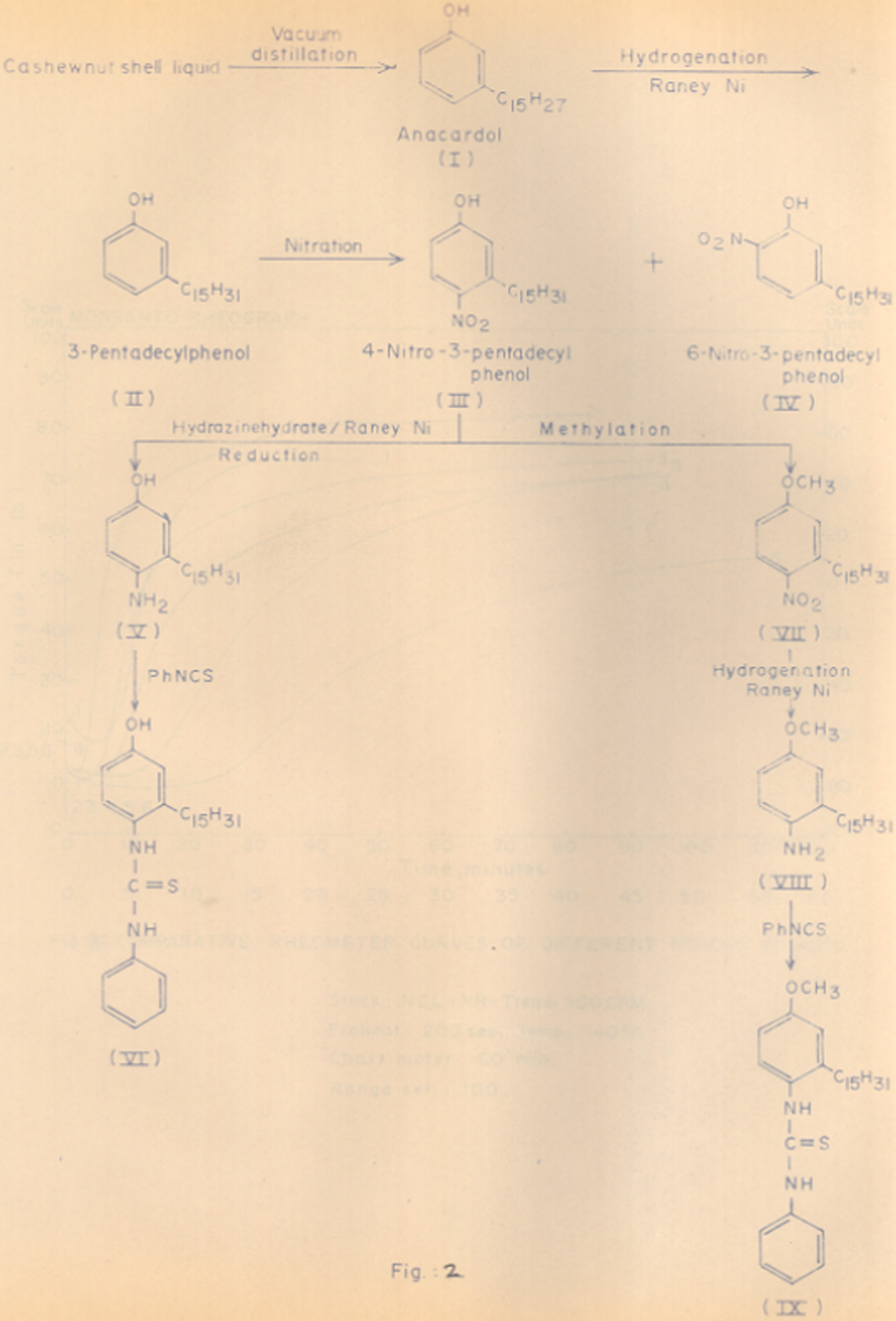

Cashewnut shell liquid
Vacuum distillation
Anacardol
(I)
Hydrogenation
Raney Ni
3-Pentadecylphenol
(II)
Nitration
4-Nitro-3-pentadecyl phenol
(III)
+
6-Nitro-3-pentadecyl phenol
(IV)
Hydrazinehydrate/Raney Ni
Reduction
Methylation
(V)
PhNCS
(VI)
(VII)
Hydrogenation
Raney Ni
(VIII)
PhNCS
(IX)

