Fat and Oil Products in Urethane Polymers

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Abstract

Urethane polymers comprise one of the most rapidly expanding areas of the organic chemical industry. Polyurethane production, estimated at about 100 million lb in 1960, is expected to rise to 500 million lb in 1965 and to have an ultimate potential in excess of a billion lb. The polymers are used in foams (flexible, semi-rigid and rigid), plastics, fibers, solid elastomers, surface coatings and adhesives. Fat- and oil-derived products have potential utility in all these applications. Fat-derived reactants include natural glycerides (e.g., castor oil), and other esters derived from reaction of fatty acids with polyols such as glycerol, pentaerythritol, sorbitol, sucrose, alkanol amines, etc., polymerized fatty acids, alkylene oxide derivatives of fatty acids and tall oil. The reactions of primary importance in the production of polyurethanes from isocyanates, including the urethane reaction, urea reaction, allophanate and biuret formation are discussed. A generalized treatment of the chemical technology involved in the preparation of representative polyurethane products is presented and the major areas in which fat and oil products are finding application in polyurethanes are noted.

Introduction

URETHANES are typically formed by the reaction of alcohols and isocyanates. The first isocyanates were synthesized more than a hundred years ago but it was not until the 1930's that the commercial potential of these compounds began to be realized. During World War II polyurethane fibers and plastics were used extensively in Germany and a well-integrated industry based on diisocyanates developed there, but in the U. S. large scale production of polyurethanes was not attained until the 1950's.

Discussion

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 have achieved significant industrial use. Some of these are illustrated in Figure 1. Of these, toluene diisocyanate (TDI) is used to a far greater extent than any of the others. Actually TDI as it is commonly used is composed of a mixture of 80% of the 2,4- and 20% of the 2,6-isomer. Although TDI is the workhorse of the polyurethane industry considerable quantities of MDI [methylene bis (4-phenyl isocyanate)] are also used. The others are used only to a relatively minor extent. Hexamethylene diisocyanate was the one most commonly used in the early days in Germany for the production of urethane fibers. Various naphthalene diisocyanates have also been investigated and the 1,5-isomer was the preferred isocyanate used in the original German work on elastomers.

As indicated earlier, urethanes are formed by the reaction of isocyanates and alcohols. However, the isocyanates are very reactive and versatile chemicals
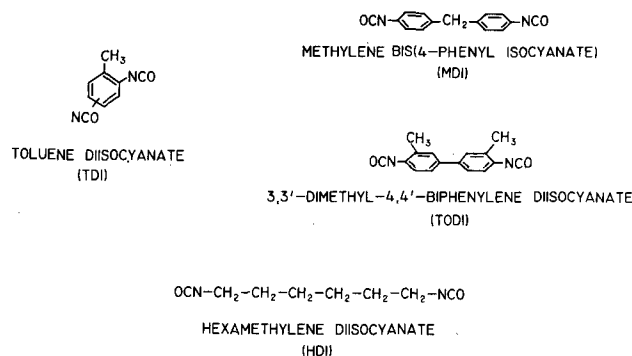

Fig. 1. Representative diisocyanates.

and they react with many different classes of compounds. These include acids, amines, amides, phenols, thiols, etc. The term polyurethane has come to be applied to the class of polymeric materials which contain urethane linkages even if polymer segments are also joined by other linkages such as ureas. Extensive reviews which are available describe the numerous reactions of isocyanates in detail (1,2). 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 and is illustrated in Figure 2. The type reaction is one in which 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.

In Figure 3 are presented some of the reactions of isocyanates which are particularly relevant to the preparation of polyurethanes. 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 the reaction products may have widely different properties. But what especially aroused great early interest in the polyurethanes was the possibility of combining the polymer forming reaction with the reaction of isocyanates with water to produce carbon dioxide gas and the obvious implications of this for the production of foams.

What are the polyurethanes used for and what is the trend? This can perhaps be indicated by use of some statistics. In Table I is given some data concerning the present and projected consumption of polyurethanes in major areas of use.

