INTRODUTION

1. INTRODUCTION

As the availability of oil and petroleum fractions has become very uncertain, this has resulted in a severe competition for oil between uses as fuel for energy and as feedstock for petrochemicals. Although the entire petrochemical industry (including fertilizers and synthetic polymers) consumes less than 10% of the supply of crude oil, the greater demand for fuel for energy makes uncertain the future supply of feedstock for petrochemicals at a reasonable price. The cost advantage of polymer materials in general over the other conventional materials has already been eroded considerably by the price rise of crude oil. Never before have plastics been faced with such tough competition from traditional materials like metals, alloys, glass, etc. This scarcity and high price of crude oil has led to research and development activities worldwide for the use of alternative, preferably renewable, resource materials as feedstock for polymers and petrochemicals.

In an attempt to find a suitable alternative and renewable substitute for petroleum-based and allied chemicals we have recently developed rosin-maleic anhydride Diels-Alder Adduct from gum rosin and maleic anhydride. Gum rosin is made to react with maleic anhydride to form the Diels-Alder adduct. The Diels-Alder adduct, MPA, is also known as maleopimaric acid. The molecule of MPA contains one carboxyl group and one anhydride group; the two reactive functionalities capable of undergoing various chemical reactions with appropriate reagents. The hydrophenanthrene ring system present in the rosin moiety of MPA offers thermal and oxidative stability to the MPA molecule. It is expected from the above structural similarities that MPA may be a suitable substitute for petrochemicals in most, if not all, of its

applications. Since rosin is a cheap and renewable material, the price of MPA and its derivatives is expected to be lower than that of petrochemical derivatives. The most important point to be noted here is that the supply of rosin will be unhindered as this is derived from a forest product abundantly available in India and many other countries.

Throughout history, the early Egyptians and Persians were known to employ gum Arabic as a binder for preparing their varnishes, and the ancient Chinese and Japanese were also known to use sap tapped from trees as vehicles in the preparation of protective lacquers [1]. Thus the coatings industry has historically been a large user of renewable resources such as seed oils and wood derivatives primarily because of availability. The Arab-Israeli war and the subsequent oil embargo of 1973 resulted in dramatic OPEC oil price increases. The recent war in the Gulf was also in part due to the supply of World oil. Both events reflect the fact that we are becoming increasingly dependent on the use of fossil fuels despite the continued decrease in global oil reserves. On the other hand, the extensive use of fossil fuels is a major contributor to global warnings. It has been estimated that if present trends in greenhouse-gas emissions continue, the earth could be committed to a warming of 1.5-4.5 ^{o}C by the middle of the next century. The key to preventing global warming is to reduce World consumption of fossil fuels by 50% or more over the next several decades [2]. With the exhaustion of readily accessible petroleum and natural gas looming in the future, and the increasing environmental concern, a shift back to an emphasis on renewable resources for raw materials is becoming imminent. It will be too late if and when the coatings industry has to be regulated by another 'Rule' or 'Act' to restrict the use of raw materials

when coal and petroleum are near exhaustion. Thus, the need to seriously consider renewable resources in coating technologies is clear. Rosin, being one of the important renewable resources, has in the past found its use in many coating applications such as adhesives, varnishes and printing inks [2]. This is largely due to factors such as fast drying properties, excellent solubility and compatibility with other resins and oils, economy and ready availability. However, the use of this renewable raw material has declined slowly since the 1950s this decline can be attributed to the increased supplies of petroleum-based resins.

Contemporary polymer synthesis places a strong demand on good control of molecular architecture. This requires a good understanding of rosin chemistry if it is to be considered as a polymer intermediate for protective coating applications. The large amount of work done in the early to mid parts of this century on the chemistry of rosin, such as isomerization upon heating, can be complicated and easily forgotten. The purpose of the next section is re-exploring knowledge of rosin chemistry and to discuss various aspects of rosin modification and its implications for protective coatings.

1.1 CHEMISTRY OF ROSIN

The chemical composition of various wood species generally consists of 35-45% cellulose, 25-35% lignin, 20-30% hemicellulose and 2-5% extractives where rosin is found. The content of extractives and their composition vary greatly among different wood species and also within different parts of the same tree. They consist mainly of rosin, fatty acids, phenolic compounds and a large variety of terpene derivatives [3]. Furthermore, the extractives content increases after the death of a living

tree due to chemical changes. Up to 12-14% extractives were found in some dead pine species [3] and up to 27% of extractives were reported for an aged virgin pine stump [4].

There are three important methods for obtaining rosin commercially:

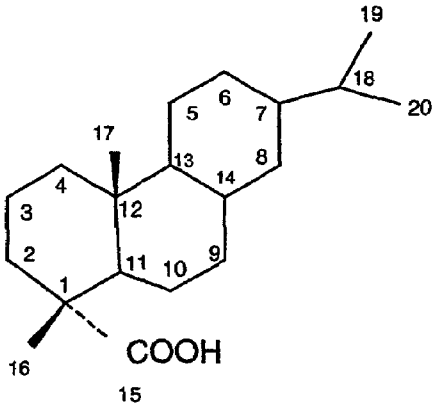
(1) Distillation of volatile turpentine from oleoresin exuded from the wound of living pine trees to obtain gum rosin;

(2) solvent extraction of pine stump wood along with the removal of the turpentine by steam distillation to obtain wood rosin; and

(3) separation of tall oil to obtain tall oil rosin.

However, since 1949s new facilities designed to recover and fractionate practically all of the crude tall oil in the pulp industry has made tall oil rosin the major source of rosin [4, 5]. The name 'tall oil' originates from the Swedish word 'tall' which means pine [5]. Traditionally, pine wood is the major source of rosin. The pulp and paper industry is the largest consumer of pine. Their principal method of separating extractives from the cellulose fibers of wood is by the sulfate or Kraft process. Generally this process involves the digestion of wood chips with sodium hydroxide and sodium sulfide under heat and pressure to form a highly alkaline solution of sodium salts. After a few washings, the fatty acid and rosin soaps are separated by skimming. Acidification with sulfuric acid yields a crude mixture of rosin and fatty acid which then undergoes acid refining or fractionation [3, 6]. The acid refining process removes odor bodies, such as mercaptans and disulfides, and a large portion of colored materials. It also dimerizes a portion of the rosin and fatty acids, which eliminates the crystallizing tendencies of the rosin. In the fractionation process, distillation temperatures of up to 280 °C [7] are used. Two major fractions are obtained: a fatty acid fraction and a rosin fraction. The

reported contents of rosin fractions in softwood, such as slash pine, are 47% [8]. Very little rosin is found in hardwood such as birch [3]. The rosin obtained from the above process is called tall oil rosin. At present, the US gum rosin industry is almost extinct since it is a labor-intensive industry. As a result, since the 1960s, the US imports a great deal of its gum rosin primarily from Portugal, Brazil and the People's Republic of China. Similarly, only one company in the US, Hercules Inc., produced wood rosin by 1989s. It should be noted that all rosin sold in the US must be described by reference to the US Standards, and subject to grading (ASTM D-509-70) based on its color or appearance (e.g., grade X, WW, WG, N and others) prior to such sale. The principal components of rosin are rosin acids, which are monocarboxylic acids of hydro-phenanthrene. Rosin acids occur in pine in a number of isomeric forms having the molecular formula $C_{20}H_{30}O_2$. Sixteen rosin acids have been identified by gas chromatography-mass spectrometry (GC-MS) in Finnish tall oil rosin [7]. The composition of rosin also depends on where the pine trees are grown and the separation process used [8]. Generally, the rosin acids can be divided into two subgroups: the pimaric type acid, characterized by both methyl and vinyl substituents at the C-7 position; and the abietic-type acid, bearing only a single isopropyl group at this position as shown in 1. The numbering system used in this review adheres to the rules for naming rosin acids as derivatives of abietane and pimarane from Klyne [9].



(1)

The structures of some of the important rosin acid isomers including abietic (2) levopimaric (3), palustric (4), neoabietic (5), dehydroabietic (6), dihydroabietic (7) and tetrahydroabietic (8) acids are shown in **Table (1.1)**. The distribution of these isomers found in pine trees varies depending on their geographic location and, perhaps equally important, on the thermal history of the rosin [9-12]. Gum rosin has total abietic-type acids of 60-65% [17], but Finnish tall oil rosin has only 39-47% [9]. It has been shown [9] that rosin acid composition between crude tall oils and tall oil rosin changes substantially during the high-temperature fractionation process. One of the most obvious changes is the large increase in the more stable dehydroabietic acid from 17.8-18.2% to 30.2-37.6% and a corresponding decrease in abietic acid from 52.9-54.9% to 32.5-39.8% [3]. Furthermore, some of the rosin acids originally not present in crude tall oil are found after distillation [6]. This is mainly due to the decomposition, dehydrogenation, isomerization and disproportionation reactions taking place during fractionation. The melting points of rosin acids and the compositional data for different rosins are given in **Table (1.2).**

Table (1.1): Structures of Major Rosin Acid Isomers

Isomers	Double-bond positions
abietic acid (2)	C-7,C-8 and C-9, C-14
levopimaric acid (3)	C-6, C-7 and C-8, C-14
palustric acid (4)	C-7, C-8 and C-13, C-14
neoabietic acid (5)	C-8, C-14 and C-7, C-18
dehydroabietic acid (6)	aromatic in the ring bearing Isopropyl group
dihydroabietic acid (7)	one double bond among C-9, C-14, C-13 and C-8 (three probable)
tetrahydroabietic acid (8)	none

Table (1.2): Composition of Tall oil, Gum and Wood Rosin.

Rosin acids	Melting point(°C)	Tall oil rosin (wt.%)	Gum rosin (wt.%)	Wood rosin (wt.%)	Ref.
abietic	172-175	27-37	18-33	39	11
neoabietic	167-169	4-5	14-16	10	11
palustric	162-167	10-14	6-35	12	12
pimaric	217-219	1-2	5-6	7	12
isopimaric	160	8-15	18	20	12
dehydroabietic	171-172	29	6-9	8	12
levopimaric	150-152	-	-	-	12

1.1.1 Isomerization of rosin acids

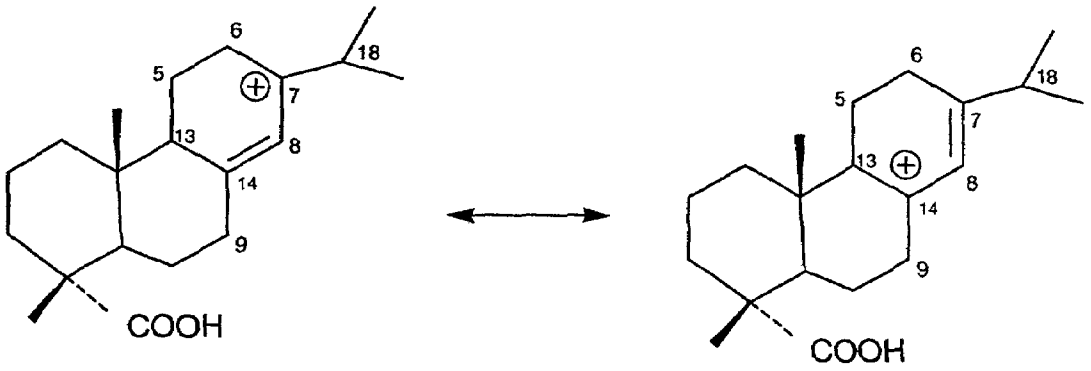
The pimaric-type acids, including pimaric and isopimaric acids, contain non-conjugated double bonds. They are more stable to heat than the abietic type rosin acids including levopimaric, palustric, abietic and neoabietic acids which contain two conjugated double bonds. Migration of the whole diene system to an adjacent position should be expected when these rosin acids are heated to above their melting point.

