



CIN - CORPORAÇÃO INDUSTRIAL DO NORTE, S.A.

Resiquímica 



High Solids Alkyd Resins



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1. Introduction

1.1. Alkyd resins

The word alkyd derives from "al" from alcohol and "cid" from acid; "cid" was changed to "kyd". Alkyd resins in a broad sense refer to polyesters [1].

Alkyd resins are made by condensation polymerization of three types of monomers of different functionalities: polyols, polybasic acids and fatty acids or triglyceride oils. In **Figures 1** and **2** is schematised alkyd production from triglyceride oils.

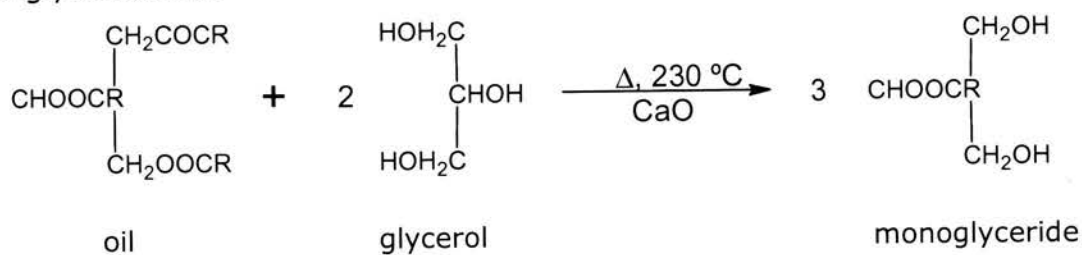


Figure 1 First step in alkyd resins: alcoholysis of oil to form monoglycerides.

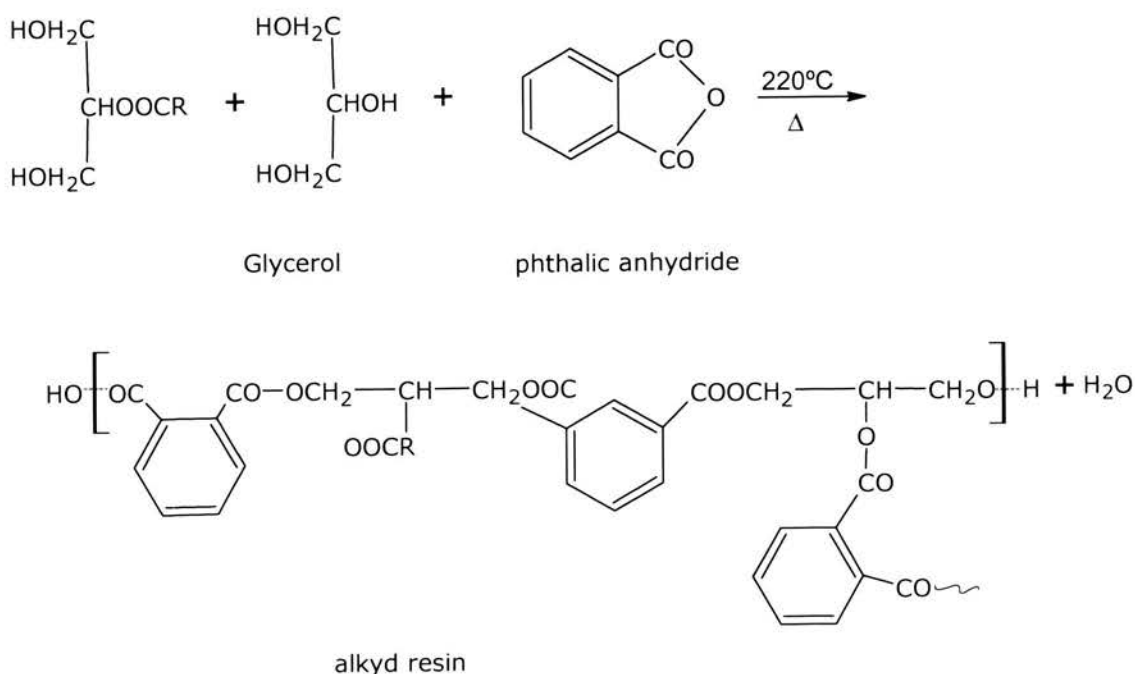


Figure 2 Monoglyceride's reaction with phthalic anhydride to form alkyd resin.

The largest use of alkyds is for surface coatings as paints, enamels, lacquers and varnishes. Alkyd resins are not the largest volume vehicles in coatings, but still are of major importance. They have lower cost than most vehicles and tend to give coatings that have fewer film defects during application, however, durability of alkyd films, especially outdoors, tends to be poorer than films from acrylic and polyurethane [2].

1.1.1. History

The development of alkyd resins can be separated into two different phases. The first period is from 1847 to the early years of the twentieth century. During this time the reaction products of polyhydric alcohol and polybasic acids were studied for academic interest and industrial applications. The second phase started after 1918, with investigations of reactions between glycerol and phthalic anhydride. These investigations were performed by researchers at two Electric firms: American General Electric Company and British Thomson Houston Company, and concerned production techniques and investigation of the effects of formulations on resins properties [3].

The first polyester resin was made by Berzelius in 1847 and in 1901 W. Smith reported a glycerol/ phthalic anhydride polymer. The General Electrical Program lead, in 1921, to glycerol/ phthalic anhydride/ fatty acids polymers. These were used commercially as adhesives in 1926.

In the 1930's linseed oil was the most common binder for architectural paints, but alkyds were starting to replace it. By the 1950's alkyds became a prominent binder for coating and water based architectural paints were being introduced. Until the 1970's, water based architectural paints captured market from alkyds. However, alkyd use continued to increase during most of this period, because of their uses in a variety of industrial and special purposes coatings and inks [4].

After the 1980's the consumption of alkyds started to decline at a slow rate.

Nowadays alkyds are well-established in specialized uses and its replacement would be difficult. Besides, the rising of petrochemical prices

have increased interest in polymers made partially from renewable resources.

1.1.2. Raw materials

Alkyd produced with triglyceride oils always contains some glycerol and other polyols can be used. Glycerol is the most widely used polyol because is present in oils from which alkyds are synthesized.

Alkyd produced with fatty acids uses any polyol or polyol mixture. Glycerol can be used but common choice is inexpensive synthetic polyols like 1,1,1-trimethylolpropane and pentaerythritol.

Dibasic acids used to prepare alkyds are usually aromatic. In alkyd processing, polybasic acids are almost never used. Instead, their internal cyclic anhydrides are used. The anhydrides are easier to polymerize, more stable and economical. They form the same polymer compositions as the acids.

Phthalic anhydride is used more than any polybasic acid for reasons of economy and easy processing. When weatherability and corrosion resistance is required, isophthalic acid is often used. Cycloaliphatic diacids have good weatherability also.

Many alkyds contain a small percentage of maleic acid. This acid reduces resin colour.

For alkyds made with fatty acid process tall oil fatty acids are usually used because they are more economical than other fatty acids.

For alkyds made by the monoglyceride process, the fatty acids used in alkyd production can be obtained by triglyceride oils hidrolisis. The fatty acid composition of the oil is not substantially changed by hydrolysis process and from this process are obtained fatty acids mixtures. Linseed oil fatty acid and soybean oil fatty acid are used worldwide. Soybean oil is economical and the supplies are reliable because it is an agriculture product. In fact, the critical factor involved in the fatty acid choice is cost.

The composition of the fatty acid mixture may vary with soil, climate and damage of plant and extraction processes.

Fatty acids compositions of some of the more common vegetable oils are shown in **Table 1**.

Besides polyols, polybasic acids and fatty acids other monomers can be added to form alkyds. These are modified alkyds.

The most important modified alkyds are chain stopped, styrenated, acrylated, silicone and thixotropic alkyds.

Table 1 Fatty acids composition of some of the more common vegetable oils.

Fatty acids	Unsaturation	Coconut oil	Castor oil	Grape seed oil	Linseed oil	Oiticica oil	Palm oil	Palm Kernal oil	Safflower oil	Sunflower oil	Soya Bean Oil	Tung oil	Tall oil	Dehydrated Castor oil
Caprylic $C_8H_{16}O_2$		6					4% of hydroxy acids	3						
Capric $C_{10}H_{20}O_2$		6						4						
Lauric $C_{12}H_{22}O_2$		44						51						
Myristic $C_{14}H_{28}O_2$		18					1	17						
Palmitic $C_{16}H_{32}O_2$		11	2	9	6	7	48	8	8	11	11	4	5	
Stearic $C_{18}H_{36}O_2$		6	1	4	4	5	4	2	3	6	4	1	2	
Oleic $C_{18}H_{34}O_2$	(-2H)	7	7	20	22	6	38	13	13	29	25	8	48	9
Ricinoleic $C_{18}H_{34}O_2$	(-2H)		87											8
Linoleic $C_{18}H_{34}O_2$	(-4H)		3	67	16		9	2	52	52	51	4	45	83
Linolenic $C_{18}H_{30}O_2$	(-6H)	2			52				2	2	9	3		
Eleostearic $C_{18}H_{30}O_2$	(-6H)											80		
Licanic $C_{18}H_{30}O_2$	(-6H)					78								

1.1.3. Definitions

- Oil length

Oil length is the fatty acid amount present in the resins (in percentage). Alkyds are short oil if fatty acid percentage is less than 45%, medium oil if fatty acid percentage is between 45-55% and long oil if fatty acid percentage is greater than 55%.

