

THE PREPARATION OF A POLYURETHANE ELASTOMER AND  
EVALUATION OF THE MECHANICAL PROPERTIES

by

Choung - Lin Lo

Thesis submitted to the Graduate Faculty of the  
Virginia Polytechnic Institute  
in candidacy for the degree of

MASTER OF SCIENCE

in

CHEMICAL ENGINEERING

August, 1960

Blacksburg, Virginia

LIBRARY  
BLACKSBURG, VA

TABLE OF CONTENTS

	Page
I. INTRODUCTION . . . . .	1
II. LITERATURE REVIEW. . . . .	3
Survey of Linear, Branching and Space Polymerization. . . . .	3
Linear Polymers. . . . .	3
Branching Polymer. . . . .	5
Cross-Linking in Space Polymer . . . . .	5
Polyurethane Development. . . . .	10
Polyurethane and its Application . . . . .	11
Chemistry of Polyurethane . . . . .	15
Nature of Polyurethane Elastomers . . . . .	17
Chemistry of Polyurethane Elastomers. . . . .	18
Condensation Method. . . . .	18
Addition Method. . . . .	19
Method of Preparation of Polyurethane Elastomers. . . . .	20
Preparation of Linear Polymer. . . . .	20
Chain Extension of the Polyester with Diisocyanate . . . . .	20
Further Chain Extension. . . . .	40
Cross-Linking of Chain Extended Copolymer . . . . .	41
The Mechanism of Network Formation. . . . .	50
Water as a Cross-Linking Agent . . . . .	50
Hydrogen Sulfide as a Cross-Linking Agent. . . . .	51



	Page
Glycols as a Cross-Linking Agent . . . . .	52
Dithiols as a Cross-Linking Agent . . . . .	54
Diamines as a Cross-Linking Agent . . . . .	54
Amino Alcohols as a Cross-Linking Agent . . . . .	55
Polymerization Process . . . . .	57
Vulcollan Process . . . . .	57
Urethane Cross-Linking with Glycols Process . . . . .	60
Chemigum SL in an Elastomeric Polyester-Urethane. . . . .	62
Properties of Polyurethane Elastomer . . . . .	65
III. EXPERIMENTAL. . . . .	75
Purpose of Investigation . . . . .	75
Plan of Experimentation. . . . .	75
The Apparatus Required. . . . .	75
Preliminary Tests . . . . .	76
Preparation of Elastomer. . . . .	76
Testing of Elastomer. . . . .	76
Materials. . . . .	77
Apparatus. . . . .	79
Method of Procedure. . . . .	86
Raw Materials . . . . .	86
Preliminary Tests . . . . .	88
Preparation of Polyurethane Elastomer . . . . .	89
Preparation of Testing Materials. . . . .	93

	Page
Determining the Solvent Absorption of Polyurethane. . . . .	96
Determining the swelling of Polyurethane Elastomer in Acetone Solution . . . . .	101
Determination of Tensile Strength, Elongation, and Breakdown Force . . . . .	102
Determination of Hardness of Polyurethane Elastomer at Room Temperature . . . . .	105
Determination of Hardness of Polyurethane Elastomer at High Temperature . . . . .	106
Data and Results . . . . .	106
Sample Calculations. . . . .	122
IV. DISCUSSION. . . . .	134
Discussion of Polymerization Process . . . . .	134
Copolymerization of Polyurethane Elastomer. . . . .	135
Chain Extension of Ethylene Glycol. . . . .	135
Molding of Polyurethane Elastomer . . . . .	136
Curing of Polyurethane Elastomer. . . . .	137
Summary of the Process Conditions . . . . .	137
Discussion of Results. . . . .	138
Varying R Values, the Mole Ratios of Diisocyanate to Polyester. . . . .	138
A Constant R Value with Varying Amount of Cross-Linking Agent, Ethylene Glycol. . . . .	140
A Constant R value of 2.5 with Varying Amount of Cross-Linking Agent, Ethylene Glycol. . . . .	141
The Solvent Absorption Properties for Varying R Values of Polyurethane Elastomer. . . . .	141

	Page
The Swelling Properties of Varying R Values of Polyurethane Elastomer. . . . .	142
The Tensile Properties for Various R Values in a Polyurethane Elastomer. . . . .	143
The Hardness by Penetration for Polyurethane Elastomers of Various R Value at 75° F. . . . .	145
The Hardness by Penetration for Polyurethane elastomers of Various R Value at 300° F . . . . .	146
The Solvent Absorption Properties of the Elastomers having R Values of 1.65 with Varying Amounts of Cross-Linking Agent, Ethylene Glycol. . . . .	148
The Solvent Absorption for R Value of 2.5 with Various Amounts of Cross-Linking Agent . . . . .	149
Swelling Properties for the Constant R Values of 1.65 and 2.5 with Various Amount of Cross-Linking Agent . . . . .	149
Tensile Properties at Constant R Value of 1.65 and 2.5 with Various Quantities of Cross-Linking Agent . . . . .	150
The Hardness by Penetration for the Elastomer with Constant R Value of 1.65 and 2.5 with various Quantities of Cross-Linking Agent. . . . .	151
Recommendations. . . . .	152
Limitations. . . . .	155
V. CONCLUSIONS. . . . .	158
VI. SUMMARY. . . . .	163
VII. BIBLIOGRAPHY . . . . .	168
VIII. ACKNOWLEDGEMENTS . . . . .	173
IX. VITA . . . . .	174



LIST OF TABLES

TABLE		Page
I.	Reaction Products of Simple Polyesters with Naphthylene-1,5-Diisocyanate. . . . .	23
II.	Reaction Products of Mixed Esters with Naphthylene-1,5-Diisocyanate . . . . .	24
III.	Mixed Esters and Mixtures of Esters. . . . .	26
IV.	Physical Properties of Cast Urethane Elastomers as Influenced by Polyester. . . . .	27
V.	Ethyleneglycol-Adipic Acid Esters of Different Hydroxyl Numbers Extended with Naphthylene-1,5-Diisocyanate to a Molecular Weight of 4000 . . . . .	32
VI.	Ethyleneglycol-Adipic Acid Esters of Different Hydroxyl Numbers Extended with Naphthylene-1,5-Diisocyanate to About 1.9 Increase in Molecular Weight . . . . .	34
VII.	Reaction Products of the Undried Polyester of Ethyleneglycol and Adipic Acid and Various Diisocyanates (Approximately 30 Per Cent in Excess of the Amounts Calculated on the Basis of Hydroxyl Groups) . . . . .	37
VIII.	Physical Properties of Cast Urethane Elastomers as Influenced by Diisocyanates. . . . .	38
IX.	Physical Properties of Cast Urethane Elastomers as Influenced by Aliphatic Glycols. . . . .	42
X.	Physical Properties of Cast Urethane Elastomers as Influenced by Aromatic Extenders . . . . .	43
XI.	Physical Properties of Cast Urethane Elastomers as Influenced by Chemical Cross-Linking. . . . .	47
XII.	Influence of the Amount of Cross-linking Agent, 1,4-Cyclohexandiol on Physical Properties . . . . .	63

TABLE		Page
XIII.	Physical Properties of Vulcanized Chemigum SL . . . . .	66
XIV.	Aged Properties of Vulcanized Chemigum SL. . . . .	67
XV.	Performance of Chemigum SL in Tread Stocks . . . . .	72
XVI.	Oxygen Absorption. . . . .	74
XVII.	Composition of Test Batches - Test Series 1. . . . .	97
XVIII.	Composition of Test Batches - Test Series 2. . . . .	98
XIX.	Composition of Test Batches - Test Series 3. . . . .	99
XX.	Determination of the Solvent Absorption of Polyurethane Elastomer for Test Series 1 . . . . .	108
XXI.	Determination of the Solvent Absorption of Polyurethane Elastomer Series 2 . . . . .	109
XXII.	Determination of the Solvent Absorption of Polyurethane Elastomer Series 3 . . . . .	110
XXIII.	Determination of the Swelling of Polyurethane Elastomer in Acetone Solution Test Series 1. . . . .	113
XXIV.	Determination of the Swelling of Polyurethane Elastomer in Acetone Solution Test Series 2. . . . .	114
XXV.	Determination of the Swelling of Polyurethane Elastomer in Acetone Solution Test Series 3. . . . .	115
XXVI.	Test Data for Tensile Properties of Poly- urethane Elastomer Test Series 1 . . . . .	118
XXVII.	Test Data for Tensile Properties of Poly- urethane Elastomer Test Series 2 . . . . .	119
XXVIII.	Test Data for Tensile Properties of Poly- urethane Elastomer Test Series 3 . . . . .	120
XXIX.	Hardness by Penetration. Test Series 1 . . . . .	123
XXX.	Hardness by Penetration Test Series 2. . . . .	124

TABLE	Page
XXXI.	Hardness by Penetration Test Series 3. . . . . 125
XXXII.	Hardness by Penetration at 300° F Test Series 1. . . . . 126



LIST OF FIGURES

FIGURE		Page
1.	Effect of Cross-linkages on Swelling . . . . .	9
2.	Modulus - Temperature Variation as Influenced by Polyester. . . . .	29
3.	Volume Swell as Influenced by Cross- Linking and Solvent. . . . .	49
4.	Cold Hardening of Chemigum SL. . . . .	69
5.	Comparative Stress-strain Curves . . . . .	70
6.	Penetration Pin for Hardness Test. . . . .	81
7.	Compression Mold . . . . .	82
8.	Electric System for Constant Tempera- ture Bath. . . . .	90
9.	Flow Diagram for the Preparation of Polyurethane Elastomer . . . . .	94
10.	Tinius Olsen Testing Machine . . . . .	103
11.	Test Specimen. . . . .	104
12.	Effect of R value on the Absorption of Acetone . . . . .	111
13.	Effect of Time on the Absorption of Acetone. . . . .	112
14.	Effect of R Value on the Swelling of Poly- urethane in Acetone. . . . .	116
15.	Effect of Time on the Swelling of Polyurethane in Acetone . . . . .	117
16.	Effect of R Value on the Tensile Strength of Poly- urethane at Different Elongations. . . . .	121
17.	Effect of R Value on the Hardness of Polyurethane at 75° F . . . . .	127
18.	Effect of R Value on the Hardness of Polyurethane at 300° F. . . . .	128

## I. INTRODUCTION

During the last few years the American market has seen the introduction of a new elastomeric material, the family of solid urethane elastomers. These materials have been noteworthy for their abrasion resistance, oil resistance, ozone and oxygen resistance and other features. This new elastomeric material has played an important role in developments other than the applications of natural rubber. Its superior properties as well as wide range of applications have led to research on the applications to space science and high speed projects.

This new elastomeric polyurethane was an outgrowth of research in Germany and the United States in the period of 1937-1945. It has approached commercial production in the United States only within the past few years. Polyurethane is prepared from polyesters and diisocyanates. Some research has been carried out on different starting materials and the products have been recommended for use in heavy duty tire for aircraft and trucks, foam material, fibers and high impact resistance plastics. Compounds can be made that are as soft as gelatin or as hard as polystyrene.

The final products of the polyurethane elastomers have been found to have superior tensile strength, tear strength, excellent oil resistance and abrasion resistance, ozone resistance and very small oxygen absorption. The abrasion resistance, ozone resistance and tensile

strength are superior to those of natural rubber and synthetic GR-S. It was considered desirable to do additional work on the possibility of controlling the degree of cross-linkage in the elastomer and determining the resulting effects on mechanical properties.

The purpose of this investigation was to study the effect of the variation of cross-linkage on the mechanical properties of the polyurethane elastomer formed from 33' Bitolylene 44' diisocyanate and the polyester of adipic acid and ethylene glycol.



## II. LITERATURE REVIEW

The available literature lacks almost entirely any information concerning the elastomeric copolymer of 33'-Bitolylene 44'-diisocyanate and the polyester of adipic acid and ethylene glycol. Many articles have been written concerning the copolymerization of polyesters and diisocyanates, and because 33'-Bitolylene 44'-diisocyanate is a derivative of diisocyanate, it was felt that the same methods might be used. A research for information concerning cross-linking was carried out and the information obtained is presented in the following sections. Sections included are chemistry, properties, bonding, established method of preparation and treatment, and testing of products.

### Survey of Linear, Branching and Space Polymerization

In dealing with masses of molecules<sup>(67)</sup> one must consider not only the intramolecular forces which hold one atom to another within a molecule but also the intermolecular forces by which the molecules as separate entities are held to one another. The former are strong primary valence forces; the latter are weaker secondary forces or intermolecular attractive forces. The term "bond" is used to describe primary valence forces and "bridge" to describe secondary intermolecular attractions.

Linear Polymers. The mers are joined in line and this type of polymer is called linear or chain polymer. The mechanical properties of a linear polymer depend upon three factors. One<sup>(67)</sup> is the short range

Brownian movement of the chain segments, and the others<sup>(17)</sup> are the slipping or displacement of entire molecules, and the tendency to re-crystallize. In a rubbery polymer<sup>(33)</sup> such as natural rubber or GR-S (Butadiene-Styrene) the molecules are intertwined and entangled in a random fashion, individual segments are free to move a short distance<sup>(45)</sup> but the motion of each molecule as a whole is restricted by virtue of its entanglement with other molecules. When a sample of this rubber is stretched by application of an external force, the first effect is distortion. If the force is immediately removed the molecules return to their original position. This is due to their internal entanglement. If the stress is maintained the material will flow like a viscous liquid and assume the new shape, due to the gradual slippage of the individual molecules. As the temperature is raised this flow becomes easier, owing to increased Brownian motion of the segments. Actually this slippage<sup>(17)</sup> is greater than is desired in commercial practice and is overcome by the use of three properties of molecular structure; (1) bulkiness of the molecules, (2) attractive forces between the molecules (e.g., hydrogen bonds, polar groups of crystallinity resulting from an accumulation of Van der waal's forces) and (3) chemical bonding (cross-linking) between individual molecules. Examples of all these structural features are seen in synthetic rubber of the GR-S type. The bulky styrene molecules prevent slippage. All rubber is cross-linked or vulcanized and when stretched crystallites (minute regions of crystallization) are formed, which raise the tensile strength enormously. Alfrey<sup>(1)</sup> and D'alelio<sup>(24)</sup> discuss more fully the relationship of structural and physical properties.

Branching Polymer. By the simple addition of monomer molecules to a free radical chain<sup>(17)</sup> it is possible to form branches, and also to form cross-links. Branching<sup>(5)</sup> may occur as a result of chain transfer between the free radical terminus of a growing chain and a polymer molecule. A very small degree of branching will vastly modify the pattern of the molecule. If the molecular weight is very large and if such branching as is attached to the main chain is small compared with the molecular weight of the linear chain, it will have no discernible effect on the properties of the polymer. On the other hand, if the molecular weight of the branching polymer is very large, such as with diolefins the polymerization is generally capable of yielding a partly insoluble product.

Cross-linking in Space Polymers. In addition to the linear growth by the simple addition of monomeric molecules<sup>(17)</sup>, it is possible for the chain to form branches, and to cross-link to other chains. A linear polymer<sup>(67)</sup> is bridged to its neighbors by secondary valence forces only, while a cross-linkage introduces strong primary valence bonds to form a three-dimensional network as a typical space polymer. This introduces strong primary-valence restraints. Separation of the main chains of the structure from one another is not possible unless the cross-links are ruptured, a process that can be classed only as chemical decomposition or degradation. Solubility, fusibility, flow and moldability are greatly reduced or entirely eliminated. A few cross-links raise the molecular weight enormously, and the kinetic translation of the resulting



giant molecules as units is reduced to the vanishing point. The introduction of a large number of cross-links tends to form rigid, spatial supermolecules of infinite molecular weight. The physical properties of a space polymer are considered by Schmidt<sup>(67)</sup>. They depend upon three fundamental structural factors; (1) the character of the main chains, (2) the character of the cross-links, (3) the number of cross-links. The term character is defined to cover the length, flexibility, and extensibility of the main chain in the cross-links. D'Alelio<sup>(24)</sup> has contrasted the properties of linear and cross-linked polymers as follows:

A. Linear (Branched and Unbranched) .

1. Unlimited faculty for swelling and the eventual formation of homogeneous solution. Every very high polymer is capable of unlimited swelling, and although the rate of solubility is slow, the polymers are still capable of being dissolved.

2. In very dilute solutions, as for example, in the limiting case of extreme dilution, the dispersed molecules behave as independent kinetic units and exhibit the property of normal viscosity. Solutions of these polymers may be used in the preparation of films or filaments.

3. These polymers have a softening temperature zone whose sharpness more or less depends on their chemical and physical nature, for example, the type of atoms in the chain, their molecular weight, cohesive forces, etc. Above this temperature zone the polymer behaves as a viscous fluid, and, below it, the behavior corresponds to an

amorphous or samicrystalline solid. Most of these polymers soften without decomposition, and the softening zone is reproducible. Decomposition does occur in some polymers having unstable groups in the chain, or when secondary forces along the chain are very high, and decomposition occurs before softening. Polyacrylonitrile, polyvinyl alcohol, certain proteins, and cellulose belong to this class.

4. If not normally so at least when stretched or otherwise worked as by rolling or cold drawing, many linear polymers give X-ray crystal diagrams indicating an oriented structure, the intensity of orientation increasing to a maximum with degree of stretching. Many polymers show liquid diagrams before stretching. If the linear or branch disorder is high, the possibility of orientation decreases.

5. These polymers readily undergo chemical reactions in the dissolved or swollen state without appreciably changing the average chain size. As a rule these reactions are reversible, and the derivative will give an X-ray pattern similar to the parent material. Typical examples are (a) the conversion of cellulose to cellulose acetate and its reconversion to cellulose, (b) the reversible conversion of polyvinyl alcohol to acetate, (c) the hydrogenation of polystyrene.

The polymer in some cases does not have to be in a dissolved or swollen state. Polyvinyl alcohol and paraformaldehyde can be made to react in an aliphatic hydrocarbon in which neither the reacting materials nor the product of reaction is soluble.



B. Cross-linked (Net and Space).

1. These polymers show a limited capacity for swelling, but they do not dissolve. The degree of swelling decreases with cross-linking. Staudinger<sup>(76)</sup> cited excellent examples of the divinylbenzene-styrene copolymers, glyceryl phthalate, rubber vulcanized to different degrees. Swelling as a function of cross-linking is shown in Figure 1, page 9 .

2. These polymers do not dissolve, but in some cases they may swell. Where solution apparently occurs, it has been accomplished through the destruction of primary chemical bonds, as for example, insoluble polydiallyl phthalate may be hydrolyzed by concentrated hydrochloric acid.

3. These polymers have no softening zone corresponding to those of the linear polymers since they never really melt. They become soft at very high temperature, at which they usually decompose. If they have a large number of cross-linkages they may not even soften but decompose directly when the temperature becomes sufficiently high. Usually such polymers are brittle. However, they have improved heat distortion value and find wide application in industrial use, and higher cross-linkages show less distortion under load.

4. As the number of cross-linkages increases, the sharp X-ray diagrams of linear polymers begin to become indistinct. When the cross-linkages are sufficiently numerous ring diagrams are obtained. Working by rolling or stretching does not produce orientation.



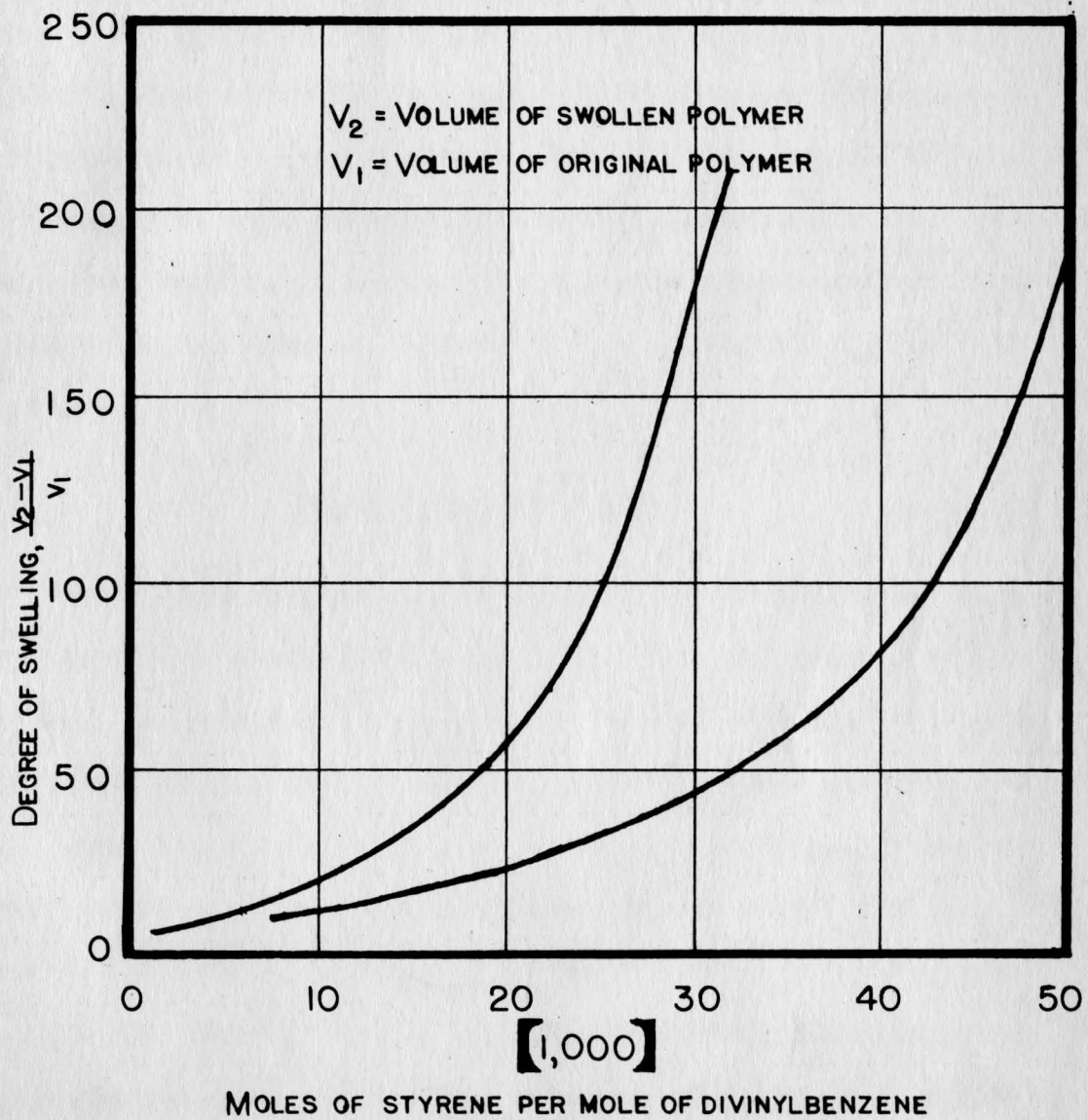


FIGURE 1 EFFECT OF CROSSLINKAGES ON SWELLING.

D'Alelio, G. F.: "Fundamental Principles of Polymerization",  
p. 164. John Wiley & Sons, Inc., New York, N. Y., 1952.

5. As cross-linkage increases permutoid reactivity decreases; and if the cross-linkage is sufficiently high, reactivity eventually disappears. This may be readily observed as the degree of esterification of copolymers of acrylic acid and divinylbenzene is studied. The esterification reactivity decreases with an increase in the ratio of divinylbenzene to acrylic acid. A more startling example is found in attempts to react polymers of polyvinyl alcohol and maleic anhydride with paraform in hexane. Formalization almost completely disappears when more than one hydroxyl in ten of the polyvinyl alcohol is cross-linked.

#### Polyurethane Development

The polyurethane polymers<sup>(11)</sup>, also known as isocyanate polymers, are perhaps the newest major entry in the field of plastics in this country. An outgrowth of research in Germany and the United States. In the period of 1937-1945, they have approached commercial production in the United States only within the period of 1954-1955. Before then both production of isocyanates and applications of the isocyanate resins were in the development stage.

In 1937 Bayer<sup>(6)</sup> and his coworkers discovered, and have since developed, the method of preparing polyurethane. This method is called polyurethane polymerization. It is also known as the diisocyanate method. As early as 1848 Wurtz<sup>(11)</sup> found that ethyl isocyanate ( $C_2H_5-N=C=O$ ) adds itself smoothly to ethyl alcohol to yield ( $C_2H_5-NHCOOC_2H_5$ ) and to dialkyl

amine ( $\text{NH} \begin{smallmatrix} \text{R} \\ \text{R}' \end{smallmatrix}$ ) to yield ( $\text{C}_2\text{H}_5\text{NHCON} \begin{smallmatrix} \text{R} \\ \text{R}' \end{smallmatrix}$ ), by shifting of the hydrogen atom of the isocyanate group. In 1849 Hoffman(11) extended these observations to the aromatic series with phenylisocyanate. Then with the recent successful German development(11) of elastic urethane forms of exceptional quality, full scale isocyanate production became economically attractive. The resulting decrease in the prices of these compounds immediately broadened their scope of practical applications. More comprehensive reviews of more recent developments are presented by Bjorksten, Tovey and Dollard(26) and by Rartz(61).

Polyurethane and its Application. Polyurethane(27) is referred to as isocyanate resin. Polyesters and polyethers(13) can be modified with diisocyanates to yield a variety of resinous products ranging from tough to rubbery plastics. The diisocyanate-modified polyesters have applications as elastomers, adhesives, foams, and molding and coating compounds.

The isocyanate-modified polyesters are primarily a German development. The German Vulcollans(41,53) opened the field of polyurethane elastomer and were followed by English "Vulcaprene"(77) and later by products from B. F. Goodrich Chemical Company(31).

The commercial production of polyurethane applications has developed rapidly within the last ten years in the United States. The successful development of elastic isocyanates forms of exceptional quality induced great interest in the development of full-scale production, and it became economically attractive. Resulting major reductions in the prices of these compounds immediately broadened their scope of applications. The major



industrial applications are fibers, flexible and rigid foams and coatings, adhesives, and synthetic elastomers.

Fibers: The advent of nylon induced an effort on the part of I. D. Farben to produce similar fibers of a different basis<sup>(27,28,29,30,31)</sup>.

Foams: During 1956, urethane foams<sup>(74)</sup> have achieved new importance with the rapid development of soft and flexible varieties. Three flexible foams are offering competition to latex foam rubber and flexible vinyl foams. Generally, both types of urethane foams<sup>(75)</sup> are prepared commercially from polyester (or polyethers), diisocyanates and water. The mechanical characteristics of the foam depend largely on the choice of polymer. By varying the degree of branching<sup>(32)</sup> one can prepare either flexible or rigid foams. When isocyanates<sup>(2)</sup> react with carboxylic groups and when water is added to polyester-diisocyanate reaction products, carbon dioxide is evolved with the production of amide and urethane linkages. Water<sup>(32)</sup> may be added in form of a metal salt hydrate.

The urethane foams available include soft, flexible, or tough, rigid types of great strength as well as an infinite number having properties between these two extremes. All types are characterized by excellent resistance to oxidation, solvents and temperature. Other properties are more specific, depending on whether the foam is flexible or rigid. Flexible foams having a predominately open cell structure are available in a density range of two to six pounds per cubic foot. Rigid urethane<sup>(43,47)</sup> foams are available in a density range of two to six pounds per cubic foot and have predominately closed cells.

Adhesives: The isocyanate-modified polyesters<sup>(16)</sup> can be polymerized in the presence of the materials to be bonded. Also, the diisocyanate component<sup>(39,60)</sup> is so reactive that it is very likely to find groups on adjacent surfaces to which it can attach itself. Other types of products based on the elastomer, such as single-component adhesives, have been developed from isocyanate, polyester resins. These adhesives have high sensitivity to moisture, which causes them to skin prematurely. There are also several kinds of applications of adhesives. Austin<sup>(4)</sup> used the diisocyanate polyester resins for binding cork for gaskets and floor covers. Harmon<sup>(34)</sup> invented adhesives for waxed paper, for bonding synthetic fibers to rubber in automobile tires, and there is also an adhesive<sup>(28)</sup> for bonding wood which was developed in Germany.

Coating: In the surface coating<sup>(21,63)</sup> field the isocyanate-urethane type coatings show excellent adhesion and resistance to chemicals and abrasion. Nonetheless, they have not yet been accepted generally because of hazards in handling the isocyanate component and because of the inconvenience of using two component systems. Polyester-derived urethane coatings are generally superior to the rubber or polyvinyl chloride coating in regard to tear strength and resistance to aging and water. A large potential field for these resins is in can coatings and in protective coatings for magnesium, iron, and zinc, where their excellent adhesion, tendency, and complete resistance and inertia to solvents, lard, greases, and flavors offer important advantages. Applications such as wire coatings and insulation are logical in view of the excellent dielectric properties

of these resins. This problem has been attacked by Breslow<sup>(18)</sup> and the Hercules Powder Company. Coffey<sup>(23)</sup> developed the use of diisocyanate-modified polyesters as non volatile plasticizers in polyvinyl chloride.

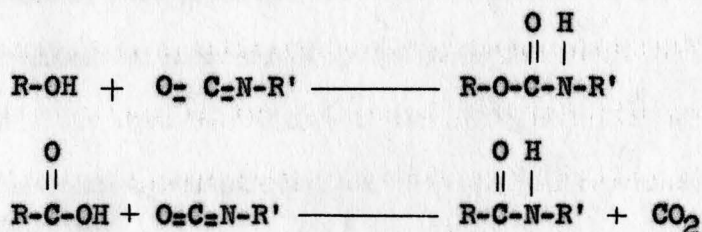
Elastomers: Polyurethane rubbers<sup>(43)</sup> are elastomeric materials prepared by reacting a polyester or polyether containing terminal hydroxyl groups with a diisocyanate (e.g., toluene diisocyanate) and so called "cross-linking" chemicals. This ties together large molecules, and hence changes the physical properties of the material and may be accomplished by radiation or other means. Basically, these polymers<sup>(16)</sup> are prepared by joining a polyester with diisocyanate to lengthen the chains and then cross-linking the modified polyester by reaction with water, glycols<sup>(29, 46, 49, 52, 73)</sup>, amide<sup>(8, 46, 72, 73)</sup>, or amine alcohol<sup>(68, 73)</sup>. When water is used as a cross-linking agent, carbon dioxide is evolved. Therefore, the material must be worked to allow the gas to escape before press curing the final products from the polymers. The final products of polymerization are characterized by high tensile and tear strengths and excellent abrasion resistance without necessity for fillers. These elastomers<sup>(14)</sup> have abrasion resistance, ozone resistance, and tensile strength far superior to those of natural rubber and synthetic GR-S. They have excellent oil resistance, and oxygen absorption is very small. Reinforcement with carbon black results in still better properties. They have fair resistance to heat. Their resistance to extreme conditions of hot water and steam is as yet relatively poor and they show some tendency to harden at low temperature. More detailed technical data on the properties of



polyurethane elastomers are given by Dinsmore(25). The full commercial application of polyurethane elastomers has been slow because of the high cost of the raw material. Also, processing is difficult and adhesion and compounding problems have only been partially solved. Potential applications include heavy-duty truck, bus, friction wheels, hydraulic gasket oil seals and related products.

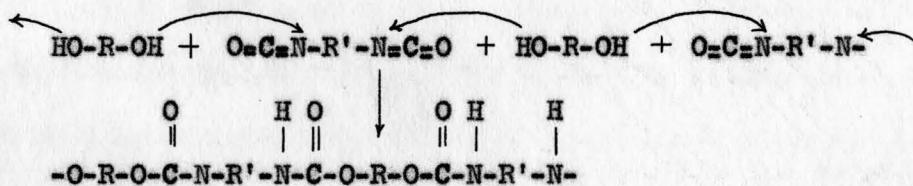
### Chemistry of Polyurethane

The urethane products are esters of carbamic acid and are formed by reaction between an isocyanate and a compounds containing a hydroxyl group. Isocyanates ( $R-N=C=O$ ) react with compounds containing reactive hydrogen atoms. A urethane linkage is formed with compounds containing hydroxyl groups, and an amide linkage is formed with molecules containing carboxyl groups:



The reaction products(22) of diisocyanates and polyester resins usually contain a mixture of two types of linkage, since the terminal groups in the original polyester molecules are usually a mixture of hydroxyl and carboxyl groups. The properties of the two types of linkage can be varied by changing the proportions of acid and glycol used in preparing the

polyester. Increasing the glycol proportion the number of urethane linkages formed is correspondingly increased. Increasing the acid proportion increases the number of amide linkages. The first step in the diisocyanate modification of polyesters results mainly in an extension of chain length, since the reaction is usually that of adding on to the polyester chain or of linking two polyesters chains together. Urethane linkages formed by hydroxyl group reaction still contain an active hydrogen which offers a point for further addition of the same diisocyanate or by adding a different diisocyanate, the polyester may be modified and cross-linked to give products with a wide range of properties. At the copolymerization stage, Dr. Otto Bayer showed<sup>(54)</sup> that in order to utilize these quantitative and strongly exothermic reactions to make polymers, diisocyanate had to be produced and added to glycols, diamines, polyhydroxy or polyamino compounds. The following simple diagram of the reaction of one diisocyanate with one glycol shows that to a large degree it parallels a pure polymerization.



The essential difference is that the chain molecule is not composed exclusively of carbon atoms but rather of heteroatoms, oxygen, carbon and nitrogen. The range of compounds made with the polyhydroxy compounds alone

has applications broader than those of known products made by polymerization or condensation methods.

#### Nature of Polyurethane Elastomers

In the field of urethane elastomers the Germans were first to develop Vulcollans (8,12,41) then followed by English production of Vulcaprenes (77): In the United States Goodyear's Chemigum SL (25) is also one of the greatest contributions in this field. These products are the practical results of research on diisocyanate-polyester elastomers. These new elastomeric products are so called diisocyanate-linked condensation elastomers. Principally it is a two-step reaction in which primary polymer chains terminating in reactive groups are treated with a bifunctional reagent adapted to react with these terminal groups and thus by uniting the primary chains, lead to molecules of the higher order of molecular weight. The material of the first step consists of a polyester or polyesteramide, the molecular weight of which is only moderately high, and the molecules of which, thanks to the choice of an appropriate ratio between the dibasic acid and glycol or aminoalcohol from which they are made by condensation, terminate in hydroxyl or amino groups.

In the second step, such primary polymer chains are linked with the consequent formation of long chains, by reaction of their terminal groups with a diisocyanate.



Chemistry of Polyurethane Elastomer

Bayer<sup>(25)</sup> showed that by means of the diisocyanate process, it is possible also to prepare new types of highly elastic and valuable products of the character of vulcanized rubber. The process is the polyaddition of diisocyanates, which in principle is the addition of diisocyanates to dihydroxy and polyhydroxy compounds and to other compounds containing two or more reactive hydrogen atoms. This makes it possible to synthesize products of high or even extremely high molecular weight, and with practically predetermined structures and properties, from small molecules.

Desmophene<sup>(20)</sup> has found application for the reactants polyhydroxy compounds which can be easily obtained by esterification of dibasic acids, with an excess of bivalent and trivalent alcohols.

Dr. Otto Bayer<sup>(11)</sup> who developed the polyurethane polymer and showed the chemical reaction of this polymerization which is complicated and manifold plastics. It is produced according to these two basic reactions, by the condensation and addition methods.

Condensation method. (1) A great number of small molecules<sup>(11)</sup> with at least two functional groups react, liberating during the process a reaction product of low molecular weight, such as water, hydrochloric acid, sodium chloride, alcohol. (2) In order to obtain the macromolecular state, several reaction conditions are often applied, such as high temperature and condensing agents. Consequently, the plastics produced in this way are mostly mixtures of products from the different

condensation stages. (3) It is a characteristic advantage of the condensation that it is possible to stop it at any intermediate stage and complete the reaction of the intermediate products in subsequent processing into moldings, cast resins or infusible protective coatings. Moreover, mixed condensates can be prepared from various intermediate condensation products.

