ALKYLPHENOLS

1. Introduction

Alkylphenols of greatest commercial importance have alkyl groups ranging in size from one to twelve carbons. The direct use of alkylphenols is limited to a few minor applications such as epoxy-curing catalysts and biocides. The vast majority of alkylphenols are used to synthesize derivatives which have applications ranging from surfactants to pharmaceuticals. The four principal markets are nonionic surfactants, phenolic resins, polymer additives, and agrochemicals.

Nonionic surfactants and phenolic resins based on alkylphenols are mature markets and only moderate growth in these derivatives is expected. Concerns over the biodegradability and toxicity of these alkylphenol derivatives to aquatic species may limit their use in the future. The use of alkylphenols in the production of both polymer additives and monomers for engineering plastics is expected to show above average growth as plastics continue to replace traditional building materials.

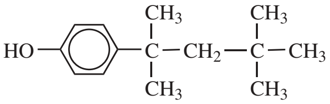
Alkylphenols containing 3–12-carbon alkyl groups are produced from the corresponding alkenes under acid catalysis. Alkylphenols containing the methyl group were traditionally extracted from coal tar. Today they are produced by the alkylation of phenol with methanol.

2. Nomenclature

An alkylphenol is a phenol derivative wherein one or more of the ring hydrogens has been replaced by an alkyl group(s). Phenol is a heading parent in the CAS indexing system. Appropriate names of alkylphenols for abstract citations can be derived by using the appropriate aids (1). The names generated in this manner are unambiguous and refer to a specific compound, but are lengthy and cumbersome to use. Common names are used on a daily basis and are especially prevalent for alkylphenols that have gained commercial importance.

Kirk-Othmer Encyclopedia of Chemical Technology.

For monosubstituted alkylphenols, the position of the alkyl radical relative to the hydroxyl function is designated either with a numerical locant or ortho, meta, or para. The alkyl side chain typically retains a trivial name. Thus 4-(1,1,3,3-tetramethylbutyl)phenol, 4-*tert*-octylphenol, and *para-tert*-octylphenol (PTOP) all refer to structure (**1**).

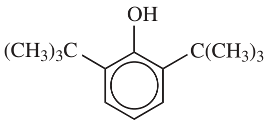


(**1**)

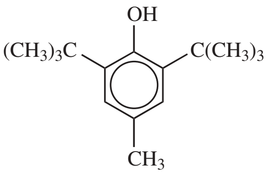
Dialkylphenols employ locants to designate the position of the alkyl groups on the ring. Thus, 2,6-bis(1,1-dimethylethyl)phenol, 2,6-di-*tert*-butylphenol, and 2,6-DTBP each refer to structure (**2**).

Other common names are cresol and xylenol for methyl- and dimethylphenols respectively, eg, *o*-cresol is 2-methylphenol, and 2,5-xylenol is 2,5-dimethylphenol.

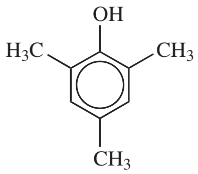
For phenols with three or more alkyl substituents, trade names, abbreviations, and associative names predominate, eg, BHT and 2,6-di-*tert*-butyl-4-methylphenol refer to structure (**3**) and mesitol and 2,4,6-trimethylphenol refer to structure (**4**).



(**2**)



(**3**)



(**4**)

3. Physical Properties

Of course, the physical properties of alkylphenols are comparable to phenol. The properties are strongly influenced by the type of alkyl substituent and its position on the ring. Alkylphenols, like phenol, are typically solids at 25°C. Their form is affected by the size and configuration of the alkyl group, its position on the ring, and purity. They appear colorless, or white, to a pale yellow when pure (Table 1).

Para-alkylphenols have higher melting points and boiling points than the corresponding ortho-isomers. The melting points of para-alkylphenols go through a maximum for *tert*-butyl and then decrease. An alkene stream consisting of a mixture of isomers produces an alkylphenol that has a depressed melting point. As the carbon chain of the alkyl group surpasses 20, the resulting phenols take on a waxy form. Alkylphenols, especially when di- and trisubstituted, tend to supercool. Alkylphenols show the same sensitivity to oxidation that phenol

Table 1. **Commercially Important Alkylphenols**

Name	CAS Registry Number	Molecular formula	Molecular weight	Physical form at 25°C	Boiling point, °C[a]	Freezing point, °C	Density[b], g/mL	Typical Assay	Flash point, °C	Molten color APHA
4-*tert*-amylphenol	[80-46-6]	$C_{11}H_{16}O$	164.0	solid	249	90.0	0.915^{107}	99	121	200
4-*tert*-butylphenol	[98-54-4]	$C_{10}H_{14}O$	150.2	solid	237	97.5	0.890^{107}	98–99	117	100
2-*sec*-butylphenol	[89-72-5]	$C_{10}H_{14}O$	150.2	liquid	224	20.0	0.938^{43}	98	>93	100
4-cumylphenol	[599-64-4]	$C_{15}H_{16}O$	212.0	solid	335	70.0	1.029^{93}	99	188	100
4-dodecylphenol	[27193-86-8]	$C_{18}H_{30}O$	262.0	liquid	334		0.914^{20}	89–95	>100	500
4-nonylphenol	[84852-15-3][c]	$C_{15}H_{24}O$	220.3	liquid	310		0.933^{43}	90–95	146	100
4-*tert*-octylphenol	[140-66-9]	$C_{14}H_{22}O$	220.3	solid	290	81.0	0.940^{25}	90–98	132	200
2,4-di-*tert*-amylphenol	[25231-47-4]	$C_{16}H_{26}O$	234.4	liquid	275	23.0	0.900^{49}	99	104	100
2,4-di-*tert*-butylphenol	[96-76-4]	$C_{14}H_{22}O$	206.3	solid	263	52.0	0.867^{82}	99	115	100
2,6-di-*tert*-butylphenol	[128-39-2]	$C_{14}H_{22}O$	206.3	solid	253	36.0	0.898^{43}	99	>99	100
di-*sec*-butylphenol	[31291-60-8]	$C_{14}H_{22}O$	206.3	liquid			0.902^{66}	90	127	500
2,4-dicumylphenol	[2772-45-4]	$C_{24}H_{26}O$	330.0	solid		65.0	1.030^{66}	99	462	100
2-methylphenol	[95-48-7]	C_7H_8O	108.1	solid	191	30.0	$1.049^{15.5}$	99	81	25
3-methylphenol	[108-39-4]	C_7H_8O	108.1	liquid	202	10.0	$1.042^{15.5}$	97	86	
4-methylphenol	[106-44-5]	C_7H_8O	108.1	solid	202	34.0	1.022^{25}	99	86	25
2,6-dimethylphenol	[576-26-1]	$C_8H_{10}O$	122.1	solid	203	48.0	1.020^{25}	99	88	

[a] At 101.3 kPa = 1 atm.

[b] At the temperature indicated by the superscript, °C.

[c] Mixture, branched chains.

does. The presence of trace amounts of metals or alkaline impurities accelerates oxidation. Oxidation products cause discoloration.

The solubility of alkylphenols in water falls off precipitously as the number of carbons attached to the ring increases. They are generally soluble in common organic solvents: acetone, alcohols, hydrocarbons, toluene. Solubility in alcohols or heptane follows the generalization that "like dissolves like." The more polar the alkylphenol, the greater its solubility in alcohols, but not in aliphatic hydrocarbons; likewise with cresols and xylenols. The solubility of an alkylphenol in a hydrocarbon solvent increases as the number of carbon atoms in the alkyl chain increases. High purity para substituted phenols, C_3 through C_8, can be obtained by crystallization from heptane.

The aromatic ring of alkylphenols imparts an acidic character to the hydroxyl group; the pK_a of unhindered alkylphenols is 10–11 (2). Alkylphenols unsubstituted in the ortho position dissolve in aqueous caustic. As the carbon number of the alkyl chain increases, the solubility of the alkali phenolate salt in water decreases, but aqueous caustic extractions of alkylphenols from an organic solution can be accomplished at elevated temperatures. Bulky ortho substituents reduce the solubility of the alkali phenolate in water. The term cryptophenol has been used to describe this phenomenon. A 35% solution of potassium hydroxide in methanol (Claisen's alkali) dissolves such hindered phenols (3).

Alkyl groups in the ortho position affect the environment about the hydroxyl group; the larger the group the greater the effect. Intermolecular hydrogen bonding decreases with the introduction of a *tert*-butyl group ortho to the hydroxyl, reducing the atmospheric boiling point of the ortho isomer by about 20°C. Substitution of the second ortho position with a *tert*-butyl group effectively precludes any hydrogen bonding as shown by the infrared spectrum of 2,6-DTBP; a sharp absorbance is found at 2.75 μm, characteristic of an unassociated hydroxyl stretching (4). The impact of an ortho alkyl substituent on hydrogen bonding can be advantageously applied to the analysis and separation of alkylphenols. A mixture of ortho and para isomers is separated effectively using normal phase chromatography (flash or hplc).

There is a health benefit associated with hindering hydrogen bonding. Alkylphenols as a class are generally regarded as corrosive health hazards, but this corrosivity is eliminated when the hydroxyl group is flanked by bulky substituents in the ortho positions. In fact, hindered phenols as a class of compounds are utilized as antioxidants in plastics with FDA approval for indirect food contact.

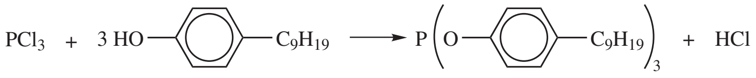
4. Chemical Properties

Alkylphenols undergo a variety of chemical transformations, involving the hydroxyl group or the aromatic nucleus that convert them to value-added products.

4.1. The Hydroxyl Group.

The unshared pairs of electrons on hydroxyl oxygens seek electron deficient centers. Alkylphenols tend to be less nucleophilic than aliphatic alcohols as a direct result of the attraction of the electron density by the aromatic nucleus. The reactivity of the hydroxyl group can be enhanced in spite of the attraction of the ring current by use of a basic catalyst which removes the acidic proton from the hydroxyl group leaving the more nucleophilic alkylphenoxide.

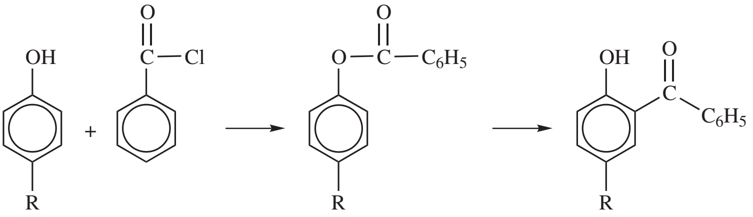
Esterification. Alkylphenols react with acid chlorides and acids to produce commercially important esters. Three equivalents of *p*-nonylphenol (**5**) react with phosphorus trichloride or tributyl phosphite to produce tris(4-nonylphenyl) phosphite (TNPP) (**6**).



(**5**) (**6**)

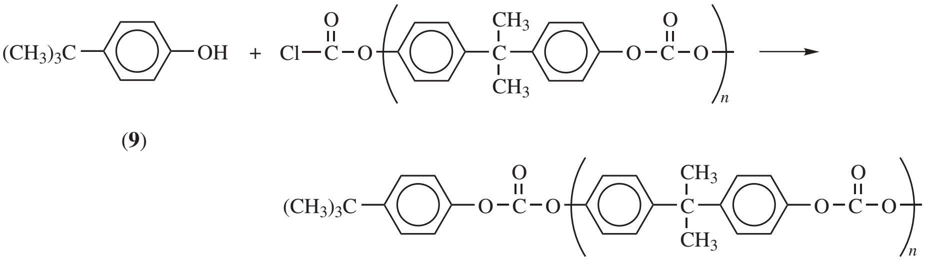
When the phenol reactant is 2,4-di-*tert*-butylphenol, a phosphite ester with greater hydrolytic stability is produced.

