

stages are too high or the time of reaction too long. The process of equilibration occurs, resulting in lower mol wt resins.

Preparative-wise little need be said of the methods used other than they may be *solvent based* where a relatively closed system is used with an azeotrope forming organic liquid to facilitate removal of the water of reaction to drive the esterification to completion or *fusion* where an inert gas is used as the means of removing the water.

One of the outstanding features of alkyd resin systems is their capability of modification with other resins. Lanson has commented on this quality at some length (6). This characteristic in the past and presently has served as the continuing basis of interest for alkyds. Whatever the explanation, be it physical or chemical modification of the alkyd resin, this ability will be the source of future need and interest for alkyds.

Statistics for this branch of industrial activity are available to show that this is no small business. Although alkyds have not continued to grow at the same rate as population, still they are maintaining a significant position. In 1959, 350 million lb of alkyd resins were produced. This must be considered in the light of other new resin developments such as latex paints, epoxies, etc. Alkyd resins fit into the coatings scheme practically everywhere.

It is obvious that achievement of a place in each of the many applications, and the continued maintenance of that position against all competition on price and performance grounds is not an easy task. This is a tough business and no quarter is given; it is on this continuing demand for performance that the versatility of the alkyd resin is called upon. By proper choice of the alkyd resin ingredients themselves and selection of the modifying resin and its

amount, an infinite series of acceptable materials are provided. As new resins are produced, the horizon is further extended.

Present interest is strong in certain areas but whether this is confirmed by specific needs requires validation. Water-soluble resins have captured the fancy of the industry, but only small segments of the market have opened for coatings due to generally higher costs and restrictive application properties. Technically, air dry water-soluble coatings are within our reach today, but again the cost is a detriment. Unless some specific need exists for a water-based vehicle as is the case with some new locations where solvent paints could create hazards, little impetus in this area is to be expected.

On the other hand, the author sees a bright future for systems which approach or are synonymous with 100% solids coatings. It is apparent that raw material costs are just about as low as industry can tolerate. It then follows that application costs must be reduced. The number of coats to achieve a given film thickness must be minimized to save labor costs, and reduce film shrinkage.

Another area of increasing value to the coatings industry and affecting alkyds is collateral resin development. Any new resin which can be used to upgrade the performance or reduce the cost (not necessarily both at the same time) has something of importance for this billion dollar industry.

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Fatty Acid Derivatives in Polyurethanes¹

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THE STUDENT of elementary organic chemistry learns that urethanes are formed by the reaction of alcohols and isocyanates. He also learns that this provides a convenient method of preparing solid derivatives of alcohols that are useful for purposes of identification by means of their characteristic mp. That is generally where his knowledge of urethanes, and his interest in them, begins and ends.

The first aliphatic isocyanate was synthesized by Wurtz in 1849, and the next year Hofmann made the first aromatic isocyanate(1). During the next 80 years, particularly between 1890 and 1920, much information concerning the preparation and properties of numerous isocyanates was developed, but it was not until the 1930's that commercial applications of these compounds began to be realized. The discovery of condensation polymers such as nylon by Carothers during the 1930's stimulated interest in all kinds of difunctional materials. During this period the diisocyanates came in for their share of attention, particularly their reaction with polyhydroxy compounds to form polyurethanes.

The earliest work on the development of technical

applications of isocyanates was apparently done in Germany where, in 1937, Otto Baeyer experimented with isocyanates as a means of producing fibers equal to or superior to nylon, which would not be covered by the Du Pont patents on nylon(2). During World War II polyurethane fibers and plastics were used extensively in Germany, and a well-integrated industry based on diisocyanates developed there. Research in the U.S. was not far behind; patents were applied for in 1939 and 1940 and granted in the early 1940's. The first commercial application in this country took place early in World War II, and isocyanates were used in the production of life rafts and "Mae West" inflatable vests(2). However, really strong interest did not develop in the U.S. until after the end of the war in Germany when a group of observers sent there by the Office of the Quartermaster General returned greatly impressed with German utilization of polyurethanes. Following that, greater industrial interest developed in the U.S. and polyurethane technology developed rapidly during the 1950's.

Isocyanates and Their Preparation

It is beyond the scope of this paper to discuss the preparation and properties of isocyanates in detail,

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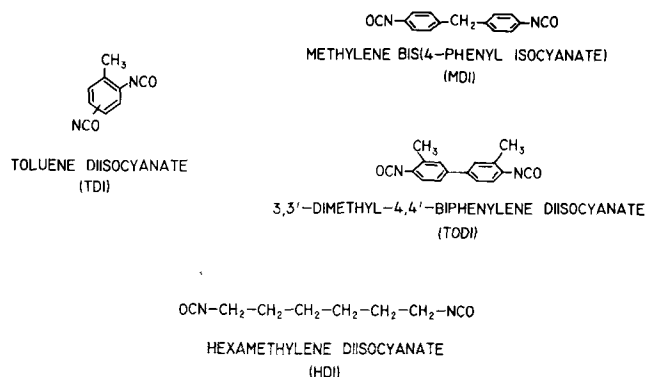


Fig. 1. Representative diisocyanates.

but some discussion is necessary for a proper appreciation of the tremendous commercial interest in these versatile materials, of their manifold potentialities in the production of all kinds of industrial products, and of some of the problems encountered in their development. A great many isocyanates are actually and potentially available and, in fact, many have been investigated for the production of polyurethanes. However, for a variety of economic and technological reasons, less than half a dozen, all diisocyanates, have achieved significant industrial use. Some of these are illustrated in Figure 1.

