

Introduction

1. INTRODUCTION

Water-soluble synthetic polymers are a family of materials that have been developed commercially and studied scientifically at an accelerating pace in recent years. Partly, this is a reflection of the increasing diversity in the applications of water-soluble polymers in mineral processing, water-treatment, and oil-recovery as surfactants. Surfactants are used together with polymers in a wide range of applications. In areas as diverse as detergents, paints, paper coatings, food and pharmacy, formulations usually contain a combination of a low molecular weight surfactant and a polymer which may or may not be highly surface active. Together, the surfactant and the polymer provide the criteria needed for specific application.

1.1. SURFACE ACTIVE POLYMERS

The name amphiphile is sometimes used synonymously with surfactant. The word is derived from the Greek word *amphi*, meaning both, and the term relates to the fact that all surfactant molecules consist of at least two parts, one which is soluble in a specific fluid (the lyophilic part) and

one which is insoluble (the lyophobic part). When the fluid is water one usually talks about the hydrophilic and hydrophobic parts, respectively. The hydrophobic part of a surfactant may be branched or linear. The polar head group is usually, but not always, attached at one end of the alkyl chain. The length of the chain is in the range of 8-18 carbon atoms. The degree of chain branching, the position of the polar group and the length of the chain are very important parameters for the physicochemical properties of the surfactant. The polar part of the surfactant may be ionic or non-ionic and the choice of polar group determines the properties to a large extent. For non-ionic surfactants, the size of the head group can be varied. The relative size of the hydrophobic and polar groups, not the absolute size of either of the two, is decisive in determining the physicochemical behavior of a surfactant in water.

The modern concept of surface-active agents, or surfactants, includes soaps, detergents, emulsifiers, wetting agents, and penetrants. Most surface-active agents have water-attracting, or hydrophilic groups on one end of the molecule, water-repelling, or hydrophobic groups on the other end. In most cases hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight

or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain, for example, $C_9H_{19}C_6H_4-$. The hydrophilic functional group may vary widely and may be:

- Anionic, e.g., $-OSO_3^-$ or $-SO_3^-$,
- Cationic, e.g., $-N^+(CH_3)_3$ or $C_5H_5^+$,
e.g. quaternary trimethylalkylammonium halides
- Zwitterionic, e.g., $-N^+(CH_3)_2(CH_2)_2COO^-$, e.g.,
alkyl betaines
- Semipolar, e.g., dimethylalkylamine
- Nonionic, e.g., $-(OCH_2CH_2)_nOH$,

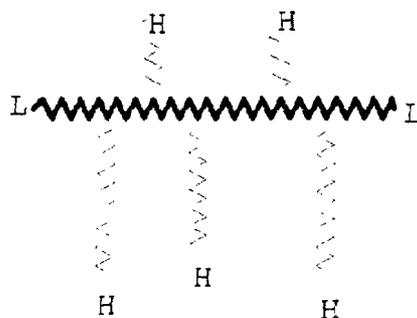
In general, the hydrophilic nature of these functional groups decreases from ionic to nonionic. Alkylbenzene sulfonates have traditionally been the workhorse among synthetic surfactants. They are widely used in household detergents as well as in a variety of industrial applications. They are made by sulfonation of alkyl benzene. Other surfactants that have found use in detergent formulations are paraffin sulfonates and α -olefin sulfonates, the latter often referred to as AOS. Paraffin sulfonates, or secondary n-alkane sulfonates are usually prepared by sulfoxidation of paraffin hydrocarbons with sulfur dioxide and oxygen under UV (ultraviolet) irradiation [Bo Jonsson et al.

(1998)]. α -Olefin sulfonates are prepared by reacting α -olefins with sulfur trioxide, typically yielding a mixture of alkene sulfonate (60-70%), 3- and 4-hydroxyalkane sulfonates (around 30%) and some disulfonate and other species. The two main α -olefin fractions used as starting material are C_{12} - C_{16} and C_{16} - C_{18} [Bo Jonsson et al. (1998)].

Surface active agents or (surfactants) are substances that at low concentrations can adsorb at some or all of the interfaces and significantly change the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it. Surfactants are amphiphilic molecules i.e. molecules that have a lipophilic tail and hydrophilic head group. When surfactants are dissolved in two-phases oil/water systems, they minimize the free energy in the system by adsorbing at interfaces (thus, lowering the interfacial tension) and, in bulk phases, by forming dynamic aggregates of colloidal dimensions termed micelles, above a critical concentration known as the critical micelle concentration CMC [Mittal(1977,79) and Rosen (1978)].

Polymers with such an amphiphilic character may be expected to exhibit the aforementioned surfactant properties. A polymer with surface-active properties can be built along two main routes: with hydrophobic chains grafted to a hydrophilic backbone or with alternating hydrophilic and hydrophobic segments [Porter(1991) and Piirma(1992)]. Polymers consisting of both the hydrophilic and hydrophobic portions have characteristic properties [Tollar et al.(1969) and Okano et al.(1978)], often referred to as amphiphilic property.

Moreover, it has been reported that the hydrophobic interaction of a water-soluble amphiphilic polymer is influenced not only by the chemical structure and composition of the hydrophobic groups but also by the distribution of these groups along the chain [Okano et al. (1977,78)]. Block and graft copolymers having the general formulae, $L - (L)_m - L - H - (H)_n - H$



Where L and H are the lipophilic and the hydrophilic moieties respectively [Ruckenstein et al.(2000)]. In random copolymer, L and H may not be segregated sufficiently (in analogy to monomeric surfactants) and hence are not expected to exhibit surface activity. Indeed, it was discussed that when propylene oxide (L) and ethylene oxide (H) were allowed to copolymerize randomly, the products did not possess the essential characteristics of surfactants[Ruckenstein et al.(2000)].

