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Phenol and Formaldehyde Free Offset Printing Ink Resins

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Abstract

The resin industry is under constant investment, representing a large portion of the chemical industry. The focus for the following years is to eliminate all phenolic compounds from modified resin’s formulations, as the field is seeking a greener future.

Offset printing process demands high-quality inks with specific properties that allow the high-speed oleophilic and hydrophilic transfers between rollers. The modified resin incorporated in the varnish in the ink’s formulations has a major influence on these specifications. For this application, rosin is modified with Resol to achieve an extremely voluminous structure with high solubility values in mineral oils.

To achieve a modified resin without the phenolic portion, with similar properties to one employed in offset printing inks, a phenol-formaldehyde free resin formulation already manufactured was taken as a base to work with and two approaches were taken. Firstly, a similar structure to Resol was attempted introducing two new species, a polyalcohol and a diacid. Intending to create a building block that supports chain growth and allows additional aliphatic ends, balancing the insolubility introduced by the extra ester linkages.

In the secund approach, a bifunctional triglyceride was introduced to the phenol free formulation, replacing the conventional soybean oil. With a hydroxyl group present in the oil’s aliphatic chains a structure increase would be expected.

In both case studies, Target values were accomplished after formulation’s adjustments, when taking into consideration raw materials quantities, acid ratio balance and addiction timings.

Keywords: offset printing ink, phenol-formaldehyde free modified resin, Resol

Resumo Alargado

A indústria de modificação de colofónia está em constante evolução. A presença de substâncias carcinogénicas e derivados de petróleo em diversas formulações leva a preocupações a nível de saúde humana e sustentabilidade. Por estas razões, existe um constante investimento e dedicação em substituir os compostos fenol e formaldeído, que asseguram propriedades únicas em diferentes produtos.

A Respol – Resinas, SA, empresa dedicada à produção de derivados de colofónia, não é exceção e nos últimos anos o departamento de I&D tem-se focado em alargar o catálogo de resinas "phenol-free".

A colofónia como matéria-prima que suporta toda esta indústria de resinas modificadas, por si só tem uma grande valorização a nível industrial e tem despertado o interesse académico. A sua estrutura química com múltiplas funcionalidades faz com que este material biorenovável, seja utilizado em diversas aplicações, tanto na sua forma nativa como modificada.

De uma parceria entre a Faculdade de Ciências da Universidade de Lisboa, o Instituto Superior Técnico, a empresa Woodchem (consultora pertencente ao grupo RESPOL) e a Respol – Resinas SA, tem origem esta dissertação de mestrado que se enquadra no tema referido, "Formulação de resinas sem compostos de fenol e de formaldeído".

Este estudo centra-se na formulação de uma nova resina isenta destas espécies para utilização em tintas de impressão offset. Uma tinta convencional para este tipo de aplicação é constituída por pigmentos, que oferecerem coloração, aditivos que permitem modificar propriedades finais da tinta, e um verniz. Este último é considerado o elemento focal, sendo composto por uma percentagem de resina modificada (20-50%), óleo vegetal e óleo mineral. Responsável por propriedades como aderência, viscosidade, estabilidade, secagem e brilho. A resina empregue tem obrigatoriamente de ter uma elevada viscosidade e solubilidade nos óleos utilizados.

Umas das resinas que a Respol comercializa para esta aplicação tem a designação R2038. O grupo metilol ao reagir com os ácidos resínicos gera uma estrutura extremamente volumosa e intrincada com cadeiras alifáticas que proporcionam um elevado ponto de amolecimento e uma alta solubilidade nos óleos minerais de Halterman.

Para iniciar as cargas piloto deste estudo, foi utilizada a formulação da resina livre de fenóis R3064, e realizadas algumas alterações de modo a entender a influência das matérias-primas na resina final. Foi substituído óleo de soja por óleo de peixe, aumentada a quantidade de ácido esteárico, reduzida a função éster e alterada a quantidade de óleo a utilizar em função de ácido esteárico.

Após uma extensa pesquisa e leitura de artigos científicos e análise de trabalho já realizado no laboratório, a ideia de que a introdução de novas estruturas químicas seria uma mais-valia para atingir o objetivo deste trabalho tornou-se evidente. Duas abordagens foram então tomadas.

