Kirk-Othmer Encyclopedia of Chemical Technology.

HYDROCARBON RESINS

Hydrocarbon resin is a broad term that is usually used to describe a low molecular weight thermoplastic polymer synthesized via the thermal or catalytic polymerization of coal-tar fractions, cracked petroleum distillates, terpenes, or pure olefinic monomers. These resins are used extensively as modifiers in the hot melt and pressure sensitive adhesive industries. They are also used in numerous other applications such as sealants, printing inks, paints, plastics, road marking, carpet backing, flooring, and oil field applications. They are rarely used alone.

Typical hydrocarbon resins range in appearance from hard, brittle solids to viscous liquids. They may come in flakes, pellets, drums, or in molten form. Depending on application requirements, many resins are available as solutions in organic solvents or oils. Anionic, cationic, or nonionic emulsion forms are also manufactured. Hydrocarbon resins typically have a number average molecular weight (M_n) of less than 2000. The colors of these resins range from water-white to dark brown. Water-white resins usually are produced from the Lewis acid polymerization of pure olefinic monomers or by the hydrogenation of catalytically or thermally produced precursors. Colors are determined on the Gardner and Saybolt scales.

The first resins to be produced on a commercial scale were the coumarone–indene or coal-tar resins (1); production in the United States was started before 1920. These resins were dominant until the development of petroleum resins, which were established as important raw materials by the mid-1940s. Continued development of petroleum-based resins has led to a wide variety of aliphatic, cyclodiene, and aromatic hydrocarbon-based resins. The principal components of petroleum resins are based on piperylenes, dicyclopentadiene (DCPD), styrene, indene, and their respective alkylated derivatives.

With the improvement of refining and purification techniques, many pure olefinic monomers are available for polymerization. Under Lewis acid polymerization, such as with boron trifluoride, very light colored resins are routinely produced. These resins are based on monomers such as styrene, α-methylstryene, and vinyltoluene (mixed *meta*- and *para*-methylstyrene). More recently, purified *para*-methylstyrene has become commercially available and is used in resin synthesis. Low molecular weight thermoplastic resins produced from pure styrene have been available since the mid-1940s; resins obtained from substituted styrenes are more recent.

Terpene-based hydrocarbon resins are typically based on natural products such as α-pinene, β-pinene, and *d*-limonene [5989-27-5], which are obtained from the wood and citrus industries, respectively. These resins, which were originally the preferred tackifiers for natural rubber applications, possess similar properties to aliphatic petroleum resins, which were developed later. Terpene-based resins have been available since the mid-1930s and are primarily used in the adhesives industry.

1. Physical Properties

Most hydrocarbon resins are composed of a mixture of monomers and are rather difficult to fully characterize on a molecular level. The characteristics of resins are typically defined by physical properties such as softening point, color, molecular weight, melt viscosity, and solubility parameter. These properties predict performance characteristics and are essential in designing resins for specific applications. Actual characterization techniques used to define the broad molecular properties of hydrocarbon resins are Fourier transform infrared spectroscopy (ftir), nuclear magnetic resonance spectroscopy (nmr), and differential scanning calorimetry (dsc).

1.0.1. Softening Point

Softening point is the temperature at which a material shows a measurable flow or softening under a given weight. This property is usually measured by a standard ring and ball method and may be done manually (ASTM E28–E67) or automatically using an instrument such as the HERZOG Automatic Ring and Ball Tester MC-753 (ASTM D36-D2398). A typical procedure involves the pouring of a molten resin sample into a brass ring of defined diameter and thickness. The resin is then allowed to cool. A ball of a specific weight is then supported on the resin-filled ring and the apparatus is heated in a glycerol or water solvent until flow is detected.

1.0.2. Color

Colors of hydrocarbon resins are routinely determined on the Gardner scale (ASTM D154) or on the Saybolt scale (ASTM D156). Saybolt colors are determined from 2 g of resin in 18 g of toluene (10% solution) and are used for very light color to water-white resins. The Saybolt scale ranges from -30 to 30 with the latter being water-white. Gardner colors are determined as a 50% solution in toluene and are used for resins ranging in color from light yellow to dark brown. The Gardner scale ranges from 1 to 18 with the latter being dark brown. Molten resin colors are also reported in Gardner units. Aged color (or heat stability) is also an important property of hydrocarbon resins, which is determined by the high temperature oven aging of resins to predict thermal and oxidative stability.

1.0.3. Melt Viscosity

Viscosities of resins at standard temperatures yield information about molecular weight and molecular weight distribution, as well as valuable information with respect to application logistics. Some customers prefer to receive resins in molten form. Melt viscosities help to determine the required temperature for a resin to be pumpable. Temperature–viscosity profiles are routinely supplied to customers by resin manufacturers. In general, a molten viscosity of 1–1.1 $\mathrm{Pa{\cdot}s}$ (1000–1100 cP) or less at process temperatures is convenient for the pumping and handling of molten resin.

1.0.4. Solubility Parameter

Compatibility between hydrocarbon resins and other components in an application can be estimated by the Hildebrand solubility parameter (2). In order for materials to be mutually soluble, the free energy of mixing must be negative (3). The solubility of a hydrocarbon resin with other polymers or components in a system can be approximated by the similarities in the solubility parameters of the resin and the other materials. True solubility parameters are only available for simple compounds and solvents. However, parameters for more complex materials can be approximated by relative solubility comparisons with substances of known solubility parameter.

1.0.5. Molecular Weight

The determination of the molecular weight and molecular weight distribution of a hydrocarbon resin is very important for the prediction of performance parameters. Molecular weights are routinely determined using gel permeation (size exclusion) chromatography, which is commonly referred to as gpc or sec (4). Gpc quickly provides the relative weight average (M_w), number average (M_n), and Z-average (M_z) molecular weights, as well as the polydispersity (M_w/M_n) of a polymer or resin. In predicting solubility and compatibility with other polymers, the Z-average molecular weight has proven very useful. Other methods for determining the absolute molecular weight of polymers are light scattering (M_w) and vapor-phase osmometry (M_n). Solvent–nonsolvent separations of hydrocarbon resins have also been described (5–7).

1.0.6. Characterization

In many cases, ftir is a timely and cost-effective method to identify and quantify certain functionalities in a resin molecule. Based on developed correlations, ftir is routinely used as an efficient method for the analysis of resin aromaticity, olefinic content, and other key functional properties. Near infrared spectroscopy is also quickly becoming a useful tool for on-line process and property control.

For most hydrocarbon resins where numerous structurally different monomers are polymerized, nmr is typically used as a general tool to quantify the aromatic and/or olefinic content of a resin. In conjunction with gpc and ftir, nmr measurements are used to identify and quantify particular functionalities or monomers present in hydrocarbon resins.

As applied to hydrocarbon resins, dsc is mainly used for the determination of glass-transition temperatures (T_g). Information can also be gained as to the physical state of a material, ie, amorphous vs crystalline. As a general rule of thumb, the T_g of a hydrocarbon resin is approximately 50°C below the softening point. Oxidative induction times, which are also determined by dsc, are used to predict the relative oxidative stability of a hydrocarbon resin.

2. Polymerization

Most commercial hydrocarbon resins produced from olefinic feedstocks are synthesized via carbocationic polymerization (8). Very similar catalyst systems are used in the synthesis of coumarone–indene, petroleum, terpene, and pure monomer-based resins (9). The first catalyst systems used were strong mineral acids, specifically sulfuric acid [8014-95-7] and phosphoric acid [766-38-2]. These acids typically afforded dark colored resins with very low softening points and molecular weights. More recently, resin synthesis technology has focused on the use of Lewis acids and Friedel-Crafts polymerization chemistry. Typical Lewis acids used in the synthesis of hydrocarbon resins are $AlCl_3$ [7446-70-7], BF_3 [7637-07-2], $(CH_3CH_2)_2AlCl$ [96-10-6], $(CH_3CH_2)AlCl_2$ [563-43-9], and complexes of these acids with various electron-donating species (see Friedel-crafts reactions).