- Acid value

Acid value is the potassium hydroxide necessary, in mg, to neutralize 1 g of resin. Acid value is used for fatty acid analysis and alkyds resins control.

- Hydroxyl number

Hydroxyl number is the potassium hydroxide equivalent, in mg, to the amount of acylation of 1 g of resin.

- Functionality

A functional group is the particular arrangement of atoms in a molecule that is capable of undergoing a polymerization reaction ^[5]. The functionality of monomer molecule is the number of functional group in the molecule.

- Molecular weight (MW)

This characteristic has considerable importance, because it has a big significance on properties like solubility, rheology, dry speed and performance.

For condensation polymers the relation between polymer molecular weight and monomer molecular weight is very complicated, depending on

functionality of monomers and extent of polymerization [5]. All polymers used in the coating industry are mixtures or distributions of polymers of different molecular weight. So, the molecular weight of a polymer is highly dependent on the measurement method used. The two most important measures of molecular weight averages are number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w). The number-average MW counts the number of molecules of a particular weight and averages this with over the total number of molecules:

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad (1)$$

N_i represents the number of molecules of the i th species and M_i is the molecular weight of the i th species.

The weight-average MW averages the weight of each of the different MW species or segments distributed all over the polymer.

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} \quad (2)$$

W_i represents the weight of molecules of the i th species. The expression can be written ($W_i = N_i M_i$):

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (3)$$

Heavier molecules affect \bar{M}_w more than the light ones, \bar{M}_w is always greater than \bar{M}_n .

- Molecular weight distribution

The ratio $\overline{M}_n / \overline{M}_w$ gives the molecular weight distribution and indicates the breadth of distribution of molecular weight species in the polymer. This is a useful measure of the polydispersity of the polymer.

- Glass transition temperature (T_g)

This temperature identifies a second order transition, characteristic of all high polymers and indicates the transition from rubbery or plastic state to the glassy state, with decreasing temperature. T_g affects the final coating hardness.

1.1.4. Polymer theory

A polymer is built by small structural units linked together with covalent bonds ^[5]. The size of the chain in weight units is the molecular weight. The subscript n in polymer structures is used to indicate the number of monomer units polymerized and the degree of polymerization. The degree of polymerization of polymers is at least 10.

Oligomers are low molecular weight polymers (short chains); they are very important to the coating industry, especially for high solids and radiation coating industry.

When a difunctional acid or anhydride (AA) and a difunctional alcohol (BB) are heated together, a stepwise reaction occurs (**Figure 3**).

Under certain conditions, polymer chains contain thousands of monomers units, so that a very high molecular mass is formed. The mixture must be heated long enough to complete reaction, equimolar quantities must be present and no alternative reactions may occur. A and B can not contain monofunctional reactive impurities.

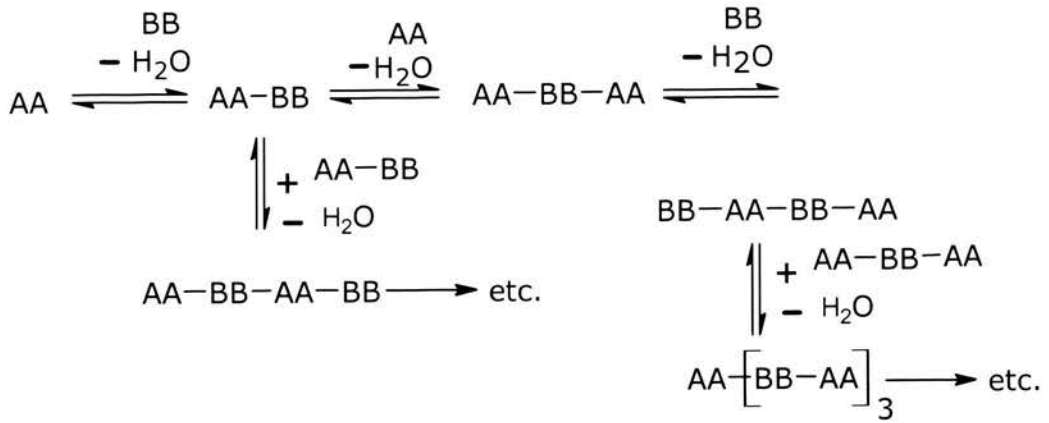


Figure 3 Stepwise reaction.

If a trifunctional monomer BBB is added then chain branching occurs. However, if substantial amounts of BBB are present, continued polymerization leads to gel formation (three dimensional network). To prepare structures that are branched but not gelled is an objective in alkyds synthesis. Gel causes loss of materials and difficult clean-up.

Carothers developed a polymerization theory: a uniform stepwise process gelation occurs as the molecular mass approaches the infinite. The gelation condition is:

$$p_g = \frac{2}{F} \tag{4}$$

p_g is the extent of reaction at the gel point and F is the average functionality of the monomer mixture. F is formally defined as the ratio between total number of effective groups and total number of molecules^[6]. Carothers p_g predictions are higher than reality.

Flory proposed that gelation occurs when a relatively small proportion of the monomer molecules first become bonded into a three dimensional network. This theory is satisfactory for straightforward monomers used to produce polymers. However, alkyds formulation deals with monomers not so simple.

A precise theory for alkyd resins is improbable because alkyd polymerization may not be homogeneous during the last stages of reaction and most alkyds contain gel particles that can be important to obtain optimum properties.

1.1.5. Film formation

There are two mechanisms to transform liquid coatings in film (cure): drying by solvent evaporation and cross-link to form a polymer network. Several coatings (based on alkyd resins) depend on both mechanisms.

The type of fatty acid regulates the properties of alkyds and they can be classified into drying or non-drying, depending on the degree of unsaturation.

In the first case, the curing mechanism involves autoxidation cross-linking of the unsaturated fatty acid that remains in the resin. Most studies in this subject involve drying oils rather than complex alkyd resins.

In non conjugated unsaturated oils the initiator group is the diallylic group (-CH=CHCH₂CH=CH-) from esters of linoleic acid and linolenic acid. The cure process is related to the number of diallylic groups per molecule. If this number is greater than 2,2, the oil is drying; if the number of diallylic groups per molecule is slightly lower than 2,2 then the oil is semi-drying. There is no line between semi-drying and no drying [2].

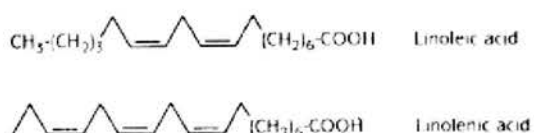


Figure 4 Linoleic and linolenic acid.

An important consideration is the drying rate. Oils with conjugated double bonds dry faster than those with non conjugated double bonds. Fatty acids containing only one double bond are autoxidized slowly and those containing two double bonds react a hundred times faster.

Useful drying rates can be achieved if high concentration of polyunsaturated fatty acids is present. However, dried films, especially with three double bonds fatty acid, yellow with aging. So, for decorative paints soybean, safflower and tall oil alkyds are preferred. They have high double bonds content (from linoleic acid, as seen in **Table 1**) and low levels of three or more double bonds. They are the least unsaturated that dry well.

When the liquid coating is applied, naturally present hydroperoxides decompose to form free radicals. The peroxy free radicals can abstract hydrogens from methylene groups between double bonds to form hydroperoxides and generate free radicals. A chain reaction is established leading to autoxidation. The formation of hydroperoxides on a methylene group can be seen in **Figure 5** and **Figure 6**:

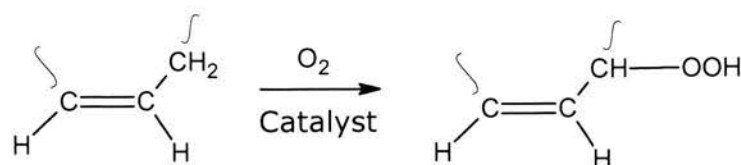


Figure 5 Formation of hydroperoxides on methylene.

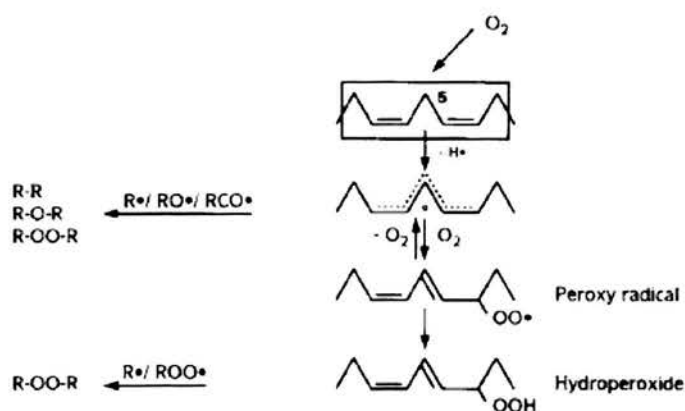


Figure 6 Mechanism of oxidative cross linking ^[7].