Fig. : 2

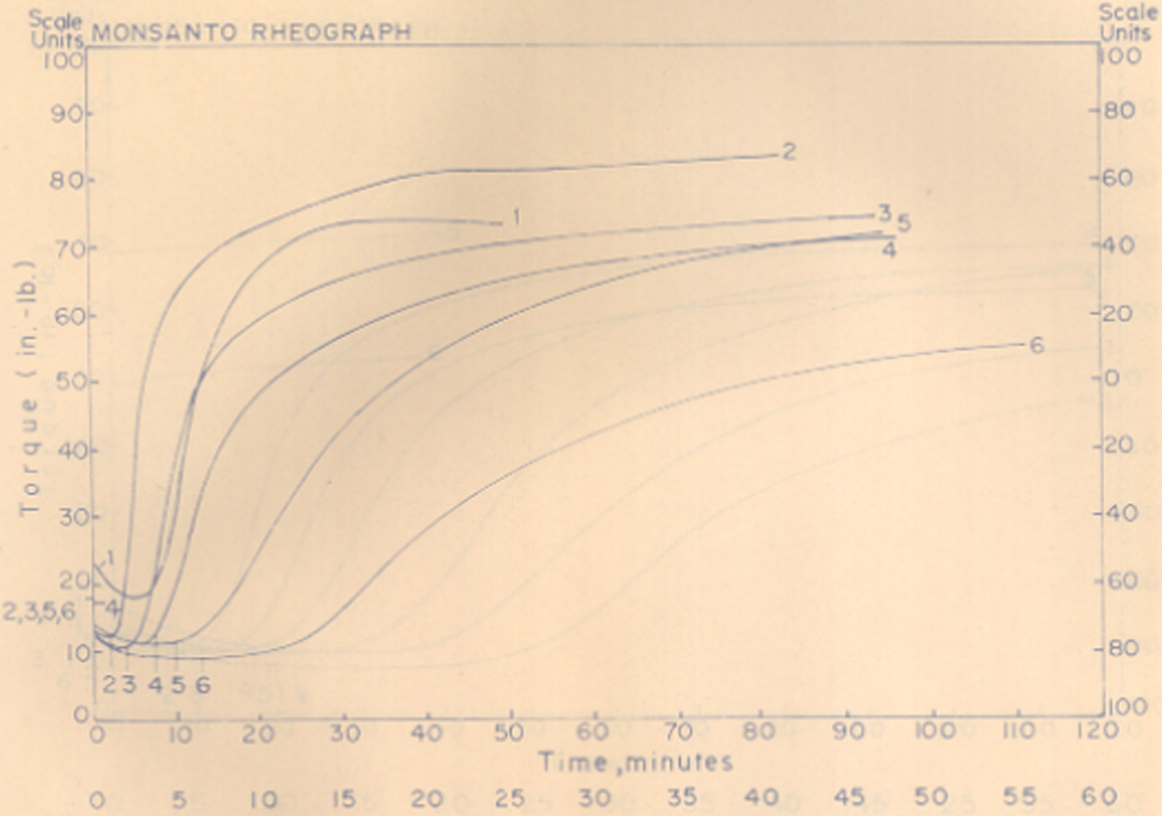


Fig. 3 COMPARATIVE RHEOMETER CURVES OF DIFFERENT STOCKS AT 140°C.

Stock : NCL - NR - Tread - 900 CPM.

Preheat : 200 sec. Temp. : 140°C.

Chart moter : 60' min.

Range sel. : 100.