Alkylphenyl esters (**7**) of aromatic carboxylic acids can be made from appropriate acid chlorides or by transesterification of benzoate esters. The resulting alkylphenyl benzoates undergo a transformation called the Fries rearrangement which involves cleavage of the ester linkage followed by the migration of the benzoyl group to the ortho or para position of the phenol. The reaction can be catalyzed by metal halides in a typical Friedel-Crafts reaction or the process can be photochemical, ie, the photo-Fries. The resulting product is a hydroxybenzophenone (**8**). These benzophenones have found applicability as uv absorbers in thermoplastics.



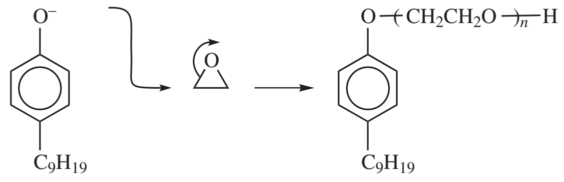
(**7**) (**8**)

Alkylphenols have been substituted for phenol as chain terminators in polycarbonates. In this role, PTBP (**9**) competes with the diol monomer for reactive chlorocarbonate sites. The ratio of butylphenol to diol controls the molecular weight of the polymer.



(**9**)

Etherification. Many of the monoalkylphenols and some of the dialkylphenols are converted into ethoxylates which find commercial application as nonionic surfactants (5). For example, *p*-nonylphenol reacts with ethylene oxide under mild basic conditions.

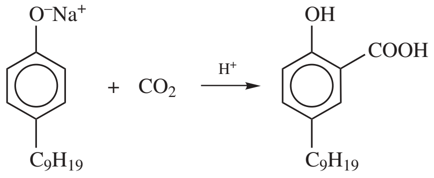


(**10**)

The number of ethylene oxide units added to the phenoxide depends on the application of the ethoxylate. This chemistry is closely related to the reaction between an alkylphenol and epichlorohydrin which is used in epoxy resins (qv).

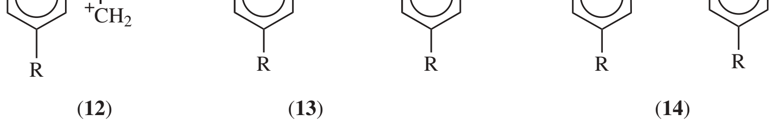
4.2. Reactions Involving the Ring. The aromatic nucleus of alkylphenols can undergo a variety of aromatic electrophilic substitutions. Electron density from the hydroxyl group is fed into the ring. Besides activating the aromatic nucleus, the hydroxyl group controls the orientation of the incoming electrophile.

Alkylphenols undergo a carboxylation reaction known as the Kolbe Schmidt reaction. In the following example, the phenolate anion of *p*-nonylphenol (10) reacts with carbon dioxide under pressure. Neutralization generates a salicylic acid (**11**) (6).



(**10**) (**11**)

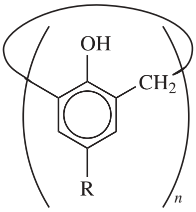
Reactions with Aldehydes and Ketones. An important use for alkylphenols is in phenol–formaldehyde resins. These resins are classified as resoles or novolaks (see PHENOLIC RESINS). Resoles are produced when one or more moles of formaldehyde react with one mole of phenol under basic catalysis. These resins are thermosets. Novolaks are thermoplastic resins formed when an excess of phenol reacts with formaldehyde under acidic conditions. The acid protonates formaldehyde to generate the alkylating electrophile (**12**).



(**12**) (**13**) (**14**)

The intermediate methylol derivative (**13**) is unstable under the reaction conditions and generates an electrophile that undergoes another substitution reaction resulting in the methylene bridge between alkylphenol groups (**14**). This reaction is repeated to propagate the polymer chain. The choice of alkylphenol as well as the alkylphenol:formaldehyde ratio allows a good deal of control over the properties of the resulting resin.

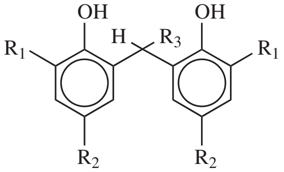
A newer development in alkylphenol–formaldehyde resins has been the application of this condensation reaction to produce calixarenes, cyclic oligomers of methylene-bridged alkylphenols (**15**). The smallest cyclic oligomer that has been isolated to date contains four alkylphenol groups.



(**15**)

These molecules are significant in the field of research devoted to host–guest complexation. Synthetic routes to a number of calixarenes have been developed (7).

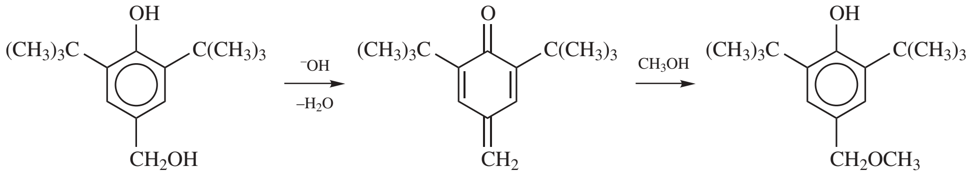
2,4-Dialkylphenols react with aldehydes similarly. A bisphenol (**16**) is formed by the condensation.



(**16**)

Commercial application of this type of reaction is used to produce 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (R^1 = *tert*– butyl; R^2 = methyl; R^3 = H) and 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) $R^1 = R^2$ = *tert* – butyl; $R^3 = CH_3$).

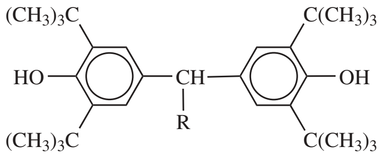
Quinone Methides. The reaction between aldehydes and alkylphenols can also be base-catalyzed. Under mild conditions, 2,6-DTBP reacts with formaldehyde in the presence of a base to produce the methylol derivative (**17**) which reacts further with base to eliminate a molecule of water and form a reactive intermediate, the quinone methide (**18**). Quinone methides undergo a broad array of transformations by way of addition reactions. These molecules are conjugated homologues of vinyl ketones, but are more reactive because of the driving force associated with rearomatization after addition. An example of this type of addition is between the quinone methide and methanol to produce the substituted benzyl methyl ether (**19**).



(**17**) (**18**) (**19**)

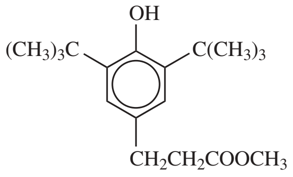
This addition is general, extending to nitrogen, oxygen, carbon, and sulfur nucleophiles. This reactivity of the quinone methide (**18**) is applied in the synthesis of a variety of stabilizers for plastics. The presence of two *tert*-butyl groups ortho to the hydroxyl group, is the structural feature responsible for the antioxidant activity that these molecules exhibit (see Antioxidants).

4,4′-Methylenebis(2,6-di-*tert*-butylphenol) (**20**) (R = H) [118-82-1], the reaction product of two molecules of 2,6-DTBP with formaldehyde under basic conditions, is a bisphenolic antioxidant. The quinone methide in this case is generated *in situ*. The product results from the addition of 2,6-di-*tert*-butylphenolate to (**18**) (8).



(**20**)

The versatility of this reaction is extended to a variety of aldehydes. The bisphenol derived from 2,6-di-*tert*-butylphenol and furfural, (**20**) where R = furfuryl (9), is also used as an antioxidant. The utility of the 3,5-di-*tert*-butyl-4-hydroxybenzyl moiety is evident in stabilizers of all types (16), and its effectiveness has spurred investigations of derivatives of hindered alkylphenols to achieve better stabilizing qualities. Another example is the Michael addition of 2,6-di-*tert*-butyl phenol to methyl acrylate. This reaction is carried out under basic conditions and yields methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate [6386-38-5] (**21**) (11).

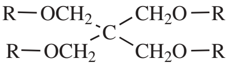


(**21**)

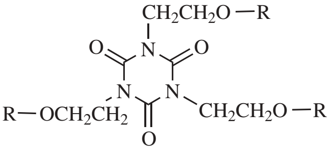
Transesterification reactions between the methyl propionate and various alcohols produce another family of stabilizers. Stearyl alcohol yields octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (**22**) (12), pentaerythritol gives the tetrakis ester (**23**) (13), and trishydroxyethyl isocyanurate gives (**24**) (14).

$R{-}OC_{18}H_{37}$

(**22**)

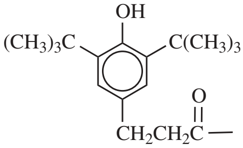


(**23**)

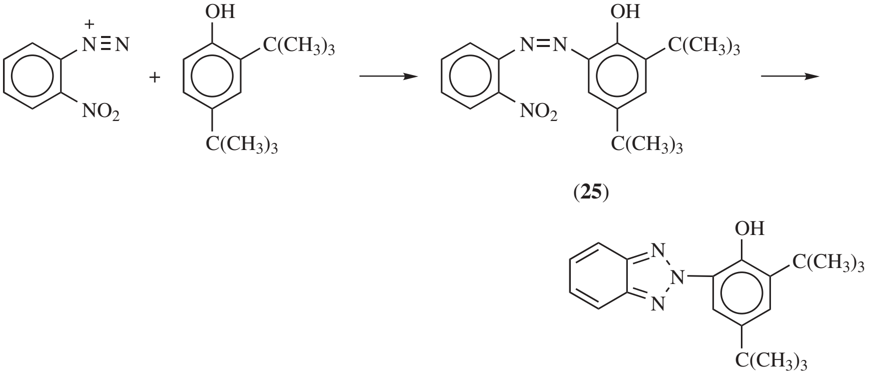


(**24**)

where R =



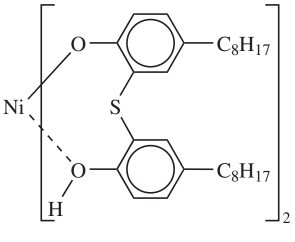
Diazo Coupling Reactions. Alkylphenols undergo a coupling reaction with diazonium salts which is the basis for the preparation of a class of uv light stabilizers for polymers. The interaction of *ortho*-nitrobenzenediazonium chloride with 2,4-di-*tert*-butylphenol results in an azo-coupled product (**25**). Reduction of the nitro group followed by *in situ* cyclization affords the benzotriazole (**26**) (15).



(**25**)

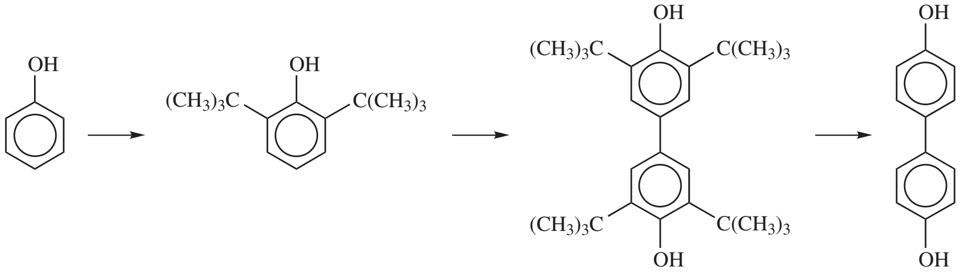
(**26**)

Benzotriazoles stabilize resins based on their ability to absorb uv radiation and re-emit the energy as thermal energy through molecular vibrations. Nickel-containing light stabilizers can act as both absorbers and quenchers of excited states of carbonyl impurities (16). One such nickel-containing stabilizer is made by coupling 4-*tert*-octylphenol with sulfur dichloride. The resulting bisphenol-sulfide is used to complex nickel(II) and form (**27**) (17).



