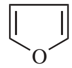
FURAN DERIVATIVES

1. Introduction

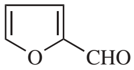
Furan (**1**) is a 5-membered heterocyclic, oxygen-containing, unsaturated ring compound. From a chemical perspective it is the basic ring structure found in a whole class of industrially significant products. The furan nucleus is also found in a large number of biologically active materials. Compounds containing the furan ring (as well as the tetrahydrofuran ring) are usually referred to as furans (1). From a manufacturing standpoint, however, furfural (**2**) is the feedstock from which all of the commercial furan derivatives are derived, as it the easiest and least expensive to manufacture. In this article, the more common name furfural is used in place of the *Chemical Abstracts* name, 2-furancarboxaldehyde.

Furan is produced from furfural commercially by decarbonylation; loss of carbon monoxide from furfural gives furan directly. Tetrahydrofuran (**3**) is the saturated analogue containing no double bonds.



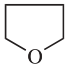
furan [*110-00-9*]

(**1**)



furfural [*98-01-1*]

(**2**)



tetrahydrofuran [*109-99-9*]

(**3**)

Furfural is derived from biomass by a process in which the hemicellulose fraction is broken down into monomeric 5-carbon sugar units which then are dehydrated to form furfural.

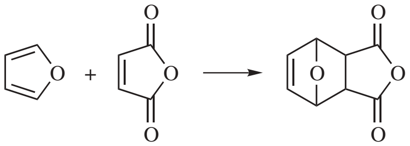
This article is limited primarily to simple furans in which the nucleus occurs as a free monocycle, and in general, does not include compounds in which the furan ring is fused to another ring. In recent years it has mistakenly become common practice to refer to polychlorinated isobenzonfurans simply as *furans*. These isobenzofurans are comprised of chlorine-containing fused rings, are not simple furans, and are not included here. The presentation is generally limited to compounds (including resins or polymers) derived from furfural. Ring closure methods to prepare furan or tetrahydrofuran compounds are not covered.

Tetrahydrofuran (**3**) is produced commercially from furfural by decarbonylation followed by hydrogenation; it is also produced by several different methods from other raw materials. A complete discussion of tetrahydrofuran is found under Ethers. Polymers of tetrahydrofuran are covered under the general topic, Polyethers. Several other compounds containing the tetrahydrofuran ring, which are most readily produced from furfural, are discussed here.

The furan nucleus is a cyclic, dienic ether with some aromaticity (2). It is the least aromatic of the common 5-membered heterocycles. A comparison of the aromaticity (3) of several of these compounds is shown below.

Property	Furan	Thiophene	Pyrolle	Benzene
Unified aromaticity index	53	81.5	85	100
Resonance energy, kJ/mol	113.8	180.0	169.4	191.6
kcal/mol	27.2	43.0	40.5	45.8

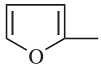
The balance between aromatic and aliphatic reactivity is affected by the type of substituents on the ring. Furan functions as a diene in the Diels-Alder reaction. With maleic anhydride, furan readily forms 7-oxabicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic anhydride in excellent yield [5426-09-5] (**4**).



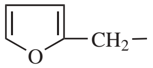
(**4**)

Alkylfurans, halofurans, alkoxyfurans, furfuryl ester and ethers, and furfural diacetate [613-75-2] behave similarly. Furans containing electron withdrawing constituents, for example, furfural, 2-furoic acid, and nitrofurans, fail as dienes even with very strong dienophiles.

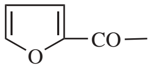
Radicals derived from furan are named similarly to analogous radicals in the benzene series. Typical radicals are 2 (or α)-furyl (**5**), 2-furfuryl (**6**), 2-furoyl (**7**), and 2-furfurylidene (**8**):



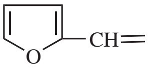
(**5**)



(**6**)



(**7**)



(**8**)

Centers of high electron density occur at the *alpha* positions of the ring which governs the behavior of furans in electrophyllic substitution reactions. Such reactions proceed readily at available alpha positions. Orientation of incoming groups is similar to that observed in benzene compounds, eg, 3-methylfuran is nitrated to yield 2-nitro-3-methylfuran (similar to *ortho*) and 3-furancarboxaldehyde gives 2-nitro-4-furancarboxaldehyde (corresponding to *meta*). Furan compounds differ from benzene analogues in the ease in which they are polymerized; resinification or polymerization is easily brought about by strong acids. Resins or polymers are the principal end products or furfural utilization and account for a high percentage of the ultimate consumption of furfural.

For reviews on furan chemistry see References (1,4–7). The monograph by Dunlop and Peters (1), published in 1953 remains as the most comprehensive review of furan chemistry available. Unfortunately, it has never been revised, has been out of print for many years, and is not readily available. An excellent, review by Dean (7) covers advances in furan chemistry up through about 1982.

2. Furfural

Furfural was first isolated in the early nineteenth century. Dobereiner is credited with the discovery. He obtained a small amount of a yellow “oil” (too little to characterize) as a by-product in the preparation of formic acid (8). Other chemists found that the same “oil” having a characteristic aroma could be obtained by boiling finely divided vegetable materials such as oats, corn, sawdust, bran, etc, with aqueous sulfuric acid or other acids (9,10). The oil was present in the liquid resulting from condensation of the vapors produced during heating. The empirical formula $C_5H_4O_2$ was determined by Stenhouse (10). Ring structure and location of the aldehyde group were established by the efforts of Baeyer, Markwald, and Harries (11–14). For some time, furfural was a laboratory curiosity and a compounding ingredient of perfumes.

It was not until the twentieth century that furfural became important commercially. The Quaker Oats Company, in the process of looking for new and better uses for oat hulls found that acid hydrolysis resulted in the formation of furfural, and was able to develop an economical process for isolation and purification. In 1922 Quaker announced the availability of several tons per month. The first large-scale application was as a solvent for the purification of wood rosin. Since then, a number of furfural plants have been built world-wide for the production of furfural and downstream products. Some plants produce as little as a few metric tons per year, the larger ones manufacture in excess of 20,000 metric tons.

Furfural can be classified as a reactive solvent. It resinifies in the presence of strong acid; the reaction is accelerated by heat. Furfural is an excellent solvent for many organic materials, especially resins and polymers. On catalyzation and curing of such a solution, a hard rigid matrix results, which does not soften on heating and is not affected by most solvents and corrosive chemicals.

Furfural is formed by a series of reactions when biomass materials containing hemicellulose are treated with acid at an elevated temperature. Hemicellulose is basically a polymer of 5-carbon sugars. Cellulose and starch are polymers of 6-carbon sugars. Most plant matter is made up of cellulose, hemicellulose, and lignin. When treated with aqueous acid, the hemicellulose is depolymerized to give primarily xylose, which under the reaction conditions loses three molecules of water and cyclizes to give furfural. The precise mechanism for the formation of furfural from C_5-sugars or their precursors has not yet been unequivocally established. Superheated steam passing through a reactor containing eg, ground oat hulls, provides heat for the conversion as well as carrying furfural away from the reaction mixture. Furfural also resinifies under the reaction conditions so the steam serves a very important function by removing the furfural as fast as it is formed. Most of the other compounds present in the reaction vessel are not volatile with steam. Condensation of the vapors gives a dilute solution of furfural in water. Furfural is isolated from the water by azeotropic distillation and phase separation, followed by dehydration and purification by distillation.

2.1. Physical Properties.

Furfural [98-01-1] (2-furancarboxaldehyde), when freshly distilled, is a colorless liquid with a pungent, aromatic odor reminiscent of almonds. It darkens appreciably on exposure to air or on extended storage. Furfural is miscible with most of the common organic solvents, but only slightly miscible with saturated aliphatic hydrocarbons. Inorganic compounds, generally, are quite insoluble in furfural.

The most important physical properties of furfural, as well as similar properties for furfuryl alcohol, tetrahydrofurfuryl alcohol and furan are given in Table 1. The tabulated properties of furfural are supplemented by a plot (Fig. 1) of the vapor–liquid compositions for the system, furfural–water (15,16).

2.2. Chemical Properties.

The chemical properties of furfural are generally characteristic of aromatic aldehydes but with some differences attributable to the furan ring. Furfural resinifies in the presence of acid and

Table 1. **Physical Properties of Furan Derivatives**

	Furfural	Furfuryl alcohol	Furan	Tetrahydrofurfuryl alcohol
General Properties				
molecular weight	96.09	98.10	68.08	102.13
boiling point at 101.3 kPa (1 atm), °C	161.7	170	31.36	178
freezing point, °C	−36.5		−85.6	< − 80
metastable crystalline form		−29		
stable crystalline form		−14.63		
refractive index, n_D				
20°C	1.5261	1.4868	1.4214	1.4250
25°C	1.5235			1.4499
density, d_4, at 20°C	1.1598	1.1285	0.9378	1.0511
vapor pressure, 100 Pa (0.75 mm Hg)				
−15°C			130	
0°C			277	
20°C			658	
50°C			1980	
60°C	21	8.5		10
80°C	56	25		28
100°C	132	58		68
120°C	280	164		156
140°C	567	361		324
vapor density (air = 1)	3.3	3.4	2.36	3.5
critical pressure, P_c, MPa[a]	5.502		5.32	
critical temperature, T_c, °C	397		214	
solubility, wt %, in water				
20°C	8.3	∞		∞
25°C			1	
alcohol; ether	∞	∞	∞	∞
Thermodynamic properties				
heat of vaporization, kJ/mol[b]	38.6		27.1	
specific heat (liq), J/(g · K)[b]				
20°C			1.699	
20–27°C				1.774
20–100°C	1.741			
25°C		2.100		
specific heat (vap), J/(g · K)[b]				
31.36°C			1.021	
98.99°C			1.251	
heat of combustion (liq), kJ/mol[b]	2344	2548	2092	2965
Fluid properties				
viscosity, mPa · s (= cP)				
20°C			0.38	6.24
25°C	1.49	4.62		
surface tension, mN/m (=dyn/cm)				
25°C		ca 38		37
29.9°C	40.7			
Electrical properties				
dielectric constant				
20°C	41.9			
23°C				13.6

Table 1 (*Continued*)

	Furfural	Furfuryl alcohol	Furan	Tetrahydrofurfuryl alcohol
	Flammability properties			
explosion limits (in air), vol %	2.1–19.3	1.8–16.3	2.3–14.3	1.5–9.7
flash point, °C				
Tag closed cup	61.7	65	−35.5	
Tag open cup				83.9
ignition temperature, °C	315	391		282

[a] To convert MPa to atm, divide by 0.101.