Addition method. (1) The addition method<sup>(11)</sup> involves linkage of many molecules (up to about 5000 in the linear chain) of a monomer into a high molecular weight polymer which has the same percentage composition as the monomer. Addition is an extremely sensitive reaction which probably occurs by the shifting of activated hydrogen atoms from molecule to molecule of the monomer. In contrast to condensation, addition proceeds smoothly. Kinetically, it is a pure chain reaction. (2) It is typical of addition that only final products can be obtained and that it is impossible to isolate reactive intermediate products as in the condensation reaction; e.g., di-, tri- or tetramers, and to further polymerize these with one another or with the monomer. On the contrary, such intermediates often inhibit the polymerization. (3) A further characteristic of polymerization is that, for all practical purposes, one can only start with reactive vinyl compounds or dienes which yield either chain or cross-linked polymers. They are all the result of the direct linkage of carbon to carbon. Mixed polymerization of two or three different polymerizable compounds makes possible a wide variety of compounds. But it is practically impossible to produce high polymers containing



heteroatoms. Polymerization reactions involving heteroatoms are rare, as examples, the polymerization of the compact ring compounds - methylene oxide and ethyleneimine - may be mentioned, as well as the vulcanization of rubber which must be considered as polymerization involving cross-linking of the linear rubber and sulfur molecules.

#### Method of Preparation of Polyurethane Elastomers

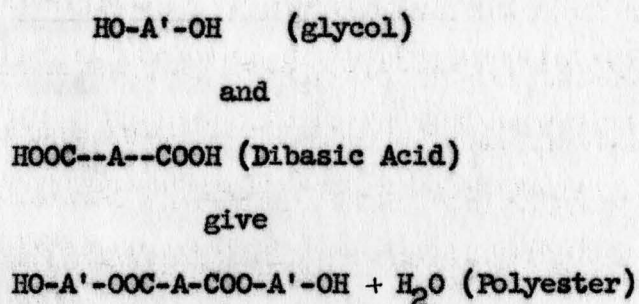
The method of preparation of polyurethane elastomers<sup>(8)</sup> can be divided in three main steps; (1) preparation of a linear polymer by using dibasic acid and glycol or aminoalcohol by condensation, with terminal in hydroxyl or amino groups; (2) chain extension of the polyester with diisocyanate, giving a linear copolymer; (3) cross-linking of the chain extended copolymer to give cured elastomers.

Preparation of Linear Polymer. A linear polymer<sup>(71)</sup> as a starting material for polyurethane is made by the polycondensation of glycol and a dibasic acid. For Vulcollan<sup>(8)</sup> a simple glycol-adipic acid polyester with hydroxyl number of 50-60 represents the ideal starting material. The choice of the polyester is extremely important because the physical properties of the final product are dependent upon the chemical structure of the starting materials and the molecular quantities of each component. There is a wide range of polyesters and extensive experiments were carried out by Harekoss, Schmidt and Bayer<sup>(7)</sup> to find materials which would not show the disadvantageous tendency to harden and to become crystalline.

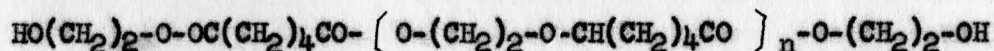


There is considerable latitude in the choice of glycols and dibasic acids as well as molal ratio of reactants in case a mixture is desired. Depending on the specific glycols and dibasic acids selected and the molal ratio desired to make a polyester, it is possible to obtain finally a curing elastomer that does not harden or crystallize on aging, yet exhibits outstanding physical properties. Bayer<sup>(12)</sup> carried out a great number of experiments and showed that it is necessary to have the polyester segment terminating in hydroxyl groups for the elastomeric polyurethane. In this way an excess of glycol is used when reacted with dibasic acid. Also the degree of polymerization or molecular weight of the polyester can be controlled within optimum limits so that elastomeric products results in the later reaction with diisocyanate.

In the preparation of polyester<sup>(71)</sup>, general formula is shown below.



The most typical polyesters<sup>(78)</sup> which result from the reaction of ethylene glycol and adipic acid carry preponderantly terminal OH group. The general formula is the polyester of ethylene glycol and adipic acid.



Schlack<sup>(64)</sup> worked in 1940 on the transformation of linear polyesters by diisocyanates, to increase greatly the chain length of these hydroxypolyesters.

In preparing polyesters, there are two possibilities. It is possible to work with individual polyesters prepared from other compounds, i.e., the polyesters prepared from one glycol and one dicarboxylic acid. Some of the results which were obtained by Bayer<sup>(12)</sup> and his coworkers with such simple polyesters are summarized in Table I, page 23. Also, it is possible to synthesize linear polyesters from more than two components. These are designated in general as mixed esters. The possible combinations with mixed esters are many, both with respect to the number of the condensed constituents and also to the proportions of the original reactants, but only a relatively few representative combinations could be studied. Some of the results which were obtained by Bayer<sup>(12)</sup> and his coworkers with mixed esters are shown in Table 2, page 24. This Table contains only mixed esters in which the ethylene glycol-adipic acid polyester, was extended by a thin bifunctional constituent.

In all experiments in this range of polyesters, the mechanical properties of the products were determined, and special attention was paid to the hardening of the products. As is evident in the tables, in no case were the mechanical properties of the ethyleneglycol-adipic acid polyester surpassed. On the other hand, it was found possible to synthesize a series of polyesters which had far less tendency to harden. With respect to any relationship between the physical properties of the polyesters and



Table I  
Reaction Products of Simple Polyesters with Naphthylene-1,5-Diisocyanate

Glycol constituent	Acid constituent	Consistency	Tensile Strength Kg./cm <sup>2</sup>	Extensibility %	Structural strength Kg./cm <sup>2</sup>	Remarks
Ethyleneglycol	Succinic acid	Solid wax	273	625	120	High permanent set; hardens and becomes leathery
Ethyleneglycol	Adipic acid	Solid wax	350	640	158	Slowly hardens
Ethyleneglycol	Pimelic acid	Liquid	-	-	-	-
Ethyleneglycol	Sebacic acid	Solid wax	-	-	-	Hardens immediately on cooling; only highly elastic at elevated temperatures
Ethyleneglycol	Decamethylene dicarboxylic acid	Solid wax	-	-	-	highly elastic at elevated temperatures
Ethyleneglycol	Diglycolic acid	Resin	270	570	147	Leathery; very easily saponified.
Ethyleneglycol	Phthalic acid	Brittle resin	107 <sup>a</sup>	261 <sup>a</sup>	87	<sup>a</sup> Processible only with 25% of dibutyl phthalate; glasshard without softener.
1,2-Propyleneglycol	Succinic acid	Liquid	180	670	96	Leathery; highly elastic at 70° C
1,2-Propyleneglycol	Adipic acid	Liquid	220	780	92	Does not harden
1,2-Propyleneglycol	Phthalic acid	Brittle resin	-	-	-	-
2,3-Butyleneglycol	Adipic acid	Liquid	179	630	92	Does not harden
1,6-Hexanediol	Adipic acid	Solid wax	248	610	122	Hardens
Hexahydroresorcinol	Succinic acid	Resin	112	223	82	Leathery

Bayer, O., E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly Elastic Substances. *Rubber Chemistry and Technology* 23, 819 (1950).



Table II  
Reaction Products of Mixed Esters with Naphthalene-1,5-Diisocyanate

Irregular component	Mole ratio based on 100 moles adipic acid	Consistency	Tensile Strength Kg./cm <sup>2</sup>	Extens- ibility %	Structural strength <sub>2</sub> Kg./cm	Hardening
1,2-Propyleneglycol	100:15	Solid wax, low m.p.	221	810	158	(+)
1,2-Propyleneglycol	100:20	Solid wax, low m.p.	272	745	122	-
1,3-Butyleneglycol	100:15	Solid wax, low m.p.	146	650	84	(+)
Diethyleneglycol	100:15	Solid wax, low m.p.	180	720	79	-
Glycerol- $\alpha$ -monomethyl ether	100:15	Solid wax, low m.p.	165	525	92	-
Thiodiglycol	100:15	Solid wax, low m.p.	-	-	-	-
Buteneglycol	100:14	Solid wax, low m.p.	306	680	86	(+)
Buteneglycol	100:33	Solid wax, low m.p.	254	650	54	-
Butine glycol	100:20	Solid wax, low m.p.	Easily cracked tarry product			
Hydroxyethylaniline	100:10	Solid wax, low m.p.	222	660	87	+
Hydroxyethylaniline	100:6	Solid wax, low m.p.	266	630	108	++
Hydroxyethylaniline	100:3	Solid wax, low m.p.	259	700	165	++
Dihydroxyethylaniline	100:15	Solid wax, low m.p.	155	680	67	(+)
$\beta$ -Dihydroxyethylnaphthylamine	100:10	Solid wax, low m.p.	230	675	92	(+)
Piperazine	100:3	Solid wax, low m.p.	151	645	95	(+)
Piperazine	100:2.2	Solid wax, low m.p.	344	720	112	+
Piperazine	100:2.1	Solid wax, low m.p.	367	820	133	+
Succinic acid	100:100	Liquid	130	590	33	-
Sebacic acid	100:100	Solid wax	-	-	-	-
Methyladipic acid	100:20	Solid wax, low m.p.	143	610	75	-
Thiodipropionic acid	100:15	Solid wax	-	-	-	++
Maleic acid	100:33	Swollen	-	-	-	-
Phthalic acid	100:35	Brittle resin	202	463	118	++

The mixed esters were mostly prepared from ethyleneglycol and adipic acid, and contain as a third component the components shown in this table.

Bayer, O. E. Müller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly Elastic Substances.

Rubber Chemistry and Technology 23, 821 (1950).

the tendency of the final products to harden, polyesters with high melting points give, as a general rule, products which tend to harden. Whereas polyesters<sup>(50)</sup> which are either liquid at room temperature or fuse at only moderately high temperatures give products which do not lose their high elasticity, even on long storage. Moreover, unsaturated constituents, such as butenediol, butinediol and maleic acid are of no particular advantage. Table II and III, pages <sup>24</sup> and <sup>26</sup> show, in addition, that the introduction of unsaturated and sulfur bearing constituents lead in some cases to difficulties in esterification.

There is another study from Mobay Chemical Company<sup>(56)</sup> of the physical properties of cast urethane elastomers as influenced by several polyesters. It is shown in Table IV, page 27.

The following general characteristics<sup>(56)</sup> from Table IV are explained. Generally it was noted that tensile strength and 300% modulus were more nearly functions of the presence of side chains than of ester group separation. This was shown by a comparison of the data for the first four polyesters listed. The tensile and modulus of the elastomer prepared from poly (1, 3-butylene adipate), a polyester containing methyl side chains, were significantly lower than for the elastomers. There was little significant difference noted between the tensile strength and modulus in elastomers of linear adipate.

Tear strength was apparently dependent on both the presence of methyl side chains and on ester group separation, since it decreased significantly in the elastomers made with poly-(1,5-pentylene adipate) and



Table III

Mixed Esters and Mixtures of Esters

Reagents	Tensile strength (Kg./cm <sup>2</sup> )	Extensibility %	Perma- nent set %	Structural strength (Kg./cm <sup>2</sup> )	Hard- ness (Shore)	Elas- ticity	Hardening
Simple ethyleneglycol-adipic acid polyester	350	640	6	158	60	69	++
Mixed ester of ethyleneglycol, 1,2-propyleneglycol and adipic acid	283	725	15	133	65	65	(+) <sup>a</sup>
Mixture of esters: 70 parts glycol-adipic acid ester and 30 parts 1,2-propyleneglycol-adipic acid ester	300	730	13	145	67	63	(+) <sup>a</sup>
Mixed ester of ethyleneglycol, 1,2-propyleneglycol (50:50) and adipic acid	270	700	20	108	71	70	-
Mixture of esters: 50 parts ethyleneglycol-adipic acid ester and 50 parts 1,2-propyleneglycol-adipic acid ester	250	680	14	117	66	70	-
Simple 1,2-propyleneglycol-adipic acid ester	220	780	14	92	69	76	-

<sup>a</sup> Only in the stretched state.

Bayer, O., E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly Elastic Substances. Rubber Chemistry and Technology 23, 822 (1950).



Table IV

Physical Properties of Cast Urethane Elastomers as Influenced by Polyester

Polyester	Tensile Strength, psi	Elongation %	Set, %	Modulus, psi at 300 % Elong.	Tear Strength lb./in.	Hardness Shore B	Specific Gravity
Ethylene adipate	6900	590	15	1550	240	60	1.25
1,4-Butylene adipate	6000	510	15	1900	280	70	1.21
1,5-Pentylene adipate	6300	450	10	1800	60	60	1.17
1,3-Butylene adipate	3200	520	15	1100	100	58	1.19
Ethylene succinate	6800	420	40	3200	200	75	1.32
2,3-Butylene succinate	3500	380	105	#	520	85	1.24
Neopentyl succinate	2600	400	70	2000	230	67	1.22

# Exhibited cold drawing

Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr, J. H. Saunders, and E. E. Hardy

Published by Mobay Chemical Company. Pittsburg 34, Pa.

with poly(1,3-butylene adipate) as compared to those made from poly(ethylene adipate). The specific gravity appeared to be a function of either the glycol chain length or the percentage of ester groups present. Where linear polyesters were used, there appeared to be a relationship indicated between glycol chain length and specific gravity, with longer chain glycol polyesters yielding elastomers of low specific gravity.

Another investigation is shown in Figure 2, page 29 by K. A. Piggott<sup>(56)</sup> on the torsional modulus as a function of temperature. It was noted that the stiffening at low temperatures varied widely and was apparently dependent on the ester group separation within the polyester. Curve (1) and (2) represent poly(1,4-butylene adipate) and poly(1,5-pentylene adipate) elastomers. These showed a significant decrease in the glass transition temperature compared to the polyethylene adipate elastomer, shown as curve (3). Closer spacing of ester groups as in the polyesters of succinic acid, curve (4), (5) and (6), resulted in the transition occurring at a higher temperature.

Generally, this study of variations in structure of polyesters shows that greater ester group separation yielded improved low temperature flexibility and lower tear strength. Closer ester group spacing reduced flexibility at low temperatures and at room temperature favored higher hardness values, higher modulus, and a marked increase in permanent elongation. These results may be attributed to increased Van der Waals forces.

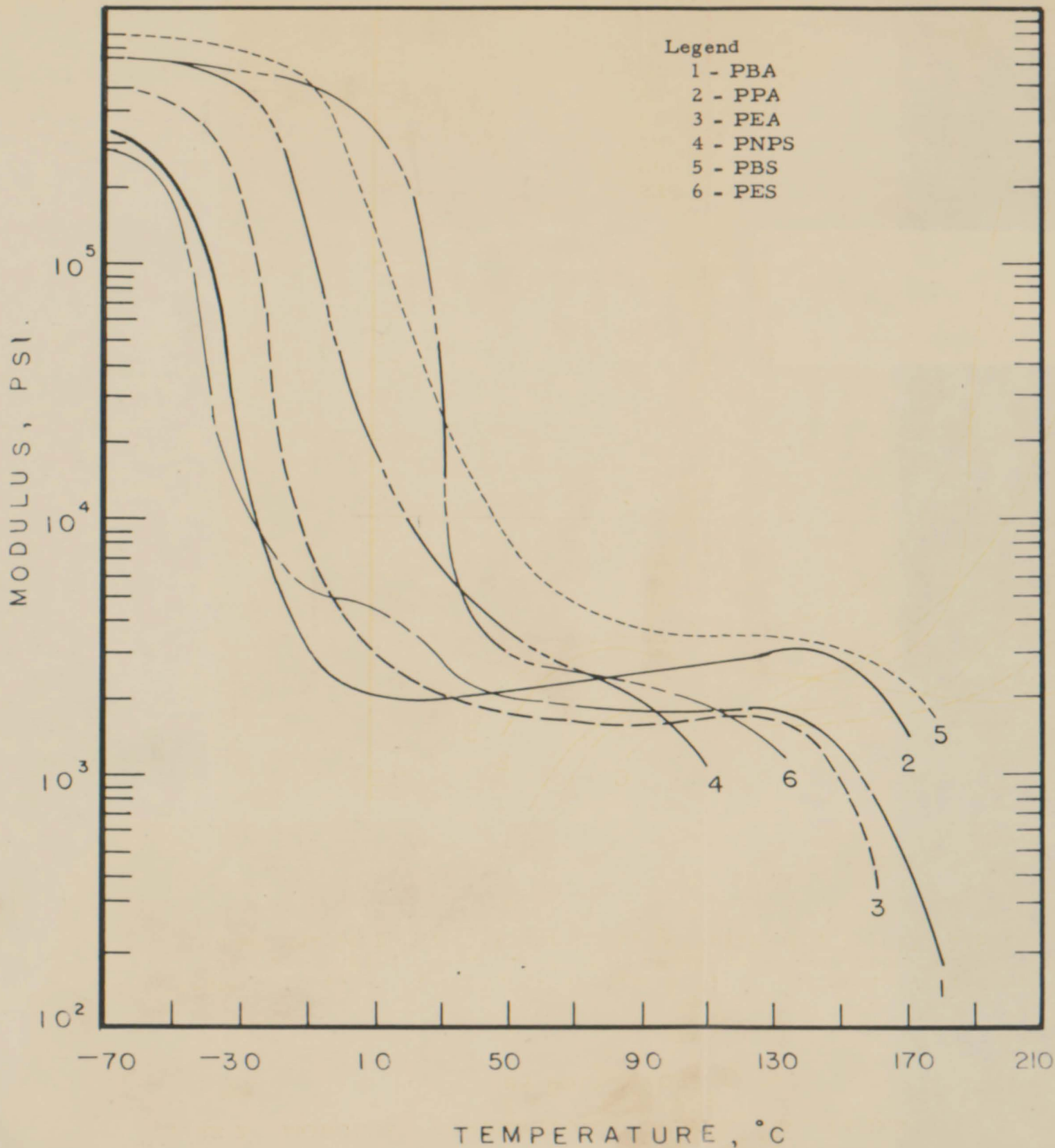


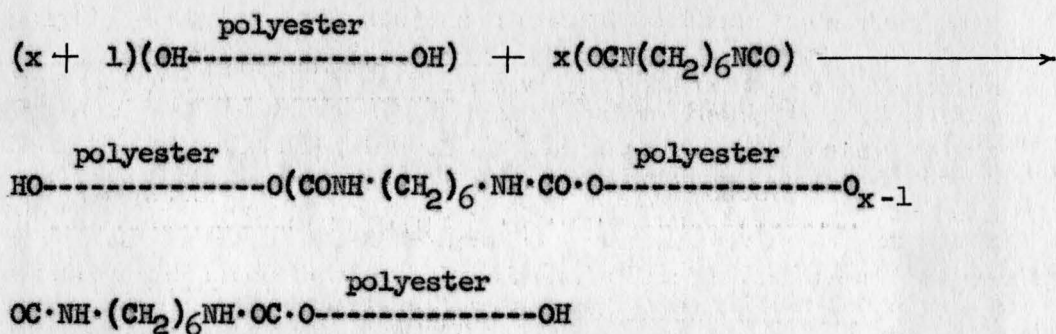
FIGURE 2 MODULUS - TEMPERATURE VARIATION AS INFLUENCED  
BY POLYESTER

Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Dan,  
J. H. Saunder and E. E. Hardy: Published Paper from Mobay  
Chemical Company, Pittsburgh 34, Pennsylvania, May 13, 1959.

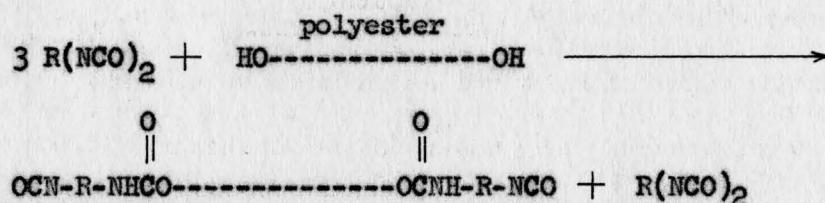


Chain Extension of the Polyester with Diisocyanate. The process of polyaddition<sup>(71)</sup>, which in principle is the addition of diisocyanates to dihydroxy and polyhydroxy compounds and to other compounds containing two or more reactive hydrogen atoms, makes it possible to synthesize from small molecules to produce of high or extremely high molecular weight, and with practically predetermined structures and properties. As pointed out before, a linear polyester<sup>(12)</sup> can be made to react with diisocyanates without any network formation only if every trace of moisture is excluded. It is always advantageous first to prepare the extended isocyanate polyester, to stop the reaction at this stage and to carry out the reaction involving network formation only as a subsequent process, but the only important consideration is to dry the polyester before reacted with diisocyanate. Dehydration<sup>(77)</sup> was effected by fusion in a vacuum at about 120° C, and either passing an inert gas through the system or employing a drying agent, Another possible way, in case it is desired to work with a solvent, is azeotropic distillation. Finally chemical dehydration is possible, e.g., by the addition of calcium carbide.

The possible reaction mechanisms are different from the reaction of two reactant polyester chains and diisocyanate, according to Schlack<sup>(64)</sup> as well as others<sup>(56)</sup>.



or



Numerous experiments have been carried out on the polyurethane elastomer to determine the influence of the hydroxyl number of the polyester and the optimum proportion of isocyanate in the simple system on the tendency to harden after extending the chain. Bayer<sup>(12)</sup> and his coworkers used ethyleneglycol-adipic acid polyester and naphthylene-1,5-diisocyanate, using fractionated polyesters having various hydroxyl numbers which were made to react with enough naphthylene-1,5-diisocyanate for the elongated product to have an average molecular weight of about 4,000. Some physical properties are listed in Table V, page 32. Under these conditions the ester with the smallest hydroxyl number gave the best mechanical properties. However, at the same time the product showed the greatest tendency to harden. Bayer<sup>(12)</sup> and his

Table V

Ethyleneglycol-Adipic Acid Esters of Different Hydroxyl NumbersExtended with Naphthylene-1,5,-Diisocyanate To aMolecular Weight of 4000

OH no.	Polyester Mol. wt.	Isocyanate (g./100 g. polyester)	Mol. wt. after extension	Tensile strength (Kg./cm <sup>2</sup> )	Extensibility %	Stress at 300% elong. Kg.	Structural strength (Kg./cm <sup>2</sup> )	Elasticity	Hardness (Shore)	Hardening
49 <sup>a</sup>	2290	15.2	4000	392	680	94	192	58	65/71	↓ decreasing tendency ↓
32	3500	11.9	4000	348	560	131	250	65	67/73	
36	3100	12.6	4000	305	610	111	172	59	68/73	
46	2440	14.6	4000	351	646	113	186	59	71/76	
54	2080	16.2	4000	385	635	130	195	60	71/76	
81	1385	21.6	4000	371	645	110	125	50	74/77	

a Unfractionated ester.

Bayer, O., E. muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly Elastic Substances.

Rubber Chemistry and Technology 23, 824 (1950).



coworkers also did a series of experiments in which the fractionated polyesters with various hydroxyl numbers were in every case extended by sufficient naphthylene-1,5-diisocyanate for the calculated molecular weight to increase about 1.8 or 1.9-fold. The results are recorded in Table VI, page 34. The products show almost the same tensile strengths and structural strengths. With higher hydroxyl numbers, i.e., lower molecular weight of polyester, the hardness and the modulus (measured in kilograms per square centimeter at an elongation of 300 per cent) are definitely higher. From these experiments and from other similar ones, it was possible to determine the most favorable conditions with respect to chain length of the polyester and the amount of excess isocyanate to be used. From a practical viewpoint, polyesters having a hydroxyl number of 50-60 and an excess of isocyanate in the range of 40-60 per cent are used.

The influence of the diisocyanate on the polyurethane elastomers has been studied in the past ten years. The polyester of ethylene-glycol and adipic acid<sup>(12)</sup>, which carries terminal hydroxyl groups, was first studied. Products with terminal networks are naturally formed directly when this polyester is treated with triisocyanates, but the resulting elastomers show only slight tear resistance. Consequently, the experiments were directed toward diisocyanates. Those containing nitro groups<sup>(51)</sup> were first tested. In 1953 N. V. Seeger<sup>(71)</sup> of Good-year Tire and Rubber Company found from great numbers of experiments that the structure of diisocyanate used in the chain extension step

Table VI

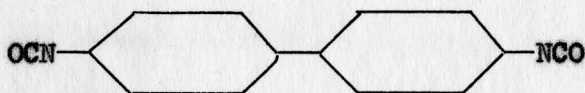
Ethylene glycol-Adipic Acid Esters of Different Hydroxyl Numbers Extended with  
Naphthylene-1,5-Diisocyanate to About 1.9 Increase in Molecular weight

OH no.	Polyester Mol. wt.	Isocyanate (./100 g. polyester)	Mol. wt. after extension	Factor <u>Extend mol. wt.</u> Mol. wt. polyester	Tensile Strength (Kg./cm <sup>2</sup> )	Extensibility (%)	Structural strength (Kg./cm <sup>2</sup> )	Elasticity	Hardness at 300 $\mu$	Stress along. Kr.	Hardening
24	4680	7.0	8920	1.90	390	770	158	-	59/63	55	decreasing tendency
32	3500	9.5	6600	1.89	352	710	158	70	64/70	73	
42	2670	12.5	5090	1.91	380	720	163	61	71/76	98	
52	2160	16.0	3885	1.80	322	726	150	60	71/86	119	
95	1180	30.5	2170	1.84	331	455	84	63	83/83	160	

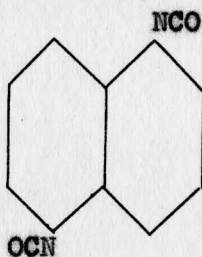
Bayer, O., E. muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly Elastic Substances.

Rubber Chemistry and Technology 23, 825 (1950).

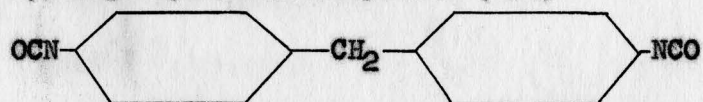
contributed markedly to the cured physical properties. The diisocyanates used in preparation of storable rubbers are symmetrical aromatic diisocyanates which are preferred over aliphatic diisocyanates. He also pointed out several diisocyanates which had a suitable character for this application. They are:



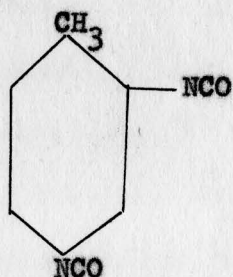
4,4' Xenylene diisocyanate (XDI)



1,5 Naphthylene Diisocyanate (NDI)



Methylene bis (4-phenylisocyanate) (MDI)



2,4 Tolyene diisocyanate (TDI)



Bayer<sup>(12)</sup> and his coworkers also carried out work and listed some results on physical properties which were obtained with the ester of ethyleneglycol and adipic acid with various diisocyanates. These results are shown in Table VII, page 37. The influence of diisocyanate in the product was studied by a Mobay research group<sup>(56)</sup>. They did a great deal of work on different diisocyanates and obtained very valuable data which are listed in Table VIII, page 38. In these experiments the polyester was polyethylene adipate (hydroxyl number 56, acid number 1) and the extender was 1,4-butandiol. The table shows the physical properties of these elastomers. It should be noted that the elastomers prepared do not necessarily represent the optimum balance of starting materials for each diisocyanate. The experiments were based on using equivalent stoichiometric amounts of the various diisocyanates in order to be able to draw conclusions on the effect of molecular structure on properties.

Pigott<sup>(56)</sup>, assuming essentially the same degree of polymerization in each case, postulated some possible effects of isocyanate structure as follows. The influence of bulky, rigid molecules was demonstrated by a comparison of the naphthalene diisocyanate (N5) elastomer with that from p-phenylene diisocyanate (p-14). With the increased bulkiness and rigidity, substantial increases in hardness and 300 per cent modulus were noted. A comparison of the elastomers from tolylene (TDI) and p-phenylene diisocyanates readily demonstrated the effect of reduced symmetry combined with methyl substituents. Where methyl substituents

Table VII

Reaction Products of The Undried Polyester of Ethyleneglycol  
and Adipic Acid and Various Diisocyanates (Approximately  
30 Per Cent in Excess of the Amounts Calculated on  
the Basis of Hydroxyl Groups)

Diisocyanate	Tensile strength (Kg./cm <sup>2</sup> )	Elongation at rupture (%)	Structural strength <sup>#</sup> (Kg./cm <sup>2</sup> )	Notes
Hexamethylene 1-Methylbenzene-2,4-	- (200-250)	- (730)	- (83)	worthless hardens at once mostly blistered difficult- ly reproducible high perman- ent set
2-Nitrodiphenyl-4,4'	188	743	122	-
2-Nitrodiphenylmethane-4,4'-	197	629	75	-
Diphenylmethanesulfone-4,4'-	240	736	108	-
Diphenylsulfone-4,4'-	215	331	138	-
Naphthalene-1,4-	315	756	134	-
Naphthalene-1,5-	311	765	167	-
Naphthalene-2,7-	402	758	163	-
Fluorene	435	660	142	-
Chrysene	300	684	133	-

# The structural strength here and as shown in the subsequent tables was measured with 4-mm.  
test-specimens (rings with 1-mm. notches) and calculated to basis of Kg. per sq. cm.

Bayer, O., E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of Highly  
Elastic Substances. Rubber Chemistry and Technology 23, 816 (1950).

Table VIII

Physical Properties of Cast Urethane Elastomers as Influenced by Diisocyanate

Diisocyanate	Tensile Strength, psi	Elongations % Set, %	Modulus, psi 300% Elong.	Tear Strength lb./in.	Hardness Shore B	
N-5	4300	500	85	3000	200	80
P-14	6400	600	25	2300	300	72
TDI	4600	600	1	350	150	40
MDI	7900	600	10	1600	270	61
DMDI	5300	500	0	600	40	47
PDI	3500	700	10	300	90	56
TODI	4000	400	10	2300	180	70

Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr, J. H. Saunders,

and E. E. Hardy: Published by Mobay Chemical Company. Pittsburg 34, Pa.

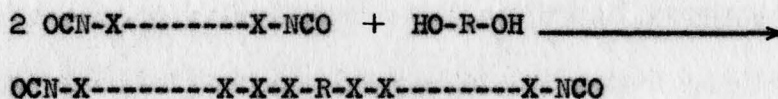


were present, and symmetry was reduced, a general decrease in tensile, modulus, tear, and hardness was found. A similar effect of methyl groups was shown in a comparison of diphenylmethane diisocyanate (MDI), dimethyl-diphenylmethane diisocyanate (DMDI), and diphenylisopropylidene diisocyanate (PDI). This effect of methyl groups can very likely be attributed to the induced spatial, separation of adjacent polymer chains, resulting in an increased mobility of local segments. Increased flexibility within the diisocyanate molecule was indicated by a comparison of the dimethyl diphenylmethane diisocyanate elastomer with that from bitolylene diisocyanate (TODI). It is likely that there is less flexibility associated with the carbon to carbon bond of the bitolylene molecule than with the methylene bridge in the diphenyl methane nucleus. The apparently decreased flexibility resulted in increased hardness, tear strength, and modulus. At the same time ultimate tensile and elongation were decreased.

Piggot<sup>(56)</sup> drew the conclusion that, generally, polymers of higher tensile strength, tensile modulus, tear strength, and harness are associated with diisocyanate molecules of greatest symmetry and rigidity. Flexibility of the molecule and spatial separation by methyl side chains were associated with softer, more elastic polymers. These observations led to the belief that the diisocyanate structure plays a major part in governing the tendency of chains to orient within the polymer. The diisocyanate structure thus exhibits an important influence on the Van der Waals forces and hydrogen bonding potential within the polymer.

Further Chain Extension. Linear polyurethane can react with water(16), glycols(46,52,57,58,72,73), diamines(8,12,46,72,73) or amine alcohols(72,73,78) and also extend their chain, except the glycols. The reactions are usually accomplished in the main stage of cross-linking, because these two reactions can not be separated. This chain extension reaction will be discussed later in the section of cross-linkage.

Glycol used as a chain extender is one of the most important constituents in polyurethane elastomers and it is used widely in the recent developments. This step of the reaction is separated from the stage of polyester-disocyanate copolymerization or cross-linkage. The reaction(56) is that the polyurethane copolymer containing excess diisocyanate is then under-reacted under controlled conditions with a low molecular weight polyfunctional compound, for example an aliphatic glycol, so that long chains with isocyanate terminals are formed, the reaction is:



where the simple formula "X's" are included to indicate the presence of urethane groups, although the actual number is not indicated.

Influence of chain extenders by using different low molecular weight glycols was studied by Pigott(56). In his investigation, elastomers were prepared from poly(ethylene asipate) and diphenylmethane

diisocyanate. Table IX, page 42 shows the physical properties of elastomers extended with a homologous series of aliphatic glycols. Examination of the data presented shows that generally optimum balance of properties was obtained with 1,4-butanediol. Other experimental work has been done by Pigott(56) on aromatic glycols, listed in Table X, page 43 showing the physical properties of elastomers extended by multrathane XA and by xylene -d.2'-diol. He also gave the conclusion that generally the properties shown indicated lower tensile, higher tear, modulus and hardness than for specimens extended with aliphatic glycols. These changes may be attributed to the greater rigidity of the aromatic glycols.

The influence of chain extenders was not as pronounced as that of either polyesters or diisocyanates. This was undoubtedly due to the relatively small quantity of extender used in comparison with the other constituents, but within the limits noted, useful changes were obtained by varying the extender.

#### Cross-linking of Chain Extended Copolymer

Cross-linking of chain extended copolymers(89) to give cured elastomers. Generally, the chain lengthening high molecular weight elastomers contain the following nitrogen linkage point in the linear chain in addition to the ester links, urethane, urea and amide. Later these serve as cross-linking points as additional diisocyanate reacts with the nitrogen hydrogen atoms. An amide link is formed when amine



Table IX

Physical Properties of Cast Urethane Elastomers as Influenced by Aliphatic Glycols

Glycol	Tensile Strength, psi	Elongation %	Set, %	Modulus, psi at 300% Elongation	Tear Strength lb/in.	Hardness Shore B
Ethylene -	6500	500	20	2000	230	61
1,3-Propanediol	6600	600	15	950	270	61
1,4-Butanediol	7900	600	10	1000	270	61
1,5-Pentanediol	7100	600	10	900	280	62
1,6-Hexanediol	7400	500	5	850	170	60

Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr, J. H. Saunders, and

E. E. Hardy: Published by Mobay Chemical Company. Pittsburgh 34, Pa.

Table X

Physical Properties of Cast Urethane Elastomers as Influenced by Aromatic Extenders

Extender	Tensile Strength, psi	Elongation % Set,%	Modulus, psi at 300% Elong.	Tear Strength lb./in.	Hardness Shore B
Multrathane XA	4500	550 45	2500	350	75
Xylene - , '-diol	6600	500 20	2200	300	73

Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr, J. H. Saunders, and

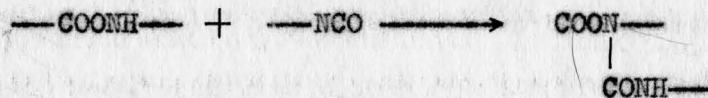
E. E. Hardy: Published by Mobay Chemical Company. Pittsburg 34, Pa.

alcohols<sup>(68,73)</sup> are used at this stage. In the early development of polyurethane elastomers<sup>(12)</sup>, water was added in the stage of cross-linking as a cross-linking agent. Bayer<sup>(12)</sup> showed from his experimental results, that urea-linkage is ten times as fast as the urethane linkage to form the network. The formation of carbon dioxide is the main disadvantage in the elastomer processes and it is necessary to dispose of the gas before curing. If a glycol<sup>(62)</sup> or diamine cross-linking agent is added in small, controlled amounts objectionable gas formation is eliminated.

If glycol<sup>(36,54)</sup> is used as the cross-linking agent, the cross-linked product can be used for compression molding. A combined casting-pressing process is also employed, in which the partly reacted mass of diisocyanate, modified polyester and cross-linking glycol is cooled to room temperature. It will retain its thermoplasticity for several days, within this time it can be formed or pressed and heat cured.