A primeira baseou-se na criação de uma estrutura semelhante ao *Resol*, utilizando um álcool e um ácido. Sendo o objetivo gerar uma estrutura de base volumosa com possíveis pontos alifáticos. Para tal, inicialmente, três novas espécies químicas foram testadas, o dietilenoglicol, o ácido isoftálico e o ácido succínico. O álcool e um dos ácidos foram adicionados ao reator após fusão

da colofónia e adição de ácido fumárico e ácido esteárico. Esta introdução tanto com o primeiro ácido como com o segundo, levou a maiores insolubilidades nos óleos de Halterman, no entanto, utilizando o ácido isoftálico a viscosidade da resina final aumentou substancialmente. O maior problema na formulação de resinas é conseguir contrariar o aumento de insolubilidades com o aumento de viscosidade. O monómero gerado não favorecia a resolução desta problemática e por isso, um novo monómero foi idealizado.

O diálcool foi substituído por um álcool de seis grupos hidroxilos, o dipentaeritritol, como forma de aumentar os possíveis pontos de alifaticidade. A formulação foi ainda ajustada na quantidade de ácido esteárico para que o comportamento viscoelástico da resina não tendesse para gel. A resina final desta primeira carga com as novas matérias-primas atingiu os valores requeridos de viscosidade e solubilidade, no entanto, após algumas alterações a sua reprodutibilidade não se verificou, acabando as cargas por gelificar.

Após o ajuste das quantidades do monómero utilizadas o comportamento elástico da resina reduziu, obtendo-se valores de descarga da mesma. Os parâmetros encontravam-se próximos dos objetivos, porém, a resina apresentava uma turvação e resíduo característico. Algumas alterações para aproximar os valores da referência R2038 foram efetuadas. Contudo, as observações de turvação e resíduo mantinham-se. O aspeto turvo foi associado ao ponto de sublimação do ácido isoftálico, por esta razão, o diácido foi substituído pelo seu isómero, anidrido ftálico. A turvação desapareceu por completo, todavia, o resíduo insolúvel em tolueno manteve-se. Procedeu-se à alteração dos catalisadores e quantidades utilizadas de modo a observar se o material estaria associado à formação de um sal, relação que não se verificou. Conclusão confirmada por uma análise termogravimétrica que comprovou a origem orgânica.

Por último nesta abordagem, alterou-se a temperatura à qual o dipentaeritritol é adicionado ao reator para 230ºC, em vez da sua adição no carregamento inicial juntamente com a colofónia. A quantidade de resíduo reduziu significativamente, mantendo-se abaixo dos 120ppm, quantidade máxima de resíduo de uma resina. Concluindo-se que este estaria relacionado com o facto de o ponto de fusão do álcool ser 218ºC e o mesmo não estar a reagir na sua forma sólida, sofrendo mais tarde reações paralelas que resultavam neste resíduo.

Na segunda parte deste estudo, um novo óleo foi introduzido à formulação base. Um triglicerídeo com bifuncionalidade, o óleo de ricínio. Com um grupo hidroxilo na posição C_{12} das suas cadeias alifáticas, o ácido gordo adquire uma reatividade superior aos típicos triglicerídeos utilizados em formulações. Este foi conjugado com o tetra-álcool da formulação, as diferenças estruturais das duas espécies químicas poderiam tornar-se interessantes. Rapidamente se entendeu que ao proceder à substituição de grupos hidroxilos de uma espécie pelo mesmo grupo funcional da outra, é possível reduzir a relação insolubilidade e viscosidade.

Por fim, após algumas alterações para aproximar a carga aos valores de referência, um último ajuste foi realizado em ambas as abordagens. Com o objetivo de aumentar tenuemente o comportamento viscoso sem modificar a solubilidade das resinas, o bloqueador de cadeias, ácido esteárico, foi adicionado em duas partes. Esta alteração processual possibilitou um maior desenvolvimento de estruturas mantendo o número de estruturas alifáticas presentes.

Embora se tenham obtido resultados próximos das propriedades da resina fenólica, no contexto pandémico em que este trabalho prático decorreu, a utilização de novas matérias-primas no complexo fabril, até à data, não se pode considerar viável economicamente.

Palavras-chave: viscosidade, solubilidade, dipentaeritritol, óleo de ricínio

Chapter 1. Respol Group

This internship was endorsed by Woodchem SA in partnership with Respol, Resinas SA.

Woochem is a research and development company, founded in 2019, to promote and support ideas and projects that aim to investigate raw materials of natural origin or waste with high potential to generate new products and energy in a circular economy framework. As well as, developing new technologies and sustainable production process or improving existing ones to make them more efficient and environmentally responsible.

