CHAPTER II

THEORETICAL CONSIDERATIONS

Rosin is a solid resinous material that occurs naturally in the oleoresin of pine trees. There are three major sources for rosin: from the oleoresin exudate of the living pine tree, from the oleoresin contained in the aged stump of the longleaf pine, and from the tall oil produced as a by-product in the kraft paper industry.

Rosin is a complex mixture of mainly resin acids and a small amount of nonacidic components. Its color, depending on the source and method of processing, can vary from a very pale yellow through dark red to almost black with a tinge of red. It is generally translucent, brittle at room temperature, and has a slight turpentine odor and taste. It is readily soluble in most organic solvents, such as ethyl alcohol, ethyl ether, mineral spirits, and benzene; it is insoluble in water.

Rosin as obtained from its three major sources is called unmodified rosin. Chemical treatment, such as hydrogenation, dehydrogenation, or polymerization, increases the stability and improves the physical properties of rosin through modification of the phenanthrene-derived moiety; the products are known as modified rosins. Unmodified and modified rosin may also be converted to carboxylic acid derivatives. These modified rosins and derivatives are of greater commercial importance than unmodified rosin. [1]

Production Method [1, 2, 3, 4]

There are three important methods of obtaining rosin commercially: distillation of the oleoresin from the living tree, solvent extraction of pine stump wood, and separation from tall oil.

1 <u>Gum Rosin</u>. The oleoresin of the living pine tree was once the only commercial source of rosin. The harvesting of the oleoresin is simple, requiring only wounding (scarification) of the tree and collection of the exudate. The streak of wound is sprayed with 50% aqueous sulfuric acid to stimulate and prolong the flow of exudate. The crude turpentine is collected by guiding the flow through gutters into metal cups. Before distillation, the collected crude turpentine was separated from the extraneous matter, such as bark, wood chips, etc., which floats on the surface of the molten rosin and is sometimes removed by skimming. The collected crude turpentine is carried to the still. Here the turpentine, to which a little water is added, is carefully heated to around 180-200°C to drive off the oil of turpentine present, together with the water added. The distillate is condensed by passing it through a coil around which cold water is flowing and collected in a barrel or any suitable containers. The two substances, water and oil of turpentine, which make up the distillate, are immiscible and soon separate, the lighter oil of turpentine rising to the top and floating on the water, which is drawn off from the bottom. Oil of turpentine is often called spirits of turpentine or in the paint trade, turpentine.

The hot residue (gum rosin) is drawn off the still into suitable containers such as tanks, drums, or bags, etc. The color varies widely, depending on the care exercised in collecting and processing the gum. The principal factor causing discoloration is heating for prolonged periods,

especially in the presence of minor amounts of iron salts, and high molecular weight materials.

2 <u>Wood Rosin.</u> Aged virgin pine stump is the source of wood rosin. It is allowed to remain in the ground for about ten years, so its bark and sapwood may decay and slough off to leave the heartwood rich in rosin. A typical analysis of an aged virgin pine stump, as it is received at the processing plant, shows 19% rosin, 4% turpentine, 4% of a gasoline-insoluble resin, 23% water, and 50% of cellulosic-and lignin-type materials.

The extraction of stump may consist of the following steps: (1) steam distillation to remove the oil, (2) heating to remove the excess moisture, (3) solvent extraction to remove the resin, and (4) steaming to remove the residual solvent from the chips. The preferred method is extraction of both the oil and resinous materials in a single step under pressure. To obtain the best results in the extraction of the resin a water-immiscible solvent is used. An aliphatic solvent is used for extracting only terpene and rosin-type materials, whereas aromatic solvents are employed to extract the additional resinous materials.

3 <u>Tall Oil Rosin.</u> [5] Tall oil contains 70-90% acidic material which is composed essentially of fatty and resin acids. In alkaline pulping processes, the acids present in the wood are solubilized in the hot cooking liquor. the spent liquor is partially concentrated and the brown curdy mass which floats to the top on cooking is skimmed off. this material, called soap skimmings, is reacted with mineral acid to obtain crude tall oil.

Tall oil can be used most effectively and profitably when separated into its two main fractions, the resin acids and fatty acids. Many processes for effecting the separation have been reported, based on the differences in both chemical and physical properties of the two classes of acids. One of the more effective means is fractional distillation of crude tall oil at reduced pressure. In

this process (Figure 2.1) crude tall oil is dehydrated to remove water completely and then flash distilled through a stripping tower to separate tall oil pitch. The vapors containing the resin acids, fatty acids, and volatile neutrals are passed through a continuous fractionating tower from which the highest-quality tall oil rosin is taken from the lower plates or off the bottom. Volatile odor-containing light ends are removed from the top of the tower. The intermediate or fatty acid fractions are collected and further fractionated to yield high-quality fatty acids and additional tall oil rosin as mixtures with varying amounts of fatty acids.