Preparation of polymeric surfactants and their application have been reported in details [Whistler et al. (1973) and Akhmedov et al.(1982)]. The emergence of synthetic polymeric surfactants is a result of increasing technical development in both polymers and surfactants [Schwartz et al. (1958), Hogen (1984) and Omar et al.(1997)]. The polyelectrolytes, in which the hydrophilic group is ionogenic, have been studied extensively [Rembaum & Eols(1975) and Skrebnev et al (1985)] since their solution properties are of great interest in theory of polymer behavior.

The polymeric surfactants are also classified as cationic, anionic, non-ionic and zwitterionic. The vast majority of cationic surfactants are based on the nitrogen atom carrying

the cationic charge. Both amine and quaternary ammonium-based products are common. The amines have only function as a surfactant in protonated state; therefore, they cannot be used at high pH. Quaternary ammonium compounds, 'quats', on the other hand, are not pH sensitive. Non-quaternary cationics are also much more sensitive to polyvalent anions. Among the cationic surfactants, the Quaternized derivatives of poly-2 and poly(4-vinyl pyridine) which have been investigated by Strauss [Strauss(1977)] and others [Woerman & Wall (1960) and Inoue (1964)].

The dodecyl-ethyl poly(4-vinyl pyridinium) salts were also reported to show marked activity at the aqueous-air and aqueous-hydrocarbon interfaces in the presence of a simple electrolyte [Jorgensen and Strauss(1961)]. Graft vinyl alcohol / 4-vinyl pyridine hydrochloride copolymer were investigated by Parker and Piirma [Packer and Piirma (1986)]. These authors reported that aqueous solutions of this polycationic surfactant exhibits no sharp critical micelle concentration value and tends to become turbid upon standing. The structure and the surface active properties of cationic surface-active pyridinium semi-carbazide urethane-containing polyoxyethylene surfactants

were studied by Shevchenko [Shevchenko et al.(1990)]. These surfactants exhibited higher surface activity than traditional surfactants from 1 to 6 orders of magnitude. Increasing molecular weight of polyoxyalkylene from 500 to 2000 increases the surface activity from 1 to 4 orders of magnitude.

Anionics are used in greater volume than any other surfactant class. One main reason for their property is the ease and low cost of manufacture. Anionics are used in most detergent formulations, and best detergency is obtained by paraffin chains in the C_{12} - C_{16} range. Carboxylate, sulfonate, sulfate and phosphate are the polar groups found in anionic surfactants. Several investigations on anionic polymeric surfactants are found in the literature [Goebel et al.(1953,1954), Bistlin et al.(1959), Dubin and Strauss (1975), Ito et al. (1985), El-Sawy et al. (1990) and Bo et al. (1992)] The influences of molecular weight and degree of dissociation of polymethacrylic acid (polyelectrolyte) on its surface activity have been studied [Katchalsky and Miller (1951), Kuchkarova and Akhmedov (1987)]. Marion and Westerman [Marion and Westerman (1978)] have copolymerized acrylic acid with dodecylmethacrylate to produce a surface-active product

useful as emulsifier. Kuchkarova and co-workers [Kuchrakarova et al. (1987)] have studied the IR spectroscopy of sodium naphthalene-2-sulfonate-formaldehyde. They revealed that the oligomerization proceeded via substitution at C-3 position of the sulfonate. A wide variety of maleic anhydride, olefin copolymers have been synthesized, these products can be hydrolyzed [Putnam (1951)] or ammoniated [Robinette and Pfeifer (1953)] to give anionic polymeric surface active and emulsifying agents. Intramolecular micelle formation in aqueous solution of maleic anhydride alkyl vinyl ether copolymers has been investigated by Twaik et al [Twaik et al. (1975)]. The preparation and properties of amphiphilic graft copolymers containing poly (ethylene oxide) grafts have been the subject of several investigations [Twaik et al. (1975), Wesslen (1989), El-Sawy et al. (1990), Yang (1990), Bo et al.(1992) and Jannasch (1993)].

Zwitterionic surfactants contain two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to 'amphoterics' but in fact the term is not precise. An amphoteric surfactant is one that

changes from net cationic via zwitterionics to net anionic on going from low to high pH. Neither the acid nor the base site is permanently charged, i.e. the compound is only zwitterionic over a certain pH range.

Many of the naturally occurring polymeric compounds such as proteins and their derivatives are amphoteric (zwitterionic) surfactants. Some have marked foaming and detergent properties but are used only as auxiliaries in detergent formulations. The physicochemical properties and surface activity of [N-(2-carboxyethyl)-N-(2-hydroxyalkyl)minoethylene have been studied [Moriya et al. (1986)]. Furthermore, Isoda and co-workers [Isoda et al. (1952)] have partially quaternized polyethylenimine with dodecyl bromide and then condensed the remaining imino groups with chloroacetic acid. The zwitterionic product was claimed to be strong surface-active agent.

Non-ionic surfactants have either polyether or polyhydroxyl as the polar group. In the vast majority of non-ionics, the polar group is polyether consisting of oxyethylene units, made by polymerization of ethylene oxide. Ethoxylation is usually carried out under alkaline conditions. Any material containing active hydrogen can be

ethoxylated.. The most commonly used starting materials are fatty alcohols, alkyl phenols, fatty acids and fatty amines. Castor oil ethoxylates, used for animal feed applications, constitute an interesting example of triglyceride-based surfactants. The two major varieties of non-ionic polymeric surfactants are the poly (alkylene oxide) block copolymers and the phenolic polymers. Block copolymers containing poly (propylene oxide) as a hydrophobic block and poly (ethylene oxide) as a hydrophilic block were synthesized and tested as non-ionic surfactants [**Vaughn et al. (1951) and Jackson (1954)**].