(**27**)

Removal of tert-Alkyl Groups. *tert*-Alkyl groups on a phenol nucleus can be removed selectively to produce a desired synthetic result. The oxidative coupling of phenol offers a good example. 2,6-Di-*tert*-butylphenol can be coupled under oxidative conditions to 3,3′,5,5′-tetra-*tert*-butyl-4,4′-dihydroxybiphenyl (**28**). The *tert*-butyl groups can then be removed under acid conditions and recovered as isobutylene. The net result is the formation of 4,4′-dihydroxybiphenyl (**29**) from phenol (18).



(**28**) (**29**)

5. Manufacture and Processing

Alkylphenols of commercial importance are generally manufactured by the reaction of an alkene with phenol in the presence of an acid catalyst. The alkenes used vary from single species, such as isobutylene, to complicated mixtures, such as propylene tetramer (dodecene). The alkene reacts with phenol to produce monoalkylphenols, dialkylphenols, and trialkylphenols. The monoalkylphenols comprise ~85% of all alkylphenol production.

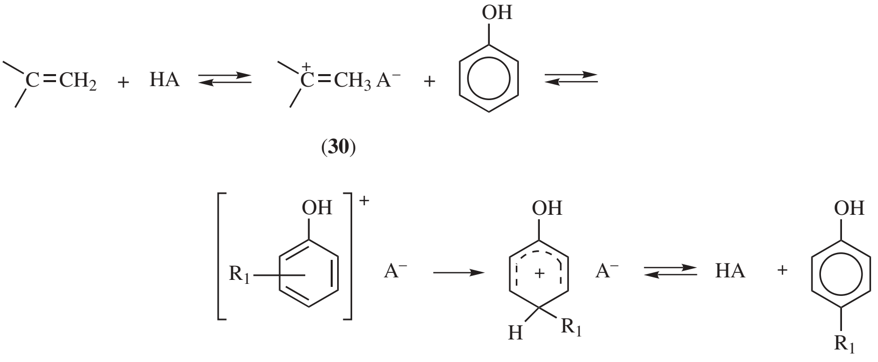
The choice of catalyst is based primarily on economic effects and product purity requirements. More recently, the handling of waste associated with the choice of catalyst has become an important factor in the economic evaluation. Catalysts that produce less waste and more easily handled waste by-products are strongly preferred by alkylphenol producers. Some commonly used catalysts are sulfuric acid, boron trifluoride, aluminum phenoxide, methanesulfonic acid, toluene–xylene sulfonic acid, cationic-exchange resin, acidic clays, and modified zeolites.

To describe the varied processes by which alkylphenols are produced, it is convenient to consider the reaction and recovery separately. In some cases this distinction is artificial because the operations are intimately linked, but in many processes the break is operationally significant.

5.1. Alkylation of Phenols.

The approach used to synthesize commercially available alkylphenols is Friedel-Crafts alkylation. The specific procedure typically uses an alkene as the alkylating agent and an acid catalyst, generally a sulfonic acid. Alkene and catalyst interact to form a carbocation and counter ion (**30**) which interacts with phenol to form a π complex (**31**). This complex is held together by the overlap of the filled π-orbital of the aromatic ring with the empty orbital of the carbocation (19). The π-complex can rearrange to the ς complex (**32**).

Loss of R^+ from complex (**32**) results in no reaction whereas loss of H^+ results in the alkylation of phenol.



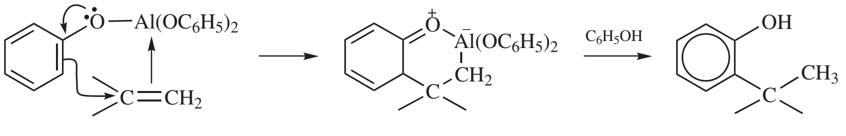
(**30**)

(**31**) (**32**)

The driving force for the formation of (**31**) can be viewed as the result of electrostatic interaction, an electron deficient species being attracted to an electron rich species. This type of interaction explains some of the by-products that are formed during these alkylation reactions. Phenylalkyl ethers are the result of an interaction between the unshared electron pairs of the phenol oxygen with the carbocation. Alkene oligomers form when the carbocation complexes with the filled π-orbital of another alkene. These alkene oligomers can in turn react with phenol to produce correspondingly higher molecular weight alkylphenols.

Alkylations of phenol can give rise to three positional isomers, ortho, meta, and para, and multisubstitution products as well. A reaction may yield some of each potential product and this product mix presents a separation problem. Fortunately, judicious choice of catalyst and/or reaction conditions allows some control over selectivity. The reactivity of the alkylating agent also controls selectivity. The reaction between phenol and isobutylene [115-11-7], wherein the alkylating agent is the *tert*-butyl carbocation, shows a very high para selectivity using acid catalysis. Tertiary carbocations are the most stable, hence least reactive species and consequently are the most selective. Isomer selectivity in Friedel-Crafts reactions (qv) has also been shown to rely on steric effects, charge distribution, and relative stability of the quinonoid intermediates (20).

In 1957 a procedure was described that selectively alkylated phenol in the ortho position (21). This approach, using aluminum catalysis, made a variety of 2,6-dialkylphenols accessible. The mechanism proposed for this ortho alkylation is outlined as follows:



(**8**)

(**33**) (**34**)

An aluminum trisphenoxide (**33**) is generated from phenol and aluminum or a trialkyl aluminum. The attraction between the electropositive aluminum and the electron-rich alkene places the latter in close proximity to the ortho position of the phenol yielding (**34**). An unreacted phenol molecule can then displace the ortho alkylated phenol. Using an alkene to phenol ratio of 2:1 yields proportionately more 2,6-dialkylphenol. The schematic representation of this reaction is a gross simplification. Some intermolecular alkylation does not take place. The aluminum catalyzed synthesis of 2,6-dialkylphenols generates several isomeric products, albeit in low yields. This procedure works well for making dialkylphenols from alkenes containing up to six carbon atoms. Thereafter, the nonpolar nature of the products and intermediates causes the aluminum trisphenoxide to fall out of solution. Given the bulkiness of the aluminum complex (**34**), terminal alkenes react more readily than internal alkenes. The use of forcing conditions with internal alkenes presents its own set of problems. At high temperatures the aluminum phenoxide produces a polymeric aluminum species accompanied by the formation of phenyl ethers (22).

The alkylation of phenol with an alkene using either acid or aluminum catalysis probably accounts for 95% of the commercially produced alkylphenols with alkyl groups of three carbons or larger. The alkenes are commercially available and environmentally kind. They do not produce by-products as do alkylations which use alcohols or alkyl halides. Together with an acid catalyst and the appropriate amount of phenol, mono-, di-, and trialkylphenols can be produced.

Several methods are available to supplement the phenol alkylations described above. Primary alkylphenols can be produced using the more traditional Friedel-Crafts reaction. Thus an *n*-butylphenol can be synthesized directly from a butyl halide, phenol, and mild Lewis acid catalyst. Alternatively, butyryl chloride can be used to acylate phenol producing a butyrophenone. Reduction with hydrazine (a Wolff-Kishner reduction) generates butylphenol.

5.2. Reactors. Reactors used to produce alkylphenols are simple batch reactors, complex batch reactors, and continuous reactors. All of these reactors have good mixing and heat removal capability. Good mixing is required for contacting the alkene and catalyst with the phenol. Typically, alkene–alkene reactions compete with phenol–alkene reactions at operating conditions. Good mixing minimizes locally high alkene concentrations and thus favors the desired reactions relative to the undesired ones. Good heat removal capability is needed to maintain controlled temperatures because of the highly exothermic nature of these reactions. The selectivity of alkylation is greatly affected by temperature (23).

The simple batch reactor generally consists of a cooled, agitated mixing tank. Figure 1 shows one type of simple batch reactor arrangement. There are four basic operating steps for this type of reactor in alkylphenol service: (*1*) the phenol is loaded; (*2*) the catalyst is loaded; (This step may be avoided if an appropriate heterogeneous catalyst is available.) (*3*) the alkene is loaded at such a rate that the reactor's heat removal capability is not exceeded and the desired reaction temperature is maintained; and (*4*) the alkylate is removed. This final step is trivial if a homogeneous catalyst is used, but it may require special equipment design if a heterogeneous catalyst is used.

The relatively low capital cost of the simple batch reactor is its most enticing feature. The inability to operate under pressure typically limits the simple batch reactor to use with the higher alkenes; ie, octenes, nonenes, and dodecenes.

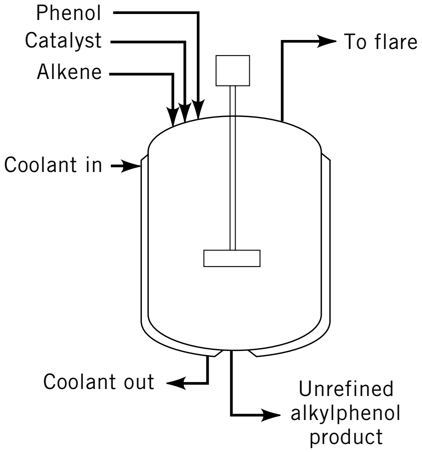


Fig. 1. Flow sheet of simple batch reactor.

For mainly economic reasons, these reactors are usually run at phenol to alkene mole ratios of between 0.9 and 1.1 to 1.

The complex batch reactor is a specialized pressure vessel with excellent heat transfer and gas liquid contacting capability. These reactors are becoming more common in alkylphenol production, mainly due to their high efficiency and flexibility of operation. Figure 2 shows one arrangement for a complex batch reactor. Complex batch reactors produce the more difficult to make alkylphenols; they also produce some conventional alkylphenols through improved processes.

The same four operating steps are used with the complex batch reactor as with the simple batch reactor. The powerful capabilities of the complex batch reactor offset their relatively high capital cost. These reactors can operate at phenol to alkene mole ratios from 0.3 to 1 and up. This ability is achieved by designing for positive pressure operation, typically 200 to 2000 kPa (30 to 300 psig), and

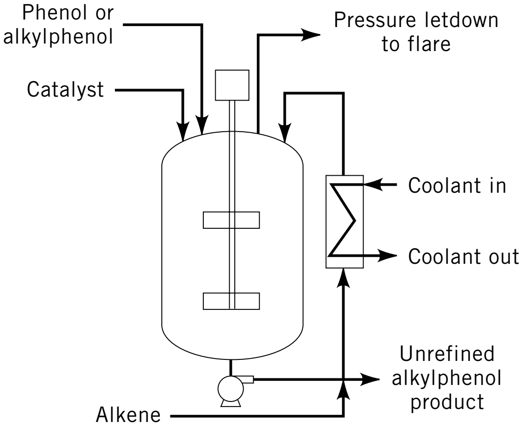


Fig. 2. Flow sheet of complex batch reactor.

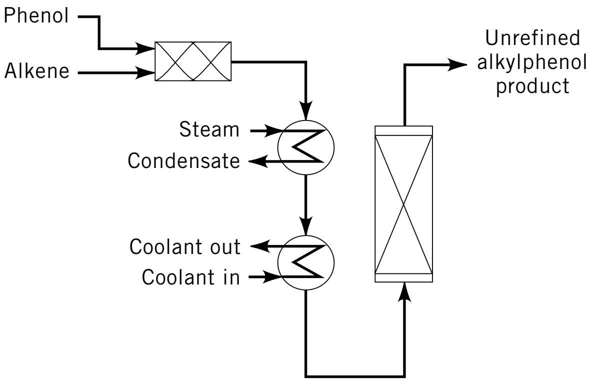


Fig. 3. Flow sheet of continuous reactor.

for the use of highly selective catalysts. Because these reactors can operate at low phenol to alkene mole ratios, they are ideal for production of di- and trialkylphenols.

