RENEWABLE RESOURCE MATERIALS FOR POLYMER APPLICATIONS

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BY

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CERTIFICATE

Certified that the work incorporated in the thesis entitled 'Renewable Resource Materials for Polymer Applications' submitted by Miss Ratnaprabha S. Khisti, was carried out by the candidate at the Division of Polymer Chemistry, National Chemical Laboratory, Pune-411008, under my supervision, such material as has been obtained from other sources has been duly acknowledged in the thesis. This work was not submitted so far for any degree.

N. D. Ghatge
(Dr.N.D. Ghatge)
Research Guide

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(Miss Ratnaprabha S.Khisti)

GENERAL REMARKS

1. All melting/boiling points are uncorrected.
2. The IR spectra are recorded on PYE UNICAM SP3-300 infrared spectrophotometer with sodium chloride/cesium bromide optics.
3. Elemental analysis of compounds is carried out by microanalytical procedures for carbon, hydrogen, nitrogen and sulphur.
4. A list of references pertaining to each chapter is given at the end of that chapter.

General Introduction

INTRODUCTION

Mankind started his life on the earth almost solely due to renewable resources such as animal proteins and vegetation for nourishment and shelter.

During 19th and 20th centuries, renewable resources have been extensively utilized for various aspects such as energy source, clothing, building materials and drugs.

The 20th century is an era of great changes ever experienced by mankind. In 20th century an unprecedented development has taken place on non-renewable resources as energy source as well as source for monomeric materials for textile, automobile, building construction and several others which are derived from renewable resources. Thus, most of the renewable resource-based materials were rapidly replaced by non-renewable-based ones. Non-renewable (synthetic) materials received great demand and attraction due to their better quality and economics over the products from naturally occurring materials.

But, the predawn of 21st century has geared back towards the use of abundantly available natural resources for technological application due to inevitable shortage of fossil fuel. Thus, in the present energy crisis, inexhaustible natural sources such as plants, wind, ocean and solar energy have been tried for polymer feed stock and energy source.

The potentially available raw materials for polymer feed stock are based on natural sources like forest, vegetation and animal tissues. The renewable resources from plant and animal origin are mostly composed of carbohydrate, lignin, fats and oils.

When plant and animal tissues are extracted with nonpolar solvent, a soluble part is called lipid which consists of fatty acids, triglycerides, waxes, prostaglandins and steroids and insoluble part consists of carbohdyrates, lignin, proteins, etc. The renewable resource materials can be grouped according to their sources and uses as follows[1]:

Sr.No.	Group	Example	Sources	Uses
A)	Carbohydrate	Cellulose, starch, sucrose, etc.	Plants	Flood, clothing and fuel
B)	Lignin	-	Wood	Fuel, additives, replacement for phenol and coatings
C)	Drying oil	Linseed, castor and tung oil	Seeds	Synthesis of various polymers
D)	Polyisoprene	Rubber	Hevea Brasiliensis	Tyres, golf ball covers, coated fabrics, molded articles and adhesives
E)	Protein	Keratin, elastin and fibroin	Skin, hair, muscles and seeds	Food and clothing

These materials have already established their position in today's industrial market as alternative for petroleum-based products. In the following sections their possible use and feasibility as alternative source has been described.

A) Carbohydrates

Carbohydrates consist of mono, di and polysaccharides which include various sugars, cellulose and its derivatives and starch.

1. Polysaccharides: 3/4th of the dry weight of the plants consists of carbohydrates. Carbohydrates vary in their structure, purity, molecular weight and site of branching according to their source as well as the location of the source.

The examples of monosaccharides are glucose, mannose and fructose and of disaccharides are sucrose, cellobiose, etc. The natural sources of glucose are corn and potatoes. Fermentation of glucose solution to ethanol in 85 to 90% yields is a commercially established technique. The further conversion of ethanol to ethylene (96%) and butadiene (70%) was carried out on commercial scale in U.S. and was proved to be lower in capital cost than the processes based on hydrocarbon conversion[2].

2. Cellulose and its Derivatives

Cellulose

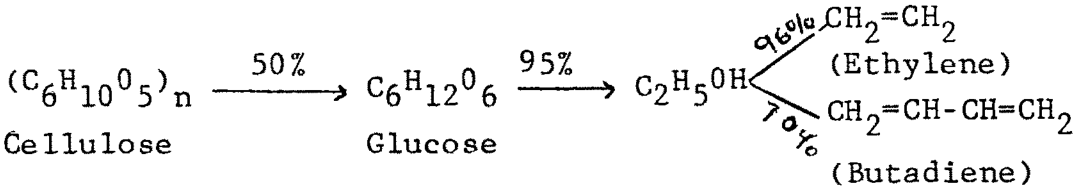
Cellulose is abundantly available raw material in the world, which is one of the few natural polymers with enough world-wide tonnage to replace the synthetics according to the requirement[3].

Cellulose and its derivatives have unique place in scientific and commercial field. A few of their uses from the point of feasibility in the industrial applications are described below:

Since long time, cellulose fibers are the greatest source of industrial and textile fibers. An improved quality of rayon- a product of modified cellulose- can be used as an alternative for nylon which is used in the tyre cord[4].

The hydrolysis of cellulose gives glucose which can be further converted to 5-hydroxy-2-furaldehyde which in turn can be readily converted to levulinic acid[5]. Levulinic acid may serve as an intermediate for several polymers[6].

The conversion of cellulose to glucose by enzymatic hydrolysis has received great importance since glucose can be converted into ethanol by fermentation. The steps involved in conversion of cellulose to industrially important monomers like ethylene and butadiene are given below[6]:



$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_n} \xrightarrow{50\%} \underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{95\%} C_2H_5OH \begin{cases} \xrightarrow{96\%} \underset{\text{(Ethylene)}}{CH_2{=}CH_2} \\ \xrightarrow{70\%} \underset{\text{(Butadiene)}}{CH_2{=}CH{-}CH{=}CH_2} \end{cases}$$

Agricultural waste also contains high concentration of cellulose, e.g., sugarcane bagasse which can be used as a filler for wall board and plastics. Furfural can be produced from bagasse[7].

Thermally molded plastics are obtained by reactions of agricultural waste with vinyl monomers. Wood fibers are converted into pulps that are useful both in the manufacture of paper and in the preparation of regenerated textile fiber[7]. Bagasse can be upgraded by bonding with resins to produce composites suitable for building materials[8].

Three hydroxyl groups present in cellulose undergo reactions to give nitrates, esters and ethers which are commercially important.

Cellulose Nitrate

Cellulose Nitrate is explosive and used as gun powder[9], with low nitrate level, cellulose nitrate has been used as lacquer .

Cellulose Acetate

Cellulose acetate (CA) generally has the degree of substitution in between 2.5 to 3. CA films are widely used in food packings[9], sausage casing, photography[9] and in battery separator .

CA membranes are versatile for desalination of water by reverse osmosis due to their dimensional stability, clarity, wet shrinkage and solute permeability[10].

These membranes are also used in food concentration[11]. Hollow fiber CA membranes are used in artificial kidney[12].

Cellulose triacetate has also been used for fiber production.

Sodium carboxymethyl cellulose is an important ether of cellulose which is used as food thickner and as anti-redepositor[13].

Hemicellulose

Hemicellulose can be readily hydrolysed to simple sugar (pentose). Prehydrolysis of the wood with dilute acidic solution provides aqueous xylose solution which can be further converted to furfural (75%)[14]. Furfural is one of the important raw chemical for production of resins, adhesives and for condensation polymers.

3. Chitin

Chitin is a biopolymer abundantly available in the nature after cellulose in the form of exoskeleton of insects which is an unbranched polysaccharide. It can be used in surgical sutures, burn dressing and contact lenses[15].

Thus, carbohydrates are valuable raw materials to serve as food and polymer feed stock to substitute hydrocarbon-based products.

B) Lignin

For many years, cheaply available bark and agricultural wastes were disposed very cheaply. However, in the era of petroleum crisis efforts have been made for their positive utilization.

Lignin, like cellulose, is abundantly available from woody structure of the higher plants which is a noncellulosic material and whose structure is complex consisting of phenol, aliphatic alcohol, ether, ketone and aldehyde group. The primary source of lignin is coniferrous wood and commercial source is waste product of paper and pulp industry.

Lignin has been suggested as raw material for polymers and plastics for more than 30 years due to its three dimensional structure which resembles to phenol formaldehyde resin[16]. Chemical modification of lignin to phenolic and aromatic chemicals by economically competitive process can improve its utility in structural polymer coatings and dispersants[17]. Pure, low molecular weight chemicals can be obtained from lignin which are useful for chemical industry[18].

Pilot plant studies are being carried out on production of phenol by hydrogenation of lignin[18]. Catechol can be obtained from lignin at much lower cost than by synthetic method utilizing benzene[19].

Unmodified lignin is used as binder, filler and resin extender[20].

Alkali lignin and lignosulphonate find applications in phenolic and urea adhesives for plywood and particle board[21]. Because of their surface activity, both are used as emulsifier and protective celluloids to stabilize emulsion. Alkali lignin and lignosulphonate are employed as precipitating and tanning agent for leather due to their reactivity with protein.

Sequestering action of alkali and sulphonated lignin serves to remove scum and insoluble salts in hard water and are also useful in agriculture[20].

Alkali lignin is used as reinforcing and stabilizing agent for rubber which provides light weight and light coloured product[20].

Lignosulphonate is used as additive in oil-well-drilling mud, industrial cleaner, production of vanillin[22] and to enhance the oil recovery[20].

Water soluble lignin derivatives are used as speciality dispersants. Lignin can replace carbon black as additive to elastomeric rubber system[20]. Glasser and co-workers[23] explored the use of lignin derivatives in rigid, low density polyurethanefoams. The foams have good strength and stability with excellent flammability resistance. Polyphenylene sulfides have been prepared[24] from its degraded product guiacol and its chloro derivative. Aromatic polyesters have also been synthesised[25] starting from degradation products[25] of the lignin.

Thus, the potential market for lignin can be in process fuel, oil field chemicals, agricultural chemicals, asphalt extender, carbon black, adhesives, engineering plastics and speciality dispersant which is feasible with refinement of technology to meet today's petroleum crisis.

C) Drying Oils

The major soluble part of plant and animal tissues in nonpolar solvents is composed of lipid which mainly contains natural oils and fats. The natural oils are mostly triglycerides which can be classified into three general groups according to their structural features.

1. Highly saturated animal fats such as tallow (non-drying).
2. The unsaturated oil such as linseed (drying).
3. Natural oil containing active groups other than double bond e.g. castor oil containing hydroxyl groups, vernonia oil having epoxy group and oiticiaca with conjugated keto group.

The other natural oils which are not triglycerides include cashewnut shell liquid (CNSL), Japanese lacquer and terpentine. CNSL is a meta-substituted phenol having a mixture of one, two or three double bonds in the side chain. Japanese lacquer has a cellular structure of polysaccharide cell wall and phenolic compound. Turpentine is a compound of α-and β-pinenes.

Soyabean, linseed, tung and castor oil are commercially important since many years. Due to their structural features they find wide applications in paints, varnishes, adhesives and coatings. Most of the alkyd resins are based on fatty acids and find various applications.

Soyabean and linseed oil are used as epoxy plasticizer and stabilizer for polyvinyl chloride (PVC)[26,27]. These oils are also used for conversion of epoxy derivatives to coatings[28], in baits to attract the ants[29] and also in various preparations of alkyd and polyester-amide resins[30].

Tung oil has been extensively employed in paints and water proofing materials and in insulating compounds[31]. Tung oil's new applications include lubricating greases[32], preparation of vinyl resin stabilizer and modification of mechanical properties of glassy polystyrene by blending with random copolymers of tung oil and styrene[33].

Japanese lacquer can be used as a coating material or as a durable polymeric material[34].

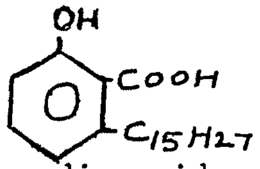
In the present work, CNSL, castor oil and cellulose acetate have been used for synthesis of new compounds/ polymers. A brief description of the uses of CNSL and castor oil for polymer applications is given below:

Cashewnut Shell Liquid (CNSL)

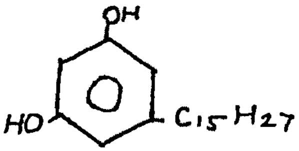
CNSL is available as a by-product in cashew processing industry. It is a versatile raw material for many industries like paint, varnishes, rubber, etc. It's applications cover almost all fields of chemistry such as polymers, organic intermediates and isocyanates.

CNSL is a dark brownish, viscous, vesicant and corrosive liquid. India is one of the major countries in the world producing cashewnuts and CNSL and is getting good export market as shown in Table 1.

Stadler[35] has studied the ether extract of cashew nuts and reported that 90% of its consists of an acid which is called anacardic acid and rest of 10% being a dihydroxy phenol known as cardol. It is now established that anacardic acid and cardol have the structures as shown below:



Anacardic acid



Cardol

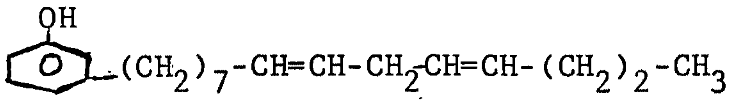
Harvey and Caplan[36] distilled the commercial CNSL under vacuum and 70% of the total distillate was found to be single phenolic component with an unsaturated side chain in meta-position. The substance they termed as 3-pentadecadienyl phenol (cardanol) is formed by decarboxylation of anacardic acid.

Table 1

Export of Cashewnut Shell Liquid (CNSL)

Countries	Year		
	1979-80	1980-81	1981-82
U.K.	2,422	1,113	710
USA	3,411	2,619	180
Japan	5,078	3,763	2,298
Australia	3	-	-
Netherland	420	71	-
Total export including other countries	13,031	9006	4,777
Values in Rs. million	145.8	68.4	21.83

Dawson and coworkers[37-39] have studied the chemistry of cardanol in detail and established the structure of cardanol as follows:



The aliphatic side chain usually consists of mixture of $C_{15}H_{29}$, $C_{15}H_{27}$ and $C_{15}H_{25}$ viz. one, two and three double bonds, respectively in a linear chain and the composition is given below:

Saturated	- 5.4%
Monoolefin	- 48.5%
Diolefin	- 16.8%
Triolefin	- 29.3%

Cardanol, which is structurally similar to m-cresol behaves as a phenol and these structural features have been utilized for various commercial applications. Reviews on chemistry and applications of CNSL in various fields of polymer chemistry are available[40,41].

CNSL, cardanol and its derivatives have been used for the manufacture of insulating varnishes, oil and acid proof cold setting cements, automobile break linings, plasticizers, mosquito larvicides[42], detergents[43], etc. Many patents and papers are available in the literature describing the uses of CNSL in lacquers, baking enamels[44], varnishes[45], coating materials[46], laminating products, adhesives, etc.

Some useful plasticizers[47,48], ultraviolet light absorbers[49] and stabilizers for PVC[50,51] and isocyanates[52-56] based on CNSL have been synthesised by Ghatge and coworkers.

CNSL has been used to develop some self catalysed aminophenol resins for use in the preparation of polyurethane rigid foams[57]. Ghatge has[58] employed CNSL based cation exchange resin as a catalyst for the preparation of polyesters.

CNSL, cardanol and its derivatives are extensively used in rubber industry. The rapid growth of rubber industry led to an increasing demand of the auxillary chemicals which are used in the compounding of rubber to promote and control the vulcanization process. Thus, a number of CNSL based compounds are utilized to promote the quality and stability of rubber products. A few of them are mentioned below:

In 1930, Harvey[59] reported that when sulphur is heated with CNSL, a gummy material is obtained which can be used for coating impregnation and as rubber substitute. He also reported that rubber like substance was obtained by heating CNSL with glycerine at about 245°C which can be used in a variety of applications. Subsequent work reported[60] that when CNSL is intermixed with natural rubber it enhances the insolubility of the vulcanizates in petroleum solvent.

Plasticizers for rubber have also been developed[61] by reacting CNSL and styrene. The addition of styrene-CNSL reaction product as plasticizer during rubber compounding improved the filler(silica) uptake of rubber and some physical properties of carbon black filled natural rubber, than using dioctylphthalate (DOP) as a plasticizer in the similar rubber compounding. Recently, cardanol dialcohols have been prepared by Ghatge et al.[62] and used to make rosin modified phenolic resins for utilization in synthetic and natural rubber.

Cation exchange resin made from CNSL and aldehydes by milling with crepe rubber has been used as cation exchange resin membrane[63]. Styrene butadiene rubber (SBR) was reinforced by the above resin to give vulcanizates with better modulus, hardness and lower Goodrich heat build up. Synthesis of modified novolac resin based on CNSL for use in natural rubber as reinforcing agent has been reported by Ghatge and Shinde[64]. The effect of addition of various commercial resins and card-phenol-paraformaldehyde resin on physical properties of natural rubber has been compared. Card phenol resin incorporated natural rubber showed better properties.

SBR has been plasticized with 'cardiolite 625' - the ethyl ether of monophenolic component of CNSL-and it has been reported that the low temperature properties were superior to the properties of similar compounds containing a naphthonic based plasticizer[65]. Banerjee and Banerjee[66,67] have used card phenol as a mixing ingredient for natural rubber as well as synthetic rubber. Banerjee et al.[68] have reported that cardanol shows plasticizing property in nitrile rubber with improved tear and solvent resistance as well as aging property.

Amino-3-petadecylphenol can be used as an intermediate for the preparation of a wide variety of useful products such as dyes and in the compoundings of the rubber[69]. Ghatge and Mahajan[70] used isomeric 6-amino-3-pentadecylphenols, in SBR to evaluate as antiradiation agent and compared their performance with standard commercial antiradiation chemicals. The conclusion drawn was that β-naphthylamine and 6-amino 3-pentadecylphenol appeared to give better protection than other compounds evaluated. Ghatge and Patil[71] have prepared sulphur containing reclaiming agents and compared their properties with commercially available sulphur containing reclaiming agents. The compounds were tested for medium pressure reclaiming process.

The chemicals obtained from CNSL have also been used in accelerating the process of vulcanization. Thus, Ghatge and Gokhale[72] obtained two unsymmetrical thioureas from 4-amino-3-pentadecyl phenol. These compounds were evaluated as secondary accelerator in typical natural rubber tyre tread E.V. compound containing low sulphur/high sulphenamide primary accelerator system. Such system was found to produce superior vulcanizates at temeprature of 140°C, than the vulcanizates produced by the conventional system.

Ghatge and Maldar[73] have reported the synthesis of a new active nonsulphur vulcanization agent-2-pentadecylbenzoquinone dioxime for vulcanization of synthetic rubber. It was used to obtain heat resistant vulcanizates from styrene butadiene rubber and butyl rubber.

Castor oil

Castor oil is derived from the beans of castor plant-Ricinus Communis L which occurs in tropical and subtropical countries either wild or cultivated. India occupies second place among castor producing countries in the world. The major part of castor seeds in the form of oil is exported (Table 2).

Castor oil is obtained either by cold pressing or solvent extraction of castor bean, cold pressing oil has low acid number while solvent extracted oil has high acid number.

Castor oil is a triglyceride of fatty acid that contains 87-90% ricinoleic acid-*cis* 12 hydroxy-octadecaenoic acid- a rare source of 18 carbon hydroxylated

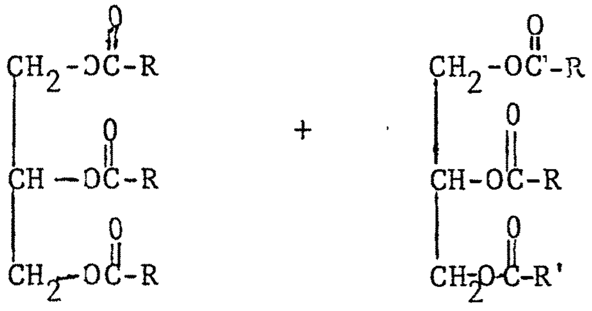
Table 2

Export of Castor Oil[*]

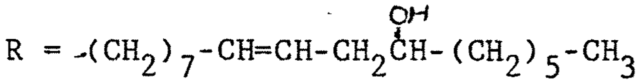
Year	Quantities (Kgs)	Values (Rs.)
1977-78	5357236	33622515
1978-79	537236	33622515
1979-80	11156352	79476473
1980-81	873881	6488896
1981-82	4423013	34068350

[*] From monthly statistics of Foreign Trade

fatty acid. Castor oil is described as triglyceride of ricinoleic acid. The chemical structure of castor oil and chemical composition is given below:



70%   30%



$$R = -(CH_2)_7-CH=CH-CH_2\overset{OH}{C}H-(CH_2)_5-CH_3$$

R' = other fatty acid

Fatty acid components of castor oil in %

Acid component	%
Ricinoleic acid	89.5
Dihydroxy stearic acid	0.7
Palmitic acid	1.0
Stearic acid	1.0
Oleic acid	3.0
Linoleic acid	4.2
Linolenic acid	0.3
Eicosanic acid	0.7

There are several possibilities for reactions of castor oil due to its three functional groups namely, the ester, the olefinic linkage and the hydroxyl group.

Castor oil is an industrially important raw material for the manufacture of complex organic derivatives[75,76]. Castor oil can be converted into other chemicals by number of processes such as dehydration[77], sulphonation[78], alkali fusion[79], oxidation[80], pyrolysis[81], hydrogenation[82] and saponification[83].

The largest single use of castor oil is in the preparation of sebacic acid and capryl alcohol. Sebacic acid is used in the manufacture of 6,10 nylon, sebacate plsticizers, sebacate polyesters, etc.

Another notable use of castor oil is in the manufacture of paints and varnishes. Since castor oil has three secondary hydroxyl groups it has been utilized in isocyanate reactions for adhesives[84], coatings[85], foams[86-89], castable elastomers[90-92], millable elastomers[93], etc. The Germans used isocyanate based adhesives from castor oil for metal to metal and metal to rubber bonding. 4,4'-Diphenylmethane diisocyanate- castor oil based isocyanate-terminated prepolymers have been used as adhesives for cements and other patching materials. Castor oil has alsobeen used for the production of superior coatings.

Castor oil based rigid and semirigid foams are well known. Recent use of castor oil is in the heat protecting foams.

Castor oil has been used in the preparation of castable elastomers. Notable work has been carried out by Patton et al. of Bakers Castor Oil Co.[87,91] and Heiss of Mobay Chemical Co.[90]. Patton has prepared polyols based on castor oil and have used them in the polyurethane preparation.

Thermal fission of castor oil yields 10-undecenoic acid which is a base material for nylon 11 and the other product is heptaldehyde- a verastile aroma ingredient. Lower ricinoleate esters are used as vehicles for solid inks for ball pens. Esterification of castor oil with lower organic acids gives PVC stabilizers.

Polyisoprene

Polyisoprene is a natural rubber available in cis form from the tree Hevea Brasiliensis. The other cis form available from natural source is Guayule-available from Parthenium argentatum Gray. Even the white sap of mildweed and dandelian contains 1.25-5% rubber. Efforts were made to extract rubber from dandelian roots during World War II.

trans Polyisoprene

Gutta percha and balata are naturally available trans polyisoprenes from the trees- Palaquin-Gutta and Bolla tree from Malaysia and Brazil, respectively.

Numerous applications of natural rubber are known since last century. To mention a few are tyres, shoes, molded articles, adhesives and coated fabrics.

Proteins

Proteins are complex molecules and are fundamental part of life. Much of the cellular content of plants and animals is protein.

Many proteinssince long have been in use such as clothing, wool, silk and leather. Graft polymers of wool and leather are under investigation to get more water resistant materials. Adhesives can be obtained from casein, blood albumin collagen and its breakdown product gelatin. Casein, soyabean and egg albumin have also been used for fiber production.

Thus, future world shortage of petrol and petroleum-based derivatives has started research activity for the alternative source for polymer feed stock. The first choice is abundantly available renewable resource from which new monomers and polymers can be developed. A new class of materials may be formed from natural monomers and polymers either by blending, grafting or chemical transformations.

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CHAPTER I

New Silane Compounds from Cardanol and Castor Oil and their Applications in Rubber Reinforcement and in Foundry Sand Cores

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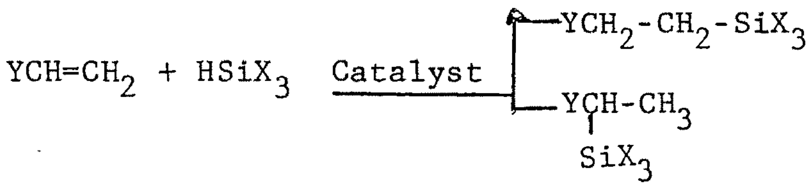
Section A

Synthesis of New Silane Coupling Agents
from
Ethers and Esters of Cardanol
and
Castor Oil Acetate

INTRODUCTION

Silanes are the compounds containing hydrogen and silicon. Mono, di and trichlorosilanes are inorganic silanes. Trichlorosilane is a predominant inorganic silane which is used in the production of high purity silicon metal and as an intermediate reagent in organic synthesis[1].

The addition of $HSiX_3$ to unsaturated hydrocarbon, termed as hydrosilylation, constitutes an important reaction from synthetic as well as industrial point of view. The reaction can be shown as:



$$\mathrm{YCH{=}CH_2 + HSiX_3} \xrightarrow{\text{Catalyst}} \begin{cases} \mathrm{YCH_2-CH_2-SiX_3} \\ \mathrm{\underset{\displaystyle SiX_3}{YCH}-CH_3} \end{cases}$$

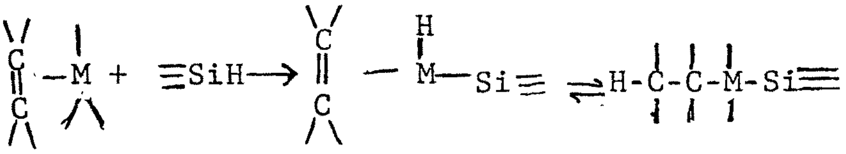
The addition of $HSiX_3$ to olefin gives organosilicon compound. The substituents X and Y can be varied widely which are either alkyl, aryl or halogen.

A number of reviews have been published on the data of hydrosilylation. Eaborn and Bott[2] have published a review on methods of synthesis and reactions of the Si-C bond. The review by Pomerantseve *et al*[3] deals with recent achievements by hydrosilylation.

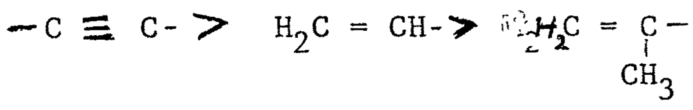
The hydrosilylation reaction is effected by catalytic, ionic and thermal conditions[4]. The variety of catalysts used include UV radiation[5], peroxides[6], azo compounds[7], platinum on carbon[8] or chloroplatinic acid[9]. Ionic conditions are used for hydride transfer to carbonium ion[4]. The reaction rate and the course of reaction depends on the substituents X and Y, catalyst and catalyst concentration[10].

The most commonly used catalyst for hydrosilylation of alkenes and alkynes is chloroplatinic acid. The addition of trichlorosilane to olefin is *cis* with respect to element H and $SiCl_3$ group and the product obtained is *trans* [11]. The reaction rate can be increased by 10^4 to 10^6 times by using lower concentration of platinum catalyst[10]. The yield of the final product depends on the rate of reaction. The low rate offers less yields[10].

The mechanism suggested for hydrosilylation reaction is similar to that of oxo process[11]. The double bond migrates from an internal to terminal position *via* a series of π and θ bonded metal complexes.



The rate of hydrosilylation in case of alkenes is slow as compared to alkynes. The order of reactivity of some alkynes and alkenes is[11]



$$-C \equiv C- > H_2C = CH- > H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}}-$$

The product obtained with peroxy catalysed hydrosilylation is a cis product with trans addition of element H and $SiCl_3$ group[11].

A literature survey reveals that hydrosilylation reaction has also been applied to olefins containing organofunctional groups[6,12]. Thus, addition of triphenyl silane to undecylenic acid in the presence of benzoyl peroxide and addition of trichlorosilane to 1-octene using diacetylperoxide as catalyst have been reported[6,12].

Saghian[13] has studied the addition of various chlorosilanes to the esters of long chain unsaturated fatty acids such as oleic, linoleic and 10-undecenoic acid with respect to catalyst, temperature and solvent.

Applications of Organosilane Compounds

Organosilanes find a wide variety of applications[1] such as:

1. Controlling orientation of liquid crystals.
2. Binding heavy metal ions.
3. Immobilizing enzymes and cell organelles.
4. Surface binding of antimicrobial agents.
5. Coupling agents for organic polymer and inorganic matrix.

A brief description of the above applications is given below :

1. Controlling Orientation of Liquid Crystals

The geometry of the interphase can also impose orientation on the bulk phase. In liquid crystal displays, clarity and permanence of image are enhanced if the display can be oriented parallel or perpendicular to the substrate. The oxide surface treated with octadecyl-(3-(trimethoxysilyl)propyl)-ammonium chloride tends to orient liquid crystal perpendicular to the surface and parallel orientation is obtained on surface treated with N-methylaminopropyl trimethoxysilane[14]. Thus, silanes help in eliminating micromachining operations.

2. Ion Removal

The ethylenediamine (en)-functional silane has been studied extensively as silylating agent on silica gel to preconcentrate polyvalent anions and cations from dilute aqueous solutions. Numerous other chelate functional silanes have been immobilized on silica gel, controlled pore glass and fiber glass for removal of metal ions from solution[15,16].

3. Immobilized Enzymes and Cell Organelles

Use of enzymes to catalyze reactions in free cell systems has been limited by the difficulty of enzyme isolation, lability of the enzymes and difficulty in effecting clean separation of enzymes from reaction mixtures. An approach that has circumvented some of these problems is to attach enzymes to solid support material[17]. The most frequently used technique for immobilizing enzymes on solid support involves reducing N-(3-silylpropyl)-p-nitrobenzamide group on silica or controlled poreglass to give aniline derivative, then converting them to diazonium salt and effecting coupling through azo linkage to the tyrosine of the proteins.

4. Surface Binding of Antimicrobial Agents

Surface bonded organosilicon quaternary ammonium chlorides have enhanced antimicrobial and algicidal activity[18]. Thus, the hydrolysis product of 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride exhibits antimicrobial activity against a broad range of microorganisms while chemically bonded to a variety of surfaces.

5. Coupling Agent for Organic Polymer and Inorganic Matrix

Organosilanes find major applications in industry as coupling agents for organic polymer and inorganic matrix. There are a number of applications in which silane adhesion promoters are employed. They are used to form primary bonds to either or both the adherends and bulk adhesives[19]. A large number of silanes of general structure $R_{(4-n)}SiX_n$ have been evaluated as coupling agents where R is a organofunctional group selected for the optimum performance with a given polymer matrix. The X group may be alkoxy , acyloxy or aracyloxy which gets readily hydrolysed under the suitable conditions of application.

A large number of coupling agents are available. A list of commercially available silane coupling agents is given in Table 3.

The organofunctional silanes find utilization in almost every type of organic polymers including elastomers, thermosetting and thermoplastic resins. Silane coupling agent can be applied either directly to inorganic surface or integrally blended with filler at room temperature or at elevated temperature.

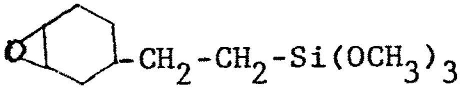
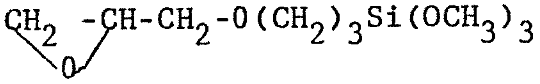
According to their reactivity in organic phase, silane coupling agents can be classified as[19].

(1) Non-reactive (2) Reactive and (3) Catalytic

1. Non-reactive silane coupling agents $R_{(4-n)} SiX_n$ have R with no functional group such as unsaturation or reactive group. R may be an alkyl or aryl group e.g. methyl trichlorosilane, dimethyl dichlorosilane, etc. These silanes find excellent use as primer for silicon rubber for binding many surfaces[20]. The large alkyl or aryl group and their halogenated derivatives are incorporated with silanes for cohesive interaction with bulk adhesives and find use in nonpolar resins

Table 3

Commercially Available Silane Coupling Agents

Chemical Name	Structure
1. Vinyltriethoxysilane	$CH_2= CH-Si(OC_2H_5)_3$
2. Vinyltris (γ-methoxyethoxysilane)	$CH_2=CH-Si(OCH_2CH_2OCH_3)_3$
3. Vinyltriacetoxysilane	$CH_2=CH-Si(OOCCH_3)_3$
4. γ-Methacryloxypropyl trimethoxysilane	$CH_2= C(CH_3)\overset{O}{\overset{\|}{C}}O(CH_2)_3Si(OCH_3)_3$
5. γ-Aminopropyl triethoxysilane	$H_2N(CH_2)_3Si(OC_2H_5)_3$
6. γ-(β-Aminoethyl)aminopropyl trimethoxysilane	$H_2N(CH_2)_2-NH(CH_2)_3Si(OCH_3)_3$
7. Mercaptopropyl trimethoxysilane	$HS(CH_2)_3-Si(OCH_3)_3$
8. γ-Chloropropyltrimethoxysilane	$Cl(CH_2)_3-Si(OCH_3)_3$
9. β-(3,4-Epoxycyclohexylethyl)trimethoxysilane	
10. γ-Glycidyloxypropyl trimethoxysilane	
11. Bis-(3-triethoxysilylpropyl)tetrasulfide	$(H_5C_2O)_3Si(CH_2)_3-(S)_4-(CH_2)_3Si(OC_2H_5)_3$

such as polystyrene and polyvinyl compound[21,22].

2. Reactive silanes have functional groups such as vinyl, epoxy, mercapto, chloro, acid or ester. They have capacity to react with bulk adhesives. These functional silane coupling agents are employed according to the end use of polymer.

3. The catalytic silane used is aminosilane which can act as a catalyst for polymerization of thermosetting and thermoplastic resins.

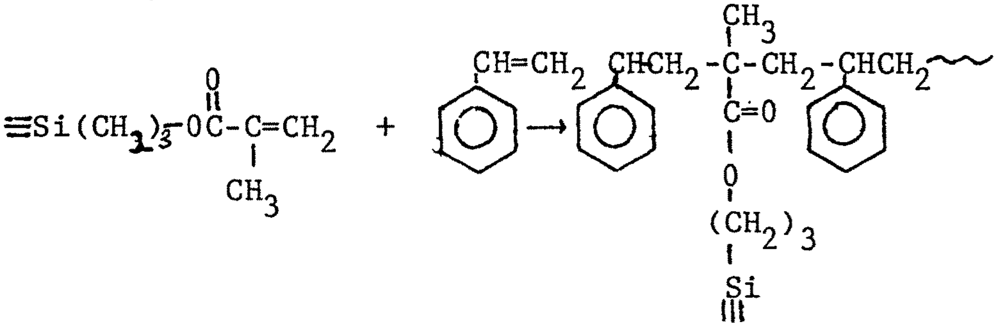
The use of silane coupling agent in polymers first started in mid 1940's. Steinman, Te Grotenhuis and Goebel and Iler[23] have reported in their patents the improvement in adhesion of matrix resin to glass fiber using methallyl silicate, vinyl siloxane and methacrylato chromic chloride.

The various applications of reinforced polymer are possible due to silane coupling agents.

A brief description of the use of silane coupling agents in various polymers is given below:

<u>Polyester</u>

Silane coupling agents find largest use in unsaturated polyesters[24-26]. Unsaturated thermoset polyesters can be modified by copolymerization with styrene. Vinyl silanes are used to improve the reinforcing properties of the polyester[24]. The better properties are obtained if there is compatability between silane and styrene than maleate portion of the polyester. The reaction can be shown as:



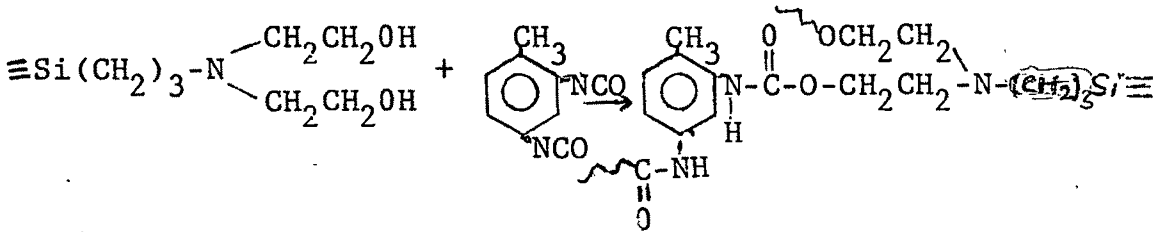
Styrene Modified Polyester

Silane incorporated polyester resins find application in large structural parts of boats and car bodies[27]. In fiber glass lay up application, glass cloth is impregnated with resin and in spray up application, a mixture of polyester and unoriented glass fiber is sprayed on to a mold or a base structure[27].

Urethanes

Urethanes can be effectively coupled with silanes[27]. Functional silanes may be used to treat the filler directly or integrally blended with isocyanates and thioisocyanates prior to cure. On the other hand, amine and alkanolamine functional silanes are blended with the polyols which further react with isocyanates to give urea linkage. Silane modified urethane resins are employed in improving bond strength with sand in abrasion resistant and sand filled flooring resin[27].

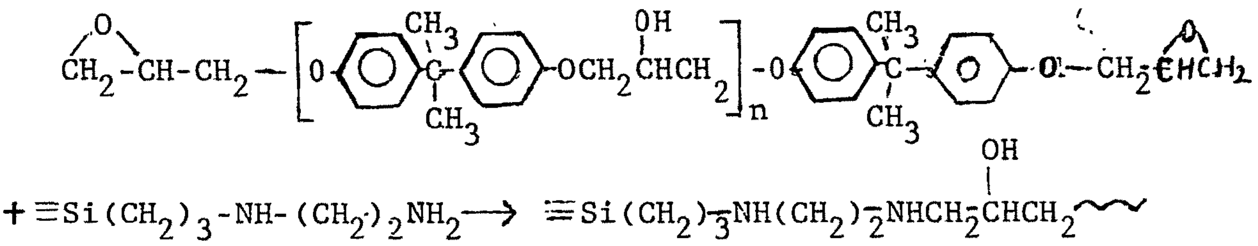
The reaction of urethane with silane takes place as follows:



Epoxies

A large application of silane modified epoxies is in the glass cloth reinforced epoxy laminates and electrical circuit board. Epoxycyclohexyl and glycidyloxy functional silanes are used to pretreat the filler or blended with glycidylbisphenol-A ether[28].

Amine functional silanes are also employed in similar fashion i.e. pretreatment of filler or blending with hardner portion. Thus, silanes help in epoxy adhesives to improve their dispersibility and increase the mechanical properties of the cured resin. The reaction of amino functional silane with epoxy resin can be shown as:



Phenolics

Although some foundry sand molds are formulated with resol and silane[29], the commercial utilization of silanes in phenolic resin is largely limited to novolak/glass fabric laminates and molding compounds. When phenolic resins are compounded with rubbers to use as structural adhesives e.g. nitrile/phenolic improved shear strength values are obtained by incorporating silanes[30]. Similar incorporation of silane in polyvinyl butyral-phenolic adhesives has improved the peel strength properties[30].

Thermoplastic Compositions

A wide range of thermoplastic applications in adhesion technology is possible due to incorporation of silane coupling agents[31]. The promoted properties of thermoplastic compositions are obtained when silanes react with polymer and not with monomeric precursors.

Aminoalkyl silane has been used as coupling agent for polymers containing reactive sites either in the backbone or in pendant groups.

Reinforcement of PVC by silane enhances its dimensional stability and increases its resistance to deformation at elevated temperature. By incorporating silane coupling agents, polyphenylene sulfide can be utilized at 500°C even under compressive load[27].

