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STUDIES IN THE SYNTHESSES AND EVALUATION
OF POLYURETHANE POLYMERS [RIGID FOAMS]

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A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY



by

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678.664 (043)
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December 1975

Acknowledgement

I am deeply grateful to Dr.N.D. Ghatge, Scientist, Division of Polymer Chemistry, National Chemical Laboratory for his valuable guidance and constant encouragement during the course of this investigation.

I wish to express my sincere thanks to Prof.B.D.Tilak, Director, National Chemical Laboratory for his kind permission to submit this work in the form of a Thesis.

I gratefully acknowledge the valuable advice and help given by Dr.S.S. Mahajen, Dr.S.P. Vernekar, Dr.S. Prebhakera Rao and Mr.D.K. Dandge.

I express my sincere thanks to all my friends and colleagues for their co-operation.

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GENERAL INTRODUCTION

The development of polyurethanes, also referred to as 'Urethanes' or 'isocyanate polymers' has been rapid during the last few years. These polymers are adaptable to almost every application for cellular plastics in their current state.

Polyurethane polymers were first discovered in Germany by Prof. Otto Bayer and his associates in the mid of 1930's as a substitute for Carother's polyamide polymers. They contain the characteristic linkage



which may be considered as a mixed amide ester of carbonic acid. Urethane polymers are generally made by the interaction of polyisocyanates with polyhydroxy compounds such as polyethers, polyesters, castor oil and glycols. The structure of these polymers has the repeating urethane groups. Other groups which may appear in the structure are urea, ether, amide, biuret, allophanate and other groups. The manner in which these groups are put together and extent of branching determines largely the major physical properties. Hence, they can be tailor-made to any desired structure and properties.

The properties of various types of urethane polymers depend primarily on molecular weight, degree of crosslinking,

effective intermolecular forces, stiffness of chain segments and crystallinity. Because of the many structural variations that are possible in their formulation, urethanes may be considered as versatile polymers in the field of fibres, soft and hard elastomers, coatings, adhesives, rigid and flexible foams, thermoplastic and thermosetting plastics etc. Still the major applications are in urethane foams.

Urethane foams

Urethane foams are formed by the reaction of an isocyanate and a polyol in presence of a catalyst, a blowing agent and a surfactant. By varying the ratio of raw materials and the foaming conditions, a broad spectrum of the end properties can be obtained for any particular foam. The most important foam properties are flexibility, resiliency and load bearing ability. The range extends from soft, flexible to rigid foams. The density of a urethane foam can be varied from one to sixty lbs./cuft. As the density increases, many of the foam characteristics change. The choice of the polyol has a major influence on the properties of the foam and its rigidity and flexibility. The crosslink density of the urethane foam determines whether the foam will be flexible or rigid.

Flexible foams are produced from polyols of moderately high molecular weight and low degree of branching, while rigid foams are prepared from lower molecular weight and highly branched polyols.

Polyols generally used for rigid and most flexible

urethanes are polyethers. The hydroxyl groups of the polyol and terminal NCO groups of the isocyanate react to build the urethane polymer chain. The most widely used isocyanate for flexible foam is toluene diisocyanate (TDI), while crude tolylene diisocyanate and diphenyl methane diisocyanate (MDI) are used for rigid foam. Catalysts are required to accelerate and control the foaming reaction to obtain proper cure. Tertiary amines or tin compounds with amines are employed as catalysts. Carbon dioxide generated when isocyanates react with water, is the primary blowing agent in flexible urethane foam. Inert chemicals such as fluorocarbons which are vaporized by the exothermic heat of the polyol and isocyanate reaction, are used as blowing agents mostly in rigid urethane foam. Surfactants which are usually silicone block-copolymers exert a stabilizing action upon cell formation. In addition to these basic components described, additives such as fillers, dyes, colourants, plasticizers and flame retardants are also used sometimes to modify the properties of urethane foam.

The wide range of physical and chemical properties of urethane foams make these cellular plastics suitable for a variety of applications. However, the current trends point toward greatly increased use of rigid urethane foam in a number of industries such as refrigeration, transportation, insulation, building materials, furniture, construction, marine, packaging and thermal insulation.

History of rigid urethane foam

The technology of the urethane foams originated in Germany late in 1930's. Prof. Otto Bayer and his coworkers¹ first discovered rigid urethane foam in the laboratories of the German I.G. Farbenindustrie. These early foams were based on polyesters having high acid number (about 30) and high viscosity. The main mechanism for foaming was the release of carbon dioxide from the reaction between the acid groups in the polyester and isocyanate. Relatively high temperature was needed for the reaction. These foams were utilized during World War II as light weight, high strength sandwich materials for aircraft construction and a flotation material for temporary bridging, submarines and tanks.

During 1945-47 surveys of wartime German developments in plastics conducted by Allied forces led to the introduction of polyurethane and rigid foam in the United States^{2,3} and attracted broad interest due to its light weight, high strength and excellent adhesion to metals. As a result, many companies from U.S. such as Good Year Aircraft, Lockheed Aircraft, Du Pont and Monsanto initiated research on polyurethanes, particularly rigid foams. Investigations also began in Great Britain and European countries.

Good Aircraft Corporation⁴ developed a low density core material to be used in random construction. They were mostly of the same type as the early German foams. The Lockheed Aircraft Company developed a one shot technique for foamed in place rigid urethane foam called Lockfoam, during 1947-48, and was awarded a

series of patents⁵ covering this process. These patents disclose the use of foam stabilizers, regulators and blending agents.

Farbenfabriken Bayer developed foam machines^{6,7} (U Machines) based on injection principle, as early as 1950 and these machines were employed for the continuous production of rigid foam based on three component system: polyester, diisocyanate and water.

Lower cost rigid and semi-rigid foams based on castor oil and TDI were developed by DuPont^{8,9} with densities ranging from 2 to 20 lbs./cuft. These foams had good adhesion, impact resistance and acoustical properties. Polyester based systems were slightly higher in cost than the castor oil foams but they had the advantage of higher closed cell contents, high strength, better solvent and temperature resistance and could be prepared in densities from 1.5 to 20 lbs./cuft.

Initially rigid urethane foams were made with TDI, which were toxic and had technical deficiencies. In early 1950s, ICI developed the low toxic system based on diphenyl methane diisocyanate (MDI) compositions^{10,11} and urethane foams using MDI and polyester resins were marketed in 1957 for the first time.

In 1956-57 urethane grade polyethers were developed on large scale. They were the best substitutes for polyester resins and had materially lowered the cost of the rigid urethane foam¹²⁻¹⁴.

In 1958, the use of fluorocarbons as a blowing agent instead of carbon dioxide was one of the most important

milestone in the development of rigid urethane foam. Apart from the lower cost, the resulting foam prepared with these fluorocarbons has improved thermal insulating properties and processing characteristics^{15,16}.

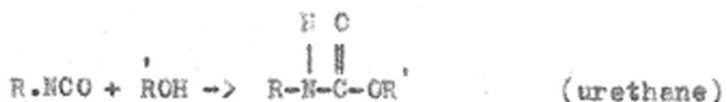
In 1959 polyether resins were employed with MDI on commercial scale for the production of rigid urethane foam. The first large scale applications¹¹ of rigid urethane foam of ICI systems based on polyether, MDI and fluorocarbons were the insulation of portable refrigerated containers, the insulation of domestic chambers of the ships and the insulation of chemical plants.

The growth of rigid urethane foam was rather slow till 1960. Literature survey reveals that a tremendous work has been reported since then on the development of rigid urethane foam technology by using suitable polyols, various isocyanates different foam systems and the modern sophisticated machines.

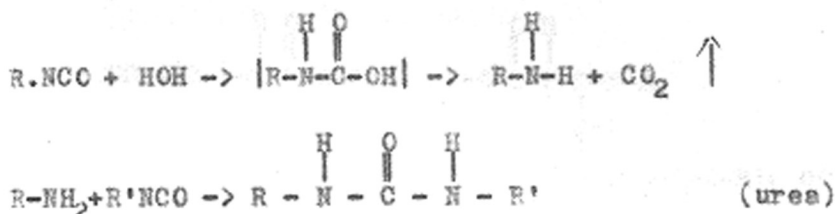
The chemistry of foam formation

The process of formation of urethane foam is complex. The detailed chemistry and manufacturing technique for urethane foams have been described in literature¹⁷⁻²⁰. The reactive ingredients of a foam system are usually an isocyanate, a hydroxyl terminated resin and water.

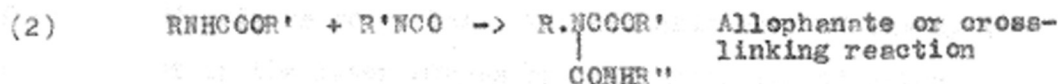
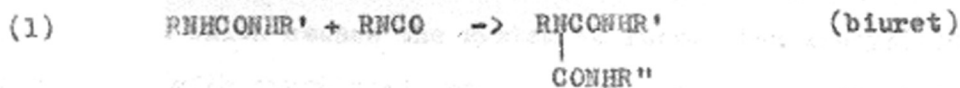
(I) The reaction of hydroxyl group with an isocyanate produces urethane



(II) The second reaction of isocyanate is with water to form an amine and carbon dioxide. The carbon dioxide thus produced acts as a blowing agent and the amine reacts with excess isocyanate to form urea.

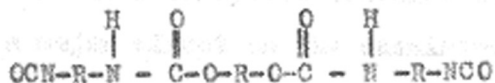
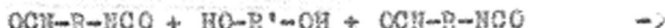


Presently water is less frequently used as a blowing agent in rigid foam system. Non-reactive liquid blowing agents (fluoro carbons) are vaporised by the exothermic heat of the polyol and isocyanate reaction to produce gas and causing the system to form. The isocyanate may also react with urea and with the urethane to give a biuret and an allophanate linkage respectively.



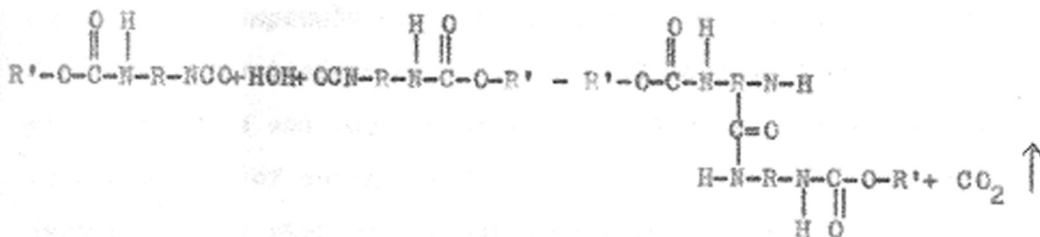
Prepolymer formation

Polyfunctional compounds react to form chains or prepolymer as shown by the following reaction:



The terminal isocyanates continue to react with hydroxyl group to form chains.

The reaction of urethane prepolymer with water culminates either in foam formation or gelling.



The function of the isocyanate in foaming

Generally 80:20 mixture of 2:4/2:6 TDI or crude TDI and MDI are used in foaming. Isocyanate reacts with water to form carbon dioxide which acts as blowing agent in foam formation. In some systems the exothermic heat produced by the reaction of isocyanate and polyol helps to vaporise the inert low boiling liquids to produce gas which causes the system to foam. The isocyanates also react with functional groups of the resin leading to the formation of polymer molecules. The stoichiometry of the system is such that in the later stages of polymerization of water blown systems, the polymer end groups are largely the very reactive isocyanate groups. This high reactivity helps greatly in further condensation.

The role of catalysts in foaming.

Generally the foam system contains one or more catalysts which have a major effect on the chemistry of the system. The catalyst accelerates the reaction between the prepolymer and

water or between isocyanate and resin and water (in water blown systems) at such rates that the foam rises and cures sufficiently fast to prevent collapse or the shrinkage of the foam. The catalysts most commonly used are tertiary amines and the tin compounds such as stannous octoate, stannous oleate, dibutyltin dioctoate and dibutyltin dilaurate. The balance of polymerization and foaming rates is controlled mostly by the proper choice of catalysts⁷⁵. The presence of alkaline or metal impurities may also contribute to the catalytic effects. Acidic impurities in the resins or isocyanate reduce the catalytic effect¹⁸.

The role of the blowing agent

The blowing agent provides sufficient gas for the formation of a number of fine bubbles in the polymerizing system. Blowing agents most frequently used in foaming are carbon dioxide (from reaction of isocyanate and water) and fluoro carbons such as trichlorofluoromethane and dichlorodifluoromethane etc.

The rate of foaming in water blown foam system is controlled by the concentration and strength of the catalyst while in solvent blown, it is controlled by the boiling point and heat of evaporation of the solvent.

The role of surfactant in foaming

The function of the surfactant is to facilitate the uniform production of very small bubbles and to impart stability to the foam process by reducing the surface tension of the system.

It also provides the elasticity and self healing character of liquid films. A variety of surfactants such as conventional soaps, amine salts of fatty acids and sulphates, poly(dimethyl siloxanes) and poly(oxyalkylene), poly(siloxane) block copolymers have been used in foaming⁷⁵.

Raw materials used in rigid urethane foam

The raw materials used in the rigid urethane foam consist of a di or poly functional isocyanate, a poly functional hydroxy compound, usually a polyol, a blowing agent, catalyst and cell size regulator. In addition to these basic raw materials, numerous additives such as fillers, plasticizers, flame retardants and pigments are used to obtain special properties.

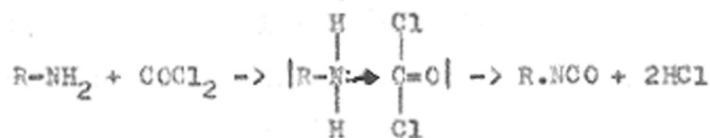
Isocyanates

The major isocyanates used for rigid urethane foams are:

- (1) Polyurethane diisocyanate (TDI) 80:20 and 65:35 isomers
- (2) Crude or undistilled TDI
- (3) Diphenylmethane diisocyanate (crude MDI)

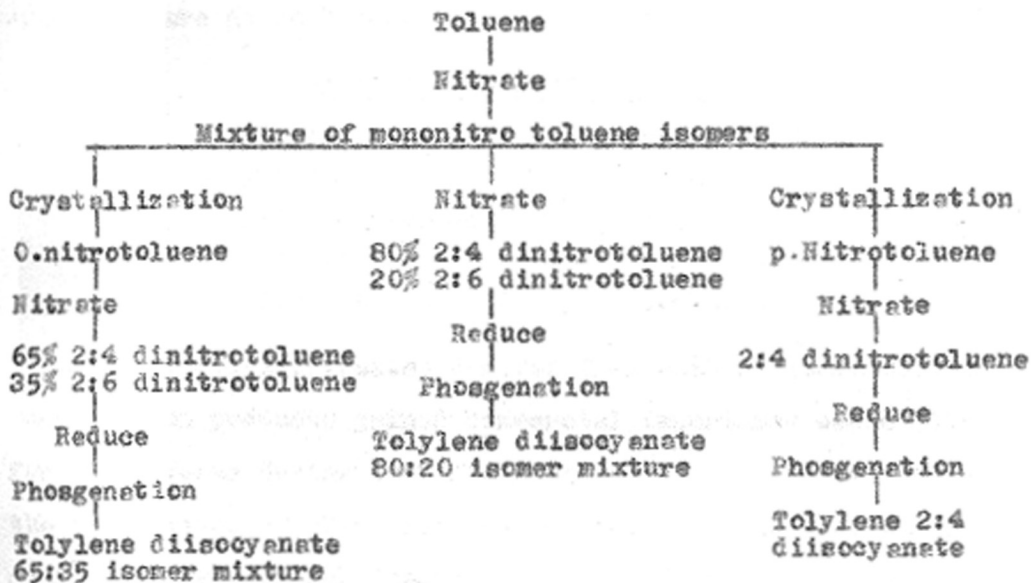
A number of methods of preparation of isocyanates are reported in scientific literature. The only method of commercial importance is the phosgenation of primary amines.

The reaction between primary amines and phosgene gives isocyanates and hydrochloric acid gas.



Commercially isocyanates are prepared in two steps, first

the amine or amine hydrochloride is mixed with phosgene at low temperature. Then the temperature is increased slowly to 120-150°C and more phosgene is passed. The isocyanate is obtained by distillation. The flowsheet of commercial preparation of tolylene diisocyanate⁷⁶ and the specifications of commercially available TDI are given below:



Specification of commercially available TDI¹⁸

Isomeric ratio	2:4/2:6 81/19
Purity	99.3% toluene diisocyanate isomers
Hydrolyzable chloride	Less than 0.004%
Boiling point	118-120°C at 10 mm.
Combining weight	87.6
Density	1.22

Early German rigid urethane foams were based on 2:4 TDI.

In the United States 80:20 mixture of 2:4/2:6 TDI is still more common while in Europe the 65:35 ratio is extensively used. More recently an undistilled grade of mixed isomers of TDI have been introduced in the United States. It has been useful particularly in the production of one shot polyether based rigid foams^{21,22}. Its chief advantages over distilled TDI are its lower cost, lower acidity and easy handling. Specifications of crude TDI are given below:

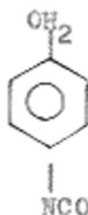
Specifications of crude TDI¹⁸

Colour	Brown
TDI %	63-65
Amine equivalent	102-108
Acidity	0.2 - 0.4
Viscosity at 25°C	50-150 cp.

A family of polyisocyanates derived from aniline formaldehyde condensation products gained commercial importance especially for rigid foams during last few years. The polyamines used in the preparation of these isocyanates are designed to provide a mixture of isomers and isocyanates of different molecular weights when phosgenated. The product is chemically related to MDI and often called as crude MDI. The resulting polyisocyanates include compounds such as:



The assay is usually about 91-93% calculated as MDI.

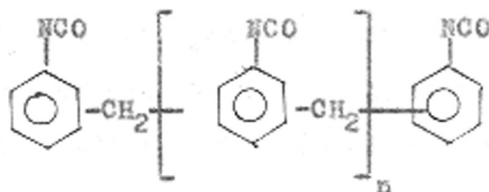


The low vapour pressure, low freezing point and the consequent easy handling of these polyisocyanates make them very useful and attractive in one shot system for spraying and "pour in place" applications²³ of rigid urethane foam. In addition these isocyanates usually provide improved dimensional stability and flame resistance^{24,25}. Specifications of crude diphenyl methane diisocyanate are given below:

Specifications of crude MDI¹⁸ Desmodur 44V

Boiling point, initial °C 1 mm Hg.	170
Freezing point	8°C (46°F)
Specific gravity 20°C	1.25
Viscosity cps. at 25°C	50-60
Assay %	approx. 88-90
NCO %	.. 30-31
Hydrolyzable chloride %	.. 0.2
Total chloride	.. 0.2
Solid contents %	.. 1.0

In addition to these polyisocyanates, a triisocyanate called as polymethylene polyphenyl isocyanate (PAPI) is also used specially in the preparation of rigid foams having high heat distortion and flame resistance²⁶. Its structural formula is:



Polymethylene polyphenyl isocyanate (PAPI)

It is composed of a mixture of low molecular weight aromatic condensation products having both ortho and para substituted isocyanate groups.