Toluene diisocyanate (TDI) is used to a far greater extent than any of the others. TDI is the workhorse of the polyurethane industry but considerable quantities of MDI (Methylene bis [4-phenyl isocyanate]) are also used. 3,3'-Dimethyl-4,4'-biphenylene diisocyanate (TODI) is representative of another structure, which has received considerable attention. The analogous compound without the two methyl groups and the homolog with a methylene group between the aromatic rings (comparable to the MDI skeleton) have also been studied extensively. Various naphthalene diisocyanates have also been investigated; the 1,5-isomer was the preferred isocyanate used in the early German work on elastomers. Hexamethylene diisocyanate is included in Figure 1 chiefly for its historical interest. In the early days in Germany, this diisocyanate was the one most commonly used for production of urethane fibers.

Other isocyanates that are produced in pilot plant or developmental quantities include phenyl isocyanate, octadecyl isocyanate, hexadecane-1,16-diisocyanate, dianisidine diisocyanate, and triphenylmethane triisocyanate.

Although numerous ways of synthesizing isocyanates have been described, the method almost universally used for their large-scale manufacture is based on the reaction of an amine or amine salt with phosgene. This procedure (Figure 2) involves essentially two steps: (1) formation of a carbamoyl chloride by reaction of an amine (or diamine) with excess phosgene and (2) thermal dissociation of this intermediate to isocyanate and HCl. Temps in the vicinity of 200°C are generally used for the dissociation. In practice both steps are frequently carried out in one operation and the isocyanates are prepared most readily by reacting a slurry of the appropriate amine hydrochloride with phosgene in a suitable solvent. Toluene diisocyanate (TDI) is the most important commercial diisocyanate. Dombrow has described its preparation in considerable detail(2). The TDI that is most commonly used is composed of a mixture of 80% of the 2,4- and 20% of the 2,6-isomer, although a 65:35 mixture and the substantially pure 2,4-isomer

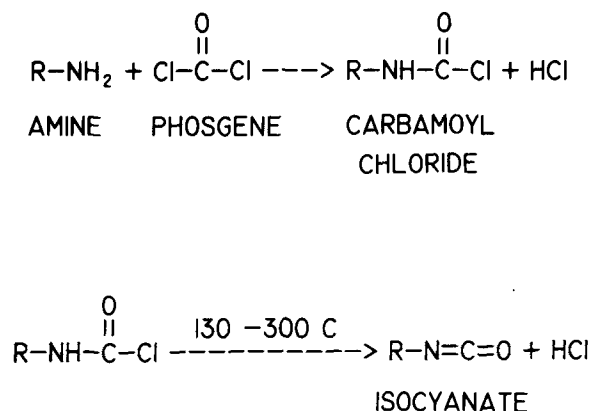


Fig. 2. Synthesis of isocyanates using phosgene.

are also available. These different isomer ratios result, in part, from the chemistry of the process (Figure 3).

Reactions of Isocyanates

As indicated earlier, urethanes are formed by the reaction of isocyanates and alcohols. However, the isocyanates are very reactive, and they react with many different classes of compounds. These include acids, amines, amides, phenols, and thiols and, of course, numerous derivatives of fats and oils contain such groups. The term "polyurethane" has come to be applied to the class of polymeric materials that contain urethane linkages even if many other linkages such as urea groups are also present.

Extensive reviews describe the reactions of isocyanates in detail(1,3). Most reactions pertinent to polyurethane technology involve reactions of isocyanates with compounds containing active hydrogen, that is, hydrogen that can be replaced by sodium. The type reaction, although it is applicable to a great many compounds, is basically very simple: the active hydrogen is transferred to the nitrogen of the isocyanate, and the rest of the molecule is linked to the adjacent carbonyl carbon atom.

If HX is an alcohol, the product is a urethane. It also may be considered as a substituted carbamate or as a derivative of carbonic acid. This product has a reactive hydrogen in the -NH portion of the urethane.