Respol Resinas is a family business registered as a company operating in CAE 20141, referring to the manufacturing of resin and its derivatives, which develop, produce, and commercialize colophony derivatives for several applications. The company focusses on maintaining a high level of client satisfaction, offering the best rosin derivatives on the market with a proactive and quick response to challenges. A common effort along all departments and 150 employees, to this day, turns this mission easily achievable.

The company is organized in the following structure:

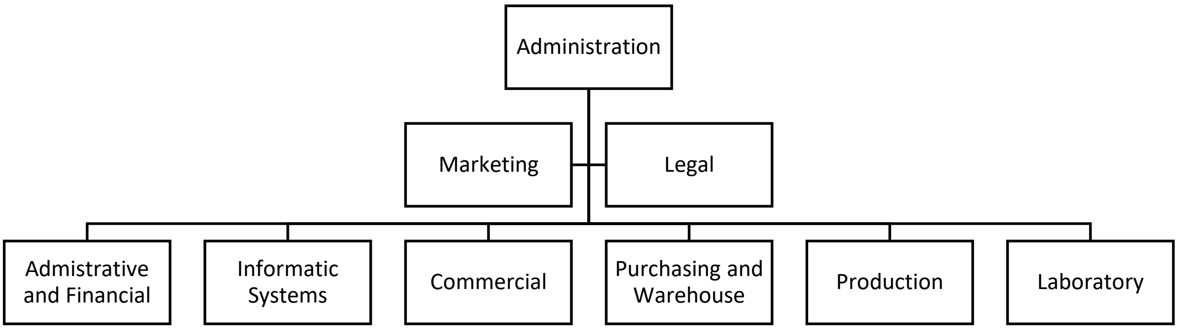

Figure 1.1 – Respol's organizational structure (2022)

1.1. History

The history of Respol, Resinas S.A. goes way back to the end of the 19th century, where in 1883 in the city of Leiria, a small familiar business explored the gum rosin tapping process.

With the business growth, in 1973, Resipez – Indústria e Comércio de Resinas LDA was founded in the town of Pinheiros. This new entity aimed to distil pine resin, primarily from pine forests in the central area, to commercialize turpentine and rosin.

Later, in 1993, in facilities adjacent to Resipez, Respol – Resinas S.A. was born. This factory was equipped with the technology of the then dismantled DSM – Resins and Functional Materials, located in Lisbon in the industrial area of Cabo Ruivo. The company's purpose was to produce and sell rosin derivatives resins, for application in paint, varnishes, chewing gum, polyester processing industry, adhesives, and printing inks.

The factory started its activity with a production capacity of 6.000 tonnes/year. This capacity quickly grew with the improvement of operational conditions of the industrial unit. Subsequently, the company expanded both in national and international market.

In 2002, with the expansion of the international market came an increase on demands for hard resins, this led to the abandonment of the production of alkyd resins, unsaturated polyester, and aqueous dispersion. The industrial complex started to focus on the production of resin derived from gum rosin of pine trees.

In the following years, with an increase in production capacity and variety of products, a rapid growth of business came. In 2007, the company exported 30.000 ton/year for the European market.

Resipez and Respol came together in 2008. Two years later, Respol purchase Cray Valley, located in Spain, thus, expanding the number of products in its portfolio.

In 2013, Forchem Oy joins the Respol family. This Tall Oil refinery in Finland is one of the world's most modern and ecologically sustainable. With the purchase Respol granted the control of its prime raw material, colophony.

Two years ago, the company dislocated its distillation complex to Albergaria dos Doze, in the town of Pombal.

Nowadays, Respol, Resinas SA is a chemical company dedicated to the manufacture of rosin derivatives, with a 50.000 ton/year production capacity and exporting 90% of the volume to the international market, namely European union, United States of America, and middle east.

1.2. Production Process

Every week the industrial complex receives new raw materials, which after passing through the proper quality control is stored in vertical cylindrical tanks, in the case of raw materials in the liquid state, in the covered warehouse for solid substances or in the outdoor paved park, where 200 kg zinc drums of rosin are kept.

The supply of raw materials to the reactor follows. Materials in the cylindrical tanks are routed through the line that directly connects these to the reactors, solid compounds are weighed and placed on the respective reactor platform to be dosed. Solid rosin is placed in one of the two melting tanks who operate in parallel, with temperatures up to 150ºC. Then filtered and sent to the intermediate storage tanks, from these the raw material is dosed to the reactors.