Polyhydroxy compounds (polyols)

Polyesters and polyethers containing terminal hydroxyl groups are generally used in the preparation of rigid urethane foam. Castor oil and its derivatives have been the basis for a number of commercial semi-rigid foams due to their low cost. They are rarely used in rigid foams. Because of their high equivalent weights and more flexible aliphatic structures, these resins do not impart sufficient rigidity to a urethane polymer.

Polyesters

During the initial development of polyurethanes, polyesters were commonly used. Since unsaturated polyesters were found undesirable for use in polyurethanes, completely saturated polyesters containing terminal hydroxyl groups rather than carboxyl are preferred. Polyesters are prepared usually by the esterification of simple dicarboxylic acids such as adipic or phthalic acid and saturated polyfunctional alcohols such as 1,2,6 hexane triol trimethylol propane and glycols. The acid to alcohol ratio is such that all the acid groups react and the hydroxyl groups are in sufficient excess to give a polyester containing hydroxyl groups as reactive sites. The polyesters with very low acid number and very low water content (<.1%) are preferred. Highly branched polyesters are used for the preparation of rigid foam and chemical resistant coatings.

Polyesters prepared from chloroendic acid or tetrachloro phthalic or tetrabromophthalic acid have excellent flame resistance properties^{27,28}. The polyester resins are used less frequently than the polyethers for the preparation of rigid urethane foams because of their high cost and high viscosity.

Polyethers

Polyether polyols are the most popular and commercially used resins in rigid urethane foams because of their low cost. Gaylor²⁹ has reviewed the general subject of polyether polyols covering the chemistry, manufacture and uses of these substances.

Commercially polyethers are manufactured by reacting alkylene oxides with polyfunctional alcohols like glycerine, trimethylolpropane, pentaerythritol, sorbitol, methyl glycoside and sucrose. The choice of the polyhydroxy compound will govern entirely the average functionality or degree of branching of the resin and has a profound influence on its final room temperature viscosity. In most cases the addition of the alkylene oxides serves primarily to convert the solid state of the alcohol to the liquid form. Although ethylene oxide is the cheapest material available for this condensation, propylene oxide is preferable because it imparts greater resistance to water absorption.

Polyethers used in rigid urethane foams are generally based on propylene oxide adducts of various polyfunctional alcohols. These polyethers have terminal secondary hydroxyl groups unless the polymer chains are terminated with ethylene oxide. This contributes directly to the chemical activity for

reaction with isocyanate.

A second type of polyethers are known as self-catalytic resins. They are prepared by condensing alkylene oxides with polyfunctional amines such as ethylene diamine or diethylene triamine or piperazine or di or triethanol amines²⁰. Because of the inherent high chemical activity caused by the presence of tertiary nitrogen, they are seldom used singly in the preparation of foam, but are combined in formulations with other polyether polyols. They are particularly useful in spraying or pour in place applications where a high order of reactivity is needed.

A third type of polyether polyol is prepared from oxy-phosphorous acids and alkylene oxides to impart flame resistance to rigid urethane foam. These phosphorous containing polyols are most often used as blends with other polyols for the preparation of rigid urethane foam²⁰.

Recently, T.H. Ferringo¹⁸ has given an excellent review on commercially available polyethers with their specific properties for the preparation of rigid urethane foam.

Catalysts

The balance of polymerization and foaming rate is controlled to a large extent by the proper choice of catalysts. The choice of catalysts for the preparation of rigid urethane foam is governed by many factors, the most important of them being:

- (a) the method of foam application e.g. spraying²³,
moulding or slabbing³¹:



- (b) the specific polyol or polyisocyanate used³², and
- (c) the activity of catalyst itself in promoting urethane reaction or gas formation³²⁻³⁵.

The catalysts, most commonly used, are tertiary amines and tin compounds. The tertiary amines are used successfully for both water isocyanate reaction and hydroxyl isocyanate reaction. Tertiary amines which are used in rigid urethane foam consist of triethylamine, triethanolamine, triethylene diamine (Dabco), N,N-diethyl cyclohexylamine, N,N-dimethyl 2 phenethyl amine and ~~N,N,N,N~~ tetramethyl butane 1-3-diamine etc. The mechanism by which tertiary amines accelerate the reaction between isocyanate and either with active hydrogen compounds or water has been described in the literature³⁶.

Metal catalysts such as organotins, stannous octoate and dibutyltin dilaurate are not frequently used in rigid foams. They are strong catalysts and are used to promote the reaction of secondary hydroxyl groups with isocyanate and chain propagation. Some times in rigid foam technology, tin catalysts are beneficial in promoting the 'surface cure' of a foam.

Combination of organotins and tertiary amines gives synergistic effect which is required in spray application of rigid urethane foam. Recently the self catalytic resins have been employed to make rigid urethane foam without additional catalysts for spray and frothing applications.

Blowing agents

No polyurethane foam will result unless the reacting resin/isocyanate mixture is simultaneously expanded by gas generation.

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This is achieved by two ways:

- (1) carbon dioxide produced in situ by the reaction of isocyanate with water acting as a blowing agent;
- (2) inert halogenated hydrocarbons in the formulation which vaporise during the course of polymerization, acting as blowing agent.

Commercially, trichlorofluoromethane (Freon 11) is used for the preparation of rigid urethane foam. This inert low viscosity liquid takes no part in the chemical reaction. It is quickly volatilised by the exothermic hydroxyl/isocyanate reaction. Being chemically inert, no isocyanate is consumed in gas generation as in the case of carbon dioxide blowing. Moreover the gas trapped in the foam cells reduces the thermal conductivity of foams due to its low thermal conductivity (K factor). It has also the advantage of considerably reducing the viscosity of very high viscous resins. Further, the expanding gas acts as a coolant and improves the processing characteristics. By regulating the amount of trichlorofluoromethane, foam density can be varied from 1 to 30 lbs./cuft.

Recently Du Pont³⁰ has developed a frothing process in which a mixture of two different low boiling fluorocarbons (Freon 11 and 12) are used to obtain a very low density foam.

Surfactants or surface active agents

In an expanding foam, it is essential that the gas should be retained completely in the form of bubbles which ultimately gives the closed cell structure in the final cured foam.

This is achieved by adding surface active agents to the foam mix whose function is to facilitate the uniform production of very small bubbles and to impart stability to the foam process by reducing the surface tension of the system.

The choice of the surfactant is governed primarily by the type of polyol used and the method of foam preparation. The surface active agents most commonly used are silicone compounds (of the general type polyoxy alkylene polysiloxane copolymers). Surfactants employed for polyesters are usually of the ionic or nonionic type and include sulfonated castor oil, amine ester of fatty acids and polyoxyalkylene derivatives of acids or alcohols.

Silicones, particularly the polyalkyl siloxane-polyoxyalkylene copolymers, are the most common surface active agents used for polyether based foams. They usually give extremely fine cell foam of excellent uniformity and high closed cell content. They are becoming more popular and useful because they contain direct Si-C bonds which gives better hydrolytic stability.

Bondra³⁷ has presented a well organized discussion of the effect of poly(oxyalkylene) poly(siloxane) copolymers on the formation of urethane foam.

Silicone oils, polydimethylsiloxanes of relatively low viscosity have been used in polyether systems and foamed as prepolymers²⁰.

Generally the silicone surfactants are recommended at concentrations of 0.5 to 1.5% based on the total weight of foam ingredients.

Flame retardants

Flame retardants are the most widely used additives in rigid urethane foams. The demand for the flame retardant rigid foams has increased sharply in the last few years for a number of applications such as appliances, structural panels and transportation etc. Flame retardants are commonly of three types:

- (1) non-reactive additives
- (2) reactive additives, and
- (3) inherently fire retardant.

A great variety of non-reactive additives mainly organic phosphorous and/or halogen compounds or inorganic materials such as antimony oxide, ammonium phosphate or carbonate and red phosphorous are used in urethane foams. They are effective alone or in combination with other organic additives.

Although these additives are effective for flame proofing, they adversely affect thermal conductivity, water vapour permeability and dimensional stability of the foam.

A better approach for imparting flame resistance to the foam is to incorporate the flame retarding groups into the polymer backbone. Polyols containing phosphorous or halogens are preferable.

Inherently fire retardant foams based on trimerising polymeric isocyanates to make isocyanurate ring structures are the probables of the future. Today isocyanurate foams account for about 8% of the total rigid foam volume but by the end of 1975, trimers are expected to increase their share

thrice or even fourfold³⁸.

Fillers

A variety of fillers such as cellulosic derivatives, synthetic and glass fibres, asbestos, silica and silicates, calcium carbonate and others have been used to impart special properties to rigid foams and to reduce their cost³⁹. By adding fillers, no real advantage is gained since processing becomes more difficult and results in overall inferior properties. However, some exceptions have been reported in literature⁴⁰⁻⁴² that inexpensive extenders obtained as waste products in the conversion of wood to paper (tall oil and Vinsol) have been used successfully in rigid urethane foams.

Foaming processes

In general, there are three basic systems of foam preparation: (1) complete prepolymer, (2) quasi or semi-prepolymer, and (3) one shot. At present quasi prepolymer and one shot systems are widely used for the preparation of rigid urethane foams.

Complete prepolymer

In this system all of the hydroxyl compound is first reacted with the isocyanate and then water and catalyst are added for foaming. This process is relatively unimportant to the rigid foam manufacture with the exception of castor oil based foams. Quasi-prepolymer system has almost replaced the complete prepolymer system.

Quasi-prepolymer or semi prepolymer

In quasi-prepolymer system, a large molar excess of isocyanate is reacted with the polyol to give a product with a high percentage of free isocyanate groups (20-35%). The process is preferably carried out under well controlled condition of temperature and time (e.g. 60-70°C for 1 to 2 hrs.) under dry atmosphere. Under these conditions, the resulting semi prepolymer should be substantially free of any linkages other than urethanes. The semi prepolymer is then combined at the time of foaming with the additional amount of hydroxyl resin, blowing agent, catalyst and surfactant.

One shot system

The quasi prepolymer gained wide spread use during 1950s but with the advent of crude MDI and TDI, the one shot system became more popular and economical.

In one shot procedure, all the ingredients are combined at one time to produce a foam. Since in one shot systems ingredients are mixed at room temperature, it is necessary that all the components should be liquid at room temperature and they must have a moderate degree of compatibility with each other, thereby facilitating the mixing operation.

A major problem in the preparation of both polyester and polyether based rigid foam by one shot system, is the development of relatively high exotherms during foaming which may cause scorching particularly on large pours. However, this difficulty can be overcome by using crude isocyanates.

Applications

Low thermal conductivity, high mechanical strength, light weight and easy fabrication enable one to use rigid urethane foam in diversified applications.

Thermal insulation

Rigid urethane foam with its high insulating efficiency is ideal for thin wall design in commercial and residential refrigerators and freezers, cold storage cabinets and cold storage warehouses⁴³⁻⁴⁵. Refrigerated trucks, railroad cars, and shipping containers⁴⁵⁻⁴⁹ carrying milk, food products and other temperature sensitive materials are insulated with urethane rigid foam, thus rendering light weight and greater usable space to the carrier with unloading time reduced to a considerable extent. Because of its closed cell structure, the rigid urethane foam provides an effective protection against moisture and corrosive atmosphere. Industrial tanks and piping⁴⁵⁻⁵⁰ in which heat transfer must be controlled, are also efficiently insulated. Modified insulated foam products with better properties can be obtained by combining with different plastics⁵¹. Urethane foam insulation is applied in the form of precut slabs and by on site forming using spraying and pour in place technique.

Structural uses

Rigid urethane foam has been used extensively in constructions. They have been used in sandwich-panels⁵⁹ for roof, floors, exterior and interior walls, door cores and perimeter insulation. Besides having excellent insulating value, these

foams also contribute to high strength, light weight, structural reinforcement and good adhesion to any wall or panel in which it is used. They can be applied either 'foamed in place' or spray methods.

One of the biggest market potential for rigid urethane foam is building industry⁵²⁻⁵⁷. Urethane foam insulation has been extended to all building surfaces except windows, by spraying on to panel supports and filling joints and gaps by spray or pour in place technique. Foam core panels for roof decking⁵⁸ are creating wide spread interests in the building industry. These thin walls, acting as light weight roofing, are quickly and easily installed and provide excellent thermal insulation.

Pre-fabrication of small structures⁶⁰ and building components containing rigid urethane foam have been regularly used in construction industry.

Erection of barriers in coal mines by spraying urethane foam on a cloth substrate has become a standard technique. In space technology, rigid urethane foam pellets and powder have been developed to fabricate structures in space environment⁶¹.

Furniture

Rigid urethane foam has been used on large scale in furniture for decorative purposes. Rigid foam has also been used for structural support in upholstered chairs. Casted urethane foam has been utilised for artificial limbs. Recently, one-piece table⁶²⁻⁶⁴ and instrumental parts have been made from

injection moulded urethane foam. Techniques have been developed for combining with PVC, urethane and textile fabrics surfaces for padded furniture and rigid applications⁶³.

Marine applications

Rigid urethane foam is finding widespread acceptance in the marine field because of its exceptional buoyancy, light weight and structural strength. Blocks of urethane foam and foam-core sandwich construction have commonly been used to create buoyancy in small boats and dead spaces⁶⁵ (void fillings) in big naval ships, are filled with urethane foam to prevent flooding⁶⁶. Buoys and life boats⁶⁷ also extensively use urethane foam. Rigid urethane foam has been used in salvage operation⁶⁹, in which liquid raw materials are pumped into submerged hulls where they expand and displace the water.

Packaging

Strong, light weight rigid urethane foam offers unlimited possibilities in packagings. It can be premoulded to a given size or shape or it can be used in combination with paper, wood and other common packing materials⁶⁰.

Rigid urethane foam absorbs energy when crushed and has been used for protective shock proof packaging of electronic components and military hardwares^{46,51}.

Aerospace applications⁷⁰⁻⁷⁴ include protection of missile components, fuselage structures and rigidization of aircraft components.

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Part-I

SHELLAC POLYESTERS

INTRODUCTION

Shellec (lac) is the only natural resin of insect origin, which is obtained from trees in Indian jungles. It is a secretion of tiny insect on branches of trees, which is scrapped to get sticklac. This is purified and refined to obtain shellec. This is then bleached by: (1) chemical process, which involves dissolution of shellac in sodium carbonate solution, decantation, bleaching by hypochlorite solution and finally precipitation by acid. (2) physical process, which involves the treating of shellac with activated charcoal to remove colour. The lac is a mixture of inter and intraesters of hydroxy acids with molecular weights ranging from 300 to 3000. Shellac has the following composition:

<u>Components</u>	<u>Percentage</u>
Lac resin and gums	93.3
Lac dye	0.5
Wax	4.0
Volatiles	1.8

(source: Monogram of Lac IIRI 1962)

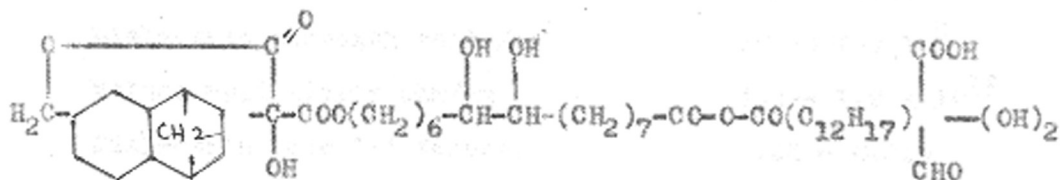
Shellec is a hard, tough amorphous resin. The mechanical and physical properties of lac are influenced by temperature and humidity. A comprehensive account of work has been published on physical, mechanical and chemical properties of

shellac¹⁻⁵. Some of the important properties are given in Table 1.

One of the important electrical properties of shellac is its non-conductivity even when it is subjected to an electric arc. Shellac retains its electrical insulation properties even under the influence of intense ultraviolet radiation¹.

Chemistry of shellac

The suggested empirical formula for shellac is C_4H_6O and its mean molecular weight is 1000, consequently $C_{60}H_{90}O_{15}$ represents the average molecule. Lac resin is generally regarded as composed of a number of polyhydroxy acids, mostly of the aliphatic series, present in the form of lactones, lactides and interesters. Shellac is an acidic resin, the ionisation constant⁶ (K) of dewaxed and decolourised shellac is 1.8×10^{-5} and the average molecule contains at least one free carboxyl and five hydroxyl and three ester groups. Two of the hydroxyl groups are on adjacent carbon atoms and the others are likely to be tertiary. The probable structure of lac molecule given by Sen Gupta³⁴ is given below:



The iodine value indicates the presence of unsaturated linkages and one of the constituent acids, shellolic acid contains a double bond. However, Kameth and Nadkarni⁷ found

Table 1.Important properties of shellac

Specific gravity	1.207
Molecular weight	964-1000
Shore hardness	60-61
Abrasion resistance (sand)	110
Ultimate tensile strength kg/sqcm.	132
Modulus elasticity kg/cm ²	13.5 x 10 ³
Adhesion p.s.i - steel	3200
Optical plane surface	6400
Copper	3300
Brass	2500-3300
Melting point	77-80°C
Softening range	30.5 - 56.5°C
Thermal conductivity mill watts/cm/°C	
at 35°C	2.42
at 63°C	2.09
Dielectric constant (K) at 20°C	3.23 - 4.61
Dielectric strength volts/cm	200-400 x 10 ³
Volume resistivity ohm/cm	1.2 - 1.8 x 10 ¹⁶
Dielectric loss 'E' Kc/sec.	0.26 - 0.329
Power factor tan ϕ at 20°	0.0044 - 0.0072
Loss factor K tan ϕ	0.0152 - 0.028
Permittivity	2.3 - 3.8

that the halogen consumption is chiefly due to the substitution at the carbon atom next to aldehydic group. Lac resin was separated into two fractions by means of ether. The soluble part is called the soft resin and the other insoluble part as hard resin. Hard resin is soluble in polar solvents. The chemical constants of shellac are given in Table II.

Polymerization of shellac

When shellac is heated above its melting point, it polymerizes very rapidly, loses its fluidity and is converted through a rubbery stage to a hard horn like infusible product. Thermal polymerization of shellac has been studied by many workers⁸⁻¹². Interesterification and interetherification are the most probable reasons for thermal polymerization of shellac. However, Battacharya¹³ has reported that as a result of thermal polymerization at 125°C, the various chemical constants such as acid value, the saponification value and iodine value remain practically the same. There is a slight initial lowering of the hydroxyl value.

Considerable efforts have been made for the separation of shellac acids from hard or pure lac and reported by different workers¹⁴⁻²⁰.