To promote autoxidation, driers (catalysts) are added to drying coatings. These driers are usually oil soluble salts like Cobalt, Calcium, Manganese and other metals. The autoxidation of uncatalyzed non conjugated alkyds is slow.

Non drying oils fatty acids can be used for preparation of alkyds used as plasticizers for polymers like nitrocellulose and thermoplastic polyacrylates. Non drying oils fatty acids do not cross link and have the advantage over monomeric plasticizers, because they do not volatilize considerably when the films are dry.

During alkyd production, an excess of hydroxyl groups are used to avoid gelation. These groups can react with polyisocyanates or others. The resulting coatings have more durability and faster curing than alkyd resins with no polyisocyanates or resins, with no big increase in price.

The films obtained from non drying oils fatty acids also have a discoloration problem but it can be reduced by using non drying oils with minimal levels of unsaturated fatty acids.

Alkyds that are used in coatings to be cured at high temperatures are usually blended with aminoplasts. Alkyds for baking enamel do not need to be autoxidable and are usually made from oils with saturated fatty acids like coconut.

1.2. High solids alkyd resins

1.2.1. Environmental concerns

After production almost all alkyds are blended with organic solvents to make them suitable to use. The organic solvents will be part of the coatings manufacture evaporates to the atmosphere. These solvents contribute to air pollution. In air, organic solvents react in photochemical process to produce ozone that is one of the constituents of photochemical smog.

The amount of solvent emitted during the coating process depends on the solid content of the paint but also on the efficiency of the application process.

The measure of emission control is the concept of Volatile Organic Compounds (VOC). The VOC of paint is measured as the paint is being used [1]:

$$VOC(kg / m^3) = \rho \frac{100 - NVs}{100} \quad (4)$$

NVs is non volatile percentage by weigh and ρ is the density of the paint in kg / m^3 .

1.2.2. High solids

Alkyd technologies are being adapted to meet modern needs. For alkyd paints there are two main alternatives to reduce VOC levels: high solids and water reducible systems. Waterborne alkyds are usually more expensive and have lower solid content. Their dry time is affected by temperature and humidity and storage stability is lower than solution alkyds^[9]. These characteristics make waterborne alkyds not very attractive. On the other hand, high solids alkyd resins have lower molecular weigh

which results on the increase of its drying time and reduces durability. In many cases they have low T_g .

There are numerous technologies to reduce organic solvents besides high solids. The most important ones are: powder coatings, waterborne coatings, radiation curable coatings and reactive diluent systems. High solids have advantages over the other technologies because the switch from conventional technologies is simple.

Conventional alkyd coatings are less fluid than high solids alkyd coatings and their viscosity increases more rapidly during drying process.

Strictly speaking, high solids means that the coatings have more than 80% non volatile content by volume. This 80% content by volume corresponds to 85-88% by weigh solids because solvent is the component with the lowest density ^[1].

The technical problem in formulating high solid coatings is to find ways to achieve low viscosity without using organic solvents, keeping the properties at high level. Too low molecular weigh must be avoided, because it leads to inferior drying properties.

1.2.3. Polymer characterisation

o Molecular weight

High solid coatings can be obtained by processing the alkyd at low enough molecular weigh. This approach is not enough because it leads to alkyds with unwanted properties. Molecular weigh influences the network formation and the type of structural elements formed.

The molecular weigh of an alkyd can be determined by the ratio between carboxy groups to hydroxyl groups (r_0).

Reducing molecular weigh has its limitations. As molecular weigh is reduced, it is necessary to increase the ratio of functional monomers in the

oligomer to increase cross linking sites during the cure to augment viscosity. This augment will balance the desired viscosity decrease from molecular weight reduction. There must be some optimum relation between molecular weight and functional group content [8].

- **Molecular weight distribution**

The molecular weight distribution is one of the most important parameters in polymers' properties control. It is desired to control the polymerization in order to obtain a better defined structure and narrower molecular weight distribution. The ratio $\overline{M}_n / \overline{M}_w$ is usually used to measure the distribution of molecular weights of individual parameters. This measurement is made with Size Exclusion Chromatography (SEC), which is not only an analytical tool but also gives preparative fractionation of the polymer. SEC is a useful tool to monitor small changes in alkyd structure as a result of variations in ratio of starting materials or in synthesis process.

As molecular weight distribution increases, weight fractions of high molecular oligomers and weight fractions of low molecular polymer increases.

- **Branching**

A practical solution apart from lowering the molecular weight of resins, is the simultaneous increase of their molecular branching. The resins may have a conventional structure, and their increased branching is obtained by introducing polyfunctional substrates. Another way is by synthesising resins of defined increased branched structure.

The polymer viscosity depends on the degree of branching. Usually branched polymers give lower viscosities than their correspondent linear polymers with the same molecular weight.

- **Functional groups**

In alkyds, hydroxyl and carboxyl groups are hydrogen bond donors and ester and carboxyl groups are acceptors. If these groups are present in high concentration, the alkyd will have high viscosity because functional groups in combination with steric accessibility results in strong intermolecular forces.

Small amounts of low molecular ketones and alcohol have a viscosity reducing effect. They compete with the alkyd: ketones as acceptor and alcohol as donor.

Unsaturated groups in fatty acid residues of air dry alkyds have effect on the viscosity of alkyds solutions. This effect is related with the reduction of the intermolecular associations.

- **Use of reactive diluents**

Reactive diluents can function as solvents in the coating formulation and during the cure are converted into a part of the film. A small amount of reactive solvent as part of the total volume of solvent is a way of further increasing the non volatile content.

Reactive solvents must have low volatility, so that they do not evaporate before curing. The properties of an ideal reactive diluent are given in **Table 2**.

Most of the commercially available reactive diluent paints show considerable drawbacks when used into high solids formulations. Fatty acid esters failed to show sufficient dilution capabilities compared to white spirit and reactive diluents based on acryloyl functional oligomers cause instabilities in the vessel. Butadiene based oligomers lead to early embrittlement during aging and weathering of the paint films and finally allyl ethers can show a substantial emission of toxic fragments during drying in the paint film.

Table 2 Key properties of an ideal reactive diluent [7].

Reactive diluent properties	In-can, application and paint film properties
Low viscosity and good alkyd compatibility	Good storage stability
Low volatility	No influence on drying times
Non-toxic	A good through drying (no wrinkling)
Low colour	No toxic degradation products
Economic replacement for solvents	No influence on hardness/no blocking
	No influence on gloss and durability

The reactive diluent must have some of the physical specifications of conventional solvents and reactive sites that enables cross link into the alkyd film. Two aspects must be considered: types and number of reactive sites. The activity of an allylic methylene group is adversely affected by the increasing electronegativity of adjacent groups. Although the number of reactive sites present can also have an influence, the magnitude of this effect is much smaller.

- **Oil length**

Increasing oil length has three consequences. The first one is lower molecular weight. It also leads to less hydrogen bond-forming groups and reduction of intermolecular action. These three effects result in lower viscosity [8].

1.3. Particular cases

Some particular examples are mentioned because they were studied in recent years and the results have significant importance.

1.3.1. Use of Styrene Allyl Alcohol (SAA) Resinous Polyols (based on ref. [9])

SAA polyols are co-polymers of styrene and allyl alcohol. They are hard, low molecular weight and highly functional resins that are not susceptible to hydrolysis.

In the study made by Lyondell Chemical Company is described the use of SAA (SAA-100, SAA-101 and SAA-103) to produce high solids alkyd resins with improved properties compared to conventional alkyd resins.

Conventional long oil alkyd resin was prepared with refined soybean, pentaerythritol and phthalic anhydride. Mineral spirits were added to 60-70% solids.

SEC analysis (**Figure 7**) shows that the polymer had a broad molecular weight distribution (equal to 20) but contained high amounts of high molecular weight polymer.

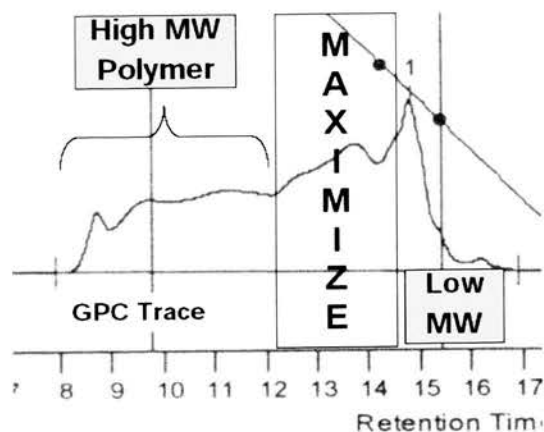


Figure 7 SEC trace of 60% alkyd.

High molecular weight impurities have an unbalanced effect on resin viscosity, so eliminating high molecular weight fraction reduces the solvent required to achieve desired viscosity. Reducing low molecular weight fraction improves drying time and film properties. Reducing polydispersity is a key to lowering VOCs and maintaining M_n is a key to preserving properties.