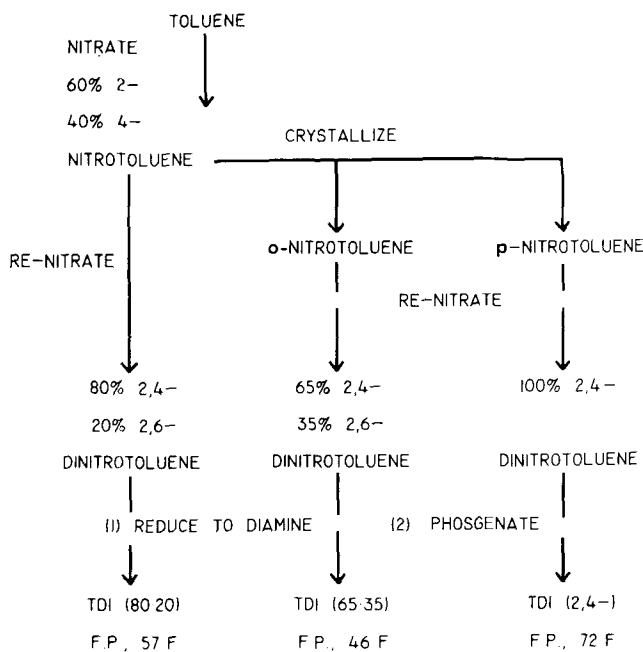


Fig. 3. Preparation of toluene diisocyanates.

Although this hydrogen is not as reactive as the hydroxyl hydrogen of most alcohols it competes with other reactive hydrogens for any isocyanate that is present. Some of the reactions of isocyanates particularly relevant to the preparation of polyurethanes are presented in Figure 4.

The widespread and intense commercial interest in polyurethanes is readily understood if one considers that numerous polyisocyanates and co-reactants are actually or potentially available and, hence, a tremendous number of different reaction products are possible. Depending upon the starting materials used, the reaction products may have widely different properties. What especially aroused great early interest in polyurethanes was the possibility of combining the polymer-forming reaction with the reaction of isocyanates with water to produce CO₂ gas. The implications of this for the production of foams are obvious. In practice, the reaction products have been used as

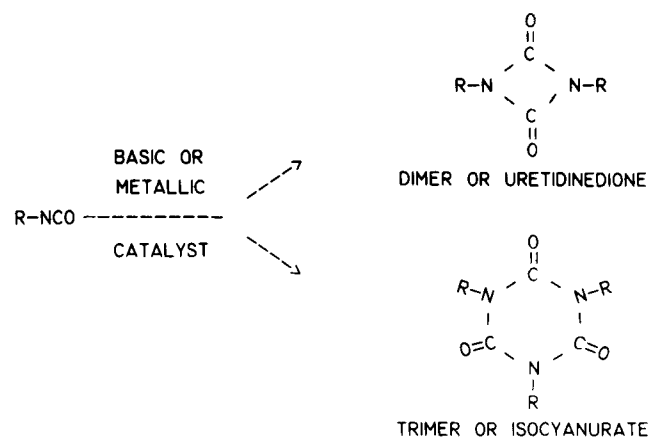
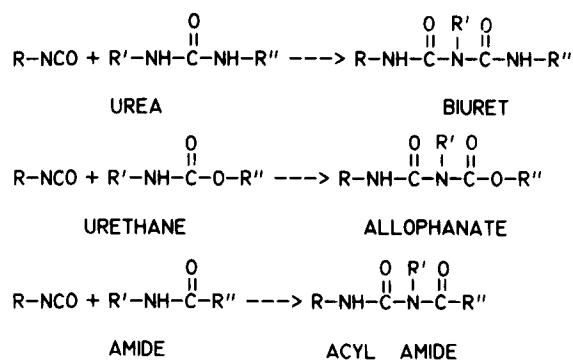
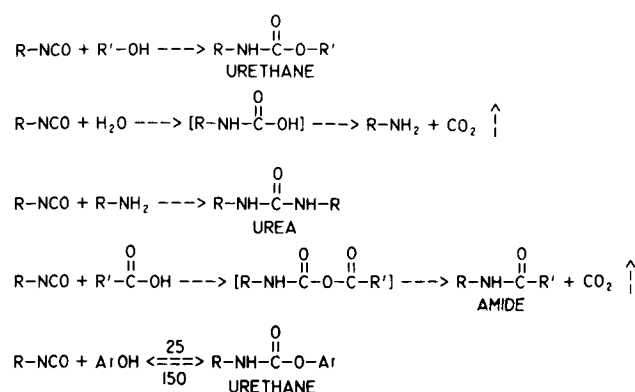


Fig. 4. Reactions of isocyanates relevant to formation of polyurethanes.

TABLE I
Relative Effects of Substituent Groups on Isocyanate Reactivity

Substituent group	Approx relative rate
Sulfone (para).....	>50
Nitro (para).....	>35
Chlorine (meta).....	7
Isocyanate (meta or para).....	6
Methyl (meta or para).....	0.5
Methyl (ortho).....	0.08
Methoxy (ortho).....	0.04

adhesives, resins, plastics, rubbers, surface coatings, and fibers, as well as foams.

