

The Chemistry of Tackifying Resins

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INTRODUCTION

Resins are low molecular weight amorphous polymers. Their main applications are in adhesives, inks, and chewing gum. In adhesives, resins are used to generate tack and specific adhesion. Mostly they are used together with larger polymers, which form the backbone of the adhesive and thus generate cohesion. Formulators use resins to create the best balance between adhesion and cohesion. There are many different resins available to the marketplace.

Tackifying resins can be divided into three groups: hydrocarbon resins, rosin resins and terpene resins. Hydrocarbon resins are based on a petroleum feedstock, i.e., a synthetic source, rosin resins are based on a natural feedstock: gained from pine trees and terpene resins are generated from a natural source, wood turpentine or from the kraft sulphate pulping process.

This paper will discuss the chemistry of these three types of resin and their various modified forms.

Tools to characterize resins will be given, which make it easier for formulators to choose the right resin for the right application.

ROSIN RESINS

Rosin is one of the oldest raw materials for the adhesives industry, either as such or converted to rosin ester. Three types of rosin are used for resin manufacture, gum rosin, wood rosin and tall oil rosin, all generated from the pine tree.

Gum rosin was once the only commercial source of rosin. It is the oleoresin (pine gum) of the living pine tree. The harvesting of the oleoresin is simple, involving only periodic wounding of the tree and collecting of the exudate into cups.

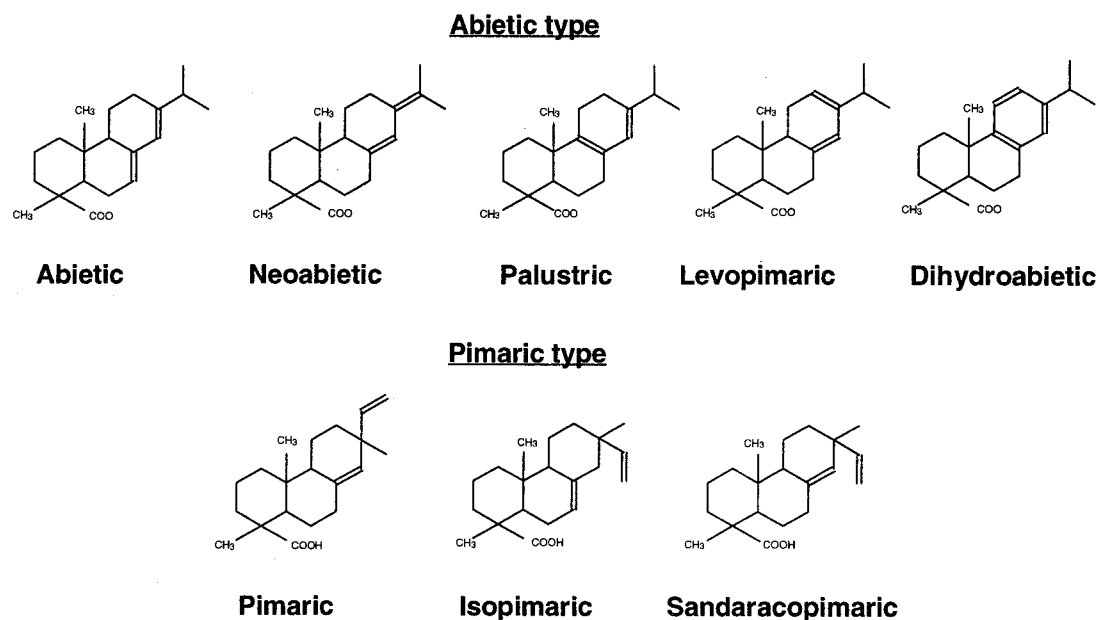
Wood rosin. After harvesting pine trees the stump is allowed to remain in the ground for about ten years so that its bark and sapwood may decay and slough off to leave the heartwood rich in resin. Resinous material is extracted from the stump.

Tall oil rosin is obtained by distillation of crude tall oil (CTO), a by-product of the kraft sulphate pulping process. CTO contains 70-90% acidic material, which is composed essentially of fatty acid and tall oil rosin. Tall oil rosin (TOR) has a tendency to crystallize and usually contains 200-600 ppm sulfur. Highly distilled TOR can produce esters which are competitive with gum and wood rosin derivatives.

Rosin Chemistry

Rosin resins, unlike hydrocarbon resins, are not polymers. In fact, they are a blend of different molecules. Figure 1 displays some of the structures of rosin molecules.