Replacing a portion of the Pentaerythritol with SAA-100 (**Figure 8**) in standard high solid alkyds reduces polydispersity while maintaining M_n above 4000 (**Figure 9**).

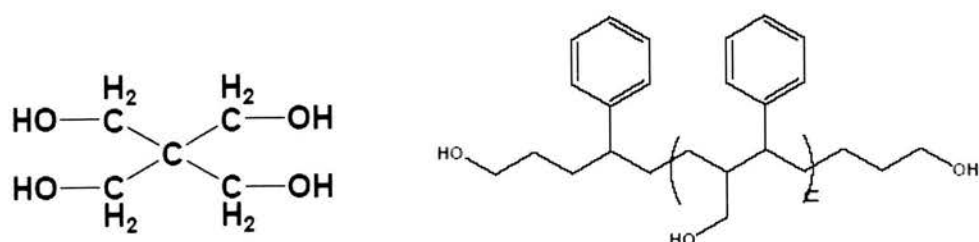


Figure 8 Pentaerythritol and SAA polyol.

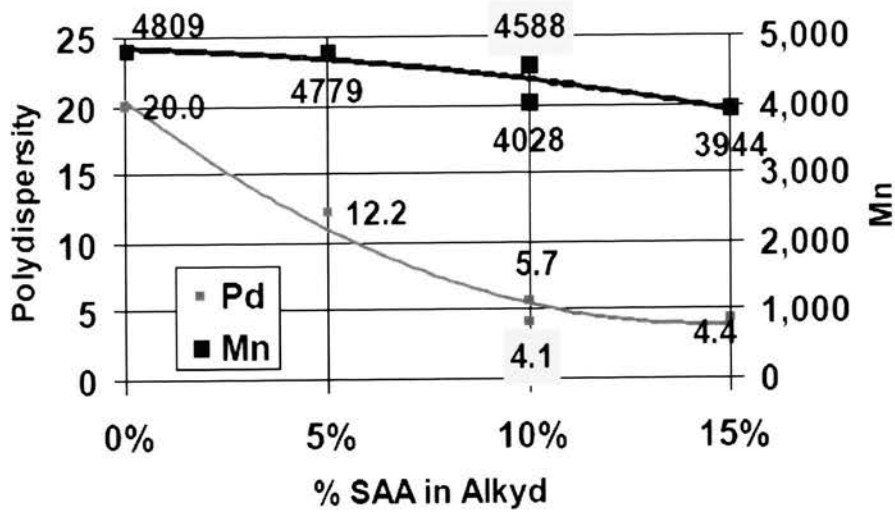


Figure 9 Effect of SAA polyol on M_n and polydispersity.

The use of SAA oleate (alcoholises of vegetable oils with SAA polyols) further improves resin properties.

Solution viscosity was reduced due to decrease in high molecular weight polymer fraction (**Figure 10**)

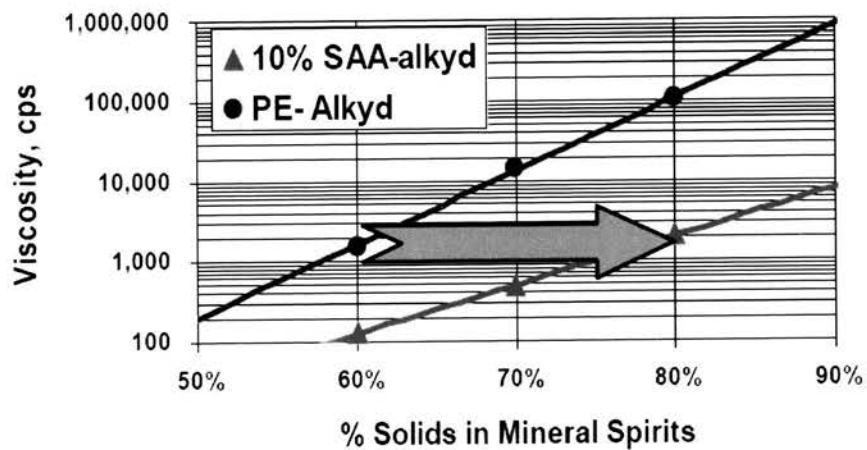


Figure 10 Viscosity profile of long-oil alkyds in Mineral Spirits as function of SAA content.

SAA modified alkyds were used to formulate alkyd coatings. **Figure 11** compares the hardness development of 10% SAA-100 modified alkyds to a commercial high solid alkyds and a conventional solids alkyds.

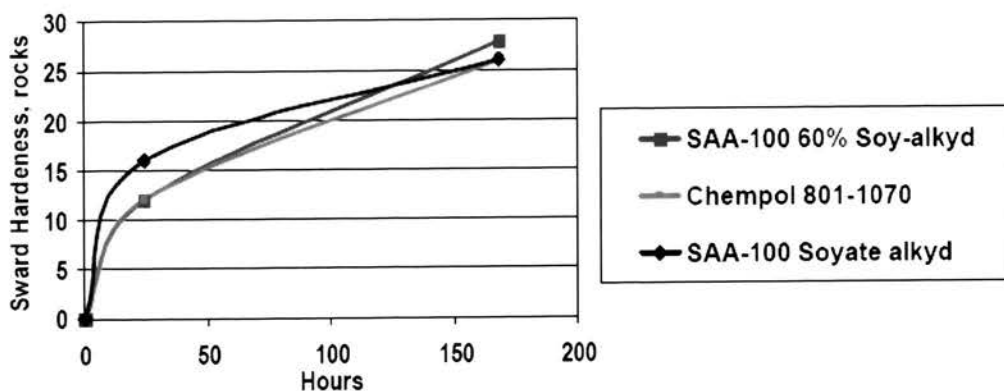


Figure 11 Hardness development of SAA-100 modified alkyd vs. commercial long oil alkyd.

The SAA modified alkyd developed hardness faster than commercial high solid alkyds. The alkyd prepared from pre-reacted SAA soyate hardened faster than the one prepared with solid SAA.

The effect of oil length and type of SAA were also studied: at equal length alkyds modified with SAA-100 formed faster dry coatings with lower ultimate hardness than those based in SAA-103 (that has lower OH content). On other hand, the increase of oil length in SAA modified alkyds has the same effect in all the alkyds: decrease in VOCs, cure speed and a softening of the final cure coating.

Other properties were studied: there was an improvement in humidity resistance and weatherability compared with commercial high solid alkyds.

1.3.2. Design and incorporation of reactive diluents for air-drying high solids alkyd paints (based on ref. [7])

A new class of reactive diluents based on octadienyl fumarate/succinate (OFS class) has emerged.

2,7-octadienyl maleate and fumarate (**Figure 12**) have three different types of olefin sites available for cross linking (site *a* is a allylic

olefin, site *b* a terminal olefin and *c* and *c'* are types of central sites (trans and cis-double bond)).

Allyloxysuccinate (**Figure 13**) was prepared by addition of 2,7-octadienol to the maleate or fumarate. Site *d* represents allyl ether.

An optimal paint performance could be achieved by combination of allyloxysuccinate with maleate and fumarate (**Figure 14**).

The performance of the OFS class was observed using H NMR and mass spectrometry. The progress of OFS incorporation was followed by monitoring the vanishing of the reactive sites.

After 100 h of drying, the disappearance of the double bonds is faster than the decrease of the methylene groups from the fatty acids (**Figure 15**).

All sites seems to react in similar rate, however the decrease in fumarate is faster than that of the malate.

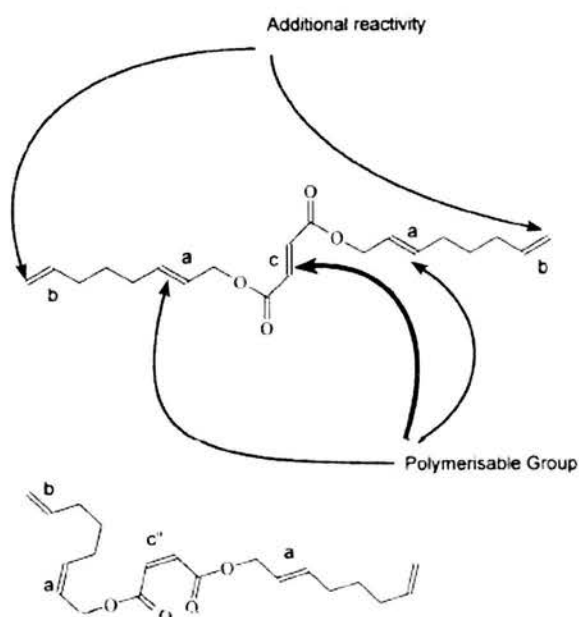


Figure 12 Reactive sites of di-2,7-octadienyl fumarates and -maleates.