[b] To convert J to cal, divide by 4.184.

heat. Open chain compounds are formed from furfural under strong oxidizing conditions. Because furfural has a fairly low degree of aromaticity, the ring is more easily saturated than the benzene ring on catalytic hydrogenation. Depending on catalysts and conditions, products of hydrogenation can include furfuryl alcohol [98-00-0], tetrahdrofurfuryl alcohol [97-99-4], 2-methylfuran [534-22-5] and even 2-methyltetrahydrofuran [96-47-9]. Under strongly reducing conditions, the ring is opened.

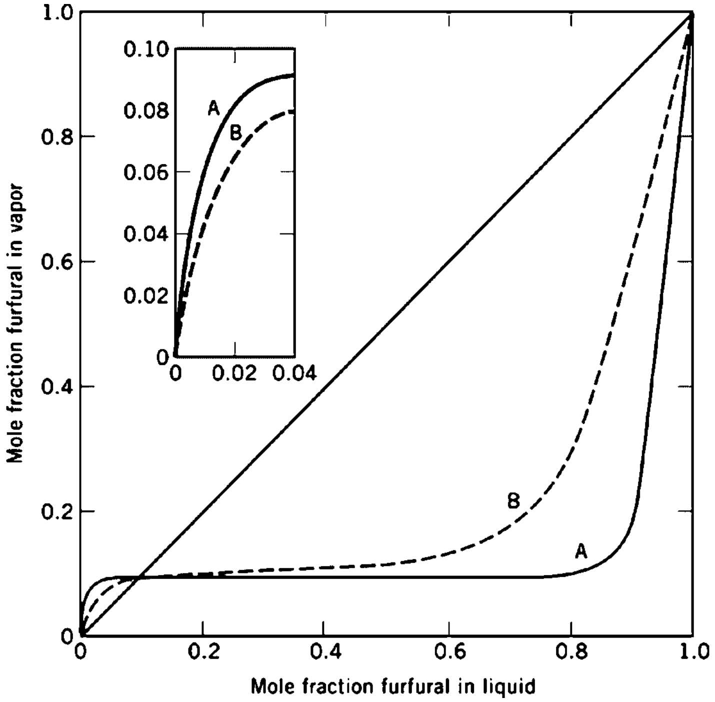


Fig. 1. Vapor–liquid equilibria in the furfural–water system. A at 101 kPa (1 atm) (15). B at 598 kPa (5.92 atm) (16).

Furfural is very thermally stable in the absence of oxygen. At temperatures as high as 230°C, exposure for many hours is required to produce detectable changes in the physical properties of furfural, with the exception of color (17). However, accelerating rate calorimetric data shows that a temperature above 250°C, in a closed system, furfural will spontaneously and exothermically decompose to furan and carbon monoxide with a substantial increase in pressure. The pressure may increase to 5000 psi or more, sufficient to shatter the container (18).

Furfural can be oxidized to 2-furoic acid [88-14-2], reduced to 2-furanmethanol [98-00-0], referred to herein as furfuryl alcohol, or converted to furan by decarbonylation over selected catalysts. With concentrated sodium hydroxide, furfural undergoes the Cannizzaro reaction yielding both 2-furfuryl alcohol and sodium 2-furoate [57273-36-6].

Acetals are readily formed with alcohols and cyclic acetals with 1,2 and 1,3-diols (19). Furfural reacts with poly(vinyl alcohol) under acid catalysis to effect acetalization of the hydroxyl groups (20,21). Reaction with acetic anhydride under appropriate conditions gives the acylal, furfurylidene diacetate [613-75-2] (22,23).

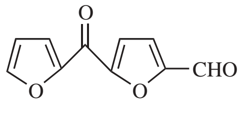
Nitration and halogenation of furfural occurs under carefully controlled conditions with introduction of the substituent at the open 5-position (24,25). Nitration of furfural is usually carried out in the presence of acetic anhydride, resulting in the stable compound, 5-nitrofurfurylidene diacetate (26,27). The free aldehyde is isolated by hydrolysis and must be used immediately in a reaction because it is not very stable.

Just as most other aldehydes do, furfural condenses with compounds possessing active methylene groups such as aliphatic carboxylic esters and anhydrides, ketones, aldehydes, nitriles, and nitroparaffins.

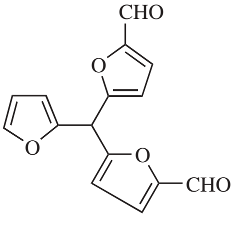
The electron-withdrawing character of the aldehyde group makes furfural quite resistant to hydrolytic fission. Even at high temperatures, long exposure is required to effect extensive ring opening destruction of furfural by dilute acids (28). Under these conditions a competing reaction takes place: black polymer results, and the rate of its formation is dependent upon the hydrogen ion concentration and temperature.

Furfural is a resin former under the influence of strong acid. It will self-resinify as well as form copolymer resins with furfuryl alcohol, phenolic compounds, or convertible resins of these. Conditions of polymerization, whether aqueous or anhydrous, inert or oxygen atmosphere, all affect the composition of the polymer. Numerous patents have issued relating to polymerization and to applications. Although the resins exhibit a degree of brittleness, they have many outstanding properties; a number of applications are discussed under "Uses."

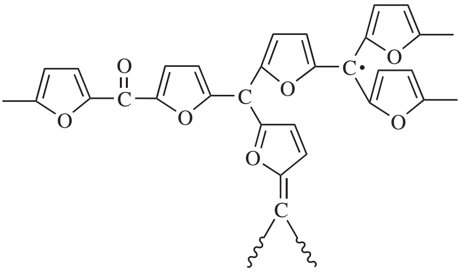
Several early interpretations of the polymerization mechanism have been proposed (1,17,29–31). Because of the complexity of this polymerization and insoluble character of the products, key intermediates have not ordinarily been isolated, nor have the products been characterized. Later work, however, on the resinification of furfural (32,33) has provided a new insight on the polymerization mechanism, particularly with respect to thermal reaction at 100–250°C in the absence of air. Based on the isolation and characterization of two intermediate products (**9**) and (**10**), structure (**11**) was proposed for the final resin. This work also explains the color produced during resinification, which always is a characteristic of the final polymer (33). The resinification chemistry is discussed in a recent review (5).



(**9**) [*57583-51-4*]



(**10**) [*72918-23-1*]



(**11**)

The presence of stable free radicals in the final polycondensate is supported by the observation that traces of (**11**) have a strong inhibiting effect on the thermal polymerization of a number of vinyl monomers. Radical polymerization was inhibited to a larger extent by a furfural resin than by typical polymerization inhibitors (34). Thermal degradative methods have been used to study the structure of furfural resinified to an insoluble and infusible state, leading to proposed structural features (35).

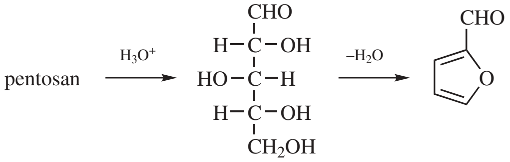
2.3. Manufacture.

Furfural is produced from annually renewable agricultural sources such as nonfood residues of food crops and wood wastes. The pentosan polysaccharides, xylan and arabinan, commonly known as hemicellulose, are the principal precursors of furfural and are always found together with lignin and cellulose in plant materials.

By-products such as corncobs, cottonseed hulls, oat hulls, rice hulls, and cereal grasses constitute one large natural storehouse; bagasse, a by-product of sugar-cane harvesting, another; and wood and wood products yet another. The chief constituent of the pentosan fraction of these materials is xylan, a polysaccharide having backbone chains of β-D-xylopyranosyl residues (33). According to published data (34), xylan with a small amount of arabinan, a highly branched polysaccharide of α-araibinofuranosyl residues (35), accounts for 2–30% of cereal straws and grains, approximately 15–25% of deciduous woods and 5–15% of coniferous woods, based on the dry matter of these plants.

Theoretically, all pentosan-containing substances are potentially usable for the production of furfural. Only a relatively few, however, are commercially significant (1,36,37). Corncobs, oat hulls, rice hulls, and bagasse contain sufficient levels of pentosans and are often easily available in large tonnages within a limited radius of a furfural-producing plant. The simultaneous occurrence of side reactions complicates the recovery of furfural and limits its practical yield, which is far from quantitative under any commercial mode of operation. The average weight yield of furfural based on the dry weight of these raw materials is 10% or less. Thus, the economics of furfural production is highly dependent upon pentosan content, availability, and cost of raw materials, as well as the expense of collecting, shipping, and handling them.

Furfural is commercially produced in batch or continuous digesters (37) where the pentosans are first hydrolyzed to pentoses (primarily xylose (**12**), which are then subsequently cyclodehydrated to furfural:



(**12**)

Strong inorganic acid can be used as a reaction catalyst, or if the temperature is raised high enough, sufficient acetic acid is produced by the heat to catalyze formation of furfural.

In all processes, raw material is charged to the digester and heated with high pressure steam. Enough excess steam is used to drive the furfural out of the reaction zone as vapor. The condensed reactor vapors are fed to a stripping column from which an enriched furfural–water distillate mixture is taken overhead and condensed. The liquid passes into a decanter where it separates into two layers. The furfural-rich lower layer containing about 6% water is processed further to obtain the furfural of commerce, and the water-rich layer containing about 8% furfural is recycled back to the stripper column as reflux. The last process steps are dehydration and distillation. The furfural isolation and recovery process is illustrated in Figure 2. Flow charts for the Escher-Wyss and Rosenlew, two slightly different processes can be found in Ref. 38. In general, regardless of the process employed, the cellulose in the raw material undergoes only partial degradation and remains with the lignin in the by-product residue.

Most laboratories now use gas chromatographic methods for the analysis of refined furfural. For dilute aqueous solutions, wet methods are sometimes more appropriate. A number of wet analytical methods for quantitative estimation of furfural have been reported (1), yet none have universal acceptance. For the most part, they can be divided into two general categories: those involving reactions of the aldehyde group, and those that are dependent upon the unsaturated characteristics of the furan ring. Accordingly, the determination of furfural is generally subject to interference by carbonyl compounds or other unsaturated substances. The quantitative measurement of furfural in water may be carried out by uv spectroscopy; absorbance is measured at 276 nm (39). This method is best used on dilute solutions. However, uv-absorbing impurities such as phenolic compounds interfere with the analysis. The Hughes-Acree method, based on the reaction of bromine with the double bonds in furfural was at one time the method of choice (1).