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

A typical formulation using castor oil is 60 parts castor oil, 40 TDI, 0.5 surfactant such as Dow Corn-
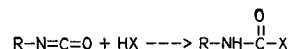
$$R-N=C=O + HX \longrightarrow R-NH-\overset{O}{\underset{||}{C}}-X$$

Fig. 2. Generalized reaction of isocyanates.

$$R-NCO + R'-OH \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-R'$$
URETHANE

$$R-NCO + H_2O \longrightarrow [R-NH-\overset{\overset{\textstyle O}{\|}}{C}-OH] \longrightarrow R-NH_2 + CO_2 \uparrow$$

$$R-NCO + R-NH_2 \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-NH-R$$
UREA

$$R-NCO + R'-\overset{\overset{\textstyle O}{\|}}{C}-OH \longrightarrow [R-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-\overset{\overset{\textstyle O}{\|}}{C}-R'] \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-R' + CO_2 \uparrow$$
AMIDE

$$R-NCO + ArOH \underset{150}{\overset{25}{\rightleftharpoons}} R-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-Ar$$
URETHANE

$$R-NCO + R'-NH-\overset{\overset{\textstyle O}{\|}}{C}-NH-R'' \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle R'}{|}}{N}-\overset{\overset{\textstyle O}{\|}}{C}-NH-R''$$
UREA   BIURET

$$R-NCO + R'-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-R'' \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle R'}{|}}{N}-\overset{\overset{\textstyle O}{\|}}{C}-O-R''$$
URETHANE   ALLOPHANATE

$$R-NCO + R'-NH-\overset{\overset{\textstyle O}{\|}}{C}-R'' \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-\overset{\overset{\textstyle R'}{|}}{N}-\overset{\overset{\textstyle O}{\|}}{C}-R''$$
AMIDE   ACYL AMIDE

R-NCO —— BASIC OR METALLIC CATALYST —→ DIMER OR URETIDINEDIONE / TRIMER OR ISOCYANURATE
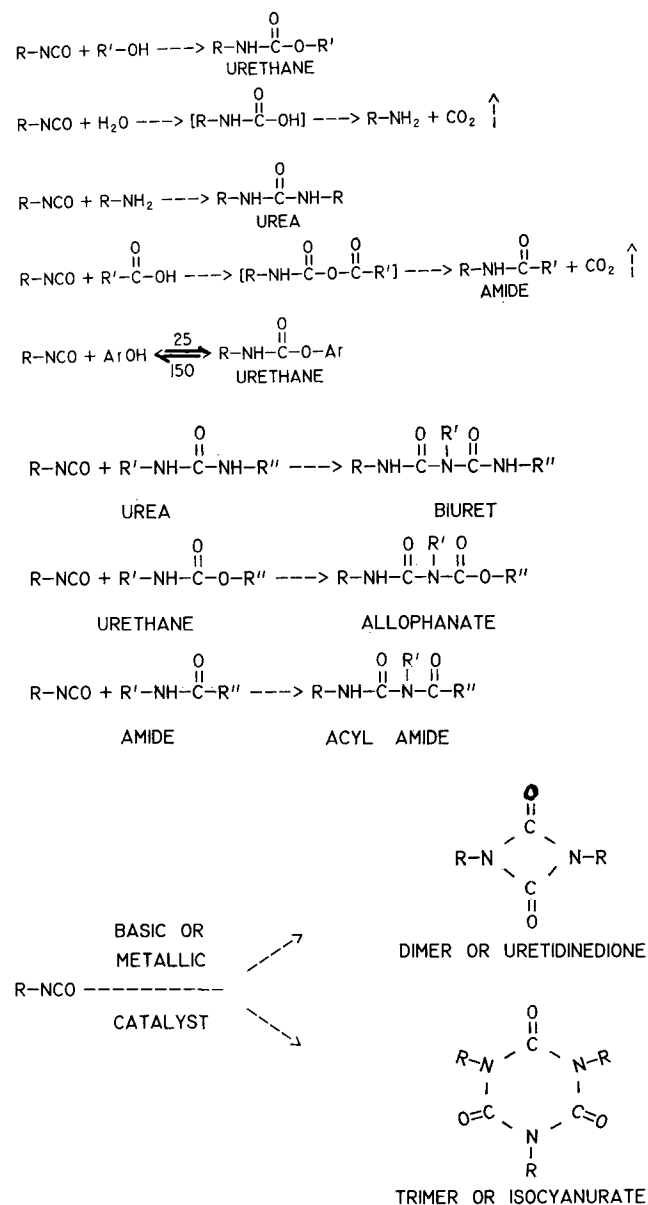
FIG. 3. Reactions of isocyanates.