Mechanism of Adhesion

Coupling of polymer to filler involves chemical as well as mechanical modification. A number of studies reveal that bulk structure of silane film formed on various substrates is due to interfacial interaction between silane coupling agent and substrate.

Vasenin[32] tried to classify the mechanism from mechanical, absorption, diffusion, chemical and physical point of view. The first three involves intermolecular forces, whereas chemical and physical mechanisms are due to chemical bonding and electrostatic forces respectively.

Considerable attempts[33] have been made to study whether the interaction between substrate and silane is actually through chemical bonding or through physical absorption.

Kans and Kardos[34] studied the interaction of silane coupling agent with high silica surface powder by IR spectroscopy and showed that the interaction is taking place by chemical bonding between γ–amino-propyl triethcxy-silane and silica surface and hydrogen bonding is playing minor role.

Koening and Shin[35] investigated the interaction of glass fiber, silane and resin by laser Raman technique. The conclusion drawn was that, vinyl triethoxysilane (VTES) used as coupling agent had been polymerised and chemical bonding through Si-O linkage to the surface of E glass fiber had taken place. Koening has also investigated the polymerization of methylmethacrylate in presence of VTES coated fiber surface and observed that vinyl group had been copolymerized with methylmethacrylate. Ishida and Koening[36] have found by FTIR that covalent bond was formed through silica-silane interface when VTES was deposited on high surface area silica powder[37].

The interface between silane and the oxidised surface of mild steel has been studied by X-ray[37] photoelectron spectroscopy and static secondary ion mass spectroscopy. The presence of $FeSiO^+$ radical on mild steel pretreated with 1% aqueous γ-glycidyloxypropyltriethoxysilane suggest the formation of chemical bond, probably $FeO\text{-}\overset{+}{Si}$, between the iron oxide surface and polysiloxane polymer.

Present Investigation and Results

A great emphasis is being made on utilization of renewable resources as an alternative for petroleum-based products due to limited supply of petrol and coal and their escalating prices. Most of these renewable resources are composed of agricultural products such as starch, sugars, cellulose, proteins, fats and oils. Agricultural products are becoming important as renewable resources for polymer synthesis and additives also.

Vegetable oils of plant origin are one of the major sources for replacement of petroleum-based products. A number of fatty acids derived from vegetable oils find uses in various industrial applications due to their functional and structural features such as presence of unsaturation and reactive group.

In the present study, cardanol and castor oil which are the agricultural products have been used for synthesis of silane compounds. Cardanol, 3-pentadecadienyl phenol (3-PDP) is indigeneously available raw material from cashew industry and castor oil, 12-hydroxy triglyceryl ricinoleate is available from plant Ricinus Communis L.

The structural features of cardanol and castor oil were explored to synthesise new hydrosilylated products. Methyl ether of cardanol, allyl ether of cardanol, ester of cardanol with oleic acid, ester of cardanol with

5023
A

linoleic acid and castor oil acetate were prepared. The new hydrosilyated products were synthesised from these ethers and esters using trichlorosilane as hydrosilylating agent and chloroplatinic acid as catalyst. These hydrosilylated products were further converted into methoxysilyl derivatives by alcoholysis. Also, polysulphide from 3-pentadecylphenol was prepared and reacted with trichlorosilane to get chlorosilane derivative which was further converted into methoxysilyl derivative by alcoholysis. Thus, the following new compounds were synthesised:

(A) Benzene, 1-methoxy, 3-[8,11-bis(trimethoxysilyl)] pentadecyl (BMMS) (Methoxysilane derivative of methyl ether of cardanol).

(B) Benzene, 1-(3-trimethoxysilyl) propanyloxy, 3-(8, 11-bis-trimethoxysilyl) pentadecyl (BMSP) (Methoxysilane derivative of allyl ether of cardanol)

(C) 1-(9-Trimethoxysilyl) octadecanoate, 3-(8,11-bis-trimethoxysilyl) pentadecyl phenol (9-TOMSP)-(Methoxysilane derivative of ester of cardanol with oleic acid)

(D) 1(9,12-Bis(trimethoxysilyl) octadecanoate, 3-(8,11-bis-trimethoxysilyl) pentadecyl phenol (9,12-TOMSP)-(Methoxysilane derivative of ester of cardanol with linoleic acid).

(E) Methoxysilane of polysulphide from 3-pentadecyl phenol (MPSP)

(F) Methoxysilane of castor oil acetate [MCA]

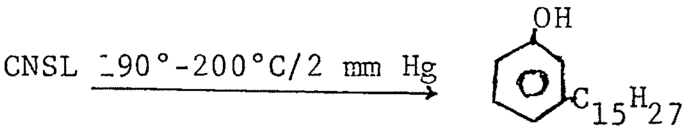
The compounds BMMS, BMSP, 9-TOMSP, 9,12-TOMSP, MPSP, and MCA in the course of the text will be referred as A, B, C, D, E and F, respectively.

The scheme for synthesis of compounds A to D is given in Fig.1, for compound E in Fig. 2 and for compound F in Fig. 3.

A brief description of each step involved is given below

3-Pentadecadienyl phenol (3-PDP)

When commercial cashewnut shell liquid (CNSL) was distilled under reduced pressure, 3-pentadecadienyl phenol (cardanol) was obtained as pale yellow liquid



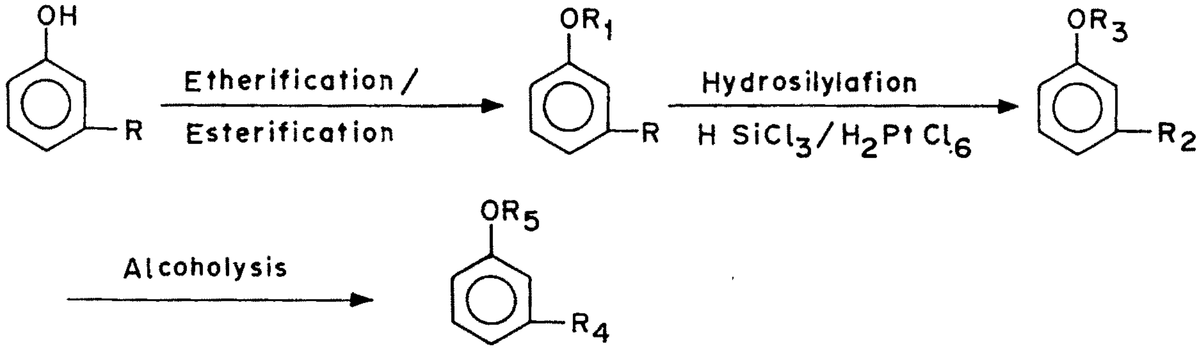
cardanol

Yield - 50%.

b.p. - 195-200°C/2 mm Hg

Benzene, 1-methoxy, 3-pentadecadienyl (Methyl ether of cardanol)(BMP)

Methyl ether of cardanol was prepared by refluxing acetone solution of cardanol with dimethyl sulphate in presence of sodium hydroxide. The excess of dimethyl

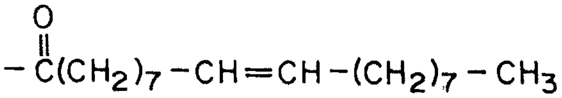


Where ,

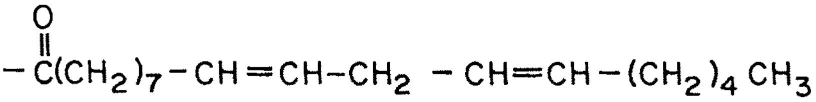
$R = -(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_2-CH_3$ -[3-PDP].

$R_1 = -CH_3$ - BMP.

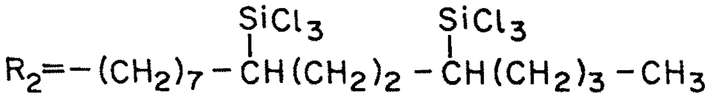
$-CH_2CH=CH_2$ - BPP.



$-\overset{O}{\overset{\|}{C}}(CH_2)_7-CH=CH-(CH_2)_7-CH_3$ 9-OPP.



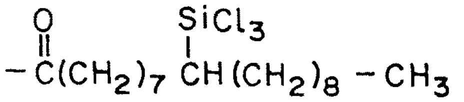
$-\overset{O}{\overset{\|}{C}}(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4CH_3$ 9,12-OPP.



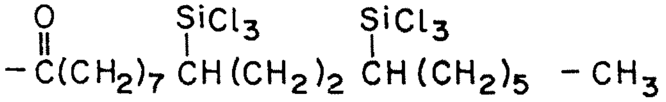
$R_2 = -(CH_2)_7-\overset{SiCl_3}{\overset{|}{C}}H(CH_2)_2-\overset{SiCl_3}{\overset{|}{C}}H(CH_2)_3-CH_3$.

$R_3 = -CH_3$, Chlorosilane Derivative of BMP,

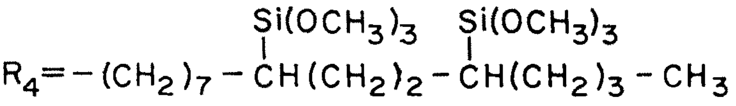
$-CH_2-CH_2-CH_2SiCl_3$ Chlorosilane Derivative of BPP,



$-\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{SiCl_3}{\overset{|}{C}}H(CH_2)_8-CH_3$, Chlorosilane Derivative of 9-OPP,



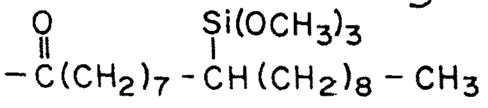
$-\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{SiCl_3}{\overset{|}{C}}H(CH_2)_2\overset{SiCl_3}{\overset{|}{C}}H(CH_2)_5-CH_3$, Chlorosilane Derivative of 9,12-OPP.



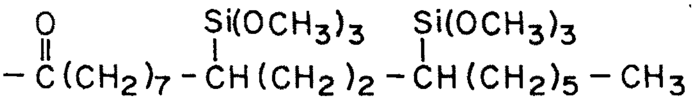
$R_4 = -(CH_2)_7-\overset{Si(OCH_3)_3}{\overset{|}{C}}H(CH_2)_2-\overset{Si(OCH_3)_3}{\overset{|}{C}}H(CH_2)_3-CH_3$.

$R_5 = -CH_3$, BMMS [A]

$-CH_2CH_2CH_2-Si(OCH_3)_3$ BMSP [B]

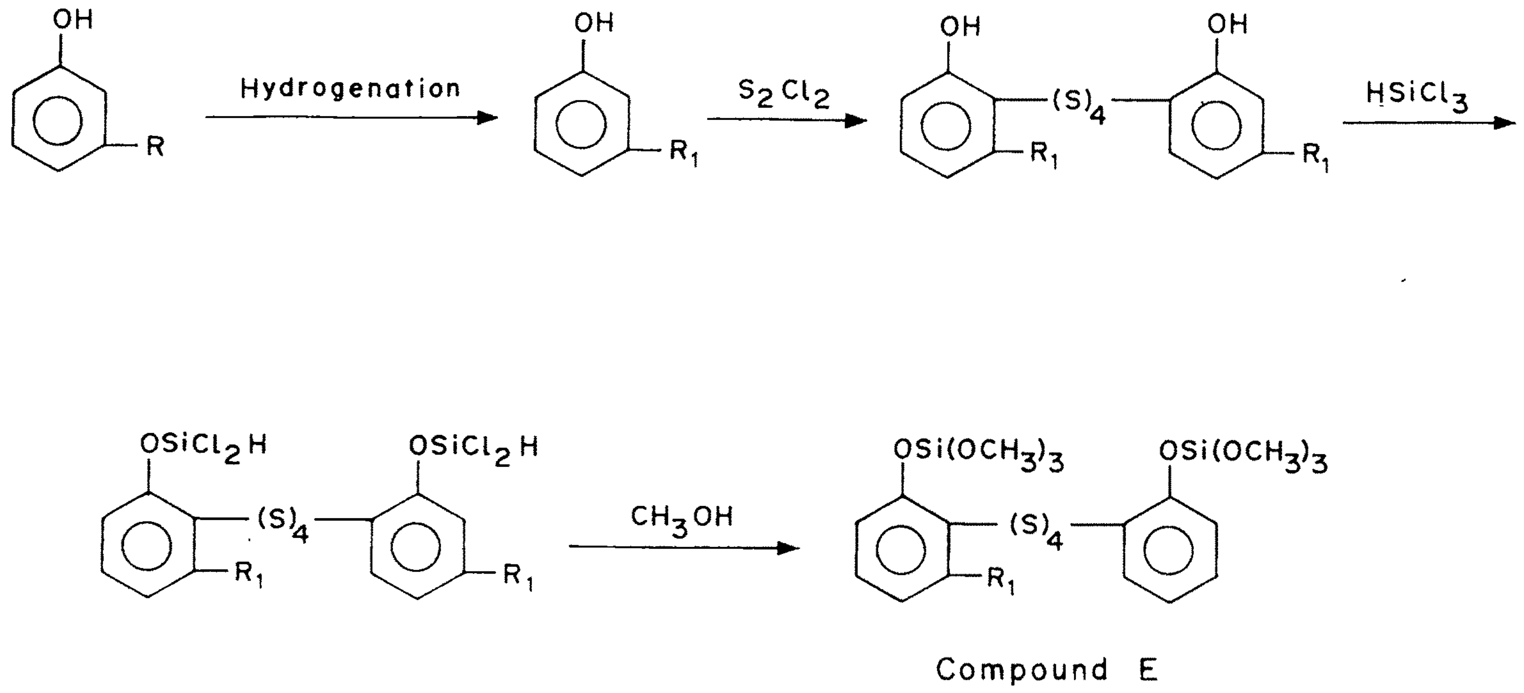


$-\overset{O}{\overset{\|}{C}}(CH_2)_7-\overset{Si(OCH_3)_3}{\overset{|}{C}}H(CH_2)_8-CH_3$, 9-TOMSP , [C]



$-\overset{O}{\overset{\|}{C}}(CH_2)_7-\overset{Si(OCH_3)_3}{\overset{|}{C}}H(CH_2)_2-\overset{Si(OCH_3)_3}{\overset{|}{C}}H(CH_2)_5-CH_3$ 9,12-TOMSP , [D]

FIG. 1 : SCHEME FOR SYNTHESIS OF COMPOUNDS **A** TO **D**.



$R = -(CH_2)_7-CH=CH-(CH_2)CH=CH-(CH_2)_2-CH_3$

$\longrightarrow C_{15}H_{27} \longleftarrow$

$R_1 = C_{15}H_{31}$

FIG. 2 : SCHEME FOR SYNTHESIS OF COMPOUND E.

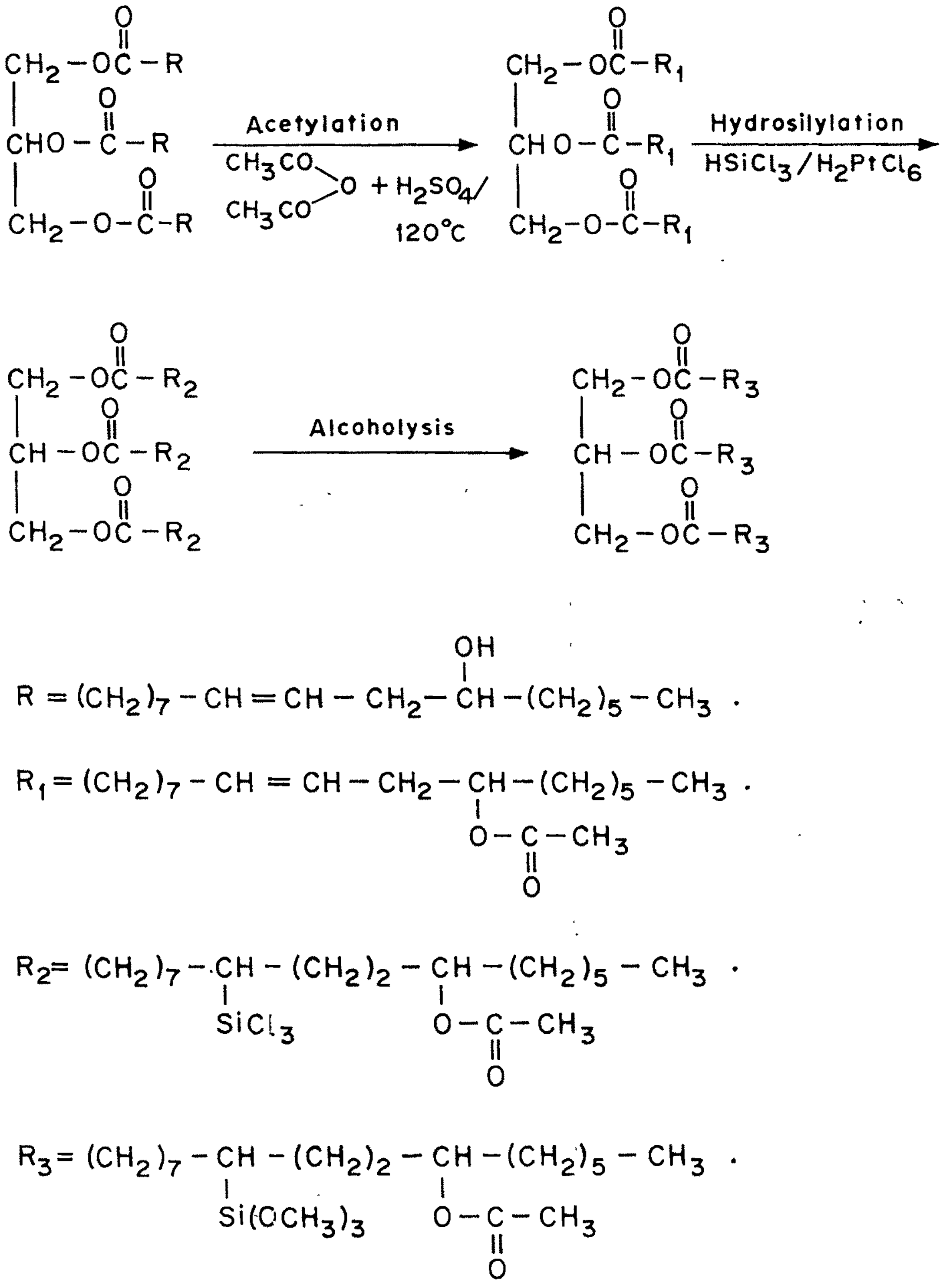


FIG. 3 : SCHEME FOR SYNTHESIS OF COMPOUND F.

sulphate was destroyed by washing with water. The compound was purified by column chromatography to remove the last traces of unreacted cardanol. The elution of column with petroleum ether (60°-80°C) and benzene (70:30) solvent system afforded a compound showing a single spot on thin layer chromatography (TLC). The physical characteristics of this compound such as b.p., refractive index and elemental analysis were in good agreement with the reported values. The IR spectrum of BMP is given in Fig. 4. The physical characteristics are given in Table 4.

Benzene, 1propenyloxy,3-pentadecadienyl (Allyl ether of cardanol) (BPP)

Allyl ether of cardanol was prepared by reported procedure[38] which involves the dropwise addition of allyl chloride to cardanol at room temperature (28°C) with stirring, which was followed by the addition of sodium hydroxide and refluxing the reaction mixture. The compound was washed with hot water, neutralised and dehydrated at 120°-130°C. This ether was also purified by silica gel column chromatography. A pure compound was obtained when petroleum ether (60°-80°C) and benzene mixture (50:50) was used as eluent. The compound was characterised by b.p., refractive index and elemental analysis. The physical characteristics were found to be in agreement with the reported ones (Table 4). The IR spectrum is given in Fig. 5.

1-(9-Octadecenoiate), 3-pentadecadienyl phenyl (Oleic acid ester of cardanol), (9-OPP) and 1-(9-12-Octadecenoiate) 3-Pentadecadienyl phenyl (Linoleic acid ester of cardanol) (9,12-OPP)

A number of procedures are described in the literature for direct esterification of phenol with fatty acids. However, direct esterification was not of much success in case of cardanol with both oleic and linoleic acid. Ghatge and Vaidya[39] have reported a method for the esterification of cardanol with fatty acids which gives better yields than the other known methods. Hence, in the present work, method of Ghatge and Vaidya was followd to prepare the esters of cardanol with oleic and linoleic acid. Thus, esterification was carried out by condensation of fatty acid chloride and sodium salt of cardanol in ether under dry conditions. It was essential to get pure esters, free of cardanol and acid chloride. Therefore, these esters were also purified by column chromatography on silica gel (60-120 mesh) with benzene as eluent. Both the compounds showed single spot on TLC. The physical characteristics of these esters were matching with those of reported ones and are given in Table 4. Fig. 6 shows the IR spectrum of oleic acid ester of cardanol.

Polysulphide from 3-Pentadecyl Phenol [PSP]

3-Pentadecyl Phenol

3-Pentadecadienyl phenol was catalytically reduced over Raney Ni catalyst at 600 psi ... and at 70°C in Parr autoclave to give 3-pentadecyl phenol. The compound was purified by crystallization from petroleum ether (40°-60°C). m.p.. 51°-52°C.

Polysulphide from 3-Pentadecyl Phenol

This was obtained by reacting 3-pentadecyl phenol with sulphur monochloride in an inert solvent such as carbon tetrachloride to give a resinous product . The resinous mass obtained, after distillation under reduced pressure, gave a fraction, boiling at 250°-260°C/1.5 mm Hg which was a polysulphide from 3-pentadecyl phenol. The physical characteristics are reported in the Table 4.

Castor Oil Acetate

Castor oil acetate was prepared under controlled conditions of temperature in the presence of acid catalyst. First, castor oil and sulphuric acid (10%) were heated with stirring upto 110°C, followed by the slow addition of acetic anhydride. After the addition was over, the temperature was raised to 160°C and maintained there for 3 h. The compound was purified by column chromatography to remove unreacted castor oil. The elution of column

Table 4

Physical Properties of Ethers and Esters of 3-Pentadecadienyl Phenol, Polysulphide of 3-Pentadecyl Phenol and Castor oil Acetate

No.	Compound	Boiling point °C/mm Hg	Refractive index at 25°C	Elemental analysis, %				Yield, %
					C	H	S	
1	BMP	195°C/2 m	1.510	Calcd	84.09	10.83	-	90
				Found	84.25	11.12	-	
2	BPP	195-191°C/2mm	1.504	Calcd	80.91	10.11	-	85
				Found	80.93	10.49	-	
3	9-OPP	240-245°/C/7mm	1.499	Calcd	82.96	11.39	-	70
				Found	83.01	11.61	-	
4	9,12-OPP	245-252°C/5mm	1.503	Calcd	83.18	11.14	-	70
				Found	83.05	11.40	-	
5	PSP	250-260°C/1.5mm	-	Calcd	68.60	9.50	17.40	70
				Found	68.90	9.70	17.90	
6.	Castor Oil Acetate	-	1.469	Calcd	71.45	10.39	-	70
				Found	71.36	10.20		

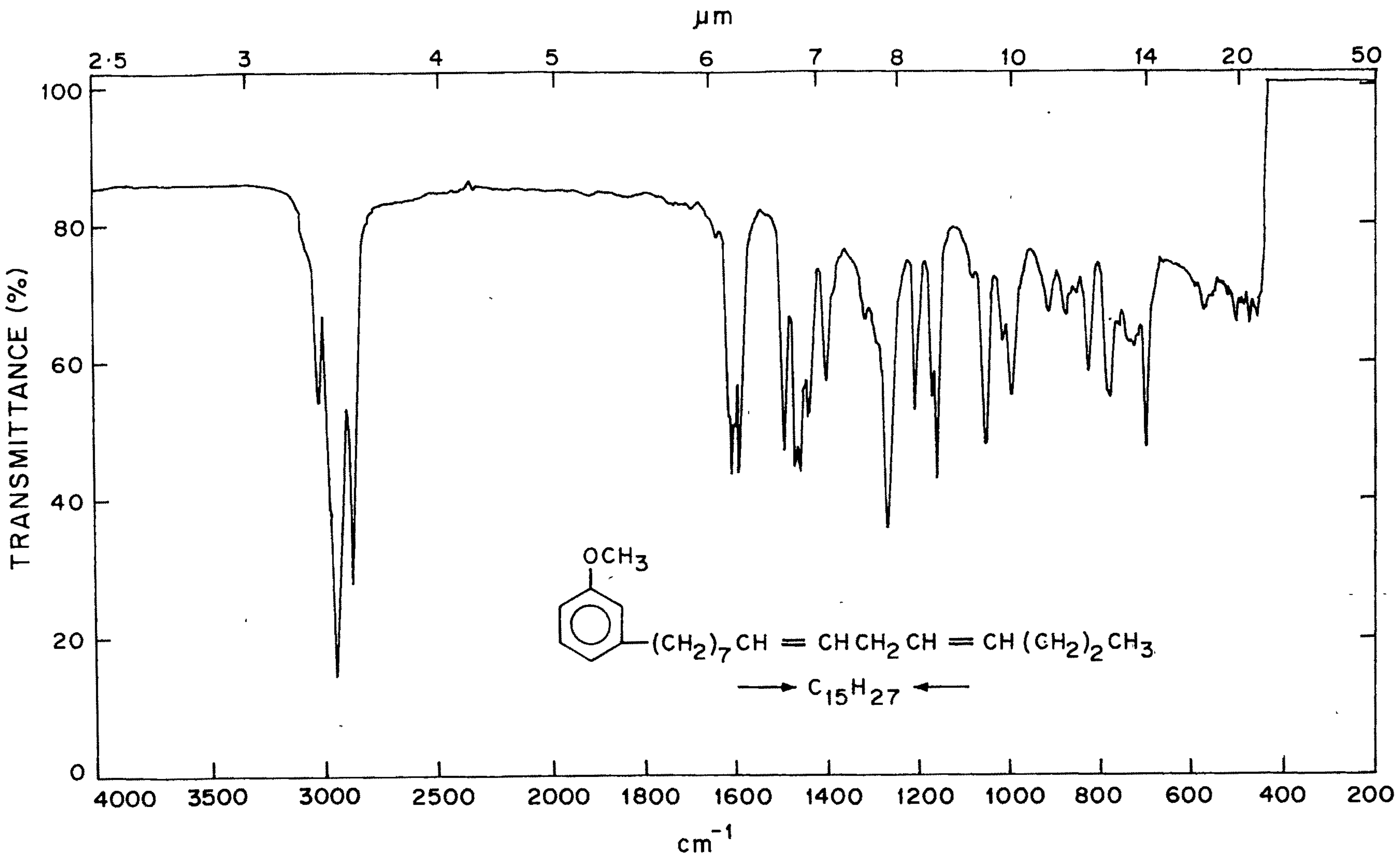


FIG. 4 : IR SPECTRUM OF BENZENE, 1-METHOXY, 3-PENTADECADIENYL. (METHYL ETHER OF CARDANOL).

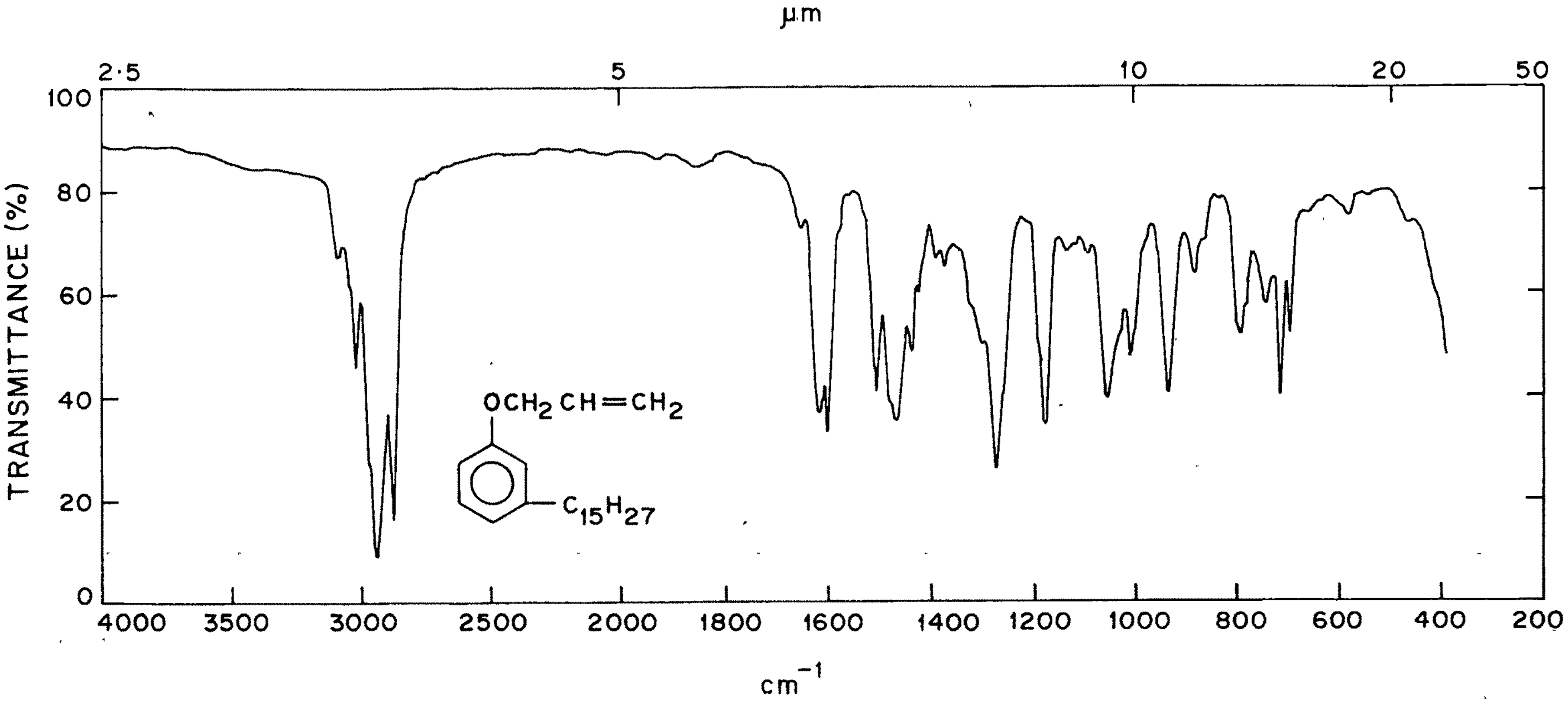


FIG. 5 : IR SPECTRUM OF BENZENE, 1-PROPENYLOXY, 3-PENTADECADIENYL. [ALLYL ETHER OF CARDANOL].

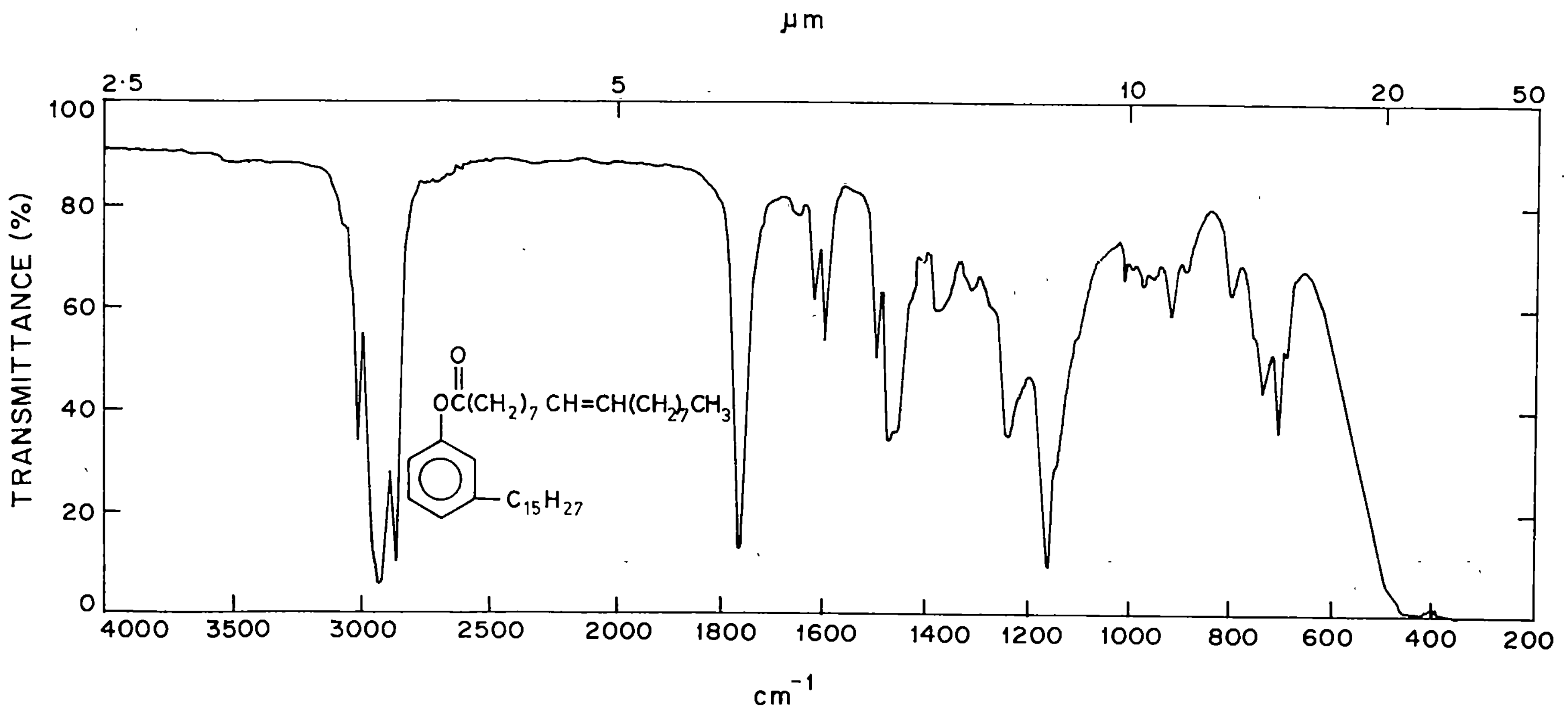


FIG. 6 : IR SPECTRUM OF 1,[9-OCTADECENOATE],3-PENTADECADIENYL PHENYL. [ESTER OF CARDANOL WITH OLEIC ACID].

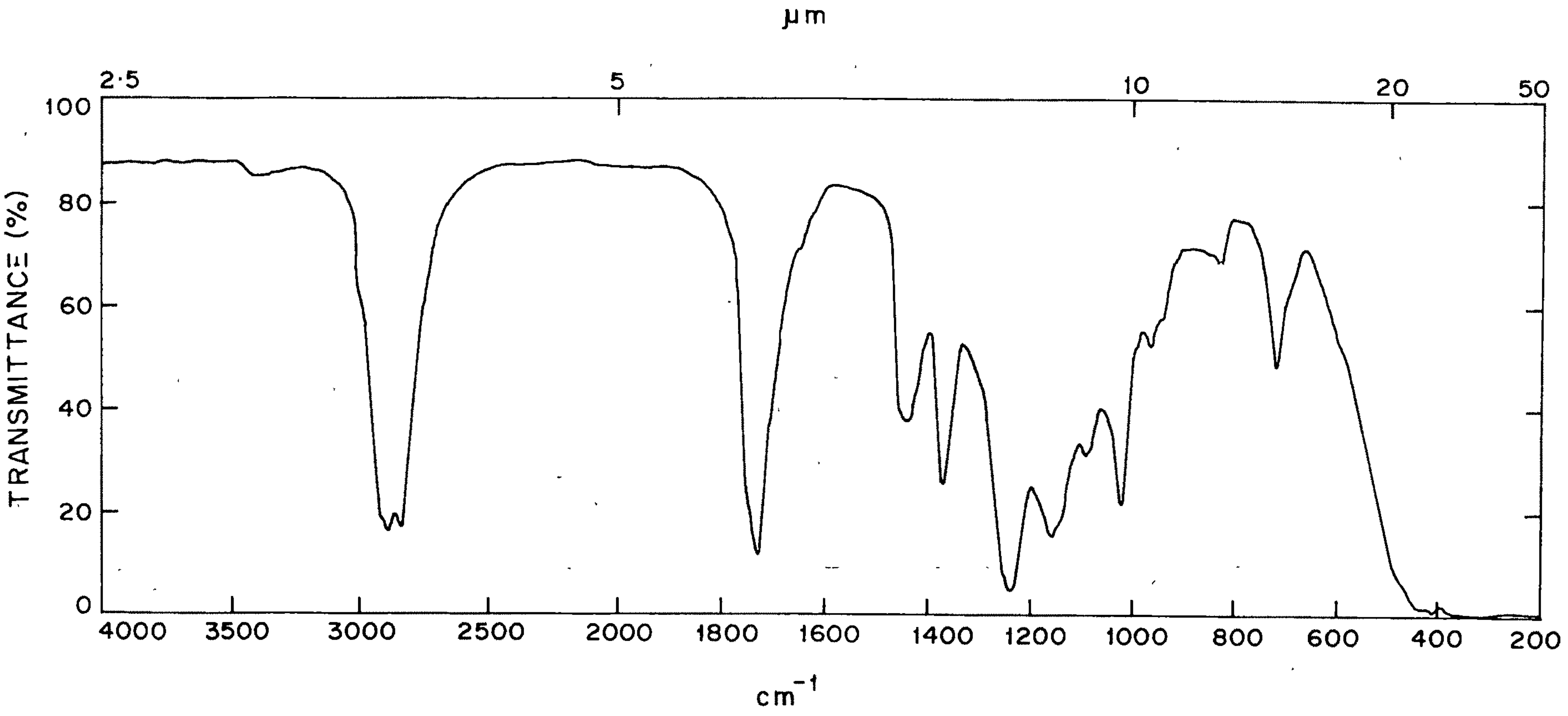


FIG. 7 : IR SPECTRUM OF CASTOR OIL ACETATE.

with benzene and ethylacetate (95:5) solvent system afforded a compound showing a single spot on TLC. The compound was characterised by elemental analysis and refractive index measurements (Table 4).

Synthesis of Hyrdosilylated Products from Ethers and Esters of Cardanol and Castor Oil Acetate

In the present investigation, hydrosilylation of the following compounds was carried out to obtain the corresponding hydrosilylated derivatives.

1. Methyl ether of cardanol
2. Allyl ether of cardanol
3. Ester of cardanol with oleic acid
4. Ester of cardanol with linoleic acid

and 5. Castor oil acetate

The hydrosilylation reactions were carried out in thick walled glass ampoules using trichlorosilane as hydrosilylating agent and chloroplatinic acid as catalyst. The amounts of hydrosilylating agent and catalyst used in each case are given in Table 5.

Thus, the respective compound was placed in the glass ampoule and cooled to 0°C. Then, trichlorosilane was added slowly, followed by the addition of isopropanolic solution of chloroplatinic acid. Finally, the glass ampoule was sealed after three freeze thaw cycles and heated at 90°C for 8 h. Then the ampoule

Table 5

Hydrosilylation of Ethers and Esters of 3 Pentadecadienyl Phenol and Castor oil Acetate

No.	Compound	Trichlorosilane in g	Chloroplatinic Acid (0.1 M isopropanolic solution) ml
1	BMP (Methyl ether of cardanol) 3.14 (0.01 mole)	5.4 (0.04 mole)	0.332
2	BPP (Allyl ether of Cardanol) 3.56 g (0.01 mole)	8.10 (0.06 mole)	0.498
3	9-OPP(Ester of cardanol with oleic acid) 5.64 g (0.01 mole)	8.10 (0.06 mole)	0.498
4	9,12-OPP (Ester of cardanol with linoleic acid) 5.62 g (0.01 mole)	10.8 (0.08 mole)	0.660
5	Castor oil Acetate 10.58 g (0.01 mole)	8.10 (0.06 mole)	0.498

6 Polysulphide of 3 pentadecyl phenol 17.34 g (0.01 mole) was reacted with 8.10 g (0.06 mole) of trichlorosilane

was cooled to 0°C and opened. The excess of trichlorosilane was removed under reduced pressure. Pure hydrosilylated products could not be separated by distillation under reduced pressure at high temperature.