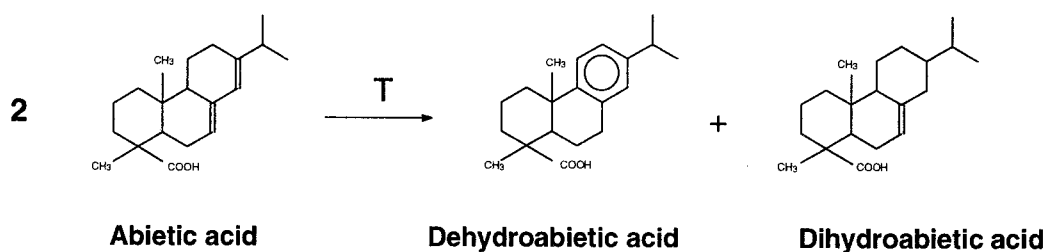
Figure 1 Rosin Structures



Rosin molecules have poor stability caused by unsaturation. Stability can be improved by various methods such as disproportionation and hydrogenation.

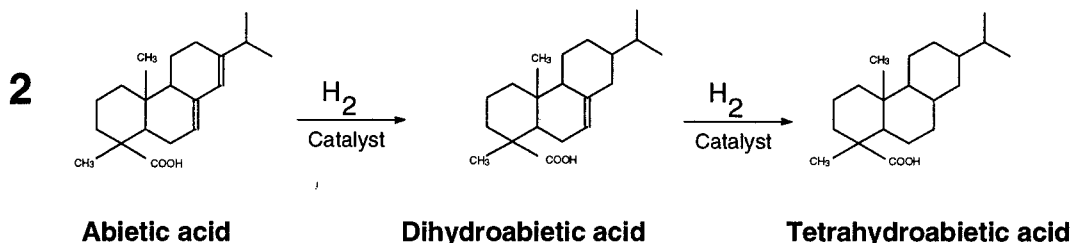
Rearrangement of the double bonds by disproportionation leads to improved stability (see Figure 2).

Figure 2 Disproportionation of Rosin Acids



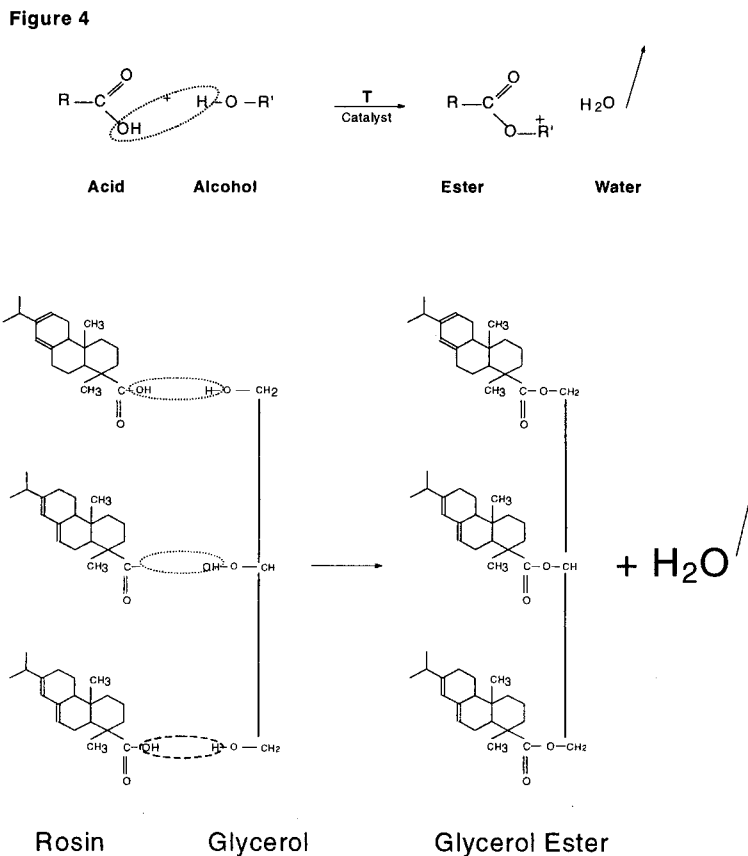
Another method to improve stability is to hydrogenate the rosin molecules (see Figure 3).

Figure 3 Hydrogenation of Rosin Acids



The carboxylic acid can be converted to an ester using various alcohols. The molecular weight of the alcohol determines the softening point of the subsequent ester. Glycerol and pentaerythritol are the most commonly used alcohols. Methanol and tri-ethylene-glycol are used to produce lower softening point esters. In Figure 4 glycerol is used as the alcohol.

Figure 4



The reaction is an equilibrium reaction, which is driven to near completion. However, there will always be some unreacted acidic and hydroxyl groups. A typical acid number for a pure rosin acid is around 170. A glycerol ester typically has an acid value below 20. The type of alcohol chosen is key to the molecular weight of the rosin ester and its softening point. A typical softening point for glycerol esters is 85°C, and 105°C for pentaerythritol esters. The difference in softening point affects their compatibility and hence adhesive performance.

Rosin resins have a wide span of compatibility with almost all polymers. They are well known for their peel and tack contribution to the adhesive, but generally decrease cohesive strength.

