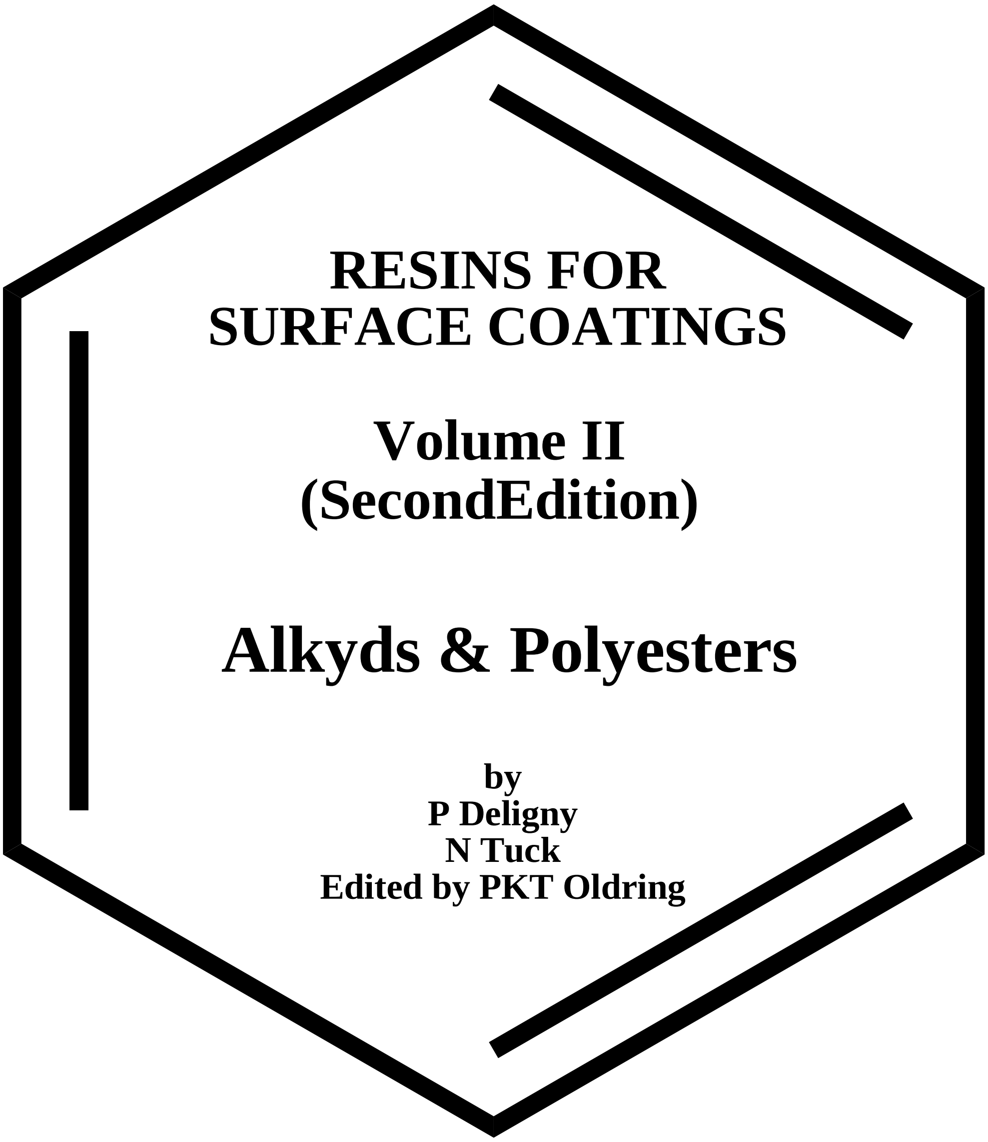

RESINS FOR SURFACE COATINGS

Volume II
(SecondEdition)

Alkyds & Polyesters

by
P Deligny
N Tuck
Edited by PKT Oldring

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Resins for Surface Coatings

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Since the 1980's there have been many significant changes in surface coatings which have necessitated major changes in the resins used, even though many may still be referred to by generic names. Thus it is appropriate that a series of books written for graduates new to the resins and surface coatings industries, which became recognised globally as an overview of the technology of resins for surface coatings should be revised and issued in time for the new millennium to reflect the recent advances within these industries, whilst retaining the basic understanding for which this original series of books was renowned.

It is reported that there was a time when the surface coatings industry dealt with a relatively small number of materials and processes for making paints and varnishes. Indeed it is claimed that between 1736 and 1900, Watin's book on varnish formulations was reprinted 14 times with only minor modifications. This was claimed(4) to be the industry standard. Compare that with today's situation. A book which lasts for 200 years to the turn of the century, followed by a series of books) published in the 1940's which last 40 years to be superseded by a set which lasts 20 years before needing to undergo major revisions. It is not the writing which is inadequate, but it is a true reflection of the increasing rate of change of the surface coating industry.

Reference to some of the earlier text books written for the surface coatings industry reveal how far this industry has progressed over the last 50 or so years. Examination. of a 5 volume set of books published by Wiley will be used to illustrate the changes and progress which have occurred and the approximate dates for introduction of what were considered new technologies over the last hundred or so years. Dates for new technology developments may be the Aject of debate, because it was often different between North America and Europe and even within some parts of Europe. Dates are given to try and put this industry and its developments into perspective.

In the early 1900's resins used for surface coatings were based upon naturally occurring materials, albeit with some degree of modification or processing in some cases. Some of the early resins for surface coatings resembled alchemy, with secret ingredients and/or processing techniques being handed down from father to son (at the turn of the century, there were few female resin chemists).

In the opening paragraph of Volume III, Chapter 4 of Mattelio's book written in the early 1940's as reproduced here, the reader will note a lot of similarities to the above paragraph and some would question if the situation had changed. Rest assured it has changed beyond all recognition from. the 1940's let alone prior to 1900!

"The art and skill of the old-time varnish maker have yielded slowly-to more scientific control and to the developments of the chemists and engineers who have entered the coating-materials industries. The complexity of the organic: molecules which they have had to deal with, however, has necessitated the continued use of methods which, although wore exact and more scientifically grounded than those of their predecessors, nevertheless are still quite empirical.

“it is well to remember that the molecular complexity of the drying oils and resins which are now (1943) in commercial use has provided a formidable variety of problems, which have long proved perplexing... Under such circumstances, one hardly need wonder that empiricism has so long prevailed or why there have been so many recorded differences of opinion and conflicting experimental observations".

To quote a recognised industry standard publication 55 years ago, “manufacture was in the hands of untrained men. Chemists or engineers, if there were any in this industry one hundred years ago (ca 1850), were a curiosity. The breadth of science had not yet touched it, and most manufacturers at that time saw no reason why it should”

When resins were processed, early controls consisted of mainly empirical factory, such as string length - how long a piece of resin could be stretched before breaking. The objective was to process a resin as close to its 'gel point', without actually gelling.
Much thermal processing was on gas fired open iron vessels, which resembled a pan on a gas cooking ring. Foam over and associated fires were common place. Indeed, folklore has it that some resin processing was controlled by processing until it "foamed over" or ignited.

Early surface coatings were limited to mainly air drying systems which film formed by either evaporation of solvent, to leave a dried film of the natural resin or oxidative cross-linking of any unsaturation present in vegetable oil based binders. French polish, based upon shellac is an example of the first type of coating, whilst alkyds or oleo-resinous based systems are examples of the latter.

Alkyds and oleo-resinous based coatings were originally used for many surface coating applications, where there was a performance demand, such as increased durability or resistance to water or alkali, compared to alterative systems. The unsaturation in the vegetable oil portion of the resin enabled cross-linking reactions, induced by oxygen in the air, to form resistant and durable films. Some decorative paints, based on linseed oil, for example, could easily yellow. Other systems (varnishes, rather than coatings), were often based upon solutions of hard, naturally occurring resins.

Today coatings can be divided into thermoplastic and thermo-set. Thermoplastic systems primarily film form by evaporation of solvent. As a general rule, thermoplastics coatings are based on high molecular weight polymers. solutions of high molecular weight thermoplastic resins are normally too high in viscosity for the desired applications solids, hence dispersions of thermoplastic resins are frequently used. A dispersion in water, maybe an acrylic latex or emulsion, typically used in home decorative emulsion wall paints.

Thermoplastic polymers may also be dispersed in organic solvents, although the solvent is not a solvent for the polymer. An example would be a dispersion of PVC in organic solvents, commonly known as an organo-sol.
Organo-sol coatings are used for architectural coil for claddings and the internal coatings, mainly coil applied, of easy open ends for beer and beverage cans.

Another approach to obtaining a resistant film of high molecular weight, whilst having good application solids viscosity relationships is to use thermo-set systems. Here relatively low molecular weight resins with chemical functionality. Being of low molecular weight, they give relatively low viscosity at the required application solids. Film formulation is induced by either mixing the two components, as in a two pack epoxy, polyamine heavy duty coating, or by the application of heat to a one pack epoxy phenolic can coating. The stability of a thermo-set coating, once mixed, is of great importance. Should chemical reaction be prematurely induced, then the viscosity could rapidly and easily increase to a point where the coating is unusable. For one pack coatings the unusable period is referred to as die shelf life, normally measured in months, whilst for two pack coatings it is the pot life, normally measured in hours.

Protective coatings have been used for many years. They are no restricted to industrial coatings and include house paints, because the paint or varnish protected die wooden parts of the house. Varnishes are also covered by the term 'protective coatings', because vanishes, such as spar varnishes, protect the spars on sailing ships.

Not only were die paints and varnishes derived from vegetable oils and natural materials, many of which have disappeared, but they were classified in a way which few resin and paint chemists would recognise today, particularly if they are relatively new to this industry.

Varnishes in the past were divided into two types, with many sub-divisions, as follows:

Oleo-resinous varnishes

- Oil plus natural resins
- Oil plus synthetic resin
- Oil
- Oil modified glycerol phthalate
- Oil modified chlorinated rubber

Spirit varnishes

- Solvent plus natural resins
- Solvent plus synthetic resins

The first group dry by oxidation or process initiated by oxidation, whilst he second dry by evaporation.

Before 1905 house paints consisted of white lead, linseed oil, driers and thinners (solvent). Later, zinc: oxide was used at about 20-30% of the pigment by weight. Extenders, such as barites and magnesium silicate, only started to be used from about 1910 onwards. A red lead primer was often used for metal structures, such as bridges. The mid 1900's saw a rise in the use of aluminium top coats for metal structures.

Lacquers referred to certain natural products used in the Chinese and Japanese or solutions of resinous materials in volatile solvents. However, this term also came to cover solutions of nitrocellulose. These became of great importance to the automobile industry in the 1920's, seeking a faster finish than that obtainable for oleo-resinous materials. The commercial availability of ketonic: and ester solvents greatly assisted the market penetration of nitrocellulose lacquers. These lacquers came to also be used on furniture. However, due to its brittle nature, nitrocellulose films needed plasticizing. Alkyds were developed for this purpose and the resulting properties of an alkyd nitrocellulose film were beneficial.

Some of the natural resins used in the protective surface coatings industry in the past were dammar, kauri, copal, congo, east india, zanzibar, sandarac, manila and amber. As the name suggest, they often reflected their geographic origin.
Natural resins were often 'run' to impart oil solubility. This involved heating to some extent to depolymerise the resin. Weight losses up to 30% could occur and the process generated copious fumes. With synthetic resins, such as phenolics, polymerisation occurs.
Spirit varnishes used lacs, which are of insect origin. It has been estimated that 1,500,000 insects are required to produce sufficient: lac for 0.5 kg of shellac.
The use of natural resins has decreased in the USA since about 1930, with them being replaced by synthetic resins. Rosin was, and is, an important member of this family. It is used in the preparation of both varnishes and synthetic resins and as such its usage did no drop to the same extent as other natural resins. Rosin is used to form ester gums, which are based upon the glycerol reaction with rosin, plus other components in many cases.

In 1938, 61% of linseed oil consumption was for paints and varnishes. Other uses included linoleum, oil cloth, printing and patent leather. Certainly at this time as in days before, linseed oil was of major importance to the surface coatings industry.

Linseed oil was subdivided into numerous types depending upon its processing. Some of these were raw linseed oil, alkali refined linseed oil, acid refined linseed oil, oxidised linseed oil, heat bodied drying oils, air bodied versus vacuum bodied. Linseed oil was normally pre-bodied before combination with natural resins, whilst this was not needed for tung oil.

Tung oil was first imported into the USA about 1870. It took time for formulators to learn how to process the oil to avoid the problems of wrinkling, crow's feet, rapid bodying or onset of gelation and matt appearance. Between 1915 and 1925, varnish making was adapted to utilise this new material by gas-checking the oil, which involved heating it to 500'F. Many of the varnishes used 90% tung oil and 10% Linseed oil(4). Phenolic resins had a major impact on the use of tung oil.

Perilla oil, which has similar properties to those of linseed oil, with faster drying and harder films, only came into importance during the 1030's. It was often used m combination with tung oil (75% tung and 25% perilla) and alone in alkyds.

Otocacia oil was first used in about 1923 and was believed to be similar to tung oil, but later this was found not to be the case, being inferior in water and lacking alkali resistance and with behaviour more like that of a resin than an oil causing embitterment However, by modification of the resins used with this oil, it could be used as a replacement for tung oil. Ester gums based on this oil have also been prepared.

Castor oil, not being a drying oil, was used as a plasticizer for lacquers. Whilst the dehydration of this oil was the subject of Much study over many years, it was not until about 1937 to 1939(4-6) that dehydrated castor oil (DCO) became commercially available. Even then, it was only 75 to ~M% dehydrated, which gave rise to a tackiness in the dried films.
By late 1938, 95% to 98% dehydrated castor oil was available, and many of the earlier obstacles and objections to the use of this oil were overcome. Bodying the oil under vacuum gave low acid value stand oils, which could be used to replace, fully or partially, tung oil.

Soybean oil was unknown in 1909 as a raw material for paints and varnishes. It became an important oil in the mid-1930's. It was used for non-yellowing, white baking enamels. When fortified with tung oil, alkyd resins suitable for automotive finishes were obtained. Combination with phenolic: resins also gave acceptable varnishes.

Fish oils, such as sardine oil, have been used, but today this practice has virtually ceased. Odour and variable composition of the oils were two main reasons, with availability as fish stocks decline being an additional one.
Synthetic resins used in the middle of the 20 century included:
Ester gums, based upon reaction of rosin with glycerol or other polyhydric alcohols, were used from about 1900 onwards, and were important raw materials. Nowadays their use is limited. Other natural resins, such as copal, were sometimes used to produce ester gums.

Coumarone indene resins were in commercial production in the USA before 1920 and as such could be considered as the first commercially available synthetic resins. They impart alkali, acid and brine resistance, good adhesion and fast drying. They were also used in combination with phenolic resins.

The reaction of phenol with aldehydes was documented in 1872. Phenolic resins have been used commercially since about 1916 in Europe, and in 1922 in the USA. Many of the phenolic resins used today would bear little resemblance to the early phenolic resins. They were primarily based upon phenol and formaldehyde.

It was not until about 1926 that intensive developments of modified phenolic: resins got underway in earnest. In 1931 p-ter-butylphenol and p-phenylphenol based phenolic resins were introduced, whilst 1937 saw the use of bisphenol A in phenolic resins. Many of these modifications were brought about by attempts to improve the oil solubility of the phenolic resins. Reaction of modified phenolic resins with rosin or copal made the resulting product oil-soluble. Modification of phenolic resins with ester gums was common practice. Fast drying times of touch dry within 4 hours were achieved. Tung oil varnishes modified with phenolic resins gave vastly improved water and alkali resistance finishes. Even when modified with ester gums, significantly improved water and alkali resistance was obtained compared with that from natural resin based varnishes.

It has been known since 1901 that phthalic anhydride reacts with glycerol, a by-product of refining oils (triglycerides) to form fatty acids. This was the foreigner to the largest class of synthetic resins which are still in use today, namely alkyds. They are based upon oils or fatty acids with polyhydric alcohols, such as glycerol or pentaerythritol, and polybasic acids such as phthalic anhydride. In addition, monofunctional acids or alcohols may also be present Initially, drying oils or fatty acids were used for baking or air-drying finishes. In 1929, differentiation between air (oxygen) and heat convertible alkyds was made. Alkyds have been a major resin in the surface coatings industry since about 1928-1930. Automobile finishes (enamels) were based upon alkyd resins, even though they required baking at higher temperatures than the alterative nitrocellulose lacquers. Even nitrocellulose based automotive lacquers contained a proportion of alkyd resin. Due to the final properties of the alkyd, the complexity of combinations of type of oil or fatty acid and other components and the various ways of processing, a generation of alkyd chemists emerged.

Polyvinyl acetate was the first important vinyl resin and was available in about 1912. Aldehyde treated polyvinyl acetate resins were used for spirit type varnishes, lacquers and enamels which has good weathering properties. Some of the higher aldehyde modified polyvinyl acetates gave good baking varnishes. Copolymers of vinyl acetate and vinyl chloride then became available. They tended to be more used in Europe, whilst the USA tended to use polyvinyl chloride resins for surface coatings. One reason was the rubber-like characteristics of polyvinyl chloride. Indeed, it was used as a rubber substitute.

Acrylic resins were first used in surface coatings in about, 1935. Since this time, hundreds of different acrylic based resins have been made commercially available, with a wide range of characteristics. Many in the coatings industry tend to consider styrene as an acrylic co-monomer Polystyrene is claimed 61 to be the oldest synthetic resin, having been 'discovered' about 1800. They are commercially available in Europe in the 1920's and it was not until the late 1930's that they were produced in the USA

Chlorinated rubber is soluble in many solvents and has good compatibility with many materials used in paints. It imparts alkali and moisture resistance to films containing it. Chlorinated rubber resins were used in the USA from about 1934 onwards, having been used in Europe for a few years before.

Urea formaldehyde resins, which are part of the aminoplast family, and their use with alkyd resins were reported in about 1930. Applications reported in the 1940's included metallic articles requiring resistance to adverse conditions, whilst retaining good appearance, of which automobiles, refrigerators and bicycles were three such examples. In 1945 it was stated that the era of urea formaldehyde resins as coasting materials was just beginning. Viewed from today's perspective, this was a very apt vision, especially when one considers the other aminoplast resins now available which complement the early urea formaldehyde resins. Melamine formaldehyde resins started to become available from about 1940 onwards. These materials are co-curing resins, which means that in addition to film forming themselves they can crosslink with other resins containing functional groups, such as hydroxylic groups in alkyds, polyesters, epoxies and acrylics, acidic groups in alkyds, polyesters and acrylics, epoxy groups m epoxy resins and amine groups in acrylics. Phenolic resins can also be considered as co-cure resins.

Epoxies resins only became commercially available in about 1947. Since then their usage has grown to over 550,000 tonnes per year (1990), but all are not for coating applications. They impart outstanding resistance properties and find many applications, including 1 and 2 pack air drying systems. The latter includes, the polyamine, polyamide or polyamino-amide heavy duty coatings, where the amine functionality cross~ the epoxy resin to give a durable and resistant film They are typically used for marine applications such as ship's hulls,-decks, superstructure and tanks, oil rigs and other off-shore installations, storage tanks for food, chemicals and water, pipe linings and paints for concrete and cement. Heat cured coatings based on epoxy resins are used for can linings or internal lacquers, automotive primers and powder coatings.

Epoxy resins can be reacted with other materials to improve the performance of either. There are two types of epoxy esters. One is for air drying coatings and the other is for stoved ones. For air drying epoxy esters, epoxy resin is reacted with air drying oils or fatty acids. For good colour retention, fatty acids with low degrees of unsaturation, such as coconut, would be reacted with the epoxy resin/ film formation would be through cross-linking, probably through the use of an aminoplast.

Polyurethanes did not gain any prominence in surface coatings until he latter half of the 20 Century. Based upon isocyanates and hydroxyl functional materials, a wide range of properties could be attained. Additionally, isocyanates are used to crosslink resins.

In he period 1930-1940, pigments consisted of white lead, basic lead sulphate, litharge, red lead, zinc oxide, leaded zinc, lithopone and blanc fixe. Titanium dioxide started to become commercially available in about 1918 and even in 1943 it was stated(41 that the tonnage consumed by the paint industry had grown considerably. High opacity rutile titanium dioxide was available from 1941. It had superior exterior durability and hiding power compared to anatase titanium dioxide.

Synthetic: organic pigments which had a usable level of light-fastness were made possible in 1914, when it was realised that reaction of the dyes with complex inorganic acids imparted such properties. Phthalocyanine based pigments came into being about 1927.

For air drying oils or fatty acids to dry efficiently, it was normal practice to add 'driers' which were mainly based upon lead, manganese and cobalt. They were often used in the form of naphthenates or linoleates. Today, whilst driers are still required they are based upon less toxic metals such as calcium, barium or zinc.

As the demands on surface coatings increased, and as the complexity of the resins needed to meet these demands also increased, so the resin raw materials and processing techniques changed out of all recognition.

Some of the earliest modem resin process controls used 'wet chemistry' techniques such as acid value in conjunction with solids (non-volatile content - NVQ and viscosity measurements. By plotting acid value against viscosity during the process it was (and is) possible to safely continue a reaction to close to the 'gel point', without gelation. This approach also ensured a greater degree of reproducibility. In essence, the monitoring of acid value and viscosity for alkyds and polyesters, was a means of controlling the molecular weight of the resin. With analytical techniques rapidly improving, it is now possible to routinely monitor molecular weights using Gel Permeation Chromatography (GPC).

Improvements in Spectroscopy, such as Fourier Transform Infra Red (FTIR), enables rapid checking of quality of either raw materials or finished products. The area of Statistical Process Control (SPC) is now commonplace in resin and coating manufacture. As the requirements for coatings increase and formulations have to balance numerous opposing properties, the need for consistency of product becomes more important.

In the early days the quality of the raw materials could be variable, to say the least. With many being based on naturally occurring materials, their composition could vary due to variable climatic conditions during the growing season(s) or geographic region(s). This is true of some of these materials even today. For example, the compositions of North American and Scandinavian tall oil fatty acids, which are derived from the stumps of trees, is different. For some applications this doesn't matter, but for other more sensitive ones, this difference can exclude the use of tall oil fatty acid from a particular source. With ever improving analytical techniques and understanding of the science of processing of raw materials, variations in composition are now much reduced.

Raw material innovations and developments have been fundamental for the development of resins and coatings with improved performance, lower cost and improved environmental acceptability. The more sophisticated the raw materials, the greater the process control necessary and the better the product consistency.

Initially, most coatings were solvent based, many of low solids content. With environmental pressures, there has been a move towards waterborne or high solids content systems. However, many waterborne systems still contain organic solvent. Additionally, neutralising amine is also present. Both solvent borne and water borne systems have to meet VOC (volatile organic compounds) legislation. The applicators and users of coatings have the option of incineration of solvent or waterborne to reduce their emissions of organic materials. However, it has to be borne in mind that incineration of solvent whilst reducing the fuel costs of the incinerator will increase the emissions of carbon dioxide, which has the potential for being the subject of a future tax for some European countries. However, with the environmental requirement of some countries, it may be necessary to continue to incinerate to comply with 'odour' emissions at the boundary fences of the factory site, even for waterborne systems.
Hence there will. be the balance of costs of incinerator fuel verses calorific value of solvent versus size of incinerator - incineration of a waterborne system requires a much smaller incinerator that that for an equivalent volume of solvent based coatings.

Before the Second World War many surface coatings were based on-alkyds. The rate of change in the last 40 years is truly remarkable. The demise of alkyds has been predicted many times, but the fact that they are still a major class of surface coating resin is a tribute to their versatility. Alkyds have been modified to suit the demands placed upon them. Today waterborne and high solids alkyds are commonplace. Twenty or so years ago, these alkyd technologies were in their infancy. It would take a brave person wagering against the alkyd technology continuing for another 100 years due to the ability to relatively easily modify them and the face that they are based upon the renewable raw materials (vegetable oils) and are extremely cost competitive. Many of the traditional areas of surface coating will continue with modifications to suit external pressures.

Heavy duty coatings will continue to be, for the main part, based upon epoxy polyamine/polyamide technology. For certain applications, waterborne heavy duty coatings are commonly used as are some solvent-less systems. One of the reasons for the continued use of tried and trusted technologies, is the fact that they are tried and trusted. In the case of heavy duty and many industrial coatings, the cost of the coating is small compared to the article being coated, and normally results in an enhanced value or prolonged lifetime of the article. Thus, the fabricators of articles and applicators of coatings tend to be conservative and use tried and trusted coatings, albeit with modifications to suit environmental or other concerns. The can coating business, with its use of epoxy phenolic internal lacquers, is another example of tried and trusted technology surviving.

In some areas, however, there have been dramatic changes in the coating technologies used. One such example would be "white goods" which are domestic appliances such as washing machines and refrigerators. This market is now predominantly powder coating, whereas a few years ago acrylic technology dominated. The automotive market is another which has seen 'leaps' of technology. Electro deposition, initially anodic and now cathodic, dominates for automotive primers.

Some areas have seen rapid adoption of what were considered at the time as radical technologies, with powder coatings and radiation curable being two good examples. Both of these technologies whilst being solvent free, are unable to meet all of the demands of the end applications. Hence, there is and will continue to be a place for liquid solvent based or waterborne coatings, even if major modifications are required to enable them to meet environmental legislation.

In some cases, such as wood coatings. geographic preferences dictate the technology used. The choices are alkyd aminoplast or radiation curable unsaturated polyesters or epoxy acrylates.

The success of many solvent based and waterborne industrial coatings depends upon the correct amount of cross-linking occurring to give a balance between, for example, the opposing properties of resistance and flexibility. As a general rule, for a given system, the higher the crosslink density, the greater the resistance, but the less the flexibility. There have been great advances in understanding cross-linking, consequently there have been great advances in developing improved cross-linking or co-curing resins, such as aminoplasts or phenolplasts.

Another factor driving the thermally cured industrial coating market today is reduced temperature curing systems. This is to reduce energy cost and greenhouse gas emissions.

It should not be forgotten that coatings are not only protective and decorative, but they can play a major role in the fabrication or filling of articles. For example, some can coatings are used to enable cans to be formed through deformation of a flat sheet. Can coatings also impart the mobility to beverage cans to allow them to be filled at up to 2,000 cans per minute. As the speed of fabrication or filling increases, so the technology of the coating needs to be changed. In some cases this, way be a minor modification such as changing an additive, but in others it may necessitate the adoption of a new technology.

Coatings can be applied to many articles per minute, as m beverage can coatings with up to 2,000 cans being made and coated per line per minute, or one article over several days or weeks as in the heavy duty coatings for the hold of a ship or oil. rig.

Industrial coatings have to be formulated for their conditions of use. Arguably, more sophisticated systems can be used under factory conditions than by a semi skilled person painting an oil rig under adverse weather conditions in the North Sea.

Many systems, such as powder, radiation curable and thermally cured ones, can only be applied satisfactorily under factory conditions and for the best and reproducible results, these conditions have to be carefully and rigorously controlled.

In this set of books the chemistries of different types of resins for surface coatings are explained. Radiation curable coatings is the subject of a separate series of books. For the reader interested in more detailed information, there are books dedicated to each class of resin.

CHAPTER I

PAINT TECHNOLOGY –
SOME IMPORTANT FACTORS

by

Dr PKT Oldring

Chapter I

I INTRODUCTION.

Before discussing the different technologies employed in the various categories of resins, it may be useful to the reader to discuss some important points of basic paint technology common to all the resins referred to in the chapters of this series of books. The first two sections refer to testing or quantifying the performance of wet and dry paint films and the third discusses paint application techniques. There is also a section briefly discussing the pigmentation of paints.

II PRINCIPAL TESTS FOR PALM AND PAINT FILMS.

The paint industry has a series of tests enabling the testing and evaluation of paints, all of which are part of the readily accessible DIN standards. Those which are commonly used will be discussed, in order to helps formulators with their selection.

1. Tests on liquid paints.

(i) Measurement of the fineness-of-grind.

This test is carried out with a fineness-of-grind gauge, which is made up of a polished metal plate with 2 grooves whose depth varies uniformly from nothing to a set depth. By depositing a little paint spread over the entire surface, one can determine, during the first five seconds of the measurement the fineness-of-grind of the paint. This is the point at which, surface imperfections (bits) can be first observed. The gauge is marked and the point at which the bits are first seen is read from the gauge. This will give an indication of die gloss and the surface, appearance of the applied and dry paint film, and the resistance to settlement of the liquid paint prior to application. The gauge is cither calibrated in microns or 'Hegman numbers', after the originator. The US uses Hegman numbers, the Europeans microns. The fineness of an undercoat is between 6 - 7 Hegman (30 - 40 im) and a finish or topcoat, 8 - 10 (20 to 1 ìm)

(ii) Measurement of the viscosity.

The paint industry uses metal containers (flow cups) with an. orifice (diameter varying between 1.5 - 6 mm) at their lowest point for the determination of the viscosity of a paint. The efflux (flow) time (normally in seconds) for a fixed volume of paint at a fixed temperature is a useful, simple measurement to compare flow properties of paints, typically at application viscosities. This method is only valid for paint which have little or no thixotropy i.e. Newtonian flow. In Table 1-1 flow times for various standard flow cups commonly employed in the European paint industry, compared with a dynamic viscosity approach. All values are at 20°C.

TABLE 1-1: FLOW TIME IN SECOND

Viscosity in mPa	Ford 4 cup	AFNOR 4 cup	DIN 4 cup
20	10	12	11
25	12	14	12
30	14	16	14
40	18	20	16
50	22	25	20
60	25	29	23
70	28	32	25
80	30	34	26
90	33	37	28
100	35	40	30
120	40	45	34
140	44	50	38
160	50	56	42
180	54	61	45
200	58	66	49
220	62	70	52

Below are listed some typical viscosities which paints would be adjusted to (thinned) prior to application by the mentioned application techniques (AFNOR 4 cup):

Brush application	60-100s
Spray gun application	20-45s
Electrostatic application	20-30s
Dipping	25-40s

It should be noted that there are other viscosity measurement techniques. The flow cup is one of the simplest methods. Examples of other techniques are rotating spindle, such as Brookfield, rotating concentric cylinders and cone and plates. Refer to Vol. VI Test Methods for UV & EB Curable Systems by Dr. Chris Lowe, SITA Technology 1998, ISBN 094 7798 072 for further information.