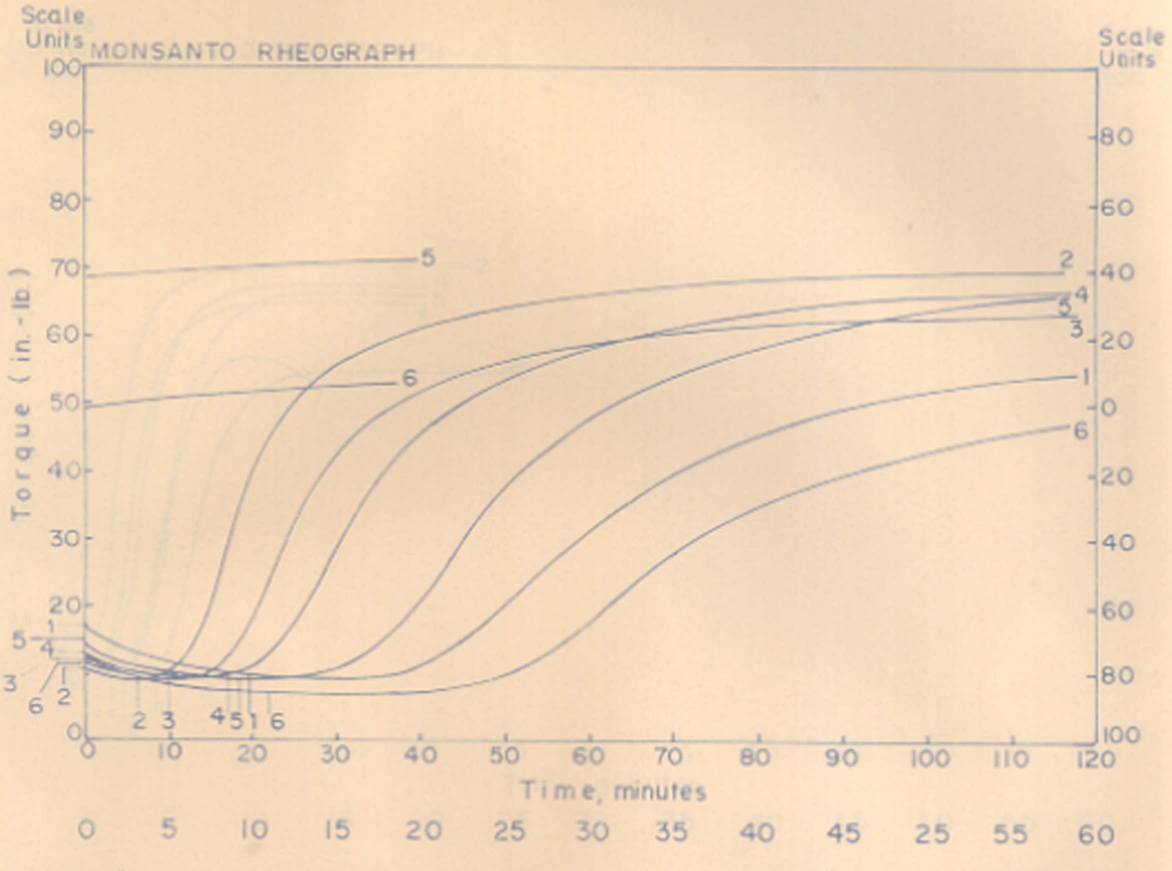


Fig 4 COMPARATIVE RHEOMETER CURVES OF DIFFERENT STOCKS AT 160°C.

Stock : NCL - NR - Tread - 900 CPM.
Preheat : 20 sec. Temp. : 160°C.
Chart moter : 12' min.
Range sel. : 100.