Several workers have studied this versatile resin for variety of reactions, since shellac consists of carboxyl, hydroxyl and ester groups. The major work involves esterification²¹⁻²⁴ or partial esterification of carboxyl or hydroxyl groups of the shellac. Battacharya and Gidwani²⁵ have

Table II

	Shelloc	Soft resin	Hard resin
Acid value	65-75	103-110	50-55
Saponification value	220-230	207-229	218-225
Ester value	155-165	104-119	163-165
Hydroxyl value	250-280	116-117	235-240
Iodine value			
Wijs (1 hour)	14-18	50-55	11-13
Hübl.	6-12	-	-
Carbonyl value	7.8 - 27.5	17.3	17.6
Molecular weight (Rast method)	1006	513-536	1900-2000

esterified the hydroxyl groups of the lac with acetic, butyric, caprylic, lauric, iteanic, oleic and linseed oil acids. They found that in some cases, all the five hydroxyl groups can be esterified under controlled conditions. These esters are suitable for varnishes, paints and in other surface coatings. With alcohols, the free carboxyl group readily forms esters²⁶⁻²⁸ in the presence of mineral acid. It has been esterified with glycols, glycerols and pentaerythritol. These esters are more viscous than the shellac esters of monohydric alcohols. The reaction in the case of shellac and glycol is more complex and is accompanied by the formation of shellac glycol ethers⁸. Esters have been prepared using various dicarboxylic acids or their anhydrides with or without solvents. These modified products have properties such as gloss, water resistance, elasticity and adhesion to glass and metal⁵. Cockeram and Levine⁴ have esterified shellac with polyols such as ethylene glycol, diethylene glycol and sorbitol. They obtained soft products some of which adhere to metals with surprising tenacity. They prepared esters with low acid number also (2-3) but they are very viscous and sticky. These esters are used as coating compositions where it enhances the adhesion and flexibility. Kerath²⁹ has prepared glycol esters using hydrolysed lac and ethylene glycol and the films were reported flexible even at low temperature (-40°C). Polyesters based on shellac have also been prepared by esterification of hydrolysed lac with glycols and aliphatic dicarboxylic acids to produce flexible urethane coatings on textiles³⁰⁻³¹ such as nylon and cotton. Thus,

shellac esters have been utilized for a number of applications.

Some of the important applications of shellac are given below:

- (1) Spirit varnishes - furniture finishes, french sealers, undercoats and enamels
- (2) Glazes for confectionary and tablets
- (3) Aqueous varnishes for wood, paper and leather
- (4) Flexographic and other shellac based inks
- (5) Hair lacquers and cosmetics
- (6) General moulding compositions, grinding wheels, gramophone records and sealing wax
- (7) Rubber compounding
- (8) Electrical insulation, including moulded insulations, laminated paper and insulating varnishes
- (9) Adhesives and cements

From the foregoing discussion, it is evident that shellac with its several peculiar characteristics, can be explored as a source of hydroxy and ester groupings suitable for reaction with isocyanates to obtain polyurethane foams.

PRESENT INVESTIGATION AND RESULTS

Polyhydroxy compounds are one of the important starting materials for making rigid urethane foam. Today thousands of polyhydroxy compounds are known. They are polyesters and polyethers or simply called as polyols. At present the raw materials required for making urethane foams (flexible and rigid) are not manufactured in India. The demand for these foams is expected to increase in near future. In view of the growing commercial importance of polyurethane polymers, it is of interest to substitute new polyhydroxy compounds for the preparation of urethane foam and evaluate the characteristics of the resulting foams.

Shellac (lac) is indigenously available in India. Therefore it was considered desirable to exploit the potentiality of shellac esters for making rigid urethane foam. As discussed in the Introduction Section, lac has got attractive properties like high dielectric strength, low thermal conductivity, good adhesion and gloss, which could be considered as added features for shellac esters.

In the present investigation, the shellac polyesters are prepared by esterifying the free carboxyl group present in lac with different glycols. These polyesters are highly viscous. To reduce the viscosity of these polyesters, they are blended with other hydrogen donors or reacted with diisocyanate to give

semiprepolymers. These are further processed for the preparation of rigid urethane foams.

Several workers have prepared lac esters with different glycols but no one has evaluated esters with low acid value for making urethanes. It is observed that diethylene glycol is more compatible with lac as compared with ethylene glycol, propylene glycol or polyglycols and hence diethylene glycol is the most suitable glycol for the esterification of lac.

1(a) Esters of shellac with diethylene glycol

Literature²⁵ survey reveals that the esterification of lac with glycol is generally carried out in 1:10 molar ratio. A series of experiments have been carried out for the esterification of orange lac and bleached lac with diethylene glycol in the presence of p-toluene sulphonic acid as a catalyst at different molar ratios, time intervals and temperatures. It is of interest to note that when one mole of lac was condensed with less than five moles of glycol (without solvent) the reaction product has a tendency to gel before appreciable amount of ester is formed. The conditions for the preparation of different polyesters and their properties are given in Table III and IV.

(b) Effect of catalytic concentration

Para toluene sulphonic acid has been used as catalyst in the preparation of all polyesters. As the efficiency of the catalyst depends upon its concentration, several attempts were made for the preparation of polyesters with higher concentrations of p-toluene sulphonic acid. The reaction time is reduced with

Table III

Orange lac polyesters with diethylene glycol

Expt. No.	Orange lac in parts	Diethylene glycol in parts	Temperature in °C.	Time in hrs.	Catalyst in parts	Hydroxyl value mgs of KOH/gm	Acid value mgs of KOH/gm
A	100 gm.	106.0	90-180	8	0.5	510	13.0
B	100 gm.	84.8	90-180	8	0.5	480	16.6
C	100 gm.	63.6	90-180	8	0.5	440	18.4
D	100 gm.	53.0	90-180	8	0.5	435	18.0

Table IV

Bleached lec polyesters with diethylene glycol

Expt. No.	Bleached lec in parts	Diethylene glycol in parts	Temperature in C.	Time in hrs.	Catalyst in parts	Hydroxyl value mgs of KOH/gm	Acid value mgs of KOH/gm
E	100 gm.	106.0	90-180	8	0.5	475	14.5
F	100 gm.	84.8	90-180	8	0.5	400	15.8
G	100 gm.	63.6	90-180	8	0.5	375	18.0
H	100 gm.	53.0	90-180	8	0.5	370	18.0

higher concentrations of the catalyst but the removal of catalyst is tedious and uneconomical. Moreover, the properties of the foam are affected by excess of the residual catalyst. The catalyst was found to be most suitable at 0.5% concentration on shellac basis.

(c) Esters of shellac-glycols-dibasic acids

In the present work, apart from the polyester obtained with shellac diethylene glycol, several shellac modified polyesters were also prepared with different molar proportions of adipic, succinic, sebacic, phthalic acid, ethylene glycol, diethylene glycol, polyglycol and glycerol at constant time and temperature with p-toluene sulphonic acid as catalyst. The conditions for the preparation of different polyesters and their properties are given in Table V.

Though some of the modified polyesters have required acid and hydroxyl value, they cannot be used as such for making urethane foams by one shot technique due to their high viscosities. A number of foams were prepared using these highly viscous resins by semi prepolymer method but the foams were found to be inferior in all respects as compared to foams obtained from shellac-diethylene glycol polyester. Therefore the present study was concentrated only on shellac diethylene glycol polyester.

(d) Preparation of semi prepolymers from shellac polyesters

Since the shellac polyesters are viscous, it is difficult to adopt one shot foam system for their foam

Table V

Preparation of different polyesters and their properties

Sr. No.	Bleached Ethylene glycol	Diethylene glycol	Glycerol	Polyglycol 400 mol.wt.	Composition in parts					OH value in mgs of KOH per gm.	Acid Value in mgs of KOH per gm.
					Adipic acid	Phthalic acid	Succinic acid	Sebacic acid	Time		
1.	100	62.0	-	-	-	-	-	-	gelled	-	-
2.	100	124.0	-	-	-	-	-	-	620.0	24.0	24.0
3.	100	-	26.5	9.2	100.0	-	-	-	300.0	20.5	20.5
4.	100	-	53.0	9.2	-	-	-	-	350.0	20.0	20.0
5.	100	-	106.0	-	-	29.2	-	-	440.0	25.0	25.0
6.	100	-	63.0	-	-	14.6	-	-	410.0	23.3	23.3
7.	100	-	26.5	27.6	-	43.8	7.4	-	550.0	26.0	26.0
8.	100	-	26.5	75.44	-	-	14.8	11.8	375.0	80.0	20.0

preparation. Therefore semi prepolymer system was preferred.

In semi prepolymer or quasi prepolymer system, a part of polyester is reacted with excess diisocyanate, the NCO:OH ratio being usually 4.5:1 to get a prepolymer of low viscosity. Generally toluene diisocyanate (TDI) is preferred to make prepolymers for one shot foam system because the partial reaction of TDI with polyol provides lower exotherm when the two components (polyol and isocyanate) are mixed in the foaming operation.

Lac polyesters were reacted with different isomers of TDI to give semi prepolymers of reduced viscosity.

- (A) A shellac polyester D (Table III) (one mole equivalent) was reacted with 4.5 mole equivalent of 80:20 mixture of 2:4/2:6 TDI under dry and inert atmosphere. The resultant semi prepolymer had 28.1% free isocyanate content.
- (B) A shellac polyester H (Table IV) (one mole equivalent) was reacted with 5.5 mole equivalent of 65:35 mixture of 2:4/2:6 TDI under dry and inert atmosphere. The resultant semi prepolymer had 29.8% free isocyanate content.

(c) Preparation of rigid urethane foams from semi prepolymer

The foams were prepared from shellac polyester, silicone oil, semi prepolymer, catalyst and water (various proportions). The foam formulations and foam properties are tabulated in Table VI and VII.

In the present study, the semi prepolymer method was found to be most suitable as the polyesters were viscous. The one shot method was also adopted for making rigid urethane foams by blending these viscous resins with suitable hydrogen donors for comparative study.

Table VI

Rigid foams from semi prepolymer A

	F	G	H	I	J
<u>Foam formulation</u>					
Shellac polyester ^b in parts	100	100	100	100	100
Silicone oil 201 Dow	0.5	0.5	0.5	0.5	0.5
Triethanol amine	0.25	0.25	0.25	0.25	0.25
Semi prepolymer A	149.0	142.0	135.5	134.0	132.5
Water	1.5	1.0	0.5	0.4	0.3
<u>Processing characteristics</u>					
NCO:OH	----- 1.05:1 -----				
Cream time min.	2.0	2.0	2.5	2.5	2.5
Rise time min.	3.0	4.0	4.5	5.0	5.0
Tack free time min.	6.0	6.5	7.0	7.0	7.0
<u>Foam properties</u>					
Density lbs/cuft.	8.2	13.0	16.0	17.6	18.2
Compression strength, psi. at 10% deflection	115	210	285	310	340
Closed cells %	96	98	98	98	98
Water absorption lbs/sqft. of surface area	----- less than 0.035 -----				
Permeability perm inches	----- less than 1.0 -----				
Thermal conductivity BTU/hr/sq.ft/°F/inch	0.26	-	0.28	-	0.3
Dimensional stability % volume change					
at 70°C for 28 days	----- less than 1.0 -----				
at 110°C for 28 days	----- less than 1.5 -----				

A - semi prepolymer prepared with 80:20, 2:4/2:6 TDI
(28.1% free isocyanate content)

B - shellac polyester D from Table III.

Table VII

Rigid foams from semi prepolymer B

	A	B	C	D	E
<u>Foam formulation</u>					
Shellac polyester ^a in parts	100	100	100	100	100
Silicone oil 201 Dow	0.5	0.5	0.5	0.5	0.5
Triethanol amine	0.25	0.25	0.25	0.25	0.25
Semi prepolymer B	142.5	135.0	127.5	126.0	124.5
Water	1.5	1.0	0.5	0.4	0.3
<u>Processing characteristics</u>					
NCO:OH	----- 1.05:1 -----				
Cream time min.	2.0	2.0	2.5	2.5	2.5
Rise time min.	3.0	4.0	4.5	5.0	5.0
Tack free time min.	6.0	6.5	7.0	8.0	8.0
<u>Foam properties</u>					
Density lbs/cuft.	8.0	12.0	15.5	17.0	18.0
Compression strength, psi. at 10% deflection	110	200	260	300	330
Closed cells %	96	98	98	98	98
Water absorption lbs/sqft. of surface area	----- less than 0.04 -----				
Permeability perm inches	----- less than 1.0 -----				
Thermal conductivity BTU/hr/sq.ft/°F/inch	0.26	-	0.28	-	0.3
Dimensional stability % volume change					
at 70°C for 28 days	----- less than 1.0 -----				
at 110°C for 28 days	----- less than 2.0 -----				

a - shellac polyester D from Table III.

B - semi prepolymer prepared with 65:35, 2:4/2:6 TDI
(23.8% free isocyanate content)

(f) Modification of bleached lac polyester

As the bleached lac polyester was viscous, many difficulties encountered in further processing. Therefore this polyester H (Table IV) was blended with polyethylene glycol (mol.wt. 400) to reduce its viscosity. This blended product was utilised in making foams by one shot technique. The specifications of this modified bleached lac polyester K are given in Table VIII.

Table VIII

Specifications for polyester K

Appearance	Dark brownish liquid
OH number	326 mgs of KOH/gm
Acid number	10.0 mgs of KOH/gm
Moisture content	0.1%

(g) Preparation of rigid foams from polyester K by using one shot technique

The polyester K, polymeric MDI, silicone oil, catalyst and water was mixed together simultaneously. By varying the water proportion, foams with different densities were obtained. The foam formulations and foam properties are reported in Table IX. The solvent and chemical resistance characteristics of all the foams prepared from shellac polyesters are listed in Table X.

Table IX
Rigid foams from modified polyester K

	P	Q	R	S	T
<u>Foam formulations</u>					
Modified polyester K in parts	100	100	100	100	100
Silicone oil 201 Dow	0.5	0.5	0.5	0.5	0.5
Triethylene diamine	0.25	0.25	0.25	0.25	0.25
Polymeric MDI	101.0	93.5	86.0	84.0	82.5
Water	1.5	1.0	0.5	0.4	0.3
<u>Processing characteristics</u>					
NCO:OH	----- 1.05:1 -----				
Cream time min.	2.0	2.0	2.5	2.5	2.5
Rise time min.	3.0	4.0	5.0	5.5	5.5
Tack free time min.	6.0	7.0	7.5	8.0	8.0
<u>Foam properties</u>					
Density lbs/cuft.	8.1	12.8	16.4	17.8	18.4
Compression strength, psi. at 10% deflection	120	265	300	330	360
Closed cells %	98	98	98	98	98
Water absorption lbs/sqft. of surface area	----- less than 0.045 -----				
Permeability perm inches	----- less than 1.0 -----				
Thermal conductivity BTU/hr/sq.ft./°F/inch	0.265	-	0.29	-	0.3
Dimensional stability % volume change					
at 70°C for 28 days	----- less than 1.0 -----				
at 100°C for 28 days	----- less than 1.0 -----				

Table X

Solvent and chemical resistance of the foams prepared
from shellac polyesters

(at room temperature for 8 days)

<u>Material</u>	<u>Resistance</u>
<u>Mineral acids</u>	
conc.	Poor
dilute	Good
<u>Alkali</u>	
conc.	Good
dilute	Excellent
<u>Organic solvents</u>	
alcohol aliphatic	Fair (shrinkage)
ketone	Poor
aromatic hydrocarbon	Good (slight swelling)
chlorinated hydrocarbon	Fair
<u>Brine solution</u>	
conc.	Good
Dilute	Good
<u>Water</u>	Good

DISCUSSION

Polyesters having low acid number and high hydroxyl value are generally used for the preparation of rigid urethane foams. To obtain the desired acid number and hydroxyl value, shellac (bleached and orange lac) was esterified with diethylene glycol in 1:5 ratio (polyester D and polyester H - Table III and IV) without solvent. Both these polyesters have an acid number of 18 and hydroxyl value of 370 for bleached lac and 435 for orange lac.

p-Toluene sulphonic acid was found to be the effective catalyst for the esterification, however, a concentration of more than 0.5% adversely affects the properties of the foam. This may be due to the hydrolysis of polyesters in presence of high concentration of acid catalyst. The moisture content of the shellac polyesters was found to be less than 0.5%.

The polyesters were dark brown in colour and highly viscous. In order to reduce the viscosity, the polyesters were blended with polyethylene glycol (mol.wt. 400) or reacted with excess TDI to give semi prepolymers. These blends have been utilised for the preparation of rigid urethane foams by one shot method using polymeric isocyanate (MDI), triethylene diamine (Dabco) as a catalyst, silicone oil (Dow 201) as a surface active agent and water as a blowing agent. Rigid urethane foams from semi prepolymers were prepared by mixing shellac polyester, silicone oil and semi prepolymer together

followed by the addition of the catalyst triethanol amine and water.

In semi prepolymers triethanol amine was found to be a suitable catalyst while in blends, triethylene diamine (Dabco) gave the best results. It was found that 0.25% of the catalyst concentration is optimum for both cases. The use of silicone oil (Dow 201) in 0.5% concentration was found to be the best in getting foams with uniform and closed cell structure.

Foam characteristics

In the present investigation, different density foams were prepared by using water as a blowing agent, which helps as a chain extender and further crosslinking without any side reactions. The density of the foams was controlled by varying the amount of water. The density increases with decreasing amount of water. The foams were obtained with the density ranging from 5 to 20 lbs./cuft. It was observed that water upto 1.5 parts yields foams with overall good properties. Any excess of water imparts higher shrinkage and brittleness to the foam, resulting in undesirable mechanical properties.

The compression strength values of the foams were found to increase (Table VI, VII) with increasing density. It was observed that the compression strength of the foam made from MDI was higher than the foam made from TDI or semi prepolymers (Table IX). This may be due to high functionality of MDI.

From the Tables VI, VII and IX, it can be seen that the foams have low water absorption and low water vapour permeability

which may be due to the high closed cell structure of the foams (96-98%). The water vapour permeability was found to be less than one perm inches while water absorption values are less than 0.045 lb/sq.ft. of surface area in all the cases.

The thermal conductivity (K factor) was found in the range of 0.26 to 0.3 BTU/hr/sq.ft./^oF/inch. It has been observed that K factor increases with increasing density. The K factor for initial foams (freshly cut samples) was found to be 0.24 to 0.26, while at equilibrium, it attained a value of 0.26 to 0.28 BTU/hr/sq.ft./^oF/inch.

It was observed that most of the foams have good solvent resistance. However, in some polar solvents, they somewhat loose their shape and in concentrated acids, the foams were found to disintegrate completely.

These foams have good thermal dimensional stability since no measurable change was observed in weight, colour and volume after aging them for 28 days at 70^o and 100^oC.

After successful preparation of high density foams from shellac polyesters, the possibility of obtaining low density foams from the latter by using trichlorofluoromethane as a blowing agent was explored. Only a limited success could be achieved since the trichlorofluoromethane has very poor compatibility with shellac polyesters.

Applications

High density rigid urethane foams are suited to several applications such as artificial limbs (as substitute to wood),

furniture, reinforcing materials in aeroplanes, in void fillings, construction field etc. The most attractive is the one for artificial limbs for a country like India. In western countries, mostly rigid urethane foams are being used for this purpose. In India, wood is still being used for artificial limbs with several disadvantages. To evaluate the suitability of high density rigid urethane foams prepared from shellac polyesters, they were compared with polyethylene foams (German product) which is used for artificial limbs as the reference standard. The comparative properties are given in Table XI. It could be seen from the table that shellac foam is quite comparable with the German product in all respects and can be used for making artificial limb as a substitute to wood. An artificial limb prepared from shellac polyester rigid urethane foam has been shown in Fig. 1 .