Commercial grades of tall oil rosin produced in this process contain as little as 2-4% fatty acids are of pale color, and have a high acid number.
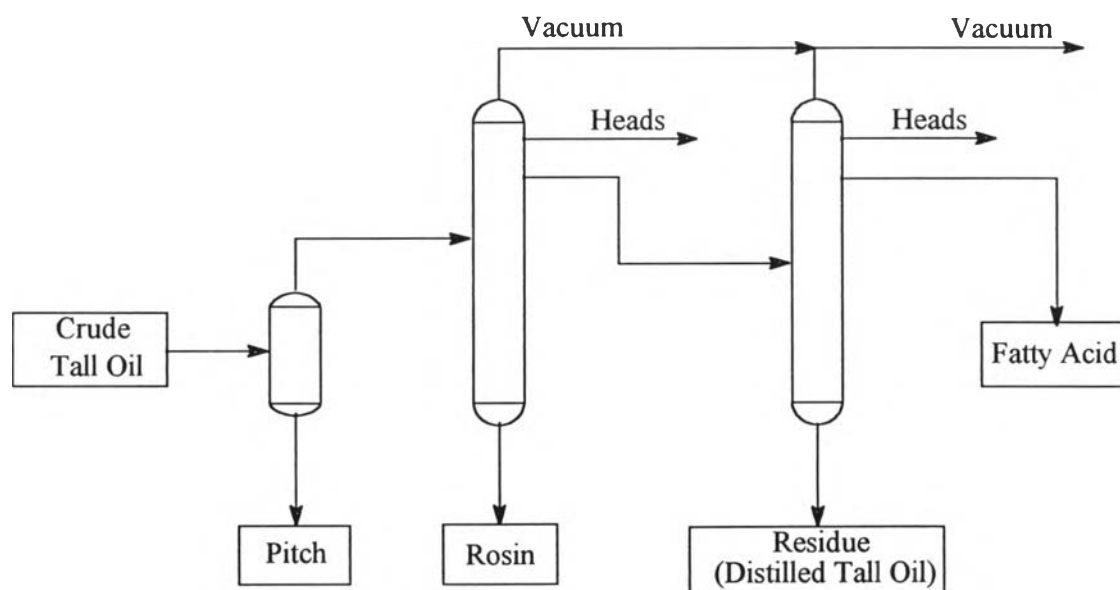
Figure 2.1 Process for producing tall oil rosin from crude tall oil.

Rosin Grades and Tests [2, 6]

Rosin is graded by color and tested for foreign matter, softening point, acidity, and sponification number.

1 <u>Color Grades</u>. The color varies considerably from very pale yellow to a dark reddish-brown and even black. Standards issued by the Department of Agriculture, USA, are designated by letters. Thus the darkest grades occur in the range from A to F, with the palest grades from N to X. A good series for adoption as color standards would include samples of D, E, F, G, H, I, K, N, WG, WW, and X. D grade is almost black. FF is specially reserved for wood rosin and is really a red F grade. WW is sometimes described as water white although this description is not strictly true. WG is described as window glass grade. Spectral transmission curves for rosins of each standard grade are shown in Figure 2.2.

Figure 2.2 Spectral transmission curves for rosin samples selected to match the glass standard in color

2 Foreign Matter. Rosin should be bright and clear and free from foreign substances such as dirt, sand, bark or wood chips. The amount of insoluble matter is determined gravimetrically by using toluene as a solvent according to ASTM D-269.

3 Softening Point. The preferred method for interlaboratory reference work is ASTM ring and ball softening-point method (E-28-58T). However, for control purposes, a more rapid method is frequently desired. The Hercules drop softening-point method is a typical widely used technique. It consists of determining the temperature at which a given weight of rosin begins to droop from the bulb of special standard thermometer mounted in a test tube immersed in a constant-temperature bath. Drop softening points determined by this method are quite reproducible and are a few degrees higher than those determined by the more tedious ring-and-ball method.

4 Acid Number. The acid number of rosin is expressed as the number of milligrams of KOH required to neutralize one gram of sample.

5 Sponification Number. The sponification number of rosin is expressed as the number of milligrams of KOH required to sponify one gram of sample.
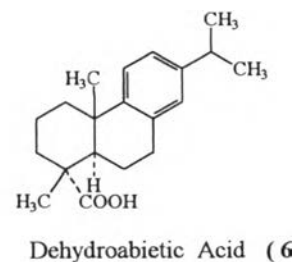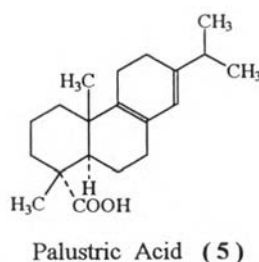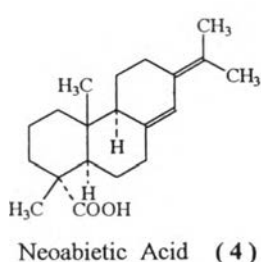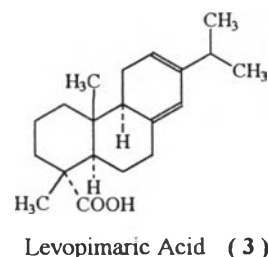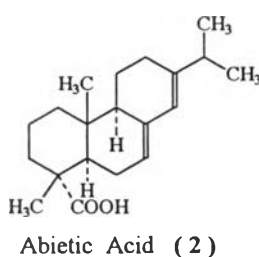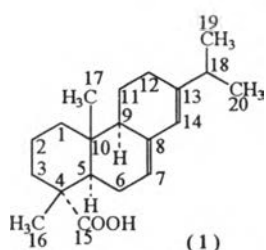
Use of Unmodified Rosins Unmodified rosin was used extensively in the production of printing inks, linoleum, vanishes, electrical insulation, foundry core oil, leather, matches, adhesives, paper sizing agent, resins for paint, and solder fluxes. In several instances it was not well suited for these applications because of three properties: the tendency to crystallize from the solvents employed, oxidation by atmospheric oxygen because of its unsaturation, and reaction with heavy metal salts as in vanishes.
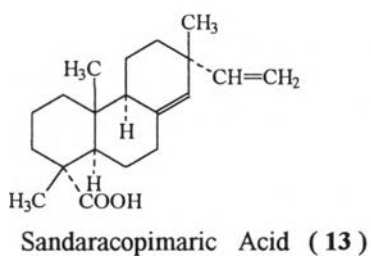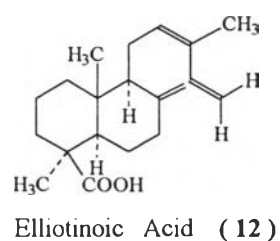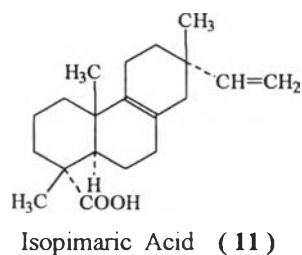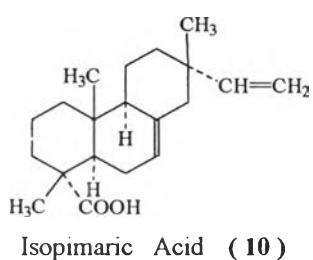
In present-day applications many of these difficulties have been eliminated by the development of processes to produce modified rosins and rosin derivatives. Today, more rosin is used modified than unmodified. The chief uses of the various rosin products are in the manufacture of paper size, synthetic resins, and rubber chemicals.