Hydrosilylation reactions are affected by various reaction parameters such as time, temperature and ratio of reactant to hydrosilylating agent. In the present work, attempts have been made to achieve complete hydrosilylation of cardanol ethers, esters and castor oil acetate. The hydrosilylations were conducted under various conditions of reactions such as time, temperature and ratios of reactants to achieve maximum hydrosilylation.

Thus, the time of the reaction was increased from 8 h to 10 h. However, complete hydrosilylation was not achieved which is evident from the spectral data. The presence of unsaturation was seen in the IR spectra.

To observe the effect of temperature, the temperature of reaction was raised from 90°C to 110°C. Still, the unsaturation was observed in the IR spectra, indicating, hydrosilylation of the compound was incomplete.

The IR spectra of chlorosilane derivatives of BMP, BPP, 9,12-OPP and castor oil acetate are given in Figs. 8,9,10 and 15, respectively.

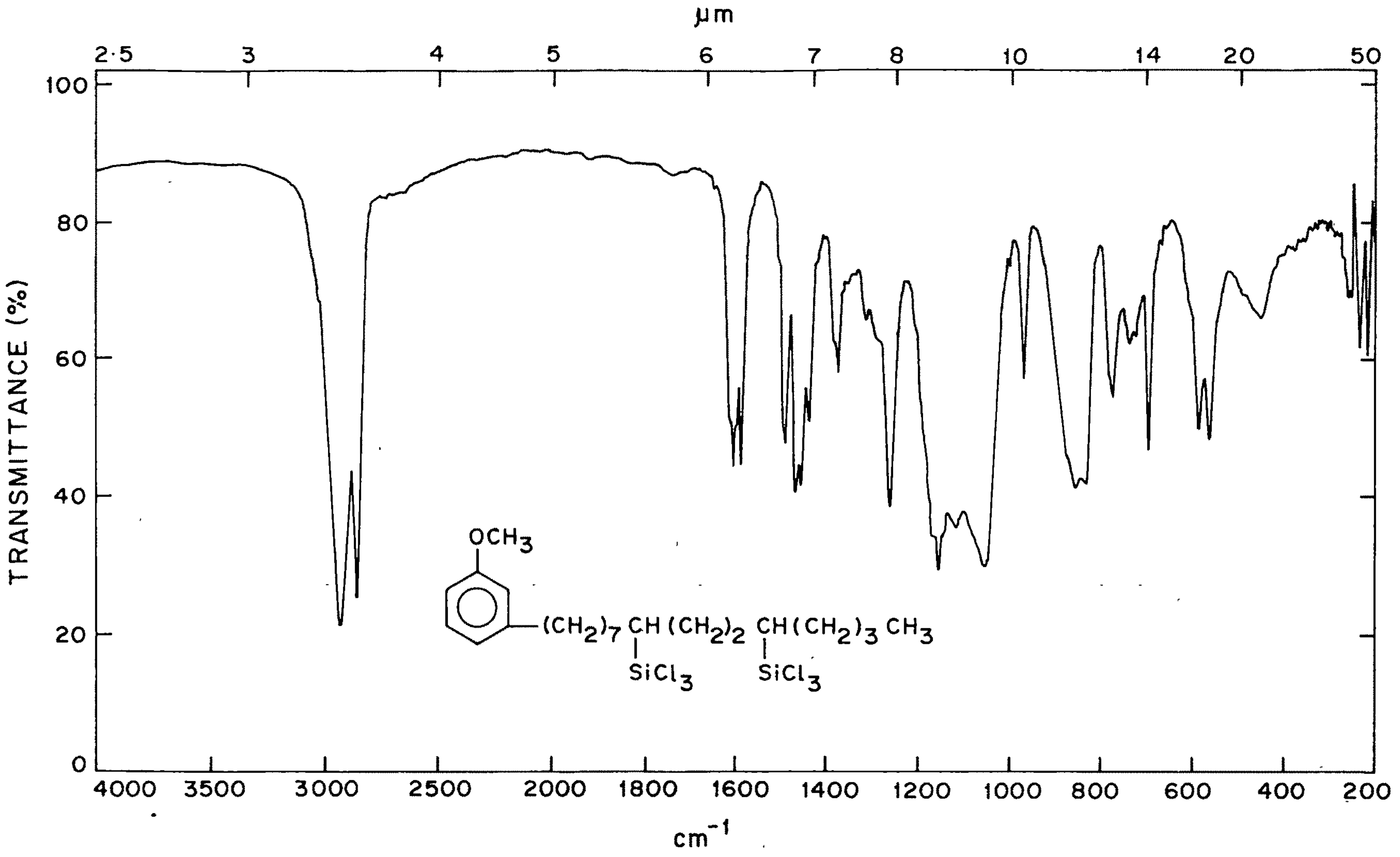


FIG. 8 : IR SPECTRUM OF BENZENE, 1-METHOXY, 3-[8,11 BIS(TRICHLOROSILYL)] PENTADECYL.

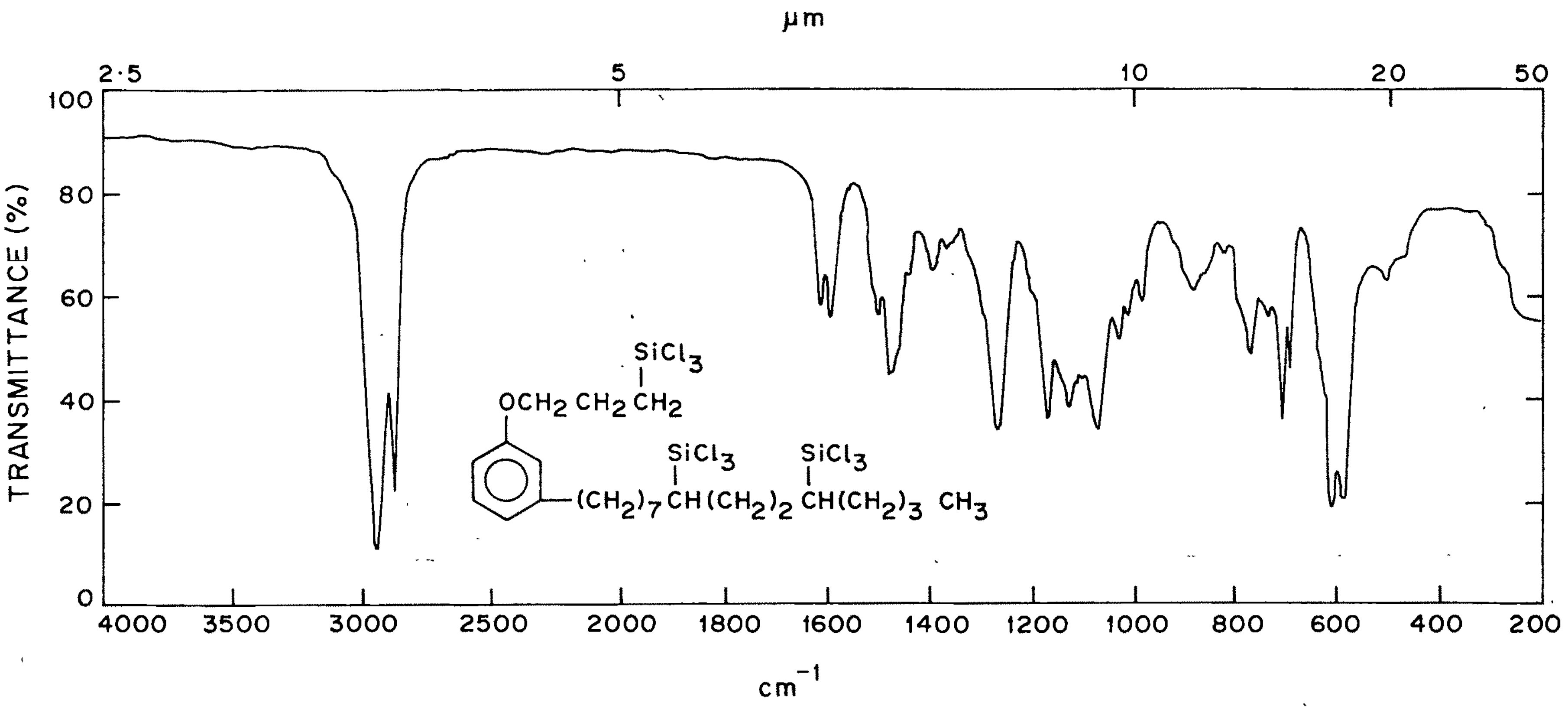


FIG. 9 : IR SPECTRUM OF BENZENE , 1-[3-(TRICHLOROSILYL) PROPANYLOXY]
3-[8,11 BIS(TRICHLOROSILYL)] PENTADECYL .

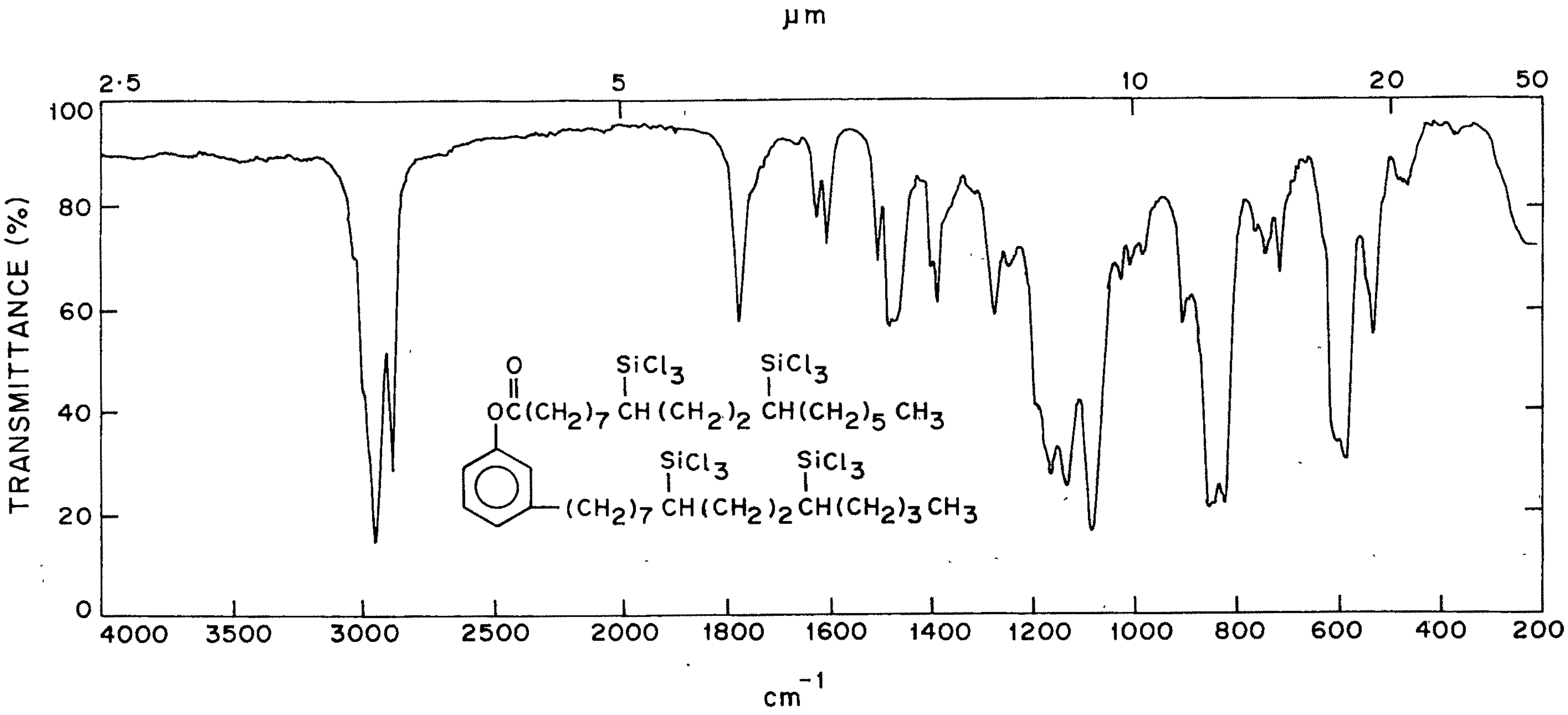


FIG. 10 : IR SPECTRUM OF 1-[9,12 BIS(TRICHLOROSILYL)] OCTADECANOATE, 3-[8,11 BIS(TRICHLOROSILYL)] PENTADECYL PHENYL.

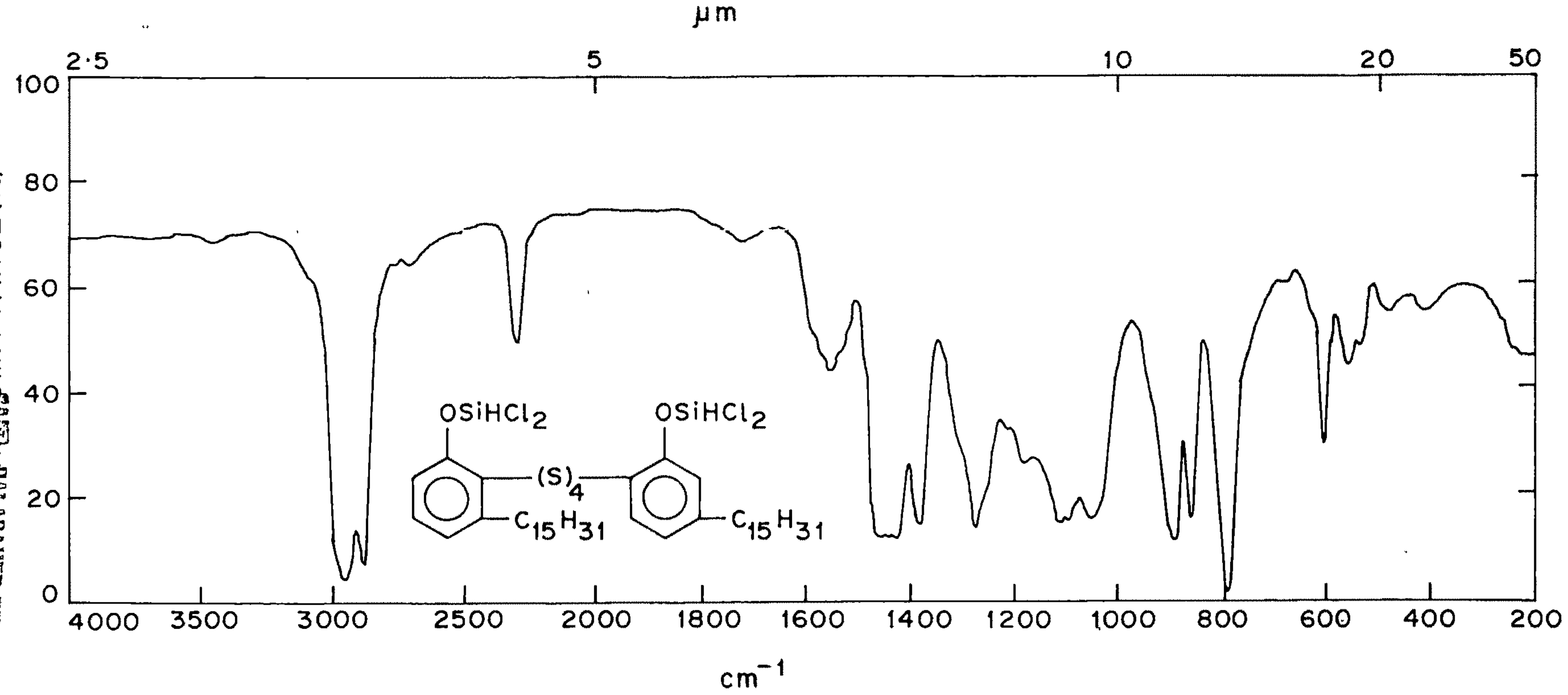


FIG. 11 : IR SPECTRUM OF CHLOROSILYL DERIVATIVE OF POLYSULPHIDE OF 3-PENTADECYLPHENOL.

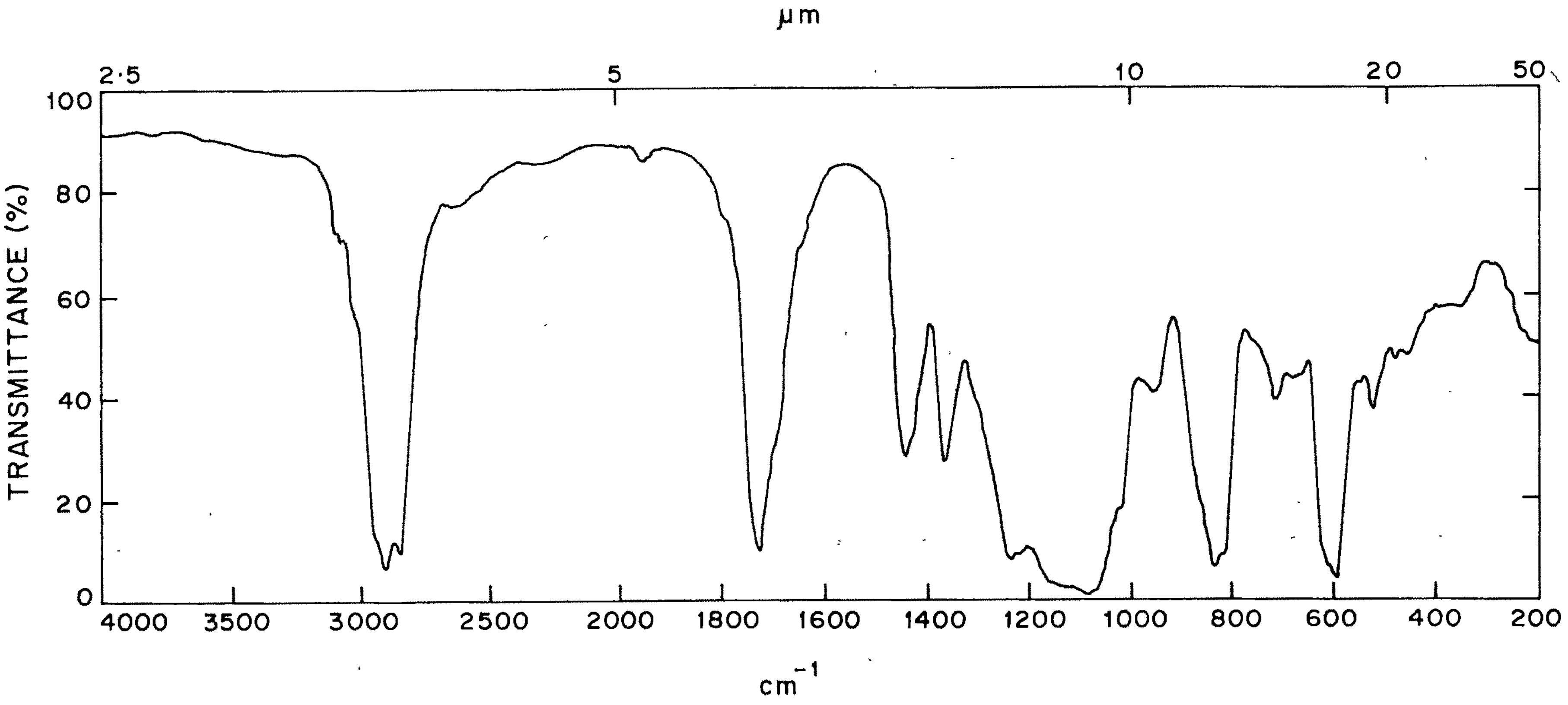


FIG. 15 : IR SPECTRUM OF CHLOROSILANE DERIVATIVE OF CASTOR OIL ACETATE.

Reaction of Polysulphide from 3-Pentadecyl Phenol with Trichlorosilane

The reaction of polysulphide from 3-pentadecyl phenol with trichlorosilane is depicted in Figure 2. The reaction was carried out by slow addition of trichlorosilane to the benzene solution of polysulphide from 3-pentadecyl phenol at 10-15°C under dry conditions with stirring. After the addition was over, the reaction mixture was stirred for 3 h at 50°C. Then the unreacted trichlorosilane and benzene were removed under reduced pressure.

The IR spectrum of chlorosilyl derivative is given in Fig. 11.

Synthesis of Methoxysilyl Derivatives

The reactions of chlorosilane derivatives with dry methanol in dry benzene afforded new methoxysilyl derivatives. The slow addition of methanol to chlorosilane compounds was done at 20°C temperature with stirring (Table 6). Then the reaction mixture was refluxed till the evolution of HCl ceased (3-4 hr.). The procedure was repeated twice to ensure the complete conversion of chlorosilane derivatives to methoxysilane compounds. The IR spectra of BMMS, 9-TOMSP and 9,12-TOMSP are given in Figs. 12,13 and 14, respectively. These methoxysilyl compounds were brown coloured

Table 6

Alcoholysis of Chlorosilane Compounds

No.	Compound	Benzene, ml	Methanol, gm
1.	Chlorosilane of BMP (0.01 mole)	50	1.92 (0.06 mole)
2.	Chlorosilane of BPP (0.01 mole)	50	2.88 (0.09 mole)
3.	Chlorosilane of 9-OPP (0.01 mole)	75	2.88 (0.09 mole)
4.	Chlorosilane of 9,12-OPP (0.01 mole)	75	3.84 (0.12 mole)
5.	Chlorosilane of PSP (0.01 mole)	75	1.92 (0.06 mole)
6.	Chlorosilane of castor oil acetate (0.01 mole)	70	2.88 (0.09 mole)

viscous liquids.

The compounds were found to be sensitive to atmospheric moisture. Hence, these compounds were stored under dry conditions.

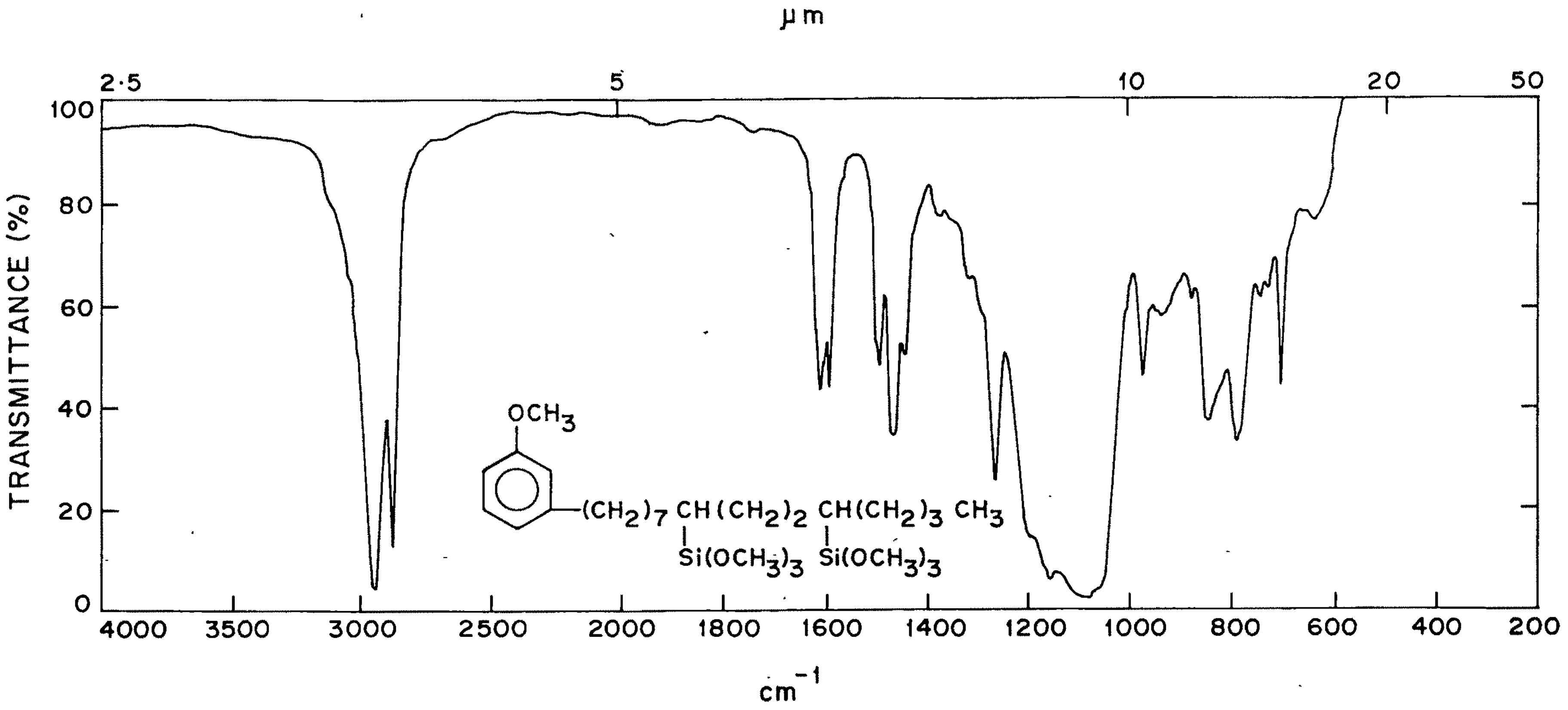


FIG. 12 : IR SPECTRUM OF BENZENE, 1-METHOXY, 3-[8,11 BIS(TRIMETHOXYSILYL)] PENTADECYL.

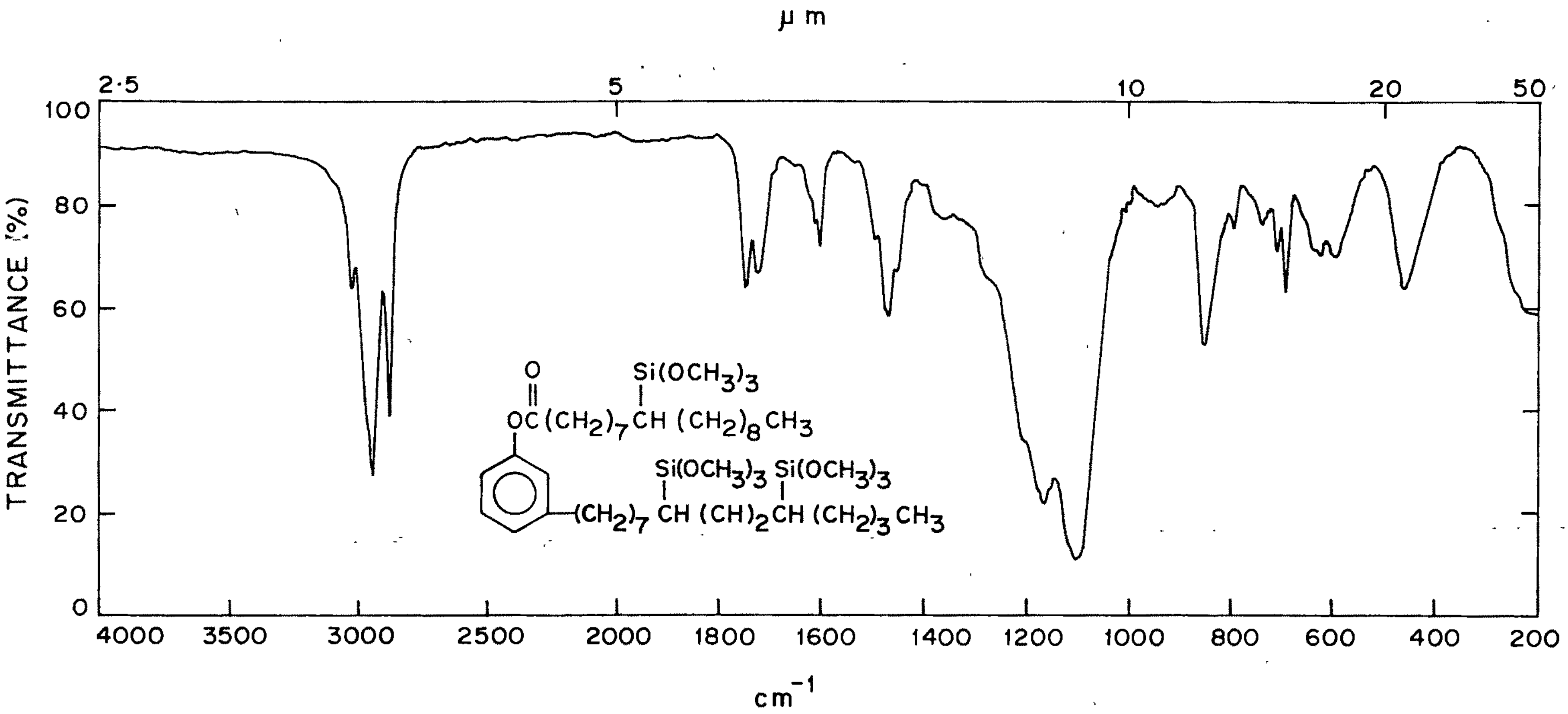


FIG. 13 : IR SPECTRUM OF 1-(9 TRIMETHOXYSILYL) OCTADECANOATE, 3-[8,11 BIS(TRIMETHOXYSILYL)] PENTADECYL PHENYL.

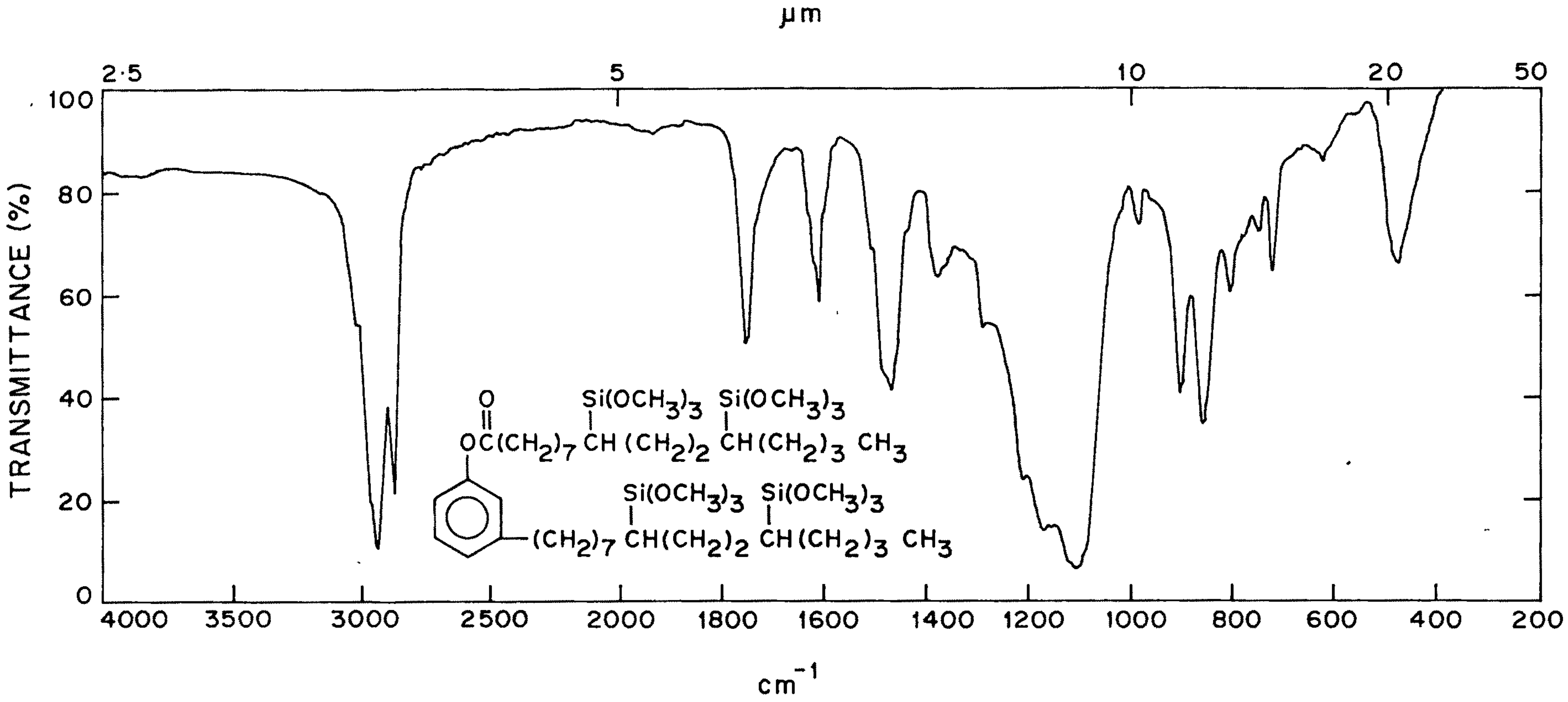


FIG. 14 : IR SPECTRUM OF 1-[9,12 BIS(TRIMETHOXYSILYL)] OCTADECANOATE, 3-[8,11 BIS(TRIMETHOXYSILYL)] PENTADECYL PHENYL.

DISCUSSION:

In the present study, new silane compounds were synthesised from 3-pentadecadienyl phenol (cardanol)- an indigineously available raw material- with a view to utilize them for various polymer applications.

Cardanol is a major constituent of CNSL. The reactive sites present in 3-PDP are phenolic hydroxyl group and double bonds in the side chain. The aliphatic side chain present in 3-PDP is a mixture of one, two and three double bonds (i.e. $C_{15}H_{29}$, $C_{15}H_{27}$ and $C_{15}H_{25}$). But for our experimental purpose it was assumed that it contains two double bonds only. The hydrosilylation reaction was carried out by protecting the hydroxyl group.

Thus, the methyl ether of cardanol was prepared from cardanol and dimethyl sulphate. Further, the etherification of cardanol was carried out with allyl chloride so that the resulting allyl ether derivative will have more number of double bonds available for hydrosilylation. The reactive sites were further increased by esterification of cardanol with oleic and linoleic acid. In castor oil also the hydroxyl groups were protected by acetylation.

For hydrosilylation reaction, it is important to have compounds free of cardanol. There is possibility of contamination of cardanol even after separating the ethers and esters of cardanol by vacuum distillation at high temperature. Therefore, pure products were obtained by column chromatography.

These ethers and esters were characterised by IR spectra (Figs. 4 to 7). All the spectra showed disappearance of hydroxyl band at 3400 cm^{-1}. The appearance of new band at 1280 cm^{-1} due to C-O-C stretch in case of methyl ether of cardanol, at 920 cm^{-1} due to vinyl stretching in case of allyl ether of cardanol and at 1770 cm^{-1} due to ester carbonyl stretching in esters of cardanol and in castor oil acetate also indicated the formation of ethers and esters.

The attempts for complete hydrosilylation of the ethers and esters of cardanol and castor oil acetate were unsuccessful. This is evident from the IR spectra of the hydrosilylated products (Figs. 8-10). The IR spectra of hydrosilylated products showed appearance of new bands in 600-550 cm^{-1} and in 860-845 cm^{-1} regions which are characteristic of Si-Cl and Si-C stretching, respectively suggesting that the hydrosilylation had taken place. However, the weak band at 690 cm^{-1} characteristic of C=C _cis_ stretching was still present which indicates that hydrosilylation was not complete. To get pure hydrosilylated products attempts were made to distill the chlorosilyl derivatives under reduced pressure but the attempts were unsuccessful. Therefore, these chlorosilyl derivatives were used as such for their further conversion to methoxysilane compounds.

The reaction product of polysulphide from 3-pentadecylphenol with trichlorosilane showed absence of OH band at 3400 cm^{-1} and appearance of new bands in 600-550 cm^{-1} regions due to Si-Cl stretching indicating that hydroxyl group is reacting with trichlorosilane.

Synthesis and Characterization of Methoxysilyl Compounds

The conversion of Si-Cl groups to $Si-OCH_3$ groups was achieved by usual alcoholysis reaction. The alcoholysis reaction was repeated twice with methanol to ensure the complete conversion of chlorosilane groups to methoxysilane groups which is supported by IR spectra.

The disappearance of bands in 600-550 cm^{-1} region due to Si-Cl stretching in the IR spectra (Figs. 12-14) and appearance of broad band in 1120-1080 cm^{-1} region due to Si-0-C stretching supported that the complete convesion had taken place.

Although methoxysilyl compounds of cardanol ethers and esters and castor oil acetate contain unreacted respective starting unsaturated compounds these unreacted compounds should not impose any limitation on their use as coupling agents for rubber reinforcement and for foundry sand cores.

EXPERIMENTAL

Materials

Cahewnut shell liquid (CNSL) was obtained from Card Chem. Industries, Hyderabad (India).

Dimethyl sulphate was procured from IDPL, Hyderabad (India) and was kept over potassium carbonate and distilled before use.

Allyl chloride was obtained from M/s. Koch Light Laboratory Chemicals, England and was purified by distillation under dry conditions.

Oleic acid and linoleic acid were purchased from local market and were purified by distillation under reduced pressure at 234°C/15 mm Hg and at 230°C/15 mm Hg, respectively.

Phosphorous trichloride of commercial grade was distilled before use.

Sulphur monochloride (99%) was obtained from Riedel, GDR.

Trichlorosilane was distilled before use (31°C).

Chloroplatinic acid was procured from Jonson Mathey and Co.Ltd. (London) Pt. approx. 40%.

Solvent ether was carefully dried and stored over fresh sodium ribbon.

Solvents like ptroleum ether (40°-60°C) and (60°-80°C), benzene, acetone and carbontetrachloride were purified by distillation before use.

PREPARATIONS

Distillation of CNSL

The refined CNSL was used throughout the work.

Specifications of CNSL of export variety (Kerala State, Govt. of India) were

Specific gravity	- 0.985
Viscosity	- 434.1 cps
Moisture content	- 1.17% (max)
Matter insoluble in toluene	- 0.20% (max)
Volatiles	- 5.2% (max)
Iodine value	- 234.0

3-Pentadecadienyl phenol (cardanol)

Raw commercial CNSL (heat extracted) 900 g was distilled from 2 litre round bottomed flask under reduced pressure. The flask was heated slowly till initial frothing subsided and the distillate was collected between 190°-220°/2 mm Hg. This was redistilled to give pale yellow cardanol.

Yield 410 g, b.p.195-200°/2 mm Hg.

Benzene, 1-methoxy, 3-pentadecadienyl (Methyl ether of cardanol) (BMP)

In a 500 ml round bottomed flask equipped with a reflux condenser, a mixture of 30.0 g (0.1 mole) of cardanol in 80 ml of acetone, 31.0 g (0.75 mole) of sodium hydroxide in 40 ml of water and 16.8 g (0.13 mole) of dimethyl sulphate were placed. The reaction mixture was refluxed for 2 h on the water bath. Then, reflux condenser was removed and acetone was distilled off. The reaction mixture was cooled to room temperature and extracted with ether. The ether layer was washed with water to destroy excess of dimethyl sulphate. The ether layer was dried over anhydrous sodium sulphate. Ether was removed and the product obtained was distilled under reduced pressure at 195°-210°C/3 mm Hg. It was further purified on silica gel column (60-120 mesh). A pure compound was obtained with 70:30 petroleum ether (60°-80°C): benzene solvent system. It was identified by b.p., refractive index, elemental analysis and IR spectrum.