ings' DC 200 (50 Cs), 1.9 catalyst such as 2-diethyl-aminoethanol, and 2.5 parts water (3). 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 hydroxyl groups per mole, and the diisocyanate at a temperature of 100 to 130C for about an hour. To produce a foam the prepolymer which contains about 10% by weight of unreacted —NCO groups is mixed with the surfactant and then the catalyst, which has been buffered and dissolved

TABLE I
Consumption of Polyurethanes
(Millions of lb)

	Foams[a]		Elasto-mers[b]	Coat-ings[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).

TABLE II
Effect of Proportion of Castor Oil on Foam Properties

Castor oil (%)	Type	Density, lb/ft³	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

in sufficient water to react with residual isocyanate, is stirred in. An exothermal reaction sets in almost at once but the mixture can be stirred for about a minute before significant foaming, resulting from evolution of CO_2, begins. With the above formulation the foam continues to rise for about 20 min but the foaming time can be varied considerably by suitable changes in the 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 above formulation affords a semi-rigid foam. The data in Table II indicate some of the different properties obtainable by such a relatively simple change as that of the proportions of castor oil, TDI and water, the amount of catalyst and surfactant being kept constant (3). It will be noted that as the proportion of castor oil was increased from 50 to 80% the character of the foam changed from rigid (or semi-rigid) to flexible and the density increased. The examples given in Table II feature the use of castor oil but in suitable formulations other polyols could be used. These include blown oils, castor or other oils alcoholyzed with polyols such as glycerol, pentaerythritol, sorbitol, trimethylolpropane, etc. The use of tall oil in the production of polyurethane foams has recently been proposed (4).

Some of the early German work employed castor oil but most was based on the use of polyesters. These 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. 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.

The whole foaming procedure was revolutionized in the late 1950's by the introduction of the solvent blowing technique. This has taken over almost entirely in the production of polyurethane foams. In this technique a low-boiling fluorocarbon solvent such as trichlorofluoromethane (CCl_3F) is used to supply the gas required for foaming. This liquid boils at 24C, just above room temperature, and the heat evolved during the urethane reaction is sufficient to vaporize the CCl_3F. It is actually cheaper to use these fluorocarbons to produce a given amount of gas than it is to use CO_2 obtained by reaction of the relatively expensive isocyanate with water and the fluorocarbon blown foams have better thermal insulation properties.

The composition and some properties of two typi-

TABLE III

Composition and Properties of Castor-Urethane Foams

Composition (g) :	I	II
TDI	49.3	46.1
Pentaerythritol monoricinoleate	35.9	
Castor oil		21.0
Trimethylol propane	14.8	
Triisopropanolamine		21.2
Hexol [a]		11.7
CCl₃F	15.0	16.0
Surfactant	1.5	1.5
Catalyst	0.6 [b]	0.65 [b+c]
Properties :		
Density (lb/ft³)	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.

cal castor based, solvent blown foams are given in Table III (5).

In using such a system, an isocyanate containing prepolymer is prepared by reacting all of the diisocyanate with a portion of the polyol. The desired amount of CCl_3F 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 minutes although the foaming time can be varied to a moderate extent by suitable changes in the catalyst system.

One of the most recent developments in urethane foam technology is frothing (6). In the frothing technique a fluorocarbon boiling well below room temperature is used and pressure equipment is required. The most distinguishing feature of the frothing technique is that the mixture has the appearance of an aerosol shaving cream as it discharges from the processing equipment, whereas, in the older solvent-blown procedure it is discharged from mixing equipment as a liquid. The fluorocarbon most commonly used in frothing is dichlorodifluoromethane (b.p. −28C).

One of the more promising fields of utilization of polyurethanes is in elastomers. 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. They 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 million lb in 1959 and 6.8 million lb in 1960 and was an estimated 11 million lb in 1961 (7). 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 In each procedure a polyol is generally first reacted 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 United States are TDI and MDI.