2. Tests on wet paint films.

(i) Measurement of drying time.

Three types are noted here. (In each case the three parameters which have to be controlled and recorded are temperature, humidity and paint film thickness).

(a) Dust Method.

Drying is evaluated by placing grit of a well-defined size onto a freshly. applied film of paint. After a period of time, a brush goes over the paint film in order to see whether the film retains the grit or not. Drying corresponds to the drying time necessary for the grit to stick to the film no longer.

(b) Touch Dry: (or handling ability).

This is the time for which a cigarette paper placed on the paint film (and subjected to a weight of 400 g) can become detached under the action of its own weight, by just turning the film over.

A commonly used, but subjective, alterative method for assessing touch dry times is by touching the paint periodically with one's thumb.

An anti-corrosion primer will have a touch dry time of 10 to 20 minutes whereas a typical DIY gloss paint will take around 3 hours.

(c) Through Dry.

This is the time of drying of the film after which a metallic sheet placed on the film and subjected to a pressure of 0.4 bar, over 10 minutes, leaves no trace on the paint film. It is therefore the time after which the paint will be capable of coping with normal working, handling and storage conditions.

There are alterative methods for measuring dryness. There are various pieces of test equipment available to measure surface and through drying. One such common piece of equipment is the BK recorder. The principle is that a weighted needle is slowly propelled through the wet film of paint at a constant rate. This leaves a visible trail in the wet film. As the paint dries, so the trail starts to disappear. When fully dry no sign of the track of the needle remains. The distance related to time for the partial and complete disappearance of marks is a measure of the drying time.

3. Tests on dry paint films.

The most frequent tests are: measurements of thickness, hardness, impact resistance, stamping, adhesion, resistance to traction tear, resistance to abrasion and scratching, measurement of colour, gloss and orange peel.

(i) Pendulum hardness.

This test is carried out using a Persoz or Koenig pendulum and gives a measure of the hardness properties associated with the through film and not just the surface. The oscillations of a pendulum supported by the film (by two steel beads) are more or less dampened depending on the hardness of the film- The hardness is expressed in seconds.

Examples of maximum Persoz hardness on aged paint films follow:

Chlorinated rubber:	120-130 s
Nitrocellulosic:	120 s
Vinylic:	130-150 s
Silicones:	130-150 s
Baked alkyds:	160-180 s
Baked acrylics:	280-320 s
Baked epoxides:	280-300 s
Polyurethanes:	250-300 s
Glass reference:	420 s

(It is always necessary to measure this at the same time as the paints and to quote for comparison)

(ii) Impact resistance.

The resistance of the film of paint to the impact of a 1 kg mass at varying heights can be determined. The mass is placed in a tube which guides its fall. This test is carried out on the painted substrate side (direct impact) or on the reverse side (reverse impact), which is the tougher test. The result is given in cm and corresponds to the minimum height from which flaking (or cracking) in the film of paint can be observed. The test may be slight1y refined by quoting two values, the first is where cracking is first observed but the coating still adheres to the substrate. The second value is for cracking and flaking, when the coating begins to lack adhesion.

(iii) Grid or cross-hatch adhesion test.

The aim of this test is to monitor the adhesion of a film of paint on a given substrate and to Check the interlayer adhesion of a multilayer system. By using a multi-bladed cutting object, a grid is made by drawing it over the paint film and then in a direction at right angles. This results in small squares of approximately 1 mm2 being formed. An adhesive tape, (typically Sellotape), is applied to the scored film and then removed in a rapid but controlled movement. The score of this test is evaluated as a function of pre-established values and ranges from 0 (excellent) to 5 (the area of paint removed represents significantly more than 35 % of the grid area).

(iv) Pencil Hardness.

Using a pencil holder, the point of the pencil is applied at an angle. of 30' with a 30Og force on the paint film. The instrument is removed and the surface is examined. Failure is at the point at which a pencil, (10H, 9H, 8H, H, F, B, 6B, soft) which has scratched the surface.

(v) Measurement of gloss.

The measurement of specular gloss is carried out using a reflectometer which measures the reflection of a light beam falling onto the film of paint at a specified angle of incidence.

20° angle for high gloss coatings
60° angle for medium gloss coatings
85° angle for matt surfaces

Using the general 60° meter the following values would be typical:

Absolute gloss = 100 %
Gloss = 70-85 % (D1Y gloss alkyd = 85%)
Average satin finish = 20-30 %
Matt satin finish = 10-20 %
Matt = 0-5 %

Gloss is expressed as a percentage of light retransmitted.

(vi) Exterior exposure (weathering).

Of particular importance to the paint industry is the period during which a paint film will retain its gloss and integrity. Of course, it can be decided by exposing the paint film to the elements, but that will require several years wait hopefully! Therefore the paint industry has devised several accelerated tests to predict the longevity of a Paint film as far as resistance to loss of gloss is concerned. The correlation between the accelerated result and real time weathering varies with the nature of the resin system used and results are interpreted with caution. Xenon lamps and frequent water sprinkling weatherometers are quoted as equating to 1500 to 2000 hours exposure with 2 to 3 years' external natural exposure. During this test, the loss of gloss and change in colour are regularly evaluated.

There is also the QUV cabin^ where resistance to UVA and/or UVB radiation interspersed with condensation cycles are used until film destruction occurs. For this particular test, alkyd resins perform poorly as UV radiation wavelengths destroy the resin. This test is high1y controversial since the transmitted UV dose is very high compared to reality and it is difficult to find a relationship between 1000 hours of QUV and natural exposure, such as in Florida, for example.

(vii) Corrosion resistance.

The evaluation of corrosion resistance remains one of the more important tests for some sectors of the coating industry. The resistance of a film of paint is evaluated by exposing it to a marine atmosphere in a closed cabinet. This atmosphere is achieved using a 5% brine solution. The cabinet is heated to 35'C. This is the well known ASTNI B 117 Accelerated Salt Spray Resistance test. A film of paint is deposited at the required film thickness on the substrate of interest and allowed fully to dry or cure. The painted panel is usually scribed with a cross, which penetrates the paint film through to the substrate, running from the four comers of the panel. The panel is then placed at an angle to the salt spray in the cabinet. Corrosion resistance is evaluated by measuring the density of the pinholes which appear, the blister area, the corrosion creep from the scribe and the loss of gloss. Scales are available which enable a score to be allocated after a certain number of hours of salt spray exposure. Every day, a paint formulator somewhere is working on a project to develop a coating with 250 or 500 hours of salt spray resistance, in addition to the other film attributes desired.

III PAINT APPLICATION METHODS.

To a paint chemist, formulating the paint for film performance properties is only half the job. The other, and arguably more difficult part is to formulate for the application technique that is to be used to apply the paint.

Many methods for painting different substrates under various conditions and constraints have been developed, and the choice of the application method depends on many factors. Some key ones are listed below:

- The geometry of the article(s) to be painted, their weight, dimensions and composition.
- The type of paint (liquid or powder).
- The rate at which the parts are to be painted. The cost of the painting process.
- Safety and pollution considerations.

Some of the more common application techniques are discussed below:

1. Brushes and rollers.

These simple application methods are still used in industry for painting heavy, bulky objects or those for which access is difficult, for examples the holds of 'ships. The brush method offers the advantage of good penetration into all areas of roughness or accessibility of the substrate - particularly important when applying an anti-corrosion primer. A roller does not offer quite the same advantages although a more even paint film thickness can be achieved with automatic airless feed rollers. Both techniques remain rather slow and offer little flexibility with regard to today's economic constraints.

Of course, for household decorative paints, the brush and roller are the principal application tools, whether it be for the professionals or DM During paint application to a wall, a roller gives rise to a shear rate of 10,000 s^{-1} enabling good spreading, flow and substrate wetting.

But, once applied, the paint will have to rapidly adopt a certain structure so as not to sag or run from the wall.

To minimise sagging or running, thixotropic alkyds are used which allow the paint to flow under shear and for a certain period after the shear is removed, to allow levelling, but then a rapid increase in viscosity occurs to prevent sagging and slumping. Naturally, the degree of thixotropy is adjustable to anow for the desired amount: of flow and levelling. For example, for a finish and a high build primer

Finishing gloss paint → weak thixotropy
High build primer → strong thixotropy

2. Spray techniques.

There are variations on spray techniques, some of which are described below. Spray application is ideally suited to rapid application of large volumes of paint.

(i) Pneumatic spraying.

This is the most frequently employed application method in industrial finishing. It is cheap and easy to use. The principal disadvantage is the paint and solvent overspray which needs to be removed continuously with appropriate extraction. Fully extracted water backed spray booths are usually used to cope with this. The paint ed for spray guns may be gravity or pressure pot.

(ii) Airless spraying.

In this technique, air is no longer used to atomise the paint. The paint is fed at a very high pressure, typically 200 bar, through a fine nozzle or spray tip. The sudden drop in pressure causes the paint to atomise. This system necessitates a high-pressure pump, such as a piston or one of the membrane (diaphragm) types. A number of versions are available, depending on the final use (small or large ratio, hot application paints, two component paints). The airless process brings the following advantages:

Total elimination of overspray mists. High throughput and thick coats after one coat. Possibility of applying very heavy paints.

On the other hand, this remains a dangerous process and the paint formulation demands are very specific. Airless spraying also yields a relatively poorly atomised paint and thus lay down and flow are often impaired. However, the technique is ideally suited for many applications and is very widely used in heavy duty paint sectors such as marine and maintenance coatings.

(iii) Air-mix spraying.

This type of spraying enables practically overspray mist-free paint application and better atomisation, a combination of the advantages of the first two methods. The paint which is ready to spray is pumped to the nozzle by means of a low pressure pump (35 bars) and atomisation is assisted with a light air stream (1.5 bars). The reduction of misting is due to the slow particle speed (around 0.6 ms- l). This process has the following advantages:

Economical in terms of paint, solvent and compressed air. Reduced misting and hence reduced pollution.

(iv) Electrostatic spraying.

This process consists of giving the paint particles a negative electrical charge which, once placed in an electric field, will be attracted to the earthed part. Figure 1-1 is a schematic representation of an electrostatic spray set up.

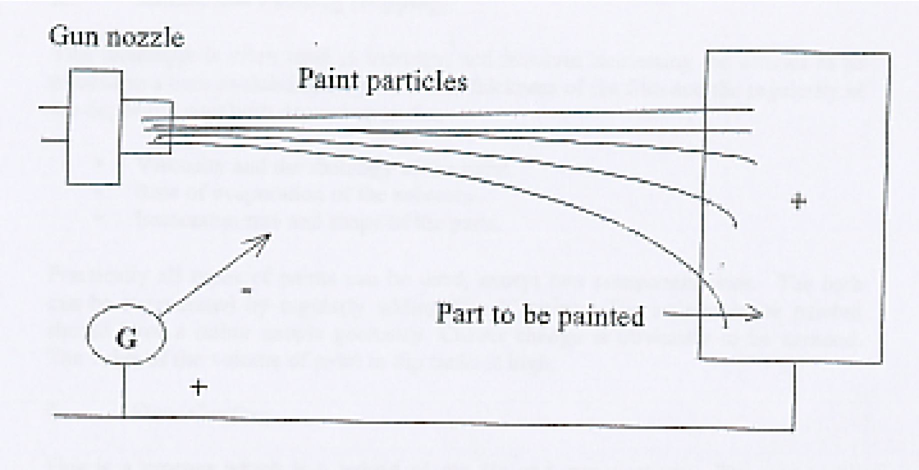


Figure 1-1: Schematic representation of an electrostatic spray set up.

The advantages and disadvantages of this technique are summarised in Table 1-1

TABLE 1-2: THE ADVANTAGES AND DISADVANTAGES OF ELECTROSTATIC SPRAYING

Disadvantages	Advantages
Cavity coating difficult (Faraday cage effect)	20 - 30% more efficient compared with traditional spraying
Need for special solvent to lower resistivity	Coatings of sharp edges and hidden corners Easy to automate
Article to be painted must be an electric conductor	Possible application of water-dilutable paints

The existing equipment can be classified into two types:

- Electrostatic guns.
- Rotating disc or bell appliances.

Rotating bell appliances spray due to the high speed of rotation (40-,000 to 70,000 rotations per minute) of a disc or bell mounted on a compressed air turbine.

These are connected to a high tension generator. The paint flow rates are around 0.4 litres min^{-1}. Transfer efficiencies are very high, rivalling those of powder coatings.

(v) Comparison of different spray application techniques.

In Tables 1-3 and 1-4 different spray techniques are compared.

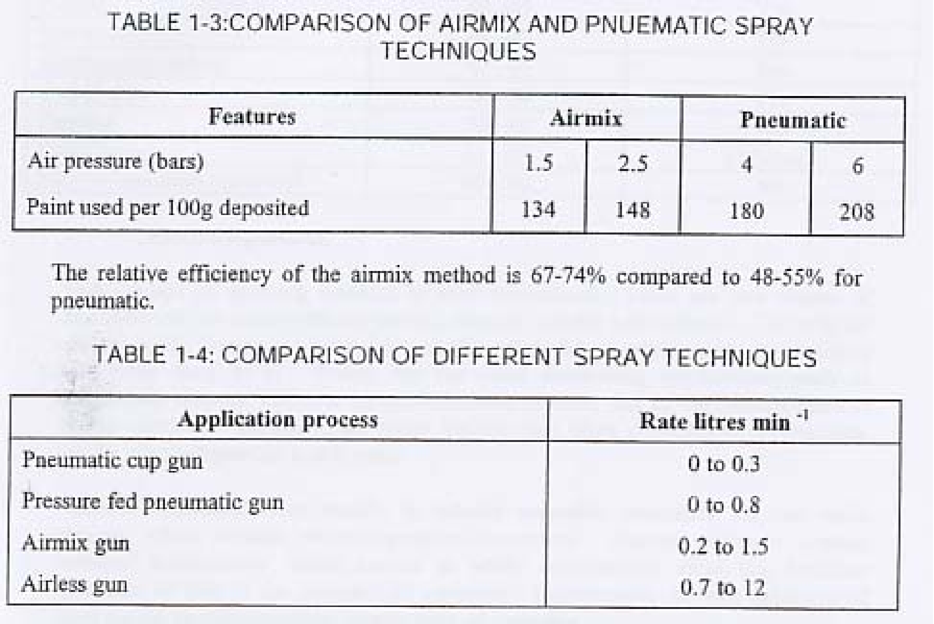


TABLE 1-3:COMPARISON OF AIRMIX AND PNUEMATIC SPRAY TECHNIQUES

Features	Airmix		Pneumatic	
Air pressure (bars)	1.5	2.5	4	6
Paint used per 100g deposited	134	148	180	208

The relative efficiency of the airmix method is 67-74% compared to 48-55% for pneumatic.

TABLE 1-4: COMPARISON OF DIFFERENT SPRAY TECHNIQUES

Application process	Rate litres min $^{-1}$
Pneumatic cup gun	0 to 0.3
Pressure fed pneumatic gun	0 to 0.8
Airmix gun	0.2 to 1.5
Airless gun	0.7 to 12

All these processes may have the option of a hot mode whereby paint heated to 60 80'C is applied. This variant offers the following advantages:

- Savings on thinners and time.
- Thicker layer deposited per coat (higher solids).
- Shortened dry time - less solvent to evaporate and higher temperature for flash off.
- Reduced VOC’s.

In the case of alkyds, only those which are non or poor drying can be used, otherwise oxidative cross linking will occur during application.

3. Immersion Painting (Dipping).

This technique is often used in industry, and involves immersing the articles to be painted in a bath containing the paint. The thickness of the film and the regularity of the deposited coat both depend upon the:

- Viscosity and the rheology of the pain
- Rate of evaporation of the solvents.
- Immersion rate and shape of the parts.

Practically all types of paints can be used, except two component ones. The bath can be regenerated by regularly adding "fresh" paint. The articles to be painted should have a rather simple geometry. Colour change is obviously to be avoided. The value of the volume of paint in dip tanks is high.

4. Flow Coating.

This is a process which is a hybrid of the dip and gun methods. The part to be painted is introduced into a closed vessel and is sprinkled by a large amount of paint mist. Excess paint is recycled after filtration. The installation is rather costly and not very flexible with regard to changes in colour.

5. Curtain coating.

Curtain coaters are especially used in the wood industry for coating large fiat areas at a rate of 1 to 2 m/s. The part passes under an extended hopper with an adjustable slit which regulates the rate at which the paint is applied. The amount of product deposited varies from 100 to 300 g/m^2.

6. Coil Coating.

In this process, the coil of steel is unrolled and passes through two or more rollers impregnated with paint. The coating rates are very high, varying between 60 and 150 min^{-1}. The steel sheet passes through a high temperature oven where the paint is dried and then cooled and recoiled. The coated coil of steel is then used to fabricate articles such as washing machines which are therefore pre-painted. The flexibility requirements of the coating are obviously extremely high.

In Table 1-5 the transfer efficiencies of the different application methods are compared.

TABLE 1-5: COMPARISON OF THE EFFICIENCIES OF DIFFERENT APPLICATION TECHNIQUES.

Application method	**% paint deposited on the substrate**	**Used for alkyds or polyesters**
Pneumatic	35-50	Yes
Airless	40-65	Yes
Electrostatic	60-70	Yes
Electrostatic airless	45-80	Yes
Bell or disc	80-90	Yes
Dipping	70 ~80	Yes
Coil Coating	85-90	Polyester
Electro-deposition (cationic)	90-98	No

7. **Electrodeposition.**

This method of applying coatings is very specialised. There are two classes of electro-deposition paints (electro-paints), namely, anodic: and cathodic. The original electro-paints were anodic, whilst cathodic paints are a more recent development (since the early 80's). Today, for the more demanding applications, such as automobile primers, cathodic electro-deposition is used, due to the better corrosion results obtained. However, for some limited, and often non-critical applications, anodic electro-deposition is still used.

Anionic: electro-deposition results in inferior corrosion resistance for two main reasons, which cationic electro-deposition overcomes. Anionic polymers contain carboxyl functionality, which creates an acidic environment which can facilitate corrosion of iron in the presence of moisture. Furthermore, anionic oxidation of steel during electro-deposition creates sites of corrosion.

The article to be painted acts as an electrode. It is immersed in a bath containing the coating or paint. Another electrode is in the bath and a current is passed. The paint particles carry the charge and are deposited onto the substrate. This ensures 'hard to reach' parts of a complex shaped object can be painted, for example, an automobile chassis. When the paint film reaches a certain thick-ness it acts as an insulating barrier and no longer conducts electricity at that coated part. Paint is then deposited to other parts which have not yet reached this film thickness. This method ensures that a uniform film is applied over the whole of the object.

The paint is, obviously, waterborne. Normally the non-volatile content of an electro-deposition bath is low (15-20%). The voltage, current, time, temperature of bath and nature of the paint all determine the film weight applied. This technique can only be used for the first coating applied and the article to be coated has to be an electrical conductor. Colour change is difficult, due to the large volumes of the electro-deposition tanks. B ath stability is also important. This method of application is ideally suited to production lines, such as automobiles and central heating radiators. Some advantages and disadvantages of electro-deposition are summarised below.

Advantages
- Ideally suited for automation on a production line.
- Uniform film weight applied.
- Consistent film weight applied to every article coated, which gives good q. control.
- Excellent penetration of hard to reach parts of a complex shaped article.
- Fast.
- Excellent corrosion resistance possible.

Disadvantages
- Articles to the coated must be electrical conductors.
- High capital investment required.
- Potential effluent problems due to low solids.
- Limited colour changes.
- Need high throughput of articles of the same type.
- Changing the article to be coated may require the bath settings to be altered.

IV EFFECTS OF PIGMENTS AND RILLERS ON FILM PERFORMANCE.

Pigments and fillers used in the paint can provide:

- A decorative function.
- An anticorrosive function.
- Mechanical, chemical or rheological functions.
- An extending or cheapening function.

1 Pigments.

For decoration and opacifying purposes, coloured pigments are used, which can be:

- Dye stuffs.
- Inorganic and organic pigments.

Dye stuffs include natural or synthetic substances, which are soluble in the suspension media and which have zero or very weak opacity.

Organic pigments are generally made up of metallic salts with good to moderate opacity. They are bright and transparent and their resistance to degradation in light is variable. Inorganic pigments such as titanium dioxide, red and yellow iron oxides have excellent opacities and are stable (or can be stabilised) in light. Both the organic and inorganic pigments are insoluble in the paint medium or solvents.

The choice of pigment or colorant will be based on the following considerations:

- Colouring and opacifying ability.
- Stability to light, temperature and weathering.
- Compatibility with resins.
- Price.

Table 1-6 lists the majority of organic and inorganic pigments used in paints.

TABLE 1-6: INORGANIC AND ORGANIC COLOUR PIGMENTS

Colour	Description	Colouring Powder	Opacity	Light Resistance	Heat Resistance	Base Resistance	Acid Resistance	Solvent Resistance	Weathering Resistance	Observations
WHITE	TiO_2 anatase	VG	VG	G	*	G	G	*	*	Use in interior
	TiO_2 rutile	VG	VG	VG	*	G	G	*	VG	Most used as
	Lithopone	P	P	G	*	G	P			Under coat
	Zinc oxide	A	P		*	G	P		*	Used in anticorrosion
BLACK	Iron oxides		*	VG	P	*	*	*	VG	Antirust, Anti acid,
	Graphite		VG	*	*	VG	VG	VG	VG	Anti acid,
BLUE	Ultramarine blue	VG	P	A	A	A	A		A	
	Prussian blue	VG	VG	VG	A	p	A	*	A	
	Cobalt blue	P	P	VG	VG	G	G		VG	
GREEN	Chrome oxide	G	VG	VG	VO	G	G	*	*	
YELLOW	Lemon chrome	A	G	P	*		P		P	Darkens readily
	Medium chrome		G	P		P	P		G	Darkening tendency
	Orange chrome		G	P	VG					Does not darken
	Cadmium yellow			A		A	P		P	
						VG	G		G	
	Iron oxide yellow	VG	VG	VG						Contains sulphides
ORANGE **RED**	Molybdenum	VG	VG			G	P		G	
	Cadmium red		VG	VG	VG	G	P		G	
	Red iron oxide	VG	G	VG		VG	G		G	
VIOLET	Manganese violet	P	P	VG	VG					
	Cobalt violet	P		VG						
BROWN	Iron oxide	VG	VG	VG		G	G	G	VC	
	Sienna	P	A	VG	VG	G				
BLACK	Carbon black	VG	VG	VG	VG	VG	G		VG	
	Animal black	A	VG	VG	VG		P			
BLUE	Phthalocyanine	VG			VG	VG	VG	VG	VG	Flocculation tendency
	Indanthrone	VG			VG	VG	*			
GREEN	Phthalocyanine	VG	A		VG	VG	VG		VG	
	Azoic nickel									
YELLOW	Flavanthrone	VG		VG	G		VG		VG	
	Benzidene	VG				*	*			
	Isoindoline	VG	*	VG		VG	VG		VG	-
RED	Quinacridone	G		G	G	VG				
	Thio indigo	*	*		*	*	VG			
	Naphtol	*	*		*	VG	VG			
	Toluidene	VG			*	P	P		G	
	Perilene	VG		VG	VG		VG		VG	
BROWN	Alizarine	*	*		*					

VG = Very good G = Good A = Average P = Poor * = Possible Use

2. Anti-corrosion Pigments.

Pigments used in anti-corrosion primers play a particular role. These can be divided into:

- Anodic protection pigments (chromates and phosphates).
- Metallic: pigments providing cathodic protection (zinc or lead).
- Inert pigments: these act by the formation of thick lamella structures.
  They are barriers to water (aluminium, talc, graphite and mica).

For information purposes, Table 1-7 lists many commonly used anticorrosion pigments

TABLE 1-7: SOME COMMONLY USED ANTI-CORROSION PIGMENTS

Material	**Supplier**
Actirox	Colores Hispania
Anticor	Bayer
Alcophor	Henkel
Bayerferrox	Bayer
Butrol	Buckmam
Diroval	Plússtaufer
Delaphos	Isc alloys
Ferrinox	SNCZ
Halox	Lawrence industries
Hispafos	Colores Hispania
Heucophos	Heubach
Heucosil	Heubach
Jacor	CSF
K WIIITE	Teíkoku
MOLY WHITE	PMC
Nalzin	NL Chemical
Oncor	wrnn 5
Novinox	SNCZ
Phosphìnal	SNCZ
Phosphinox	SNCZ
Precor	CSF
Schieldex	Grace
sicor	BASF
Strontium chromate AT	Habich
ZEOLEX	Zeofmn Oy
Zinkphosphat	SNCZ
Zinkoxyd	Lehnwm Voss
Zinkchromat	BASF
Wacor ZBP	Waardals

3. Fillers

Inorganic fillers can do more than just act as a low cost filling material. They can also improve certain properties of the coating. They can be classified according to their chemical and physical properties.

(i) Talc.

Tale is a magnesium silicate with a hardness equal to 1, with terminal hydroxyl groups and a large specific surface area. The latter point explains the higher quantity of resin than expected required to completely wet out a given amount of tale. (The requirement to entirely wet out the surface of a pigment or filler with a resin in a paint formulation is self evident. Each pigment or filler has a value referred to as its 'oil absorption' and that is determined by the amount of linseed oil required to completely wet out 100g of pigment or filler. The value of oil absorption varies with pigment or extender, for example the oil absorption of titanium dioxide pigment is 20 and the value for a fumed silica extender is around 200.) Talc is insoluble in acids and remains one of the most widely used fillers in alkyd resins. Chlorite is similar to talc. Some of the magnesium is replaced by aluminium in the crystal lattice, giving rise to thicker flakes.

The high hydrophobicity of talc imparts a high impermeability to the system towards water and prevents swelling. In solvent systems, its incorporation is easy but in water-dilutable systems, the use of wetting agents is imperative. All lamella products and, in particular, tale, influence the rheological behaviour of the paint. This structure is certainly due to the formation of hydrogen bonds between the resin and the hydroxyl groups of the talc. However, a true thixotropic structure will never be obtained through this system, it is a structured effect.

(ii) Mica.

Mica is generally used as its Potassium derivative termed moscovite which corresponds to flakes which can undergo bending. During grinding these yield fine flakes of large dimension and hardness (2.5). Mica is chemical and weathering resistant. Plastorite is a type of Mica blended with quartz and chlorite, in a sandwich structure. 1 t is elastic (Mica) to flexible (chlorite), and weathering as well as heat resistant. Plastorite has a smaller specific surface area than talc, which is translated through a lower oil absorption. One can thereby formulate with a higher density concentration of pigment, which is found to be economically favourable. With this filler, a better adhesion on inorganic substrates than with talc or mica is also observed. In the case of talc, a more rapid sedimentation upon storage is also noticeable.

(iii) China clay.

Kaolin (china clay) is a hydrated aluminium silicate, with yellowish colour and hardness 1.5.

(iv) Carbonates.

Carbonates are fillers with a cubic structure whose principal asset is their weak self colour and their good compatibility with other pigments. They can be used as single extending agents in white and pigmented paint systems, in order to achieve pure tones.

The fineness of the carbonate used determines the quantity of expensive white pigment, TiO_2, which can be replaced and therefore enables cost saving in the formulation.

In sealants (mastics) and filler coating systems, both carbonates and talc are used in order to improve the sealing properties and sanding ability. Carbonates are also found in low cost anti-corrosion systems. Here, they act as sacrificial pigments., lf there is a corrosion attack, the carbonate goes into solution at the same time as the protons of the acid and thereby buffers them, which reduces the rate of corrosion, at least in its initial phase.

Today, the low price of fillers remains one of the important factors in their favour, especially when the price of titanium dioxide tends to rise. A well-conceived formulation enables one also to save costs on pigments as well as additives which remain a lot more expensive. In Table 1-8 the principal fillers used are listed.

TABLE 1-8: COMMONLY USED PAINT FILLERS

Fillers	**Thixotropy**	**Matting agent**	**Wear resistance**	**Flame resistance**	**Electrical resistance**	**Conductivity**	**Decorative Effect**
Kaolin	x						
Mica				x	x		
Tale	x	x					
Pumice			x				
Glass bead		x	x		x		x
Colloidal silica	x	x					
Calcite chalk			x				
Aluminium paste							x
Graphite						x	
Carbon black						x	
Aluminium powder				x		x	
Zinc powder							x

4. Effect of the amount of pigment on paint properties.

(i) Pigment by volume concentration (PVC).

Research has shown that the properties of a paint depend essentially on the ratio of the volumes of the pigments and fillers used and the volume of the dry film. Therefore a most useful calculation is given by the concentration of pigment by volume or PVC.

The pigment volume concentration is defined as the fractional volume of pigment (including fillers) in a unit volume of a given pigment binder mixture.

$$PVC = V_P/(V_P+V_b)$$

Where V_p = volume of pigments and filler,
V_b = volume of binder, volatiles excluded.

It follows that as the PVC of a paint film increases, a point will be reached when the pigment and filler particles have effectively used up all the available resin for surface wetting and addition of further pigment will result in pigment to pigment contact rather than pigment: to resin contact in the film. This point is known as the Critical Pigment Volume Concentration, or CPVC.

The critical pigment volume concentration CPVC, corresponds to the limit beyond which significant modifications in the paint film properties can be observed, such as an increase in permeability of a film to water vapour or a reduction in the resistance to corrosion. The following discussion lists the main trends as a function of the amount of filler expressed as PVC. A very useful concept in paint formulating is to use the function of the pigment volume concentration as a percentage of the CPVC. Note that, beyond a certain PVC/CPVC percentage, a sudden drop in properties occurs.

The best results depend on the nature of the pigments but they are generally with the following PVC range:

Primers:	$30\ \% < PVC < 50\ \%$ (Except for primers with high zinc content $PVC > 95\%$)
Intermediate coats:	$30\ \% < PVC < 35\ \%$
Finishing coats:	$PVC < 20\ \%$

(ii) Changes in characteristics as a functions of the amount of pigmentation.

(a) Gloss.

Between 20% and 30%, PVC has only a small influence, but thereafter a very sharp fall is found which reaches the start of its asymptote at around 42% of the CPVC which then levels off.

(b) Blistering.

This parameter starts to decrease above 30% of the CPVC, reaching its minimum at 60%.

(c) Corrosion.

Corrosion resistance remains very low up to a value of around 42% of the CPVC, and then it strongly increases, reaching its maximum at 55 %.