1.1.1.1- *Isomerization of abietic-type rosin acids*

The establishment of the isomerization among the various rosin acids was a result of much work during the 1940s and 1950s with the use of improved separation techniques, such as chromatographic and ultraviolet absorption analysis [11]. This led to the identification of neoabietic acid [12], isopimaric acid and palustric acid [13].

a- Acid-catalyzed isomerization of rosin acids

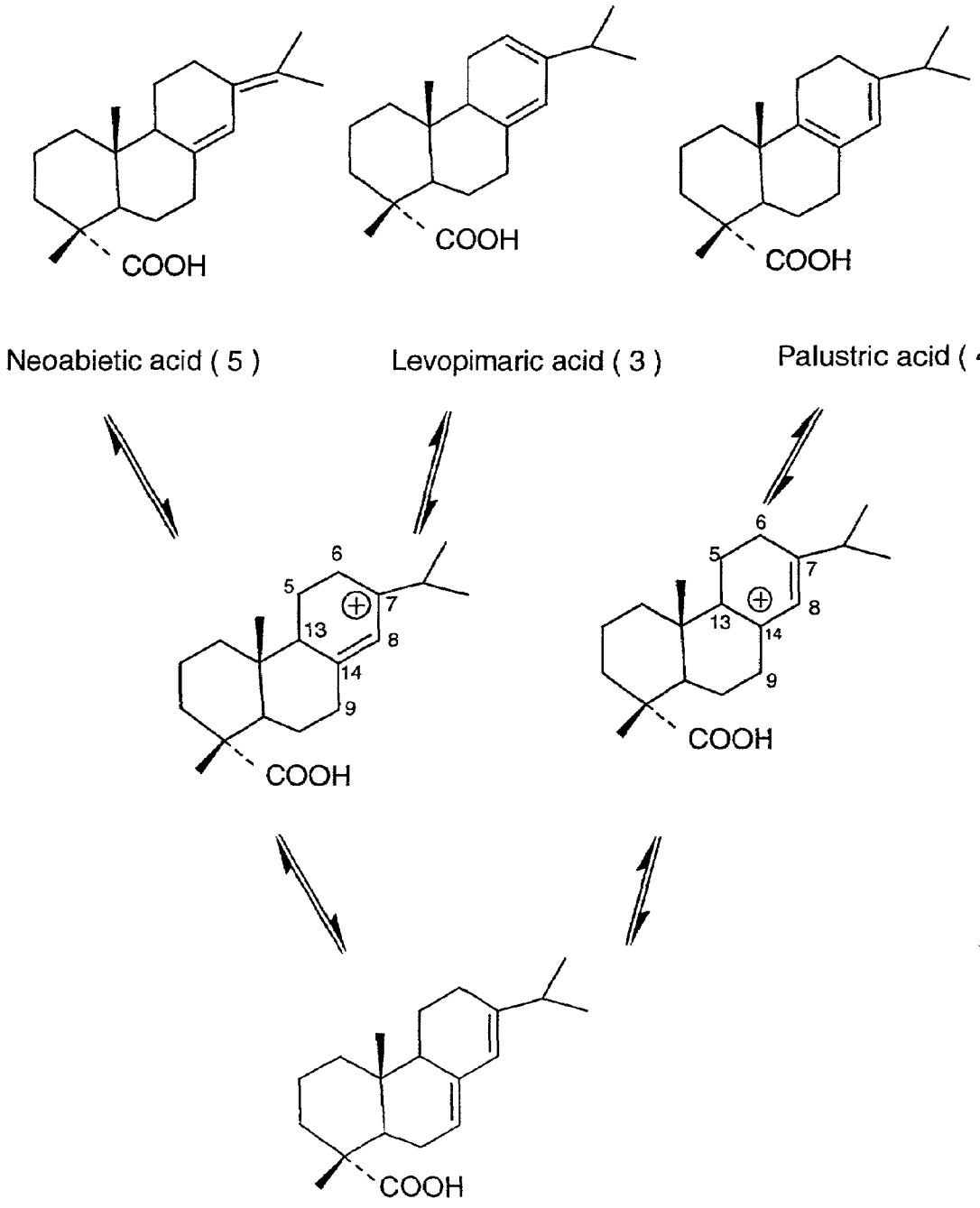
In the presence of strong acid catalysts, such as hydrochloric acid and p-toluenesulfonic acid, levopimaric acid [14] and neoabietic acid [15] were found to isomerize rapidly to reaction mixtures which contain over 90% of abietic acid and a small amount of starting material. In both cases it was demonstrated [14, 15] that the isomerization were catalyzed by the solvated protons in anhydrous ethanol with the same activation energy (21.4 + 0.4 kcal mol^{-1}) involved, being first order with respect to the catalyst and the rosin acids. It was rationalized that the rate-controlling step in the isomerization was the addition of solvated proton to either levopimaric or neoabietic acid to form a resonance hybrid of tertiary carbonium ions 6 and 7.



(9) **(10)**

It is to be noted that 9 can lose its charge by expulsion of a proton either at C-6 or C-18 to regenerate levopimaric acid and neoabietic acid [13]. On the other hand, 10 can lose its charge by expelling a proton from C-9 to form the abietic acid. However, if 10 loses its charge by expelling a proton from C-13, the result would be a new unknown rosin acid. Later, with the use of partition chromatography it was discovered [13] that this unknown rosin acid was palustric acid.

The formation of resonance hybrid 9 and 10 proposed by Ritchie and Mc Burney [14, 15] implies that all four conjugated rosin acids are interexchangeable upon acid-catalyzed isomerization. This was demonstrated by Baldwin et al. [16], Takeda *et al* [17] and Enoki i.e. in the presence of acid catalyst, all four rosin acids eventually reached the same equilibrium distribution of rosin acids (92-95% abietic, 3-5% palustric and 2-3% neoabietic acids) in dilute (0.7-2.0 %) ethanolic solutions at room temperature. In all the isomerization studies, no detectable amount of levopimaric acid was found in the final equilibrium mixture. Based upon the above information, a generalized reaction path may be drawn [15]and shown in **Scheme (1.1)**.


COOH
COOH
COOH
Neoabietic acid (5)
Levopimaric acid (3)
Palustric acid (4)
6
5
7
13
8
14
9
COOH
6
5
7
13
14
8
9
COOH
COOH
Abietic acid (2)

Scheme (1.1)

It can be seen that levopimaric, palustric, neoabietic and abietic acids can all yield the same resonance carbonium ions upon attack of a proton at appropriate locations. The subsequent or concurrent loss of a proton from appropriate positions α to the electron-deficient carbon atoms can lead to the formation of all four acids in question. In the case of palustric acid, protonation must occur from the α side exclusively at C-13 or else abietic and neoabietic acid would be formed [16]

The relative instability of a homoannular diene system, coupled with the lack of full substitution at C-6, would explain the considerable reactivity of levopimaric acid. The heteroannular distribution of the diene system in abietic acid may well be responsible for its stability. It was determined [17] from NMR spectra that the rate of isomerization of levopimaric acid to palustric acid was faster than that of neoabietic acid to levopimaric acid, and that both levopimaric and neoabietic acids isomerized to abietic acid through palustric acid [17].

b- Thermal isomerization of rosin acid

It has been shown [18] that levopimaric acid, originally present in commercial pine oleoresins, is completely isomerized to other rosin acids during gum distillation and that the major end-product is abietic acid. In the mid-1950s to early 1960s there was a substantial increase in tall oil and gum rosin production utilizing high-temperature distillation and fractionation. Thermal isomerization of rosin represents a practical interest because it defines the product distribution.

When levopimaric acid was heated at 155 °C, just above its melting point, for 4 h, it was completely isomerized. After 221 h isomerization, the product contained 7% palustric, 86% abietic and 8% neoabietic acids. When palustric acid was heated at 170 °C for 24 h, the product

contained 13% palustric, 80% abietic and 7% neoabietic acids [18]. Similarly, when neoabietic acid was heated at 200 °C for 72 h, the product approached an equilibrium mixture of 13% palustric acid, 82% abietic acid and 5% neoabietic acid [19]. While abietic acid was found to be the most dominant product of the thermal isomerization of levopimaric, neoabietic and palustric acids, Lawrence et al.[17] discovered that abietic acid also isomerized thermally. At 200 °C abietic acid undergoes a rapid isomerization after 1 hour to give an equilibrium mixture of 81% abietic acid, 14% palustric acid and 5% neoabietic acid [17]. No levopimaric acid was found in any of the final product equilibrium mixtures. These results of the thermal as well as the acid-catalyzed isomerizations of rosin acids are summarized in ***Table (1.3).*** Data shown in **Table (1.3)** indicate that the abietic acid content in the acid catalyzed isomerization is higher than in the thermal isomerization at different temperatures. The difference has been attributed [17] to the different rates of reaching dynamic equilibrium during each isomerization. Thus, it is not surprising to see that in the absence of a catalyst, all four rosin acids isomerized in dilute (0.67%) chloroform-ethanol solutions at 25 °C in the dark under a nitrogen atmosphere to give a final equilibrium mixture of 92% abietic acid, 5% palustric acid and 3% neoabietic acid determined by specific rotation, NMR and GC-mass spectral techniques. It should be noted that levopimaric acid was shown to exhibit no observable isomerization at temperatures below its melting point (150-152 °C).However; it completely isomerized at 155 °C to abietic, palustric and neoabietic acids which possess a higher melting point. It can be reasonably assumed that at 155 °C, levopimaric acid

Table (1.3): Product Distribution between Acid-Catalyzed and Thermal Isomerization of Rosin Acids.