Among continuous reactors, the dominant system used to produce parasubstituted alkylphenols is a fixed-bed reactor holding a solid acid catalyst. Figure 3 shows an example of this type of reactor. The phenol and alkene are premixed and heated or cooled to the desired feed temperature. This mix is fed to the reactor where it contacts the porous solid, acid-impregnated catalyst. A key design consideration for this type of reactor is the removal of the heat of reaction.

Phenol and alkenes react quite exothermically. The reaction between 1 mole of phenol and 1 mole of isobutylene to yield 1 mole of *p-tert*-butylphenol PTBP liberates approximately 79.8 kJ/mol (19.1 kcal/mol) (24). In an adiabatic system, this reaction, if started at 40°C, would result in a reaction product at about 250°C. Temperatures above 200°C are considered unacceptably high in the reactor so design measures are employed to keep the temperature down.

The most common approach to maintaining the desired reaction temperature is to operate with a significant excess of phenol in the reactor. An adiabatic reactor fed with 2 moles of phenol and 1 mole of isobutylene at 40°C would reach about 180°C if all the isobutylene formed PTBP. The selectivity towards the desired monoalkylphenol product almost always improves as the phenol to alkene mole ratio increases. These gains must be weighed against the higher costs associated with higher mole ratio operation. Both the capital cost and the operating costs increase as the mole ratio is increased, since larger equipment that consumes more energy is needed to separate the excess phenol from the unrefined alkylphenol stream.

5.3. Purification. The method used to recover the desired alkylphenol product from the reactor output is highly dependent on the downstream use of the product and the physical properties of the alkylphenol. The downstream uses vary enormously; some require no refining of the alkylphenol feedstock; others require very high purity materials. Physical property differences affect both the basic type of process used for recovery and the operating conditions used within that process.

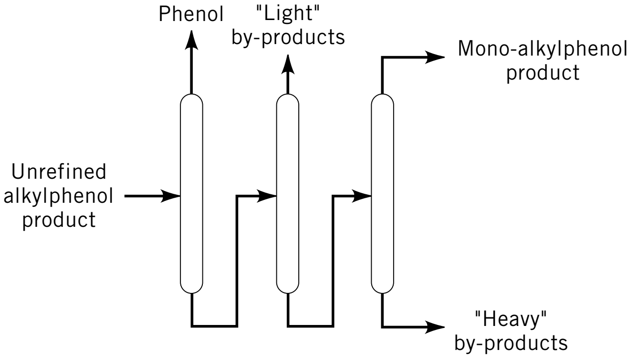


Fig. 4. Monoalkylphenol distillation train.

Some alkylphenol applications can tolerate "as is" reactor products, most significantly in the production of alkylphenol–formaldehyde resins. These resins can tolerate some of the reactant and by-product from the alkylphenol reactor because they undergo purification steps. This resin production route has both capital and operating cost advantages over using purer alkylphenol streams as feedstock. For these savings, the resin producer must operate the process in such a way as to tolerate a more widely varying feedstock and assume the burden of waste disposal of some unreactive materials from the alkylphenol process.

Most alkylphenols sold today require refinement. Distillation is by far the most common separation route. Multiple distillation tower separations are used to recover over 80% of the alkylphenol products in North America. Figure 4 shows a basic alkylphenol distillation train. Excess phenol is removed from the unrefined alkylphenol stream in the first tower. The by-products, which are less volatile than phenol but more volatile than the product, are removed in the second tower. The product comes off the third tower overhead while the heavy by-products come out the bottom.

The design of these distillation systems and the operating conditions used depend on the physical properties of the alkylphenols involved and on the product requirements. Essentially all alkylphenol distillation systems operate under vacuum, but the actual pressures maintained vary considerably. Vacuum operation allows reasonable reboiler temperatures (200–350°C) so that thermal dealkylation reactions of the alkylphenols are slow.

Some alkylphenols in commercial production have low vapor pressures and/or low thermal decomposition temperatures. For these products, the economics of distillation are poor and other recovery processes are used. Crystallization from a solvent is the most common nondistillation method for the purification of these alkylphenols.

6. Shipment

Most commercially important alkylphenol production is of three types, unrefined alkylphenols, monoalkylphenols, and dialkylphenols. Together, these processes comprise over 95% of all alkylphenol production in the United States. The boundaries between types of production are not rigid; and some commercially important production is through a combination of these processes.

Unrefined alkylphenols are generally produced in the simple batch reactors described earlier. An alkene with between 8 and 12 carbon atoms reacts with phenol to produce a mixture of reactants, monoalkylphenols, and dialkylphenols. These mixtures usually do not freeze above 25°C and so are liquid at production and storage conditions. The product is generally used in the same factory or complex in which it is produced so shipment typically consists of pumping the material from the reactor to a storage tank.

Monoalkylphenols are generally produced in specialized plants that have both continuous reactors and continuous vacuum distillation trains. Alkenes with between 4 and 24 carbon atoms react with phenol to produce an unrefined phenol–alkylphenol mixture. This mixture is fed to the distillation train where the phenol is removed for recycle and the product is isolated. The product is then stored in heated tanks made of stainless steel or phenolic resin lined carbon steel. These tanks are blanketed with inert gas to avoid product discoloration associated with oxidation.

Large volumes of monoalkylphenols are shipped in liquid form by railcar, tank wagon, or export container. These shipping vessels must be stainless steel or phenolic resin lined carbon steel. For smaller volumes, drums and tote-tanks are used. For high freezing point alkylphenols, such as PTBP, the product is flaked and shipped in either bags or supersacs. For low freezing point products, such as *p*-nonylphenol (PNP) (fp $< 20°C$), the product is shipped in drums or tote-tanks.

Dialkylphenols are also produced in specialized plants. These plants combine complex batch reactors with vacuum distillation trains or other recovery systems. Alkenes with carbon numbers between 4 and 9 react with phenol to make an unrefined alkylphenol mixture, which is fed into the recovery section where very high purity product is isolated. The product is stored, handled, and shipped just as are the monoalkylphenols.

7. Economic Aspects

Among the key variables in strategic alkylphenol planning are feedstock quality and availability, equipment capability, environmental needs, and product quality. In the past decade, environmental needs have grown enormously in their effect on economic decisions. The manufacturing cost of alkylphenols includes raw-material cost, nonraw-material variable cost, fixed cost, and depreciation.

Raw-material costs are the largest cost items over the lifetime of a plant and typically make up between 40 and 90% of the total manufacturing cost. The placement of plants near production facilities making alkenes and/or phenol is important to producers of alkylphenols. The raw-material costs are so important that a large fluctuation in a raw material price can drive a product from a reasonably profitable situation to a clearly unprofitable one.

Nonraw-material variable costs consist largely of utility costs, but other costs can be significant in this area. For example, operating costs for additional waste treatment are in this category. Nonraw-material variable costs account for 5–20% of the total manufacturing cost of an alkylphenol operation.

Fixed costs include corporate overhead and administration costs as well as those plant-related costs that do not vary with production and contribute 5 to 30% of the total manufacturing cost.

Depreciation costs can drop from as high as 50% of the total manufacturing cost to less than 10% as the plant ages. The effect of the changing depreciation rates is tempered if after-tax analysis is used.

Schenectady International Classes is the leading global supplier of alkylphenols. Plants are located in Rotterdam Junction, N.Y, and Freeport, Texas (25).

8. Health and Safety Factors

As a class of compounds the toxicity of alkylphenols range from moderately toxic (oral rat LD_{50} 50–500 mg/kg) to practically nontoxic (oral rat LD_{50} 5,000–15,000 mg/kg) and most are irritants or corrosive toward skin (Table 2). Sensitization to alkylphenols has been reported. 4-*tert*-Butylphenol is known to cause leucoderma (depigmentation of the skin) in sensitive individuals. In general, precautions should be taken when handling alkylphenols to avoid contact with the skin by wearing appropriate protective gloves, clothing, and a face shield or goggles. Most of the alkylphenols are combustible when heated and emit irritating vapors upon decomposition the Dot label for octyl phenol is 6.1. KEEP AWAY FROM FOOD (27). Alkylphenols should only be stored and handled in well-ventilated areas and appropriate respiration equipment with carbon filters should be worn if PEL or TLV limits are exceeded.

9. Uses and Derivatives of Alkylphenols

Typical physical properties and assays of the commercially most important alkylphenols in terms of worldwide volume were given in Table 1.

9.1. 4-*tert*-Amylphenol.

p-*tert*-Amylphenol (PTAP) or 4-(1,1-dimethylpropyl)phenol is commercially produced by the alkylation of phenol with isoamylene under acidic catalysis. Isoamylene is a mixture of 2-methyl-1-butene and 2-methyl-2-butene, which is produced by dehydration of the corresponding alcohol or backcracking of the corresponding methyl ether. The highest purity isoamylene is available from the backcracking of *tert*-amyl methyl ether (TAME), produced from a C_5 raffinate stream by reaction with methanol under acid catalysis.

The crude product formed from the alkylation of phenol with isoamylene contains principally 2-*tert*-amylphenol, 4-*tert*-amylphenol, and 2,4-di-*tert*-amylphenol. 4-*tert*-Amylphenol is purified to its typical assay of 99+% by fractional distillation. 4-*tert*-Amylphenol [80-46-6] is commercially available as a solid, flaked material packaged in paper or plastic bags (25 kg net weight) or as a molten material in tank wagon or railcar quantities.

4-*tert*-Amylphenol is employed as a germicide in cleaning solutions (28), but it is being replaced by environmentally safer quaternary ammonium salts.

Table 2. **Health and Safety Data**[a]

			Toxicity data				
Name	CAS Registry Number	RTECS NO.[b]	Skin (rabbit)	Oral (rat) LD$_{50}$, mg/kg	Skin (rabbit) LD$_{50}$, mg/kg	Dot skin	Eye (rabbit)
4-*tert*-amylphenol	[80-46-6]	SM6825000	open, 100 μg/24 h	severe, 500 mg	1830	2000	yes
4-*tert*-butylphenol	[98-54-4]	SJ8925000	mild, 500 mg/24 h	severe, 50 μg/24 h	2951	2288	yes
2-*sec*-butylphenol	[89-72-5]	SJ8920000	severe (2 mg/24 h)	severe, 50 μg/24 h	340	5560	yes
4-cumylphenol	[599-64-4]	SL1942450			1770		yes
4-dodecylphenol	[27193-86-8]	SL367500	severe, 8.0–8.0/24 h	moderate, 33.3/110	2140	5000	yes
4-nonylphenol	[84852-15-3]	SM5630000	severe, 10 mg/24 h	severe, 50 μg/24 h	1620	2140	yes
4-*tert*-octylphenol	[140-66-9]	SM9625000	moderate, 20 mg/24 h	severe, 50 μg/24 h	2160		yes
2,4-di-*tert*-amylphenol	[25231-47-4]	SL3500000		moderate, 100 mg	330		yes
2,4-d-*tert*-butylphenol	[96-76-4]	SK8260000			1500		yes
2,6-di-*tert*-butylphenol	[128-39-2]	SK8265000	mild, 0.5 g/24 h	minimal, 100 mg/24 h	>5000		no
2,6-di-*sec*-butylphenol	[5510-99-6]	SK8225000	severe, 500 mg/24 h	severe, 50 μg/24 h	1320		yes
2,4-di-cumylphenol	[2772-45-4]						yes
2-methylphenol	[95-48-7]	G06300000	severe, 524 mg/24 h	severe, 105 mg	121	620	yes
3-methylphenol	[108-39-4]	G06125000	severe, 517 mg/24 h	severe, 103 mg	242	1100	yes
4-methylphenol	[106-44-5]	G06475000	severe, 517 mg/24 h	severe, 103 mg	207	750	yes
2,6-dimethylphenol	[576-26-1]	ZE6125000		severe, 100 mg	296	1000	yes

[a] Ref.26.