(d) Permeability.

This follows the same behaviour as corrosion resistance with a slower evolution.

Note the presence of a PVC 'zone' around 45% of the CPVC where all the characteristics cross. This corresponds to a "no-go zone" for the parameters studied. In this zone, almost all parameters are at their minimal level, or conversely the paint formulation is 'optimised'.

CHAPTER II

ALKID RESINS

by

Phillipe Deligny
Dr. N. Tuck

Edited by

Dr. P. K. T. Oldring

I INTRODUCTION

For many years, resins resulting from the polycondensation of polyacids and polyols have been used in the paint industry. They have been named in many different ways which have led to ambiguities, as to the composition and utilisation of these products.

"Alkyds, Polyesters, Glycerols, Glycerophthalics, Oil-free Polyesters"

The term "Alkyds", which is one of the more commonly employed definitions, was created in *1914* by Kienle. It corresponds to the euphonic contraction of the words '1alcohol" and "acid" indicating the polycondensate obtained from fatty acids, polyols and polyacids.

The term "Glycerophthalic" arises from the fact that the first resins were based on glycerol and phthalic anhydride.

The first attempts at polycondensation were carried out by Belzelius, in *1847,* who prepared glyceryl polytartrate, then by Smith, in *1901,* who synthesised glycerol polyphthalate. The film-forming property of this product was improved by Kienle *(1914)* who modified it with natural oil fatty acids. The thereby formed resins were sold by General Electric under the name “Glyptal”

However, the real credit for the development of alkyd resins in paints can be given to chemists working in Bayer laboratories (at the time of 1 G Farben) who discovered, in *1927,* the transesterification process of oils which enabled the direct use of these oils as basic components without having to use fatty acids. This process enabled the development of the range of "Alkydal" resins for paints.

In this chapter alkyd resins will be considered as those which result from the polycondensation of polyols with polyacids and for which, at least a part of the polyacids (the most frequent case) will comprise a fatty acid or oil, of natural or synthetic origin, and which will possess either oxidative drying ('drying') or non-oxidative drying ('non-drying') properties.

II ALKYDS

1. Types of alkyds.

Alkyd resins of various oil lengths and degrees of modification are still widely used in industrial and D1Y applications. Below is a discussion of the various types of alkyd, a brief description of their properties and some comments on their suitability for various end uses.

It is interesting to note that some oils, precursors for alkyd resins, are still. directly used in paints or for the preparation of certain coatings. For this reason linseed oil is used alone or in stand oils for wood or early anticorrosion primers. China wood (Tung) and Soya bean oils as well as stand oil-based oils can also be found. Lime based oils are still found in matt paints for ceilings for application and brushability reasons, as well as for coating old substrates for either authenticity or preservation purposes.

(i) Long oil alkyds: air drying and aliphatic solvent compatible.

Long oil alkyds, containing >55% of a drying oil, are used in building interiors and D1Y paints, such as matt, satin, gloss finishes, primers and for wood (stains and varnishes). They are stilly widely used in marine and maintenance applications as primers and finishes.

Advantages

- Air drying in 5 to 8 hours, low viscosity, excellent gloss, and wetting of pigments. They can be formulated at 100% solids and as emulsions in water. Thixotropic variants can be formulated.

Disadvantages

- Poor hardness, solvent, alkali and hydrocarbon sensitive, poor exterior resistance. The long oil alkyds can exhibit a tendency to yellowing in darkness, an undesirable feature in white D1Y finishes where areas that are not exposed to light exist next to areas that are, on a window sill for example that may have pot plants. The area under the pot yellows and when the pot is subsequently moved, a yellows area is revealed. The yellowing will eventually disappear, bleached by the light. They are susceptible to specifications, and therefore degrade relatively rapidly.

(ii) Medium oil alkyds: air and oven drying; aliphatic and aromatic solvent compatible.

Medium oil alkyds, containing 45-55% of oil, are often used in low cost anticorrosion primers, D1Y paints (especially matt and satin-finish) and some industrial stoving enamels such as for agricultural machinery.

Advantages

- Air drying in 3 hours, rather high viscosity, induced or assisted air drying (50 – 80°C), good gloss. They can be used in paints along with long oils to improve metal adhesion of the long oils.

Disadvantages

- Poor hardness, hydrocarbon, alkali and oil sensitive.

(iii) Short oil alkyds: air and oven drying; aromatic hydrocarbon and ester solvent compatibility.

The main application of short oil alkyds, containing <45% oil, is in the industrial coating sector, as anti-corrosive primers, finishes, stoving enamels, agricultural machinery finishes, commercial and car refinishes, DIY household radiator finishes and road paints. The short oil length minimises the so called over-coating window for finish over primer because the degree of oxidative drying is low, thus the solvent from the top coat can penetrate the primer, softening it and. then subsequently evaporate without causing any swelling of the primer resin. In the longer oil alkyds, the crosslinking is greater and solvent choice in a topcoat must be carefully considered to minimise the potential swelling of a medium or long oil alkyd primer.

Advantages

- High viscosity, good substrate adhesion and hardness. Good flexibility, water and weathering resistance. Short oil alkyds can be used as primers or as top coat. They can be used in two components systems with isocyanate curing agents.

Disadvantages

- Limited compatibility with many aliphatic (low toxicity) solvents.

2. Modified alkyds.

The following alkyds are modified as indicated and the comments refer to the improvements, or otherwise, in properties compared to the unmodified alkyd.

(i) Styrene-based alkyds: air drying and aromatic solvent compatible.

Styrenated alkyds are widely used in industrial paints for rapid air drying, spray application primers and finishes, one coat metal finishes, solderable zinc powder paints, and anti-corrosive primers.

Advantages

- These resins contain 15 - 40% styrene, and give improved speed of drying, hardness, water and alkali resistance results. Styrenated alkyds have good adhesion to difficult metals.

Disadvantages

- Poor solvent resistance due to lowered oxidative crosslinking and sensitive to scratches.

(iii) Vinyltoluene-based alkyds: air and induced air drying: aliphatic solvent compatible.

These are used in knife-applied coatings, anti-corrosive primers, two-component systems for large-scale machinery and quick drying industrial paints.

Advantages

- These contain 10-30% vinyltoluene and have improved through drying, (compared to styrenated alkyds), hardness, water and alkali resistance. They are compatible with anti-corrosive pigments. They can be used in two component systems with isocyanate pre-polymers such as Desmodur N. (Bayer)

Disadvantages

- Poor solvent resistance, again due to low oxidative crosslinking.

(iii) Acrylic (methylmethacrylate, for example) modified alkyds: air drying and aliphatic solvent compatible.

These are found in car refinish undercoats and topcoats. Varnishes are resistant to autoclaves and are used in food can coatings.

Advantages

- Very fast drying, excellent chemical, water and alkali resistance. Good light stability and therefore weatherability.

Disadvantages

- Depending on the extent of modification, poor mechanical performance.

(iv) Epoxy modified alkyds (epoxy esters): air and oven drying: aliphatic solvent compatibility.

Epoxy esters are used in anti-corrosion paints due to their low cost instead of epoxy coatings. One coat finishes are used for heavy goods vehicles and in can coatings.

Advantages

- Very good adhesion to metal, excellent resistance to corrosion. Epoxy esters are less expensive than. a system containing only epoxy resins, exhibiting good chemical resistance, but without reaching the levels of chemical resistance and toughness of a two pack epoxy system.

Disadvantages

- Possibility of flaking and loss of gloss if there is too much epoxy component. (Due to the sensitivity of the bisphenol A component of the epoxy to degradation in UV light). Rather poor mechanical properties.

(v) Urethane alkyds: air and oven drying: aliphatic solvent compatible.

Urethane modified alkyds can be used for parquet varnish preparation, garage floor paints, marine varnishes, many types of primers and urethane based thixotropic resins. They unproved the drying of unmodified alkyds, when blended with them in paint formulations.

Advantages

- Good surface hardness and better drying. Improved chemical resistance, abrasion and scratch resistance, good resistance to water and to specification.

Disadvantages

- Urethane alkyds can yellow in light (if an aromatic isocyanate is used) and can be brittle if too much toluene di-isocyanate, TDI, is present. The free TDI content of a urethane alkyd requires monitoring, due to the highly pneumotoxic nature of TDI.

(vi) Phenolic modified alkyds: (Long oil varnishes) air and induced air drying: aliphatic solvent compatible.

This type of resin is used to a lesser extent today as it remains rather expensive. Their principal application was for quick drying anti-corrosive primers.

Advantages

- Quick drying, good chemical and corrosion resistance

Disadvantages

- Prone to yellowing

(vii) Nitrocellulose alkyds. air drying and aliphatic solvent compatible.

These are employed in the automobile and cycle industry, and on different surfaces such as glass, wood and plastics.

They are not really a modified alkyd, as they are a blend of alkyd and cellulose resins.

Advantages

- They exhibit: rapid drying and a high gloss.

Disadvantages

- Limited resistance to temperature and solvents.

(viii) Long oil silicone modified alkyds: air drying and aliphatic and aromatic solvent compatible.

These resins were used for a long time in the American Navy as anticorrosion paints at thicknesses of 80im. They are used when exterior durability is important, but where two component polyurethanes are unsuitable for either health and safety (of applicators) or application complexity reasons. Therefore, they are suited to large exterior applications such as paints for the fronts of houses, shutters, marine applications, etc.

Advantages

- Quick air drying, hard, flexible films, excellent water resistance, and excellent exterior durability.

Disadvantages

- Expensive resins.

(ix) Short oil silicone modified alkyds: oven drying and aliphatic and aromatic hydrocarbon solvent compatibility.

These resins are used in higher quality stoving finish industrial paints, particularly when their temperature resistance properties are required - ships funnels, tractor exhausts, domestic equipment such as ovens, toasters, saucepans.

Advantages

- Very good general qualities and excellent temperature resistance (150-200°C)

Disadvantages

- Expensive resins.

(x) Urea formaldehyde and melamine formaldehyde blended with short oil alkyds: oven drying and ketone, alcohol, ester and aromatic hydrocarbon solvent compatible.

They enable the preparation of stoving finishes (80-1501C), for industrial applications. They are still used in the car industries of developing countries because of their tolerant application characteristics when compared to acrylic or polyester stoving systems.

Advantages

- Flexible films, water impermeable, resistance to acids and bases, good hardness, stable towards light and heat.

Disadvantages

- Resistance to aggressive solvents sometimes limited, minimum cure temperature 80°C.

(xi) New developments - waterborne and high solid alkyds.

Alkyd emulsions in. water enable the preparation of all types of paint as can be seen in the paint formulation section. High solids alkyd resins (100 % solids) have found it difficult to penetrate the market despite their extremely low volatile organic compound content, VOC « 250g/l). Their properties are still too different from those of traditional alkyds, especially with regard to through drying, which remains the biggest problem associated with these products. Many paint users avoid this issue and opt for water-dilutable paints.

III RAW MATERIALS FOR ALKYD RESINS

1. oil and Fatty Acids.

Oils and fats are very much part of daily life (butter, bacon, soy bean oil or sunflower oil). Although fats are solids and oils liquids, they both share the same basic organic structure. They are glycerol esters (glycerine) and are also termed triglycerides. When heated in die presence of an alkali, followed by acidification, they give glycerol and a mixture of fatty acids. This is known as saponification. The composition of fatty acids is given in Table 2-1.

TABLE 2-1: SOME FATTY ACD COMPOSITIONS

Common Name	No. of Carbon	Type	Formula
Lauric	12	Saturated	$CH_3\text{-}(CH_2)_{10}\text{-}COOH$
Myristic	14	Saturated	$CH_3\text{-}(CH_2)_{12}\text{-}COOH$
Palmitic	16	Saturated	$CH_3\text{-}(CH_2)_{14}\text{-}COOH$
Stearic	18	Saturated	$CH_3\text{-}(CH_2)_{16}\text{-}COOH$
Arachidic	20	Saturated	$CH_3\text{-}(CH_2)_{18}\text{-}COOH$
Oleic	18	Unsaturated	$CH_3\text{-}(CH_2)_7CH{=}CH(CH_2)_7\text{-}COOH$
Ricinoleic	18	Unsaturated	$CH_3\text{-}(CH_2)_4\text{-}CHOH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$
Linoleic	18	Unsaturated	$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$
Linolenic	18	Unsaturated	$C_2H_5\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$
Oleostearic	18	Unsaturated	$(CH)_3\text{-}(CH_2)_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$
Liconic	18	Unsaturated	$CH_3\text{-}(CH2)_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH2)_4\text{-}CO\text{-}(CH_2)_2\text{-}COOH$

Apart from a few rare examples, fatty acids possess unbranched chains and an even number of carbon atoms. When double bonds are present, they are usually in the cis form and are not conjugated. Ricinoleic acid has two cis double bonds; linoleic has two cis, linolenic three cis, olcostearic and licanic one cis and two trans.

Two types of triglycerides exist. Simple triglycerides are based on three, identical fatty acids and mixed triglycerides are made up of different fatty acids. The majority of oils are made up of complex mixtures of triglycerides. For example, olive oil mainly consists of oleic, palmitoleic and linoleic acids. The fatty acid compositions of some commonly used oils are given in Table 2-2.

TABLE 2-2: FATTY ACID COMPOSITION OF SOME OILS

Type of Fatty Acid and % present	**Copra**	**Palm**	**Castor Oil**	**Dehydratated Castor oil**	**Olive**	**Groundnut**	**Rape**	**Cottonseed**	Soy been	Sunflower	Poppy seed	Safflower	Linseed	Perilla	Oitica	Tung oil	Refined tall	Tallow
Saturated																		
Caprylic	8																	
Capric	7																	
Lauric	49																	
Mystiric	17	2									1							4
Palmitic	9	39	1	1	14	7	2	20	7	6	4	5	6	4	6	4	4	31
Stearic	2	5	1	1	1	3	1	2	3	4	3	2	5	3	4	1	3	17
Arachidic						4	2	1	1									
Behenic						2												
Unsaturated																		
Oleic	6	45	2	2	76	64	20	35	30	42	36	20	21	8	8	7	46	43
Ricinoleic			92	11														
Erucic							50											
Linolenic	2	9	4	85	9	20	22	42	54	47	62	72	17	38	8	10	35	5
Linoleic							3		5	1		1	51	47			12	
Oleostearic																78		
Licanic															74			
Iodine Value	9	54	84	60	88	92	100	107	127	130	145	145	178	190	150	163	130	45

The Iodine value, which is the number of grams of iodine that will react with 100 g of oil or fatty acid by opening the double bonds, is a measure the degree of unsaturation in an oil or a fatty acid. Hence, it is possible to predict the oxidative drying capabilities of an oil. For example, linseed oil has an iodine value of 180 and tall oil fatty acid has an iodine value of 130-150.

The type of unsaturation also influences the rate at which the oil dries. Indeed, double bond conjugation accelerates the oxidative drying process. It is for this reason that the isomerisation of non-conjugated oils is widespread so as to increase this property. Oils such as linseeds are often heated either in air or under vacuum to encourage rearrangement of the non-conjugated double bonds to increase the amount of conjugation present.

Oils are in fact divided into three types - drying, semidrying and non-drying. The drying oils have a high percentage of unsaturation present and high iodine values.

The best drying oils have considerable conjugation. Semidrying oils have a smaller percentage of unsaturation and medium iodine values. Non-drying oils have low unsaturation and low iodine values.

For certain types of alkyd resins (top of the range short or long oils), fatty acids are preferred over oils although in general they are less economic. Their advantage resides in the fact that they can be used as such in resin formulations, without having to resort to the transesterification phase. Moreover, glycerine present in the oils is known to decompose into acrolein, which is a harmful and irritant product, but it is not present in fatty acids.

The production of some oils is given in Table 2-3.

TABLE 2-3: OIL PRODUCTION (EUROPEAN UNION, 1993) IN TONNES

GROLTNDNUT	193,000
SOYABEAN	1,677,000
RAPESEED	1,620,000
SUNFLOWER	1,698,000
VARIOUS	2,758,000
TOTAL	8,029,000

(i) Types of Oils.

(a) Linseeds Oil.

Linseed oil has a significant fraction of linolenic acid which gives the oil good drying and adhesion. But it also suffers from a strong propensity to yellowing. The new variety (not yet distributed) LINOLA has a 4% linolenic content as opposed to 55-70%, which could rekindle interest in this type of oil.

(b) Soya bean Oil.

This oil has a balanced composition of fatty acids and is good value-for-money, as it is derived from an extensively planted crop. It can lead to slight yellowing. Its drying to completion (through film drying) is quicker film linseed oil, big it has significantly slower surface dying. The presence of unsaturated acids may lead to cloudiness especially in pigmented paints.

(e) Safflower Oil.

With a low linolenic yet high linoleic content, this is a high quality oil. Its excellent drying capacity and low levels of yellowing in darkness are only hindered by the high cost of this raw material. This oil enables the preparation of paints with high brightness levels.

(d) Corn and Grape-seed Oil

These two by-products from the transformation of corn. and grapes are used in the food industry and are, therefore, of limited availability to the resin industry, despite having similar basic qualities to safflower oil.

(e) Cottonseed Oil.

This very expensive oil is of limited availability and enables the formulation of paints with very good resistance to yellowing. Its lower unsaturation level makes it unsuitable as a drying oil and it is largely used in stoving enamels such as paints for radiators.

(f) Sunflower Oil.

This oil has a similar iodine value (degree of unsaturation) to that of soy bean oil whilst its fatty acids content is similar to that of safflower oil. It dries in an analogous fashion to soy bean oil with a higher starting Level of paint whiteness and a lower level of yellowing in darkness. Only the quality of fallow sunflower oil (given its price) can be used in the resin industry.

(g) Tall Oil Fatty Acid (TOFA).

This product is a by-product of the paper industry being derived from the stumps of pine trees. TOFA is composed of acids of very high quality giving it the following characteristics: Excellent drying, brightness and gloss retention as well as limited yellowing. Its price fluctuates although it is one of the cheapest fatty acids on the market and its availability and quality are often variable (American or Scandinavian).

(h) Fish Oil.

This oil is only used in lowest cost alkyd resins, for anti-corrosive finishes. Odour is no longer a problem with the qualities available today.

(i) Castor Oil.

This oil merits particular attention since Ricinoleic acid, its principal constituent, has a secondary alcohol function This can be dehydrated to give an extra double bond, directly during the manufacture of the alkyd resin This oil dries quickly, has high gloss and excellent elasticity. When hydrogenated, this gives a non-yellowing oil with excellent adhesion to steel.

G) Coconut, Palm and Groundnut Oil.

These oils have minimal drying properties and are used in stoving finish alkyd resins but their adhesion to metal is not optimal. Groundnut oil has excellent applications in nitrocellulose varnishes, due to its excellent ability for loosing solvent which, therefore does not detract from the fast drying nature of these varnishes. Supplies of these oils remain irregular and difficult.

(k) China Wood (Tung), Oitica, Perilla Oil.

These are very rich in unsaturated fatty acids, and are only used in alkyd resins when extremely fast drying is required. Very high degrees of hardness and adhesion are obtainable, but a degree of brittleness is often the penalty. Marine applications for alkyds made from these oils include spar varnishes. Of course, blends of oils or alkyds are used in resin or paint formulations so that properties can be optimised. A lot of china wood oil (commonly known as tung oil) is used in blends with linseed for example.

A high propensity to discoloration and viscosity increase due to in situ oxidation are problem during alkyd resin manufacture using these oils.

(l) Synthetic Dying Oils.

A number of modified synthetic drying oils can be made by chemically altering synthetic drying oils or natural oils.

Pentaerythritol can be used to produce synthetic drying oils of good quality by esterification reaction with linseed oil, tung oil, or other natural drying oils, or by ester exchange and other reactions with fatty acid esters. Such synthetic drying oils dry quickly, and because they have outstanding properties, such as lustre, water resistance, alkali-resistance and flexibility, they are widely used in producing printing inks and processing paper.

(ii) Oil Length.

The amount of oil in an alkyd resin is the biggest single variable in the properties of an alkyd. Oil length is a highly practical concept. It corresponds to the percentage of oil present in the resin expressed as triglyceride. Different formulators may use slightly different values for oil length, but one set of definitions is :

SHORT OIL ALKYDS: 45 % oil
MEDIUM OIL ALKYDS: 50 % 2:45 % oil
LONG OIL ALKYDS: k 55 % oil

It should be noted that for trans conjugated structures, not only is oxidative drying favoured but also other reactions such as Diels Alder additions to double bonds can be important. An example of a commercially available product resulting from this principle is conjuvandol which has remarkable drying and gloss properties as well as low yellowing properties although, unfortunately its high cost limits it to certain applications.

(iii) Air Drying of Alkyds.

It is useful to discuss the oxidative drying process and how it is used to make alkyds the most widely used of synthetic resins. The principal crosslinking or drying mode when considering alkyd resins is oxidative drying. The mechanism is somewhat better understood today and includes four steps.

1. The induction period which starts the moment the paint film is applied until it starts to absorb oxygen.
2. The formation of peroxides
3. Decomposition of peroxides
4. Polymerisation

FIGURE 2-1: **REPRESENTATION OF STEPS IN OMDATIVE DRYING OF AN ALKYD RESIN**

The oxidative drying mechanisms with conjugated and non-conjugated double bonds are shown in Figures 2-2 and 2-3.

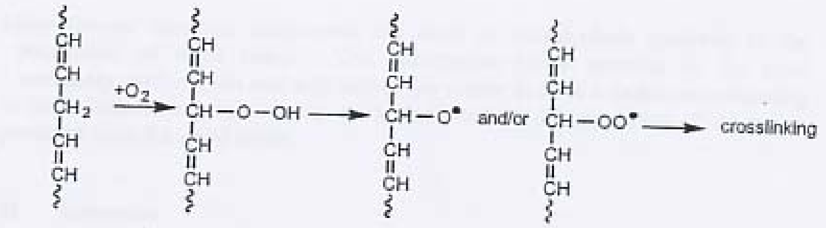


FIGURE 2-2: OXIDATIVE DRYING MECHANISM FOR AN ALKYD WITH NON-CONJUGATED DOUBLE BONDS

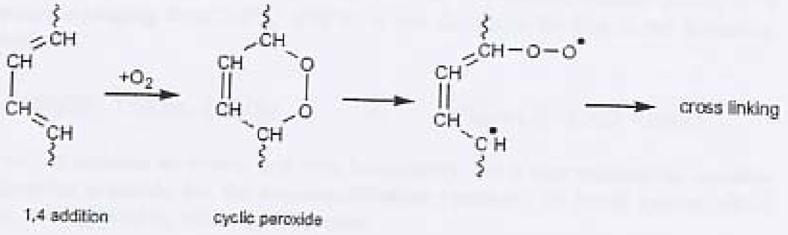


FIGURE 2-3: OXIDATIVE DRYING MECHANISM FOR AN ALKYD WITH CONJUGATED DOUBLE BONDS:

In order to accelerate the oxidative drying period, especially the phases of oxygen adsorption and polymerisation, which can. take several weeks, drying agents can. be added to the paint. These are termed 'driers' and are carboxylate derivatives of different metals used in paints at room or high temperatures in order to optimise their drying. Driers exert the following effects:

1. Reduction of the induction period
2. Increase in oxygen absorption rate
3. Assist the formation and decomposition of peroxides
4. Reduce the quantity of oxygen necessary

These driers can be classified into three groups.

(a) Oxidation catalysts.

These are also called primary driers and help oxygen absorption by the film of paint as well as the formation and decomposition of peroxides. These products, hence, control the surface drying of the paint film and are based principally on cobalt, manganese, cerium, vanadium and iron (HI). Cobalt remains the most efficient in this role, Cerium and iron are only used for high temperature applications.

(b) Polymerization catalysts.

These help the drying to completion of the paint film and are called secondary driers or through film driers. These include principally lead, zirconium, rare earths, aluminium and bismuth.

Lead is still the best metal in this category but its use is now prohibited, for toxicity reasons. It has been replaced by zirconium which is, however, slight1y less active. Rare earths and aluminium are used in special formulations such as high solids paints.

(c) Auxiliary catalysts.

These are based principally on calcium, lithium, potassium and zinc. The first three, used alone, do not improve drying at all. However, they do play a synergestic role with cobalt or zirconium. because they improve film formation. Calcium remains the most widely used and zinc is used to reduce the rate of surface drying, thereby permitting better oxygen absorption through the paint film and also avoiding orange peel phenomena.

Table 2-4 lists the usual recommended amount of drier to use for each of the metals (relative to the non-volatile content of alkyd resin used).

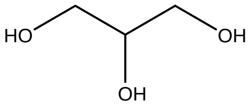
TABLE 2-4: AMOUN-WOF DRIER REQUIRED

cobalt	0.02 - 0.1%
manganese	0.02 - 0.05%
cerium	0.05 - 0.15%
iron	0.04 - 0.15%
calcium	0.1 - 0.25%
zinc	0.05 - 0.25%
potassium	0.05 - 0.25%
lithium	0.05 - 0.2%
lead	0.3 - 1%
zirconium	0.1 - 1%
rare earths	0.1 - 0.3%
aluminium	0.2 - 1%

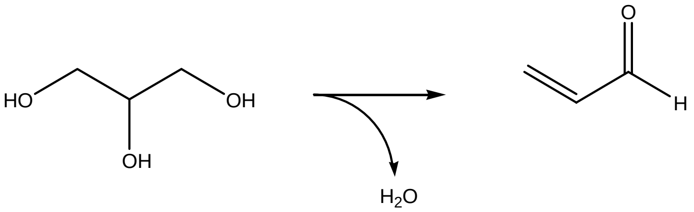
2. Polyols.

Many diverse chemical compounds are used as polyalcohol (polyols) in the preparation of alkyd resins. The information below pertains to the more commonly used polyols and will enable the reader to have a better understanding of the influence they have in the resin itself and on the properties of the paints produced from the alkyd resins.

(i) Glycerine.

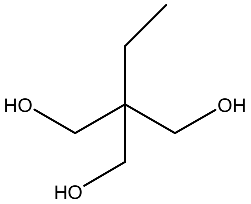


Glycerine, (also known as glycerol), is a triol and was the first polyol to be used in the production of alkyd resins. When used in the monoglyceride phase, at a temperature ranging from 260'C -290'C, it can dehydrate leading to the formation of acrolein:



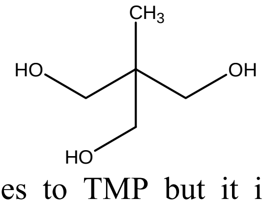
Not only is acrolein an irritant and very lachrymatory, but it also reduces the quantity of glycerine available for the transesterification reaction. In better quality alkyd resins, it is replaced by trimethylolpropane.

(ii) Trimethylolpropane, TMP.



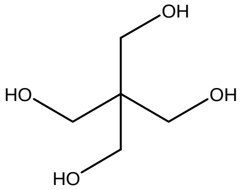
This polyol contains only primary hydroxyl groups. Resins formulated with TMP instead of glycerine have lower viscosity, potentially allowing the formulation of paints with increased film thickness per coat. Exterior durability is improved, as are water and alkali resistance. This is because all hydroxyls are primary and therefore equally reactive. Branched chains result with consequent resistance to hydrolysis of the alkyd produced.

(iii) Trimethylolethane, TME.



This molecule has similar properties to TMP but it is nowadays only available in large quantities and at an acceptable price on the North American continent. It gives a slight improvement in heat resistance of the alkyd resin compared with TMP.

(iv) Pentaerythritol, PENTA.

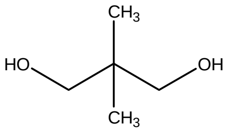


Alkyd paints made with Pentaerythritol, frequently termed PENTA, have superior adhesion, weather-resistance, colour, lustre, water resistance and chemical resistance properties in comparison with trihydric alcohols, such as glycerol, and also dry faster than trihydric alcohols.

Penta is used principally in long oil alkyd resins as the long and middle oil lengths make it possible to take advantage of pentaerythritol’s properties. If pentaerythritol is mixed with a dihydric alcohol, it may be used in short oil alkyds.

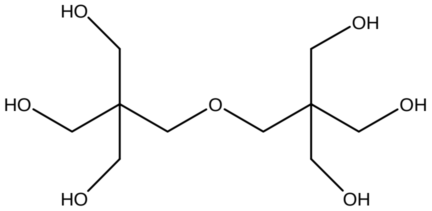
The above polyols are the most widely used, mostly because of low cost and wide if availability, but other polyols are used either in small amounts or for very specific applications.

(v) Neopentylglycol NPG.



This interesting diol is common in the polyester industry but is less well known in the alkyd resin industry. The presence of two methyl groups, which protect the central carbon, impart good resistance to hydrolysis which therefore improves the weathering properties of alkyds produced from. it.

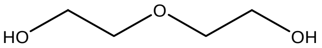
(vi) Dipentaerythritol.



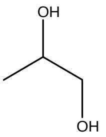
This hexafunctional alcohol enables the formation of very long oil length alkyd resins (80 - 90%) and is often used in high solids alkyds. It leads to an improvement in drying compared with PENTA but lowers exterior resistance due to the presence of an ether linkage. A few percent of this product can be found in technical PENTA (ca. 7-9%) which improves the drying qualities of the prepared resin compared with the use of pure PENTA.

(vii) Glycols.

Diethylene Glycol:



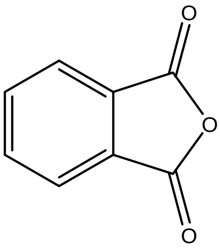
Propylene Glycol:



These products impart a lower viscosity and high flexibility coupled with a low hardness to alkyd resins.

3. Polyacids.

(i) Phthalic Anhydride (PA).

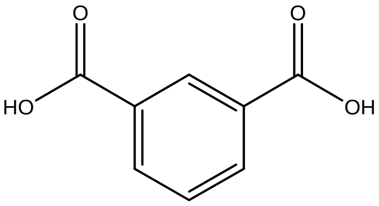


Orthophthalic acid, is only used as its anhydride derivative. It remains the most widely used diacid in the alkyd resins industry. Originally, phthalic anhydride was produced solely from the oxidation of coal-tar-derived naphthalene and its availability depended on the availability of coal tar from coking operations. In 1960, when coal-tar naphthalene was in short supply, output was erratic and prices fluctuated. As a result, petroleum-derived naphthalene was commercialised as a new feedstock for phthalic anhydride. However, naphthalene supplies remained unstable, causing many producers to start using o-xylene as a raw material. Since that time, the petrochemical industry has rapid1y expanded, making large quantities of o-xylene available at competitive prices. Consequently, o-xylene has become the predominant starting material for the production of phthalic anhydride.