Composition Gum and Wood Rosins [2]

Just as the oleoresin from which gum rosin is obtained yields substantial quantities of split of gum turpentine, the stump wood from which wood rosin is obtained yields wood turpentine and other liquid products. The rosins derived from both oleoresin and aged stump wood are composed of approx. 90% resins and 10% nonacidic material.

Rosin is composed of resin acids which are monocarboxylic acid having the typical molecular formula $C_{20}H_{30}O_2$. Most naturally occurring resin acids contain two double bonds. The resin acids are divided into the abietic acid type (2)-(8); pimaric acid type (9)-(11); and other resin acids, (12) and (13).

Abietic Acid (2)

Levopimaric Acid (3)

Neoabietic Acid (4)

Palustric Acid (5)

Dehydroabietic Acid (6

Dihydroabietic Acid (7)
(3 probable)

Tetrahydroabietic Acid (8)

Pimaric Acid (9)

Isopimaric Acid (10)

Isopimaric Acid (11)

Elliotinoic Acid (12)

Sandaracopimaric Acid (13)
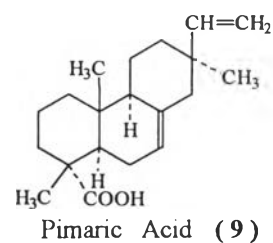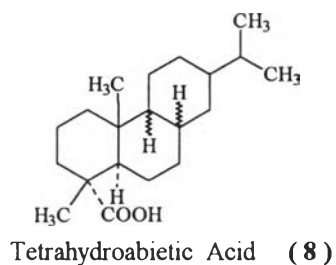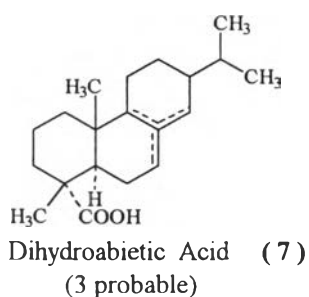
These resin acids are easily isomerized and oxidized by heating or acid. They are changed into the most stable abietic acid and oxidation products. Therefore, the rosin, which goes through the usual heat treatment process, is mostly composed of abietic acid. Some of the physical properties of the known resin acids and their methyl esters are tabulated in Table 2.1

Table 2.1 Physical Properties of Rosin Acids and their Methyl Esters

Sample	Mp, ^{O}C	$[\alpha]^{25}_{D}$ in	Spectrum (EtOH)	
		95% EtOH	λ, nm	ε
isopimaric acid	106-107	+113		
methyl isopimarate	68-70	+118		
elliotinoic acid		+40	232	29,000
methyl elliotinoate	105-106	+48	232	27,800
pimaric acid	217-219	+73		
methyl pimarate	68-69	+72		
sandaracopimaric acid	173-174	-20		
methyl sandaracopimarate	68-69	-21		
palustric acid	162-167	+72	266	9060
methyl palustrate	24-27	+67	265-266	8530
levopimaric acid	150-152	-276	272	5800
methl levopimarate	62-64.5	-269	272	5690
isopimaric acid	162-164	0		
methyl isopimarate	61.5-62	0		
dehydroabietic acid	173-173.5	+62	268,276	698,774
methyl dehydroabietate	63-64.5	+61	268,276	724,740
abietic acid	172-175	-106	241	24,150
methyl abietate		-96	242	24,300
neoabietic acid	171-173	+161	252	24,540
methyl neoabietate	61.5-62	+148	252	24,460

Partial hydrogenation of abietic-type acids under mild conditions, 250-270°C, results in the production of dehydroabietic acid. The abietic–type is readily susceptible to isomerization by heat or acid and to oxidation by atmospheric oxygen, whereas the pimaric–type is relatively stable under these conditions. The abietic-type acids are isomerized by heat or acid to an equilibrium mixture containing chiefly abietic acid.

Hydrogenation can result in a number of resin acid derivatives, depending on the reaction conditions. There are a number of dihydro isomers

obtained from the abietic-type acid, the most stable being the dihydro compound, and at least five possible dihydro acids from the pimaric acids. Complete hydrogenation of rosin gives a mixture of tetrahydro derivatives from acids of both abietic and pimaric types.

Reactions and Derivatives. [2]

The resin acid molecule possesses two chemically reactive centers, the double bonds and the carboxyl group. Through these, along with many modifications in structure and number of resin acids, the chemistry of its reactions is relatively complex. The reactions at the double bonds are intended to alter the double bond configuration of the two-double-bonds abietic–type acids. Therefore, for the sake of clarity, the description of reactions on rosin for the preparation of derivatives will be preceded by a description of the same reactions on the two- double-bond abietic-type acids.