Temperature (°C)	Abietic acid(wt.%)	Palustric acid(wt.%)	Neoabietic acid(wt.%)	Ref.
Acid-catalyzed isomerization				
Room temp.	92-95	*3-5*	*2-3*	*14-17*
Thermal isomerization				
155	*86*	*7*	*8*	*12*
170	*80*	*13*	*7*	*18*
200	*80*	11	7	18
200	82	13	5	19
200	81	14	5	16

Probably isomerizes directly to other rosin acids irreversibly. This may be supported by the fact that, at 155 °C, the abietic acid content in the final product distribution was higher (86%) than at 170-200 oC (80-82 %) as shown in **Table (1.3).**

c-Carboxylic acid-catalyzed thermal isomerization

In attempts to determine whether or not the isomerization of rosin acids in the absence of acid catalysts was due to hydrogen ions from the carboxy group, the use of methyl esters of rosin acids provide a convenient way for such investigations. When methyl levopimarate was isomerized at 155 °C for 18.5 h, it was found that about 50% methyl levopimarate was still present. At the same temperature, it requires only 4 h for levopimaric acid to completely isomerize to other acids. When methyl neoabietate was isomerized at 200 °C, it was found [19] that, after 168 h, 88% of the ester remained unchanged. This compares to 8 h at the same temperature for neoabietic acid to completely isomerize to the final equilibrium mixture containing 13% neoabietic acid. Similarly, it was estimated [18] that the isomerization rate of palustric acid at 200 °C was about 2000-times as fast as that of methyl ester. Consequently, the extent of isomerization of rosin acids was controlled by adding an alkali such as sodium hydroxide, sodium carbonate or potassium hydroxide to the crude oleoresin before it was processed into rosin [20]. In dilute chloroform solutions without the presence of a catalyst (in the dark under nitrogen), levopimaric, palustric and neoabietic acids were found to begin isomerizing after 6, 7 and 80 h, respectively, and rapidly approached an equilibrium state. However, in the presence of hydrochloric acid (7 ppm), the above rosin acids were found to isomerize immediately under similar conditions. Clearly, the so-called

thermal isomerization of rosin acids is actually ionic in character, being catalyzed by the proton of the carboxy group [21].

d- Isomerization temperature and product distribution

The results of the thermal isomerization of rosin acids indicate that the relative stability of rosin acids upon heating is in the order abietic acid> palustric acid > neoabietic acid > levopimaric acid, and that the final product distribution is dependent on the isomerization temperature. Data shown in **Table (1.4)** demonstrate that as the isomerization temperature increases, the abietic acid content decreases and the palustric acid content increases in the final product distribution. While this may be due to the sensitivity of the rosin acids towards acid catalysis [13, 16] at higher isomerization temperatures, reactions other than isomerization may be involved. It was suggested by Radbil and Kushnir [21] that at higher isomerization temperatures (> 210 °C), other processes, such as decarboxylation and disproportionation, were involved. These authors reported that when abietic acid was heated at 260 °C for 3 h, the product consisted of 64.1% abietic, 19.9% palustric, 8.3% neoabietic, 1.1% dihydroabietic and 6.6% dehydroabietic acid. It has been long established that the isomerizations of abietic [17], palustric [18] and levopimaric [12, 18] acids at temperatures between 155 °C and 200 °C are first-order reactions. However, neoabietic acid did not give a reaction curve characteristic of a first- or second-order reaction [18, 19]. This was attributed [18] to the back-reaction of neoabietic acid (5) forming the carbonium species (as represented in **Scheme (1.1),** which tends to progressively retard the reaction rate, and therefore the isomerization fails to behave in a first-order kinetic manner. This explanation is also partially reflected in the data shown in **Table (1.4),** which indicate that

Table (1.4): Isomerization Temperatures and Final Product Distribution.

Isomerization temp. (°C)	Abietic acid (Wt %)	Palustric Acid (Wt %)	Neoabietic Acid (Wt %)	K_{iso}	K_{pal}
190	83	11	5	0.20	0.13
200	81	13	5	0.23	0.16
210	78	15	5.5	0.28	0.19
220	76	16	6	0.32	0.21

The concentration of neoabietic acid remains small and constant (0.5%) at 190-220 °C. As can be seen from the data listed in **Table (1.4)**, the calculated equilibrium rate constants for the isomerization of abietic acid ($K_{iso,}$) and the formation of palustric acid (K_{pal}) increase as the isomerization temperature increases. This suggests that at higher temperatures the reverse reaction is important, as was also suggested from thermodynamic equilibrium considerations [22]. When the data shown in **Table (1.3)** were plotted as ln K vs. 1/T according to the Van't Hoff equation, it was found [21] that both the plots corresponding to abietic acid isomerization and palustric acid formation have the same slope. Since the formation of neoabietic acid remains constant, a similar slope indicates that the thermal isomerization of abietic acid is reversible.

e-Formation of levopimaric acid during thermal isomerization

Fomin et al. [23] have studied the thermal isomerization of abietic acid at 180 °C and 200 °C and found that levopimaric acid is present in the product mixture throughout the isomerization. The 200 °C isomerization data are shown in **Table (1.5)**. contradict the results of all previous investigations which indicate that levopimaric acid is not present in the equilibrium mixtures. Levopimaric acid, for example, was found [23] to completely isomerize at 155 °C after 4 h, and at 200 °C after 0.5 h. The thermal Isomerization was generally acquired By optical rotation measurements, UV absorption and chromatographic analyses.

Table (1.5): Isomerization of Abietic Acid at 200 °C.

Time (min.)	Abietate (Wt. %)	Palustrate (Wt. %)	Levopimarate (Wt. %)	Neoabietate (Wt. %)
0	100.0	-	-	-
5	92.3	1.0	4.6	2.1
10	82.0	2.4	12.6	2.9
15	78.9	3.8	11.6	4.6
20	80.1	3.1	11.6	4.2
25	76.1	4.3	14.3	4.8
40	74.5	5.3	14.8	4.7
60	74.9	4.1	13.0	4.2
90	78.5	4.7	11.8	4.3
540	77.0	5.4	13.2	4.4
600	78.7	2.8	14.0	4.5

Data shown in **Table (1. 5)** were largely dependent on the use of improved GLC methods. Fomin *et al.* [23] showed that methyl abietate (obtained through room-temperature reaction with diazomethane [24] gave a single peak in the chromatogram before isomerization. When abietic acid was isomerized followed by methylation, it gave four resolved peaks in the chromatogram. The peak of levopimarate was identified by UV and IR spectroscopy. To further confirm the levopimarate peak, these authors added maleic anhydride to the methyl esters of isomerized samples at room temperature for 24 h and found that the peak for levopimarate decreased with the appearance of an additional new peak. This new peak was attributed to the methyl maleopimarate. Since only levopimaric acid reacts with maleic anhydride at room temperature, this confirms that the original peak in the GLC chromatogram was methyl levopimarate. It is difficult to judge the results shown in **Table (1. 5)**. Brooks et al [25] showed that methyl levopimarate selectively isomerized to palustrate as a result of acid catalysis in a GLC column (Versamide 900). This caused an unresolved levopimarate and palustrate peak in the chromatogram. It is possible that either the palustrate or neoabietate of the isomerized products shown in the work of Fomin et al. [23] may have selectively isomerized to levopimarate in the GLC column. It is also possible that the palustric and neoabietic acids of the isomerization products may have isomerized to levopimarate selectively during the methylation process using diazomethane.

1.1.1.2 *Isomerization of pimaric-type rosin acids*

An important explanation of the relative stability of pimaric-type acids toward thermal isomerization is that the 18,19-double-bond migration is prevented by tetra- substitution at C-7 [26]. In earlier studies, it was reported [13] that pimaric and isopimaric acids remain unchanged by the processing of gum and tall oil rosins at temperatures normally encountered in tall oil distillation. Although it has been shown [7], during the distillation of crude Finnish tall oil rosin at 280 °C, that pimaric-type acids also undergo isomerization, the extent was small (1-2%).

1.1.2 Other reactions of rosin acids

Since gum and tall oil rosins come from living trees, the different methods involved in obtaining these products account for most of the differences in their composition. In the case of gum rosin, these changes involve the isomerization of levopimaric acid to palustric, neoabietic and abietic acids. The rosin acids from which tall oil rosin is obtained are exposed to oxidation and high temperatures. The former is responsible for the increased concentrations of the dehydroabietic acid [2], and the latter is responsible for the increase of the abietic acid content in rosin. Since at high reaction temperatures, other reactions such as decarboxylation, disproportionation and polymerization can also occur, it will be helpful to discuss these reactions.

1.1.2.1 Oxidation and disproportionation

It is known that when rosin is exposed to air over a prolonged period of time, the exposed surface darkens. When pure abietic acid is exposed to air, ultraviolet absorption characteristics indicate the disappearance of the double-bond chromophore and the saturation of the conjugated double-bond system by oxygen [4].This is because abietic-type acids with

conjugated double-bond systems readily take up oxygen. In studies of the photosensitized oxidation of pine gum rosin, Schuller *et al.* [27] showed that levopimaric acid, palustric acid and neoabietic acid all gave transannular peroxide with oxygen content in the neighborhood of 3%. Undoubtedly, the oxidation of rosin dienes takes place readily at high temperatures.

As was described earlier, the fractionation of tall oil rosin at high temperatures results in the formation of large amounts of dehydroabietic acid and a significant decrease in the abietic acid content. Because of greater stability due to the formation of a rigid aromatic ring system in dehydroabietic acid, the oxidation products of rosin have been the subject of much investigation. In the thermal dimerization of tall oil, gum and wood rosin, it was found that [27] the dehydroabietic acid content increased to 28.3% (from 6-9%, as shown in **Table (1.2)** when gum rosin was heated at 230 °C for 16 h in air. When the reaction was conducted at 275 °C for 29.4 h, the dehydroabietic acid content further increased to 49.2%. In the presence of an oxidizing agent such as iodine, abietic acid was also shown to oxidize and give a product mixture consisting of dehydroabietic acid (40%) and dihydroabietic acid [5].(20%) (at temperatures of 160-170 °C. Hence, an important consequence of the oxidation of rosin acid is the formation of dehydroabietic acid. It has been shown that dilute chloroform solutions of homoannular diene, such as levopimaric and palustric acids, isomerize in the dark under aeration to dehydroabietic acid in about 50% yield. The formation of dehydroabietic acid presumably occurs by hydrogen abstraction from palustric or levopimaric acids [28]. Although heteroannular dienes such as abietic or neoabietic acids do not form

dehydroabietic acid under similar conditions, they give unidentified oxygen adducts [28]. Because of the transfer of part of the hydrogen from other rosin acids, the reaction leading to the formation of dehydroabietic acid frequently has been described as a disproportionation. When the abstracted hydrogen is consumed by the pimaric-type acids present in the rosin, it leads to the formation of stable dihydropimaric acid [4]. Similarly, in the study of the conditions affecting the dimerization of pure rosin acids and rosin, part of the by-product was found to be dehydro- and dihydro-abietic acids.

1.1.2.2 Hydrogenation and dehydrogenation

Hydrogenation and dehydrogenation are important methods for modifying the rosin acids in rosin to reduce its air-oxidation tendencies. The former involves the addition of hydrogen to double bonds in the rosin acid, typically catalyzed by nickel compounds [29] or noble metals , to form saturated ring structures. The latter consists in the removal of two atoms of hydrogen from the abietic-type acids and the rearrangement of the double bond system, catalyzed by iodine to form an aromatic nucleus such as dehydroabietic acid [28].Both methods are typically carried out above 250 °C.

In ordinary hydrogenation reactions of rosin, it is generally difficult to completely hydrogenate the rosin without causing decarboxylation and the formation of dehydroabietic acid [29, 30]. This is because endocyclic double bonds are generally more difficult to hydrogenate than exocyclic double bonds [29]. However, since the residual double bond is highly resistant to air oxidation, much of the desired stability is obtained even by hydrogenation to the dihydro stage. Analysis of the various types of rosin acids in highly hydrogenated rosin, such as Foral AX (Hercules

Inc.), showed the complete absence of abietic-type acids with the presence of 1-14% dihydroabietic acids and 66-80% tetrahydroabietic acids [4]. Because the hydrogenated product is so resistant to oxidation, it is used as a tackifier and plasticizer in pressure-sensitive adhesives [31]. On the other hand, dehydrogenation of abietic acid was studied at 250 °C in the presence of platinum catalysts and found to lead to disproportionation to dehydroabietic and dihydroabietic acids plus a small amount of tetrahydroabietic acid [30]. At an even higher temperature (275 °C), the main product of the reaction was dehydroabietic acid [30] .A similar conclusion was reached when palladium was used as a catalyst at 230 °C. Since the formation of dehydroabietic acid requires the loss of hydrogen from abietic acid, it should come as no surprise that hydrogenation and dehydrogenation in abietic acid occur through disproportionation.