Production floor is equipped with ten reactors (Figure 1.2). Up to eight batches can be produced simultaneously, being that each batch can last up to two days or more. Reactions are monitored by the production laboratory and when at the desired specifications, the final product is unloaded to one of the four flakers. Located at a level below the reactor, these metal double screens with water flow, serving as a cooling fluid, forward the resin to the big bags, where the product will be stored and moved into the final product warehouse to posterior expedition.

During reaction process, from esterification of resin acids a by-product is formed, water. Its removal is essential and done through the condenser existing at the top of the reactor. To ensure complete removal of this by-product, vacuum is applied to the reactor at the end of each reaction. Water is then forward to Respol's ETARI for further treatment

Figure 1.2 - Production's reactor floor

1.3. Laboratories

Respol's laboratory, equipped with the most advanced resources for its area of expertise, is divided in three sections: the research and development, industrial pilot unit and quality control, where quality of incoming raw materials is verified.

Research and development, figure 1.3b, area focuses on developing innovative eco-friendly and sustainable products to attain clients and market demands, collaborating with external research centers. The laboratory is provided with many equipment, all able to perform reference analytical techniques on rosin derivatives and on customer's products. The team sets new solutions for clients, develops tailor-made products, renders technical support to the resin market, and cooperates with external research centres or complexes on subjects such as rosin derivatives and analytical techniques. Lab facilities hold a pilot scale-unit (Figure 1.3c) destinated to optimize and speed-up the technical transfer of our products from lab to plant scale production.

This internship was carried out at the R&D lab. Integrating the lab's team, the necessary laboratory material and equipment to achieve this thesis purpose was at my disposal. The study was accomplished with a level of autonomy and the help and guidance of colleagues.

Figure 1.3 - Respol's headquarters (a); I&D laboratory (b); pilot scale-unit where formulations were tested (c)

1.4. Health, Safety and Security Policies

1.4.1. Coronavirus Pandemic

This thesis took place during a world pandemic situation. In this subchapter I will describe how a common effort between me and Respol, allowed me to not interrupt my internship.

In December 2019 the first case of the new coronavirus SARS-CoV-2 appeared in Wuhan (China). Quickly the disease spread throughout the world, being recognized as a pandemic on 11th March. To attenuate the spread of this disease, Portugal government declared Emergency State for 45 days, ending on 2nd May 2020. During this time, companies had to take certain precautions. Respol implemented rules like social distancing, the obligatory use of masks, body temperature scans as interring the factory and more alcohol gel dispersers. Also, by recommendation of Portuguese Public Health department, the number of people working in the factory was reduced to only the necessary, meaning that interns were sent home during this Emergency State. During the rest of the year Portugal was under the necessary measures to control the virus dissemination, masks were mandatory in closed and opened spaces, hands disinfection and social distance was recommended.

Though due to coronavirus mutations to variants more transmissible, the country declared another Emergency State on January 14th, 2021, lasting until April 30th 2021. This secund emergency state was during my internship, though by this time the number of people working in the laboratory was inferior to the year before. The company was able to assure my practical work, rearranging work schedules so that only four workers were in the lab at the same time.

Chapter 2. Framing

One of rosin derivatives application is in ink making for offset printing. The origin of the printing process dates to the 18th century and today dominates the printing industry all over the world, as it offers the highest printing speed and quality.

As the target of this thesis is for this usage, the whole printing process will be unveiled in this chapter, as well as ink formulations and requirements.

2.1. Offset Printing Process

Offset printing was initially conceived to be an inexpensive method of reproducing artwork. The breakthrough was based on the phenomena of hydrophobicity and hydrophilicity [1]. Initially the process was limited to use on flat porous surfaces because the printing plates were produced from limestone. Though, quickly the stone was replaced by a metal cylinder and the first rotary offset lithography printing press was created.

Offset lithography process, figure 2.1, starts with a plate cylinder whose surface comprises areas covered with either oleophilic or hydrophilic coatings. These two areas correspond to image areas and non-image areas, respectively. As the plate cylinder rotates, its first point of contact is with the water rollers, who spread a mixture of water and other chemicals to the non-image areas of the plate cylinder. This pre-treatment with water, prevents the ink from staining the non-image areas. Next, the ink roller wets the image-areas with ink and, when fully coated, the plate cylinder transfers the ink images onto the blanket cylinder, also called offset cylinder. The substrate runs in between the impression cylinder and the blanket cylinder and pressed onto the blanket cylinder by the printing one. The images are at this point printed onto the substrate. Hence, the offset lithography gets its name "offset", due to the fact that the plate cylinder is not directly touching on the substrate [1] [2] [3].