[b] RTECS = Registry of Toxic Effects of Chemical Substances.

Another commercial application of 4-*tert*-amylphenol is in phenolic resins (qv) (novolaks and resoles). These resins are used in paints and varnishes and as printing ink resins. The ethoxylated novolaks are used as oil field demulsifiers. Because of the high cost of 4-*tert*-amylphenol, which is related to the high cost of isoamylene, many of the resin applications have been reformulated using 4-*tert*-butylphenol. 4-*tert*-Amylphenol is also used as a vulcanizing agent as the disulfide derivative for the curing of rubber.

9.2. 4-*tert*-Butylphenol. *p*-*tert*-Butylphenol (PTBP) or 4-(1,1-dimethylethyl)phenol is produced from the alkylation of phenol with isobutylene under acid catalysis. Isobutylene [115-11-7] is commercially produced mostly from the dehydration of *tert*-butyl alcohol or from the cracking of methyl *tert*-butyl ether (MTBE). The principal products of this alkylation are 2-*tert*-butylphenol, 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, and minor amounts of 2,4,6-tri-*tert*-butylphenol and 4-*tert*-octylphenol. 4-*tert*-Butylphenol is available in a technical grade which is used in the production of phenolic resins. A high purity grade is available for the production of glycidyl ethers and for the chain termination of polycarbonates. 4-*tert*-Butylphenol [98-54-4] is available as a flaked solid packaged in paper or plastic bags (25 kg net weight), and as a molten material in tankwagon and railcar quantities.

Phenolic resin applications account for 60–70% of all 4-*tert*-butylphenol consumed worldwide. These resins are used in a wide range of applications which include paints, coating resins, and printing inks (29). 4-*tert*-Butylphenol novolak resins react with ethylene oxide to form oil field demulsifiers or are converted into phosphate esters for use as hydraulic fluids and synthetic lubricants. 4-*tert*-Butylphenol resoles react with alkaline-earth metal hydroxides to produce metal resinates. The resinate is combined with a rubber component to give an adhesive. Other uses of 4-*tert*-butylphenol include the chain termination of polycarbonates where its use in the place of phenol gives a polycarbonate with better heat distortion characteristics and improved processability for injection grade material. 4-*tert*-Butylphenol is converted to its corresponding glycidyl ether by the reaction with epichlorohydrin followed by dehydrohalogenation. The glycidyl ether is used as a hardner in epoxy resins (qv). 4-*tert*-Butylphenol can be reduced with hydrogen to a mixture of *cis*-4-tert-butylcyclohexanol and *trans*-4-*tert*-butylcyclohexanol under nickel catalysis. The corresponding acetate derivative is widely used as a perfume in soaps and detergents. The sodium salt of the phosphoric ester of 4-*tert*-butylphenol, sodium bis(4-*tert*-butylphenyl) phosphate, is used as a nucleating agent for polypropylene (30). The use of a nucleator provides a polypropylene with improved thermal properties and increased clarity. 4-*tert*-Butylphenol is used in the production of pesticides such as 2-(4-*tert*-butylphenoxy)cyclohexyl-2-propynyl sulfide [2312-35-8]2-(4-*tert*-Butylphenoxy), which is used on a variety of fruits and vegetables (31).

The consumption of 4-*tert*-butylphenol in the production of phenolic resins represents an application in a mature market and little growth is projected. Its use in end-capping polycarbonates, in the production of glycidyl ethers, and in the production of nucleation agents for polypropylene was expected to grow.

9.3. 2-*sec*-Butylphenol. *o*-*sec*-Butylphenol (OSBP) or 2-(1-methylpropyl) phenol is produced by the alkylation of phenol with butene under aluminum or acid catalysis. The aluminum catalysis route selectively yields 2-*sec*-butylphenol whereas the acid catalysis route yields a 2:1 mixture of 2-*sec*-butylphenol and 4-*sec*-butylphenol. 2-*sec*-Butylphenol [89-72-5] is a liquid available in 55-gal drums (208-L) and in bulk quantities in tank wagons and railcars.

Up until 1986 the major use for 2-*sec*-butylphenol was in the production of the herbicide, 2-*sec*-butyl-4,6-dinitrophenol [88-85-7], which was used as a pre- and postemergent herbicide and as a defoliant for potatoes (32). The EPA banned its use in October 1986 based on a European study which showed that workers who came in contact with 2-*sec*-butyl-4,6-dinitrophenol experienced an abnormally high rate of reproduction problems. France and the Netherlands followed with a ban in 1991. A significant volume of 2-*sec*-butyl-4,6-dinitrophenol is used worldwide as a polymerization inhibitor in the production of styrene where it is added to the reboiler of the styrene distillation tower to prevent the formation of polystyrene (33). OSBP is used in the Far East as the carbamate derivative, 2-*sec*-butylphenyl-*N*-methylcarbamate [3766-81-2] (BPMC) (34). BPMC is an insecticide used against leaf hoppers which affect the rice fields.

Because of environmental concerns about 2-*sec*-butylphenol-based derivatives, the market growth was expected to be negative in the future, with the exception of possible significant growth in the use of the carbamate insecticide.

9.4. 4-Cumylphenol. *p*-Cumylphenol (PCP) or 4-(1-methyl-1-phenylethyl)phenol is produced by the alkylation of phenol with α-methylstyrene under acid catalysis. An inexpensive and selective method has been reported (35). α-Methylstyrene is a by-product from the production of phenol via the cumene oxidation process. The principal by-products from the production of 4-cumylphenol result from the dimerization and intramolecular alkylation of α-methylstyrene to yield substituted indanes. 4-Cumylphenol [599-64-4] is purified by either fractional distillation or crystallization from a suitable solvent. Purification by crystallization results in the easy separation of the substituted indanes from the product and yields a solid material which is packaged in plastic or paper bags (20 kg net weight). Purification of 4-cumylphenol by fractional distillation yields a product which is almost totally free of any dicumylphenol. The molten product resulting from purification by distillation can be flaked to yield a solid form; however, the solid form of 4-cumylphenol sinters severely over time. PCP is best stored and transported as a molten material.

The major use of 4-cumylphenol is as a chain terminator for polycarbonates. Its use in place of phenol gives a polycarbonate with superior properties (36). For a low molecular weight polycarbonate used for injection-molding applications, the use of 4-cumylphenol as a chain terminator significantly lowers the volatility of the resin. Other uses of 4-cumylphenol include the production of phenolic resins, some of which have applications in the electronics industry (37). Another application of 4-cumylphenol involves its reaction with ethylene oxide to form a specialty surfactant.

The growth rate of 4-cumylphenol is expected to parallel the growth rate of polycarbonates, particularly the grades used to produce compact discs.

9.5. 4-Dodecylphenol. *p*-Dodecylphenol (PDDP) may be produced by the reaction of phenol with dodecene under acid catalysis, but commercial 4-dodecylphenol is produced from propylene tetramer. Dodecene differs significantly from the idealized tetramer of propylene because of skeletal rearrangements which occur during the oligomerization process, producing a complex mixture of tri- and tetrasubstituted monoolefins. Although dodecene is purified by fractional distillation, it contains olefins with carbon numbers ranging from C_{10} to C_{14}; the C_{12} content is typically 60–70%. Two grades of 4-dodecylphenol [27193-86-8] are commercially available. A technical grade of 4-dodecylphenol is a nondistilled product and contains approximately 10% 2-dodecylphenol, 85% 4-dodecylphenol, and 5% 2,4-didodecylphenol. A high purity grade is fractionally distilled and contains approximately 5% 2-dodecylphenol, 95% 4-dodecylphenol, and only a trace of 2,4-didodecylphenol. The technical grade of 4-dodecylphenol is amber in color, whereas the high purity grade is colorless. 4-Dodecylphenol is available in 55-gal drums (208-L) and as bulk shipments in tank wagons and railcars.

The major use of technical grade 4-dodecylphenol is in lube oil additives. 4-Dodecylphenol is converted to a calcium phenolate [50910-68-4] and used as a detergent in lubricating oils (38). The phenolate combines with combustion debris to prevent the accumulation of the debris on engine parts and neutralizes the strong acids formed during combustion and oxidation. The reaction product of 4-dodecylphenol with ethylene oxide and propylene oxide is used as a corrosion inhibitor in oil. It coats the inner surfaces of an engine to prevent the corrosion of moving parts. 4-Dodecylphenol is used in the production of a zinc dithiophosphate ester [54261-67-5], which is used as an antioxidant and antiwear additive for high temperature applications (39).

High purity 4-dodecylphenol is used to produce specialty surfactants by its reaction with ethylene oxide. The low color of high purity 4-dodecylphenol is important in this application from a standpoint of aesthetics. 4-Dodecylphenol is also used to produce phenolic resins which are used in adhesive applications and printing inks. 4-Dodecylphenol is also used as an epoxy curing catalyst where the addition of 4-dodecylphenol accelerates curing of the epoxy resin to a hard, nontacky solid.

The worldwide consumption of 4-dodecylphenol is difficult to estimate since the majority of 4-dodecylphenol produced is captively used.

9.6. 2-Methylphenol.

This phenol, commonly known as *o*-cresol, is produced synthetically by the gas phase alkylation of phenol with methanol using modified alumina catalysis or it may be recovered from naturally occurring petroleum streams and coal tars. Most is produced synthetically. Reaction of phenol with methanol using modified zeolite catalysts is a concerted dehydration of the methanol and alkylation of the aromatic ring. 2-Methylphenol [95-48-7] is available in 55-gal drums (208-L) and in bulk quantities in tank wagons and railcars.

The majority of 2-methylphenol is used in the production of novolak phenolic resins. High purity novolaks based on 2-methylphenol are used in photoresist applications (40). Novolaks based on 2-methylphenol are also epoxidized with epichlorohydrin, yielding epoxy resins after dehydrohalogenation, which are used as encapsulating resins in the electronics industry. Other uses of 2-methylphenol include its conversion to a dinitro compound, 4,6-dinitro-2-methylphenol [534-52-1] (DNOC), which is used as a herbicide (41). DNOC is also used to a limited extent as a polymerization inhibitor in the production of styrene, but this use is expected to decline because of concerns about the toxicity of the dinitro derivative.

2-Methylphenol is converted to 6-*tert*-butyl-2-methylphenol [2219-82-1] by alkylation with isobutylene under aluminum catalysis. A number of phenolic anti-oxidants used to stabilize rubber and plastics against thermal oxidative degradation are based on this compound. The condensation of 6-*tert*-butyl-2-methylphenol with formaldehyde yields 4,4′-methylenebis(2-methyl-6-*tert*-butylphenol) [96-65-1], reaction with sulfur dichloride yields 4,4′-thiobis(2-methyl-6-*tert*-butylphenol) [96-66-2], and reaction with methyl acrylate under base catalysis yields the corresponding hydrocinnamate. Transesterification of the hydrocinnamate with triethylene glycol yields triethylene glycol-bis[3-(3-*tert*-butyl-5-methyl-4-hydroxyphenyl)propionate] [36443-68-2] (42). 2-Methylphenol is also a component of cresylic acids, blends of phenol, cresols, and xylenols. Cresylic acids are used as solvents in a number of coating applications. An oxidative hair dye precursor composition containing 5-amino-2- methyl phenol has been reported (43).

9.7. 3-Methylphenol. *m*-Cresol is produced synthetically from toluene. Toluene is chlorinated and the resulting chlorotoluene is hydrolyzed to a mixture of methylphenols. Purification by distillation gives a mixture of 3-methylphenol and 4-methylphenol since they have nearly identical boiling points. Reaction of this mixture with isobutylene under acid catalysis forms 2,6-di-*tert*-butyl-4-methylphenol and 2,4-di-*tert*-butyl-5-methylphenol, which can then be separated by fractional distillation and debutylated to give the corresponding 3- and 4-methylphenols. A mixture of 3- and 4-methylphenols is also derived from petroleum crude and coal tars.