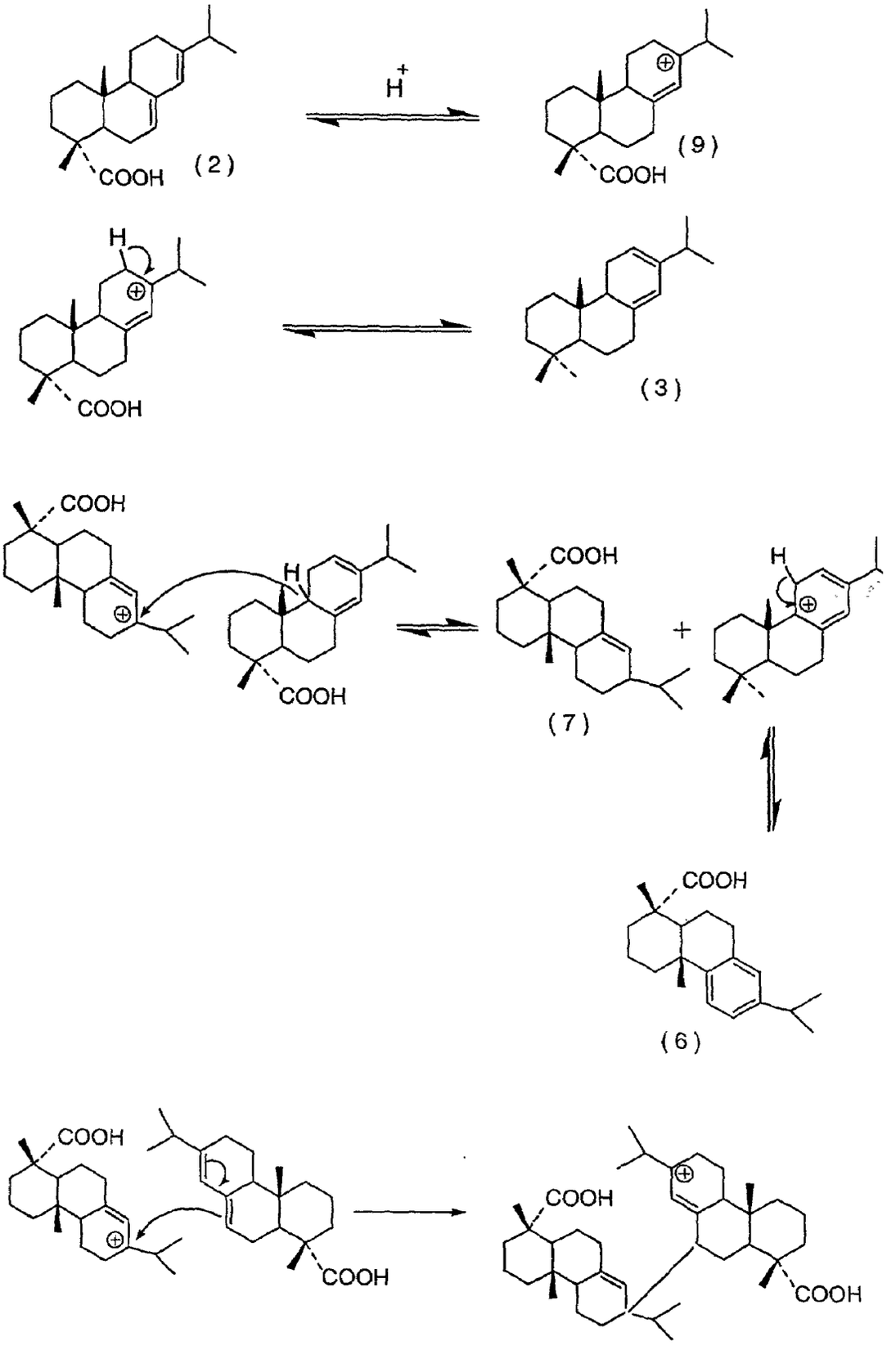
1.1.2.3 Dimerization and polymerization

The dimerization and polymerization of rosin has been subjected to investigations from the 1940s to the 1960s. Much work [32, 33] has been centered around the reaction conditions necessary for 'dimerizing' or 'polymerizing' the rosin acids. This was due to the increasing commercial use of dimerized rosin in adhesives, lacquers, varnishes and printing inks. These applications generally require rosin molecules to have good solubility and compatibility with high ***Tg*** values. A variety of reactions were investigated for optimizing the yield of dimerized rosin. Generally, mineral acids are required to dimerize the tall oil, wood and gum rosin in 50-60% yield [33, 34]. However, weaker acids such as a sulfonic acid were also found by Olechowski and Lawson [35] to yield 32% dimer. In the presence of acid catalysts such as sulfuric acid, boron

trifluoride, phosphoric acid or aluminum chloride, the dimerization products of rosin can be complicated [6]. One should not forget that isomerization reactions can also occur during the dimerization process. Su and Han [36] have studied the polymerization process of rosin acids in the presence of sulfuric acid in chloroform solution. These authors found that the rate of isomerization of abietic-type acids is faster than the rate of polymerization, and that isomerization equilibrium among abietic, palustric and neoabietic acids remains the same throughout the reaction. The reaction consisted of a fast isomerization step and a rate-determining dimerization step in agreement with earlier results obtained by Sinclair *et al* [34].

Sinclair et *al.* [34] dimerized abietic acid, levopimaric acid and methyl abietate in the presence of a mineral acid catalyst, such as sulfuric acid, at 44 °C using chloroform as the solvent. These authors found [34] that the rate of dimer formation was dependent on the concentration of the monomer and the acid catalyst. The product mixture consisted of 80% dimer with a loss of 20% of the original acid functionality. Furthermore, dehydroabietic and dihydroabietic acids have been identified among the by-products. The loss of acid functionality suggests that either ester formation or decarboxylation may have occurred. The presence of dehydroabietic and dihydroabietic acids is probably the result of disproportionation and, more importantly, oxidation of the rosin acids. A general chemical kinetic scheme consistent with the kinetic data has been proposed [34] and is shown in **Scheme (1.2)**. Thus the structures of dimerized rosin acids can be mixtures of various polymeric forms depending on the reaction conditions. The thermal dimerization of gum rosin under various conditions was studied.

These authors isolated 15-30% of a polymeric material. For example, when gum rosin was heated at 300 °C for 10 min, it yielded 16% isolated polymeric residue and dehydroabietic acid. The polymeric residue had an acid number equivalent weight of 645, a saponification equivalent weight of 408 and a molecular weight (determined by vapor pressure osmometry) of 654. The above information suggests that the polymerized materials were essentially a mixture of monobasic dimer acids. This was further supported by the strong peaks at 1700 $cm^{-1}$and 1730 cm^{-1} in the IR spectrum, which indicated the presence of carboxylic acid and ester groups. Presumably the reaction was the result of the addition of the rosin carboxylic acid across one of the double bonds of another rosin acid, such as abietic acid, to form ester dimers. In the dimerization of abietic acid or levopimaric acid, Sinclair *et al.* [34] determined by MS and GC methods that there were at least 12 structures. The most important dimerization conditions were found to be the solvent ($CHCl_3$) employed, the acid strength of the catalyst and the $CHCl_3$: H_2SO_4 : AA ratio. Under the most favorable dimerization conditions, the rosin-acid dimer was limited to 80-90% yield by side-reactions. The remaining undimerized materials were inert to further dimerization because they lacked conjugated diene structures. It is clear from the above information that the important changes in composition during the polymerization of rosin are the decrease in carboxy functionality, the disappearance of a large portion of the abietic-type acid and the increase in dimer and dehydroabietic acid content. These changes make the dimerized rosin mixture less susceptible to attack by


COOH
(2)
H+
(9)
COOH
H
COOH
(3)
COOH
H
COOH
COOH
(7)
+
H
COOH
(6)
COOH
COOH
COOH
COOH

Scheme (1.2)

atmospheric oxygen so that the desired stabilization of the abietic-type acids is produced.

A polymerized rosin has the further advantage of requiring less maleic anhydride [4] or phenol-formaldehyde condensate,yield maleic-modified or phenolic-modified rosin esters to achieve a given hardness and viscosity. Consequently, it also requires less polyol for esterification than the unmodified rosin to achieve low acid number and high softening point.

1.2 MODIFICATIONS OF ROSIN FOR COATING APPLICATIONS

Rosin has been recognized to have excellent solubility and compatibility with a variety of other synthetic resins. This is because resin acids have a hydrophobic skeleton in combination with hydrophilic carboxy groups. It is advantageous to modify these resin acids for many coatings applications. For example, when rosin or its adduct were incorporated into alkyds and varnishes for coatings applications, faster drying and better chemical resistance have been reported [37-40]. The faster drying property is primarily due to the higher *Tg* value of rosin and its adducts in coatings that impart a lacquer-dry characteristic. The versatility of rosin applications has been summarized in the report by Hedrick et al. [41].

1.2.1 Carboxy functionality and esterification

Esterification is an important part of rosin modification. The carboxy group of rosin acids is bonded to a tertiary carbon and is therefore sterically hindered. Furthermore, three rings in the rosin acids are fused together to form relatively rigid structures which make rosin possess

A relatively high melting point (as shown in **Table 1.1**). Consequently, high temperatures are normally required for esterification to occur. Ester gum finds its use in adhesive applications and is obtained by modifying rosin with glycerol or pentaerythritol at temperatures in the range 200-240 °C. Even higher reaction temperatures (260-275 °C) and longer reaction times are required for some rosin ester preparations. Much information may be found in the work by Ellis [42]. As would be expected, the high-temperature esterification process results in a decrease in abietic acid and an increase in dehydroabietic acid due to isomerization and oxidation. However, this is not the only consequence. In an attempt to prepare a Diels-Alder adduct of abietic acid and fumaric acid (200 °C for 2.5 h), Halbrook and Lawrence [43] noted a 2% weight loss based on abietic acid. These authors found that this was mostly due to decarboxylation as evidenced by the carbon dioxide trapped as barium carbonate from the exhaust gas. This leads to the formation of abietenes or rosin oil [44], which generally results in products with a lower softening point. The decarboxylation products at least explain, in part, the yellow, gummy, neutral materials which often accumulate in the condenser during a typical rosin ester preparation. In comparison to Su and Han's finding [36] that the isomerization equilibrium among abietic, palustric and neoabietic acids was not disrupted throughout the acid-catalyzed polymerization of rosin acids, the presence of esters during esterification was also found to have no effect on the isomer redistribution of rosin acids during the high temperature (290 °C) esterification of rosin.