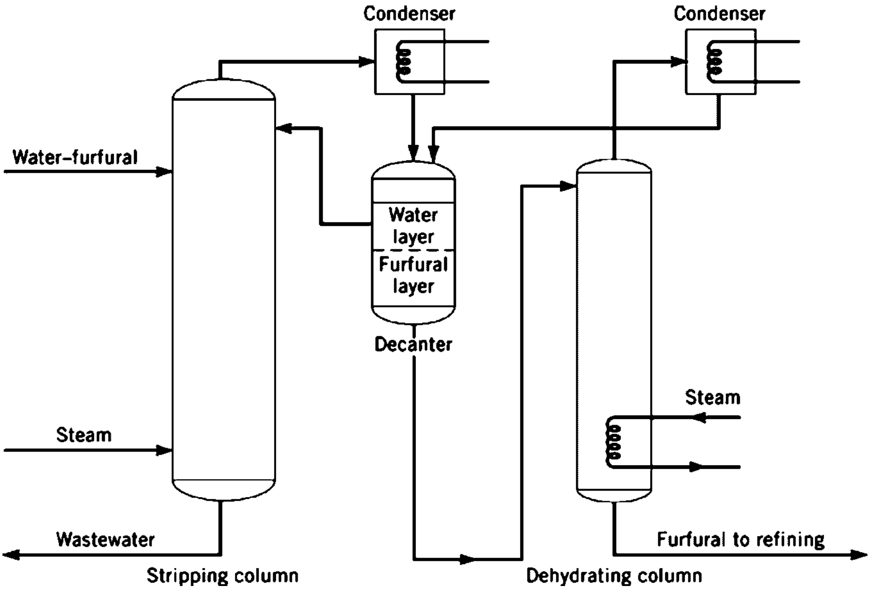


Fig. 2. Furfural recovery from aqueous solutions.

The estimation of furfural potential of various raw materials is best done by the AOAC method (1). Although liquid chromatographic methods are now available for the estimation of polymeric pentosans, results do not always correlate well with furfural formation.

Furfural is not corrosive to metal and can be shipped in mild-steel tank cars or trucks or steel drums. Storage in either aboveground or underground installations is satisfactory. For extended storage with maximum stability, cool storage conditions and nitrogen blanketing are recommended. Because furfural is an excellent solvent and penetrant, care must be taken that all joints are secure and that the pump and valve packings are in good condition. Unopened drums may be stored in cool locations for months without appreciable change in physical properties.

The flash point of furfural is 143°F by Tag Closed Cup. Because of its chemical reactivity, furfural should be kept away from strong acids, alkalies or strong oxidizing chemicals. When furfural is stored for long periods in contact with air, there is a gradual darkening of color, increase in acidity, and formation of a soluble polymer.

According to the latest available information (40), in 1992, total world-wide capacity for furfural was 240,000 metric tons (t) (530,000,000 lb). Production capability is moving away from developed countries into developing nations. The Peoples' Republic of China has become a significant factor in furfural production, with an estimated total capacity of 50,000 t, most of it being produced in small plants. New capacity has come on stream or is being planned in other Asian countries as well as in Indonesia. South African capacity is rated at 17,000 t. United States capacity was estimated at 73,000 t (30% of the world total), production at 40,000 t and consumption at 43,000. Western Europe capacity was

Table 2. **U.S. Consumption of Furfural**

Use	t	(10^6 lb)
raw material for furfuryl alcohol	24,460	(54)
raw material for tetrahydrofurfuryl alcohol	905	(2)
raw material for tetrahydrofuran	13,590	(30)
solvent applications	3,625	(8)
other uses	1,815	(4)

8,000 t (down from 27,000 in 1988). Production was 6,000 t and consumption was 36,000 t, a significant amount being imported from the western hemisphere. Japan is not presently a producer of furfural, importing approximately 9,000 t, mostly from China. At this time there is significant overcapacity worldwide; consumption is steady or declining slightly. The United States list price for furfural was \$0.79/lb in 1992; it has not changed significantly since then.

2.4. Uses. Furfural is primarily a chemical feedstock for a number of monomeric compounds and resins. One route produces furan by decarbonylation. Tetrahydrofuran is derived from furan by hydrogenation. Polytetramethylene ether glycol [25190-06-1] is manufactured from tetrahydrofuran by a ring opening polymerization reaction. Another route (hydrogenation) produces furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyltetrahydrofuran. A variety of proprietary synthetic resins are manufactured from furfural and/or furfuryl alcohol. Other chemicals that have been derived, on a lesser scale are described in a later section. In this country more than 90% of the furfural produced is used as feedstock for other compounds. A breakdown of U.S. consumption in 1992 is shown in Table 2.

As can be seen, most of the furfural produced in this country is consumed as an intermediate for other chemicals. Hydrogenation to furfuryl alcohol is the largest use. Some of the furfuryl alcohol is further hydrogenated to produce tetrahydrofurfuryl alcohol. The next major product is furan, produced by decarbonylation. Furan is a chemical intermediate, most of it is hydrogenated to tetrahydrofuran, which in turn is polymerized to produce polytetramethylene ether glycol (PTMEG).

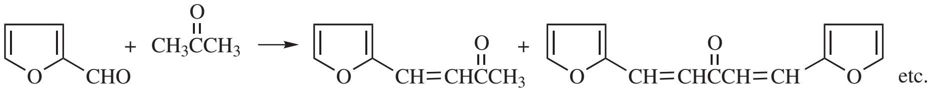
Furfural and furfuryl alcohol are specialty solvents. They also are reactive solvents and contribute low viscosity to resin formulations. Thermosetting resins containing furfural and/or furfuryl alcohol. "Furan resins" demonstrate specialty properties including corrosion resistance, high carbon yield, stability at elevated temperature, low fire hazard, and excellent physical strength. These properties are of industrial importance in making foundry molds and cores, fiberglass composites, mortars, cements, plastic insulation foams, refractory mixes, high carbon composites, and aggregate binders, among others.

The principal direct application of furfural is as a selective solvent. It is used for separating saturated from unsaturated compounds in petroleum refining, for the extractive distillation of butadiene and other C_4 hydrocarbons in the manufacture of synthetic rubber; and for the production of light-colored wood rosin. These applications for furfural are mature and volume is declining. Furfural is both a solvent and a processing aid for refining anthracene. It is an ingredient in furfuryl alcohol resins and in phenol–aldehyde resins. Furfural is also used as a resin solvent and wetting agent in the manufacture of abrasive wheels and brake linings. Furfural is used as a reactive solvent in cold-blending of pitch. The mixture gives resinous impregnants that interact at carbonization temperatures. These resin pitch combinations have curing and carbonization characteristics better than those of either component alone. The cold-blending process significantly improves the environmental acceptance of pitch and offers industry an alternative to hot processing.

High quality carbon fibers have been produced (41) by pyrolyzing, in a nonoxidizing atmosphere, resinous fibers prepared from a viscous copolymer of furfural and pyrrole. Yield of carbon fiber having a glossy surface and only 3% voids was 66%. Compared with other graphite-type fibers, these carbon fibers had improved mechanical strength, higher oxidation resistance, and lower density.

Useful thermosetting resins are obtained by interaction of furfural with phenol. The reaction occurs under both acidic and basic catalysis. Other large uses of furfural together with phenol are in the manufacture of resin-bonded grinding wheels and coated abrasives (5).

Furfural reacts with ketones to form strong, crosslinked resins of technical interest in the former Soviet Union; the U.S. Air Force has also shown some interest (42,43). The so-called furfurylidene acetone monomer, a mixture of 2-furfurylidene methyl ketone [623-15-4], (**13**), bis-(2-furfurylidene) ketone [886-77-1] (**14**), mesityl oxide, and other oligomers, is obtained by condensation of furfural and acetone under basic conditions (44,45). Treatment of the "monomer" with an acidic catalyst leads initially to polymer of low molecular weight and ultimately to cross-linked, black, insoluble, heat-resistant resin (46).



(**13**) (**14**)

Furfural–acetone resins have been used to form resin-aggregate mixtures referred to as organic concretes. Despite the reportedly excellent properties, there has been virtually no commercial use of such resins outside the former Soviet Union. The structures and polymerization mechanisms of these furfural–aldehyde–ketone polymers are discussed in a review (6).

Furfural has been used as a component in many resin applications, most of them thermosetting. A comprehensive review of the patent literature describing these uses is beyond the scope of this review. A few, selected recent patents and journal articles have been referenced. Resins prepared from the condensation products of furfural with urea (47), formaldehyde (48), phenols (49,50), etc, modified by appropriate binders and fillers are described in the technical literature; for earlier applications, see reference 1, which contains many references in an appendix.

3. Furfuryl Alcohol

3.1. Physical Properties. Furfuryl alcohol (2-furanmethanol) [98-00-0] is a liquid, colorless, primary alcohol with a mild odor. On exposure to air, it gradually darkens in color. Furfuryl alcohol is completely miscible with water, alcohol, ether, acetone, and ethyl acetate, and most other organic solvents with the exception of paraffinic hydrocarbons. It is an excellent, highly polar solvent, and dissolves many resins.

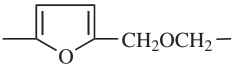
The physical constants of furfuryl alcohol are listed in Table 1. When exposed to heat, acid or air the density and refractive index of furfuryl alcohol changes owing to chemical reaction (51), and the rate of change in these properties is a function of temperature and time of exposure.

3.2. Chemical Properties. The chemical properties of furfuryl alcohol are characteristic of the hydroxymethyl group; however, in the presence of acid the reactivity of the furan ring is significantly enhanced through allyl carbonium ion formation. Furfuryl alcohol undergoes the typical reactions of a primary alcohol such as oxidation, esterification, and etherification. Although stable to strong alkali, furfuryl alcohol is very sensitive to acid, thus imposing limitations on the conditions used in many of the typical alcohol reactions. For example, esterifications must be performed under neutral or basic conditions, or via base-catalyzed transesterification. Likewise, etherifications are done under basic condensation conditions to suppress polymerization of the furan ring. Yet it is this very sensitivity to acid that is the basis for most of the commercial uses of furfuryl alcohol. It is a more reactive solvent than furfural and easily resinifies under the influence of acid and heat.

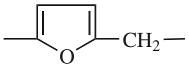
Under acidic conditions, furfuryl alcohol polymerizes to black polymers, which eventually become crosslinked and insoluble in the reaction medium. The reaction can be very violent and extreme care must be taken when furfuryl alcohol is mixed with any strong Lewis acid or Brönstad acid. Copolymer resins are formed with phenolic compounds, formaldehyde and/or other aldehydes. In dilute aqueous acid, the predominant reaction is a ring opening hydrolysis to form levulinic acid [123-76-2] (52). In acidic alcoholic media, levulinic esters are formed. The mechanism for this unusual reaction in which the hydroxymethyl group of furfuryl alcohol is converted to the terminal methyl group of levulinic acid has recently been elucidated (53).

Hydrogenation of furfuryl alcohol can yield 2-tetrahydrofurfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, or straight-chain compounds by hydrogenolysis of the ring. Ethoxylation and propoxylation of furfuryl alcohol provide useful ether alcohols.