Table XI

Comparative properties of polyurethane rigid foams

	Pedilene sample (imported)	shellac based rigid foam
Density lbs/cuft.	20.2	18-20
Compression strength, psi. at 10% deflection	400-420	340-360
Water absorption lbs/sq.ft of surface area	0.03	0.04
Water vapour permeability perm inches	<1.00	1.00
Closed cells %	98	96-98
'K' factor BTU/hr/sq.ft/°F/inch	0.24	0.26 - 0.28
Dimensional stability % volume change		
at 70°C for 28 days	<1.0	1.0
at 100°C for 28 days	<1.0	1.2
Flame resistance	No self extinguishing	No self extinguishing
Burning rate in/min.	1.6	1.0
Solvent resistance properties		
acids conc.	----- degraded-----	
solvents	No change after removal of the solvents.	

EXPERIMENTAL

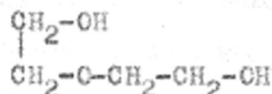
Raw materials

Shellac - Shellac was obtained from M/s. Angelo Bros., Calcutta. Specifications of lac are given below:

Lac	Form	Colour	Acid No. mgs of KOH/gm	Hydroxyl No. mgs of KOH/gm
Orange lac	Flakes	Dark brown	70.55	263.6
Bleached lac	Powder	Pale yellow	73.47	286.4

Diisocyanates - Toluene diisocyanate (TDI) and Desmudur 44 V (polymeric MDI) were obtained from Farbenfabriken Bayer (Germany). Specifications of the both diisocyanates have already been reported on pages 11 & 13.

Diethylene glycol -



Molecular weight: 106.12, b.p. 245°C,

Viscosity at 20°C: 36.0 centipoises,

Specific gravity at 20/20: 1.1184 Purity: Reagent grade.

Diethylene glycol was obtained from NOCIL, India.

p-Toluene sulphonic acid - Anhydrous and freshly prepared p-toluene sulphonic acid was used for esterification.

Dibasic acids and glycols - Adipic acid, sebacic acid, succinic acid, phthalic acid, polyglycols, ethylene glycol and

glycerol used in the present study were analytical grades.

(a) General method for the preparation of shellac polyester

In a two litre four necked round bottom flask equipped with a stirrer, a nitrogen gas inlet, a thermometer and a reflux condenser, different molar ratios of diethylene glycol (reported in Table III and IV) were mixed. The mixture was heated upto 80-90°C with constant stirring. Powdered shellac (0.1 mole) was added slowly with stirring under nitrogen flushing. The reaction temperature was maintained at 80-90°C till a homogenous mass was formed. Then 0.5% of p-toluene sulphonic acid catalyst (based on shellac) was added. The heating was increased slowly to 180°C with constant stirring. The sample was taken out intermittently and tested for the acid number. When a desired acid number was obtained the reaction was stopped. Finally, the excess of diethylene glycol and water was removed under vacuum (0.2 mm). The final ester was analysed for acid number and hydroxyl number which have been reported in Table III and IV. The moisture content in all the shellac polyesters was found to be <0.1%.

(b) Preparation of esters of shellac-glycols and dibasic acids

In a two litre four necked round bottom flask equipped with a stirrer, a nitrogen gas inlet, a thermometer and a reflux condenser, powdered shellac and/or dibasic acids and glycols were mixed in proportions indicated in Table V, at 80-90°C, with constant stirring and under inert atmosphere till a homogenous mass was formed. Then 0.5% p-toluene sulphonic acid catalyst

(based on shellac) was added. The heating was increased slowly upto 180-200°C. At this temperature, the mixture was heated for 8 hours with slow stirring and nitrogen flushing. At definite intervals, the sample was taken out and tested for acid number. At the end of 8 hours, the reaction was stopped and the excess glycol was removed under reduced pressure. In each case the residual product was determined for acid and hydroxyl number which have been reported in Table V.

(c) Preparation of semi prepolymer from shellac polyester

(A) In a two litre four necked round bottom flask equipped with a stirrer, a gas inlet, a thermometer and a dropping funnel, polyester D (Table III)(one mole equivalent) was placed. To this TDI (4.5 mole equivalent) 80:20 was added slowly with gentle stirring under nitrogen flushing at room temperature for $\frac{1}{2}$ hour. Then the temperature was raised to 70°C and maintained this temperature for 1 hour with constant stirring. The final product was analysed for free isocyanate content.

(B) This semi prepolymer was prepared with polyester H (Table IV) using the procedure described above. In this prepolymer 65:35 TDI (5.5 mole equivalent) was used instead of 80:20 TDI. The final product was analysed for free isocyanate content.

(d) Preparation of rigid foams from semi prepolymers

The weighed quantities of shellac polyester, silicone oil, semi prepolymer as mentioned in Table VI and VII were

mixed in a polyethylene beaker till a homogenous suspension was obtained. Then triethanol amine and water were added to it with vigorous stirring. When the creamy stage was attained, the mass was poured into polyethylene trays coated with wax paper. Foams were kept at room temperature for 3-4 hours and then cured at 50°C for $\frac{1}{2}$ hour.

Test samples were cut out from the centre of the foam block parallel to foam rise and evaluated for their physical, mechanical and chemical properties. The foam formulations and foam properties have been reported in Table VI and VII.

(e) Preparation of polyester K (modified bleached lac polyester)

In a two litre four necked round bottom flask equipped with a stirrer, a gas inlet, a thermometer and a reflux condenser, equal parts of polyester H (Table IV) and polyethylene glycol (mol.wt. 400, OH 285) were blended at 70°C to 80°C for 2 hours with constant stirring under nitrogen atmosphere. After 2 hours the blend was dried under reduced pressure. The final product was tested for acid number, hydroxyl number and moisture content and have been reported in Table VIII.

(f) Preparation of rigid urethane foam from polyester K and polymeric MDI by one shot technique

Weighted quantities of polyester K, silicone oil, triethylene diamine, polymeric MDI and water as mentioned in Table IX were mixed together with vigorous stirring (2000 rpm.) till the creamy stage was observed. Then the homogenous mass was transferred to moulds (polyethylene or wooden trays) coated

with wax paper. The foams were kept at room temperature for 3-4 hours and then cured at 50°C for 30 minutes.

Test samples were cut from the centre of the foam block parallel to foam rise and tested for their physical and mechanical properties. The foam formulations and foam properties have been reported in Table IX.

Analytical Methods

Testing procedure for polyesters or polyols

Determination of acid number - Accurately weighed sample (about 1 gm.) was dissolved in 50 ml. alcohol: benzene mixture (1:1) and the resulting homogenous solution was titrated against standard 0.1 N alcoholic potassium hydroxide solution. Acid number was calculated in terms of milligrams of KOH per gram of the sample as follows:

$$\text{Acid number} = \frac{(A-B) \times N \times 56.1}{W}$$

where A = ml. of KOH required for the titration of the sample

B = ml. of KOH required for the blank

N = normality of KOH

W = weight of the sample in gms.

Determination of hydroxyl number

About 0.5 gm. of the sample was accurately weighed and dissolved in 20 ml. of monochlorobenzene in 250 ml. Erlenmeyer flask. 10 ml. of phenyl isocyanate solution (10 ml. phenyl isocyanate diluted to 100 ml. with dry toluene) was added. The solution was refluxed on a sand bath for 1 hour. Then it was cooled to room temperature and 20 ml. of dibutyl amine solution (10 ml. of dibutyl amine diluted to 100 ml. with dry toluene) was added and refluxed for 15 minutes. Then it was cooled to room temperature and 50 ml. of dry methanol was added

through the condenser. The excess amine was titrated with 0.5 N HCl using bromophenol blue as indicator. A blank run was carried out in a similar manner. The hydroxyl number was calculated in terms of milligrams of KOH per gram of the sample as follows:

$$\text{Hydroxyl number} = \frac{(A-B) \times N \times 56.1}{W}$$

A = ml. of HCl for the sample

B = ml. of HCl for the blank

N = normality of HCl

W = weight of the sample in grams

Determination of NCO percentage

TDI or MDI was reacted with dibutylamine to form urea. The excess amine was estimated by back titration with HCl. Percent NCO was calculated as follows:

$$\text{Percent NCO} = \frac{(0.042) \times 100 \times N (B-S)}{W}$$

where: S = ml. of HCl required for the sample

B = ml. of HCl required for the blank

N = normality of HCl

W = weight of the sample in gms.

Specific gravity - Specific gravity was found out by using pycnometer (25 ml.)

$$\text{Specific gravity } 25/25^{\circ}\text{C} = \frac{S}{W}$$

where: S = weight of the sample in the pycnometer

W = weight of the water in the pycnometer.

Determination of moisture content by Karl Fisher method (using a direct dead stop technique)

This was tested according to the ASTM D 1638. The method

is based on the reduction of iodine by sulphur dioxide in the presence of water. The reaction is quantitative when pyridine and alcohol are combined to react with sulphur trioxide to produce hydrochloric acid.

Preparation of Karl Fischer reagent (KF)

- (A) Iodine (127 gms.) was dissolved in a mixture of 650 ml. of dry methanol and 100 ml. of dry pyridine under dry conditions.
(B) Sulphur dioxide (100 gms.) was absorbed in 100 ml. of dry pyridine under strictly dry conditions.

Both these solutions A and B were mixed together and kept overnight in a dark place in an air tight bottle.

Karl Fischer (KF) reagent was standardised by using anhydrous methanol and water sample.

Method of estimation

Equivalency factor F. - It was calculated in terms of milligrams of water per millilitre of the reagent as follows:

$$F = A/B \quad \begin{array}{l} A = \text{milligrams of water added} \\ B = \text{milligrams of KF added} \end{array}$$

Moisture content in polyol - The sample was weighed (about 2 gm.) accurately in the titration flask and titrated against the KF reagent using dead stop technique.

The moisture content or percentage of water was calculated as follows:

$$\text{Water \%} = \frac{VF}{10W}$$

where V = ml. of KF required for sample

F = equivalency factor for KF in milligrams per millilitre of reagent

W = weight of the sample.

Testing of foam

Apparent density was found out according to ASTM No. D 1622-63.

Test specimen - 2" x 2" x 1". Specimen was weighed accurately and its volume was noted at room temperature. Density was calculated and expressed in pounds per cubic feet.

$$D = \frac{W}{V} \times 3.8$$

D = density of specimen in lbs. per cubic feet

W = weight of the specimen in gms.

V = volume of specimen in cubic inches.

Compression strength

Compression strength was found out according to ASTM No. D 1621-64.

Test specimen - 2" x 2" x 1" free from visible flaws or imperfections. Dimensions were measured accurately.

Specimen was kept in the compression machine and the load was applied in such a manner that it was distributed as uniformly as possible on the entire specimen. The rate of crosshead movement was kept 0.1 inch per minute per inch of specimen thickness. The specimen was compressed to 10% of its measured thickness. The load was measured at 10% deflection. The compression strength was calculated by dividing the maximum load in pounds by the area of the specimen in square inches. The average value was determined and expressed as pounds per square inch at 10% deflection.

Tensile strength

The tensile strength of the rigid foam was determined

according to ASTM No.D 1623-64.

Test specimen - 2"x2"x6" piece was turned on a lathe to give dumbbell shape having a throat diameter of 1.129 inches. The cross-sectional dimension of test specimen was measured at several points. Specimen was placed in the grips and aligned properly to the central axis. The load was measured as the specimen was ruptured. The rate of the head movement was kept 0.05 inch per minute per inch of test specimen gauge length. The tensile strength was calculated by dividing the breaking load in pounds by the original minimum cross sectional area of the specimen in square inches and expressed in pounds per square inch.

Dimensional stability

The effect of temperature on rigid foam was determined according to ASTM No.D 2126-62 T.

Test specimen - 10 x 10 x 2.5 cms. The specimens were aged at 70°C and 100°C for 28 days in an air circulating oven. The samples were examined before and after aging for:

- (1) percentage change in weight
- (2) percentage change in volume
- (3) shape and colour.

Thermal conductivity (by thermal conduction tester - Feutron type 4110)

The plate method³² is applied by inserting the material to be tested between the two plain plates with different temperatures. The plate having the higher temperature designated as heating plate and it is maintained at the same temperature by electrical heating. The other plate having lower temperature

is designated as cooling plate and it is maintained at constant temperature by the dissipation of heat. The sides and back surface of the heating plate are surrounded with a plate having the same temperature, designated as the protective heating plate. Side and back heat transfer of the heating plate are avoided so that in the quasi-stationary condition the electric power fed to the heating plate is proportional to the heat current by the material to be tested.

Test specimen - 25 x 25 x 2.5 cm.

Procedure:- The test specimen was accommodated between the heating plate and the cooling plate. Both the plates were stabilised using thermostatic control. Heating of the plate was carried out electrically and dissipation of heat by means of tap water. The temperature of the heating plate and protective heating plate was controlled by regulating circuit which is composed of the thermopiles, a two point regulator and the heating plate. Readings were taken at $\frac{1}{2}$ hour interval. The average thickness of the sample and different temperatures were noted accurately. From this data the thermal conductivity was determined as kilo calories/hr/meter/ $^{\circ}$ C. It was converted into BTU/hr/sq.ft/ $^{\circ}$ F/inch by multiplying the factor 8.064.

Water vapour permeability

Permeability was determined according to BS No.3887.

Procedure:- The specimen was a right cylinder of 2 ± 0.05 inches in height and a diameter of 0.03 inch greater than the internal diameter of glass beaker of approximately $2 \frac{1}{2}$ inch internal

diameter and $3\frac{1}{2}$ inch in height. Top of the beaker was slightly belled out. The beaker was filled with granulated anhydrous calcium chloride to about $1/4$ inch below the expected lower surface of the specimen. The specimen was inserted into the beaker so that top of the surface was flushed with the top of the beaker. Melted wax (90% microcrystalline + 10% plasticizer i.e. dibutyl phthalate) was run to seal the space between the belled out rim and the upper edge of the perimeter of the specimen. Care was taken to avoid softening of the foam sample. The whole assembly was then weighed accurately and kept at room temperature and at 40 to 42% relative humidity. Successive weights were taken after 24 hour intervals and the cumulative weight increase was plotted against time. Water vapour permeability was calculated as follows:

$$\text{Permeability} = \frac{240 x}{AY} = \text{g/m}^2/\text{day}$$

where x = the weight increased in mgs. in y hours
 A = the area expressed in cm^2 .

The final value was multiplied by the factor 0.0598 in order to get permeability in perms inches.

Water absorption

Water absorption was determined by ASTM No.2127-62T.
Test specimen - 4" x 4" x 1".

Specimen was weighed accurately and immersed in a horizontal position under a 2 inch head of distilled water. Sample was removed after 10 seconds and allowed to drain for 10 seconds and then weighed again for zero absorption

value - (A) again sample was immersed for 24 hours and then drained and weighed - (B) water absorption was calculated as B-A and expressed as pounds per square feet of surface area.

Closed cell content

The relative proportion of open to closed cells in the foam was determined by the water absorption method³³.

Test specimen - 2"x2" x1".

Electrical properties

Electrical properties such as dielectric constant and dielectric loss factor were determined according to ASTM No. D 150-70 and dielectric constant by ASTM No. 149-64. Test specimens were made up of very thin sheets.

Flammability

The flammability test was carried out according to ASTM D 1692-59T.

Test specimen - 2"x6"x $\frac{1}{8}$ " free from dust and cut particles.

Specimen was marked across its width by two lines, 1 and 5 inches from one end of the specimen. The specimen was held horizontally on standard hardware cloth and the Bunsen burner flame was applied. The observations were noted as follows:

- (1) If no evidence of ignition as flame or progressive glow is seen after removal of burner flame, the result was noted as non-burning.
- (2) If the specimen continued to burn and reached upto the first mark after removing the burner flame, the time

required (in seconds) to reach the second mark was noted. The burning rate was calculated as follows:

$$\text{The burning rate} = \frac{240}{t}$$

where t = time required for burning in seconds.

The rate of burning is expressed as inch per minute.

- (3) If the specimen continued to burn even after removal of the burner flame, but does not reach upto the second mark, the result was noted as self extinguishing.

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Part-II

SELF CATALYTIC RESINS OR AMINOPOLYOLS

INTRODUCTION

The choice of polyol for the polyurethane synthesis largely determines the properties of the foam. Self catalytic resins or aminopolyols have received considerable attention in the preparation of rigid urethane foam^{1,2}. These polyols exert a pronounced effect on urethane reaction due to the presence of tertiary nitrogen in them. These types of resins are generally prepared by the condensation of di or trifunctional amines with alkylene oxides. The more common amines used in their manufacture are diethanolamine, triethanolamine, ethylenediamine, diethylenetriamine and piperazine. Foams have been obtained by coupling these resins with isocyanate.

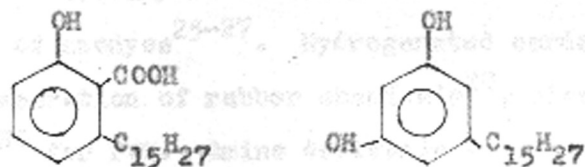
Recently Mannich base polyols³ have come into effect as self catalytic resins for the preparation of rigid urethane foam. These resins are generally prepared by condensing phenol^{3,4} or alkyl phenol⁵ with di or triethanolamine or further reacted with alkylene oxides. Under certain conditions the amino polyols are used exclusively as the polyol source or they may be combined with other polyhydroxy compounds for the preparation of rigid urethane foam. They are used particularly in systems designed for spraying and pour in place technique where a high order of activity is needed. Sometimes auxiliary catalysts such as 'organotins' are also used along with aminopolyols to provide an adequate balance of properties to the foam. These polyols have very good compatibility with polymeric isocyanates. Foams

produced from these polyols have greater fire retardancy, water resistance and dimensional stability³.

PRESENT INVESTIGATION AND RESULTS

New polyhydroxy compounds are frequently explored in the development of polyurethane foams. Self catalytic resins or aminopolyols have been marketed in United States of late by many entrepreneurs. These are generally prepared by condensing phenol or alkylphenol with di or triethanolamine and formaldehyde. In the present investigation, cardanol obtained from cashewnut shell liquid is utilised for the preparation of such polyols.

Cashewnutshell liquid (CNSL) is indigenously available in India as a by product from cashew industries. It is a dark blackish brown, viscous and corrosive liquid. The chemistry of cashewnutshell liquid has been the subject of extensive study by several investigators. Stadler⁶ has studied the ether extract of cashewnuts and reported that 90% of it consisted of an acid which he called anacardic acid, the rest 10% being a dihydroxy phenol known as cardol. The structure of anacardic acid and cardol is established as shown below:

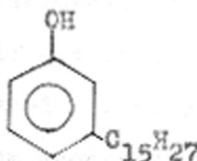


Anacardic acid.

Cardol.

Harvey and Caplan^{7,8} distilled the commercial CNSL under vacuum and 70% of the total distillate was found to be a single phenolic component with an unsaturated side chain in the meta

position. This is known as cardenol. The structure of cardenol is established as shown below:



Cardenol (3 pentadecenyl phenol)

Dowson and coworkers⁹⁻¹³ and many others have studied the detailed chemistry of cardenol.