The largest markets for phthalic anhydride, plasticizers, unsaturated polyester resins and alkyd resins are all relatively mature and therefore subject to the influence of general economic conditions. Phthalic anhydride gives alkyd resins hardness and chemical resistance, due to the phenyl group's resistance to rotation. This structure also causes alkyds made from phthalic anhydride (acid) to be susceptible to hydrolysis.

In many ways, the choice of phthalic: acid and a fatty acid defines all that is both good and bad about alkyds. Phthalic: is the acid of choice because of cost, fatty acids are used to enable ambient cure, case of surface wetting and cheapness. This sums up alkyds, cheap, effective, easy to use. Disadvantages are poor exterior durability and yellowing. Both of these can be avoided by not using phthalic: acid and fatty acids, but that destroys both the economics and the case of use.

(ii) Isophthalic Acid (IPA).



EPA is principally used in polyester resins and is little used for alkyd resins due mostly to cost constraints. In general, it leads to higher molecular weights dial with phthalic acid because of its greater tendency to cyclisation with diols. It enables, however, one to improve resistance to corrosion, hydrolysis, and yellowing. It improves the drying rate, as well as hardness.

Its applications relate to high performance alkyd resins for external paints whose durability is improved. This is especially true for silicone alkyds, where the cost of the silicone modification outweighs the cost increase involved in the use of IPA. IPA is useful in alkyds for exterior wood paints to which it imparts both exterior resistance as well as improved mechanical properties (elongation, deformation) which allow the paint to cope with the deformations in changing climatic: conditions on a wood substrate.

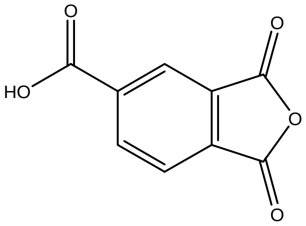
However, its very high melting point leads to longer reaction times during alkyd manufacture than with phthalic acid as well as leading to an increase in the final resin coloration. It should be noted that it also reduces the compatibility of the resin obtained.

Terephthalic acid finds no application in alkyd manufacture. Its very high melting point renders it difficult to use and it can only be found in fibres and polyester resins.

(iii) Maleic Anhydride (MA).

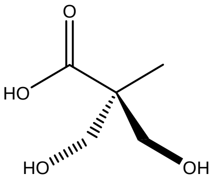
The use of this anhydride gives notable improvements in the drying properties and hardness of the resin. It is also employed in the maleinisation of fatty acids (see section referring to associated reactions) which can lead to water-dilutable alkyds. It is often used to effectively increase the viscosity of a resin which will then. require a large volume of dilution solvent, thus reducing the cost of the alkyd.

(iv) Trimellitic Anhydride. (TMA)



TMA is often used for water soluble alkyds, since it gives a free carboxyl function which is readily accessible to an amine for neutralisation. It is also used in high solids alkyds.

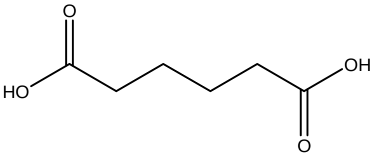
(v) Dimethylolpropionic acid (DMPA).



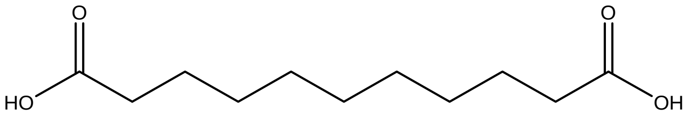
The diol function of this molecule is employed for esterification reactions leaving the acid functionality free for the preparation of water-dilutable alkyd resins of superior quality to those obtained with TMA. It remains, however, a very expensive product for the alkyd resins industry.

(vi) Aliphatic Diacids.

Adipic acid:

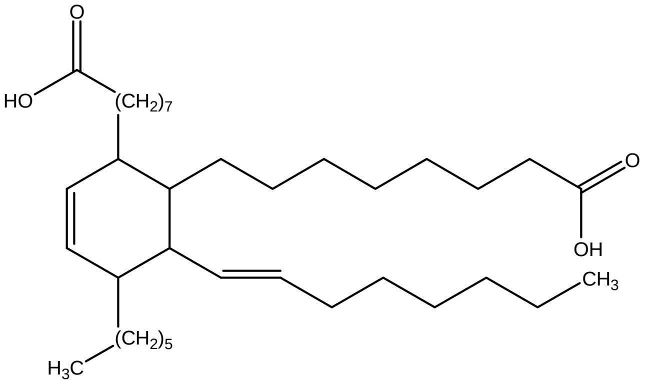


Azelaic acid:



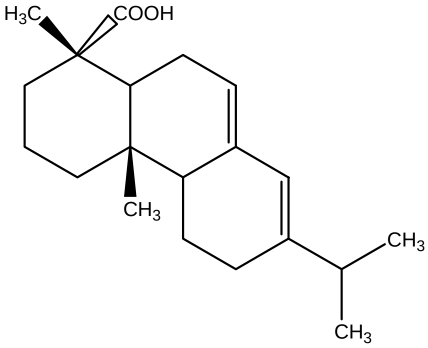
These linear diacid are used to plasticize alkyd resins by imparting flexibility, shock and impact resistance, but compromise hardness, chemical resistance and durability.

(vii) Dimer Acid.



Dimer acid is obtained by the addition of two moles of C_{18} fatty acids, usually tall-oil fatty acid. It is actually composed of many isomers and its probable structure includes a C_6 core. It greatly improves the flexibility of the resin, yet it remains a product which has seen little use in alkyds because of its price and its extreme flexibility. It is very widely used in polyamides for adhesives and curing agents for epoxies.

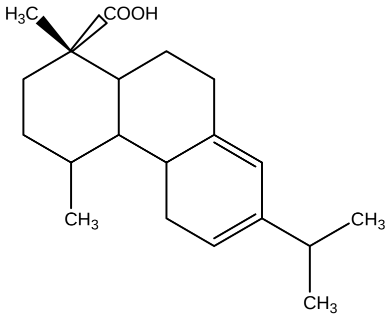
(viii) Monoacids.



Rosin (Abietic Acid)

Rosin is a natural resin which comes from trees and their stumps. It is composed of 90% of varying rosin acids depending on the country of origin as well as its degree of coloration, but its main constituent is abietic acid. At a temperature of 15VC this compound undergoes isomerisation giving levopimaric acid.

Levopimaric Acid

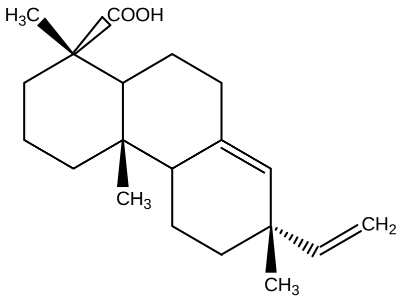


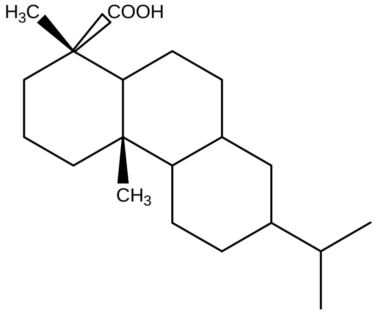
The carboxyl functionality is sterically hindered and only reacts with diols at above 250'C. On the other hand, the ester obtained is difficult to hydrolyse and leads to excellent water, alkali and acid resistance. However, the conjugated double bonds are readily oxidised leading to fragmentation of the molecule. As a result, rapid exterior degradation of the paint film can occur, if other than small amounts of rosin modified alkyds are used in exterior quality paints.

Rosin used in quantities ranging from 3 to 10% (often called hard rosin) in alkyd resins, lowers the viscosity of the final paint product whilst improving the gloss of the paint film. Drying is perceived as being faster due to the hard nature of the rosin after solvent evaporation.

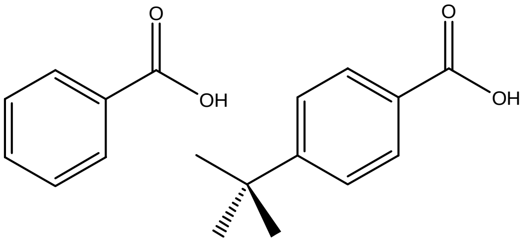
Another method for incorporating rosin in the alkyd involves the use of tall oil fatty acid with a 25% rosin acid content (such as RESINOLINE BD25). Here, principal component is not abietic acid but a mixture of two acids, dextropimaric and tetrahydroabietic, which do not have conjugated double bonds and whose resistance to exterior exposure is much improved.

Dextropimaric and Tetrahydroabietic Acids





Benzoic Acid and Para-t-butylbenzoic Acids



Monoacids such as benzoic acid or para-t-butylbenzoic acid are used as chain length limiters or so called chain stoppers. They reduce the functionality of the system without changing the length of the oil. Their esterification reactions resemble termination reactions. They improve the physical drying of resins (very attractive for stoving finish resins) as well as hardness. Hence, these acids are used to produce what the industry refers to as 'chain stopped alkyds'. They improve the solubility parameters of the resins and enable rather low viscosities even for high solids alkyds.

(ix) Other Acids Used in Alkyd Resins.

(a) Crotonic acid is used in certain instances to improve the adhesion of alkyd resins.
Non-drying synthetic fatty acids with linear fatty chains can also be found, such as isononoic acid or n-heptanoic acid which are added to stoving alkyd paints in order to improve flexibility, gloss and pigment wetting.

(b) Cardura E 10 (SHELL) or Glydexx 10 (EXXON).
This the glycidyl ester of versatic acid and it possesses a branched structure. Versatic acid is a neo-acid containing 9, 10 or 11 carbon atoms, which is roughly equivalent to a low molecular weight fatty acid chain. Cardura E10 has a unique highly branched carbon-rich structure which enhances resistance to water and other polar materials such as alcohol. 7be branched structure sterically protects the ester bonds and the adjacent monomer units against hydrolysis, thus providing excellent alkali resistance.
The epoxide group is highly reactive towards the carboxylic groups of an alkyd resin and enables, in certain cases, the iodine value of the resin to be reduced to almost zero. This is necessary for resins combined with zinc powder. This raw material gives the alkyd resin an excellent degree of gloss, resistance to yellowing as well as a very high degree of flexibility. Moreover, with its “Fatty" structure, the pigment wetting of an E10 modified alkyd is considerably increased. As it has no drying ability, it can only be used in blends with drying fatty acids. or in stoving resins, which remains its principal application.

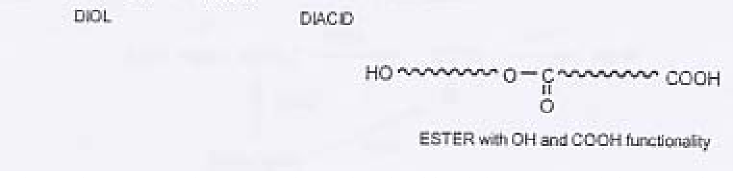
IV CHEMISTRY OF ALKYD RESINS

l. Polymerisation Mechanisms.

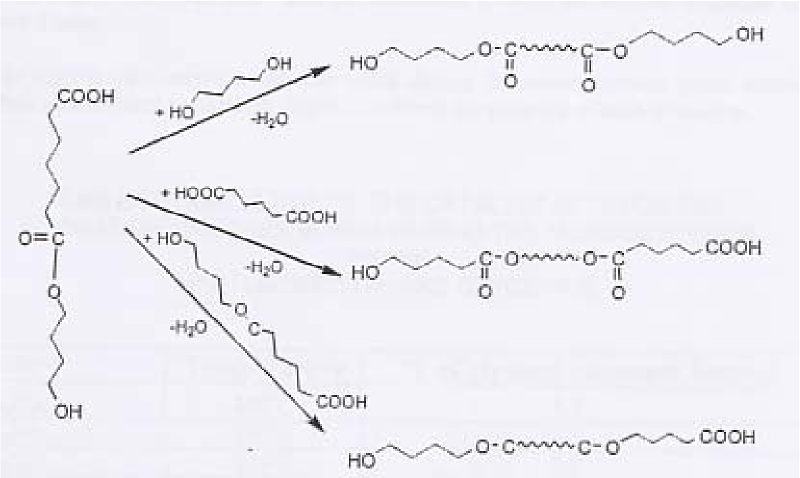
Many polymers or resins can be classified according to two main polymerisation mechanisms:

(i) **Polyaddition,** in which the propagation process typically involves unsaturated monomers which can react with each other by a free radical mechanism, (or catalytically), hence giving a polymer made up of the same atoms, in the same proportions as the monomer (e.g. polyethylene).
(ii) **Polycondensation,** whereby the polymer is formed by the reaction of two functional groups with the loss of a small molecule, such as water, hence the resulting resin is not made up of the same atoms or in the same proportions as the basic monomer (e.g. polyesters).

This second synthetic method for the synthesis of resins is, therefore, generally achieved by the reaction of two monomers, both of which are at least difunctional molecules.



The next step may involve reaction of the alcohol/acid ester with another diol, a diacid, or with itself. For simplicity of representation, the ester is represented as being OH and COOH terminated. In practice, depending upon the amounts of diols and diacids present, the ester could be terminated with two hydroxyl groups, two carboxyl groups or a hydroxyl and a carboxyl group, as shown. The reality is that most polyesters and alkyds contain trifunctional polyols.



The principal features of polycondensation are:

1. Stepwise reaction between functional groups.
2. Progressive increase in molecular weight. (Slow in comparison to polymerisation by a free radical addition mechanism)
3. Approximately similar reactivity of monomers and intermediates.
4. Increase in reaction rate for all steps by the use of catalysts.

In general, the polymer is a mixture of molecules of different sizes and of different weights. The given molecular weight always corresponds to an average molecular weight:

M_w: Weight average molecular weight
M_n: Number average molecular weight

These are defined by the formulae:

$$M_n = \frac{\sum N_X M_X}{\sum N_X} = \frac{W}{N}$$

$$M_W = \frac{\sum N_X M_X^2}{\sum N_X M_X} = \frac{\sum N_X M_X}{W}$$

Here $\mathbf{N_X}$ represents the number of molecules in a polymer fraction of weight $\mathbf{W_X}$, all having the same molecular weight $\mathbf{M_X}$, and **W** and **N** represent the total weight and the total molecules, respectively, for the polymer mixture.

Molecular weights are determined by the measurement of the intrinsic viscosity, gel permeation chromatography, or by high-pressure liquid chromatography (HPLC). Viscosity measurements yield a weight average molecular weight whereas osmotic pressure and end group analysis yields a number average molecular weight.

The ratio $\mathbf{M_w/M_n}$ determines the polydispersity of the polymer which is symbolised by I or P. This value can be rather high in the case of alkyd resins, indicating the presence of high and low Mw fractions.

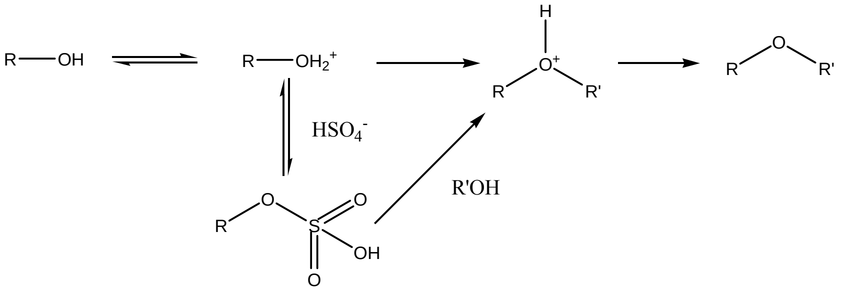
Molecular weights of resins have a strong influence on the behaviour of paints made from them, notably during application and also on the properties of the paint film. Higher molecular weight polymers or resins will yields paints with higher viscosities and lower solids, but also with improved dry film properties such as durability and faster drying. Conversely, high solids paints can be made from lower molecular weight resins but a compromise of paint properties is often required.

2. Secondary or Competing Reactions.

During polycondensation, several competing or secondary reactions can occur and lead to undesirable effects on the properties of the alkyd resin.

(i) Etherification.

This reaction, which corresponds to the dehydration of polyols, catalysed by protonic acids is shown in Figure



This reaction is especially undesirable since it increases the level of crosslinking in the system, with the risk of Premature gel formation. Moreover, too high a percentage of ether linkages would be detrimental towards the exterior resistance of such a resin.

The etherification reaction can also occur during the monoglyceride phase which often uses an alkaline catalyst. Table 2-5 shows the progress of such a reaction.

TABLE 2-5: INFLUENCE OF THE CATALYST (0.1 %) ON THE FORMATION OF ETHER BONDS DURING THE MONOGLYCERIDE PHASE
WITH LINSEED OIL AND GLYCERINE.

Catalyst	Temperature	% of glycerol oligomer formed
Na_3PO_4	240°C	3.5
Na_3PO_4	280°C	27.3
NaOH	240°C	8.0
NaOH	280°C	25.6

(ii) Cyclisation.

This type of reaction is observed particularly when phthalic anhydride is used. The following structures have been identified in alkyd resins.

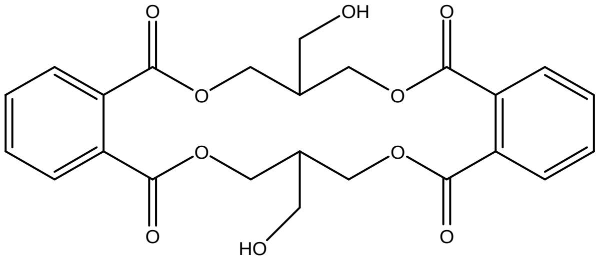


Figure 2-5: Termination reaction - chain breaking

This reaction can be considered as a termination reaction acting as a chain breaking process. If much of this reaction occurs during the condensation polymerisation, achieving a high molecular weight polymer and the expected viscosity increase will be difficult, if not impossible. It appears that the synthesis of alkyds via the fusion method leads to more cyclisation reactions than with the azeotropic method.

(iii) Maleinisation.

Maleic anhydride is frequently used for the preparation of alkyd resins. The double bond present in this molecule can react with those present in the oil or fatty acid. With a suitable system, a Diels Alder reaction can take place at temperatures around 60-80°C. With less favourable systems, temperatures around 200°C are necessary. In general, the functionality of this product should be considered as > 2.

3. Important Parameters for Formulating Alkyd Resins.

The formulator of a resin has to develop one which will be fit for a specific end use. For a specific paint application, there are several resin-related parameters which must be considered. They may be quantitative or qualitative, and the experienced resin chemist uses them. knowing their effect in the final paint formulation.

(i) Hydroxyl Value.

This is die percentage of hydroxyl groups expressed in mg of KOH per g of solid resin (i.e. excluding solvent content of the resin). It enables the determination of the amount of free and available hydroxyl functionality in the alkyd resin.

This parameter will influence the following properties of the resin:

- Pigment wetting - increasing hydroxyl value favours the wetting of polar pigments.
- Polarity of the resin, and therefore its dilution properties in solvents.
- Water resistance - a high OH value is undesirable from a water resistance point of view.
- Crosslinking - a certain OH value is essential if the OH groups on the alkyd are to be used in cure or crosslinking reactions with isocyanate or amino-resins
- Adhesion to substrate.

(ii) Nature of oil and oil length.

These are extremely important parameters since the oil length and properties of the oil used will fundamentally determine the nature of the alkyd resin. The nature of the oil and oil length of an alkyd controls the following parameters of any paint formulated from the alkyd:

- gloss
- hardness
- drying
- cost
- colour
- yellowing
- exterior durability
- chemical resistance
- dilution properties and compatibility

Oil length is a highly practical concept which facilitates the classification of alkyd resins into different groups. It corresponds to the percentage of oil present in the resin expressed as triglyceride. Consider an example of an alkyd resin consisting of *878* g (1 mole) of Soya bean oil*, 184* g *(2* moles) of glycerol and *444* g (3 moles) of phthalic anhydride. The alkyd resin obtained has an oil length of:

$$\frac{878*100}{878+444+184-54}=60.5\%$$

As a function of this parameter or criterion, the following classification can be established:

SHORT OIL ALKYDS	<45%
MEDIUM OIL ALKYDS	>45%; <55%
LONG OIL ALKYDS	>55%

As explained earlier, the definition of short medium and long oil alkyds may vary from formulator to formulator. The differences are normally only a few percent.

When the oil length is greater than *75* %, the resin is no longer considered as an alkyd resin but a modified oil instead. The properties obtained will be closer to those of the base oil. Table *2-6* and Figure *2-15* indicate the influence of oil length on the resin properties:

TABLE 2-6: EFFECT OF OIL LENGTH ON PROPERTIES OF ALKYD

R

Oil length	Air drying	Stoving finish	Self colour	Flexibility	White spirit solubility	Easy of application
30 70	↓	↑	↓	↓	↓	↓

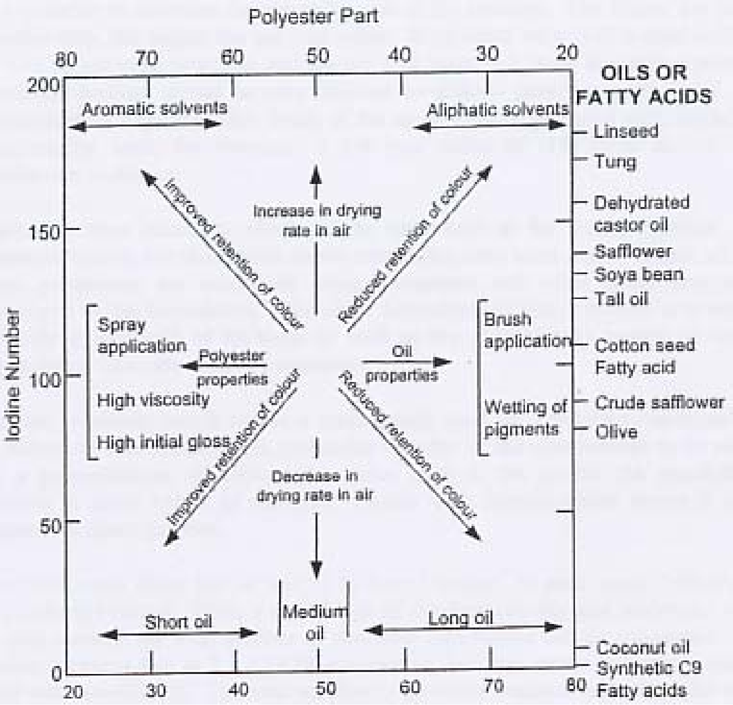


TABLE 2-7: EFFECT OF OIL LENGTH AND DEGREE OF UNSATURATION (IODINE VALUE) ON THE PROPERTIES OF ALKYD RESIN.

Air drying obviously requires the presence of fatty acids, so it is obvious that air drying increases as oil length increases. Stoving (baking) systems require compatibility of the crosslinking resin, frequently melamine, with the alkyd, and as oil length increases, this compatibility decreases. The yellowing tendencies of an alkyd are related lo unsaturation, so yellowing increases with increasing oil length.

Fatty acid chains are inherently flexible, hence flexibility increases with oil length. Compatibility with white spirit increases with increasing oil length as does ease of application, as the fatty acid chains confer low surface tension and hence ease of surface wetting.

(iii) Functionality.

A knowledge of the functionality of the resin system enables the formulator to predefine the level of crosslinking and condensation (the amount of reaction or polymerisation).

A functionality equal to 2 is obtained uniquely with difunctional monomers. The degree of condensation will influence, amongst others, the following properties of the paint and resin:

1 . molecular weight
2. hardness
3. drying characteristics
4. compatibility
5. the relationship between viscosity and non-volatile content (solids) levels
6. gloss
7. flexibility

The value of the functionality can be easily calculated using the theory of condensation, after ascribing to each basic component of the resin a real (practical) and non theoretical functionality. As examples, the functionality of trimethylolpropane is three, because it has three primary and non sterically hindered hydroxyl groups. Contrast this to the triol glycerol whose practical functionality is two, despite the presence of three OH groups. This is because only two of the OH groups are primary and a single secondary OH group has little actual reactivity in the polymerisation reaction. Hence a polymer of phthalic anhydride and glycerol will yield an essentially linear polyester with little branching or crosslinking, assuming equal moles of the two reactants. If the glycerol is replaced with pentaerythritol, of functionality four, with its four primary OH groups, extensive branching and crosslinking would occur with equal moles of anhydride and polyol.

A knowledge of the functionality of the resin system also enables one to estimate whether the resin can be manufactured. The performance of many alkyd resins improves the nearer they are processed to the point of gelation. Thus it is necessary, particularly for air drying alkyds, to process as close to the point of gelation as possible without loosing the resin through the formation of a gel. The functionality of a system is a good indicator as to how far the resin can be processed without gelling.

The Carothers and Patton equations enable the measurement, for an alkyd resin, of the Patton gel value. During the condensation polymerisation, the acid value of the resin gradually reduces with a simultaneous elevation in the viscosity as a function of the following parameters:

1. functionality.
2. hydroxyl value.
3. final acid value of the resin.

It is possible to calculate the gel acid value of the reaction. The higher die selected functionality, the higher the gel acid value. If an alkyd resin with a final acid value of 5 to 10 has to be prepared, and the gel acid value is 0, there is a strong possibility that the product would be very difficult to make - gelation could occur during manufacture. On the other hand, if the same resin is prepared with slightly less functionality with, for example, a gel acid value of -15, there should be no production problems.

There are other constants which can be used such as the Patton constant or the hydroxyl excess, but those cited above remain the ones most used. Today, all of the cited parameters are calculated using computers and often using programmes developed by the formulators. Therefore, nowadays, all that is needed is to enter the different constituents of the resin as well as the quantities by weight in order to immediately have the desired parameters.

Another approach, which has been traditionally used for estimating functionality, is to utilise the functionality and molecular weights of the components to be reacted. As a generalisation, the closer this value is to 2, the greater the possibility of gelation at some extent of reaction. Resins with functionalities above 2 can be prepared without gelation.

The alkyd resin either has an acid or hydroxyl excess. In most cases (>99.9%) this is a hydroxyl excess. From a knowledge of the functionality and molecular weight of each reactant the total number of reactable equivalents can be calculated. For a hydroxyl excess this is 2 x COOH equivalents, because every OH group can only react with one COOH. The total number of moles of reactants present at the start of the reaction is also required. The average functionality ($F_{(average)}$) can then be calculated as follows:

($F_{(average)}$) = total number of reactable equivalents / total number of moles of reactants

Consider some examples.

Example 2-1.

nHO-R-OH + nHOOC-R'-COOH → HO-R-O-$\{CO-R'-C0-0R-O\}_{(2n-2)}$-CO-R'-COOH + nH_2O

Reactable equivalents = 2 COOH and 2 OH = 4n. Note that there is no hydroxyl or acid excess. This does not happen in practice for alkyd resins and this is only being used as an illustration.
Total number of moles present at start = 2n
($F_{(average)}$) = 4n/2n = 2
Note that this case is unique, in that although the functionality is 2, gelation should not occur because the system is linear. No reactant has a functionality greater than 2.

Example 2-2.

2 HO-R-OH + HOOC-R'-COOH → HO-R-OOC-R'-COO-R-OM

Reactable equivalents = 2 COOH and only 2 of the 4 OH groups = 4 Total number of moles present at start = 3
($F_{(average)}$) = 4n/3n = 1.33
Consider now a system with a trifunctional polyol which would more closely resemble an alkyd formulation. Here because at least one reactant present has a functionality greater than two, gelation is a real possibility unless the amounts of reactants are carefully controlled.

Example 2-3.

Consider stoichiometric amounts of trimethylolpropane and phthalic anhydride reacting.

2 TMP + 3 PA → polyester + water

Reactable equivalents = 2 x 3 OH (from TMP) + 3 x 2 COOH (from PA) = 12. In this example there is neither acid nor hydroxyl excess.
Total number of moles present at start = 2 + 3 = 5
($F_{(average)}$) = 12n / 5n = 2.4

At some point during the preparation of this alkyd gelation will occur.

There are two ways to avoid gelation. The first, which is unsatisfactory, is to stop the reaction short at an acid value higher than the predicted gelation acid value. The other, which is used in practice is to incorporate a proportion of monofunctional material. This is normally a fatty acid or benzoic acid or derivatives. In this role the acid is often referred to as a 'chain stopper'. In practice it limits the growth of the chains, thereby stopping. the build up of a network. Consider the previous reaction with benzoic acid (BA) present. For this example, there is no excess of hydroxyl to enable comparison with the above calculation.

Example 2-4.

2 TMP + 2 PA + 2 BA → Polyester + water

Reactable equivalents = 2 x 3 (TW) + 2 x 2 (PA) + 2 x 1 (BA) = 12. This is the same value of reactable equivalents as in the previous example.
Total number of moles present at start = 2 (TMP) + 2 (PA) + 2 (BA) = 6

$(F_{(average)}) = 12n/6n = 2.$

As can be seen the functionality of the system has been significantly reduced. There is still the possibility of gelation at low acid values. In practice a hydroxyl excess would be used. Consider the above reaction with excess TMP.

Example 2-5.

2.1 TMP + 2 PA + 2 BA → polyester + water

The number of reactable equivalents remains at 12, because there are only 6 COOH groups available for reaction.
The number of moles present at the start is increased to 6. 1.

$(F_{(average)}) = 12 / 6.1 = 1.97$

It should be possible to prepare this alkyd at low acid value without gelation, provided no losses occur. Some of the low molecular weight polyols are sufficiently volatile at reaction temperatures to be distilled along with the water of reaction. This tends to be a greater problem. with polyesters than alkyds, due to the nature of the polyols commonly used. Phthalic anhydride can also be lost. Obviously any change in the number of moles or reactable equivalents through losses or purity of the starting materials will affect the functionality. A difunctional material containing some trifunctional material has a functionality greater than two. In practice, this is not a problem. for alkyds used for surface coatings, unless low grade low cost raw materials are being used.

V MANUFACTURE OF ALKYD RESINS

Alkyd resins are prepared by the polycondensation of polyols and polyacids until predetermined values for viscosity, acid value or theoretical water loss are obtained. The reaction is carried out under an inert gas atmosphere in order to minimise oxygen exposure and therefore to avoid strong coloration of the final product.