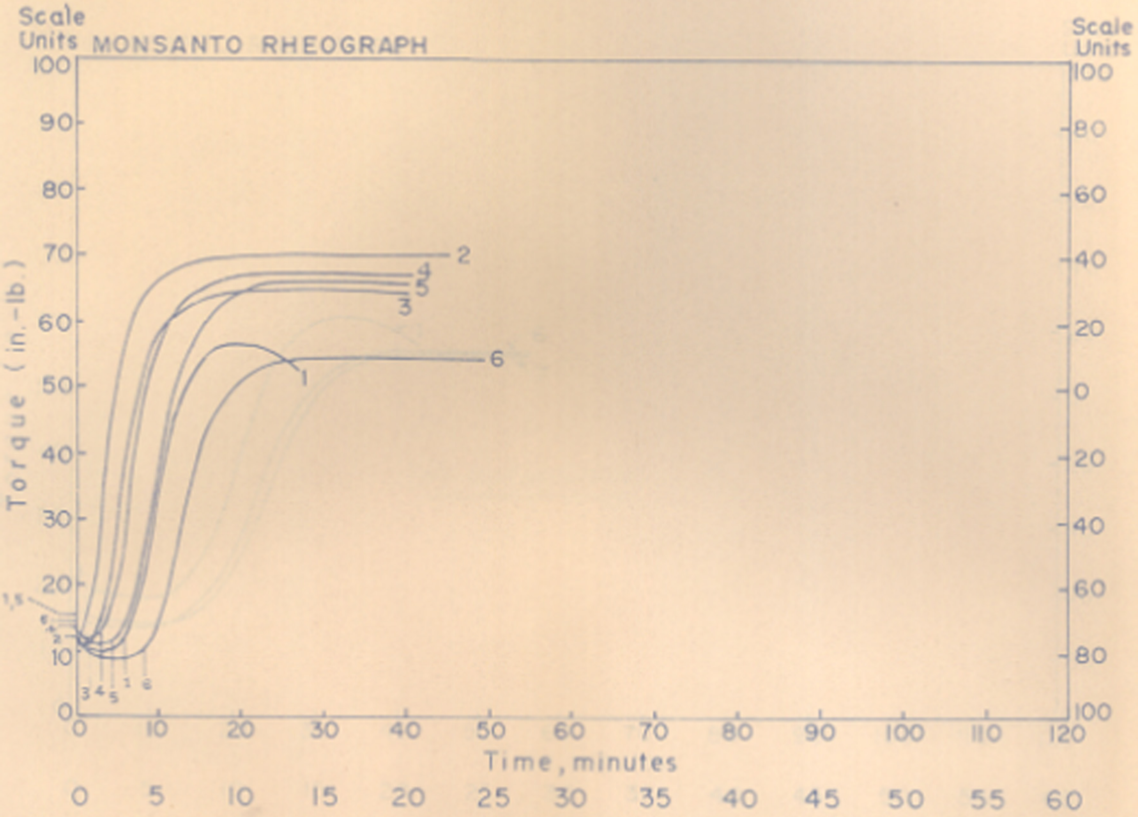


Fig.: 5 COMPARATIVE RHEOMETER CURVES. OF DIFFERENT STOCKS AT 180°C

Stock: NCL - NR - Tread - 900 CPM.
Preheat: 20 scc. Temp.: 160°C.
Chart moter: 30'min.
Range sel.: 100.