The structural features of commercial CNSL and its derivatives impart several useful properties to it as a commercially useful intermediate. Among the various uses proposed for CNSL, cardenol and its derivatives are the manufacture of varnishes and paints¹⁴⁻¹⁸ resins^{19,20}, mosquito larvicides²¹, detergents and pesticides²². A useful collection of patents was listed²³ on different applications of these products in insulating varnishes, waterproofing materials, adhesives, automobile break linings and plastic components. Tetrahydro anacardol sulphides, amines and ureas have been recommended as oil soluble antioxidants and gasoline gum inhibitors²⁴. Tetrahydro cardenol has also been used for the preparation of azodyes²⁵⁻²⁷. Hydrogenated cardenol has been used for the preparation of rubber chemicals²⁸, plasticizers²⁹ and stabilizers³⁰ for PVC. Amino derivatives of hydrogenated cardenol are used for the preparation of mono and polyisocyanates³¹⁻³⁴. Teikichi and others³⁵ have prepared urethane oils from cardenol.

This investigation was undertaken with a view to exploit the use of cardenol in the preparation of self catalytic resins

(amino polyols) and rigid urethane foams therefrom. In the present work cardenol (3-pentadecenyl phenol) was condensed with diethanolamine and formaldehyde in different molar ratios to obtain aminopolyols. Self catalytic resins from nonyl phenol were also been prepared for comparative study.

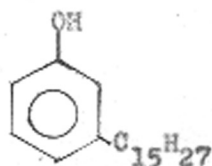
Different steps for the preparation of self catalytic resins are given below.

Distillation of CNSL

Commercial cashewnut shell liquid was distilled under reduced pressure to obtain cardenol (3-pentadecenyl phenol) as a pale yellowish liquid.

Cashewnutshell
liquid (CNSL)

Distillation
b.p. 195°/2 mm. ->



Cardenol
(3-pentadecenyl phenol)

Iron-free formaldehyde

The commercial formaldehyde was passed through the ion-exchange column to remove iron impurities. The formaldehyde content was estimated by the standard procedure.

Diethanolamine

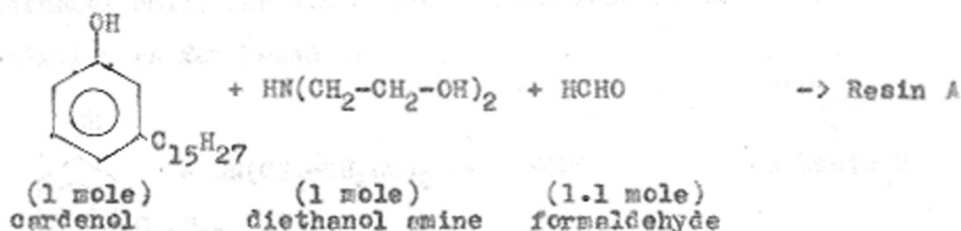
A.R. grade diethanol amine with following specifications was used.

Formula wt.	105.14
Sp. gravity	1.097 at 20°C

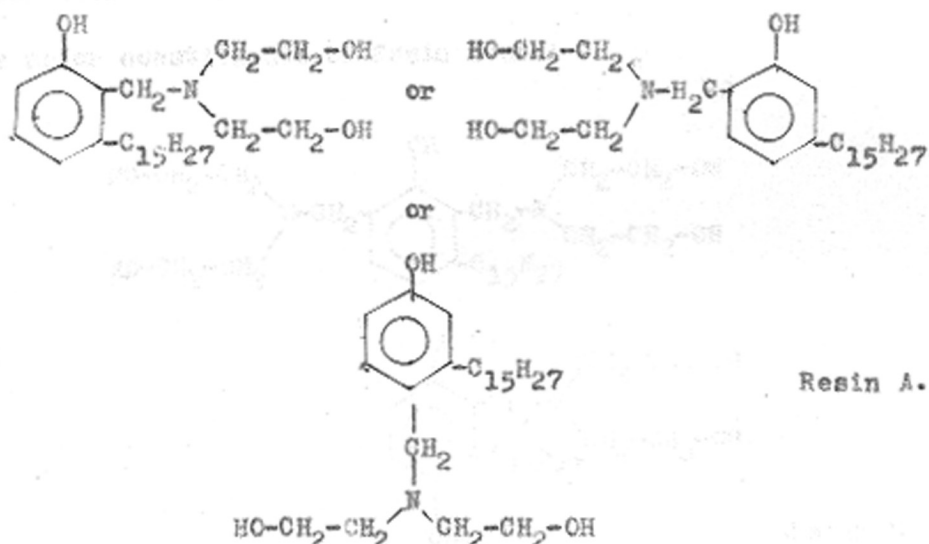
B.P. °C	271 (760 mm.)
Refractive index	1.4776 at 20°C.

Preparation of aminopolyol (self catalytic resin) from cardenol

Resins A. One mole of cardenol was condensed with one mole of diethanol amine and 1.1 mole of formaldehyde under controlled conditions (see Experimental page 105). The product was dried under reduced pressure at 90°C.



The major constituents of Resin A are:



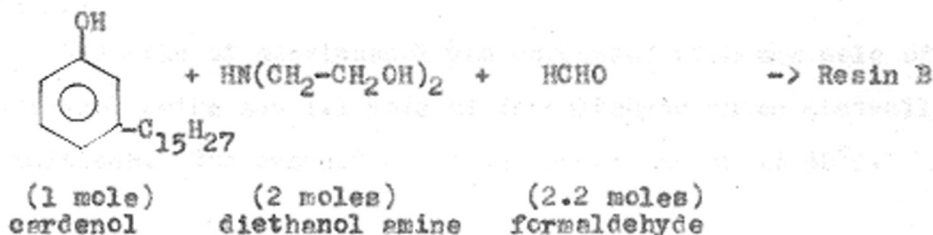
The properties of Resin A are given below:

Acid number	0.1 mgs. of KOH/gm
Hydroxyl number	400 mgs. of KOH/gm

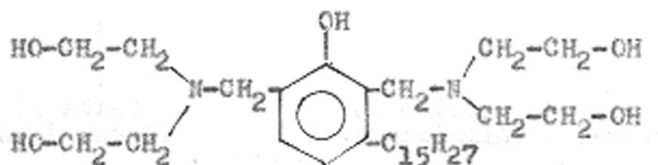
Sp. gravity	1.0214 at 25°C
Nitrogen content	3.4% (weight %)
Moisture content	0.2%
Viscosity	Flow time of 960 seconds in Ford Cup No.4
Appearance	Viscous dark brown liquid
Mol. wt.	418.

Resin B

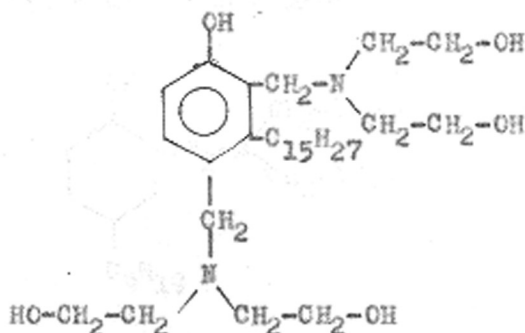
One mole of cardenol was condensed with two moles of diethanol amine and 2.2 moles of formaldehyde under the same condition as for Resin A.



The major constituents of Resin B are:



or



Resin B.

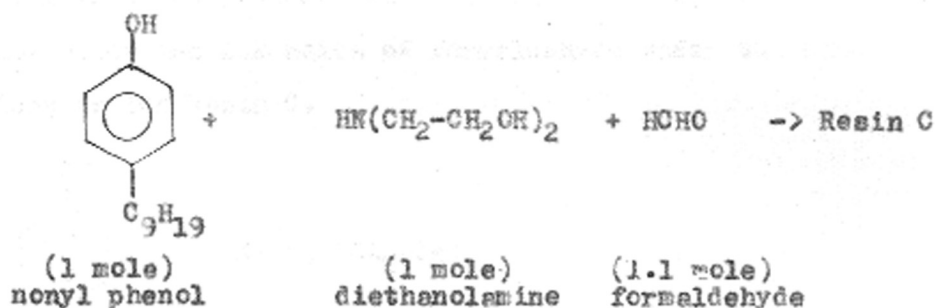
The properties of Resin B are given below:

Acid number	0.1 mgs. of KOH/gm
Hydroxyl number	580 mgs. of KOH/gm
Specific gravity	1.042 at 25°C
Nitrogen content	5.2% (weight %)
Moisture content	0.3%
Viscosity	Flow time of 1200 seconds in Ford Cup No.4
Mol.wt.	540
Appearance	Viscous dark brown liquid

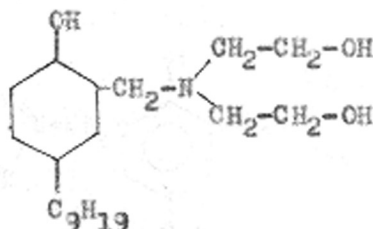
Preparation of aminopolyol from nonylphenol

Resin C.

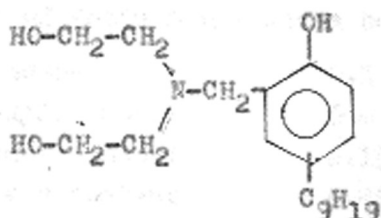
One mole of nonylphenol was condensed with one mole of diethanol amine and 1.1 mole of formaldehyde under controlled conditions. The product was dried under vacuum at 90°C.



The major constituents of Resin C are:



or

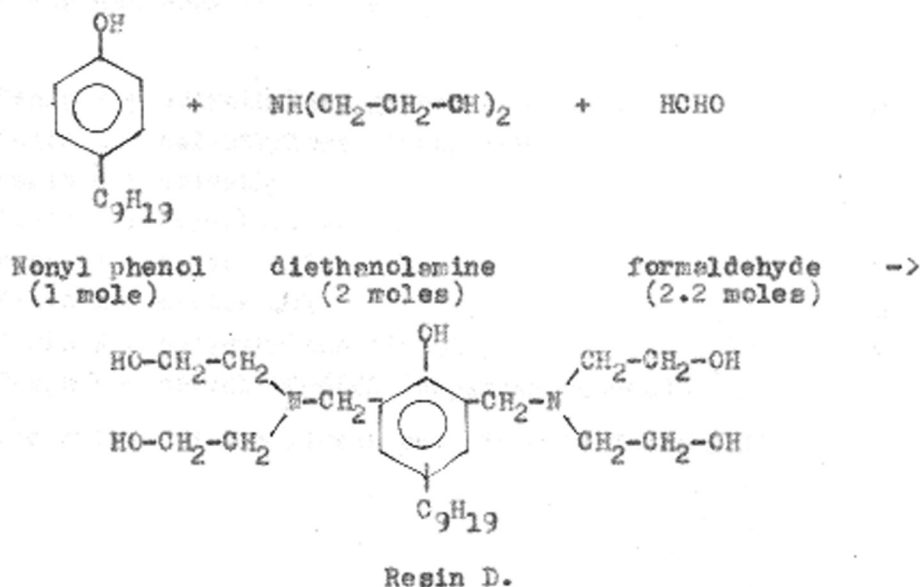


The properties of Resin C are given below:

Acid number	0.1 mgs. of KOH/gm
Hydroxyl number	498 mgs. of KOH/gm
Sp. gravity	1.028 at 25°C
Nitrogen content	4.1% (weight %)
Moisture content	0.24%
Viscosity	Flow time of 940 seconds in Ford Cup No.4
Appearance	Viscous yellow liquid.

Resin D.

One mole of nonylphenol was condensed with two moles of diethanol amine and 2.2 moles of formaldehyde under the same conditions as for Resin C.



Properties of Resin D are given below:

Acid number	0.1 mgs. of KOH/gm
Hydroxyl number	640 mgs. of KOH/gm
Nitrogen content	6.15% (weight %)
Moisture content	0.28%
Sp. gravity	1.058 at 25°C
Viscosity	Highly viscous
Appearance	Viscous yellow liquid.

Since the amino polyols obtained are highly viscous and reactive, they could not be used as such for making rigid urethane foams. Therefore, they were blended with low molecular polyhydroxy compounds such as polyethylene glycols of different molecular weights or urethane grade castor oil to obtain the required viscosity. The properties of the polyethylene glycols and castor oil used for moderating the amino polyols are given in Table XII.

The blending of the aminopolyols with different polyhydroxy compounds was done in 1:1 (w/w) proportion as indicated below:

	<u>Resin</u>
(1) Resin A + polyethylene glycol 200 (mol.wt.)	P
(2) Resin B + polyethylene glycol 400	Q
(3) Resin C + polyethylene glycol 200	R
(4) Resin D + polyethylene glycol 400	S
(5) Resin A + castor oil	T
(6) Resin B + castor oil	U
(7) Resin A + polyethylene glycol 300	V
(8) Resin V + polyol CC-460N (Japanese source)	W

The properties of the blends are given in Table XIII.

Table XII

Properties of polyethylene glycols and castor oil

	Polyethylene glycol		Castor oil
Molecular weight	200	300	400
Acid number mgs of KOH/gm	nil	-	1.0
Hydroxyl number mgs/KOH/gm	560.0	385.0	280.0
Viscosity at 25°C in Ford Cup No.4 flow time in seconds	22.0	30.0	35.0
Moisture content %	less than 0.005		
Colour	colourless		pale yellow

Table XIII

Properties of the blends

	P	Q	R	S	T	U	V	W
Acid number mgs of KOH/gm.				less than 0.05	0.60	0.65	0.05	0.05
Hydroxyl number mgs of KOH/gm	480.0	430.0	530.0	460.0	280.0	370.0	390.0	425.0
Moisture content %	0.1	0.15	0.12	0.14	0.1	0.16	0.1	0.05
Viscosity at 25°C by Ford Cup No.4 flow time in seconds.	110.0	120.0	108.0	135.0	115.0	140.0	115.0	145.0
Appearance		dark brown liquid			pale yellow		dark	brown liquid

The specifications and source of different additives used in the foam preparation

Isocyanate

Polymeric MDI or Desmudur 44V. It is obtained from M/s. Bayer and Co., Germany. Its specifications have already been given on page 13.

Surfactant - silicone base 201 Dow Corning.

Colour	- light yellow
Viscosity at 77°C centistokes	2000 - 3000
Hydroxyl content %	nil.
Water solubility	completely soluble
Water stability	stable

Non-ionic surfactant - ALK, obtained from Hice Products, Bombay.

Colour	pale yellow
Viscosity	highly viscous
Hydroxyl content	nil.
Water solubility	completely soluble

Flame retardant - Trioresyl phosphate obtained from SISCO Products, Bombay.

Sp. gravity at 20°C	1.18
Boiling range	430-440°C
Refractive index at 20°C	1.561

Blowing agent - Trichlorofluoromethane obtained from Freon Gas Co., Bombay.

Mol. wt.	137
B.P. at 1 atm.	23.77°C
Freezing point	-111°C
Appearance	very thin liquid
Density at 25°C	1.476
Solubility in water 1 atm. at 25°C	0.11

Crosslinking agent - Glycerine obtained from SISCO Products, Bombay.

Mol. wt.	92.10
Density at 20°C	1.225
Refractive index	1.4746
Hydroxyl number mgs of KOH/gm.	1833.0

Preparation of low density foams

Resins P, Q, R, S, T, U and V were utilised for the preparation of a series of low density foams (2-3 lbs./cuft). Resin V was found to yield a low density rigid urethane foam with superior properties. A number of foams were therefore prepared starting from Resin V by varying the proportions of blowing agent, surfactant, crosslinking agent, flame retardant and the NCO/OH ratio. The detailed observations of these studies are described in the 'Discussion'.

Having studied the effect of various foam ingredients, a suitable formulation was developed which yielded low density foam equivalent to those available commercially. Three foams, namely A, B and C were prepared according to the standard formulation. The foam formulations, processing characteristics and comparable properties of foams A, B and C are listed in Table XIV.

Resin V was further blended with polyol OC-460 N (Japanese polyol) and was named the Resin W, as indicated in Table XIII. Resin W was also utilised to see whether it can yield low density rigid urethane foams of quality superior to other such foams studied. The foam formulation, processing characteristics

Table XIV

Foam formulations and foam properties made from Resin V, polymeric MDI and trichlorofluoromethane.

Foam formulation	A	B	C
<u>Component B (premix) in parts</u>			
Resin V	100	100	100
Surfactant ALK	1.5	1.5	1.5
Crosslinking agent (Glycerine)	6.5	6.5	6.5
Trichlorofluoromethane	30	45	45
Tricresylphosphate	-	-	5
<u>Component A</u>			
Polymeric MDI	108	108	108
<u>Processing characteristics</u>			
NCO:OH	----- 1.05:1 -----		
Premix temperature °C	20	20	20
Isocyanate temp. °C	25	25	25
Agitator design	----- screw type -----		
Mixing speed (rpm)	3000	3000	3000
Mould temperature °C	40	40	40
Cream time in seconds	11-12	9-10	10-11
Rise time in seconds	150-160	140-150	130-140
Tack free time in seconds	150-160	150	150
<u>Foam properties</u>			
Density panel, lbs/cuft.	3.0	2.2	2.2
Density core, lbs/cuft.	2.9	2.1	2.1
Compression strength psi. in direction to foam rise at 10% deflection	45-50	35-40	30-35

cont....

Table XIV (cont.)

Foam formulation	A	B	C
Perpendicular to foam rise at 10% deflection	30-35	20-22	15-18
Tensile strength, psi. in the direction to foam rise	56-60	45-50	35-40
Closed cells %	34.0	32.0	92.0
Thermal conductivity (K factor) at room temperature.			
BTU/hr/sq.ft./°F/in. initial	0.146	0.122	0.126
(cut from sample) at equilibrium	0.16	0.16	0.16
Water vapour permeability (dry cup method), perm. inches	1.96	2.30	2.40
Water absorption, lbs/sq.ft. of surface area	0.055	0.060	0.065
Flammability (self extinguish)	No.	No.	Yes.
Burning rate, inch/min.	4	4	2
Dielectric constant (1000 cps.)	1.06	1.04	1.05
Dielectric strength, vol/ml.	36	35	35
Dielectric loss	0.005	0.005	0.005
Dimensional stability at 70°C for 28 days volume change %	<1	1	1
at 100°C ,,	4	5	5
at 70°C at 100% R.H. 1 week	6.8	7.5	8.4
-40°C for 24 hours	----- No change -----		

and foam properties are given in Table XV. Solvent and chemical resistance characteristics of the low density foams studied are listed in Table XVI.

Preparation of high density foams

High density foams have been prepared with Resins P, Q, R, S, T and U, polymeric MDI and water by the one shot technique.

Different densities were obtained for the foam by varying the proportion of water in the foam formulations. All the foams were cured at room temperature for 3 to 4 hours and then at 50°C in an oven for 30 minutes. The foam formulations, processing characteristics and foam properties are given in Table XVII to XXI.

Table XV

Foam formulations and foam properties made from
Resin W, polymeric MDI

<u>Foam formulation</u>	
<u>Component B</u> in parts.	
Resin W	100
Trichlorofluoromethane	45
Silicone surfactant 201	0.5
Non-ionic surfactant ALK	1.0
<u>Component A</u>	
Polymeric MDI	102
<u>Processing characteristics</u>	
NCO:OH	1.05:1
Premix temperature °C	20
Isocyanate temperature °C	25
Mixing speed (rpm.)	3000
Mould temperature °C	40
<u>Foam properties</u>	
Density panel, lbs./cuft.	2.12
Density core, lbs/cuft.	2.0
Compression strength, psi.in direction to foam rise at 10% deflection	40-42
Tensile strength, psi.	50-55
Closed cells %	92.00
'K' factor, BTU/hr/sq.ft/°F/in.	0.12
Flammability - self extinguishing	Yes
Burning rate, inch/min.	1.5
Water absorption, lbs./sq.ft. of surface area	0.045
Water vapour permeability, perm inch	2.2
<u>Dimensional stability</u>	
at 70°C for 28 days volume change %	<1
at 70°C for 7 days at 100 W.H volume change	6.1
at -40°C for 24 hours	No change.