The isocyanate cross-linking reactions are: For urethane formation,

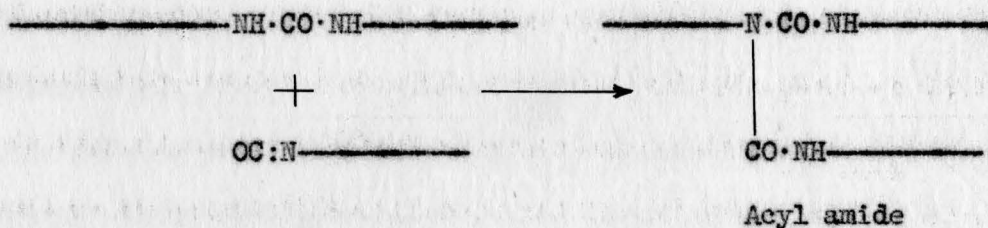
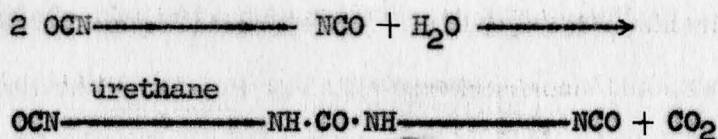




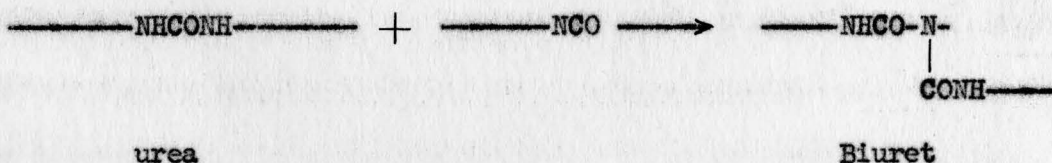
Urethane

Alliphatic ester

when water is added,  $\text{CO}_2$  will be evolved and the reaction proceeds as follows,



For amide formation,



In an early study, Bayer(12) noted that normal cross-linking in the urethane polymer was reported to occur by reaction of terminal isocyanate groups with urethane groups to form alliphatic linkages(42). Pigott(56) studied the influence of chemical cross-linking on the

physical properties. He used another method to obtain and control chemical cross-linking. Cross-linking by way of urethane groups can be easily accomplished by substitution of a trifunctional hydroxyl compound in place of the normal glycol extender. In this case the degree of cross-linking is a function of the amount of triol used. His experimental results are shown as Table XI, page 47. Data for samples prepared by substituting trimethylol propane for 1,4-butanediol are in order of increasing average molecular weight per branch point,  $\bar{M}_c$ , or decreasing degree of cross-linking, calculated from the triol content of the polymer. In general it was observed that decreased  $\bar{M}_c$  values in the range of 21,000-5,300 resulted in decreased values of physical properties with two exceptions; compression set and permanent elongation. Both of these values decreased, indicating greater elasticity. These observations are contrary to results of similar work with hydrocarbon elastomers, where increased cross-linking results in increased values of physical properties, especially modulus. In the case of the polyester-urethane elastomers it appears that increased chemical cross-linking of this type actually causes a general weakening of the polymer. This is probably due to a reduction in orientation of chains and hence a reduction in probability of obtaining hydrogen bonding and benefit of other intermolecular attractive forces. In other words, with increased chemical cross-linking, there is obtained a spatial separation of chains which reduces intermolecular attractions. This observation in part confirms the

Table XI

Physical Properties of Cast Urethane Elastomers as Influenced by Chemical Crosslinking

Mc	Tensile Strength, psi	Elongation %	Set, %	Modulus at 100% Elong. psi	Tear lb./in.	Hardness Shore B	Compression Set, %
2100	1800	170	0	570	30	57	1.5
3100	1750	200	0	420	25	53	16
4300	1450	280	0	300	30	49	10
5300	2800	350	0	270	30	46	5
7100	4500	410	0	330	40	51	25
10900	5600	491	5	460	60	55	40
21000	5500	510	10	500	140	56	45
	6750	640	15	630	300	61	55

Compression Set - ASTM395, Method B, 158° F. for 22 hours.

Tear Strength - FTMS-601  
M 4221

Tensile Strength, Elongation, Elongation Set and Modulus - ASTM 412.

Hardness - ASTM 676

Pigott, K. A., B. F. Frye: Published by Mobay Chemical Company. Pittsburg 34, Pa.



belief that a major portion of the strength of urethane elastomers is due to forces other than primary valence bonding. In this series, in the  $\bar{M}_c$  range of 5,300-2,100 the modulus increased with lower  $\bar{M}_c$  values, indicating the primary crosslinks eventually became dominant in controlling the modulus.

In order to test these premises, a series of volume swell measurements was made on the elastomers previously described. It was found necessary to use a very strong solvent to obtain significant changes in volume for the specimens of varying cross-linking. Figure 3, page 49 shows the effect of three solvents tested, acetone, tetrahydrofuran, and dimethylacetamide. It is apparent that dimethylacetamide was the most powerful in overcoming intermolecular attraction. Figure 3, page 49 shows both the volume swell and 100 per cent modulus as functions of the calculated  $\bar{M}_c$ . The curve for volume swell increased with decreased cross-linking in conformity with theoretical conditions. This confirms qualitatively that changes in the degree of cross-linking had been obtained as expected.

The modulus curve shows a decrease with increased cross-linking, passes through a minimum, and then increases to a maximum value for the highest degree of cross-linking studied. It is noted that the decreased modulus observed is contrary to general behavior of this type of hydrocarbon elastomers. If the modulus were only a function of chemical cross-linking, as was the volume swell, then the modulus curve would be opposite in slope to the volume swell curve, and would not

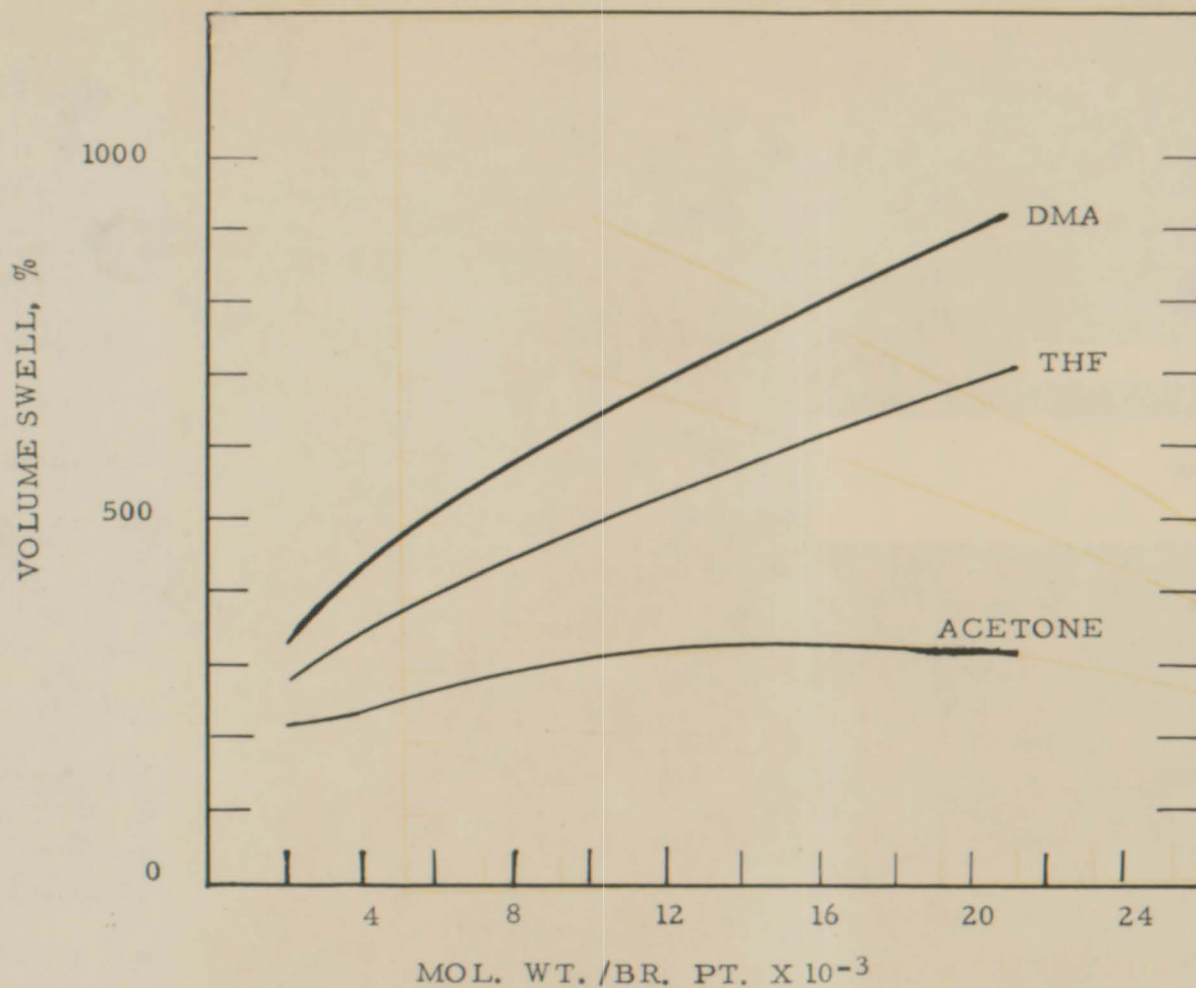


FIGURE 3 VOLUME SWELL AS INFLUENCED BY CROSS-LINKING AND SOLVENT

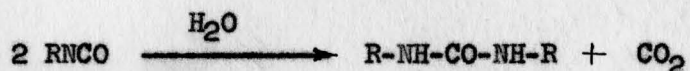
Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Dan, J. H. Saunder and E. E. Hardy: Published Paper from Mobay Chemical Company, Pittsburgh 34, Pennsylvania, May 13, 1959.

display a minimum, this set of experiments shows a definite indication that hydrogen bonding and other intermolecular forces contribute in a large degree to the ultimate properties of the polyester-urethane elastomers. As noted earlier, modulus apparently is affected primarily by intermolecular attractions at high  $\bar{M}_c$  values, and by primary cross-links at low  $\bar{M}_c$  values.

#### The Mechanism of Network Formation

It is known from Bayer<sup>(12)</sup> and his coworkers' work that for the polyesters containing isocyanate groups, these groups lead to network formation. It<sup>(16)</sup> is also interesting that different cross-linking agents cause different mechanisms of network formation. It is known<sup>(54)</sup> that water, hydrogen sulfide, glycols, dithiols, diamines, amino alcohols and dicarboxylic acids have been studied for use as cross-linking agents. The possibilities of various cross-linking mechanisms for isocyanate polyesters will be discussed as follows.

Water as a Cross-linking Agent. It is known that isocyanates react with water to form ureas and carbon dioxide:



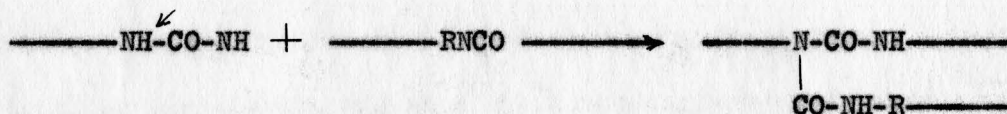
The water couples two isocyanate molecules to symmetrical urea groups, with simultaneous formation of carbon dioxide.

The hydrogen atoms of the urea group are now capable of reacting in turn with isocyanate polyester still present. Such reactions of

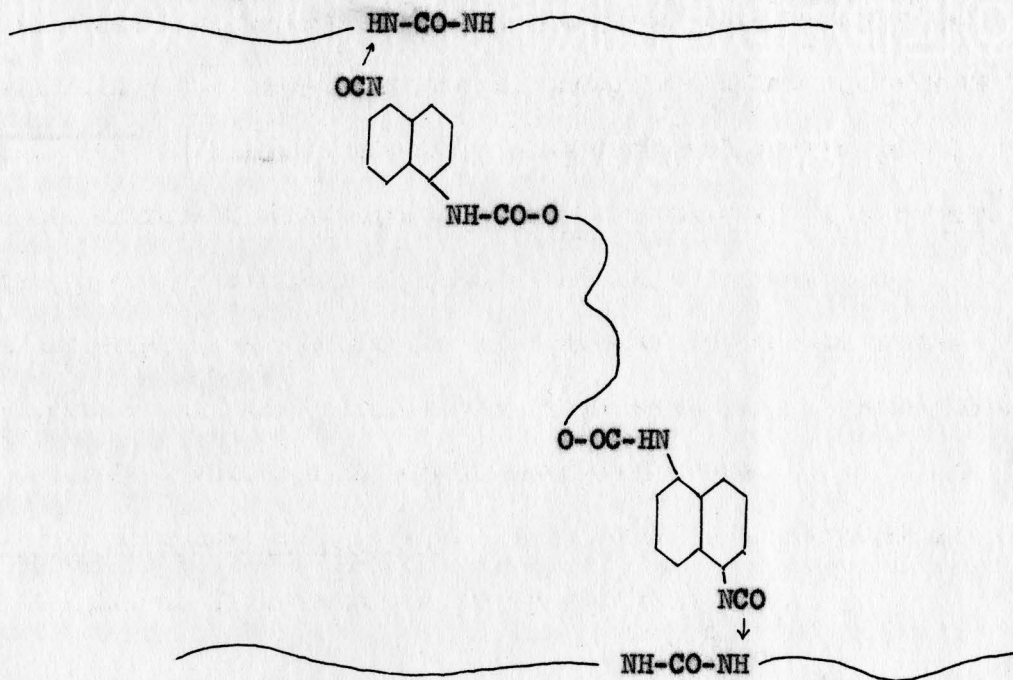


low molecular weight distributed ureas with isocyanates are known.

The reaction is as follows:



With polyesters containing isocyanate groups, the reaction furnishes cross-linking sites which lead to three dimensional supermolecules.



Hydrogen Sulfide as a Cross-Linking Agent. The use of hydrogen sulfide, the sulfur analog of water, was obvious. Hydrogen sulfide<sup>(12)</sup> reacts with isocyanates to form symmetrical ureas and carbon oxysulfide<sup>(44)</sup>,

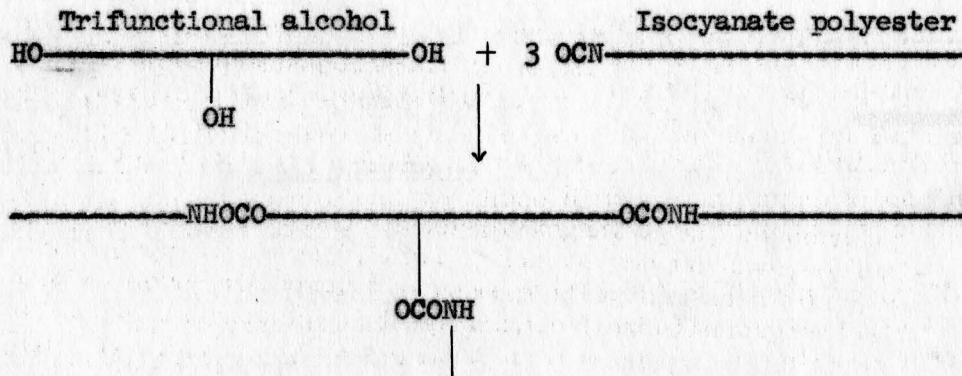


The reaction takes the same course with isocyanate polyesters to give sulfur-free products which are identical to those obtained by cross-linking with water. Since the two are indistinguishable in composition, it is not surprising that the overall course of the reactions as well as the physical properties of the products are identical. Since hydrogen sulfide offers no advantage over water cross-linking it is without commercial significance because of the unpleasant properties of hydrogen sulfide.

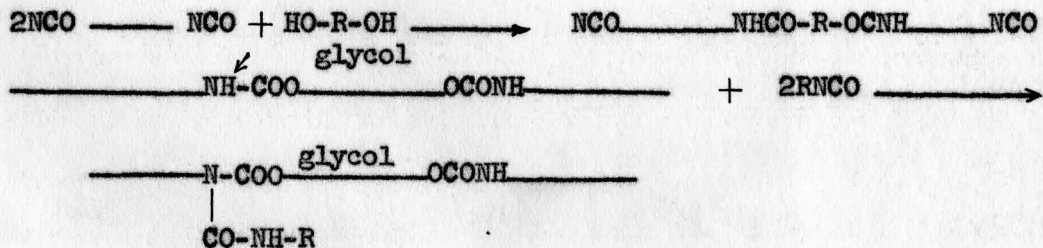
Glycols as a Cross-linking Agent. It<sup>(12)</sup> is now of interest to determine how other bifunctional compounds such as glycols behave toward the isocyanate polyesters. As was to be expected, a lengthening of the isocyanate polyesters occurred here also, not by the way of the urea group, but through two closely adjacent urethane groups.

This stage of the reaction is associated with a certain increase of viscosity. If the proportions are so chosen that the glycol is present in deficient amount or in amount nearly equivalent to the free isocyanate content of the isocyanate polyester, the reaction does not stop at this stage but leads gradually through a highly viscous condition to a crumbly insoluble material which, by further processing, gives valuable rubbery products. The course of the cross-linking reaction is at first not quite clear. From earlier work it was known that tri-functional alcohols when reacted with the isocyanate polyester gave cross-linked products which showed very poor tear resistance. In

this type of structure there appear on the ends of each isocyanate-ester group cross-linkages which are regularly distributed through the molecule,

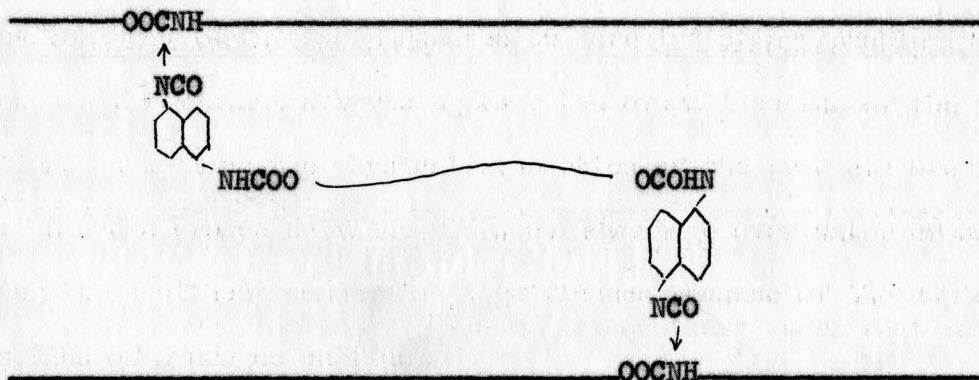


With the use of bifunctional glycols this cross-linking site is not present and one must, therefore, be inclined toward the assumption that, analogous to the urea cross-linking, the hydrogen atoms of the adjacent urethane groups are susceptible to reaction with isocyanate groups. It remains undetermined as to whether one or both of the urethane groups enter into the reactions. Such reactions of low molecular weight substituted urethanes with isocyanates are known. They proceed as follows:





Hence in the isocyanate-ester-glycol product the cross-linking site apparently lies in the newly formed urethane group,



It is strongly emphasized that the overall glycol cross-linking process is possible only with reactive isocyanate, such as was designated(29) as "bulky and open".

Dithiols as a Cross-Linking Agent. If the oxygen in glycols is replaced by sulfur, the compounds are dithiols. These react similarly, although very slowly to form thiourethanes. The reaction is too slow to be practical significance.

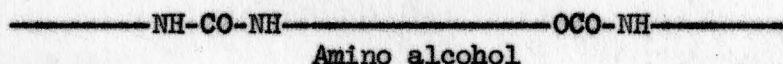
Diamines as a Cross-Linking Agent. In the course of work with new kinds of cross-linking agents, Muller(54) and his coworkers included diamines. The idea was that isocyanates react with amines to form symmetrically disubstituted ureas, the significance of which, in water cross-linking, was indicated before. By treatment of isocyanate polyesters with diamines, coupling of the isocyanate polyester chains occurs through two closely adjacent urea groups.

At the same time the excess of diisocyanate groups reacts with the hydrogen atoms of the urea groups, whereby the cross-linking reaction take place. The urea group thus furnishes the pivot point for cross-linking with diamine as well as with water cross-linking. An essential difference between the two lies in the fact that, with water coupling, two isocyanate polyester chains are linked through one urea group with formation of  $\text{CO}_2$ , whereas the amine cross-linking proceeds by addition, and two isocyanate-polyester chain are coupled through two adjacent urea groups.



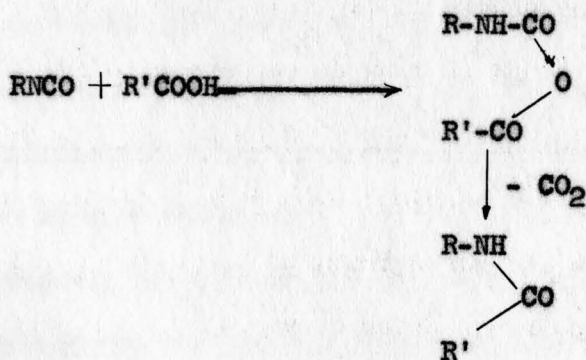
The amine cross-linking has great significance in the Vulcollan field, and in particular offers extensive possibilities for variation of the diisocyanate as well as the diamine.

Amino Alcohols as a Cross-Linking Agent. Amino alcohols<sup>(54)</sup> such as ethanolamine can be used instead of diamines as cross-linking agents. Hence the coupling of two isocyanate-polyester chains occurs through a urethane and a urea group which are closely adjacent,

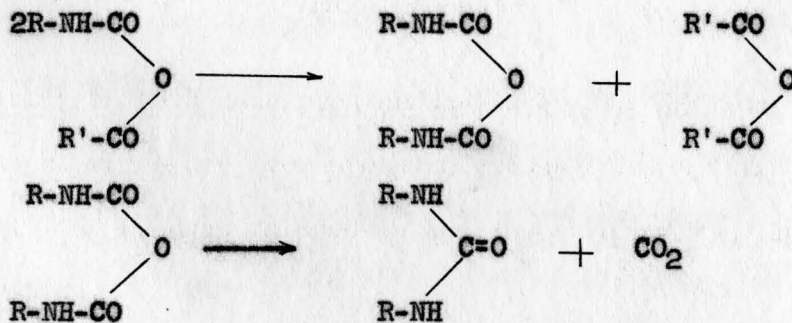


Apparently in this case urea cross-linking is the more ready reaction, and takes precedence over urethane cross-linking. The typical amino alcohol link product is used in the Vulcaprenes<sup>(40)</sup>, as prepared by the British.

Dicarboxylic Acids as a Cross-Linking Agent. When isocyanate<sup>(54)</sup> reacts with carboxylic acid which also produces cross-linked products. From Nageli<sup>(55)</sup> and his coworkers' study that isocyanate react with carboxylic acid to give mixed anhydrides of carboxylic and carbamic acid, these then split off CO<sub>2</sub> to produce symmetrical disubstituted ureas. But immediate of splitting CO<sub>2</sub> and also occur, which leads to substituted amides. In both cases groups are formed which contain labile hydrogen atoms capable of reacting with isocyanate. The reaction mechanism was also defined by Nageli<sup>(55)</sup>. He showed many cases where the reaction of an aryl isocyanate with a carboxylic acid gives significant yields of the symmetrical diarylurea and the anhydride of the carboxylic acid. The following mechanism was proposed:



In many cases it is also:





Thus, if isocyanate polyester is treated with a dicarboxylic acid, such as maleic acid, coupling can occur through two adjacent urea or amide groups which in known monomers react with excess isocyanate to establish cross-linking.

### Polymerization Processes

Vulcollan Process. Well known as an excellent process for polyurethane elastomers, the Vulcollan process<sup>(77)</sup> was developed in Germany in 1950. An excess of diisocyanate is used in bringing about the union of the initial polyester chains. Curing is effected by treatment with water, which reacts with the free terminal isocyanate groups.

Synthesis of these new highly elastic products<sup>(10,12)</sup> involves three steps, (1) preparation of the linear polyester; (2) increase in chain length, with formation of the polyester isocyanate; (3) formation of urea with water, and development of a network. It is of advantage in the processing of Vulcollan to carry out step (2) and (3) separately and successively. Only anhydrous polyesters are used.

Linear polyesters as starting materials for Vulcollan. The simple glycol-adipic acid polyester<sup>(12)</sup> with hydroxyl number of 50-60 represents the ideal starting material as far as physical properties, particularly structural strength, and technical availability, are concerned. The "hydroxyl Number"<sup>(77)</sup> is defined as the milligrams of potassium hydroxide required per gram of polyester, and is determined

by adding pyridine and acetic anhydride and titrating the acetic acid formed with potassium hydroxide solution.

Esterification(12) is carried out either by heating adipic acid and ethylene glycol or by first fusing the adipic acid and then adding the ethylene glycol extremely slowly. The acid(77) is melted at 170° C, and the glycol is then added gradually, the temperature being raised until it finally reaches 200° C. The reaction(12,77) is carried out in 20 to 40 hours. The water is distilled off at a gradually rising temperature, and the esterification is completed by subsequent heating in a vacuum. The polyester(15,77) is then dried (to about 0.02 per cent moisture) by heating with agitation in an autoclave under vacuum for one hour at 130° C. The product is wax-like material melting at 50 to 70° C and having a low viscosity above 80° C. In order to insure the presence of terminal hydroxyl groups, an excess of the glycol is used in the preparation of the polyester. From Bayer's results(12) with a hydroxyl number of 40 (1.2 per cent of OH groups) the molecular weight of the polyester chain averages above 2,800. About 16 structure units ( $--OC(CH_2)_4COOCH_2CH_2O--$ ) are linked together in chain formation, with a hydroxyl number of 60 (1.8 per cent of OH groups). The average molecular weight is 1870, and the number of structural units is 10-11.

The reaction with the diisocyanate, which is usually carried out at 100-130° C is exothermic, and reaction is carried in an internal mixer. Since the amount of diisocyanate is in excess of the calculated proportion, 15.5 parts naphthalene-1,5 diisocyanate per 100 parts of polyester are

reacted. The chain growth and consequent observed increase in viscosity are not very marked. The desired transformation is complete in a few minutes; however, the reaction mixture can be heated for several hours longer without any noticeable change. The product<sup>(12)</sup> is a highly viscous liquid above 70° C. It hardens on standing at room temperature and therefore can be worked on a rubber mill. In this step the diisocyanate reacts with the terminal hydroxyls of the polyester, forming urethane linkages and lengthening the chains. As the diisocyanate is in excess, the product formed carries terminal isocyanate groups. It has been indicated by Peterson<sup>(8)</sup> that the molecular weight at this stage is about 4000.

The final stage<sup>(12)</sup> involves the formation of a network structure by the extended isocyanate polyester through the agency of water. This can be effected in various ways. For example, steam can be passed through the viscous mass of isocyanate-polyester at a temperature above 100° C until the mass becomes progressively more viscous and finally becomes a brittle solid. This process is best carried out on a large scale in a kneading machine. When the network development has reached the desired stage, the mass is ejected by the blades of the machine. It is also simple to add water very gradually. The reaction follows the same course, and the amount of water can be controlled better (0.4-1.4 grams per 100 grams of mixture). It is important that the friable product obtained is in a condition to be milled out into a coherent sheet on a friction roll mill. The sheet



from the mill can be stored for some time, and under favorable conditions for days before it is molded. A few hours' storage before molding appears to be advantageous. The sheet can be molded, e.g., under a pressure of 50 to 200 Kg. per square centimeters for 10 to 15 minutes at 150-170° C. The molded products are pale yellow to brownish when they do not contain filler. Molding<sup>(9)</sup> to form thick sheets is impracticable because the development of a network structure in the isocyanate polyester involves the liberation of carbon dioxide. As a result, every solid molded article is necessarily blistered. This was originally a disadvantage of such products over isocyanate elastomers, which, thanks to their different mechanism of network formation, behave satisfactorily in molding processes and in centrifugal casting.

Urethane Cross-Linking with Glycols Process. This process was developed by Muller<sup>(52)</sup> and his coworkers. They used glycols instead of water as a cross-linking agent at the stage of cross-linking. Recently the Mobay Chemical Company<sup>(56)</sup> has applied this process and developed the new highly elastomeric materials called Cast Urethane Elastomers.

Muller<sup>(54)</sup> and his coworkers used ethylene glycol adipic acid polyester and 1,5-naphthalene diisocyanate as starting materials. The preparation is carried out as follows. First, the ester is carefully dried by melting at 120-130° C in a vacuum, whereby water is eliminated as a cross-linking agent. The dried ester is then treated at 130° C with the diisocyanate. The reaction is slightly exothermal and is

complete in a few minutes. The proportions are so chosen that normally 2-3 polyester chains are coupled together, which at an OH number of 50 requires the use of 15-16 per cent by weight of 1,5-naphthalene diisocyanate, based on the polyester. This isocyanate polyester makes a pourable melt, and is stable for several hours at elevated temperatures if protected from moisture. On very long heating or on storage of solutions, gelling due to cross-linking occurs in one to two weeks, even with most careful exclusion of moisture. This effect is evidently ascribable to the urethane groups present in the chain-lengthened isocyanate polyester.

The cross-linking of the isocyanate polyester proceeds very rapidly when a glycol such as 1,4 butanediol is added to the melt at about 130° C. After a few minutes a noticeable increase of viscosity occurs and this finally proceeds through various intermediate stages to a crumbly material which can be milled to a cohesive sheet. The sheet can be pressed as usual at 150-170° C and about 700-2,800 pounds per square inch to the desired form.

Various types of glycols can be used as cross-linking agents, including aliphatic, cycloaliphatic, aromatic, and unsaturated glycols. The amount of glycol must be so controlled that there are not enough hydroxyl groups present to be stoichiometrically equivalent to the isocyanate groups, that is, there must be a certain excess of isocyanate present in every case. With an excess of glycol, products are obtained which are thermoplastic and of higher elongation. With



decreasing amounts of glycol the physical properties of the condensation product improve at first, until finally, beyond a certain isocyanate content, side reactions set in. These latter are apparently reactions of isocyanate groups with each other. They are characterized by gas formation (blowing) and by decline of physical properties. Table XII, Page 63 illustrates the influence of the amount of cross-linking agent on physical properties. In his experimental work, Muller<sup>(54)</sup> used 1,4-cyclohexanediol as cross-linking agent, the polyethylene adipate used had a hydroxyl content of 1.5 per cent (OH number of 50). The quantity of 1,5-naphthalene diisocyanate was calculated to be 9.3 grams; 15.4 grams was used. Thus, the excess was 6.1 grams. This excess of 6.1 grams of diisocyanate was equivalent to 3.37 grams of 1,4-cyclohexanediol. As shown in Table XII the amount of 1,4-cyclohexanediol was reduced stepwise, whereby the number of excess isocyanate groups increased proportionately. The most favorable results of Muller's work were obtained in the range of about 2.05 per cent excess of 1,5-naphthalene diisocyanate over the equivalent of cross-linking agent.

Chemigum SL - An Elastomeric Polyester-urethane. A new elastomeric polyurethane, Chemigum SL, was described<sup>(72)</sup> by the Goodyear Tire and Rubber Company<sup>(46,59,73)</sup>. These rubbers are first made as processible and storable raw gum that has many of the characteristics of pale crepe natural rubber. They can then be mixed on the mill or in the Banbury mixer with additional curatives, such as diisocyanates and other compounding agents and then cured in standard rubber molds.



Table XII

Influence of The Amount of Cross-linking Agent, 1,4-Cyclohexanediol on Physical Properties

1,5-Naphthalene Diisocyanate gram.	1,5-Naphthalene Diisocyanate mole	1,4-Cyclo- hexandiol gram	1,4-Cyclo- hexanediol mole	Excess of Diisocyanate gram	Tensile Strength lb./in. <sup>2</sup>	Tear Strength lb./in. <sup>2</sup>	Permanert Set %
15.4	0.0734	3.37	0.0291	0	1660	590	48
15.4	0.0734	3.09	0.0266	0.525	1560	474	34
15.4	0.0734	2.81	0.0242	1.03	1910	1130	15
15.4	0.0734	2.22	0.0191	2.10	4840	2630	9
15.4	0.0734	1.68	0.0145	3.03	4580	2320	6
15.4	0.0734	0.84	0.0075	4.54	----- Blown -----		

Molecular Weight of 1,5 Naphthalene Diisocyanate = 210

Molecular Weight of 1,4 Cyclohexanediol = 116

100 grams Polyester = 9.3 grams Diisocyanate

Muller, E., O. Bayer, S. Petersen, H. Pipenbrink, W. Schmidt, and E. Weinbrenner: Rubber

Chemistry and Technology 26, 493 (1953).

The preparation<sup>(71)</sup> of storable Chemigum SL can be described in the following steps; (1) preparation of the linear polyester, (2) chain extension of the polyester with diisocyanate, giving the storable elastomer, (3) cross-linking of the raw gum to give cured Chemigum SL.

The polyester<sup>(12)</sup> is made by condensation of ethylene glycol and adipic acid. Since it is necessary to have the polyester segment terminated in hydroxyl groups, an excess of glycol is used when reacted with adipic acid. In this way also the degree of polymerization or molecular weight of the polyester can be controlled within optimum limits so that elastomeric products result in the reaction with diisocyanates. In the second step in the preparation of the rubber, the polyester segment is "chain extended" with diisocyanate. Melted polyester at 120° C is mixed with the appropriate amount of diisocyanate until thoroughly blended and polymerization can be completed either in an internal mixer or by heating the blend in shallow trays in an oven. The critical amount of diisocyanate to be used for the most useful range at the "chain extended" stage is from 0.70 to 0.99 mole of diisocyanate to 1 mole of polyester for optimum storability and processing. Thus, molecular weight is controlled by the amount of excess polyester used. Then, in the last step of cross-linking, polyester-urethane rubbers are cross-linked by an entirely different type of chemical reaction. This reaction begins as soon as additional isocyanate curative is added to the millable raw gum. The

diisocyanates use as curatives may be the same as, or different from, the ones used in the preparation of the storable rubber.

#### Properties of Polyurethane Elastomer

The isocyanate-polyester elastomer<sup>(27)</sup> has better tensile strength than natural rubber and extraordinary abrasion resistance. It is also superior to natural rubber in its oil resistance. However, it has poor resistance to temperature extremes and to alkalies and acids. Generally this new class of elastomeric materials<sup>(69)</sup> possesses certain outstanding physical properties, good solvent resistance, and excellent ozone resistance, high abrasion resistance and versatile processibility. The final products of the polyurethane elastomers are characterized by high tensile and tear strengths and excellent abrasion resistance without the necessity for fillers. These elastomers have abrasion resistance, ozone resistance, and tensile strength far superior to those of natural rubber and synthetic GR-S. They have excellent oil resistance, and oxygen absorption is very small. Reinforcement with carbon black results in still better properties. They have fair resistance to dry heat. Their resistance to extreme conditions of hot water and steam is as yet relatively poor and they show some tendency to harden at low temperature.

Vulcanized poly-urethane<sup>(71)</sup> has poor resistance to high temperatures, hot water, and steam. Tables XIII, page 66 and XIV, page 67 list the physical properties of vulcanized Chemigum SL.



TABLE XIII

Physical Properties of Vulcanized Chemigum SL

(Cured 15 minutes at 280° F)

---

Tensile strength Lb/Sq. inch	5450
Hot tensile at 200° F Lb/sq. inch	2860
Elongation %	750
Hot elongation at 200° F, %	845
Modulus (300 %) Lb/sq. inch	675
Hardness (Shore A)	65
Hot cut flex. min.	300
Bur. of Standards abrasion (Index=100)	200
Hot rebound %	84
Cold rebound %	80
Schopper tear (nicked), Lb/sq. inch	2000
Freezing point °C	-35
Ozone resistance	Excellent
Ultraviolet resistance	Excellent

---

Seeger, N.V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Finelli; and E. A. Sinclair. Ind. Eng. & Chem. 45,2538 (1953)

TABLE XIV

Aged Properties of Vulcanized Chemigum SL

(Cured at 280° F)

	Tensile	Elongation
	Lb/sq. in.	%
<u>Aged in dry heat.</u>		
30 days heat at 158° F	4700	685
14 days heat at 250° F	500	580
<u>Aged in Water.</u>		
3 months heat at 77° F	5000	---
2 days heat at 200° F	1700	---
14 days heat at 158° F	1000	---

Seeger, N. V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Finelli; and E. A. Sinclair: Ind. Eng. & Chem. 45, 2538 (1953).

Another disadvantage of these polymers<sup>(71)</sup> is the tendency to harden at low temperatures. Figure 4, page 69 illustrates cold properties as measured by the Gehman twist method. Chemigum SL freezes at  $-35^{\circ}$  C, compared with  $-65^{\circ}$  C for cured natural rubber gum.