In order to facilitate the esterification, Arimoto and Zinkel [45, 46] showed that a rosin ester with an acid number of 5.1 can be prepared at 40 °C by

reacting a rosin acid quaternary ammonium salt, such as tetrabutylammonium dehydroabietate, with alkyl or alkenyl halides. More commonly, catalysts such as zinc dust or boric acid are used [47]. On the other hand, the carboxy group in a rosin acid can be converted to a variety of other functional groups which are less sterically hindered. For example, the carboxy group can be converted into a hydroxy group by hydrogenolysis [48] or by reaction with ethylene oxide [49]. Blazhko [50] showed that a flexible transparent film was obtained from products of reactions of dehydroabietic acid or disproportionated rosin acids with glycidyl ether.

1.2.2 *Condensation with dienophile*

One of the important synthetic reactions of rosin is the formation of an adduct with dienophiles such as maleic anhydride or fumaric acid, via the Diels-Alder reaction at temperatures of 180-210 °C. Portions of the rosin are converted to tribasic acids capable of being reacting with polyols to form high molecular weight rosin esters. Generally, the optimum Diels-Alder reaction conditions for rosin are temperatures of 180-190 °C for 2 h [11]. Above 200 °C, evaporation of maleic anhydride, decarboxylation and darkening of the product were reported [11].

1.2.2.1 *Condensation with maleic anhydride*

In a Diels-Alder reaction between rosin acids and maleic anhydride, abietic-type acids are first isomerized to levopimaric acid before forming the maleopimaric acid[11]. It was reported by Wienhaus and Sandermann[51] that with abietic acid maleic anhydride addition products formed only at temperatures above 100 °C, and were identical to those

obtained in quantitative yield from levopimaric acid in benzene at room temperature. Similarly, palustric acid and neoabietic acid were shown to be inert toward maleic anhydride at room temperature, but reacted at 150-200 °C to yield maleopimaric acid. It has been assumed that as the trace quantities of levopimaric acid present in tall oil rosin react with maleic anhydride, the equilibrium is displaced until eventually all of the abietic-type acids capable of isomerizing to levopimaric acid are converted to the Diels-Alder adduct. Thus, when commercial rosin is heated together with maleic anhydride above 180 °C, it has been commonly accepted [11] that the reaction is driven to completion due to the continuous supply of levopimaric acid (originally present in trace quantities) by maintaining an active isomerization of the other abietic-type acids. Of course the assumption may not be entirely correct if the data shown in Table 1.5 are true. It is also possible that maleic anhydride may induce rosin acid isomerization to form dipolar or zwitterionic intermediates based on the known [52] mechanism of the Diels-Alder reaction.

It should be noted that pure maleopimaric acid is converted to the monoether ester in alcoholic KOH solution and may be titrated as a dicarboxylic acid. This shows an acid number of 280, but this is not due to the third carboxylic group, which is sterically protected, as reported by Shukla et al. [53]. Generally in Diels-Alder reactions, the original geometry in the dienophile is retained. When a cyclic diene and a dienophile are allowed to react via the Diels-Alder reaction, the endo isomer is generally favored [52]. Thus, the adduct from anthracene and maleic anhydride is the cis-anhydride, and fumaric acid is a trans-dicarboxylic acid [54]. Although it has been established in the reaction

between maleic anhydride and furan that the isolated product was exo, the reaction was kinetically controlled. The initial rate of endo-adduct formation was 500-times faster than that of the exo- adduct but the former was less stable by 1.9 kcal mol^{-1} [52]. In the Diels-Alder reaction between abietic-type acids and maleic anhydride, it should be noted that only one isomer (m-p., 225-227 °C; [(α], -25°) of the product, maleopimaric acid, has been reported [55]. However, in the studies of the reaction between maleopimaric acid and 3- phenyl-l-propanol at 240 °C, Molhoek [56] has observed that the anhydride functionality in maleopimaric acid exhibits a large difference in reactivity toward-hydroxy groups. The difference in reactivity was attributed [56] to the suspected presence of isomers of maleopimaric acid, but the author failed to isolate them. Molhoek's observations of different anhydride reactivities were based on measurements of the changes in the peak height at 1782 cm^{-1} (C=O stretch-vibration) in the IR spectrum, which has long been established [57]. However, data shown in this author's work are largely incomplete, and it is probably best not to speculate.

Burgstahler and Coworkers[58] have shown that the isopropyl-bearing ring in levopimaric acid. is skewed in such a manner that the β face is shielded by the angular methyl group at C-12, while the α face is free for attack by the dienophile. This would indicate a back-side approach in the Diels-Alder reaction between levopimaric acid and maleic anhydride. This was also reflected in the low Arrhenius kinetic parameters *A* ($10^{5.1}$) and E (3.6 kcal mol^{-1}) for the reaction between levopimaric acid and maleic anhydride, which suggest the absence of a strain [55]. Thus, the anhydride moiety of maleopimaric acid was shown [59] to be cis to the double bond. Similarly, with the intention of confirming the

configuration at C-13 in levopimaric acid, Ayer and McDonald [60] examined the NMR spectra of a series of 22 compounds derived from maleopimaric acid. From a comparison of the proton shifts and the observed long-range shielding effect of the olefinic bond, these authors concluded that the anhydride group is in the endo position. One should not that, the carbonyls in the anhydride ring shown are oriented differently; one is in the endo position, and the other is in the exo position.

1.2.2.2 *Condensation with other dienophiles*

When pure abietic acid, or a mixture of abietic, neoabietic, palustric and levopimaric acids in a ratio commonly found for rosin, was reacted with excess fumaric acid at 200 °C for 2-3 h, fumaropimaric acid in two isomeric forms was produced [43]. They were crystalline fumaropimaric acid (major, 50-72% yield) and non-crystalline tricarboxylic acid. The non-crystalline portion of the product was separated and found to contain 9% maleopimaric acid and 16% non-crystalline fumaropimaric acid based on the weight of the abietic acid used. The presence of maleopimaric acid was due [43] to the isomerization of fumaropimaric acid. It was demonstrated [43, 58] that pure fumaropimaric acid will isomerize to maleopimaric acid (m.p., 228-229 °C [10] in 62% yield by heating at its melting point (280-282 °C) under nitrogen. The non-crystalline form of fumaropimaric acid was presumably [59] the mixture of the additional isomers.

Similarly, reaction of levopimaric acid or rosin with acrylic acid, P-propiolactone [59], methyl acrylate [59] and acrylonitrile through the Diels-Alder reaction all resulted in isomeric products. In the reaction

between levopimaric acid and acrylonitrile, the resulting isomers were isolated and found to possess a large difference in melting point. Depending on the sources and application requirements, various amounts of maleic anhydride or fumaric acid are used to react with rosin. A typical commercial rosin adduct for coating applications is prepared by incorporating rosin with c. 4-6 wt.% maleic anhydride [10,11]. High concentrations of adducts in the rosin generally lead to high melting points, viscosity and gelation upon esterification with polyols. Generally, fumaric acid-rosin adducts have about a 20 °C higher softening point than maleic anhydride-rosin adducts. For example, Halbrook and Lawrence [61] studied the thermal reactions of fumaric and maleic anhydride with gum, wood and tall oil rosin under various conditions. When 100 parts of gum rosin were reacted with 20 parts of fumaric acid for 3 h, the softening point was 138 °C, while the maleic anhydride-rosin adduct had a softening point of 117 °C. It should be realized that the maximum molar yield of such adducts produced in typical rosin is approximately equivalent to the total mole fraction of the abietic type acids present.

In recent years, trifunctional anhydrides such as trimellitic anhydride or oligomers terminated by anhydride groups have been used [62] to crosslink epoxy resins in powder coating compositions. The rosin-maleic adducts or rosin-fumaric adducts present an interesting possibility in this area. Penczek et al. [63] reported that acid anhydrides obtained from rosin were used as epoxy crosslinkers for curing at 210 °C with phenol as an accelerator, to give resins with good mechanical strength for stove varnishes. Conceivably, these adducts may be used in many alkyd formulations [39, 42] to replace phthalic acid for fast drying.

Shukla and Vasishtha reported [40] that fast drying coatings and industrial finishes were obtained with styrenated alkyds based on maleopimaric acid. The maleopimaric acid was also reported [64] to react with hexamethylenediamine to form a polyamideimide with excellent thermal stability. Similarly, coatings based on unsaturated polyesters derived from rosin modification with P-propiolactone were shown [65] to have excellent resistance to water, base and acid. It should be noted that, due to the shortage of phthalic anhydride during World War II, the maleinization and styrenation of rosin was developed and subsequently produced in tank car volumes.

1.2.3 *Condensation with formaldehyde*

While the Dieles-Alder reaction of abietic-type acids with maleic anhydride produces tribasic acid, a considerable effort was also made in the early 1960s to make hydroxy-functional rosin acids. This can be accomplished by condensing rosin acids with formaldehyde. The reaction of formaldehyde with unsaturated hydrocarbons to produce unsaturated alcohols is well known [66]. However, the condensation of formaldehyde and rosin acids usually gives a complex mixture of hydroxymethyl-substituted rosin acids. Parkin *et al.* [67] reacted levopimaric acid with paraformaldehyde under reflux conditions (100 °C) to yield the cyclic ether of the levopimaric acid-formaldehyde adduct. Treatment of this adduct with dilute mineral acid gave 6-hydroxymethylabietic acid, quantitatively. To increase the thermal stability, the 6-hydroxymethylabietic acid can be hydrogenated by palladium on carbon to give 6-hydroxymethyldihydroabietic acid, or by

copper-chromite reduction to give 6-hydroxymethyltetrahydroabietinol [67].

The reaction between levopimaric acid and formaldehyde is time-temperature-sensitive as a result of competition with the isomerization of levopimaric acid, [13], condensation with formaldehyde and further conversion of the adduct to 6-hydroxymethylabietic acid. However, in the reaction between abietic-type rosin acids and formaldehyde in the presence of acetic acid, the products were shown [68] to be mixtures of various methylol, dimethylol and dioxan derivatives. The heterogeneous nature of the various condensation products suggest that reactions other than Diels-Alder are involved in the acid-catalyzed condensation reactions.

The paraformaldehydes commonly used in the trade have a degree of polymerization ranging from 10 to 100 and contain up to 7% water. At temperatures above 100 °C, paraformaldehyde depolymerizes to release methylene glycol rather than formaldehyde [69]. One can expect that this highly reactive intermediate is capable of alkylating rosin acids to form a mixture of hydroxymethyl- and dihydroxymethyl-substituted rosin acids with small amounts (5%) of unreacted rosin acids [70]. Of course the condensation of rosin acids with formaldehyde is not the only method to produce hydroxymethyl derivatives. A so-called 'oxo' process can also be used to increase the functionality of rosin acids. This process is generally used in the production of alcohols and aldehydes by passing olefin hydrocarbon vapors over cobalt catalysts in the presence of CO and H_2 under high pressure. Levering and Glasebrook [71] used the 'oxo' process to prepare hydroxymethylated rosin with 89.5% yield. The actual product composition of oxonated rosin was studied by Rohde and

Hedrick [72]. These authors used gum rosin with $CoCO_3$ as a catalyst to produce a mixture of products consisting of the saturated monohydroxy-/dihydroxy-addation products, together with unoxonated material. The unoxonated material was presumably due to the unreactive rosin acids, e.g., dehydro- and tetrahydro-abietic acids [73]. It should be realized that, under oxonation, the pimaric-type acids are capable of converting to hydroxymethylated rosin acids [71]. The resulting polyhydroxy-functional rosin can be reacted with a variety of fatty acids or drying oils in an alkyd formulation to obtain improved air -drying properties for varnishes [74]. These hydroxy-functional rosins were also shown [48] to control the crosslink density in film-forming reactions with isocyanates to form urethane foams [48].