A major use of 3-methylphenol [108-39-4] is in the production of phenolic based antioxidants which are particularly good at stabilizing polymers in contact with copper against thermal oxidative degradation. The alkylation of 3-methylphenol with isobutylene under acid or aluminum catalysis yields 2-*tert*-butyl-5-methylphenol [88-60-8]. Condensation of 2-*tert*-butyl-5-methylphenol with butyraldehyde yields the corresponding 4,4′-butylidenebis(6-*tert*-butyl-3-methylphenol) [85-60-9] which is used in the stabilization of rubber and latex (44). Condensation of 2-*tert*-butyl-5-methylphenol with crotonaldehyde yields a corresponding trisphenol derivative, 1,1,3-tris(5-*tert*-butyl-2-methyl-4-hydroxyphenyl)butane [1843-03-4], which is used to stabilize polymers for high temperature applications (45). The reaction of 2-*tert*-butyl-5-methylphenol with sulfur dichloride yields 4,4′-thiobis(6-*tert*-butyl-3-methylphenol) [96-69-5] which is widely used in curable rubber.

Another significant use of 3-methylphenol is in the production of herbicides and insecticides. 2-*tert*-Butyl-5-methylphenol is converted to the dinitro acetate derivative, 2-*tert*-butyl-5-methyl-4,6-dinitrophenyl acetate [2487-01-6] which is used as both a pre- and postemergent herbicide to control broad leaf weeds (46). Carbamate derivatives of 3-methylphenol based compounds are used as insecticides. The condensation of 3-methylphenol with formaldehyde yields a curable phenolic resin. Since 3-methylphenol is trifunctional with respect to its reaction with formaldehyde, it is possible to form a thermosetting resin by the reaction of a prepolymer with paraformaldehyde or other suitable formaldehyde sources. 3-Methylphenol is also used in the production of fragrances and flavors. It is reduced with hydrogen under nickel catalysis and the corresponding esters are used as synthetic musk.

9.8. 4-Methylphenol. *p*-Cresol is produced synthetically from toluene. Toluene is sulfonated to yield *para*-toluenesulfonic acid, which is then converted to 4-methylphenol via the caustic fusion route. A minor amount of 4-methylphenol is also derived from petroleum crude and coal tars. 4-Methylphenol [106-44-5] is available in 55-gal drums (208-L) and in bulk quantities as a molten material.

The bulk of 4-methylphenol is used in the production of phenolic antioxidants. The alkylation of 4-methylphenol with isobutylene under acid catalysis yields 2-*tert*-butyl-4-methylphenol [2409-55-4] and 2,6-di-*tert*-butyl-4-methylphenol [128-37-0]. The former condenses with formaldehyde under acid catalysis to yield 2,2′-methylene bis(6-*tert*-butyl-4-methylphenol) [119-47-1],which is widely used in the stabilization of natural and synthetic rubber (47). The reaction of 2-*tert*-butyl-4-methylphenol with sulfur dichloride yields 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) [90-66-4]. 2,6-Di-*tert*-butyl-4-methylphenol, which is commonly known as BHT (butylated hydroxy toluene), is a widely used phenolic antioxidant in the stabilization of oils, rubber, and polyolefins (48). BHT is also one of the few *phenolic antioxidants* approved by the FDA as a direct food additive where it is used to retard the oxidation of naturally occurring oils in food.

Other uses of 4-methylphenol include its conversion to a benzotriazole uv stabilizer, 2-(2′-hydroxy-5′-methylphenyl)benzotriazole [2440-22-4] (49). The benzotriazole-based uv stabilizer makes possible the extended use of thermoplastics in outdoor applications. Other minor applications for 4-methylphenol include its use in the production of novolak or resole phenolic resins. It is also used in the production of certain dyes and fragrances.

9.9. 4-Nonylphenol. *p*-Nonylphenol (PNP) is produced by the alkylation of phenol with nonene under acid catalysis. All commercially produced PNP is made from nonene based on the trimerization of propylene. Because of the skeletal rearrangements which occur during the oligomerization of propylene, commercial grade nonene does not have a high percentage of the idealized structure, 4,6-dimethyl-2-heptene. Rather it is a complex mixture of olefins, mostly tri- and tetrasubstituted monoolefins. Nonene is fractionally distilled from other oligomers and contains approximately 90% C_9 olefins; the remaining 10% is C_8 and C_{10} olefins. The two commercial purity grades of 4-nonylphenol are a technical grade which is composed of 10–12% 2-nonylphenol, 85–90% 4-nonylphenol, and up to 5% 2,4-dinonylphenol, and a high purity grade which contains 5% maximum 2-nonylphenol, 95% minimum 4-nonylphenol, and only a trace of 2,4-dinonylphenol. 4-Nonylphenol [84852-15-3] is available in 55-gal drums (280-L) and in bulk quantities in tank wagons and railcars.

The major use for 4-nonylphenol is in the production of nonionic surfactants (10) and constitutes 80% of usage (50). 4-Nonylphenol reacts with ethylene oxide in a mole ratio that varies from 1–40 under base catalysis. 4-Nonylphenol based nonionic surfactants are the largest volume alkylphenol based ethoxylate. The most common nonionic surfactant based on 4-nonylphenol is the nine-mole ethoxylate. Higher mole ratios in the range of 12–15 moles of ethylene oxide per mole of 4-nonylphenol are used as emulsifiers for agrochemicals. Other major applications for alkylphenol ethoxylates are as cleaners of metal surfaces; detergents for car washes, commercial laundries, and the rug cleaning industry; as a dispersant for wood pulp in the production of paper, and as an emulsifier in the production of latex paint (51). 4-Nonylphenol based ethoxylates can be converted to phosphate esters or sulfonated to the corresponding sulfate to yield higher performing surfactants. Phosphate esters of 4-nonylphenol are also reported to be excellent flame retardants (52). Nonylphenol nonionic geminic surfactants are extremely effective in improving detergency (53).

Another significant use of 4-nonylphenol is in the production of tris(4-nonylphenyl) phosphite [3050-88-2] (TNPP) (54), a secondary antioxidant which protects organic materials against oxidative degradation by decomposing hydroperoxides. In this process, the hydroperoxide is converted to the corresponding alcohol and the phosphite is converted to the corresponding phosphate. Phosphites form synergistic mixtures with phenolic-based antioxidants. Tris(4-nonylphenyl) phosphite is widely used in the stabilization of natural and synthetic rubber, vinyl polymers, and polyolefins and styrenics; and it has the distinction of being one of the few commercially available liquid triaryl phosphites. Other uses of 4-nonylphenol include its conversion to barium [41157-58-8] and calcium [100842-25-9] phenolates, which are used as heat stabilizers in poly(vinyl chloride) (55). 4-Nonylphenol also has application as a catalyst in the curing of epoxy resins (56,57). Hydrogen bonding of the acidic proton on the hydroxyl group of 4-nonylphenol with the oxygen of the oxirane ring may assist in the opening of the epoxide.

The worldwide consumption of 4-nonylphenol is somewhat difficult to ascertain because of the captive consumption by some producers. Future growth in the consumption of 4-nonylphenol is predicted to be at the rate of 2%, but some market share in surfactants has been lost to the linear alcohol surfactants because of environmental concerns over aquatic toxicity and biodegradability of alkylphenol based ethoxylates (50). The use of alkylphenol ethoxylates was banned in Switzerland in 1986 and Germany is undergoing a voluntary phase out by the early 1990s. An industry group of 4-nonylphenol producers and surfactant producers is currently operating under a consent order from EPA to carry out a wide range study on the biodegradability of 4-nonylphenol-based ethoxylates and toxicity studies on aquatic life forms of the resulting break-down products. Early results from testing of sediments from river beds and waste plant sludge show that nonylphenol-based ethoxylates are readily biodegraded and the residual level of 4-nonylphenol is very low. Tests on endocrine interference potential are incouraging, but research continues (50).

The use of 4-nonylphenol in the production of tris(4-nonylphenyl) phosphite is also not expected to show much growth because of its replacement in many polymers by higher performing and more hydrolytically stable phosphites.

9.10. 4-*tert*-Octylphenol. *p-tert*-Octylphenol (PTOP) or 4-(1,1,3,3-tetramethylbutyl)phenol is produced by the alkylation of phenol with diisobutylene under acid catalysis. Diisobutylene is a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. A small amount of skeletal rearrangement during alkylation leads to a second 4-*tert*-octylphenol isomer which has the proposed structure of 1,1,2,3-tetramethylbutyl as the alkyl radical. The crude alkylation product typically contains 4-*tert*-butylphenol (from the backcracking of the diisobutylene), 2-*tert*-octylphenol, 4-*tert*-octylphenol, butyloctylphenol, and 2,4-dioctylphenol. 4-*tert*-Octylphenol is purified by fractional distillation under reduced pressure; it is available as a technical grade which contains 5–8% 2-*tert*-octylphenol, 90–95% 4-*tert*-octylphenol, and 1–2% butyloctylphenol. A high purity grade is also available which contains less than 2% 2-*tert*-octylphenol, 98–99% 4-*tert*-octylphenol, and only a trace of higher boiling alkylphenols. 4-*tert*-Octylphenol [140-66-9] is packaged as a flaked solid in paper or plastic bags (25 kg net weight) or as a molten product for bulk shipments in tank wagons and railcars.

4-*tert*-Octylphenol reacts with ethylene oxide under base catalysis and the resulting ethoxylates are used in many of the same applications as the 4-nonylphenol-based surfactants. A major use area for ethoxylates based on 4-*tert*-octylphenol is as a surfactant in the emulsion polymerization of acrylic and vinyl monomers (58). The 4-*tert*-octylphenol ethoxylate aids in the dispersion of the monomers in the aqueous medium and stabilizes the latex formed as a result of polymerization.

Another important application for 4-*tert*-octylphenol is in the production of phenolic resins. Novolak resins based on 4-*tert*-octylphenol are widely used in the tire industry as tackifiers. The tackiness of these resins binds the many parts of an automobile tire prior to final vulcanization. A specialty use for novolak resins based on 4-*tert*-octylphenol is the production of a zincated resin, which is formulated as a dispersion in water and coated onto paper in combination with encapsulated leuco dyes to yield carbonless copy paper (see MICROENCAPSULATION). Pressure from writing bursts the encapsulated leuco dye, which is converted from its colorless form to its colored form by the *zincated resin* (59). Novolak resins based on 4-*tert*-octylphenol are also used in the production of specialty printing inks.

Resoles based on 4-*tert*-octylphenol react with alkaline-earth metal hydroxides to yield metal resinates. The resinate is combined with natural or synthetic rubber to produce an adhesive. The 4-*tert*-octylphenol-based resin gives the adhesive its initial tack which holds the two surfaces undergoing bonding together while the other components of the adhesive undergo final curing.

Other applications for 4-*tert*-octylphenol include chain termination of polycarbonates (60). The properties of low molecular weight polycarbonates used in injection-molding applications to form compact disks are enhanced when the polymer is terminated using 4-*tert*-octylphenol.

Another use of 4-*tert*-octylphenol is in the production of uv stabilizers. 4-*tert*-Octylphenol reacts with sulfur dichloride to yield the thio-bisphenol derivative, which then reacts with nickel acetate to form 2,2′-thiobis(4-*tert*-octylphenolate)-*N*-butylamine nickel [14516-71-3]. This type of stabilizer is widely used in the production of outdoor carpeting based on polypropylene fibers. Nickel compounds give a green discoloration which limits their applications. A second class of uv stabilizers based on the benzotriazole structure. 2-(2′-hydroxy-5′-*tert*-octylphenyl)benzotriazole [3147-75-9] is produced from 4-*tert*-octylphenol (61).