But polyurethane products represent a new and valuable group of highly elastic materials with other valuable physical properties, such as Vulcollan<sup>(12)</sup> for instance. A comparison of Vulcollan products prepared from various polyesters with loaded and unloaded natural rubber and Buna-S, Vulcollan showed the superior properties. This comparison of the different properties of Vulcollan makes it evident that it cannot replace these older elastomers, as would hardly be expected in view of its totally different chemical structure, but it does represent a new type of synthetic material which is destined to win an important place among already known materials. Its resistance to tearing and extensibility do not give clear evidence of its distinctive properties. Vulcollan products of the highest quality are particularly outstanding when not loaded, and in complete contrast to natural rubber and Buna-S, they have, when loaded with carbon black, a tendency to show lower tear resistance. The stress modulus at 300 per cent elongation and the hardness of Vulcollan are high. Figure 5, page 70 shows the stress-strain curves of Vulcollan in comparison with stress-strain curves of natural rubber containing carbon black. Polyurethane elastomer represents, therefore, a stiff material which shows great resistance to reversible mechanical deformation. This



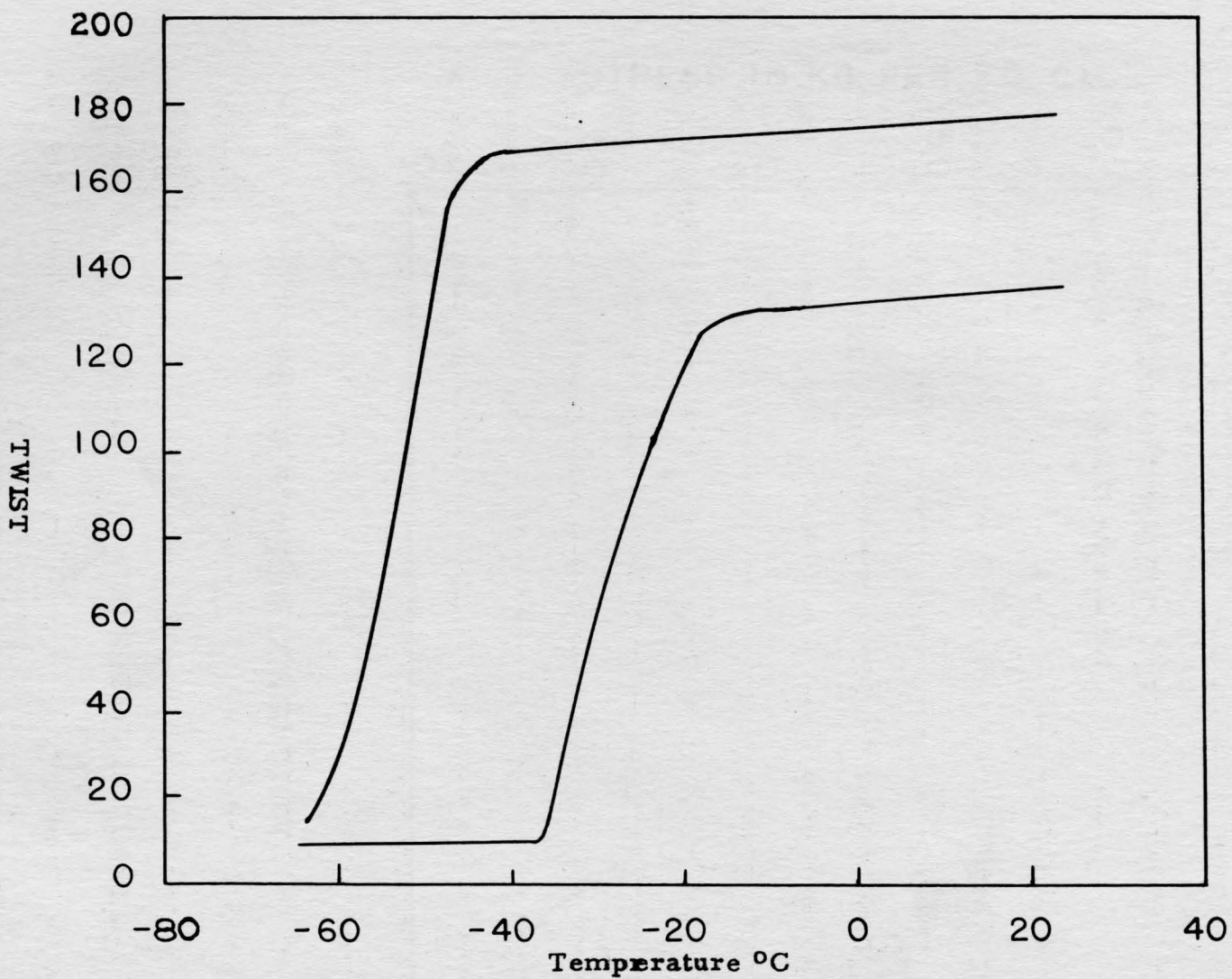


FIGURE 4 COLD HARDENING OF CHEMIGUM SL

Seeger, N. V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Finelli  
and E. A. Sinclair: Chemigum S. L. - An Elastomeric Polyester-Urethane,  
Ind. Eng. Chem. 45, 2538-42 (1953).

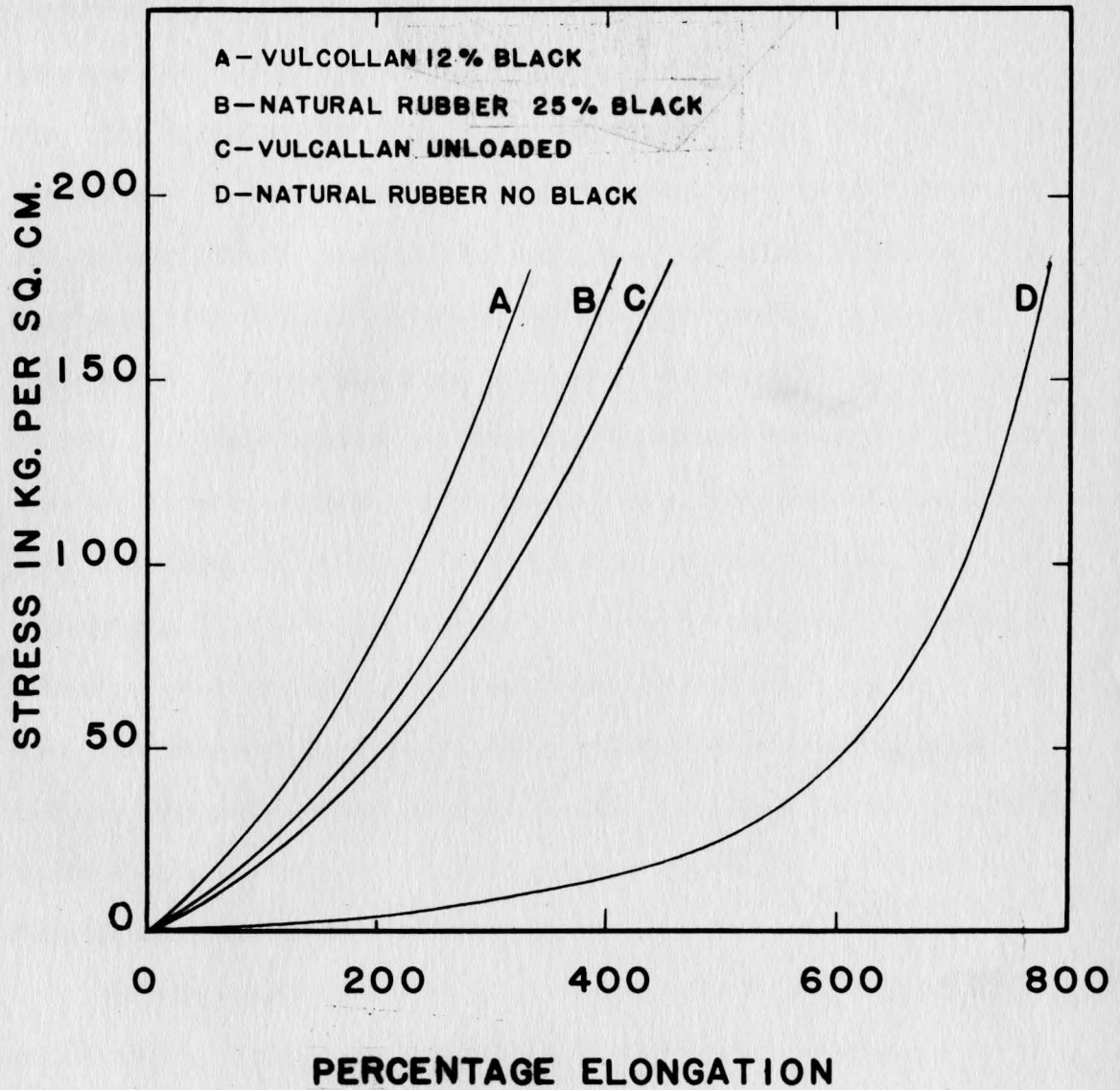


FIGURE 5 COMPARATIVE STRESS-STRAIN CURVES

Bayer, O., E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of High Elastic Substances, Vulcollans, Rubber Chem. & Tech., 23, 812-35 (1950).

characteristic is a drawback in some finished products, but is an advantageous one in the carcass of tires, in transmission belting, etc. The structure in relation to resistance to the initiation and propagation of tearing and to notched tearing also is of importance and, as has already been pointed out, this structure is more highly developed than that of any other rubber-like material. The abrasion resistance<sup>(77)</sup> is outstanding, being five to ten times that of natural rubber. In tests against an emery paper surface the losses by volume were as follows; natural rubber tread stock, 200, Buna-S tread stock, 150; Vulcollans 20 to 30. The dynamic properties of cured Chemigum SL of Goodyear Tire and Rubber Company<sup>(71)</sup>, are compared with natural rubber and oil extended GR-S tread stock in Table XV, page 72. These data were obtained by means of the Goodyear vibrotester. The conclusion is that polyurethane rubber compares favorably with standard tread stock, having higher resilience and generating less heat on flexing than the hydrocarbon rubbers.

The resistance of polyurethane elastomer<sup>(69)</sup> to aging is also outstanding. Published information on elastic polyurethane has emphasized the resistance that this class of polymers shows to the degradative action of oxygen<sup>(8,35,71)</sup>, ozone<sup>(8,19,35,71)</sup>, aging<sup>(54)</sup>, weathering<sup>(8)</sup>, and ultra-violet light<sup>(8)</sup> but improvement has been great in the newly developed polyurethane elastomer, polyurethane VC<sup>(69)</sup>, a virtually cross-linked elastomer showing outstanding properties. The data<sup>(71)</sup> for oxygen absorption are shown for chemigum SL by means



TABLE XV

Performance of Chemigum SL in Tread Stocks

Rubber Stock	Dynamic Properties			Relative heat generation
	Dynamic modulus Kg./sq.cm	Internal friction Kilopoises	Dynamic resili- ance %	
Chemigum SL	84.4	15.9	63.3	65
Chemigum SL plus 30 parts Mpc black	196.0	49.1	54.5	128
Natural rubber tread	91.8	35.1	39.6	109
Oil-extended GR-S tread	116.0	59.3	29.0	141

Seeger, N. V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Finelli; and E. A. Sinclair; Ind. Eng. & Chem. 45, 2538 (1953).

of the comparison of typical natural rubber tread and GR-S tread stocks in Table XVI, page 74. It is appreciable at 100° C after 300 hours.

After 910 hours at 100° C only 0.25 ml. of oxygen per gram of Chemigum SL was absorbed.

The resistance of urethane elastomer<sup>(69)</sup> to swelling in benzene and even in aromatic hydrocarbons is noteworthy, e.g., only about 40 per cent in benzene. Acetone and methylene chloride have the greatest swelling action. With increase in swelling, the strength decreases, but with no subsequent shrinkage. In contrast to this good resistance to swelling is the very poor resistance to acids and alkalies, which likewise is dependent on the polyester structure. With regard to the physical properties of polyurethane elastomer, at the elevated temperature, it is of interest to note that the tensile stress is decreased as the temperature increases. Schollenburger<sup>(69)</sup> and his coworkers determined the stress-strain relationships between -20 and 250° F. The testing material was polyurethane V. C. prepared from diphenylmethane-p-p'-diisocyanate, adipic acid, and butanediol 1,4.

Polyurethane elastomer<sup>(70)</sup> is characterized by outstanding physical and mechanical properties, high tensile strength as well as good tear, abrasion, solvent, oil and ozone resistance. Resistance to outdoor exposure and ultra-violet-initiated autoxidation have been estimated as good.

TABLE XVI

Oxygen Absorption


---

O<sub>2</sub> Absorbed ML/Gr. of polymer at 100° C

---

Time Hours	Natural rubber tread stock (*)	GR-S tread stock (*)	Chemigum SL
0	0	0	0
40	10	4	0.01
80	27	10	0.02
120	58	14	0.04
160	92	18	0.08
240	--	27	0.11
320	--	36	0.13
450	--	--	0.16
910	--	--	0.25

---

\* Natural rubber and GR-S tread stocks contain 45 parts of carbon black per 100 parts of natural rubber and 1.25 parts of N-phenyl-B-naphthylamine as antioxidant.

Seeger, N. V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Finelli; and E. A. Sinclair: *Ind. Eng. & Chem.* 45, 2538 (1953).



### III. EXPERIMENTAL

#### Purpose of Investigation

The purpose of this investigation was to study the effect of varying the degree of cross-linkage on the mechanical properties of the polyurethane elastomer formed from 33' Bitolyene 44' diisocyanate and the polyester of adipic acid and ethylene glycol.

#### Plan of Experimentation

The plan of experimentation comprised four phases. The first phase consisted of the construction of apparatus required. The second phase consisted of preliminary work in order to determine the general conditions of copolymerization, molding, chain extension and curing of polyurethane elastomer. The third phase consisted of preparation of elastomeric specimens by copolymerization of linear polyester and diisocyanate, chain extension and cross-linking by ethylene glycol, molding and curing. The fourth phase consisted of making absorption and swelling tests, hardness tests and tensile tests.

The Apparatus Required. All apparatus which will be needed in this investigation will be assembled and constructed in the laboratory. A resin kettle with assembled oil bath will be used for preparing the elastomer, the mold will be constructed, a hydraulic press with heater will be assembled for press molding. A Tinius Olsen tensile machine

will be used for the test and the hardness tester will be constructed and assembled for hardness test.

Preliminary Tests. The preliminary tests will be conducted in order to determine the general conditions of copolymerization, molding, chain extension and curing of polyurethane elastomer. These preliminary tests will be carried out in accordance with the available information from the literature and the theoretical view point. The copolymerization temperature will be tested from 85° C to 150° C, molding temperature will be tested from 100° C to 200° C, curing temperature will be also tested from 85° C to 185° C and curing time will be tested from the range of one hour to 24 hours.

Preparation of Elastomer. All conditions of preparing the elastomer will be used in accordance with the results of preliminary tests.

Testing of Elastomer. The testing of elastomer will consist of four phases. The first phase is solvent absorption test. Acetone will be used as a solvent. The second phase of the test is swelling test. The third phase of the test is tensile properties test. The fourth phase of the test is hardness test. All these tests will be carried out at 75° F and 50 per cent humidity. In addition to these tests the hardness at 300° F will be tested for the comparison to the properties at 75° F.



### Materials

The following section contains a list of the materials that were used to perform this investigation.

Acetone. Reagent grade, 99.7 per cent, lot number 9559.

Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used as solvent for the swelling and absorption tests and for solubility tests.

Butanediol 1,4. Reagent grade, lot number p-6526. Manufactured by Eastman Organic Chemicals, Rochester 3, New York. Used as a cross-linking agent in preliminary work.

Calcium Chloride. Technical grade. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, 40 Rector Street, New York 6, New York. Used as a dehydrating agent.

Calcium Oxide. C. P. Obtained from stockroom of Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to prepare calcium hydroxide solution for CO<sub>2</sub> test.

Calcium Stearate. Technical grade. Obtained from the stockroom of Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as mold lubricant.

Cellosolve. Ethylene glycol monoethyl ether. Purified grade. Obtained from Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as sensitive liquid in mercury thermostat.

Ethylene Glycol. Reagent grade, lot number 700759, Cat. No. E-177. Obtained from Fisher Scientific Company, Silver Spring, Maryland, Used as cross-linking agent.



Lubricating Oil. Lubricating oil No. 15, technical grade with light color. Obtained from Shell Oil Company, Blacksburg, Virginia. Used as liquid in oil bath and hydraulic pressure oil in press.

Multrathane R-14. Linear ethylene glycol adipic acid polyester, technical grade, average molecular weight 2000. Lot number E-6222. Manufactured by Mobay Chemical Company, Pittsburgh 34, Pennsylvania. Used as an initial material of copolymerization.

Nacconate 200. 33' Bitolylene 44' diisocyanate, purity of 99.5 per cent. Obtained from National Aniline Division, Allied Chemical and Dye Corporation, 40 Rector Street, New York 6, New York. Used as an initial material of copolymerization.

Potassium Dichromate. Technical grade. Obtained from stockroom of the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as the component of cleaning solution.

Pyridine. C. P. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as catalyst for polyester and 33' Bitolylene 44' diisocyanate copolymerization in preliminary work.

Silicone Fluid. Trade mark (SF-96(100)) technical grade. Manufactured by General Electric, Silicone Products Department, Waterford, New York. Used as lubricating agent for molding, and roller mill in preliminary work.

Sulfuric Acid. Technical grade. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used as component of cleaning solution.

### Apparatus

The apparatus which was used for this investigation is listed here.

Absorbing Paper. One roll. Obtained from Rose store, Blacksburg, Virginia. Used to dry the solvent from test specimen.

Balance. Analytic "Chainomatic". Manufactured by Christian Becker, Inc., New York, New York. Used for determining solvent absorption and for weighing various sample specimens.

Balance. Triple beam balance, model CG 311, capacity 311 grams, Manufactured by the Ohaus Scale corporation, Union, New Jersey. Used to weigh solid samples.

Constant Temperature Bath. Constant temperature bath is assembled by the following items; mercury thermostat, jar and base unit, thermometer, motor stirrer, 500 w. immersion heaters. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to heat the resin kettle.

Copper Tubing. Dead soft, seamless 3/8 inch outside diameter, five feet long. Manufactured by National Copper and Smelting Company, Cleveland, Ohio. Used for oil bath cooling coil to carry circulating water.

Die for the Specimen Cutter. Die for the specimen for absorption and swelling test. Brass tube, 0.25 inches, inside diameter, four inches long. Obtained from stockroom of Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to cut the specimen for absorption and swelling test.

Hardness Tester. Based on the A.S. T. M. method No. D 676-58T of hardness test, a pin was made corresponding to the typical durometers. A high carbon steel nail, 0.12 inches diameter and 2 inches long was machined to dimensions as shown in Figure 6, page 81. Then this small pin was fixed on the head of a six inch long bolt. This was then used on the Tinius Olsen Electromatic Tester, in Wood Construction Laboratory, Virginia Polytechnic Institute, Blacksburg, Virginia, for hardness test.

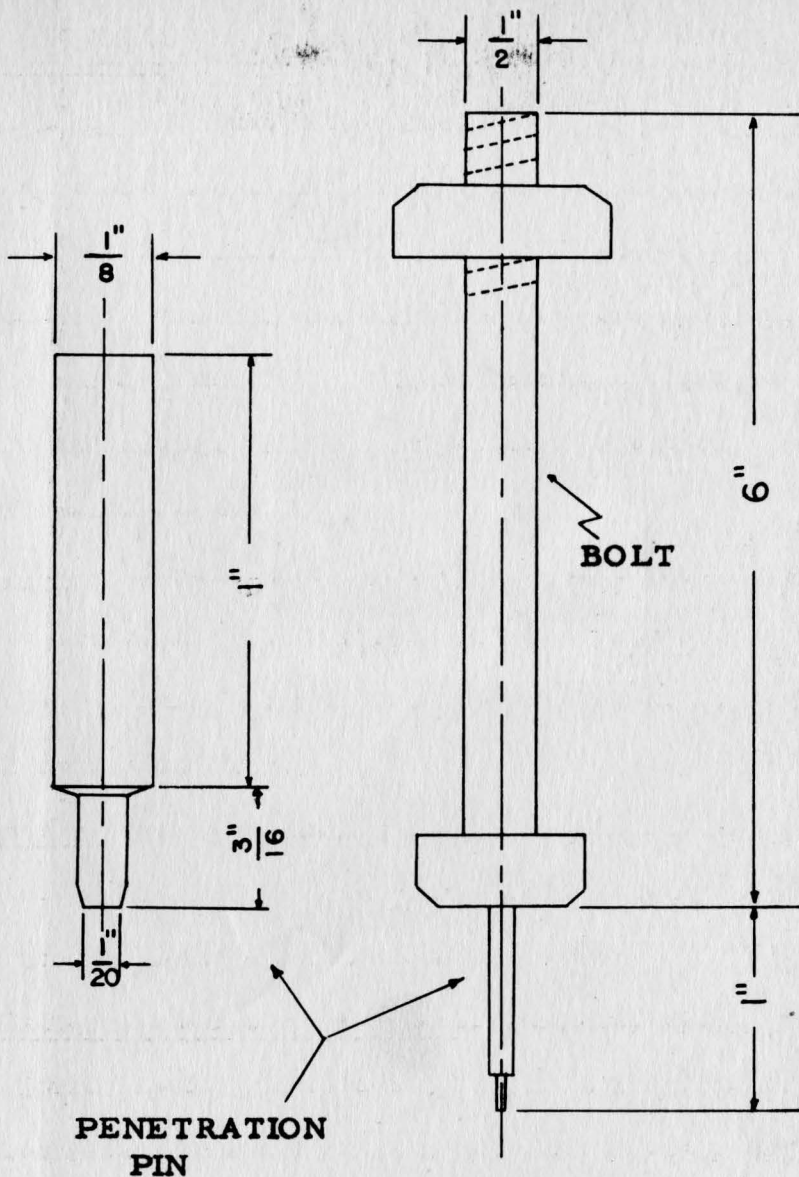
Hot Plate. Electric heating plate with thermostat, Model 2500, 110V. 60 cy. 660 watt. Obtained from Thermo-electric Manufacturing Company, Dubuque, Iowa. Used to heat 500 ml. beaker oil bath for small scale preliminary work.

Micrometer. One inch maximum length, 0.001 inch graduation with vernier. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to measure the specimens.

Miscellaneous Laboratory Equipment. Beakers, flask, graduated cylinders, jars, pipets, rubber tubing, glass tubing, stoppers. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used in the general laboratory work of this investigation.

Mold, Compression. Aluminum alloy, three pieces. Dimensions six inches diameter, 1.6 inches high, 0.3 inches thickness molded specimen. Made in Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. The mold was composed of four parts as shown in Figure 7, page 82. These four parts were top force of mold, polished brass surface sheet, steel cavity and bottom



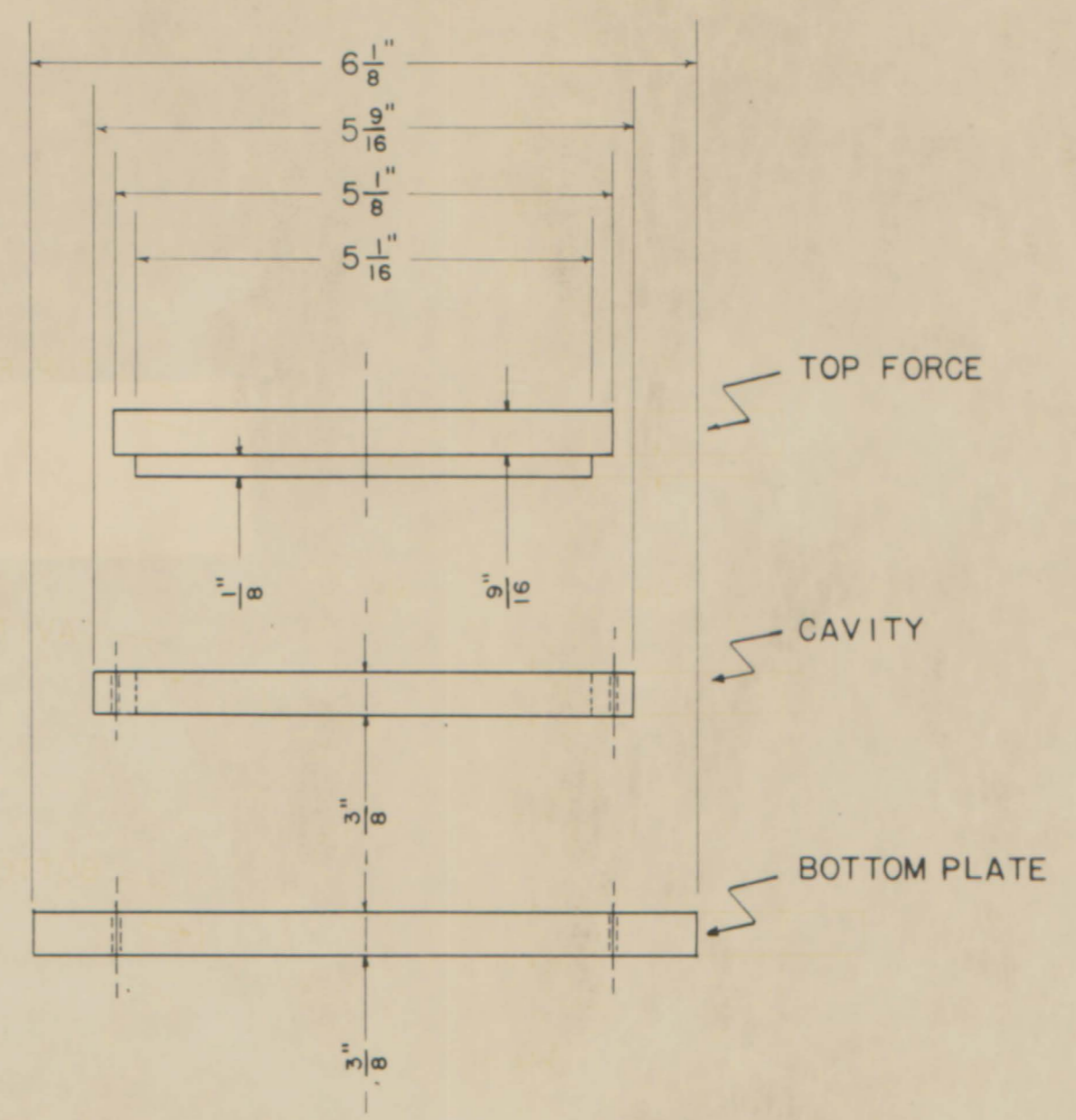
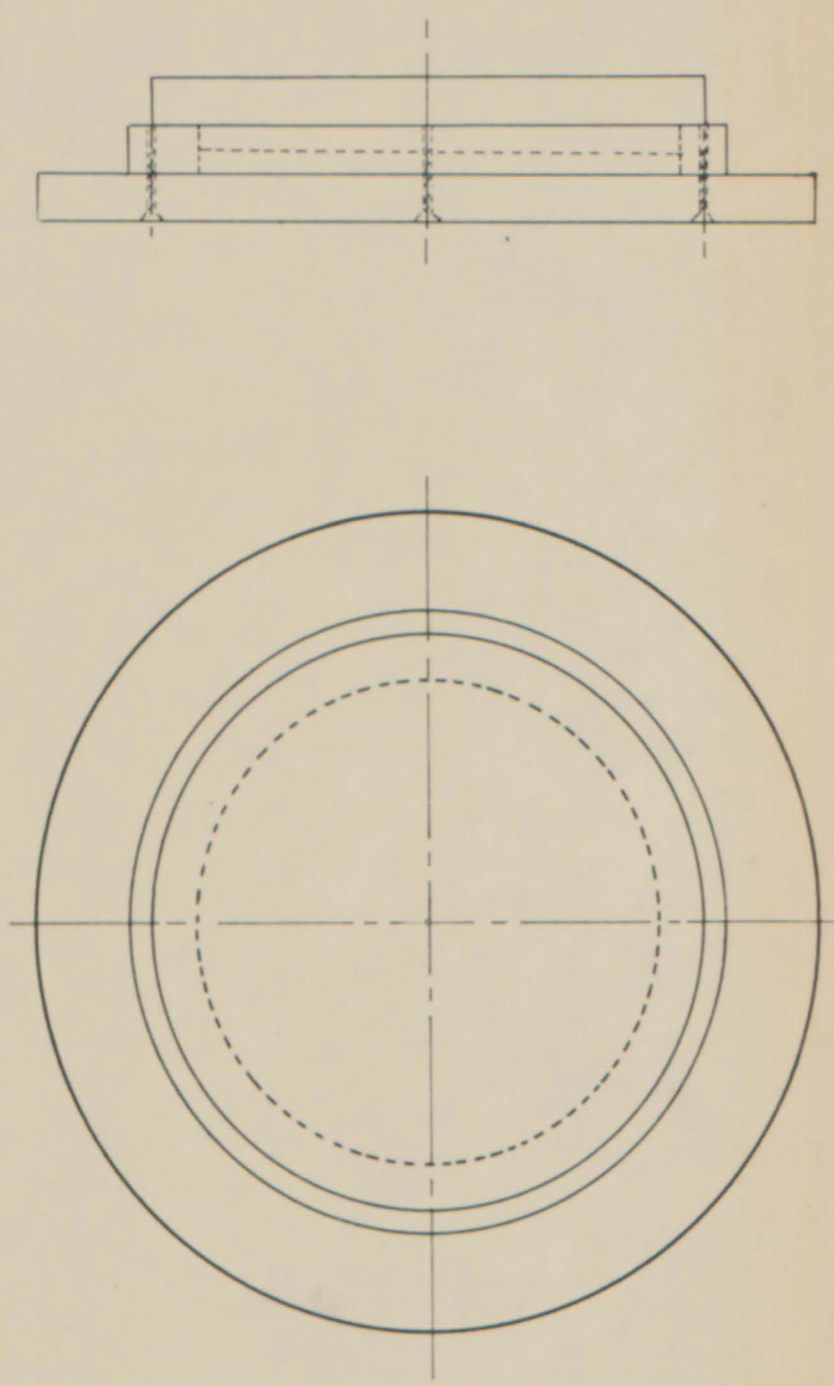


**PENETRATION  
PIN**

DEPARTMENT OF CHEMICAL ENGINEERING  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

**PENETRATION PIN FOR HARD-  
NESS TEST**

SCALE: 1" = 1"      DATE 7/3/60 CASE NO: 599  
DRAWN BY: C L L      FILE NO:  
CHECKED BY: CAR      FIGURE NO: 6  
APPROVED BY: R A F      SHEET NO:



DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VIRGINIA

**COMPRESSION MOLD**

SCALE: 1:1  
 DRAWN BY: **CLL**  
 CHECKED BY: **CAR**  
 APPROVED BY:

DATE  
 CASE NO: **599**  
 FILE NO:  
 FIGURE NO: **7**  
 SHEET NO:



plate. Top force and bottom plate of mold were made of aluminum alloy, and both surfaces were carefully polished by means of different grades of sand paper. The dimensions and shape are shown in this figure. Brass plate was obtained and cut in machine shop in Industrial Engineering Department, Virginia Polytechnic Institute. It was finished in 1/8 inch thick, six inches diameter plate. One side of plate was polished by means of chemical and mechanical treatment. Plate was first treated in hydrochloric acid solution and polished by fine sand paper, then finished by applying toothpaste and polished by fine emery cloth.

Steel ring (cavity) was cut from steel pipe, and smoothed by sand paper, dimension is 6 inches inside diameter,  $\frac{1}{4}$  inch thick,  $\frac{5}{8}$  inch high. The steel ring is mounted on the bottom plate of the mold by means of three  $\frac{3}{4}$  inch long bolts. Bottom plate is  $\frac{1}{2}$  inch thick, 7 inches diameter with five screw holes; three for fastening steel ring and two on each end for disassembling the mold by applying force on these bolts. One face of bottom plate was smoothed as on top force of the mold. Five bolts were three  $\frac{3}{4}$  inch, and two bolts were one inch.

This mold is used for molding and curing polyurethane elastomer.

Oven, Electric. Constant temperature oven, serial No. 1078 rating 110 v. 660 w. 6 amp. Equipped with thermo-electric pyrometer, range  $25^{\circ}$  C -  $175^{\circ}$  C, one degree graduations. Manufactured by Will Corporation, Rochester, New York. Used to cure the polyurethane elastomer.



Press, Hydraulic. Carver Laboratory press No. 16600-50, capacity 20,000 pounds on  $\frac{1}{4}$  inch ram. Equipped with electric heating plates. Manufactured by Fred S. Carber, Inc., Summit, New Jersey. This press was assembled with two six by six inch square inside electric nichrome wired hot plate which was controlled and adjusted by a needle type thermostat inserted in the side hole of top plate. Six by six inch square and  $\frac{3}{4}$  inch thick asbestos and two six by six inch steel wire nets were also assembled. The asbestos plates were placed between the hot plates and steel nets which were placed next to the platens of the press. This press assembly was used to mold elastomer.

Resin Kettle. Pyrex glass with three hole cover, capacity 2000 cc. Cat. No. 11-847-30 obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to prepare copolymer.

Stainless Steel Tweezers. Small tweezers. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to pick the specimens from solvent in absorption test.

Tensile Strength Testing Machine. Tinius Olsen, capacity 12,000 pounds. Manufactured by Tinius Olsen Company, Willow Grove, Pennsylvania. Located in the Wood Construction Laboratory, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to test samples of polyurethane elastomer.

Thermometers. Mercury, range -5 to 360° C, one degree graduations, Cat. No. 15-005 two required. Obtained from Fisher Scientific Company,

Silver Spring, Maryland. Used for general thermometric purposes.

Thermometers. Mercury, range  $-20$  to  $150^{\circ}$  C one degree graduations. Cat. No. 15-166, G-1. Three required. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for general thermometer purpose.

Timer, Electric. "Time-It" range 9999.9 second, 0.1 second graduations, 110 v. 60 cy. ac, power supply. Manufactured by Precision Scientific Company, Chicago, Illinois. Used for timing various tests.

Vacuum Pump. Vacuum pump with electric motor, maximum speed of pumping 600 rpm. Model A-7386. Obtained from Central Scientific Company, Chicago, Illinois. Used to keep vacuum on copolymerization reaction in preliminary work.

Variac Resistance. Capacity 110 v. one volt graduation. Obtained from General Radio Company, Cambridge, Massachusetts. Used to control speed of electric stirred.

Weighing Bottle. Weighing bottle and glass stopper, for analytical use, one needed. Obtained from Fisher Scientific Company. Used to weigh samples for solution absorption test.

### Method of Procedure

The plan of experimentation was carried out according to the following procedure.

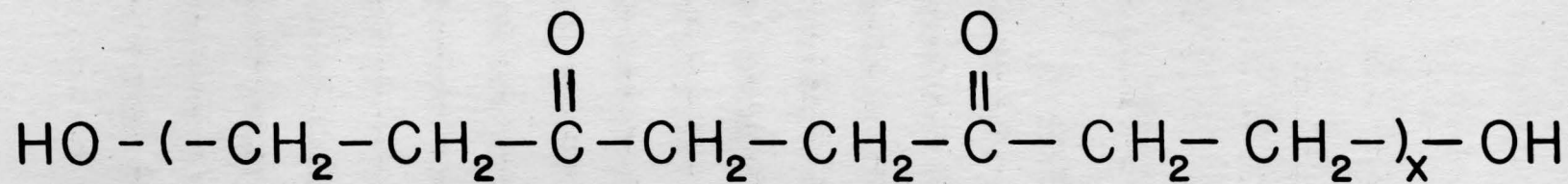
Raw Materials. A linear polyester of adipic acid and ethylene glycol, and 33' Bitolylene 44' diisocyanate was choice as the initial material for the polyurethane elastomer for this investigation. These are described as follows:

Linear Polyester. A linear polyester was one of the starting materials for the polyurethane elastomer. The linear polyester was prepared from adipic acid and ethylene glycol by Mobay Chemical Company in accordance with the method developed by O. Bayer<sup>(25)</sup>. It is marketed under the trade name Multrathane R-14.