TERPENE RESINS

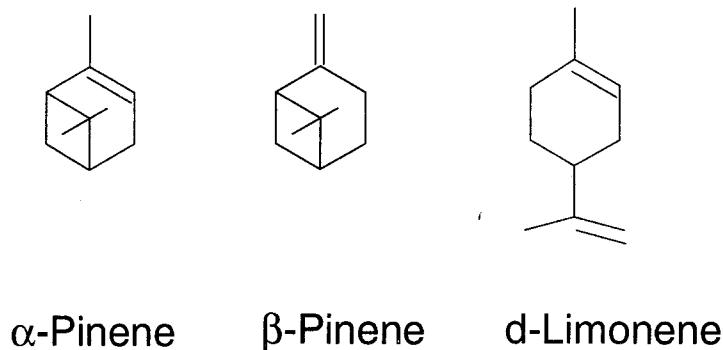
Terpene resins are based on three feedstreams (Figure 5). These resins are formed by a cationic polymerization reaction using a Lewis acid catalyst.

These resins have excellent initial color and have a broad range of softening points and have been produced for many years.

Alpha-pinene and beta-pinene are derived primarily from two processes: stump extraction leading to the isolation of steam distilled wood turpentine and the kraft sulfate pulping process leading to the isolation of sulfate turpentine. The individual terpene compounds are isolated by distillation from these two streams.

d-Limonene is obtained from citrus sources and a similar compound, dipentene, is obtained by distillation from petroleum sources.

Figure 5



The main difference for the formulator between these resins is that the d-limonene (and dipentene based) resins are not compatible with SBR polymers.

There are other resins based on these terpene feedstocks:

- Styrenated terpenes - mixed aliphatic/aromatic resins
- Terpene phenolics - polar resins with excellent adhesion and broad compatibility with polar polymers.
- Hydrogenated terpenes - improved color by hydrogenation

HYDROCARBON RESINS

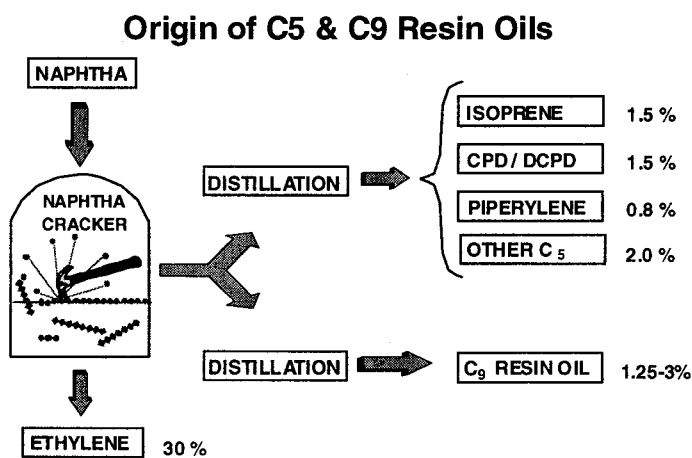
There are three major types of hydrocarbon resins:

C5 aliphatic resins
C9 aromatic resins
DCPD cycloaliphatic resins (dicyclopentadiene)

A fourth category, hydrogenated hydrocarbon resins will also be discussed.

The feedstocks to produce C5 and C9 hydrocarbon resins are fractions from a naphtha cracker (Figure 6).

Figure 6



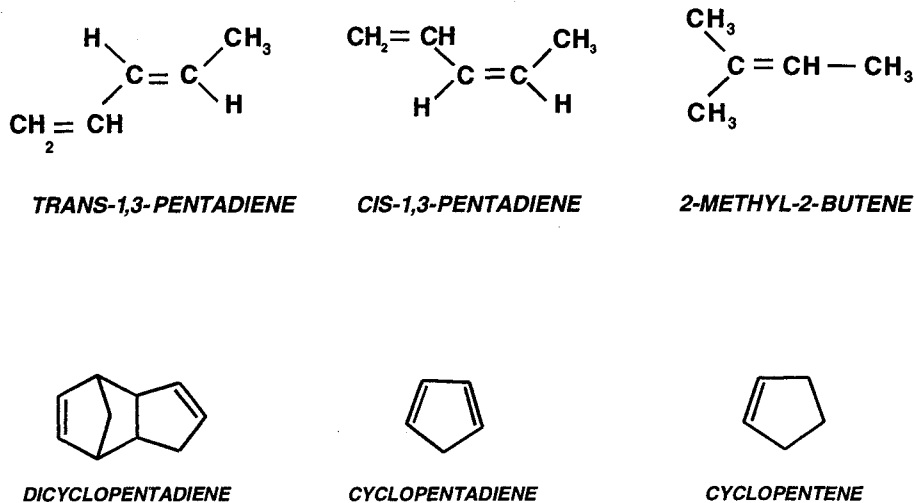
The feed streams to produce hydrocarbon resins can be divided into two groups: C5 piperylene feedstock and C9 resin oil.

C5 Aliphatic Hydrocarbon Resins

C5 piperylene contains various monomers, illustrated in Figure 7.