1. Chemical processes.

(i) Monoglyceride process.

When an oil is used as feedstock, it is necessary to carry out the synthesis in two stages, since there is a compatibility problem. between the different raw materials particularly with the oil. These two stages are:

I. Alcoholysis of the oil by a part of the polyol used
2. Esterification by a polyacid and the remainder of the polyol.

The oil and part of the polyol are mixed and heated to between 240 – 270°C in the presence of a catalyst, generally alkaline, (NaOH, KOH, LiOH) or without catalyst if the reaction proceeds around 270°C. The quantities of catalyst used are around 0.01- 0.05 % with respect to the oil. The formation of a monoglyceride is shown idealistically in Figure 2-6.

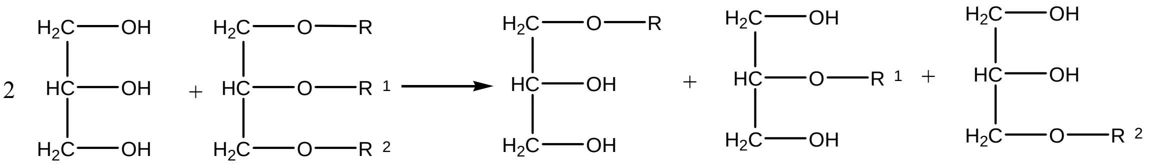


Figure 2-6: Formation of a monoglyceride

The monoglyceride obtained is in fact a mixture of monoester, diester, triester and glycerol. In general it does not contain more than 40% of monoglyceride, irrespective of the reaction conditions, but this proportion remains sufficient to homogenise the reaction medium and allow the process to proceed to the second step.

The following scheme in Figure 2-7 shows the change in monoglyceride composition if the polyol is pentaerythritol:

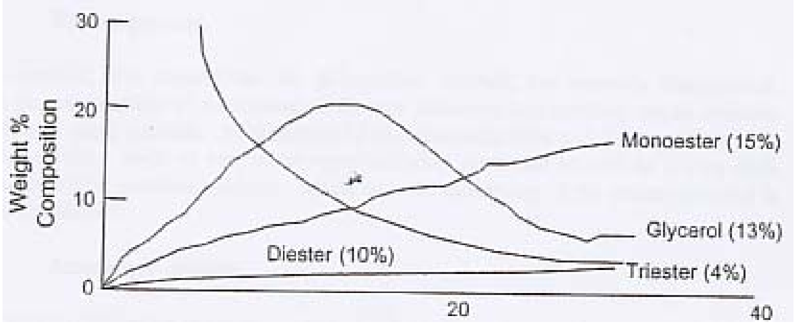


Figure 2-7: Change in monoglyceride composition with time at reaction temperature using pentaerythritol.

The transesterification reaction is monitored by a solubility test of the reaction medium in methanol or ethanol. The starting oil is insoluble in alcohol, but when sufficient transesterification has taken place to ensure full compatibility of all reactants for the polymerisation reaction, the polyol and oil mixture is soluble in alcohol.

This phase lasts in general 2 to 4 hours at the reaction temperature. The temperature is then lowered to 180°C and the remaining polyol and diacid, (such as phthalic anhydride, for example), are added. The reaction continues at a temperature of between 200°C and 240°C and it is monitored by the reduction in acid value and viscosity increase until the desired viscosity and acid value are obtained. Acid value is expressed in mg of KOH per gram of sample. The diglycerides generated during the first phase take part in the polymerisation by undergoing numerous transesterification reactions.

(ii) Fatty Acid Process.

This is only applicable when a fatty acid is a major component. This technique is the quickest since it requires no intermediate step. All the raw materials are compatible and are added from the start and are heated in an inert gas atmosphere at a reaction temperature between 190°C and 240°C. All the acid components therefore directly compete to react with the polyols. Since the primary hydroxyl groups of glycerol react faster with the phthalic anhydride carboxyl groups than with those of the fatty acid, the dominant structure of the alkyd obtained can be represented as shown in Figure 2-8:

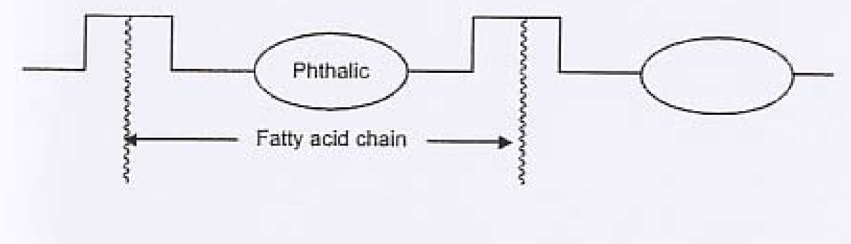
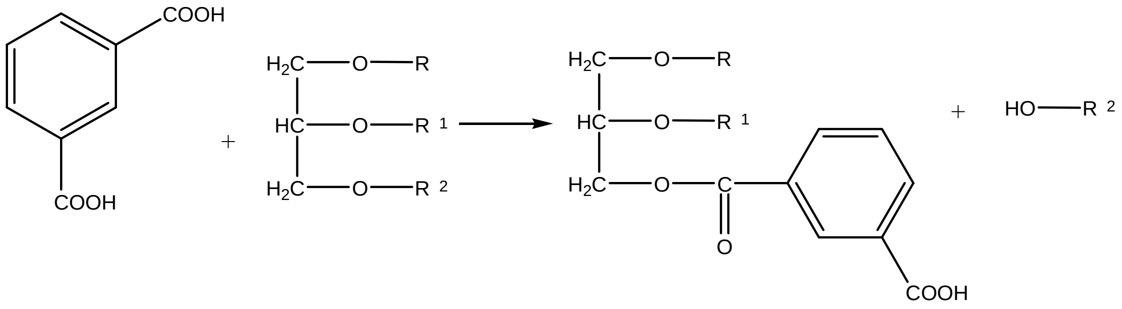


Figure 2-8: Idealised structure of the alkyd resin obtained

Here, the fatty acid is in the a Position whereas in the monoglyceride process it is in the a position. This process has certain advantages compared with the monoglyceride process. It enables better control of the reaction as well as greater freedom for the formulator. It can be started by reacting the polyol with the diacid to give the desired condensation level and then esterifying the polyol with the fatty acid, corresponding to the so-called "high polymer" process. Alkyd resins are thereby obtained with high viscosity, improved drying and hardness properties.

(iii) Acidolysis process.

This process is only used in cases where the diacid is insoluble in the reaction mixture or when it has a high melting point. This is the case for isophthalic and especially terephthalic acids. Acidolysis is schematically represented in Figure 2-9.



The intermediate reaction occurs at a temperature around 270°C – 290°C until perfect compatibility is attained. The reaction mixture obtained is then cooled and polyol is added. The polycondensation reaction is then carried out as for the previous processes.

2. Physical processing techniques.

Two methods are used for polycondensation reactions, whether it be the alcoholysis or acidolysis process.

(i) Fusion process.

This method, also termed the 'all in together' method, bas virtually disappeared. This process consists of combining all the raw materials and carrying out an aqueous extraction using vacuum. Sublimation of phthalic anhydride and the loss of polyols (NPG, glycols) leads to very poor reproducibility problems as well as a very high viscosity of the reaction medium. Moreover, the darkening of the resins obtained is quite significant.

(ii) Azeotropic process.

The polycondensation reaction is carried out in the presence of a solvent which is miscible with the reaction bulk and immiscible with water when cooled. The boiling point of this solvent, (xylene, white spirit) is lower than the polycondensation temperature. Water given off by the reaction is carried over as an azeotrope with the solvent. This then condenses into a separation funnel (receiver) known as a Dean and Stark receiver where the two separate. Water is drawn off (and measured) and solvent is returned to the reaction vessel.

Phthalic losses are reduced, compared to the fusion process, because the whole reaction vessel is enveloped by the solvent vapours which wash the reaction vessel walls and recycle the products which have sublimed and crystallised. This process is readily carried out and enables the preparation of highly specialised products as well as clear resins.

However, when it is desirable to prepare a resin which is not diluted by the solvent used for the azeotropic circulation, this solvent, present at an amount of 3 to 8% in the resin bulk, has to be distilled under vacuum. Moreover, for top of the range alkyd resins, vacuum stripping is necessary lo eliminate decomposition products which could reappear during the drying of the alkyd resin and cause problems.

In plants where alkyd resins are produced, the reactors are made of stainless steel and have a capacity ranging from 2,000 to 40,000 litres. Their effective capacity depends on the non-volatile component of the resin to be produced. They are equipped with a vertical (packed) column, a horizontal condenser and separation vessels which collect both the water and solvent. Heat is provided either by electricity or thermal fluids, the latter circulating via a double envelope. Cooling is provided by water which circulates alternately in the double envelope or in a cooling coil at the core of the reactor, and hence at the core of the resin. Alternatively cooling is sometimes achieved by cooling the heating fluid externally to the reactor. Dilution and mixing tanks ere connected to the reactor in order to carry out the final dilution. and adjustments to the product. The product is then filtered. A schematic of an alkyd reactor is shown in Figure 2-10.

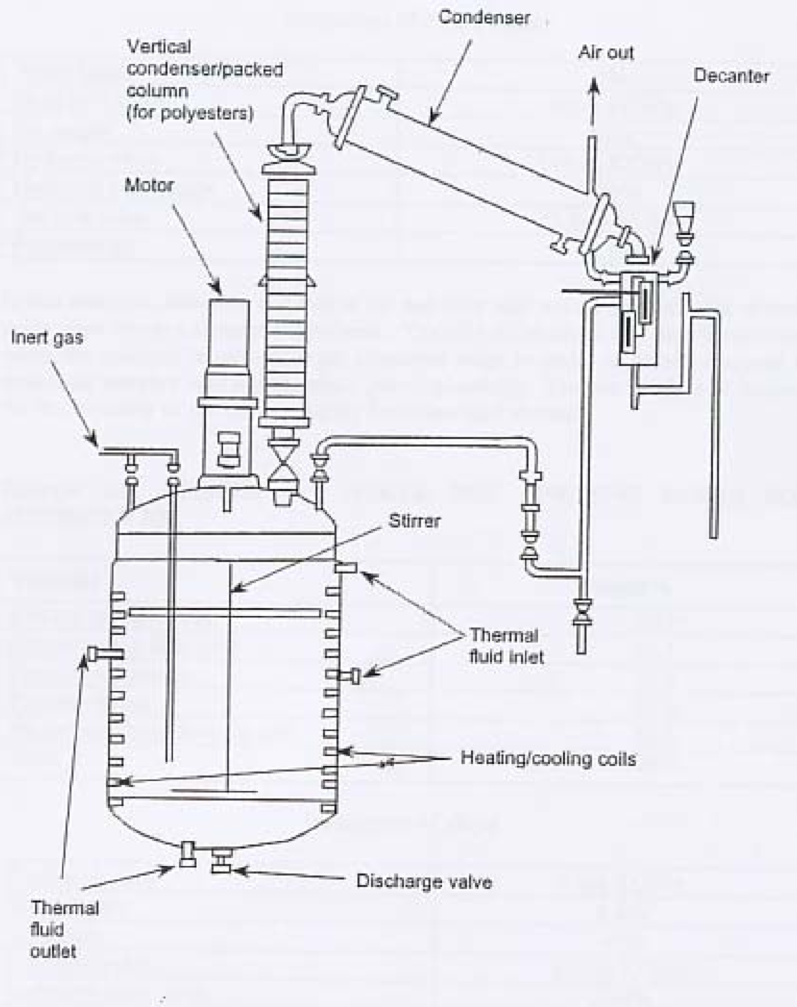


Figure 2-10: Schematic of an industrial reactor for alkyd manufacture

VI TYPICAL ALKYD FORMULATIONS AND SUGGESTED END USES

1. Examples of alkyd formulations.

Some examples of alkyd resin formulations with their different calculated parameters follow:

Example 2-6: LONG OIL ALKYD FOR DIY GLOSS PAINT.

Material	**Weight** %
Soya bean oil	62.0
Phthalic anhydride	24.2
Pentaerythritol	13.0
Maleic anhydride	0.8
Total	100.0

Parameters of Alkyd

Final acid value	8 mg_KOH/g
Water losses	2.7%
Oil length	64%
Hydroxyl value	45mg KOH/g
Hydroxyl percentage	1.4%
Gel acid value	-4mg KOH/g
Functionality	2.10

By increasing the maleic anhydride content, the apparent viscosity of the resin will increase. For improved drying speed the oil length can be increased. Replacing the soy bean oil by sunflower or tall oil will improve the yellowing resistance.

Example 2-7: MEDIUM OIL ALKYD FOR MATT HOUSE PAINTS.

Material	**Weight** %
Soya bean oil	25.3
Tall fatty acid with 25% resins	23.1
Phthalic anhydride	28.6
Glycerol	21.0
Maleic anhydride	2.0
Total	100.0

Parameters of Alkyd Resin.

Water losses	5%
Final acid value	10mg KOH/g
Oil length	46%
Hydroxyl value	114mg KOH/g
Hydroxyl percentage	3.46%
Gel acid value	-25.5mg KOH/g
Functionality	2.14

In this example, there is a mixture of oil and fatty acid with a large amount of rosin acids since this is a sequential synthesis. The oil will be added at a high temperature when the reaction is already at an advanced stage in order to obtain a spread of molecular weights which gives some pseudo-plasticity. The use of glycerol reduces the functionality of the already highly functionalised system.

Example 2-8: **MEDIUM OIL ALKYD FOR FINISHING PAINTS FOR CARS.**

Material	Weight %
2 % tall oil fatty acid	28.2
Conjuvandocl fatty acid	14.5
Phthalic anhydride	25.0
Pentaerythritol	22.0
P-ter-butyl-benzoic acid	10.
Total	100.

Parameters of alkyd

Final acid value	8 mg KOH/g
Water losses	6.6%
Oil length	47%
Hydroxyl value	67 mg KOH/g
Hydroxyl percentage	2.04%
Gel acid value	4 mg KOH/g
Functionality	2.21

This resin is highly condensed and controlled due to the use of a chain stopping agent such as p-ter-butyl-benzoic acid PTBB, which also allows the resin to be diluted in white spirit. Molecular weights will be rather high.

Material	Weight %
Sunflower fatty acid	32.6
Phthalic anhydride	35.7
Benzoic acid	8.2
Trimethylolpropane	14.2
Pentaerythritol	9.3
Total	100.0

Parameter of Alkyd resins

Final acid value	15 mg KOH/g
Water losses	66g
Oil length	32 %
Hydroxyl value	88 mg KOH/g
Hydroxyl percentage	2.67%
Gel acid value	-1 mg KOH/g
Functionality	2.20

In this case, the resin has to be diluted in aromatic type solvents (xylene) and/or glycol ethers. The molecular weights are medium. for an alkyd and the functionality is high despite the rather low gel Acid value. The viscosity will be low and the non-volatile content during application will, therefore, be higher. This resin is cross-linked with a melamine formaldehyde resin at temperatures between 80 and 100'C. This formulation is for a low cure temperature paint. Normally higher stoving temperatures are used. The compatibility of this type of resin with the other resins, such as medium oil alkyds and various melamine resins, is very good.

Example 2-10: SHORT OIL AIKYD FOR ANTICORROSION PRIMERS.

Material	Weight %
Linseed oil	22.7
China wood oil (Tung oil)	13.1
Glycerine	16.7
Rosin	19.56
Phthalic anhydride	27.94
Total	100.0

Parameters of Alkyd Resin

Final acid value	22 mg KOH/g
Water losses	3.9%
Oil length	37%
Hydroxyl value	80 mg KOH/g
Hydroxyl percentage	2.47%
Gel acid value	20 mg KOH/g
Functionality	2.058

This oil mixture gives a resin which is well suited for use in anticorrosion primers. It dries extremely rapidly, obviously a most important requirement for primers. These resins are rather brittle and very hard. Primers formulated with these types of resins are intended to be coated very quickly with a topcoat.

Example 2-11: EPOXY ESTER.

Material	Weight %
Soya bean fatty acid	40.0
Epikote 1004 resin	60.0
Total	100.0

Parameters of epoxy ester

Final acid value	5
Water losses	1.2%
Oil length	42%
Hydroxyl value	42 mg KOH/g
Hydroxyl percentage	1.26%
Gel acid value	- 12 mg KOH/g
Functionality	1.98

Epikote 1004 is a product of bisphenol A and epichlorhydrin. It is diepoxy functional and has secondary OH groups along the resin backbone which will also condense with the soy fatty acid. This resin can be used for the preparation of one coat gloss paints applied to metals for applications such as lorry cabins and farm appliances. The anticorrosion resistance obtained will reach 300 hours salt spray (ASTM B 117) for gloss formulations and it will have a gloss around 80% at 20°. A linear diacid can be added in order to improve the mechanical characteristics as well as the durability.

Epoxy esters are considered in detail in epoxy book "Solvent based and Waterborne Resins for Surface Coatings and their End Use Applications - Vol. 2: Epoxy", SITA Technology, 1999.

2. Modified Alkyd Resins.

An alkyd resin can be chemically modified with the objective of improving specific properties such as drying, application, exterior resistance or corrosion resistance. In paint terms, this modification can be envisaged in two ways:

1. Mixing with another type of resin. However, in this case, compatibility problems are rapidly encountered between resins, and the blended resins often show the weaknesses of both resins rather dm any combined strengths.
2. By chemical modification, which today is the most widespread case.

(i) Reactions of the Double Bonds of the Alkyd.

This involves modification of the alkyd resins by acrylic, or vinylic compounds or by styrene. The copolymerisation of one of these compounds is carried out with the double bonds present in the fatty chain of the alkyd. The process involves first preparing an alkyd resin to which the relevant monomer and peroxide initiator are added in order to carry out the free radical addition polymerisation. The following compounds are often used for this type of process:

- ***Styrene, Vinyl toluene, methylmethacrylate, or (even) cyclopentadiene***.

The principal advantages and disadvantages these modifications contribute to the resin are as follows:

Advantages:

1. Rapid surface drying due to the introduction of some thermoplastic characteristics.
2. Improved resistance to water and bases.
3. Less prone to yellowing.

Disadvantages:

1. Poor hardening because of reduced amount of unsaturation for oxidative drying.
2. Scratch-sensitive, (same reason).
3. Appreciably lower compatibility in aliphatic solvents.

Styrene has a tendency to undergo homopolymerisation rather than copolymerisation with the alkyd, due to the relative reactivity of the double bond in styrene compared to that of the fatty acid chain. Therefore the alkyd resin must contain the highest possible quantity of double bonds in order to favour copolymerisation.

The resultant alkyd is in fact composed of a mixture of polystyrene, non-modified and styrene-grafted alkyd.

In a styrenated alkyd, the styrene content varies between 15 and 40 %. A small amount of á-methylstyrene can be added which reduces the tendency of styrene to undergo homopolymerisation.

Vinyl toluene (VT) is less prone to homopolymerisation. However its copolymerisation is a lot slower. As a result, the final alkyd resin has shorter chains and this fact means that VT alkyds can have reasonable compatibility with aliphatic solvents. The amount of VT varies between 10 and 35% and it improves the drying and hardness as well as the water resistance of the basic alkyd resin.

Methylmethacrylate (MMA) is also prone to homopolymerisation. Copolymerisation with the alkyd can only occur in the presence of a solvent. MMA improves the exterior resistance, water and chemical resistance as well as the drying, of the initial alkyd.

In all cases, the synthesis is carried out by feeding the monomer(s) into the alkyd resin at a temperature between 130° - 160°C in the presence of initiators and sometimes chain transfer agents. Solvent is added to the reaction medium prior to the monomer addition, for better control of the reaction.

(ii) Reactions of the functional groups.

(a) Epoxy Modification.

Epoxy resins are used and considered as polyols which will react with the carboxylic functions of the alkyd resin. This type of modification (for example, with EPIKOTE 1004) improves adhesion to light metals such as copper and aluminium, resistance to bases, and above all resistance to corrosion. Paints based on epoxy modified alkyds show a strong tendency towards chalking and a resulting loss of gloss, (see later), which makes it difficult to use them as top coats except in the case of one coat finishes. Epoxy modified alkyd resins are less expensive than epoxy resins and are used in low cost anticorrosion primers. A fatty acid alone can also be used which will react with the epoxy resin to give what is termed an epoxy ester (safflower, Soya bean oil fatty acid).

(b) Silicone Modification.

The polysiloxanes which are used are phenyl-methyl derivatives of low molecular weight containing reactive hydroxyl groups. The resins obtained are characterised by their strong heat resistance and above all by their extraordinary resistance to weathering. They also have an excellent level of resistance towards hydrolysis.
Silicone modified alkyds find limited use as alterative to two pack polyurethanes in commercial vehicle and yacht refinishing. The superb resistance to weathering is not matched with toughness and therefore the comparison with PU finishes is flawed, particularly as they can cost more than the two pack PU. Moreover, solvent resistance is rather disappointing for this type of product.

(c) Isocyanate Modification.

Addition reactions to Bis-Hydroxyl groups of the alkyd resin can be carried out using a diisocyanate (generally toluene diisocyanate TDI or isophorone diisocyanate, IPDI). This reaction leads principally to the formation of urethane linkages. The resultant resins are referred to as urethane alkyds, and the paints produced as polyurethanes, although this is somewhat inaccurate and confusing! The goal of this modification is to improve the hardness of the film and the compatibility and the solubility parameters of the base alkyd resin. Chemical resistance is one of the qualities brought about by this modification as well as a significant improvement: in scratch resistance.

These products are often used as the base resins for parquet varnishes. The resins obtained display particular characteristics, in that they have a certain pseudo-plasticity or thixotropy. It should be noted that, due to their weak acidity, these can be used with basic pigments or metallic powders.

Highly modified isocyanate resins are used for the preparation of interior matt and satin-finish varnishes, floor paints, and industrial coatings with increased chemical resistance (note the intercoat adhesion in these applications). Their better resistance to saponification on alkaline substrates such as fresh concrete than traditional alkyds which do not have such a resistance should also be noted. For this reason, they are used in paints for primers on concrete. The use of LPDI (aliphatic non-yellowing type) allows one to contemplate exterior applications such as varnishes for boats.

(iii) Use of Polyamides and Urethanes as Rheology Modifiers in Alkyds.

When applying paints to vertical surfaces or to ceilings, problems of applicability as well as drip and sag resistance are encountered. This type of modification is aimed at improving the rheology of the alkyd resin and, hence, of the paint, by giving it a thixotropic structure.
The principle involves the high temperature reaction of a polyamide resin with an alkyd resin of a well-defined structure. Depending on the intended end use of the resin, (gloss paint for example), the alkyd is prepared as if it were to be used as such.
The reactions with the polyamides are rather complex and can be envisaged as follows:

$$\text{RCOOH} + \text{R'CONHR''} \longrightarrow \text{R'COOH} + \text{RCONHR''}$$

$$\text{ROH} + \text{R'CONHR''} \longrightarrow \text{R'COOR} + \text{R''NH}_2$$

$$\text{R''NH2} + \text{RCOOH} \longrightarrow \text{RCONHR''} + \text{H}_2\text{0}$$

The thixotropy of the resin is obtained by the formation of hydrogen bonds resulting from the proximity of the NH and CO bonds
Thixotropic alkyd resins allow the preparation of paints which have:

1. Low drip tendency at a shear rate of 10000 s^{-1}, which is that applied to paint during application with a brush.
2. Low settlement during storage.
3. Very good levelling and excellent application characteristics.

These resins take the physical form of a more or less firm gel. Very firm gels have applications in matt or satin-finish paints or are used in applications where extremely rapid gel formation is required.

Alkyd gloss finishes use thixotropic resins with low gel structure to maximise the gloss level of the finish.

Unfortunately, these thixotropic alkyd resins have a strong tendency towards yellowing and their synthesis is sometimes delicate. The polyamide resins used are generally derived from dimerised or trimerised tall oil fatty acids with molecular weights in the range 2000 to 6000. They are not compatible with basic alkyd resins. As the reaction progresses, compatibility is achieved and the cloudy starting mixture becomes clear. In industry the reaction is monitored by a nephelometer which measures this cloudiness. The end point of the reaction will influence the strength of the gel or the thixotropy of the resin (as well as the type of polyamide resin used). At the start of the reaction the gel strength will increase only to rapidly decline.

During the manufacturing process, a 20 to 30 minute deviation is sufficient for an industrial batch to fail. Each end point of the reaction is a function of:

1. The polyamide resin used (M_w, reactivity).
2. The anticipated final gel strength.
3. The end use of the resin.

Instead of polyamide resins, urethanes can be used which will also lead to thixotropic resins, which in comparison with those modified with polyamides, bring about the following improvements:

Better heat resistance - the thixotropy induced by the amide-carboxyl-hydroxyl hydrogen bonding is destroyed by heat and this precludes the use of polyamide modified alkyd in industrial stoving systems.

1. Improved thixotropy conservation even in the presence of highly polar solvents (such as in wood stains)

Thixotropy adjustment by the addition of solvents such as glycols or equivalent solvents (swelling occurs which can be altered to the desired effect).

These somewhat specialised urethane alkyds remain a lot more expensive than their polyamide homologues and are not used as extensively. Moreover, their industrial use is rather delicate and the reproducibility in altering the paint's thixotropy is difficult.

This technology has been extensively developed by the Cray Valley company under the trade name "Supergelkyd"

Generally, thixotropic alkyd resins are used in blends with traditional alkyd resins in order to give the desired structure. This is, therefore, a thixotroping alkyd resin. Cost and degree of thixotropy can very effectively be optimised by the paint formulator, and very few DIY interior gloss paints are formulated without the use of some polyamides modified alkyd.

(iv) Crosslinking reactions via hydroxyl and carboxyl groups.

The alkyd hydroxyl and carboxyl groups can be used for reaction with urea-formaldehyde or melamine-formaldehyde resins at temperatures ranging from 80°C to 150°C. The reactions are catalysed by acids such as p-toluene-sulphonic: acid, or indeed by the carboxyl groups on the alkyd itself. Industrial stoving finish paints can be prepared, or in some countries low temperature automotive OEM body work finishes (80°C to 120°C) are prepared, (for economic reasons).

Crosslinking of alkyd resins can sometimes be carried out with hardeners such as polyisocyanates. Therefore, two pack polyurethanes are formulated which combine some of the attributes of alkyds and top of the range polyester or acrylic and isocyanate paints. The case of application of the alkyd is retained and some difficult applications benefit from this, such as large yacht finishing and commercial vehicle finishing. However, the exterior weathering of the true two pack PU finishes is lost and although costs are lower than PU finishes, its end uses are limited. For this application, a hydroxide number of at least 60 is a minimum requirement.

3. Current industry suppliers and trade references.

In the field. of alkyd resins, and in particular solvents, numerous various manufacturers of resins can be found. They are sometimes totally different in size. They may have national or international capabilities depending on their layout and the range of their product portfolio. Table 2-8 lists the principal manufacturers as well as the trade names of their products.

TABLE 2-8 PRINCIPAL SUPPLIERS OF ALKYD RESINS

CRAY VALLEY	Synolac, GeIkyd, Supergelkyd, Unithane, Synagua
DSM	Uraiac, Urathíx, Uradil, Uramax
VIANOVA	Vialkvd, Daotans, Resydrols
WORLEE	Worleekyd, Woricethix, Worleesol
BAYER	Alkydal
CRODA	Crodakyd
BEP	Beetle
SYNTHOPOL	Synthalat, Lioptal
LIXOL	Lìxoglyp, Lixothan id
AKZO	Setal
BLAGDEN	Valithanc,Valircs, Valithix
NOVANCE	Chemporob, Coporob
GALSTAFF	Sintal
NESTE	Rhenalyd
KRAEMER	Rokaplast
PLUESSTAUFER	Plusol, Plusagua
ALBUS	Albukyd
REICHHOLD CBENIICALS	Acropiaz, Beckosol, BeckoLel, Balkyd
DYNO INDUSTRIE	Dynotal
ALBERTUS	Ha1weftal, Halweplast
RESISA SYNTETICA	Reactal
BERGUE	Bergalkyd
JAGGER(EASTMANN)	Jágalyd
SICAP	Sicalyd
SOAB	Soakd
McVMORTER	Durarnac:
BASF	Laropal

WATER-DELUTABLE RESINS

1. Introduction.

The introduction of legislation pertaining to air pollution was implemented in Los Angeles in 1966. The so-called 'Rule 66' was the starting point for environmental, control for the paint industry. Since then industry has been subjected to pressure, mostly relating to air pollution by organic solvents used in paint, by different official (governments, European Commission, American states) and unofficial (ecological associations and movements) groups. Apart from. solvents, various other prime components of paint formulations have been, or will soon be, subjected to legislation. These include hexavalent chrome, tri-butyl tin in antifouling paints, cadmium pigments, lead pigments, driers and many more will follow. In California, even carbon black must be labelled as a carcinogen!

Today, the notion of pollution applies to all of the elements, air, water and earth. Moreover, these aspects complement already existing issues, namely health and safety of raw materials during paint and resin manufacture and paint application.

The paint sector is targeted because of its use and, hence, disposal of pollutants, mainly organic solvents. Methods have been around for some time to limit these releases to a minimum but only a few of the larger industry sectors are involved and this does not solve the whole problem.

The automobile industry has highly developed electrostatic painting which limits consumption of paint and hence the release of solvents and volatiles during flash off and stoving, as well as the installation of incineration systems which connect solvent effluents for burning. The waste solvent is actually used partially to fuel the incinerator and heat the factory. This technique is also used in the coil and can coating sector.

In order to regulate these solvent emissions, it is common to refer to the VOC of a paint, which corresponds to the volatile organic compound content. (Sometimes referred to as the volatile organic content for simplicity) Unfortunately, the definition and especially the calculation of VOC are not always made in the same way, depending on the country or continent. Indeed there are significant differences between the way VOC's are calculated in North America and the UK. Sometimes, some compounds additives for example, are left out of the calculation and there are two distinct methods of calculation - with and without water content! This situation is resolving itself and firm guidelines are being drawn up with the participation of the paint industry.

Some countries or legislating bodies are well advanced in their plans to reduce organic solvent pollution. The-European Commission and the US EPA have issued solvent reduction legislation - different in each continent of course! – detailing permitted solvent contents in various paint types and applications against time scales. In most cases the paint industry has been consulted during the legislative process. Some of the regulations are already implemented in countries which have a pioneering role in environmental issues - Holland and Germany for example.