Benzene, 1-propenyloxy, 3-pentadecadienyl (Allyl ether of cardanol) (BPP)

3-Pentadecadienyl phenol 30 g (0.1 mole), was placed in a 250 ml three necked round bottomed flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel. Allyl chloride 10 g (0.13 mole) was added slowly with stirring. Then 5.3 g (0.13 mole) of sodium hydroxide dissolved in 15 ml of water was added to the reaction mixture with stirring. After the addition was over, the reaction mixture was refluxed for 5 h when two layers separated. The reaction mixture was neutralised with hydrochloric acid and the water layer was separated out. The separated layer was further washed twice with hot water and dehdyrated by heating on oil bath at 120°-130°C. Allyl ether of cardanol was purified on silica gel column (60-120 mesh) to remove last traces of unreacted cardanol. A pure compound was obtained with petroleum ether (60-80°C): benzene (70:30) mixture as eluent.

1-(cis 9-Octadecenoate), 3-pentadecadienyl phenyl (Ester of cardanol with oleic acid) (9-OPP)

Sodium salt of cardanol

In a 250 ml three necked round bottomed flask fitted with a reflux condenser, mechanical stirrer and thermowell 30 g. (0.1 mole) of 3-pentadecadienyl phenol and 2.3 g (0.1 mole) of freshly cut sodium pieces were placed and heated on oil bath at 120°-125°C with vigorous stirring for 4 h. A dark brown viscous liquid was obtained.

cis-9-Octadecenoic acid chloride (Oleyl chloride)(9-OAC)

In a 500 ml three necked round bottomed flask fitted with a reflux condenser with calcium chloride guard tube, a dropping funnel with calcium chloride guard tube and a thermowell, 28.2 g (0.1 mole) of oleic acid was stirred at 70°-75°C with magnetic stirrer. Then, 27.4 g (0.1 mole) of phosphorus trichloride was added dropwise during 30 min. The reaction mixture was maintained at 70°-75°C for 2 h. The reaction product was cooled to room temperature and viscous liquid was decanted. The decanted liquid was heated to 150°C in vaccuo (water aspirator), cooled to room temperature and again decanted from small amount of viscous material. The residual decanted product on vacuum distillation gave oleyl chloride as a pale yellow liquid. Yield 70%, b.p.180°-185°C/5 mm Hg.

cis 9 cis 12-Octadecadienyl acid chloride (Linoleyl chloride) (9,12, LAC)

9,12-LAC was prepared as per the method used to prepare 9-OAC. Yield 70%, b.p. 190°-195°/4 mm Hg.

cis 9-Octadecenoiate 3-Pentadecadienyl Phenyl(Ester of cardanol with oleic acid) (9-OPP)

Sodium salt of 3-pentadecadienyl phenol 32.2 g (0.1 mole) and dry ether (300 ml) were placed in a 500 ml three necked round bottomed flask, fitted with a mechanical stirrer, a reflux condenser with a calcium chloride guard tube and a dropping funnel having calcium chloride guard tube. Oleyl chloride (30.9 g) (0.1 mole) was added dropwise over a period of 1 h under dry conditions. The reaction mixture was refluxed for 5 h and then cooled to room temperature and solvent ether was removed. The product obtained was purified on silica gel column (60-120 mesh) and identified by b.p., refractive index, elemental analysis and by IR spectroscopy.

1-(cis 9, cis 12 Octadecadienoiate 3-pentadecadienyl) phenyl

9,12-OPP (Ester of caradanol with linoleic acid) was prepared under similar reaction conditions employed for 9-OPP.

Polysulphide from 3 Pentadecyl Phenol

Cardanol (300 g) was hydrogenated at 70°C in a Parr autoclave under 600 psi pressure of hydrogen in the presence of Raney nickel catalyst (0.3-0.5 g) which was prepared according to the W-2 method. When no more absorption was noticed, the reaction was stopped, the catalyst was filtered and solvent was distilled out. Recrystallization from petroleum ether (40°-60°C) gave white waxy solid of 3-pentadecyl phenol. Yield 270 g, m.p.51°-52°C.

3-Pentadecyl phenol 6 g (0.02 mole) was dissolved in carbontetrachloride (30 ml) and was placed in 250 ml three necked round bottomed flask fitted with a reflux condenser, a dropping funnel and a mechanical stirrer. Sulphur monochloride 0.84 ml (0.01 mole) in 6 ml of carbontetrachloride was added dropwise at low temperature (20°C) with stirring. Then the temperature was brought to 30°C and maintained for ½ h. The reaction mixture was refluxed for 3 h in the oil bath. The solvent was removed under reduced pressure and the soft resinous mass obtained was further distilled under reduced pressure. The first fraction boiling at 220°C/1.5 mm Hg gave unreacted 3-pentadecyl phenol. The second fraction obtained at 225-240°C/1.5 mm Hg was 3-pentadecylphenol contaminated with sulphur monochloride and third fraction distilling at 250-260°C/1.5 mm Hg was polysulphide from 3-pentadecyl phenol.

Castor oil acetate

In a 500 ml three necked round bottomed flask fitted with a mechanical stirrer, a thermowell and a reflux condenser 93.2 g (0.1 mole) of castor oil was placed. Then 3 ml of sulphuric acid (10%) was added with stirring. The mixture was heated to 110°C. Then 30.6 g (0.3 mole) of acetic anhydride was added slowly. After the addition was over the temperature was raised to 160°C and maintained for 3 h. Castor oil acetate was purified by silica gel (60-120 mesh) column chromatography using benzene:ethylacetate solvent system to obtain pure product free of castor oil.

Hydrosilylation of Ethers/Esters of Cardanol and Castor Oil Acetate

Hydrosilylation reaction was done in a thick walled, dry glass ampoule. The respective ether/ester (0.01 mole) was taken in the ampoule and cooled to 0°C.

Then the corresponding amount of trichlorosilane (Table 5) was added slowly. The temperature was maintained at 0°-5°C throughout the addition. Then the addition of isopropanolic solution of chloroplatinic acid (Table 5) was done. Finally, the glass ampoule was sealed after three freeze thaw cycles and heated at 90°C for 8 h. The ampoule was cooled to 0°C and opened. The product was transferred to 100 ml round bottomed flask and the excess of trichlorosilane was removed under reduced pressure at 30°C/10 mm Hg.

Reaction of Polysulphide from 3-Pentadecyl Phenol(PSP) with Trichlorosilane

In a three necked 250 ml round bottomed flask fitted with a reflux condenser, a stirrer and a dropping funnel 0.01 mole of PSP (Table 5) and 30 ml of benzene were placed and stirred. The reaction mixture was cooled to 10°C and trichlorosilane was added slowly with vigorous stirring to drive off HCl gas formed during the reaction. The mixture was stirred for 3 h at 50°C. Then the unreacted trichlorosilane and benzene were removed under reduced pressure at 30°C/10 mm Hg.

Methoxysilyl Derivatives from Chlorosilane Derivatives of Ethers and Esters of Cardanol, Castor Oil Acetate and Chlorosilyl Ether of Polysulphide from 3-pentadecyl phenol

In a three necked 250 ml round bottomed flask fitted with a reflux condenser, a mechanical stirrer and a dropping funnel 0.01 mole of respective ether/ ester was placed with 50 ml of benzene. Then required amount of methanol (Table 6) was added at 20°C with vigorous stirring. After the addition was over, the reaction mixture was refluxed for 3 h. Then methanol and benzene were removed under reduced pressure at 30°C/10 mm.Hg The above procedure was repeated twice to ensure the complete conversion of chlorosilane to methoxy silane compound. The compounds were found to be sensitive to moisture. Therefore, these compounds were stored under dry conditions.

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Section B

Evaluation of Silane Coupling Agents in Rubber Reinforcement

INTRODUCTION

The current world position of petroleum reserves has fostered sincere efforts to utilize alternate materials which are less dependent upon petroleum. Highly reinforced rubber is one of the major needs of rubber industry for various applications. Carbon black, a petroleum-derived filler- is no longer a cheap extender due to its escalating prices. An extensive research is going on for replacement of cost effective reinforcing carbon black filler in rubber compounding by low cost fillers like silica, clay and calcium carbonate.

A number of papers[1-4] have been published during the last decade for promoting reinforcing action of mineral fillers by surface treatment. The traditional means of treatments include the use of bases such as sodium hydroxide or sodium carbonate which modify the pH and effect dispersibility in water as well as improve rubber compound cure properties[5].

The modification of clays by incorporating organo-functional silane is important both from commercial as well as technical significance. Fillers may be pretreated with silanes or silanes may be integrally blended or added at the time of rubber compounding. Many research workers are working for the effective improvement in physical properties of mineral filled elastomers using silane coupling agents.

The use of silane coupling agent for mineral filled elastomers was first reported by Fusco in 1960's[6]. Since then a number of research papers have been published. A brief account of the use of silane coupling agents in mineral filled elastomers is given below:

The electrical properties of ethylene propylene rubber (EPR), which is widely used in wire and cable insulation compounds, were significantly improved by use of vinyl silane. Wolf and Roche[7] described the retention of electrical properties even under wet conditions and higher modulus with vinyl silanes in clay filled EPR.

Ranney and Pagano[8] studied the special performance of mineral filled EPDM compounding and related it to dual functionality of organofunctional silanes. They further stated that the organofunctional silanes must be reactive with cure system and have ability to interact with the elastomer through copolymerization or addition. The dynamic testing improvement such as flex life, abrasion, heat build up and road wear properties along with improvement in normal physical properties were observed by using mercaptosilane in mineral filled sulphur cured EPDM. In case of talc/kaolin clay/precipitated silica filled, sulphur cured EPDM, higher tear and 300% modulus were obtained when mercapto or aminosilanes were incorporated than using alkoxy silanes. They have also evaluated monomeric alkoxy silanes $(R'-CH_2)_n-Si(OR)_3$ as surface modifiers for various grades of carbon black and silica filled natural rubber compoundings and observed increase in permanent set values and reduced heat build up.

Ranney et al.[9], have also published a review on the performance of silane modified mineral fillers in rubber compounding. Fitter[10] has reported that the original properties of natural rubber filled with N-330 (HAF) black could be maintained by partial (15-20 phr) or full loading (45-50 phr) of HS-200 silica and silane coupling agents. Similar type of improvement was also noticed in SBR, CR and NBR.

Wagner[11] has done the comparison of silica and carbon black filled SBR and demonstrated that the use of coupling agent was an efficient method of reducing heat build up. Other properties were also readily optimised due to coupling bond and cross-linking net work.

Plueddemann[12] has investigated the importance of proper selection of silane coupling agent, elastomer and curing system. The effect of various silane coupling agents on physical properties of sulphur and peroxy cured elastomer was studied. Plueddemann has also proposed that the mechanism of rubber reinforcement is similar to bonding mechanism of reinforced plastics.

Burg[13] has observed improved physical properties by employing mono and dimercapto polymeric siloxanes as coupling agents in clay and silica filled SBR.

Wolf[14] has reported that the precipitated silica filled (VN-2) natural rubber tread compound using Si-69 and thiuram disulphide curing system gave the same tread wear as obtained by natural rubber reinforced with N-110 (SAF 135 m^2) carbon black.

The precipitated silica offers closest alternative to cost effective reinforcement of rubber. The use of mercapto-silane in many rubber compoundings offers reinforcement with hydrated silica which is comparable to that of carbon black reinforcement. In truck tyre test N-200 (ISAF) black was replaced with Hi-Sil 210 using 2% mercaptosilane which gave comparable modulus and tensile strength. Wagner[15] has further reported that the tyre wear test of 150 m^2/g hydrated silica filled tread composition is 65-70% and can be increased by incorporating silane coupling agent.

Wolf[16] has studied the modification reaction of silica which reveals the information about filler-silane interactions and its practical and economical use.

Elastomers consisting of polybutadiene filled with glass beads pretreated with silane coupling agent showed increased tear and tensile strength by 25%[17].

Stenberg et al.[18] observed improved mechanical properties of calcium silicate filled natural and EPDM rubber when mercapto silane was used as coupling agent instead of titanium alkoxide.

Good friction resistance of butadiene styrene rubber blend even in wet condition was observed by Yamada Hiroshi[19] by incorporating silane coupling agent (0.5) and antifriction agent such as Al_2O_3.

Dujan, et al.[20] have noticed increased physical properties of SiO_2 filled SBR in which oils were used as plasticizers and silanes as surface modifiers.

The effect of different silane coupling agents (mercapto and amino) on clay filled sulphur and peroxide cured NR has been analyzed by studies on network structure, physical properties of vulcanizates and scanning electron micrographs of fracture surface. The promoted physical properties were observed by incorporation of silanes. The lower values of compression and dynamic set and heat buildup by incorporating silane coupling agent was explained on the basis of polymer filler interaction[21].

Present Investigation and Results

Reinforcement in rubber compounding is achieved by incorporating small size particle substances which give to vulcanizates high abrasion resistance, high tear and tensile strength and some increase in hardness. These small size particle substances are called reinforcing fillers.

Carbon black is the most important filler used in rubber industry. Fillers other than carbon black are mineral fillers such as fine silica, clay and calcium carbonate and are commonly known as non black fillers.

The physical properties of rubber products depend on the nature and type of the filler used. Carbon black reinforced vulcanizates give better properties than vulcanizates with non black fillers. Carbon black industry is severely affected by energy crisis due to which it is no longer a cheap reinforcing filler for rubber industry. Therefore, attempts are being made all over the world for replacement of carbon black by mineral fillers. A number of studies report the improvement in physical properties of mineral filled vulcanizates by treatment with silane coupling agents.

In 1960's Fusco[6] has first reported improved physical properties of mineral filled peroxide cured ethylene propylene rubber (EPR) with retention of properties even under severe conditions of wet aging by incorporating silanes. Thus, low cost mineral fillers can be upgraded with organofunctional silanes to have improved performance as reinforcing fillers in rubber compoundings.

A literature survey reveals that a number of rubber reactive silane compounds are known which can react with mineral surface and improve the filler dispersion with reduced compound viscosity to give better physical properties.

Cost and its control has become an important factor in evergrowing rubber industry. In the present study, attempts have been made to replace energy sensitive reinforcing filler--carbon black-by low cost mineral filler such as china clay which is abundantly available on the earth's crust. Thus, the present work involves a comprehensive evaluation of new silane compounds (A to F), synthesised from renewable resource, in the upgradation of physical properties of mineral filled natural rubber (NR) and mixture of styrene butadiene rubber (SBR) and natural rubber (RMA).

Fast extrusion furnace (FEF) carbon black is one of the major type of carbon black used for tyre inner liners, hose and extrusion goods. Vulcanizates from FEF carbon black show medium to high reinforcement, high modulus and hardness and smooth extrusion.

In the present work attempts were made to find out substitute for FEF carbon black as reinforcing fillers for rubber compounding. Thus, rubber compoundings were made with

1. FEF carbon black
2. Mixture of FEF carbon black and china clay

and 3. China clay alone

with and without silane coupling agents. In all rubber compoundings sulphur and cyclohexylbenzothionyl sulfenamide (CBS) were used as curing agent and accelerator, respectively. Silane compound 1% on the weight basis of filler was added while compounding the rubber on two roller rubber mill. Addition of silane compound in rubber compoundings was done after the filler has been added. The recipe for compoundings is given in Table 7. The physical properties of the rubber vulcanizates such as modulus at 200% and 300%, elongation and tensile strength were determined on Scott testing machine according to ASTM Designation number D-412-68. The Shore A hardness was tested according to ASTM Designation number D-2240-68 and % compressibility was determined according to ASTM Designation number D395-67 (Table 8).

The physical properties of the rubber vulcanizates obtained by incorporating newly synthesised methoxysilanes were compared with the properties of rubber vulcanizates in which commercially available silane coupling agent Si-69 was used (Table 8).

Table 7

Recipe for Rubber Compounding

Rubber Compounding Ingredients	Formulations I	II	III	IV	V	VI
Natural Rubber	100	100	100	-	-	-
SBR (1502) + RMA	-	-	-	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	105	1.5	1.5
FEF Carbon black	50	-	-	50	-	-
FEF Carbon black + China clay	-	25 + 25	-	-	25 + 25	-
China clay	-	-	60	-	-	60
Mineral oil	5	5	5	5	5	5
PBNA	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
CBS	1	1	1	1	1	1

Silane coupling agents (1% on weight basis of fillers)were added after the addition of filler while compounding

Table 8

Physical Properties of Rubber Compoundings Cured at 140°C/15 min

Rubber compounding	Silane coupling agent	Modulus at 300% in Mpa	Elongation %	Tensile strength Mpa	Shore A hardness	Compression set, %
I	—	10.5	450	20.4	65	25
	A	11.2	420	22.1	64	23
	B	12.4	420	23.4	64	21
	C	12.6	422	24.8	64	21
	D	13.3	430	25	64	20
	E	14.8	410	26.2	64	19
	F	12.7	420	24.6	64	21
	Si-69	15.9	410	27.8	63	18
II	-	3.8	520	14	55	30
	A	4.2	500	15.2	53	28
	B	5	500	17	53	27
	C	5	490	18.2	53	27
	D	6.4	485	18.4	54	25
	E	7.6	470	19.6	58	24
	F	5.1	505	18.2	53	27
	Si-69	8.9	475	21.2	60	24

continued

Table 8 (continued)

Rubber compounding	Silane coupling agent	Modulus at 300% in Mpa	Elongàtion %	Tensile strength Mpa	Shore A hardness	Compression set, %
III	-	2.2	650	6.8	59	40
	A	2.9	630	8.2	59	37
	B	3.2	625	9.6	57	35
	C	3.4	625	10	57	35
	D	3.6	615	11.2	62	33
	E	4.8	600	12.4	62	33
	F	3.5	625	9.8	57	35
	Si-69	5.2	580	14.2	62	32
		Modulus at 200% in Mpa				
IV	-	9.3	320	16.8	76	33
	A	10.2	290	18.2	74	30
	B	11.1	280	19	74	29
	C	12.1	285	19.4	74	29
	D	12.2	270	20.6	75	27
	E	13.4	250	21.9	75	26
	F	12.3	285	19.5	74	29
	Si-69	14.1	250	23.6	75	25

continued

Table 8 (continued)

Rubber compounding	Silane coupling agent	Modulus at 100% in Mpa	Elongation %	Tensile strength Mpa	Shore A hardness	Compression set, %
V	-	2.8	350	11.2	69	35
	A	3.1	335	12.8	67	33
	B	3.6	330	14.6	68	31
	C	3.8	330	15	68	31
	D	4.6	320	15.8	67	30
	E	5.2	305	16.8	66	30
	F	3.6	335	14.8	68	31
	Si-69	6.8	300	18.2	66	28
VI	-	1.2	400	5.6	65	45
	A	1.9	390	7.8	64	43
	B	2.4	380	8.2	63	42
	C	2.6	380	8.4	63	42
	D	3	365	9.6	63	41
	E	3.8	350	11.8	68	40
	F	2.7	380	8.4	63	42
	Si-69	5	350	13.2	68	40

DISCUSSION

The oil embargo in today's space age has a great deal of impact on research field to find out alternative source for petroleum-based products. Carbon black is a petroleum-based reinforcing filler. High cost and potential shortage of reinforcing carbon black filler has stimulated interest in research field for replacement of carbon black by low cost mineral fillers.

The low modulus and tensile strength of clay filled elastomers can be improved by combination of clay with reinforcing filler. The combination of clay and carbon black is practised in a number of commercial applications to get unique properties of both the fillers. Such combination offers good balance of reinforcement and low cost. Attempts are being made to improve physical properties of such combination by incorporating silane compounds. Silica, clay and other silicates, in presence of suitable silane coupling agents exhibit improved properties as reinforcing fillers. Silane compounds have capacity to react with filler particles. The cross-linking takes places between organic and inorganic component by coupling which helps in enhancing the reinforcing properties of the rubber.

In the present investigation readily hydrolyzable alkoxysilanes (A to F) were incorporated with the elastomers such as (1) NR and (2) mixture of SBR and RMA. The rubbers were compounded with the following reinforcing fillers.

1. Carbon black
2. Mixture of carbon black and china clay

and 3. China clay

From the Table 8 it is observed that the vulcanizates, prepared by incorporating silane compounds exhibit improved physical properties. This may be due to the fact that the methoxysilyl groups present in silane compounds get readily hydrolyzed in the presence of atmospheric moisture while compounding, and silane-filler bonding may be taking place. This may be promoting reinforcing properties of the filler. The reaction of anhydrous silica and methyltrimethoxysilane was studied by Hertl[22]. According to the study, the by-product methanol reacts with the surface of silica as follows:

$$Si(OH) + (CH_3O)_3\text{-}SiCH_3 \longrightarrow CH_3Si\text{-}O\text{-}Si(OCH_3)_2 + CH_3OH$$

$$2\ \ SiOH + (CH_3O)_3\text{-}SiCH_3 \longrightarrow (SiO)_2\text{-}Si(OCH_3)_3 + 2\ CH_3OH$$

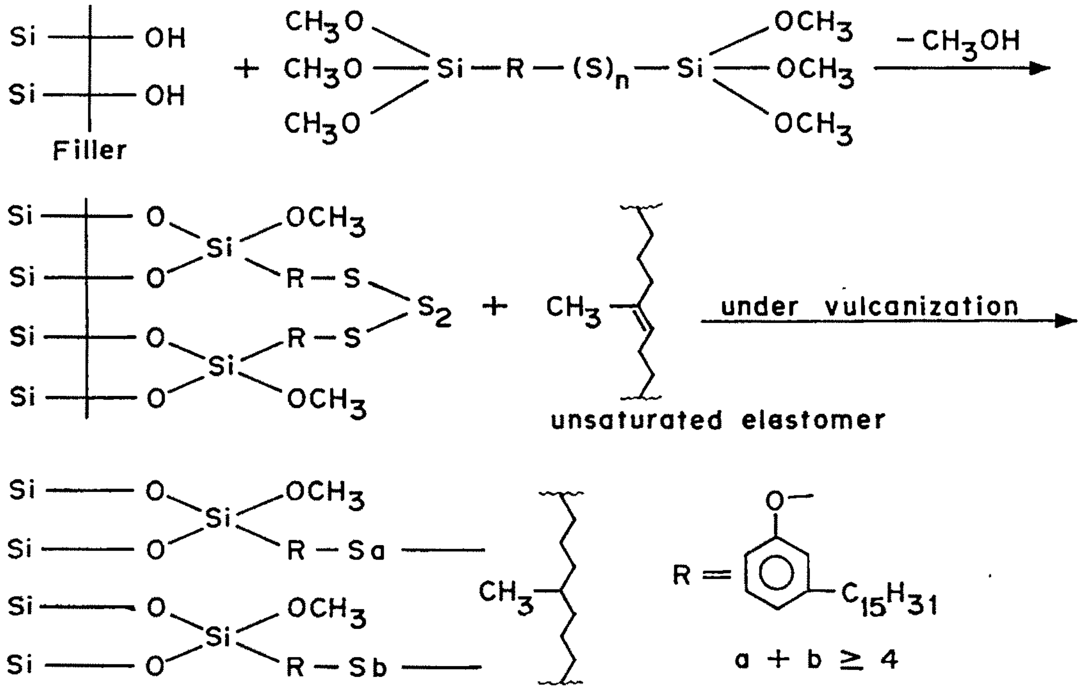
$$SiOH + CH_3OH \longrightarrow SiOCH_3 + HOH$$

In case of nonsiliceous filler, highly cross-linked siloxane membrane (Si-O-Si) is formed during vulcanization which enhances the physical properties of the elastomer.

Hertl and others[23] have also reported that the trifunctionality in the silica reactive moiety (chloro or alkoxysilanes) had greater functionality than di or monofunctional silane.

Thus, a comparison of the tensile strength of vulcanizates (Table 8) in which silane compounds (A to D) were incorporated, indicated that the vulcanizates in which silane compound D was incorparated exhibited higher tensile properties than the vulcanizates obtained by incorporating other silane compounds.

The vulcanizates in which silane E was incorporated showed maximum tensile strength as it contains sulfidic linkages in addition to methoxysilyl moities. The improved elastomeric properties may be due to interaction between elastomer, coupling agent and filler which can be shown as:



Sulfidic as well as nonsulfidic cross-links were produced during vulcanization. Thus, silane-filler, silane-rubber interaction involved in the methoxysilane of polysulphide from 3-pentadecyl phenol may be responsible for producing better properties in elastomer than the other methoxysilanes.

The tensile strength values of vulcanizates obtained by incorporating silane compound E were comparable with those obtained by incorporating commercial silane coupling agent Si-69 [Bis(tri-ethoxysilylpropyl)] tetrasulphide.

Again, higher tensile strength values were exhibited by carbon black reinforced vulcanizates than the other vulcanizates obtained by incorporating mineral fillers such as mixture of carbon black and china clay or china clay alone. The cross-linking density of the elastomers may be decreased by silica fillers which is responsible for producing poor physical properties (Table 8).

The compression set values of silane incorporated vulcanizates were decreased (Table 8) which may be due to high cross-linking produced by coupling action between silane and filler.

EXPERIMENTAL

Materials

Rubber:

Natural Rubber (NR), mixture of styrene butadiene rubber (SBR) and natural rubber (RMA) were obtained from M/s. Rathi Rubber Products, Pune, (India).

Fillers

Reinforcing Filler

Commercial grade fast extrusion furnace (FEF) carbon black was used.

Non Black Filler

China clay (90%) of mesh size 300 and moisture content 0.3% was procured from M/s. Rathi Rubber Products, Pune (India).

The other compounding ingredients such as zinc oxide, stearic acid, mineral oil, β-phenylnaphthylamine (PBNA) and sulphur were ISI grade rubber chemicals and used as received.

Silane Coupling Agents

Si-69 [Bis (triethoxysilylpropyl) tetrasulphide]- a commercial silane coupling agent was procured from Degussa AG.

Newly synthesised silane coupling agents (A to F) were used as coupling agents. Their synthesis is given in Section A.

Rubber Compounding

All mixes were prepared on a conventional laboratory size 6" x 12" two roll rubber mixing mill. Rubber was mascicated on cold mill till a band was formed. Then the ingredients were added according to the order given in the compounding recipe (Table 7). The mix was cut thrice from either side and rolled six times through tight mill and sheet out. The vulcanized sheets of compounded rubber of size 15 cm x 15 cm x 0.02 cm were prepared by compression molding at 140°C/15 min. under hydraulic press (15 $kg/_{psi}$) for evaluation of various properties.

The cured rubber sheets were cut into dumbbell shaped specimens as per ASTM D-412-68 Dic Noc for determination of physical properties such as modulus at 200%, 300%, elongation and tensile strength.

Shore A hardness of specimens was determined on test specimens using durometer hardness tester according to ASTM D-2240-68.

For compression set measurements, specimens were prepared according to ASTM-D 395-67.

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Section C

Evaluation of Silane Coupling Agents
in
Rubber to Metal Adhesion

INTRODUCTION

Development of rubber to steel adhesion using synthetic adhesives is an important goal in the rubber industry. These adhesives are used for a variety of automobile assembly applications. Structural bonding adhesives are increasingly used to replace welding and riveting during assembly of car parts made up of light weight plastics and metals.

The need for bonding rubber to metal units has been most evident in the engineering industries where they are used to reduce vibrations, absorb shocks and help in reduction of noise.

Over the years a number of methods have been used to bond vulcanizates to metals. One of the earliest methods but still of great commercial importance is brass plating in which ordinary sulphur vulcanizing compounded natural rubber adheres to the metal[1].

The normal procedure for achieving high performance of rubber to metal adhesion is to bond rubber with metal during vulcanization process. A good adhesion is achieved by placing adhesive coated metal part and vulcanized elastomer in the mold and by curing under hydraulic press under suitable conditions of temperature and time.

The first proprietary bonding agents for natural and synthetic rubbers were based on chlorinated elastomers[2].

A number of natural rubber stock recipes with various cure rates as well as synthetic elastomers containing polar groups have been developed for rubber to metal adhesion[3].

The next breakthrough for rubber to metal adhesion was the use of isocyanates. In 1945 American patent first disclosed the use of polyisocyanates in rubber to metal adhesion[4].

Phenolic resins are the earliest employed synthetic adhesives for bonding rubber to metal to withstand severe environmental conditions. To overcome the drawback of phenolics such as brittleness, modifications of phenolic resins with synthetic rubbers and other flexible resins were reported. Nitrile/phenolic or chloroprene/phenolic mixtures were used where high peel strength, thermal stability and moisture resistance were required.

For many years, silane coupling agents have been successfully used for glass reinforced plastic systems. The bonding of rubber to metal surface such as copper, aluminium, steel, etc. has been improved by the use of aminosilane either by pretreatment of metal or by incorporating them into elastomers[5]. Vanderbilt[6] used silanes, unsaturated monomers and peroxides to bond rubber and ethylene propylene co-polymer to metal or glass fiber.

The effect of silane adhesion promoters in polysulphide and polyurethane sealant compositions has been described by Toogood and Sterman[7]. Adhesive strength of urethane elastomers to glass, steel and aluminium can be improved by addition of aminosilane prior to pouring. The bonding of silicon elastomers was enhanced either by incorporation of aminosilanes into silicon rubber or by pretreatment of metal surface by methylsilane[8]. Polaniazek and Schaufflberger[9] have evaluated mercapto and aminofunctional silane compounds as additives for various structural adhesive systems such as nitrile-phenolic, polyvinylbutyral-phenolic, epoxy, polysulfone and vinyl plastisol sealants. The authors observed that the functional silanes can improve the adhesion of these adhesives and inorganic substrates like aluminium, glass and steel. The adhesion of polyurethane to aluminium metal was greatly increased by pretreatment of metal surface with amino or epoxy containing silanes[10]. The bonding of copper treated with aminoalkyl silane to silicon elastomer was greatly increased with exceptional bond stability at elevated temperature[11]. Swanson and Price[12] have developed the shelf stable two component urethane adhesive by incorporating silane coupling agent as integral blend additive and observed improvement in initial adhesion by manyfold with retention of adhesion after aging.

Severnyi et al.[13] have studied the effect of silane coupling agents on adhesion properties of silica filled rubber to steel and aluminium. The adhesion of silicon rubber to metal has been promoted by using acetoxysilane in primer composition[14]. The improved adhesion of steel rubber composite was achieved using 3-glycidyloxypropyltrimethoxysilane along with formaldehyde-phenol-resorcinol adhesive[15].

Present Investigation and Results

Adhesion phenomenon which helps in reducing vibrations and shocks in rubber to metal bonding is industrially becoming more vital in today's space, engineering and automobile technology.

Various techniques are known for bonding elastomers to the metals. Use of ebonite as bonding agent is well-known since last century. Brass plating system with natural and synthetic rubbers was known prior to 1940. As brass plating technique has certain drawbacks like poor resistance to chemicals and environment and unpredictability, synthetic adhesives based on polymers came into practice since 1950. These include isocyanates, phenolics, epoxies and polysulfones.

It has become essential to have a strong bond between rubber and metal in order to ensure a long life and resistance to withstand severe conditions of temperature, when rubber is enforced with metal using these compounds. Adhesion of these compounds can be improved by using coupling agents[9].

The unique ability of silane compounds to adhere dissimilar surfaces has been explored for the adhesion of rubber to metal bonding. Rubber reactive silane compounds which help to reinforce the properties of rubber are also reported as adhesion promoters for rubber to metal bonding.

There are number of adhesives in which natural or synthetic rubbers are blended with resin to obtain unique properties of both the components[9]. Rubbers are rarely used alone as adhesives. By blending the rubber with resin, improved properties such as tack, cohesive strength, heat resistance and specific adhesion to the surface is achieved.

Improved adhesion of rubber to metal has been reported by blending nitrile-phenolic, polyvinylbutyral-phenolic along with silane coupling agent[7]. This prompted us to find out the utility of new silane coupling agents synthesised from renewable resource material as adhesion promotor

Use of Silane Coupling Agents in Rubber Solution

In the present work following adhesive solution were prepared from compounded natural rubber solution (Recipe for compounding is given in Table 9):

Rubber Solution (20% in toluene) as Adhesive

(1) Compounded natural rubber solution.

(2) Compounded natural rubber solution and phenolic resin (5%)

(3) Compounded natural rubber solution
\+ Phenolic resin (5%)
\+ Silane coupling agent (1%) (A to F)

Also, new silane coupling agents were evaluated along with commercially available rubber to metal bonding agent - Chemlock-220.

Table 9

Compounding of Rubber Solution Used as Bonding Agent for Rubber to Metal

Rubber Compounding Ingredients	Formulation I	 II	 III
Natural rubber	100	100	100
Zinc oxide	10	10	10
FEF Carbon black	30	30	30
Phenolic resin*	-	5	5
Silane coupling agent**	-	-	1
PBNA	1	1	1
Sulphur	1.5	1.5	1.5
CBS	0.5	0.5	0.5

*Phenolic resin was added on the weight basis of rubber.

**Silane coupling agents (A to F) were added (1% on the weight basis of filler)

A 20% solution in toluene of each compounding was made

Elastomers used for bonding studies were:

1. Natural rubber (NR)
2. Mixture of styrenebutadiene rubber (SBR) and Natural Rubber (RMA)
3. Neoprene (Neo) rubber

Compoundings of these elastomers is given in Table 10. Phenolic resin and silane coupling agents were added at the time of compounding the rubber on the mill. To study the effect of silane coupling agents, rubber compoundings were done with and without silane coupling agents.

Preparation of Test Specimens

One coat of bonding agent (0.015mm) was applied at the centre of thoroughly cleaned degreased, sand blasted mild steel plate (2" x 1") and dried in the air. Then adhesive coated metal plates were kept in the preheated mold (~80°C). Compounded uncured rubber strips of 6" x 1" were pressed on the metal plates immediately. The mold was heated at 140°C/15 kg/cm^2 for 15 min, then cooled and kept at room temperature for 24 h.

Testing of Cured Specimens

The strength of adhesion of joint for each rubber compounding with and without silane coupling agent was determined as ASTM D 429-73 (180° peel) test. The test was done at room temperature (26-27°C) on an Instron

Table 10

Compounding of Rubbers used as Adherend

Rubber Compounding Ingredients	Formulation I	II	III
Natural rubber	100	-	-
SBR (1502) + Natural rubber (RMA) 50 + 50	-	100	-
Neoprene	-	-	100
Zinc oxide	5	5	5
Magnesium oxide	--	-	5
Stearic acid	1.5	2	1
FEF carbon black	30	30	30
Silane coupling agent*	1	1	1
Mineral oil	5	5	-
Dioctyl phthalate	-	-	5
PBNA	-	-	1.5
Sulphur	1.5	2.2	-
N-22	-	-	0.2
CBS	1.5	-	-
TMT	-	-	0.5

*Silane coupling agent was added 1% on weight basis of filler while compounding the rubber on two roll mill after the filler.

testing machine which measures the strength to debond the substrate and adherend at constant cross head speed of ½"/min at 50 lb load. The results of rubber failure (peel strength) are given in Tables 11 and 12.

Table 11

Rubber to Metal Adhesion Using Rubber Solution as Bonding Agent*

	Peel strength values (kg/cm^2)(Rubber Failure)		
	Natural rubber**	Mixture of SBR and RMA**	Neoprene** rubber
Formulation I*	10.6	7.4	9.9
Fomrulation II*	15.4	9.8	14.8
Formulation III* + Silane A	15.9	10.0	15.1
Formulation III + Silane B	16.4	10.4	15.4
Formulation III + Silane C	16.4	10.5	15.6
Formulation III + Silane D	17.2	10.9	16.5
Formulation III + Silane E	17.8	11.2	15.0
Formulation III + Silane F	16.2	10.6	15.5

*Rubber solution formulation is given in Table 9.

**Rubber Compounding is given in Table 10.

Table 12

Rubber to Metal Adhesion using Chemlock 220 + Silane Coupling Agent as Bonding Agent

Adhesive	Peel strength in kg/cm^2 (Rubber failure)		
	Natural rubber*	SBR + RMA*	Neoprene*
Chemlock-220	24.2	21.5	23.2
Chemlock-220 + Silane A	25.8	22.8	26.2
Chemlock-220 + Silane B	26.1	23.6	27.9
Chemlock-220 + Silane C	26.9	24.0	27.9
Chemlock-220 + Silane D	27.2	25.4	28.5
Chemlock-220 + Silane E	28.0	26.1	24.2
Chemlock-220 + Silane F	26.2	23.4	27.7

*Rubber compounding is given in Table 10

DISCUSSION

Evaluation of Silane Coupling Agent in Natural Rubber-Solution Used as Bonding Agent for Rubber to Metal

Compounded natural rubber solution is used as bonding agent for many substrates due to its inherent property to act as adhesive. This property is also used for rubber to metal bonding. The peel strength values were lower when compounded rubber solution was used as adhesive for rubber to metal bonding. To improve peel strength values, phenolic resin which acts as bonding agent for rubber to metal was added while compounding the rubber on the mill. Higher peel strength values were obtained when rubber solution containing phenolic resin was used as bonding agent for rubber to metal adhesion (Table 11). A slight improvement in peel strength values was observed when new silane coupling agents (A to F) were incorporated in rubber compounding which was containing phenolic resin.

Evaluation of Silane Coupling Agents along with Chemlock-220

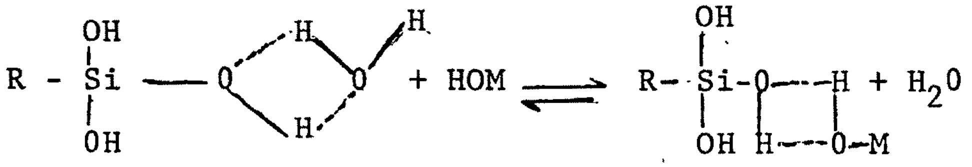
The improved adhesion phenomenon of elastomer to metal was also observed when silanes were incorporated with various rubber compoundings and chemlock-220 was used as bonding agent for rubber to metal adhesion (Table 12).

The mechanism for improved peel strength values by incorporating silanes may be explained on the basis of reversible hydrogen bonding which result in formation of the hydrogen or oxane bond formation.

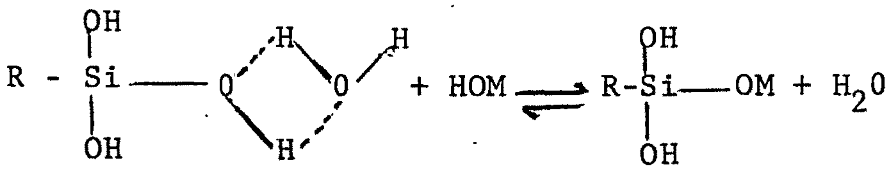
Silane coupling agents (A to F) employed in the present study are methoxysilanes which readily get hydrolysed by atmospheric moisture while compounding as follows:

$$R\text{-}Si(OCH_3)_3 \xrightarrow{3H_2O} R\text{-}Si\text{-}(OH)_3 + 3CH_3OH$$

and further reacts with metal surface which contains metal hydroxyl via reversible hydrogen bond mechanism resulting in the formation of hydrogen or oxane bond due to which adhesion is promoted.



Oxane bond



The peel strength value of rubber to metal bonding also depends upon the type of elastomer used as adherend. When compounded NR and Neo rubbers were used as adherend for rubber to metal bonding, the peel strength values obtained were higher than the mixture of SBR and RMA. This may be due to the fact that NR and Neo themselves act as adhesives for a number of substrates.

EXPERIMENTAL

Materials

Elastomers:

Natural rubber (NR), mixture of styrene butadiene rubber (SBR) and natural rubber (RMA) and neoprene rubber (Neo) were obtained from M/s. Rathi Rubber Products, Pune (India).

Mild steel plates were purchased from local market and cut into size of 2" x 1". They were thoroughly cleaned, degreased and sand blasted. The plates were preserved into petroleum ether (60-80°C), until use.

Filler

Commercial grade fast extrusion furnace (FEF) carbon black was used as reinforcing filler.