Their versatility arises from the flexible structure and their properties can be modified through variations in: the total molecular weight, the ratio of molecular weights of the blocks, the arrangement of the blocks and the type of initiator used.

Synthesis, properties and applications of block copolymers have been reviewed in details [**Schmolka (1966)**]. The relation between surface activity and molecular structure of nonionic polymeric surfactants synthesized by grafting of polypropylene glycol onto hydrophilic polymer has been investigated by Nakamura [**Nakamura and Sasaki (1970)**].

Furthermore, preparation and properties of comb-shaped amphiphilic copolymers composed of hydrophobic polymethacrylate backbone and hydrophilic poly (ethylene glycol) side chains were reported [Lee et al.(1995)]. The polymers were synthesized through grafting of poly (ethylene glycol) monomethyl ethers onto acrylic copolymers by transesterification. Several types of comb-shaped copolymers have been synthesized by the use of macro monomers [Xia and Smid (1984), Ito et al. (1985), Nankwo et al. (1988), Tsukahava et al. (1989) and Jin Ho et al. (1990)]. The success of the method relies to a large extent on the reactivity of the macro monomers in copolymerizations with other monomers. It has been reported that, the reactivity of any macromonomer is lower than that of its corresponding analog [Ito et al. (1985)]. This was attributed to the intramolecular interactions, which reduce the reactivity of the polymer chains.

On the other hand, the probability of chain transfer to polymer may be high, which would lead to the formation of cross- linked gels at relatively low conversions. Using atom transfer radical polymerization (ATRP), amphiphilic di- and triblock copolymers between n-butyl acrylate (n-BA) and 2-hydroxyethyl methacrylate (HEMA) were synthesized [Curran (1988)]. ATRP has been

demonstrated to proceed via the establishment of equilibrium between active (radical) species and dormant species (alkyl halide) [Wang (1995) and Matyjaszewski et al. (1997)]. Alkylphenols condensate with formaldehyde [Wang and Matyjaszewski (1995)]. afforded linear polymers, which were ethoxylated to give surface-active graft copolymers.

Insoluble surfactants such as silicone and polyacrylate of various molecular weights are widely employed in the petroleum industry as antifoaming agents [Congxiang and Hua (1994)]. Newly developed polysiloxane fluids having highly fluorinated chains showed very low surface tensions and were examined as antifoaming compounds [Kobayashi and Owen (1993)]. Finely divided insoluble solid particles constitute an important class of emulsifying agents. Colloidal particles that are partially wetted by both the aqueous and the oleic phases are capable of effectively stabilizing emulsions. The effectiveness of these solids in stabilizing emulsions depends on factors such as particle size, interparticle interactions and the wettability of the particles [David and Mukul (1993)].

1.2. SOLUBILIZATION AND ASSOCIATION PROPERTIES OF SURFACTANTS

A surfactant is characterized by its tendency to adsorb at surfaces and interfaces. The term interface denotes boundary between any two immiscible phases; the term surface indicates that one of the phases is gas, usually air.

Altogether five different interfaces exist:

- Solid - vapor
- Solid - liquid
- Solid - solid
- Liquid - vapor
- Liquid - liquid

The major effect of surfactant when adsorbs at an interface is the reduction of free energy of that phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface. The term interfacial tension is often used instead of interfacial free energy / unit area. Thus the surface tension of water is equivalent to the interfacial free energy / unit area of the boundary between water and air above it. When that boundary is covered by surfactant molecules, the surface tension (or the amount of work required to expand the

interface) is reduced. The denser of surfactant packing at the interface is the larger reduction in surface tension [Bo Jonsson et al. (1998)]. Surfactants may adsorb at all above-mentioned types of interfaces. The tendency to accumulate at interfaces is a fundamental property of a surfactant. The degree of surfactant concentration at a boundary depends on surfactant structure and also on the nature of the two phases that meet at the interface. Therefore, there is no universally good surfactant, suitable for all uses. The choice will depend on the application. A good surfactant should have low solubility in the bulk phases. Some surfactants (and several surface active macromolecules) are only soluble at the oil - water interface. Such compounds are difficult to handle but are very efficient in reducing of the interfacial tension. There is, of course, a limit to lower the surface and interfacial tension by the surfactant. In the normal case that limit is reached when micelles start to form in bulk solution.

At low concentrations, most properties of a surfactant are similar to those of a simple electrolyte. One notable exception is the surface tension, which decreases rapidly with surfactant concentration. At a higher concentration, which is varied for different surfactants, unusual changes

are recorded. For example, the surface tension takes on an approximately constant value, while light scattering starts to increase and self-diffusion starts to decrease. All these observations are consistent with a change-over from a solution containing single surfactant molecules or ions, unimers, to a situation where the surfactant occurs more and more in a self-assembled or self associated state. The first-formed aggregates are generally approximately spherical in shape. The concentration where the aggregates micelles start to form is called the critical micelle concentration, abbreviated as CMC [Bo Jonsson et al. (1998)]. The CMC is the most important characteristic of a surfactant in consideration of the practical uses. The two most common and generally applicable techniques, for measuring the CMC are surface tension and solubilization. For an ionic amphiphile, the conductivity offers a convenient approach to obtain the CMC. The CMC is not an exactly defined quantity, which causes difficulties in its determination. For long-chain amphiphiles, an accurate determination is straightforward and different techniques give the same results. However, great care must be taken not only in the measurements but also in evaluating the CMC from the experimental data. Critical micelle concentration (CMC), surface tension, and surface tension

at CMC were compared for N-Alkyl - substituted HCHO-m-phenylenediamine copolymer hydrochlorides [**Ismailov et al. (1994)**].