1.2.4 Condensation with phenolic resin

One important area of rosin modification is phenolic-modified rosin esters, which are frequently used in printing inks and varnishes. These materials offer improved drying, gloss and wet ability. Generally, two processes are used to prepare phenolic-modified rosin esters. In the direct condensation process, the reaction is brought about by reacting rosin ester with alkaline-condensed reactive phenolic resin at temperatures of 250-270 °C. In this type of reaction, it was at one time suggested by Krumbhaar that there was no chemical linkage between rosin and phenolic resin and that self-condensation of the phenolic portion was responsible for the increased softening point. Krumbhaar's comments reflected the uncertainty during the late 1940s on the reaction between phenolic derivatives and drying oils. However, the reaction of

o-hydroxymethyl phenols with unsaturated compounds such as oleic acid was found [75] to occur at 180 °C.

The rigidity of the molecular structure was assumed to be responsible for the increase in melting point when rosin is combined with a phenolic resin [76]. However, one should note that in order for rosin to form a chroman ring with reactive phenols, two 'active methylene hydrogen' from rosin acids are needed. This appears to be possible only with pimaric-type acids. Since the pimaric-type acid concentration in rosin is usually low, and the concentration of phenol derivatives employed in the modification of rosin esters is normally less than 15%, it appears unlikely that the formation of the chroman ring would play a major role in the reactions of phenolic-modified rosin esters. The other process for the preparation of phenolic-modified rosin ester involves condensing rosin (in which a portion is a maleic anhydride adducts) with paraformaldehyde and phenol at 100-130 °C. Following the addition of polyols, the reaction temperature is increased to 260-270 °C for esterification to occur and is maintained until the desired properties are obtained. One can see that, in this process, the reactions can be even more complex than in the one previously described. The highly reactive hydroxyalkylating agent not only reacts with rosin acids to form the hydroxy ethyl-substituted rosin acids, but also reacts with phenol derivatives to form the reactive benzyl carbonium ion [69].

1.3. ROSINS AS POLYMER CHEMICALS

Rosin and its derivatives have been extensively used in various applications within the chemical industry. In almost all of these applications, rosin and its derivatives are used as industrial chemicals to modify the properties of existing formulations or to bring forth altogether new performance characteristics of the products. Rosin and rosin derivatives are widely used in paints, varnish and coatings, ink formulations, adhesives, etc.

1.3.1 Rosin in paint, varnish and coatings

The application of rosin derivatives in paint, varnish and coatings had begun before 1960 in an effort to improve the properties and performance of these materials [77].Research has been carried out on rosin as a potentially cheap source of ingredients for paints, varnishes, etc. during the last twenty-five years.

In rosin-modified alkyd resins, generally rosin is used as a part of the monobasic acid ingredient. The presence of rosin or rosin derivatives in the polymer imparts better brushing, faster drying, better gloss and gloss retention, greater hardness, and better adhesion. It is also used as a substitute for phthalic anhydride to reduce cost. Uses of rosin derivatives in surface coatings have been reviewed earlier. The adhesive strength of a sound-deadening paint containing polyisobutylene, polyethylene, polyvinyl acetate, natural rubber, etc. was found to increase ten times when rosin along with starch was added to it. The water resistance and drying time of enamels prepared from water soluble alkyd resin and Linoleic acid, etc. were improved by the addition of Pentalyn 255 (rosin-maleic acid-pentaerythritol resins). The drying time of paint for printed

circuit boards was decreased, and the solubility of the film in alkali was increased, by the addition of an alkyd resin modified with linseed oil, rosin and maleic anhydride. Formaldehyde-modified rosin and hydroxymethylated rosin were heated at 270°C with zinc oxide to obtain a Zn-salt which was used to prepare an anticorrosive paint with good resistance to H_2SO_4 and H_2S gas, for fertilizer plants .Rosin or rosin esters have been used in the manufacture of conductive paints [78]. A paint having hardness and gloss values similar to those of alkyd resin was reported to contain a rosin derivative which was prepared by heating rapeseed oil, rosin and maleic anhydride at 200°C, then treating the product with polyester fiber at 260°C and finally esterifying with pentaerythritol.

a. Antifouling paint formulations

Rosin and rosin derivatives are important chemicals in antifouling paint formulations. They may be used either as the vehicle or as the antifouling agent. Maleated rosin bis (tributyltin) oxide was reported to be used in antifouling paint formulations used for fishing nets. A marine antifouling paint for ship bottoms contains a reaction product of rosin and hydrazine as the toxicant. Triphenyltin rosinate, obtained by reacting triphenyltin hydroxide and rosin, was also used as an antifouling agent. An antifouling paint with good resistance to the erosive effects of water motion was reported to contain a chlorinated rubber-rosin matrix, Cu_2O and ZnO toxicant mixtures, $CaCO_3$ extenders, etc. . Acoustically transparent, camouflage antifouling paints for coating rubber substrates without adversely affecting their chemical stability or

sound absorbing characteristics, have been prepared from polyisobutylene rubber, rosin, Tributyl tin florid (Bu_3SnF) and pigment [79]. A paint with a completely seawater soluble film forming base and a long service life has been reported to contain a rosin ester prepared from rosin and a hydroxy acid such as salicylic acid as the binder. Good performance was observed for antifouling paints based on rosin-chlorinated rubber mixtures plasticized with tricresyl phosphate containing Cu_2O and a small amount of ZnO as toxicants [80]. Cu_2O, ZnO, $CaCO_3$, chlorinated rubber, rosin, chlorinated paraffin etc. were mixed to formulate an antifouling paint with good performance [81].

b. Traffic paint –

A hot-melt traffic paint giving films resistant to abrasion, impact and weather, was prepared from maleic acid modified rosin ester resin, sunflower oil modified alkyd resin, talc, TiO_2, glass fiber, etc.. Rosin or modified rosin was blended with the reaction product of an ethylenically unsaturated carboxylic acid or derivative with a resin made by copolymerizing a linear conjugated diene with styrene, to obtain a pavement marking composition with improved compressive strength at low temperature. Maleated rosin, alkyd plasticizer, MgO, TiO_2, and glass beads were mixed to prepare a road marking composition with good compressive strength, abrasion, weather and chemical resistance. Water thinnable traffic marking paints were prepared from maleated rosin, drying oil, NH_3, shellac, etc. and were reported to have better performance than commercial brands [82]. A reaction product of a cyclopentadiene derivative, rosin and a fatty acid was esterified with an alcohol. This ester was used as the main ingredient in a hot-melt traffic

marking composition forming a pinhole free coating with excellent crack resistance

A varnish containing rosin, cyclohexanone-formaldehyde resin, polyvinyl butyral, polyethylsiloxane, etc. was reported. In a thermoplastic varnish composition, modified rosin was used. Electrically insulating varnishes containing rosin modified phenolic resins, and an electrically conductive varnish containing rosin were reported. An air drying varnish suitable as an anticorrosive primer for construction and metallic equipment was formulated from rosin, phenol-formaldehyde resin and esters. A modified alkyd resin prepared by reacting rosin, phthalic anhydride, a phenolic resole and partial esters of linseed oil fatty acids with glycerol and pentaerythritol was used to manufacture drying varnishes resistant to water and alkali solutions. The properties of oil based paints were improved by using wood rosin modified with maleic anhydride and formaldehyde, and rosin polymers (a by-product from the distillation of flotation oils in the manufacture of wood rosin. Coating compositions containing castor oil and rosin were reported to have good adhesion, gloss and scratch resistance [83]. Scale formation during the polymerization of vinyl chloride was prevented by coating the reactor with modified rosin . The shock resistance of a coating has been increased by adding industrial oil, rosin and fatty acid to a coating composition containing rubber latex, vulcanizing agent, etc.. Reaction products of rosin with ethylene terephthalate oligomers or fatty acids were used as components of a protective and decorative coating with high hardness and strength. A polymeric product is expected to be formed after curing. Rubber, phenol-formaldehyde oligomers, dimerized rosin, etc. were mixed to prepare a spray able undercoating composition

for automobiles. Uses of rosin modified phenolic resins in oil based coatings were recently discussed [84]. Radiation curable colored coating compositions for metals contained Harimac 135 G (a rosin-modified maleic acid resin). Reaction products of rosin with unsaturated dicarboxylic acids or anhydrides were esterified with a compound having hydroxyl groups and radically polymerizable unsaturated groups to prepare a component for photocurable coatings. Polyfunctionality compounds synthesized by the reaction of maleic anhydride with renewable raw materials like cashew nut shell liquid, rosin, sunflower oil, etc. can be used in water-borne coatings]. Polyurethanes have been combined with polyol esters of rosin acids to prepare water thinned coating compositions. Another water thinned composition forming a coating with excellent water and blister resistance was found to contain an epoxy resin and a rosin-modified maleated linseed oil varnish. Blends of chlorinated polypropylene and the glycerol ester of rosin acids were mixed with water to form storage stable dispersions useful as coatings and adhesives. A reaction product of castor oil, rosin, glycerol, maleic anhydride, phthalic anhydride and propylene glycol, along with triethanolamine and water, was used to manufacture an electrophoretic coating for metals.

c. *Rosin in printing ink formulations*

Applications of rosin and rosin derivatives in printing inks were previously reviewed. An electron beam curable offset printing ink containing rosin esters and acrylic monomers has been reported. It was claimed that resistance of the print to water and acid has been increased by using a pentaerythritol ester of fumarated rosin with a molecular

weight of 1100-1400 along with an organic amine. A reaction product of rosin with 2-alkenoic acid derivatives was treated with calcium-compounds and then used as binder in inks useful in intaglio printing. Carbon black, aromatic oil, phenol-formaldehyde resin, modified rosin, etc. was used in a printing ink formulation for rotary presses. Vehicles for printing inks for plastics have been prepared from polyamide-rosin esters and nitrocotton. Rosin and an acrylic isocyanate were used to prepare a photo curing resin for printing inks [85]. A dispersant prepared by condensing polyethylenimine with esters of hydroxystearic acid and rosin was used in oil-based printing inks. Phenolic resins modified by rosin and esterified with pentaerythritol, and pentaerythritol esters of maleated rosin, were used as components for inks with increased smearing resistance, abrasion resistance, gloss and sharpness. A lithographic ink with excellent physical properties contained a phenolic resin modified by rosin and polyhydroxy compounds.