Rubber Chemicals

ISI grade commercial rubber chemicals such as zinc oxide, stearic acid, mineral oil, dioctylphthalate (DOP), PBNA, sulphur, CBS and N-22 were used as received.

Silane Coupling Agents

Newly synthesised silane coupling agents (A to F) were used. The synthesis is given in Section A.

[illegible] Chemlock-220 a commercially availablebonding agent was procured from Lords Chemicals, USA.

Rubber Compounding

All the mixes weere prepared on a conventional laboratory size 6" x 12" two roll rubber mixing mill. The rubber was mascicated on cold mill till the band was formed. Then the ingredients were added according to the ordergiven inthe compounding recipe (Table 9). The mixture was cut thrice from either side and rolled six times through tight mill and sheet out. In all compoundings silane coupling agents were added on the rubber mill while compounding. The rubber strips of size 6" x 1" were cut from the compounded slab.

Compounded Natural Rubber Solution as Bonding Agent

The compounding of the natural rubber was done on the rubber mill by similar procedure as described above.

The ingredients were added according to the order given in the compounding recipe (Table 9).

Phenolic resin was added at`the time of compounding of the rubber on the mill (Table 9). The rubber compoundings were done as follows:

1. Rubber compounding without phenolic resin
2. Rubber compounding with phenolic resin.
3. Rubber compounding with phenolic resin and silane coupling agent.

A 20% solution in toluene of each natural rubber compounding mentioned above was made and used as adhesive.

Preparation of Test Specimens for Peel Strength

One coat of bonding agent (0.015 mm) was applied to thoroughly cleaned, sand blasted metal plates. Then the plates were air dried and kept in the preheated mold (~80°C). Compounded uncured rubber strips of 6" x 1" size was pressed on the metal plates immediately. The mold was heated in the hydraulic press at 140°C for 15 min. Then it was cooled and kept at room temperature for 24 h.

Testing of the Cured Specimens

The strength of adhesion of joint for each rubber compounding with and without silane coupling agent was determined on Instron testing machine at constant cross head speed of ½"/min. at 50 lb. load. The peel strength measurement was done according to ASTMD-429-73 at room temperature, which measures the strength to debond the substrate and adherend (Table 12).

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Section D

Evaluation of Silane Coupling Agents alongwith Nobake Binder in Foundry Sand Cores

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INTRODUCTION

No bake binders are important materials used in foundry sands for producing sophisticated castings with dimensional accuracy and for ease of handling of complicated castings. These were first developed in Europe and are in foundry practice since 1950's. No bake binders are of inorganic as well as organic type.

The silicates are inorganic type of binders which have certain drawbacks like poor collapsibility and sand cannot be reclaimed.

Organic binders include drying oil based alkyd, furan, phenolics and urethanes resin.

Alkyd based no bake compositions for sand cores are in practice for last two decades. They are mostly based on drying and vegetable oils which can be cured by metallic dryers such as cobalt naphthanate, lead naphthanate or by peroxides. China wood oil treated with cobalt or lead naphthanate has been used with lead oxide as cold setting binder[2] for the sands. Fast curing of oil bonded sand cores has been achieved by addition of barium or calcium oxide[3].

Furan resin used for no bake composition consists of urea modified, furfuryl alcohol - formaldehyde condensate. They are cured at room temperature by acids such as phosphoric, mixture of phosphoric and sulphonic, gaseous hydrochloric acid or p-toluene sulphonic acid.

Novolac as well as resol resins are used as no bake binders for sand cores. The uniform distribution of resin on sand particles is made by making the solution of resin in suitable organic solvent. Phenol-cresol formaldehyde resin and mixture of furfural and furfuryl alcohol resin in presence of reactive substance such as acid has been utilized as self curing binder for the sand core.

The urethane family of binder system has been devloped in 1960's. The first urethane system was alkyd isocyanate based no bake oil binder. Alkyd resin binder in combination with isocyanate and metal ion catalyst cures at room temperature[4]. The second type of urethane no bake binder is known as phenolic urethane and has been developed in 1970's[5]. The phenolic polyol with polymeric isocyanate cures in presence of a base. It has been observed that phenolic urethane no bake binders are superior to no bake oil binder and low nitrogen-containing furan resin binder as well as high performance furan resin binders.

Foundry sand cores are low cost materials, consisting of small to medium size sand particles and resin. By incorporating silanes to phenolic or furan/ sand mix, stronger sand cores are obtained that resist handling damage and degradation in adverse environment. Thus, use of silane coupling agent is cost effective as one can achieve increased performance in sand cores' properties at reduced resin concentration. The incorporation of silanes also helps in improving working conditions of foundries because emission of gases while pouring the molten metal becomes less due to reduced binder consumption[6].

Sterman and Marsaden[7] have first reported the use of silane coupling agents in phenolic resin composition used for foundry shell molding sand.

Quaker Oats Company has published[8] the data on the use of silane coupling agents for no bake sand core composition containing furan resin cured by phosphoric acid.

Sand cores have been prepared by incorporating N,N' bis trifurfuryloxy silyl propyl pentane -2,2' diamine in formaldehyde furfuryl alcohol resin based core binder cured by oxalic acid[9].

A foundry core with improved tensile strength has been made by curing monomeric binder containing aqueous urea- formaldehyde mixture (2-10%), furfuryl alcohol, water with phosphoric acid and incorporation of amino silane coupling agent[10]. A foundry mold with improved strength and humidity resistance has been prepared by employing phenolic isocyanate system cured by gaseous amine and silane compound[11]. Higher tensile properties of phenol formaldehyde resol resin have been obtained by incorporating SiH_4[12].

The hardner/catalyst has important role in curing of no bake binders. A comparative study of acid concentration on curing of phenol formaldehyde, furan urea and furan phenol resin has been carried[13] out. The increase in stability of sand cores has been achieved by decreasing resin amount along with addition of silane compound[13].

Aminosilane has been mixed with acid cured sand core binder like furan, phenolic or urea resin to give a binder composition having long storage life[14].

Various alkoxysilanes have been used[15] in phenolic resin as adhesion promoters to improve the strength of sand molds prepared with these combinations. Their effect on adhesion property after storage has also been studied.

An attempt has been made to decrease the consumption of urea furan resin binder by employing silane coupling agents. Pure sand has been reported to give better properties to sand cores due to silane coupling agent than reclaimed sand[16].

Phenolic or urea formaldehyde resin showed 2-3 fold increase in flexular strength and thermal stability when used as sand core binder along with amino or phenoxysilane[17].

Present Investigation and Results

Foundry sand cores are composites of sand and resin which provide the casting to various precise sizes for engineering industries. The requirements of sand cores are more specific as compared to molds as the shapes are more complex in nature. They have to maintain their shapes under all conditions of temperature until they collapse after the solidification of castings. Sand cores prepared with heat curing resins impart poor green strength. Hence, handling of unbaked cores for heavy and complicated casting becomes difficult. It is known that these difficulties can be eliminated by the use of no bake binders. Phenolic, furan and urea formaldehyde resins are generally used as no bake sand core binders. No bake binders are usually cured at lower temperature either by acids or isocyanates.

Silane coupling agents have been incorporated with various no bake sand core binders to achieve better physical properties of the sand cores. Thus, in the present investigation, newly synthesised silane coupling agents (A to D) from renewable resources were integrally blended with phenolic resin with a view to improve flexular strength of sand cores.

Preparation of Phenolic Resol Resin[18]

A number of acid cured resins are used as a core binder which include furan and phenolics. In the present work, phenolic resol resin was prepared for a specific use as core binder from phenol and formaldehyde using barium hydroxide as a catalyst. The characteristics of resin are given in Table 13.

For proper mixing and processing, 50% solution of the phenolic resol resin in ethanol was used.

Preparation of Sand Cores

Sand, free of clay and chlorine, having acid demand value of 7-8 and American foundry men's Society (AFS) fine number 67-71 was used for making sand cores which were evaluated for dry tensile strength according to AFS standard.

The composition of sand mix is given in Table 14.

Sand cores were prepared as follows: First, sand and phosphoric acid were mixed thoroughly for two minutes. Then, a mixture of phenolic resin and silane compound was added and was mixed well. All the mixings were done with a paddler mixer and each mix cycle was [illegible] of two minutes.

AFS standard dry tensile strength sand core specimens (2" x 2") were prepared using three ram technique and cured at 70°C for various time intervals.

Table 13

Physical Properties of Phenolic Resin

Appearance	Dark reddish brown
Viscosity	1600 cps
Free HCHO	1.02%
Solid content	1.2%
Methylol content	34.42%

Table 14

Composition of Sand Mix

Sand	100 g
Phenolic resin	2 g
Phosphoric acid	variable (0.1 to 0.2%)
Silane coupling agent	0.2% (wt%based on ~~sand~~ resin)

After curing, the specimens were tested for Shore A hardness and dry tensile strength on universal sand core testing machine. The results are given in Table 15. The cured specimens were also exposed to atmospheric humidity (42-45%) for 168 h to determine the wet tensile strength of the sand cores.

Table 15

Formulation and Physical Properties of Sand Cores

No.	Sand in g	Phenolic resin in g	Phosphoric acid (85%) in ml	Silane Coupling Agent					Bench life in min.	Tensile strength of sand cores cured for		Tensile strength kg/cm^2 after exposing the sand cores to 42-45% humidity for 168 h	Shore A hardness	
				A	B	C	D	A-1100		12 h	24 h		12 h	24 h
1	100	2	0.10	-	-	-	-	-	20	8.6	11.2	11.5	40	40
2	100	2	0.15	-	-	-	-	-	20	10	13.9	14.0	42	42
3	100	2	0.20	-	-	-	-	-	17	11.1	16	16	45	45
4	100	2	0,10	0.2	-	-	-	-	15	10	14	14.3	50	55
5	100	2	0.15	0.2	-	-	-	-	15	12.4	20.2	21.1	58	60
6	100	2	0.20	0.2	-	-	-	-	15	17.6	23.1	24.8	65	68
7	100	2	0.10	-	0.2	-	-	-	13	11.6	16	17.1	57	60
8	100	2	0.15	-	0.2	-	-	-	13	19.2	23	23.9	65	70
9	100	2	0.20	-	0.2	-	-	-	13	21.4	27.1	28.0	70	73
10	100	2	0.10	-	-	0.2	-	-	13	12	16.1	17	57	60
11	100	2	0.15	-	-	0.2	-	-	13	19.5	23.4	24	65	70
12	100	2	0.20	-	-	0.2	-	-	13	21.5	27.3	28	70	75
13	100	2	0.10	-	-	-	0.2	-	11	16	21.5	23	70	72
14	100	2	0.15	-	-	-	0.2	-	10	24	28	29.1	72	78
15	100	2	0.20	-	-	-	0.2	-	10	25	30	Above 30	78	82
16	100	2	0.10	-	-	-	-	0.2	13	11.2	14	14.9	55	60
17	100	2	0.15	-	-	-	-	0.2	12	18.6	20.9	21.2	62	68
18	100	2	0.20	-	-	-	-	0.2	10	20.2	24.4	25.2	68	73

DISCUSSION

The interaction of silanes with composite materials leads to increase in mechanical properties. Thus, the use of silane coupling agents in foundry sand core binders increases the physical properties of the sand cores.

In the present work, increased dry tensile strength values of sand cores were observed in which newly synthesised silane coupling agents were incorporated along with phenolic resol resin (Table 15). These results can be explained on the basis of splitting of Si-0-C bond which was taking place in presence of acid to give silanol groups. The silanol groups further react with silica surface to give highly cross-linked siloxane membrane.

Again, when acid percentage in the sand mix was increased, tensile strength values were promoted. This is obvious as the autopolymerization reaction of methylol groups present in resol resin is known to be enhanced by acid which in turn helps in curing of sand cores by crosslinking.

The effect of curing time on dry tensile strength values of sand cores was also studied. Thus increase in dry tensile strength values were observed when sand cores were cured for 24 h at 70°C than when they were cured for 12 h at 70°C. This may be due to further crosslinking.

A comparative study of dry tensile strength values of silane incorporated sand cores illustrate that the maximum improvement in tensile properties of sand cores was obtained when silane D was incorporated than other silane compounds.

It was also observed that the dry tensile strength values of sand cores prepared by incorporating new silane coupling agents (except A) were slightly higher than the tensile strength values of sand cores prepared from commercially available silane coupling agent A-1100 (γ-aminopropyl triethoxy silane) (Table 15).

There was not much difference observed in tensile strength values of sand cores after exposing the sand cores to atmospheric moisture (42-45% humidity) for 168 h.

EXPERIMENTAL

Materials

Phenol, obtained from S.D. Chemicals, Bombay (India) was distilled at 180°C before use.

Formaldehyde was procured from local market. Formaldehyde content - 34.2%.

Barium hydroxide octahydrate was obtained from S.D. Chemicals, Bombay (India).

Sand obtained from M/s. TELCO, Pune (India) was clay and chlorine free, AFS fine number 67-71. SiO_2 content 98.5% and acid demand value 7-8.

Phosphoric acid (85%) was obtained from local market.

Commmercial silane coupling agent A-1100 was procured from Union Carbide Corporation, USA.

The synthesis and characterization of silane coupling agents (A to D) is given in Section A.

Preparation of Phenolic Resol Resin

In a four necked 500 ml round bottomed flask equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and a thermowell, 47 g (0.5 mole) of phenol and 2.35 g of $Ba(OH)_2 \cdot 8\ H_2O$ were placed. Then 64 g (1.5 mole) formaldehyde was added through dropping funnel with stirring at 50°C. Then, the temperature was increased gradully upto 70°C and maintained for 2 h. The reaction mixture was cooled and neutralised with 10% H_2SO_4. The water was removed under vacuum till the inside temperature of reaction mixture reached to 70°C. The resin obtained was reddish brown viscous liquid. The methylol content was determined according to the known method.

Preparation of Sand Cores

Sand mix
Sand - 100 g
Phosphoric acid - variable (0.1 to 0.2% on the weight basis of ~~resin~~ ~~sand~~ Sand)
Phenolic resin 2 g
Silane coupling agent 0.2% (based on wt basis of ~~sand~~ resin)

Sand cores were prepared as follows:

All the mixes were done with a paddler mixer. First, sand and phosphoric acid were mixed for two minutes. Then a mixture of resin and coupling agent was added to sand acid mixture and thoroughly mixed.

AFS sand core specimens for measuring tensile strength were prepared using 3 ram technique and cured at 70°C for different time intervals. The cured specimens were tested for dry tensile strength on universal sand core testing machine.

The tensile strength of the cured sand cores was also determined by exposing sand cores to atmospheric moisture (42-45% humidity).

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CHAPTER II

Modification of Cellulose Acetate by Trimethylchlorosilane for use in Desalination of water by Reverse Osmosis

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INTRODUCTION

Water, like air, is assumed to be there in adequate quantity. But with increasing population and industrialization of the world the potable water of nature is becoming insufficient. Fresh and pure water is the basic need of mankind. The world's 97% water is in the form of saline water (sea) which is inexhaustible and scarcely used source which cannot be used without purification. This is where "Desalination" comes into picture. Thus, advanced countries like USA, Japan, Denmark, Israel, etc. have taken up the project of converting the saline water to potable water using various desalination techniques and different polymeric membranes.

Desalination is a process in which saline water is converted into potable water by application of external energy. A number of processes are known for desalination of water and they can be classified as follows:

Processes for Desalination of Water

A) Processes using a phase change of water

1. Distillation
2. Freeze separation
3. Hydrate separation

B) Processes dependent on membrane technology

1. Electrolysis
2. Reverse osmosis (RO)

C) Processes utilizing ion selective properties of solids and liquids:

1. Ion exchange
2. Solvent extraction

Electrodialysis and reverse osomosis (RO) are the current important techniques used for desalination of brackish water. RO is an effective means for purification, separation and concentration of the dissolved solids from their aqueous solution under suitable process conditions[1].

Since many years, cellulose acetate (CA) has been used for desalination of water by RO. Some of the synthetic polymers such as polyamide, polyamide-hydrazides or polybenzimidazolone[2,3] have also been used recently as membrane materials for desalination.

Reverse Osmosis (RO)

RO is a process in which an applied pressure is used to reverse the normal osmosis flow of water across a semipermeable membrane. In osmosis process the normal direction of water flow across the membrane is from the solution of lower solid concentration to a solution of higher solid concentration. If a pressure ΔP) is applied to the concentrated solution just equal to the osmotic pressure, difference between the two solutions will be ($\Delta\pi$), water flow ceases and is known as osmotic equalibrium. When applied pressure is higher than osmotic pressure water will flow from concentrated solution to dilute solution. This process can be used to desalt the concentrated solution by using sufficiently semipermeable membrane.

The success and the acceptability of the process is associated firmly with the type of semipermeable membrane and thus, the improvement of CA membrane has resulted in the advancement of the process to a pilot plant scale with respect to brackish water desalination.

Advantages of Reverse Osmosis

1. Separation of salt from marine water is achieved at ambient temperature without phase changes.
2. This process in addition to desalination helps in removing bacteria and virus from feed stock.
3. This process is cost effective from the point of energy consumption, operation and maintenance cost.
4. RO unit can be built and operated with locally available materials and man power and no elaborate shop fabrication facilities are required.
5. The same plant can be used for brackish water of different salt concentrations (bet. 0.2 to 1% of total

dissolved solids) as process is not very sensitive to the salinity.

Theory of Semipermeability

A number of mechanisms have been suggested to explain the semipermeability phenomenon of the membrane by various investigators such as sieve mechanism[4], distillation mechanism[5] and adsorption theory[6-8]. However, these theories are insufficient to explain the desalination mechanism of the membrane. The latest proposed and generally accepted theory is the hydrogen bond theory which was postulated by Breton while studying the solvent solute transport mechanism in cellulose acetate membrane.

Hydrogen Bond Theory[9]

According to this theory, the pure water which passes through the 'perfect' portion of the membrane's active layer, is transported by successive forming and breaking of hydrogen bond between the water molecule and the sites. Under the driving force of the applied pressure, the water molecule approaches a membrane site at which one or more water molecules are already bound. The next approaching water molecule forms a new bond at the active site displacing the previously bound water molecule. The feed water molecule moves immediately down-stream to approach another active site. By a succession of such transfer from site to site, bound water diffuses through the surface layer in the body or the porous structure of the membrane. The membrane is swollen and the quantity of capillary water is so large that the movement of water is same as through the huge pore.

The hydrogen bonding mechanism does not exclude the sieve mechanism. The size of the holes that are continuously appearing and disappearing plays a secondary role. The rate of diffusion of solute that cannot enter into hydrogen bonding depend upon pore size. However, in case of ions and molecules that can enter into hydrogen bonding the permeability depends upon their ability to fit into ice like structure of the membrane.

The solute solvent transport mechanism of CA membrane has been shown in Figs 16A and 16B.

Though hydrogen bond theory has been considered as one of the reasonable and logical approaches for explaining the solute solvent transport of asymmetric membrane, other approaches also play a significant role. One of such approaches is solution diffusion model.

Solution Diffusion Model[4,6,10]

In 1885 Ferry suggested that ultra filtration, a very closely related technique to RO, may occur by a

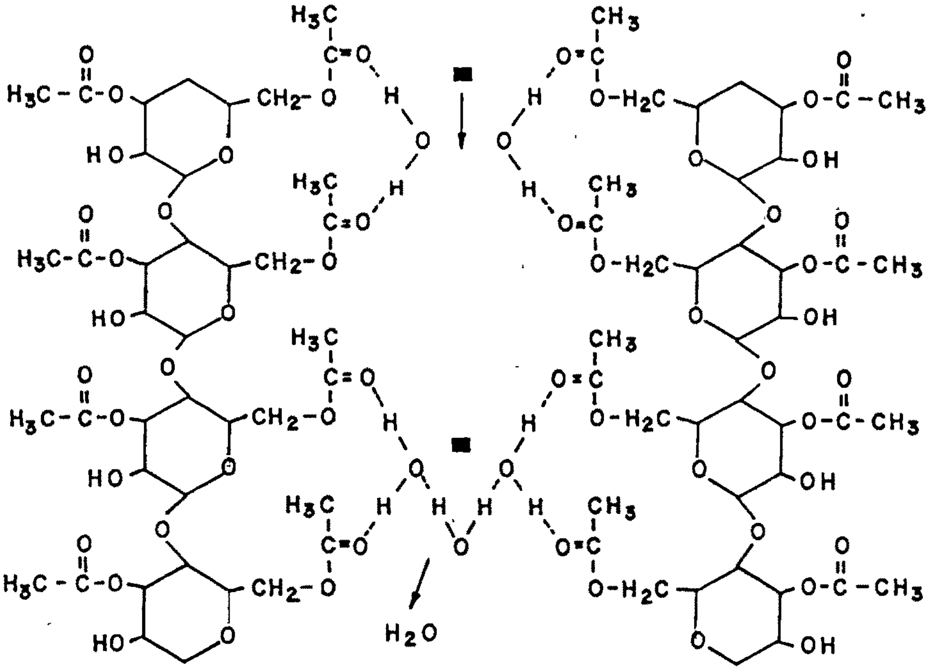


FIG 16A PERMEATION OF SALT [■] AND WATER
NON ANNEALED MEMBRANE

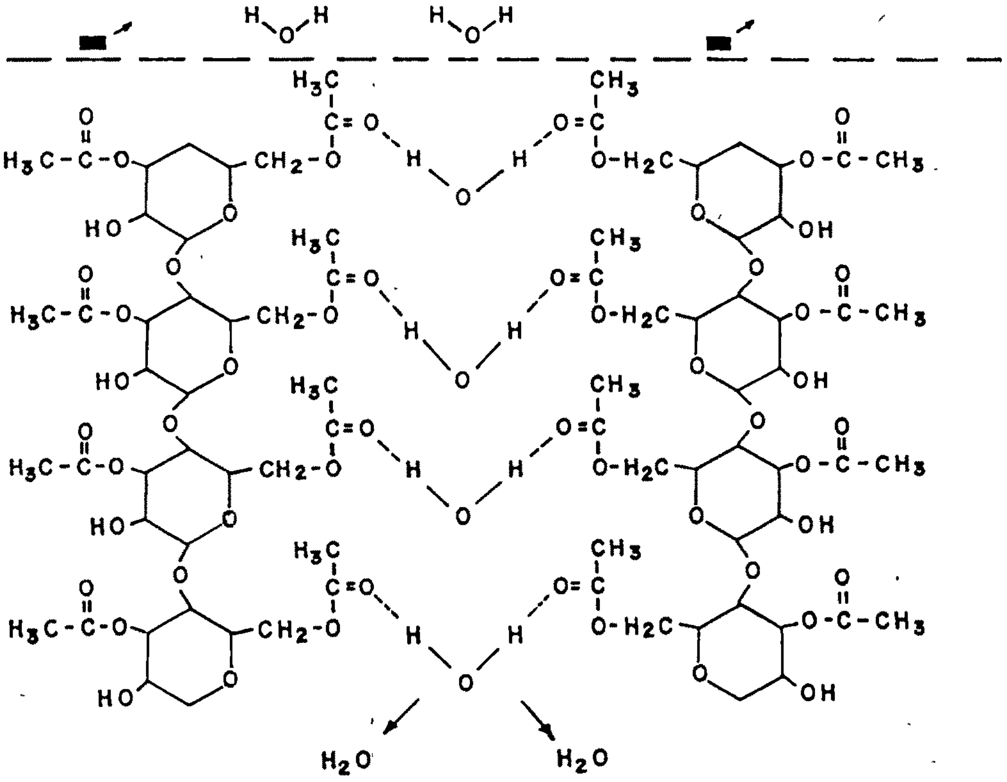


FIG 16B ANNEALED MEMBRANE

mechanism termed as the solution diffusion mechanism. While explaining the transport by the aid of this model certain assumptions were made and accordingly the transport through asymmetric membrane has been explained.

The solution diffusion model for the transport through the membrane could be explained by the following equation. The water flux F_1 is given by

$$F_1 = \frac{D_1 C_1 V_1}{RT} = \frac{\Delta P - \Delta \pi}{\lambda}$$

Where D_1 = Diffusion coefficient of water in the membrane ($cm^2\ sec^{-1}$)

C_1 = Concentration of water in the membrane.

V_1 = Partial molar volume of water in membrane

$\Delta P - \Delta \pi$ = Applied pressure minus osmotic pressure difference, across the membrane (atm)

R = Gas constant

T = Temperature (^oK)

λ = Effective thickness of the membrane (cm)

Similarly, the diffusion of solute through the membrane is given by

$$F_2 = D_2 K \frac{\Delta C_2}{\lambda}$$

where D_2 = Diffusion coefficient for the solute in the membrane material

K = Distribution coefficient constant

C_2 = Concentration difference across the membrane

λ = Effective membrane thickness

However, for any other systems than NaCl-H_2O the equation may have to be modified, taking into consideration the chemical potential gradient for that particular system under investigation.

Development of RO

Yuster et al.[11] first suggested the possibility of desalination of water by skimming out surface layer of pure water from that of sodium chloride solution. This suggestion had stimulated the research on the desalination of water at University of California and simultaneously at the University of Florida, USA in 1956.

The osmosis phenomenon was first discovered by Abbe Nollet in 1748 using animal membrane. In 1867, Traube reported first artificial membrane for osmosis. Pleffer[6,12] made the first quantitative measurements using a membrane consisting of copper ferrocyanide precipitated in the pores of porcelain. The perfection of the diffusion technique for preparing and handling of the membrane was done by Morse et al.[13]. The theoretical development started with Von't Hoff and thermodynamic treatment was developed largely through sound theoretical understanding of the osmosis phenomenon by Gibb's.

The flow through an osmotic membrane has been explained mathematically by following general equation[10].

$$F_1 = A(\Delta P - \Delta \pi)$$

Where F_1 = Fresh water flux through the membrane (g/cm^2 sec)

A = Membrane constant (g/cm^2 sec-atm)

P = Pressure drop across the membrane (atm)

$\Delta \pi$ = Osmotic pressure of the feed (atm)

Greater the ΔP lower the $\Delta \pi$ (which is dependent on the concentration of the solution), and then higher will be the output of pure water (i.e. flux). This also depends upon the membrane characteristic (i.e. membrane constant A) which determines the quality of the membrane.

Mathematical models for analysing the flow of water through osmotic membranes have been presented by Merten[6]. For desalination, concentration or separation by RO, the semipermeable membrane must meet the following requirements.

1. It mustdesalinizea given saline feed water adequately.
2. It must have adequate desalinized water flux (flow rate per unit area of membrane) at reasonable pressure
3. It must possess the above two characteristics for a reasonable length of time.

In reverse osmosis, more innovation has taken place than any other membrane application. Literature survey reveals that RO is one of the most powerful techniques for desalination of brackish water in terms of economics and technical simplicity. Large scale RO sea water desalination plants have recently gone on stream in Middle East[14].

Development of Membrane Materials - Cellulose Membrane

Many polymeric materials have been scrutinized over past twenty five years for the preparation of semipermeable membranes for use in RO technique for desalination.

A partially hydrolysed product of cellulose triacetate is known as secondary cellulose acetate which has shown to have excellent potential as RO membrane due to its semipermeable and hydrophobic nature. Cellulose acetate (CA) possesses primary as well as secondary hydroxyl groups, the ratio of which depends upon the amount of water used for hydrolysis.

Reid and Breton[9] first reported the use of cellulose acetate as promising material for RO membranes. The conclusions drawn by Sourirajan and Bernstein[11] were also similar to that of Reid.

The salt rejection obtained by CA membrane was on higher side with reduced water flux. Loeb and

Sourirajan attempted to increase the water flux through the use of Schleicher and Schuell type commercial membrane[15]. They studied the effect of heating on membrane performance and concluded that

1. Salt rejection is improved by heating the membrane in hot water for 3 to 10 minutes.
2. Degree of desalination is directly proportional to the heating temperature.
3. Water flux rate is inversely proportional to the heating temperature.

Loeb and Sourirajan[16-18] further studied the effect of heating temperature and pH on Schleicher and Schuell type cellulose acetate membrane and developed their own technique for casting cellulose membrane. Loeb and Sourirajan also found out that it is possible to fabricate CA membrane with improved water flux maintaining higher percent salt rejection by incorporating acetone as additional component in casting solution and introducing several other changes to original Dobry method[19].

The solubility of CA is critical for preparation of asymmetric membrane than for films or fibers. Since the membranes are prepared from polymeric solutions which must tolerate the incorporation of high concentration of relatively incompatible pore producing constituents.

Thus, Sourirajan and Govindan[20] used solution of 17% cellulose acetate, 68% acetone, 1.5% magnesium perchlorate and 13.5% water known as perchlorate system to cast a film at -10°C with 4 minutes evaporation time. The % salt rejection and water flux rate were improved by this system than the original Loeb Sourirajan formula and indicated that the earlier method was not optimised with respect to casting solution composition. Various additives in the membrane casting solutions have been studied to modify and to improve the membrane performance[21].

A number of useful membrane casting solutions containing only non-electrolytes have been developed by Majikian, Loeb and Mccutchan[22] which gave similar performance to above, by a method which allows room temperature casting of the membrane (although the immersion water temperature should be in the range of 0-5°C). They have reported the composition consisting of cellulose acetate, formamide, acetone in the ratio of 25:30:45 wt% appeared to be optimum. It was also reported that the presence of formamide in CA casting was responsible for creation of pores in the resulting membrane. The average pore size in the membrane was independent of the amount of formamide used but the number of pores increased with increasing quantity of formamide in the casting solution.

Membranes from cellulose esters and mixed esters have been reported[23-28] to give 99% salt rejection with acceptable water flux, using salt concentration similar to the sea water.

Although Loeb type CA membranes have been used for desalination of brackish/sea water by RO technique, these membranes suffer from some drawbacks such as

1. High rate flux decline under operating conditions.
2. Low specific water content for flux for maintaining adequate salt rejection.
3. Since cellulose acetate is polyglucose and ester, it is susceptible to microbial attack[29] at low and high pH causing rapid loss of semipermeability.
4. They can be used only with aqueous solution since organic solvents either dissolve or plasticize it causing its collapse. Secondly, most of these membranes must be kept in wet condition because if they are allowed to dry they irreversibly consolidate and loose semi-permeability.
5. These membranes cannot be operated at high temeprature.

Considerableattempts are being madeto modify cellulose acetate by chemical means to make effective polymer for preparation of RO membrane.

The functional groups present in the cellulose acetate are secondary free hydroxyl groups and ester.

An extensive literature is available[23-28] on modification of CA by chemical means. The transport properties of cellulose acetate membranes are greatly affected by substitution of functional groups.

Phenyl isocyanate and α-naphthyl isocyanate react quantitatively with free hydroxyl groupsof cellulose acetate without disturbing the acetyl group[30]. Membranes have been prepared from CA - methyl carbamate polymer and the reverse osmosis data of these membranes has been compared with cellulose triacetate[27].

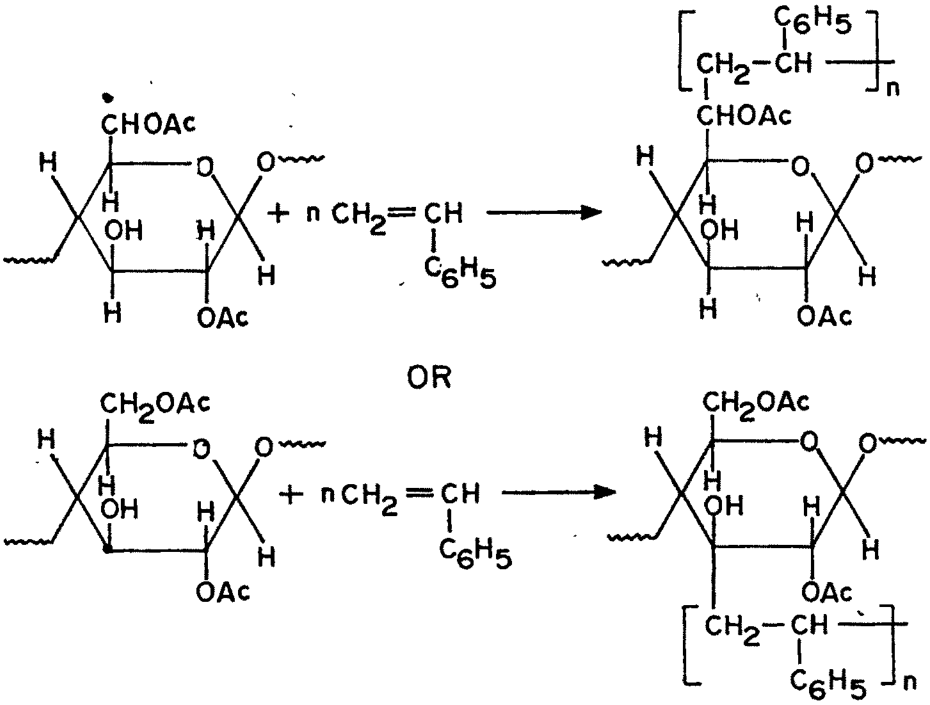
Modified cellulose ion exchange compounds have been prepared by reacting cellulose or its derivatives with excess of polyisocyanate and with aliphatic polyamines under anhydrous conditions[31].

Surface modification of cellophane has been carried out by Matsunaga and Ikada[32] by reacting it with different isocyanates. The enhanced hydrolytic stability was observed in these isocyanate modified cellophanes. Improved composite reverse osmosis membraneshave been prepared from crosslinked, regenerated cellulose with an ultra-thin film of cellulose triacetate. The cross-linking of regenerated cellulose has been effected by toluene diisocyanate. This composite membrane has been found to exhibit slightly better creep resistance at high applied pressure than the Loeb type membrane[28].

Dry reverse osmosis membranes have been prepared from cellulose acetate modified by using small amount of blocked isocyanates[33]. Monofunctional isocyanates are not as effective as diisocyanates for carbamate formation. It has been reported that the cellulose acetate membrane containing neutral carbamate group [illegible], decreases the permeability but not the perselectivity.

Modification of Cellulose Acetate by Grafting

Reverse osmosis using cellulose acetate membrane is a time dependent phenomenon in which compressive compaction occurs which results in reduced flux rate and % salt rejection. A compression and compaction of the membrane can be reduced by grafting the base polymer with the compound which has low creep value and insensitivity to water. Thus cellulose acetate has been grafted with styrene by radiation method. The grafting takes place as per the scheme shown below:



GRAFTING OF STYRENE ONTO CELLULOSE ACETATE.

The direct grafting of styrene has been reported[34,35] on

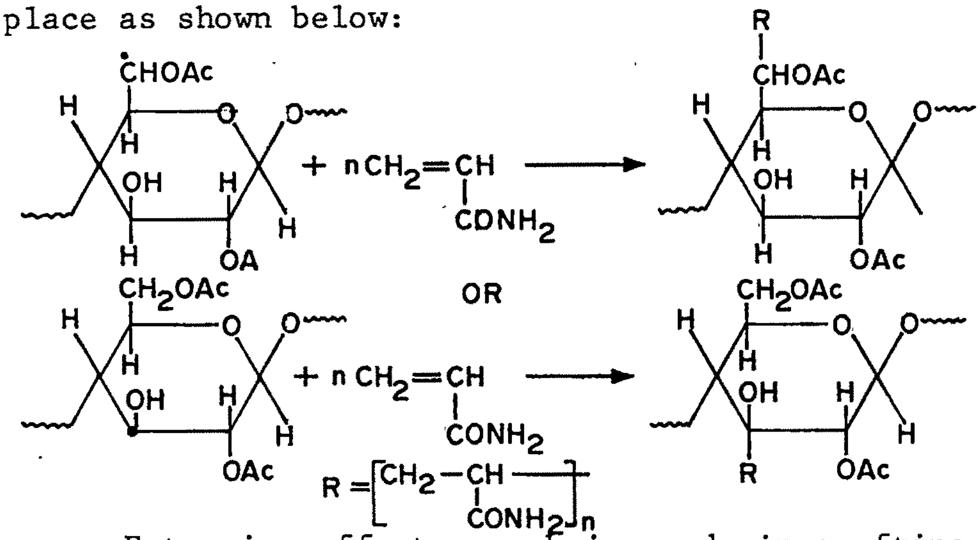
1. Dense symmetrical membrane
2. Loeb Sourirajan type asymmetric membrane
3. Purified styrene - CA copolymer,

by combining irradiation and casting technique

The above study reveals that the wet tensile creep has been reduced and also short chain grafting is significantly effective than long chain grafting.

In case of styrene or α-methyl styrene- cellulose acetate membrane, vapour sorption equilibria, sorption kinetics and related osmosis behaviour have also been studied[36,37]. The salt rejection for both styrene-cellulose acetate and methyl styrene-cellulose acetate system is identical upto a dose of 4Mrad, at higher dose, the rejection reaches to zero for α-methylstyrene. Increased water flux was observed over a significant range of grafting of styrene or α-methyl styrene on cellulose acetate without altering the creep and salt rejection.

The methyl methacrylate series has excellent salt rejection accompanied by high flux as compared to styrene cellulose acetate[37]. Acrylamide- cellulose acetate membrane prepared by radiation grafting has been used for reverse osmosis studies[38]. Radiation grafting of acrylamide as cellulose acetate takes place as shown below:



Extensive efforts are being made in grafting vinyl monomers on cellulose acetate. The co-polymer graft of methyl methacrylate and 2-vinyl pyridine show similar results to that of styrene graft[37].

Non-Cellulosic Membranes

To overcome the certain drawbacks of cellulosic membranes, considerable efforts have been made in recent years in development of number of polymeric materials which exhibit superior transport, mechanical, thermal, biological and chemical properties to those of cellulose membrane. Aromatic polyamides, polyimides and nitrogen containing aromatic backbone polymers are most promising polymers for membrane application.

Polyamides

The technique for the fabrication of asymmetric membrane from aromatic polyamide does not differ from that developed for cellulose derivatives.

Aromatic polyamides show better hydrolytic stability than the aliphatic polyamides and remarkable gamma radiation resistance. This property has been utilized in solving the effluent problem from the atomic reactors and radioactive waste concentration and recovery .

Chandorikar *et al*.[39] have studied the fabrication technique of osmotic flat membrane of poly*meta*phenylene terephthalamide and it's performance at high pressure.

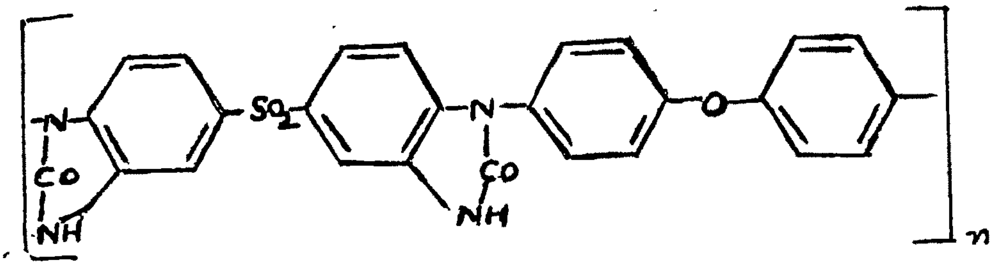
Polybenzimidazole

Polybenzimidazole (PBI) a class of polymer has been recently developed for reverse osmosis membrane application[40]. Poly 2-2' (*m*-phenylene)-5,5' bibenzimidazole is prepared from 3,3' diaminobenzidine and diphenyl isophthalate. PBI has very high moisture affinity and also possesses outstanding thermal, physical and chemical stability over a wide range of pH. The membrane performance of PBI polymer is superior to that of cellulose acetate at high temperature and pressure.

Polybenzimidazolone (PBIL)

Aromatic polymer containing benzimidazolone ring in the main chain has been found to show excellent performance as a RO membrane as compared to cellulose acetate membranes[2,3].