1.3. THE HYDROPHILE - LIPOPHILE BALANCE (HLB) CONCEPT

An emulsion is a dispersion of two immiscible liquids (oil and water). Under intense agitation fine droplets of one phase in the other may be formed. Such dispersants are not stable without any stabilizing agent. The droplets will coalesce and the coalescing process normally starts immediately as agitation is stopped. In order to enhance the dispersion process and to stabilize the emulsion, emulsifying agents and/or emulsion stabilizers are added. Water-soluble polymers are often used as stabilizers of emulsions formed by the action of low molecular weight surfactants, i.e. emulsifiers. They offer further stabilization through steric forces between adsorbed polymer layers on the dispersed droplets and are referred to protective colloids. The finely divided hydrophobic particles accumulate at the oil-water interface. The presence of polymers or particles or a combination of the two as emulsion stabilizers is very common in biological emulsions [**Shinoda and Friberg (1986)**]. The rule of

thumb in emulsion technology is that water-soluble emulsifiers stabilize o/w emulsions meanwhile oil-soluble emulsifiers stabilize w/o emulsions. This concept is known as Bancroft's rule and dates back to the beginning of this century. Bancroft's rule is entirely qualitative. In an attempt to extend it into some kind of quantitative relationship between surfactant hydrophilicity and function in solution, Griffin introduced the concept of hydrophil-lipophil balance (HLB) of a surfactant. HLB numbers for normal non-ionic surfactants were determined by simple calculation [Griffin (1949)].

1- For alcohol ethoxylates and alkylphenol ethoxylates:

$$HLB = \frac{\text{weight \% ethylene oxide}}{5} \quad (1.1)$$

2- For polyol ethoxylate:

$$HLB = \frac{\text{weight \% ethylene oxide} + \text{weight \% polyol}}{5} \quad (1.2)$$

3- For fatty acid esters of polyol:

$$HLB = 20 \left[1 - \frac{\text{saponification number}}{\text{acid number}} \right] \quad (1.3)$$

Davies, who introduced a scheme to assign HLB group numbers to chemical groups composing a surfactant, later extended Griffin's HLB number concept. Davies' formula

and typical group numbers are shown in *Table (1.1)*. From the table it can be seen, for instance, that sulfate is much more potent polar group than carboxylate.

Table (1.1): Determination of HLB number according to Davies

1. Hydrophilic group numbers	
-SO₄Na	35.7
-CO₂K	21.1
-CO₂Na	19.1
-N (tertiary amine)	9.4
Ester (sorbitan ring)	6.3
Ester (free)	2.4
-CO₂H	2.1
-OH (free)	1.9
-O-	1.3
-OH (sorbitan ring)	0.5
2. Lipophilic group numbers	
-CF₃	-0.870
-CF₂-	-0.870
-CH₃	-0.475
-CH₂-	-0.475
-CH-	-0.475

$$\text{HLB} = 7 + \Sigma(\text{hydrophilic group numbers}) + \Sigma(\text{lipophilic group numbers})$$

Table (1.2): Use of Griffin's HLB number concept

1- Appearance	
<i>HLB</i>	<i>Appearance of aqueous solution</i>
1-4	No dispersibility
3-6	Poor dispersibility
6-8	Milk dispersion after agitation
8-10	Soluble milky dispersion
10-13	From translucent to clear
13-20	Clear solution
2- Applications	
<i>HLB</i>	<i>Application</i>
3-6	w/o emulsifier
7-9	wetting agent
8-18	o/w emulsifier
13-15	Detergent
15-18	Stabilizer

The HLB number concept, and particularly Griffin's version (which is restricted to non-ionics), is completely useful as a first selection of surfactant for a given application. *Table (1.2)* shows how the appearance of aqueous surfactant solutions depends on surfactant HLB. It also indicates typical applications of surfactants of different HLB numbers. It can be seen that an emulsifier for a w/o emulsion should be hydrophobic with an HLB number of 3-6 and an emulsifier for an o/w emulsion should be in the HLB number range of 8-18. This is obviously in line with Bancroft's rule. For room temperature operations, the HLB numbers calculated according to Griffin (or Davies) give a useful selection of surfactant according to need. Non-ionic surfactants of polyoxyethylene type are very temperature sensitive, this must be considered when applying them. Also, factors such as electrolyte concentration in the water, oil polarity and the water-to-oil ratio may also influence what type of emulsion forms.

1.4. ORIGIN OF OIL SPILL

The main sources of spilled oil were outlined by the National Research Council [**National Research Council (1985)**] as follows:-

1. From municipal and industrial wastes (urban and river runoff, sewage, refineries, and industrial sources).
2. Atmospheric - borne particulates.
3. National sources (marine seeps, sediment erosion).
4. Marine transportation - tankers, barges, and lighters and offshore operations for the exploration and production of hydrocarbons are the key sources of interest in regard to marine oil spills.

On a global basis, marine transportation accounts for the largest single portion of petroleum inputs, more than 40% on the basis of NRC [**National Research Council (1985)**] and 30 - 50% depending on the ranges of other sources [**James (1989)**].