The chemistry of furfuryl alcohol polymerization has received much attention over the years. Several recent reviews have been written (5,6,54). Based on the accumulated data, furfuryl alcohol has to be considered a bifunctional monomer in the initial stage and its "normal" reactions give linear chains or oligomers containing essentially two repeating units (**15,16**) with (**16**) predominating.

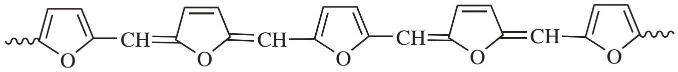


(**15**)



(**16**)

In 1996, the mechanism of resinification was clearly and elegantly established (55). Development of color (a phenomenon which up until now has never been adequately explained) has been shown to be due to conjugated sequences along linear oligomeric chains (**17**). Branching and crosslinking, which cause gelation and isolubilization are described to take place through the reaction of terminal methylol groups or disubstituted furan rings with nonfuranic double bonds in the oligomeric chain.



(**17**)

3.3. Manufacture. Furfuryl alcohol has been manufactured on an industrial scale by employing both liquid-phase and vapor-phase hydrogenation of furfural (56,57). Copper-based catalysts are preferred because they are selective and do not promote hydrogenation of the ring.

Furfuryl alcohol is shipped in bulk or drums. Although not corrosive to metals, it is a powerful solvent and penetrant; containers, tanks, lines, and valves need to be in good condition to avoid potential leakage. Furfuryl alcohol can be stored in containers lined with baked phenolic resin coatings; however, it should not be put in containers that are coated with lacquers, varnishes, or epoxy resins because it is an excellent solvent for many such coatings.

Furfuryl alcohol, on long storage, becomes progressively darker and less water soluble, a change that is also caused by heat, acidity, and exposure to air. The reactions responsible for this change in water solubility may be retarded by the addition in small quantity of an organic or inorganic base. Commercial furfuryl alcohol, however, usually does not contain any additives.

Furfuryl alcohol is comparable to kerosene or No. 1 fuel oil in flammability, the Tag Closed Cup flash point is 170°F. In the presence of concentrated mineral acids or strong organic acids, furfuryl alcohol reacts with explosive violence. Therefore, precautions should be taken to avoid contact of such materials with the alcohol. Caution is also recommended to avoid over-catalysis in the manufacture of furfuryl alcohol resins.

Worldwide furfuryl alcohol capacity in 1993 was estimated to be 110,000 metric tons (38). As with furfural, new capacity in developing countries is replacing older capacity in developed countries. China and South Africa have become significant producers of furfuryl alcohol. New plants have been built in Asia and Indonesia as well. Consumption of furfuryl alcohol is spread over the globe; the largest use is in the foundry industry which is increasingly moving away from heavily industrialized countries.

3.4. Uses. Furfuryl alcohol is widely used as a monomer in manufacturing furfuryl alcohol resins, and as a reactive solvent in a variety of synthetic resins and applications. Resins derived from furfuryl alcohol are the most important application for furfuryl alcohol in both utility and volume. The final cross-linked products display outstanding chemical, thermal, and mechanical properties. They are also heat-stable and remarkably resistant to acids, alkalies, and solvents. Many commercial resins of various compositions and properties have been prepared by polymerization of furfuryl alcohol and other co-reactants such as furfural, formaldehyde, glyoxal, resorcinol, phenolic compounds and urea. In 1992, domestic furfuryl alcohol consumption was estimated at 47 million pounds (38).

The polymerization or resinification of furfuryl alcohol is highly exothermic, and requires careful control of the reaction conditions. Proper attention to safety cannot be overemphasized. The addition of too much strong acid will lead to a violent, almost explosive, reaction. The resinification of furfuryl alcohol is autocatalytic in the sense that the rate increases geometrically with temperature. During a resinification reaction, temperature control is generally accomplished with refluxing solvent and/or external cooling. As a safety precaution, to prevent a runaway reaction, provision for emergency neutralization of the catalyst is essential. At temperatures above 250°C, in a closed system, furfuryl alcohol undergoes a strong exothermic reaction which is not controlled by base (18). Furfuryl alcohol should not be heated to above 250°C in a closed system.

In practice, intermediate, liquid resins, capable of further reaction are usually prepared. Polymerization is carried to an established end-point as determined by viscosity or other measurements. When the proper end-point has been reached, the reaction is terminated by adjusting the pH of the system to 5–8. Such liquid resins can be stored for six months or longer, then catalyzed and reacted further to obtain the final, desired product.

Furfuryl alcohol is an excellent solvent for many resins. A number of applications are based on its reactive solvent properties. When a resin solution is cured, a hard, rigid, thermoset matrix results. The final, cured product often has many outstanding properties. For example, furfuryl alcohol is a reactive solvent for phenolic resins in the manufacture of refractories for ladles holding molten steel. The furfuryl alcohol provides a low viscosity to allow good mixing of the resin with the refractory particles, then reacts with the phenolic resin during curing. When heated to high temperatures, the matrix carbonizes, producing a strong refractory bond.

The industrial value of furfuryl alcohol is a consequence of its low viscosity, high reactivity, and the outstanding chemical, mechanical, and thermal properties of its polymers, corrosion resistance, nonburning, low smoke emission, and excellent char formation. The reactivity profile of furfuryl alcohol and resins is such that final curing can take place at ambient temperature with strong acids or at elevated temperature with latent acids. Major markets for furfuryl alcohol resins include the production of cores and molds for casting metals, corrosion-resistant fiber-reinforced plastics (FRPs), binders for refractories and corrosion-resistant cements and mortars.

Metal-Casting Cores and Molds. In the foundry industry there is a highly significant binder technology based on furfuryl alcohol resins. These binders are cured at ambient temperature or at elevated temperatures. Microwave curing has been used. Even curing with acidic gases is feasible. Total furfuryl alcohol based binder consumption by the foundry industry in 1992 has been estimated at 35 million pounds, representing 27 million pounds of contained furfuryl alcohol (38).

Furan No-Bake (FNB) resins are used worldwide in competition with several other chemical binder systems. FNB binders are used in the production of sand cores and molds that cure without heat (58–61). The FNB process uses a reactive furan resin binder with strong organic acid or phosphoric acid as catalyst. Based on the requirements of the particular system, slow or rapid curing can be accomplished at ambient temperatures, eliminating the need for long ovenbaking cycles. Accelerators are sometimes used to increase curing rate (62–65). The catalyst is added to the sand, followed by the binder, often in a continuous mixer. The characteristics of the acid and the binder as well as the mixing ratio determine curing rate characteristics. Other money saving benefits that accrue include: fewer or no reinforcing rods; less pattern wear; dimensional accuracy of the castings; easy shakeout of core sand after pouring; and minimal clean-up of the finished casting. The used sand can easily be reclaimed by mechanical means. Most important, the process is simple, requiring fewer steps to produce cores, and can be operated by semiskilled personnel.

Furan hot-box resins are used in both ferrous and nonferrous foundries (66,67). In this process, resin and catalyst are intimately mixed with dry sand and then blown into heated metal boxes containing a cavity the shape of the desired core. In seconds, the surface of the sand mass hardens and, as soon as the core has cured sufficiently to be rigid and handleable the box is opened and the core removed. Automotive cores with excellent dimensional accuracy and high strengths are made via this forty-year-old process.

Both FNB and Hot Box applications are mature and declining as new technology is being used more and more in the foundry industry. Technological advances continue to be made, several recent patents describe advanced pheno–formaldehyde–furfuryl alcohohol binder systems (68–70). These systems are free of nitrogen compounds that can be detrimental to metal integrity. Systems with extended bench life have also been developed (71).

One newer application, however, is not yet mature. Warm Box systems, curing at significantly lower temperatures, are becoming more widely used. The warm-box resin is based on 2,5-bis(hydroxymethyl)furan (BHMF) resins. Lower binder levels are reported effective at core-curing temperatures of 149–177°C (72). The binders do not contain any nitrogen compounds. An essential part of the new technology is new latent curing catalysts (73,74). Core production rate using warm-box resins is equivalent to the rate with hot-box resins and provides significant improvement in working environment. Lower emissions, both at core-making and pour off are claimed.

Corrosion Resistant Fiber-Reinforced Plastic (FRP). Fiber glass reinforcement bonded with furfuryl alcohol thermosetting resins provides plastics with unique properties. Excellent resistance to corrosion and heat distortion coupled with low flame spread and low smoke emission are characteristics that make them valuable as laminating resins with fiber glass (75,76). Another valuable property of furan FRP is its strength at elevated temperature. Hand-layup, spray-up, and filament-winding techniques are employed to produce an array of corrosion-resistant equipment, pipes, tanks, vats, ducts, scrubbers, stacks, and reaction vessels for industrial applications throughout the world.

Reinforced furan resins have been used for many years in process piping and in underground sewer or waste-disposal systems. With a wide range in pH acceptability and good solvent resistance, furan piping has been a logical choice for many services.

The highly cross-linked thermoset character of cured furan resin provides substantially greater corrosion resistance than other resins used in fiber glass-reinforced plastics. Hence, furan FRP is recommended (77) for high performance chemical process equipment in service with chlorinated aromatics, highly oxygenated organic solvents, and other admixtures of organics and aggressive aqueous media of a nonoxidizing nature. Commercially manufactured corrosion-resistant off-the-shelf pipe using furan resins and fiber glass has been available since 1977 (77).

The inherent fire resistance and low smoke properties of furan resins appear to be related to the high degree of charring that takes place with minimum evolution of volatiles when exposed to fire.

Cements and Mortars. One of the original applications for furan resins was in the jointing of bricks and masonry. Furan resins have been extensively used for formulating mortars, grouts, and "setting beds" for brick linings in structures exposed to corrosive media, especially concentrated acids, and for setting tile in floors exposed to alkaline cleaning solutions or other corrosive chemical media. Mortars and grouts for these applications are usually formulated as two-package systems and mixed just prior to use. Silica fillers are satisfactory for many applications, but carbon flour (ground coke or other nongraphitic, nonactivated carbon) is used where resistance to hydrogen fluoride, fluoride salts, or hot, concentrated alkaline cleaning solutions is required.

High Carbon Yield. Furfuryl alcohol and furfural are reactive solvents (monomers) and are effective in producing high carbon yield (heat induced carbonization in a reducing atmosphere). They function as binders for refractory materials or carbon bodies. Furfuryl alcohol usually requires acidic catalysis and furfural basic catalysis. Mixtures of furfuryl alcohol and furfural are generally catalyzed with acid although some systems may be catalyzed with base.

Furfuryl alcohol alone, or in combination with other cross-linkable binders such as phenolic reins, chemical by-products and pitch, catalyzed with acid, gives carbon yields of 35–56%. Furfural together with cyclohexanone, pitch, or phenolic resins gives, under acid catalysis, yields of 35–55% carbon; under basic catalysis yields of 5–50% are achieved. Furfurylideneacetone resins (**13** and **14**), catalyzed by acid or base, give carbon yields of 48–56 and 30–35%, respectively (78).