PBIL polymer is synthesised by polycondensation of aromatic diamine and diacid dichloride, followed by ring formation reaction. PBIL polymer has a following benzimidazolone repeating unit in the backbone.



The asymmetric membranes prepared from PBIL polymer exhibit higher salt rejection and higher water flux as compared to cellulose acetate membrane. Teijin Ltd., Japan, has successfully developed RO plant using PBIL membranes[3].

Polyethyleneimine crosslinked by polyisocyanate, sulfonated polysulfone, polyphenylene oxide and poly-piperazineamide have also shown promise as membrane materials for RO application.

Industrial Applications of Reverse Osmosis

Reverse osmosis finds various industrial applications such as :

1. Production of boiler feed water.
2. Production of pharmaceutical water (i.e. free from bacteria and virus)[41].

3. Sewage treatment.
4. Purification of industrial effluents such as that from nuclear power plant, etc.[42-44].
5. Production of quality water for beverage, semi-conductors and other industries.
6. Concentration of fruit juices and other liquid food. such as sugarcane, beet and tomato juice[45-49].
7. Concentration of dairy and pharmaceutical products[50,51].
8. Water alcohol separation[52].

The Japanese government is planning a ten year $ 45-6 million development programme for membrane application including water alcohol separation, uranium recovery and others. The Italian government has also launched a similar programme in this area.

Present Investigation and Results

Reverse osmosis (RO) is an effective membrane separation technique in which more and more innovations are taking place due to its industrial importance. This process is widely used in industry for concentration of juices, industrial wastesand for treatment of industrial effluents.

One of the major applications of RO process is in the desalination of water. RO is an effective means of obtaining potable water from brackish and sea water in the growing population and industrialization of the world.

Since last twenty years, secondary cellulose acetate (CA) membranes are successfully used for desalination purpose due to their unique asymmetric nature and hydrophobic character. However, these membranes have some limitations such as poor chemical resistance, fast biodegradability, rapid flux decay due to membrane compaction under influent pressure, etc. Therefore, a considerable attention is being given for its better chemical, microbial, radiation and mechanical resistance by modifying CA by chemical means. A number of chemical modifications of CA have been reported in the literature for its use as RO membrane for desalination of water.

The effective chemical modifications of CA using aromatic as well as aliphatic isocyanates have been reported by Ghatge *et al.*[53-55]. They have studied the effect of urethane linkage of the modified CA on transport properties of the membranes obtained therefrom.

It has been reported that silyl derivative of cellulose exhibits a relatively high degree of hydrolytic stability. Methyldiphenyl silyl-cellulose has been reported[56] to be hydrolytically stable even under severe conditions which is explained on the basis of steric hindrance. CA has been known for its hydrophobic nature. Thus, the present study deals with the partial modification of residual hydroxyl groups of secondary CA with trimethylchlorosilane(TMCS) to enhance its hydrophobic character by introducing Si-O-C linkage. The modified polymers were characterised for their physical properties such as softening point, intrinsic viscosity, molecular weight determination, silicon content, acetyl content, tensile strength, thermal stability and by IR spectroscopy.

The membranes were cast from these modified polymers and used for desalination of water by RO process. The effect of Si-O-C linkage on the transport properties of the membrane such as % salt rejection, water flux rate and pure water permeability were studied.

The physical characteristics of the membrane like average pore diameter, membrane constant and specific water content were also determined.

A brief description of each step involved in the modification of CA is given below:

Preparation of Trimethyl Silyl Cellulose Acetate(TMSCA):

CA was partially reacted with TMCS in pyridine as follows:

Dry CA was completely dissolved in pyridine at 50-55°C under nitrogen atmosphere. Then TMCS in pyridine was added dropwise during 30 min. with stirring. The temperature was then gradually raised to 114°C and maintained for 6 h . After cooling the reaction mixture, the slurry was filtered through a sintered glass funnel holding a 1" layer of alumina with a layer of tightly packed glass wool on top to remove pyridine hydrochloride. The polymer in the form of white powder was obtained by precipitating with methanol. The polymer was filtered and the powdered polymer obtained was dried under vacuum at 110°C/15 mm Hg for 1 h. The modification of CA was effected by using various proportions of TMCS. The modified polymers thus obtained are designated as TMSCA (0.2), TMSCA (0.4), TMSCA (0.6) and TMSCA (0.8). The number in the parenthesis denotes the molar proportions of TMCS used for the partial modification of CA.

Characterisation of Trimethylsilyl Cellulose Acetate

The intrinsic viscosity of the polymer was determined in acetone at 30° ± 1°C using Ubblehode viscometer.

The molecular weight was calculated from intrinsic viscosity of the polymer[57] by the equation $\eta = KM^{\alpha}$

The silicon content of the polymer was determined according to the reported procedure[58].

The % acetyl content of modified CA was determined according to ASTM designation number D871-61T[59].

The tensile strength of the modified polymer was determined according to ASTM designation number D882-52T on Scott testing machine[60].

The above mentioned physical properties are given in Table 16.

The thermal stability of the polymer was studied by thermogravimetric analysis on MOM BUDAPEST DERIVATOGRAPH and the data is given in Table 17. The thermogravimetric curves are shown in Fig. 18. The IR spectrum of the modified CA was recorded as film on Perkin Elmer Model 683 IR Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1} (Fig. 17).

Table 16

Physical Characteristic of Trimethyl Silyl Cellulose Acetate (TMSCA)

Polymer	Softening point°C	(Intrinsic viscosity) dl/g	Molecular weight	Total Degree of substitution	% Acetyl content	%Si	Tensile strength of membrane kg/cm^2
TMSCA(0.2)	243-247	1.45	60,200	2.392	39.20	0.14	120.2
TMSCA(0.4)	245-250	1.5	62,800	2.371	38.98	0.35	125.7
TMSCA(0.6)	247-250	1.55	64,860	2.327	38.57	0.42	132.8
TMSCA(0.8)	247-252	1.6	65,920	2.306	38.3	0.50	140.0
CA	243-245	1.4	57,800	2.446	39.9	-	105.0

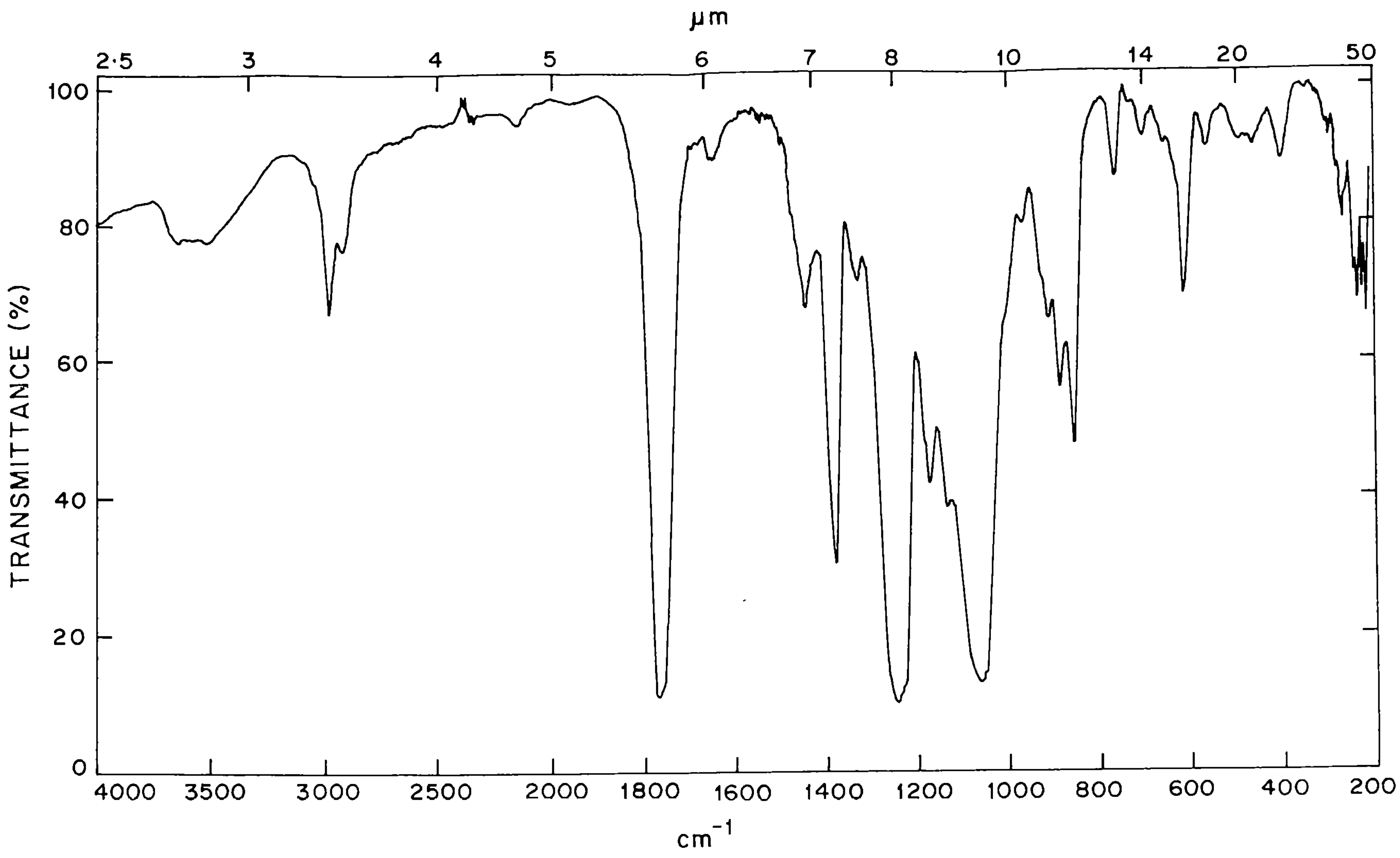


FIG. 17 : IR SPECTRUM OF SILYL DERIVATIVE OF CELLULOSE ACETATE.

Table 17

Percentage weight LOss at Different Temperatures for TMSCA and CA

	Weight Loss %				
Temperature °C	TMSCA (.2)	TMSCA (.4)	TMSCA (.6)	TMSCA (.8)	CA
100	4	4	3.6	3	6
200	4.5	4	3.5	3	6.5
300	6	5.5	5	4.5	10
400	85	80	80	75	85
500	90	85	85	83	90
600	100	97	95	92	100

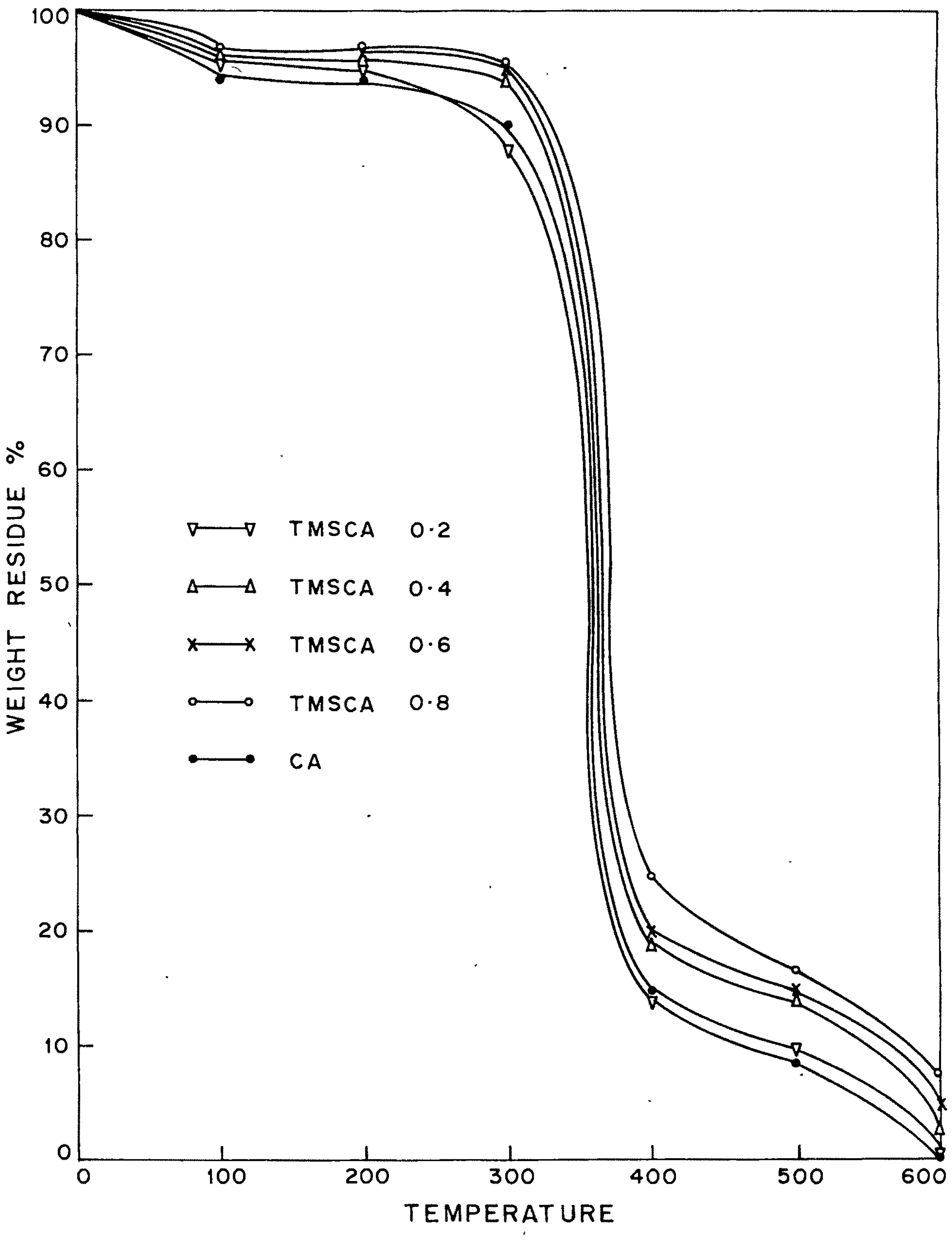


FIG. 18 : TG CURVE IN AIR AT 10°C / min. FOR TMSCA.

Trimethylsilyl Cellulose Acetate Membrane for Desalination of Water by Reverse Osmosis

Membrane Casting

The flat membranes were prepared from a solution of polymer in acetone and formamide as per the method described by Loeb and Sourirajan[15].

Annealing of the Membrane

Cellulose acetate membrane in primary gel stage exhibits high water flux and low salt rejection. Therefore annealing of the membrane was done at two different temperatures viz. 80°C and 88°C for 15 minutes. The transport properties of the annealed membranes were studied. The annealed membranes were preserved in 0.2% formalin solution.

Performance of Modified CA Membranes

The transport properties of the flat membrane such as % salt rejection, pure water permeability and water flux rate were determined on the RO unit fabricated in this laboratory at operating pressures of 600 psi and 900 psi with 5000 ppm of NaCl solution as a feed. These properties are given in Tables 18 to 21.

The pure water permeability was determined from the constant flux rate of distilled water at operating pressure of 600 psi and 900 psi. The % salt rejection by the membrane was determined by measuring the

Table 18

Transport Properties of TMSCA Membranes

Operating Conditions

Applied pressure - 600 psi
Feed concentration - 5000 ppm NaCl
Feed temperature - 23-25°C
Operating period - 6 h
Membrane area - 18.6 cm^2

Sample No.	Sample (Membrane)	Annealing temperature °C	Pure water permeabiligy gfd	Water flux gfd	% salt rejection
1.	TMSCA (0.2)	80	17	18	69
2.	TMSCA (0.4)	80	17	14.5	74
3.	TMSCA (0.6)	80	14.8	13	78
4.	TMSCA (0.8)	80	12.5	11.1	83
5.	CA	80	23	20	67

Table 19

Transport Properties of TMSCA Membranes

Operating Conditions

Applied pressure	900 psi
Feed concentration	5000 ppm NaCl
Feed temperature	23-25°C
Operating period	6 h
Membrane area	18.6 cm^2

Sample No.	Sample (Membrane)	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1.	TMSCA (0.2)	80	20.5	19	72
2.	TMSCA (0.4)	80	19	16.5	77
3.	TMSCA (0.6)	80	17.2	14	81.5
4.	TMSCA (0.8)	80	15	12	86
5.	CA	80	37	34	71

Table 20

Transport Properties of TMSCA Membrane

Operating Conditions

Applied pressure	600 psi
Feed concentration	5000 ppm NaCl
Feed Temperature	23-25°C
Operating period	6 h
Membrane area	18.6 cm^2

Sample No.	Sample (Membrane)	Annealing temperature °C	Pure water Permeability gfd	Water flux gfd	%Salt rejection
1.	TMSCA (0.2)	88	14	12	77.8
2.	TMSCA (0.4)	88	13.2	10.9	80.2
3.	TMSCA (0.6)	88	11.8	9.4	83.1
4.	TMSCA (0.8)	88	10	8.1	85.8
5.	CA	88	16.0	12.1	76

Table 21

Transport Properties of TMSCA Membranes

Operating Conditions

Applied pressure	900 psi
Feed concentration	5000 ppm NaCl
Feed temperature	23-25°C
Operating period	6 h
Membrane area	18.6 cm^2

Sample No.	Sample (Membrane)	Annealing temperature °C	Pure water permeability gfd	Water flux gfd	% Salt rejection
1.	TMSCA (0.2)	88	16.5	13	80.9
2.	TMSCA (0.4)	88	14.9	12.4	82.5
3.	TMSCA (0.6)	88	13.2	11	85.1
4.	TMSCA (0.8)	88	11	9.8	87.6
5.	CA	88	18	15	80.1

conductance of feed and permeat solution.

Membrane Characteristics

The membrane characteristics such as specific water content[62], membrane constant and average pore diameter at different annealing temperatures is given in Tables 22 and 23. Membrane constant and average pore diameter of the membranes were calculated from pure water permeability. Specific water content of the membrane was determined according to Ferry's method[4].

Table 22

Membrane Characteristics of TMSCA and CA at 600 psi Operating Pressure

SNo.	Membrane	Annealing temperature °C	Specific water content g/cm^3	Membreane constant x 10^{-5} g/cm^2-sec-atm	Average pore diameter A°
1..	TMSCA (0.2)	80	0.69	2.1	30.3
2.	TMSCA (0.4)	80	0.62	1.8	28.1
3.	TMSCA (0.6)	80	0.54	1.52	25.9
4.	TMSCA (0.8)	80	0.45	1.49	23.1
5	CA	80	0.74	2.6	32.20

Table 23

Membrane characteristic of TMSCA and CA at 600 psi Operating Pressure

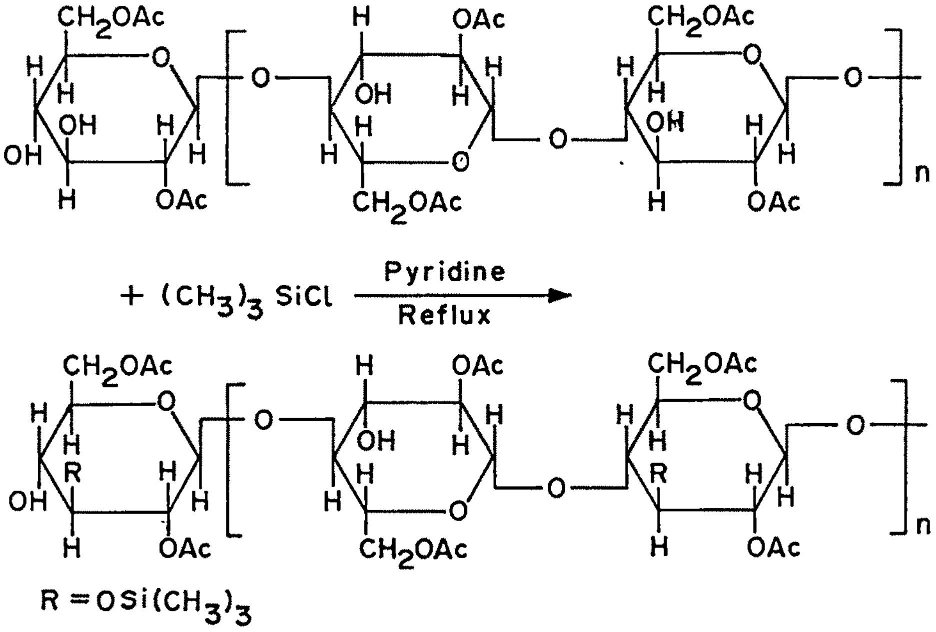
S.No.	Membrane	Annealing temperature °C	Specific water constant g/cm^3	Membrane constant x 10^5 g/cm^2-sec-atm	Avrerage pore diameter A°
1.	TMSCA (0.2)	88	0.58	1.21	24.3
2.	TMSCA (0.4)	88	0.51	1.12	22.1
3.	TMSCA (0.6)	88	0.46	0.91	20.4
4.	TMSCA (0.8)	88	0.40	0.82	19.1
5.	CA	88	0.70	1.5	23.8

DISCUSSION

Silylation of a number of natural products including various sugars is known for many years. Silylation of polyhydroxy compounds such as carbohydrate is generally done for their characterisation or analysis by gas liquid chromatography.

Cellulose has been successfully silylated by many workers. Klebe[56] has reported various silyl derivatives of cellulose and studied their hydrolytic stability. Noshay and Matzmer[61] have also investigated the hydrolytic stability of polymers containing Si-0-C linkage. This prompted us to modify CA (D.S. 2.5 to 2.6) partially with TMCS and evaluate the resulting polymer for preparation of RO membrane for desalination of water.

The effective partial silylation was carried out in pyridine using dry CA and specially purified TMCS under dry conditions. The reaction of CA with TMCS can be shown as below:



Softening Point

The gradual increase in softening point of TMSCA was observed (Table 16) when the modification of CA was carried out with high molar proportions of TMCS.

Viscosity and Molecular Weight

The molecular weight of polymer has been determined from intrinsic viscosity at 30° ± 1°C in acetone.

The molecular weight of the polymer was calculated from the equation $\eta = KM^{\alpha}$

$K = 1.56 \times 10^{-4}$
and
$\alpha = 0.83$
in acetone at 30° ± 1°C

% Acetyl and silicon content

The % acetyl and silicon content data were consistent with structural formula (Table 16).

IR Spectrum

In the IR spectrum of TMSCA (Fig. 17) characteristics bands of Si-C stretching at 860 cm^{-1} and 845 cm^{-1} were observed along with OH band frequency at 3400 cm^{-1} and 1750-1700 cm^{-1} band of ester C=0 group, thus supporting the partial silylation of CA.

Tensile strength

The tensile strength values obtained with TMSCA were higher than that of unmodified CA.

Thermal Stability

The thermal stability of CA has been reported in the literature. The effect of silicon moiety on the thermal stability of the CA modified by TMCS has not been reported so far in the literature. Therefore, the work was further extended to study the thermal stability of these modified polymers in dry state by thermogravimetric analysis. The loss in weight of polymers at various temperatures was determined from primary thermograms and is given in Table 17. In general, TMSCA showed higher thermal stability than unmodified CA (Fig. 18).

Performance of Modified CA Membranes

The transport properties like pure water permeability, water flux rate and % salt rejection of partially modified CA membranes as well as unmodified CA membranes were tested on RO unit at operating pressures of 600 and 900 psi with 5000 ppm of sodium chloride solution as feed. The % salt rejection was calculated from the conductance of feed and permeat solution. The modified CA membrane exhibited higher salt rejection compared to unmodified CA membrane. This may be due to partial modification of secondary hydroxyl group of CA. The % salt rejection inreased as the molar proportion of TMCS for the partial modification of CA was increased which can be again explained due to the surface modification of CA by TMCS.

Effect of Annealing Temperature

The membranes were annealed at two different temperatures (80°C and 88°C) to study the effect of annealing treatment on the transport properties of modified as well as unmodified CA membranes. Increase in % salt rejection and low water flux rate was exhibited by the membranes when annealed at 88°C than the membranes annealed at lower temperature (80°C).

Effect of Operating Pressure

The operating pressure on the semipermeable membrane has profound effect on % salt rejection and water flux rate. When the pressure is applied to the membrane, a restriction in Brownian movement inside the polymer takes place which further compresses the polymer structure. The water within the amorphous region becomes more tightly bound and the membrane becomes impermeable barrier to sodium chloride. This is observed in case of TMSCA membranes also, when the operating pressure was increased, higher water flux rate with marginal increase in salt rejection was noted (Table 18 to 21).

Membrane Characteristics

The specific water content of the membrane and the water flux rate of the membrane have been explained on the basis of solution transport mechanisms[62,63]. The rate of water flux through the semipermeable membrane increases with increase in water content of the membrane. The specific water content values of TMSCA membranes were lower than unmodified CA membranes. Therefore, TMSCA membranes exhibit lower water flux rate (Table 22 to 23). Membrane constant and average pore diameter in case of TMSCA membranes were lower than unmodified CA membranes.

EXPERIMENTAL

Materials

Secondary cellulose acetate (CA) (39.9% acetyl) was procured from M/s. Mysore Acetate, India, and was dried at 100°C/15 mm Hg for 5 h before use.

Trimethylchlorosilane (95%) obtained from Fluka AG, West Germany, was distilled and further purified by heating with sucrose.

Solvents such as pyridine, methanol, acetone, formamide were distilled before use. Analytical grade sodium hydroxide, hydrochloric acid and sodium chloride were used.

Preparations

Partial Modification of Cellulose Acetate by Trimethylchlorosilane

A 500 ml four necked flask fitted with a mechanical stirrer, a reflux condenser, a dropping funnel and a nitrogen gas inlet was flushed with nitrogen and 25 g. of dry CA and 300 ml of dry pyridine were placed and stirred at 50-55°C till CA was completely dissolved. Then appropriate amount of trimethylchlorosilane in pyridine was added dropwise with stirring during 30 min. The temperature was gradually raised 113°-114°C and the reaction mixture was refluxed for 6 h. The slurry was filtered through a sintered glass funnel holding a 1" layer of alumina with a layer of tightly packed glass wool to remove pyridine hydrochloride. The clear colourless filtrate was precipitated with methanol to get white solid powder. The powdered polymer was further dried under vacuum at 110°C/15 mm Hg for 1 h.

Characteristics of TMSCA

1) Softening Point

The softening point of the polymer was determined on Campbell electronics melting point apparatus.

2) Determination of Intrinsic Viscosity

A solution of polymer (1%) was prepared in acetone and filtered through sintered funnel. The filtered solution was transferred to Ubblehode viscometer and the viscosity measurements were made at 30 ± 1°C. The intrinsic viscosity was determined from the plots of η sp/c vs concentration. Thus, the molecular weight of the polymer was determined from the intrinsic viscosity.

$$\eta = KM^{\alpha}$$

where $K = 1.56 \times 10^{-4}$

and $\alpha = 0.83$

3) Determination of Acetyl Content

The acetyl content of the modified cellulose acetate was determined according to ASTM Designation

D871-61T.

Accurately weighed (1 g) polymer was taken in 250 ml Erlenmeyer flask with stopper and was swollen in 40 ml of ethyl alcohol (75%). The flask was warmed on water bath at 50°-60°C with intermittent stirring. Then 40 ml of 0.5N NaOH solution was added to it and heating was continued for another 15 min. at 50°-60°C. The flask was allowed to stand for 72 h with intermittent stirring. At the end of this period the excess of NaOH was back titrated with 0.5N HCl using phenolphthalein as indicator. Then one ml excess of 0.5N HCl was added to the flask and kept overnight. The disappearance of pink colour indicates the complete neutralization of NaOH.

Excess of HCl was titrated with 0.5N NaOH solution using phenolphthalein as an indicator. Percentage acetyl content was calculated as follows:

$$\% \text{ Acetyl content} = [(D-C)\,Na + (A-B)\,Nb]\,F/W$$

A = ml of NaOH required for the titration of sample
B = ml of NaOH required for the titration of the blank.
Nb = Normality of the NaOH solution
C = ml of HCl required for the titration of the sample
D = ml of HCl required for the titration of the blank
Na = Normality of HCl solution
F = 4.305 for acetyl
W = Weight of sample taken in gms

The degree of substitution (D.S.) of cellulose acetate polymer was also determined by above procedure.

4) IR Studies

IR spectrum: The infra red spectrum of the modified cellulose acetate was recorded as a film prepared from the polymer solution in acetone and dried in vacuum oven. The spectra were recorded on Perkin Elmer model 683 Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1}.

5) Tensile Strength

The tensile strength of both modified and unmodified CA membranes was measured according to ASTM Designation D 882-52T on Scott testing machine.

6) Silicon Content by Gravimetric Analysis

Silicon content was determined by gravimetric estimation. A weighed amount of TMSCA was digested with analar sulphuric acid (1-1.5 ml) in a crucible. The acid was evaporated with a low flame, then the crucible was heated on full flame for 30 min. The contents were heated after cooling till the constant weight was obtained.

7) Thermal Stability

The thermogravimetric analysis was done on MOM BUDAPEST DERIVATOGRAPH at heating rate of 10°C/min in air.

Characteristics of Membrane

Transport Properties of Membrane

The transport properties such as pure water permeability, water flux and % salt rejection were determined on the RO unit.

Preparation of Modified Cellulose Acetate membrane

Casting Solution

For the preparation of membrane a solution of polymer, formamide and acetone in 20:25:55 (weight ratio) was prepared and ball milled for 24 h for uniform mixing. Then the flat membrane was prepared as per the procedure given by Loeb and Sourirajan[15]. On a clean, dry glass plate with multiple electric tapes as guide and a casting knife, a 15 cm x 30 cm film was cast at room temperature. After evaporation of solvent for 1 min, the membrane cast plate was immersed in a cold water bath (2º4°C) for 1 h and the membrane was released by removing the glass plate from the cold water bath. The membranes were annealed at 80°C/88°C for 15 min and preserved in 0.2% formaline solution. Membranes were also cast from unmodified CA using similar procedure.

Pure Water Permeability

A circular membrane having area 18.6 cm^2 was cut from the flat membrane and was placed along with a circular filter paper and a stainless steel porous plate having similar dimensions as a support in the RO cell. The membrane surface which was in contact with air during casting was directed to high pressure side of the feed solution (Distilled water). The feed water reservoir was filled with distilled water. The RO cell was pressurised initially with low pressure to avoid any error in the permeat volume due to imperfection in the membrane. Then the cell was pressurised to known pessure (600 and 900 psi) and the reading for the product flux were noted at regular intervals of time till two consecutive readings (nearly constant) of the flux were obtained. The final flux readings were converted into gallon

% Salt Rejection (% SR)

The salt rejection by various membranes were measured as per the procedure employed for pure water permeability except the change in feed water reservoir that was filled with 5000 ppm sodium chloride solution instead of distilled water.

The % salt rejection by the membrane was calculated by measuring the conductance of feed and permeat solution on conductivity meter. The % salt rejection (SR) was calculated as follows:

$$\%SR = \frac{\text{Conductance of feed - Conductance of permeat}}{\text{Conductance of feed}} \times 100$$

Determination of Membrane Constant

The membrane constant 'A' was measured from the pure water permeability using following equation:

$$A = \frac{V}{a \times t \times \Delta P}$$

where V = Volume of permeat in time t

a = Effective membrane area

t = Time taken in collecting V mL of permeat in seconds

Δ p = Applied pressure in atmosphere

Determination of Average Pore Diameter

Average pore diameter of the membrane was determined according to the following equation [62]

Average pore diameter -

$$J = 2r = 4 \left[2 \cdot \frac{VnL}{SAPT} \right]^{\frac{1}{2}}$$

V = Volume of the permeat collected in time t

n = Viscosity of pure water in cps.

L = Membrane thickness in cm .

S = Specific water content of the membrane

A = Effective membrane area (cm^2)

P = Applied pressure in atmosphere

T = Time taken in collecting VmL of permeat in seconds

Determination of Specific Water Content

The specific water content of the membrane was estimated by the method reported by Ferry[62]. A small cut piece of known area from the membrane was carefully dried with the pair of blotting papers superficially. Then it was immediately placed in previously weighed crucible and the contents were accurately weighed again. The sample was dried at 105°C to constant weight. The specific water content was calculated from the following formula:

Specific water content

$$= \frac{\text{Loss in weight after drying}}{\text{Membrane area x Thickness of the membrane}}$$

$$= \text{g/cm}^2.$$

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CHAPTER III

Synthesis of Castor Oil Dithioglycolate and its Utility as Room Temperature Setting Elastomeric Materials and as a Flexibilizer for Epoxy Resin

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Section A

Synthesis of Dithioglycolates

INTRODUCTION

The future of organosulphur compounds which centres around thiols looks brighter when the possibility of oxygen based compounds such as alcohols is exhausting. Mercaptans have roots that go back to millions of years as ingredient in natural products. The sulphide and disulphide linkages are vital parts of the chemical structures of proteins such as insulin and keratin and amino acids such as cystine, methionine, etc.

The discovery of thiols in 1834 has been accredited to Zeise[1]. Since then, a large number of thiols have beeen synthesised and addition of new ones to the evergrowing thiol compounds is taking place. The organosulphur compounds due to their application potential are becoming more widely known. The unique properties of sulphur compounds to enter the reactions beyond the reach of their oxygen analogues finds special interest in studies of bio-chemical research and in various commercial applications.

Many aspects of thiol chemistry and early work has been reviewed by Malisoff *et al.*[2]

Methods of Synthesis of Thiols

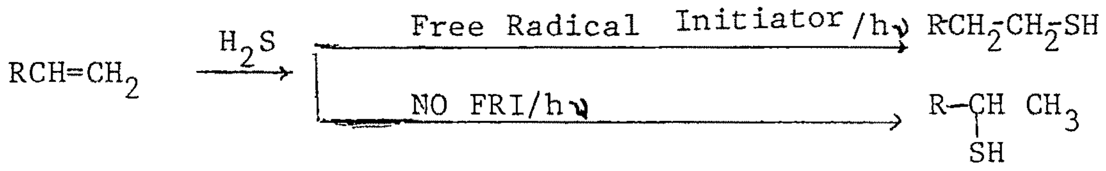
New methods of synthesis are worked out as a consequence of evergrowing development in chemistry of thiols. Following are the methods used for the synthesis of thiols:

1. Addition of hydrogen sulphide to olefins.
2. Reaction of alkyl halides with various reagents.
3. The hydrolysis of thiol esters.
4. Esterification of polyhydroxy compounds with mercapto acids
5. Reduction of disulphide and other sulphur compounds.

These methods are described briefly below:

1. Addition of Hydrogen Sulphide to Olefins

Hydrogen sulphide addition to olefins is[2,3] an important method for thiol synthesis. The addition of hydrogen sulphide to terminal olefins using free radical initiators (FRI) or by photochemical means leads to anti-Markownikoff product and in absence of these, usual Markownikoff addition takes place.



$$RCH{=}CH_2 \xrightarrow{H_2S} \begin{cases} \xrightarrow{\text{Free Radical Initiator}/h\nu} RCH_2{-}CH_2{-}SH \\ \xrightarrow{\text{NO FRI}/h\nu} R{-}\underset{SH}{\underset{|}{C}}H\ CH_3 \end{cases}$$

Radical addition of H_2S to olefins is commonly used for terminal, internal or cycloolefins. UV radiation below 3×10^4 nm, γ-irradiation[5,6] and X-rays[7] have also been used for effective addition. Promoters or sensitisers have been used to increase the reaction rate.

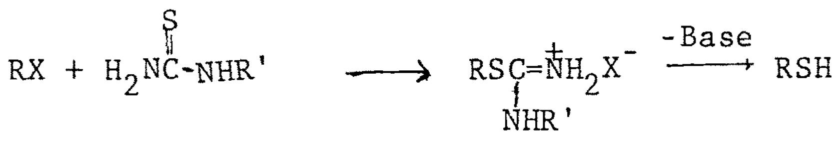
Ionic addition of H_2S to olefins in presence of many protic[8] and Lewis acid[9] catalyst afforded synthesis of thiols. Alkyl aluminium chloride was found to be effective catalyst for such addition[10]. Alkali hydroxides and amines are employed for the ionic addition to unsaturated carbonyl compounds[11,12].

2. By the Reaction of Alkyl Halides with Various Reagents

Alkyl halides have been used extensively for the laboratory scale preparation of thiols. A brief description of reactions and reagents involved in the synthesis is given below.

a) Using Thiourea

This method is widely used for small scale preparation of thiols. An alkyl halide reacts with thiourea or substituted thiourea[13] to give an isothiouronium salt which cleaves on treatment with base to yield thiol.



$$RX + H_2N\overset{\overset{S}{\|}}{C}\text{-}NHR' \longrightarrow RS\underset{NHR'}{\underset{|}{C}}=\overset{+}{N}H_2X^- \xrightarrow{-Base} RSH$$

b) Alkali Metal Hydrosulphide

Thiols have been synthesised by reacting alkyl halides with sodium or potassium hydrosulphide.

$$R\text{-}X + NaSH \longrightarrow RSH + NaX$$

c) Reaction with Sodium Polysulphide Followed by Reduction

Alkyl diahlides react with sodium polysulphide to form alkyl polysulphide which can be reduced to yield the dithiols. Good yields were obtained by this method due to stereochemical control[14].

$$X\text{-}(CH_2)_n\text{-}X \xrightarrow[DMF]{Na_2S.9\ H_2O} \overline{S(CH_2)_nS} \xrightarrow{2H} HS(CH_2)_nSH$$

d) By the Hydrolysis of Thiol Esters

Olefin-based thiols are generally synthesised by the hydrolysis of thiol esters (-RCOSR'-).

Addition of thiols e.g. thiol acetic acid CH_3COSH is similar to the addition of hydrogen sulphide to olefin.

Thiol acids add to olefins under free radical conditions or photochemical reactions and give anti-Markownikoff products which are readily hydrolysed in presence of base[15] or ammonia[16] to give thiol.

$$RCH=CH_2 + CH_3COSH \xrightarrow[h\nu]{\text{FRI or}} RCH_2\text{-}CH_2\text{-}S\text{-}COCH_3$$

$$RCH_2CH_2SCOCH_3 \begin{cases} \xrightarrow{NaOH} RCH_2CH_2SH + NaOAc \\ \xrightarrow{NH_3} RCH_2CH_2SH + NH_2Ac \end{cases}$$

High molecular weight polythiols having 6-7 thiol groups per molecule have been synthesised by this method[15,17].

e) From Polyhydroxy Compounds and Mercapto Acid

Esterification of hydroxy compounds with mercapto acid in presence of acid catalyst to yield thiol terminated compounds is an industrially important method.

$$HO\text{-}R\text{-}OH + 2\ HSCHR'COOH \longrightarrow R(OCOCHR'SH)_2$$

Thiols have been prepared using variety of hydroxy compounds such as glycerols, pentaerythritol, polyalkylenediols. Good yields were obtained using this method[18,19]. Ghatge and Murthy[20] have prepared castor oil tris thioglycolate by the reaction of castor oil and thioglycolic acid.

5. Synthesis of Thiols by Reduction of Disulphides

A number of reducing agents have been used to effect the reduction e.g. zinc-acid, tin-acid, sodium borohydride[21] and lithium aluminium hydride[22].

$$RSSR \xrightarrow{2H} 2RSH$$

Sodium hydrogen selenide has been reported as an effective reducing agent for good yields of thiols by Woods and Klayman[26].