Friedel-Crafts (Lewis) acids have been shown to be much more effective in the initiation of cationic polymerization when in the presence of a cocatalyst such as water, alkyl halides, and protic acids. Virtually all feedstocks used in the synthesis of hydrocarbon resins contain at least traces of water, which serves as a cocatalyst. The accepted mechanism for the activation of boron trifluoride in the presence of water is shown in equation 1 (10). Other Lewis acids are activated by similar mechanisms. In a more general sense, water may be replaced by any appropriate electron-donating species (eg, ether, alcohol, alkyl halide) to generate a cationic intermediate and a Lewis acid complex counterion.

$$BF_3 + H_2O \rightleftharpoons H^+BF_3OH^- \qquad (1)$$

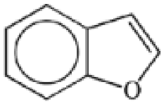
The polymerization of monomers to form hydrocarbon resins is typically carried out by either the direct addition of catalyst to a hydrocarbon fraction or by the addition of feed to a solvent–catalyst slurry or solution. Most commercial manufacturers use a continuous polymerization process as opposed to a batch process. Reactor temperatures are typically in the range of 0–120°C.

In order to facilitate heat transfer of the exothermic polymerization reaction, and to control polymerizate viscosity, percent reactives are adjusted through the use of inert aromatic or aliphatic diluents, such as toluene or heptane, or higher boiling mixed aromatic or mixed aliphatic diluents. Process feed streams are typically adjusted to 30–50% polymerizable monomers.

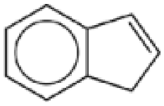
Polymerizations are typically quenched with water, alcohol, or base. The resulting polymerizates are then distilled and steam and/or vacuum stripped to yield hard resin. Hydrocarbon resins may also be precipitated by the addition of the quenched reaction mixture to an excess of an appropriate poor solvent. As an example, aliphatic C-5 resins are readily precipitated in acetone, while a more polar solvent such as methanol is better suited for aromatic C-9 resins.

3. Coumarone–Indene or Coal-Tar Resins

Coumarone–indene or coal-tar resins, as the name denotes, are by-products of the coal carbonization process (coking). Although named after two particular components of these resins, coumarone (**1**) and indene (**2**), these resins are actually produced by the cationic polymerization of predominantly aromatic feedstreams. These feedstreams are typically composed of compounds such as indene, styrene, and their alkylated analogues. In actuality, there is very little coumarone in this type of feedstock. The fractions used for resin synthesis typically boil in the range of 150–250°C and are characterized by gas chromatography.



(1)



(2)

Cationic polymerization of coal-tar fractions has been commercially achieved through the use of strong protic acids, as well as various Lewis acids. Sulfuric acid was the first polymerization catalyst (11). More recent technology has focused on the Friedel-Crafts polymerization of coal fractions to yield resins with higher softening points and better color. Typical Lewis acid catalysts used in these processes are aluminum chloride, boron trifluoride, and various boron trifluoride complexes (12). Crude feedstocks typically contain 25–75% reactive components and may be refined prior to polymerization (eg, acid or alkali treatment) to remove sulfur and other undesired components. Table 1 illustrates the typical components found in coal-tar fractions and their corresponding properties.

As a result of incorporating rigid monomers such as indene and its alkylated derivatives, resin softening points of 150°C and greater are obtainable (13, 14). Colors typically range between 8–12 Gardner. Although much of the market has been replaced by hydrocarbon resins, coumarone–indene resins are employed in coatings, flooring, tiles, printing inks, and adhesives. They are also utilized as processing aids and pigment dispersing agents in the compounding of natural and synthetic rubber.

4. Petroleum Resins

Petroleum resins are low molecular weight thermoplastic hydrocarbon resins synthesized from steam cracked petroleum distillates. These resins are differentiated from higher molecular weight polymers such as polyethylene and polypropylene, which are produced from essentially pure monomers. Petroleum resin feedstocks are

Table 1. Properties of Coal-Tar Monomers

Monomer	CAS Registry Number	Bp, °C	Density, g/mL at 20°C	n_{D}^{20}	Fp, °C
cyclopentadiene	[26912-33-4]	41–42	0.8041	1.4461	−85
dicyclopentadiene	[77-73-6]	170	0.988	1.512	−32.9
styrene	[100-42-5]	145.2	0.9059	1.5467	−30.6
o-methylstyrene	[611-15-4]	169.8	0.9036	1.5465	−68.6
m-methylstyrene	[100-80-1]	171.6	0.9113	1.5439	−86.3
p-methylstyrene	[622-97-9]	172.8	0.9106	1.5450	−34.2
coumarone	[271-89-6]	171.4	1.0948	1.5663	−28.9
2-methylcoumarone	[4265-25-2]	197	1.0534	1.5584	
indene	[95-13-6]	182.6	0.9960	1.5768	−1.6
2-methylindene	[2177-47-1]	187–199	0.9947	1.5723	

composed of various reactive and nonreactive aliphatic and aromatic components. The resins are usually classified as C-5 (aliphatic), C-9 (aromatic), C-5/C-9 (aromatic modified aliphatic), and cycloaliphatic diene-based resins. These range from viscous liquids to hard, friable solids, with colors ranging from water-white to dark brown. Petroleum resins are widely used in pressure sensitive and hot melt adhesives, as well as in sealants, inks, paints, coatings, plastics, carpet backing, road marking paints, and oil field applications.

4.0.7. Raw Materials

During the 1940s, while improved techniques for petroleum refining were being developed, the presence of reactive olefins was undesirable in aromatic solvents. In order to improve the purity of these aromatic fractions, methods were developed to remove reactive olefins and diolefins through the catalytic polymerization of these species using protic (15) and Lewis acids (16). During the same period of time, extensive surveys were being carried out to determine the best methods for cracking crude oil. These cracking methods were aimed at obtaining high yields of ethylene and propylene, as well as optimizing the formation of reactive monomers such as butadiene [106-99-0], isoprene [78-79-5], piperylene, styrene, and indene (17).

The feedstocks used in the production of petroleum resins are obtained mainly from the low pressure vapor-phase cracking (steam cracking) and subsequent fractionation of petroleum distillates ranging from light naphthas to gas oil fractions, which typically boil in the 20–450°C range (16). Obtained from this process are feedstreams composed of aliphatic, aromatic, and cycloaliphatic olefins and diolefins, which are subsequently polymerized to yield resins of various compositions and physical properties. Typically, feedstocks are divided into aliphatic, cycloaliphatic, and aromatic streams. Table 2 illustrates the predominant olefinic hydrocarbons obtained from steam cracking processes for petroleum resin synthesis (18).

4.0.7.1. Aliphatic: C-5–C-6. Aliphatic feedstreams are typically composed of C-5 and C-6 paraffins, olefins, and diolefins, the main reactive components being piperylenes (*cis*-[1574-41-0] and *trans*-1,3-pentadiene [2004-70-8]). Other main compounds include substituted C-5 and C-6 olefins such as cyclopentene [142-29-0], 2-methyl-2-butene [513-35-9], and 2-methyl-2-pentene [625-27-4]. Isoprene and cyclopentadiene may be present in small to moderate quantities (2–10%). Most steam cracking operations are designed to remove and purify isoprene from the C-5–C-6 fraction for applications in rubbers and thermoplastic elastomers. Cyclopentadiene is typically dimerized to dicyclopentadiene (DCPD) and removed from C-5 olefin–diolefin feedstreams during fractionation (19).

4.0.7.2. Cycloaliphatic Diene: CPD–DCPD. Cycloaliphatic diene-based hydrocarbon resins are typically produced from the thermal or catalytic polymerization of cyclopentadiene (CPD) and dicyclopentadiene (DCPD). Upon controlled heating, CPD may be dimerized to DCPD or cracked back to the monomer. The heat of cracking for DCPD ($\Delta H_{\text{cracking}}$) is 24.6 kJ/mol (5.88 kcal/mol). In steam cracking processes, CPD is removed from C-5

Table 2. Unsaturated Monomers Obtained From Steam Cracking[a]

Component	Boiling range, °C
Olefins	
pentenes	20–40
hexenes	41–73
heptenes	72–98.5
Diolefins	
pentadienes	34–48
hexadienes	59–80
Cycloaliphatic olefins and diolefins	
cyclopentene	44
cyclopentadiene	41.5
cyclohexene	83
methylcyclopentadiene	73
Cycloaliphatic diolefin dimers	
dicyclopentadiene	170
methylcyclopentadiene dimer	200
Vinyl aromatic hydrocarbons	
styrene	145.2
α-methylstyrene	164
vinyltoluenes	166–170
indene	182.6
methylindenes	187–199

[a] Ref. 18.

and higher fractions by heat soaking to form the dimer, which is separable by controlled fractional distillation (18) (see Cyclopentadiene and dicyclopentadiene).