3.5. Other Uses.

Anisotropic and isotropic carbon are produced from furfural-modified systems; glassy carbon is produced primarily from furfuryl alcohol or BHMF resins (78,79).

Furfuryl alcohol is used alone or in combination with other solvents for various cleaning and paint removing operations. The ethylene oxide adduct of furfuryl alcohol is especially useful in this type of application (80–83).

4. Furan

4.1. Physical Properties.

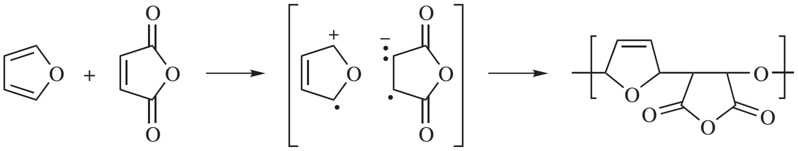
Furan, a colorless liquid with a strong ethereal odor, is low-boiling and highly flammable. It is miscible with most common organic solvents but only very slightly soluble in water. The physical properties of furan are listed in Table 1.

4.2. Chemical Properties.

Furan is a heat-stable compound, although at 670°C in the absence of catalyst, or at 360°C in the presence of nickel, it decomposes to form a mixture consisting mainly of carbon monoxide, hydrogen, and hydrocarbons (84). Substitution and addition reactions can be effected under controlled conditions, with reaction occurring first in the 2- and 5-positions. Gas-phase reaction with ammonia over a modified silica–alumina catalysts gives pyrrole in good yield, 80% conversion with 72% selectivity (85). Carrying out the reaction in steam using HZSM-5 catalyst gives 65% conversion with 99% selectivity (86). The reaction of furan with primary amines gives *N*-substituted pyrroles although in low yield (87). Acylation under Friedel-Crafts conditions goes readily.

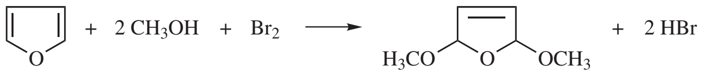
Furan and maleic anhydride undergo the Diels-Alder reaction to form the tricyclic 1:1 adduct, 7-oxabicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**4**) in excellent yield. Other strong dienophiles also add to furan (88). Although both endo and exo isomers are formed initially, the former rapidly isomerize to the latter in solution, even at room temperature. The existence of a charge-transfer complex in the system has been demonstrated (89,90).

The radical-catalyzed polymerization of furan and maleic anhydride has been reported to yield a 1:1 furan-maleic anhydride copolymer (89,91). The structure of the equimolar product, as shown by nmr analyses, is that of an unsaturated alternating copolymer (**18**) arising through homopolymerization of the intermediate excited donor–acceptor complex (91,92).



(**18**)

Furan can be catalytically oxidized in the vapor phase with oxygen-containing gases to maleic anhydride (93). Oxidation with bromine or in an electrochemical process using bromide ion gives 2,5-dimethoxy-2,5-dihydrofuran [332-77-4] (**19**) which is a cyclic acetal of maleic dialdehyde (94–96).



(**19**)

Catalytic hydrogenation of furan to tetrahydrofuran is accomplished in either liquid or vapor phase. Hydrogenation of the double bonds is essentially quantitative over nickel catalysts but is generally accompanied by hydrogenolysis over the noble metals.

4.3. Manufacture. Furan is produced commercially by decarbonylation of furfural in the presence of a noble metal catalyst (97–100). Nickel or cobalt catalysts have also been reported (101–103) as well as noncatalytic pyrolysis at high temperature. Furan can also be prepared by decarboxylation of 2-furoic acid; this method is usually considered a laboratory procedure.

Furan, a Class 3 DOT hazard, is shipped in tank cars, tank trucks and in heavy duty drums. The selling price of furan in bulk is listed at $1.60/lb.

Furan should be kept from heat and flame because of its low boiling point, low flash point, and high flammability. Unstabilized furan slowly forms an unstable peroxide on exposure to air and, therefore, care should be taken when using furan. When distilling furan, remove peroxides first by chemical reaction, and never distill to dryness.

4.4. Uses. Furan is utilized as a chemical building block in the production of other industrial chemicals for use as pharmaceuticals, herbicides, stabilizers, and fine chemicals. There are a great many references to the use of furan as an intermediate in these applications. For a recent review, see Reference 104. Several of the principal uses are described below.

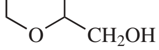
Furan is readily hydrogenated, hence it is a source of commercial tetrahydrofuran (THF). Reaction with hydrogen sulfide over alumina produces thiophene. A recent patent describes a catalyst based on cobalt and molybdenum oxides supported on alumina for this reaction (105). Furan undergoes the Diels-Alder reaction with strong dienophiles. Hydrogenation of the product resulting from reaction with maleic anhydride, followed by hydrolysis and neutralization gives a herbicide, Endothall.

The oxidative reaction of furan with bromine in methanol solution or an electrochemical process using sodium bromide produces 2,5-dimethoxy-2,5-dihydrofuran (**19**), which is a cyclic acetal of maleic dialdehyde. The double bond in (**19**) can be easily hydrogenated to produce the corresponding succindialdehyde derivative. Both products find application in photography and as embalming materials, as well as other uses.

Washing and cleaning agents containing salts of maleic acid–furan copolymers (106) form complexes with alkaline-earth ions. These cleaning compositions do not contain phosphorus or nitrogen and find use in metal, foodstuff, and machine dishwashing products.

5. Tetrahydrofurfuryl Alcohol

5.1. Physical Properties. Tetrahydrofurfuryl alcohol (2-tetrahydrofuranmethanol) [97-99-4] (**20**) is a colorless, high-boiling liquid with a mild, pleasant odor. It is completely miscible with water and common organic solvents. Tetrahydrofurfuryl alcohol is an excellent solvent, moderately hydrogen-bonded, essentially nontoxic, biodegradable, and has a low photochemical oxidation potential. Most applications make use of its high solvency. The more important physical properties of tetrahydrofurfuryl alcohol are listed in Table 1.



(**20**)

5.2. Chemical Properties. Without inhibitors, tetrahydrofurfuryl alcohol is susceptible to autoxidation, developing color and carbonyl functionality. In the absence of air, however, no observable changes occur even after several years storage. In the presence of air, if a stabilizer such as Naugard is added, tetrahydrofurfuryl alcohol remains colorless after protracted periods of storage. Peroxide accumulation is low, not dangerous, and readily dischargeable on redistillation.

The reactions of tetrahydrofurfuryl alcohol are characteristic of its structure, involving primary alcohol and cyclic ether functional groups. As a primary alcohol, it undergoes normal displacement or condensation reactions affording new functional groups, (eg, halides, esters, alkoxylates, ethers, glycidyl ethers, cyanoethyl ethers, amines, etc). As a cyclic ether, it is typically unreactive, but the ring can be forced to open by hydrolysis or hydrogenolysis to give a variety of open-chain compounds, some of which may be recyclized to different heterocyclic species.

All the common monobasic (107) and dibasic esters (108) of tetrahydrofurfuryl alcohol have been prepared by conventional techniques; the dibasic esters and some of the mono esters are effective as primary or secondary plasticizers for vinyl polymers. Tetrahydrofurfuryl acrylate [2399-48-6] and methacrylate [2455-24-5], specialty monomers, have been produced by carbonylation (nickel carbonyl and acetylene) of the alcohol (109) as well as by direct esterification (110–112) and ester interchange (111).

Tetrahydrofurfuryl alcohol reacts with ammonia to give a variety of nitrogen containing compounds depending on the conditions employed. Over a barium hydroxide-promoted skeletal nickel–aluminum catalyst, 2-tetrahydrofurfurylamine [4795-29-3] is produced (113–115). With palladium on alumina catalyst in the vapor phase (250–300°C), pyridine [110-86-1] is the principal product (116,117); pyridine also is formed using Zn and Cr based catalysts (118,119). At low pressure and 200°C over a reduced nickel catalyst, piperidine is obtained in good yield (120,121).

Tetrahydrofurfuryl alcohol is oxidized to 2-tetrahydrofurfural [7681-84-7] in good yield by passage, with oxygen, over silver gauze at 500°C (123,124). With chromate oxidizing agents, lactones are also formed (124,125).

Tetrahydrofurfuryl alcohol is surprisingly resistant to hydrogenolysis; under vigorous conditions, however, cleavage of the ring or side chain occurs (126,127).

When tetrahydrofurfuryl alcohol is passed over a variety of alumina-containing catalysts at temperatures ranging from 200–500°C, it undergoes dehydration and ring expansion to 3,4-dihydro-2*H*-pyran, a major chemical intermediate for 1,5-difunctional open-chain aliphatic compounds (128–131) as well a hydroxyl group protecting agent. The analogous 3,4-dihydro-2*H*-thiopyran is similarly prepared by reaction of tetrahydrofurfuryl alcohol with hydrogen sulfide over alumina at 300°C (132,133).

5.3. Manufacture. Tetrahydrofurfuryl alcohol is produced commercially by the vapor-phase catalytic hydrogenation of furfuryl alcohol. Liquid phase reduction is also possible.

Normal precautions for chemicals of mild toxicity are applicable to the safe handling and storage of commercial tetrahydrofurfuryl alcohol. Discoloration in storage rarely occurs if the proper precautions are observed; prevention of exposure to air will prevent autoxidation. The list price of tetrahydrofurfuryl alcohol (1997) is $1.15/lb.

5.4. Uses. Tetrahydrofurfuryl alcohol is of interest in chemical and related industries where low toxicity and minimal environmental impact are important (134). For many years tetrahydrofurfuryl alcohol has been used as a specialty organic solvent. The fastest growing applications are in formulations for cleaners (135) and paint strippers (136), often as a replacement for chlorinated solvents (137). Other major applications include formulations for crop sprays, water-based paints, and the dyeing and finishing of textiles and leathers. Tetrahydrofurfuryl alcohol also finds application as an intermediate in pharmaceutical applications.

A major use of tetrahydrofurfuryl alcohol is as an ingredient in proprietary stripping formulations. These formulations are used broadly in the automotive industry to remove protective coatings, paint, and grime prior to final painting and finishing (138). Stripping formulations containing tetrahydrofurfuryl alcohol are also available for the lifting and removal of epoxy coatings (139). Tetrahydrofurfuryl alcohol is being widely used as a replacement for chlorinated solvents, especially in the electronics industry.

Because tetrahydrofurfuryl alcohol is virtually colorless, it is used in lacquer formulations for all colors as well as water-white clear products. More specifically, tetrahydrofurfuryl alcohol is a wetting dispersant for most pigments. It has a high boiling point, high toluene dilution ratio, and good miscibility with oils, eg, linseed and soya, and is an excellent solvent for a wide range of resins.