Table XVI

Solvent and chemical resistance of low density foam

Active material	Resistance	
	at 25 ⁰⁰	at 50 ⁰⁰
Water	E	E
n-Hexane	E	-
Xylene	G	G
Benzene	G	-
Toluene	G	-
O-dichlorobenzene	G (swelling)	F
Butyl acetate	F (shrinkage)	F
Ethyl alcohol	F ..	-
Methyl alcohol	F ..	-
Methyl ethyl ketone	P ..	P
Carbon tetrachloride	G	G
Acetone	P (swelling)	-
Trichloroethylene	G	F
Methyl isobutyl ketone	P	P
Kerosene	E	G
Motor oil	E	E
Brine (saturated)	G	G
Brine (10%)	E	G
Conc. H ₂ SO ₄	S	S
10% H ₂ SO ₄	G	G
Conc. HCl	S	S
10% HCl	G	F
Conc. HNO ₃	S	S
Conc. NH ₄ OH	G	-
10% NH ₄ OH	G	G
Conc. NaOH	G	F
10% NaOH	E	G

E = Excellent resistance

G = Good

F = Fair

P = Poor

S = Severe attack

Table XVII

High density foams from Resin P with water variation

Foam formulation	I	II	III	IV	V	VI
Resin P in parts	100	100	100	100	100	100
Surfactant 201	0.5	0.5	0.5	0.5	0.5	0.5
Water	2.5	2.0	1.5	1.0	0.5	0.2
Polymeric MDI	149	141.5	134	127.5	120	116
<u>Processing characteristics</u>						
NCO:OH	----- 1.05:1 -----					
Mixing speed, rpm.	----- 3000 -----					
<u>Foam properties</u>						
Density, lbs./cuft.	5.15	8.2	11.4	14.6	17.8	20.0
Compression strength, psi. in direction to foam rise at 10% deflection	50	80	140	230	320	360
Tensile strength, psi.	80	115	118	260	370	440
Closed cells %	96	98	98	98	98	98
'K' factor at room temperature BTU/hr/sq.ft/°F/in.	0.24	0.26	-	-	0.28	-
Water vapour permeability, perm inches	1.65	1.55	-	-	1.0	-
Water absorption lbs/sq.ft of surface area	0.05	-	-	0.035	-	0.03
<u>Dimensional stability at</u>						
70°C for 28 days volume change	----- less than 1% -----					
100°C for 28 days volume change	----- less than 1.5% -----					
Burning rate, inch/min.	1.5	-	1.0	-	-	1.0

Table XVIII

High density foams from Resin Q with water variation

	VII	VIII	IX
<u>Foam formulation, in parts</u>			
Resin Q	100	100	100
Surfactant 201	0.5	0.5	0.5
Water	2.0	1.5	0.5
Polymeric MDI	131	124	110
<u>Processing characteristics</u>			
NCO:OH	-----	1.05:1	-----
Mixing speed, rpm.	-----	3000	-----
<u>Foam properties</u>			
Density, lbs/cuft.	6.8	15.2	18.0
Compression strength, psi. in direction to foam rise at 10% deflection	70	180	385
Tensile strength, psi.	90	220	410
Closed cells %	98	98	-
'K' factor BTU/hr/sq.ft/°F/in.	0.24	-	0.28
Water vapour permeability, perms inch.	1.66	-	0.9
Water absorption, lbs/sq.ft. of surface area	0.045	-	0.035
Dimensional stability at			
70°C for 28 days volume change	-----	less than 1	-----
100°C for 28 days volume change	-----	less than 2	-----
Burning rate, inch/min.	1.5	-	1.0

Table XIXHigh density foams from Resin R with water variation

	X	XI	XII	XIII
<u>Foam formulation</u>				
Resin R in parts	100	100	100	100
Surfactant 201	0.5	0.5	0.5	0.5
Water	2.0	1.5	1.0	0.5
Polymeric MDI	153	146	139	132
<u>Processing characteristics</u>				
NCO:OH	----- 1.05:1 -----			
Mixing speed, rpm.	----- 3000 -----			
<u>Foam properties</u>				
Density, lbs/cuft.	7.0	10.8	14.2	17.0
Compression strength, psi. at 10% deflection	80.0	130.0	210.0	330.0
Tensile strength, psi.	110.0	160.0	240.0	350.0
Closed cells %	98.0	-	-	-
'K' factor, BTU/hr/sq.ft/°F/in.	0.24	-	0.28	0.3
Water vapour permeability, perm inches.	1.55	-	0.9	0.8
Water absorption, lbs/sq.ft of surface area	0.045	-	0.035	0.035
<u>Dimensional stability at</u>				
70°C for 28 days volume change	----- less than 1.0% -----			
100°C for 28 days volume change	----- less than 2.0% -----			
Burning rate, inch/min.	1.4	-	-	1.0

Table XXHigh density foams from Resin S with water variation

	XIV	XV	XVI
<u>Foam formulation</u>			
Resin S in parts	100	100	100
Surfactant 201	0.5	0.5	0.5
Water	2.0	1.5	0.5
Polymeric MDI	133	126	112
<u>Processing characteristics</u>			
NCO:OH		1.05:1	
Mixing speed, rpm.		3000	
<u>Foam properties</u>			
Density, lbs/cuft	6.4	14.8	18.36
Compression strength, psi. at 10% deflection	65	170	375
Tensile strength, psi.	80	195	410
Closed cells %	98	-	-
'K' factor, BTU/hr/sq.ft/°F/in.	0.23	-	0.29
Water vapour permeability, perm inches	1.72	-	0.85
Water absorption, lbs/sq.ft.of surface area	0.045	-	0.034
Dimensional stability at			
70°C for 28 days volume change		less than 1.0%	
100°C for 28 days volume change		less than 1.5%	
Burning rate, inch/min.	1.4	-	1.0

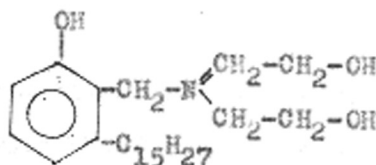
Table XXIHigh density foams from Resin T and U with water variation

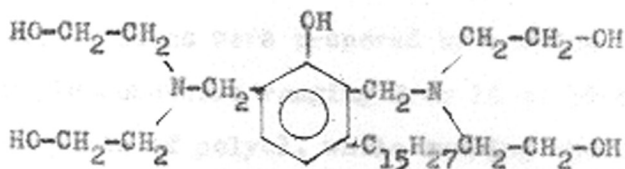
	XVII	XVIII	XIX	XX	XXI	XXII
<u>Foam formulation in parts</u>						
Resin T	100	100	100	-	-	-
Resin U	-	-	-	100	100	100
Surfactant 201	0.5	0.5	0.5	0.5	0.5	0.5
Water	2.0	1.5	0.5	2.0	1.5	0.5
Polymeric MDI	96	89	75	116	109	95
<u>Processing characteristics</u>						
NCO:OH	----- 1.05:1 -----					
Mixing speed, rpm.	----- 3000 -----					
<u>Foam properties</u>						
Density, lbs/cuft.	5.1	8.4	10.6	5.8	9.2	11.0
Compression strength, psi. at 10% deflection	35	60	110	45	80	135
Closed cells %	97	98	-	97	98	-
Water absorption, lbs/sq.ft. of surface area	0.04	0.03	-	0.04	-	0.03
Water vapour permeability, perm inches	1.4	-	1.1	1.35	-	1.0
Dimensional stability at 70°C for 28 days volume change	----- less than 5.0% -----					
Burning rate, inch/min.	1.3	-	1.0	1.4	-	1.0

DISCUSSION

The reaction between isocyanate and phenol is slower as compared to the reaction between isocyanate and aliphatic alcohols³⁶. The presence of substituents on the aromatic nucleus of the phenol has a strong influence on the reaction rate. The rate of urethane formation can be accelerated by using certain types of catalysts. It has been reported in the literature⁴ that when phenols are reacted with diethanolamine and formaldehyde, the resultant aminopolyols have high reactivity towards urethane formation due to the presence of tertiary nitrogen and primary hydroxyl groups in the moiety. The primary hydroxyl groups have greater reactivity towards isocyanates whereas the tertiary nitrogen provides catalytic effect to the reaction. The phenolic hydroxyl group also can react with isocyanates under the influence of strong catalysis. The presence of aromatic ring in the aminopolyols provides stability. The aminopolyols (self catalytic resins) prepared from cardenol (3-pentadecenyl phenol) have the following structures.

Resin A.





Resin B.

It can be seen that the aminopolyols A and B have the necessary structure required for high reactivity. Furthermore, presence of side chain at the meta position may impart plasticising property.

Aminopolyols prepared from cardenol and nonylphenol are highly viscous and hence it is necessary to blend them with polyglycols and other hydrogen donors to reduce their viscosity for easy processing during the preparation of foams. The blended polyols are shown on page 78. Resins P, Q, R, S, T, U and V have been utilised for the preparation of low density foams (2-3 lbs/cuft.) Among them, Resin V was found to give low density urethane foam with the most desirable properties. The rest were used for the preparation of high density urethane foams. A number of foams were prepared from Resin V by varying the proportions of blowing agent, surfactant, crosslinking agent, flame retardant and the NCO/OH ratio.

Effect of blowing agent

Several blowing agents such as dichlorodifluoromethane, methylene chloride, trichlorofluoromethane etc. were investigated in the preparation of low density rigid urethane foam. Among them, trichlorofluoromethane (Freon 11) was found to be the best suited for the preparation of low density foam from Resin V.

A number of foams were prepared by varying the proportion of trichlorofluoromethane ranging from 10 to 55 parts on the basis of 100 parts of polyol, while keeping the other additives constant. It was observed that those prepared with 30 to 45 parts of trichlorofluoromethane had a foam density ranging between 3 to 2 lbs/cu.ft. Though low density foams (less than 2 lbs.) could be obtained by using more than 45 parts of Freon 11, these suffer from the disadvantage of large cell structure which ultimately affects the foam properties. Therefore the optimum quantities of 30 and 45 parts of trichlorofluoromethane on the basis of polyol were chosen for the preparation of low density foams and their properties are listed in Table XIV.

Effect of surfactant

Surfactants are added to the foam formulation to impart stability during the foaming process. They are intended to control the cell structure by regulating the cell size. The choice of the surfactant is governed primarily by the type of polyol used and by the method of foam preparation. The most common surfactants are silicones. In the present study, the use of a silicone surfactant 201 (Dow Corning) resulted in an uneven blowing and shrinkage of the foam. The non-ionic surfactant ALK was found to give better foaming characteristics. The percentage of closed cell structure at a given density of the foam was optimized by varying the proportion of non-ionic surfactant. It was observed that the surfactant ALK at 1.5 parts per hundred parts of polyol, yielded a foam of uniform

and fine closed cell structure (90-92%), without sacrificing other foam properties.

Effect of crosslinking agent

When low molecular weight polyols are used for the preparation of polyurethane rigid foam, it is necessary to use a crosslinking agent to improve the crosslink density of the foam. The crosslinking agents tried were trimethylol propane, pentaerythritol, triethanol amine, sorbitol, glycerol etc. Glycerol was found to be the most suitable in the foam formulations. At the optimum proportion of 6.5 parts per hundred parts of polyol, the resultant foam on the whole had balanced properties.

Effect of flame retardant

The variety and utility of rigid urethane foams and their commercial acceptance has made them indispensable materials in many applications especially where fire hazard is an important problem. Polyurethane foams, like other organic materials, tend to be combustible unless they are rendered flame retardant. The flame retardancy of the urethane foams is achieved by any of the following methods:

- (1) Incorporation of non-reactive flame retardants in foam formulations.
- (2) Addition of flame retardant compounds containing functional group, that become chemically bound in the polymer chain.
- (3) Coating of the flammable foam by flame retarding material.

In the present study, the non-reactive additive, tricresylphosphate was studied in different proportions with respect to polyol for fire retardancy. At a dosage of five parts per hundred parts of polyol, the resultant foam had self extinguishing characteristics without significant alteration in the foam properties.

Effect of isocyanate index (NCO/OH ratio)

It has been reported that the tensile and compression strengths of the foam are dependent on the NCO/OH ratio. In the present study, it was observed that when the NCO/OH ratio increased from 0.9 to 1.1, tensile and compression strength values also increased proportionately. Best results were obtained at the NCO/OH ratio of 1.05:1. Brittle foams were obtained at higher isocyanate content.

On the basis of the foregoing considerations, the foams labelled A, B and C were prepared (Table XIV). Foams A and B were prepared with different amounts of blowing agent whereas in foam C, tricresyl phosphate was added as a fire retardant.

The overall foam properties depend mostly on the density. The densities of B and C were found to be nearly the same, i.e. 2.2 lbs/cuft. as compared to that of foam A (3 lbs/cuft.). The higher density of the latter may be due to ^{to} less amount of blowing agent in the formulation. For all the foams, the panel density was more than the core density.

It has been reported³⁷⁻³⁹ that the strength properties of rigid urethane foams are related to the density. The values obtained for compression and tensile strength in the case of

all the three foams confirm this fact. The slight lowering in the mechanical properties (strength) of foam C may be due to the fire retardant used in the foam formulation. The compression strength in the direction of foam rise at 10% deflection for foams A, B and C was found to be 45-50, 35-40, 30-35 psi. respectively, whereas the same for perpendicular to foam rise was lower and found to be 30-35, 20-22, 15-18 psi. respectively. The tensile strength for all the three foams measured in the direction of foam rise was found to be 56-60, 45-50, 35-40 psi. respectively.

The closed cell content depends mainly on the degree of crosslinking and the surfactant used during foaming. The mixing conditions also influence the closed cell structure. The closed cell content in all the three foams (A, B, C) was found to be ranging from 94 to 92%.

Thermal conductivity (K factor)

Rigid urethane foams find use commercially as insulating materials because their 'K factor' is superior to other commercial insulators used. The initial value of thermal conductivity in all the three foams was of the order of 0.146 - 0.122 BTU/hr/sq.ft/^oF/inch and at equilibrium, the K factor remained constant at 0.16 BTU/hr/sq.ft/^oF/inch. The slight higher value for initial thermal conductivity might be due to the presence of small amount of water in the polyol (0.1 - 0.2%).

As reported in the literature, we find that the low thermal conductivity of the foam prepared with trichlorofluoromethane

as a blowing agent is due to its presence in high concentrations in the foam cells and its low K factor (0.058 BTU/hr/sq.ft/°F/inch.).

Thermal conductivity of the urethane foams has been discussed by several workers^{38,41-47}. The literature reviews reveal that the 'K' factor depends largely on the open cell content of the foam, cell size, mean temperature and cell orientation. It was also reported⁴⁸ that the 'K' factor drift of cut foam samples is caused by the inward diffusion of atmospheric gases (air, CO₂ and moisture) through the cell walls. The drift in K factor continues until the partial pressure of the gases diffusing into the foam is equal to the partial pressures of the gases in the atmosphere. However, when the foams were enclosed between steel plates, the 'K' factor drift was not observed and remained at the initial low level.

Water vapour permeability and water absorption

The water vapour permeability and water absorption of the rigid urethane foam depends on the cell structure, the degree of crosslinking and the bulk density of the foams. The contributory factors towards low water vapour permeability and water absorption of the foams are the high closed cell structure, use of hydrophobic foam components, aromatic structures, a high degree of crosslinking agents, etc. Generally, plasticisers and fillers adversely affect water vapour permeability. In all the cases of the low density foams studied, the water vapour permeability was in the range of 1.96 - 2.40 perm inches

and the water absorption values varied between 0.05 to 0.065 lbs/sqft. of surface area. The water vapour permeability for foam C was slightly higher than that for foam B. This could be attributed to the use of tricresyl-phosphate in the formulation of foam C. The water vapour permeability can be lowered by increasing the density as in the case of foam A. The lower water absorption values for the foam indicate that the absorption of water is almost entirely due to the cut cells of the foam surface.

Flammability

In case of foam A and B the self extinguishing character was not observed. The burning rate of both the foams was found to be four inches per minute. Foam C showed self extinguishing character which is evidently due to the presence of tricresyl phosphate. The burning rate of this foam was found to be two inches per minute.

Electrical properties

It is reported⁵² that the electrical properties of fluorocarbon blown foams are superior since the fluorocarbon has good dielectrical properties. The results obtained for low density foams confirm the above observation.

Dimensional stability

Rigid urethane foams are used for different applications such as in transportation, refrigeration systems etc. at different environmental conditions. It is essential that the

foam must have dimensional stability at operating temperatures. The dimensional stability of urethane foam depends on the polymer structure, foam density and environmental conditions⁴⁷⁻⁵¹. When foams A, B and C were aged for 28 days at 70°C and 100°C the percent volume change was observed to be one percent and 4-5 percent respectively. When these foams were aged at 70°C in controlled humidity chamber (R.H.100%) for one week, the percent volume change was found to be 6.8, 7.5 and 8.4. The higher values obtained in the latter case may be due to the absorption of moisture. No volume change was observed when the foams were aged at -40°C for 24 hours.

Solvent and chemical resistance

Foams A, B and C were studied for their chemical and solvent resistance (Table XVI) at 25°C and 50°C. All the foams are resistant to most of the solvents but they are severely attacked by strong acids and alkalies. Strongly polar solvents caused swelling and shrinkage. In most of the cases, the foams regained their original shape after the removal of solvent.

The foam prepared from Resin V and Japanese polyol OC-460 N (Table XV) has properties comparable with foam B, which is prepared by using only resin V. Unlike foam B, the former is found to have self extinguishing character. The burning rate of the foam was observed 1.5 inches/minute.

High density foams

Different high density foams were prepared from Resins P,

Q, R, S, T and U (page 78) by varying the amount of water as the blowing agent. Their foam formulations and foam properties are given in Tables XVII-XXI. Foams prepared from Resin T and U were found to be semi-rigid. Their properties are inferior to those of the other high density foams studied in the present work.

Foams prepared from Resins P, Q, R and S are found to have comparable properties. It is noted that foams of different densities ranging from 5-20 lbs/cuft. could be prepared by varying the amount of water (2.5 - 0.5 parts) in the foam formulation. When the water content in the formulation was more than 2.5 parts per hundred parts of polyol, the resultant foams showed a tendency to friability. Optimum properties were retained upto a water content of <2 parts per hundred parts of polyol.

The strength properties are found to increase with increasing density. When the foam samples were tested in the direction of foam rise, the compression strength and tensile strength values ranged from 80-375 psi. and 90-440 psi. respectively.

The closed cell content of all the foams was found to be in the range of 96-98%. Since the foams have a high content of closed cell structure, it is obvious that these would have lower water absorption and low water vapour permeability values. The water absorption was found to be in the range of 0.05 to 0.03 lb./ft² of surface area and water vapour permeability in the range of 1.65 - 0.8 perm inches.