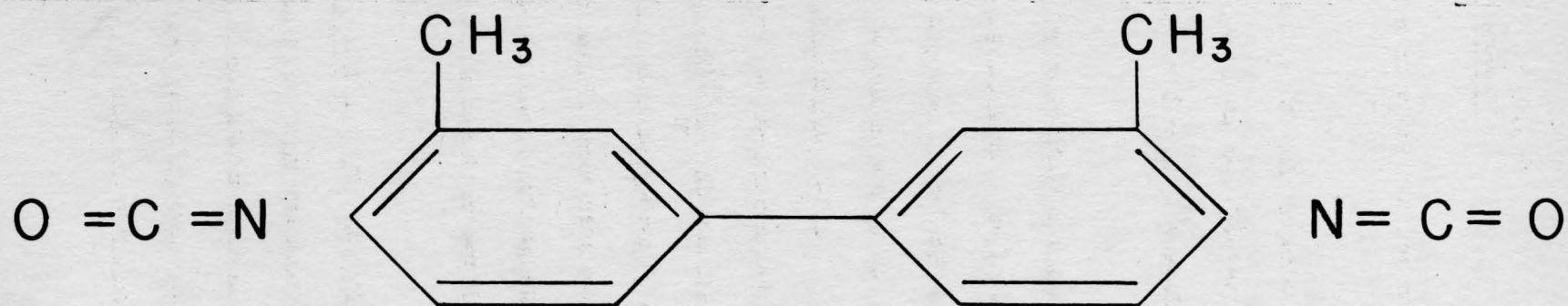
This linear polyester was a waxlike white colored material at room temperature. The average molecular weight was 2000, with less than 0.1 per cent of water content, and with hydroxyl number of 56. For ideal results in the final elastomeric product a polyester with hydroxyl number of 50 to 60 represents the ideal starting material as far as technical availability and physical properties, particularly structural strength, are concerned.

33'Bitolylene 44' Diisocyanate. 33' Bitolylene 44' diisocyanate is another starting material for polyurethane elastomers. 33' Bitolylene 44' diisocyanate was produced and supplied by National Aniline Division, Allied Chemical and Dye Corporation. Some of the physical and chemical properties are listed as follows:





POLYESTER



33' BITOLYLENE

44' DIISOCYANATE

Purity:	99.5 %
Hydrolyzable chlorine:	Less than 0.004 %
Solidification point:	69.5° C
Specific gravity:	$d_{4}^{30}$ 1.197

Solubility: Soluble in acetone, benzene, kerosene, carbon tetrachloride, chlorobenzene, and nitro benzene.

Trade name: "Nacconate 200".

Preliminary Tests. A great many preliminary tests were carried out in order to determine the general conditions and processes of preparing polyurethane elastomer. The range of each condition and process was chosen in accordance with information in the available literature, and the fundamental theories of polymerization. The copolymerization test of polyester and diisocyanate was carried in a 100 cc. beaker in a 500 cc. beaker of hot oil with the range of temperature from 85° C to 150° C at 5° intervals. Eighteen tests were conducted. Then the larger scale reaction in a resin kettle was carried out to provide material for the determination of the favorable molding and curing process, after the conditions of copolymerization and chain extension were fixed. More than 30 tests were tried. The casting, cold molding, rolling and hot molding were tried individually as well as in combination. The curing temperature and time were tested from 100° C to 150° C at 10° intervals and at 1, 2, 3, 4 hours and at two hour intervals to 24 hours.

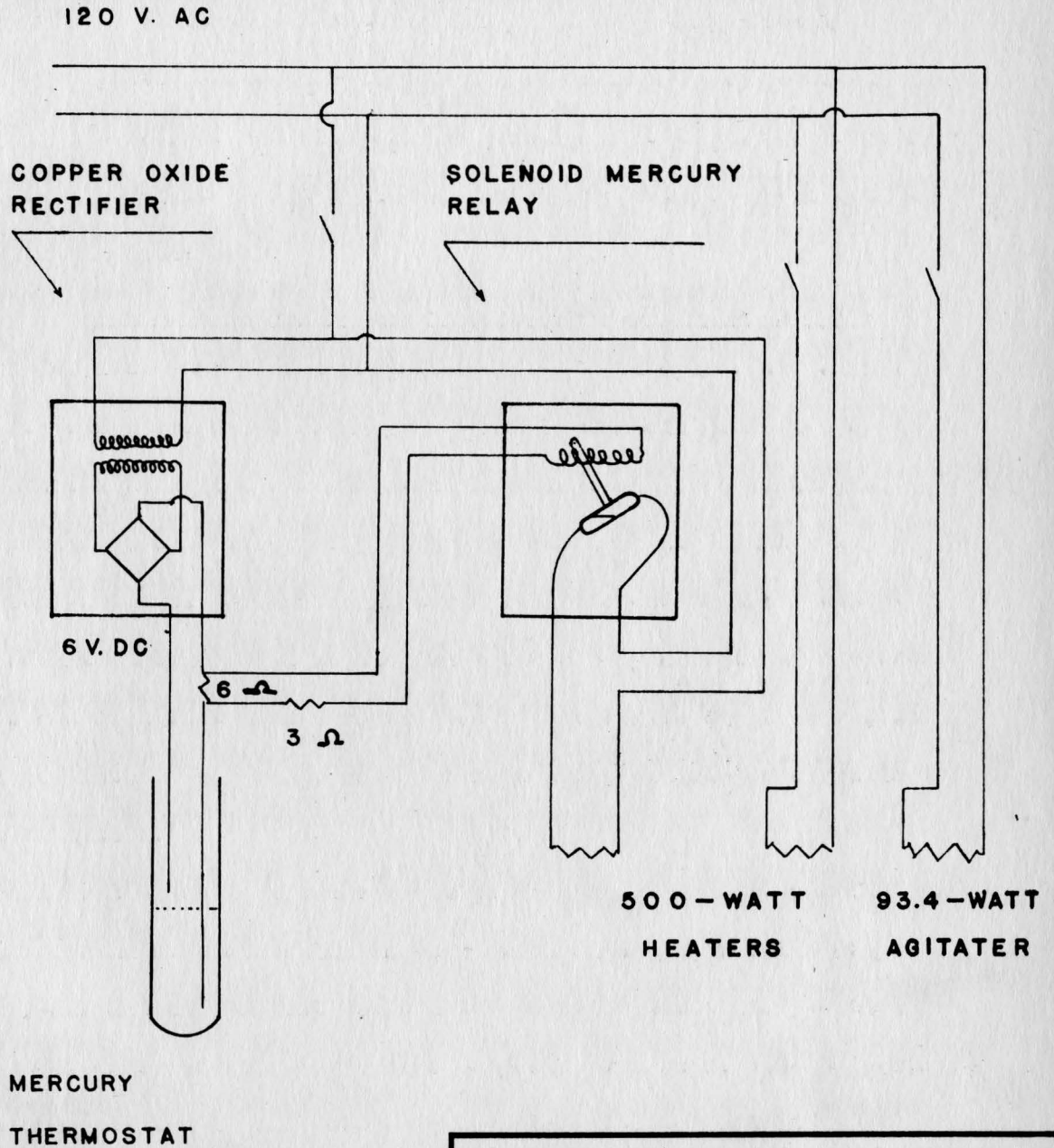
Preparation of Polyurethane Elastomer. The process of preparing polyurethane elastomer consisted of four steps; copolymerization of linear polyester and diisocyanate, chain lengthening and cross-linking, molding and curing. The process and general conditions of preparing polyurethane elastomer used were in accordance with the best results of preliminary study.

Copolymerization of Linear Polyester and diisocyanate.

Copolymerization of linear polyester and 33' Bitolyene 44' diisocyanate was carried out in a Pyrex glass resin kettle, heated by an oil bath, with agitation. The resin kettle was placed in the oil bath, held by two pieces of 3/8 inch copper tubing. A motor was mounted on the stand, and a glass rod with one end bent to U-shape dipped into kettle for agitation when the copolymerization proceeded. The speed of agitation was controlled by a variable electric resistance regulator. Figure 8, page 90, showed the diagram of electric heating system.

The resin kettle was covered with a glass cap and it was fastened by three clamps. Before its reaction with diisocyanate, the ethylene glycol-adipic acid polyester was a hard waxlike material. In this series of experiments, 80 grams of polyester was used. The polyester, upon being heated in the kettle in the oil bath, began melting at 60 to 70° C. Then the temperature was raised to 130° C and the melt was agitated. The amount of 33' Bitolyene 44' diisocyanate to give the desired ratio of reactants was then added gradually with agitation. This ratio was varied in different experiments. The mole ratio of 33'





DEPARTMENT OF CHEMICAL ENGINEERING  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

ELECTRIC SYSTEM FOR CON-  
STANT TEMPERATURE BATH

SCALE: - DATE 7/1/60 CASE NO: 599  
DRAWN BY: CLL FILE NO:  
CHECKED BY: *par* FIGURE NO: 8  
APPROVED BY: *RAF* SHEET NO:

Bitolyene 44' diisocyanate to polyester was varied in order to obtain different degrees of chain lengthening and cross-linking. This ratio will hereafter be referred to as the R value. The reaction is slightly exothermal and is completed in a few minutes according to Muller(54). The reaction was carried out for 30 minutes at a constant temperature of 130° C and with moderate stirring. The reaction produced a marked increase in viscosity, and the product had a brownish color. The rate of stirring was maintained by increasing power to the stirrer. In this step the diisocyanate reacted with the terminal hydroxyls of the polyester, forming urethane linkages and lengthening the chains. It was advantageous first to prepare the so-called extended isocyanate polyester or copolymer and stop the reaction at this stage by cooling down to room temperature, and to carry out the reaction involving network formation only as a subsequent process. The copolymer is stable for several hours at elevated temperatures, if protected from moisture. On very long heating or on storage of solutions, gelling due to cross-linking occurs in one to two weeks even with most careful exclusion of moisture.

Chain Lengthening and Cross-Linking. The copolymer in the resin kettle was melted, with the oil bath at 130° C. The oil bath was then cooled down from 130-125° C by running cooling water through the cooling coil. The chain lengthening and cross-linking reaction was carried out at 125° C. The amount of ethylene glycol required to produce the desired effect was then added drop by drop with rapid agitation. The cross-linking of the diisocyanate polyester proceeded very rapidly



when ethylene glycol was added to the melted copolymer. The reaction was carried out for four minutes, when the heating was stopped and the viscous copolymer poured into the mold. The reaction was stopped at this intermediate stage by cooling.

Molding of Polyurethane Elastomer. Molding of polyurethane elastomer can be divided into three phases of work. The first phase consisted of a casting process, the second phase consisted of cold molding and the third phase consisted of hot molding.

After the chain lengthening and cross-linking reaction, the molten viscous copolymer was poured into the mold. Next the mold was placed in an oven and heated at  $110^{\circ}$  C for 30 minutes. The viscous material proceeded through various intermediate stages to a brittle material. The volume increased visibly and became a porous material with a quantity of air bubbles in this material. The color changed from a brownish to very light yellow. The crumbly product was removed from the mold. Its removal was facilitated by applying before casting a small amount of calcium stearate powder to the surface of mold as a lubricating agent which prevented the product from sticking to the mold.

The cold molding was used after the casting stage. The material and mold were cooled down to room temperature and the sheet was turned over and the brass plate and top force of mold were placed on the mold over the crumbly material. The mold was then placed in a hydraulic press and pressed under 4000 pounds per square inch gage pressure for ten minutes. The crumbly material was thus pressed into a solid



rubberlike material, but it was still not possible to avoid the formation of air bubbles in the product.

Hot molding was carried out without removing the sheet from the mold at a temperature of 125° C, with the same pressure used in the cold molding - 4000 pounds per square inch gage. In hot molding the deviation of temperature was considered to be - 1.5° C. The operating time was 20 minutes. In this stage the cross-linking reaction went rapidly, and the final product was a solid elastomer sheet completely free of air bubbles. The material was cooled in the mold and removed.

Curing of the Final Product. The elastomeric polyurethane sheet, after being treated by the molding process was at least partially cured. In order to assure the completion of the curing process, the material was baked in an oven at 110° C for 12 hours. The color of the final product was from light brown to deep brown depending on the ratio of the starting materials of polyester and 33' Bitolylene and 44' diisocyanate. The amount of cross-linking agent, ethylene glycol, was also an important factor in the color and appearance of the product. The flow diagram of the preparation of elastomer was shown in Figure 9, page 94.

Preparation of Testing Materials. The above procedures were adopted for the preparation of the material to be tested. The variables such as temperature, reaction time and pressure and proportion of starting materials were fixed at optimum values or varied as a result of the experience gained through the preliminary work.

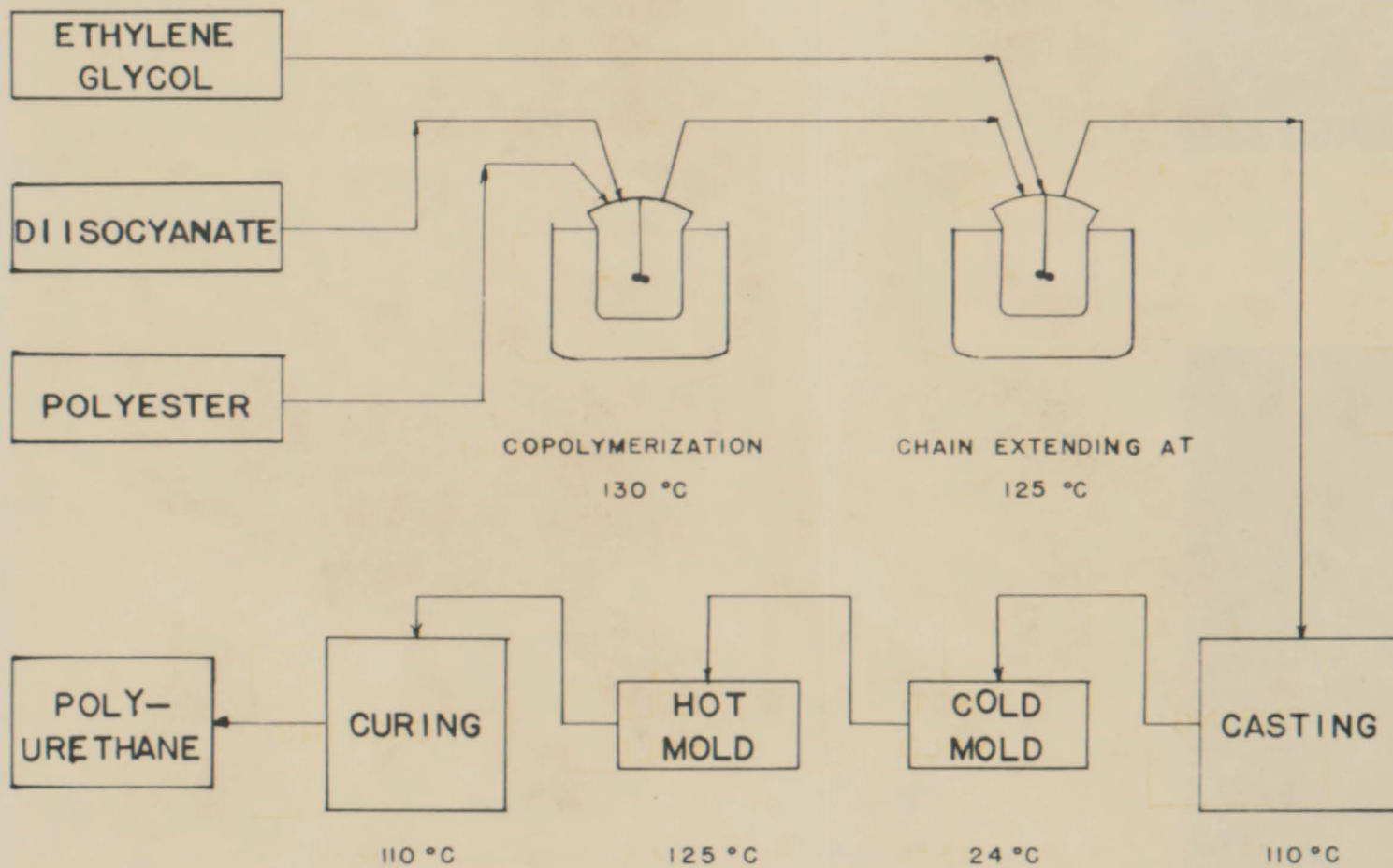


FIGURE 9 FLOW DIAGRAM FOR THE PREPARATION OF POLYURETHANE ELASTOMER

For this investigation the tests were divided into three series. The procedures, methods and reaction conditions to produce material for testing were all fixed to be identically the same and to require the minimum deviation as far as possible.

These three series were as follows: In the first series the R value, ratio of diisocyanate to polyester, was varied and fixed amounts of excess 33' Bitolylene 44' diisocyanate were used after chain extension by adding the proper amount of ethylene glycol. The second series consisted of fixing the R value at  $R=1.65$ , and varying the amounts of excess diisocyanate after chain extension by controlling the added quantity of ethylene glycol. The third series consisted of fixed R value at 2.5 and varying the amounts of excess diisocyanate after chain extension by controlling the quantity of ethylene glycol added.

Series 1: Series 1 consisted of varying R values, the ratio of polyester to 33' Bitolylene 44' diisocyanate. The R ratios used were 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5. At the R values of 4.5 the elastomeric product became very rigid, similar to hard rubber. For R values over 4.5 the product became a rigid plastic. The amount of cross-linking agent, ethylene glycol was adjusted in order to obtain the same amount of excess diisocyanate after the chain extension. The amount of excess diisocyanate in this set of tests was 0.008 moles of diisocyanate to 0.04 moles of polyester on copolymerization.

This excess amount of glycol must be fixed so that there are not enough hydroxyl groups present to be stoichiometrically equivalent to



the diisocyanate groups. That is, there had to be a certain excess of diisocyanate present in every test. This test series is listed in Table XVII, page 97.

Series 2: Series 2 consisted of tests with various amounts of cross-linking agent, ethyleneglycol, with a polymer of constant R value of 1.65, the ratio of polyester to diisocyanate. The excess of diisocyanate functional groups after chain extension was varied from 0 to 0.020 mole in this series of tests. The quantity of diisocyanate functional groups went from 0.012 mole per 0.066 mole of diisocyanate on copolymerization. Beyond a certain isocyanate content, side reactions set in which were apparently reactions involving diisocyanate groups with one another. These were characterized by gas formation, "Blowing", and by reduction of desirable mechanical and physical properties. In Table XVII, page 98 are shown the starting compositions for these tests.

Series 3: Series 3 consisted of tests with various amounts of cross-linking agent, ethylene glycol, with a constant R value. The diisocyanate functional groups varied from 0 to 0.056 mole per 0.10 mole of diisocyanate. The quantity of diisocyanate functional groups up to 0.48 mole per 0.10 mole diisocyanate on copolymerization started gas formation, "blowing". In Table XIX, page 99 is shown the schedule for this series of tests.

Determining the Solvent Absorption of Polyurethane. The solvent absorption of polyurethane elastomer samples was determined for acetone solvent. Duplicate determinations of the solvent absorption of

TABLE XVII

Composition of Test Batches - Test Series 1

Test No.	Polyester mole	Polyester gram	R Ratio	Diisocyanate		Excess <sup>a</sup> Diisocyanate mole	Glycol mole	Glycol gram	Glycol cc
				mole	gram				
PT-58	0.04	80	1.0	0.04	10.56	0	0	0	0
PT-52	0.04	80	1.5	0.06	15.84	0.02	0.012	0.768	0.69
PT-77	0.04	80	1.65	0.066	17.44	0.026	0.018	1.117	1.002
PT-78	0.04	80	2.0	0.08	21.12	0.04	0.032	1.985	1.78
PT-66	0.04	80	2.5	0.10	26.40	0.06	0.052	3.221	2.894
PT-55	0.04	80	3.0	0.12	31.68	0.08	0.072	4.463	4.00
PT-56	0.04	80	3.5	0.14	36.96	0.10	0.092	5.170	5.12
PT-57	0.04	80	4.0	0.16	42.24	0.12	0.112	6.945	6.23
PT-59	0.04	80	4.5	0.18	47.52	0.14	0.132	8.184	7.34

<sup>a</sup> Excess Diisocyanate = Mole of Diisocyanate - Mole of Polyester

No elastomer on PT-58

TABLE XVIII

Composition of Test Batches - Test Series 2

Test No.	Polyester mole	Diisocyanate mole	R Ratio	Excess <sup>a</sup> Diisocyanate mole	Chain Extending mole	Chain Extending gram	Excess <sup>b</sup> Diisocyanate mole	Excess <sup>b</sup> Diisocyanate gram
PT-75	0.04	0.066	1.65	0.026	0.028	1.738	0	0
PT-73	0.04	0.066	1.65	0.026	0.026	1.612	0	0
PT-74	0.04	0.066	1.65	0.026	0.024	1.490	0.002	0.528
PT-63	0.04	0.066	1.65	0.026	0.022	1.364	0.004	1.055
PT-77	0.04	0.066	1.65	0.026	0.018	1.117	0.008	2.110
PT-64-a	0.04	0.066	1.65	0.026	0.014	0.868	0.012	3.168
PT-64-b	0.04	0.066	1.65	0.026	0.010	0.620	0.016	4.220
PT-64-c	0.04	0.066	1.65	0.026	0.006	0.372	0.020	5.280

<sup>a</sup> Excess Diisocyanate = Mole of Diisocyanate - Mole of Polyester

<sup>b</sup> Excess Diisocyanate = (Mole of Diisocyanate - Mole of Polyester) - Mole of Chain Extending

PT-64a, PT-64-b, and PT-64-c are characterized by gas formation (blowing).



TABLE XIX

Composition of Test Batches - Test Series 3

Test No.	Polyester mole	Diisocyanate mole	R Ratio	Excess <sup>a</sup> Diisocyanate mole	Chain Extending mole	Chain Extending gram	Excess <sup>b</sup> Diisocyanate mole	Excess <sup>b</sup> Diisocyanate gram
PT-71	0.04	0.10	2.5	0.06	0.060	3.72	0	0
PT-66	0.04	0.10	2.5	0.06	0.052	3.21	0.008	2.110
PT-72	0.04	0.10	2.5	0.06	0.044	2.73	0.016	4.220
PT-68	0.04	0.10	2.5	0.06	0.036	2.235	0.024	6.336
PT-76	0.04	0.10	2.5	0.06	0.028	1.775	0.032	8.448
PT-70	0.04	0.10	2.5	0.06	0.020	1.240	0.040	10.560
PT-79	0.04	0.10	2.5	0.06	0.012	0.746	0.048	12.672

a Excess Diisocyanate = Mole of Diisocyanate - Mole of Polyester

b Excess Diisocyanate = (Mole of Diisocyanate - Mole of Polyester) - Mole of Chain Extending

PT-79 is characterized by gas formation (blowing).

polyurethane elastomer samples were made. The absorption samples consisted of a cylinder of the elastomer with an average diameter of 0.2 inch and a length of 0.3 inch. The weight range was 0.20 to 0.28 grams. The tests were made at a room temperature of 75° F.

The cylinders of polyurethane elastomer used for these tests were cut from six inch diameter sheets prepared to the test described previously. These samples were cut by means of a cylinder die prepared by the investigator. This die consisted of a brass tube of 0.408 cm. inside diameter and 10 cm. height with 0.06 cm. thick walls. Cutting of the sample was effected by applying pressure hydraulically. Fifty milliliter beakers filled with 40 ml. of acetone were used for the absorption phase of these tests. One sample specimen per beaker was used in each test. An analytic chainomatic balance with capacity of 100 grams with one milligram graduations and a vernier for tenths of milligrams was used to weigh the samples. Each sample specimen was weighed and then immersed in the acetone and a timer was used to record the time of absorption. For the first series of this investigation, weights were recorded at ten minute intervals for the first hour, then again at 1.5 hours, two hours, 2.5 hours, three hours, four hours, six hours, and twenty hours. For test series 2 and 3 of this investigation weights were recorded at 1, 1.5, 2, 2.5, 3, 3.5, 4, 6 and 20 hours.

The procedure for weighing sample specimens for each case was as follows. The specimen was taken out of the solution with stainless steel tweezers and put into a weighing bottle. Before the specimen was put into the weighing bottle, the film of acetone solution was removed

with absorption paper and the sample surface air dried. The total time for operation was ten seconds in each case. The sample was then quickly weighed using the balance, an average of 40 to 60 seconds was required to weigh in each case.

Determining the Swelling of Polyurethane Elastomer in Acetone

Solution. The swelling test was carried out using a procedure similar to that of the solvent absorption test. Again acetone was used for the determination. The sample specimen of polyurethane elastomer consisted of a cylinder with an average diameter of 0.2 inch and a length of 0.3 inch. The weight range was from 0.20 to 0.28 grams. The sample was cut by means of die prepared by the investigator described in a previous section. These tests were carried out at room temperature of 75° F.

A micrometer was used for the swelling measurements of this investigation. The specimen was measured before starting the test, which yielded the original dimension.

A fifty milliliter beaker filled with 40 ml. of acetone was used in these tests. A sample specimen from each batch was used in these tests as in the solvent absorption tests. For these tests, all three series of samples were measured after soaking times of 1, 1.5, 2, 2.5, 3, 3.5, 4, 6 and 20 hours.

The procedure of these measurements in each case involved the measurement of the diameter and the length of the sample cylinder with the micrometer. Each dimension was measured three times changing the point of measurement each time, then the mean value of each dimension



was recorded and volume calculated. In this investigation volume per cent of swelling was taken as the unit of measurement and comparison.

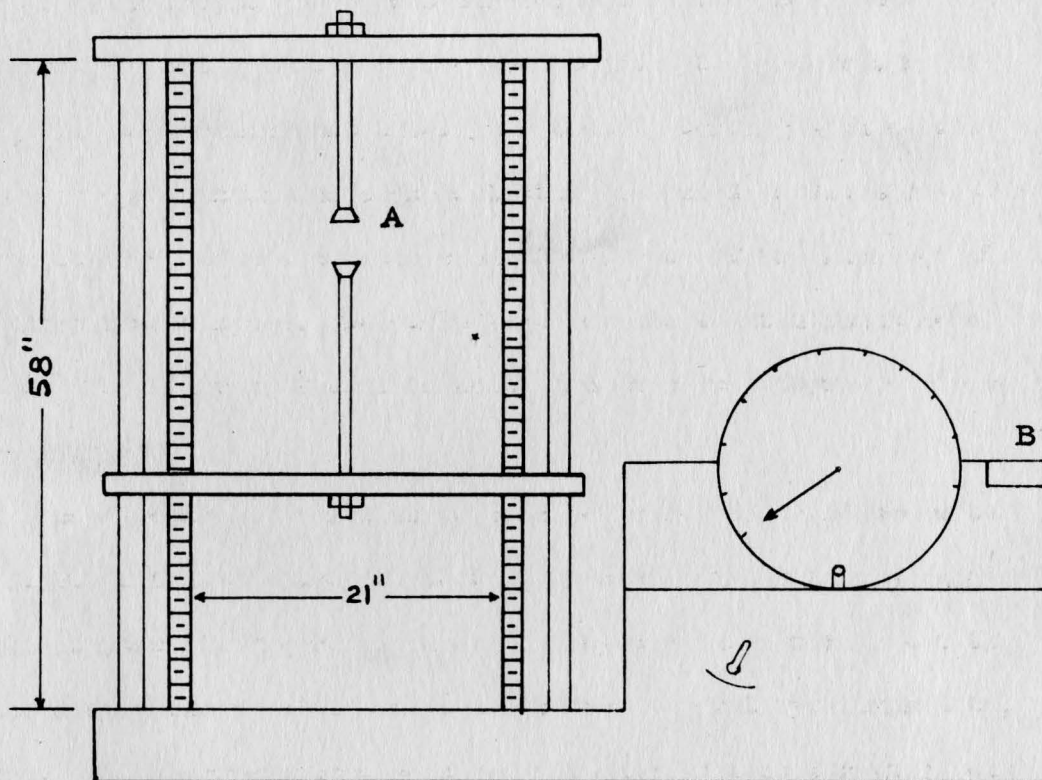
Determination of Tensile Strength, elongation, and Break Down Force. This investigation was carried out by the use of a Tinius Olsen Electromatic Tester in the Wood Construction Laboratory of Virginia Polytechnic Institute. The tensile testing machine was used for compression and tensile tests. The machine was model number 51, with 12000 pounds maximum capacity at rate of two inch per minute at maximum head speed, and 0.015 inch per minute at minimum head speed. The diagram of tensile testing machine was shown in Figure 10, page 103.

The dimensions of a tensile specimen were in accordance with A. S. T. M. tensile strength testing specimen preparation method<sup>(3)</sup> which is shown in Figure 11, page 104. The specimens were cut with a space die by the Monsanto Plastic Research Laboratory, Texas City, Texas. All specimens were measured with micrometers for thickness and for proper width. The tensile strength tests were carried out in accordance with the A. S. T. M. tensile strength testing method<sup>(3)</sup>. The procedure was as follows: To set a specimen in the Tinius Olsen tensile testing machine, the specimen was placed in the jaws of the machine so that the jaws came to the outer edge of the fillets in the wide section of the specimen. The dial setting on the machine was set for each division on the scale to equal 600 pounds. The head speed was adjusted to two inches per minute. The yield stress was

Legend

A - Specimen clamps

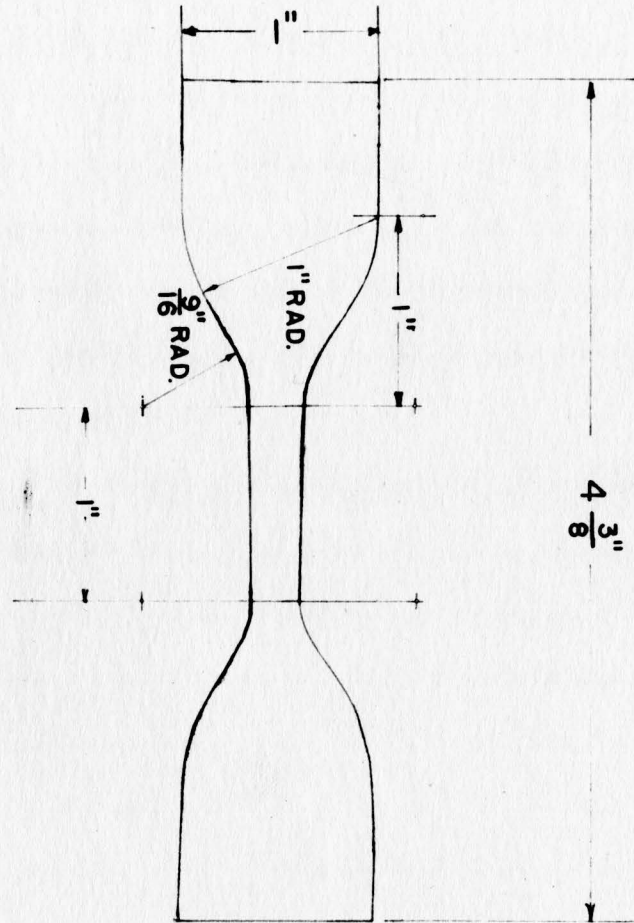
B - Automatic recorder



DEPARTMENT OF CHEMICAL ENGINEERING  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

TINIUS OLSEN TESTING MACHINE

SCALE:	DATE 7/3/60	CASE NO: 599
DRAWN BY: CLL		FILE NO:
CHECKED BY: CAR		FIGURE NO: 10
APPROVED BY: R A F		SHEET NO:



DEPARTMENT OF CHEMICAL ENGINEERING  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

**TEST SPECIMEN**

SCALE: 1" = 1"

DRAWN BY: CLL

CHECKED BY: CAR

APPROVED BY: RAF

DATE 7/1/60

CASE NO: 599

FILE NO:

FIGURE NO: 11

SHEET NO:



automatically graphed by the testing machine. Thus, a series of tests were made at room temperature of 75° F and 50 per cent humidity for certain of the batch samples previously described.

A conditioning procedure is needed for the sample specimens before the tests. The sample specimens were placed in the conditioning room, where the temperature and humidity were controlled automatically. The sample specimens were conditioned at the temperature of 75° F 50 per cent humidity for 72 hours. The testing procedure was also carried out in the conditioning room.

Determination of Hardness of Polyurethane Elastomer at Room Temperature. This investigation was carried out by the use of a Tinius Olsen Electromatic Tester in the Wood Construction Laboratory of Virginia Polytechnic Institute. A needle type testing apparatus was made as previously described. The needle was fastened by a six-inch long bolt on the movable horizontal plate of the Tinius Olsen machine, the sample specimen was placed on the steel foot stand, and the needle point was adjusted at the surface of specimen. The dial setting on the machine was set for each division on the scale to equal 0.1 pound. The head speed was adjusted to 0.3 inch per minute, and the total distance of travel was set within 0.25 inch. The yield hardness data were automatically graphed by the testing machine. Thus, a series of tests was made at room temperature for certain of the batch samples previously described. The sample specimens were conditioned at 75° F and 50 per cent humidity for 72 hours as described in tensile strength.

Determination of Hardness of Polyurethane Elastomer at High Temperature. This investigation was carried out by the use of a Tinius Olsen Electromatic Tester as described in previous section. The sample specimens were heated in the electric oven at 300° F for 12 minutes, then the specimen was moved from oven to the testing machine. In order to prevent the heat loss during the test, the test was carried out as quickly as practical. Thus, a series of tests were made at the temperature of 300° F for certain of the batch samples previously described.

#### Data and Results

The tabulated data and results with accompanying figures are presented in the following sections. The data and results include those for the determination of the reaction conditions and processes for making polyurethane elastomer in the preliminary study, absorption tests, swelling tests, tensile properties tests and hardness tests: Each test conducted in this investigation was included in three series of experiments.

Preliminary studies were conducted to determine the optimum conditions for the process. These conditions were employed in the preparation of polyurethane elastomer. Figure 9, page 94, shows the flow diagram for the preparation of the polyurethane elastomer as determined from the preliminary studies.

Absorption Test. The absorption properties of polyurethane elastomer were obtained by conducting tests to determine the weight per cent increase through a period of time in acetone solution. Table XX, page 108, Table XXI, page 109, and Table XXII, page 110, contain the absorption data and results for each series of tests.

Figures 12 and 13, page 111 and 112, indicates the comparison of the weight per cent increase for each R value.

Swelling Test. The swelling properties of polyurethane elastomer were obtained by conducting tests to determine the volume increase through a period of time in acetone solution. Table XXIII, page 113, Table XXIV, page 114, and Table XXV, page 115 contain the swelling data and results for three series.

Figure 14 and 15, page 116 and 117 indicates the comparison of volume per cent increase for each R value.

Tensile Properties Test. The tensile properties are presented in Table XXVI, page 118, Table XXVII, page 119, and Table XXVIII, page 120 for these three series of tests. For each table contained yield stress, strength at 200%, 300%, 400% and 600% elongation. Rupture strength and Young's modulus are also listed. All these data and results were obtained from automatic recording charts which were automatically recorded by Tinius and Olsen tensile strength machine.

Figure 16, page 121 indicates the comparison of the tensile properties for each R value.