1 Reaction at the Double Bond. [7, 8, 9, 10]

Isomerization The three abietic–type acids containing two conjugated double bonds (that is, abietic, neoabietic, and levopimaric acids) are unstable to heat and to acid condition. (The pimaric type, lacking the conjugating system of double bonds, does not undergo such changes). Isomerization is of practical significance in view of the changes that occur on processing oleoresin or wood extracts in the production of rosin and also because the reaction is used to produce more stable, modified rosins and derivatives.

When any of the three acids are subjected to heat or dilute acid, an equilibrium mixture of acids results in each instance. Thus, in a solution of 2 % hydrochloric acid in 95 % ethanol.

The equilibrium mixture from mineral acid isomerization of levopimaric acid was 4% palustric, 93% abietic, and 2% neoabietic acid; the equilibrium mixture of a thermally isomerized palustric acid was 13% palustric, 80% abietic, and 7% neoabietic acid.

These facts do not indicate the presence of any levopimaric acid in the isomerized mixture. Trace quantities, however, are assumed to be present as evidenced by the reaction of rosin with maleic anhydride.

Addition of Maleic Anhydride. The trace of levopimaric acid in the equilibrium mixture is assumed from the following evidence; levopimaric acid, by virtue of its double-bond configuration, conjugated within one ring, reacts with maleic anhydride at room temperature in the absence of mineral acid to form a crystalline Diels-Alder adduct in quantitative yield. Under similar condition, abietic and neoabietic acids do not react with maleic anhydride. However, if maleic anhydride is added to the equilibrium mixture (Scheme 2.1), reaction takes place at once with the trace of levopimaric acid. If the reaction is carried out in benzene in the presence of strong acid, more levopimaric acid is produced, again in trace quantities, and reacts with maleic anhydride so that the equilibrium is displaced and eventually the whole acid mixture resin acids and maleic anhydride is heated above $100^{\circ}C$. For example, if pure abietic acid is mixed with an equivalent amount of maleic anhydride and heated above $100^{\circ}C$ a quantitative yield of the adduct is obtained. The reaction proceeds at these temperatures through the formation of trace quantities of levopimaric acid which reacts with maleic anhydride to displace the equilibrium, thus permitting the formation of more levopimaric acid.

Frequently the adduct is used as the ester and prepared by reaction of glycerol or pentaerythritol with rosin and maleic anhydride. This is an example of the many instances in which both functionalities, the carboxyl group and the double bonds, must be altered to obtain a modified rosin with the desired characteristics. These esters are used extensively in protective-coating and printing-ink formulations. In the protective–coating industry they are intended primarily for compounding with film-forming materials to obtain lacquers or with drying oils to obtain faster–bodying and quicker–drying varnishes. Maleic acid–modified rosin esters contribute the properties of hardness, high luster, and adhesion in rotogravure inks, particularly those based on niaucellulose.

Fumaric acid also is used in large quantities to modify rosins for use in resins. Fumaric acid reacts more slowly than maleic anhydride but yields products of higher softening points. These resin are used primarily in printing inks.

Maleopimaric acid anhydride   Fumaricpimaric acid
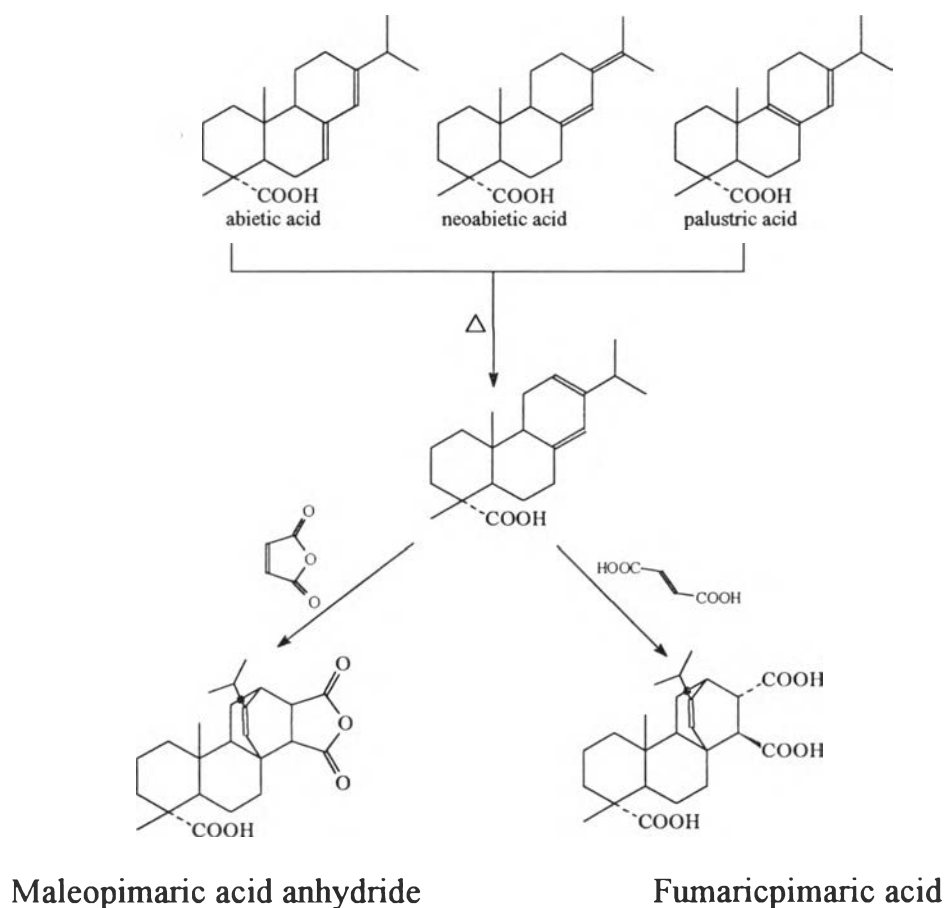
Scheme 2.1