Figure 7

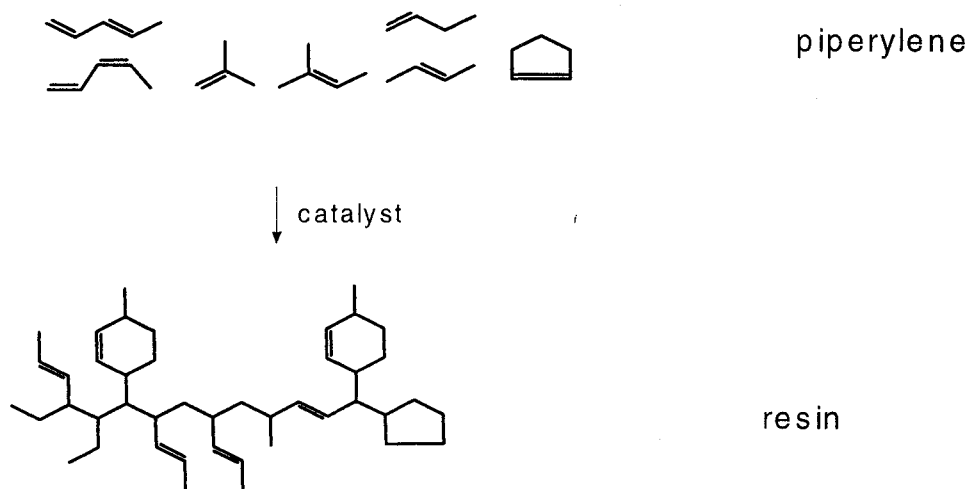
C5 Resin Oil Composition



The liquid C5 feedstock can be polymerized to a hard resin using a Lewis acid catalyst and carefully selecting temperature and pressure to obtain the desired softening point and molecular weight (Figure 8).

Figure 8

C5 Resin Oil Polymerization

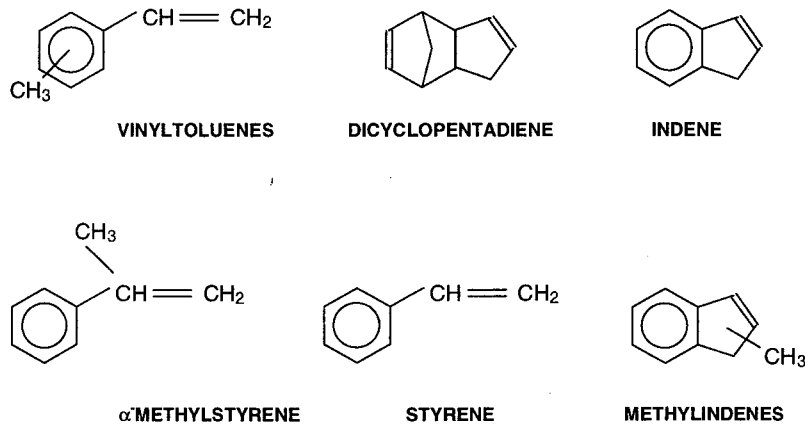


C5 resins are in essence aliphatic materials. They are available in a wide range of softening points and molecular weights.

C9 Aromatic Hydrocarbon Resins

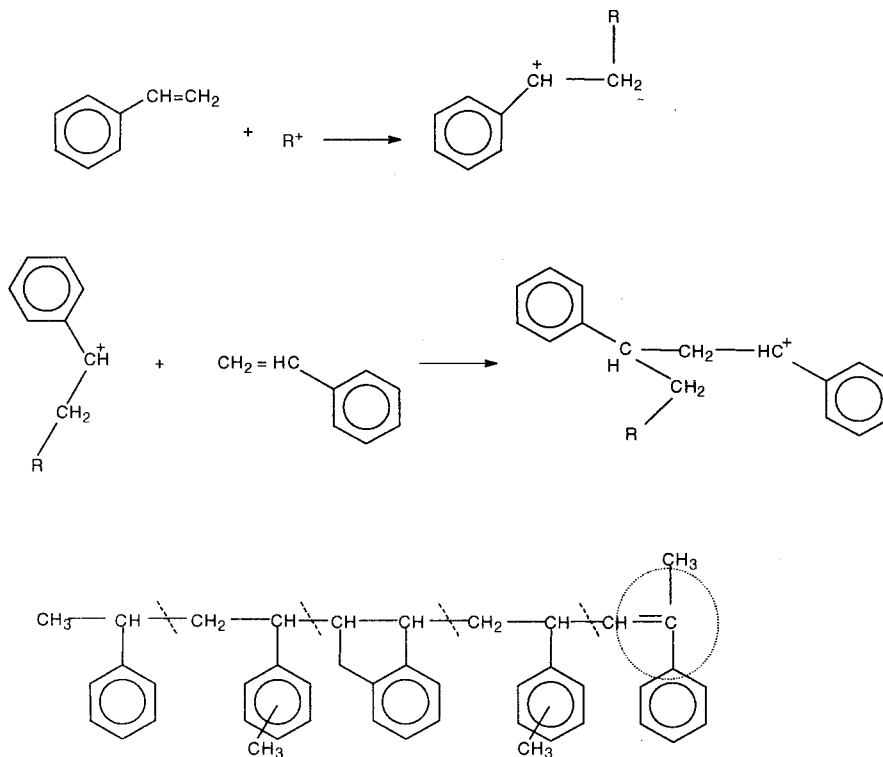
C9 resin oil contains various monomers as illustrated in Figure 9.