Hardness Test. The hardness properties of polyurethane elastomer were obtained by conducting the tests to determine the force of



Table XX

## Determination of the Solvent Absorption of Polyurethane Elastomer for

## Test Series 1

Test NO.	Sample No.	R Ratio	Minutes								Hours				
			0 gram	10 gram	20 gram	30 gram	40 gram	50 gram	60 gram	1.5 gram	2.0 gram	3.0 gram	4.0 gram	6.0 gram	
	PT-58	1.0	-	-	-	-	-	-	-	-	-	-	-	-	
wt.	ST-5	PT-52	1.5	0.1683	0.1986	0.2136	0.2263	0.2354	0.2445	0.2518	0.2578	0.2841	0.3070	0.3269	0.3584
wt.%	ST-5	PT-52	1.5	0	18.0	26.9	34.45	39.9	45.3	49.6	55.8	68.8	82.45	94.0	112.9
wt.	ST-2	PT-78	2.0	0.2213	0.2608	0.2761	0.2882	0.3089	0.3199	0.3310	0.3497	0.3652	0.3809	0.4255	0.4556
wt.%	ST-2	PT-78	2.0	0	17.86	24.8	30.16	39.6	44.6	49.6	58.1	65.1	81.2	92.4	106.0
wt.	ST-3	PT-66	2.5	0.2410	0.2708	0.2861	0.2972	0.3070	0.3162	0.3196	0.3319	0.3403	0.3644	0.3784	0.4100
wt.%	ST-3	PT-66	2.5	0	12.37	18.72	23.30	27.40	31.20	32.60	37.65	41.20	51.3	57.00	70.20
wt.	ST-4	PT-55	3.0	0.2462	0.2728	0.2840	0.2908	0.2968	0.3056	0.3115	0.3264	0.3267	0.3544	0.3574	0.3802
wt.%	ST-4	PT-55	3.0	0	10.8	15.35	18.1	20.55	24.10	26.5	32.5	32.64	44.43	45.10	54.4
wt.	ST-9	PT-56	3.5	0.2415	0.2621	0.2720	0.2766	0.2845	0.2874	0.2908	0.2995	0.3098	0.3132	0.3302	0.3530
wt.%	ST-9	PT-56	3.5	0	8.55	12.62	14.54	17.63	19.03	20.0	24.01	28.3	29.35	37.0	46.2
wt.	ST-7	PT-57	4.0	0.231	0.2488	0.2574	0.2633	0.2684	0.2740	0.2779	0.2912	0.3015	0.3159	0.3300	0.3491
wt.%	ST-7	PT-57	4.0	0	7.71	11.33	14.0	15.5	18.6	20.3	26.05	30.58	37.15	42.8	51.2
wt.	ST-8	PT-58	4.5	0.270	0.2822	0.2890	0.2921	0.2942	0.2964	0.2992	0.3050	0.3104	0.3205	0.3224	0.3339
wt.%	ST-8	PT-58	4.5	0	4.52	7.04	8.18	8.96	9.78	10.81	12.96	14.95	18.7	19.4	23.65

Testing temperature = 75° F.

Solvent: acetone.

Table XXI

Determination of the Solvent Absorption of Polyurethane ElastomerSeries 2

Sample No.	Chain Extending mole	0 Hour		1 Hour		2 Hours		4 Hours	
		Weight gram	Weight %	Weight gram	Weight %	Weight gram	Weight %	Weight gram	Weight %
PT-75	0.028	0.184	0	0.2457 <sup>a</sup>	46.7	0.2855 <sup>b</sup>	55.0	- <sup>c</sup>	-
PT-73	0.026	0.1989	0	0.3073 <sup>d</sup>	52.8	0.3572 <sup>a</sup>	80.8	- <sup>c</sup>	-
PT-74	0.024	0.1901	0	0.3107	63.3	0.3436 <sup>e</sup>	80.9	0.4538 <sup>d</sup>	138.5
PT-63	0.022	0.1753	0	0.2530	44.3	0.2795	59.5	0.3390	93.4
PT-77	0.018	0.1821	0	0.2929	60.8	0.3054	67.7	0.3853	111.5
PT-64-a	0.014	-	-	-	-	-	-	-	-
PT-64-b	0.010	-	-	-	-	-	-	-	-
PT-64-c	0.006	-	-	-	-	-	-	-	-

a Begin to dissolve during the first hour.

b Partially dissolve in the solvent.

c Dissolve and loss original shape.

d Became sticky at the surface of the specimen.

e A tendency to dissolve.

No product formed on PT-64-a, PT-64-b and PT-64-c.

Testing temperature = 75° F.

Solvent: Acetone

Table XXII

## Determination of the Solvent Absorption of Polyurethane Elastomer

## Series 3

Sample No.	Chain Extending mole	0 Hour		1 Hour		2 Hours		4 Hours		9.5 Hours	
		Weight gram	Weight %	Weight gram	Weight %	Weight gram	Weight %	Weight gram	Weight %	Weight gram	Weight %
PT-71	0.060	0.2152	0	0.2768 <sup>a</sup>	28.65	0.2767 <sup>a</sup>	28.60	0.3080 <sup>a</sup>	34.1	0.3094 <sup>a</sup>	43.8
PT-66	0.052	0.1976	0	0.2757	29.54	0.2930	48.30	0.3481	76.2	0.4030	103.9
PT-72	0.044	0.1799	0	0.2353	30.80	0.2443	35.75	0.2815	56.5	0.3115	73.2
PT-68	0.036	0.1602	0	0.2010	25.41	0.2113	31.90	0.2401	43.6	0.2598	62.2
PT-76	0.028	0.1808	0	0.2370	31.00	0.2502	38.36	0.2786	54.1	0.3002	66.1
PT-70	0.020	0.1472	0	0.1897	28.90	0.1951	32.50	0.2208	49.3	0.2331	58.4
PT-79	0.012	-	-	-	-	-	-	-	-	-	-

<sup>a</sup> Partially desolved in the solvent.

No product obtained on PT-79.

Testing temperature = 75° F.

Solvent: Acetone



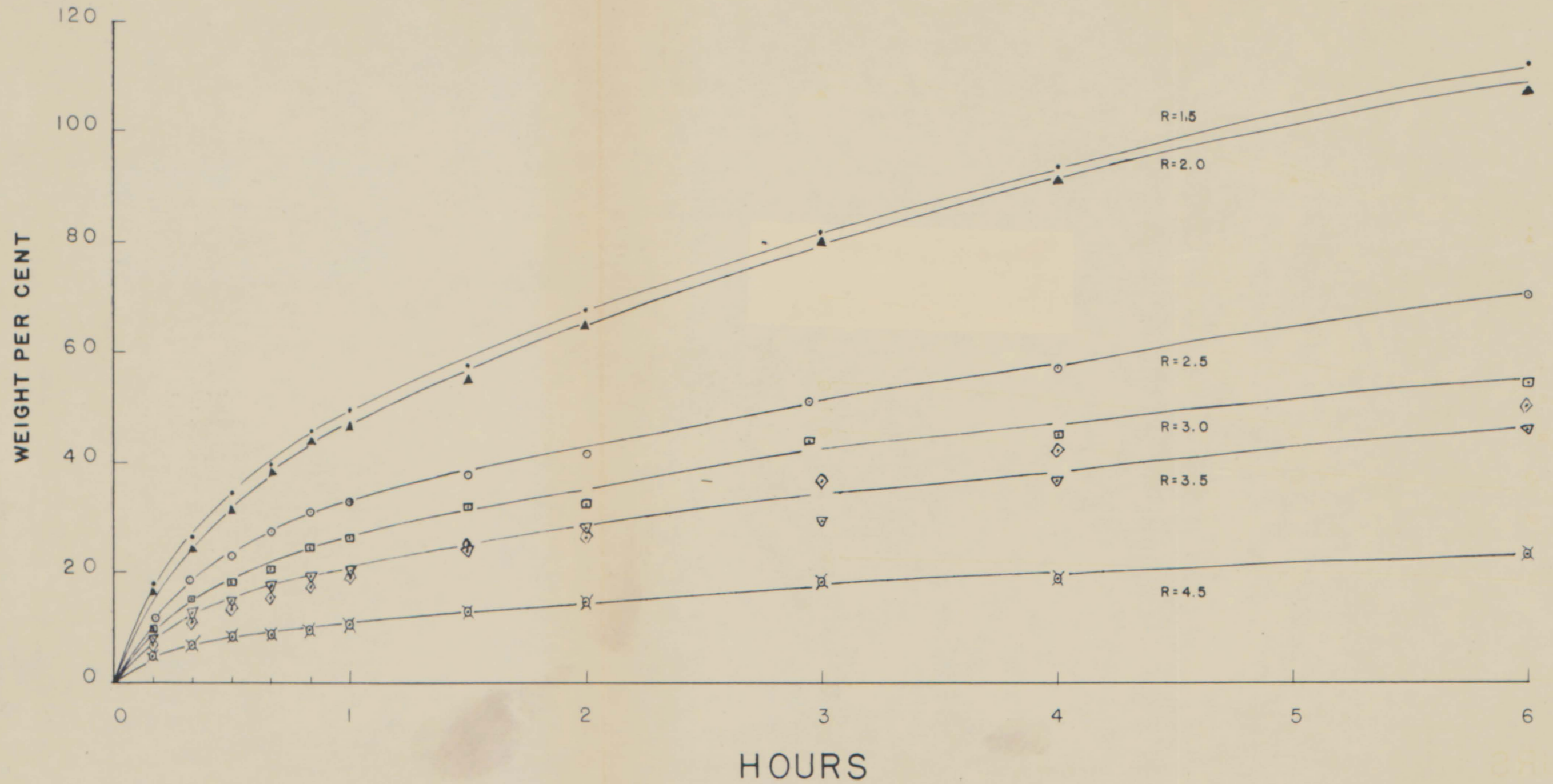


FIGURE 12 EFFECT OF R VALUE ON THE ABSORPTION OF ACETONE

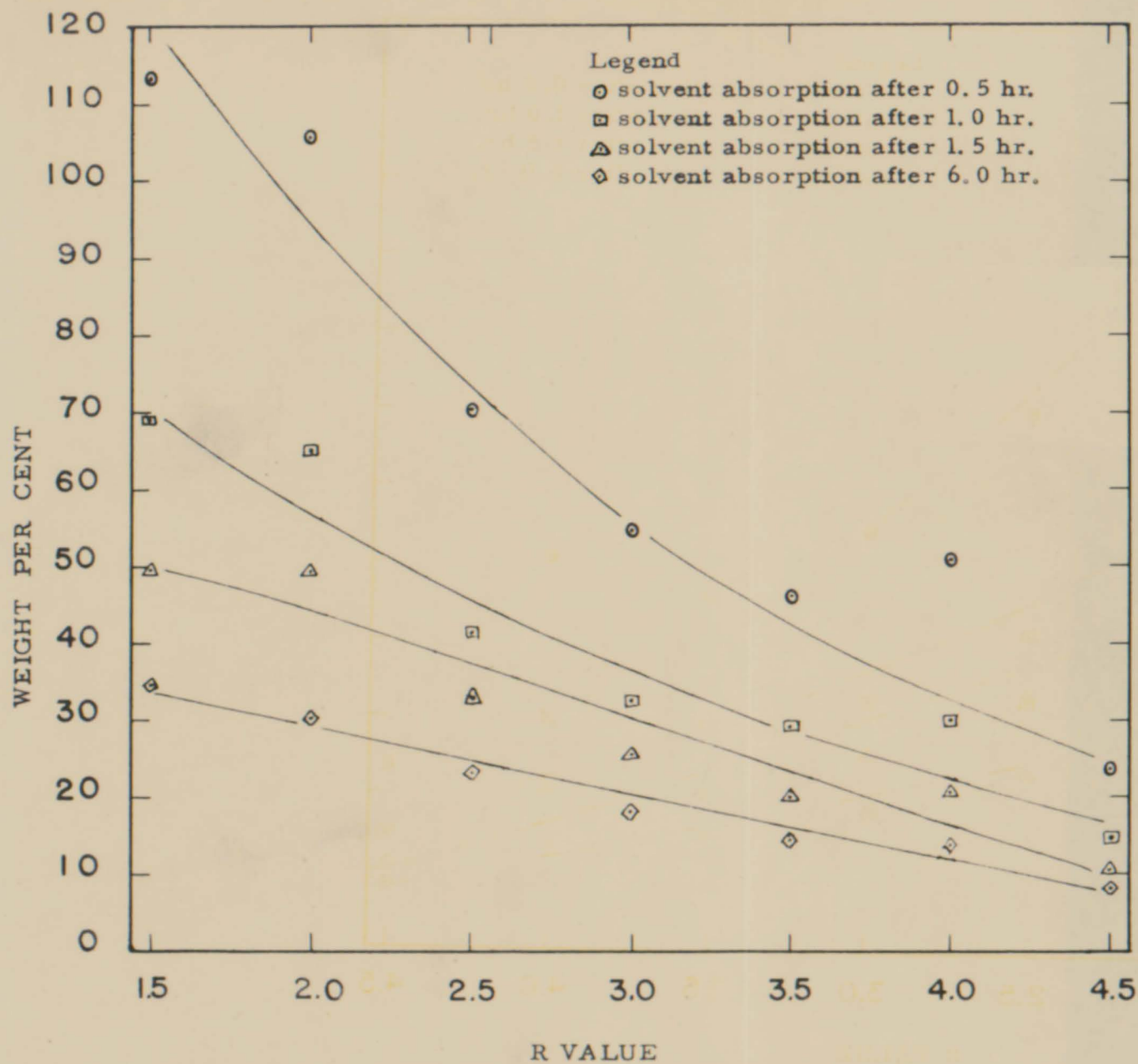


FIGURE 13 EFFECT OF TIME ON THE ABSORPTION OF ACETONE

Table XXIII

## Determination of the Swelling of Polyurethane Elastomer in Acetone Solution

## Test Series 1

Sample No.	R Ratio	0 Hour				1 Hour				1.5 Hours				2 Hours				20 Hours				
		Diameter <sub>-1</sub> in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter <sub>-1</sub> in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter <sub>-1</sub> in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter <sub>-1</sub> in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter <sub>-1</sub> in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	
PT-58	1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PT-52	1.5	2.17	20.57	96.864	0	2.493	25.37	157.375	61.780	2.577	25.97	172.909	78.507	2.661	26.57	188.142	94.233	3.213	30.43	314.129	224.300 <sup>a</sup>	
PT-78	2.0	2.338	23.33	127.522	0	2.567	26.73	175.589	77.633	2.742	27.87	209.387	64.196	2.912	28.37	240.598	88.656	3.103	32.67	314.579	146.686	
PT-66	2.5	2.390	27.97	136.917	0	2.553	26.54	165.739	76.425	2.727	27.15	201.915	47.473	2.763	27.57	210.469	53.720	3.143	31.20	308.225	125.118	
PT-55	3.0	2.633	21.00	145.593	0	2.810	24.14	190.609	70.919	2.945	24.60	139.112	36.759	2.868	24.77	203.733	39.933	3.217	29.23	302.501	107.772	
PT-56	3.5	2.540	22.55	145.493	0	2.707	24.27	177.024	21.672	2.880	24.75	205.277	41.091	2.891	24.99	208.882	43.569	3.220	27.53	285.431	92.142	
PT-57	4.0	2.397	23.47	128.631	0	2.658	24.98	175.777	36.652	2.737	25.13	188.249	46.348	2.790	25.88	201.450	56.611	3.158	30.02	299.390	132.751	
PT-59	4.5	2.577	24.17	173.202	0	2.823	25.15	200.420	15.715	2.882	25.43	211.374	22.039	2.900	25.60	215.296	24.303	3.120	28.30	273.472	59.047	

<sup>a</sup> Volume per cent of the sample after 24 hours.

Testing temperature = 75° F.



TABLE XXIV

## Determination of the Swelling of Polyurethane Elastomer in Acetone Solution

## Test Series 2

Sample No.	Chain Extending mole	0 Hour				1 Hour				2 Hours				4 Hours			
		Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %
PT-75	0.028 <sup>a</sup>				0												
PT-73	0.026	2.47	20.47	124.867	0	2.773	23.53	80.946	44.911	3.13	26.33	258.034	106.732	- <sup>a</sup>	-	-	-
PT-74	0.024	2.35	20.27	111.951	0	2.703	23.73	173.371	54.863	2.94	27.10	235.364	110.238	3.17	31.0	311.519	178.264
PT-63	0.022	2.18	23.30	110.722	0	2.493	26.53	163.765	47.907	2.657	28.50	201.210	81.725	2.86	30.9	252.762	128.285
PT-77	0.018	2.383	22.43	127.380	0	2.633	25.60	177.485	39.335	2.883	27.80	231.074	81.405	3.023	31.97	292.174	129.370
PT-64-a	0.014	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PT-64-b	0.010	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PT-64-c	0.006	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

No product obtained on PT-64-a, PT-64-b, PT-64-c.

a Sample dissolved.

Testing temperature = 75° F

Table XXV

## Determination of the Swelling of Polyurethane Elastomer in Acetone Solution

## Test Series 3

Sample No.	Chain Extending mole	0 Hour				1 Hour				2 Hours				4 Hours				9.5 Hours			
		Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %	Diameter in. x 10 <sup>-1</sup>	Length in. x 10 <sup>-2</sup>	D <sup>2</sup> x L	Vol. %
PT-71	0.060	2.581	19.58	130.442	0	2.768	21.93	168.028	28.814	2.690	22.30	161.363	23.705	-	-	-	- <sup>a</sup>	-	-	- <sup>a</sup>	-
PT-66	0.052	2.525	22.78	145.245	0	2.690	25.58	185.097	27.438	2.740	26.37	197.986	36.118	2.763	26.83	204.793	40.998	2.927	28.63	245.273	68.869
PT-72	0.044	2.297	24.50	129.264	0	2.560	26.72	175.123	35.479	2.337	26.58	184.837	42.994	2.587	28.43	190.254	47.185	2.673	29.23	208.848	61.570
PT-68	0.036	2.377	22.20	125.430	0	2.380	24.10	136.502	8.834	2.387	24.23	138.063	10.072	2.470	25.15	153.440	22.331	2.623	26.13	179.774	43.326
PT-76	0.028	2.283	23.57	122.847	0	2.523	25.70	163.606	33.179	2.660	27.27	192.963	57.076	2.677	27.90	199.931	62.748	2.723	29.88	221.560	80.354
PT-70	0.020	2.227	19.73	97.861	0	2.585	21.62	144.465	47.619	2.550	21.87	142.221	45.332	2.507	22.97	144.367	47.523	2.630	24.40	168.775	72.464
PT-79	0.012	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

No. product obtained on PT-79

a Sample dissolved.

Testing temperature = 75° F.



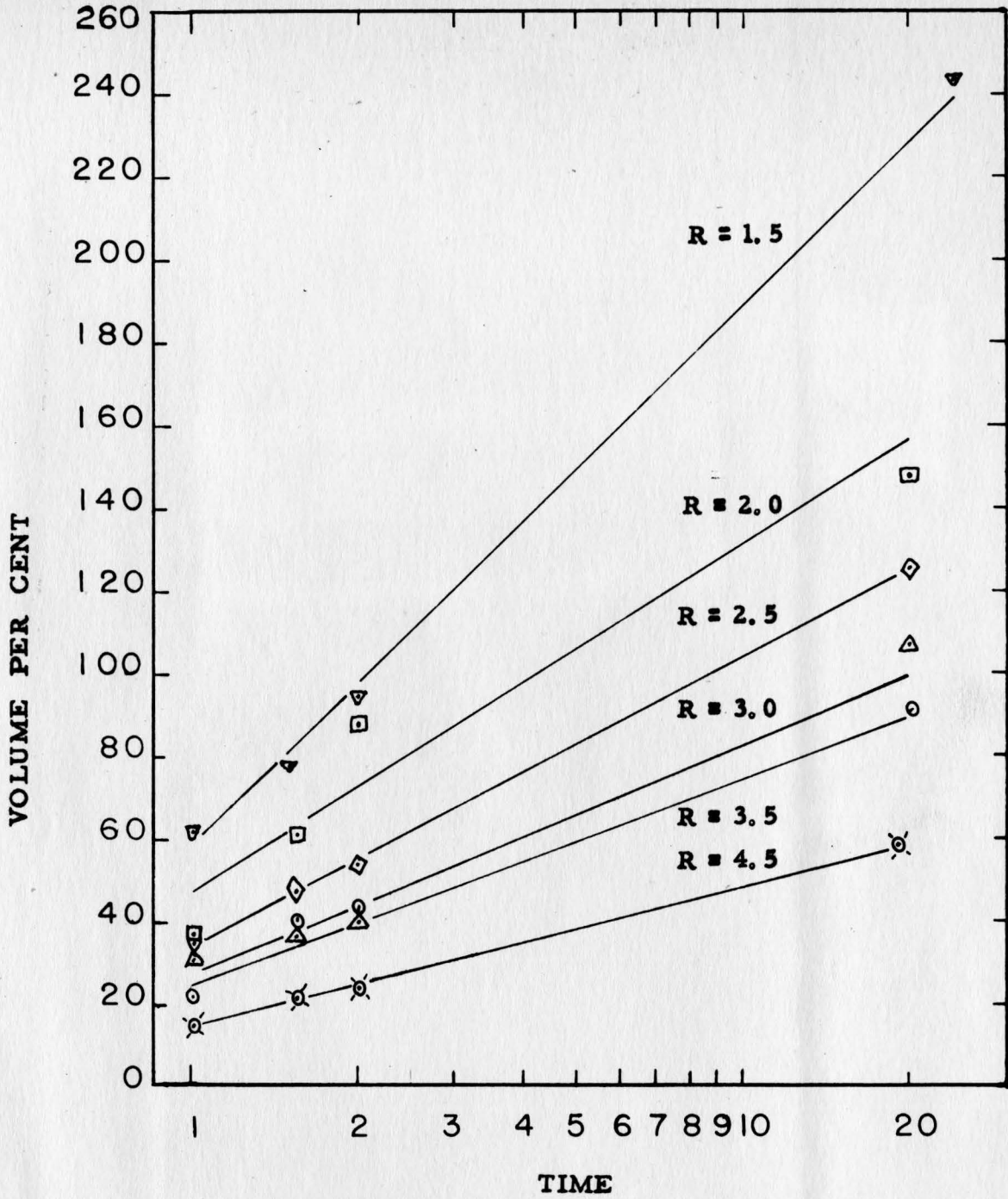


FIGURE 14 EFFECT OF R VALUE ON THE SWELLING OF  
POLYURETHANE IN ACETONE



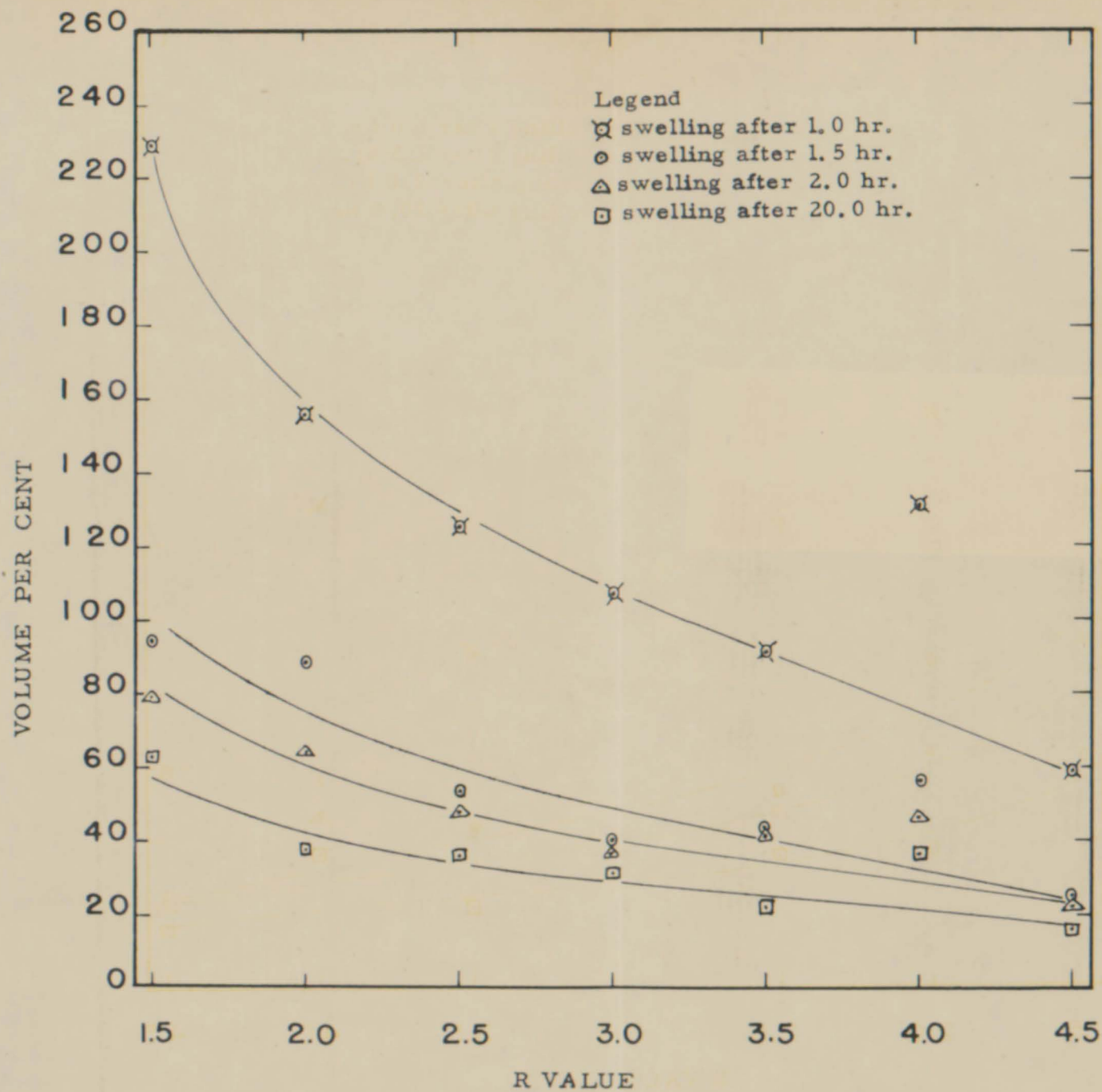


FIGURE 15 EFFECT OF TIME ON THE SWELLING OF POLY-  
URETHANE IN ACETONE

Table XXVI

## Test Data for Tensile Properties of Polyurethane Elastomer

## Test Series 1

Sample No.	R Ratio	Mean Width in.	Mean Thickness in.	Yield Stress lb./in.	200 % Elong. lb./in <sup>2</sup> .	300 % elong. lb./in <sup>2</sup> .	400 % Elong. lb./in <sup>2</sup> .	600 % Elong. lb./in <sup>2</sup> .	800 % Elong. lb./in <sup>2</sup> .	Rupture Stress lb./in <sup>2</sup> .	Young's Modulus lb./in <sup>2</sup> :	Notes
PT-58	1.0	-	-	-	-	-	-	-	-	-	-	No product obtained
PT-52	1.5	0.2665	0.2157	69.59	243.56	313.15	347.95	513.22	721.99	-	6.959	Slipped out <sup>a</sup>
PT-77	1.65	0.2457	0.2311	70.45	264.18	281.79	378.65	528.36	748.50	-	7.045	Slipped out
PT-78	2.0	0.2383	0.2196	171.99	443.34	554.18	659.18	968.58	1349.13	-	11.466	Slipped out
PT-66	2.5	0.2469	0.2551	193.61	508.10	619.24	651.00	1111.46	1381.49	-	11.115	Slipped out
PT-55	3.0	0.2501	0.2246	284.85	747.73	904.40	1068.19	1477.66	1904.93	3177.85	16.023	Ruptured
PT-56	3.5	0.2448	0.2300	426.29	1039.08	1257.55	1513.32	2078.15	2735.35	3818.38	26.643	Ruptured
PT-57	4.0	0.2475	0.2333	467.61	1082.44	1264.29	1480.78	2017.66	-	2234.15 <sup>b</sup>	30.308	Ruptured
PT-59	4.5	0.2389	0.2449	712.79	1418.96	1927.49	2378.61	3584.32	4798.23	6200.79	65.617	Ruptured

Testing condition is at the temperature of 75° F and 50 per cent relative humidity.

a Slipped out from the clamps before ruptured.

b Ruptured at 700 per cent elongation.

Table XXVII

## Test Data for Tensile Properties of Polyurethane Elastomer

## Test Series 2

Sample No.	Chain Extending mole	Mean width in.	Mean Thickness in.	Yield Stress lb./in <sup>2</sup> .	200 % Elong. lb./in <sup>2</sup> .	300 % Elong. lb./in <sup>2</sup> .	400 % Elong. lb./in <sup>2</sup> .	600 % Elong. lb./in <sup>2</sup> .	Rupture Stress <sub>2</sub> lb./in.	Young's Modulus lb./in <sup>2</sup> :	Notes
PT-75	0.028	0.2694	0.1991	200.50	484.75	554.70	646.80	1261.25	1751.77	11.181	Ruptured
PT-73	0.026	0.2571	0.196	53.15	526.80	584.49	707.68	807.46	1168.97	13.283	Ruptured
PT-74	0.024	0.2431	0.2100	55.75	313.42	391.77	421.79	548.48	-	5.877	Slipped out <sup>a</sup>
P.-53	0.022	0.2482	0.2309	87.25	331.53	348.59	400.26	436.36	-	3.490	Slipped out
PT-77	0.018	0.2457	0.2311	167.45	264.18	281.79	378.65	528.36	-	7.045	Slipped out
PT-74-a	0.024	-	-	-	-	-	-	-	-	-	No product obtained
PT-74-b	0.020	-	-	-	-	-	-	-	-	-	No product obtained
PT-74-c	0.016	-	-	-	-	-	-	-	-	-	No product obtained

Test conditions at the temperature of 75° F and 50 per cent relative humidity.

<sup>a</sup> Slipped out from the clamps before ruptured.



Table XXVIII

Test Data for Tensile Properties of Polyurethane ElastomerTest Series 3

Sample No.	Chain Extending mole	Mean width in.	Mean Thickness in.	Yield Stress lb./in. <sup>2</sup> .	200 % Elong. <sub>2</sub> lb./in.	300 % Elong. <sub>2</sub> lb./in. <sup>2</sup> .	400 % Elong. <sub>2</sub> lb./in. <sup>2</sup> .	600 % Elong. <sub>2</sub> lb./in. <sup>2</sup> .	Rupture Stress lb./in. <sup>2</sup> .	Young's Modulus lb./in. <sup>2</sup> .	Notes
PT-71	0.060	0.2582	0.2028	42.02	553.86	620.70	706.65	878.53	964.48	22.918	Ruptured
PT-66	0.052	0.2469	0.2551		508.10	619.24	651.00	1111.46	-	11.115	Slipped out <sup>a</sup>
PT-72	0.044	0.2466	0.2610	23.31	605.97	761.34	932.26	1413.96	-	12.430	Slipped out
PT-68	0.036	0.2435	0.2374	17.30	527.59	631.38	778.41	1254.46	-	12.974	Slipped out
PT-76	0.028	0.2519	0.2428	45.48	523.22	727.60	940.16	1394.18	-	9.810	Slipped out
PT-70	0.020	0.2392	0.1991	65.09	545.87	818.81	1091.75	1847.58	-	12.597	Slipped out
PT-79	0.012	-	-	-	-	-	-	-	-	-	No product obtained

Test condition is at the temperature of 75° F and 50 per cent relative humidity.

<sup>a</sup> Slipped out from the clamps before ruptured.

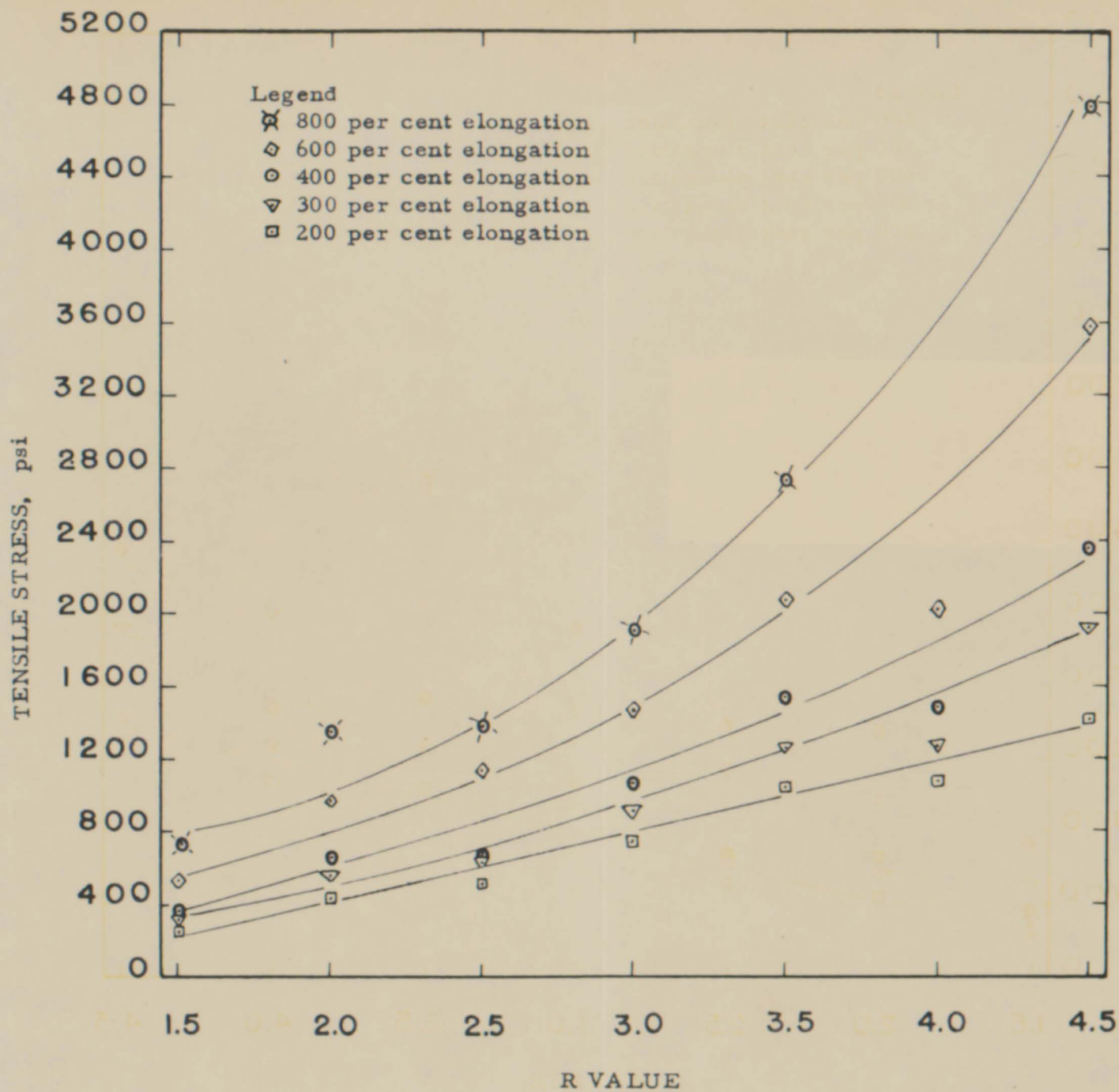


FIGURE 16 EFFECT OF R VALUE ON THE TENSILE STRENGTH OF POLYURETHANE AT DIFFERENT ELONGATIONS

penetration through the elastomer. Table XXIX, page 123, Table XXX, page 124 and Table XXXI, page 125 contained the hardness data and results at 75° F for these three series. Table XXXII, page 126 shows the data and results at 300° F for the variable R value.

Figure 17, page 127 and Figure 18, page 128 shows the comparison of the hardness for each R value at 75° F and 300° F respectively.

### Sample Calculations

Example of the major calculations used to evaluate the data and results obtained in the course of this investigation are presented in the following sections.

#### Mole of Polyester and Diisocyanate.

$$\text{mole of polyester} = \frac{\text{weight of polyester, grams}}{\text{molecular weight of polyester}}$$

$$\text{mole of diisocyanate} = \frac{\text{weight of diisocyanate, gram}}{\text{average molecular weight of diisocyanate}}$$

$$\text{mole of polyester} = \frac{8}{2000}$$

$$\text{mole of polyester} = 0.04$$

$$\text{mole of diisocyanate} = \frac{15.84}{264}$$

$$\text{mole of diisocyanate} = 0.06$$

Mole Ratio of Diisocyanate to Polyester. The mole ratio of diisocyanate to polyester is defined as R value.

$$\text{R Value} = \frac{\text{Mole of Diisocyanate}}{\text{Mole of Polyester}}$$



Table XXIX  
Hardness by Penetration  
Test Series 1

Sample No.	R Ratio	Distance travelled by needle (inch)							Maximum force	Notes
		0.025 lb.	0.050 lb.	0.075 lb.	0.100 lb.	0.125 lb.	0.150 lb.	0.175 lb.		
PT-58	1.0	-	-	-	-	-	-	-	-	No product formed
PT-52	1.5	0.8	1.8	2.7	3.7	4.9	6.7	9.0	11.4	No max. penetration
PT-77	1.65	0.9	2.0	2.9	4.0	5.4	7.2	9.4	14.8	No max. penetration
PT-78	2.0	1.1	2.5	3.8	5.3	7.1	9.4	12.5	19.6	No max. penetration
PT-66	2.5	1.1	2.6	4.0	5.7	7.9	10.2	13.4	23.9	No max. penetration
PT-55	3.0	1.2	3.7	6.2	8.9	12.3	16.2	20.9	24.2	Max. pt. at 0.1925 in.
PT-56	3.5	4.5	8.6	12.8	17.7	23.2	24.1	24.1	25.5	Max. pt. at 0.1375 in.
PT-57	4.0	5.0	9.6	14.0	19.6	25.7	24.2	24.6	27.1	Max. pt. at 0.1350 in.
PT-59	4.5	9.5	17.7	26.0	36.5	35.0	40.1	46.4	39.4	Max. pt. at 0.1088 in.