It is difficult to estimate the world consumption of 4-*tert*-octylphenol because a significant volume is captively consumed as a crude alkylphenol by producers of phenolic resins. The overall growth rate of 4-*tert*-octylphenol is expected to track the growth in the GNP. As with 4-nonylphenol-based surfactant, the surfactants based on 4-*tert*-octylphenol have also lost market share to the linear alcohol ethoxylates because of concerns over biodegradability and product aquatic toxicity. The use of 4-*tert*-octylphenol in the production of phenolic resins is a mature market and little growth is forecasted. However, the use of 4-*tert*-octylphenol in the chain termination of polycarbonates and in the production of uv stabilizers is expected to have an above average growth rate.

9.11. Dialkylated Phenols. *2,4-Di-tert-amylphenol (2,4-DTAP)* or 2,4-bis(1,1-dimethylpropyl)phenol is produced by the alkylation of phenol with isoamylene under acid catalysis in a mole ratio of 2:1 (isoamylene to phenol). The crude alkylation product contains 4-*tert*-amylphenol, 2,4-di-*tert*-amylphenol, and 2,4,6-tri-*tert*-amylphenol. The 2,4-di-*tert*-amylphenol is purified via fractional distillation under reduced pressure. 2,4-Di-*tert*-amylphenol [25231-47-4] is available in 55-gal drums (208-L) and bulk quantities in tank wagon and railcar shipments.

A major use for 2,4-di-*tert*-amylphenol is in the production of uv stabilizers; the principal one is a benzotriazole-based uv absorber, 2-(2′-hydroxy-3′,5′-di-*tert*-amylphenyl)-5-chlorobenzotriazole [25973-55-1], which is widely used in polyolefin films, outdoor furniture, and clear coat automotive finishes (62). Another significant use for 2,4-di-*tert*-amylphenol is in the photographic industry. A number of phenoxyacetic acid derivatives of 2,4-di-*tert*-amylphenol are used as developing agents in color photography (qv) (63). Other uses include its reaction with ethylene oxide under base catalysis to form a specialty surfactant used to treat cotton fibers to prevent the redeposition of dirt onto the fibers during the production of cotton-based fabric. A phenoxy poly(ethylene oxide) based on 2,4-di-*tert*-amylphenol also has an application as a fuel additive where it is used as a corrosion inhibitor.

The growth rate for 2,4-di-*tert*-amylphenol is predicted to be above GNP growth rate, mainly driven by the use of the benzotriazole derivative as a uv stabilizer for clear-coat applications in auto finishes.

2,4-Di-tert-butylphenol (2,4-DTBP) or 2,4-bis(1,1-dimethylethyl)phenol is produced by the alkylation of phenol with isobutylene under acid catalysis using a mole ratio of 2:1 (isobutylene to phenol). The crude product contains 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, and 2,4,6-tri-*tert*-butylphenol. The 2,4-*tert*-butylphenol is purified by fractional distillation under reduced pressure. 2,4-Di-*tert*-butylphenol [96-76-4] is available in 55-gal drums (208-L) and in bulk as a molten material.

The primary use for 2,4-di-*tert*-butylphenol is in the production of substituted triaryl phosphites. 2,4-Di-*tert*-butylphenol reacts with phosphorus trichloride typically using a trialkylamine or quaternary ammonium salt as the catalyst. Hydrogen chloride is formed and either complexed with the amine or liberated as free hydrogen chloride gas forming the phosphite ester, tris(2,4-di-*tert*-butylphenyl)phosphite [31570-04-4] (64). The phosphite-based on 2,4-di-*tert*-butylphenol is a solid and very hydrolytically stable. Because of this hydrolytic stability it has replaced the use of tris(4-nonylphenyl) phosphite and other less stable phosphites in polyolefins and engineering resins. Another secondary antioxidant based on 2,4-di-*tert*-butylphenol is the diphosphite derived from pentaerythritol, bis(2,4-di-*tert*-butylphenyl)pentaerythrityl diphosphite [26741-53-7] (65). It too is widely used in polyolefins, and in engineering resins where high performance is required. 2,4-Di-*tert*-butylphenol is also used in the production of a benzotriazole-based uv stabilizer, 2-(2′-hydroxy-3′,5′-di-*tert*-butylphenyl)-5-

chlorobenzotriazole [3864-99-1]. Another uv stabilizer is the phenyl ester based on the carboxylic acid of 2,6-di-*tert*-butylphenol, 2,4-di-*tert*-butylphenyl 3′,5′-di-*tert*-butyl-4′-hydroxybenzoate [4221-80-1] (66). 2,4-Di-*tert*-butylphenol condenses with acetaldehyde under acid catalysis to produce a phenolic-based primary antioxidant, 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) [35958-30-6] which is used in the stabilization of polyolefins, styrenics, synthetic and natural rubber against thermal oxidative degradation.

The growth rate for 2,4-di-*tert*-butylphenol is estimated to be above average as the market share for high performance phosphites increase. *2,6-Di-tert-butylphenol (2,6-DTBP)* or 2,6-bis(1,1-dimethylethyl)phenol is produced from phenol by alkylation with isobutylene under aluminum catalysis. The crude alkylated phenol contains 2-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, and 2,4,6-tri-*tert*-butylphenol. Pure 2,6-di-*tert*-butylphenol is produced by vacuum fractional distillation. Aluminum trisphenoxide is very selective in the formation of 2,6-di-*tert*-butylphenol and yields in excess of 80% are possible. 2,6-Di-*tert*-butylphenol [128-39-2] is packaged in 55-gal drums (208-L) and sold as a molten material in bulk quantity shipments in tank wagons and railcars.

The principal use for 2,6-di-*tert*-butylphenol is in the production of hindered phenolic antioxidants and this application accounts for 80–90% of all of this compound produced. Reaction of 2,6-DTBP with formaldehyde under base catalysis forms the methylene bisphenolic, 4,4′-methylenebis(2,6-di-*tert*-butylphenol) [118-82-1] which is used as a primary antioxidant in the stabilization of greases (67). In an excess of formaldehyde the hydroxymethyl compound is obtained. This hydroxymethyl derivative condenses with trimethylbenzene on a 3:1 mole ratio to yield 1,3,5-trimethyl-2,4,6,-tris(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)benzene [1709-70-2], which is widely used in the stabilization of polypropylene, particularly polypropylene fibers (68).

A large number of hindered phenolic antioxidants are based on the Michael addition of 2,6-di-*tert*-butylphenol and methyl acrylate under basic catalysis to yield the hydrocinnamate which is a basic building block used in the production of octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, [2082-79-3], tetrakis(methylene-3(3,5-di-*tert*-butyl-4-hydroxylphenyl)propionate)methane [6683-19-8], and many others (69,70). These hindered phenolic antioxidants are the most widely used primary stabilizers in the world and are used in polyolefins, synthetic and natural rubber, styrenics, vinyl polymers, and engineering resins. 2,6-Di-*tert*-butylphenol is converted to a methylene isocyanate which is trimerized to a triazine derivative 1,3,5-tris(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)isocyanurate [27676-62-6]; this molecule has a special application in the protection of articles made from polypropylene fibers, such as surgical gowns, that are sterilized by ionizing radiation (71). Other uses for 2,6-di-*tert*-butylphenol include the production of a diisopropylidene sulfide derivative which is a cholesterol-lowering drug. Another sulfur derivative is useful as an antiinflammatory agent (72). 2,6-Di-*tert*-butylphenol is also used in the production of 4,4′-biphenol [92-88-6] which is used as a replacement for bisphenol-A in the production of liquid crystal polyesters, polysulfones, and polyetherimides. In these applications biphenol imparts an increased rigidity and higher heat distortion temperature to the polymer. Pure 2,6-di-*tert*-butylphenol is used as is as an antioxidant in oils and greases and the crude alkylate from the alkylation of phenol with isobutylene is commonly used in gasoline, diesel fuels, and jet fuels (73).

With the growth in thermoplastic materials replacing more traditional materials such as glass, wood, paper, and metal, the growth rate for 2,6-di-*tert*-butylphenol is estimated to be above average.

Di-sec-butylphenol (DSBP) is produced by the alkylation of phenol with 1-butene or 2-butene under acidic or aluminum catalysis. The production of di-*sec*-butylphenol under acid catalysis gives a 2 to 1 mixture of 2,4-di-*sec*-butylphenol and 2,6-di-*sec*-butylphenol [2,4-bis(1-methylpropyl)phenol and 2,6-bis(1-methylpropyl)phenol]. Under aluminum catalysis 2,6-di-*sec*-butylphenol is produced in greater than 90% yield. Di-*sec*-butylphenol [31291-60-8] is available in 55-gal drums (208-L) and in bulk shipments in tank wagons and railcars.

The only significant use for di-*sec*-butylphenol is a specialty nonionic surfactant produced by reaction with ethylene oxide under base catalysis. This surfactant is registered with EPA for use in emulsifying agrochemicals.

2,4-Dicumylphenol (2,4-DCP) or 2,4-bis(1-methyl-1-phenylethyl)phenol is produced by the alkylation of phenol with α-methylstyrene under acidic catalysis. The crude alkylation product contains 4-cumylphenol, 2,4-dicumylphenol, and 2,4,6-tricumylphenol along with some olefin oligomers. Pure 2,4-dicumylphenol can be obtained either by vacuum fractional distillation or crystallization from a suitable solvent. 2,4-Dicumylphenol [2772-45-4] is packaged in 55-gal drums (208-L) and sold as a bulk material in molten form.

The largest use for 2,4-dicumylphenol is in a production of a uv stabilizer of the benzotriazole class, 2-(2′-hydroxy-3′,5′-dicumylphenyl)benzotriazole [70321-86-7] which is used in engineering thermoplastics where high molding temperatures are encountered (74). The high molecular weight of 2,4-dicumylphenol makes this uv stabilizer the highest molecular weight benzotriazole based uv stabilizer in commercial production.

2,6-Dimethylphenol (2,6-xylenol) is produced by the gas phase alkylation of phenol with methanol using modified alumina catalysis. The crude product contains 2-methylphenol, 2,6-dimethylphenol, a minor amount of 2,4-dimethylphenol, and a mixture of trimethylphenols. The 2,6-dimethylphenol is purified by fractional distillation. The mixture of di- and trimethylphenols is sold as cresylic acid for use as a solvent. 2,6-Dimethylphenol [576-26-1] is available in 55-gal drums (208-L) and in bulk shipments in tank wagons and railcars.

The oxidative coupling of 2,6-dimethylphenol to yield poly(phenylene oxide) represents 90–95% of the consumption of 2,6-dimethylphenol (75). The oxidation with air is catalyzed by a copper–amine complex. The poly(phenylene oxide) derived from 2,6-dimethylphenol is blended with other polymers, primarily high impact polystyrene, and the resulting alloy is widely used in housings for business machines, electronic equipment and in the manufacture of automobiles (see POLYETHERS, AROMATIC). A minor use of 2,6-dimethylphenol involves its oxidative coupling to 3,3′,5,5′-tetramethyl-4,4′-biphenol [2417-40-1] (76). Tetramethylbiphenol is used as a monomer in the production of specialty polycarbonates and reacts with epichlorohydrin to produce an epoxy resin.

The worldwide consumption of 2,6-dimethylphenol is difficult to estimate accurately because the majority is captively consumed. Growth rate for

2,6-dimethylphenol is directly related to the growth of engineering resins, which is generally predicted to be above average.