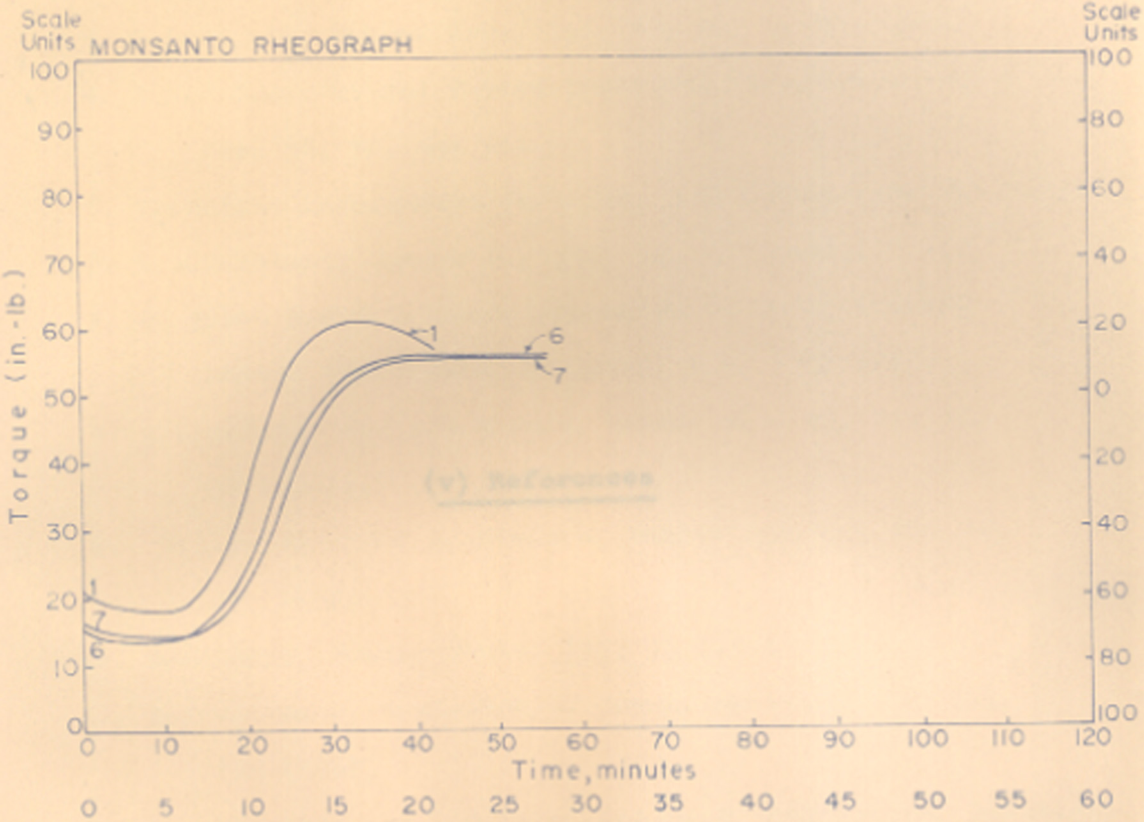


Fig.:6 RHEOMETER CURVES OF BOOSTER-ACCELERATORS BASED ON HYDROXYPHENYL AND METHOXYPHENYL THIOUREAS FROM C.N.S.L.* ALONG WITH CURVE OF CONVENTIONAL STOCK.

Stock : NCL - NR - Tread-900 CPM.
Preheat : 20 sec. Temp. : 180 °C.
Chart moter : 12'min.
Range sel. : 100.

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# SYNOPSIS

## Object of the present investigation

India is one of the major cashewnut (Anacardium occidentale) producing countries of the world, and meets about 90% of the total world demand for cashew kernels.

During the hot processing of the cashewnut shells, a dark brownish-black, viscous, vesicant liquid is oozed out, which is called cashewnut shell liquid (CNSL).

The commercial heat treat~~ment~~ed cashewnut shell liquid contains 90% of anacardol, meta-pentadecadienyl phenol and 10% of cardol, 5-pentadecadienyl resorcinol. The side alkyl chain $C_{15}H_{27}$ contains mono and a diolefinic unsaturation. The industrial uses of CNSL include surface coating materials, typewriter rolls, automobile break linings, detergents, dyes, petroleum antioxidants, germicides, insecticides, ion exchange resins, heat exchange media, etc. During the past few years, nearly 10,000 metric tons per annum of cashewnut shell liquid was exported from India to other foreign countries such as the U.K., the U.S.A., the U.S.S.R. and Japan.

The Rubber Industry in India is growing very rapidly. By 1971-72, the consumption of rubber in India will be about 200,000 M. tons. This will require about 5,000-6,000 tons of Rubber chemicals per annum. At present, only two units are engaged in the manufacture of rubber chemicals, starting from imported raw materials.

The present investigation was undertaken with a view to systematically exploring the possibilities of obtaining some

some useful new rubber chemicals from cashewnut shell liquid and to evaluate their activity in natural rubber compounds. The new rubber chemicals were mainly - (1) Antioxidants and (2) Accelerators.

A summary of the research work done for the doctoral dissertation is given below.