Kinetics of Polyurethane Formation

In the production of polyurethanes we have a series of competing reactions and, frequently, there is a difference in the rates of reaction of identical functional groups. The reactivity of the isocyanates is dependent upon the influence of neighboring groups and on the configuration of the molecule. In toluene diisocyanate, the isocyanate in the 4-(para) position is some eight times as reactive as the one in the 2-(ortho) position, at least toward alcohols at room temp. This difference in reactivity of the two isocyanate groups in 2,4-toluene diisocyanate can be utilized advantageously in forming polyol adducts. The different in reactivity is even greater between isocyanate groups in different classes of molecules. In general, the aliphatic and alicyclic isocyanates are less reactive than are the aromatic isocyanates, and the naphthalene isocyanates are more reactive than the benzene-derived isocyanates. Introduction of electron-withdrawing groups such as nitro- or halogen serves to enhance the reactivity of an isocyanate group, while electron-donating substituents such as alkyl or alkoxy groups diminish the reactivity. The presence of a second isocyanate group in an aryl ring enhances the reactivity of the first isocyanate group, in accord with its electron withdrawing character. Bailey and coworkers(4) have constructed a table of the relative effect of substituents on the reactivity of isocyanates. Their data in Table I indicate that simple changes in substituents can alter the rate of reaction more than a hundred fold. Baker and Holdsworth(5) reported that, for the triethylamine-catalyzed reaction with methanol, the relative reactivities of cyclohexyl-, p-tolyl-, phenyl- and p-nitrophenyl-isocyanate are in the ratio of 1:590:1762: ca 145,000.

The nature of the alcohol also greatly affects the rate of reaction. In general, primary alcohols react more readily than secondary alcohols, and these react much more rapidly than tertiary alcohols. Davis and Farnum(6) gave the relative reaction velocities as 1:0.3:0.005, respectively. Neighboring unsaturation also may decrease the rate of reaction of alcohols with isocyanates(7).

But generalizations concerning relative rates of reaction can be quite misleading. Cooper and co-

TABLE II
Reaction Velocity Constants $\times 10^4$ (Liter Mol⁻¹ sec⁻¹) at 100C

Isocyanate	Hydroxyl ^a	Water	Urea ^b	Amine ^c	Urethane ^d
p-Phenylene diisocyanate.....	36.0	7.8	13.0	17.0	1.8 at 130C
2-Chloro-1,4-phenylene diisocyanate.....	38.0	3.6	12.0	23.0	
2,4-Toluene diisocyanate.....	21.0	5.8	2.2	36.0	0.7 at 130C
2,6-Toluene diisocyanate.....	7.4	4.2	6.3	6.9	
1,6-Hexamethylene diisocyanate.....	8.3	0.5	1.1	2.4	0.2 at 130C

^a Polyethylene adipate.

^b Diphenyl urea.

^c 3,3'-Dichlorobenzidine.

^d p-Phenylene dibutyl urethane.

workers(7) compared the reactivity of several isocyanates toward active hydrogen in various classes of compounds (Table II). It will be noted that, although hexamethylene diisocyanate is nearly 20 times as reactive to alcoholic hydroxyl as to water, 2,6-toluene diisocyanate is barely twice as reactive. Also, although p-phenylene diisocyanate reacts with the alcohol almost twice as fast as does 2,4-toluene diisocyanate, the ratio is almost exactly reversed in the reaction of these isocyanates with the amine. And, in the case of 2,6-toluene diisocyanate, the velocity of the reaction with the alcohol is substantially the same as it is for the amine. Temp also is important. In general, low temps favor urethane formation. At higher temps allophanates, ureas, biurets, dimers and trimers may tend to form.

The kinetics of the reactions of isocyanates have been studied extensively. Although simple equations for the type reactions can be written, the kinetics are not as straightforward as the equations indicate. The reaction of an isocyanate with an alcohol appears to follow second order kinetics, with the complication that the rate const obtained is dependent upon the ratio of the alcohol-isocyanate concentration. Also, the urethane formed is a weak catalyst for the reaction(5).

Numerous catalysts accelerate isocyanate reactions, and catalysts are generally employed in the production of urethane polymers. The relative effects of some commonly used catalysts on the reactivity of phenyl isocyanate, as reported by Hostettler and Cox(8), are given in Table III. Catalysts vary in their effects on specific reactions. For example, although triethylamine increases the rate of reaction of phenyl isocyanate with butanol nearly a hundred fold, it scarcely doubles the rate of reaction with the urea. Of particular interest is the relative ratio of alcohol and water reaction rates when different catalysts are used. 1,4-Diazabicyclo-(2,2,2)-octane and organotin catalysts show relatively large ratios, up to 6 to 1. This is particularly significant in water-blown foam technology where a fast polymer-forming reaction, in relation to CO₂ evolution, is desired to prevent collapse of the foamed polymer.