d. *Rosin in adhesive formulations*

Rosin has been widely used in various adhesive formulations. In a recent review such applications of rosin in adhesive formulations have been discussed [86]. Electro conductive hot-melt adhesives were reported to contain thermoplastic resin and/or wax, silver, nickel and rosin. Glycerol esters of hydrogenated rosin acids, ethylene vinyl acetate copolymer and fluorinated surfactants were used as components of a foamed hot-melt adhesive useful for rough substrates. A transparent hot-melt adhesive was reported to contain ethylene-vinyl acetate copolymer, a rosin ester and wax. An adhesive for bonding foamed polystyrene or poly (vinyl chloride) to various substrates contained styrene-butadiene

rubber, rosin, etc. [87]. Reaction products of rosin and phenol, neoprene, ammonia etc. were used to prepare an adhesive with excellent bonding strength for metal to cotton cloth. A vulcanizable composition with good adhesion to brass contained natural rubber, a nickel salt and Vinsol (Na rosinate). A heat sensitive adhesive polymer dispersion, which becomes a good pressure sensitive adhesive upon heating, has been manufactured from butyl *methacrylate-N,N-dimethyl*aminoethyl methacrylate-lauryl methacrylate copolymer, a glycerol ester of rosin acids, ethylene-vinyl acetate copolymer, etc. A blend of an alkyl acrylate/acrylic acid copolymer with rosin or rosin derivatives was used in the preparation of a water dispersible pressure sensitive adhesive. This adhesive was useful for repulpable splicing tapes which are used to splice carbonless paper without deactivating its color generating system. Polypale (a rosin-type resin) was used as a radiation curable tackifier in a radiation curable pressure sensitive adhesive. Certain adhesives used in making adhesive paper contained a rosin ester or a natural rubber-rosin ester mixture. Pentaerythritol esters of rosin and partially polymerized rosin were used to formulate tackifiers for adhesives. Properties and uses of rosin acid derivatives as tackifying resins have been discussed earlier [88].

e. *Miscellaneous uses of rosin and rosin derivatives*

It has been reported that the addition of polyol esters of rosin acids to an ethylene-alkyl acrylate copolymer gave films having a lower heat sealing temperature. A mixture of Penseru A (pentaerythritol ester of rosin acids) and CI Pigment Violet 19 was coated on an aluminum-laminated film support to obtain an electrophotographic film [89]. Pressure sensitive copying desensitizer compositions were reported to

contain the reaction product of rosin with an alkylene oxide or a polyalkylene glycol as one of the components. Synthetic amber was prepared by curing a mixture of rosin, unsaturated polyester containing a curing agent, and the reaction product of succinic acid and nitric acid. An electrophotographic photoreceptor with high sensitivity to white light was prepared by treating the surface of the selenium-containing photosensitive layer with an isoparaffinic solution containing a rosin-modified maleic acid polymer, rosin-modified polyester and an acrylic polymer.

Rosin amides were reported to behave as multifunctional ingredients in rubber compounds. Incorporation of these amides facilitated the dispersion of filler, minimized mill sticking and improved the plasticization, flow properties and moldability of the compounds. Dewaxed and hydro-refined petroleum distillation residues were mixed with rosin and/or polyolefin to give an impregnating composition for the paper insulation of electric cables [90].

1.4. ROSINS AS POLYMER FEEDSTOCKS

Rosin acids are monocarboxylic acids based on alkylated hydrophenanthrene nuclei. They have two reactive sites - one being the carboxylic acid group and the other being the latent conjugated unsaturation centre. These reactive sites can be used for further modification of the rosin molecule to convert it to a monomer or various suitable intermediates to be used for the synthesis of polymers. Various types of polymers from rosin have been reported in the literature. Most of the information regarding rosin polymers is found in the patent literature. Copolymers have been prepared from rosin or rosin

derivatives with vinyl monomers. Copolyimides, polyurethanes, and epoxy resins from rosin have also been reported. Rosin has also been polymerized or dimerized using its reactive sites. The reports available in literature on these different types of rosin based polymers are discussed below.

Copolymers have been synthesized using rosin or rosin derivatives as comonomers. Though the structure of the polymers was not reported, it is expected that the double bond of rosin or its derivatives took part in the copolymerization with vinyl monomers. Copolymerization of ethylene with esters of unsaturated fatty acids such as abietic acid to form materials useful in agricultural products was claimed. This copolymerization reaction, although reported, is somewhat doubtful because rosin is a solid containing a sterically hindered double bond which would be expected to have low tendency to copolymerize with ethylene. Rosin acids were copolymerized with terpenes from turpentine oil with hydrofluoric acid as catalyst. The softening point and melting point of the polymer were found to be higher than those of unmodified rosin. The use of glycerol, acrylic acid-colophony condensate and bis (3-aminopropyl) amine-acrylic acid-colophony condensate in synthetic resins was reported.

Marvel and coworkers [91] reported the polymerization and copolymerization of a vinyl ester of perhydrogenated rosin. Since the polymerization involved the vinyl group a somewhat higher molecular weight polymer having an inherent viscosity of 0.16 dl/g was obtained. Copolymerization with vinyl chloride, vinyl acetate or butadiene resulted in a copolymer having 90% vinyl chloride and 10% rosin ester, 80% vinyl acetate and 20% rosin ester or 39% butadiene and 61% rosin

ester units in the copolymer chain. Inherent viscosity values for the above copolymers were 0.68, 2.23 and 0.52dl/g, respectively. However, the inherent viscosity of the copolymer decreased with an increase in the ratio of rosin ester to vinyl monomer in the feed. The authors also prepared terpolymer from rosin ester with styrene and acrylonitrile. The terpolymer contained 10.8% rosin ester, 61.2% styrene and 28% acrylonitrile. It had an inherent viscosity of 5.44dl/g. With increase in the concentration of rosin ester in the monomer feed, the inherent viscosity of the terpolymer decreased. This indicates that the polymerization of rosin ester is hindered by the bulky rosin moiety. Such polymers could be crosslinked with peroxides.

A rosin copolymer was prepared by reacting rosin with a polyol and then with an α, β-unsaturated dicarboxylic acid or anhydride to form a half acid ester mixture. The mixture was treated with a vinyl monomer to form the product. The polymerization proceeds through the vinyl double bond rather than through the unsaturation of the diene group present in the rosin molecule.

Diels-Alder adducts of rosin with maleic anhydride or fumaric acid were copolymerized with styrene in the presence of peroxide initiators using hydrocarbons, esters or ketones as solvents at 150-300°C and 0-50 atm. Oligomers obtained by reacting maleated rosins with vinyl monomers containing hydroxyl groups were mixed with vinyl monomers containing acryloyl or methacryloyl groups to give crosslinkable coating compositions which could be hardened. The problem of steric hindrance was also observed here. When the concentration of rosin derivative was increased, the molecular weight of the product was found to decrease.

Most of the rosin residues were found as pendent groups attached to the polymer chain.

a- *Alkyd resins*

The carboxyl group of rosin may react with alcohols to form alkyd resins. Since rosin has only one carboxyl group, it must either be modified to form a difunctional molecule or else mixed with a diacid in the reaction medium with a polyol in order to undergo this type of polymerization. In the second case the rosin molecule will be present either as an end group or as a pendent group on the main chain. Alkyd resins useful for coating compositions were prepared by esterifying the adduct of a rosin acid and an, β -unsaturated polycarboxylic acid with a polyhydric alcohol [92]. Another alkyd resin was prepared by reacting plant oil with an acrylic acid or maleic anhydride adduct of rosin followed by esterification with an alcohol. An oil-free alkyd resin was prepared by adding acrylopimaric acid and a rosin acid to a reaction product of a polyol, maleic anhydride and aliphatic acids.

b. *Polyurethanes*

Rosin can be converted to hydroxy terminated compounds which can then be reacted with diisocyanates to obtain polyurethanes. Polyurethane was prepared by reaction a polyisocyanate with polyester having a viscosity of 5,000-10,000 MPa at 25°C in the presence of a blowing agent. The polyester was obtained by the reaction of tall oil containing 15-35% (by weight) rosin acids with a polyhydric alcohol. The reaction product of rosin with ethylene or propylene oxide was used in the manufacture of polyurethane foam.

Hydroxymethylated derivatives of rosin acids, tolylene diisocyanate and a polyol were reacted to obtain a polyurethane elastomer. Polyols obtained by reacting rosin acids with formaldehyde and alkoxylating the hydroxymethylated product with an alkene oxide were mixed with conventional polyols and polyisocyanates to give rigid polyurethane foams with reduced flammability. Polyurethane fibers were prepared using N-(2-hydroxyethyl) maleimidopimaric acid salts. Then, the effects of incorporation of these compounds on mechanical properties and oxidative thermal aging properties of polyurethanes were studied [93].

c. Epoxy resins

Epoxy resins were prepared by the reaction of the carboxyl groups of rosin or rosin derivatives with epichlorohydrin. Penczek[94] reviewed the synthesis of epoxy resins from rosin derivatives. Epichlorohydrin and the glycidyl ester of rosin were polymerized in the presence of a catalyst. Rosin maleic anhydride adduct was reported to be used as a curing agent for epoxy resin [95]. Poly(propylene glycol) or polyoxypropylene diamine was heated with rosin and maleic anhydride at 300°C to obtain an abietic acid-levopimaric acid-maleic anhydride-polypropylene glycol/polyoxypropylene diamine copolymer containing terminal anhydride groups for use as a plasticizer and crosslinking agent for epoxy resin. Mixtures of the epoxy resin and this curing agent were cured at 100-200°C to a solid material. Rosin was refluxed with acetic anhydride to give an anhydride of rosin acids. This anhydride in turn was reacted with maleic anhydride to form an acid anhydride (softening point 102°C) that yielded a thermosetting composition when mixed with a low molecular weight bisphenol A type epoxy resin and N, N-dimethylbenzylamine. The same acid anhydride, when treated with an

additional amount of maleic anhydride, produced a more reactive hardener for epoxy resin.

Polymers with good heat and chemical resistance were prepared by first esterifying epoxy resins prepared from maleopimaric acid and epichlorohydrin with acrylic or methacrylic acid and then crosslinking with styrene [96]. Maleic anhydride modified rosin has been treated with potassium hydroxide and epichlorohydrin to give an epoxy resin which could be hardened with acid anhydrides. Rosin was reacted with the reaction product of bisphenol A and epichlorohydrin at 200-300°C for 5 hr to obtain a modified epoxy resin (softening point 114°C). Epoxy resins were also prepared from epichlorohydrin and a reaction product of rosin with maleic anhydride, [97] acrylic acid [98, 99] or methacrylic acid. Methyl epichlorohydrin has also been used in place of epichlorohydrin. Some of these resins were cured by anhydrides to yield products having good processability at 80-90°C and physical-mechanical properties similar to those of commercial epoxy resins [98]. Epichlorohydrin-maleopimaric acid copolymers of molecular weight 675 + 20 and 1080 + 80 respectively were synthesized and crosslinked and their dielectric and physical-mechanical properties were reported [100].

Cycloaliphatic epoxy resins based on rosin acids were synthesized from condensed rosin acid-formaldehyde resins. This was completed by reaction of series of rosin acid formaldehyde resins with epichlorohydrine to produce a series of multifunctional glycidyl ester and ether. The structure of the produced resins was determined by IR and ^{1}HNMR analysis. The molecular weight of the produced resins was determined by GPC technique. Series of poly (amide - imide) hardener were prepared from condensation of Diels Alder adducts of rosin acid -

maleic anhydride and acrylic acid with triethylene tetra mine and pent ethylene hexamine. These amines were also condensed with Diels Alder adducts of rosin ketones. The curing exotherms of the produced epoxy resins with poly (amide-imide) hardeners were investigated. The data of mechanical properties, solvent and chemical resistance indicates the superior adhesion properties of the cured epoxy resins based on rosin acid formaldehyde resins [101].