Tetrahydrofurfuryl alcohol is used as solvent and carrier for industrial and commercial cleaning formulations. Product applications include the commercial cleaning of aircraft, ships, and trucks as well as the industrial cleaning requirements for machine tools and dies. The solvent properties of tetrahydrofurfuryl alcohol and its low rate of evaporation are utilized in biocides and pesticides where it serves as solvent–carrier. In a recent paper, tetrahydrofurfuryl alcohol is compared to other solvents as an agricultural adjuvent (140). Tetrahydrofurfuryl alcohol has been cleared by the EPA for use in formulations sprayed on growing food crops. The fact that tetrahydrofurfuryl alcohol is totally miscible with water and easily biodegradable enhances its use in agricultural sprays used for pest control, weed control, and growth retardation.

Tetrahydrofurfuryl alcohol also has been cleared for use in California under Rule 66. It meets the rigid specifications for uv degradation in environmentally sensitive areas. In addition to domestic use, a substantial amount of tetrahydrofurfuryl alcohol is used as a solvent for agricultural chemicals in Europe.

Tetrahydrofurfuryl alcohol is a solvent and coupling agent for a phosphate-type insecticide used to control the gypsy moth. Esters of tetrahydrofurfuryl alcohol are used in preparations employed as insect repellents. Tetrahydrofurfuryl alcohol is also used as a solvent–carrier for an EPA-approved paper slimicide formulation. In this application, the exceptional solvent action of tetrahydrofurfuryl alcohol prevents separation of the active ingredient, especially at low operating temperatures.

Tetrahydrofurfuryl acrylate and methacrylate reactive unsaturated monomers, are readily polymerized and easily cross-linked by exposure to heat, peroxide catalysts, or uv radiation.

Tetrahydrofurfuryl acrylate is used as a co-reactive viscosity depressant for vinyl terminated epoxy systems. It is also used in the formulation of uv-curable printing inks, coatings, paints, and adhesives. Tetrahydrofurfuryl methacrylate serves as a reactive curing agent in the peroxide-catalyzed production of nitrile rubber. The monomer functions as plasticizer during processing and polymerizes during cure to yield hard vulcanizates useful in electrical cable coatings.

Tetrahydrofurfuryl alcohol is used in elastomer production. As a solvent for the polymerization initiator, it finds application in the manufacture of chlorohydrin rubber. Additionally, tetrahydrofurfuryl alcohol is used as a catalyst solvent-activator and reactive diluent in epoxy formulations for a variety of applications. Where exceptional moisture resistance is needed, as for outdoor applications, furfuryl alcohol is used jointly with tetrahydrofurfuryl alcohol in epoxy adhesive formulations.

In dyeing applications, tetrahydrofurfuryl alcohol permits higher dye concentrations and wider latitude in solution temperature because of its high solvency for dyes. Through swelling action on synthetic fibers and polarity with respect to leather, tetrahydrofurfuryl alcohol facilitates deeper penetration of dye into the substrate circumventing mere surface tinting. As a dye leveling agent, tetrahydrofurfuryl alcohol aids in the attainment of evenness in color shade.

6. Other Furan Derivatives

Other furan compounds, best derived from furfural, are of interest although commercial volumes are considerably less than those of furfural, furfuryl alcohol, furan, or tetrahydrofurfuryl alcohol. Some of these compounds are still in developmental stages. Applications include solvents, resin intermediates, synthetic rubber modifiers, therapeutic uses, as well as general chemical intermediates.

6.1. Solvents. Compounds containing the furan ring are generally excellent solvents. Some are miscible with both water and with hexane. Presence of the ether oxygen adds polarity as well as the potential for hydrogen bonding. Ring-substituted derivatives of furfural and furfuryl alcohol are reactive solvents, similar to the parent compounds. Reaction of the aldehyde group on furfural or the alcohol group on furfuryl alcohol give products that are merely solvents, no longer reactive. Ethers of furfuryl alcohol are easy to prepare; most simple ethers have been synthesized. Ethylene oxide adducts [31692-86-1] are used in paint stripping formulations (136,141–143). The esters of furfuryl alcohol are effective solvents, but must be synthesized carefully owing to the reactivity of furfuryl alcohol with acids. Both esters and ethers of tetrahydrofurfuryl alcohol are excellent solvents and are easily prepared. Since double bonds are no longer present, these compounds are more stable than the corresponding furan derivatives. Tetrahydrofurfuryl alcohol–ethylene oxide adducts [31692-85-0] are also useful solvents for paint stripping formulations (136,141,143). 2-Methylfuran is a good solvent, but 2-methyltetrahydrofuran (METHF), is completely saturated and is less reactive, less toxic, and has greater potential for a number of solvent applications. It is a more convenient solvent than tetrahydrofuran for Grignard reagents (144), is higher boiling, and wet METHF is more easily recovered and made anhydrous for recycle and reuse. METHF has also found application as a solvent for other organometallic reagents (145), as well as in lithium batteries (146). Ultimately, when fully commercialized, the cost of METHF should approximate that of tetrahydrofuran.

6.2. Resins. As mentioned above, both furfural and furfuryl alcohol are widely used in resin applications. Another resin former, 2,5-furandimethanol [1883-75-6] (BHMF), is prepared from furfuryl alcohol by reaction with formaldehyde. It is usually not isolated because oligomerization occurs simultaneously with formation (competing reaction). Both the monomer and oligomers are very reactive owing to difuntionality, and are used primarily as binders for foundry sand (72) and fiberglass insulation (147,148).

6.3. Therapeutics. Compounds containing the furan or tetrahydrofuran ring are biologically active and are present in a number of pharmaceutical products. Furfurylamine [617-89-0] is an intermediate in the diuretic, furosemide. Tetrahydrofurfurylamine [4795-29-3] may also have pharmaceutical applications. 5-(Dimethylaminomethyl)furfuryl alcohol [15433-79-1] is an intermediate in the preparation of ranitidine, which is used for treating ulcers. 2-Acetylfuran [1192-62-7], prepared from acetic anhydride and furan is an intermediate in the synthesis of cefuroxime, a penicillin derivative. 2-Furoic acid is prepared by the oxidation of furfural. Both furoic acid [88-14-2] and furoyl chloride [527-69-5] are used as pharmaceutical intermediates. 2-Tetrahydrofuroic acid [16874-33-2] also finds application.

6.4. Rubber Modifiers. Derivatives of furan and tetrahydrofurfuryl alcohol are used in the polymerization of synthetic rubber to control stereoregularity and other properties (149,150).

6.5. Intermediates. 3,4-Dihydro-2*H*-pyran [110-87-2] is prepared by a ring-expanding dehydration of tetrahydrofurfuryl alcohol. It is used as a protecting agent for hydroxyl compounds and as an intermediate. 2-Methylfuran is a chemical intermediate for 5-methylfurfural [620-02-0] (151) and 3-acetyl-1-propanol [1071-73-4] (152), and is also used in perfume. α-Methylfurfuryl alcohol [4208-64-4] is prepared by the reaction of furfural with methylmagnesium bromide. It is an intermediate in the synthesis of maltol [118-71-8], which is used as a flavoring agent.

7. Health and Safety Factors

As with all chemical compounds, the Material Safety Data Sheet (MSDS) for each of the specific furan derivatives should be reviewed before starting to work with these materials. Caution should be the keyword when handling chemicals. Additional information on toxic effects of most of these compounds can be found in RTECS (*Registry of Toxic Effects of Chemicals*), HSDB (*Hazardous Substances Data Bank* from the National Library of Medicine), and standard works on toxicology such as Patty's (153). Toxicology studies are taking place on a continuing basis with many chemicals; furan derivatives are no exception. New data may change the perspective on toxicity of these chemicals.

Over the years, many people have been exposed to low levels of these furan derivatives with no evidence of any significant long-term effects. Proper precautions, however, should be taken when working with these compounds as furfural, furfuryl alcohol, and furan are moderately toxic, tetrahydrofurfuryl alcohol is

Table 3. **Toxic Effects of Furfural and Main Derivatives**[a]

	Value for			
Property	Furfural	Furfuryl alcohol	Furan	Tetrahydrofurfuryl alcohol
oral toxicity	149 mg/kg	451 mg/kg	300 mg/kg	2500 mg/kg
inhalation toxicity	1037 ppm 1 h	692 ppm 1 h	3464 ppm	$LC_{2/3}$ 12650 ppm
dermal toxicity	620 mg/kg	667 mg/kg	not established	>5000 mg/kg
skin irritation	slight	slight	not established	slight
eye irritation	moderate	moderate	not established	moderate
ACGIH carcinogen	not listed	not listed	not listed	not listed
IARC carcinogen	not listed	not listed	not listed	not listed
NIOSH carcinogen	not listed	not listed	not listed	not listed
NTP carcinogen	not listed	not listed	not listed	not listed
OSHA carcinogen	not listed	not listed	not listed	not listed

[a] Ref. 154.

less so. Protective clothing should be worn; skin absorption is a likely route of entry. Eye protection is required. Proper ventilation is needed, especially with highly volatile furan. The odor threshold for these compounds is such that they can be detected at levels below the PEL (Permissible Exposure Level), and appropriate action taken as soon as the odor is detected. Specific recommendations from the manufacturer regarding exposure and protective measures should be followed. Since regulations change from time to time, up-to-date exposure limit recommendations from OSHA (Occupational Safety and Health Agency) or ACGIH (American Council of Governmental Industrial Hygienists) need to be consulted and followed.

Toxicity information is summarized in Table 3.

BIBLIOGRAPHY

"Furfural and Other Furan Compounds" in *ECT* 1st ed., Vol. 6, pp. 995–1008, by H. R. Duffey, The Quaker Oats Company, and H. J. Barrett, E. I. du Pont de Nemours & Co., Inc.; "Furfural and Other Furan Compounds" in *ECT* 2nd ed., Vol. 10, pp. 237–250, by A. P. Dunlop, The Quaker Oats Company; "Furan Derivatives" in *ECT* 3rd ed., Vol. 11, pp. 499–527, by W. J. McKillip and E. Sherman, The Quaker Oats Company; in *ECT* 4th ed., Suppl. Vol., pp. 155–183, by R. H. Kottke, Great Lakes Chemical Corporation.

CITED PUBLICATIONS

1. A. P. Dunlop and F. N. Peters, *The Furans* ACS Monograph 119, Reinhold Publishing Corp., New York, 1953.
2. M. J. Cook, A. R. Katritzky, and P. Linda, *Adv. Heterocycl. Chem.* **17**, 255 (1974).
3. C. W. Bird, *Tetrahedron* **48**, 335 (1992).
4. M. V. Sargent and T. M. Cresp "Furans" in D. Barton and W. D. Ollis, eds., *Comprehensive Organic Chemistry; The Synthesis and Reaction of Organic Compounds,* Vol. **4**, Pergamon Press Ltd., Oxford, U.K., 1979, 693–744.