DCPD of varying purity is produced and used in the synthesis of hydrocarbon resins. Typically, cyclic feedstocks have DCPD concentrations ranging from 30–80%, although high purity ($>95\%$) DCPD is available on a commercial scale and is sometimes used.

4.0.7.3. Aromatic. Aromatic feedstreams (C-8, C-9, C-10) derived from the steam cracking of petroleum distillates are composed of styrene, indene, vinyltoluenes (eg, *meta*- and *para*-methylstyrene), and their respective alkylated analogues. A typical aromatic feedstream might contain 50% reactive olefins with the remainder being alkylated benzenes and higher aromatics.

4.0.8. C-5 Aliphatic Petroleum Resins

Carbocationic polymerization of C-5 feedstreams has been accomplished with various Friedel-Crafts catalyst systems. Table 3 compares the efficiencies of selected Lewis acids in the polymerization of a typical C-5 stream containing 43 wt % C-5–C-6 diolefins and 47 wt % C-5–C-6 olefins (20). Based on weight percent yield of resin at equimolar concentrations of catalyst $(5.62\,\text{mmol}/100\,\text{g})$, efficiency follows $AlCl_3 \approx AlBr_3 > BF_3\text{etherate} - H_2O > TiCl_4 > SnCl_4$. The most commonly used catalyst in petroleum resin synthesis is $AlCl_3$.

Although most referenced catalyst systems do not indicate the presence of water, typical feedstreams derived from steam cracking operations contain parts per million quantities of adventitious water unless they are scrupulously dried before polymerization. Water serves as a cocatalyst in Lewis acid catalyzed systems. In addition to powdered or gaseous single catalyst systems, liquid complexes containing $AlCl_3$ and anhydrous hydrochloric acid in aromatic solvents such as *ortho*-xylene have also been used and shown to exhibit similar activity based on weight percent $AlCl_3$ (20–24). $AlCl_3$ complexes with aqueous mineral acids, such as 86% H_3PO_4, have been used as well (25). Acidic liquid $AlCl_3$ sludges obtained from the alkylation of benzene and

Table 3. Comparative Efficiencies of Friedel-Crafts Catalysts[a, b]

Parameter	$AlCl_3$	$AlBr_3$	BF_3 etherate	BF_3 etherate/H_2O	$TiCl_4$	$SnCl_4$	$AlCl_3$/HCl/*o*-xylene	DDB[c] sludge
concentration								
wt %	0.75	1.50	0.75^{d}	0.38^{d}	1.06	1.46	0.75^{e}	0.75^{e}
mmol/100 g	5.62	5.62	11.06^{d}	5.62^{d}	5.62	5.62		
resin								
yield, wt %	36.8	36.0	23.0	17.0	25.0	15.6	35.9	34.7
oligomer								
yield, wt %	1.9	1.5	17.4	16.0	3.4	3.4		
resin color (Gardner)	4−	4.5	2.5	4+	7	>18	6−	6+
after heating at 150°C								
3 h	8+	11+		8+	14+	>18		
16 h	14	15+	14+	14−	16+	>18		
resin softening point, °C	95	101	<20	<20	40	<20	107	113

[a] Ref. 20.

[b] At 50°C, 60 min.

[c] DDB = dodecylbenzene.

[d] As BF_3.

[e] As $AlCl_3$.

other aromatics have also been shown to have similar efficiency to $AlCl_3$. Table 3 contains an example using acidic sludge from a dodecylbenzene production facility (20).

$AlCl_3$ efficiency (based on g resin/g catalyst) can be markedly improved by polymerizing dry feeds (<10 ppm H_2O) with an $AlCl_3$/anhydrous HCl system. Proceeding from 250 ppm H_2O down to 10 ppm H_2O, catalyst efficiency improves from 30.6 to 83.0 (26). Low levels of tertiary hydrocarbyl chlorides have been shown to greatly enhance the activity of $AlCl_3$, while yielding resins with narrow molecular weight distributions relative to systems employing water or HCl (27).

The composition of feedstocks is very important for obtaining the desired properties of hydrocarbon resins such as softening point, color, and molecular weight profile. High C-5 diolefin content typically leads to higher softening points, as well as higher and broader molecular weights. These properties may be balanced by branched tertiary olefins, which typically lower softening point and lower/narrow molecular weight.

Under $AlCl_3$ catalysis, monomeric systems of greater than 85 wt % piperylenes tend to form unstable polymerization systems resulting in gel formation, which is undesirable in hydrocarbon resins (28). Softening point control in C-5 resins can be achieved by either the use of chain-transfer agents and/or through the use of alternative catalyst systems. Isobutylene [115-11-7] and branched tertiary alkenes function as chain-transfer agents due to the formation of a stable tertiary carbonium ion at the end of a growing polymer chain. This is illustrated in Figure 1 (counterions are not shown).

The $AlCl_3$ catalyzed polymerization of piperylenes in the presence of butadiene, isobutylene, and methylbutenes yields tackifying resins with softening points ranging from 25–80°C (29). When polymerized alone under $AlCl_3$ catalysis, isobutylene gives rubbery polymers, butadiene gives gummy materials, and methylbutenes form only low molecular weight residual oils (30). Due to their increased chain-transfer activity resulting in greater oligomer content, resin yields begin to decrease with greater concentrations of butadiene or isobutylene (31).

Blends of piperylenes and amylenes (mixed 2-methyl-1-butene and 2-methyl-2-butene) or UOP propylene dimers can be adjusted to produce softening points of 0–100°C and weight average molecular weights of <1200 (32, 33). Careful control of the diolefin/branched olefin ratio is the key to consistent resin properties (34).

When used as chain-transfer agents in catalytic polymerizations, branched terminal olefins (eg, 2-methyl-1-butene) have been shown to suppress the softening point to a greater extent than branched internal olefins (ie,

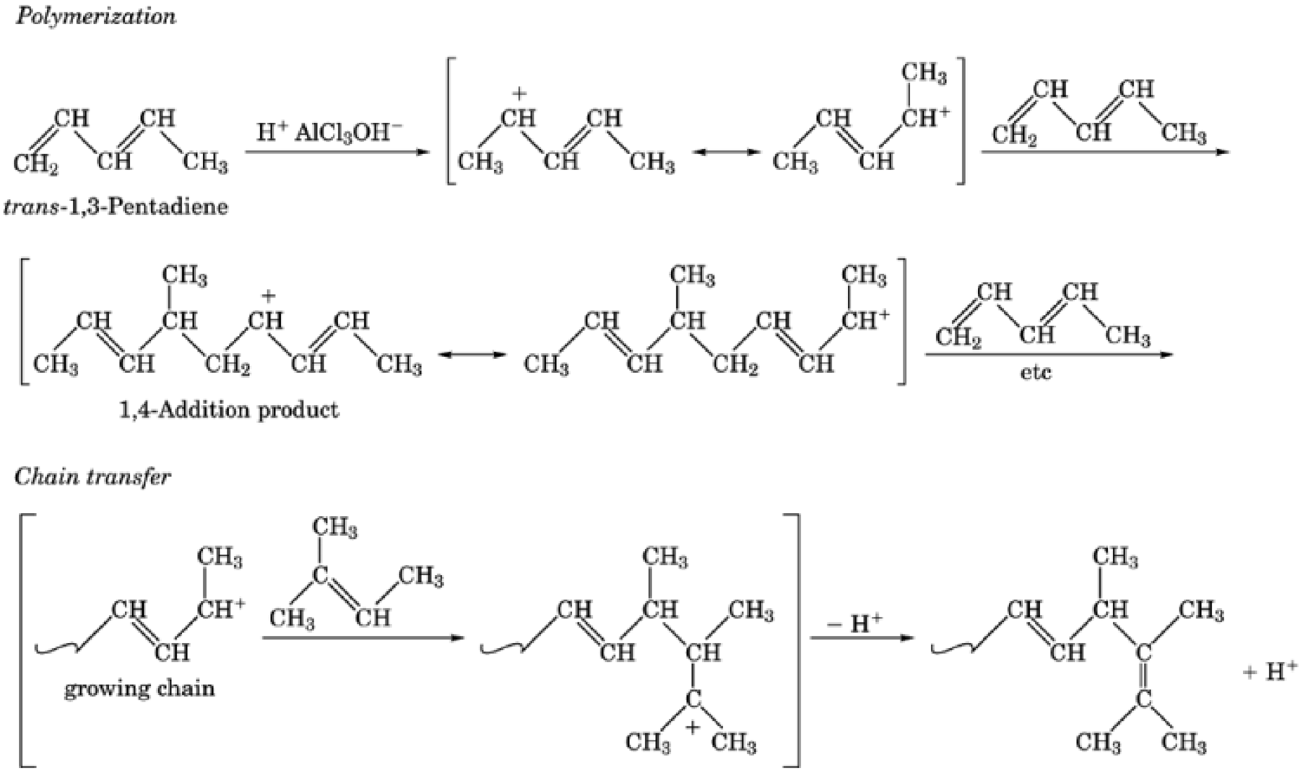


Fig. 1. Polymerization of piperylenes.