The paint industry has been researching methodologies to reduce solvent contents of coatings whilst at the same time endeavouring to maintain film performance and application characteristics. The emergence of water-dilutable, high solids, powder and radiation cured paint systems are potential solutions to environmental problems. Today, when a paint plant is installed or modernised, it is done in favour of a more ecologically sound technology.

Some countries have witnessed a significant development in ecological paints as a function of national decisions concerning the environment (or collective realisation) and large shifts in major industrial sectors. For example:

Scandinavia: Use of alkyd emulsions for decorative paints and wood stains.

Germany: Widespread use of water based alkyd emulsion undercoats for cars.

In the industrial sector, Switzerland and Holland have many years' experience in the use of water-based alkyd resins. Table *2-9* gives an illustration of the penetration of the different paint technologies.

TABLE 2-9: PENETRATION OF THE DIFFERENT PAINT TECHNOLOGIES IN WESTERN EUROPE AND USA AND JAPAN FOR 1994.

Coating type	**W Europe**	USA	**Japan**
Solvent borne	57.4%	55.3%	83.3%
Waterborne	11.6%	11.4%	11%
High solids	14.8%	26.9%	1.4%
Powder	12.3%	5.2%	3.6%
Radiation Cure	3.9%	1.2%	0.7%
Total	100%	100%	100%

From all the range of paint resin chemistries, the categories which are able to sometimes claim two-digit development perspectives are rare. Alkyd resins, powders and UV crosslinking products are three such examples.

In Table 2-10, different types of reduced (compared to traditional solvent based) VOC paints are compared, whilst Table 2-11 gives typical VOC's for these different types of competing technologies.

TABLE 2-10: APPLICATION POTENTIAL OF DIFFERENT SYSTEMS WITH LOW LEVELS OF VOC AND THEIR RESULTS

Application type	**Dispersion PU**	**High Solid Alkyd**	**Alkyd Emulsion**	**2K HS Alkyd**	**2K HS Epoxy**	**2K WB PU**	**2K WB Epoxy**	**Powder**
Wall paints	X	X	X					
House wood decoration	X	X	X					
Industrial maintenance	X	X	X					
Heavy duty				X	X	X	X	
Vehicle refinish				X		X		
Automotive OEM				X		X		X
Industrial equipment				X				X

TABLE 2-11: VOC OF THE COMPETING TECHNOLOGIES

Paint types	**% Solids**	**Solvent content**	**VOC Reduction**	**Solvent used for application Reduction ***
Powders	100	NONE	100%	40%
Radiation Cure	100	NONE	100%	40%
High Solids	80	20%	83%	33%
Water-Dilutable	50	10%	90-5%	20%
Solvent-based	0-60	40-70%	NONE	

* compared to solvent based

2. Review of Different Waterborne Alkyd Technologies.

The terminology in the field of water-based resins sometimes leads to confusion and this is certainly the case when discussing alkyd resins in water. The term water-dilutable comes from the fact that a part of the liquid portion of the resin is water, but not necessarily the entirety. A water-soluble organic solvent is more often than not present.

Today, three following classes of polymer in water exist:

1. Aqueous dispersions where the resin is a dispersion of solid particles which are essentially in an aqueous phase. The size of the particles is in the 50 to 500 nm range. In most cases, the resin is produced by an emulsion polymerisation, which generates the so-called latex polymers. The polycondensation mechanism enables the production of dispersions such as polyurethane dispersions.

2. Aqueous emulsions represent a small fraction of the total water-soluble resin market. They correspond to a resin which is a liquid polymer in emulsion in water. Alkyd and epoxy emulsions in water are examples of this class.

3. Water-soluble resins represent a large group of products, formed from resins in colloidal dispersion in water. In all of the cases, water-soluble resins are transparent because of the small size of the particles of the resin. They are made up of a polymer solution which contains hydrophilic segments which are soluble in water and also compatible with organic solvents. They can be almost infinitely diluted with water. The hydrophobic parts of the polymer tend to form colloidal particles which are stabilised only by the hydrophilic parts.

The first water soluble resins date back to 1960 and involved preparing a resin with a high acid value which, after neutralisation with an amine, forms a colloidal solution in water and glycol ethers. Many disadvantages are associated with this technology, notably:

1 Abnormal fall in viscosity in water, a non-linear dilution/viscosity curve which is usually at its steepest at the point of application viscosity of the paint formulation!
2 Instability in water (hydrolysis because of pH).
3 Poor drying.
4 Yellowing due to amines present.

(i) Alkyd Emulsions.

The past few years have witnessed major developments in alkyd emulsions. Today, two types of alkyd resin emulsions exist.

- Internally emulsified or self-emulsifying alkyd emulsions
- Externally emulsified alkyd emulsions

(a) Internally Emulsified Alkyd Emulsions.

In order to produce an alkyd emulsion, it is necessary to add polar groups to the resin (self-emulsifying) or to use a surface tension agent (surfactant) which leads to external emulsifiers.

Polar groups can be introduced into the alkyd resin either by using ionic or steric groups. lie emulsion will, therefore, be stabilised ionically or sterically. Hydrophilic: groups are also useful for the wetting of pigments and the possible emulsification of components of the paint. One tries all the same to use the minimum amount possible of these in order not to reduce the water resistance of the final film.

Only carboxylic groups are suitable as ionic groups. They are then neutralised with ammonia or suitable amines. Phosphoric or sulphuric groups have poor compatibility with metal salt driers, therefore they significantly affect drying. They are only used in the case of baked systems. It is also theoretically possible to use cationic groups such as ammoniums but the pH resulting from their neutralisation is in the acidic range.

The first high acid value alkyd resins posed the problem of poor resistance to saponification in water. In particular, the semi ester bond in phthalic anhydride has such a problem. This phenomenon is well known under the name “anichimeric effect”.

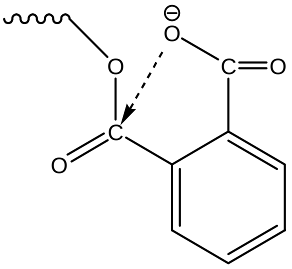


Figure 2-13: **Anichimeric effect**

The best protection against this effect is to protect the ester bond from hydrolysis by substituting the phthalic anhydride by isophthalic acid. The preparation principle of a self-emulsifying alkyd, which also takes into account the prevention of hydrolysis, includes three production steps which are:

1. The first step involves preparing a low molecular weight alkyd resin with high hydroxyl value and an acid value lower than 5 mg KOH/g.
2. The second step involves preparing a copolymer by radical copolymerisation between a fatty acid for oxidative drying and acrylic acid or one of its ester derivatives.

Step 3 involves partial esterification of the two components of the two previous phases. Since the reactivity of the primary and tertiary carboxylic groups is totally different, partial esterification enables the elimination of all the p~ groups by esterification. In this way, there is a hydrophobic: alkyl chain between the ester linkage and carboxylic group.
The product obtained ideally corresponds in theory to a core-shell whose structure is shown in Figure 2-23.

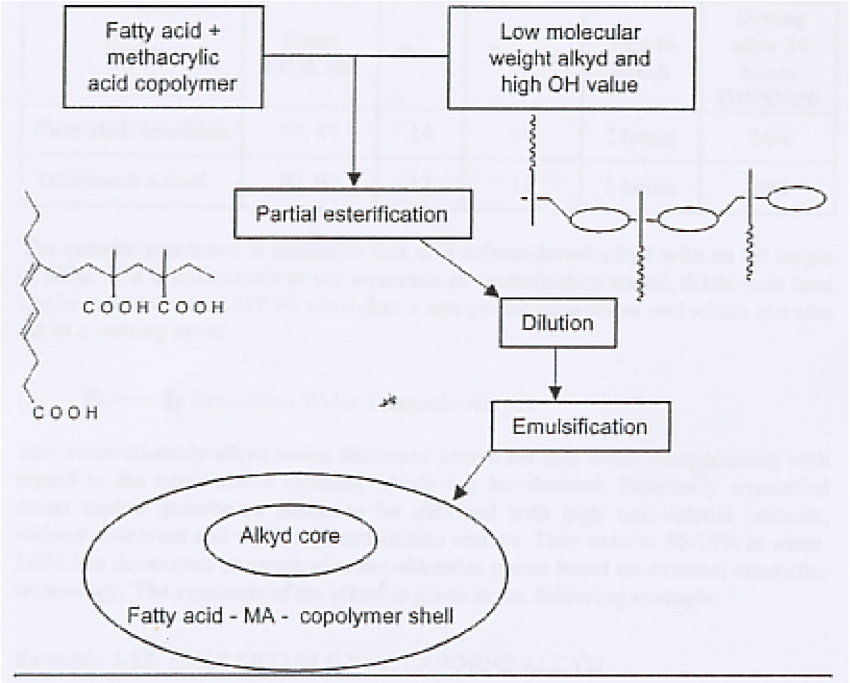


Figure 2-14: Self-emulsifying alkyd core-shell structure: Resydrol (Vianova)

In the model, shown in Figure 2-23, the alkyd resin forms the core of this structure and the surface consists of the copolymer and segments of incorporated polyethylene glycols. The alkyd core has a large influence on the final properties of
the paint film, such as chemical resistance or crosslinking, whereas the surface is responsible for the interactions with drying agents, pigment and the substrate wetting properties as well as the rheology. This type of self-emulsifying alkyd has a pseudo-plastic behaviour, that is its viscosity increases when the shear rate decreases. However, it should be noted that viscosity also strongly depends on the pH.

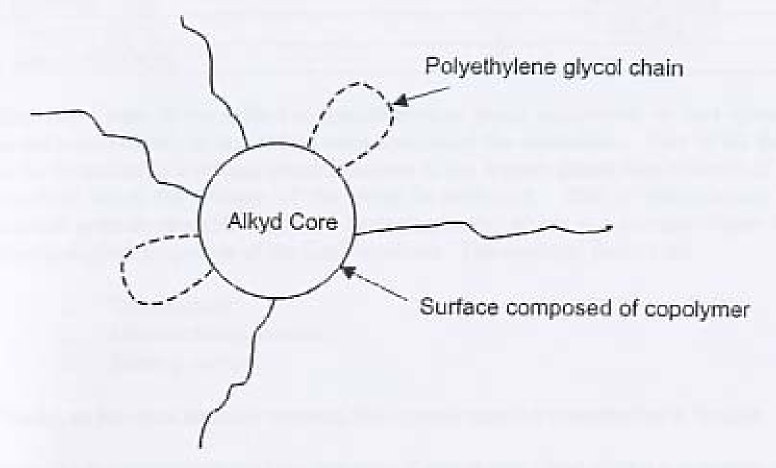


Figure 2-15: Model of alkyd core-shell

An increase in pH leads to an increase in the number of carboxylate ions and the large particles initially present divide into much smaller particles which increase the surface area. When an amine is added as neutralising agent, the resin becomes clearer with an increase in pH. The viscosity of the paint should in all cases be measured at a shear gradient rate which corresponds to the rate observed during paint application, that is around 10000 s-'.

In the structure of this self-emulsifying water-dilutable alkyd, styrene and other acrylic monomers can be used for an improvement in the physical drying of the system, whilst enabling an improvement in resistance to yellowing (in the dark). With this resin system, it is possible to prepare a water-based alkyd resin modified by Polyamide resins or by polyurethanes, which enables the formulation of water-dilutable thixotropic alkyd resins (amides or urethanes).

There is a complete range of resins based upon using this technology, with oil le,19ths ranging from 20% to 60% and all types of chemical modifications, urethane, epoxy or acrylic of the base resin are available in order to offer the formulator all the features of solvent based alkyd resins but in water.

These types of water-dilutable resins have excellent pigment wetting qualities and are stable to grinding. it is, therefore, easy to achieve a full gloss white paint.

The most important point during paint preparation is the monitoring of the pH. lf it drops too much, then there are problems with wetting and stability. A top coat with *50%* non volatile content will include between 0 and 6 % organic co-solvents. The use of fluorinated additives to reduce surface tension will sometimes be necessary in order to improve adhesion to non-prepared substrates. Table 2-12 gives a comparison of the results obtained with these types of alkyd emulsions.

TABLE 2-12: COMPARISON OF CORE-SHELL AND TRADITIONAL SOLVENT-BASED ALKYD PAINTS

Resin	Gloss 20° & 60°	Haze	Tension	Dry to touch	Dry after 24h DIN 53150
Core-shell emulsion	70,85	14	14	2 h	24/6
Traditional alkyd	80,90	12	12	5 h	30/3

The exterior resistance is similar to that of a solvent-based alkyd with an oil length of 60%. lf it is undesirable to use ammonia as neutralisation amine, dilute can be used or even AW *90* which has a less pronounced odour and which can also act as a wetting agent.

(b) Externally Emulsified Water-Dilutable Alkyds.

The water-dilutable alkyd resins discussed above are still rather disappointing with regard to the non-volatile contents which can be obtained. Externally emulsified resins enable waterborne resins to be obtained with high non-volatile contents,
without co-solvent and without neutralisation amines. They exist at 50-55% in water. DSM has developed its range of water-dilutable paints based on external emulsifier technology. The synthesis of the alkyd is given in the following example.

Example 2-12: EMULSIFIABLE WATERBORNE ALKYD.

Materials	Weight %	Molar %
Tall oil acid	65	50
Pentaerythritol	18	28
Isophthalic acid	17	22
Total	100	100

Properties of Alkyd

Non volatile component	> 99.5
Acid value	8 mg KOH/g
Hydroxyl value	50 mg KOH/g
Viscosity 23 °C	650 dPa s
Ratio OH/COOH	1/2

This alkyd resin is emulsified in special reverse phase equipment; so that water is added progressively to the molten resin containing; the emulsifiers. First of all, there is the formation of a reverse water emulsion in the organic phase then reversal of the emulsion when the volume of the water is sufficient. This is characterised by reduced particle size (500 nm) and homodispersity, which is a stability factor and the rheological properties of the final. emulsion.

The essential factors are:

1. Temperature.
2. Manufacturing control.
3. Stirring method.

Finally, as for most aqueous systems, this system must be protected by a biocide.

The paint formulations made from this type of waterborne alkyd exhibit penetration into porous substrates, almost equivalent to that obtained with solvent-based alkyds, and is due to:

1. The natural hydrophilicity of substrates.
2. The very low glass transition temperature of the binder (60'C).
3. The reduced size of the particles.
4. The high hydroxyl value of the resin.

Some studies have been made on the penetration of different alkyd resins on wood, using results by fluorescent microscopy, expressed as the average number of wood ceils penetrated. These are summarised in Table 2-13.

TABLE 2-13: PENETRATION OF DIFFERENT WOODCELLS
PENETRATED FOR DIFFERENT WATERBORNE SYSTEMS

Styrene-acrylic dispersion	3
Solvent-based alkyd	40
Emulsion alkyd	10
Externally emulsified alkyd	30

Whilst The results indicate a large improvement over the acrylic emulsion for the externally emulsified alkyd, they do not yet quite match the solvent borne system.

This substrate penetration feature is a very significant step forward in waterborne paint systems. The earlier waterborne systems, typically based on acrylic emulsions, had a tendency to sit on top of porous substrates such as wood, and were easily removed when the painted substrate was exposed to weathering. The weathering resistance of the above resin based systems on wood is much improved.

The development of this technology involved initially improving the general features of the resin, that is, drying, hardening, non-yellowing etc. The following stages consist of developing a whole range derived from this technology, such as resins based on urethane, acrylic, epoxy alkyds, and, of course, the need to avoid the use of alkyl-phenoxyethoxylates which are toxic towards fish -another regulation imposed for overseas transportation of paints.

A further improvement in this technology is to use an emulsifier which will also be a drier, which will prevent its surface migration during the formation of the film with all the problems that this could represent.

As already indicated, the penetration of this type of resin is rather good in general, and on wood, in particular.

Water sensitivity is not excellent because the presence of surfactants on the surface of the film induces a degree of hydrophilic sensitivity. Moreover, there is an interaction between the driers and the surfactant which can affect drying and, hence, delay crosslinking and, therefore, water resistance.

Paint formulations prepared from alkyd emulsions are low in viscosity, normally below a useful application viscosity. Therefore, techniques to increase the viscosity of the paint formulation are required and the use of associative thickeners has become widespread.

(c) Comparison with Acrylic Dispersions.

When discussing alkyd emulsions, their principal competitors are not only solvent-based alkyds, whose application qualities are desirable, but also styrene - acrylic dispersions. Tables 2-14 and 2-15 compare the two systems:

TABLE 2-14: COMPARISON OF SOME PROPERTIES OF ALKYD RESINS COMPARED WITH ALKYD WATERBORNE RESINS

Resin	**Gloss 20° & 60°**	**Haze**	**Tension**	**Dry to touch**	**Dry after 24h DIN 53150**
Self-emulsifying	70 - 85	14	14	2 hours	24/6
Core-shell emulsion	80 - 90	12	16	4 hours	28/3
Alkyd solvent	70 - 90	12	12	5 hours	30/3

TABLE 2-15:COMPARISON OF SOME PROPERTIES OF ALKYD AND ACRYLIC WATERBORNE SYSTEMS

Properties	Core - shell emulsion	Acrylic dispersion	Core - shell emulsion	Acrylic dispersion
Substrate	Wood	Wood	Metal	Metal
Drying	+ -	+ +	+ -	+ +
Open time	-	--		--
Gloss	+ +	+ -		+ -
Gloss retention-	+ -	+	+ -	+
Adhesion	+ +	+ -		+ -
Adhesion to dirty surface	+ -	- -	+ -	- -
Yellowing	+ -	+ +	+ -	+ +
UV resistance	+ -	+ +	+ -	+ +
Water Permeabifl	+	- -	+	- -
Water vapour permeability	+	+ +	+	- -
Blocking resistance	+ +	-	+ +	-
Corrosion protection			+	- -
Cost small thicknesses	+ -	+ -	+ -	+ -
Total	7+	2+	8+	4-

Obviously, when the next generation of alkyd emulsions was under development the idea was to combine the qualities of alkyd emulsions with those of acrylic dispersions. These are called "hybrid" systems and they correspond to in situ modified alkyd emulsions (and not to a simple mixture), with an acrylic dispersion, (which, for most of the time is also a core-shell of the hard-soft type). Depending on the degree of modification, the mixture will tend towards the features of one of the two families.

TABLE 2-16: COMPARISON OF SOME PROPERTIES OF
HYBRID ALKYD WATERBORNE SYSTEM

Resin	**Gloss 20° & 60°**	**Haze**	**Tension**	**Dry to touch**	**Dry after 24h DIN 53150**
Core - shell	70 – 85	14	14	2 h	24/6
Hybrid	60 – 85	16	20	30 min	20/4
Alkyd solvent	80 – 90	12	12	5 h	30/3

The use of a hybrid system means that driers can be avoided (because the acrylic dispersion portion leads to rapid surface drying) and also the coalescent solvent necessary for acrylic dispersions. This role is in fact taken up by the alkyd emulsion component. A 50/50 ratio gives no improvement from a practical point of view and, more often, 75/25 and 25/75 ratios are to be found which will all have their own applications.

In general, drying and durability are considerably improved, unfortunately, to the detriment of the film appearance.

Today, one can witness the development of the latest generation of alkyd emulsions with high non-volatile contents (between *55%* and *70%)* using new emulsifiers. These resins are without neutralisation amines. Moreover, their application is similar to conventional alkyd resins because they contribute body to the paint due to a better drying action (higher non-volatile content) and also because their oil length is > 60%.

3. Future developments.

Water based alkyd resins have an important role to play in the years to come but to compete with acrylic dispersions for the replacement of solvent borne alkyds, the excellent application properties of alkyd resins in solvent media need to be matched. It is important for the non-volatile content of resins in today's emulsions, which are at a level of *50%,* to be able to reach *60* or *70%* in order at last to be able to compete economically with acrylic; dispersions, without obviously compromising the drying properties.

The third millennium. should enable a third generation of alkyd emulsions to appear on the market which may be compatible with acrylic dispersions and which will have oil lengths of at least up to *65%,* non-volatiles over *60%* and with co-solvent levels below 5%. Today, polyamide and also urethane thixotropic: alkyd resin technology is already available in water as solvent medium.

Today, high solid alkyd resins, only offer a single positive point, the significant reduction in VOC. They also strongly diminish all the basic properties of conventional alkyds especially their low cost. En order to respect the environment, or conform with local legislation, many paint users have moved directly from the conventional alkyd to the emulsion alkyd.

VIII PAINT FORMULATIONS WITH ALKYD RESINS

1. Solvent Based Paint Formulations.

The following examples of paint formulations demonstrate the wide range for formulating with alkyd resins. The end use for these formulations encompasses almost all paint markets, from retail through to highly specialised industrial, from architectural through to transportation. Alkyd resins m both solvent and waterborne media will be discussed. The formulations are ambient air dried unless stated otherwise.

FORMULATION 2-1: TWO COMPONENT WOOD VARNISH ACID CATALYSED, HIGH GLOSS WITH VERY LITTLE ODOUR

Component 1	**%**	**Component 2 (hardener)**	**%**
Piastopal EBS 100/63	28.30	Para toluene-sulphonic acid	1.35
Vialkyd AC 4211801PA	49.40	Ethanol	8.65
Ethanol	22.30		
Total	100.00	Total	10.00

1) Mixing ratio by volume, component	10/1
2) Non-volatile content	52%
3) Touch dry 25°C	20 min
4) Through dry, 25°C	45/60 min
5) Viscosity 4 mm cup, 20°C	40 sec

Plastopal EB5 100/63 is a urea formaldehyde resin with a low free formaldehyde content and Vialkyd AC421 is a medium oil length coconut oil based alkyd which gives good flexibility. With the same resins, a single component varnish can be made using mono-butyl-phosphoric acid and the drying rate can be increased by adding a nitrocellulose resin such as Floches A20, 2% on solids, to the formula.

FORMULATION 2-2: INDUSTRLAL VHITE TOPCOAT & RED OXIDE PRIMER, AIR OR INDUCED AIR DRYING

Raw Material	**Primer %**	**Topcoat %**
Vialkyd AF 342 or Setal 142160X	42.0	53.0
Kronos 2059, Titaniurn Dioxide		25.0
Red iron oxide H3006	13.0	
Blane Fixe	10.0	
Zinc Chromate	6.0	
Mìcronised Talc, AT Extra	9.0	
Bentone 38, (10 % solution in xylene/methanol 95/5)	4.0	1.0
Baysilon OL 17 @ 1% (Slip aid)		0.5
4% Calcium octoate, drier.		0.8
6 % cobalt octoate, drier	0.6	0.8
6 % zirconium octoate, drier	1.5	1.5
50 % MEKO, anti - skin agent	0.6	0.8
Ethyl Glycol	4.0	3.0
Xylene	9.3	13.6
Total	100.0	100.0

Typical properties of paint

Viscosity DIN 4 cup 20°C	80 seconds	100 seconds
Pigment volume concentration, PVC	31%	17.5%
Pigment 1 binder	1.5/1	0.8/1
Touch Dry, 25°C	5 minutes	30 minutes
Through dry, 25°C	8 hours	8 hours
Gloss 60°C		98%

Typical primer film thickness, 25µ topcoat, 25 µ

Some film performance testing was carried out on the paint system by using an accelerated curing scheme of 14 days of air drying and 3 days at 60°C.

Cross Hatch Adhesion Test:

Substrate	**Result**
Steel	Excellent
Aluminium	Excellent
Zinc	Excellent

Erichsen indentation: Substrate: Mild steel, Primer only: 7.5nun
Scheme: 9.Omm

The alkyd resin choice is between two manufacturers chain stopped short oil alkyds (32 %) based on sunflower oil fatty acid.

The primer is manufactured by high speed disperser to a grind size of 10- 15 g. The zinc oxide anti corrosive pigment may be replaced with zinc phosphate if the toxicity of the zinc chromate is unacceptable.

The bentonite gel (Bentone 38 is the trade name) is a 10 % solution in xylene/methanol 95 : 5, the methanol being required to “gel the Bentone”. The function of the Bentone is to aid sag resistance and settlement resistance. The methyl ethyl ketoxime (MEKO) is a 50% solution in xylene and is used as an anti-skinning agent to prevent premature gelling or skinning during manufacture or storage.

The topcoat is made by high speed dispersion followed by a fast pass over a horizontal bead mill. The dispersion or grind size is 'off the gauge' after the high speed dispersion (FISD) stage, but it has been found that an extra dispersion via the superior shear achieved in a bead mill will enhance gloss and prevent settlement on storage (or at least delay the onset of settlement). This is typical of formulations pigmented with titanium dioxide as the sole or major pigment.

The TiO_2 grade is a chloride grade with good exterior durability. The calcium drier used in the topcoat but not in the primer is there to prevent the absorption of the primary driers onto the pigment.

The Baysilone is a siloxane slip additive, to enhance surface 'feel' and to aid in application.

Both primer and topcoat are formulated for spray application, cither conventional or airless, the WA is used as a tail or slow solvent, to aid levelling.

FORMULAITON 2-3: GREY BLUE FINISH FOR AGRICULTURAL MACHINES BASED ON MEDIUM OIL ALKYD WITH GOOD RESISTANCE TO YELLOWING

Material	**Weight** %
Alkyd with 48 % oil/ 60% in xylene	61.70
Kronos 2059, TiO_2	22.20
Phthalocyanine blue, LBG (BASF)	0.25
Carbon black, Printex V, (Degussa)	0.05
6 % cobalt octoate	0.35
18 % zirconium octoate	0.90
4 % calcium octoate	1.10
MEKO	0.15
Dipentene	1.00
Xylene	
Total	100.00

Dilute in xylene until spray application viscosity, typically 25 seconds BS134 flow cup.

Pigment / Binder, 0.6/1

A suitable alkyd would be Reactal 947165, a 47% oil length linoleic rich penta alkyd, supplied at 65% in xylene. The formulation is manufactured by high speed dispersion and horizontal bead mill. The pigments may be added as powders, but the product could be more simply manufactured as a white only dispersion and the blue and black pigments added as 'universal' colorants, particularly as the volumes required. will be very small.

The drier combination is the classical primary and secondary blend, with the cobalt as surface drier, the zirconium as the through drier and the calcium there to 'fend off the TiO_2's tendency to adsorb the cobalt.

MEKO is the anti-skin and the dipentene performs the function of an extremely slow solvent, assisting in levelling and ensuring a long wet edge time. Application would inevitably be by conventional or airless spray and dilution with xylene until application viscosity, typically 25 seconds BS134 flow cup.

The xylene in the formulation could be partially replaced by Solvesso 100 to extend the wet edge, particularly if the agricultural machinery to be painted is very large.

The formulation shows good petrol and diesel resistance, reasonable weathering and good flexibility. The use of pentaerythritol as the polyol gives a branched resin, which after oxidative crosslinking has good solvent resistance.

FORMULATION 2-4: MATT PAINT FOR CEIILINGS, BASED ON MEDIUM OIL HIGHLY CONDENSED SOYA ALKYDS

Material	**weight** %
Synolac 6823 or Vialkyd AF 5 12151	19.930
Bentone gel 32 (10 % WS – 1% ethanol 95/5)	3.790
Kronos 2063, Ti02	11.380
Dureal 2 (Ornya)	19.920
DRB 8125 (numeral whites)	21.810
Tale standard (0 / 10 min) Luzennac	3.320
Durcal 15	5.220
5 % calcium octoate	0.160
10 % zirconium octoate	0.045
6 % cobalt octoate	0.040
5 % zinc octoate	0.075
NEKO	0.380
Exxol D80 (Exxon)	1.230
White spirit	12.700
Total	100.000

Properties of paint

Theoretical non volatile component	70%
Viscosity, rotothinner 20°C	11.5 poise
Pigment / binder	7.8/1
PVC	75%
Density	1.53

The formulation is based on either Synolac 78W from Cray Valley or Vialkyd AF512151, which are medium oil length, soy alkyds. The formulation is near or slightly above the CPVC and three fillers are used to achieve the required flatness, talc, barites and chalk without introducing too much thixotropy that would prevent flow and levelling. A 10% Bentone 32 gel is used to reduce the onset of pigment settlement. This would be a very low cost formulation, used in industrial applications rather than DIY. The solvent Exxsol D 80 is a dearomatised hydrocarbon used as a very slow tail solvent.

FORMULATION 2-5: LONG OIL (FATTY ACID) ALKYD PAINT, ODOUR FREE GLOSS WHITE FINISH FOR BUILDINGS

Material	**Weight** %
Part I	
Vialkyd AF 600/50 isopar G	62.66
Kronos 2065	25.07
Part II	
Cobalt octoate 11 %	0.14
Calcium octoate 4%	0.79
Zirconium octoate 6%	2.61
MEKO	0.63
Additol VXL 4930 (levelling agent)	0.17
Isopar G or L	7.93
Total	100.00

Disperse part I for 30 minutes in a bead mill then add H and homogenise.

Properties of paint

Non volatile component	56%
Pigment / Binder	0.8/1
Viscosity, 1000 s^{-1} 23°C	370mPa.s
Dry to touch (150 ìm 23°C)	3 hours

This is an extremely simple formulation, with no thixotropy and therefore not suitable for a DIY application However, many professional paint applicators who specialise in brush application of high gloss finishes do not want any thixotropic properties in the paints that they use as they consider that flow control detracts from flow and levelling, gloss and indeed their application skills.

The alkyd is a long oil linoleic rich in isoparaffinic solvent to give a very low odour formulation. Isopar G and L are supplied by Exxon, G having a boiling point of 161°C and an evaporation rate of 16 (butyl acetate is 100), and L has a BP of 191'C and an evaporation rate of 3.