## PART I - ANTIOXIDANTS

### Section A - Synthesis of phenolic sulphide type antioxidant from CNSL and its evaluation in natural rubber

In the present investigation, 3-pentadecyl phenol was reacted with sulphurmonochloride in the presence of inert solvent, carbon tetrachloride, and the resulting dark resinous mass consisting of a mixture of mono and disulphides of 3-pentadecyl phenol, was used as a phenolic antioxidant in natural rubber. A similar phenolic sulphide type commercial antioxidant, 'Santowhite MK' of Monsanto Chemicals, was used as a standard antioxidant for comparison. The evaluation of the two sulphide type antioxidants was made in natural rubber gum and channel Black compounds. A blank was run containing no antioxidant. In channel black compound, synergistic activities of above sulphides in conjunction with phenyl-β-naphthyl amine were studied, and the mixtures showed better ageing properties than those of the phenyl-β-naphthyl amine used singly, thus showing a good synergistic effect. The ageing studies made at 70°C. revealed that the sulphide of 3-pentadecyl phenol showed a good antioxidant activity and compared favourably with the commercial antioxidant Santowhite MK of Monsanto.

### Section B - Constitution of disulphide of 3-pentadecyl phenol by infrared spectroscopy

A comperative infrared spectroscopic study of the disulphide of 3-pentadecyl phenol and a commercial phenolic sulphide type antioxidant 'Santowhite crystals' of Monsanto, was made both in nujol and carbontetrachloride. Absorption in the hydroxy region was selected for study. The changes in the spectra, in this region, in nujol and solvent ($CCl_4$) in both the sulphides, were correlated to their inter and intramolecular hydrogen bonding of the phenolic hydroxyl group with sulphur link. This study revealed that the sulphide link in the disulphide of 3-pentadecyl phenol was ortho to the phenolic hydroxyl group.

### Section C - Syntheses of substituted phenyl-β-naphthyl amine and aryl ureas from 4-amino-3-pentadecyl phenyl and evaluation of their antioxidant activity in natural rubber

The following four new compounds were synthesized from 4-amino-3-phentadecyl phenol:-

(1) Symmetrical aryl urea from 4-amino-3-pentadecyl phenol
(2) Unsymmetrical aryl urea from - do -
(3) Mono aryl urea from - do -
(4) Substituted phenyl-β-naphthyl amine from the mono-aryl urea of 4-amino-3-pentadecyl phenol.

The antioxidant activity of compounds 1, 2 and 4 was studied in natural rubber gum and channel Black compound. Commercial Phenyl-β-naphthyl amine was used for comparison.

The oxidation study was made on a quantitative oxygen absorption apparatus, similar to that developed by J.R. Shelton and co-workers of Case Institute of Technology, Cleveland, Ohio, U.S.A. The apparatus was fabricated in this Research Laboratory.

From the above studies, a correlation was established between the antioxidant activity and the molecular structure of these new antioxidants, in the light of modern concepts of electronic theory. One of these antioxidants showed a better performance than the commercial antioxidant, Phenyl-β-naphthyl amine.

## PART II - ACCELERATORS

### Development of new accelerator systems in 'Efficient Vulcanization' of natural rubber

The recent trend in the development of heat resisting 'Efficient Vulcanization Systems' has led to a new opening for the injection molding of natural rubber at high temperatures. Recent studies in literature has indicated the application of some secondary accelerators such as thiourea in conjunction with primary vulcanizing accelerator systems, for improving heat resistance of natural rubber. The use of thiourea in Efficient Vulcanization systems has shown that it gave a maximum crosslinking with better scorch delay and improved heat resistance to vulcanizates.

In the present study, two new unsymmetrical thioureas have been synthesised from 4-amino-3-pentadecyl phenol and

4-amino-3-pentadecyl anisole. They were evaluated in a typical natural rubber tyre tread E.V. compound containing low sulphur/High sulphenamide primary accelerator system.

Different proportions of thiourea/unsymmetrical aromatic thioureas, in the above E.V. compound were evaluated on a Monsanto Oscillating Type Rheometer Model MP. It was further found that a 50:50 proportion of thiourea/unsymmetrical aromatic thiourea of 4-amino-3-pentadecyl phenol showed higher crosslinking and a good scorch delay, and matched with the conventional tyre tread compound. It showed the highest stability in ageing carried out at 100°C.

The E.V. compounds containing above aromatic thioureas, showed no reversion of natural rubber, even at 180°C, indicating a good promise of this accelerator system, in the application of injection molding of natural rubber.

# PUBLICATIONS