2-methyl-2-butene) (35). Branched internal olefins, as opposed to the terminal olefins, can be used to decrease wax cloud point and molecular weight while maintaining the softening point (32). Wax cloud point is typically determined by the slow cooling of a molten blend of tackifier, wax, and polymer. The temperature at which the blend first begins to turn opaque is taken as the wax cloud point.

Due to the fact that BF_3 is a weaker Lewis acid than $AlCl_3$, structurally distinct resins are obtained upon the respective polymerization of a piperylenes–2-methyl-2-butene system with the two different Lewis acids. Much lower levels of branched olefin are required to achieve a softening point of $<40^\circ C$ with the BF_3 catalyzed system (33, 36). In fact, due to its weaker acidity, BF_3 is not useful for producing high softening point resins based on C-5 hydrocarbon feeds.

Levels of cyclopentadiene (CPD) and dicyclopentadiene (DCPD) in C-5 feedstreams have a great effect on the softening point, as well as the color and thermal stability of the resin. Typically, DCPD is added to C-5 feedblends to increase softening point. However, increased DCPD incorporation generally leads to higher color in the resin. Oligomers of CPD and alkylated analogues have been catalytically polymerized with piperylenes to yield resins with softening points greater than 200°C for printing ink applications (37).

In normal steam cracking operations, CPD levels in the C-5–C-6 hydrocarbon fractions are reduced to approximately 1–3 wt %. Studies have shown that these levels may be reduced to <0.5 wt% by heat soaking at 90–140°C followed by distillation. Heat soaking conditions of C-5 streams are usually optimized at 90–140°C to prevent dimerization of CPD with acyclic dienes. These studies have also shown that by increasing the piperylenes:CPD ratio in a C-5 feedblend from 42 to 247, the resulting resin color obtained from $AlCl_3$ improves three Gardner color units (38). Another less common method for reducing CPD levels in C-9 polymerization feedstocks is the prepolymerization of feedstocks with polar dienophiles. At initial CPD levels of <1 wt%, the resulting Diels-Alder adducts do not hinder the polymerization reaction (39).

4.0.9. C-5–C-9 Aromatic Modified Aliphatic Petroleum Resins

Compatibility with base polymers is an essential aspect of hydrocarbon resins in whatever application they are used. As an example, piperylene–2-methyl-2-butene based resins are substantially inadequate in enhancing the tack of 1,3-butadiene–styrene based random and block copolymers in pressure sensitive adhesive applications. The copolymerization of α-methylstyrene with piperylenes effectively enhances the tack properties of styrene–butadiene copolymers and styrene–isoprene copolymers in adhesive applications (40, 41). Introduction of aromaticity into hydrocarbon resins serves to increase the solubility parameter of resins, resulting in improved compatibility with base polymers. However, the nature of the aromatic monomer also serves as a handle for molecular weight and softening point control.

Aromatic modified aliphatic resins are typically referred to as C-5–C-9 resins, although typical aromatic feedstreams contain C-8 to C-10 vinyl aromatic monomers. Aromatic monomers are typically introduced as either pure monomers or as C-8–C-10 aromatic fractions obtained from steam cracking operations. Styrene and its alkylated analogues are used to introduce aromaticity into hydrocarbon resins, although each has a different effect on softening point and molecular weight. Polymerization of C-5 diolefins and olefins in the presence of 20–40 wt % α-methylstyrene [98-83-9] produces resins with softening points in the range of 60–80°C when diolefin:olefin ratios are maintained from 0.6:1 to 1.4:1, respectively (40). Catalytic resins produced from 10–25 wt % styrene with C-5 diolefins and olefins possess similar properties, although softening points tend to be reduced to 40–60°C (42). This can be attributed to the structural differences and the differing chain-transfer mechanisms of styrene and α-methylstyrene. Higher softening point C-5–styrene resins may be obtained with vinyltoluenes or *para*-methylstyrene. Copolymerization of 5–30 wt % *p*-methylstyrene with a C-5 diolefin–olefin stream yields resins with softening points in the range of 75–120°C (43).

Although most aromatic modified C-5 resins are typically higher softening point resins, certain applications, such as adhesives, require lower softening points. Copolymerization of a C-8–C-10 vinyl aromatic fraction with piperylenes in the presence of a C-4–C-8 mono-olefin chain-transfer stream yields resins with softening points ranging from 0–40°C (44). A particular advantage of these liquid resins is the fact that they eliminate the need for plasticizers or oils in some pressure sensitive adhesive applications.

Catalysts used in the polymerization of C-5 diolefins and olefins, and monovinyl aromatic monomers, follow closely with the systems used in the synthesis of aliphatic resins. Typical catalyst systems are $AlCl_3$, $AlBr_3$, $AlCl_3$–HCl–*o*-xylene complexes and sludges obtained from the Friedel-Crafts alkylation of benzene. Boron trifluoride and its complexes, as well as $TiCl_4$ and $SnCl_4$, have been found to result in lower yields and higher oligomer content in C-5 and aromatic modified C-5 polymerizations.

The conversion of aromatic monomers relative to C-5–C-6 linear diolefins and olefins in cationic polymerizations may not be proportional to the feedblend composition, resulting in higher resin aromaticity as determined by nmr and ir measurements (43). This can be attributed to the differing reactivity ratios of aromatic and aliphatic monomers under specific Lewis acid catalysis. Intentional blocking of hydrocarbon resins into aromatic and aliphatic regions may be accomplished by sequential cationic polymerization employing multiple reactors and standard polymerization conditions (45).

4.0.10. C-9 Aromatic Petroleum Resins

Feedstocks typically used for aromatic petroleum resin synthesis boil in the approximate range of 100–300°C at atmospheric pressure, with most boiling in the 130–200°C range. The C-9 designation actually includes styrene (C-8) through C-10 hydrocarbons (eg, methylindene). Many of the polymerizable monomers identified in Table 1 for coumarone–indene type crudes from coal tar are also present in aromatic fractions from cracked petroleum distillates. Therefore, the technology developed for the polymerization of coal-tar crudes is also applicable to petroleum-derived aromatic feedstocks. In addition to availability, aromatic petroleum resins offer several advantages over coumarone–indene resins. These include improved color and odor, as well as uv and thermal stability (46).

Several methods have been developed for the further improvement of color and stability in aromatic resins. Thermal pretreatment of an aromatic fraction with a boiling range of 140–280°C with an α,β-unsaturated dicarboxylic acid anhydride has been found to be an effective method for color improvement. Treatment of an aromatic fraction with 8.1 wt % maleic anhydride (based on the total weight of polymerizable monomers) for 2 h at 100°C, followed by distillation and subsequent polymerization with a BF_3-phenol complex, yielded resins with color improvements of up to three Gardner units over resins produced without the prepolymerization feed treatment. Heat stability (3 h at 200°C) was also improved by four Gardner units (47). A related method involves the sequential treatment of a cracked petroleum fraction of boiling range 80–260°C with an acidic agent such as H_2SO_4 or acidic solid ion-exchange resins (eg, Amberlyst 15), followed by vacuum distillation and subsequent catalytic polymerization (48).

Catalyst systems used in the commercial synthesis of aromatic petroleum resins are very similar to those systems used in the manufacture of C-5 and C-5–C-9 type resins. The principal catalysts are $AlCl_3$ and BF_3 and their respective complexes. BF_3 catalysis usually yields resins with improved color over $AlCl_3$ catalyzed systems.