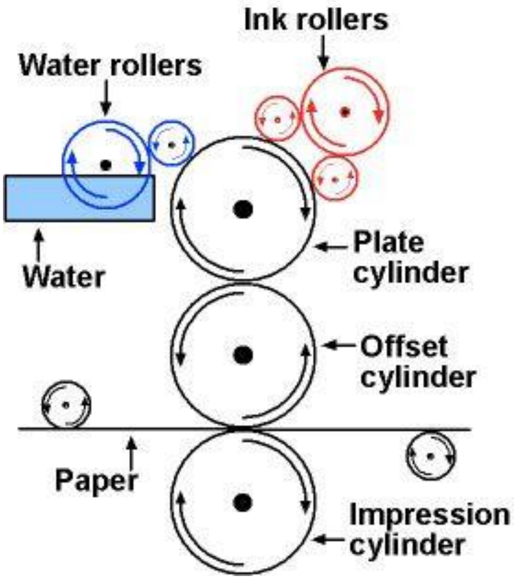

Figure 2.1 - Scheme of the offset printing process

2.2. Requirements for Offset Printing Inks

Colourants, vehicle, and the carrier substance or solvents are the main components of the ink. Moreover, to enhance or modify the final ink properties, additives may be added to the ink formulation[4] [5].

Colourants are responsible for providing colouration. Vehicle is the liquid who holds particles of pigments and carries them to the paper. Responsible for properties such as tack, viscosity, stability, drying, setting speed and gloss, the vehicle is the most important element. The carrier substance transports the colourants[4][6].

Inks used on an offset press must be able to carry the full-intended colour and covering power to the paper despite the split-film action. This occurs because the blanket cylinder picks up only a portion of the ink from the plate cylinder and delivers just a portion of that to the substrate[1][3]. The film of ink reaching the plate, then, is very thin, therefore, the ink must be able to show its full colour and opacity with this film. For this reason, offset printing inks need to have a specific composition that allow high quality printing.

In inks destinated to offset printing the vehicle is a mixture of resins or polymers, from natural or synthetic origin (rosin or phenol derivates, respectively), and a mineral or vegetable oil. Resins or polymers play an important role when thinking of offset inks characteristics. These require solubility in the carrier substance, as well as high viscosity when in solution with the oils and a good pigment wetting ability[2]. The aforementioned capabilities favour the highly viscous behaviour, the viscoelastic properties and the high tack values, characteristics of these inks that allow the high printing speeds associated to the process[7].

A conventional ink blend for offset printing process is [2]:

- Varnish, including the vehicle and the carrier substances, consists of 20-50% hard resins with a high proportion of colophony, 0-20% alkyd resins, 0-30% vegetable oil and 20-40% of mineral oils.
- Pigments, 10-30%.
- Additives, 0-10%.

Chapter 3. Introduction to Modified Rosin

3.1. Rosin

Pine genus (*genus Pinus*) of about 120 species of evergreen conifers of the pine family (*Pinaceae*), are distributed throughout the world, but primarily native to northern temperate regions [8].

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 within different parts of the same tree [9].

Being the specie of this family with the most resin ducts, *pinus pinaster* is cultivated not only for its timber but mainly for its ability to produce resin. The resin is formed in epithelial cells and accumulated in resin ducts. With more resin ducts than other conifers, the specie has the ability to form new resin ducts following biotic and abiotic attacks [6] [10]. This characteristic is extremely important, since only 2-5%, of the chemical composition of wood species, are extractives where rosin is found.

The harvest is made by pine tapping, a process based on the defence system of the tree, which secretes resin as a defensive response to external factors [6].

Resin products from pines are commonly called naval stores. The term dates back to the days when the British Royal Navy used large quantities of resin products to waterproof ships [6]. Today, rosin is still largely obtained from turpentining, so-called gum rosin, however other techniques are being used. From the kraft process in paper making rosin is obtained as a by-product, called tall oil rosin. A third way of obtaining the raw material is by solvent extraction from harvested wood, the so-called wood rosin [6] [8].

The exuded resin is now put throw a distillation process and the outcome is a volatile fraction, the turpentine (30%), and a non-volatile portion, the rosin or colophony (70%) [6] [10].