As indicated earlier, in the production of polyurethanes we have a series of competing reactions. Not only is there a difference in the rate of reaction of identical functional groups, but these rates are affected differently by changes in temp or catalysts. In addition, the primary products of the isocyanate reaction may not only react further but may also act as catalysts. Nevertheless, reasonable reaction rates are required, and a suitable balance must be maintained between different reactions, e.g., between polymer-forming or cross-linking reactions and gas-releasing reactions. Obviously, the chemistry involved in the preparation of useful urethane polymers is

TABLE III
Relative Rates of Reaction of Phenyl Isocyanate

Catalyst	Mol % catalyst	Relative rates		
		Butanol	Water	Diphenyl urea
None.....	1.0	1.1	2.2
N-Methylmorpholine.....	10	40	25	10
Triethylamine.....	10	86	47	4
N,N,N',N',-Tetramethyl-1,3-butanediamine.....	10	260	100	12
1,4-Diazabicyclo-[2,2,2]-octane.....	10	1200	380	90
Tributyltin acetate.....	0.1	800	140	80
Dibutyltin diacetate.....	0.1	5600	980	120
Dibutyltin dilaurate.....	0.1	5600		

TABLE IV
Consumption of Polyurethanes
(million of lb)

	Foams ^a		Elastomers ^b	Coatings ^c
	Flexible	Rigid		
1960.....	85	12	6.8	3.6
1965-66.....	190+	115+	65	28
Ultimate.....	500	1,000	300	35

^a Chem and Eng. News, 39, No. 27, 27-28 (1961).

^b *Ibid.* 40, No. 11, 101 (1962).

^c *Ibid.* 39, No. 14, 39 (1961).

quite complex. Much of the technology is still art, but much is being learned concerning the chemistry involved, and the technology is improving and changing rapidly.

Uses of Polyurethanes

What are the polyurethanes used for, and what is the trend? This can be indicated best, perhaps, by use of some statistics (Table IV). Derivatives of fats and oils can be used in all of the products listed in Table IV.

Foams. Unquestionably the greatest use of polyurethanes is in preparation of foamed products. Polyurethane foams range from flexible and resilient foams useful as cushioning materials to strong and rigid products used in the construction industry. In between are the semi-rigid foams for shock absorption, for example, in crash pads for automobiles.

A typical formulation for a semi-rigid foam made from castor oil is given in Table V (9). Foams of this composition are prepared by the prepolymer or two-stage method rather than a one-stage or "one shot" method, which is most commonly used. A prepolymer is formed by heating the castor oil, which contains about three hydroxyls/mole, and the diisocyanate at a temp of about 110-130C for about an hr. To produce a foam, the prepolymer containing about 10% by wt of unreacted-NCO groups is mixed with the surfactant, and then the catalyst, which has been buffered and dissolved in sufficient water to react with residual isocyanate, is stirred in. An exothermic reaction sets in almost at once, but the mixture can be stirred for about a min before significant foaming, resulting from the evolution of CO₂, begins. With the formulation given in Table V the foam continues to rise for about 20 min, but the foaming time can be varied considerably by changing catalyst. One of the major advantages of this type of foam is that it can be foamed in place. That is, the desired amount of mix can be poured into an odd-shaped void, for example, a portion of a boat hull, and the foam will fill the entire space. The character of the cells produced, that is, their size and uniformity and whether they are open or closed, is materially affected by the type and amount of surfactant, the rate of foaming, the degree of mixing, and how much air is stirred in, as well as by the nature of the polymer that is being formed. All these factors have an effect on the properties of the foam. Obviously there must be a good balance among the reactants and fine control to obtain suitable production of CO₂ gas throughout the mass

TABLE V
Components of Castor-Oil Urethane Foams

Component	G
Castor oil.....	60
Toluene diisocyanate.....	40
Surfactant ^a	0.5
Catalyst ^b	1.9
Water.....	2.5

^a Dow Corning DC 200 (50 cs).

^b 2-Diethylaminoethanol.

TABLE VI
Effect of Proportion of Castor Oil on Foam Properties

Castor oil (%)	Type	Density (lb/ft ³)	50% Compression modulus (psi)
50	semi-rigid	1.7	7.6
60	semi-rigid	2.8	10.4
70	flexible	3.5	1.19
80	flexible	6.4	0.52

of the polymer during the entire time of its formation. The key to producing a good foam of min density lies in balancing the blowing and the viscosity build-up so that at the completion of gas evolution the strength of the polymer will be just sufficient to maintain the network structure.

The data in Table VI indicate some of the different properties obtainable by a relatively simple change from the formula given in Table V. The proportion of castor oil is changed; the amount of catalyst and surfactant is kept const(9). As the proportion of castor oil is increased from 50%–80%, the character of the foam changes from rigid (or semi-rigid) to flexible, and the density increases. The examples given in Table VI feature castor oil, but any suitable polyol could be used. These include blown oils and castor or other oils alcoholized with polyols such as glycerol, pentaerythritol, sorbitol, or trimethylolpropane. The use of tall oil to produce polyurethane foams has recently been proposed(10).