1.5. METHODS OF OIL SPILL TREATMENTS

Transportation of petroleum from oil fields to consumers may require 10 to 15 transfers.. Accidents may occur during each of these transportation and storage steps. Offshore and shoreline waters can be polluted by runoff from offshore oil exploration and production and spills from ship transport of oil. Water can be polluted by runoff from oil fields and refinery areas and, in some cases

process effluent from petroleum and petrochemical plants [Bo Johnson et al. (1998)]. Crude oil consists of different hydrocarbons that range from a light gas (methane) to heavy solids. The most important and prevalent elements in petroleum are hydrogen and carbon. Which comprise up to 98% of some crude oils and 100% of many refinery products. Other constituents of petroleum are hydrocarbon derivatives containing oxygen, sulfur, nitrogen, and inorganic metal such as vanadium, nickel and mineral salts. When oil is spilled on water or on land, the physical and chemical properties of oil change progressively. This process is known as weathering. The volatile components evaporate quickly. Some of the medium-sized polycyclic aromatic hydrocarbons are slightly soluble. Some of the products, which are degraded by sun and microorganisms, become highly soluble. Weathering rates are not constant but are usually highest in the first few hours. Major processes of weathering of oil spilled on water include evaporation, dissolution, oxidation, emulsification, and microbial degradation. If the residue oil is adsorbed to other material of high specific gravity such as silt or clay suspended in the water, the specific gravity of the residual oil may exceed 1.0 and sink. The residue continues to spread from an area of denser saline water to less denser

freshwater and may then sink. In the case of crude oil evaporation, it plays an extremely important role in its volumetric loss after a spill. [James 1989)].

The spilled oil contributes an undesirable taste and odour to drinking water and causes severe environmental damage [Wardley (1976)]. Contaminated water cannot be used for municipal water supply, for industry, nor for irrigation. Public concern for sustaining a healthy environment has resulted in stronger environmental regulations regarding water quality and use of hazardous chemicals and substances. This concern has resulted in the need for improved techniques and methods for the use and reuse of hazardous chemicals where contacts with the environment occur. Improved techniques for control and removal of oil slicks is an area of research under active development. [Bloch et al(1972)].

Natural cleaning oil spill, allowing oil to be degraded and removed by natural means, takes long time to be fully effective. Oil dispersant or an oil-sinking agent can enhance this method. Oil gelling act as a surface-tension modifier, coagulating the spilt oil, and enhance the potential for mechanical removal techniques, for example recovery of

solidified oil with a net. In both cases the disadvantage is that the spilt oil cannot be reused. Therefore, recent trials of spilt oil treatment have been focused on oil absorbents.

1.5.1 Mechanical Recovery of oil spill

Mechanical recovery is the transfer of oil from the spilled area to somewhat transportable form as temporary stored by the help of oil-booms or skimmers.

- Oil booms are floating barriers, used to prevent spreading of oil on water, and sometimes to thicken the layer of oil by reducing the area into which it has spread [Blaser et al. (1964)].
- Oil skimmer is a mechanical pick up device, which physically removes oil from the seawater surface. It contains three basic components: the pickup head, the pump system, and the oil water separator.

Various types of skimmers are available, most of which rely on the ability to physically skim the oil off the water surface, to adhere the oil to a solid surface, or to absorb it into a porous material.

a) Adhesive surface devices

They mainly on the adhesion of oil to a solid surface. This type employing a rotating drum or cylinder covered with oil

absorbent materials that have ability to absorb the oil from an oil /water mixture. Oil adhered to the drum can scraped off the surface by a knife blade or by rollers and transferred to a storage tank.

b) Weir devices

The weir type of skimmer depends on gravity to drain the oil off the surface of sea-water. The weir devices employ adjustable weirs over which the oil film, riding on the surface of the water, may flow. The recovered liquid usually collected may be pumped away. Once oil collected, it may be pumped into a gravity separation tank as a secondary operation. The oil separates and floats to the surface. The sea-water is discharged through valves in vessels bottom weir type skimmers, these skimmers generally work best with heavier and thicker oils [Lanier (1972) and Sittig (1976)].

c) Centrifugal or vortex devices

Several oil recovery devices based on the use of a centrifugal force to separate oil from water. One of the interest variants of centrifugal devices is the Bertin skimmer [Canevari (1985)].

d) The floating suction devices

The floating suction skimmer can easily be put into action by placing it on the sea-water and adjusting it to float at the oil/sea water interface. Oil accumulates at surface and sea-water is displaced through a baffled opening in the bottom. When an oil layer has accumulated, it is pumped away by conventional means to storage [Tamaki (1967)].

1.5.2. Using of Chemicals as Oil Spill Dispersants

The use of surfactants has been, and still is, the most widely employed and immediately effective method of combating oil pollution both on open sea and on beaches. When oil, which is floating on the surface of the sea, is treated with a suitable surface-active agent the oil is broken up into particles of different sizes. Because of its amphipathic nature, the surfactant molecule locates and orients itself at the oil- water interface of an oil slick, its polar end in the water and its non-polar end in the oil. Because of this orientation it is able to reduce the interfacial tension and thereby aids in the generation of finely dispersed oil droplets. Once dispersed, the surfactant will prevent them from coalescing again [Beynon (1974)].

An initial reason for using dispersants is to respond to public and governmental concerns by preventing potential

damage to birds, fish, marine mammals, and other natural resources; fouling of shorelines and boats; and contamination of drinking water sources. Dispersing an oil spill will make it less visible, and may reduce its economic and ecological impact provided the water volume, which it disperses into, is great enough. Dispersants may be especially valuable when other countermeasures fail, for example when an open-ocean spill is moving oil onshore, but waves are too high to permit the use of booms and skimmers.

On the other hand, microbial degradation of oil appears to be enhanced by dispersion because of the larger surface area available. However, to some degree, the lower concentration of nutrients available in open water may limit the potential for growth of the hydrocarbon - utilizing microbial species.

Dispersant formulation effectiveness may depend on interaction with the indigenous surfactants at the interface. Such an interaction appears to affect dispersant performance even more than the physical properties of crude oil [Canevari (1985)].

Laboratory studies [National Research Council (1989)] have shown that metalloporphyrins, which are naturally occurring components of crude oil, with some surface-active properties, favor formation of water-in-oil emulsions (mousse).