Figure 9 C9 Resin Oil Composition



A cationic polymerization reaction converts the liquid feed to a hard resin (Figure 10).

Figure 10 C9 Resin Oil Polymerization



C9 resins are aromatic molecules. They are also available in a wide variety of softening points and molecular weights.

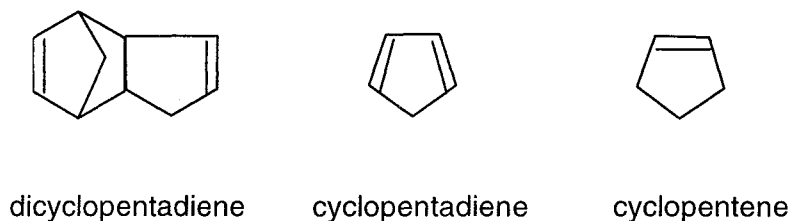
C5 and C9 resins can be modified by mixing the two feed streams together in certain ratios. This ratio determines the aliphatic/aromatic balance of the resin, which is essential to formulators. A useful method to characterize the aliphatic/aromatic balance of a resin will be discussed later.

The aliphatic C5 feed can be replaced with a terpene feedstock and modified with styrene to form "styrenated terpenes" which have excellent color and stability and are very good tackifiers for SBS block copolymers.

Dicyclopentadiene Hydrocarbon Resins

Dicyclopentadiene (DCPD) feedstock contains various structures such as those shown in Figure 11, but is primarily made up of dicyclopentadiene. The feed stock also contains codimers with dienes such as isoprene, butadiene and methylcyclopentadiene. At elevated temperature (170-190°C), dicyclopentadiene will crack into cyclopentadiene.

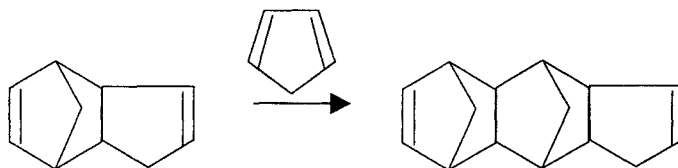
Figure 11



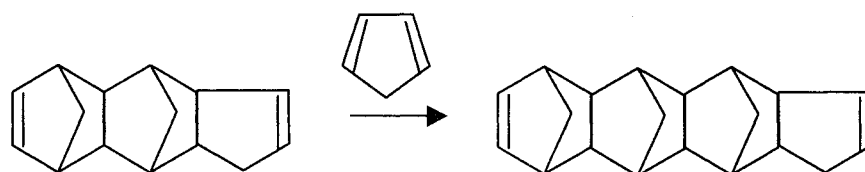
Although the exact structure of DCPD resins is not known, early steps of the thermal polymerization most likely involve the addition of cyclopentadiene to the norbornene olefin followed by continued additions of this type by additional cyclopentadiene to propagate the growing chain.

Figure 12

Cycloaddition of CPD to the norbornene ring of DCPD



Cycloaddition of CPD to the growing chain



Dicyclopentadiene is polymerized either thermally or with a catalyst to form relatively dark and unstable resins with a characteristic odor. They are normally used for construction adhesives and inks.

They are more commonly used as a base resin for subsequent hydrogenation to form water white resins with excellent stability and low odor and will be discussed in the section below.

Hydrogenated Hydrocarbon Resins

Hydrogenating the hydrocarbon resins described above produces another class of hydrocarbon resins.

Hydrogenation is primarily used to improve color and stability of the resin by removing vulnerable double bonds.

Partial and selective hydrogenation are methods used to produce resins with broad compatibility and good stability.

The most common base resins used for hydrogenation are as follows:

- C9 and C9/C5 resins
- DCPD and modified DCPD resins

The first hydrogenated hydrocarbon resins were fully hydrogenated C9 or DCPD resins producing aliphatic resins with excellent initial color and stability. These resins are ideal for tackifying SIS and SEBS block copolymers.