4.0.11. Cyclopentadiene/Dicyclopentadiene-Based Petroleum Resins

1,3-Cyclopentadiene (CPD) is just one of the numerous compounds produced by the steam cracking of petroleum distillates. Due to the fact that DCPD is polymerized relatively easily under thermal conditions without added catalyst, resins produced from cycloaliphatic dienes have become a significant focus of the hydrocarbon resin industry.

Hydrocarbon resins based on CPD are used heavily in the adhesive and road marking industries; derivatives of these resins are used in the production of printing inks. These resins may be produced catalytically using typical carbocationic polymerization techniques, but the large majority of these resins are synthesized under thermal polymerization conditions. The rate constants for the Diels-Alder based dimerization of CPD to DCPD are well known (49). The ability to polymerize without Lewis acid catalysis reduces the amount of aluminous water or other catalyst effluents/emissions that must be addressed from an environmental standpoint. Both thermal and catalytically polymerized DCPD/CPD-based resins contain a high degree of unsaturation. Therefore, many of these resins are hydrogenated for certain applications.

Dicyclopentadiene-based feedstreams are routinely used in petroleum resin synthesis as a means of increasing softening point. High softening point resins (130–160°C) have been synthesized for adhesives and ink applications using a DCPD-based stream obtained from isoprene extraction operations. The $AlCl_3$ catalyzed polymerization of a hydrocarbon fraction containing 52% DCPD and 22.3% codimers of cyclopentadiene and C-5 diolefins, using a xylene solvent, has been shown to yield a resin having a softening point of 152°C (50). Xylene has been found to provide a lower polymerizate viscosity over toluene resulting in better heat-transfer properties and a higher softening point.

Gel formation and high levels of unsaturation are problems encountered with resins produced from the thermal polymerization (250–300°C) of high purity DCPD streams. Reduction of these undesirable properties has been accomplished by the use of acyclic conjugated dienes and codimers of CPD and acyclic dienes. Polymerization of a feedblend containing 432 g DCPD (93.5% purity), 48 g piperylenes, and 120 g xylene at 260°C under nitrogen for 3 h yielded a toluene-soluble resin with a softening point of 172°C and a color of 3–4 Gardner. Control experiments using 480 g DCPD (93.5% purity) and 120 g xylene, and the same polymerization conditions, produced a resin with a softening point of 218°C, which had a color of 5–6 Gardner and was only partially soluble in toluene (51). Monomer-to-solvent ratio has a significant effect on resin softening point and gel formation in thermal processes (52).

Table 4. Effect of Cyclopentadiene–Acyclic Diene Codimers on DCPD-Based Thermal Polymerizations[a, b]

Example	1	2	3	4	5	6
DCPD, wt %	30	70	30	40	55	40
THI, wt %			48	41	30	
xylene, wt %	70	30	22	19	15	40[c]
yield, wt %	76.1	82.2	48.0	59.9	79.2	60.1
softening point,[d] °C	129.0	150.0	86.5	112.0	149.0	114.0
bromine value	114	95	125	118	101	112
color, Gardner	10	11	7	7	8	7
heat stability, °C	+15.0	+20.0	+3.0	+4.0	+4.0	+3.0

[a] Ref. 53.

[b] Polymerization conditions: 5 h at 260°C; finishing conditions: 210°C at 0.27 kPa (2 mm Hg).

[c] And 20 wt % vinylnorbornene.

[d] The increase in softening point measured after heating each resin at 220°C for 3 h. The smaller the increase, the better the heat stability.

In addition to the use of C-4–C-5 acyclic conjugated dienes as a means of controlling resin properties, CPD codimers with conjugated acyclic dienes, specifically CPD–butadiene codimers, are also effective (53, 54). Thermal polymerization of a blend of 30% DCPD (80% purity), 48% tetrahydroindene (THI) [7603-37-4], and 22% xylene, followed by removal of solvent and oligomers, produced a resin having a softening point of 86.5°C and a bromine value of 125. A comparative example using 30% DCPD and 70% xylene yielded a resin having a softening point of 129°C and a bromine value of 114 (53). Table 4 illustrates the effect of CPD–acyclic diene codimers on CPD-based polymerizations.

Distillation and stripping temperatures used for nonhydrogenated CPD-based resins are typically kept below 250°C and are usually conducted at reduced pressure (54). This is due to the high levels of unsaturation remaining in these resins and to the fact that thermal polymerization can be reinitiated at normal finishing temperatures of 250°C. Reactive, heat-reactive, or unsaturated resins react with drying oils in the range of 232–260°C to give products with improved performances in paints and varnishes.

In order to increase the solubility parameter of CPD-based resins, vinyl aromatic compounds, as well as other polar monomers, have been copolymerized with CPD. Indene and styrene are two common aromatic streams used to modify cyclodiene-based resins. They may be used as pure monomers or contained in aromatic steam cracked petroleum fractions. Addition of indene at the expense of DCPD in a thermal polymerization has been found to lower the yield and softening point of the resin (55). Compatibility of a resin with ethylene—vinyl acetate (EVA) copolymers, which are used in hot melt adhesive applications, may be improved by the copolymerization of aromatic monomers with CPD. As with other thermally polymerized CPD-based resins, aromatic modified thermal resins may be hydrogenated.

Printing inks such as heat set or gravure inks typically employ polar resins such as rosin derivatives and alkyd resins, both of which have good affinity for pigments and solubility in drying oils. Petroleum resins obtained from the copolymerization of cyclopentadiene with polar monomers, such as unsaturated acid anhydrides or fatty acids followed by esterification, have also been shown to have comparable performance to rosin derivatives in these applications (56–61). As an example, CPD-based resins for printing ink applications have been produced by the reaction of 730 g DCPD (97% purity), 70 g maleic anhydride [108-31-6], and 190 g oleyl alcohol [143-28-2] in 300 g xylene for 5 h at 270–275°C. Distillation followed by steam stripping yielded a resin having a softening point of 135°C and an acid number of 21. In order to obtain gel-free resins when using unsaturated anhydrides such as maleic anhydride, stoichiometry should not exceed 0.5–1.0 moles of anhydride per mole of CPD (56).

The majority of thermal polymerizations are carried out as a batch process, which requires a heat-up and a cool down stage. Typical conditions are 250–300°C for 0.5–4 h in an oxygen-free atmosphere (typically nitrogen) at approximately 1.4 MPa (200 psi). A continuous thermal polymerization has been reported which utilizes a tubular flow reactor having three temperature zones and recycle capability (62). The advantages of this process are reduced residence time, increased production, and improved molecular weight control. Molecular weight may be controlled with temperature, residence time, feed composition, and polymerizate recycle.

4.0.12. Hydrogenation of Petroleum Resins

Most petroleum resins produced by the catalytic or thermal polymerization of cracked petroleum fractions are colored and contain a certain degree of nonaromatic olefinic unsaturation. This unsaturation leads to reduced thermal and oxidative stability. High olefinic content may also lead to decreased resin compatibility with other components used in an application. Hydrogenation is used as a means of reducing resin color and odor, as well as improving stability and compatibility. The hydrogenation of petroleum resins may be achieved in solution or molten state and is usually accomplished by either a batchwise or, more commonly, a continuous process. The key parameters to be addressed with resin hydrogenation are catalyst activity, pressure, temperature, and feed rate.

Catalysts employed for the hydrogenation of petroleum resins are typically supported monometallic and bimetallic catalyst systems based on the group VI and VIII transition elements. Hydrogenations of thermally polymerized cyclopentadiene-based resins have been accomplished using excess hydrogen or a hydrogen-rich gas over a γ-Al_2O_3 supported sulfided nickel–tungsten (Ni–W) or nickel–molybdenum (Ni–Mo) catalyst system (63). Operating parameters for a 21% resin solution in Varsol were established at 250–330°C using a hydrogen pressure of 15–20 MPa (150–200 atm). Optimum resin decoloration and overall catalyst life were achieved using a catalyst with a specific fresh surface area of 181 m_2/g (64).

Processes for the hydrogenation of catalytic resins are usually carried out using the same catalysts and reaction conditions as those used for thermally polymerized precursors. Rainey nickel has been shown to be an effective catalyst for the hydrogenation of catalytic aromatic resins (65). By varying reaction times at a temperature of 280°C and a pressure of 19.6 MPa (200 kg/cm_2) in an autoclave, the degree of hydrogenation of the aromatic rings may be optimized to between 30 and 80%. Optimizing the reduction of the aromatic nuclei within a resin, as measured by the absorbance at $700\ cm^{-1}$, is conducted to optimize resin compatibility with ethylene–vinyl acetate copolymers.