Meanwhile, Canevari [Canevari (1985)] showed that the trace of metalloporphyrins would tend to inhibit dispersion (oil-in-water formation) rather than enhance it.

The most widely used surfactants as oil spill dispersants are classified into two main groups, ionic and nonionic surfactants:

a) Ionic surfactants

This type includes soaps of fatty acids or the alkyl sulfate and sulfonates. A large number of natural oils are capable of being sulfonated to technically useful products. The oils which contain more than one double bond per molecule are undesirable to be sulfonated. These oils tend to polymerize and oxidize forming colored and gummy products. The use of sulfated hydrogenated castor oil in preparing ointment base has been fully described by Fiero and Loomis [Fiero and Loomis (1945)].

The olefins corresponding to the higher aliphatic alcohols yield sulfated products having surface-active properties

substantially identical to those of the corresponding sulfated alcohols. This fact is of considerable practical importance as in many instances it is easier to obtain an olefinic raw material than a hydroxylated one. A wide variety of methods are used for obtaining olefins suitable for sulfation to act as surface-active agents.

Squalene, a highly unsaturated hydrocarbon occurring in shark liver oil and other marine oils, having the formula:

$\{(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2-\text{CHCH}_2-\}_2$, has been sulfated to produce an emulsifying agent [**Bloch et al. (1972)**].

Mixed di-, tri-, and tetra-isobutylenes were obtained by treating butyl alcohol with sulfuric acid. The sulfated products are in general excellent wetting agents and detergents but the sulfation process is usually difficult to be carried out [**Lanier (1972)**]. Furthermore, Olefins and alcohols have been prepared from saturated petroleum hydrocarbons [**Sittig (1976)**].

Moreover, kerosene was sulfated to prepare sulfated wetting agent from a kerosene fraction [**Padgett and Degerig (1940)**]. The sulfation of the higher olefins with the formation of secondary alkyl sulfates was carried out for the purpose of manufacturing synthetic detergents

[Padgett and Degerig (1940)]. These detergents are known under the name "Teepol".

Cracked olefins were used as starting materials for surfactant preparation [Swaminathan (1953)]. These olefins were obtained by thermal cracking of paraffin wax from petroleum or from brown coal. Salts of secondary monoalkyl sulfates were prepared by sulfation of C8-C22 alkenes in C8-C22 secondary alcohols, as reaction medium, followed by neutralization of the resultant monoalkyl sulfates [Bakker et al. (1976)].

b) Nonionic surfactants

In this type, the ester and ethers of polyethylene glycol or high-molecular-weight polymers of propylene oxide are the most common surfactants used in commercial dispersant formulations. Examples are Sorbitan monooleate (hydrophilic-lipophilic balance, HLB = 4.3), sold under the name "Span 80", and ethoxylated sorbitan monooleate (HLB=15), trade name "Tween 80". In addition, polyethylene glycol ester of unsaturated fatty acids and ethoxylated or propoxylated fatty alcohols were used. In general, the preparation of nonionic surfactants is based on enhancing the hydrophilicity of the hydrophobic molecules

by reacting them with polyethylene oxide chain, which acts as the hydrophilic moiety. In most cases, the hydrophobic residue is an alcohol, phenolic compound or fatty acid [**Anthony and James (1978)**].

The most strongly hydrophilic groups encountered in surface-active agents are the ionogenic groups, and the majority of water-soluble surface-active agents are in fact ionogens. There are, however, certain configurations, which are hydrophilic, but non-ionogenic. The two best-known radicals in this class are ether oxygen and hydroxyl. Other groups containing oxygen, such as carboxylic ester, and those containing non-basic nitrogen, such as the amide group, -CONH-, are also distinctly hydrophilic [**Anthony and James (1978)**].

A considerable number of modifications of nonionic surfactants and procedures have been described [**Carter (1959)**]. Successive treatments with ethylene and propylene oxide for example have been used to attain increased solubility. Most of the modifications, however, are concerned with the type of hydroxy compound used as a base material for reaction with ethylene oxide. Among these are:

1) Higher alcohols made by the reaction of olefins, carbon monoxide, and hydrogen [Phillips (1967)].

2) Ether alcohols of the type $R-O-CH_2-CHOH-R'$ made by etherifying an alcohol or phenol, with a halo- ketone such as chloroacetophenone: $R'-CO-CH_2Cl$.

The main concerns supporting the cautious attitude toward dispersants use after the Torrey Canyon spill were:

- (1) Toxicity of the products themselves.
- (2) The effective dispersants would make oil constituents more available to biota and thus enhance toxicity of oil components.

In order to reduce toxicity, non-aromatic hydrocarbons, water miscible solvents such as ethylene glycol or glycol ethers, as well as less toxic surfactants, have been used in more recent formulations. The modern dispersant formulations contain one or more nonionic surfactants (15-75% of the formulation) and may also contain an anionic surfactant (5-25% of the formulation) and include one or more solvents. Some of the nonionic surfactants used in different dispersants are sorbitan esters of oleic or lauric acid, ethoxylated sorbitan ester of oleic or lauric acid, polyethylene glycol ester of oleic acid, ethoxylated and propoxylated fatty alcohols, and ethoxylated octylphenol.

On the other hand, anionic surfactants, such as sodium dioctyl sulfosuccinate and sodium ditridecanoyl sulfosuccinate, are used in different dispersant formulations. These formulations usually contain a solvent to dissolve solid surfactant and to reduce the viscosity, so that, the dispersant can be sprayed uniformly. Usually, the solvent is chosen to promote rapid solubility of the surfactant in the oil and to depress the freezing point of the dispersant mixture to be used at lower temperature.