5. A. Gandini "Furan Polymers" in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Technology*, 2nd ed., Vol. **7**, John Wiley & Sons, Inc., New York, 1967, 454–473.
6. A. Gandini, *Adv. Polym. Sci.* **25**, 47 (1977).
7. F. M. Dean, *Advances in Heterocyclic Chemistry* **30**, 168; **31**, 237 (1982).
8. Dobereiner, *Ann.* **3**, 141 (1832); quoted in Ref. 1, p. 272.
9. Emmet, in *J. Pract. Chem.* **12**, 120 (1837); *Ann.* **28**, 249 (1939); quoted in Ref. 1, p. 272.
10. Stenhouse, *Phil. Mag.* **18**, 122 (1840); *Ann.* **35**, 301 (1840); quoted in Ref. 1, p. 272.
11. Baeyer, *Ber.* **10**, 355, 695, 1358 (1877); quoted in Ref. 1, p. 4.
12. Markwald, *Ber.* **20**, 2811 (1887); quoted in Ref. 1, p. 5.
13. Markwald, *Ber.* **21**, 1398 (1887); quoted in Ref. 1, p. 5.
14. Harries, *Ber.* **34**, 1488 (1901); quoted in Ref. 1, p. 5.
15. G. H. Mains, *Chem. Met. Eng.* **26**, 779 (1922).
16. R. G. Curtis and H. H. Hatt, *Aust. J. Sci. Res.* **A1**, 213 (1948).
17. A. P. Dunlop and F. N. Peters, Jr., *Ind. Eng. Chem.* **32**, 1639 (1940).
18. The Quaker Oats Company, Unpublished data.
19. T.-S. Li, S.-H. Li, J.-T. Li, and H.-Z. Li, *J. Chem. Res. Synop.*, 26–27, (1997); *Chem. Abst.* **126**, 144440 (1997).
20. V. V. Girdyuk, Yu. K. Kirilenko, L. A. Vol'f, and A. I. Meos, *Zh. Prikl. Khim.* **39**, 2601 (1966).
21. I. V. Kamenskii, S. M. Filimonova, Ngo Van Lam, B. Ya. Eryshev, and N. B. Krovyakova, *Plast. Massy* **5**, 5 (1973); *Chem. Abstr.* **79**, 79683n (1973).
22. Pais, C. G. Godwin; A. Keshavaraja; K. Saravanan, and P. Kumar, *J. Chem. Res. Synop.* **9**, 426 (1996).
23. N. Deka, D. J. Kalita, R. Borah, and J. C. Sarma, *J. Org. Chem.* **62**, 1563–1564 (1997).
24. W. J. Chute and G. F. Wright, *J. Org. Chem.* **10**, 541 (1945).
25. H. Gilman and G. F. Wright, *J. Am. Chem. Soc.* **52**, 2550 (1930).
26. V. I. Sakhnenko, M. V. Sokolov, V. V. Kashmet, A. N. Chernobrovyi, *Khim.-Farm. Zh.* **27**, (3), 53–7 (1993) *Chem. Abst.* **121**, 160125 (1994).
27. H. Li and M. Gao, *Hebei Daxue Xuebao, Ziran Kexueban*, **12**, 78 (1992).
28. D. L. Williams and A. P. Dunlop, *Ind. Eng. Chem.* **40**, 239 (1948).
29. J. Z. Marcusson, *Z. Angew. Chem.* **32**, 113 (1919).
30. G. Illari, *Gazz. Chim. Ital.* **77**, 389 (1947).
31. Y. Nakamura and M. Saito, *Kogyo Kagaku Zasshi* **62**, 1173 (1959).
32. N. Galego, Ph.D. Thesis, University of Havana, 1975.
33. N. Galego and A. Gandini, *Rev. CENIC Cent. Nac. Invest. Cient. I Cienc. Fis.* **6**, 163 (1975).
34. N. Galego and F. Lopez, *Rev. Cubana Quim.* **6**, 107 (1992).
35. R. Sanchez, C. Hernandez and G. Keresztury, *Eur. Polym. J.* **30**, 43 (1994).
36. R. L. Whistler and E. L. Richards, "Hemicelluloses" in W. Pigman and D. Horton, eds., *The Carbohydrates*, Vol. IIA, Academic Press, Inc., New York, 1970, 447–467.
37. G. O. Aspinall, *Polysaccharides*, Pergamon Press Ltd., Oxford, U.K., 1970, 103–115.
38. *Making and Marketing Furfural; Added Value for Agro-Industrial Wastes*, International Trade Center UNCTAD/GATT, Geneva, 1979.
39. J. E. Stone and M. J. Blundell, *Can. J. Res.* **28B**, 676 (1950).
40. R. Will, "Furfural," *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, Calif., Mar. 1994.
41. Jpn. Pat. 78 19,693 (June 22, 1978), M. Futamoto, U. Kawabe, and S. Hosoki (to Hitachi Ltd.).
42. *AID* (*Air Information Division*) *Report 61–19*, Armed Services Technical Information Agency, NTIS (National Technical Information Service), Springfield, Va., Feb. 1961.

43. *AID Report 61-5*, Armed Services Technical Information Agency, NTIS, Springfield, Va., Jan. 1961.
44. D. A. Isacescu, I. Gavat, C. Stoicescu, C. Vass, and I. Petrus, *Rev. Roum. Chim.* **10**, 219 (1965); *Chem. Abst.* **63**, 16284 (1965).
45. A. A. Patel, Ashok, and S. R. Patel, *Eur. Polym. J.* **19**, 231 (1983); *Chem. Abst.* **98**, 216122 (1983).
46. I. V. Kamenskii, N. V. Ungurean, B. M. Kovarskaya, and I. V. Itinskii, *Plast. Massy* **12**, 9 (1960); *Chem. Abst.* **55**, 15985 (1961).
47. Hungarian Pat. 58780 (Mar. 30, 1992); *Chem. Abst.* **117**, 193648 (1993).
48. U.S. Pat. 5,037,453 (Aug. 6, 1991), K. S. Narayanan and M. S. Ramakrishnan (to the Norton Co.).
49. U.S. Patent 4,348,343 (Sep. 7, 1982), D. W. Akerberg, G. W. Huffman, and C. A. Rude (to The Quaker Oats Co.).
50. S. A. Suvorov, D. E. Denisov, V. F. Timofeev, G. I. Kuznetsov, A. A. Kortel, Yu. D. Kuznetsov, G. I. Borovikov, A. I. Shullman, and A. F. Radionov, *Ogneupory* **11**(11), 16 (1993).
51. A. P. Dunlop and F. N. Peters, Jr., *Ind. Eng. Chem.* **34**, 814 (1942).
52. V. Sunjic, J. Horvat, B. Klaic, and S. Horvat, *Kem. Ind.* **33**, 593 (1984); *Chem. Abst.* **102**, 151194 (1985).
53. J. Horvat, B. Klaic, Branimir, B. Metelko, S. Biserkaand, and V. Sunjic, *Croat. Chem. Acta* **59**, 429 (1986).
54. A. Gandini, *ACS Symp. Ser. 433, Agric. Synth. Polym.: Biodegrad. Util.*, 195 (1990).
55. M. Choura, N. Belgacem, and A. Gandini, *Macromolecules* **29**, 3839 (1996).
56. R. H. Wojcik, *Ind. Eng. Chem.* **40**, 210 (1948).
57. U.S. Pat. 2,754,304 (July 10, 1956), S. Swadesh (to The Quaker Oats Co.).
58. W. D. Wakefield, *Production* (Oct. 1976).
59. R. F. Frankenberg, *Foundry Met. Treat.*, 87 (Jan. 1979).
60. *Int. Mod. Foundry* **2**, 2 (1978).
61. S. Pal, *Indian Foundry J.* **35**, 27 (1989); *Chem. Abst.* **112**, 143743 (1990).
62. U.S. Pat. 4,495,316 (Jan. 22, 1985), D. R. Armbruster (to Acme Resin Corp.).
63. U.S. Pat. 4,543,373 (Sept. 24, 1985), R. W. Krawiec and J. E. Menting (to QO Chemicals).
64. U.S. Pat. 4,644,022 (Feb. 17, 1987) R. Iyer (to Acme Resin Corp.).
65. Eur. Pat. Appl. 698,432 A1 (Feb. 28, 1996) K. Kiuchi, S. Nakai, M. Sawa, M. Kato, M. Sakaiand, and S. Nomura (to Kao Corp.).
66. W. H. Buell, *Foundry* **89**(2), 64 (1961).
67. A. Dorfmuller, Jr., *Foundry* **90**(4), 54 (1962).
68. PCT Int. Appl. 96-36,448 (Nov. 21, 1996), K. K. Chang, T. E. Dando, and A. L. Haugse (to Ashland Inc.).
69. U.S. Pat. 5,607,986 (Mar. 4, 1997), Y. D. Kiom and A. L. Haugse (to Ashland Inc.).
70. U.S. Pat. 4,255,554 (Mar. 10, 1981), J. P. Wuskell (to The Quaker Oats Co.).
71. Eur. Pat. Appl. 653,260 (Jan. 11, 1995), J. W. Ward, R. A. Llitar, and B. E. Wise (to Borden Inc.).
72. R. H. Kottke and A. E. Bloomquist, *AFS Trans.* **86**, 215 (1978).
73. U.S. Pat. 4,543,374 (Sept. 24, 1997), J. E. Menting (to QO Chemicals Inc.).
74. U.S. Pat. 4,451,577 (May 29, 1984), W. W. Coss (to The Quaker Oats Co.).
75. M. B. Launikitis, *Manag. Corros. Plast. Series* **3**, 190 (1977).
76. R. H. Leitheiser, K. B. Bozer, and D. D. Watson, *Furan Resins for FRP Composites*, National Association of Corrosion Engineers, Annual Meeting, San Francisco, Calif., Mar. 14–18, 1977.
77. R. M. Webster, National Association of Corrosion Engineers, Annual Meeting, San Francisco, Calif., Mar. 14–18, 1977.