To produce light colored and stable resins with the correct compatibility to tackify SBS block copolymers and to adjust properties in high styrene SIS block copolymers, two methods were introduced:

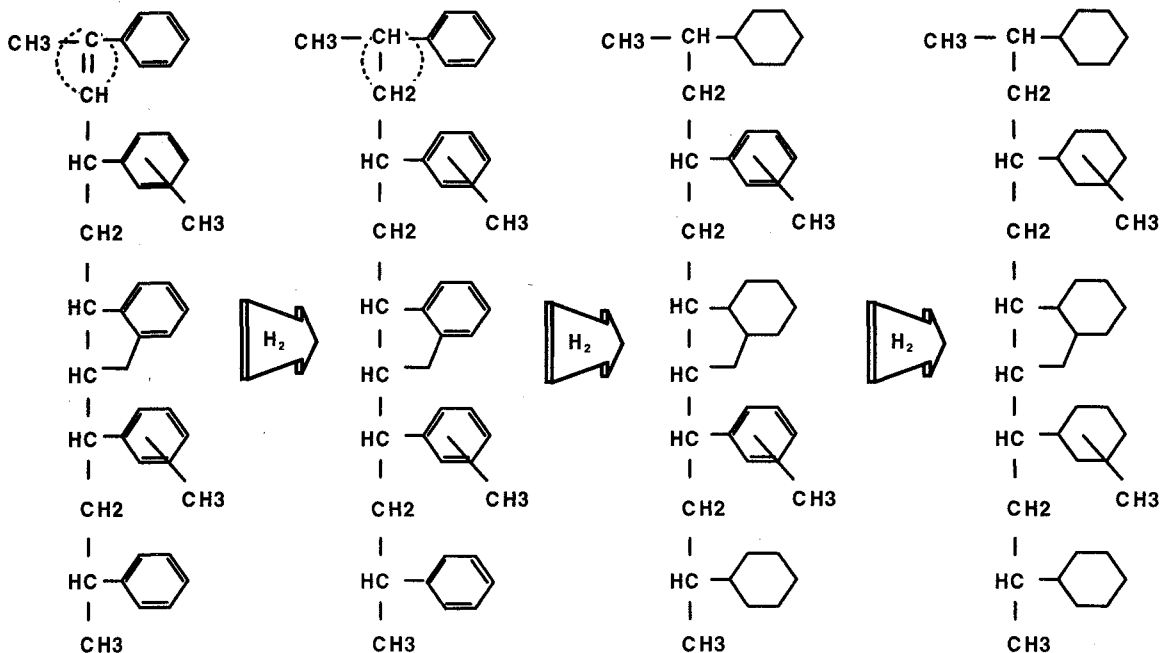
- Partial hydrogenation of C9 aromatic resins
- Selective hydrogenation of mixed feedstocks

Hydrogenated C9 Hydrocarbon Resins

C9 resins contain double bonds, which are relatively unstable. A useful way to stabilize these resins is to hydrogenate them. C9 resins have predominantly aromatic ring structures with an overall aromaticity around 40%, measured by proton NMR. Resins are hydrogenated in solution with very specific operating parameters: temperature, pressure, hydrogen concentration and catalyst level. Changing any one of these operating parameters will bring a change in the degree of hydrogenation of the final resin. During hydrogenation, the aromatic ring structures gradually lose their aromatic nature and become cyclo-aliphatic (Figure 13).

Figure 13

Varying the Degree of Hydrogenation



When the process is allowed to go to completion, the result is a fully hydrogenated hydrocarbon resin with full aliphatic character. The process can also be adjusted so that partially hydrogenated resins are the end result (Figure 13). This is very necessary in order to prepare resins for wide use in adhesive formulations and is achieved through sequential, but not total hydrogenation of the rings. This means that partially hydrogenated resins still have some aromatic rings. The ability to be hydrogenated to varying degrees, resulting in various aliphatic/aromatic balances, gives these resins their unique properties. In theory any degree of hydrogenation can be manufactured. Hercules resins carry a range of hydrogenation levels, varying from 50% to 100%.

Selective Hydrogenation of Mixed Feedstocks

To obtain resins with comparable compatibility to partially hydrogenated C9 resins, aromatic modification of DCPD (and other cycloaliphatic structures) and C5 resins is necessary.

Subsequent hydrogenation needs to be selective in order to reduce unsaturation and improve color of the cycloaliphatic and aliphatic structures without significantly affecting the aromatic content.

CHARACTERIZATION OF HYDROCARBON RESINS

There are various physical and chemical parameters that are important to characterize the resins. The aromatic/aliphatic balance of the resin is of special interest to adhesive formulators since it largely determines compatibility and ultimately, adhesive performance. Hercules uses the following criteria to define resin quality:

- Color, Gardner and Hunter Lab,
- Softening point, Ring & Ball,
- Molecular Weight,
- Melt Viscosity,
- Thermal Stability,
- Compatibility and Polarity, Cloud Points

In this paper only compatibility will be discussed.

Compatibility

The molecular weight of the resin is critical to allow for the correct compatibility with, for example, a block copolymer. Hydrocarbon resins can be designed with a specific molecular weight distribution and proper aliphatic/aromatic balance to impart the correct compatibility with the mid-block for tackification and for the styrenic end-block to optimize melt viscosity and to impart the correct cohesion to the adhesive.

Cloud Points and their Applications

The performance characteristics of a resin in a polymer system, such as an adhesive or rubber compound, are directly related to the compatibility of the resin with the polymer. Compatibility can be defined as the ability of the resin to dissolve a polymer. Knowing the compatibility of a resin with a polymer is essential to the formulator. The addition of a compatible resin to a polymer changes bulk polymer properties such as modulus and glass transition temperature (T_g).