Reduction of the aromatic nuclei contained in catalytic C-9 resins has also been accomplished in the molten state (66). Continuous downward concurrent feeding of molten resin (120°C softening point) and hydrogen to a fixed bed of an alumina supported platinum–ruthenium (1.75% Pt–0.25% Ru) catalyst has been shown to reduce approximately 100% of the aromatic nuclei present in the resin. The temperature and pressure required for this process are 295–300°C and 9.8 MPa (100 kg/cm_2), respectively. The extent of hydrogenation was monitored by the percent reduction in the uv absorbance at 274.5 nm.

5. Resins from Pure Monomers

Thermoplastic resins produced from pure monomers such as styrene, alkyl-substituted styrenes, and isobutylene are produced commercially. An advantage of these resins is the fact that they are typically lighter in color than Gardner 1 (water-white) without being hydrogenated. Among the earliest resins in this category were those made from styrene and sold as Piccolastic. Styrene and alkyl-substituted styrenes such as α-methylstyrene are very reactive toward Friedel-Crafts polymerization catalysts.

α-Methylstyrene resins possessing softening points of up to 165°C have been synthesized using BF_3, $AlCl_3$, $(C_2H_5)AlCl_2$, and $(C_2H_5)AlCl$ at reaction temperatures of 0 to $-50°C$ (67). Reaction temperature and monomer concentration must be carefully controlled to achieve the desired softening point and to minimize the dimer and trimer content of the finished polymerizate. Finishing techniques are comparable to those used for other petroleum-type resins.

Blends of vinyltoluene and α-methylstyrene (3:1, respectively) have been polymerized using BF_3 catalysis to yield resins with softening points ranging from 100–130°C and colors less than Gardner 1 (68). Polymerization of similar vinyltoluene: α-methylstyrene blends in ratios of 2.5:1 to 4.5:1, respectively, over an acidic clay catalyst (69) has been found to yield resins with softening points of up to 100°C. As compared to resins produced with boron trifluoride and having similar softening points, the maximum chain lengths of the acidic clay produced resins, as measured by gel permeation chromatography, were significantly shorter. This difference resulted in improved solubility in paraffinic waxes (70). BF_3 produced α-methylstyrene–styrene copolymers have also been synthesized for uses in the sizing and retexturing of fabrics (71), as well as in pressure sensitive adhesive applications (72–74).

Terpolymers from dimethyl-α-methylstyrene (3,4-isomer preferred)–α-methylstyrene–styrene blends in a 1:1:1 weight ratio have been shown to be useful in adhesive applications. The use of ring-alkylated styrenes aids in the solubility of the polymer in less polar solvents and polymeric systems (75). Monomer concentrations of no greater than 20% and temperatures of less than $-20^\circ C$ are necessary to achieve the desired properties.

tert-Butyl styrene has been copolymerized with various vinyl aromatic and aliphatic monomers to yield resins with unique softening points and solubility profiles. *t*-Butylstyrene–α-methylstyrene copolymers having softening points of up to 140°C have been produced using BF_3 catalysis. Process control leads to aromatic resins soluble in low Kauri-butanol solvents at temperatures as low as 0°C (76). Increased amounts of either monomer beyond an approximate 3:2 ratio (α-methylstyrene:*t*-butylstyrene) may lead to linear blocks of respective monomer in the polymer, which is detrimental to performance properties. Copolymers of *t*-butylstyrene with piperylenes (77) and diisobutylene (78) have been prepared as tackifiers for pressure sensitive and hot melt adhesives. Polymerization of *t*-butylstyrene with piperylenes requires 1–2 wt % $AlCl_3$ or 0.25–1.0 wt % BF_3. Homopolymers of *t*-butylstyrene possessing softening points of 155°C have been produced by the use of 0.1–8.0 wt % zirconium tetrachloride as a polymerization catalyst (79).

In many cases, the softening points of vinyl aromatic resins are controlled by monomer concentration and polymerization temperature. Two general rules are that the lower the monomer concentration, the higher the softening point, and the lower the polymerization temperature, the higher the softening point. These techniques may also lead to high molecular weights, which may be detrimental to many applications. Recent processes have revealed the production of high softening point ($>140^\circ C$) α-methylstyrene–*para*-methylstyrene resins which do not rely on low monomer concentration. Resin yields of greater than 96% (based on reactive monomers) have been obtained using 1.2 wt % BF_3 as the catalyst system (80).

6. Terpene-Based Resins

Terpenes, specifically monoterpenes, are naturally occurring monomers that are usually obtained as by-products of the paper and citrus industries. Monoterpenes that are typically employed in hydrocarbon resins are shown in Figure 2. Optically active *d*-limonene is obtained from various natural oils, particularly citrus oils (81). α and β-pinenes are obtained from sulfate turpentine produced in the kraft (sulfate) pulping process. Southeastern U.S. sulfate turpentine contains approximately 60–70 wt % α-pinene and 20–25 wt % β-pinene (see Terpenoids). Dipentene, which is a complex mixture of *d,l*-limonene, α- and β-phellandrene, α- and γ-terpinene, and terpinolene, is also obtained from the processing of sulfate liquor (82).

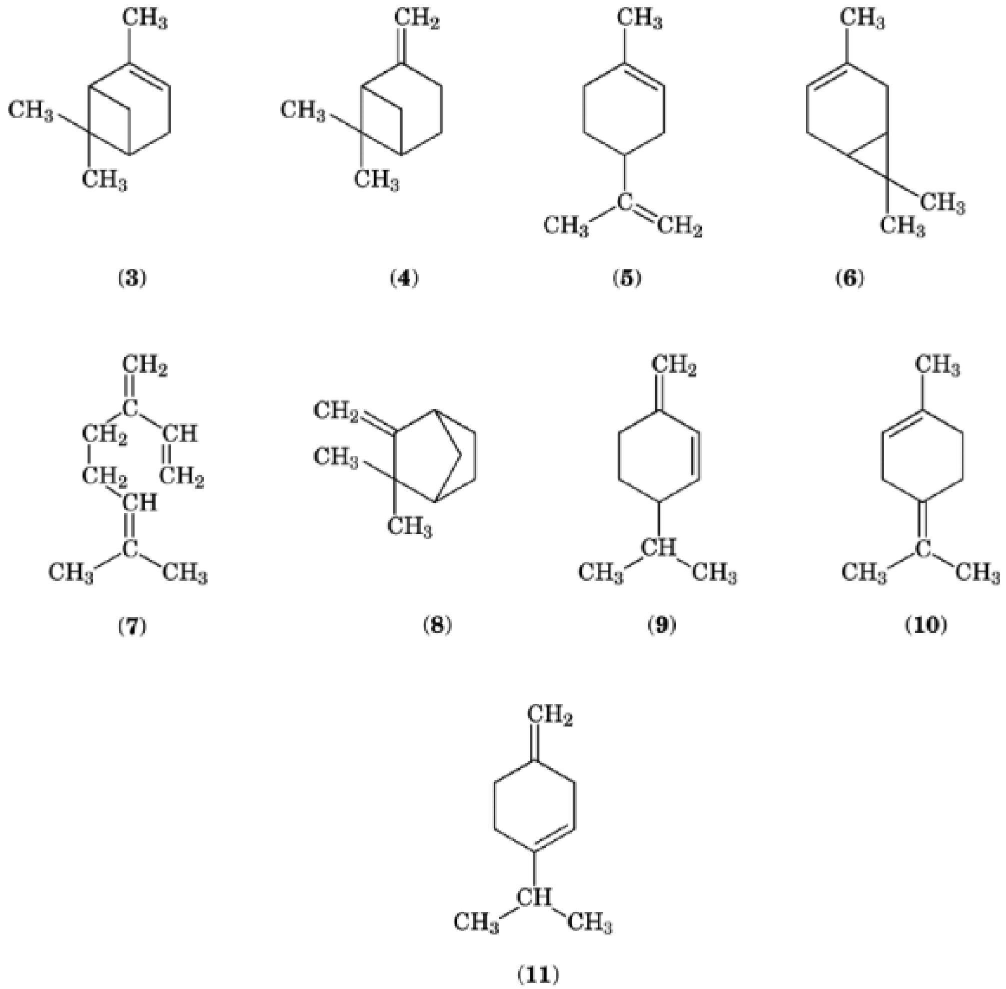


Fig. 2. Monoterpenes in hydrocarbon resins: α-pinene [2437-95-8] (**3**), β-pinene [18172-67-3] (**4**), limonene [7705-14-8] (**5**), 3-carene [13466-76-9] (**6**), myrcene [123-35-3] (**7**), camphene [5794-03-6] (**8**), β-phellandrene [555-10-2] (**9**), terpinolene [586-62-9] (**10**), and β-terpinene [99-86-5] (**11**).