Turpentine is composed of terpenes, primarily the monoterpenes alpha- and beta-pinene, with lesser amounts of carene, camphene, dipentene and terpinolene. Mainly used as a solvent, matching rosin and those of petroleum origin. Used as a raw material for the industries of soap, printing inks, varnishes, rubber, paper sizing, pharmaceuticals, pressure adhesives among many others [6] [8].

3.2. Rosin Composition

The raw material is mainly composed of diterpenic monocarboxylic acids, commonly known as resin acids, whose generic formula is $C_{19}H_{29}COOH$. This composition does not vary according to its origin, normally rosin is mainly composed of 90-95% resin acids [6] [11]. The residual components are primarily made up of neutral compound, nature of which depends on the specific origin of the raw material [6] .

Pine resin acids belong to four basic skeletal classes, three of which with a tricyclic carbon skeleton: abietane, pimarane, isopimarane, and a less common with a bicyclic skeleton: labdane [11] [9] (table 3.1). Percentage of each resin acid varies to different species, though, the processing and handling conditions (e.g. temperature and pH) can also be a critical factors, as it can induce isomerization of the double bond system or result in a disproportionation process [9] [12]

Table 3.1 – Rosin composition (%) in resin acids[6]

Rosin Acid	Elliotti (Brasilian Rosin) %	Tall Oil Rosin %	Portuguese Rosin %
Abietic	32,2	44,3	30,1
Levopimaric + Palustric	15,0	7,7	22,1
Neoabietic	17,3	4,2	17,5
Dehydroabietic	4,5	21,7	7,2
Pimaric	5,2	2,8	10,1
Isopimaric	16,9	5,9	9,9
Sandaracopimáric	1,5	1,0	1,5
Comunic	3,6	0,0	0,0
Other Acids	3,9	12,3	1,6

The abietane skeletal class divides in five different acids differing only on the position of the double bonds (Figure 3.1) [9] [11] . The arranging of these bonds is an important characteristic since it affects their chemical reactivity and, consequently, the applications of resultant products [9], hence, these types of resin acids being the ones associated to rosin chemical reactions. Dehydroabietic acid is among all the less relevant to this topic, having an aromatic ring which bring stability to the molecule.

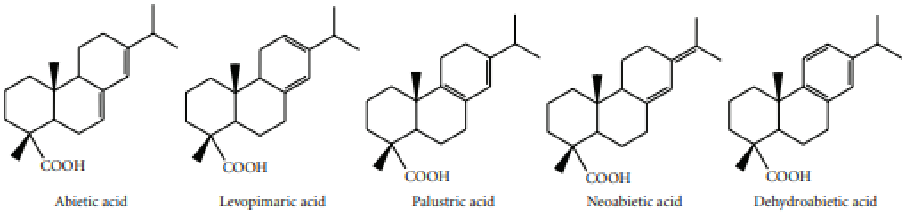

Figure 3.1 – Abietane skeletal class molecular structures

3.3. Rosin Modifications

Nowadays, rosin is modified to reach improved properties, thus, accommodates a wide variety of applications and technological purposes. In ink manufacture, rosin is never used in an unmodified form. As mentioned before, these modifications involve rosin acids.

Rosin acid’s chemical reactivity is determined by the presence of both the double bond system and the carboxylic group [13]. The conjugated double bond system present in abietic-type acids, enhances the reactivity associated with it. Thus, the olefinic system can be involved in oxidation, hydrogenation, dehydrogenation and isomerization, Diels-Alder, and phenol-formaldehyde reactions. On the other hand, the carboxylic group is mainly responsible for esterification, salt formation and decarboxylation reactions [9] [11].

3.3.1 Methylol Phenol – Lederer-Manasse Reaction

This reaction is associated to the condensation of phenol and formaldehyde, leading to the formation of methylol phenol, at temperatures, normally, not higher than 60ºC. The molecule formed can suffer another addition reaction with formaldehyde or condensate with an analogous unit of methylol phenol [14] (figure 3.2).