Reactions of Thiols

Thiols react with a variety of organic and inorganic compounds. The reactions of thiols are similar to that of their oxygen analogues but some differences in their reactions are observed due to (1) higher acidity of thiols, (2) ease with which thiols undergo oxidation and (3) ability of thiols to enter free radical reactions with ease. Some of the important reactions are briefly described below:

1) Oxidation

A characteristic and facile reaction of thiol is its capacity to easy oxidation to yield disulphide.

$$2\ RSH + \tfrac{1}{2}\ O_2 \longrightarrow RSSR + H_2O$$

The oxidation of thiols to disulphide by oxygen goes rapidly in presence of base and metals (iron and copper). Metal chelates and amine also catalyze this reaction.

A variety of other oxidizing agents are also used e.g. metal oxides[24]. This oxidative coupling in presence of metal oxides forms the basis for the curing of the industrially very important thiol containing liquid polymers which find applications as a leather impregnant, in manufacture of oil seals, in rubber industry as repair and coating materials, in aircraft industry as sealant for fuel tank and pressurised cabin sealant and in marine industry as deck and hull caulking material

Oxidation with iodine forms the basis for the analytical determination of thiols by iodimetry.

$$2\ RSH + I_2 \longrightarrow RSSR + 2\ HI$$

Lowe[26] has reported the complete oxidation of thiols and disulphide to the corresponding sulphonic acids by dimethyl sulphoxide containing hydrogen halide as the catalyst.

Oxidation with dimethyl sulphoxide has been used for the synthesis of cyclic disulphide[26].

$$HS-(CH_2)_n-SH + (CH_3)_2SO \longrightarrow \overline{S-(CH_2)_n-S} + (CH_3)_2S + H_2O$$

2) Reaction with Halogens Under Controlled Conditions

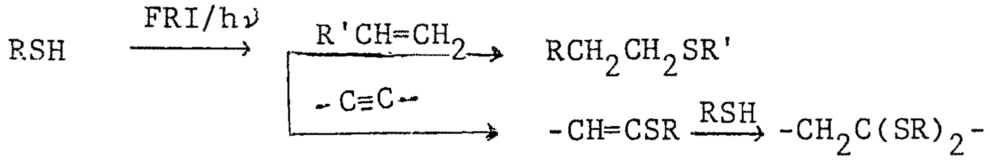
Halogens, particularly chlorine, react under controlled conditions to give sulphenyl halide.

$$RSH + Cl_2 \longrightarrow RSCl + HCl$$

Ross[23] has reported the synthesis of the bis-(sulphenyl chloride) of 1,2,4,5-tetrachloro-p-xylene dithiol, a cross linking agent for natural rubber.

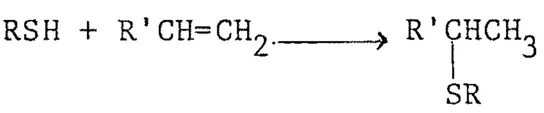
3. Addition to Olefins and Acetylene[3]

The addition of thiols to olefins and acetylenes takes place easily either by free radical or ionic mechanism which is similar to the addition of hydrogen sulphide to unsaturated compounds[28]. Radical addition of thiols in presence of the free radical initiators e.g. oxygen, peroxides, azo initiators or photo-chemical radiation yields the anti-Markownikoff product with acetylenes, it results in vinyl sulphide which on further addition forms diadduct[28,29].



$$RSH \xrightarrow{FRI/h\nu} \begin{cases} \xrightarrow{R'CH=CH_2} RCH_2CH_2SR' \\ \xrightarrow{-C\equiv C-} -CH=CSR \xrightarrow{RSH} -CH_2C(SR)_2- \end{cases}$$

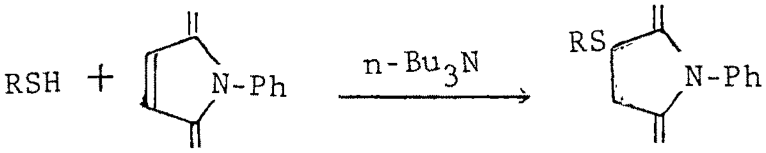
Addition of thiols to unsaturated compounds can also occur by ionic mechanism promoted by acid or sulphur and the resulting product is normal Markownikoff addition product.



$$RSH + R'CH=CH_2 \longrightarrow R'\underset{\displaystyle SR}{\underset{|}{C}}HCH_3$$

4) Addition to Activated Double Bonds

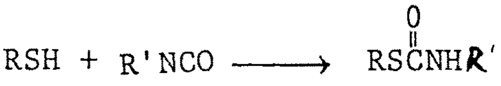
Thiols readily add to activated double bond e.g. maleimides and N-substituted maleimides in presence of tertiary amine as catalyst to form imidothioether.



Polyimidothioether polymers have been prepared by reacting bisthiols with bismaleimides[30].

5) Reaction with Isocyanate

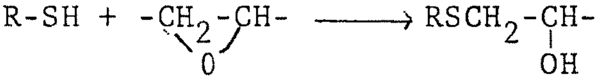
Thiols react with isocyanates to form thiourethanes[31] in presence of tin or titanium Lewis acid catalyst[32].



$$RSH + R'NCO \longrightarrow RS\overset{O}{\overset{\|}{C}}NHR'$$

6) Reaction with Epoxide

Thiols readily react with epoxy compounds to form 2-hydroxy thioethers[33]. The reaction is catalyzed by base catalyst.



$$R\text{-}SH + \text{-}\underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH}\text{-} \longrightarrow RSCH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}$$

Many polythiols have been used as curing agent for epoxy resin to impart specific properties to the end product which include mercapto acids[34] and their esters[35], polyether thiols[36], reaction product of hydrogen sulphide with diglycidyl ether[37]. Cycloaliphatic polythiols[38-40] are increasingly used in the curing of the epoxy resins for preparation of enamels, paints, potting-compositions, casting laminates and adhesives. The improved adhesive strength of epoxy resin to metal has been obtained using toluene bis(polymercaptopropyl thiocarbamates)[41].

7) Reaction with Elemental Sulphur

Thiols react with elemental sulphur to form stable organic polysulphides.

$$2\ RSH + nS \longrightarrow RS_{(n+1)}R + H_2S$$

This reaction renders it possible to synthesise organic polysulphide in a convenient way. This is the one reaction which oxygen analogues find it difficult to enter into. Sodium polysulphide also reacts with thiols to form polysulphides.

8) Formation of Mercaptides

Metal salts of thiols are called mercaptides. Thiols react with many metallic cations to form the mercaptides, a majority of which are insoluble in water.

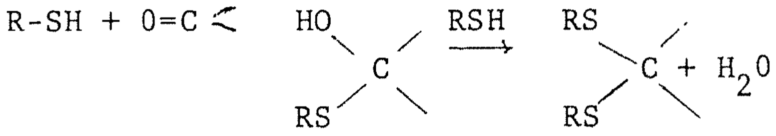
$$RSH + M^{+} \longrightarrow RSM + H^{+}$$

$$2\ RSH + M^{2+} \longrightarrow (RS)_2M + 2H^{+}$$

One of the important application of this reaction is in the sweetening of petroleum distillate. This process involves the formation of lead mercaptide followed by further reaction to form lead sulphide and organic sulphide.

9) Reaction with carbonyl compounds

Thiols, similar to their oxygen analogues, undergo acid catalysed addition to carbonyl compounds resulting in the formation of hemimercaptal and mercaptal.



Uses of Thiols

Thiols have come to occupy an important and unique position in the study of polymer synthesis and protection. They are used as important intermediates for various biochemical and in many other industrial applications. The applications of thiols are described below with a special emphasis to their applications in polymer chemistry.

1. As Chain Transfer Agent in the Polymerization of Unsaturated Compounds

Aliphatic thiols are extensively used in the polymerisation of unsaturated monomers to control the polymerisation and to give the product with required processing characteristics and properties. Thiols are used in the manufacture of industrially important rubbers based on acrylonitrile, styrene, butadiene[42,44,38] ethylene[45], styrene-butadiene graft copolymers[46] and neoprene rubber[47].

2) As Thermal Stabilizer for Synthetic Polymers

Thiols have been used in the stabilization of vinyl chloride polymers[48], polyamide fibres[49] and polyoxyphenylenes[47]. The discoloration prevention of PVC by the use of organo tin derivatives of thiols is well-known[4].

3) As Antioxidant

The antioxidant properties of thiols and their derivatives have been attributed to their ability for peroxide decomposition which helps in polymer stabilization. Thiol-antioxidants have been used for polyolefins, vinyl chloride polymer[50] and polyoxymethylenes[51]. Recently, Nakamura *et al.*[52] have described the use of thiol-s-triazine compounds as antioxidants for epichlorohydrin rubber.

4) As Vulcanizing Agent and Vulcanization Accelerator

The thermal vulcanization of epihalohydrin elastomers has been effected through polythiol[53]. Polythiols have been employed in radiation vulcanization of polydienes[54] and chlorobutyl elastomers[55]. Roos[23] has reported the use of mono, di and tri-sulphenyl chlorides as vulcanizing agents for natural rubber.

2-Mercaptobenzothiazole and derivatives constitute a well-known and important class of rubber vulcanization accelerators[56]. Ghatge and Patil[57] have synthesised accelerators from mercaptobenzothiazole disulfide and amine.

5) In Epoxy Resin Curing

Polythiols are among the important curing agents for epoxy resins[41]. Some of the polythiols used are mercapto acid esters of polyols, thiol- terminated polysulphide liquid polymers, cycloaliphatic and heterocyclic polythiols[34]. Many new polythiols have been used to cure epoxy resins at room temperature to give product with good flexibility, reduced water absorption and having desired hardness.

6) In Rubber Reclaiming Process

N,N'Dialkylarylamine sulphide[58] and sulphur containing compounds in combination with metal salt are used as reclaiming agents.

Ghatge and Patil[59] have prepared sulphur containing reclaiming agent for medium pressure reclaiming process.

7) For Shrink Proofing and Crease Resistant Finishing of Woolen and Cotton Fibers

Polythioglycolates and poly 3-mercapto propionates find wide application in shrink proofing and crease resistant finishing of woolen fibers. Some of the thiols used are thioglycolates of glycerols, trimethylol propane, pentaerythritol, polyalkylene diols and triols[60].

8) In Biological Research[61]

Mercaptans have been used as model compounds in understanding the reactivity of enzymes containing sulphydryl groups.

Miscellaneous Uses

9) Thiols find important uses in wide variety of [illegible] fields such as in photography, cosmetics, and hair waving preparation. Thiols are also important in the synthesis of bactericides, bacteriostate, pharmaceuticals, biocides, antidandruff agents and surfactants.

Present Investigation and Results

Thioglycolates, which are esters of polyhydric alcohols with mercapto carboxylic acids. are a class of thiol compounds of high industrial importance due to their ability and reactivity to take part in a wide variety of reactions. They occupy unique place in polymer chemistry as they can also act as catalyst, accelerator or chain transfer agent in polymer synthesis.

Among the thiol group containing organic polymers, thiol-terminated liquid polymers are of great industrial importance due to their facile oxidation with a wide variety of organic as well as inorganic oxidising agents to disulphide linkages at ambient temperature.

A new castor oil tristhioglycolate (COTT) synthesised by Ghatge and Murthy[20] from castor oil and thioglycolic acid was also susceptible for facile oxidation. Rubbery products were obtained by oxidative cure of COTT using lead peroxide (PbO_2) curing system. However, the rubbery products exhibited certain drawbacks like low elongation and high crosslinking density due to trifunctional nature of COTT. In the present investigation, a new castor oil dithioglycolate (CODT) was synthesised with a view to prepare elastomeric products with improved physical properties. The elastomeric products were prepared from CODT using manganese dioxide (MnO_2) as curing agent. Also, ethylene glycol bis(thioglycolate) (EBT) and polyethylene glycol-400 bis (thioglycolate) (PET-400) were prepared with a aim to obtain better elastomeric products from the combination of CODT and EBT and CODT and PET-400.

The silane coupling agents are known to enhance physical properties of elastomers when they are incorporated along with the fillers. In the present work, new silane coupling agent- castor oil silane(COS) was synthesised from castor oil and used for improvement in physical properties of elastomers obtained from CODT alone and CODT in combination with liquid polysulphide.

The following thioglycolates were prepared:

1. Castor oil dithioglycolate (CODT)
2. Ethylene glycol bis(thioglycolate) (EBT)
3. Polyethylene glycol-400 bis(thioglycolate) (PET-400)

Synthesis of Thioglycolates

Castor oil dithioglycolate was synthesised from difunctional castor oil (DCO) according to the scheme shown in Figure 19.

Preparation of Difunctional Castor oil[62] (DCO)

Castor oil is a mixture of 70% of tri and 30% of diglycerylricinoleate.

A number of methods such as acylation, benzolylation, methylation, dehydration and urethane formation are

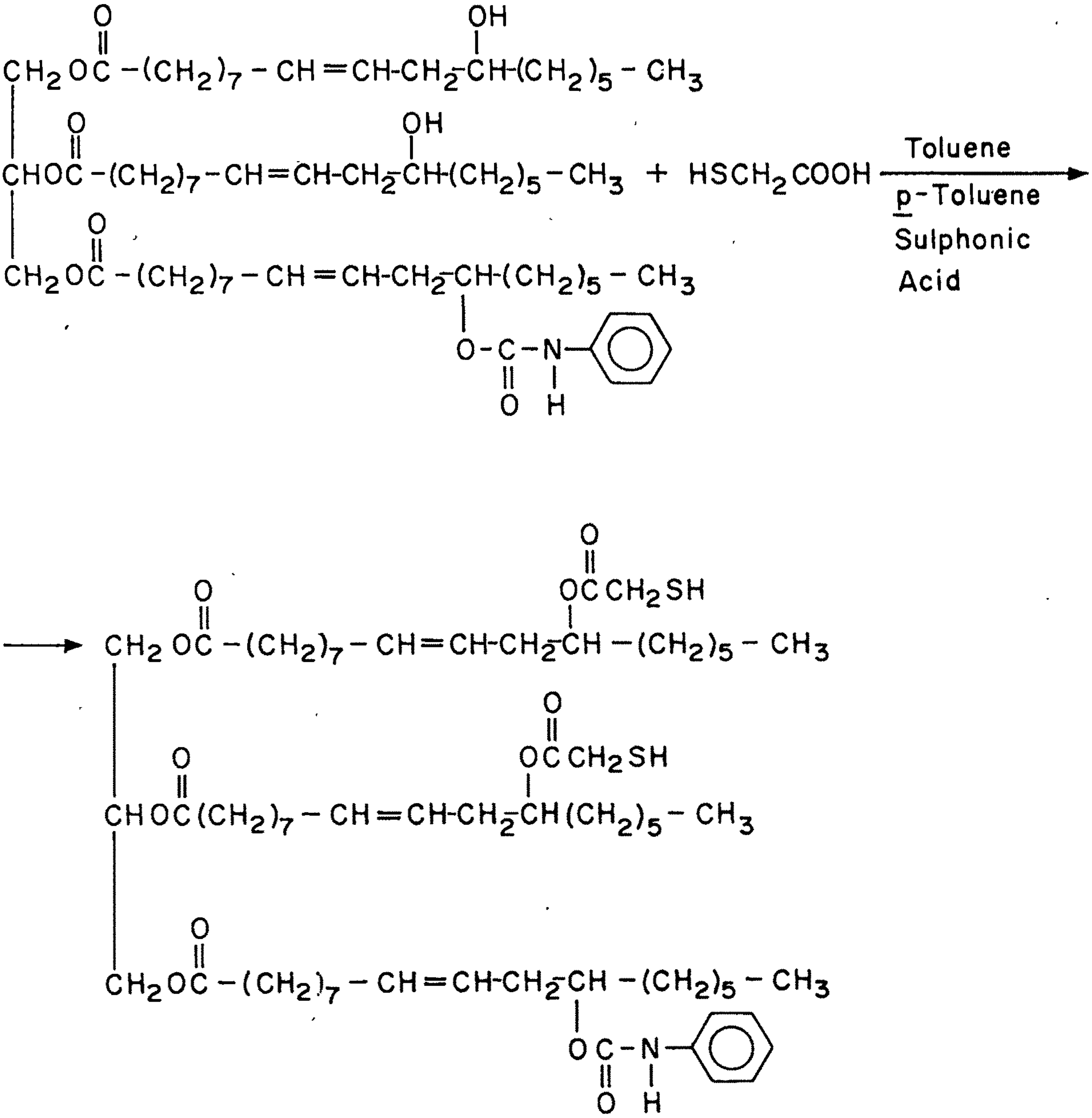


FIG. 19 : SCHEME FOR SYNTHESIS OF CASTOR OIL DITHIOGLYCOLATE.

known to block one of the hydroxyl groups of castor oil. In the present investigation, one of the hydroxyl groups of castor oil was blocked by reacting one mole of castor oil (2.7 equivalent of OH) with 0.7 mole of phenyl isocyanate assuming that the major part of phenyl isocyanate would react with one of the hydroxyl groups of 70% triglycerylricinoleate[60].

Thus, 1 mole (2.7 equivalent) of dried castor oil was heated to 100°C with stirring and then phenyl isocyanate was added dropwise during ½ h and continued heating at 100°C for 1 h. The reaction product was dried under vacuum. The physical properties of DCO and of castor oil are given in Table 24.

The major advantages of using this method are: (1) Blocking of the hydroxyl group can be done at low temperature in short time and (2) No further treatments like washing etc. of the final product are necessary.

Synthesis of Castor Oil Dithioglycolate

Thioglycolic acid (2.5 mole) was added dropwise to solution of DCO (1 mole) in toluene (400 ml) at 90°C during 15 min. with stirring. Thioglycolic acid addition was followed by the addition of _p_-toluenesulphonic acid (1.5%w/w of polyol). The reaction mixture was refluxed with azeotropic removal of water. The reaction mixture was repeatedly washed with hot water, dried over

Table 24

Properties of Difunctional Castor Oil and Castor Oil

No.	Property	Difunctional castor oil	Castor oil
1.	Appearance	Viscous liquid	Viscous liquid
2.	Colour	Brown	Yellow
3.	Specific gravity	0.9725	0.9666
4.	Refractive index at 25°C	1.483	1.474
5.	Viscosity cps at 25°C	900	575
6.	Acid number	1.67	1.35
7.	Hydroxyl number, mgm KOH/g	118.0	166.6

anhydrous sodium sulphate and after the solvent removal, dried under vacuum. The product was characterized by elemental analysis, viscosity, refractive index and SH content[63] and the molecular weight was determined from SH content (Tables 25 and 26). Figure 20 shows the IR spectrum of CODT.

Thioglycolatesof ethylene glycol (EBT) and polyethyleneglycol-400 (PET-400) were prepared similarly and characterised (Table 25 and 26).

Castor Oil Silane (COS)

Castor oil silane was synthesised as follows: First, dry castor oil was reacted with trichlorosilane in dry benzene to obtain chlorosilane derivative of castor oil. The addition of trichlorisilane to castor oil was done at low temperature with stirring. The temperature of reaction mixture was gradually increased to 50°C and maintained for 4 h. The unreacted trichlorosilane was removed under reduced pressure. The IR spectrum of chlorosilyl derivative of castor oil (CSCO) is depicted in Fig. 21. The chlorosilyl derivative was further converted to methoxysilyl derivative of castor oil by reacting it with dry methanol in dry benzene. For complete conversion of CSCO to methoxysilyl castor oil, the procedure was repeated twice. The compound obtained was stored under dry conditions as it was found to be sensitive to atmospheric moisture. The IR spectrum of COS is given in Fig. 22.

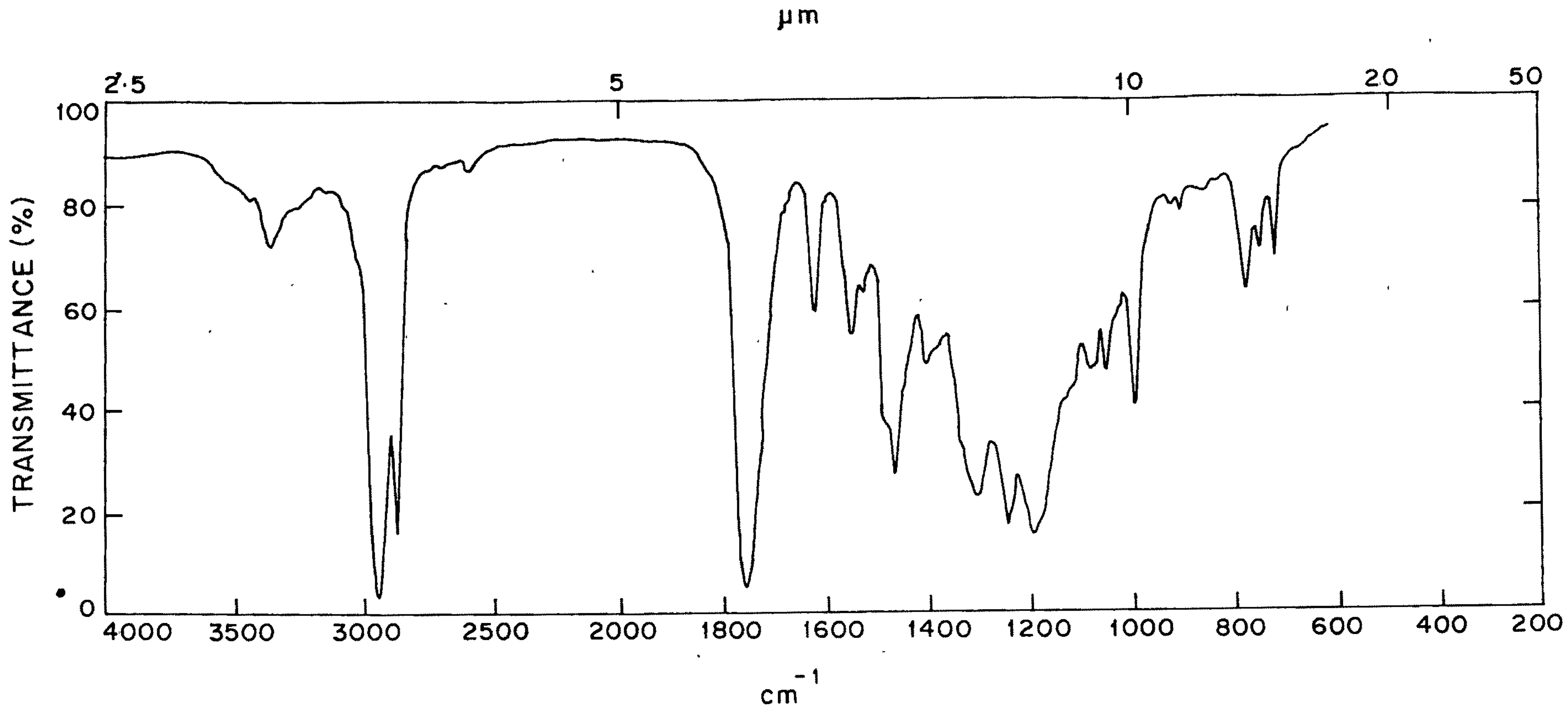


FIG. 20 : IR SPECTRUM OF CASTOR OIL DITHIOGLYCOLATE .

Table 25

Physical Properties of Castor Oil Dithioglycolate, Ethylene Glycol Bis(Thioglycolate) and Polyethylene Glycol- 400 Bis (Thioglycolate)

No.	Compound	Yield %	Boiling point °C mm Hg	Density g/ml	Refractive index at 25°C	Viscosity* cps at 25°C		Elemental analysis			
								C %	H %	N %	S %
1.	Difunctional castor oil	91	-	0.972	1.483	900	Calcd:	72.80	10.37	1.33	-
							Found:	73.20	10.40	1.28	
2.	Castor oil dithioglycolate	90	-	1.493	1.493	1700-1800	Calcd:	68.00	9.23	1.33	5.3
							Found:	67.33	9.44	1.04	6.02
3.	Ethylene glycol bis(thioglycolate)	89	148/3	1.330	1.514	-	Calcd:	34.28	4.76	-	30.40
							Found:	34.81	5.14	-	29.90
4.	Polyethylene glycol-400 bis(thioglycolate)	81	-	1.227	1.492	-	Calcd:	46.92	7.40	-	11.39
							Found:	47.13	7.72	-	11.60

*Brookfield viscosity

Table 26

Thiol Content and Molecular Weight Data of Thioglycolates

No.	Thioglycolate	Molecular formula	SH content		Molecular weight	
			Calcd	Found	Calcd.	Found
1.	Ethylene glycol bis (thioglycolate)	$C_6H_{10}O_4S_2$	31.49	31.61	210	209.1
2.	Polyethylene glycol-400 bis(thioglycolate)	$C_{22}H_{42}O_{12}S_2$	11.77	11.90	562	555.6
3.	Castor oil dithioglycolate	$C_{68}H_{113}O_{12}S_2N$	5.31	4.90	1245	1346

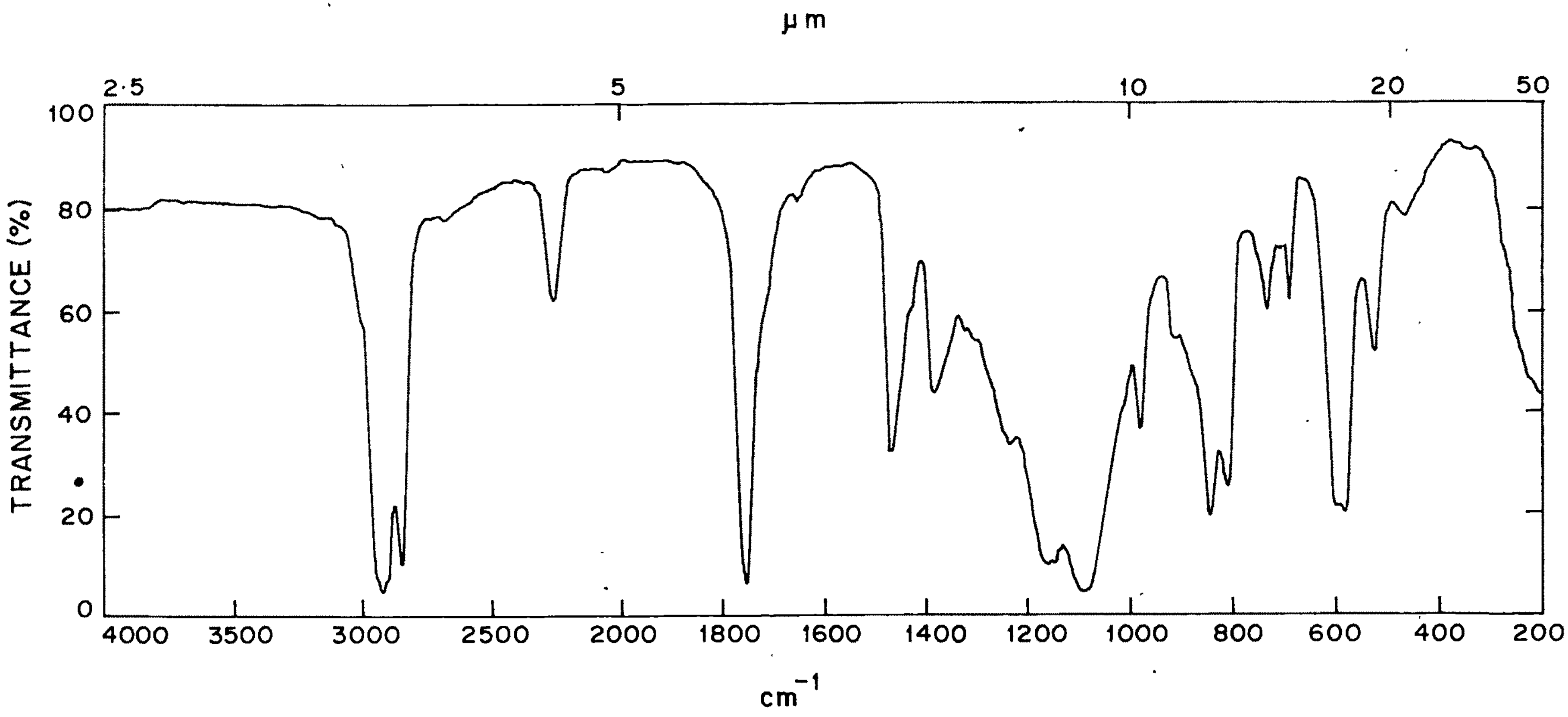


FIG. 21 : IR SPECTRUM OF CHLOROSILANE DERIVATIVE OF CASTOR OIL.

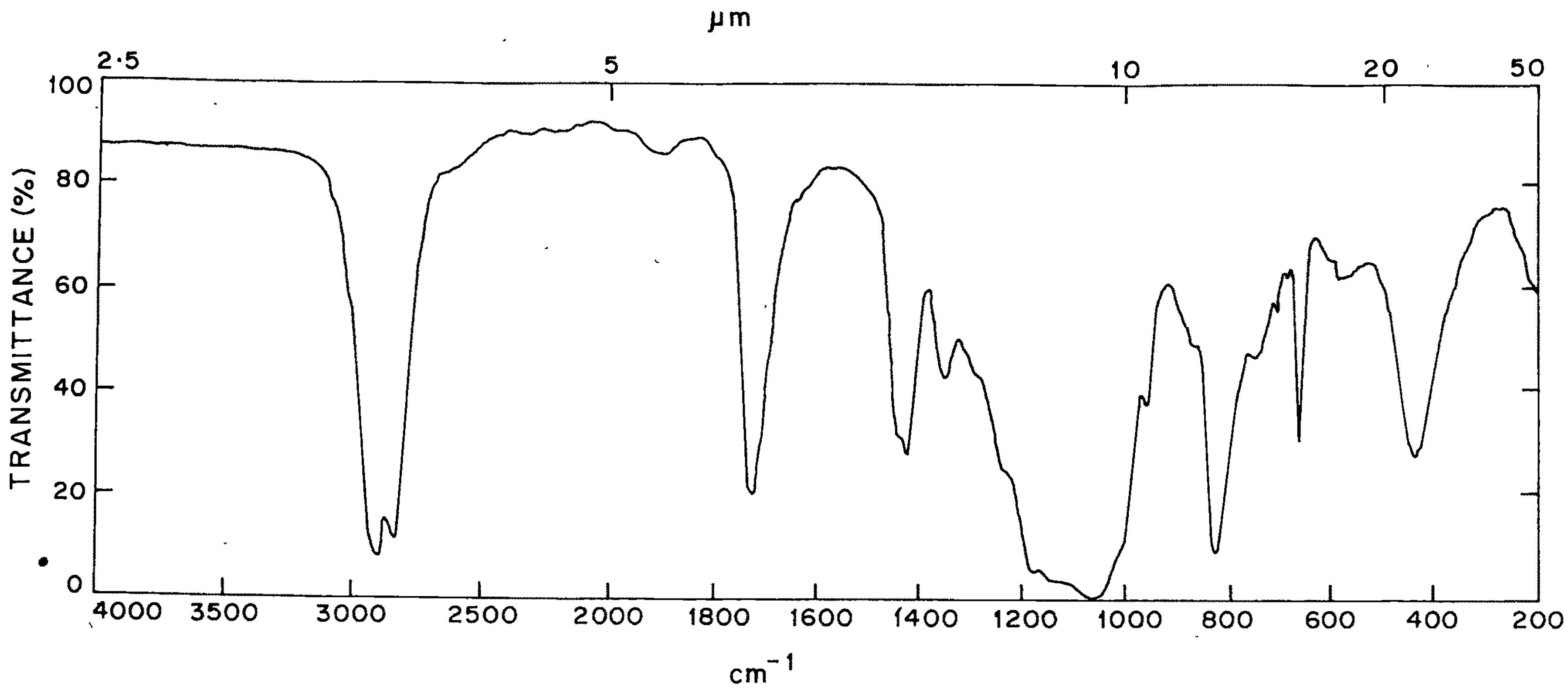


FIG. 22 : IR SPECTRUM OF METHOXYSILYL DERIVATIVE OF CASTOR OIL.

DISCUSSION

In the present study castor oil dithioglycolate was synthesized from difunctional castor oil and thioglycolic acid and utilized as a room temperature setting elastomeric product using oxidative cure. Also, EBT and PET-400 were prepared from ethylene glycol and polyethylene glycol-400, respectively.

These thioglycolates were characterized by elemental analysis, refractive index, SH content[61] and by IR spectroscopy. The physical properties and spectral information supported the structures assigned to them. The IR spectrum of CODT (Figure 20) shows absence of hydroxyl band at 3400 cm^{-1} and appearance of a new band at 2570 cm^{-1} of low intensity characteristic of SH group. The band at 1720-1750 cm^{-1} is due to carbonyl group and bands at 3350 cm^{-1} and 1520 cm^{-1} are due to N-H stretching and N-H bending respectively. The double bonds in triglyceryl-ricinoleate are of <u>cis</u> configuration which can be detected by broad band at 690 cm^{-1} in the castor oil spectrum[64]. However, on esterification the band at 690 cm^{-1} became less intense and a sharp band of medium intensity appeared at 970 cm^{-1} which is characteristic of double bond with <u>trans</u> configuration [64]. It may be concluded therefore that <u>cis-trans</u> isomerization accompanies the esterification reaction in CODT,a phenomenon which has also been observed by Ghatge and Murthy during the synthesis of COTT[20]. Thus, CODT contains both *cis* and *trans* double bonds.

The chlorosilyl derivative of castor oil (CSCO) was readily obtained by reacting castor oil with trichlorosilane and the methanolysis of the resulting CSCO afforded methoxysilyl derivative of castor oil (COS). IR spectrum of CSCO (Fig. 21) shows complete disappearance of hydroxyl group at 3400 cm^{-1} and appearance of new bands at 845 cm^{-1} and in the 600-550 cm^{-1} region characteristics of Si-C and Si-Cl stretching, respectively.

The IR spectrum (Fig. 22) of COS shows absence of Si-Cl bands in the 600-550 cm^{-1} region indicating that Si-Cl groups were converted to $Si\text{-}OCH_3$ groups by alcoholysis. The *cis* *trans* double bond isomerization as observed in the preparation of CODT was also observed in the preparation of COS. Thus, IR spectrum of COS shows a weak band at 970 cm^{-1} due to *trans* C=C and a sharp band at 690 cm^{-1} due to cis C=C .

EXPERIMENTAL

Materials

Castor oil was procured from local market and dried at 90°C/20 mm Hg for 3 h.

Ethylene glycol and polyethylene glycol - 400 were obtained from M/s. NOCIL, Bombay (India).

Phenyl isocyanate was procured from Fluka AG, West Germany.

p-Toluenesulfonic acid was used as received.

Thioglycolic acid (80%) was purchased from Veblabor Chemie, Apolda, Germany and used as received. Trichlorosilane (b.p. 31°C) was distilled before use. Silver nitrate was used as received. Solvents, such as benze, toluene etc. were purified by known methods.

Preparations :

Difunctional Castor Oil

In a 500 ml three necked round bottomed flask equipped with a mechanical stirrer, a dropping funnel with calcium chloride guard tube and a thermowell castor oil 93.2 g (0.1 mole) was placed and heated in an oil bath upto 100°C with stirring. Then, 7.08 ml (0.7 equivalent) phenylisocyanate was added dropwise with vigorous stirring during 30 min. The stirring was continued for 1 h with heating at 100°C. The resulting reaction product was dried at 100°C/5 mm Hg for 1 h.

The product was characterised by IR spectrum and elemental analysis. The physical properties are given in Table 24.

Castor Oil Dithioglycolate

A 100 ml three necked, round bottomed flask fitted with a mechanical stirrer, a thermowell and a Dean and Stark arrangement for azeotropic removal of water, was charged with 400 ml of toluene and 105.1 g (0.1 mole) difunctional castor oil. The reaction flask was heated to 85-90°C with constant stirring and then 28.5 g (0.25 mole) of thioglycolic acid was added slowly during 15 min. The acid addition was followed by the addition of p- toluenesulfonic acid (1.57 g [illegible]). The contents were refluxed with continuous stirring to remove water azeotropically. After all the water was removed, the refluxion was continued further for 25 h. The reaction was monitored by IR spectroscopy. The disappearance of OH band at 3400 cm^{-1} and appearance of new weak band at 2570 cm^{-1} due to SH in the IR spectrum indicated the completion of the reaction. Then the reaction mixture was cooled, washed several times with hot water and then dried over anhydrous sodium sulphate. After filtration, the solvent was removed under reduced pressure and the product was dried under vacuum at 30°C/5 mm Hg.

The physical properties of CODT are given in Table 25.

Ethylene glycol Bis (Thioglycolate) (EBT)

In a three necked 500 ml round bottomed flask equipped with a mechanical stirrer, a thermometer and a Dean and Stark arrangement for azeotropic removal of water, toluene (150 ml), ethylene glycol (6.2 g, 0.1 mole) and thioglycolic acid (28.5 g 0.25 mole) were placed. The reaction mixture was refluxed till all the water was removed (10 h). The contents of the flask were cooled, washed with hot water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the compound was purified by distillation under reduced pressure.

The physical characteristics of EBT are given in Table 25.

Polyethylene glycol - 400 Bis(Thioglycolate) (PET-400)

Polyethylene glycol-400 bis(thioglycolate) was prepared by similar procedure employed for ethylene glycol bis (thioglycolate).

The physical properteis are included in Table 25.

Estimation of Thiol Content and Determination of Molecular Weight

A weighed amount of the sample (0.1 g) was dissolved in pyridine (15 ml) and 15 ml aqueous silver nitrate solution (5%) was added by pipette. The flask was stoppered and kept aside for 5 min. Then 100 ml of distilled water was added at the end of this period and the content was titrated against standard sodium hydroxide solution using phenolphthalein as indicator.

Calculations

$$\% \text{ SH} = \frac{\text{V.N. } (33.06) \times 100}{1000 \text{ W}}$$

Where V = Volume of NaOH required for the sample
N = Normality of NaOH solution
W = Weight of sample in gm

Note = In these titrations blank correction is not necessary because a simple mixture of silver nitrate and pyridine was found to be sensitive to one drop of NaOH solution.

Molecular weight

The molecular weight was calculated from the SH group content using the relation.

$$M = 100 \text{ ZE/e}$$

Where Z = Number of end groups per molecule
E = Molecular weight of the end group
e = Experimentally found content of the end group (-SH) in percent.

Castor Oil Silane

In a 250 ml three necked round bottomed flask, fitted with a reflux condenser, a dropping funnel and a thermowell 9.32 g (0.01 mole) of dry castor oil and dry benzene (50 ml) were placed and stirred with magnetic stirrer. The contents of the flask were cooled to 15°C and 4.73 g (0.35 mole) of trichlorosilane was added dropwise during 15 min. Then temperature of the reaction mixture was increased gradually to 50°C and maintained till the evolution of HCl ceased (4 h). Then the unreacted trichlorosilane and benzene were removed under reduced pressure (CSCO).

The chlorosilane derivative was further converted to methoxysilyl derivative by methanolysis.

In a 250 ml three necked round bottomed flask fitted with a reflux condenser, a dropping funnel and a thermowell 12.26 g (0.01 mole) of chlorosilane derivative of castor oil and 30 ml of benzene were placed and stirred with magnetic stirrer. The contents of the flask were cooled to 20° and then 2.88 g (0.09 moles) of methanol was added slowly with stirring when the addition was over, the temperature of the reaction mixture was raised to 50°C and maintained for 3 h. Then benzene was removed. The procedure was repeated twice to ensure complete conversion of $SiHCl_2$ group to $Si(OCH_3)_3$ group. After the solvent removal the product was stored under dry condition as it was found to be sensitive to atmospheric moisture.

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Section B

Room Temperature Setting Elastomeric Materials
from
Castor Oil Dithioglycolate

INTRODUCTION

The propensity for facile oxidation of thiols to disulphide structure with a wide variety of organic and inorganic oxidising agents is an important characteristic for their wide applications in the industries. Among thiols, thiol-terminated liquid polymers find wide utilization in sealant industries. Thiol-terminated polymers form high molecular weight solid rubbery products by the action of oxidizing agents[1]. This is explained on the basis of oxidation of terminal thiol groups to disulphide structure.