Elastomers are generally prepared from the prepolymers by chain extension with either water, a polyol or a diamine. At this stage the elastomers

may 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 prepolymers with diols, water and to a limited extent with diamines. The plastic polymers formed by chain extension must then, in most cases be cured. Most correct polymers of this type are crosslinked with added curing agents such as polyisocyanates, peroxides, or formaldehyde and in the case of some polymers containing unsaturation, the conventional sulfur and its compounds normally used in curing rubber.
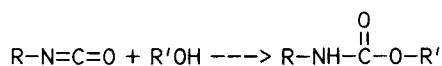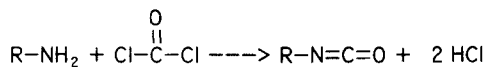
No matter what type of curing agent is used, a large measure of the strength, abrasion resistance and other desirable properties of these polyurethane elastomers is due to strong intermolecular forces such as hydrogen bonding (8). In fact, a linear thermoplastic urethane elastomer has been developed (9) which has no covalent crosslinks and may be milled, extruded and molded but possesses most of the properties of a true elastomer.

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 (8,10,11). Some properties of elastomers prepared using two of the better formulations are listed in Table IV. These castor oil containing elastomers have low moisture absorption compared to analogous polyether based elastomers. Urethane elastomers have also been prepared 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 (12).
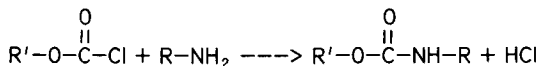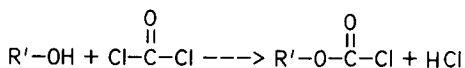
The largest single area of use of urethane elastomers at present is in the production of mechanical goods such as seals, rings and diaphragms which accounts for about 25% of urethane elastomer consumption (7). A small but rapidly increasing use is in fibers. Spandex fibers as designated by the Textile Fiber Products Identification Act, includes elastomeric fibers in which the fiber-forming substance is a long chain polymer consisting of at least 85% segmented polyurethane (13). Spandex fibers are reported to be superior to rubber in dyeability, strength, elasticity, flex life, and resistance to ultraviolet light, weathering, chemicals and oils, and it has been predicted (7)

TABLE IV

Castable Urethane Elastomers Containing Castor Oil

Composition (%) :	I	II
TDI	28.1	18.8
PPG-400	33.6	
PPG 2000		47.6
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

$$R-NH_2 + Cl-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-N=C=O + 2\ HCl$$

$$R-N=C=O + R'OH \longrightarrow R-NH-\overset{\overset{O}{\|}}{C}-O-R'$$

CONVENTIONAL URETHANE FORMATION

$$R'-OH + Cl-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R'-O-\overset{\overset{O}{\|}}{C}-Cl + HCl$$

$$R'-O-\overset{\overset{O}{\|}}{C}-Cl + R-NH_2 \longrightarrow R'-O-\overset{\overset{O}{\|}}{C}-NH-R + HCl$$

IFP URETHANE FORMATION

FIG. 4. Urethane formation reactions by conventional and interfacial polymerization routes.

that they will replace much of the rubber thread now used in stretch fabric applications such as foundation garments and swim suits. Production of spandex fibers amounted to less than a million pounds in 1961 but is expected to rise to 4 million lb in 1962 and to about 18 million lb in 1967 (7).

Perhaps not entirely unrelated is a potential application in imparting shrink resistance to wool. Research at the Western Regional Research Laboratory has resulted in the development of a successful process which 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 sebacoyl chloride (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 (COCl₂) 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 4, the phosgene is reacted with the diol while 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.

Urethane coatings present an increasing and potentially large volume use of polyurethanes. It is an area of special interest to the fats and oils chem-

ist 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 which contains a minimum of 10%, by weight, of polyisocyanate monomer (non-volatile vehicle ba-

TABLE VI

Formulations of Urethane Oil Resins

Component	Charge (pounds)	
	I	II
Linseed oil	60.0	70.0
TDI	29.0	21.2
Glycerol	11.0	......
Pentaerythritol	......	8.8
	100.0	100.0

sis). With this as a basis, five types of urethane vehicles were then defined (14). These are illustrated in Table V.

The vast majority of the urethane coatings used now are of the one package type and, of these the most common is the air-dried, ASTM type-1. This is sometimes referred to as a urethane oil or a urethane alkyd as 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 VI (14). 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.