Testing condition at temperature of 75° F and 50 per cent relative humidity.

Table XXX  
Hardness by Penetration  
Test Series 2

Sample No.	Chain Extending mole	Distance travelled by needle (inch)							Maximum force
		0.025	0.050	0.075	0.100	0.125	0.150	0.175	
		lb.	lb.	lb.	lb.	lb.	lb.	lb.	
PT-75	0.028	1.6	2.4	3.2	4.0	6.2	8.7	8.2	9.3 <sup>a</sup>
PT-73	0.026	1.2	2.5	3.8	4.6	5.4	6.5	7.9	9.3
PT-74	0.024	1.0	1.8	2.6	3.1	4.0	5.2	7.1	9.1
PT-63	0.022	1.2	2.1	2.9	3.8	4.9	6.3	8.5	11.8
PT-77	0.018	0.9	2.0	2.9	4.0	5.4	7.2	9.4	14.8
PT-64-a	0.014	-	-	-	-	-	-	-	-
PT-64-b	0.010	-	-	-	-	-	-	-	-
PT-64-c	0.006	-	-	-	-	-	-	-	-

a Maximum penetration point is at 0.1650 inch.

No product obtained on PT-64-a, PT-64-b and PT-64-c.

Testing condition is at temperature of 75° F and 50 per cent relative humidity.

Table XXXI  
Hardness by Penetration  
Test Series 3

Sample No.	Chain Extending Mole	Distance travelled by needle (inch)							Maximum force lb.
		0.025	0.050	0.075	0.100	0.125	0.150	0.175	
		lb.	lb.	lb.	lb.	lb.	lb.	lb.	
PT-71	0.060	1.8	3.3	5.1	7.5	9.7	12.8	16.3	20.8 <sup>a</sup>
PT-66	0.052	1.1	2.6	4.0	5.7	7.9	10.2	13.4	23.9
PT-72	0.044	2.0	4.2	6.5	9.3	12.2	16.7	22.0	38.8
PT-68	0.036	2.6	4.9	7.8	11.1	15.3	21.0	29.0	39.2
PT-76	0.028	2.0	4.1	6.4	9.4	12.7	17.4	23.5	38.6
PT-70	0.020	2.4	5.0	8.2	12.0	17.1	25.1	-	36.4
PT-79	0.012	-	-	-	-	-	-	-	-

a Maximum penetration point is at 0.1975 inch.

No product obtained on PT-79.

Testing condition is at temperature of 75° F and 50 per cent relative humidity.



Table XXXIII  
Hardness by Penetration at 300° F

Test Series 1

Sample No.	R Ratio	Distance travelled by needle (inch)							Maximum force	Notes
		0.025 lb.	0.050 lb.	0.075 lb.	0.100 lb.	0.125 lb.	0.150 lb.	0.175 lb.		
PT-58	1.0	-	-	-	-	-	-	-	-	No product obtained
PT-52	1.5	0.5	1.3	1.8	2.2	3.0	3.9	5.6	7.0	NO max. penetration
PT-77	1.65	0.2	0.4	0.9	1.0	1.3	1.7	2.1	5.6	No max. penetration
PT-78	2.0	1.0	1.8	2.5	3.3	4.2	5.0	8.1	11.8	No max. penetration
PT-66	2.5	0.8	1.8	2.6	3.5	4.1	5.2	6.7	12.2	No max. penetration
PT-55	3.0	1.9	3.0	4.1	5.2	6.8	8.9	11.2	12.9	Max. pt. at 0.1825 in.
PT-56	3.5	2.3	4.6	6.5	8.9	11.2	13.8	14.7	19.1	Max. pt. at 0.1675 in.
PT-57	4.0	1.4	2.4	3.4	4.6	5.9	7.8	7.0	9.9	Max. pt. at 0.1700 in.
PT-59	4.5	4.6	9.1	13.0	17.8	22.4	29.0	24.0	30.2	Max. pt. at 0.1560 in.

Testing condition is at the temperature of 300° F

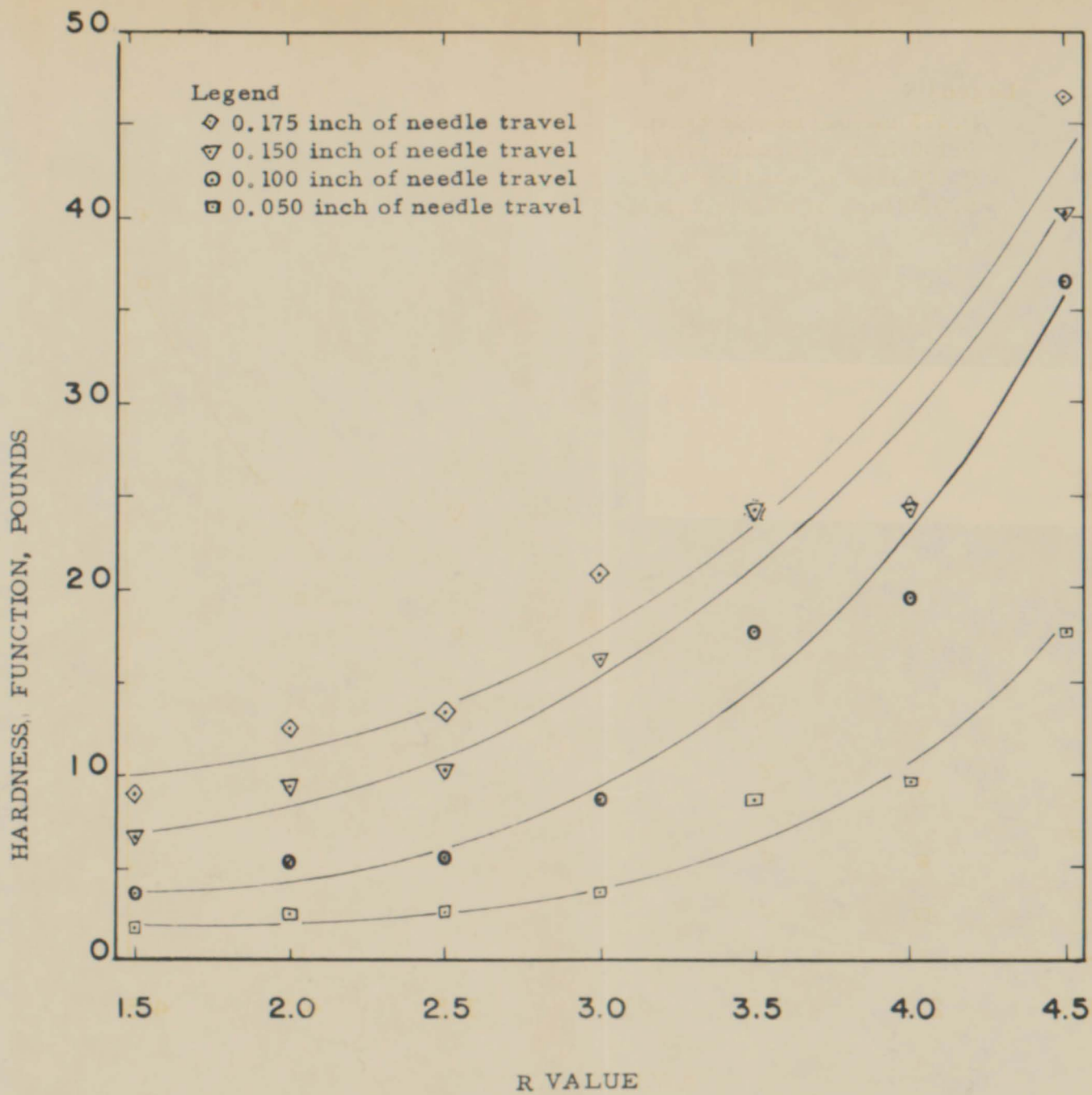


FIGURE 17 EFFECT OF R VALUE ON THE HARDNESS OF  
POLYURETHANE AT 75° F

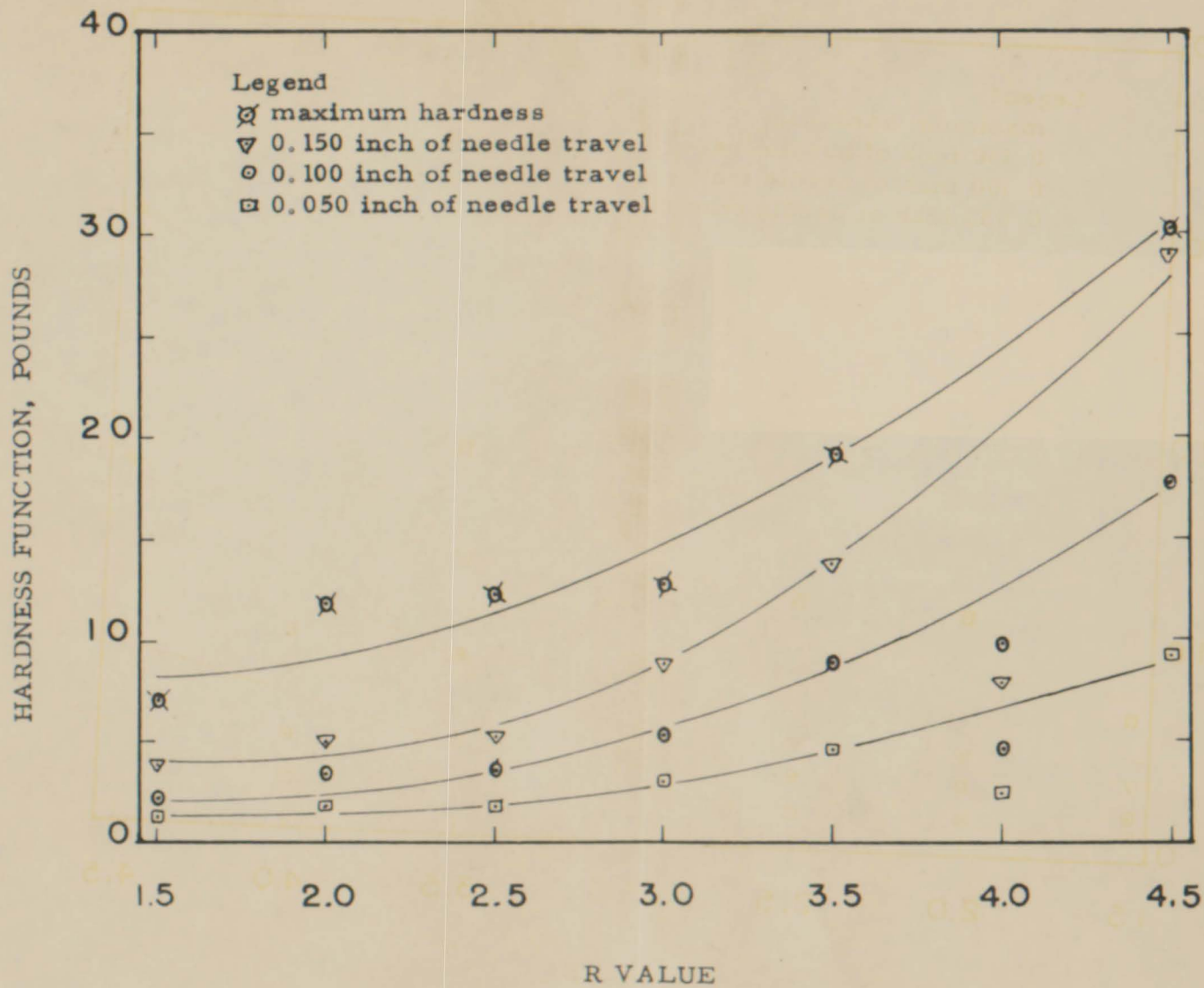


FIGURE 18 EFFECT OF R VALUE ON THE HARDNESS OF  
POLYURETHANE AT 300° F



$$R \text{ Value} = \frac{0.06}{0.04}$$

$$R \text{ Value} = 1.5$$

Excess Diisocyanate after Copolymerization Mole.

$$\text{Excess Diisocyanate} = \text{mole of diisocyanate} - \text{mole of polyester}$$

$$\text{Excess Diisocyanate} = 0.06 - 0.04$$

$$\text{Excess Diisocyanate} = 0.02$$

Excess Diisocyanate After Chain Extension, Mole.

$$\text{Excess Diisocyanate} = (D - p) - E$$

where:

D = amount of 33' Bitolylene 44' diisocyanate, mole

P = amount of polyester, mole

E = amount of cross-linking agent, ethylene glycol

$$\text{Excess Diisocyanate} = (0.06 - 0.04) - 0.012$$

$$\text{Excess Diisocyanate} = 0.008$$

Solvent Absorption in Weight Per Cent. The solvent absorption data in weight per cent increase was obtained by dividing the weight increase for the given length of time by the original weight.

$$A = \frac{W_1 - W}{W} \times 100$$

where:

A = weight per cent of solvent absorption, per cent

$W_1$  = weight of the sample specimen after immersion in the acetone solution, gram

W = weight of the sample specimen before immersion in the acetone solution, gram

$$A = \frac{0.1986 - 0.1683}{0.1683} \times 100$$

$$A = 18.0 \text{ per cent}$$

Mean Diameter and Length. The diameter and length of the sample specimen in the swelling test were measured three times for each sample specimen. The mean diameter and length are obtained by dividing the sum of each set of readings by three.

where:

$$A = \frac{A_1 + A_2 + A_3}{3}$$

A = mean diameter or length, inch

A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> = reading measurement of diameter or length, inch

$$\text{Length } A = \frac{0.2055 + 0.2055 + 0.206}{3}$$

$$A = 0.2057$$

$$\text{Diameter } A = \frac{0.218 + 0.2055 + 0.206}{3}$$

$$A = 0.217$$

Volume Per Cent of Swelling. The volume per cent swelling of the sample specimen was calculated by dividing the volume increase by the original volume.

$$A = \frac{V_1 - V.}{V.} \times 100 \quad \frac{\frac{1}{4} (D_1^2 L_1 - D^2 L.)}{\frac{1}{4} D^2 L.} \times 100$$

$$\frac{D_1^2 L_1 - D^2 L.}{D^2 L.} \times 100$$

where:

$V_1$  = volume of the specimen after immersion in the acetone solution, inch<sup>3</sup>

$V_2$  = volume of the specimen before immersion in the acetone solution, inch<sup>3</sup>

$D_1$  = mean diameter of the specimen after immersion in the acetone solution, inch

$D_2$  = mean diameter of the specimen before immersion in the acetone solution, inch

$L_1$  = mean length of the specimen after immersion in the acetone solution, inch

$L_2$  = mean length of the specimen before immersion in the acetone solution, inch

substituting data,

$$A = \frac{157.675 - 96.864}{96.864}$$

$$A = 62.780 \times 10^{-2}$$

Original Average Cross-Sectional Area for Tensile Specimen. Original average cross-sectional area was determined by multiplying the average specimen width by the specimen thickness.

$$A = m \times t$$

where:

$A$  = original average cross-sectional area, square inch

$m$  = average specimen width, inch

$t$  = average thickness of specimen, inch

substituting the data from Table XXVI, page 118.



$$A = 0.2665 \times 0.2157$$

$$A = 5.748 \times 10^{-2}$$

Tensile strength. The tensile strength of the polyurethane elastomer specimens was determined by dividing the maximum load on the specimen by the original average cross sectional area of the specimen.

$$T = \frac{L_m}{A.}$$

where:

T = Tensile strength, lbs/ sq. inch

L<sub>m</sub> = maximum load on specimen, lbs.

A. = original average cross sectional area, sq. inch

Substituting the data,

$$T = \frac{15}{5.748 \times 10^{-2}}$$

$$T = 243.56$$

Yield Stress. The yield stress of the polyurethane elastomer specimens was determined by dividing the load at the yield point on the specimen by the original average cross sectional area of the specimen.

$$Y = \frac{P}{A.}$$

where:

Y = yield stress of specimen, lbs. sq. inch

P = yield point of specimen, lbs.

A. = original average cross sectional area, sq. inch

$$Y = \frac{4}{5.748 \times 10^{-2}}$$

$$Y = 69.589$$

Young's Modulus. The Young's modulus of the polyurethane elastomer specimens was determined by the force at any point on the elastic section of the force strain curve multiplied by the original length of the specimen divided by the original cross-sectional area of the specimen times the elongation.

$$Y = \frac{f \times L}{A \times s}$$

where:

Y = Young's modulus, lbs./sq. in.

f = force on specimen, lbs.

A = original average cross-sectional area, sq. in.

L = Original length, in.

s = elongation of the specimen, in.

$$Y = \frac{4 \times 1}{5.748 \times 10^{-2} \times 0.1}$$

$$Y = 6.959$$

#### IV. DISCUSSION

The purpose of this investigation was to prepare and evaluate different degrees of cross-linkage of polyurethane elastomer formed by various ratios of diisocyanate to the polyester and the cross-linking agent, ethylene glycol. The experiments consisted of the preparation of polyurethane elastomer and testing of the sample material.

Using the results obtained during this investigation an intelligent design of the experimental unit was possible. On the basis of the results and unit design from preliminary study, recommendations have been made concerning further experimental work and a process of preparation of the polyurethane elastomer has been outlined. Limitations of the experiments have also been considered for the purpose of defining the operational and natural boundaries.

##### Discussion of Polymerization Process

Since the available literature lacks almost entirely any information concerning the elastomeric copolymer of 33' Bitolylene 44' diisocyanate and polyester of adipic acid and ethylene glycol, the reaction and process were studied and determined by preliminary experimental study. Also the limitations imposed by the lack of equipment and facilities particularly suited to reaction and processes are discussed in this section. Each step of the preparation, copolymerization, chain extension, molding and curing has been considered separately.



Copolymerization of Polyurethane Elastomer. The copolymerization of 33' Bitolyene 44' diisocyanate and the polyester of adipic acid ethylene glycol was performed by bulk polymerization. A disadvantage of this process was the fact that as the polymerization proceeds the dissipation of exothermic heat of reaction becomes increasingly difficult by virtue of the increasing viscosity. The resulting temperature gradients and local superheating create a situation of poor control over the size distribution, the average molecular weight and the color of product. For this reason, the polymerization must be carried out in small batches. The maintenance of a relatively low temperature is recommended during this reaction step. Naturally, rapid agitation is necessary for good temperature distribution. For this investigation 80 grams of polyester was used as the basis for each batch. A 2000 cc. resin kettle was used. The polymerization at any temperature above 150° C was to be avoided, and temperature range from 85° C to 150° C was suitable. In fixing the reaction temperature, the reaction time desired at a particular temperature was the main factor.

Chain Extension of Ethylene glycol. For chain extension, extremely high temperature is also unsuitable, because side reactions and decomposition of diisocyanate functional group will result. On the other hand at a temperature above 150° C the cross-linking reaction goes very rapidly, and the control of this reaction was almost impossible at this high temperature. For this particular reaction of this investigation, 125° C was found to be the most suitable temperature condition.

Molding of Polyurethane Elastomer. At the stage of copolymerization and chain extension viscosity of the polymer increased very rapidly, and became a sticky mass. A large quantity of air bubbles formed in the material as a result of rapid agitation. Hence, a simple hot mold process was not capable of releasing the air bubbles and forming a clear elastomer sheet. To overcome this difficulty a three step process was developed consisting of casting, cold molding and hot molding. Casting was carried out at  $110^{\circ}$  C in an oven for 30 minutes. Reaction of cross-linking was controlled to increase step by step by means of this three step process. During the casting process the cross-linking reaction proceeded partially, the material changed from a high viscosity thixotropic liquid to a crumbly foam rubber-like solid. The reaction temperature of  $110^{\circ}$  C and time of 30 minutes was used to control and to avoid the high degree of cross-linkage. When the temperature was too high or the time was too long, the high extent of cross-linkage was obtained at the surface of sheet as well as through every part of sheet, then an air bubble in the material was impossible to remove in the next step of the process. In case of an extremely high temperature such as  $195-200^{\circ}$  C local overheating and decomposition occurred.

Cold molding was performed by applying hydraulic pressure on the disc of foam rubber-like material at  $24^{\circ}$  C. Air bubbles were removed generally in this stage. This was classified as a simple mechanical effect. Yet, considerable amounts of air bubbles were still left in this rubber-like material.

Hot molding was conducted at 125° C for 20 minutes with hydraulic pressure at 4000 pounds per square inch gage. The cross-linkage was generally completed at this stage. The temperature of hot molding was maintained in the range of 110-140° C to attain the most favorable condition. The temperature of 125° C yielded the best elastomer product of this investigation. At this temperature, the air bubbles can be removed completely and the color of the product is very uniform.

Curing of Polyurethane Elastomer. Polyurethane elastomer sheets from hot molding were cured at 110° C for 12 hours to yield the final elastic products. With this treatment the cross-linking reaction of the product was completed. Because the elastomer became thermoset after treating by molding and curing, no solubility and softening properties will be found after these processes except thermal decomposition at extreme high temperature. Curing temperature above 150° C should be avoided because of local overheating.

Summary of the Process Conditions. The conclusions reached on the bases of this preliminary work were that the most favorable conditions were summarized in this section.

The preparation of polyurethane elastomer by bulk polymerization was conducted as copolymerization of polyester of ethylene glycol-adipate and 33' Bitolyene 44' diisocyanate. The reaction was carried out at atmospheric pressure and 130° C, for a period of 30 minutes with mechanical agitation. Chain extension was propagated by the use of ethylene glycol at 125° C for four minutes with



rapid mechanical agitation. For the molding process, casting, cold molding and hot molding were combined. In this preparation; the casting step was conducted at 110° C for 30 minutes; the cold molding step was conducted at 24° C under 4000 pounds per square inch gage pressure, for 10 minutes; the hot molding step was conducted at 125° C, at 4000 pounds per square inch gage pressure for 30 minutes; and the curing step was conducted at 110° C for 12 hours.

### Discussion of Results

The various degrees of cross-linkage which were obtained by using various ratios of diisocyanate to the polyester and cross-linking agent, ethylene glycol, were macroscopically evaluated by means of the tests of physical properties. The tests of physical properties consisted of a solvent absorption test, a swelling test, a tensile properties test and a hardness test. The results of this experimental work were used in the interpretation and evaluation of the effects of different degrees of cross-linkage.

#### Varying R Values, the Mole Ratio of Diisocyanate to Polyester.

The varying mole ratios of 33' Bitolyene 44' diisocyanate to polyester were 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5. The amount of cross-linking agent, ethylene glycol was adjusted in order to obtain the same amounts of excess diisocyanate after the chain extension. For R value at 1.0 (the mole ratio of diisocyanate to polyester), no product formed in this process, because an excess of the diisocyanate functional groups was needed for chain extension and cross-linking.

Hence, for R value of 1.0, there was no excess diisocyanate functional group concerned. No cross-linking was carried out in this process, no cross-linkage occurred at the molding stage, and the material became wax-like upon cooling down to room temperature. This material was characterized as a rigid thermoplastic with brittle behavior at room temperature. With the use of an excess of greater than 400 per cent (R value over 5) diisocyanate the product became so inelastic that it was characterized as a rigid urethane, because the cross-linkage was beyond the range of an elastomer. Considering the overall relationship of diisocyanate to polyester, the excess of isocyanate was controlled so that a chain lengthening occurred, then further increased the amount of diisocyanate which would repress the chain lengthening reaction and so increase the concentration of free isocyanate groups. If an excess of 100 per cent (R value of 2) over the amount of calculated diisocyanate is used essentially no chain-lengthening occurs, and the effect consists simply of converting the hydroxyl polyester to an isocyanate polyester.

Further increasing the amount of diisocyanate in the presence of unreacted diisocyanate in the mixture and subsequent treatment with cross-linking agents such as ethylene glycol affects a coupling of diisocyanate polyester through urethane bridges. Free diisocyanates react to form polyurethanes. Since, in general, a molecular deficiency of cross-linking agent with respect to free isocyanate groups is used, there are always free isocyanate groups remaining, which react with

the urethane groups to establish cross-linking. The finished product may, therefore, be considered as a polyurethane into which polyester units which function as softeners are built.

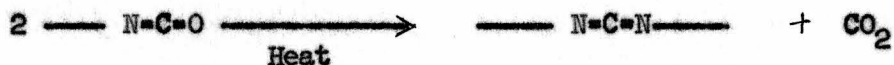
By use of 150-200 per cent excess (R values of 2.5-3.0), a considerable increase of the physical properties occurs in comparison to that of the elastomer with R values of 1.5 to 2.0. By further increasing the diisocyanate and cross-linking agent to 300-350 per cent excess (R values of 4.0 to 4.5), the elasticity and elongation properties decrease, while the hardness increases, and greater tensile strengths are obtained.

A Constant R Value with Varying Amount of Cross-linking Agent, Ethylene Glycol. A constant value of the mole ratio of diisocyanate to polyester was maintained while varying the amounts of cross-linking agent, ethylene glycol. For a ratio of diisocyanate to polyester of 1.65 (R value of 1.65) the moles of cross-linking agent, ethylene glycol used were 0.028, 0.026, 0.024, 0.022, 0.020, 0.018, 0.014, 0.010 and 0.006 moles. To obtain the results of this investigation, the amount of glycol must be so controlled that the hydroxyl groups are not stoichiometrically equivalent to the isocyanate groups. That is, there must be a certain excess of isocyanate present in every case. If there is an excess of ethylene glycol, products are obtained which are thermoplastic and of higher elongation than desired. With decreasing amounts of ethylene glycol, the desirable physical properties of the condensation product improve at first. Finally, beyond a certain isocyanate content, side reactions set in which are apparently reactions



of isocyanate groups with each other. They are characterized by gas formation and occurred at 0.014, 0.010 and 0.006 mole of ethylene glycol used. No elastomeric products were obtained in this series of preparations.

The chemistry of this gas formation (blowing) which was caused by the reactions of isocyanate groups with each other, can be considered as reaction of two moles of isocyanate functional groups with the splitting out of a mole of carbon dioxide, the reaction is shown as follows:



A Constant R Value of 2.5 with Varying Amount of Cross-linking Agent, Ethylene Glycol. The constant value of the mole ratio of diisocyanate to polyester was 2.5 (R value of 2.5) and the various amounts of cross-linking agent, ethylene glycol, used were from 0.060, 0.052, 0.044, 0.036, 0.028, 0.020, and 0.012 mole. Physical properties of these products were similar to those described in the previous section. The formation of gas (blowing) occurred in the batch with 0.012 mole of ethylene glycol.

The Solvent Absorption Properties for Varying R Values (test series 1) of Polyurethane Elastomer. The weight per cent of acetone solvent absorbed at 75° F decreased in relation to an increase of the R value at each time for the test. For instance, for the sample specimen with an R value of 1.5, the weight per cent increase was from 18.0 per cent to 112.9 per cent during test period from 10 minutes to six

hours of immersion. For an R value of 4.5, the weight per cent increase was from 4.52 per cent to 23.65 per cent during the same period of time. The results were given in Table XX, page 108, Figure 12 and 13, page 111 and 112. The R values between these two extremes have percentage weight increases corresponding to their intermediate R value. There was, however, a slight deviation at the R value of 4.0

The theoretical interpretation of the solvent absorption and consequently the swelling indicates that the per cent increase is a function of decreasing cross-linkage. This is because the solvent will decrease the secondary attractive force (bridges) and hydrogen bonds between two main chains and result in the solvent absorption and swelling. If no cross-linkage or very little cross-linkage exists in the polymer, the material is characterized as a thermoplastic and is dissolved in the solvent.

For the R value of 4.0 from the results of this investigation, the weight per cent increased irregularly in comparison to the other R values. It appears that there is less cross-linkage present than in the case of the R value of 3.5. This is very likely caused by an accidental error during the preparation of the sample material.

The Swelling Properties of Varying R Values (Test Series 1) of Polyurethane Elastomer. The swelling of the elastomer in acetone solvent at 75° F decreased in relation to increasing R values for each test. The Table and Figure showing this effect are Table XXIII, page 113 Figure 14 and 15, page 116 and 117. For an R value of 1.5, the per cent of increase in swelling was from 62.78 per cent to 224.3 per cent

for a swelling time on from one to 24 hours. For an R value of 4.5 the per cent of increase in swelling is from 15.715 per cent to 57.047 per cent, when the swelling time is from one hour to 20 hours. It is interesting to note that the rate of swelling decreases greatly at a higher R value than a lower R value as the time of immersion increases, because the greater amount of cross-linkage will decrease the rate of swelling. The theoretical viewpoint of swelling is as described in a previous section. It is affected by the relative amount of cross-linkage in the elastomer. These results are similar to those of the previous section in that the R value of 4.0 of swelling test yielded an abnormal result. It is believed that an accident during the process of preparation was the cause of this abnormality.

The Tensile Properties for Various R values (Test Series 1) in a Polyurethane Elastomer. The tensile properties of the polyurethane elastomer were increased to relate the tensile properties to the relative size of the R value. The tensile properties were determined by using a Tinius Olsen Tensile Machine in the Wood Construction Laboratory of Virginia Polytechnic Institute. This machine was originally designed for determining the tensile and compression properties of wood and steel. The elongation limit for one cycle is less than 100 per cent. When elastomeric material is to be tested a modified technique must be used for testing because of great elongation. Even with modification rupture stress still could not be obtained with this machine with R values of 1.5, 1.65, 2.0 and 2.5. These



elastomer sheets were very flexible and great elongation was possible. A difficulty encountered during the testing procedure was that there was not a suitable clamp that would hold the specimen ends without slipping. Because of this no ruptured stress data were obtained for the R values of 1.5, 1.65, 2.0 and 2.5 in this investigation. However, the tensile properties at 200, 300, 400, 600 and 800 per cent elongation were obtained with satisfactory results. For an R value of 1.5, the tensile strength increased from 243.56 pounds per square inch original cross sectional area to 721.99 pounds per square inch as the elongation increased from 200 per cent to 400 per cent, and for an R value of 4.5, the tensile strength increased from 1418.96 pounds per square inch to 4798.23 pounds per square inch. For R values of 3.0, 3.5, 4.0, and 4.5, the ruptured stress values were obtained. The ruptured stress value increased from 3177.85 pounds per square inch to 6200.79 pound per square inch with increasing R values from 3.0 to 4.5. On the contrary, the per cent of elongation at rupture decreased with the increase of R value. The results are presented in Table XXVI, page 118, Figure 16, page 121.

On the theoretical interpretation of the tensile properties, these were not entirely a function of chemical cross-linking. The forces affecting the tensile properties can be divided into three types. These are cross-linking (primary bonding force), intermolecular force (Secondary bonding force) and hydrogen bonding, especially for the long molecular chains like these polymers. Hydrogen bonding and intermolecular forces contribute to a large degree to the ultimate

properties of the high polymers. So the physical properties are apparently affected primarily by intermolecular forces, hydrogen bonding and cross-linking.

At the R value of 4.0 the results of this investigation indicated an irregularity which gave the appearance of reduced cross-linkage and a smaller average molecular weight than the results for R values of 3.5 and 4.5. This was believed to be the result of an error during the preparation of the sample material.

The Hardness by Penetration for Polyurethane Elastomers of Various R value (Series 1) at 75° F. The hardness by penetration values increased with respect to the increase in the R values at each degree of penetration. This test was conducted at several degrees of penetration. The depth of penetration is the distance travelled by the needle head, with readings taken at 0.025, 0.050, 0.075, 0.100, 0.125, 0.150 and 0.175 inch of needle head penetrated. The maximum penetration was also obtained. This testing device was constructed by modifying an A. S. T. M. durometer hardness tester design. No standard values of hardness were obtained for this test, and only the relative value of hardness for purposes of comparison of hardness values for the variation in the R value of each elastomer

The data and results are shown in Table XXIX, page 123, and graphically in Figure 17, page 127. For an R value of 1.5, the pounds force required was 0.8 pounds to 9.0 pounds for the distance of penetration from 0.025 inch to 0.175 inch. For an R value of 4.5 the pounds mass required for penetration was from 9.5 pounds to 46.4

pounds, respectively. No maximum penetration values were obtained on the smaller R values, such as 1.5, 1.65, 2.0 and 2.5 sample specimens which were very flexible compared to the others. However, the maximum penetration values were obtained for the R values of 3.0, 3.5, 4.0 and 4.5. It is also interesting to note that the distance of penetration at the maximum penetration decreased with respect to an increase in the R value. The maximum penetration load was from 24.2 pounds to 39.4 pounds as R values varied from 3.0 to 4.5, and the distance penetrated by the needle head at the maximum penetration load decreased from 0.1925 inch to 0.1088 inch, respectively.

The increase in hardness is a function of the amount of cross-linkage. There is an increase in the average molecular weight to a considerable degree while on the other hand an increase of cross-linking will act to prevent slipping between two molecular chains due to external movement or force. These two factors are considered to be the main factors that affect the hardness of the elastomer in this investigation.

The Hardness by Penetration for Polyurethane Elastomers of Various R value (Test Series 1) at 300° F. The hardness by penetration values increased with respect to the increase in the R values for each degree of penetration at this temperature. The methods and procedures of this test followed those described in the previous section. The data and results are shown in Table XXXII, page 126, and illustrated in Figure 18, page 128. For the R value of 1.5, the pounds force required for penetration was from 0.5 pounds to 5.6 pounds for distances



of penetration of 0.025 inch to 0.175 inch, respectively. For an R value of 4.5, the pounds mass required for penetration was from 4.6 pounds to 24.0 pounds, respectively. No maximum penetration data was obtained at the smaller R values, such as 1.5, 1.65, 2.0 and 2.5. For this part of the test series the sample specimen was more flexible compared to the others at 75° F. However, the maximum penetrations were obtained for the R values of 3.0, 3.5, 4.0 and 4.5, the maximum penetration values ranging from 3.0 to 4.5. The depth of penetration at maximum penetration decreased with respect to an increase in the R value. The depth of penetration varied from 0.1825 inch to 0.1560 inch. Overall results from these investigations of the hardness at these two temperatures showed that the hardness decreased rapidly when the temperature increased to 300° F. And the per cent of maximum penetration decreased with an increase in the R value for both temperatures. The per cent of maximum penetration was from 87.5 per cent to 30.42 per cent for an R value increase from 3.0 to 4.5.

From the theoretical viewpoint an increase in temperature should cause an increase in the potential energy of the polymer molecular so that the molecules become activated and the external mobility of the molecule will increase comparatively. Then the polymer chains tend to slip and the hardness decreases at a higher temperature. Hence, a higher degree of cross-linkage possesses a stronger ability to prevent this external movement, therefore, a cross-linkage increase will decrease the relative hardness at a given temperature. In the test of hardness at 300° F the operating technique caused several errors in the data.

The Solvent Absorption Properties of the Elastomers Having R Values of 1.65 with Varying Amounts of Cross-linking Agent, Ethylene Glycol. The solvent absorption at 75° F for the elastomer with an R value of 1.65 and amounts of cross-linking agent, ethylene glycol varying from 0.028 mole to 0.006 mole was used. After four hours of immersion, the weight per cent of absorption was decreased first from 138.5 per cent to 93.4 per cent, then again this value increased to 111.5 per cent when the cross-linking agent, ethylene glycol, was decreased from 0.024 mole to 0.022 mole and then to 0.018 mole. For this series of tests the cross-linking agent used between 0.022 and 0.018 mole is considered to be the most favorable range. Beyond this uppermost value, the polymers were characterized by gas formation (blowing), because of side reactions which occurred during the molding step. The chemistry of this side reaction has been described in a previous section. On the other hand the samples made with 0.028, 0.026 and 0.024 mole of cross-linking agent dissolved in acetone during the test, and the rate of solution was increased with respect to the increased amount of cross-linking agent used which was in the order of 0.024, 0.026 and 0.028 mole. This is apparently because the excess of diisocyanate functional groups was controlled by the amount of cross-linking agent to obtain an elastomer with no functional or very few functional groups which would form cross-linking bonds. So these elastomers are classified as linear polymers since they are soluble in the solvent. The data and results are presented in Table XXI, page 109.