The equilibrium thermal conductivity of the foams was

in the range of 0.26 - 0.3 BTU/hr/sq.ft/°F/inch. The high thermal conductivity of these water blown foams (in comparison with fluorocarbon blown foams) might be caused by the presence of carbon dioxide (high K factor - 0.102) in the foam cells.

The dimensional stability of these foams was studied by aging the foams at 70°C and 100°C for 28 days. The percent volume change was found to be in the range of 1-2%.

Most of the high density foams are resistant to a large number of solvents but they are severely attacked by strong acids. In polar solvents, slight swelling was observed.

Conclusion

Polyurethane rigid foams of various densities (low and high) could be prepared by using self-catalytic resins prepared from cardenol - an indigenously available raw material in India. These foams have the advantage of possessing several important properties such as insulating efficiency, light weight strength, buoyancy, good heat resistance, excellent adhesion to wood, metal, glass etc. and ease of fabrication. These foams may find wide range of applications in insulation, transportation, construction, building materials, packaging, furniture, substitute for wood and marine equipments.

EXPERIMENTAL

Isolation of cardenol (3-pentadecenyl phenol) by distillation of commercial cashewnutshell liquid

Heat extracted raw commercial cashewnutshell liquid (CNSL) (3 kg.) was distilled under vacuum in a five litre round bottom flask. The contents were heated slowly till the initial frothing subsided. 1.5 kg. of brown coloured distillate (yield 50%) was collected between 190-240°C/2-4 mm Hg pressure. This was redistilled to obtain a pale yellow cardenol. It had the following specifications:

Density at 25°C	0.9272 - 0.9335
Volatile losses	Max. 1%
Ash content	Negligible
Iodine value	210
Acid value	5 mgs of KOH/gm
Hydroxyl value	185-190 mgs of KOH/gm
Colour	Pale yellow.

Purification of formaldehyde

One kg. of cation exchange resin (Tulsion-42) packed in a glass column was regenerated with 5% hydrochloric acid and then washed with distilled water till it was free from acid. The commercial formaldehyde solution was passed through this column at a slow rate. A colourless and iron-free effluent was obtained and was estimated for purity, as described below.

Estimation of formaldehyde

The deionized effluent was weighed accurately (1 gm.) in a capsule. The capsule was placed in a 125 ml. Erlenmeyer flask. To this, 10 ml. of a 10% solution of hydroxylamine hydrochloride was added and the contents were thoroughly mixed. A similar experiment was carried out for the blank. After 15-20 minutes, the contents of both the flasks were titrated against 0.1 N KOH solution using bromophenol blue as an indicator. The percentage of formaldehyde was calculated as follows:

$$\% \text{ formaldehyde} = \frac{(A-B) N \times 3.003}{W}$$

where:

A = ml. of KOH for the sample

B = ml. of KOH for the blank

N = Normality of KOH

W = weight of the sample in gms.

Preparation of self catalytic resins or aminopolyols

Resin A

In a two litre four necked round bottom flask, equipped with a stirrer, a nitrogen gas inlet, a thermometer and a reflux condenser, 1.1 mole (93.4 ml.) of formaldehyde solution (37%) were placed. To this, a mixture of 1 mole of cardenol (300 gms.) and 1 mole of diethanolamine (105 gms.) was added slowly during an interval of 45 minutes at 15-20°C. The reaction mixture was kept at room temperature for one hour and then the temperature was increased to 85°C. The stirring was continued at this temperature for one hour under nitrogen atmosphere.

Then water was distilled off under reduced pressure (2-3 mm.) for 3 to 4 hours. Finally the product was tested for its chemical and physical characteristics. Yield 95%.

Resin B

Resin B was prepared by condensing 1 mole of cardenol (300 gms.) with 2 moles of diethanol amine (210 gms.) and 2.2 moles of formaldehyde (187 ml. of 37%) under the same conditions described in the preparation of Resin A. Yield 94%.

Resin C

In a two litre four necked round bottom flask equipped with a stirrer, a nitrogen gas inlet, a thermometer and a reflux condenser, 1.1 mole (93.4 ml.) of formaldehyde solution (37%) were placed. To this, a mixture of 1 mole of nonyl phenol (220 gms.) and 1 mole of diethanol amine (105 gms.) was added slowly during one hour interval at 15-20°C. The reaction mixture was kept at room temperature for one hour and then the temperature was raised to 85°C. The stirring was continued at this temperature for one hour under nitrogen atmosphere. Then water was removed under reduced pressure (2-3 mm.) for 3 to 4 hours. Finally the product was tested for its chemical and physical characteristics. Yield 95%.

Resin D

Resin D was prepared by condensing 1 mole of nonyl phenol (220 gms.) with 2 moles of diethanol amine (210 gms.) and

2.2 moles of formaldehyde (187 ml. of 37%) under the same conditions as described in the preparation of Resin C. Yield 93%.

The properties (chemical and physical) of Resins A, B, C and D have been given in 'Present Investigation' Section.

Blending of Resin A,B,C,D with other polyhydroxy compounds

Different blends of Resin A, B, C and D were prepared by mixing them in 1:1 w/w proportion either with polyethylene glycol, mol.wt. 200 or 300 or 400 or castor oil at 70°C for 2 hours. Then they were dried at 90°C under reduced pressure for one hour. The different blends along with their physical and chemical properties are given in 'Present Investigation and Results' Section (Table XIII).

Testing procedures for aminopolyols and blends

The methods for the determination of acid number, specific gravity and moisture content were the same as adopted for polyester in Part I. The hydroxyl number for aminopolyols and blends was determined by the acetylation method.

Determination of hydroxyl number

The resin was weighed accurately (0.2 gm.) in a capsule and was transferred into the 250 ml. Erlenmeyer flask. 10 ml. of acetylating reagent (20 ml. of pure acetic anhydride + 0.35 ml. of distilled water + 100 ml. of pyridine) was added to the flask and the contents were refluxed at 90°C for one hour

on a water bath. Then the flask was cooled to room temperature and 20 ml. of ice cold distilled water and 50 ml. of alcohol: benzene mixture (1:1) were added. Then the flask was cooled in ice for 30 minutes and the mixture titrated against 0.5 N KOH solution using bromothymol blue as an indicator. A similar experiment was carried out for blank.

Hydroxyl number was calculated in terms of milligrams of KOH per gram of sample used, as follows:

$$\text{Uncorrected hydroxyl number} = \frac{(B-A) \times N \times 56.1}{W}$$

where A = ml. of KOH required for the sample

B = ml. of KOH required for the blank

N = Normality of KOH

W = Weight of the sample in gms.

The hydroxyl number was corrected by adding the acid number or subtracting the alkalinity number.

Viscosity measurements

Viscosity of aminopolyol or blends was measured in terms of its flow time in Ford Cup No.4. The flow time was measured in seconds.

Preparation of low density foams

The component A (polymeric MDI) and component B (polyol + blowing agent + surfactant + flame retardant) (Table XIV) were metered accurately in a mixing chamber and mixed intimately by the agitator. The prefoam mixture was then dispensed through the orifice into the mould and subsequently cured at

40°C in an oven for 20 minutes. Test samples were cut from the centre of the foam block parallel to foam rise and evaluated.

Preparation of high density foams

High density foams were prepared by mixing all the ingredients given in foam formulation (Table XVII-XXI) by one shot technique. As soon as the creamy stage was observed, the homogeneous mass was poured into polyethylene moulds coated with wax paper. After foaming, the foams were kept at room temperature for 3-4 hours and then cured at 50°C for 30 minutes. Test samples were cut from the centre of the foam block parallel to foam rise and evaluated.

The foam properties of all the foams (low and high density) were tested according to the same procedures mentioned in Part I. The foam properties for low and high density foams have been given in Table XIV - XXI.

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Part-III

METHOD OF MANUFACTURE

METHODS OF MANUFACTURE

The manufacturing technique of both flexible and rigid urethane foams was reviewed by several authors¹⁻⁷. Normally the following processes are adopted for the manufacture of polyurethane rigid foam.

Batch process

This method consists of mixing the formulations in a batch in containers such as beakers, pails or buckets with mechanical stirring as the mixing device. Quasi prepolymer formulations are mostly carried out by this method since the rise time of the foam can be controlled accurately. Better results can be achieved by this method by controlling the parameters such as temperature and mixing time. This process has certain disadvantages⁸ such as lack of uniformity, high scrap and loss of materials due to its adhering to the sides of the mixing container.

Continuous slab process⁹

This process involves the accurate metering of all foam ingredients to a common mixer operating at a high rotational speed (2000-5000 rpm.). The intimately mixed chemicals are then poured onto the paper lined conveyor which moves away from the mixer. At the same time, the mixer is swung in a reciprocating motion from one side of the conveyor to the other. In this fashion, the liquid prefoam mixture is

deposited as a thin layer on the conveyor and subsequently foams to form a continuous slab of foam. The foam is cut into sections by a verticle cutter which is synchronized with the speed of the conveyor.

Foaming in place process

This method involves the addition of intimately mixed liquid or froth foam mixture into the mould or cavity, which gets filled completely by the resulting foam¹⁰⁻¹¹. Best adhesion can be obtained on a clean oil-free, dry and roughened surface.

The frothing system for the production of both rigid and flexible foam has been introduced by Du Pont¹² and Farbenfabriken Bayer¹³ and is currently gaining widespread use in the foaming in place method. The process consists of incorporation of a volatile liquid such as dichlorofluoromethane (fluorocarbon 12) into the foam reactants under pressure. Frothing occurs as the volatile liquid in the foam mixture vaporises by reduction in pressure as the material is discharged from the mixer.

By employing a combination of fluorocarbons of different boiling range (fluorocarbon 11 and 12) a two stage expansion can be achieved. In this process the lower boiling fluorocarbon produces immediate frothing on pouring and the higher boiling fluorocarbon subsequently completes the foaming process in the cavity in the second stage. Very low density foams can be manufactured by this technique.

Lower mould pressures, uniform cell structure, smooth

filling of voids or cavities and greater consistency in foam density are the main advantages of this process.

Spraying process

Spraying involves the same step of metering and mixing of chemicals as required by all rigid urethane foam processes. However, it differs from other processes in that the prefoam mixture is dispensed as a spray rather than a stream. A number of suitable spraying units have been developed for rigid foam applications¹⁴.

The spraying system generally consists of two components having relatively low viscosity which facilitate mixing and atomization. In general the spraying systems are highly catalysed to effect a very rigid foaming and gelation on the surface being sprayed. Presently self catalytic resins (amino polyols) have been successfully used in spraying system. Best spraying results are obtained on clean and dry surfaces.

The froth spray system is adaptable for either pouring or spraying¹⁵. Froth spray has several advantages which include high deposition rates, low over-spray, ready applications to cold surfaces, efficient utilization of expanding agent and uniformity of the foam density.

Recently a new process producing rigid urethane foam with a thick high density skin and a cellular core called 'Duromer urethane' has been reported by Pischota¹⁶. These foams are produced from special polyols and isocyanates in a single step operation, on a conventional equipment. In some

respects, the process is similar to the injection moulding of thermoplastics in which the reactive foam ingredients are injected into heavily jugged moulds wherein the combination of special ingredients and foaming pressure produces foam structure with thick skin. The resulting foam exhibits high strength and stiffness.

Equipment

The selection of the proper equipment for rigid urethane foam preparation is determined by the application as well as the desired production capacity. It will also depend on whether the foam is to be produced by frothed, sprayed or poured in place technique.

Literature¹⁷⁻²⁴ is available on the use of different foam equipments for foam processing and operating conditions for maximum efficiency. Depending on the applications, highly sophisticated machines have been designed by many engineering firms in Europe and U.S.A. for rigid urethane foams²⁵⁻³⁰. The successful production of rigid urethane foam largely depends on a reliable metering and mixing unit.

Metering unit

The function of a metering unit is to deliver two or more components (streams) to the mixing head in correct proportions under controlled conditions of temperature and pressure.

A metering or pumping unit comprises of a storage tank, pumps, a pump driving system, piping, a heat transfer unit and

associated controls for regulating temperature, pressure and flow. Among the different types of pumps available, axial piston pump or gear pump with variable speed drives are found to give the best results for metering polyols and isocyanates.

Mixing head

The 'mixing head' of the foam machine is considered to be the heart of the rigid foam production unit, which determines the successful production of urethane foam in industry.

The function of the mixing head is to provide for the homogenous mixing of the components irrespective of their ratios and their viscosities for obtaining uniform cell structure and optimum physical properties of the resultant foam. Insufficient mixing will result in a weak foam with coarse and irregular cell structure.

The degree of mixing achieved in the head is largely dependent on the agitator design, the clearance between the housing and agitator, the size of the outlet orifice and the agitator speed. Several agitator designs are used for rigid foam production. Normally pin type agitator provides low shear agitation while helical gear type provides high shear agitation with uniform fine cell structure. The specific clearance to be used for a particular system between the housing and agitator depends on ingredient viscosities. The size of the orifice may be so chosen to keep the cell size to a minimum. The speed of agitator is normally maintained in the range of 3000-6000 rpm. Injection of nitrogen or dry air into the

mixing chamber is recommended as it provides additional nucleating sites which improve the cell structure.

In addition to the mixing head and the mould design considerations, the foam quality also depends on other factors such as mould packing, direction of foam rise, mould temperature, mould thickness and curing conditions.

Spraying equipment

Most of the urethane spray equipment is designed for the use of a two component system whose polyol to isocyanate ratio is 1:1. It is designed primarily for field applications and comprises of a piston pump arrangement for each component. The components are metered to the mixing head and the prefoam mixture is dispensed as a spray by a single power source. Different types of spray guns such as the air support type or airless spray type are generally used in the spraying technique.

Fabrication of laboratory scale foam making machine

The rapid advance in the technology of rigid urethane foams during the last few years, has resulted in the development of new techniques and processing units. Recently many engineering companies in western countries have developed special type of machinery for processing rigid foam chemicals²⁵⁻³⁰. The machines range from small to large dispensing units in which the liquid chemicals are pumped in metered quantities to a mixing chamber. After mixing, the prefoam mixture can be discharged in the form of a liquid stream or as a spray by

fitting special nozzles to the discharge tube of the mixing chamber.

Considerable developmental work is in progress by several engineering firms for designing urethane foam machines with sophisticated controls using special propriety chemicals. Since no such small scale machine was readily available and considerable amount of foreign exchange is involved in importing a polyurethane foam machine, it was felt necessary to design and fabricate our own dispensing unit.

Better foams are obtained by proper blending of foam ingredients in the mixing head which depends on mixer design, the feed rate, the mixing time and the viscosity of the ingredients. The above observations were kept in view while designing and fabricating different components of the machine.

Mixing head

The mixing head constructed for the machine designed in the present study is of a simple design (Fig. 2). It consists of two circular plates A and B which can be tightened together over a small glass cylinder C by means of two screws E' and E". The glass cylinder C serves as a mixing chamber where the ingredients are metered from the inlet tubes F and G. These ingredients are blended homogenously by means of the stirrer D. The glass mixing chamber C has the advantage over a metal mixing chamber in that the volume (size) of the chamber can be easily changed to the desired level at very little cost. Another advantage of this type of glass chamber is that it

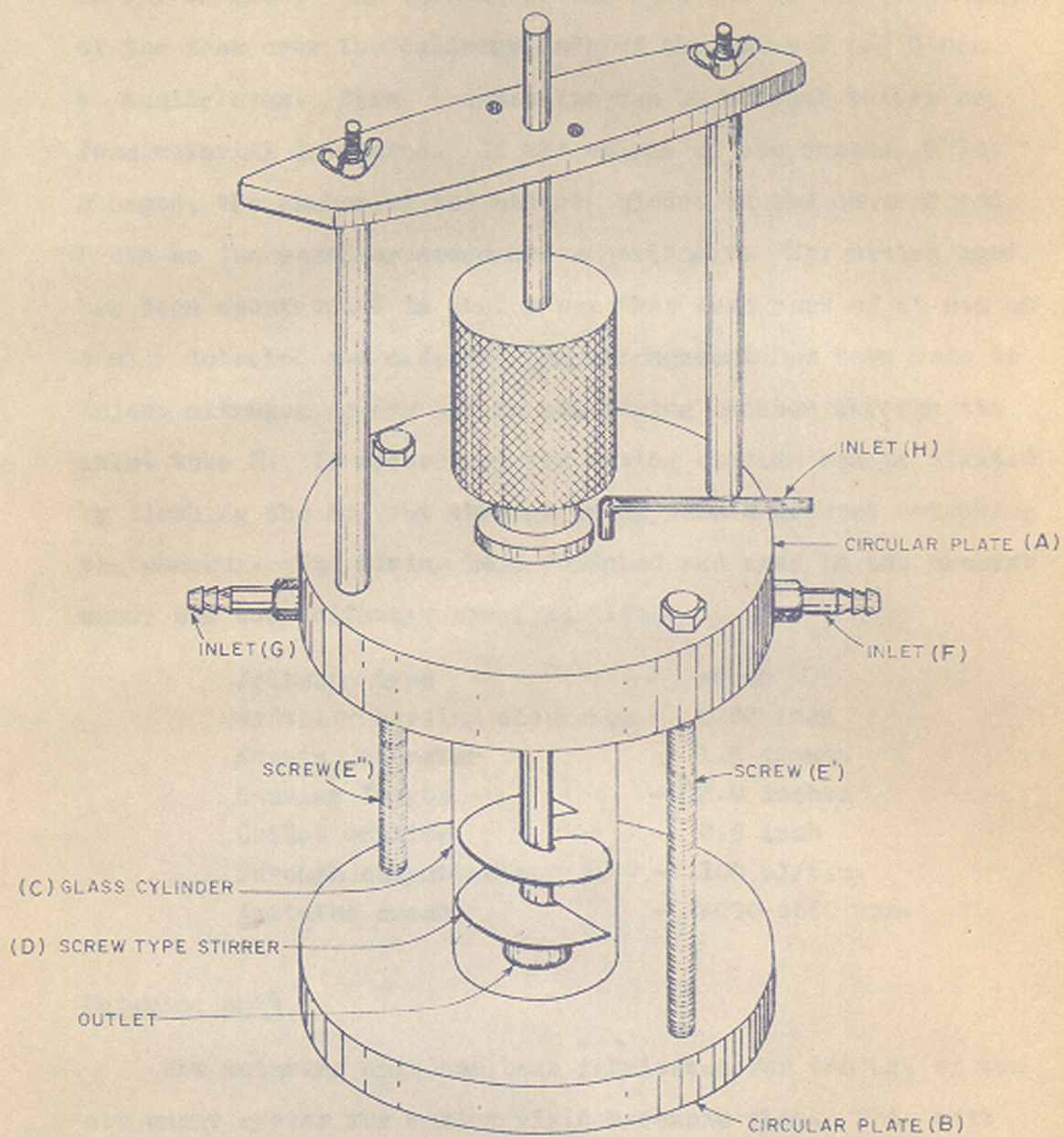


FIG. 2. THE MIXING HEAD

facilitates visual observations of the changes taking place in the chamber. Any choking of the feed due to the splashing of the foam over the delivery ends of the tubes F and G can be easily seen. Thus, the machine can be stopped before any foam material is wasted. If the volume of the chamber C is changed, the number of the stirrer blades on the central rod D can be increased or decreased accordingly. The mixing head has been constructed in such a way that each part of it can be easily detached and cleaned. An arrangement has been made to inject nitrogen or dry air in the mixing chamber through the inlet tube H. If necessary, the mixing chamber can be cleaned by flushing the solvent through inlet tube H without detaching the chamber. The mixing head designed and used in the present study had the following specifications:

Agitator type	- screw
Agitator housing clearance	- 0.02 inch
Housing diameter	- 1.5 inches
Housing length	- 2.0 inches
Outlet orifice	- 0.5 inch
Through output rate	- 100 ml/min.
Agitator speed	- 3000-4000 rpm.