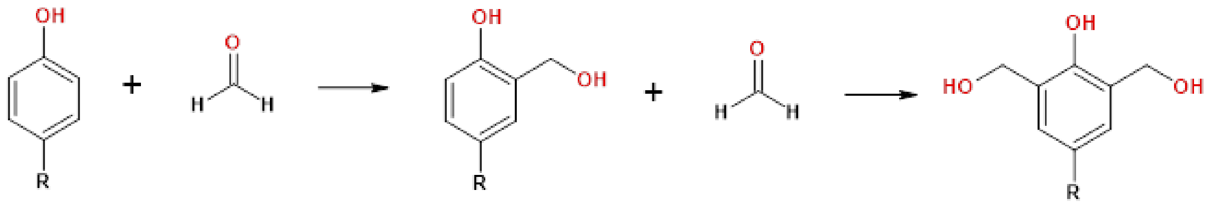

Figure 3.2 - Addition of formaldehyde to a para-alkyl phenol and post addiction with formaldehyde

3.3.2 Oligomerization

Above 60ºC oligomerization reactions take place, hence, occurs condensation between methylol phenol units until a resol resin structure is formed [14]. A by-product is formed as seen in figure 3.3, water.

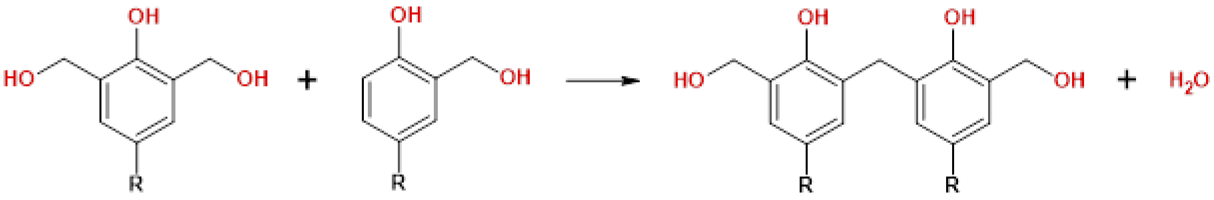

Figure 3.3 – Condensation reaction between methylol phenol units, adapted from [15]

3.3.3 Chroman Ring Formation

Resol condensates forming a polymer that reacts, by Diels-Alder addition, with abietic acids, developing a particular structure intituled by Chroman ring [14] (figure 3.4). It is considered the structure generated with the resin acids is associated with the increased solubility, this theory is discussed later in chapter 4.

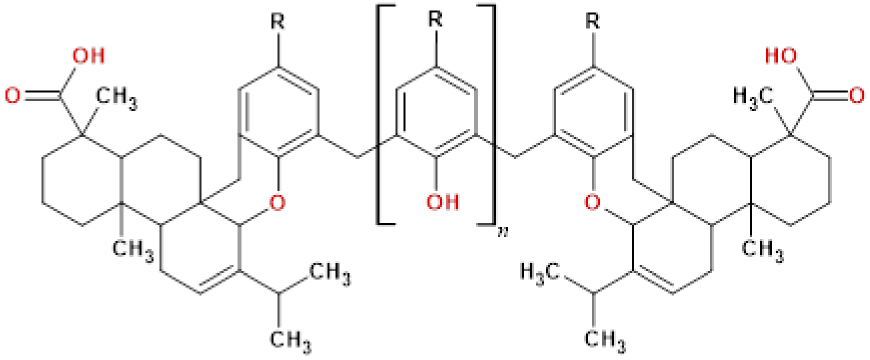

Figure 3.4 - Chromane-like structure. Resol bridge between two resin acids, adapted from [15]

3.3.4 Diels-Alder Addition

The addition reaction occurs between a diene and a dienophile at 150ºC, allowing adduct formation. The reaction is optimized by the simultaneous isomerization process giving levopimaric acid (diene), which is the major isomer able to undergo the reaction [9] [6]. Dienophiles can be of a wide variety, though, when modifying rosin, the highly used are fumaric acid and maleic anhydride, figure 3.7**.** Resin acid adducts presence is significant to this matter, providing molecular weight, viscous behaviour, higher softening point and lower solubilities.

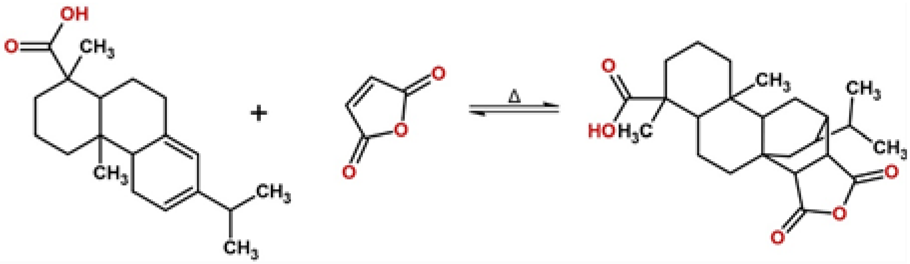

Figure 3.5 - Maleic adduct formation via Diels-Alder reaction, adapted from [15]

3.3.5 Esterification

Esterification occurs between carboxylic acids and hydroxyl groups, producing water as a by-product (figure 3.8). The presence of this secondary product is unsought as it can reverse the reaction and unfold the ester linkage, therefore water is removed during the process. Esterification of resin acids is performed industrially at high temperatures (260-300ºC) in presence of metal oxides or hydroxides as catalysts. This is the most important reaction in modified resin.