6.0.13. Polymerization

Polymerization of monoterpenes is most commonly accomplished by carbocationic polymerization utilizing Friedel-Crafts-type catalyst systems, such as aluminum chloride. High energy radiation and Ziegler-type catalysts (83) have also been demonstrated to be effective. A number of Friedel-Crafts-type catalysts have been evaluated with respect to β-pinene (84). They are arranged here in a decreasing order of effectiveness: $AlCl_3 = AlBr_3$, $ZrCl_4$, $AlCl_3O(C_2H_5)_2$, $BF_3O(C_2H_5)_2$, $SnCl_4$, $BiCl_3$, $SbCl_3$, and $ZnCl_2$. Typical polymerization procedures entail the addition of monomer to a cooled solvent–catalyst slurry over a determined period of time. Routine reaction temperatures are 20–55°C, although some polymerizations may employ lower temperatures. Finishing procedures are identical to those used for catalytic petroleum resins.

Colors of commercial terpene-derived resins typically range from 2 to 5 Gardner. β-Pinene and limonene generally give better yields of hard resin than α-pinene in solution polymerization using $AlCl_3$. However, the addition of trialkylsilicon halides (85), silicon tetrahalides (86, 87), or dibutyltin dichloride (88) as cocatalysts have been shown to significantly improve the yields of α-pinene polymerizations. Typical cocatalyst ratios are 5:1, $AlCl_3$:R_3SiX ($X = Cl$,Br,I).

Particular drawbacks of using alkylsilicon and alkyltin halides with $AlCl_3$ for the cationic polymerization of terpenes are low yields and the fact that they require rigorously dried feeds ($\leq$50 ppm H_2O) to be effective. Increased water content results in lower yields and lower softening points (85). Catalyst systems comprised of $AlCl_3$ with antimony halides in the presence or absence of a lower alkyl, alkenyl, or aralkyl halide are particularly effective in systems containing up to 300 ppm H_2O (89, 90). Use of 2–12 wt % of a system composed of 2–3 parts $AlCl_3$, 0.7–0.9 parts $SbCl_3$, and 0–0.2 parts of an organic halide provides good resin yields (94% based on reactive monomers) and softening points greater than 110°C. Softening points of 150°C have been achieved for β-pinene resins produced with an $AlCl_3$–$SbCl_3$ catalyst system (90).

Organogermanium halide cocatalysts have also been shown to be effective in the cationic polymerization of less reactive terpenes, as well as other hydrocarbon streams (91). Slow addition of 300 g α-pinene to a slurry of 2 wt % $AlCl_3/(C_2H_5)_3GeCl$ (5:1, respectively) in 210 g xylene at $-15°C$ was followed by gradual warming to 20°C. Catalyst deactivation was accomplished with a volume of water equal to the value of α-pinene used. Atmospheric distillation followed by steam stripping yielded a 120°C softening point resin in a 96.7% yield based on reactive monomers (92). Addition of an organic halide to the $AlCl_3$–R_3GeX catalyst system reduces the amount of organogermanium halide needed without affecting yield or resin properties. This reduction results in a more economical catalyst system than the antimony, silicon, or tin-based systems (93, 94).

To avoid high resin chloride content associated with the use of high concentrations of aluminum trichloride, a trialkylaluminum–water cocatalyst system in a 1.0:0.5 to 1.0 mole ratio has been used in conjunction with an organic chloride for the polymerization of β-pinene (95). Softening points up to 120°C were achieved with 1–3 Gardner unit improvement in color over $AlCl_3$ produced resins.

Boron trifluoride etherate–*n*-hexanol complexes have successfully been used to polymerize β-pinene, as well as dipentene, to yield resins with softening points $\geq 70°C$ (82). Limonene or dipentene sulfate has been polymerized with aluminum chloride in a mixed toluene/high boiling aliphatic naphtha to give high yields of light colored resins (96). For the polymerization of dipentene or limonene, 4–8 wt % of $AlCl_3$ has been used. Polymerization of β-pinene typically requires lower levels of catalyst relative to limonene or dipentene.

6.0.14. Terpene Copolymers

Terpenes are routinely polymerized with other terpenes or with nonterpene-type monomers (97–102). The $AlCl_3$ catalyzed polymerization of β-pinene, dipentene, and terpene oligomers (oily dimers and trimers) has been found to yield resins with softening points ranging from 0–40°C (103).

Copolymerization of 10–40 wt % Δ-3-carene with a heat soaked C-5–C-6 olefin and diolefin stream under $AlCl_3$ catalysis has been shown to yield resins having softening points in the range of 60–140°C (104). These resins exhibit superior peel strength and tack properties over low softening point C-5 petroleum resins in pressure sensitive adhesive applications. Δ-3-Carene provides a rigid cyclic structure in the polymer backbone, which contributes to high softening points. This monomer also provides resins with narrower molecular weight distributions and better wax compatibilities than DCPD-modified resins.

A process of polymerization of isomerized α-pinene or turpentine with vinylbenzenes has been disclosed (105). α-Pinene or turpentine is isomerized by flash pyrolysis at $518 \pm 5°C$ in a hot tube reactor to yield a mixture of predominantly dipentene and *cis*-alloocimene (2,6-dimethyl-2,4,6-octatriene [673-84-7]). Catalytic copolymerization of the isomerized fraction with styrene yields resins with softening points ranging from 70–110°C and properties suitable for tackifiers in hot melt and pressure sensitive adhesive applications.

Equal portions of styrene and β-pinene have been copolymerized using a 1:1 $AlCl_3$–organic ketone complex to yield resins having narrower molecular weight properties, lower softening points, and lighter color than resins produced from $AlCl_3$ catalysis alone (106). This Lewis acid–ketone complex has been demonstrated to be

Table 5. Worldwide Hydrocarbon Resin Demand, 10^3 t

	United States		Europe		Asia		Total	
Resin	1980	1990	1980	1990	1980	1990	1980	1990
petroleum	197	304	97	127	48	137	342	568
natural[a]	121	239	109	173	72	60	302	472
Total	*318*	*543*	*205*	*300*	*121*	*197*	*644*	*1040*

[a] Rosin esters and terpenes.

effective for monomers of differing reactivities by producing unimodal molecular weight distributions. Although producing equivalent number average molecular weights (M_n) to polymerizations using the complex, $AlCl_3$-catalyzed polymerizations of β-pinene with styrene or C-5 dienes tend to yield resins with higher softening points and broad bimodal molecular weight distributions. Other Lewis acid complexes utilizing oxygenates such as alcohols, ethers, esters, or carboxylic acids tend to give high oligomer contents and lower yields.

Heteroatom functionalized terpene resins are also utilized in hot melt adhesive and ink applications. Diels-Alder reaction of terpenic dienes or trienes with acrylates, methacrylates, or other α, β-unsaturated esters of polyhydric alcohols has been shown to yield resins with superior pressure sensitive adhesive properties relative to petroleum and unmodified polyterpene resins (107). Limonene–phenol resins, produced by the BF_3 etherate-catalyzed condensation of 1.4–2.0 moles of limonene with 1.0 mole of phenol have been shown to impart improved tack, elongation, and tensile strength to ethylene–vinyl acetate and ethylene–methyl acrylate-based hot melt adhesive systems (108). Terpene polyol ethers have been shown to be particularly effective tackifiers in pressure sensitive adhesive applications (109).

7. Economic Aspects

The approximate regional demands for hydrocarbon resins in 1980 and 1990 are shown in Table 5. Based on these figures, the average worldwide total growth rate of petroleum resins from 1980 to 1990 was 22, 600 t/yr. The average worldwide total growth for natural resins for the same time period was 17, 000 t/yr. The projected annual growth rate for hydrocarbon resins through the early to mid-1990s has been approximated at 4–8% based on various sources. Production figures may be gained from the U.S. International Trade Commission reports or from various consulting firms, which specialize in monitoring hydrocarbon resin and related industries. Consumption and growth predictions with respect to specific end uses may also be gained from these sources.