The Solvent Absorption For R Value of 2.5 with Various Amounts of Cross-linking Agent. The solvent absorption was carried out at 75° F, the amount of cross-linking agent, ethylene glycol, used ranged from 0.060 to 0.012 mole. The solvent absorption after 9.5 hours varied from 103.9 to 53.4 per cent as the amount of cross-linking agent varied from 0.052 to 0.012 mole. For this series of tests, the amount of cross-linking agent between 0.028 to 0.020 is considered to be the most favorable range. Beyond the upper value, the polymer suffered side reactions (gas formation). However, the sample which was formed by the reaction with 0.060 mole of cross-linking agent dissolved in acetone solvent during the absorption test. It is apparent that no or very few cross-linking bonds had been formed in this elastomer because the isocyanate functional groups had all reacted with the ethylene glycol. So this elastomer is classified as a linear polymer, which, of course, dissolved in the solvent. The data and results are presented in Table XXII, Page 110.

Swelling Properties for the Constant R value of 1.65 and 2.5 with Various Amount of Cross-linking Agent. The swelling properties at 75° F for an R value of 1.65 were determined. The amount of cross-linking agent, ethylene glycol, used in the chain extension varied from 0.028 to 0.006 mole. The volume per cent swelling increase for 4.0 hours immersion was from 178.264 to 129.37 per cent. For amounts of cross-linking agent, ethylene glycol, 0.024, 0.022 and 0.018 mole the swelling decreased first then increased to 129.370 volume per cent. For this series of tests the amounts of cross-linking agent of 0.022



and 0.018 mole were considered to be the range which gave the smallest swelling increase. Beyond this amount of cross-linking agent the elastomer was characterized as a thermoplastic which suffered from gas formation as described in a previous section. The data and results are presented in Table XXIV, page 114.

For the elastomer having R value of 2.5 with the amount of cross-linking agent used from 0.060 to 0.012 mole the volume per cent increase by swelling for immersion of 9.5 hours decreased from 68.689 per cent with 0.052 mole to a minimum value, then increased to 72.262 per cent with 0.020 mole. A test of the polymer with 0.012 mole could not be made because the polymer could not be molded on account of gas formation. From the standpoint of swelling properties it was considered that the copolymer reacted with 0.036 mole of cross-linking agent was the best. The results of these tests reveal that the use of an amount of cross-linking agent greater than 0.036 mole causes an excess of isocyanate functional groups which is large enough to start side reactions and cause a decline of the desirable physical properties.

Tensile Properties at Constant R values of 1.65 and 2.5 with Various Quantities of Cross-linking Agent. The tensile properties were tested at 75° F. For the R value of 1.65 the quantities of cross-linking agent, ethylene glycol, were from 0.028 to 0.006 mole. The tensile properties at 600 per cent elongation were such that the tensile stress was a function of the quantity of cross-linking agent, varying from 1261.25 pounds per square inch to 528.36 pounds per square inch, for quantities of cross-linking agent varying from 0.028 mole to 0.018

mole. As described in a previous section, the major factors affecting the tensile strength were considered to be intermolecular forces, hydrogen bonding and cross-linking. For an R value of 1.65, chain length of the copolymer is rather long in comparison to the high R value, hence, the intermolecular as well as the hydrogen bonding forces contribute in a large degree to the ultimate macroscopic physical properties. These physical properties were apparently affected to a greater degree by hydrogen bonding forces and intermolecular forces than by cross-linking.

For an R value of 2.5 the amount of cross-linking agent, ethylene glycol, used in this test series varied from 0.060 to 0.020 mole. The tensile strength of 600 per cent elongation varied from 878.53 pounds per square inch to 1847.58 pounds per square inch with respect to corresponding quantities of cross-linking agent varying from 0.060 mole to 0.020 mole in the elastomer. The best condition from the standpoint of tensile properties was at 0.02 mole of ethylene glycol, cross-linking agent in the elastomer. At this value apparently the tensile strength was in the main determined by the intermolecular attractions, hydrogen bridge and cross-linking.

The Hardness by Penetration for the Elastomer with Constant R Values of 1.65 and 2.5 with Various Quantities of Cross-linking. The hardness by penetration tests were conducted at 75° F, using 0.175 inch of needle head travel for R value of 1.65. The pounds mass required for penetration decreased from 8.2 pounds to 7.1 pounds then increased to 9.4 pounds, with the corresponding quantities of cross-linking agents

used varying from 0.028 to 0.018 mole. The best condition from the standpoint of hardness was considered to be when the quantity of ethylene glycol used was 0.018 mole.

For an R value of 2.5, similar results were obtained when the quantity of cross-linking agent used was from 0.060 to 0.020 mole. The pounds mass required for a penetration of 0.150 inch of needle head travel varied from 12.8 pounds to 10.2 pounds then to 25.1 pounds. The quantity of cross-linking agent of 0.020 mole yielded the better value which was the most favorable condition of this test series.

As discussed in a previous section the intermolecular attraction and the amount of cross-linkage primarily affected the hardness. The hardness of the sample with 0.060 mole of cross-linking agent was considered to be due to the intermolecular attraction primarily.

#### Recommendations

As a result of the investigation dealing with the preparation and the testing of the physical properties of polyurethane elastomers, the following recommendations are offered.

Process and Preparation of Polyurethane Elastomer. The copolymerizations of 33' Bitolylene 44' diisocyanate and ethylene glycol-adipate polyester were conducted in a resin kettle. It is recommended for bulk polymerization, that using a shallow tray will improve the heat transmission of the system aiding in the uniform reaction of the polymer



during copolymerization and chain extension. A vacuum system would improve the molding processes, a pressure of 50-75 mm of mercury should be maintained. This should result in the removal of air or gases evolved during the polymerization step.

Molding and Curing Processes. For this investigation the molding process involved the use of a combination of casting, cold molding and hot molding. The process was rather complicated and inconvenient. For large scale preparation the author recommends the copolymer be milled after cooling instead of cast and cold molded. Because for an R value over 3.0 the linear copolymer at the room temperature is very soft and viscous, it is impossible to conduct the operation by milling. For an R value over 3.0, the diisocyanate should be added in two steps. Initially, the amount of diisocyanate to polyester should be adjusted to maintain the R value at 1.0 to 2.0, then the remainder of the calculated amount of diisocyanate should be added at the milling stage. Then the polymer passes to hot molding and curing stages.

Specimen Cutter. A specimen cutter should be obtained to assure uniform specimens for the tensile tests. Since the polyurethane elastomer is particularly tough, a specimen cutter is absolutely necessary for any further work along the lines of this investigation.

Tensile Strength Machine. Obtain a tensile strength machine for elastomeric material. The tensile strength machine used in this investigation was a Tinius Olsen Tensile Machine which is designed for testing steel and wood material. The maximum elongation for one cycle was 100 per cent elongation. No suitable clamps to hold the elastomeric

specimen were available, so no ruptured stress data could be obtained for several sample specimens. If extensive investigations are to be continued in this area, the testing machine is needed.

Hardness Tester. Obtain a hardness tester. Such a device as a durometer or a Shore A hardness tester which are described in A. S. T. M. hardness testing method should be adequate. The results obtained in this investigation were not a standard method of hardness testing, but were the relative pounds mass applied by each degree or depth of penetration and the hardness tester was designed and constructed by the author in accordance with the specifications of the A. S. T. M. durometer.

Duplicate Test of R Value of 4.0. From the results of the experimental study, the R value of 4.0 yielded irregular results, such as the results of solvent absorption test, swelling test, tensile strength and the hardness test at 300° F. These results were considered to be due to an error in the experimental work. It is recommended that a duplicate test is necessary for this particular material.

Additional Standard Tests. As mentioned in a previous section, there was no ruptured stress obtained for several samples because of the inadequate clamps on the testing machine. The hardness test also yielded non-standard data. Additional standard tests using adequate testing machines are recommended.

Further Study of Polyurethane Elastomer at Various Temperatures. No information was obtained at different temperatures for the polyurethane made by copolymerization of 33' Bitolylene 44' diisocyanate

and polyester of ethylene glycol and adipic acid except for hardness. The effect of temperature on the physical properties would be a valuable and interesting study to further complete the knowledge of this elastomer. The temperature range should be from  $-50^{\circ}$  F to  $550^{\circ}$  F.

Study of the Applications of Polyurethane Elastomer. The polyurethane elastomer has certain exceptional physical properties which make it favorable for wide application. The different R values cause different degree of hardness from a flexible rubber-like material to a rigid plastic. More complete information concerning the chemistry and properties is needed for the further development of wide applications. The author recommends that the research be extended to R values as far as 8 or 10.

Absolute Value of the Degree of Cross-linking. So far no absolute degree of cross-linking determination is available to this field of research. The author is convinced that it is possible to obtain an absolute degree of cross-linkage with further refinement of phototechnology. Further study by the use of X-rays and infrared spectrum would possibly elucidate the problem although considerable experience and technique must be gained yet.

#### Limitations

The limitations on this investigation are presented in the following section. These limitations include the preparation of polymer and tests of polymer. The quantitative boundaries of concentration, temperature, time, and pressure have also been given.



Component of the Reactant. Diisocyanate, polyester and ethylene glycol are the starting materials of polyurethane elastomer. There were three testing series of polyurethane elastomers prepared.

1. Series 1; the various ratios of diisocyanate to polyester (R value) were 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5.

2. Series 2; the constant amount of R value at 1.65 was used with variable amounts of ethylene glycol from 0.006 to 0.028 mole.

3. Series 3; the constant amount of R value at 3.5 was used with variable amounts of ethylene glycol from 0.012 to 0.060 mole.

Preparation of Polyurethane Elastomer. Preparation of elastomer consisted of six steps.

1. The copolymerization was carried out at 130° C, atmospheric pressure for 30 minutes reaction time with moderate agitation.

2. The chain extension was carried out at 125° C, four minutes with rapid agitation.

3. The casting stage was conducted at 110° C for 30 minutes in the oven.

4. The cold molding stage was carried out by applying 4000 pounds per square inch gage pressure for ten minutes at 24° C.

5. The hot molding was conducted at the temperature of 125° C with 4000 pounds per square inch gage pressure for 20 minutes.

6. Curing stage was conducted by oven at 110° C for twelve hours.

Testing Conditions. All tests including the solvent absorption, swelling, tensile properties and hardness were conducted at 75° F. In addition, to these tests, hardness tests of series 1 was conducted at 300° F.

Conditioning. For tensile properties test and hardness test at 75° F, the specimens were conditioned for 72 hours at 75° F and 50 per cent humidity.

Tensile Properties Test. The tensile properties test was carried out by Tinius Olsen Testing Machine.

1. The head speed of the tensile machine was maintained at two inches per minute.
2. The maximum elongation for one cycle was maintained one inch.
3. The accuracy of machine measurements was plus or minus 0.1 pounds force.

Hardness Test by Penetration. The hardness test was carried out by Tinius Olsen Testing Machine.

1. The head speed of the tensile machine was maintained at 0.3 inch per minute.
2. The accuracy of machine measurements was plus or minus 0.05 pounds force.
3. The maximum distance of travel was set within 0.25 inch.

## V. CONCLUSIONS

This investigation dealt with the preparation and evaluation of the different degrees of cross-linkage in an elastomer. The elastomers were prepared by using different ratios of 33' Bitolylene 44' diisocyanate to the polyester of adipic acid and ethylene glycol and the cross-linking agent, ethylene glycol. This investigation consisted of six parts, specifically the preparation of the polyurethane elastomer, the absorption tests at 75° F, swelling tests at 75° F, the tensile properties tests at 75° F, the hardness tests at 75° F and the hardness tests at 300° F.

The preparation of polyurethane elastomer by bulk polymerization was conducted as a copolymerization of polyester of ethylene glycol-adipate and 33' Bitolylene 44' diisocyanate. The optimum conditions for the reaction were found to be atmospheric pressure and 130° C, for a period of 30 minutes with rapid mechanical agitation. For the molding process, casting, cold molding and hot molding were used. In this preparation the casting step were conducted at 110° C for 30 minutes; the cold molding step was conducted at 24° C under 4000 pounds per square inch gage, for ten minutes; the hot molding step was conducted at 125° C at 4000 pounds per square inch gage pressure for 20 minutes; and the curing step was conducted at 110° C for 12 hours.

A. For various ratios of diisocyanate to polyester (R value) which controlled the degree of cross-linking through the functional



groups and established the value of the excess of the isocyanate group corresponding to the quantities of ethylene glycol added, the effect was studied by a series of investigations consisting of five sections, specifically an absorption test at 75° F, a swelling test at 75° F, a tensile properties test at 75° F, a hardness test at 75° F and a hardness test at 300° F. The following conclusions were drawn from these tests.

1. The properties associated with cross-linking varied in such a way as to indicate an increase in cross-linking as the R value increased.

2. The weight per cent of acetone solvent absorbed at 75° F in one hour decreased in comparison with an increase of the R value and was in the range from 49.6 per cent to 10.81 per cent with the R values varying from 1.5 to 4.5. For six hours the range was from 112.9 per cent to 23.65 per cent with the R value varying from 1.5 to 4.5.

3. The swelling test for the various R values resulted in the per cent volume increase values decreasing with increasing R values. Swelling property of the elastomers in an acetone solvent at 75° F for two hours was such that the range of the relative volume increase was from 94.233 per cent to 24.303 per cent with the corresponding R values increasing from 1.5 to 4.5.

4. The tensile properties increased in comparison with an increase of the R value. At 300 per cent elongation the tensile strength was in a range from 313.15 pounds per square inch to 1927.49

pounds per square inch with the corresponding R values increasing from 1.5 to 4.5. For 600 per cent elongation, the range was from 513.22 pounds per square inch to 3584.32 pounds per square inch as the corresponding R values increased.

5. For the hardness test by penetration at 75° F and 50 per cent humidity, the force required increased with each degree of greater penetration. At 0.175 inch of needle head penetration, pounds mass required for penetration was from 9.0 pounds to 46.4 pounds as the R value varied from 1.5 to 4.5, respectively. The maximum penetration values were obtained for R values of 3.0, 3.5, 4.0 and 4.5 in which the pounds mass applied varied from 24.9 pounds to 39.4 pounds, respectively. The distance of needle head travel was at most 0.1925 inch and was as low as 0.1088 inch at maximum penetration, as the corresponding R values varied from 3.0 to 4.5

6. Hardness tests by penetration were conducted at 300° F. The force in pounds required increased with respect to corresponding increases in the R values for each degree or depth of penetration. At 0.175 inch of needle head penetration, pounds mass required for penetration varied from 5.6 pounds to 24.0 pounds corresponding to respective R values from 1.5 to 4.5. Maximum penetration for R values of 3.0, 3.5, 4.0 and 4.5 varied from 12.9 pounds to 30.2 pounds for corresponding variation in the R values from 3.0 to 4.5.

B. For the R value at 1.65 with a fixed excess of the isocyanate group and various amounts of ethylene glycol to provide functional cross-linking molecules or chains, this series of tests may be divided

into four sections. These are the absorption test at 75° F, the swelling test at 75° F, the tensile properties test at 75° F, and the hardness test at 75° F. The results of these tests led to the following conclusions.

1. For elastomer with R value of 1.65 the best results were obtained with 0.022 and 0.018 mole of ethylene glycol.

2. Solvent absorption with various amounts of cross-linking agent, ethylene glycol in acetone at 75° F at two hours was in the range of 80.8 weight per cent to 67.7 weight per cent for amounts of ethylene glycol from 0.026 mole to 0.018 mole, respectively.

3. The polymer prepared with 0.028 mole ethylene glycol was completely soluble in acetone at 75° F in two hours. The polymer prepared with 0.026 mole ethylene glycol was partially soluble in acetone at 75° F in four hours.

4. Swelling of polymer with various amounts of cross-linking agent, ethylene glycol in acetone at 75° F in two hours was in the range of the volume per cent increase from 106.732 per cent to 81.405 per cent for corresponding amounts of ethylene glycol from 0.026 mole to 0.018 mole.

5. At 400 per cent elongation the tensile strength was from 646.80 pounds per square inch to 378.65 pounds per square inch for corresponding amounts of ethylene glycol from 0.028 mole to 0.018 mole.

6. The hardness by penetration was conducted at 75° F. At 0.175 inch of needle head penetration the pounds mass required for penetration was from 8.2 pounds to 9.4 pounds for amounts of ethylene glycol from 0.028 mole to 0.018 mole, respectively.



C. For the R value at 2.5 with other conditions the same as before for comparison with the effects with the R value at 1.65, the following conclusions were drawn.

1. For elastomer with R value of 2.5 the best results were obtained with 0.028 and 0.020 mole of ethylene glycol.

2. The solvent absorption tests for the various amounts of cross-linking agent, ethylene glycol, for the R value of 2.5 in acetone at 75° F for 9.5 hours was in the range of 43.8 per cent to 58.4 per cent for amounts of ethylene glycol from 0.060 mole to 0.020 mole, respectively.

3. The swelling of polymer with various amounts of cross-linking agent, ethylene glycol in acetone at 75° F in 9.5 hours was in the range of the volume per cent increase from 68.869 per cent to 72.464 per cent for corresponding amounts of ethylene glycol from 0.052 mole to 0.020 mole.

4. The tensile properties for 600 per cent elongation, tensile strength was from 878.53 pounds per square inch to 1847.58 pounds per square inch for corresponding amounts of ethylene glycol from 0.060 mole to 0.020 mole.

5. The hardness by penetration was conducted at 75° F. At 0.150 inch of needle head penetration the pounds mass required for penetration was from 12.8 pounds to 10.2 pounds for amounts of ethylene glycol from 0.060 mole to 0.020, mole, respectively.

## VI. SUMMARY

The elastomeric polyurethane was an outgrowth of research in Germany and the United States in the period of 1937-1945. It has approached commercial production in the United States only within the past few years. The polyurethane has superior properties as well as a wide range of applications.

The purpose of this investigation was to study the effect of the variation of cross-linkage on the mechanical properties of the polyurethane elastomer formed from 33' Bitolyene 44' diisocyanate and the polyester of adipic acid and ethylene glycol.

Considerable work has been done in the past few years but the available literature lacks almost entirely any information concerning the elastomeric copolymer of 33' Bitolyene 44' diisocyanate and the polyester of adipic acid and ethylene glycol.

This investigation consisted of the preparation of polyurethane elastomer, solvent absorption and swelling tests, tensile properties tests and hardness tests. Three groups of polymer material were prepared. In the first group the R value (the ratio of diisocyanate to polyester) was varied from 1.0 to 4.5, and fixed amounts of excess diisocyanate were used. Ethylene glycol was used as the cross-linking agent. In the second and third groups the R value was fixed at 1.65 and 2.5, and the amount of excess diisocyanate after chain extension was varied. The preparation of the elastomer was accomplished by the

steps of copolymerization, chain extension, casting, cold molding, hot molding and curing. All tests were conducted at 75° F. In addition to these tests the hardness test was carried out at 300° F.

The following conclusions were drawn the basis of this work.

A. For various ratios of diisocyanate to polyester, test series

1.

1. The properties associated with cross-linking varied in such a way as to indicate an increase in cross-linking as the R value increased.

2. The weight per cent of acetone solvent absorbed at 75° F in one hour decreased in comparison with an increase of the R value and was in the range from 49.6 per cent to 10.81 per cent with the R values varying from 1.5 to 4.5. For six hours the range was from 112.9 per cent to 23.65 per cent with the R value varying from 1.5 to 4.5.

3. The swelling test for the various R values resulted in the per cent volume increase values decreasing with increasing R values. Swelling property of the elastomers in an acetone solvent at 75° F for two hours was such that the range of the relative volume increase was from 94.233 per cent to 24.303 per cent with the corresponding R values increasing from 1.5 to 4.5.

4. The tensile properties increased in comparison with an increase of the R value. At 300 per cent elongation the tensile strength was in a range from 313.15 pounds per square inch to 1927.49 pounds per square inch with the corresponding R values increasing from 1.5



to 4.5. For 600 per cent elongation, the range was from 513.22 pounds per square inch to 3584.32 pounds per square inch as the corresponding R values increased.

5. For the hardness test by penetration at 75° F and 50 per cent humidity, the force required increased with each degree of greater penetration. At 0.175 inch of needle head penetration, pounds mass required for penetration was from 9.0 pounds to 46.4 pounds as the R value varied from 1.5 to 4.5, respectively. Maximum penetration values were obtained for R values of 3.0, 3.5, 4.0 and 4.5 in which the pounds mass applied varied from 24.9 pounds to 39.4 pounds, respectively. The distance of needle head travel was at most 0.1925 inch and was at low as 0.1088 inch at maximum penetration, as the corresponding R values varied from 3.0 to 4.5.

6. Hardness tests by penetration were conducted at 300° F. The force in pounds required increased with respect to corresponding increases in the R values for each degree or depth of penetration. At 0.175 inch of needle head penetration, pounds mass required for penetration varied from 5.6 pounds to 24.0 pounds corresponding to respective R values from 1.5 to 4.5. Maximum penetration for R values of 3.0, 3.5, 4.0 and 4.5 varied from 12.9 pounds to 30.2 pounds for corresponding variation in the R values from 3.0 to 4.5.

B. For constant amount of R value at 1.65 with various cross-linking agent, test series 2.

1. For elastomer with R value of 1.65 the best results were obtained with 0.022 and 0.018 mole of ethylene glycol.

2. Solvent absorption with various amounts of cross-linking agent, ethylene glycol in acetone at 75° F at two hours was in the range of 80.8 weight per cent to 67.7 weight per cent for amounts of ethylene glycol from 0.026 mole to 0.018 mole, respectively.

3. The polymer prepared with 0.028 mole ethylene glycol was completely soluble in acetone at 75° F in two hours. The polymer prepared with 0.026 mole ethylene glycol was partially soluble in acetone at 75° F in four hours.

4. Swelling of polymer with various amounts of cross-linking agent, ethylene glycol in acetone at 75° F in two hours was in the range of the volume per cent increase from 106.732 per cent to 81.405 per cent for corresponding amounts of ethylene glycol from 0.026.

5. At 400 per cent elongation the tensile strength was from 646.80 pounds per square inch to 378.65 pounds per square inch for corresponding amounts of ethylene glycol from 0.028 mole to 0.018 mole.

6. The hardness by penetration was conducted at 75° F at 0.175 inch of needle head penetration the pounds mass required for penetration was from 8.2 pounds to 9.4 pounds for amounts of ethylene glycol from 0.028 mole to 0.018 mole, respectively.

C. For constant amount of R value at 2.5 with various cross-linking agent, test series 3.

1. For elastomer with R value of 2.5 the best results were obtained with 0.028 and 0.020 mole of ethylene glycol.

2. The solvent absorption test for the various amounts of cross-linking agent, ethylene glycol, for the R value of 2.5 in acetone at 75° F for 9.5 hours was in the range of 43.8 per cent to 58.4 per cent for amounts of ethylene glycol from 0.060 mole to 0.020 mole, respectively.

3. The swelling of polymer with various amounts of cross-linking agent, ethylene glycol, in acetone at 75° F in 9.5 hours was in the range of the volume per cent increase from 68.869 per cent to 72.464 per cent for corresponding amounts of ethylene glycol from 0.052 mole to 0.020 mole.

4. The tensile properties for 600 per cent elongation tensile strength was from 878.53 pounds per square inch to 1847.58 pounds per square inch for corresponding amounts of ethylene glycol from 0.060 mole to 0.020 mole.

5. The hardness by penetration was conducted at 75° F. At 0.150 inch of needle head penetration the pounds mass required for penetration was from 12.8 pounds to 10.2 pounds for amounts of ethylene glycol from 0.060 mole to 0.020 mole, respectively.



VII. BIBLIOGRAPHY

1. Alfrey, T. J.: "Mechanical Behavior of High Polymers", p. 236. Interscience Publishers Co., Inc., New York, N. Y., 1948.
2. Anon.: Isocyanate Formed-in Place Resins, Tech. Bull., 44, Monsanto Chemical Co., Revised June 1, 1953.
3. A. S. T. M.: "1958 Book of A. S. T. M. Standards Part 9", pp. 1361-69. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa., 1958.
4. Austin, P. R." U. S. 2,365,508, September 9, 1940.
5. Bawn, C. E. H.: "The Chemistry of High Polymers", p. 55. Interscience Publishers Co., Inc., New York, N. Y., 1948.
6. Bayer, O.: Angew Chem., 59, 257-72 (1947);  
Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
7. \_\_\_\_\_: Ann. 549, 286 (1941);  
Seeger, N. V.: Ind. Eng. Chem., 45, 2538-42 (1953).
8. \_\_\_\_\_, E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth,: Angew Chem. 62, No. 3, 57-66 (1950);  
Muller, E.: Rubber Chem. and Tech., 26, 493 (1953).
9. \_\_\_\_\_: German Patent Application J. - 77, 394 (May 15, 1944);  
Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
10. \_\_\_\_\_, E. Muller, H. F. Piepenbrink, E. Windemuth, Bunge, and S. Petersen: German Patent Application J. - 77, 781 (July 10, 1944);  
Bayer, O: Rubber Chem. and Tech., 23, 812-35 (1950).
11. \_\_\_\_\_: Modern Plastic 24, No. 10, 149-52, 250-60 (1947).
12. \_\_\_\_\_, E. Muller, S. Petersen, H. F. Piepenbrink and E. Windemuth: New Type of High Elastic Substances, Vulcollans, Rubber Chem. and Tech., 23, 812-35 (1950).
13. Beilly, C. B. and O. Milton: Preparation and Properties of Polyurethane Coatings, Ind. Eng. Chem., 48, 59-63 (1956).
14. Bello, F.: Fortune 51, No. 3, 110-3, 166, 169 (1955).

15. B. I. O. S.: Final Report, No. 1166.
16. Bjorksten Research Laboratory: "Polyesters and Their Applications", pp. 226-30. Reinhold Publishing Corporation, New York, N. Y., 1956.
17. Bovey, F. A., I. M. Kotthoff, A. I. Medalia and E. J. Meehan: "Emulsion Polymerization," pp. 6, 38. Interscience Publishers Co., Inc., New York, N. Y. (1955).
18. Breslow, D. S.: U. S. 2,531,392, September 8, 1948.
19. Buist, J. M.: Rubber Chem. & Tech. 28, No. 1, 230 (1955).  
or Rev. Gen. Coautchouc 31, No. 6, 479 (1954).
20. Bunge, O. Bayer, S. Petersen and Spielberger: German Patent 756,058. Seeger, N. V.: Ind. Eng. Chem., 45, 2538-42 (1953).
21. Christ, R. E. and W. E. Hanford: U. S. 2,333, 639, July 2, 1940.
22. C. I. O. S. Report, Item No. 22, File No. XXII-16, and B. I. O. S. Item No. 22, Final Report No. 1498.
23. Coffey, D. H.: U. S. 2,606,162.
24. D'Alerio, G. F.: "Fundamental Principles of Polymerization", pp. 164-66. John Wiley & Sons, Inc., New York, N. Y., 1952. 1 ed.
25. Dinsmore, R. P.: Address before Washington, D. C., Rubber Group, Goodyear Rubber Co., March 18, 1953.
26. Dollard, H. L., Jr., J. A. Bjorksten and H. Tovey: Polyurethane Resins, Modern Plastics, 31, No. 8, 143-4, 228-30, 233 (1954).
27. Encyclopedia of Chemical Technology, First Supplement Volume: "Polyurethane Resins", pp. 686-88. The Interscience Encyclopedia Inc., New York, N. Y. (1957).
28. German Patent Application 73, 726. (PB Report 20, 544); Bayer, O.: Rubber Chem and Tech., 23, 812-35 (1950).
29. German Patent Application, F-2824 39/C and F-2972 39/C; Bayer, O.: Rubber Chem and Tech., 23, 812-35 (1950).
30. Givens, J. H.: "Continuous and Staple Fiber Plants of Germany", PB Report 337, 1946.

31. Goodrich Service Bulletin G-18: "Estane Polyurethane Materials", B. F. Goodrich Chem. Company, August, 1959.
32. Goodyear Aircraft Co.: Report on U. S. A. F. Contract No. 33-038-AC-15228, Wright-Patterson Air Force Base, Dayton, Ohio.
33. Harkins, W. D.: General Theory of Mechanism of Emulsion Polymerization, J. Polymer Sci., 5, 217 (1950).
34. Harmon, J.: U. S. 2,393,987.
35. Hill, F. B., C. A. Young, J. A. Nelson and R. G. Arnold: Ind. Eng. Chem., 48, No. 5, 927 (1956).
36. Hochtlen, A.: Kunststoffe 42, 302-10 (1952); Seeger, N. V.: Ind. Eng. Chem., 45, 2538-42 (1953).
37. Hoff, G. P.: "Fiber-forming Polymers and Intermediate", PB Report 1357, 1945.
38. Hoff, G. P. and D. B. Wacker: "Perton U; Polyurethanes of I. G. Farben Bobingen, Augsburg", PB Report 1122, 1945.
39. Imperial Chemical Industries, Ltd.: Brit. 573-932.
40. Imperial Chemical Industries: Vulcaprene Manual.
41. Kline, G. M.: Review on German Plastic 1938-45, Modern Plastic 23, No. 2, 152A-152B (1945).
42. Kogon, I.C.: J. Org. Chem. 24, 83 (1959).
43. Kolley, L.: U. S. 2,302,037.
44. Ladenburg: Ber., 2, 30 (1869); Muller, E.: Rubber Chem. and Tech., 26, 493 (1953).
45. Mark, H.: Trans Faraday Soc., 43, 447 (1947).
46. Mastin, T. G. and N. V. Seeger: U. S. 2,625,535 (Jan 13, 1953).
47. Mediger, H.: U. S. 2,342,679.
48. Modern Plastic Encyclopedia, 35, No. 1A, 18 (issue September 1957).
49. Muller, E. and O. Bayer: Angew Chem., 64, 523-31 (1952).
50. \_\_\_\_\_ and Traube: German Patent Application, J-77, 127 (April 3, 1944).



51. Muller, E. , S. Petersen and O. Bayer: German Patent Application J-76, 584 (Jan. 17, 1944).
52. \_\_\_\_\_, H. F. Piepenbrink, W. Schmidt and E. Weinbrenner: German Patent 831,722 (Feb. 24, 1949). (U. S. Priority, Jan. 12, 1949).
53. \_\_\_\_\_; A Review on German Plastics with Polyester Base, Kunststoffe 41, 13-9 (1951).
54. \_\_\_\_\_, O. Bayer, S. Petersen, H. F. Piepenbrink, F. Schmidt and E. Weinbrenner: Polyurethanes IX, New Types of Highly Elastic Products, Rubber Chem. and Tech., 26, 493-509 (1953).
55. Nageli and Tyabji: Helv. Chem. Acta., 17, 247 (1934); Muller, E.: Rubber Chem. and Tech., 26, 493 (1953).
56. Pigott, K. A., B. F. Frye, K. R. Allen, S. Steingiser, W. C. Dan, J. H. Saunder and E. E. Hardy: "The Development of Cast Urethane Elastomers for Ultimate Properties", Published Paper from Mobay Chemical Company, Pittsburgh 34, Pa., May 13, 1959.
57. Pinten, H.: German Patent Application, D 90260; Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
58. \_\_\_\_\_: German Patent Applications F2824 39/C and F 2972 39/G; Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
59. Popper, F.: Rubber Age (N. Y.), 73, 81 (1953).
60. Pratt, B. C. and H. S. Rothrock: U. S. 2,430,479.
61. Rartz, I.: Papers Presented at 11th Annual Nat. Tech. Conf. Soc, 2, 149-72, Plastics Eng. Inc., (1955).
62. Rinke, H., H. Schild and W. Siefken: U. S. 2,511,544.
63. Robinson, E. B. and R. B. Waters: Properties of Urethane Oils, Chem. Age 54, No. 1655, 481-4 (1951).
64. Schlack, P.: German Patent Application J-66, 330 (Jan. 17, 1940), and French Patent 869,243.; Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
65. \_\_\_\_\_: U. S. 2,325,552 (Versted in Alien Properties Custodian).
66. \_\_\_\_\_: U. S. 2,343,808 (Versted in Alien Properties Custodian).

67. Schmidt, A. X. and C. A. Marlies: "Principles of High Polymer Theory and Practices", pp. 1-3, 61, McGraw-Hill Book Company, Inc., New York, N. Y. (1948).
68. Schmidt, W. and K. E. Muller: U. S. 2,621,166.
69. Schollenberger, C. S., H. Scott and G. R. Moore: Rubber World 137 No. 4, 549-55 (1948).
70. Sczquare, M.: J. Polymer Sci., 19, No. 93, 589 (1956).
71. Seeger, N. V., T. G. Mastin, E. E. Fauser, F. S. Farson, A. F. Fiucelli and E. A. Sinclair: Chemigum S. L. - An Elastomeric Polyester-Urethane, Ind. Eng. Chem. 45, 2538-42 (1953).
72. \_\_\_\_\_: U. S. 2,625,531 (Jan. 13, 1953).
73. Seeger, N. V.: U. S. 2,625,532 (Jan. 13, 1953).
74. Simons, H. R.: "A Concise Guide to Plastics", pp. 171-73. Reinhold Public Co., New York, N. Y. (1957).
75. \_\_\_\_\_ and F. W. Thomas: U. S. 2,577,279.
76. Staudinger, H. and E. Huseman: Ber., 68, 1618 (1935); Muller, E.: Rubber Chem. and Tech., 26, 493 (1953).
77. Whitby, G. S.: "Synthetic Rubber", pp. 25-6, 922-32, John Willy & Sons, Inc., New York, N. Y. (1955).
78. Windemuth, E.: German Patent 826,641; Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).
79. \_\_\_\_\_: German Patent Application, J-75, 922 (Sept. 22, 1943); Bayer, O.: Rubber Chem. and Tech., 23, 812-35 (1950).

VIII. ACKNOWLEDGEMENTS

The author wishes to express his deep appreciate to Dr. R. A. Fisher, Professor of the Chemical Engineering Department, Virginia Polytechnic Institute, for his guidance, encouragement, and inspiration during the course of this investigation.

He is also grateful to \_\_\_\_\_ for his help in English and many of the figures in this thesis, and \_\_\_\_\_ for his valuable suggestions.

Thanks are also extended to \_\_\_\_\_ for operation of the tensile testing equipment, Dr. Y. K. Pan of the Plastic's Research Laboratory, Monsanto Chemical Company, Texas, for cutting the tensile testing specimens.

All the members of the faculty of the Chemical Engineering Department assisted with helpful suggestions.



**The two page vita has been  
removed from the scanned  
document. Page 1 of 2**

**The two page vita has been  
removed from the scanned  
document. Page 2 of 2**

## ABSTRACT

### The Preparation of a Polyurethane Elastomer and Evaluation of the Mechanical Properties

This thesis was a study of the effect of the variation of cross-linkage on the mechanical properties of a polyurethane elastomer prepared from 33' Bitolylene 44' diisocyanate and the polyester of adipic acid and ethylene glycol. The investigation consisted of the preparation of polyurethane elastomer, solvent absorption and swelling tests, tensile properties test and hardness test. Three groups of polymer material were prepared. In the first group the R value was varied from 1.0 to 4.5, (the ratio of 33' Bitolylene 44' diisocyanate to polyester) and fixed amounts of excess diisocyanate were used. Ethylene glycol was used as the cross-linking agent. In the second and third groups the R value was fixed at 1.65 and 2.5, and the amount of excess diisocyanate after chain extension was varied.

The preparation of the elastomer was accomplished by a method based on the literature and preliminary experiments carried out for the purpose of determining optimum conditions for the specific polymer under investigation. All mechanical tests were accomplished by conventional and standard methods. All tests were conducted at 75° F. In addition to these tests the hardness test was carried out at 300° F.



The preparation of polyurethane elastomer by bulk polymerization was conducted at atmospheric pressure and 130° C with the reaction requiring a period of 30 minutes for completion. For the molding process, casting, cold molding, hot molding and curing were used. The various degrees of cross-linkage could be obtained by using different ratios of 33' Bitolyene 44'diisocyanate to polyester and by varying the amount of cross-linking agent, ethylene glycol. The properties associated with cross-linking varied in such a way as to indicate an increase in cross-linking as the R value increased. The solvent absorption and swelling properties decreased with an increase of the R value. The mechanical properties improved with an increased R value. Also the hardness increased with an increase of the R value.