Some of the early German work employed castor oil, but most was based on the use of polyesters. The latter were formed by the reaction of dibasic acids such as adipic or phthalic with polyols such as ethylene and propylene glycols, butanediol, glycerol and trimethylolpropane. In some cases polyesters with a moderately high acid value were employed, and the reaction of the acidic groups with isocyanate was used to generate some of the CO₂ used in blowing. Materials of fatty origin that can be, and sometimes are, used to make suitable polyesters include azelaic acid obtained by ozonolysis of oleic acid, sebacic acid made from castor oil, and dimer acid obtained by polymerization of linoleic acid. More recently hydroxy-terminated polyethers based on propylene oxide or tetramethylene oxide were introduced as the co-reactant for the isocyanate, and these polyethers are the polyols now used most extensively.

Foaming procedures were revolutionized in the late 1950's by introduction of the solvent blowing technique, in which a low-boiling fluorocarbon solvent supplies the gas required for foaming. Trichlorofluoromethane (CCl₃F), which boils at 24C, is generally used, and the heat evolved during the urethane reaction is sufficient to vaporize it. It is actually cheaper to use these fluorocarbons to produce gas than it is to use CO₂ obtained by reaction of the relatively expensive isocyanate with water. In addition,

TABLE VII
Composition and Properties of Castor-Urethane Foams

	Foam I	Foam II
Composition, g		
Toluene diisocyanate.....	49.3	46.1
Pentaerythritol monoricinoleate.....	35.9	
Castor oil.....		21.0
Trimethylol propane.....	14.8	
Triisopropanolamine.....		21.2
Hexol ^a		11.7
CCl ₃ F.....	15.0	16.0
Surfactant.....	1.5	1.5
Catalyst.....	0.6 ^b	0.6 ^{b-c}
Properties		
Density (lb/ft ³).....	2.16	2.12
Compressive strength (psi).....	43	37
Closed cells, %.....	93	95

^a Atlas G-2406. ^b Triethylenediamine. ^c 0.05 g Stannous octoate.

tion, use of the fluorocarbons lowers the exotherm and so reduces the high temp that sometimes develops in large blocks of foam during their preparation. Fluorocarbons have the advantage over other solvents with similar volatility in that they are non-toxic, non-inflammable and have relatively little odor; in addition, the fluorocarbon-blown foams have better thermal insulation properties.

The composition and some properties of two typical castor-based, solvent-blown foams are given in Table VII(11).

In the solvent blowing system, an isocyanate containing prepolymer is prepared by reacting all of the diisocyanate with a portion of the polyol. The desired amount of CCl₃F and surfactant is dissolved in the prepolymer, and a solution of the catalyst in the additional polyol is stirred in. Foaming begins in about 30 sec and is completed in about two min, although foaming time can be varied to a moderate extent by suitable changes in the catalyst.

One of the most recent developments in urethane foam technology is frothing(12). In the frothing technique a fluorocarbon boiling well below room temp is used, and pressure equipment is required. The froth looks like an aerosol of whipped cream as it is discharged from the processing equipment, whereas, the solvent-blown mixture is discharged as a liquid. The fluorocarbon most commonly used in frothing is dichlorodifluoromethane (CCl₂F₂) which boils at -28C. Mixtures of fluorocarbons are sometimes used, and the frothing system can be varied considerably.

Elastomers. One of the more promising uses of polyurethanes is in elastomers, sometimes called urethane rubbers. Just what constitutes a polyurethane elastomer is rather hard to define because, depending on the classification used, it may include anything from adhesives and sealing and caulking compounds through elastic thread and tires to mechanical goods and potting and encapsulating compounds which may be quite hard. A tremendous amount of research in this country has gone into the development of suitable polyurethane elastomers. Although the 100,000 mile tire, about which a good deal was heard 5–10 years ago, has not yet materialized, there are still recurrent rumors that the many problems involved in developing a successful automobile and truck tire will be solved within a few years(13). Urethane rubbers are being used in such products as industrial tires, printing rolls, mechanical goods, belt stocks, heels and shoes, and elastic fibers. Output of polyurethane elastomers of all types was reported as 2.2 M lb in 1959 and 6.8 M lb in 1960 and was an estimated 11 M lb in 1961(14). Optimists envision an ultimate production comparable to that of neoprene, even if the polyurethane automobile tire never materializes.

Several routes are used in the preparation of urethane elastomers. Generally, a polyol is reacted first with an excess of a diisocyanate to form an isocyanate-terminated prepolymer, analogous to the prepolymers described previously for the preparation of castor oil urethane foams. The polyols commonly used are polyesters, polyethers, or castor oil or its derivatives. The isocyanates used in most urethane elastomers prepared in the U.S. are TDI and MDI.