78. *Impregnating Formulations Based on Furan Chemicals*, Technical Bulletin No. 190, Chemicals Division, The Quaker Oats Company, Chicago, Ill., 1979.
79. Jap. Pat. Appl. 06171918 A2 (June 21, 1994), (to Hitachi Chemical Co. Ltd.).
80. U.S. Pat. 4,619,706 (Oct. 28, 1986), D. G. Squires, L. Hundley, and R. A. Berry (to Texo Corp.).
81. U.S. Pat. 4,366,022 (Dec. 28, 1982), C. M. Carandang (to Amchem Products, Inc.).
82. U.S. Pat. 5,259,993 (Nov. 9, 1993), S. M. Short (to Cook Composites and Polymers).
83. Jap. Pat. Appl. 03062898 (Mar. 18, 1991), K. Kitazawa and M. Takeda (to Kao Corp.).
84. C. D. Hurd and A. R. Goldsby, *J. Am. Chem. Soc.* **54**, 2558 (1932).
85. Jpn. Pat. 58090548 A2 (May 30, 1983) (to Daicel Chemical Industries, Ltd.): *Chem. Abst.* **99**, 105121 (1983).
86. Jpn. Pat. 01301658 A2 (Dec. 5, 1989), T. Yamamoto and M. Iwasaki (to Asahi Chemical Industry Co., Ltd.); *Chem. Abst.* **112**, 198124.
87. Yu. K. Yur'ev, *J. Gen. Chem. USSR* **8**, 1934 (1938).
88. A. Norton, *Chem. Rev.* **31**, 319 (1942).
89. G. B. Butler, J. T. Badgett, and M. Sharabash, *J. Macromol. Sci. Chem.* **4**(1), 51 (1970).
90. B. Kamo, I. Morita, S. Horie, and S. Furusawa, *Polym. J.* **6**(2), 121 (1974).
91. N. G. Gaylord, S. Maiti, B. K. Patnaik, and A. Takahashi, *J. Macromol. Sci. Chem.* **6**, 1459 (1972).
92. N. G. Gaylord, M. Martan, and A. B. Deshpande, *J. Polym. Sci. Polym. Chem. Ed.* **16**, 1527 (1978).
93. N. A. Milas and W. L. Walsh, *J. Am. Chem. Soc.* **57**, 1389 (1935).
94. K. G. Akopyan, A. G. Dzhomardyan, A. P. Sayadyan, G. K. Garibyan, and N. M. Morlyan, *Arm. Khim. Zh.* **41**, 451–454 (1988); *Chem. Abst.* **110**, 212078 (1989).
95. Ger. Pat. DE 2710420 (Aug. 24, 1978), D. Degner, H. Nohe, and H. Hannebaum (to BASF).
96. R. E. W. Jansson and N. Tomov, *Chem. Ind. (London)*, 96–98 (1978).
97. Russian Pat. Ru 2,027,714 (Apr. 28, 1992), N. G. Zheltonog, G. E. Kramerova, N. N. Machalaba and V. E. Oleinikov, *Chem. Abst.* **124**, 86804 (1995).
98. N. N. Machalaka, G. F. Tereshchenko, A. G. Bazanov, and N. G. Zheltonog, *Gidroliz. Lesokhim. Prom-st*, 25 (1993).
99. K. J. Jung, Ph. Lejemble, Ph. Kalck, J. Molinier, and A. Gaset, *Inf. Chim.* **283**, 135 (1987).
100. K. J. Jung, A. Gaset, and J. Molinier, *Biomass* **16**, 89 (1988).
101. U.S. Pat. 2,846,449 (Aug. 5, 1958), W. H. Banford and M. M. Manes (to E. I. du Pont de Nemours & Co., Inc.).
102. U.S. Pat. 3,021,342 (Feb. 13, 1962), D. G. Manly (to The Quaker Oats Co.).
103. R. Paul, *Compt. Rend.* **206**, 1028 (1938).
104. B. A. Keay and P. W. Dibble, in C. W. Bird, ed., *Comprehensive Heterocyclic Chemistry II*, Vol. 2, Elsevier, Oxford, U.K., 1996, p. 395.
105. Belg. Pat. BE 1,008,868 (Aug. 6, 1996), J. E. Shaw and W. E. Sattich (to Phillips Petroleum Co.).
106. U.S. Pat. 3,850,832 (Nov. 26, 1974), (to Hankel & Cie GmbH).
107. R. T. Wragg, *J. Chem. Soc.*, 7162 (1965).
108. L. H. Brown and J. W. Hill, *J. Chem. Eng. Data* **5**, 56 (1960).
109. W. Reppe and co-workers, *Ann.* **582**, 1 (1953).
110. Jpn. Pat. JP58174346, (Oct. 13, 1983) (to Yokkaichi Chemical Co., Ltd.).
111. Jpn. Pat. JP50050313 (May 6, 1975), K. Kimura, K. Suzuki, E. Kondo, N. Motoyama, G. Terada, and H. Mishina (to Toa Gosei Chemical Industry Co., Ltd.).
112. Jpn. Pat. JP50013313 (Feb. 12, 1975), K. Suzuki, K. Kimura, Y. Kato, H. Mishina, and E. Kondo, (to Toa Gosei Chemical Industry Co., Ltd.).

113. U.S. Pat. 2,636,902 (Apr. 28, 1953), A. W. C. Taylor, P. Davies, and P. W. Reynolds (to Imperial Chemical Industries Ltd.).
114. Jpn. Pat. JP60178877 (Sept. 12, 1985), S. Mori, T. Aoki, R. Hamana and Y. Nomura (to Mitsubishi Petrochemical Co., Ltd.).
115. L. S. Glebov, G. A. Kliger, A. N. Shuikin, and V. G. Zaikin, *Neftekhimiya* **36**, 344 (1996).
116. U.S. Pat. 3,238,214 (Mar. 1, 1966), D. G. Manly, J. P. O'Halloran, and F. J. Rice (to The Quaker Oats Co.).
117. J. H. Choi and W. Y. Lee, *Appl. Catal. A* **98**, 21 (1993).
118. Soviet Pat. SU1524917 (Nov. 30, 1989), K. M. Akhmerov, D. Yusupov, U. D. Nazirova, and A. B. Kuchkarov, (to Tashkent Polytechnic Institute).
119. U. D. Nazirova and K. M. Akhmerov, *Dokl. Akad. Nauk. UzSSR* 40 (1988).
120. U.S. Pat. 3,163,652 (Dec. 29, 1964), D. G. Manly, J. P. O'Halloran, and F. J. Rice (to The Quaker Oats Co.).
121. Jpn. Pat. JP60174776 (Sept. 9, 1985), S. Mori, T. Aoki, R. Hamana and Y. Nomura, (to Mitsubishi Petrochemical Co., Ltd.).
122. Brit. Pat. GB593,617 (Oct. 21, 1947), J. G. M. Bremner and R. R. Coats (to Imperial Chemical Industries).
123. R. A. Karakhanov, V. Vagabov, N. P. Karzhavina, O. M. Ramazanov, Y. S. Mardashev, and M. M. Vartanyan, *Zh. Prikl. Khim. (Leningrad)* **54**, 454 (1981).
124. S. Baskaran, I. Islam, and S. Chandrasekaran, *J. Chem. Res. Synop.* 290 (1992).
125. S. Baskaran and S. Chandrasekaran, *Tetrahedron Lett.* **31**, 2775 (1990).
126. E. P. Goodings and C. L. Wilson, *J. Am. Chem. Soc.* **73**, 4801 (1951).
127. S. Landa and J. Mostecky, *Collect. Czech. Chem. Commun.* **20**, 430 (1955).
128. O. W. Cass, *Chemurgic Dig.* **8**(6), 6 (1949).
129. R. Paul, *Bull. Sec. Chim. France* **14**, 158 (1947).
130. O. W. Cass, *Ind. Eng. Chem.* **40**, 21C (1048).
131. U.S. Pat. 3,518,281 (June 30, 1970), D. C. Holtman (to Emery Industries, Inc.).
132. R. F. Naylor, *J. Chem. Soc.*, 2749 (1949).
133. Yu. K. Yur'ev and E. G. Vendel'shtein, *J. Cen. Chem. USSR* **22**, 751 (1952).
134. *QO Tetrahydrofurfuryl Alcohol, Bulletin 206*, QO Chemicals, part of Great Lakes Chemical Corporation, West Lafayette, Ind.
135. U.S. Pat. 5,514,294 (May 7, 1996), G. W. Bohnert and co-workers (to Allied Signal Inc.).
136. U.S. Pat. 4,737,195 (Apr. 12, 1988) C. M. Caranding and R. E. Koch (to Amchem Products, Inc.).
137. U.S. Pat. 5,128,057 (July 7, 1992), M. L. Bixenman and G. C. Wolf (to Kyzen Corp.).
138. U.S. Pat. 4,514,325 (Apr. 30, 1985), A. Russo and T. Mauthner (to J. Hall Co.).
139. U.S. Pat. 5,456,853 (Oct. 10, 1995), M. M. Myers (to Rust-Oleum Corp.).
140. K. J. Doyel and co-workers, C. L. Foy, ed., *Adjuvants Agrichemistry*, CRC, Boca Raton, Fla., 1992, 225–234.
141. U.S. Pat. 5,259,993 (Nov. 9, 1993), S. M. Short (to Cook Composites and Polymers Co.).
142. U.S. Pat. 4,619,706 (Oct. 28, 1986), D. G. Squires, L. Hundley, and R. A. Barry (to Texo Corp.).
143. U.S. Pat. 4,666,002 (Dec. 28, 1981), C. M. Carandang (to Amchem Products, Inc.).
144. L. Poppe, K. Recseg and L. Novak, *Syn. Com.* **25**, 3993 (1995).
145. WO. Pat. 97/06097, (Feb. 20, 1997), T. Rathman and co-workers (to FMC Corp.).
146. S. Tobishima and co-workers *J. Appl. Electrochem.* **27**, 902 (1997).
147. U.S. Pat. 5,486,557 (Jan. 23, 1996), D. W. Akerberg (to QO Chemicals, Inc.).
148. U.S. Pat. 5,589,536 (Dec. 31, 1996), (to QO Chemicals, Inc., and Schuller International, Inc.).

149. U.S. Pat. 4,429,091 (Jan. 31, 1984), J. E. Hall (to Firestone Tire and Rubber Co.).
150. A. F. Halasa and W. L. Hsu, "New Ether Modifiers for Anionic Polymerization of Isoprene," *Polym. Prepr.* **37**(2), (1996).
151. Jap. Pat. 57091982 A2 (Nov. 28, 1980) (to Sumitomo Chemical Co., Ltd.).
152. V. N. Pavlychev and co-workers, *Khim. Prom-st.*, (7), 394 (1980).
153. G. D. Clayton and F. E. Clayton, eds., *Patty's Industrial Hygiene and Toxicity*, 4th ed., John Wiley & Sons, Inc., New York, 1991.
154. Great Lakes Chemical Corp., information summarized from Material Safety Data Sheets.

GENERAL REFERENCES

Refs. 1,7–9.

M. V. Sargent and T. M. Cresp "Furans" in D. Barton and W. D. Ollis, eds., *Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds*, Vol. **4**, Pergamon Press Ltd., Oxford, U.K., 1979, 693–744.

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