Metering unit

The metering unit has been fabricated for the use of two component system for making rigid urethane foam. This unit consists of two positive displacement pumps for metering of liquid components (polyol and isocyanate). Metering can be adjusted accurately by changing the pump displacement volume

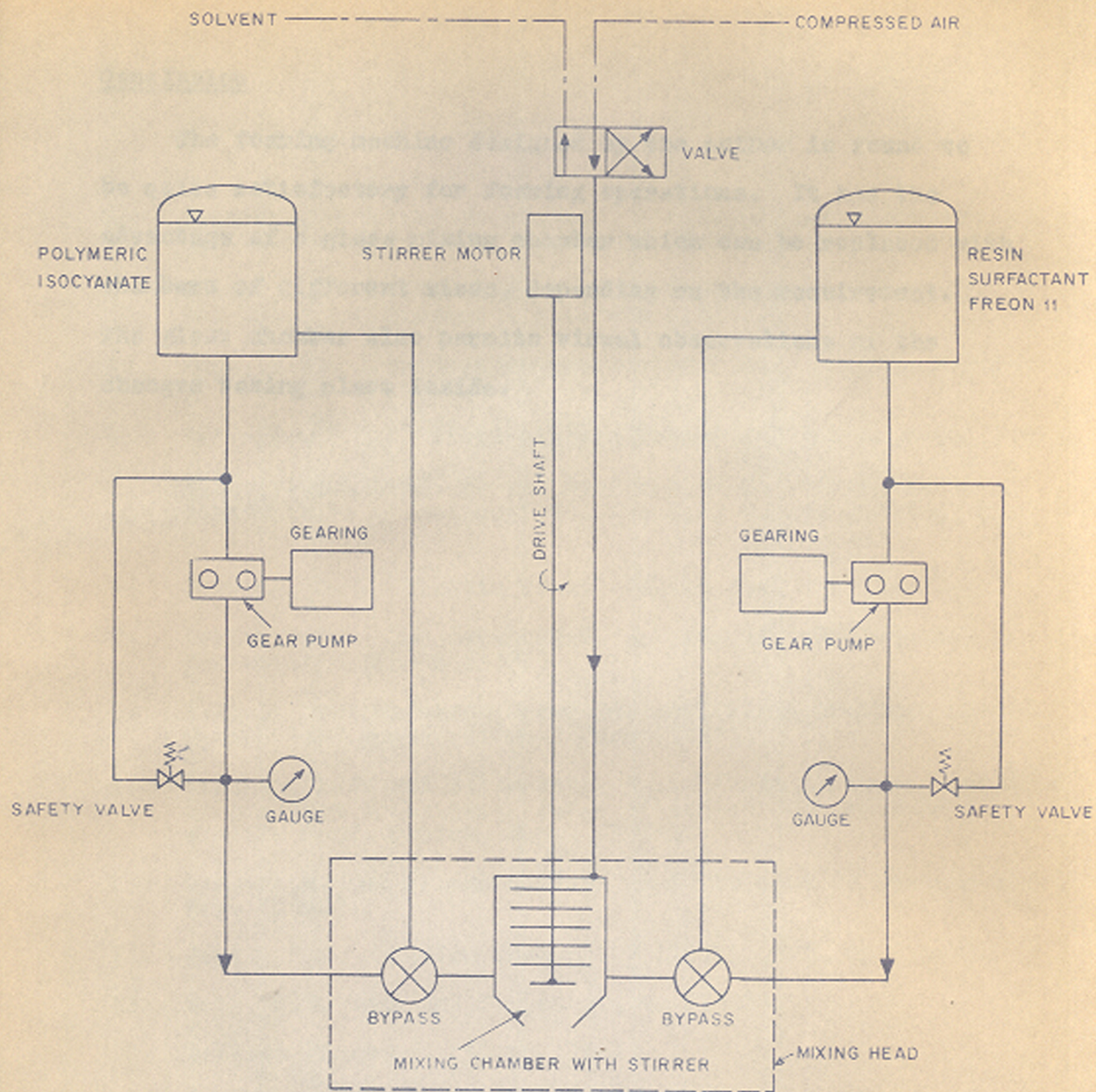


FIG. 3. WORKING CYCLE OF THE FOAMING MACHINE

Conclusion

The foaming machine designed by the author is found to be quite satisfactory for foaming operations. It has the advantage of a glass mixing chamber which can be replaced with chambers of different sizes, depending on the requirement. The glass chamber also permits visual observations of the changes taking place inside.

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SYNOPSIS

of the Thesis to be submitted by

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to the University of Poona for the award of Ph. D. Degree
in Chemistry.

Title: STUDIES IN THE SYNTHESIS AND EVALUATION OF
POLYURETHANE POLYMERS (RIGID FOAMS)

Introduction

Rigid urethane foams were first discovered by Prof. Otto Bayer and coworkers during World War II¹. Early foams were based on polyesters, toluene diisocyanate and water. These foams were utilised in aircraft construction and as insulation materials in submarines and tanks. After the World War II, aircraft companies in U.S.A. were attracted by the light weight and high strength properties of the foam as well as their excellent adhesion to metals. The Lockheed Aircraft Company developed 'one shot technique' during 1947-48 for 'foamed in place' rigid urethane foam². Low cost rigid and semi-rigid foams based on castor oil and TDI were developed by the Du Pont with densities ranging from 2 to 20 lbs/cu.ft.^{3,4}.

Initially rigid urethane foams were made with TDI (toluene diisocyanate) which was toxic and had technical deficiencies. The ICI developed the low toxicity system based on Diphenyl Methane Diisocyanate (MDI) composition⁵ in 1950. The product based on MDI and polyester resin was marketed in 1957.

The development of polyether resins as effective substitutes for polyester resins has materially lowered the cost of rigid urethane foams. Rigid urethane foam based on polyether resin and MDI was marketed in 1959.

The use of trichlorofluoromethane as a blowing agent instead of carbondioxide was one of the most important milestones in the development of rigid urethane foam. Apart from the lower

cost, and the resulting foam prepared with trichlorofluoromethane as a blowing agent has greatly improved thermal insulating properties. Literature survey reveals that tremendous work has been reported since 1960 on the development of rigid urethane foam technology.

Rigid urethane foams have many unique properties such as insulating efficiency, light weight, high strength adhesion, low water-vapour transmission, buoyancy, solvent, chemical resistance, fire retardancy and ideal electrical properties.

Since the last few years, industrial applications of rigid urethane foam extended to several areas such as domestic and industrial refrigeration, transportation, insulation, packaging, structural reinforcement, building materials in construction, automobiles, substitute to wood in furniture and in artificial limbs etc.

These foams have dominated other plastic foams due to their simple method of preparation and ease of application.

Polyhydroxy compounds are one of the important starting materials for making these foams. Their chemistry is developing tremendously in recent years. Today thousands of different polyhydroxy compounds are known. They are polyesters and polyethers or simply called as polyols. The choice of the polyol has a major influence on the properties of the foam.

At present, the raw materials required for making urethane foams (flexible and rigid) are not manufactured in India. The demand for these foams is expected to increase in near future. In view of the growing commercial importance of polyurethane polymers, it is of interest to substitute new polyhydroxy compounds for rigid urethane foams manufacture.

In the present investigation polyhydroxy compounds have been synthesised by using indigenously available raw materials such as shellac and cashewnut shell liquid (CNSL). These polyhydroxy compounds were used for making rigid urethane foams of different densities. Since these foams have commercial

importance, a continuous metering and foaming unit was also fabricated.

PART I

Shellac Polyesters

Shellac is a naturally occurring hard, brittle resin containing small amount of wax. It is not a single compound but an intimate mixture of several components. Its natural colour varies from dark red to light yellow.

It is an acidic resin, phenolic in nature, and the average molecule contains at least one free carboxyl group, five hydroxyl groups and three ester groups. Two of the hydroxyl groups are in adjacent carbon atoms and others may be tertiary.

Useful intermediates are obtained by the modification of shellac by esterification or etherification of the free carboxyl and hydroxyl groups of the lac resin.

Shellac formulations have outstanding physical properties such as high dielectric strength, low thermal conductivity, good adhesion, gloss and great dimensional stability, which are the most desired properties in rigid foam, and hence shellac is an attractive and alternative raw material for rigid urethane foam.

A series of polyesters were prepared by refluxing shellac-glycol or shellac-glycol-dibasic acid mixtures under nitrogen. These polyesters were found to be highly viscous. Semi pre-polymers were made by reacting these polyesters with diisocyanates which were subsequently converted to rigid foams by reacting with original shellac polyester. The physical, mechanical and chemical properties of these foams were studied.

The studies were conducted to investigate the usefulness of the shellac polyester resin for making rigid polyurethane foams in 'artificial limbs' application.

PART II

Self-catalytic resins or amino polyols

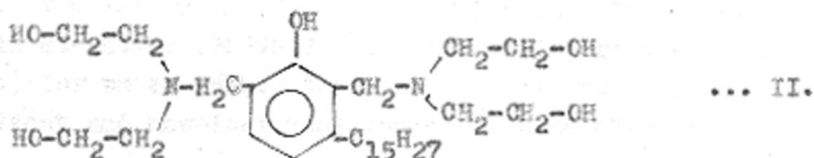
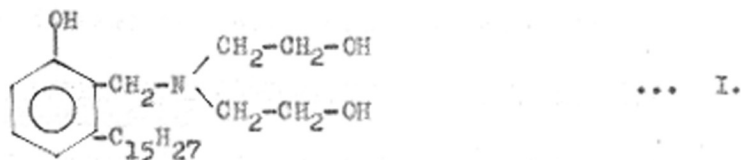
New polyhydroxy compounds are coming into effect regularly for new developments. Self-catalytic resins are marketed in United States recently by many entrepreneurs. The polyols contain bonded tertiary nitrogen in their molecule which presumably acts as a catalyst. These types of resins are generally prepared by condensing phenol or alkyl phenol with diethanolamine or triethanolamine and formaldehyde.

India is one of the major cashewnut shell liquid (CNSL) producing countries of the world. CNSL is a mixture of about 90% monhydroxyphenol (cardenol) and 10% of dihydroxy phenol (cardol).

Cardenol or 3-pentadecenyl phenol was obtained by distilling CNSL under reduced pressure. This phenol has an unsaturated hydrocarbon chain of 15 carbon atoms at meta position with respect to the phenolic 'OH' group.

Various amino polyols were prepared from CNSL or cardenol or nonyl phenol by condensing with diethanol amine and formaldehyde in different molar ratios.

The structures of the aminopolyols can be presented as I and II.



The primary hydroxyls are readily reactive to polyisocyanates and the tertiary nitrogen can act as a catalyst. The phenolic

hydroxyl is somewhat less reactive but under conditions of strong catalysis the reactivity may be enhanced. The presence of benzene ring provides stability and the side chain should have a plasticizing effect.

Hydroxyl number, moisture content, specific gravity, viscosity, molecular weight and nitrogen content of these polyols were determined. These polyols were found to be slightly viscous and difficult for metering. Therefore they were blended with natural and synthetic hydrogen donors such as castor oil and polyglycols (mol.wt. 200-600). Specific properties of these blended polyols were also studied.

Polyglycols of mol.wt. 200, 300 and 400 were found to be suitable for blending and metering the compositions for making rigid urethane foams.

These mixed polyols were then reacted with diisocyanates to obtain low and high density foams.

Low density foams for refrigeration and packaging

2 lbs/cuft. density foam was prepared by using trichloro-fluoromethane as blowing agent. These foams have closed cell structure (90%), light weight, low thermal conductivity (0.12 - 0.14 BTU/hr (ft³)(°F)/in.), low water vapour transmission (2.2 to 2.5 per m. inches) and good dimensional stability.

High density foams for furniture, buoyancy and building materials in construction

Foams of density 5 to 20 lbs/cuft. were prepared by varying the amount of water in the foaming formulation. These foams have closed cell structure (96-98%) high compression strength (50-400 lbs/sq.in.) low water vapour transmission (1.5 to 1 per m.inches) flame, solvent and chemical resistance and good dimensional stability.

Rigid urethane foams made from amino polyols were studied for foam structure and their properties by varying the proportions of chemicals such as blowing agents, silicone surfactants,

NCO:OH ratios, plasticizers and fillers.

PART III

Mechanical methods of manufacture of foams

Rigid polyurethane foams can be manufactured by batch process, by foaming in place, by continuous slab process and by spraying. Foam properties are generally dependent upon the mode of preparation and the mechanical factors encountered in these processes. In the early development of urethane foam, it was necessary for chemical suppliers to develop the special equipment necessary and also establish the basic principles which should be adopted for the given system. Recently, many engineering companies⁶⁻¹¹ have developed special types of machinery for processing rigid foam chemicals. The machines range from small to large dispensing units in which the liquid chemicals are pumped in metered quantities to a mixing chamber. After mixing, the chemicals can be discharged in a liquid stream (dispensing) or as a fine spray (spraying) by fitting special nozzles to the discharge tube from the mixing chamber. Sophisticated controls have been designed for several machines.

Active design development is in progress by many engineering firms for developing urethane foam machines. Special machines have been developed for making rigid urethane foams using special propriety chemicals.

Since no such small scale machine was available for use with our polyols, it was felt necessary to develop our own dispensing unit.

A laboratory scale foam making machine has been designed and fabricated. A special feature of the machine is its glass mixing chamber, enabling visual observations of the contents and provision for altering the volume of chamber easily. Other salient features such as metering unit, mixing head, agitator speed, have been discussed.

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INDIAN PATENTS AND DESIGN ACT 1911

COMPLETE SPECIFICATION

Patent Application No. 417/Cal/75.

PREPARATION OF AMINOPOLYOLS USING CNSL
AND MAKING POLYURETHANE RIGID FOAMS

Council of Scientific & Industrial Research
Refi Merg, New Delhi, India, an Indian
Registered body incorporated under
the Registration of Societies
Act (XXI of 1869)

The following specification describes the
nature of the invention.

This is an invention by MANASAHEB DATTAJIRAO
GHATGE and KANTILAL BALARAM GUJAR, both of
the National Chemical Laboratory, Poona,
citizens of the Republic of India.

PREPARATION OF AMINOPOLYOLS USING CNSL
AND MAKING POLYURETHANE RIGID FOAMS

This invention relates to the use of CNSL (cashewnut shell liquid) and 3-pentadecenyl phenol (cardenol), the main constituent of the commercially available CNSL, for making rigid polyurethane foams and their application in household and industrial refrigerators as thermal insulation; for structural reinforcement, artificial limbs, packaging, transportation, as building materials in construction; substitute for wood in furniture and marine applications such as void filling, buoys and life rafts etc.

Cashewnutshell liquid is commercially obtained by the well known process involving cold pressing, heating at a suitable temperature, or extraction with solvent. It is a mixture of about 90% cardenol and 10% cardol.

3-Pentadecenyl phenol was obtained from CNSL by distillation under reduced pressure. This phenol has a hydrocarbon chain of 15 carbon atoms at meta position to the phenolic OH-group with unsaturation in side chain and is described in scientific papers and in Current Science, 9, 362 (1940).

The following examples illustrate the preparation of aminopolyols and their use in foam formulations according to the present investigation.

Example 1: Preparation of aminopolyol from CNSL

1 Mole of commercial CNSL was condensed with diethanolamine (1 to 2 moles) and formaldehyde (1 to 3 moles) at 20-85°C for 2-10 hours under nitrogen atmosphere. Water was removed under reduced pressure. This product was dark in colour and highly viscous.

Example 2: Preparation of aminopolyol from cardenol

1 Mole of 3-pentadecenyl phenol was condensed with diethanolamine (1 to 3 moles) and formaldehyde (1 to 3 moles) at 20 to 90°C for 2-10 hours, with vigorous stirring under nitrogen flushing.

Water was removed under reduced pressure. This product was brown black in colour and had pourable consistency.

Example 3: Preparation of aminopolyol from cardenol and castor oil

1 part of aminopolyol from Example 2 was mixed with castor oil (1 to 3 parts) at 40-70°C for about 2 hours. The product was dried under reduced pressure and had pale brown colour.

Example 4: Preparation of aminopolyol from cardenol and polyglycols

1 part of aminopolyol from Example 1 was mixed with 1 to 4 parts of polyglycols (200 to 600 mol.wt.) at 40 to 70°C for about 2 hours. The product was dried under reduced pressure and had dark brown colour.

Example 5: Preparation of aminopolyol from cardenol, glycerine and polyglycols

1 part of aminopolyol from Example 2 was mixed with glycerine (0.1 to 1 mole) and polyglycol (1 to 4 parts) at 40 to 70°C for about 2 hours.

Formulations for rigid foams

Example 1:	Polyol	100 parts
	Diisocyanate	98 parts
	Emulsifier	0.5 to 1 part
	Water	1 to 3 parts
	Plasticizer	5 to 10 parts
Example 2:	Polyol	100 parts
	Diisocyanate	78 parts
	Emulsifier	0.5 to 1 part
	Fluorocarbon	10 to 50 parts
	Plasticizer	5 to 10 parts
Example 3:	Polyol	100 parts
	Diisocyanate	98 parts
	Emulsifier	0.5 to 1 part
	Blowing agent	1 to 3 parts
	Filler	5 to 20 parts

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that we claim:

- (1) A process for the preparation of aminopolyols by condensing cashewnutshell liquid with formaldehyde and ethanolamines in different proportions and at a temperature range from 0 to 100°C and blending the aminopolyol with polyhydroxy compounds and plasticizers and reacting these with polyisocyanate and blowing agents to make cellular products at a temperature from 10°C to 50°C.
- (2) A process as claimed in Claim 1, where the cashewnutshell liquid is a product of commerce or fractionation product thereof, distilling between 190-200°C/0.7 mm.
- (3) A process as claimed in Claim 1, wherein the ethanolamines are monoethanolamine or diethanolamine.
- (4) A process as claimed in Claim 1 wherein the ratio of cashewnutshell liquid to ethanolamines varies between 1 to 3, cardenol with formaldehyde and diethanolamine by using different molar proportions.
- (5) A process as claimed in Claim 1 wherein the polyhydroxy compounds are polyesters or polyglycols of molecular weight 200-1000 or castor oil or glycerine or trimethylol propane.
- (6) A process as claimed in Claim 1, for making rigid castable or sprayable foams by reacting these aminopolyols with diisocyanates such as toluene diisocyanate (80:20, 65:35) or diphenyl methane diisocyanate (liquid).
- (7) A process as claimed in Claim 1 for making rigid foams by using blowing agents such as water or fluorocarbons etc.
- (8) A process as claimed in Claim 1 of making foams by reacting the reactants at temperature from 10° to 50°C.