Elastomers are prepared, generally, from the prepolymers by chain extension with water, a polyol or a diamine. At this stage the elastomers can be classified into two broad groups based essentially on how

the elastomers are processed. One group comprises those elastomers in which the final shaping or molding and curing is accomplished during the chain extension step, i.e., the castable or liquid curable elastomers. In the other group an intermediate plastic polymer is formed. This may be milled, mixed with curing agents, fillers, etc., extruded, molded or shaped in some manner, and cured to the final elastomer. Chain extension and curing of the castable urethane elastomers is accomplished by use of diamines such as 4,4'-methylene-bis-(2-chloroaniline) (MOCA), polyols such as castor oil or mixtures of the two. The millable polyurethanes have been formed by chain extension of the prepolymer with diols, water and to a limited extent, diamines. Plastic polymers formed by chain extension must then, in most cases, be cured. Early types of water-extended elastomers were not storage stable and were cured by residual excess isocyanate left from the extension step. Most current polymers of this type are storage stable and are cross-linked with added curing agents such as polyisocyanates, peroxides, or formaldehyde and, in some polymers containing unsaturation, the traditional sulfur and its compounds normally used in curing rubber.

No matter what type of curing agent is used, a large measure of the strength, abrasion resistance and other desirable properties of these polyurethane elastomers is due to strong intermolecular forces such as hydrogen bonding(15). In fact, a linear thermoplastic urethane elastomer has been developed(16) which has no covalent crosslinks. It can be milled, extruded and molded, but possesses most of the properties of a true elastomer. Urethane elastomers have been prepared by the "one-shot" method, also, in which a diisocyanate, a polyol and, in some cases, a diamine are reacted in one step to form the finished elastomer (17,18).

Urethane elastomers are characterized by their extreme resistance to abrasion and high tensile strength, and these properties can be obtained without loading with fillers. In addition, these elastomers are largely saturated and hence are resistant to oxygen and ozone. They are oil resistant but are not resistant to steam and cannot be used at temp above about 250F(14).

Several vegetable oils or derivatives of fats and oils have been used in the preparation of urethane elastomers. Many formulations have been reported using castor oil(15,19,20). Some properties of elastomers based on two of the better formulations are listed in Table VIII. These castor oil-containing elastomers have low moisture absorption compared with analogous polyether-based elastomers. Urethane elastomers have been prepared, also, from various diol esters of dimer acid, sebacic acid, and azelaic acid. These polyester-based elastomers have been reported to be well suited for use as rocket fuel binders(21).

The largest single use of urethane elastomers is in mechanical goods such as seals, rings and diaphragms, which accounts for about 25% of urethane elastomer consumption(14). A small but rapidly increasing use is in fibers. Spandex fibers, as designated by the Textile Fiber Products Identification Act, are elastomeric fibers in which the fiber-forming substances is a long-chain polymer consisting of at least 85% segmented polyurethane" (22). Spandex fibers are reported to be superior to rubber in dyeability, strength, elasticity, flex life, and resistance to ultraviolet light, weathering, chemicals, and oils. It has been predicted(14) that they will replace much of the rubber thread now used in stretch fabric applications such as foundation

TABLE VIII
Castable Urethane Elastomers Containing Castor Oil

	Formulation	
	I	II
Composition, %		
Toluene diisocyanate.....	28.1	18.8
Polypropylene glycol—400.....	33.6	
Polypropylene glycol—2000.....		47.6
4,4'-Methylene-bis-(2-chloroaniline) (MOCA).....	6.3	12.1
Castor oil.....	32.0	21.5
Properties		
Tensile strength, psi.....	4,450	2,920
Elongation, %.....	300	290
Shore A hardness.....	97	74
Bashore rebound.....	30	25

garments and swim suits. New outlets are expected also in sportswear and men's clothing. Production of Spandex fibers amounted to less than a M lb in 1961 but is expected to rise to 4 M lb in 1962 and 18 M lb in 1967(14).

Perhaps not entirely unrelated is a potential application in imparting shrink resistance to wool. Research at the Western Regional Research Laboratory has resulted in development of a successful process that comprises grafting nylon on wool by interfacial polymerization (IFP). In the process currently used, wool is impregnated with a solution of a diamine, hexamethylene diamine, and is then passed through a solution of sebacyl chloride (which of course is derived from castor oil). This produces the familiar nylon 6-10 on the wool. More recent research has been directed toward application of a polyurethane to wool by IFP. In this procedure a diol is treated with phosgene to produce a bis-chloroformate. This is then treated with a diamine to produce the desired polyurethane on the wool. Essentially the same components are involved here as in the usual procedure for making urethanes from isocyanates. However, as shown in Figure 5, the phosgene is reacted with the diol, whereas in the usual synthesis of isocyanates it is reacted with the diamine. One of the diols currently being investigated for this application is ricinoleyl alcohol derived from ricinoleic acid of castor oil.

Coatings. Urethane coatings present an increasing and potentially large volume use of polyurethanes. It is an area of special interest to the fats and oils chemist, partly because oil-based materials have traditionally been used extensively in surface coatings and partly because a large proportion of the polyurethanes used in surface coatings contain significant amounts of fat derived materials. The particularly desirable properties generally associated with urethane coatings are toughness, abrasion resistance, chemical (corrosion) resistance and durability.