BIBLIOGRAPHY

"Alkylphenols" in *ECT* 2nd ed., Vol. 1, pp. 901–906, by R. W. G. Preston and H. W. B. Reed, Imperial Chemical Industries Limited; Supplement, pp. 27–31, by Gerd Leston, Koppers Company; "Alkylphenols" in *ECT* 3rd ed. Vol. 2, pp. 72–96, by H. W. B. Reed, Imperial Chemical Industries Limited; in *ECT* 4th ed., Vol. 2, pp. 113–143 by John F. Lorenc, Gregory Lambeth, and William Scheffer, Schenectady Chemicals Inc.

CITED PUBLICATIONS

1. *CAS Index Guide*, Chemical Abstract Service, Columbus, Ohio, 1982, Appendix 4.
2. Z. Rappoport, *Handbook of Tables for Organic Compound Identification*, 3rd ed., The Chemical Rubber Co., Cleveland, Ohio, 1967, p. 434.
3. R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. C. Morrill, *The Systematic Identification of Organic Compounds*, 6th ed., John Wiley & Sons, Inc., New York, 1980, p. 102.
4. C. J. Pouchert, ed., *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Company, Inc., Milwaukee, Wis., 1981.
5. *SURFONIC N-Series Surface Active Agents*, Technical Product Bulletin, Texaco Chemical Company, Houston, Tex., 1987.
6. A. S. Lindsey and H. Jeskey, *Chem. Rev.* **57**, 583–620 (1957).
7. C. D. Gutsche in J. F. Stoddart, ed., *Monographs in Supramolecular Chemistry, Calixarenes*, Royal Society of Chemistry, Cambridge, England, 1989.
8. *Ethyl 702, Technical Bulletin*, Ethyl Corporation, Baton Rouge, La.
9. U.S. Pat. 4,222,883 (Sept. 16, 1980), E. Clinton (to Ethyl Corporation).
10. P. R. Dean, *Index of Commercial Antioxidants and Antiozonants*, Technical Bulletin, Goodyear Chemicals, Akron, Ohio, 1983.
11. Fr. Pat. 1,343,301 (Nov. 15, 1963), E. A. Meier and M. Dexter (to J. R. Geigy A-G).
12. U.S. Pat. 3,330,859 (July 11, 1967), M. Dexter, J. D. Spivack, and D. H. Steinberg (to Geigy Chemical Corporation).
13. U.S. Pat. 3,644,482 (Feb. 22, 1972), M. Dexter, J. D. Spivack, and D. H. Steinberg (to CIBA-GEIGY Corporation).
14. U.S. Pat. 3,678,047 (July 18, 1972), G. Kletecka and P. D. Smith (to B. F. Goodrich Company).
15. U.S. Pat. 4,226,763 (Oct. 7, 1980), M. Dexter and R. A. E. Winter (to CIBA-GEIGY Corporation).
16. J. W. Chien, W. P. Connor, *J. Am. Chem. Soc.* **90**, 1001 (1968); D. J. Harper, J. F. McKellar, and P. H. Turner, *J. Appl. Polym. Sci.* **18**, 2805 (1974); N. S. Allen, J. Homer, and J. F. McKellar, *Macromol. Chem.* **179**, 1575 (1978).
17. U.S. Pat. 2,971,968 (Feb. 14, 1961), A. M. Nicholson and B. Zurensky (to Ferro Corporation); U.S. Pat. 2,971,941 (Feb. 14, 1961), S. B. Elliott, C. H. Furchman, and A. M. Nicholson (to Ferro Corporation).
18. U.S. Pat. 4,447,656 (May 8, 1984), L. D. Kershner, L. R. Thompson, and R. M. Strom (to Dow Chemical Company); U.S. Pat. 4,205,187 (May 27, 1980), J. N. Cardenes and W. T. Reichle (to Union Carbide Corporation).

19. J. March, *Advanced Organic Chemistry Reactions, Mechanisms, and Structure*, 3rd ed., John Wiley & Sons, Inc., New York, 1985, p. 448.
20. *Ibid*, p. 463; S. H. Patinkin and B. S. Friedman in G. A. Olah, ed., *Friedel-Crafts and Related Reactions*, Vol. 2, Wiley-Interscience, New York, 1964, p. 7.
21. A. J. Kolka and co-workers, *J. Org. Chem.* **22**, 642 (1957).
22. U.S. Pat. 4,360,699 (Nov. 23, 1982). W. E. Wright (to Ethyl Corp.).
23. C. B. Campbell, A. Onopchenko, and D. C. Young, *Ind. Eng. Chem. Res.* **29**, 642–647 (1990).
24. W. A. Pardee and W. Weinrich, *Ind. Eng. Chem.* 36, Vol. 7, 602 (1944).
25. B. Schmeth, *Chem. Week* (Jan 2, 2002).
26. *Registry of Toxic Effects of Chemical Substances*, National Institute for Occupational Safety and Health, Cincinnati, Ohio, July 1990.
27. R. J. Lewis, Sr., *Sax's Properties of Industrial Materials*, 10th ed.,Vols. 2 and 3, John Wiley & Sons, Inc., New York, 2000.
28. *Pentaphen, Technical Bulletin*, Pennwalt Chemicals, Philadelphia, Pa., March 1981.
29. Jpn. Pat. 62,050,186 (March 4, 1987), K. Ogawa (to Matsushita Electric Industrial Company).
30. U.S. Pat. 4,258,142 (Mar. 24, 1981), M. H. Fisch, S. S. Ahluwalia, and B. A. Hegranes (to Witco Corporation).
31. Neth. Pat. Appl. 6,406,854 (Jan. 19, 1965) (to United States Rubber Company).
32. U.S. Pat. 3,694,513 (Sept. 26, 1972), S. W. Tobey and M. Z. Lourandos (to The Dow Chemical Company).
33. D.E. Pat. 3,539,776 (May 21, 1987), D. Lansberg, M. Lieb, H. Moeckel, and H. Uho (to BASF A.G.).
34. D.E. Pat. 2,545,389 (April 29, 1976), I. Yamamoto, Y. Takahashi, and N. Kyomura (to Mitsubishi Chemical Industries Company).
35. U. S. Pat. 6, 448,453 (Sept. 10, 2002), J. Oberholtzer and co-workers (to General Electric Company).
36. Eur. Pat. 305,214 (Mar. 1, 1989), M. Okamoto (to Idemitsu Petrochemical Company).
37. U.S. Pat. 4,837,086 (June 6, 1989), T. K. Hiroshi, M. H. Naohiro, and T. S. Shir (to Hitachi Chemical Company).
38. U.S. Pat. 3,761,414 (Sept. 25, 1973), H. Hangen and H. Chafetz (to Texaco, Inc.).
39. U.S. Pat. 4,089,791 (May 16, 1978), H. Hangen and D. G. Weetman (to Texaco, Inc.).
40. E.P. Pat. 204,659 (Dec. 10, 1986), C. E. Monnico and S. A. C. Sheik (to CIBA-GEIGY A.G.).
41. U.S. Pat. 3,737,480 (June 5, 1973), E. E. Stahly and E. W. Lard (to W. R. Grace Company).
42. Jpn. Pat. 62,053,942 (Mar. 9, 1987), M. Sasaki and co-workers (to Sumitomo Chemical Company, Ltd.).
43. U.S. Pat. 6,554,871 (April 29, 2003) H. J. Braun (to Wella A6).
44. U.S. Pat. 3,170,893 (Feb. 23, 1965), S. Steinguseo and I. D. Salyer(to Monsanto Company).
45. Brit. Pat. 951,935 (Mar. 11, 1964), D. Ranson (to Imperial Chemical Industries Ltd.).
46. U.S. Pat. 3,679,736 (July 25, 1972), I. C. Popuff and K. I. H. Williams (to Pennwalt Corporation).
47. U.S. Pat. 2,762,787 (Sept. 11, 1956), I. Goodman and A. Lambert (to Imperial Chemical Industries, Ltd.).
48. U.S. Pat. 4,433,181 (Feb. 21, 1984), S. N. Holter (to Koppers Company, Inc.).
49. D.E. Pat. 2,621,006 (Dec. 2, 1976), C. E. Ziegler and H. J. Peterli (to CIBA-GEIGY A.G.).
50. "Nonylphenol, Chemical Profile, "*Chemical Market Reporter* (July 2, 2001).

51. D.E. Pat. 270,726 (Aug. 9, 1989), A. Kirchhof and A. Strauch (to Veb Galvanotechnik Leipzig).
52. Eur. Pat. 324,716 (July 19, 1989), B. Holt (to CIBA-GEIGY Corp.).
53. U.S. Pat. 5,900,397 (May 4, 1999), D. J. Tracy and R. Li (Rhodes, Inc.).
54. U.S. Pat. 2,220,845 (Nov. 5, 1940), C. L. Moylet to The Dow Chemical Company).
55. B.R. Pat. 7,803,418 (May 8, 1979), J. M. Bohen (to Pennwalt Corporation).
56. U.S. Pat. 4,668,757 (May 26, 1987), G. Nichols.
57. U.S. Pat. 4,828,879 (July 30, 1987), K. B. Sellstrom and H. G. Waddill (to Texaco, Inc.).
58. Jpn. Pat. 01,138,275 (May 31, 1989), Y. Masuda (to Agency of Industrial Science and Technology).
59. Jpn. Pat. 1,042,288 (Feb. 14, 1989), H. Hasegawa (to Richo Company).
60. D.E. Pat. 3,506,680 (Aug. 28, 1986), W. Paul, U. Grigo, P. R. Mueller and W. Nouvertne (to Bayer A.G.).
61. U.S. Pat. 4,224,451 (Sept. 23, 1980), R. D. Roberts and W. B. Hardy (to American Cyanamid Company).
62. D.E. Pat. 2,620,897 (Nov. 25, 1976), C. E. Tiegler (to CIBA-GEIGY A.G.).
63. U.S. Pat. 4,443,536 (April 17, 1984), G. J. Lestina (to Eastman Kodak Company).
64. U.S. Pat. 4,312,818 (Jan. 26, 1982), R. M. Larsch, E. O. Linderfels, and H. Z. Ernsthofin (to CIBA-GEIGY Corporation).
65. Ger. Offen. 2,709,528 (Sept. 15, 1977), J. F. York (to Borg-Warner Corporation).
66. U.S. Pat. 4,128,726 (Dec. 5, 1978), V. G. Grosso and R. L. Hillard (to American Cyanamid Company).
67. U.S. Pat. 3,211,652 (Oct. 12, 1965), J. B. Hinkamp (to Ethyl Corporation).
68. U.S. Pat. 3,026,264 (Sept. 12, 1962), A. L. Rocklin and J. L. Van Winkle (to Shell Oil Company).
69. U.S. Pat. 3,330,859 (July 11, 1967), M. Dexter, J. D. Spivack, and D. H. Steinberg (to Geigy Chemical Corporation).
70. U.S. Pat. 3,642,868 (Feb. 15, 1972), M. Dexter and co-workers, (to CIBA-GEIGY Corp.).
71. U.S. Pat. 3,531,483 (Sept. 29, 1970), J. C. Gilles (to B.F. Goodrich Company).
72. U. S. Pat. 5,684,204 (Nov. 4, 1997), R. S. Matthew (to Procter and Gamble).
73. *Ethyl Antioxidants in Fuels, Technical Bulletin*, Ethyl Corporation, Baton Rouge, La., 1977.
74. U.S. Pat. 4,275,004 (June 23, 1981), R. A. E. Winter and M. Dexter (to CIBA-GEIGY Corp.).
75. U.S. Pat. 3,306,874 (Feb. 28, 1967), A. S. Hay (to General Electric Company).
76. U.S. Pat. 3,247,262 (April 19, 1966), W. W. Kneding (to The Dow Chemical Company).

JOHN F. LORENC
GREGORY LAMBETH
WILLIAM SCHEFFER
Schenectady Chemicals, Inc.