Polymers obtained by oxidative cure are of more utility since the oxidation process does not result in the introduction of oxidant fragments into the polymer backbone. The presence of curing agent fragment in the polymer backbone have undesirable effects on the final properties of the cured products. The following classes of oxidising (curing) agents are used in the oxidation process of thiol group containing compound[2].

1. Metal oxides, such as oxides of lead, zinc, magnesium, calcium, barium, iron, cobalt and copper.
2. Metal peroxides such as peroxides of lead, zinc, magnesium, calcium, manganese, tellurium, selenium, tin, iron, arsenic and antimony.

3. Inorganic oxidizing agents such as chromates, dichromates and perchlorates of sodium and potassium.

4. Organic peroxides such as benzoyl and dicumyl, cumene and t-butyl hydroperoxide and t-butyl perbenzoate.

5. Other organic oxidizing agents such as mono and polynitro derivatives of benzene, trinitrotoluene, p-quinone dioxime, organic titanates, borates, silicates, quinones, reactive phenols, di- and polyisocyanates and epoxides.

A brief account of the curing action of some of the above mentioned curing agents is given below:

1. Metal Oxides

Generally, the compounds of this class are not very active and leads to the formation of mercaptide structures with metal atom in the main chain when thiols are cured with metal oxides e.g. reaction with zinc oxide can be shown as follows:

$$2\ RSH + ZnO \longrightarrow Rs\text{-}Zn\text{-}SR + H_2O$$

The satisfactory cures are possible with oxides of zinc, manganese, calcium, cadmium, cobalt and copper when processed at 158°F for longer time.

2. Metal Peroxides

The complete cure of thiols are obtained by using these compounds. Lead peroxide is generally used for the curing of thiols at room temperature as well as at elevated temperature[3-5]. The reaction of lead peroxide with thiol group, as a typical example of curing by inorganic peroxide, may be shown as:

$$2RSH + PbO_2 \longrightarrow RSSR + PbO + H_2O \qquad (i)$$

$$2RSH + PbO \longrightarrow RSPbSR + H_2O \qquad (ii)$$

$$RSPbSR \longrightarrow RSR + PbS \qquad (iii)$$

$$RS.Pb.SR + PbO_2 \longrightarrow RSSR + 2PbO \qquad (iv)$$

The presence of mercaptide bonds introduces number of defeciencies[3] such as loss of adhesion and weight loss by cyclodepolymerization reaction. These drawbacks can be minimised by incorporation of small amount of sulphur. The reaction of mercaptide with sulphur may be shown as:

$$RSPbSR + S \longrightarrow RS\text{-}SR + PbS$$

The presence of disulphide linkage is essential for good chemical resistance. Oxidative cure with tellurium dioxide, manganese dioxide and various chromate salts are reported with fewer side reactions than lead peroxide. The reaction of thiol with manganese dioxide can be illustrated as follows[6]:

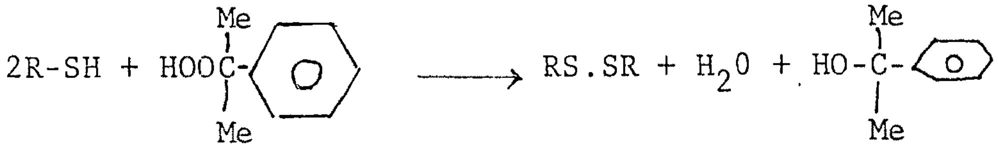
$$RSH + Mn\overset{iv}{O_2} \longrightarrow RS\ HOMnO^{iii} \qquad (i)$$

$$RSH + Mn\overset{iv}{O_2} \longrightarrow RS + Mn^{ii}O + H_2O \qquad (ii)$$

$$2RS \longrightarrow RSSR \qquad (iii)$$

3. Organic Peroxides

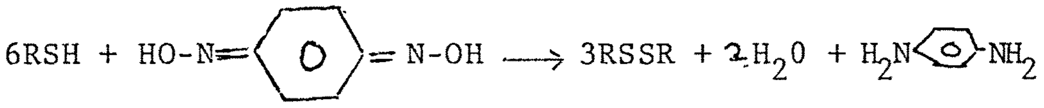
The curing of thiols with cumene hydroperoxide can be shown as:



Diphenyl or triphenyl guanidine is generally used as activator for cumene hydroperoxide.

4. Dioximes

p-Quinone dioxime gives effective cure for low molecular weight thiol-terminated polymers.



5. Epoxy Resin and Polyisocyanates

Curing of thiols with epoxy resins and polyisocyanates is widely used in sealant combinations because in these reactions side products are not formed.

Present Investigation and Results

The present study aims to prepare room temperature setting elastomers from castor oil dithioglycolate using oxidative cure, Manganese dioxide was selected as curing agent for CODT as it gives better physical properties to the vulcanizates. The effect of manganese dioxide as curing agent on the physical properties of the cured products obtained from CODT alone and in combination with EBT, PET-400 and commercially available liquid polysulphide LP-33 were studied (Tables 28 and 29).

For preparation of curing paste, commercially available MnO_2 as well as magnetite coated MnO_2, prepared by the known method[7] was used. The particle size of MnO_2 was measured by Electron Scanning Microscope (Fig. 23). The MnO_2 content of commercial MnO_2 and magnetite coated MnO_2 was determined by reported method. These results are given below:

	Commercial MnO_2	Magnetite coated MnO_2
Particle size	0.638	0.563
MnO_2 content	70.81%	61.8%
pH	7.2	8.5

Preparation of Curing Paste

The recipe for curing paste is given in Table 27. The curing paste was prepared from both MnO_2 samples.

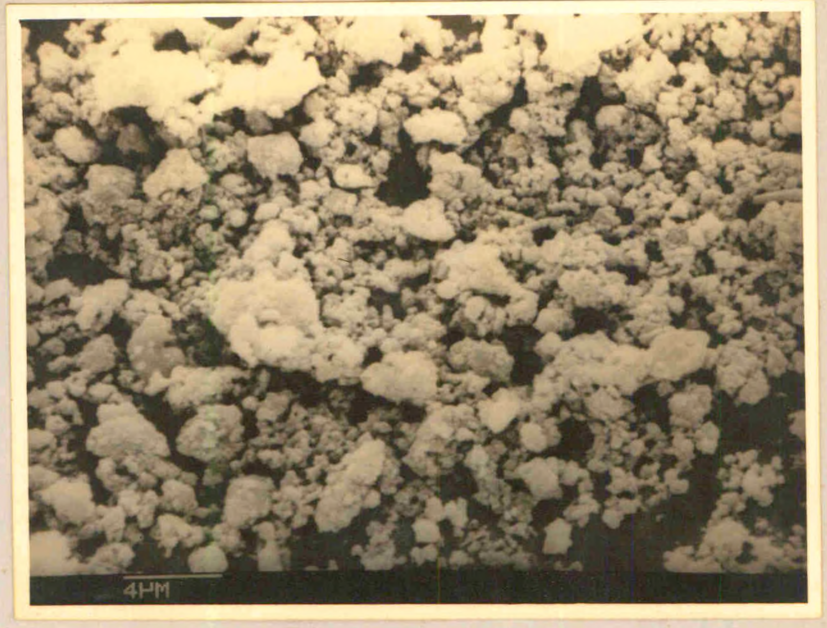


FIG.23 SCANNING ELECTRON MICROGRAPH
OF
COMMERCIAL MnO_2

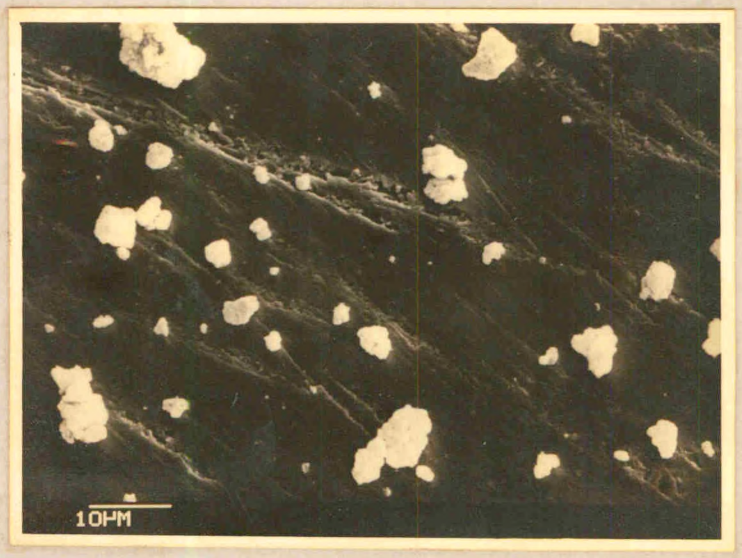


FIG.23 SCANNING ELECTRON MICROGRAPH
OF
MAGNETITE COATED MnO_2

Table 27

Recipe of Curing Paste

No.	Component	Amount taken in gms
1.	Manganese dioxide	50
2.	Dibutyl phthalate	45
3.	Stearic acid	3

First, stearic acid was dissolved in hot dibutyl phthalate and mixed thoroughly. After cooling, MnO_2 was added with stirring. Finally, a fine paste was obtained by mixing it on the paint mill.

The effect of reinforcing fillers on physical properties of vulcanizates is also significant. In the present study semireinforcing carbon black (SRF) and medium thermal carbon black (MT) were used as fillers and their effects on the physical properties of vulcanizates obtained from CODT alone and in combination with polysulphide were studied (Tables 28 and 29).

The newly synthesised silane coupling agent from castor oil was incorporated with CODT and in combination of CODT with LP-33 to promote the physical properties of the elastomers obtained therefrom by oxidative cure (Table 31).

Compounding and Testing

The mixing ratios of CODT, liquid polysulphide, filler and curing paste is given in Table 28.

The amount of curing paste added was calculated from the reported formula[8].

The initial mixing of component I for all the systems from Table 28 was carried out in a pug mixer and finally on three roll paint mill till a creamy consistency was obtained. A number of mixes were prepared by mixing components I, I and II (Table 28).

Table 28

Mixing Ratios of CODT, CODT-EBT, CODT-PET-400 and CODT - Liquid Polysulphide (LP-33)

			Component I				Component I	Component III
System	CODT (g)	EBT (g)	PET-400 (g)	LP-33 (g)	Carbon black (g)		Curing paste*	Diphenyl guanadine (g)
					SRF	MT	(g)	
A	100	-	-	-	30	-	19.00	0.40
	100	-	-	-	50	-	19.00	0.40
B	100	-	-	-	-	30	19.00	0.40
	100	-	-	-	-	50	19.00	0.40
C	100	10	-	-	30	-	19.5	0.40
	100	10	-	-	50	-	19.5	0.40
D	100	-	10	-	30	-	19.5	0.40
	100	-	10	-	50	-	19.5	0.40
•	100	-	-				19.5	0.40
E 1)	75	-		25	30	-	19.5	0.40
	75	-	-	25	50	-	19.5	0.40
2)	100	-	-	100	30	-	20	0.40
	100	-	-	100	50	-	20	0.40

System C Components gelled while mixing. Therefore specimen could not be drawn.

*Curing paste was prepared from commercial MnO_2

Table 29

Physical Properties of Cured Vulcanizates from CODT, CODT-PET-400 and CODT-LP-33

System	Carbon black % SRF	Carbon black %MT	Tensile strength (MPa)	Elongation %	Residual elongation %	Shore A hardness	Pot life (h)
A	30	-	1.05	100	5	35	4
	50	-	1.12	120	5	40	3
B	-	30	0.97	90	3	30	4½
	-	50	1.03	105	3	30	4
D	30	-	1.02	100	3	32	3½
	50	-	1.04	110	4	37	3
E (1)	30	-	1.00	140	2	30	2
	50	-	1.10	180	2	35	1.5
(2)	30	-	1.3	250	4	30	1
	50	-	1.4	210	4	30	0.75

Table 30

Physical Properties if Cured Vulcanizates from CODT using Commercial/Magneite Coated $Mn0_2$

CODT	Carbon black % SRF	Curing Paste		DPG in g	Tensile strength in Mpa	Elongation %	Shore A hardness	Pot life in h
		$Mn0_2$ in g	Magnetite coated $Mn0_2$ in g					
100	30	19	-	0.4	1.05	100	35	4
100	50	19	-	0.4	1.12	120	40	3
100	30	-	19	0.4	0.98	95	30	1½
100	50	-	19	0.4	1.01	100	30	1

The pot life of each system is given in Table 29.

The mixing ratios of CODT, liquid polysulphide, filler, curing paste and silane coupling agent are given in Table 31. Silane coupling agent was added on the weight basis of filler. It was added before the addition of DPG (Table 31).

For determination of physical properties sheets were prepared from Π shaped template (11 cm x 3 cm x 0.2 cm) and cured at room temperature (29°C) for 24 h. and then thermostated for 24 h at 70°C. Dumbbell shaped specimens were cut from the cured samples and tested for tensile strength, elongation and hardness according to ASTM designation D412-68 and D2240-68. The results are given in Tables 29,30 and 31.

Table 31

Effect of Silane Coupling Agent on Physical Properties of Vulcanizates from CODT and CODT-LP-33 Combination

CODT in g	LP-33 in g	Carbon black(SRF) (in g)	Curing* paste in g	Silane coupling agent		DPG in g	Tensile strength in MPa	Elongation %	Shore A hardness	Pot life h
				COS	A-1100					
100	-	30	19	-	-	0.4	1.05	100	35	4
100	-	30	19	0.5	-	0.4	1.15	100	40	2
75	25	30	19.5	-	-	0.4	1.00	140	30	2
75	25	30	19.5	0.5	-	0.4	1.3	145	30	2
100	-	30	19	-	0.5	0.4	1.4	105	45	1½
100	25	30	19.5	-	0.5	0.4	1.55	150	45	1

* Commercial MnO_2

DISCUSSION

The petroleum crisis has created uncertainties concerning the availability and price of monomers on which synthetic rubbers are based. The emphasis is now centered on the use of renewable resource for industrial needs. Thus, the availability of reactive liquid materials from renewable resources which could be converted into elastomeric products appear attractive and offers various opportunities in present energy crisis situation.

Polythiols can be easily converted into polymeric structure by curing them with a wide variety of inorganic and organic oxidising agents.

It has been reported in the literature that MnO_2 gives oxidative cure with a fewer side reactions than PbO_2. Thus, in the present study MnO_2 was used as the curing agent for CODT.

Combination of CODT with EBT was done with a view to improve the physical properties of elastomers obtained therefrom using manganese dioxide as curing agent (Table 28). However, gelling occured immediately when curing paste was added to CODT and EBT mixture. This may be explained on the basis of higher reactivity of EBT due to its low molecular weight. There was not much improvement observed in physical properties of elastomers obtained from the combination of CODT and

PET-400 (Table 29). Then our next choice was LP-33.

CODT and LP-33 were mixed in various proportions. On gradual increase in the ratio of LP-33 to CODT, a corresponding increase in tensile strength and elongation of elastomers was observed (Table 29). The cured specimens of CODT alone exhibited low tensile strength which could be due to the presence of long alkyl chain in its molecule which might be reducing the effectiveness of the intermolecular forces between the chains.

The reinforcing fillers also have significant effect on physical properties of cured products. Thus, SRF carbon black reinforced elastomers exhibited higher tensile strength than the MT carbon black reinforced elastomers (Table 27). Higher loading of fillers showed marginal effect on the physical properties of the cured elastomers.

The oxidative cured products obtained from CODT using manganese dioxide curing paste prepared from commercial manganese dioxide exhibited better tensile strength and elongation than magnetite coated manganese dioxide (Table 30). This may be due to higher % of manganese dioxide content present in commercial manganese dioxide and its less alkalinity.

When castor oil silane was used as coupling agent for promotion of reinforcement between filler and elastomer, considerable increase in reinforcing properties of the elastomers was observed. The incorporation of commercial silane coupling agent A-1100 in combination of CODT and LP-33 showed higher reinforcement in properties than castor oil silane (Table 31).

EXPERIMENTAL

Materials

Castor oil dithioglycolate: Synthesis and characterization is given in Section A.

Liquid polysulphide LP-33 was obtained from Thiokol Corporation, New Jersey, USA.

Manganese dioxide was procured from M/s. Hindustan Mineral Products, Bombay (India).

Magnetite coated manganese dioxide was prepared by reported method.

SRF carbon black and MT carbon black were used as received.

Dibutylphthalate, stearic acid and diphenyl guanidine (DPG) were ISI rubber grade chemicals and used without further purifications.

Preparations

Curing Paste

In a 250 ml beaker, DBP (45 g) was taken and heated to 90°C and then stearic acid (3.0 g) was added followed by addition of 50 g manganese dioxide. Initially, these components were mixed in pug mixer and then finally on three-roll paint mill till a creamy consistency was obtained.

surface. The compound was levelled in the direction of length. Afterwards the template was removed and the sheet was allowed to dry at room temperature (29°C) for 24 h and then thermostatedat 70°C for 24 h. Dumbbell shaped specimens were cut from the cured specimens and tested for elongation, tensile strength and hardness according to ASTM designation D 412-68 and D 2240-68.

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Section C

Evaluation of Castor Oil Dithioglycolate as a Flexibilizer for Epoxy Resin

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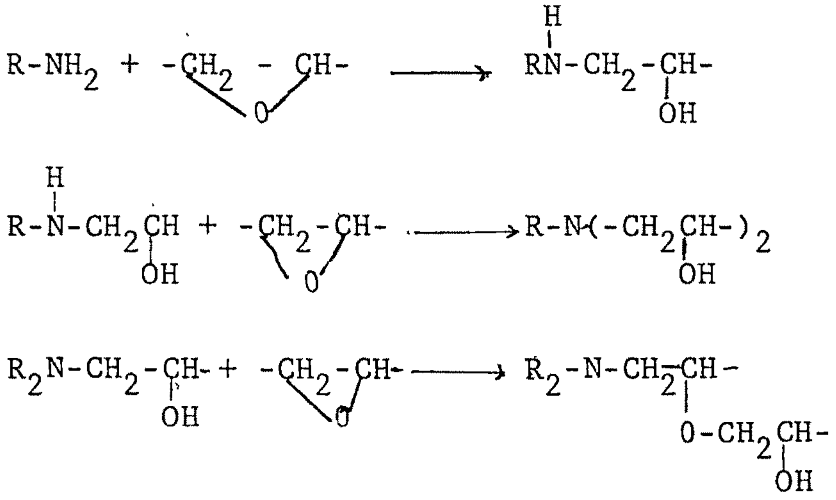
INTRODUCTION

Epoxy resins contain both epoxy terminal groups and pendant hydroxyl groups and are cured according to the available sites in a given resin. The curing of epoxy resin is a process of transformation of epoxy resin into a infusible crosslinked structure. This process of transformation is used for various industrial applications to obtain desirable properties according to their end uses. The curing takes place either by the reaction between the epoxide molecules themselves or by the reaction between the epoxide group and other reactive molecules with or without the help of a catalyst i.e. either by homopolymerization or by polyaddition reaction[1]. Depending on the curing agent and curing conditions it is possible to obtain products having high electrical insulating properties, good thermal resistance, mechanical properties ranging from flexibility to high strength and solvent resistance. Polyaddition reactions take place by curing agents such as polyamines, polyamides, polymercaptans, polyacids, anhydrides and polyphenols. A brief account of the curing process by some of the above mentioned curing agents is given below.

Curing of Epoxy Resins with Polyamines

Polyamines are most widely used for curing of epoxy resins which contain aliphatic, aromatic, cycloaliphatic and heterocyclic groups. Curing occurs by chain extension process. The amine is incorporated into the structure of the crosslinked polymer and forms part of the backbone.

The reaction of an amine with an epoxide group may be represented[2,3] as



Polyamines may be aliphatic or aromatic. Aromatic amines react with epoxy group at a slower rate than the aliphatic amines. Aromatic amines although require elevated curing temperatures provide good solvent resistance and high heat distortion temperature to the cured system. Recently, siloxane-containing polyalkylene polyamines have been used as curing agent which increase the surface hardness[4-6]. Ghatge and Murthy[7] have synthesised new aminofunctional curing agents from polythiol, paraformaldehyde, diethylene triamine, phenol and 3-pentadecadienyl phenol and studied the curing of epoxy resin at room temperature and at 50°C.

Curing of Epoxy Resins with Polyamides

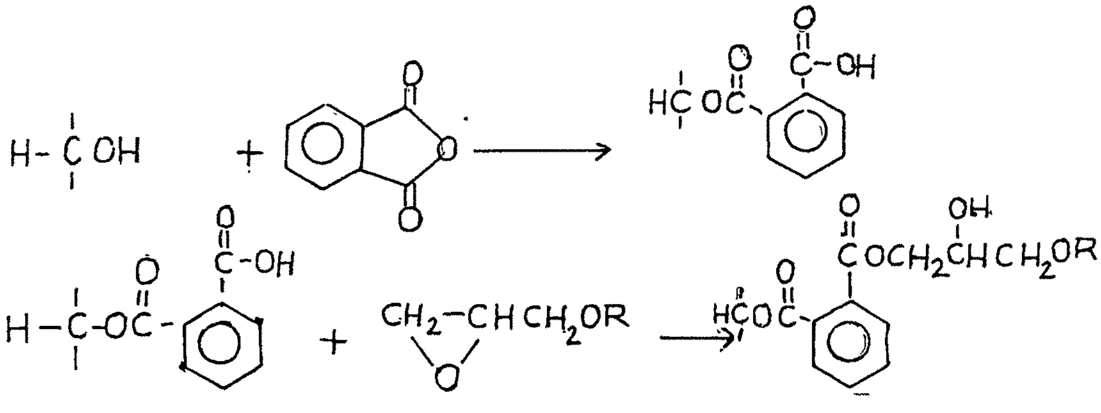
Polyamides are used for epoxy resin curing to achieve lower toxicity, good water resistance, improved flexibility and longer pot life. Modified polyamides i.e. polyamidoamines resulting from the reaction of polymeric fatty acids and amines are extensively used as hardner for epoxy resins[8-10].

Curing of Epoxy Resins with Polyphenols

Curing of epoxy with novolac resins is known in the literature[11]. Curing takes place in presence of catalysts which include inorganic bases, nitrogeneous bases and stannous salts[12].

Curing of Epoxy Resins with Carboxylic Acids and Anhydrides

Carboxylic acids or anhydride cured epoxy resins find wide applications in coating, laminates, adhesives and molding powder. The reaction can be represented as follows[13-15].



Curing of Epoxy Resins with Polythiols

Polythiols are important curing agents for epoxy resin which give cured product with reduced water absorption as well as desired hardness. Thiol-terminated polysulphide polymers are most widely used in epoxy resin technology[16]. The other polymercaptan curing agents include mercapto-carboxylic acids and their esters,[17,18] polyether thiols[19] and cyclo-aliphatic polythiols. Cycloaliphatic polythiols are used in the curing of epoxy resin for preparation of enamels, paints, potting compositions, casting laminates and adhesives[20,22].

Present Investigation and Results

Epoxy resins are inherently hard and brittle in the cured state. The reaction of epoxy resin with liquid polysulphide polymer at room temperature results in flexible compound which has excellent properties for casting and embedment application[23]. Polysulphides, in addition to their flexibilizing action, co-cure with the epoxy resin in the presence of catalyst which is either amine or an acid anhydride thus, offering a wide range of property control applications. These applications include high impact strength, good stress and strain properties, dimensional stability and resistance to most solvents and chemicals. Mercapto carboxylic acids and their esters, polyetherthiols, reaction product of hydrogen sulphide with diglycidyl ether[24] and cycloaliphatic thiols are also used as modifier /flexibilizer for epoxy resin.

In the present investigation, an attempt has been made to explore the possibility of use of castor oil dithioglycolate (CODT), a dithiol obtained from castor oil- a renewable resource material as a flexibilizer for epoxy resin. Various combinations of CODT and commercial epoxy resin Sympol-200 (epoxy equivalent 190) were made. Room temperature curing of these compoundings was facilitated by diethylene triamine. For a comparative study LP-33 was also evaluated as a flexibilizer/modifier for epoxy resin.

Compounding and Testing

The mixing ratios of CODT and epoxy resin and LP-33 and Synpol-200 are given in Table 32. The initial mixing of components I and II (Table 32) was done by similar method employed for CODT and polysulphide (See Section B). Various combinations were prepared by mixing components I and II in a glass or porcelain dish. A sheet was prepared from π shaped template and was cured at room temperature for 7 days. For determination of properties like elongation, tensile strength and Shore D hardness, dumbbell shaped specimens were cut from the cured sheet and tested according to ASTM designation D 412-68 and D 2240-68. The results are given in Table 33.

Table 32

Mixing Ratios of Epoxy Resin - CODT and Epoxy Resin- LP-33

System	Component I Epoxy resin (Synpol-200) in g.	CODT in g.	LP-33 in g.	Component II Diethylene triamine in g.
I				
	100	-		10
1)	100	25		10
2)	100	50		10
3)	100	75		10
4)	100	100		10
II	100	-	25	10
1)	100	-	50	10
2)	100	-	75	10
3)	100	-	100	10
4)				

Table 33

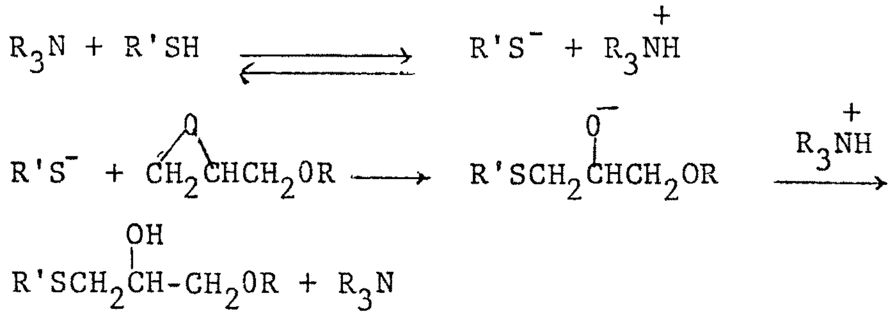
The Effect of CODT/LP-33 on the Physical Properties of Liquid Epoxy Resin Sheets Cured for 7 Days at Room Temperature

System	Tensile strength MPa	Elongation %	Shore hardness Shore D	Pot life (h)
I				
1)	17.8	0	90	0.5
2)	18.70	10	88	4
3)	18.00	20	87	2
4)	6.30	30	85	2
	3.80	50	80	1
II				
1)	24.8	8	88	4
2)	20.7	17	85	2.5
3)	10.8	30	85	2
4)	7.5	45	80	1.5

DISCUSSION

In epoxy resins, reactive modifiers such as polyamide resins, polysulphide polymers and polyester flexibilizers[25] have been widely used. Polysulphide-epoxy formulations find extensive applications in casting of complex shapes, and for improving impact resistance.

The reaction of liquid polysulphide with epoxy resin was first studied by Gannon and Fettes[26]. Primary and tertiary amines generally facilitate the reaction at room temperature. The mercapto groups in presence of an amine are converted to mercaptide ions which readily react with epoxy group at room temperature and enter into the backbone of epoxy resin. The reaction can be represented as follows[27]:



$$R_3N + R'SH \rightleftharpoons R'S^- + R_3\overset{+}{N}H$$

$$R'S^- + CH_2CHCH_2OR \longrightarrow R'SCH_2\overset{O^-}{C}HCH_2OR \xrightarrow{R_3\overset{+}{N}H}$$

$$R'SCH_2\overset{OH}{C}H\text{-}CH_2OR + R_3N$$

Epoxy resin, after curing gives rigid structure which can be modified to flexible structure by incorporation of polysulphide. In the present study CODT and LP-33 were used as flexibilizer/modifier for epoxy resin cured by diethylene triamine. The effect of addition of CODT as well as LP-33 on the physical properties of cured epoxy resin is given in Table 33. It is interesting to note that increase in tensile strength of epoxy resin by adding CODT or LP-33 upto 50%. When the amount of CODT or LP-33 was increased above 50% in the combination, a sharp drop in the tensile strength was observed. This may be due to the plasticizing action of CODT or LP-33. Thus the effect of increased tensile strength and elongation upto 50% addition of CODT in Synpol-200 epoxy resin indicates that these combinations may find applications as flexible epoxy adhesives, coatings, as water proofing materials, pottings, laminates, etc.

EXPERIMENTAL

Materials

Castor oil dithioglycolate (CODT) synthesis and characterization is given in Section A.

Liquid polysulphide, LP-33 was obtained from Thiokol Corporation, New Jersey, USA.

Epoxy resin, Synpol-200 was purchased from Synthetic and Polymer Industries, Gujarat (India) and used as received.

Diethylene triamine was obtained from Ciba Geigy (India).

Preparations

Compounding of CODT with Epoxy Resin

CODT and epoxy resin were weighed separately and mixed well in pug mixer (Table 32) followed by the addition of diethylene triamine as hardner and mixed well. The pot life of various combinations is given in Table 33

Preparation of Test Specimens

A sheet was prepared from π shaped template according to the procedure given in Section B. The sheet was cured at room temperature (29°C) for 7 days. Dumbbell shaped specimens were cut from the cured sheet and tested for elongation, tensile strength and hardness according to ASTM designation number D 412-68 and D 2240-68 (Table 33).

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SUMMARY

The thesis deals with

General Introduction

(1) Synthesis of New Silane Compounds from Cardanol and Castor Oil and their Applications in Rubber Reinforcement and in Foundry Sand Cores.

(2) Modification of Cellulose Acetate by Trimethyl chlorosilane for use in Desalination of Water.

(3) Synthesis of Castor Oil Dithioglycolate and its Utility as Rcom Temperature Setting Elastomeric Material and as Flexibilizer for Epoxy Resin.

General Introduction

This part covers a brief and comprehensive review of literature on the possibility of use of renewable resource materials as an alternative source for petroleum-based monomers and polymers.

Chapter I: New Silane compounds from Cardanol and Castor Oil and their Appplications in Rubber Reinforcement and in Foundry Sand Cores.

Section A : Synthesis of New Silane Coupling Agents from Ethers and Esters of Cardanol and Castor Oil Acetate.

Organofunctional silanes have been used successfully for many years as coupling agents for composite materials because of their unique ability to bond polymers with dissimilar materials such as silica, alumina and glass. The use of silane coupling agents for improvement in adhesion of matrix resin to glass fibers was first reported in mid 1940's[1].

In this section the structural features of cardanol-a by-product obtained from cashew industry -3,pentadecadienylphenol and castor oil-12 hydroxy triglyceryl ricinoleate-have been exploited to synthesise new silane coupling agents. Thus, methyl and allyl ether of cardanol, ester of cardanol with oleic acid and linoleic acid, and castor oil acetate were prepared. The new hydrosilylated products were synthesised from these ethers and esters and castor oil acetate using trichlorosilane as hydrosilylating agent and chloroplatinic acid as catalyst. Also polysulphide of 3-pentadecyl phenol was prepared and reacted with trichlorosilane. These chlorosilyl derivatives were further converted into methoxysilyl compounds by alcoholysis. Thus, the following new silane compounds were synthesised:

(A) Benzene, 1-methoxy-3-(8,11 bistrimethoxysilyl) pentadecyl.

(B) Benzene, 1-(trimethoxysilyl) propanyloxy 3-(8,11 bistrimethoxysilyl) pentadecyl.

(C) 1-(9-trimethoxysilyl) octadecanoate,3-(8,11 bistrimethoxysilyl) pentadecyl phenyl

(D) 1-(9,12 bistrimethoxysilyl) octadecanoate 3-(8,11-bistrimethoxysilyl) pentadecyl phenyl.

(E) Methoxysilane from polysulphide of 3-pentadecyl phenol

(F) Methoxysilane from castor oil acetate.

These compounds were characterised by IR Spectroscopy. The complete hydrosilylation was not achieved even under different parameters of reaction which is evident from spectral data.

Section B: Evaluation of Silane Coupling Agents in Rubber Reinforcement

The oil embargo in today's space age has a great deal of impact on research field to find out alternative source for petroleum-based products. High cost and potential shortage of carbon black - a petroleum based reinforcing filler-has stimulated interest in the replacement of carbon black by low cost mineral fillers.

In 1960's, Fusco[2] has reported the improved physical properties of mineral filled peroxide cured ethylene propylene rubber by incorporating silane compounds. The physical properties of mineral filled elastomers can also be improved by using vinyl, mercapto and alkoxy silane[3].

In the present investigation, an attempt has been made to improve the physical properties of clay filled elastomers by incorporating silane coupling agents. Thus, natural rubber (NR), combination of styrene butadiene rubber (SBR) and natural rubber (RMA) were compounded with fast extrusion furnace (FEF) carbon black, mixture of FEF carbon black and china clay and china clay alone using sulphur and cyclohexylbenzothiozylsulfenamide (CBS) as curing agent and accelerator, respectively and silane

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The physical properties like modulus, elongation, tensile strength, compression set and Shore A hardness of the resulting elastomers were determined and compared with the physical properties of the elastomers in which commercially available silane coupling agent Si-69 was incorporated. Silane incorporated elastomers showed improved physical properties. The maximum tensile strength was obtained by incorporating methoxysilane from polysulphide of 3-pentadecyl phenol. This may be due to sulfidic linkages present in the compound. The results obtained were comparable to Si-69, (Bis triethoxysilylpropyl) tetrasulfide. The properties of the vulcanizates obtained from the mixture of carbon black and china clay and silane coupling agent were higher than china clay alone and comparable to those vulcanizates obtained when carbon black was used as reinforcing filler.

Section C: Evaluation of Silane Coupling Agents in Rubber to Metal Adhesion.

Adhesion of rubber to metal is industrially becoming more important in today's space, engineering and automobile industry as it helps in shock absorption and in reducing vibrations. The adhesion of conventional adhesives such as blend of natural rubber with phenolic resin can be further improved using silane coupling agents[4].

Thus in the present work, silane coupling agents (A to F) have been evaluated as adhesion promoters for rubber to metal bonding along with adhesive prepared from a blend of natural rubber and phenolic resin and commercially available bonding agent Chemlock-220. NR, combination of SBR and RMA, and neoprene rubber (Neo) were used as substrate. Silane compounds were added while compounding the rubber on the mill. The compoundings were done with and without silane coupling agents to study the effect on physical properties such as Shore A hardness and peel strength after curing the specimens under hydraulic press and subsequent cooling at room temperature for 24 hr.

Section D: Evaluation of Silane Coupling Agents along with No Bake Binder in Foundry Sand Cores.

A number of no bake binders are available for foundry sand cores such as drying oil alkyd, phenolics and furan resins which can be cured at room temperature or at slightly elevated temperature by isocyanates or acids. Silane coupling agents have been advantageously used to increase the flexular properties of sand cores prepared from various no bake binders[5,6].

In the present study phenolic resol resin was prepared and used as no bake binder for sand cores using phosphoric acid as hardner. An attempt has been made to improve the physical properties of the sand cores by incorporating silane coupling agents (A to D ~~and~~ [illegible]), along with phenolic no bake binder. The effects of acid concentration and curing time on the physical properties of the sand cores were also studied. The performance of silane coupling agents was compared with commercially available silane coupling agents A-1100.

Chapter II: Modification of Cellulose Acetate by Trimethylchlorosilane for Use in Desalination of Water.

Since last twenty years, cellulose acetate (CA) membranes are successfully used for desalination of water by reverse osmosis (RO) due to their unique assymetric nature and hydrophobic character.

Modification of cellulose acetate membranes by chemical means is being carried out all over the world due to their certain limitations such as poor chemical resistance, fast biodegradibility, etc.[7].

It has been reported in the literature that the introduction of silyl moiety in the cellulose increases its hydrolylitic stability[8]. Thus, the present study deals with the partial modification of residual hydroxyl groups of secondary cellulose acetate with various proportions of trimethylchlorosilane to enhance its hydrophobic character by introducing Si-O-C linkages. The modified polymers were characterised by intrinsic viscosity, molecular weight, acetyl content, silicon percentage, thermal stability and IR spectra.

The membranes were cast from the modified CA as per the reported procedure. The transport properties of the membranes such as water flux, pure water permeability and % salt rejection were determined on the RO unit fabricated in this laboratory at different operating pressures. The effects of annealing temperature on the transport properties of the membranes were also studied and compared to the properties obtained with unmodified cellulose acetate membrane. The annealed membranes were characterised for the properties such as specific water content, membrane constant and average pore size diameter. The modified cellulose acetate membranes exhibited better salt rejection than unmodified membrane while water flux rate and membrane constant were reduced as compared to that of the unmodified cellulose acetate membrane.

Chapter III: Synthesis of Castor Oil Dithioglycolate and its Utility as Room Temperature Setting Elastomeric Material and as Flexibilizer for Epoxy Resin.

Section A: Synthesis of Dithioglycolates

Thioglycolates, which are esters of polyhydroxy compounds with mercapto carboxylic acid, occupy unique place in polymer chemistry as they can act as catalyst, accelerator or chain transfer agent in polymer synthesis.

Among the thiol group containing organic polymers, thiol terminated liquid polymers are of great importance due to their facile oxidation with a wide variety of organic as well as inorganic oxidising agents to disulphide linkages at ambient temperature. Recently, Ghatge and Murthy[8] synthesised castor oil tristhioglycolate (COTT). The rubberyproducts obtained by oxidative cure from COTT exhibited certain drawbacks such as low elongation and tensile strength which may be due to its high cross-linking density. To overcome these drawbacks, castor oil dithioglycolate (CODT) was synthesised from difunctional castor oil and thioglycolic acid with a view to reduce its cross-linking density and prepare room temperature setting elastomeric products with improved properties by oxidative cure. Ethylene glycol bis thioglycolate (EBT), polyethylene-glycol-400 bis thioglycolate(PET-400) and castor oil silane (COS) were prepared with an aim to obtain elastomers with improved properties from the combination of these compounds with CODT. These thioglycolates were characterised by IR spectroscopy, elemental analysis, viscosity, SH content and molecular weight determination.

Section B: Room Temperature Setting Elastomers from Castor Oil Dithioglycolate

In the present study, elastomeric products from liquid

CODT alone and in combination with EBT, PET-400 and commercially available liquid polysulphide LP-33 from Thiokol were prepared by oxidative cure. The oxidative curing paste was prepared from commercial $Mn0_2$ as well as from laboratory synthesised magnetite coated $Mn0_2$. Both $Mn0_2$ samples were characterised by Electron Scanning in Chemical Analysis (ESCA), Mn^{++}% and pH to study the effect of these characteristics on the curing of thiol compounds. The effect of reinforcing fillers on physical properties of cured product was studied by employing semi-reinforcing (SRF) carbon black and medium thermal (MT) carbon black. The effect of COS as coupling agent on reinforcing properties of elastomers from CODT alone and in combination with LP-33, was studied. The oxidative cured products of CODT exhibited better tensile strength and elongation. When CODT was mixed with LP-33 increase in tensile strength and elongation was observed.

Section C: Castor Oil Dithioglycolate as Flexibillizer for Epoxy Resin

Epoxy resins are inherently brittle and hard in the curedstate. The reaction of epoxy resin with liquid polysulphide polymer at room temperature results in flexible compound which has excellent properties for casting and embedment application.

In the present investigation, an attempt has been made to explore the possibility of use of CODT as a flexibilizer for epoxy resin (Synpol-200). Various combinations of CODT and Synpol-200 were made. The room temperature curing of these combinations was facilitated by diethylene triamine. The physical properties such as % elongation, tensile strength, hardness and pot life were studied. The increase in tensile strength and elongation of epoxy resin by adding CODT upto 50% was observed.

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