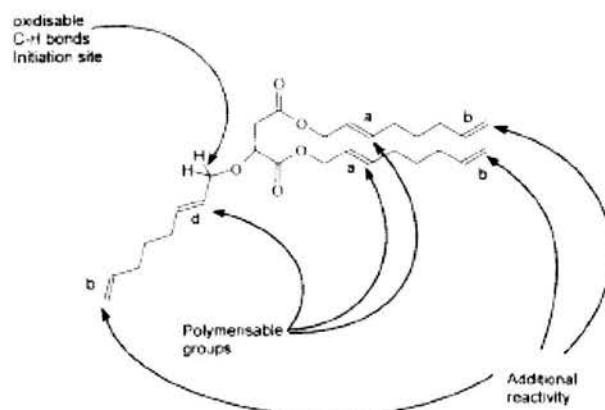


Figure 13 Reactive sites of 2-(2,7-octadienoxy)-di-2,7-octadienylsuccinate.

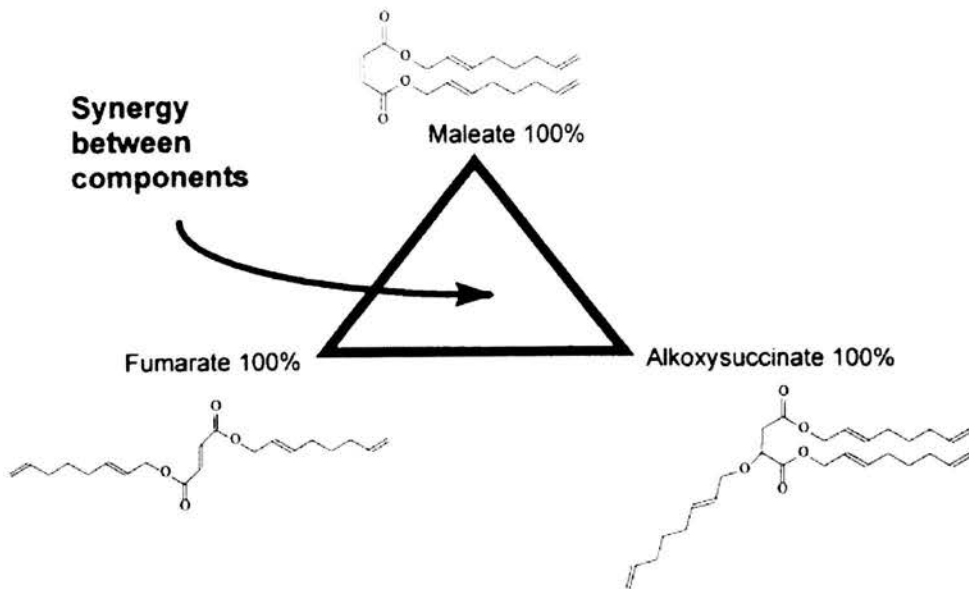


Figure 14 The OFS class of reactive diluents, components.

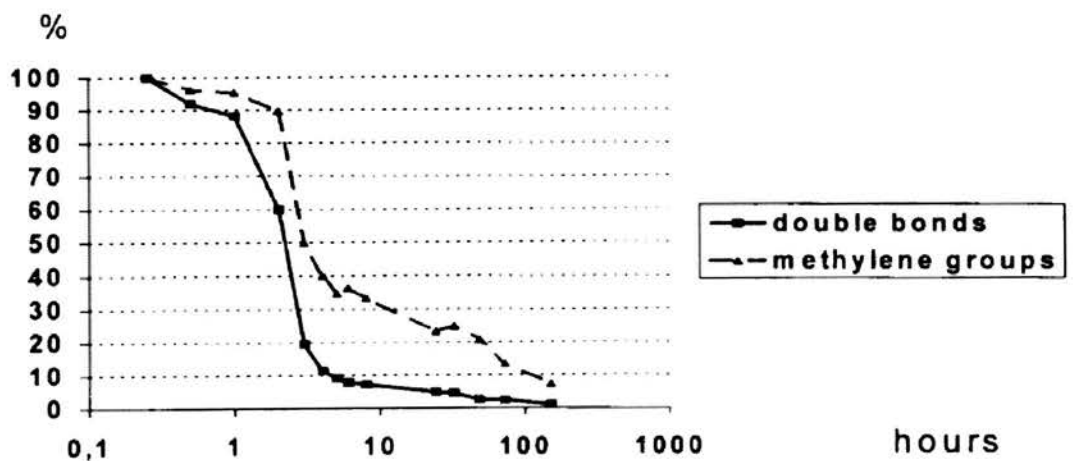


Figure 15 NMR signal decrease of methylene groups and double bounds of a drying alkyd film.

NMR measurements confirm a good incorporation of these reactive diluents in alkyd paint films (facilitated by presence of fumarate and allylic ether succinate).

Also, weigh changes prove that these reactive diluents incorporate and do not evaporate (**Figure 16**).

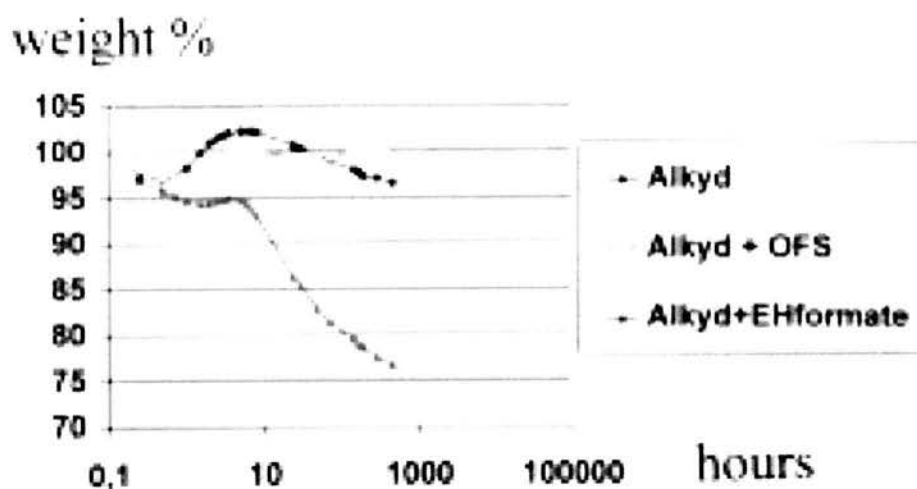


Figure 16 Weight changes during drying of films.

By replacing a part of alkyd solvent by OFS reactive diluent, low VOCs levels can be achieved (**Table 3**).

Table 3 VOC reduction by OFS-class reactive diluent

System ^a	Solids content (wt.%)	VOC level (g/l)
Conventional opaque	69	370
Conventional opaque + 2% OFS ^b	72	340
Conventional opaque + 4% OFS ^b	74	320
Conventional opaque + 9% OFS ^b	78	290

^a White TiO₂ pigmented alkyd system (PVC = 15%).

^b Reactive diluent (%) on total paint formulation.

Combining OFS with higher solid alkyds makes it possible to obtain systems with less VOC content.

Paints with OFS class reactive diluents have good drying performance (**Table 4**) and increased harness.

Table 4 Drying performance of OFS-class alkyd system

Paint	BK drying 23°C (h)		BK drying 10°C (h)	
	Open time	Tack free	Open time	Tack free
Conventional opaque ^a	1.4	4.8	0.5	4.8
Conventional opaque + 8% OFS ^b	1.8	2.5	2.0	5.5

^a White TiO₂ pigmented alkyd paint (PVC = 15%), VOC = 370 g/l.

^b Reactive diluent (%) on total paint formulation, VOC = 300 g/l.

1.3.3. Highly branched high solids alkyd resins (based on ref. [10])

Two types of highly branched alkyd resins were synthesised. Properties of these resins and of coatings obtained from them were compared with the properties of conventional alkyd resins.

High solids alkyd resins having a conventional structure were synthesised with dipentaerythritol as a single polyol with fatty acids of high content of linoleic acid and phthalic anhydride.

The star-like resin (**Figure 17**) is composed of three types of molecules: dipentaerythritol esterified with fatty acids, star-like molecules in which three or four arms extend from one core and a mixture of star-like structure linked by linear fragments.

Hyperbranched (**Figure 18**) alkyd resins was synthesised with Trimethylolpropane, dimethylolpropionic acid and unsaturated fatty acids.

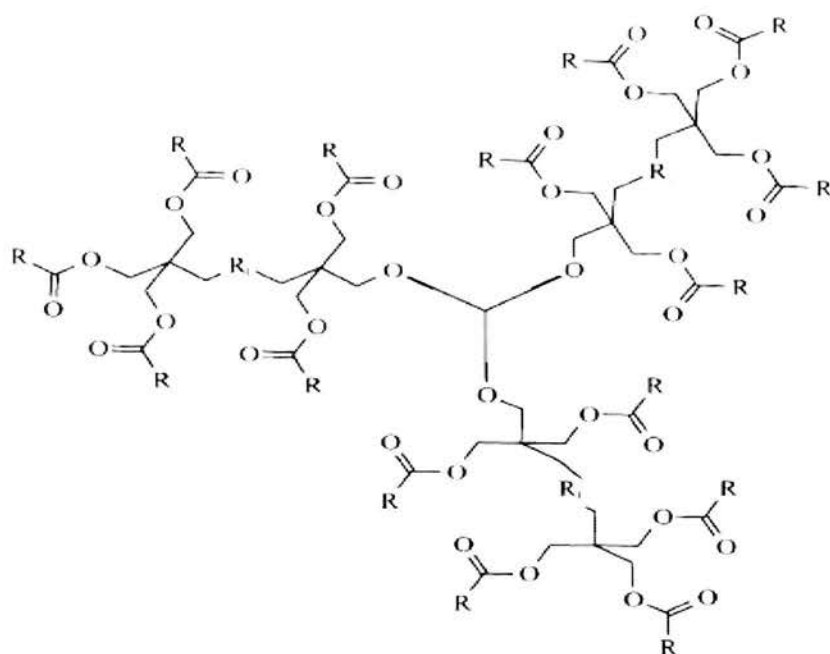


Figure 17 Model of star-like resin molecule (with three arms).