In recent years, the commercial availability of dispersants, containing less toxic chemicals and more efficient surfactants, has renewed interest for basic studies on dispersant effectiveness and on the fate of dispersed oil in the marine environment [**Mackay et al. (1984) and Lewis & Laskey (1985)**].

During the last two decades, significant reviews and descriptions of dispersants were published [**Pastorak et al. (1958), Canevari(1969), Dodd (1974), and Brochu et al. (1987)**]. Surface-active formulation with spreading force > 40 dyne/cm was found to be useful for protecting beaches from petroleum spills at sea by either collecting or dispersing the oil slick [**Lepain (1980)**].

The effectiveness of sodium dodecyl sulfate, Tween 20 and Span 20 with different methods of addition in the treatment of oil spills was studied [Gonzalez et al(1988)].

Dispersants have disadvantages, the principal one being that many of them are much more toxic than the oil which they are acting on. In addition, dispersed oil may be even more toxic than non-dispersed oil because more dissolved hydrocarbons are present in the water column when the oil is dispersed. A great deal of research to produce low toxic oil dispersant was subsequently carried out (after 1967). New less toxic and more effective dispersants consist essentially of low aromatic content. At present they must be used with extreme care and only after detailed study.

The difficulty with the use of dispersants is how to apply them rapidly and effectively to large areas. This can be done by use of ships or aircrafts, but the application time is long, the ability to evenly distribute the dispersant is questionable, and the cost is enormous. Application of dispersants in shallow water remains an issue of debate within the spill response community.

1.5.3 Using of Oil Sorbers to Control Oil Spill

The most urgent technique of elimination of emergency spread of oil and petroleum products is collecting of thin layers from the water surface with the help of sorbents. Sorbents are materials that suck up liquids. They can be used to recover oil through the mechanisms of absorption, adsorption, or both. Absorbents allow oil to penetrate into pore spaces in the materials they are made of while adsorbents attract oil to their surfaces but don't allow it to penetrate into the material. To be useful in combating oil spills, sorbents need to be oleophilic or hydrophobic although they may be used as sole cleanup method in small spills. Sorbents are most often used to remove final traces of oil or in areas that cannot be reached by skimmers. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed or cleaned for re-used.

Other alternative methods for oil removal using biodegradable materials were developed [Swaminathan (1993)]. Also Non-woven fabrics or melt-blown polyesters and polyurthane foam sheets have been used. These materials have a serious disadvantage of bulkiness that is, inconvenient shipping and storage. For polyurethane foam

these disadvantages were resolved by using an oil-recovery machine designed for an on-site foaming method [Shulka et al. (1985)].

In spite of the development of polymer for oil absorption, there have been few reports on the synthesis of such polymers. Synthesis of ethylene-propylene-diene polymer (EPDM) containing an aromatic moiety was reported [Davis et al. (1996)]. Due to the non-polar hydrocarbon nature of the polymer, EPDM has excellent water resistance but poor oil resistance. As known, ethylene-propylene-diene (EPDM) is an artificial rubber, which has elasticity and outstanding resistance to degradation by heat, light, oxygen, ozone, and water but poor resistance to oil.

Other kinds of polymers have been widely used to absorb oil spilled on water [Bronchu et al. (1987)]. Among them, alkyl acrylate and aromatic polymers, which have hydrophobicity and gel-type structure consisting of an elastic network and interstitial space, have been attracting much interest in the field of environment [Matyjaszewski & Wang (1995), Shevchenko et al. (1990), Saito et al. (1993), Martel & Morcellet (1994), Zhou & Cho (2000), Champ et al. (2001), Sayil & Okay (2001), Atta (2002) and Atta & Arndt (2002)].

Crosslinked polymers are important in chemical research and practice owing to their wide range of other applications. Chemical resistance, water treatment, chromatographic techniques, solid phase organic synthesis, enzyme immobilization, soil conditioning, solvent, ion separation, organic coating and oil sorber are using crosslinked polymers as the principal substrate. [Malik et al. (2002)].

1.6. MODIFICATIONS OF ROSIN FOR DIFFERENT APPLICATIONS

Rosin has been recognized to have excellent solubility and compatibility with a variety of other synthetic resins. This is because rosin acids have a hydrophobic skeleton in combination with hydrophilic carboxy groups. It is advantageous to modify these rosin 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 [Putnam (1951), Robinette & Pfeifer (1953), Twaik et al. (1969), Marion & Westerman (1978) and Wesslen (1989)].

1.6.1. Chemistry Of Rosin

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. 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 gum rosin was developed to fulfill these purposes. 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. Furthermore, the supply of rosin will be unhindered as this is derived from a forest product abundantly available in India and many other countries.

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 petroleum 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 petroleum uses and applications.

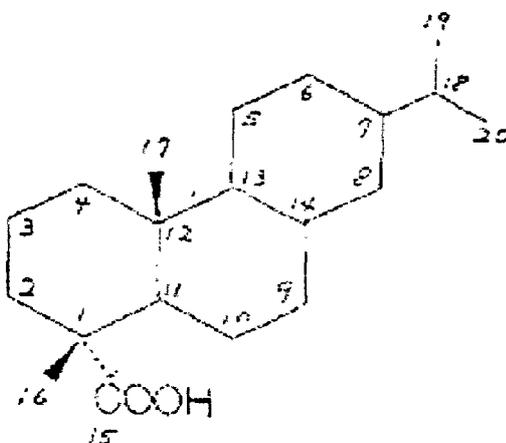
There are three important methods for obtaining rosin commercially:

- (1) Distillation of volatile turpentine from oleoresin extruded 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.

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 [**Zachary et al. (1956) and Sjostrom (1981)**]. 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 [**HoImbom et al. (1974)**] are used. Two major fractions are obtained: a fatty acid fraction and a rosin fraction.