Additol VYL 4930 is a levelling aid

FOMULATION 2-6: SEMI-GLOSS PAINT, WHITE NON PENETRATING LONG OIL CONDENSED ALKYD

Material	**Weight %**
Alkyd 60% White spirit	35.70
(M_w controlled by distribution Soya oil + Penta)	
10 % Bentone gel 34	5.00
Iron oxide extra	5.65
Kronos 2061	13.61
Lithopone	27.50
Kaolin	5.90
10 % zirconium octoate	0.45
6 % cobalt octoate	0.11
10 % calcium octoate	0.34
MEKO	0.40
White spirit	5.34
Total	100.00

Properties of paint

Non volatile component	75%
PVC	38%
Pigment / Binder	2.5/1

FORMULATION 2-7: ZINC PHOSPRATE PRIMER BASED ON A SHORT OIL LENGTH TUNG OIL, LINSEED AND ROSIN

Material	Weight%
Vialkyd AM 342/60X	40.00
Zinc phosphate	13.50
Yellow iron oxide	4.50
Microtalc AT 1	11.00
Red iron oxide	16.00
Aluminium stearate	0.10
Soya lecithin	0.20
Pm-acetate	2.00
10 % zirconium octoate	0.25
6 % cobalt octoate	0.17
MEKO	0.30
Butyraldoxime	0.20
Xylene	6.00
Butanol	1.78
Solvesso 100	4.00
Total	100.00

Properties of paint

Non volatile component	65%
Pigment / Binder	2.25/1

The alkyd chosen for this primer is a rosin modified short oil linseed/ tung. The rosin modification provides fast lacquer dry and the tung, good through drying. The presence of butyraldoxime in the formulation is important.

Methyl-ethyl-ketoxime is not an efficient anti-skinning agent for tung oil resins, whereas butyraldoxime is and so is favoured over MEKO, where toxicity considerations will allow. Unfortunately, butyraldoxime is a particularly unpleasant chemical and is not allowed in many end users (or paint companies) formulations.

It appears that European users and producers are more concerned about butyraldoxime than their US counterparts.

The soy lecithin is in the formulation as an anti flocculent. The application is either by airless or conventional pneumatic spray

FORMULATION 2-8: HIGH PERFORMANCE, LOW BAKE WHITE FINISH, SHORT OEL SAFFLOWER BASED ALKYD

Material	**Weight** %
Vialkiyd AR 280/60X	41.20
Kronos 2059	28.00
Bentone 34 10%	3.20
Aerosil 200	0.50
Solvesso 100	3.00
Butanol	2.00
Setamine US 143/55 (melamine resin)	17.00
Silicone oil AK 35/ 1% Xylene	0.30
Xylene / Solvesso 100 (1/1)	4.80
Total	100.00

Property of paint

Pigment / Binder	0.8/1
Alkyd: Melamine ratio, on solid resins	72.5/27.5
Application Viscosity DIN 4	25 seconds
Baking conditions	30 to 40 minutes at 80-90°C

A standard alkyd melamine formulation with a low temperature bake schedule (although the time cycle is consequentially lengthened.) The alkyd resin chosen for such a low bake must have a significant acid value, as no external acid catalyst is included in the formulation. The melamine resin must be partially methylolated, which makes it suitable for weak acid catalysis.

A certain percentage of the cured films' properties will undoubtedly come from oxidative crosslinking of the safflower alkyd, at such a low bake schedule.

This formulation is an example of both Bentone and Aerosil being used as thixotrope additives.

FORMULATION 2-9: GLOSS NITROCELLULOSE VARNISH

Material	**Weight %**
Nitrocellulose H 24 / 65% wet butanol	14.60
Toluene	18.10
Butyl acetate	39.40
Ethyl acetate	3.60
Pm-acetate	1.60
Butanol	3.60
Di-butyl phthalate	2.80
Levelling agent	0.50
Vialkyd AT 432/60X	15.80
Total	100.00

Properties of paint

Non volatile component	Ca. 22%
Viscosity, DIN 53211 / 20°C	45 s
Dry to touch (under 30 im film, dry at 20°C)	10 min

The alkyd is used to plasticize the nitrocellulose and it must, therefore, be compatible with it, and enable good solvent release.

FORMULATION 2-10: AIR DRYING GREY MIETALLIC VINYL TOLUENE MODIFIED ALKYD

Material	**Weight %**
Vinyltoluene alkyd resin, 45 % oil length at 60% solids in xylene	78.6
Blitz 6260/ 73 % Aluminium paste	3.7
Toluene	7.0
Ethyl acetate	7.0
Cobalt octoate, 1% in white spirit	2.4
MEKO	0.5
Additol VXL 5905 (special additive for metallic)	0.8
Total	100.0

Properties of paint

Paint non-volatile component	50%
Viscosity DIN 4 1 200C application	45s
Pigment / binder	0.06/1
Touch dry (under 1500 wet film, at 200C)	2 hours

Additol VXL 5905 is a wetting agent, specifically designed for wetting out aluminium pastes. The aluminium is wetted out in the additive and toluene prior to the addition of the resin. The driers and the antiskin are added and viscosity adjusted with the fast solvent, ethyl acetate. Application is by conventional spray. A 50R wet film would be touch dry within 15 minutes. The exterior durability is indifferent, as vinyl-toluene is no more resistant to UV than styrene.

FORMULATION 2-11: ZINC RICH GREY PRIMER BASED ON AN EPOXY MODIFIED ALKYD

Material	**Weight** %
Duroxyn EF 900160X	11.00
Zinc powder	79.00
10 % Bentone 34 paste	3.90
Lampblack 700, carbon black-	0.70
6 % cobalt octoate	0.02
MEKO	0.02
Phenolic antioxidant	0.12
Calcium oxide (desiccant)	0.50
Xylene	4.74
Total	100.00

Bentone paste: Bentone 34 (10g) + Xylene (86g) + Methanol (4g).

Properties of paint

Pigment / binder	12/1

The alkyd resin is an epoxy ester resin based on a 40% oil length DCO, supplied at 60% solids in xylene. Zinc rich primers are standard in the protective coatings markets where the very high levels of zinc offer excellent corrosion resistance via passivation and sacrificial corrosion mechanisms.

FORMULATION 2-12: EXTERIOR GREEN SILICONE ALKYD FINISH

Material	**Weight %**
Vialkyd TS 354 1 70WS	65.50
Chrome green T 255 (BASF)	18.30
Cobalt octoate 1%	2.30
Zirconium octoate 10%	2.30
Calcium octoate 2%	2.30
MEKO	0.60
Slip and levelling agent	0.20
White spirit	8.50
Total	100.00

Properties of paint

Non volatile content	64%
Viscosity DIN / 20°C	171s
Dry to touch	2.5-3 hours
Pigment / Binder	0.4 / 1

The alkyd is a silicone modified resin, supplied at 70% in white spirit. The formulation is intended for brush or roller application and the dull green chromic oxide pigmentation compliments the durability of the silicone alkyd. The Byk 310 is used to reduce surface tension to aid substrate wetting and to resist cratering.

A step further in durability in silicone alkyds can be taken by using isophthalic acid in place of phthalic anhydride in the alkyd and by using a UV absorber package in the paint formulation.

FORMULATION 2-13: WHITE GLOSS HIGH SOLIDS DECORATIVE ALKYD.

Material	**Weight** %
Synolac 6095WP85	28.31
Tiona 535	34.56
Super Gelkyd 3910WP90	24.72
Drier package	2.67
MEKO	0.22
Isane 1P175	8.63
Propylene glycol	0.89

Viscosity mPas.s @ 25°C	410
Pigment / Binder	0.75/1
SG	1.35
Vehicle solids	72.4%
Total Solids	82.4%
PVC	16.2%
VOC g/L	238

Synolac 6095WP85 is a 70% linoleic rich alkyd supplied at 85% in isoparaffinic solvent and Synolac 3910WP90 is a urethane modified Super Gelkyd thixotropic alkyd at 84% linoleic fatty acid supplied at 90% solids in isoparaffinic solvent.

The drier combination, Combi APB, from Servo, is a blend of cobalt, calcium and lithium driers, 0.05%, 0.2% & 0.04% respectively as metal on solid resin. Isane IPI75 is an isoparaffinic solvent from Total Solvents. Application is by brush or roller. The long oil length means that the use of surface tension reducing additives may not be required.

FORMULATION 2-14: LEAD AND CHROMATE-FREE PRUVIER BASED ON AN ACRYLIC MODIFIED ALKYD

Material	**Weight %**
Acrylic modified alkyd resin, 50% in xylene	32.00
Sicorin RZ (BASF)	1.3
Kronos 2160 Ti02	9.6
Talc AT extra	4.8
Blanc fixe	6.6
Zinc phosphate ZNP 1 S	7.4
Bentone 38	0.3
Zinc oxide WS	3.2
Lampblack L TD	0.1
Drying agent 173	0.9
MEKO	0.3
Tungophen B 50 (Bayer)	0.3
Desavin (Bayer)	0.3
Solvent	32.9
Total	100.0

Properties of paint

Non volatile content	49%
Dry to touch	15 min
Viscosity CAF 4	140s
Pigment /Binder	2/1

The alkyd is a styrenated 36% linoleic /DCO supplied at 50% solids in xylene. The anticorrosive pigments are essentially zinc based and are extended with barites and talc in the classic fashion.

A 50p wet film is touch dry in only 15 minutes and there will be no significant over coating issues, with such a short oil length. Because the product is a primer, the fact that the durability is poor will have no relevance and the excellent adhesion of this resin will ensure that the barrier properties of the formulation are enhanced by the good substrate adhesion.

2. Waterborne Paint Formulations

FORMULATION 2-15: GREY WATER-DILUTABLE ONE COAT BAEING FIMSH BASED ON TWO WATER-DILUTABLE SELF-EMULSIFYING ALKYDS

Millbase for Sandmill

Material	**Weight %**
Resydrol. AX 246/ 70 BG	13.30
Anti foaming agent	2.35
utylgIyc01	1.65
Dimethylethanolamine	0.55
Demineralised water	28.05
Special black 4	0.20
Kronos 2190 TiO2	18.05
Aluminium silicate ASP 600	3.00
Bentone 34	0.40
Microtalc AT extra	1.85
Let Down:	
Resydrol AX 9061 (55% in water)	12.85
Cymel 303 Hexamethoxy methyl melamine (Cyanamid)	2.25
Water	15.50
Total	100.00

Disperse the millbase over 30 minutes then reduce with the let down.

Properties of paint

Non-volatile content	47 % (at 25 s cup 4)
Viscosity DIN4	110s
Pigment/Binder	1.4/1
pH value	8
Baking	20 min at 130-700°C

The AX 246 alkyd is supplied in butyl glycol and is adjusted to pH 8 with the dimethylethanolamine. The AX 906 is co-solvent free and the cross linking amino is hexamethoxymethylmelamine. The application method is dipping and this was a very common application for waterborne paint systems, both air-drying or as in this case, for stoving. It is far safer from a fire risk point of view, to have a large dip tank full of waterborne paint than inflammable solvent. The dipping viscosity is 25 s BSB4 cup and the formulation is reduced to this viscosity with demineralised water.

Waterborne dipping paints are not easy to formulate however, as during the flash off period, the water comes off slowly and has a washing effect on the deposited paint film. Of course, solvent borne dipping formulations have the same issue, but the time taken for water to flash off is very difficult to alter! In the case of electrodeposition paints, the water washing effect is not present as the deposited paint film is no longer water soluble.

The formulation would be much improved by using a waterborne dispersion of the black pigment, to ensure consistency of colour.

The following series of test results given in Table 2-17 were obtained with this formulation at various baking schedules

FORMULATION 2-16- MATT WMTE WATER DILUTABLE HOUSE PAINT BASED ON A SELF-EMULSIFYING ALKYD

Material	**weight %**
Millbase:	
Résydrol AY 586/ 38% in water	28.00
Anti-foam agent	0.50
Additol VXL 6208	2.00
A M P 90 (neutralisation)	1.00
Octa Soligen 421 aqua drier	0.50
Water	11.00
Kronos 2059	13.00
Omyalite 90	7.00
Durcal 5	27.00
Tale 20 MO	3.00
Let down:	
Rheolate 278	0.50
MEKO	0.50
Water	3.50
Texanol	1.00
Accematt TS 100	1.00
Total	100.00

Mix millbase and disperse for approximately 30 minutes and reduce with let down.

Properties of paint

Non-volatile content	60 %
Dilution	Water
Pigment/Binder	4.7/1

TS 100 is used as a final gloss adjustment. Texanol is a very slow evaporating co-solvent.

The formulation is a straightforward, decorative matt white and would be used in place of a vinyl emulsion. There would appear little benefit in choosing this formulation over a commercial vinyl matt wall paint.

FORMULATION 2~18: WALNUT MATT WOOD STAIN, FOR INTERIOR USE, BASED ON A WATER-DILUTABLE SELF-EMULSIFYING ALKYD

Material	weight %
Part I	
Resydrol AY 586 138% in water	65.5
Ammonia 25% in water	0.8
Additol VXW 4940 (drier)	0.3
MEKO	0.4
Surfactant	0.4
Part II	
Matting agent OK 412	3.5
Cerudust 9615 (matting agent)	1.3
Aerosil 200	0.4
Luvotix HT	0.3
Wetting agent	OA
Anti foam agent	0.4
Part III	
Water	22.7
Luconyl red 2817	1.2
Luconyl yellow 1916	1.2
Luconyi black 0066	1.2
Total	100.0

Mix in order, disperse Parts I & II well then complete with III

Properties of paint

Non-volatile content	30%
Viscosity	30s
Dry to touch (dependant on film thickness and humidity)	2 hours
Can be over coated after 2 hours	

The alkyd is adjusted for pH 8 with ammonia solution. OK 412 is a precipitated silica matting agent and Aerosil 200 is a pyrogenic silica used to impart thixotropy. Disperbyk 190 is a wetting agent, used here as an anti-flocculating aid. The LuconyFs are water dilutable dyestuffs.

To improve the exterior resistance, a compatible acrylic dispersion such as Mowilith DM 772 can be blended with the above. The drying will also be accelerated.

FORMULATION 2-19: PREVIER BASED ON A SHORT (24%) AND A LONG OIL (58%) WATER-DILUTABLE ALKYD

Material	**Weight** %
Resydrol AY *586 / 38%* in water	15.30
Dowanol DPM	1.40
Ammonia *25%* in water	0.10
Additol VXW *4940*	0.40
MEKO	0.10
Surfactant	0.10
Water	6.00
Resydrol AY *241140%* in water	14.50
Kronos *2160*	9.60
Violet label chalk (Ornya)	20.00
Barium sulphate EWO	20.00
Special extender SE SUPER(Naintsch)	9.00
Microtalc AT extra	2.90
Wetting agent	0.30
Anti foam agent	0.30
Total	100.00

Properties of paint

Non volatile content	73%
Pigment / Binder	5.3 / 1
Dry to touch (100µ film, dependent on relative humidity)	20 min

The alkyds are high acid value neutralised with ammonia and supplied in water. Additol VXW 4940 are water dilutable driers. The formulation is relatively fast drying because it contains so much extender to assist in water release. A finish formulation would be much slower in drying.

FORMULATION 2-20: LIGHT GREY STOVING PRIMER BASED ON SHORT OIL SELF-EMULSIFYING ALKYD

Material	**Weight %**
Resydrol AY 224 w 140 water	24.05
Levelling agent	0.15
Surfynol 104 E (wetting)	0.25
Water	5.20
Kronos 2190	13.75
Blane fixe F	13.75
Carbon Black	0.05
Resydrol AM 224 w / 40% in water	34.35
Cyrnel 303	4.15
Water for dilution	4.30
Total	100.00

Properties of paint

Non-volatile content	55%
Viscosity	2.3 Poises
Pigment / Binder	1/1
Amount of co-solvents	3%
Baking conditions	20 min at 160°C

Items *1-7* are high speed dispersed and items *8-10* are added as a reduction. The alkyd is a short oil soy and the crosslinking_agent is hexamethoxymethylmelamine. The alkyd amino ratio (on solids) is *85:15* which is a low amount of amino for a stoving system. The formulation would be improved for colour consistency with a pre-dispersion of carbon black.

FORMULATION 2-21: UNIVERSAL ANTICORROSION PRIMER BASED ON 32 % OIL LENGH SELF-EMULSIFYING, EPOXY AND ACRYLIC MODIFIED ALKYD

Material	**Weight %**
Part I	
Resydrol VAX 6050 / 40% water	55.8
AMP 90 (multifunction additive)	0.1
Winnofil SPT (anti sedimentation)	0.4
Zinc phosphate 3850 (Heubach)	8.5
Microtalc AT Extra	6.0
Naintsch BC super	6.0
Bayerferrox 130	12.6
Wetting agent	0.4
Additol VXW 4940 drying agents	1.5
Anti foam agents	0.4
MEKO	0.5
Part II	
Rheolate 278 18 % water	1.9
Water	5.9
Total	100.0

Properties of paint

Non volatile c2mPonent	56%
Viscosity 1000 s^{-1}	110 mPa s
Value of pH	8.4-8.8
Dry to touch (152g film, humidity dependent)	30 min

Mix part I in the disperser then grind and complete with part II. The Resydrol is a self-emulsifying short oil alkyd that is both epoxy and acrylic modified. It has good adhesion to metal substrates. AMP 90 is the pH adjusting amine, the Winnofil is an activated calcium carbonate and possess pigment antisettle properties. The Rheolate is an associative thickener.

FORMULATION 2-22: WRITE GLOSS AIR DRYING EXTERNAL EMULSIFIER ALKYD EMULSION

1 . Urad DD 518 (DSM)	0.9
2. Tamol 731 (25% in water)	0.6
3. Demin water	15.1
4. Tipure 706	29.3
5. Borchigen 706	0.4
6. Tego Foamex 8 10	0.1
7. Uradil AZ 516 Z 60	51.1
8. Cobalt Hydrocure II	0.6
9. Exskin 2	0.2
10. Acrysol RM 1020	0.6
11. Acrysol RM 8 (10% in water)	0.6
12. Surfynol 420	0.5

The externally emulsified alkyds are not sufficiently stable to shear to enable grinding of pigment. Items 1-6 are mixed and then high speed dispersed or milled in a pearl mill. The rheology can be adjusted to achieve the necessary shear conditions by using some of the rheology modifiers from the let down. A 5µ grind size should be achieved.

During film formation in a solvent borne system the polarity of the continuous phase does not change, going from solvent to alkyd etc. In an alkyd emulsion system the continuous phase changes from polar water to almost non polar alkyd and this has a profound affect on the pigment. The pigment surface needs to be hydrophilic to be wetted by the water as continuous phase and subsequently there is rapid change to lipophilic when the alkyd is the continuous phase. This is achieved by the use of surfactants that are used to coat the pigment surface during the pigment dispersion process.

DSM Resins have designed a single surfactant that will accomplish this for alkyd systems, based on polyethylene glycol and linseed oil. The DSM product is Urad DD 518. The linseed oil component of the molecule has the ability to oxidatively crosslink with the alkyd resin in an air drying formulation. Urad DD 518 has lipophilic components from the fatty acid chain of the oil and hydrophilic components from the polyethylene glycol chain and the ester/carboxyl functionality of the oil. Naturally, the DSM product is more suited to long oil air dry systems and would contribute to yellowing (due to the linseed oil) in a short oil stoving system.

Byk Chemie have a product that performs similarly but is formulated without the linseed oil component - Disperbyk 190.

DD518 therefore used as a pigment wetting agent and stabiliser. The Ti02 grade from DuPont is an exterior grade. The Tamol 731 is an amine used to adjust the pH to 7, care should be taken not to use too much of the amine as the DD 518 will dissolve completely and foam will then become a severe problem. The DD 518 should form an opalescent solution, if it is clear, then over neutralisation has taken place. In many regions, tap water is suitable in place of demineralised water. The Borchigen DFN is an ethoxylated nonyl phenol and is used to reduce surface tension. In parts of Europe nonyl phenols are now banned, alterative non-ionic surfactants should be used.

The antifoam, Tego 810 is an incompatible type. The use of antifoams is a problem in alkyd emulsions and the wetting and dispersing agents used should be altered rather than use of antifoams as far as possible. The wetting and dispersing additives should have moderate water solubility, a high molecular weight and a high affinity towards the pigment. This combination will ensure that there are minimal amounts of these agents in the water phase, yielding a low foaming grind stage.

Items 7-9 are premixed prior to adding them to the grind stage. The alkyd emulsion is a 63% oil length tall oil at 60% in water, it is amine and co-solvent free. The pH is in the region 3.5-5.0. The recommended drier package for this alkyd, based on metal content on resin solids is:

Cobalt	0.05-0.06
Calcium	0.1-0.2
Zirconium	0-3-0.5

The Acrysol rheology modifiers are added to bring the viscosity profile up to the desired level and this will vary depending on the application method. Surfynol is an anti crater agent, approved for use in alkyd emulsions.

FORMULATION 2-23: RED OXIDE SEMI GLOSS EXTERIOR FINISH

1 . Demin Water	10.00
2. Borchigen DFN	1.35
3. Orathan 731 25%	0.60
4. Agitan 295	0.10
5. Acrysol RM8	0.70
6. Bayferrox 130M	12.50
7. Microtalc AT Extra	2.00
8. Mierdol Extra	10.00
9. Demin Water	7.00
10. Uradil AZ516 Z60	45.00
11. Durham VX7	1.50
12. Acrysol RM 1020	2.00
13. Troysan Polyphase P 100	0.35
14. Dowanol PM	0.55
15. Actiside SPX	0.25
16. Demin Water	6.10

SG	1.203
PVC	20.4%
Non volatile content	52.5%
Volume solids	41.6%
VOC g/L	15

The alkyd is the same long tall oil fatty acid that was used in the previous formulation. The ethoxylated phenol is used as a wetting agent and Orathan 731 is a dispersing additive from Rohm & Haas. The Acrysol RM 8 and RM 1032 are two rheology modifiers, and on this occasion the drier package is from. Harcros Chemicals.

Two biocides are used in this waterborne formulation, the Polyphase is an algaecide and the Acticide is a broader spectrum. biocide. The Dowanol PM is a slow tail solvent to assist in wet edge extension.

The 100g notional applied wet film will dry down to 42µ giving a coverage of 10m^2/L.

FORMULATION 2-24: TRANSPARENT WOODSTAIN, BASED ON AN EXTERNALLY EMULSIFIED ALKYD.

1. Demin water	46.25
2. Triton X 405	0.05
3. Acrysol RM 8	1.65
4. Agitan 295	0.05
5. Disperfin Yellow 400 WD	3.45
6. Disperfin Red 400 WD	0.40
7. Disperfin Black 350 WD	0.10
8. Uradil AZ515 Z6	45.40
9. Durharn VX 7	1.50
10. Fluorad FC 129 10%	0.40
11. Dowanol PM	0.45
12. Troysan Polyphase P 100	0.30

SG	1.023
PVC	1.5%
Non volatile content	29.5%
Volume solids	28.1%
VOC g/L	12

The alkyd is a 73% oil length tall oil fatty acid emulsion supplied at 60% in water. It is amine and co-solvent free and has a pH of 4-5. It is flexible and has good exterior durability and hence its selection as a vehicle for a wood stain. The recommended drier package is 0.5-0.6% cobalt, 0.1-0.2% calcium and 03-0.5% zirconium metal, on solid resin.

Items 1-7 are added in order under stirring and items 8- 10 added sequentially. Items 11 & 12 are premixed and then added under stirring.

Triton X 405 is a wetting agent and the Disperfins are water dilutable pigment pastes. No pigment dispersion step is therefore required in this formulation.

The Fluorad is a fluoro tenside surface tension lowering agent.

FORMULATION 2-25: WOOD AND CONCRETE PRIMER BASED ON AN EXTRENALLY EMULSIFIED ALKYD

1. Demin Water	9.88
2. Acrysol RM 8	0.79
3. Byk 024	0.10
4. Disperbyk 190	1.998
5. Microdol A 1	12.35
6. Zinc Oxide	1.48
7. Omyalite 95 T	3,70
8. Kronos 2160	13.33
9. Demin Water	4.94
10. Uradil AZ601 Z44	45.93
11. Acrysol 2020	2.47
12. Durharn VX 71	0.84
13. Propylene glycol	0.99
14. Demin water	1.23

SG	1.325
PVC	35.2%
Non volatile content	51.5%
Volume solids	35.8%
VOC g/L	18

Items 1-8 are high speed dispersed and items 9-13 added under stirring. The viscosity is adjusted with item 14.

The alkyd is a urethane modified 25% oil length linoleic rich supplied at 44% solids in water. It is neutralised with triethylamine to p11 6.0-7.5. Byk 024 is an antifoam and Disperbyk 190 is a dispersing agent.

The application method for this formulation is spray using conventional pneumatic spray equipment.

CHAPTER III

POLYESTER RESINS

by

Phillipe Deligny

Edited by

Dr. P. K. T. Oldring

I INTRODUCTION.

The first polyesters were developed by Kienle in *1926.* After the end of the Second World War, the production of high molecular weight linear polyesters began to be developed on a large scale, especially for polyethylene terephthalate or polyethylene glycol terephthalate, discovered in *1941* by Whinfield and Dickson.

This is the most important raw material for polyester fibres whose brand names include Dacron, Terylene, Tergal, Trevira, and Terlenka. Since *1950,* a large number of novel linear polyesters have been synthesised and studied, and many chemical modifications of the polyethylene terephthalate structure have been proposed from which only a few have had industrial applications, in the fibre and plastic sectors.

Polyethylene terephthalate, moreover, has numerous industrial applications as a plastic, a laminating plastic, and as sheets for packaging material, capacitors, recording tapes (as oriented PET film) and even in satellites and other vehicles for the same purpose. Polybutylene terephthalate is a plastic material.

Another type of linear polyester which is widely used nowadays is bisphenol A based polycarbonate. The latter was first introduced in *1957.*

Linear high molecular weight polyesters cannot be used in paints and coatings, except for specific applications, such as in coatings for polystyrene (such as in hi-fi systems), which use very high molecular weight water dispersible polyesters. However, in solution, the viscosity of high molecular weight polyesters is very high and, moreover, they require solvents which cannot be used in the paint industry. Some polyesters with a number average molecular weight $M_n>10000$ are useful for coil coating combined with lower weight reactive polyesters. These polyesters are frequently based on terephthalic acid and short-chain diols such as ethylene glycol. Their high viscosity, excellent mechanical properties yet low reactivity due to two terminal hydroxyl functions for a high molecular weight polyester of M_n 10000 should be noted. Despite their high melting points, they are essentially thermoplastic resins.

Alkyds are a class of polyester and have been used commercially for paints and coatings for many years. They utilise triglycerides of fatty acids, or fatty acids themselves, with synthetic polyols and polyacids. The oils or - fatty acids are nowadays derived from vegetable oils, for example soy bean oil, or-from stumps of pine tress, for example tall oil fatty acid. The relatively low molecular weight of alkyds combined with the ability to air dry to form resistant glossy films resulted in alkyd based paints dominating the paint and coating market about 40-70 years ago. The demand for better quality industrial paints based on short oil alkyd the market appearance of the so-called "oil-free alkyds" or polyesters. As already discussed in the alkyd resin chapter, the terminology is not easy and there is no clear divide between polyester and alkyd resins. Polyesters for surface coatings are traditionally considered as being “oil free alkyds” or “oil free” polyesters.

Normally, a polyester resin is the result of a polycondensation of diols and diacids (or higher functionality derivatives triacids, tri- or tetraols) which do not have a fatty acid chain. A complication arises with what is accepted as the definition of a fatty acid chain. For example, Cardura E10 has a C_{10} branched chain which is associated with a fatty acid chain.

Products using it are often termed alkyds but also they can be considered as a polyester. Isononanoic acid is a similar case.

lf alkyds are defined as resins containing a fatty component of a natural compound (in most cases), with varying degrees of drying properties, as applies to the traditional long oil alkyds for oil based gloss paints, problems can still arise. There is a class of alkyds based on non-drying oils or fatty acids, such as coconut. Most workers refer to these products as non-drying or stoving alkyds. Modifications made with linear long chain diacids can be considered as being polyesters, or modified alkyds. Other workers may consider that the term alkyd includes those polyesters containing fatty acids or oils derived from vegetable or marine oils.

The molecular weights of most polyesters used for industrial coatings range from *2000* to 6000 and they are normally cross-linked (with a crosslinking agent) or used for plasticizing various systems such as nitrocellulose. Crosslinking agents would typically include aminoplasts and polyisocyanates or modified polyisocyanates. As discussed in the polyurethane chapter (Volume RI, Chapter 1), polyesters are also used as the basic materials for preparation of polyurethanes.

Unsaturated polyesters, which will not be considered in this chapter, appeared around 1942. Their only use, which could be considered as paints, is for gel coats but this area is very specific and the requirements are very distinct from those for paint.

Polyesters for powder coatings will be dealt with separately, to illustrate the different types used as well as their cross-linked systems , but this will not be in any detail.

II APPLICATIONS FOR POLYESTER RESINS IN SURFACE COATINGS.

1. Coil Coatings

The first coil production lines were installed in the USA in the beginning Of 1940s They were used for coating steel shutters (50 mm width and 0.3 mm thickness). Their production rate was 12 m/minute and twelve hours were required in order to produce one ton of lacquered metal. Today, a modem production line can produce 500 tonnes of steel in 12 hours. The current uses of coil coating can be sub-divided as shown in Table 3-1.

TABLE 3-1: CURRENT USES OF COIL COATING

Utilisation (in 1996)	**Steel**	**Steel**	**Aluminium**	**Aluminium**
	Area (mil m^2)	**Thousand of tons**	**Area (mil m^2)**	**Thousand of tons**
Buildings	435	2025	125	183
Transport	21	99	23	33
Household appliances	49	227	4	6
Miscellaneous	34	159	4	6
Dealers	56	264	9	14
Various export	49	227	8	12
Total	644	3001	173	254

Applications include:

- Buildings: metallic locks, roller shutters, cladding, roofing, window breasts, siding, awnings, blades for shutters
- Internal applications: roof supports, partitions.
- Transport industry: caravans, coaches.
- Miscellaneous: casing for different appliances such as televisions, radio, camping equipment, switchgear, household appliances.
- Food and beverage cans: easy open ends for food and beverage, drawn cans for food. However the use of polyester based coatings for coil applications for can coatings is, today, minimal. Epoxy and PVC based systems are the major coatings employed for can coil coatings.

Coil coatings have progressed over the years. At the beginning, all of the resin types present during this period were used. These included vinyl organosols, vinyl derivatives, alkyds, acrylics and epoxies. Failure soon became apparent, with loss of adhesion of vinyl organosols on exterior exposure and the very rapid and significant development in the physical properties of some vinyl alkyds. At this time, acrylics rapidly established themselves despite their very pungent odour and very dense fumes. A significant improvement was introduced in 1968 with polyesters and silicone based acrylics. Siliconised polyesters soon followed this.