An incompatible resin does not change the polymer properties and hence does not generate extra tack and adhesion. The fine-tuning of adhesive systems is often accomplished by the addition of a resin having limited compatibility, thus producing a lower tack level with higher cohesive strength characteristics. This is the often-delicate adhesion/cohesion balance a formulator is looking for.

Softening point and resin concentration are familiar concepts to formulation but these alone will not determine all the effects that the resin has on the performance of the formulated compound. Compatibility data is also required for a more complete understanding of resin performance.

A convenient method to characterize resin compatibility is by determination of cloud points in suitable solvent systems. From the cloud point values obtained, the resin may be characterized as being aliphatic, aromatic, or a combination of both. Additionally, polarity of resins, also an important formulating parameter, can be determined by cloud point methods.

Hercules uses several solvent systems to determine resin cloud points (Table I).

Table I - Cloud point solvent systems

MMAP	1 : 2 mixture of methylcyclohexane and aniline
DACP	1 : 1 mixture of xylene and di-acetone alcohol (4-hydroxy-4-methyl-2-pentanone)
HMDA	Hercules modified di-acetone alcohol cloud point, a proprietary solvent blend

Cloud point determination is easy to do and involves weighing a standard amount of resin which is dissolved in the solvent at high temperature. When homogeneous it is allowed to cool, with mixing. The temperature at which the resin begins to form a separate phase is defined as the cloud point.

Cloud Points and Resin Compatibility

An explanation of how these cloud points may be related to compatibility follows below.

Mixed methylcyclohexane aniline point (MMAP), being an aromatic solvent system, is a measurement of aromatic solubility and determines the aliphatic/aromatic character of the resin. The lower the MMAP value, the less aliphatic and the more aromatic nature of the resin and vice versa. This method is the least sensitive of all cloud points to differences in molecular weight.

The diacetone alcohol cloud point (DACP) method determines the polarity of the resin. Due to the polar nature of the solvent mixture, polar resins will dissolve better. In general, specific adhesion of an adhesive is related to the polarity of the resin that it contains. The lower the DACP value, the higher the resin polarity and the better the specific adhesion.

Many polar resins, such as aromatic hydrocarbon resins and rosin resins, produce DACP cloud points lower than -50°C . Working at these very low temperatures is not without problems. At about -20°C , the DACP solvent reaches its own cloud point, thereby obscuring the cloud point of the resin. Not many laboratories are equipped to operate at such low temperatures and the method thus becomes impractical.

The Hercules modified diacetone alcohol (HMDA) method was developed to measure the polarity of highly polar resins where DACP would produce results of limited use and simply reported as $< -20^{\circ}\text{C}$.

The DACP and HMDA data appeared to be linear. There is a small overlap in the temperature range between -20°C and $+30^{\circ}\text{C}$.

Cloud Point Mapping

When cloud point values are graphically displayed, application windows may be determined for the compatibility of resin families with polymers. Figures 14 and 15 display the MMAP and DACP cloud point regions for aliphatic, modified aliphatic, and

hydrogenated hydrocarbon resins. Compatibility regions for styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block copolymers have been identified, which indicate the resin type required to produce midblock compatibility, resulting in tack at room temperature.