Characteristic parameters of all the resins are given in **Table 5** and basic molecular parameters are given in **Table 6**. **Figure 19** presents their SEC molecular weight distribution curves.

Table 5 Basic properties of resins of different structure.

	High solid resin of conventional structure	Hyperbranched resin	Star-like resin	Commercial conventional resin
Content of fatty acids (%)	68	68	81	ca 55
Viscosity of 100% resins (mPa s)	26000	2800	3500	1000000
Viscosity of 80% solution in Exocel D-40 (mPa s)	1250	400	350	45000
Acid number (mg KOH/g)	10	6	8	12

Table 6 Molecular parameters of the high solids resins

Molecular weight	HS resin of conventional structure	Hyperbranched resin	Star-like resin
M_n	5195	4754	6046
M_w	22 213	7914	25 855
Polydispersity: M_w/M_n	4.28	1.66	4.26
Viscosity at 20 °C (mPa s)	20000–26000	2500–3000	2800–4000

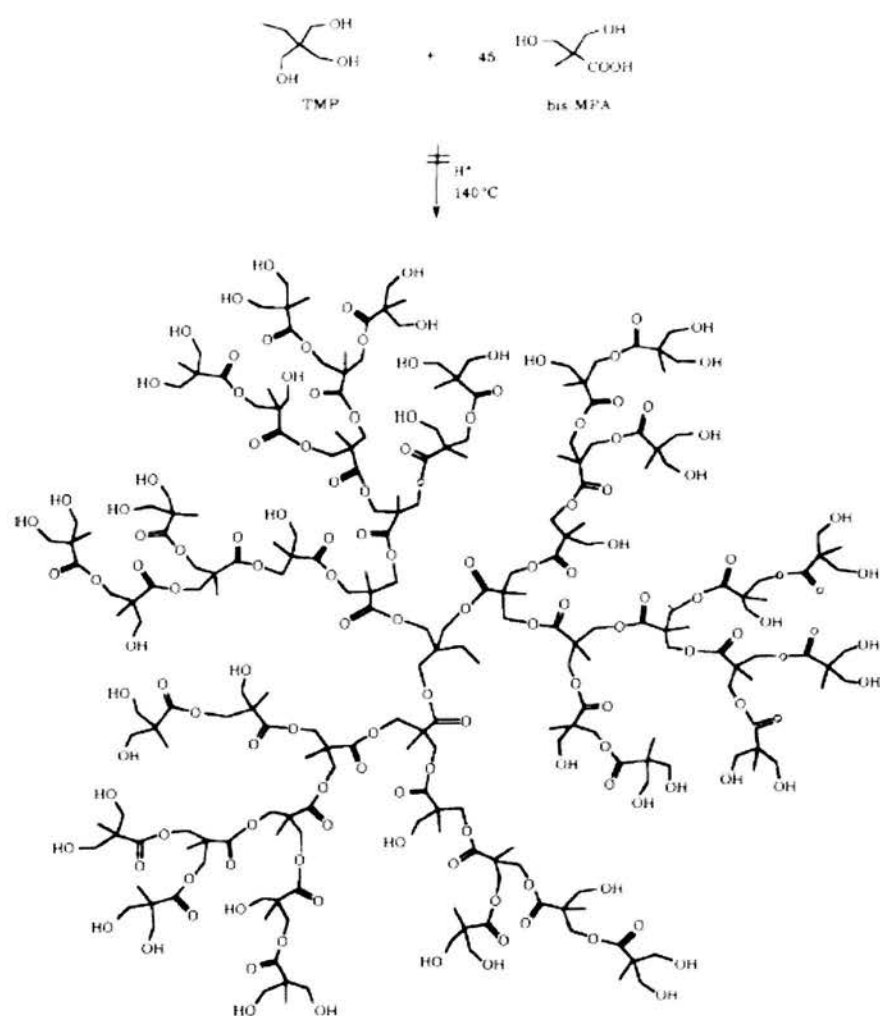


Figure 18 Scheme of the synthesis of hyperbranched saturated polyester

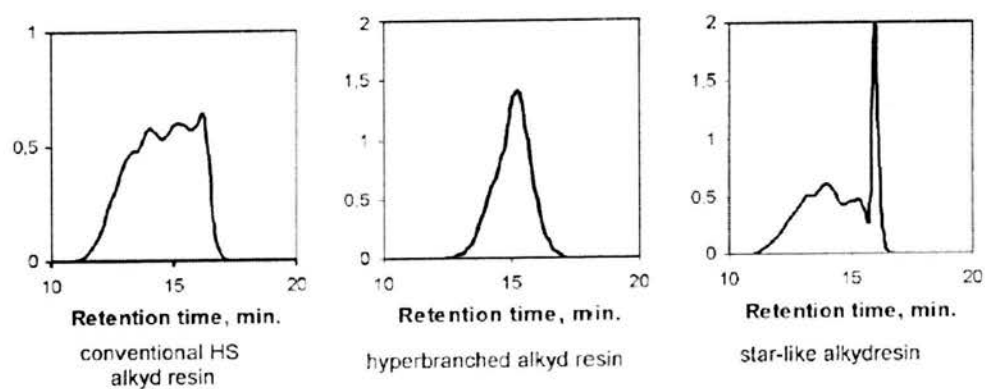


Figure 19 SEC molecular weight distribution curves of alkyd resins.

The hyperbranched resin has narrow SEC trace and low viscosity. Star-like resin has average molecular weights much higher than the

hyperbranched and conventional high solid resins and its viscosity is low owing to the effect of its structure.

All resins synthesised were tested in the form of varnishes and white enamels.

It was studied the drying process (**Figure 21**):

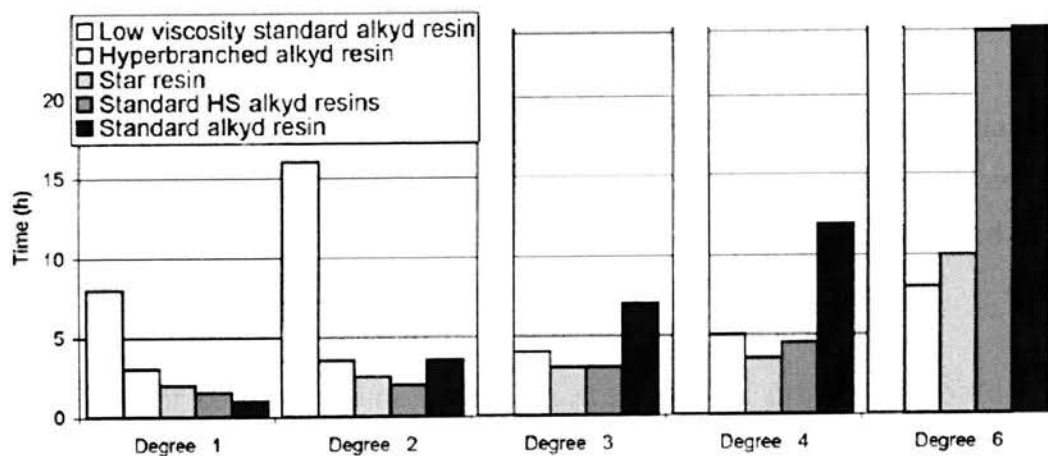


Figure 20 Drying of alkyd resins.

Conventional resins having the highest molecular weight, dry in the shortest period. When the solvent evaporates, the conventional coatings become solid while coatings made of low-molecular weight resins remain liquid. Solidification of these coatings is due to a slow oxidation process

In the case of the star-like resins, molecular weight influences the drying process as usual since resins having higher molecular weight dry faster.

Hardness of coatings was determined (**Figure 22**):

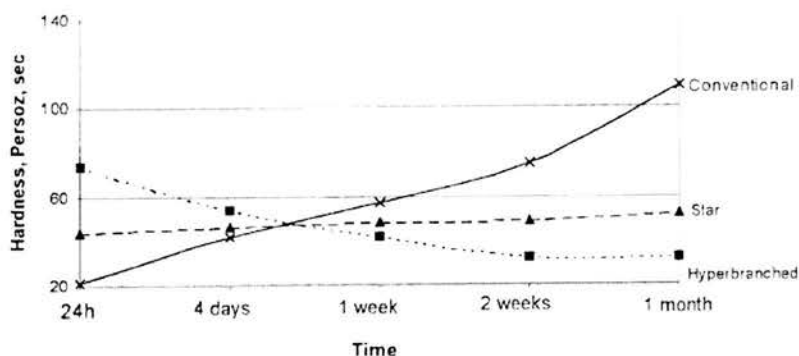


Figure 21 Effect of structure of alkyd resin on hardness of coatings.