The rosin obtained from the above process is called tall oil rosin.. 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 [HoImbom et al. (1974)]. Generally, the rosin acids can be divided into two subgroups: the pimaric acid type is 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 *formula (1)*. The numbering system used in this review adheres to the rules for naming rosin acids as derivatives of abietane and pimarane from Klyne [Klyne(1953)] as shown in *formula (1)*:



Formula (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 (1.3)*.

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 [Harris & Sanderson (1948) and Klyne (1953)]. Gum rosin has total abietic-type acids of 60-65% [Baldwin et al. (1965)].

Some of the rosin acids originally not present in crude tall oil are found after distillation [Zachary et al. (1965)]. This is mainly due to the decomposition, dehydrogenation, isomerization and disproportionation reactions taking place during fractionation. Structures of major rosin acid isomers is supplied in *Table (1.3)* whereas the melting points of rosin acids and the compositional data for different rosins are given in *Table (1.4)*.

Table (1.3): Structures of Major Rosin Acid Isomers

<i>Isomers</i>	<i>Double-bond positions</i>
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-8, C-9, C-13, C-14
neoabietic acid (6)	C-8, C-14, 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 (1.4): Composition of Tall oil, Gum and Wood Rosin.

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

1.6.2. Carboxy Functionality And Esterification

Esterification is an important method 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 a relatively rigid structure which makes rosin possess a relatively high melting point as shown in *Table (1.3)*. Consequently, high temperatures are normally required for esterification to occur. 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. Moreover, some investigators [**Arimoto & Zinkel (1982)** and **Zinkel & Arimoto(1983)**] 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. Catalysts such as zinc dust or boric acid could be used [**Bent and Johnson (1931)**]. 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 [**Harris et al. (1953)**] or by reaction with ethylene oxide [**Hedrick (1973)**].

1.6.3. Condensation with Dienophile

One of the important modification 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 temperature range for rosin is between 180-190°C for 2h [Saksena et al. (1981)]. Above 200°C, evaporation of maleic anhydride, decarboxylation and darkening of the product were observed [Saksena et al. (1982)]. In a Diels-Alder reaction between rosin acids and maleic anhydride, abietic-type acids were first isomerized to levopimaric acid before forming the maleopimaric acid [Saksena et al. (1982)]. 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 [Trivedi and Culbertson (1982)].

Depending on the sources and application requirements, various amounts of maleic anhydride or fumaric acid are used to react with rosin. 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 [**Halbrook and Lawrence (1958)**] studied the thermal reactions of fumaric and maleic anhydride with gum, wood and tall oil rosin under various conditions.

Furthermore, trifunctional anhydrides such as trimellitic anhydride or oligomers terminated by anhydride groups could be used to crosslink epoxy resins in powder coating compositions [**Mukoyama and Nishizawa (1985)**]. Penczek et al. [**Penczek et al. (1970)**] 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 to replace phthalic acid for fast drying [**Ellis (1935) and Panda (1984)**]. Other investigators reported that fast drying coatings and industrial finishes were obtained with styrenated alkyds based on maleopimaric acid [**Shukla et al. (1985)**].

The maleopimaric acid was also reported to react with hexamethylenediamine to form a polyamideimide with excellent properties [**Ray et al. (1985)**]. Similarly, coatings

based on unsaturated polyester rosins with P-propiolactone were introduced [**Halbrook and Lawrence (1963)**]. These adducts had excellent resistance to water, base and acid.

1.6.4 Condensation with Formaldehyde

While the Diels-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 [**Stapp (1976)**]. However, the condensation of formaldehyde and rosin acids usually gives a complex mixture of hydroxymethyl-substituted rosin acids [**Parkin et al. (1966)**].

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 H₂ under high pressure. This process was used to prepare hydroxymethylated rosin with 89.5% yield [**Levering and Glasebrook (1958)**]. The actual product composition of oxonated rosin was studied [**Rohde**

and Hedrick (1971)]. These authors used gum rosin with CaCO_3 as a catalyst to produce a mixture of products consisting of the saturated monohydroxy-/dihydroxy-addition products, together with unoxonated material. The unoxonated material was presumably due to the unreactive rosin acids, e.g., dehydro- and tetrahydro-abietic acids [Joye and Lawrence (1967)]. The resulting polyhydroxy-functional rosin can be reacted with a variety of fatty acids to obtain improved air -drying properties for varnishes [Minor and Lawrence(1958)].

1.6.5. 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. The rigidity of the molecular structure was assumed to be responsible for the increase in melting point [Mare and Maiti (1983)].

The 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. [Knop and Scheib (1976)]

1.6.6. 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 center. 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.

Furthermore, 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 polymerization and copolymerization of a vinyl ester of perhydrogenated rosin were also reported [Brit (1967)].

- **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 [Aktjr (1972)]. 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 [Aktjr (1972)]. It was 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 [Manovictu et al. (1971)]. 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 [Gershanova et al. (1976)]. 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) [Shepotinnik et al. (1984)].

- **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. 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 [Simo (1985)].

- **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. [Maiti (1985)] Penczek reported [Penczek and Matynia (1974,1975)] 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, poly (ethylene terephthalate) or trimethylolpropane [Schuller et al. (1964)].

- **Polyamideimides**

Schuller and Lawrence reported the preparation of polyamideimides from maleopimaric acid (APM) derivatives [Schuller & Lawrence(1967)] 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 [Schuller & Lawrence(1967)] 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 [Schuller & Lawrence(1967)].

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 [Ray et al. (1985)]. This acid chloride derivative was reacted with different diamines in equimolar proportion in the presence of an acid acceptor such as triethylamine [Vxsistha et al. (1988)]. 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 [Vxsistha et al. (1988)].