The tetra functional epoxy resins were prepared from rosin acids. This was obtained from reactions of diethanolamine with Diels-Alder adducts of rosin ketone. These adducts were reacted with epichlorohydrine in presence of NaOH as a catalyst to produce epoxy resins. The obtained resins were characterized by IR and ^{1}HNMR spectroscopy. The curing behaviours of these resins with their poly (amide-imide) derivatives were investigated by Viscometry. The curing activation energy was evaluated from the critical time, critical viscosity and gel point. The curing exotherms of the produced epoxy resins with poly (amide-imide) hardeners were investigated. The curing and gel times of the produced resins show slight differences between the synthesized resins. The chemical resistances and mechanical properties of the cured films were evaluated. The produced coats show high stability for salt spray at duration time 563 h [102].

Unsaturated polyesters with increased heat and chemical resistance were prepared by polymerizing maleic anhydride with propylene glycol in the presence of the reaction product of diglycidyl acrylopimarate with methacrylic acid. Glycidyl esters of saturated, branched chain C_{9-11} acids were reacted with an adduct of pine rosin and maleic anhydride at 200°C to give polyester resins. Glycidyl esters of rosin acids were

polymerized in the presence of cationic catalysts to give film forming polyesters with increased elasticity. A nonflammable polyester resin capable of being crosslinked and having a high molecular weight was prepared by reacting epoxy resin with chlorinated rosin in the presence of carbon dioxide. The final product (melting point 85-120°C) was reported to be useful in coating formulations. Novel rosin polyesters have been prepared by treating a dicarboxylic acid or its anhydride with rosin glycidyl esters. This patent also reported that glycidyl esters of gum rosin and hydrogenated rosin had been polymerized .

d. Polyesters

For one to prepare polyesters from rosin, the rosin needs to be converted to a dicarboxylic acid by reaction with suitable reactants before polyesterification. A method of converting rosin to a dicarboxylic acid is to react it with β-propiolactone. The dicarboxylic acid thus obtained was reacted with diethylene glycol to form polyester. In a subsequent patent, these authors have used the rosin polyester resin thus prepared in hot-melt adhesive compositions. It was further reported that gum rosin could also be modified with acrylic acid instead of the carcinogenic β-propiolactone. The polyester resin prepared from rosin, β-propiolactone and diethylene glycol was further modified with fumaric acid or maleic anhydride and mixed with styrene. The mixture was polymerized with or without glass fiber webbing to form laminated products. The preparation of propiolactone-modified rosin-based polyesters was also reported [103].
It has been reported that a Diels-Alder reaction was carried out between unsaturated polyester and a glycerol ester of rosin acids to obtain a new polyester with good chemical resistance [104]. However, the Diels-Alder reaction between the double bonds of the bulky rosin molecule and the

maleic- or fumaric-type unsaturation of a polyester is difficult and, therefore, most of the rosin molecules will be present as pendent groups on the main chain. Polyester based water-resistant coating compositions which hardened at room temperature were prepared by dissolving a maleopimaric acid-monoallyl glycerol ether-allyl glycidyl ether-diethylene glycol-sebacic acid copolymer in an isopropanol-isobutanol mixture. The copolymer was prepared by refluxing maleopimaric acid with the other constituents at 230°C with continuous removal of reaction water. Colored polyesters were recently prepared by reacting RTS-12 (pentaerythritol-esterified maleated rosin) with azo or anthraquinone disperse dyes [105]. Copolyesters useful for coatings resistant to abrasion, water, alkali, acid and solvents were prepared by esterifying glycerol simultaneously with rosin and poly(bisphenol A maleate) or poly(bisphenol A phthalate). Dimethyl terephthalate, glycerol and zinc acetate were heated for 3 hr at 210°C, and then rosin was added and the mixture was again heated at 275°C for 3 hr to obtain a modified polyester resin having a softening point of 113°C [106]. In the last two cases, rosin, being a monocarboxylic acid, will act as a chain terminating agent.

One well-known method of polyester synthesis from rosin is to react rosin with unsaturated acids like acrylic acid or fumaric acid (Diels-Alder reaction) followed by polyesterification with a diol. This type of polymer has a softening point in the range of 60-100°C and is used as a hot-melt coating material for road marking. A polyester prepared by reacting fumaric acid-modified rosin with a polyol at 220°C (softening point = 147.5°C) was further modified by dehydration followed by reaction with toluene diisocyanate and neutralization with aminoethanol

to give a copolymer which was used in printing ink. A polyester resin was also prepared by reacting a rosin-polyhydric alcohol melt with dicarboxylic acids or their anhydrides.

A new polyester was prepared from a rosin-acrylic acid adduct and hexane diol [107]. Rosin was first reacted with acrylic acid in the presence of hydroquinone at or above 150°C for 5 hr. The finely powdered white product (yield 68%, m.p. 220°C) was refluxed with thionyl chloride for 10 hr to yield a diacid chloride (yield 90%, m.p. 150°C). The diacid chloride was reacted with hexanediol in DMF:NMP (3:1) solution containing 4% LiCl, first at ambient temperature and then at higher temperature (100°C), to obtain the polyester; yield 71%, inherent viscosity 0.28dl/g.

e. *Polyamides*

Polymers for printing ink were prepared by reacting fumaric acid-modified rosin with urea or with a diamine. Rosin-maleic anhydride adduct was also reacted with urea to obtain a polymeric product. Polyamides were probably obtained in those cases. A polyamide was also prepared by reacting a diamine or amine alcohol with dimerized or more highly polymerized natural rosin. [108] An amber colored polyamide was prepared by heating at 140-225°C a mixture of rosin-maleic anhydride adduct, polymeric fatty acid, tall oil fatty acid, adipic acid and bis(hexamethylene) triamine. This polyamide was used as a binder for quick drying water resistant printing inks. A water soluble polyamide was prepared by reacting polymerized fatty acids, maleated rosin, and aromatic or aliphatic diamines for 2 hr at 200°C/50 mm. The softening point of the polyamide was about 129°C. Maiti and coworkers

have investigated the synthesis of various polymers using maleopimaric acid (MPA) or similar Diels-Alder adducts as the starting material. One of the polymers, a polyamide, was synthesized from the acid chloride of rosin-acrylic acid adduct and hexamethylene diamine in 76% yield. It had an inherent viscosity of 0.30dl/g.

f. Polyesterimides

Polyesterimides are an important class of engineering plastics due to factors such as good processability, generally high glass transition temperature, solubility in common solvents, relatively low cost, and good thermal and outdoor stability. Polyesterimides from rosin have been studied by Maiti *et al.* [109]. Penczek reported [98]. the preparation of polyesterimides from maleopimaric acid. Maleopimaric acid was reacted with an amino alcohol to form maleimidopimaric acid. Polyesterimides were synthesized by polycondensation of maleimidopimaric acid with glycols, glycerol, dimethyl terephthalate, polyethylene terephthalate, trimethylol ethane or trimethylolpropane. A polymer (mol. wt. 2,000) was thus prepared using zinc acetate as catalyst. Maiti *et al.* prepared polyesterimides by different routes. In the one-step method [110] rosin-maleic anhydride adduct (MPA) was reacted with a diamine in 2: 1 mole ratio in the presence of excess diol, with an antimony trioxidecadmium acetate mixture used as the catalyst. The mixture was first heated gently at 120°C for 30 min and then refluxed at 200°C for 3 hr. The excess diol was distilled off under reduced pressure to obtain the polyesterimide. In the two-step process [111] MPA was first converted into rosin maleimidodicarboxylic acid (RMIDA) by reacting APM with para-aminobenzoic acid (1 : 1 mole ratio) in dimethylformamide solution for 3 hr at 150°C. RMIDA was isolated,

purified and reacted with excess diethylene glycol in the presence of a mixed catalyst of antimony trioxide and zinc acetate under a nitrogen atmosphere. The reaction mixture was heated at 260°C for 3 hr, at 280°C for 2 hr and finally at 300°C for 1 hr. The final 15 min of the reaction was carried out under slightly reduced pressure (~ 93 kPa). In both the one-step and the two-step methods the yields and the inherent viscosities of the polymers are almost the same. If RIDA prepared in the two-step method is converted to the diacid chloride, the polymerization with the diol can be carried out at lower temperatures
(~ 100°C).

g. Polyamideimides

Schuller and Lawrence reported the preparation of polyamideimides from maleopimaric acid (APM) derivatives [110]. Maleopimaric acid, on treatment with thionyl chloride, was converted into maleopimaric acid chloride which was reacted with diamines to form bisamides. The bisamides were fused with diamines to give head-to-head and tail-to-tail linked polyamideimides [110]. Treatment of one mole of monoacid chloride with excess diamine in a modified Schotten-Baumann procedure followed by acidification with hydrochloric acid gave an amide amine hydrochloride salt of maleopimaric acid. This salt was then fused with a diamine to give a head-to-tail linked polyamideimide resin. Fusion of maleopimaric acid chloride with one mole of diamine gave randomly linked polyamideimides. [110]. Treatment of maleopimaric acid chloride with methyl alcohol gave trimethylmaleopimarate, which, when fused with various diamines, gave polyamideimide resins. Molecular weights of the polyamideimides were reported to be in the range of 6,000 (inherent viscosity 0.10 dl/g for a 1% solution in

dimethylformamide at 30°C. Films and fibres have been prepared from these polymers.

Schuller and Lawrence[110] reported a synthesis of dihydromaleopimaric acid from dihydrofumaropimaric acid by heating under pressure at 250-325°C in the presence of hydrochloric acid. The dihydromaleopimaric acid was converted to the acid chloride by treatment with thionyl chloride. The acid chloride derivative was then reacted with 4,4"-methylenedianiline to obtain a polyamideimide . Aldrich reported synthesis of a polyamideimide useful for ink formulations from maleopimaric acid and *hexamethylenediamine* Maleopimaric acid was mixed with hexamethylenediamine to get a salt which was heated to obtain the polymer.

Maiti *et al.* [109] prepared a polyamideimide from the imidodicarboxylic acid obtained by reacting MPA with p-amino benzoic acid. The imidodicarboxylic acid was converted to the diacid chloride derivative by refluxing with excess thionyl chloride for 15 hr. The final product was obtained by removing excess thionyl chloride under vacuum and recrystallizing the product from chloroform (yield 65-70%, m.p. 186-187°C). The diacid was then reacted with suitable diamines in equimolar proportion in dimethylformamide solution in the presence of pyridine as an acid acceptor. The reaction was carried out at room temperature for 3 hr and finally at 60-70°C for 5 hr. The polymer was isolated by precipitating in ice/water and was then purified by repeated precipitation from dimethylformamide solution by methanol.

In another method MPA was converted to the monoacid chloride by refluxing with thionyl chloride for 6 hr in the presence of a catalytic amount of dimethylformamide. The product was isolated by azeotropic

distillation with benzene and purified by crystallization from chloroform (yield: 92%, m.p. 170°C) [64]. This acid chloride derivative was reacted with different diamines in equimolar proportion in the presence of an acid acceptor such as triethylamine [111] Different solvents, mixed solvents and salt solutions were tried as the reaction medium. It was found that a mixed solvent of dimethyl formamide and N-methyl 2-pyrrolidone (DMF: NMP = 3: 1) containing 4% lithium chloride was the best reaction medium [111].