For high solid resins, with increased branching and lower molecular weight, hardness decreases. The highest values of hardness were achieved after about 6–12 h from the time when the 4th drying degree was obtained.

Hardness can be improved by addition of aluminium dryer.

Properties of coatings were tested on steel panels primarily (coated with an alkyd anticorrosive primer). Films made with enamels containing highly branched resins have lower elasticity than conventional alkyd resin. The reason is the effect of higher density of cross-linking, which was achieved by higher concentration of double bonds.

Other properties of the analysed coatings like resistance properties (resistance to UV radiation and behaviour of coatings in QUV cabinet) and weathering are similar to conventional alkyd resins.

1.4. Patents

There are some recent patents regarding high solid alkyds.

Eastman Chemical Company has assigned a few. Patent Number US 6548601 B1 of April 2003 reports an invention related to an oxidative cure composition containing an acrylate functionalized alkyd resin and the methods of preparing an oxidative cure composition containing an acrylate functionalized alkyd resin. These compositions are useful in preparing fast-dry, high solids coatings.

An acrylate functionalized alkyd resin is an alkyd modified with glycidyl acrylate via non free radical reaction. This alkyd exhibits superior dry properties and tack free properties which previously could only be improved by increasing molecular weight and T_g .

Acrylate functionalized alkyd resin requires less VOCs because this amount is related with molecular weight and T_g .

Patent Number US 6794049 B2 of September 2004 reports an acetoacetate functionalized alkyd resin and a method of preparing acetoacetate functionalized alkyd resin comprising the step of contacting an acetoacetate functionalized alkyd resin with at least one drier in the presence of an organic solvent.

The acetoacetate functionalized alkyd resin is the reaction product of an alkyd resins and an alkyd acetoacetate. This resin has the same properties as acrylate functionalized alkyd resin in drying process and also requires less VOCs.

The Patent Number 4,477,534 of October 1984, by E.I. Du Pont de Nemours and Company reports that air drying resins like acrylate or methacrylate acid drying oil resins and alkyds can be blended with up to 70% by weight of the combined weights of a vinyl oxazoline ester as a reactive diluent. In an organic solvent, the blend produces a suspension or solution which has a lower viscosity than a suspension or solution of the resin alone with the same or even higher percentage of solids. The higher percentage of solids results in lower solvent emissions and evaporation.

When applied to a substrate, the blend dries to air to a good protective and ornamental coating, similar to those produced with the resin alone.

The Patent Number 4,038,225 of July 1977, by E.I. Kansai Paint Company, Ltd stated a thermosetting high solid coating composition which is characterized by less solvents consumed in production, evolves less solvent vapour in use and consists in:

- 80 to 60 parts by weight of alkyd resin having fatty acid content of 10 to 20 % by weight, a phenol group of 10 to 25 % by weight and a dibasic acid ratio and a hydroxyl group equivalent within certain ranges,
- 20 to 40 parts by weight of melamine resin mainly comprising hexakisalkoxymethylmelamine,
- If desired, alcohol modified melamine resin replacing not more than one half of said melamine resin,
- 0.005 to 1.00 part by weight of aliphatic or aromatic sulfonic acid or their amine salts,
- 70 to 20 parts by weight of solvents at the time of spray coating.

E.I. Kansai Paint Company, Ltd registers two other patents. The Patent Number 4,224,202 of September 1980 reports a high solids coating composition containing an unsaturated fatty acid alkyd resin (50%), an alkyd dimethacrylate or trimethacrylate monomer (10-40%), a cobalt salt effective as catalyst for oxidative cross link, a complexing agent to block the cobalt catalyst, and a polar solvent (10%). These percentages are based on resin and methacrylate monomer (by weight).

The di- or trimethacrylate monomer crosslinks with the alkyd and becomes part of the solid paint film.

In Patent Number 4,140,663 of November 1977, a high solid coating composition is invented, curable at ambient temperature, which is a mixture of:

- 100 parts by weight of alkyd resin made with saturated aliphatic or polybasic acids or their anhydrides, polyhydric alcohols and unsaturated vegetable oil fatty acid. Some portion of said alkyds can be replaced by modified oils or butadiene polymers.
- Metallic alcoholates and/or chelate compounds thereof.

Because of the addition of the Metallic alcoholates and/or chelate compounds thereof, the curing property in the inner portion of the coating film can be accelerated to a great extent. Other properties of the film can be also improved. There is no greatly pollution in use.

The Patent Number 4,140,663 of February 1979, by Kureha Chemical Industry Co, Ltd. Reports an air dry high solids coating composition containing 90% or more of solid components and consisting of:

- 95-50 parts by weight of low viscosity alkyd resin having an oil length of 60 or higher and a viscosity of Z4 or lower,
- 5-50 parts by weigh of 1,1-bis-(1'-methyl-2'-ninyl-4',6'-heptadienoxy)-alkane,
- If necessary, other components as pigments, organic solvents and additives.

This composition is quite effective in the prevention of air pollution and the saving of resources.

2. Synthesis of alkyd resins

Alkyds can be made from oils or by using free fatty acids as raw materials.

2.1. Monoglyceride Process

The fusion process starting from triglyceride oils is often called the *alcoholysis* or the *monoglyceride process*. It is a two-stage process as seen in **Figure 1** and **2**.

The first stage is an ester interchange reaction. The transesterification reaction runs at 230–250°C in the presence of a catalyst like litharge (PbO) or certain Li or Ca salts.

Although the product is called a monoglyceride, it is actually a mixture of isomers of mono-, di-, and triglycerides and of polyol. The composition depends on the ratio of polyol to oil, catalyst, time, and temperature.

The reaction runs under an inert atmosphere like CO₂ or N₂ to minimize discoloration and dimerization of drying oils.

Many tests have been developed to estimate the extent of transesterification, but none is general enough.

At some relatively arbitrary point, polybasic acids or anhydrides are added and polymerized with the monoglyceride mixture to form the resin. This stage occurs at 220-255°C. Other ingredients may be added during the second stage.

A critical aspect of alkyd synthesis is deciding when the reaction is completed. Disappearance of carboxylic acid is followed by acid number,

and increase in molecular weight is followed by viscosity. In alkyd production, viscosity is commonly determined using Gardner bubble tubes.

After it is decided that the extent of reaction is sufficient, solvent is added to the reaction.

The choice to add the solvent must be made so that the acid number and viscosity of the mixture in the reactor will be between the time of sampling, determination of acid number and viscosity, and solvent addition.

Esterification is a reversible reaction. An important factor affecting the rate of esterification is the rate of removal of water from the reactor. Most alkyds are produced using a reflux solvent, such as xylene, to promote the removal of water by azeotropeing. The xylene vapors form an azeotrope with water and carry it out of the reactor. A partial condenser may be used allowing the water vapors to escape and condensing most of xylene that returns to the reactor. If a partial condenser is not used, the vapors are also condensed. Water and xylene separate into two layers; the xylene is returned to the reactor and the water is removed, usually to a measuring vessel. The amount of water collected can be monitored as one of the indicators of the extent of the reaction.

The amount of solvent is dependent on the reactor and is set so that there is enough to reflux strongly, but not so much as to cause flooding. Some of the xylene is distilled off along with the water.

Reaction time is affected by reaction temperature. Higher temperatures accelerate the reaction but if the reaction is carried too far, there is a major risk of gelation. Therefore, it is desirable to operate at as high a temperature as possible without risking gelation.

2.2. Fatty Acid Process

The fusion process starting with fatty acids is the oldest and simplest process. In this case, fatty acids must be used instead of oils, and the process can be performed in a single step.

Any oil can be saponified to yield fatty acids, but the cost of separating fatty acids from the reaction mixture increases the cost of the alkyd.

When fatty acids are used, the polyol, fatty acids, and dibasic acid are all added at the start of the reaction, which occurs in the range of 220–255°C.