The second type of vehicle listed in Table V is characterized by the presence of free isocyanate groups in the vehicle and is capable of conversion to a useful film by reaction of these isocyanate groups with ambient moisture. A typical vehicle would be composed of approximately equal weights of TDI and a suitable polyol such as a mixture of polypropylene glycol and trimethylolpropane. 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 and 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 temperature 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 urethane 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 having free isocyanate

TABLE V

Urethane Vehicle Types

Packages	ASTM coding	Cure	Free —NCO	Description
1 (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
2 (limited pot life)	4	amine	yes	Cured with *catalytic* amount of reagent
	5	polyol	yes	Cured with *substantial* amount of reagent

groups capable of forming useful films by combining with components contained in a second package. The distinguishing feature between the two types of two-package systems is that in one the second package contains a relatively *small* amount of a catalyst, accelerator or crosslinking agent such as a monomeric polyol or polyamine and in the other the second package contains a *substantial* amount of a resin such as blown castor oil which has reactive hydrogen groups. The systems have a limited pot life after the two packages are mixed.

The major applications of polyurethanes are in foams, elastomers and coatings. Derivatives of fats and oils have a place in all of these—provided adequate research is done to find and keep it.

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Reactions of Ozone. VII.

Ozonization of Fatty Acids and Their Derivatives

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Abstract

Ozone was a useful tool very early in the history of structural studies involving fatty acids and their derivatives. More recently the productions of azelaic and pelargonic acids by the ozonolysis of oleic acid has become of commercial importance. This paper reviews the chemistry of the ozonolysis of various unsaturated fatty acids and their derivatives. The products can be varied from a single starting material depending on the manner of decomposing the intermediate ozonide. Thus, variations in starting material and variations in procedure make possible a great variety of straight chain products containing one or two functional groups such as carboxyl, aldehyde, hydroxyl, and amino.

Introduction

IN THE DECADE 1951–61, ozonization chemistry has mushroomed in its use as a general chemical tool of the synthetic chemist working with unsaturated fatty acids, oils and their derivatives. This is evidenced by the accelerated growth of *primary* ozone publications explaining some new facet of organic ozone chemistry as shown in Figure 1.

In addition, numerous papers describing the use of ozone as a step in a reaction sequence have been published. No special mention of ozone was made there because of the increasing acceptance of ozone for everyday use by laboratories that have ozonators on hand. There are 450 to 475 laboratory ozonators in the U.S. to date.

The versatility and useful applications of ozone for unsaturation values, structure determinations, production of mono and polybasic acids, aldehydes, amines, omega-amino acids, amine oxides, peracids and epoxides are coming into their own as discussed below.

Discussion

Unsaturation

For years a simple, reliable, quantitative method for determining olefinic unsaturation has been sought. Existing methods such as bromination, iodination, catalytic hydrogenation and peroxide reactions have their specific limitations as discussed by numerous investigators (2,5,23,31). However, for many olefinic compounds, ozone is an excellent titrimetric reagent (23). Maggiolo (19), Boer and Kooyman (6) have shown that ozonization could well supplant these other methods. The procedure can be simplified by using commercially available apparatus. The analysis is based on determining the time required to titrate a sample of olefin with a stream of ozonized air containing a known amount of ozone.

This proposed analytical determination eliminates most of the limitations and failings found in the current bromine and iodine number procedures. The presence of tertiary hydrogens as in α-pinene does not cause the high varying results found by the bromine technique. The determination of olefinic unsaturation in the presence of an activated aromatic ring as in isosafrole is also shown to be feasible. The results given in Table I are expressed as "Ozone Values," i.e., the number of grams of ozone absorbed per 100 g of unsaturated fatty acid.

Samples containing small amounts of conjugated

TABLE I

Compound	Ozone value theory	Ozone value found
Methyl oleate	16.2	16.2, 16.4
Linoleic acid	34.2	34.2, 34.4, 34.4, 34.5
Methyl linolenate	49.2	49.2, 49.5
Isosafrole	29.5	29.0, 29.7, 29.1
α-Pinene	35.3	36.1, 35.6
Olive oil	16.4	16.3, 16.5
Sesame oil	21.3	21.7, 21.7
Safflower oil	27.1	27.5, 27.5, 27.8
Tall oil	24.3	24.3, 24.5
Tall oil	23.9	23.8