Many diverse coatings systems based on isocyanates have been developed, and the ASTM is trying to bring some order out of the chaos that now exists. An ASTM committee has defined a urethane vehicle as "one that contains a min of 10%, by wt, of polyisocyanate monomer" (non-volatile vehicle basis). With this as a basis, five types of urethane vehicles have been defined(23) (Table IX).

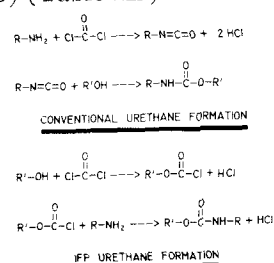


Fig. 5. Urethane formation by conventional and interfacial polymerization routes.

TABLE IX
 Urethane Vehicle Types

Class	ASTM type code number	Cure	Free -NCO	Description
One-package coatings (prolonged can stability)	1	air	no	Alkyd structure driers used.
	2	moisture	yes	Cured by ambient moisture.
	3	heat	no	Blocked; -NCO regenerated by heat.
Two-package coatings (limited pot life)	4	amine	yes	Cured with <i>catalytic</i> amount of reagent.
	5	polyol	yes	Cured with <i>substantial</i> amount of reagent.

The vast majority of urethane coatings used are of the one-package class and the most common of these is the air-dried, ASTM type-1. It is sometimes referred to as a urethane oil or a urethane alkyd, since it can be regarded as an alkyd in which the diisocyanate replaces the dicarboxylic acid such as phthalic acid normally used in an alkyd. The composition of two typical urethane oils is given in Table X(23). These urethane alkyds are formulated with the usual paint driers in normal amounts, and they dry in the same way as conventional air-drying alkyds, by virtue of the unsaturation in the fatty acid moiety of the drying oils.

The second type of vehicle listed in Table IX is characterized by the presence of free isocyanate groups. It is capable of conversion to a useful film by reaction of these isocyanate groups with ambient moisture. A typical vehicle would be composed of approx equal wt of TDI and a suitable polyol such as a mixture of polypropylene glycol and trimethylolpropane (TMP). Castor oil can replace the TMP in such a formulation on an equimolar basis to give a rubbery coating particularly suitable for elastomers or plastics.

The third type of coating is heat cured. It has found considerable application for coating electrical wiring. In this type of coating some of the isocyanate groups of the prepolymer are temporarily blocked with a suitable reactant such as a phenol. If TDI is reacted with phenol, it forms a urethane which is stable at room temp but dissociates on heating above about 140C. The isocyanate groups set free on baking are then capable of reacting with any materials deliberately added while the isocyanate was blocked. When such a blocked isocyanate coating is used on electrical wiring it is only necessary to twist two coated wires together and dip them into melted solder to get clean metal surfaces and a good soldered joint.

The ASTM committee has characterized the two package system as one wherein "one package contains a prepolymer or adduct that has free isocyanate groups capable of forming useful films by combining with components contained in a second package." The two types of two-package systems differ in that the second package of one type contains a relatively *small* amount of a catalyst, accelerator or crosslinking agent such as a monomeric polyol or

polyamine, and the second package of the other type contains a *substantial* amount of a resin with reactive hydrogen groups. The systems have a limited pot life after the two packages are mixed. For the first type, a suitable formulation is one in which one package contains the same ingredients as the moisture-cured polyurethanes dissolved in a suitable solvent such as a mixture of cellosolve acetate and xylene, and the second package contains a fraction of a percent of a catalyst such as triethylene diamine dissolved in benzene. In the second type, the first package contains a prepolymer with considerable free-NCO groups, and the second package contains a major amount of a polyol such as oxidized castor oil.

Minor Applications. Two specific examples serve to indicate the diverse uses of polyurethanes. Several artists are using the foams creatively. In one instance, the artist creates mosaics from finished colored foams. In another, the artist foams the polyurethane, which may be colored or pigmented, into free or abstract forms on a panel and then scorches or burns off portions with a blow torch. In this way, impressive, lightweight structural reliefs can be obtained.

The second specific example is in medicine. Polyurethane is used in a new surgical technique especially useful for the repair of certain long bone fractures. An advertisement(24) by a large producer of chemicals (not castor oil) states that the material is supplied to the surgeon in the form of a prepolymer and a catalyst, or "activator." The prepolymer is reported to be a mixture of "toluene diisocyanate, glycerine, castor oil, ricinoleyl alcohol, and corn oil." It is noteworthy that of the five components of the prepolymer, four are derived from fats and oils. Obviously, even in the minor applications of polyurethanes, as in the major applications, derivatives of fats and oils have a place.

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 TABLE X
 Formulations of Urethane Oil Resins

Component	Charge, lb	
	Resin I	Resin II
Linseed oil.....	60.0	70.0
Toluene diisocyanate.....	29.0	21.2
Glycerol.....	11.0	
Pentaerythritol.....		8.8
	100.0	100.0