3. Laboratory Processing

3.1. Equipment

The scheme of the laboratorial apparatus used in alkyd production can be seen in **Figure 22**:

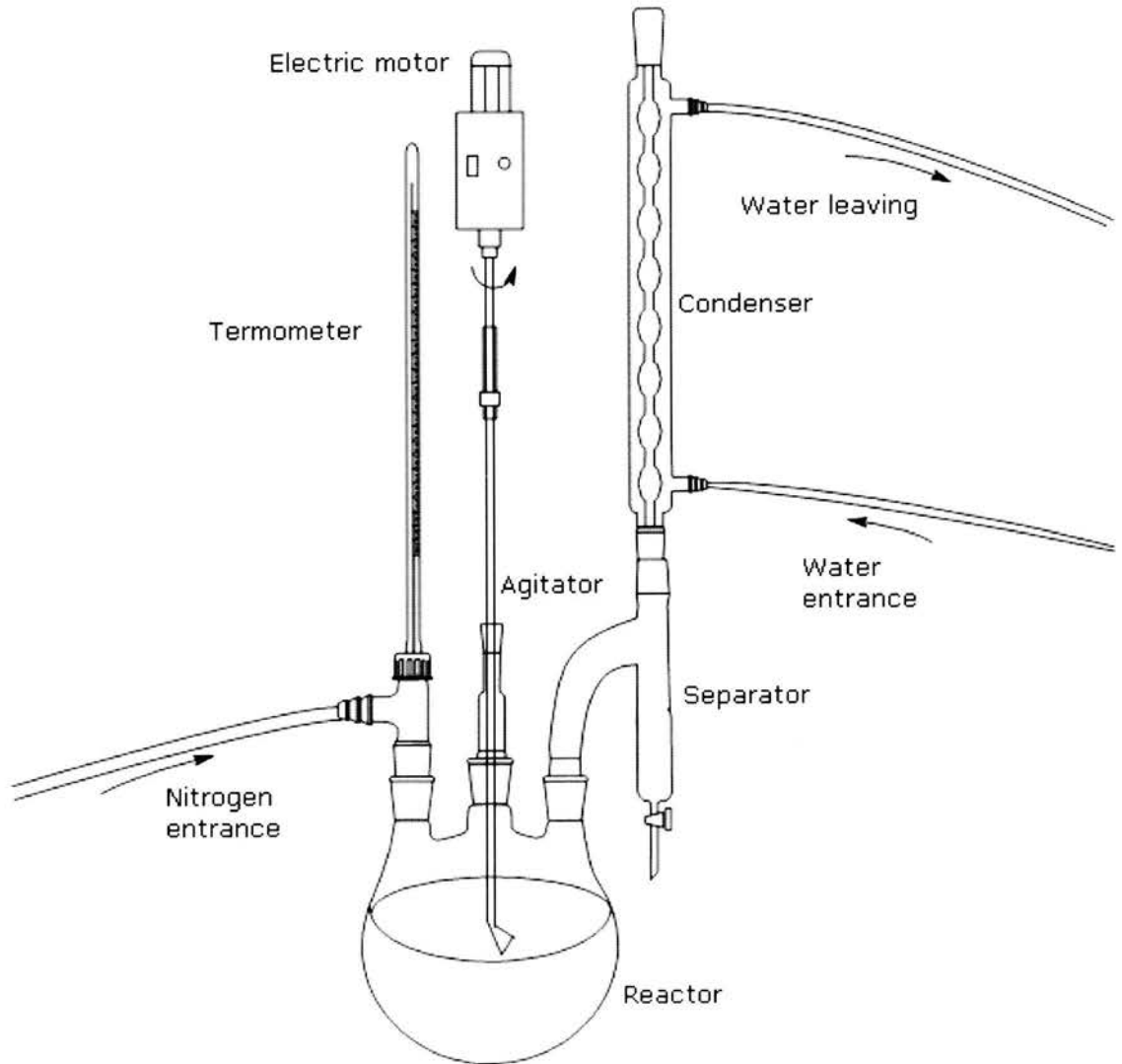


Figure 22 Laboratorial apparatus used.

The main equipment used in alkyd production consists in a 2L reactor, an agitator driven by a powerful electric motor, a condenser and a separator. Heating and cooling is reached by a heating mantle.

3.2. Raw materials used

There were synthesised tree resins. Resins 1 and 2 are adaptations of commercial resins from Resiquímica and Resin 3 is an adaptation of a resin from **Ref. [9]**.

The raw materials' weight percentages are described in the following table:

Table 7 Raw materials' weight mass percentages of the three resins produced.

	Resin 1	%	Resin 2	%	Resin 3	%
Alcoholysis	oil	60.86	oil	62.24	oil	59.94
	Polyol 1	13.95	Polyol 1	13.23	Polyol 1	6.99
	antioxidant	0.061	Polyol 2	0.65	SAA	14.98
			antioxidant	0.06	antioxidant	0.055
Esterification	antioxidant	0.12	antioxidant	0.06	antioxidant	
	anhydride 1	24.35	anhydride 1	23.65	anhydride 1	0.055
	anhydride 2	0.153	anhydride 2	0.10		17.98
	monofunctional acid	0.51				59.94
	total	100	total	100	total	100

An initiator was also used during alcoholyses. In Resin 1 was added 0.0047% of total weight, 0.0029% in Resin 2 and 0.0002% in Resin 3.

Xylol was added in esterification (5% of total weigh in Resin 1 and 2 and 4 % in Resin 3) and non aromatic solvent was added for dilution.

3.3. Example of Alkyd preparation

The following procedure was used to produce the Resin 1.

3.3.1. Alcoholysis

Oil, polyol, antioxidant and initiator are charged to the reactor. The mixture was then heated to 270°C under nitrogen and maintained at that temperature until a sample gave clear in ethanol. **Figure 23** shows an image during alcoholysis.

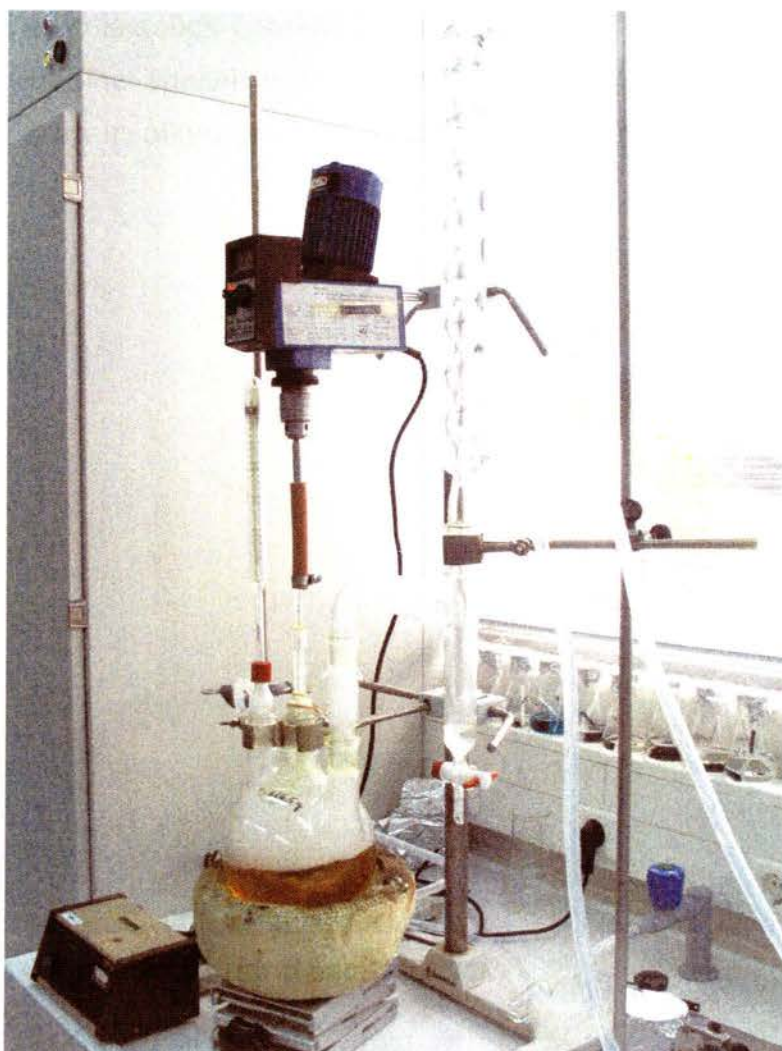


Figure 23 Apparatus during alcoholysis.

3.3.2. Esterification

After alcoholysis the reactor contents are cooled till 160°C. Anhydrides, mono-functional acid, antioxidant and part of xylene are added to the reactor. Xylene is also added to the separator (**Figure 24**). The mixture is then heated to 250°C. At that temperature, a xylene/ water azeotrope is collect overhead. The rest of xylene is added to maintain temperature.

After 2 hours the first sample is collected in the reactor and the acid number and viscosity is determined. When the specifications are reached, the reaction is stopped and the dilution with the solvent starts.

The next step is solids content determination. If the value is not the coincident with the final specification, a new dilution is necessary.

The final step in alkyd production is the determination of resin final properties.



Figure 24 Apparatus during esterification.

3.4. Final properties of Alkyd Resins

The final analysis of alkyd resins produced gave the results expressed in **Table 8**.

Table 8 Final properties of alkyd resins produced.

	Solids content (%)	Acid number	Viscosity	
			Gardner (stokes)	Brookfield (mPa.s)
Resin 1	69.0	6.6	-	10600
Resin 2	74.3	8.9	D	9160
Resin 3	80.7	9.2	Y	3765

Resin 3 properties are similar to Ref [9]. The Brookfield viscosity achieved is, as expected, lower than those from commercial resins. Solution viscosity is lower because SAA reduces the high molecular weight polymer fraction, as explained earlier. This reduction of the high molecular weight polymer fraction reduces the solvent necessary to achieve desired viscosity.

In the future new resins will be synthesised and coatings characteristics will be analysed.

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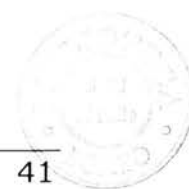
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