8. Applications

Hydrocarbon resins are used extensively as modifiers in adhesives, sealants, printing inks, paints and varnishes, plastics, road marking, flooring, and oil field applications. In most cases, they are compounded with elastomers, plastics, waxes, or oils. Selection of a resin for a particular application is dependent on composition, molecular weight, color, and oxidative and thermal stability, as well as cost. A listing of all hydrocarbon resin suppliers and the types of resins that they produce is impractical. A representative listing of commercially available hydrocarbon resins and their suppliers is included in Table 6.

Table 6. Hydrocarbon Resin Suppliers

Manufacturer	Resin type	Trade name
Arakawa	C-9 aromatic, hydrogenated	Arkon
Arizona Chemical Co.	C-5 aliphatic	Betaprene, Sta-Tac
	C-5–-C-9 aromatic modified aliphatic	Sta-Tac
	polyterpene	Nirez, Zonarez
	modified polyterpene	Nirez, Zonatec
Eastman	DCPD, hydrogenated	Eastotac
Exxon	C-5 aliphatic	Escorez 1000 series
	C-5–C-9 aromatic modified aliphatic	Escorez 2000 series
	C-9 aromatic	Escorez 7000 series
	DCPD, nonhydrogenated	Escorez 8000 series
	DCPD, hydrogenated	Escorez 5000 series
Goodyear	C-5 aliphatic	Wingtack 95
	C-5–C-9 aromatic modified aliphatic	Wingtack Plus, Extra, 86
Hercules	C-5 aliphatic	Piccopale series
	C-5–C-9 aromatic modified aliphatic	Hercotac
	pure C-9 aromatic, nonhydrogenated	Kristalex
		Piccolastic
		Piccotex
	pure C-9 aromatic, hydrogenated	Regalrez
	DCPD, nonhydrogenated	Piccodiene
	polyterpene	Piccolyte
	modified polyterpene	Piccofyn
Interesin	C-9 aromatic	Norsolene
Lawter	C-9 aromatic	Petro Rez
Neville	C-5 aliphatic	Nevtac
	C-5–C-9 aromatic modified aliphatic	Super Nevtac
	C-9 aromatic	Nevchem

8.0.15. Adhesives

The largest use for hydrocarbon resins is in Adhesives (qv). There are numerous classes of adhesives, but the largest classes utilizing hydrocarbon resins are hot melt adhesives (HMA) and pressure sensitive adhesives (PSA). Hot melt adhesives are typically composed of a higher molecular weight polymer, a tackifier, a wax, and an antioxidant. HMAs do not utilize a solvent. Typical polymers that are used in HMA applications are ethylene–vinyl acetate (EVA), ethylene–methyl acrylate (EMA), and low molecular weight polyethylene. Depending on the comonomer content (eg, vinyl acetate) of the polymers (polarity), useful tackifiers may range from C-5 aliphatic to C-9 aromatic resins and rosin esters.

Pressure sensitive adhesives typically employ a polymer, a tackifier, and an oil or solvent. Environmental concerns are moving the PSA industry toward aqueous systems. Polymers employed in PSA systems are butyl rubber, natural rubber (NR), random styrene–butadiene rubber (SBR), and block copolymers. Terpene and aliphatic resins are widely used in butyl rubber and NR-based systems, whereas PSAs based on SBR may require aromatic or aromatic modified aliphatic resins.

Styrenic block copolymers (SBCs) are also widely used in HMA and PSA applications. Most hot melt applied pressure sensitive adhesives are based on triblock copolymers consisting of SIS or SBS combinations (S = styrene, I = isoprene; B = butadiene). Pressure sensitive adhesives typically employ low styrene, high molecular weight SIS polymers while hot melt adhesives usually use higher styrene, lower molecular weight SBCs. Resins compatible with the mid-block of an SBC improves tack properties; those compatible with the end blocks control melt viscosity and temperature performance.

In general, hydrocarbon resin tackifiers used in adhesive applications serve to enhance adhesion by increasing the wetting properties of a polymer. Increased wetting allows for extensive interfacial contact between the adhesive and a substrate. From a rheological standpoint, tackifiers serve to reduce the storage modulus of a particular polymer, while increasing the glass-transition temperature (T_g). This serves to enhance cohesive strength. Alternatively, Plasticizers (qv) tend to decrease the T_g of the system and reduce cohesive strength.

8.0.16. Printing Inks

Hydrocarbon resins are used extensively in printing inks and have replaced many of the natural resins that are used as the binder portion of Inks (qv). They perform well in heat-set letterpress, heat-set web offset, publication gravure, and lithographic printing inks. Hydrocarbon resins are also used in alcohol and water-based flexographic printing inks. Resins suitable for printing ink applications, specifically heat set and gravure inks, should have a reasonably high softening point (130–160°C), light color, good solubility in typical ink solvents, the ability to wet pigment, and a reasonably high solution viscosity.

For rotogravure printing, aromatic, functionally modified aromatic or aliphatic, and cycloaliphatic-based petroleum resins perform well in Type A and B rotogravure publication inks and Type T packaging printing inks. In heat-set inks, both web-offset and letterpress, the aromatic and functionally modified aromatic resins exhibit fast solvent release, good pigment wetting properties, solvency in ink oils, acceptable compatibility with alkyds and other film formers, and the tack required for good printing.

8.0.17. Rubber Compounding

Hydrocarbon resins are used in the production of various types of rubber-based products, including tires, shoe soles and heels, hoses, industrial belting, mats, electrical wire insulation, and roll coverings. Coumarone–indene and aromatic resins reinforce mineral-loaded SBR stock and increase tensile strength, elongation, and resistance to flex cracking. The aliphatic- and terpene-based resins are used as tackifiers for NR and NR/SBR combinations in the formulation of tires and molded goods. Aromatic modified aliphatic or functionally modified aromatic resins can act as both tackifying and reinforcing resins. Normally a range of 5–15 parts of resin per 100 parts of elastomer is used in rubber compounding.

8.0.18. Protective Coatings

Paint (qv) and varnishes for industrial and trade sale applications frequently contain hydrocarbon resins. Aromatic petroleum resins are incorporated into air-dry and low bake industrial primers containing medium and long-oil alkyds, as well as in gloss and semigloss industrial and trade sale enamels to speed up drying (see Alkyd resins). Aromatic resins are also employed in leafing aluminum paints to improve leafing properties and speed drying time, and in oil and varnish stains to increase penetrating characteristics and impart water resistance.

Nonhydrogenated dicyclopentadiene-based resins are oxidizable resins that develop a degree of solvent resistance in aged films. Their unsaturation causes copolymerization in Drying oils (qv) used in cooked varnishes and alkyds, and thus reduces drying time. Pure monomer resins are used in aerosol paints where they retain pigments in excellent condition and promote high gloss and fast solvent release. The low solution viscosity of these resins is also helpful in formulating these low solids coatings.

To control the degree of moisture evaporation and setting time, freshly poured concrete is sprayed with solvent solutions of aromatic, dicyclopentadiene, or aliphatic resins (see Cement).

8.0.19. Other Uses

Large quantities of hydrocarbon resins are used in mastics, caulks, and Sealants (qv). Polymers for these adhesive products include neoprene, butyl rubber, polyisoprene, NR, SBR, polyisobutylene, acrylics, polyesters, polyamides, amorphous polypropylene, and block copolymers. These adhesives may be solvent or water-borne and usually contain inorganic fillers.

Terpene resins, because of their low odor and acceptable FDA clearance, are used as tackifiers for the natural and synthetic gum bases used in chewing gum. Selected petroleum resins are also used as gum bases.

Coumarone–indene resins and styrene-modified aromatic resins, representing 20–30% of the binder portion, are used in the manufacture of light colored asphalt floor tile. Electrostatic toners used in copy machines employ resins made from styrene and styrene copolymer resins to disperse the pigment needed to produce the image. Comonomer resins composed of α-methylstyrene and vinyltoluene or styrene are used by dry-cleaning establishments as retexturizing agents to provide the proper hand, drape, and creasability to textiles after cleaning.

High softening point modified aliphatic resins are used as diverting agents for hydraulic fracturing, acid treating, and fluid loss operations in crude oil recovery. Key attributes of suitable resins are the solubility in crude oil and softening points high enough to accommodate application temperatures.

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