Rosin-Modified Phenolics.[11]   The reaction between the abietic acid of rosin and *o*-phenol-alcohols facilitated by heating to temperatures in the range 150-300°C, yields chroman derivatives and water (Scheme2.2). Most of the carboxylic groups remain in the product and are usually esterified with glycerol or pentaerythritol in making the "modified resins" used in industry. This product finds application in low-cost paints used for the protection of metal in chemical plant.
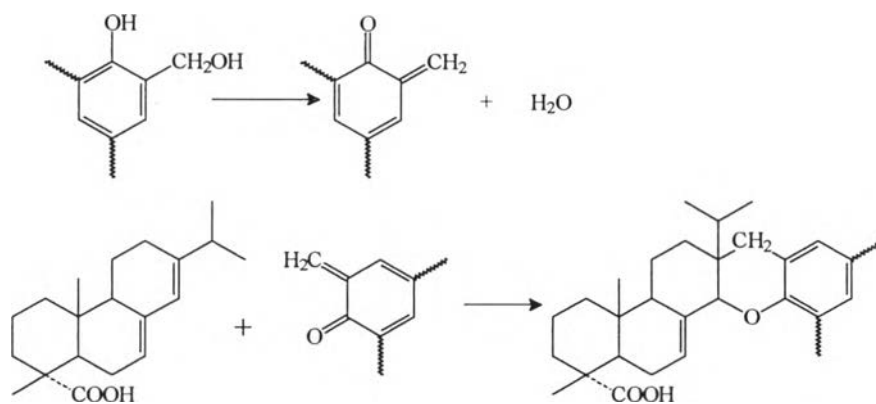
Scheme 2.2

Oxidation. [2, 12, 13] One of the more troublesome and therefore important reactions of resin acids is oxidation with atmospheric oxygen. The abietic-type acids with conjugated systems of double bonds readily take up oxygen, whereas the pimaric-type acids are relatively inert. A sample of pure abietic acid on exposure to air over a period of time takes on a decided yellow coloration. A simultaneous decrease in negative optical rotation and change in ultraviolet absorption characteristics (Figure 2.3) indicates the disappearance of the double-bond chromophore and hence saturation of the conjugated-double-bond system with oxygen. Scheme 2.3 shows some probable intermediates formed during the air oxidation of abietic acid. In one route the active methylene group at C-12 is attacked to form a hydroperoxide which decomposes to give a hydroxy or keto group in that position; in the other, the double-bond system is attacked with the formation of an epoxide which is opened to a glycol.
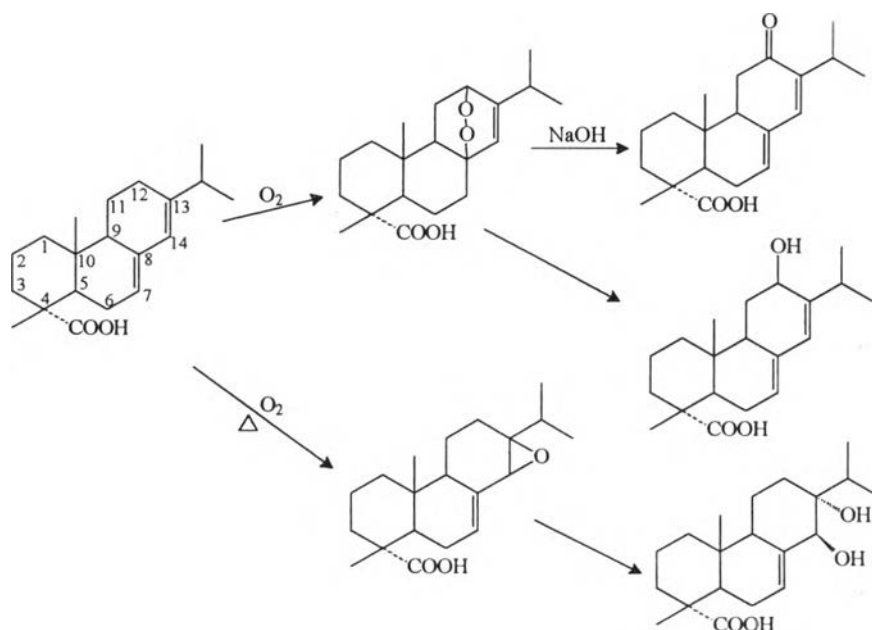
Scheme 2.3

Therefore, when rosin is exposed to air over a period of time, the exposed surface is oxidized to result in a product of considerably darker color, and for most uses of lower value. Similarly, lower-grade rosins are obtained from the molten material which is allowed to come in excessive contact with air during the refining process.

Other Oxidation. An alcoholic solution of levopimaric acid containing a sensitizing dye, e.g., methylene blue, readily absorbs one mole of oxygen when contacted with air to produce quantitatively a peroxido, 8,12-peroxido−13,14-dihydroabietic acid, by 1,4-addition. All the dienoic acids in rosin or crude pine-gum oleoresin, excepting abietic acid, react under similar photolytic conditions. Identical or similar products have been prepared by oxidizing levopimaric acid, pine-gum oleoresin, and rosin with singlet oxygen

from the reaction of hydrogen peroxide with sodium hypochlorite. Epoxidation and ozonolysis of resin acids have been studied rather extensively but the products have little industrial significance.