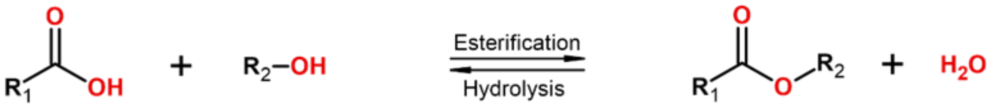

Figure 3.6- Esterification reaction

3.3.6 Transesterification

A side reaction of the previous, consisting in the ester exchange (figure 3.9). Though occurring in small scale, still need to be considered as the occurrence impacts the final product.

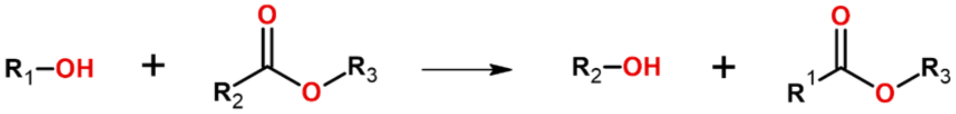

Figure 3.7 - Transesterification reaction

3.3.7 Etherification

Associated to low molecular weights, etherification is another side reaction that can take place. The reaction consumes hydroxyl groups and stops poliesterifications from happening.

3.3.8 Salt Formation

Numerous metals can react with resin acids and form the so-called secondary. Some of the most common Na, Mg, Ca, Zn, Al and ammonium [9] [13]. These salts can be produced industrially. In the past some of these were used as soaps, nowadays, resin acid salts like sodium are used as intermediates in paper sizing [9].

These reactions can sometimes be a problem when modifying rosin. Occurring as a side reaction, the salts resulted end up clogging reactor's filter.

3.4.Hansen Solubility

Systems considered on this thesis are extremely complex to be described by a theoretical prediction. Though, once the aim of this work is to reach a rosin resin soluble in a highly aliphatic oil, an understanding of Hansen Solubility theory may be of interest, to get familiar with solubility concepts.

The theory is based on molecule structure and functional groups present, the idea that "like dissolves like" where one molecule is defined as being "like" another if it bonds to itself in a similar way. Hansen solubility parameters are an alternative tool in evaluating the ability of the solvent to interact via dispersion forces, δ_d, dipole-dipole interactions, δ_p, and hydrogen bonding interactions, δ_h [16]. Allowing us to predict the solubility of a molecule in a solvent, only being familiar with the terms. Two species with similar contributions on the three parameters are soluble in each other.

It is also possible to calculate an accurate value for all contributions of the structural groups of a molecule by this theory, though, in this case it would not be accurate enough, as mentioned before due to complexity.

As noted in table 3.2 for species included in the mineral oils 6/9 AF and 6/9 AF New, dispersion forces parameter is the only relevant one [17]. The same happens in aliphatic groups (table 3.3), however, on the other hand in groups associated with polyester structures the three interactions are evident. Suggesting polyesters are less soluble in mineral oils than aliphatic structures.

Table 3.2 – Solubilities parameters for species present in Hanssen mineral oils adapted from [16]

	Liquid	**δ_d**	**δ_p**	**δ_h**
Included in 6/9 AF	Butane	14.1	-	-
	Pentane	14.5	-	-
	Hexane	14.9	-	-
	Octane	15.3	-	-
	Nonane	15.5	-	-
	Decane	15.8	-	-
	Dodecane	16.0	-	-
	Hexadecane	16.4	-	-
Included in 6/9 AF and 6/9 AF New	Cyclohexane	16.8	-	-
	Methylcyclohexane	16.0	-	-
	Cis-decahydronaphthalene	18.8	-	-
	Trans-decahydronaphthalene	18.0	-	-

Table 3.3 – Solubility parameters for groups present in aliphatic and polyester structures, adapted from [15]

Structural group	**F_d**	**F_p**	**F_h**
-CH3	419	-	-
-CH2-	270	-	-
5- or 6-member ring	190	-	-
-COO- ester	667	511	2557