Figure 14

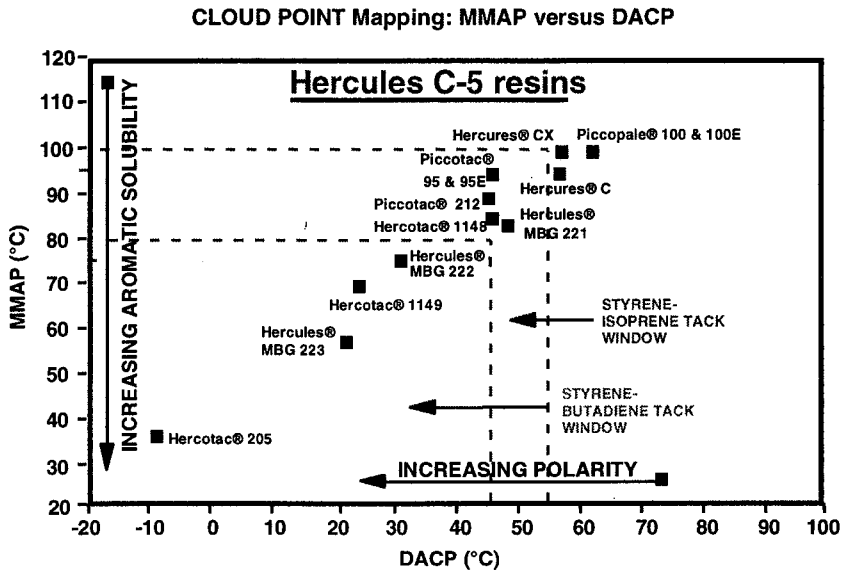
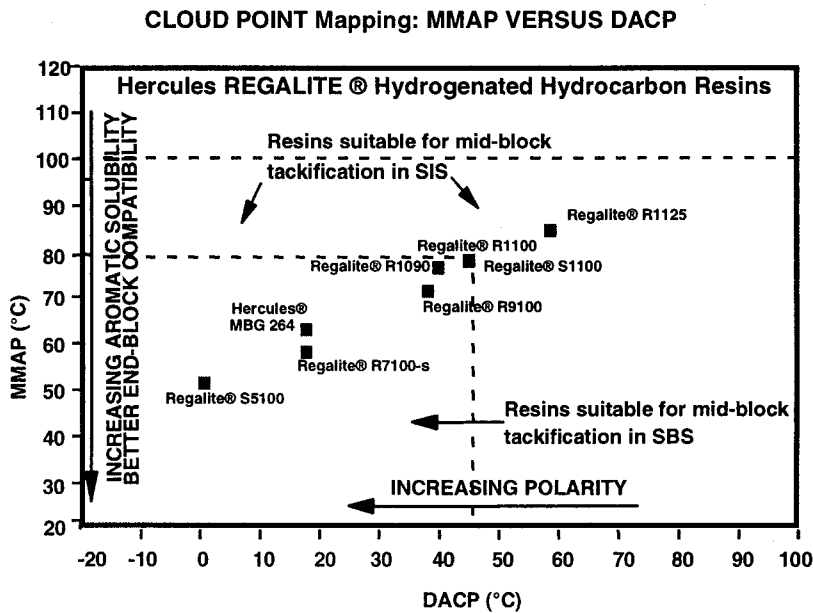


Figure 15



For adhesives used in relatively simple aliphatic polymers such as natural rubber, a high resin MMAP value can be translated into good compatibility and, in turn, into high tack, but relatively low cohesive strength. Piccotac® 95 and Piccotac® 212, being fully aliphatic resins, are a case in point. An aromatic-modified resin of comparable molecular

weight, such as Hercotac® 205, is characterized by a much lower MMAP value, and confers less compatibility with the polymer and hence imparts different performance to the adhesive.

In block copolymer systems, such as SIS copolymers, a high degree of compatibility can no longer be equated with high tack levels. The polystyrene domains of the polymer do not play a role in room temperature tack. Tackification at room temperature can only be achieved through the mid-blocks, requiring the use of aliphatic or (slightly) aromatic modified aliphatic resins. If an aromatic resin was used, there would be a tendency to soften the hard styrenic domains (evidenced by low viscosity), but tack would not be established even at high resin concentrations. In conclusion, a resin with a high MMAP value will impart tack and cohesive strength in SIS, giving a system with relatively high viscosity. A resin with a low MMAP value typically yields a softer adhesive with lower shear and tack properties and a lower viscosity.

The same arguments are valid for SBS block copolymers but the optimum resin-MMAP value for the tackification of SBS is lower than for SIS block copolymers. The SBS-compatibility window in Figures 14 and 15 is accordingly smaller than its SIS-counterpart. High molecular weight, high MMAP aliphatic resins, which show a good degree of compatibility with SIS, fall outside the SBS window. Partially aromatic aliphatic resins give the best balance of adhesion and cohesion in SBS polymers.

DACP and HMDA primarily determine the polarity of the resin but they are also dependent on the molecular weight of the resin. In a given resin family (for example pure C5 resins), DACP increases with increasing molecular weight. DACP and HMDA are more sensitive to molecular weight differences within a given resin family than MMAP.

Resin Properties

Resin molecular weight distribution, ring & ball softening point, MMAP and DACP/HMDA, are the main characteristics useful to a formulator. With these parameters in hand, formulators can easily choose their resin of choice to give optimum adhesive performance with a selected polymer.

Figure 16 shows the typical molecular weight parameter of resins with varying degrees of hydrogenation (or aromatic/aliphatic balances), together with other important parameters for resin characterization. This example only shows resins with similar (100 °C) softening points.

Figure 16**Physical Properties of Regalite® Hydrogenated Hydrocarbon Resins**

Resin Type	Degree of H ₂ , %	Aromaticity H-proton NMR, %	Mn	Mw	Mz	MMAp, °C	DACP, °C
Regalite® S1100	100	1	600	900	1120	79	45
Regalite® R9100	90	4	600	850	1280	73	38
Regalite® R7100	70	11	600	900	1500	63	22
Regalite® S5100	50	15	600	900	1700	52	0

CONCLUSION

Resins are low molecular weight amorphous additives useful in many applications. They provide tack and peel to adhesive systems. They offer a versatile chemistry with a wide range of properties. They can be synthetic or generated from natural sources. Formulators need to have a knowledge of the chemistry of resins since this is key for their compatibility in adhesive formulations. It is essential to know the softening point, molecular weight and aliphatic/aromatic balance, as well as the polarity of a resin. In this way resins provide formulators the ability to optimize their adhesives.

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