As the oxidation of abietic-type acids and rosins depends on the conjugated system of double bonds, any method for minimizing air oxidation of rosins should have as its basis the alteration of these double bonds. Such reaction as hydrogenation, dehydrogenation, and polymerization have been employed commercially to produce more stable rosins. Comparative oxygen-absorption data of rosins and some derivatives are shown in Figure 2.3. It can be seen that hydrogenation reduces to a minimum the tendency of rosin to absorb oxygen. Also the transformations in resin acids that occur during esterification reactions result in considerably decreased oxidation

Figure 2.3   Oxygen absorption by rosin derivatives at room temperature and 300 Psi of oxygen

Hydrogenation. [2, 14, 15] Hydrogenation is one of the more satisfactory methods for decreasing the susceptibility of rosin to air oxidation. Because of the structural features of the resin acids, more vigorous conditions are necessary than with ordinary olefins. Reduction with heavy metals and mineral acid or with sodium amalgam and water accomplishes only partial hydrogenation even for one double bond; on the other hand, molecular hydrogen in the presence of noble metal catalysts such as palladium or platinum, will saturate one or both double bonds depending on the polarity of the solvent employed. By taking advantage of solvent effects, the desired selectivity can be obtained with platinum oxide or palladium-carbon catalyst. One double bond is hydrogenated efficiently in hydrocarbon solvents such as methylcyclohexane; hydrogen absorption stops sharply after one mole. Complete hydrogenation to the saturated acid is accomplished in glacial acetic acid. The hydrogenation reaction is used successfully for the quantitative determination of the degree of unsaturation of rosin and its derivatives.

The relative ease of hydrogenation of the resin acids in wood and gum rosins is very nearly the same as that described for the pure acids. The first double bond, activated by conjugation, is hydrogenated with ease, whereas the second is resistant to hydrogenation under the same conditions. The residual double bond is also highly resistant to air oxidation so that much of the desired stability is obtained even by hydrogenation to the dihydro stage. This type of hydrogenation may be carried out by passing the molten rosin over Raney Nickel catalyst at 230°C under 125 atm of hydrogen pressure for 5 hours. Under these conditions most of the color components on refined rosins are bleached to produce an almost colorless product.

A typical analysis of the various types of acids in hydrogenated rosin shows only two changes, a decrease in two double-bond types of acid from 74 to 3%, and an increase in dihydro acid from 1 to 75%; hence, the overall

change is conversion of the former to the latter. The more highly hydrogenated rosins have a–double–bond–type acids with about 1–4% dihydro acids and 66–80% tetrahydro acids.

Because the hydrogenated rosin product is so oxidation resistant, it is used as a softener, tackifier, and plasticizer with natural as well as synthetic rubber. For pressure-sensitive adhesives used in industeial tapes made from synthetic rubbers, an ester is more suitable than a nonesterified hydrogenated rosin. However, in surgical tapes where natural rubber is used, the hydrogenated rosin itself is adequate. In the production of high-grade papers, however, where resistance to discoloration and retention of sheet brightness are of fundamental importance, an oxygen-resistant rosin must be used. The sodium salts of hydrogenated rosins also are used in the form of the carboxylic derivatives (esters) for specialty applications where resistance to air oxidation and discoloration by heat are of importance. Examples are chewing gum and hot-melt-applied coatings and adhesives.

Disproportionation (Dehydrogenation) [1, 15, 16, 17, 18] The disproportionation reaction is the second means of effectively modifying rosins to render them less susceptible to oxidation by atmospheric oxygen. In effect the reaction consists of the removal of two atoms of hydrogen from the two double-bond abietic-type acids and the rearrangement of the double-bond system to form an aromatic nucleus in the production of dehydroabietic acid (Scheme 2.4). Part of the hydrogen that is removed, is readily absorbed by other two-double-bond abietic-type acids present in rosin to produce the stable dihydroabietic acids and tetrahydroabietic acid.

The reaction is brought about by mineral acid and is greatly enhanced by the use of such disproportionation catalysts as iodine, sulfur, selenium, or noble metal on carbon supports. When the reaction is carried out

at higher temperatures, above 300°C, in the presence of catalyst (Scheme 2.4) complete dehydrogenation is obtained to produce the parent hydrocarbon, retene and pimanthrene.
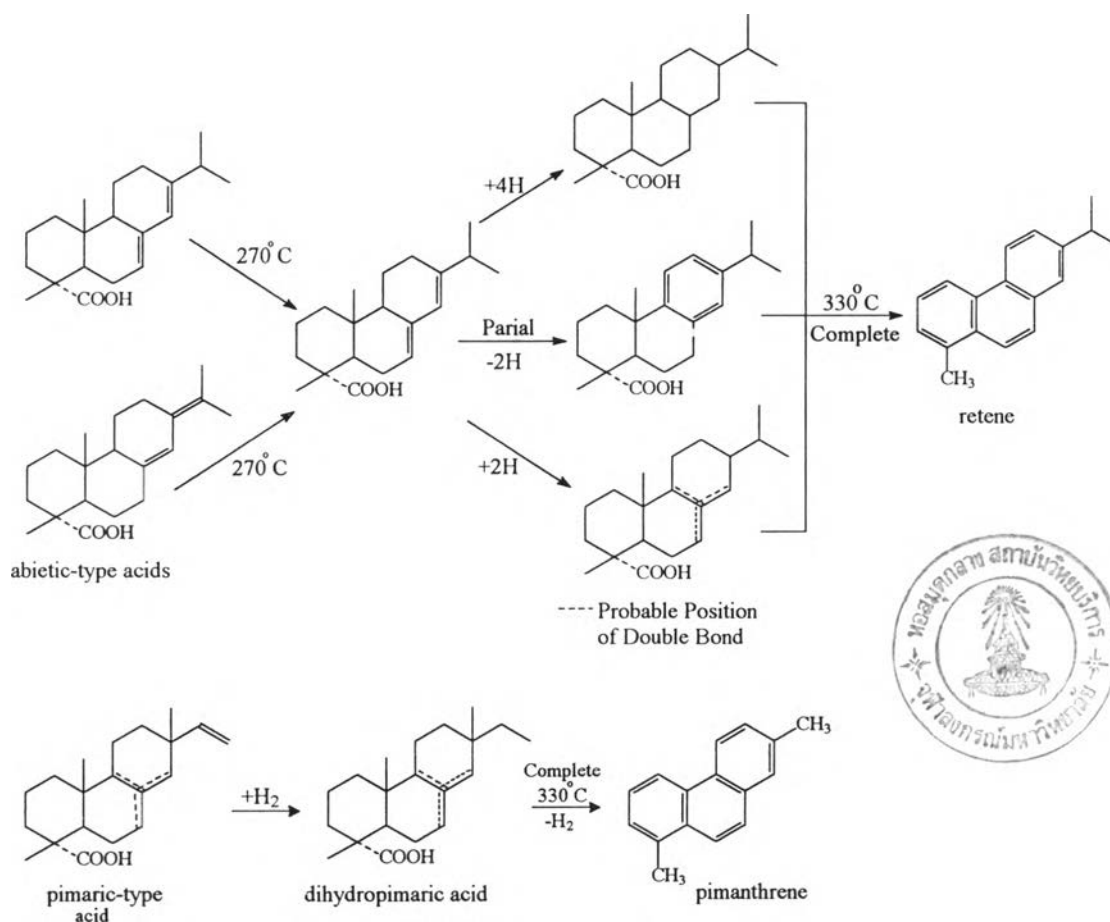
Scheme 2.4

An important use of dehydrogenated rosin is in the form of the sodium or potassium soap, as an emulsifier in the production SBR-type synthetic rubber at 50°C with peroxysulfate catalyst. In peroxysultate recipes, a soap of unmodified rosin is not suitable as an emulsifier because of the

detrimental effect of even small amounts of abietic acid on the polymerization rate.

Synthetic rubber produced with the aid of a carefully prepared dehydrogenated rosin is more tacky than SBR made with a fatty acid soap emulsifier, and is therefore superior for tire building. In addition, improved resistance to heat buildup, superior hysteresis properties, higher tensile strength and elongation, improved tear resistance, and better reinforcement in low-black compounds and non-black pigment loading add up to make a superior rubber.

More recently, sodium and potassium soaps of dehydrogenated rosin have been accepted generally for the production of "cold rubber" (SBR made at 5°C) produced by hydroperoxide-catalyzed redox recipes. These modified rosin soaps have the same advantages over fatty acid soaps at 5°C as they do at high temperatures. In addition, the soaps are more soluble at this temperature than are the sodium soaps of hydrogenated tallows and greases, which are commonly used in emulsion polymerization at higher temperatures.

Similarly, modified rosin soaps are used in other emulsion polymerizations, as of chloroprene to neoprene.

Other uses of commercial dehydrogenated rosin which depend on its relative stability to oxidation are as a compounding ingredient for rubber and as a raw material for manufacture of synthetic resins.

Polymerization. [18, 19] The abietic-type acids that are readily degraded by air oxidation also can be stabilized under conditions which result in their polymerization. Commercial polymerized rosin is prepared by the action of an alkyl or metal halide or inorganic acid on rosin at room temperature over an extended period of time. Methanesulfonic acid and its halogenated derivatives are used as catalysts for polymerization of rosin.

Their activity in promoting the polymerization of rosin are ordered from methanesulfonic acid (least reactivity) through partially halogenated and fully halogenated derivatives to trifluoromethane sulfonic acid (most reactivity). Polymerization of a rosin is carried out by heating the rosin to a temperature in the range of 60–180°C in the presence of a catalytic proportion of the methane sulfonic acid (0.3–1% by weight of rosin). The product, having a high dimer acid content, resists crystallization for moderate periods of time.

The polymerization of rosin occurs in the presence of a catalytic proportion of formic acid (1:1 to 3:1 by weight) on heating the mixture to a temperature in the range 90–150°C. Polymerization is complete within about 1 to 12 hours and produces 27–45% of dimerized rosins.

Many uses for polymerized rosin have been developed based on its desirable properties, such as high softening point, high viscosity of solution, and resistance to oxidation and crystallization. As in the case of the other forms of modified rosins, polymerized rosins, through reaction of the carboxyl group, have been converted to products such as salts, esters, and alcohols

A polymerized rosin has the advantage that it requires less glycerol than does unmodified rosin, because of its lower acid number, to obtain an ester of low acid number and high softening point. Metal salts of polymerized rosin are well adapted for use in varnishes, dryers, printing inks, and adhesives. As compared to similar salts made from unmodified rosin, they are harder, more viscous, and more resistant to oxidation. Solutions in organic solvents do not crystallize. Some of the physical properties of modified rosins are shown in Table 2.2.

Table 2.2 Important Properties of Rosin and Modified Rosins

Property	Rosin	Hydro–genated	Highly Hydro–genated	Dehy–drogenated	Poly–merized
acid number	163	165	160	153	152
saponification number	168	167	163	155	148
color, U.S. rosin std.	WG	X	<X	WG	WW
softening point, ^{o}C	81	75	75	80	102
refractive index at 20 ^{o}C	1.5453	1.5270	1.5360	1.5379	1.5440

2 Reaction at the Carboxyl Group.[1, 2]

In addition to the double-bond reactions, resin acids also undergo typical carboxyl group reactions. Salts and esters of rosin are important commercial derivatives of rosin.

Salt Formation. Salts of resin acids, such as sodium, calcium, zinc, and aluminum, are normal with the exception of the 3:1 resin acid aluminum salt, in which one molecule of the normal salt crystallizes with three molecules of the free acid. The sodium salts of the various resin acids vary markedly in their solubility in water. Those of abietic, neoabietic, and isopimaric acids are quite soluble, whereas those of levopimaric and pimaric acids are very insoluble in water. It was by this means that the last two acids were isolated from the oleoresin. The sodium salt of rosin is important commercially and is used extensively in soaps, sizing of paper, and emulsions of the oil-in-water type.

Resinates of heavy-metal salts can be prepared by one of two methods, precipitation or fusion. The precipitation method consists of the addition of a solution of the heavy-metal salt to a solution of the sodium soap of rosin at 40-75°C, thus precipitating the insoluble metal resinate, which is filtered, dried, and pulverized. Fused resinates are prepared by heating the rosin with the metal hydroxide, metal oxide, or the metal salt of a volatile organic acid.

Calcium resinate, or limed rosin, finds use in low-cost protective coating, where it serves to thicken the vanish and increase the hardness of the dried film over that obtainable with rosin alone. The type of lime used in the preparation of limed rosin is of particular importance; a high grade of hydrated lime should be used with a small amount of calcium acetate. The hydrated lime should be as free as possible of iron, manganese, and silicates. Solid limed rosin, particularly that made from polymerized rosin, has found extensive use in gravure inks.

Zinc resinate has interesting properties, such as dispersing action on gels, low reactivity with drying oil, and compatibility with ethylcellulose. In the preparation of the resinate by the fusion process, zinc oxide causes blocking. this difficulty is readily eliminated by the use of polymerized rosin, which does not form a crystalline zinc salt, or by the addition of calcium acetate which results in mixed zinc calcium resinates.

Metallic resinates find use also in ceramic colors, pyrotechnics, tile adhesives, and generally where a harder and less acidic thermoplastic resin than rosin is required.

Esterification. [20, 21, 22] The structurally hindered nature of the resin acid carboxyl group makes it necessary to use higher temperatures or generally more drastic conditions to bring about esterification. This hindrance

is, in turn, responsible for the unusual resistance of the ester linkage to cleavage by water, acid or alkali. The polyols employed in the esterification are also well known and are represented by diols such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol; triols such as glycerol; tetrols such as pentaerytritol; and hexols such as mannitol. The esterification step is carried out in the presence of esterification catalysts such as calcium hydroxide, zinc oxide, phosphoric acid, p–toluene sulfonic acid, lithium carbonate and the like. Esterification is carried out by bringing together the rosin and an equivalent excess of the polyol in an appropriate reaction vessel and heating the mixture to a temperature within the range of about 150–300°C under an inert atmosphere, such as a nitrogen gas atmosphere.

Uses of Rosin Esters. [2, 20, 21, 23]   Ester gum is used extensively in cellulose ester lacquers for interior applications because of its low cost, solubility in lacquer solvents, and the desirable properties it imparts to the lacquer. The use of ester gum in nitrocellulose lacquer increases the solids content, improves adhesion to wood, metal, and glass, and improves the gloss of the lacquer film. The requirements for an ester gum for this purpose are a low acid number and light color. There are several instances where reactions at both the carbonyl group and at the double bonds of rosin are carried out to obtain product with the desired properties. Examples are maleic-modified glycerol and pentaerytritol esters which are high-melting resins used in printing inks, coatings, and adhesives.

The hydrogenated methyl ester of rosin which acts both as resin and plasticizer, is a valuable constituent of lacquers for interior wood and furniture applications. Inexpensive, clear lacquers for wood-furniture gloss finishes can be improved measurably in adhesion, luster, and distensibility by replacing part of the hard resin with this liquid resin. It has been used

extensively as a plasticizer for film formers, such as ethylcellulose, chlorinated rubber, and some vinyl resins.

Varnish manufacturers prefer to use the soft domestic drying oils such as linseed, fish, and soybean, as they are lower in cost than tung oil. Because ester gum does not produce a satisfactory varnish with these oils, pentaerytritol esters of rosin were developed, Like other rosin esters, these are varied properties based on the type of rosin used in their manufacture as well as by modification with maleic anhydride and phenol-formaldehyde condensates. The pentaerythritol esters of rosin are prepared at temperatures sufficiently high so that some dehydrogenation takes place to form a more stable, nonoxidizable resin. Heat stability, along with a high softening point of about $135^{\circ}C$, makes the pentaerytritol ester very satisfactory for use in varnishes based on soft drying oils.

Esters of rosin and modified rosins are used in many adhesive compounds as tackifying resins in combination with rubber, waxes, synthetic rubber, and other elastomers, particularly in hot-melt adhesives. The glycerol ester of hydrogenated rosin is used in chewing gum.

Decarboxylation. [1, 2] Rosin can be decarboxylated with 5% zinc chloride as catalyst at $120–200^{\circ}C$ to obtain a 75% conversion to rosin oil. Phosphorus pentoxide can also be used in decarboxylation of rosin. The light oil obtained from decarboxylated resin acids, is the main fraction (Table2.3). A similar mixture obtained also when no catalyst was used at higher reaction temperatures on a commercial scale.

Rosin oil once was used extensively in paper-wrapped cables, greases for skidways, rubber reclaiming, linoleum, shoe polishes, and foundry core compounds.

Table 2.3 Products from Decarboxylation of Rosin

Product, %	Catalyst		
	ZnCl$_2$	P$_2$O$_5$	None
Gas	8.5	7.5	
Water	3.8	3.5	
Rosin spirits	4.5	8.0	6.0
Light oil (bp 215-260°C)	52.6	52.5	70.4
Heavy oil (bp 260°C and above)	17.5	10.0	23.5
Residue	8.7		