Coil substrates include galvanised steel and aluminium alloys. In 1980, galvalum was introduced which is a galvanized steel whose zinc coating is replaced by a mixture of aluminium - zinc. These different substrates are surface treated before being coated. These are, in particular bonded substrates (parker), alodine or even alcomet C which is deposited by a roller to give a homogeneous chemical conversion on the surface of the substrate.

The use of polyesters in coil depends on the use of the final coating. Polyester primers are used quite often in Europe although their anticorrosive properties are not as good as those from other types of primer. However, their mechanical properties are far superior.

Acrylics and polyesters cross-linked with melamine formaldehyde resins or blocked isocyanates are used in finishes. Acrylics were developed at an earlier stage for interior uses, where they are not exposed to water, chemicals or mechanical stresses. Polyester resins are suitable for a large number of applications, including those unsuitable for acrylic based coatings.

Flexible coatings, which are abrasion resistant with good durability, can be formulated from polyester resins with or without blocked polyisocyanates. The benefit of polyurethane crosslinking improves, once again, the flexibility of the coating.

Silicone modified polyesters give several years exterior resistance, enabling ten or more year guarantees to be offered on some building applications, such as claddings. The polyesters used are generally based on isophthalic or terephthalic acid in order to have maximum flexibility and exterior resistance. The use of special diols remains somewhat limited since for this application material prices must be competitive. Molecular weights (M_w) are rather low and the structure rather linear, therefore there are very few triols used. The hydroxyl value will be between 80 to 160 mg KOH/g. The blocked polyisocyanates that are used are the trimers of HDI or 1PDI. In the USA, these polyester systems are starting to become more widespread as they are more tolerant to passivated surfaces than epoxides or water dilutable primers.

Of course, polyester resins can also be found in powder coatings, which are trying to break into the coil coating market. For coil coating there is a slow but regular development of water-dilutable Polyesters which are used when a new production line is put into service. However, these add an extra constraint in that it is necessary to pre-dry the coating in order to evaporate the water.

2. Industrial

Polyesters, principally used with melamine formaldehyde resins, are particularly suited for stoving finishes on industrial articles. These are typically the rather standard type of coating being based on phthalic acid or isophthalic acid, as in general the desired properties are resistance towards chemicals, high, gloss and a good appearance. Their functionality is a little higher than for those used in coil coatings. Curing temperatures range from, 120°C to 180°C.

Polyesters modified with isononanoic acid or Cardura E10 to impart high flexibility to the system are available. They have the advantage that a fatty chain improves pigment wetting, whilst increasing the fatty acid nature of the polyesters.

In two component polyurethane systems, polyesters still have many advantages compared with resins that are principally used in this sector. Polyesters, either alone or combined with acrylics, impart flexibility which cannot be attained with acrylics alone, for example cold impact resistance. Moreover, the appearance obtained with the latter is also improved.

New cycloaliphatic: diols enable QUV resistances of 3000 hours without significant loss of gloss and practically no yellowing. Today, these products remain expensive and have rather high hydroxyl values, which increases the cost of formulations (due to the higher levels of crosslinking agent required).

New products are being developed, particularly with the objective of obtaining VOC's of ca. 350 mg/I for tints such as orange or red. At such levels, acrylics cannot compete and it is necessary to use reactive diluents that are very expensive and also reduce pot life. Reduced hardness and chemical resistance also result. Polyesters have a promising future in the field of high solids coatings.

Today, in the two-component water based system, the best results are obtained with acrylics but adding polyesters enables their properties to be improved.

Of course, in the majority of polyurethane dispersions, a polyester with varying degrees of branching, which imparts a large part of the hardness and physical drying characteristics is used.

3. Automotive.

Nowadays, the automotive industry uses a large tonnage of polyester resins that can be found in the following types of paints:

- Primers
- Metallised opaque and pearl coats
- Pigmented finishes and varnishes

(i) Car primer surfacer.

For economic reasons and above all for mechanical properties, polyester resins are predominantly used. A primer surfacer for car paint systems is applied on top of a cathodically deposited primer and may be covered by a metallised base and finishing varnish. This layer, therefore, ensures cohesion of the unit and imparts most of the mechanical properties. For example, when the birds' droppings resistance test is carried out on car coats, a varnish or a topcoat system has no influence on the result, because this is a mechanical problem and not a physical attack. Indeed, at high temperatures, the droppings adhere to the softened coat and during the drying process, lead to the mechanical contraction of the film. If the sealer cannot absorb the strains imposed on the system, the layer of paint will be stripped off down to the primer or even the electrodeposited coating layer. For grit resistance, the principal remains the same, as the primer will absorb the impact of grits and ensure that there is no detachment of the coating. Finally, this primer has a direct action on the appearance of the vehicle as it also serves as a leveller.

The better the appearance of the primer, the better the appearance of the finish which is applied afterwards. Thus as can be seen, a primer has an essential role to play and it is common to see up to three different polyesters in a formulation in order to meet different and often contradictory requirements. Sometimes polyesters are found with extreme flexibility based upon very long chain diacids or urethane modified polyesters in order to improve the appearance as well as self-crosslinking polyesters which impart chemical, adhesion and grit resistance. These products are evolving towards polyesters with higher non-volatile contents, which will impart body, and increasingly flexible products enabling the amount of blocked isocyanate in the formulation to be reduced.

Water-dilutable (water reducible) formulations which are being developed, use polyesters in two ways:

- Using water-dilutable polyesters, modified by a fatty chain acid, which assist in obtaining hardness, appearance and ease of application.

- Blending polyester with polyurethane dispersions, which are nowadays indispensable in water-dilutable primer formulations and which, due to the use of polyesters as the basic structure, (in combination with the correct diisocyanate) imparts mechanical properties.

Polyesters or hybrid polyester/acrylic systems (70/30) are used m automobile primers especially m the USA where more than two million vehicles per year (lorries and cars) are produced.

(ii) Metallised opaque and pearlescent coats.

Polyesters play an important role in these complex formulations. In most cases, these polyesters have a large degree of linear structure in order to impart maximum flexibility to the film and aluminium placement or rather metallic effect. SCA (sagging control agents) polyesters have also become indispensable so as to bring a certain rheology to the system that relies on the application and stability of the base and also on its appearance.

(iii) Pigmented finishes and varnishes.

For one coat pigmented finishes, which are most often white, red or black, polyester resins are still used but in significantly smaller amounts than previously because of the smaller demand for these systems. Instead, the use of bi-layer systems is increasing. They include metallised base plus finishing varnish because of the progress in specifications which has improved in terms of exterior resistance for car paints as well as better tint stability.

Acrylics have come into this sector bringing with them improved exterior resistance and a higher gloss although the appearance, build and mechanical properties are not the same, being inferior. All this is available at an equivalent cost. Today, new polyesters are appearing on the market with improved exterior resistance and also increased non-volatile content. It has also been observed that when gas ovens are used, acrylics give coatings with less yellowing in the oven than with polyesters.

For finishing varnishes which are applied to metallised or opaque bases, a large proportion of polyester resins are used, especially in two component varnishes or they can be used in combination with acrylic resins. Here, they improve film build and especially scratch resistance by softening the film and give a very high level of general mechanical properties. In one component varnishes, they are sometimes used in small amounts in order to impart resistance towards scratches and friction due to cleaning brushes (car wash). Their structure must be aromatic-free and relatively linear. This is why their use is limited since they reduce hardness and chemical resistance and remain slightly more expensive than traditional acrylics.

4. Powders.

In this field, polyester resins represent the predominant chemistry (with epoxy resins) and this chemistry is used with different crosslinking agents for many varied applications. They can be found in automobiles, aviation, transport material, renovation and metal supplies as well as for various machines and equipment, coil and metal containers.

Today, several types of polyesters for powder coatings can be identified as a function of their crosslinking mechanism.

- High acid value polyester (30 to 60 mg KOH/g) for crosslinking with an epoxide resin with EEW = ca. 700.
- Hydroxylated polyester for crosslinking with blocked polyisocyanates.
- Polyesters for crosslinking with amine compounds such as Primid, PT 9 10, or even the most well known TGIC
- Carboxylated polyester for crosslinking with an acrylic resin containing epoxide groups.
- Thermoplastic polyesters.

(i) Acid functional polyesters.

Acid functional polyesters primarily react and crosslink with solid epoxy resins. These are termed hybrid systems or carboxyl systems. With the all-epoxy systems, these are the two systems with the largest volume. In powder coatings, the polyester-epoxy ratio varies between 50/50 and 70/30. The greater the polyester portion, the better its exterior resistance.

Acid value is an essential characteristic of the polyester. Its acid value influences its reactivity towards epoxy resins which are most often a type 3 or even 2. The higher the acid value, the greater the reactivity of the polyester.

However, different catalysts with their different chemistries are used in order to regulate this since too high a reactivity of the system reduces the appearance. The coating must flow to form a level film before crosslinking, otherwise the surface is very uneven when cured. These polyester resins use linear structures such as terephthalic or isophthalic acid and some triacids such as trimellitic anhydride that can be used in two ways in order to utilise its third acidic function.

However, with small amounts of TMA present in the monomer composition, the flexibility of the polyester can be modified at will depending on the desired application, by replacing for example NPG, which is often used, by hexanediol or adipic acid. By varying the quantity of diacids, the exterior resistance of the polyester can be increased which will further increase, the more there is in the formulation.

By reducing the level of branching (tri-dimensional structure) and by reducing the molecular weight, the paint flow can be significantly improved as well as its reactivity. The cyclic structures, which are discussed in the section on side reactions in polycondensation, are responsible, in some cases, for the undesirable blooming effect. Today, it is possible to guarantee resins without this effect that detracts from the appearance of the paint.

Increasing the T_g, of the resins, by as much as 50'C, significantly improves stability.

A standard average paint formulation of a hybrid system comprises 60-62 % of resin (polyester + epoxy), 37-38 % of pigments and fillers, 0.7-1.2 % of surface tension modifier (flow additive) and 1% of other additives such as benzoin.

(ii) Hydroxyl functional polyesters.

Hydroxylated polyesters are cross-linked with polyisocyanates. These isocyanates can be either blocked by a blocking agent that is often caprolactam, or else they can be polyisocyanate dimers, tenned uretidiones. Consult Waterborne and Solvent Based Surface Coatings Resins, Volume 3, Chapter 1, for further details.

The polyester resins used include polyols that are partially trifunctional in order to increase the excess of hydroxyl functionality. This hydroxyl value varies between 40 to 60 mg KOH/g. In particular applications such as for anti-graffiti paints, polyesters with hydroxyl values of 100 to 300 mg KOH/g are used in order to obtain a very densely cross-linked network which gives protection from chemical attack by inks or aerosol paints. These coatings are also resistant to scratches. Often trimethylolpropane is used as the triol. Terephthalic acid is often used with flexible diacids such as adipic acid. Polyisocyanates dimers have less reactivity than caprolactam blocked isocyanates, but they do not release volatile agents during curing. The films obtained in general have excellent resistance towards ageing but still remain rather expensive compared with other systems. The usual ratios of polyester to isocyanate crosslinker vary from 70/30 to 85/15 for traditional systems, but for polyesters with high hydroxyl values, this can be as high as 30/70.

(iii) TGIC cured systems.

Another well-known powder coating system is polyester/TGIC (triglycidyl isocyanurate). As with hydride systems, there are many varied polyester systems available that enable coating systems to be formulated for a wide range of requirements:

- Changing the acid value enables crosslinking to be carried out at temperatures from 30° at 140°C to 10’ at 200°C.
- Ratios with TGIC which vary between 7 to 4 % for the more economical systems.
- Systems without blooming.

Systems with very good exterior resistance (super durable).

- Systems for mar resistant paints. o

C

The use of TGIC enables one to achieve good exterior resistance due to its absence of aromatic structures, resistance to UV combined with excellent mechanical performances. It is a product today which tends to be replaced by other polyamines that are not as toxic as TGIC. Examples are principally Primid (EMS), Araldite PT 910 (CIBA) as alterative for TGIC.

(iv) UV curable powders.

In the very popular UV powder systems of today, there are semi-crystalline or crystalline polyesters that are modified in order to have double bonds available for UV crosslinking at a later stage. Here, it is necessary to melt the powder by infrared radiation to ensure flow, before crosslinking in the presence of a photo-initiator.

(v) Miscellaneous.

In very marginal applications, carboxylated polyesters can be used to crosslink modified acrylic resins with non-aromatic epoxide groups.

As can be seen, the diversity of monomers for polyesters is well exploited in powders as well as the diversity of crosslinking. There are numerous uses and in terms of mechanical properties, the significantly more expensive acrylics have difficulty in providing similar properties.

III RAW MATERIALS:

powder coatings and some fibres.

As will be seen, chemists formulating polyester resins have a significant number of (C) Terephthalic acid (TPA).

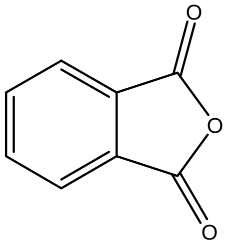
basic materials with which an infinite number of possible formulations can be envisaged. However, the resin must meet the requirements of the final user. It is, hence, important to know (or at least to try and know) the influence of both the composition and structure on its properties. This remains the eternal problem to be resolved and this distinguishes between a good and a poor formulator.

1. POLYACIDS

(i) Phthalic acids.

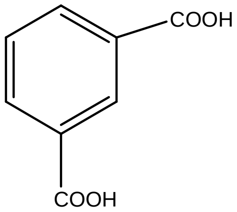
There are three acids in this category, namely phthalic anhydride, isophthalic acid and terephthalic acid. They all have important, but different characteristics when used to formulate polyester resins.

(a) Phthalic anhydride



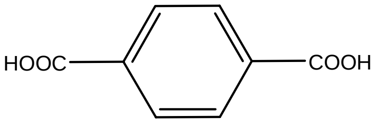
As for alkyd resins, phthalic anhydride is frequently used where cost and not performance is the overriding factor. The use of PA in polyesters is restricted. Its mechanical properties are rather limited and its exterior resistance is rather poor. In terms of its general properties, it is considered to be a bottom of the range product and it is not recommended for exterior or high performance coatings.

(b) Isophthalic acid



IPA enables the mechanical properties, chemical resistance and hardness to be significantly improved compared to those obtained by using PA. IPA also imparts some degree of physical drying. IPA is less reactive than PA and it gives resins that are slightly less soluble. However, IPA remains one of the key products for polyester resins for surface coatings. With its higher melting point, it leads to longer reaction times and is slightly more difficult to use. It is also used in polyesters for powder coatings and some fibres.

(c) Terephthalic acid



TPA further increases the heat resistance and mechanical properties of polyesters compared to either PA or IPA, but it also reduces the solubility of resins containing it and has a strong tendency towards crystallisation. In fact, TPA has to be mixed with IPA to ensure solubility in the solvents commonly used for surface coatings. TPA is less reactive than IPA and requires higher reaction temperatures and the use of catalysts.

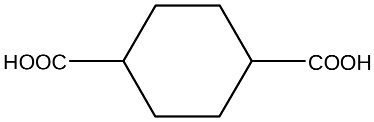
In Table 3-2, the properties of polyesters prepared from two diols (NPG + TW) and the three phthalic acids outlined above, are compared.

TABLE 3-2: COMPARISON OF MELTING POINT AND HARDNESS OF THREE POLYESTERS BASED ON DIFFERENT PHTHALIC ACIDS

Phthalic acid used	**Melting point**	**Erichsen value**
phthalic anhydride	70°C	2 mm
isophthalic acid	85°C	6 mm
terephthalic acid	100°C	10 mm

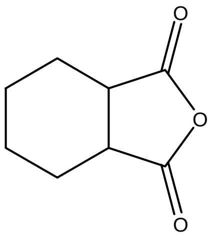
The use of the anhydride leads to angular chains, with a relatively low softening temperature and poor flexibility. Using isophthalic acid opens out the structure, which increases the melting point and improves flexibility. With terephthalic acid, a linear configuration is obtained, with extreme elasticity and a high melting point. The melting point is particularly important in the case of powder coating resins or those polyesters that are produced as a solid, prior to subsequent fragmentation (crushing or grinding) into powder. The more linear a product, the greater its tendency to crystallise and the lower its solubility in different solvents.

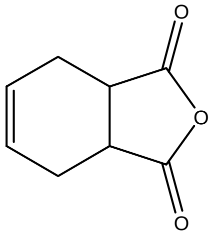
(ii) Cyclohexane dicarboxylic acid (CHDA).



This diacid, as with its diol Homologue, CHDM, represents an excellent compromise between hardness and flexibility. Corrosion resistance is better than with linear polyacids. Exterior resistance is also better than that from aromatic compounds or aliphatic/aromatic mixtures used for establishing the best compromise between hardness and flexibility. It has good solubility in most of the liquid diols used and its reactivity is quite good. It has poor dilution characteristics in solvents. Its thermal resistance is good and the ranges of colours of the resins obtained are good due mainly to its symmetrical structure.

(iii) Hexahydrophthalic and tetrahydrophthalic anhydride





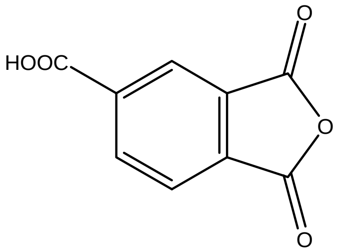
Hexahydrophthalic anhydrite is used when a very high resistance at hydrolysis and excellent yellowing and external resistance is required. However it’s expensive and is only used where its benefits justify the extra cost, such as water dilutable products, which require excellent hydrolytic: stability, or for automobile coatings which need good colour and light stability, such as white topcoats. Tetrahydrophthalic is also quite stable towards hydrolysis but is more sensitive to yellowing. This is a slightly lower cost option than using HHPA.

(iv) Isononanoic and isooctanoic acid.

These monoacids used to modify stoving finish polyesters in order, to impart certain fatty chain characteristics without the problems associated with unsaturated fatty acids, notably yellowing.

They impart excellent flexibility, limit chain length and lead to a high wetting ability for the polyester. Moreover, they improve the appearance of stoving finishes due to their fatty acid qualities.

(v) Trimellitic anhydride



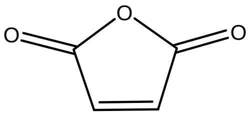
This anhydride is a trifunctional polyacid that can be used in two ways. Either, the three acid functions are reacted and the functionality of the system is increased without significantly increasing the viscosity and the molecular weight of the polyester.

In this case, it is added at the beginning of the synthesis. Or, only the first two acid functions are reacted, whilst one is kept for neutralisation at a later stage by an amine in order to form a water dispersible polyester.

In this case, TMA is added during the second phase of the condensation.

This product, like many anhydrides, is sensitive to humidity and needs to be appropriately packaged to avoid this. There are health risks associated with the handling and use of TMA. The appropriate precautions recommended by the suppliers of TMA must be strictly followed.

(vi) Maleic anhydride (MA).



Maleic anhydride can be used in powder coating polyesters for ultraviolet crosslinking technology.

The anhydride function is used for a condensation with diols and the double bond is retained in the resin which can then crosslink initiated by a UV initiator in the presence of other UV curable materials.

It is also responsible for secondary reactions during polyesterification.

Two polyester chains containing MA double bonds have difficulty in copolymerising.

Maleic anhydride has a functionality of 3 and not 2, if the functionality of the double bond is considered However for functionality calculations the functionality of MA is 2.

(vii) Linear Diacids.

Many linear diacids are available in order to provide varying size aliphatic chains for the polyester structure. The greater the number of carbons in the chain, the greater the flexibility, but the lower the hardness. The following are the most frequently used products :

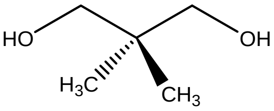
Adipic acid: $HOOC - (CH_2)_4 - COOH$
Azelaic acid: $HOOC - (CH_2)_7 - COOH$
Dodecanedioic acid: $HOOC - (CH_2)_{10} - COOH$

Adipic acid is one of the most frequently used linear diacids since it gives an excellent compromise in terms of technical performance and price.
Diacids with much longer chains are significantly more expensive, thus they are limited to specific applications.
They are used for their extremely good mechanical qualities such as their resistance towards gritting or elongation. They are also used in the fibre industry. They also improve the durability of films.

In order to find polyacids which can lead to extreme flexibility, saturated fatty acid dimers are also used in polyester preparations, which contain practically no double bonds, and which can be used sparingly since they lead to a significant drop in the level of hardness. These are in particular Pripols or equivalent products resulting from Diels Alder reactions.

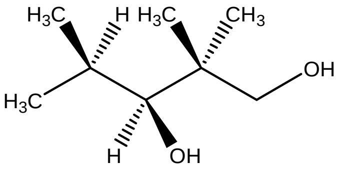
2. POLYOLS.

(i) Neopentylglycol NPG.



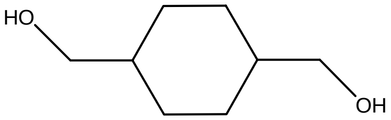
NPG has no labile β hydrogen with respect to the hydroxyl functionality, which leads to its excellent exterior durability. Its two primary hydroxyl functions ensure good reactivity not only during condensation but also during subsequent crosslinking.
The two methyl groups increase the steric hindrance that imparts chemical resistance, stability towards hydrolysis and corrosion resistance.
Its symmetrical structure improves the thermal stability of resins containing NPO and can give resins with low colour, high T_g and with low viscosity.
Moreover, these methyl groups prevent the chains from being too close to one another and, hence, as a consequence, improve the solubility of the prepared polyester.
However, during production, it is readily distilled with the water of reaction and such losses, which may significantly affect the polyester structure, must be monitored and glycol corrections must be made, unless a sufficient excess of NPG to allow for losses is added at the start of the reaction.

(ii) Trimethylpentanediol TMPD.



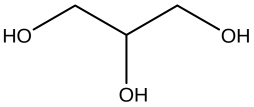
With an asymmetric structure, TMPD enables the preparation of polyester resins of low density and viscosity. Viscosity is improved compared with NPG. The hydroxyl groups are significantly hindered, which leads to corrosion and chemical resistance but this also results in lower reactivity compared with NPG. Moreover, the hardness obtained is lower than that with NPG. Exterior resistance is also lower due to the presence of β hydrogens. This polyol also leads to an extra colouration of the resin of 1 to 2 points. It enables an improvement in adhesion compared with HPHP.

(iii) Cyclohexanedimethylol CHDM.



The presence of two primary hydroxyl functions gives excellent reactivity during esterification and crosslinking. Moreover, these functions are not at all hindered. The symmetrical structure leads to thermal stability and low coloration during curing. The cycloaliphatic; structure represents par excellence a compromise between hardness and flexibility. The 1,4 position strongly influences the T, of the resin and lowers the solubility of the polymer. The presence of labile P hydrogens imparts moderate exterior durability, even though the cyclohexyl ring is completely saturated.

(iv) Glycerol

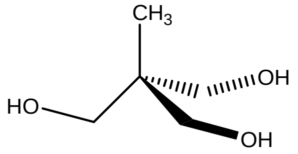


This trifunctional polyester is not frequently used in polyester resins since it leads to a *high density* of crosslinking even though it is not always easy to react the central secondary hydroxyl function. If the latter is available for crosslinking at a later stage, it can only react with difficulty. In polyesters, trimethylolpropane is preferred to glycerol. Some of the disadvantages of using glycerol were discussed in Ch. 2, but as a generalisation glycerol containing polyesters are not as clean as other based upon alterative polyols, such as TMP.

(v) Trimethylolpropane TMP.

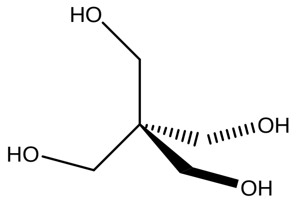
Trimethylolpropane has three primary hydroxyl functions which gives better reactivity than glycerol. Compared with glycerol, it gives resins with a lower viscosity. The exterior durability of coatings based on polyesters with this polyol is also improved because there is no labile β hydrogen in TMP.

(vi) Trimethylolethane TME.



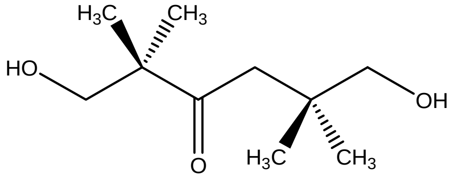
TME has very similar properties to those of TMP and is more frequently used in the USA where its price is competitive to that of TMP, which is not the case in Europe. It gives a slight improvement in polyester thermal resistance compared with TMP.

(vii) Pentaerythritol PENTA.



With its high level of functionality (4 primary hydroxyl groups) pentaerythritol is little used in polyester resins since this gives resins with too much functionality and very high viscosities. As explained in Chapter 11, its main use is in long oil alkyd resins where it imparts excellent durability to the coatings obtained as well as high reactivity.

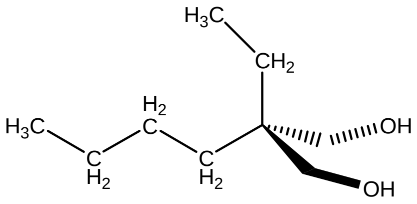
(viii) Hydroxypiralyl hydropivalate HPHP.



The absence of labile hydrogens P to the hydroxyl groups enables excellent exterior resistance to be obtained from resins based upon HPHP. The presence of two readily accessible end-of-chain primary hydroxyl groups leads to excellent reactivity and low coloration of the resulting resin.

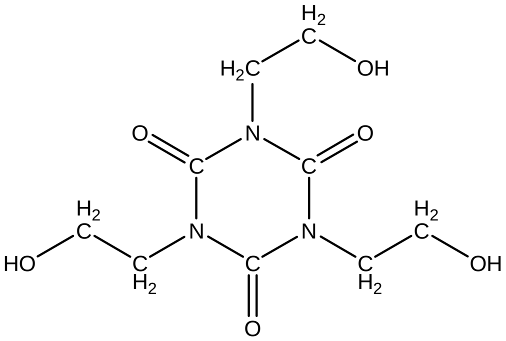
Steric hindrance, from the methyl groups, stabilises the structure and imparts good corrosion, chemical and hydrolysis resistance. The molecular weight of this diol is rather high leading to a reduction in aromatic compound content. required, hence increasing the flexibility of the system and its exterior durability.

(ix) 2 butyl-2-effly1-1,3-propanedioi BEPD.



BEPD reduces the viscosity of the system, whilst improving its solubility parameters and reducing the density of the resin. The absence of a labile β hydrogen that leads to good exterior resistance should be noted. The primary nature of the two hydroxyl functions should lead to good reactivity, but, during synthesis, it is not always the case and it is necessary to work at a slightly higher temperature than usual in the presence of a catalyst. Moreover, higher than usual levels of coloration are obtained. The partial hindrance of the hydroxyl groups leads to good hydrolysis resistance as well as good chemical and corrosion resistance.

(x) Trihydroxyethyl-isocyanurate THEIC.

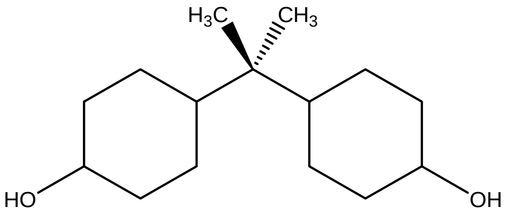


THEIC is a triol with a very stable isocyanate core. It is used to modify polyester resins in order to confer excellent heat resistance, such as in imide polyesters for wire enamels. It also leads to a high density of crosslinking as well as a good exterior resistance. The mechanical properties are also of interest.

(xi) CARDURA E10 or Glydexx N10.

This ester is in fact the glycidyl ester of versatic acid. When it is reacted with an acid during synthesis, a secondary hydroxyl functionality is formed, which can then condense as for other polyols. Its importance resides in the fact that it brings a false fatty chain to the polymer chain comprising ten carbons, but which are branched and spread over four carbons. One can thereby obtain excellent wetting characteristics towards pigments and fillers and a "fatty" effect for the topcoats. The presence of several labile hydrogens does not give it the best exterior resistance characteristics. The fatty chain gives the system a certain hydrophobic nature.

(xii) Hydrogenated bisphenol A.



This rather expensive diol in general imparts excellent solvent and chemic al resistance and does not reduce exterior resistance compared to aromatic compounds. Its reactivity is excellent due to two primary hydroxyl groups.

(xiii) Glycols.

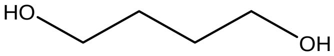
A large number of glycol compounds are available which may be used, including the following:

All these compounds contribute flexibility to the system although this is at the expense of hardness that drops very rapidly with increasing chain length of the glycol. The greater the increase in flexibility, the less the hardness. They remain relatively economic, at least for the first ones in the series. One needs to be aware of their water solubility and losses that can take place during the synthesis of the polyesters.

(a) 1,6 Hexanediol 1,6 HD.

This diol is an excellent monomer for obtaining flexible coatings with good impact resistance. It is used in applications that are demanding in terms of mechanical
characteristics since its cost remains high. In general, it is combined with isophthalic or terephthalic acid in order to compensate for the loss of hardness whilst maintaining a good level of flexibility.

(b) 1,4 Butanediol 1,4 BD.



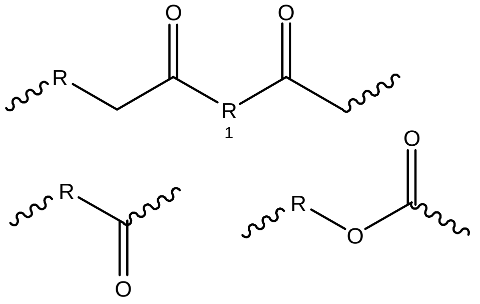
1,4 Butanediol is an alterative for 1,6 HD, but as seen in the side reactions section, this product can generate undesirable side reactions.
As an example, the influence of the polyester composition on the properties of a polyurethane film is compared in Table 3-3.

TABLE 3-3: COMPARISON OF THE EFFECT OF DIFFERENT
POLYESTER CONSTITUENTS ON THE PROPERTIES OF A POLYURETHANE

Polyester	**Phthalic**	**Adipic**	**Triol**	**Diol**	**Structure**		**Reaction Rate**	**Hardness**	**Resistance chemical Products**	**Temperature influence**
					Branched	**Rich in OH**	**Rapid**	**Hard**	**Resistance**	**Thermo Hardening**
A	+	+	+	-						
B	-	+	+	+						
C	-	+	+	+						
D	-	+	-	+						
					Linear	**Low in**	**Slow**	**Flexible**	**Swelling**	**Slight1y thermoplastic**

3. IMPORTANT CONSIDERATIONS FOR POLYESTER RESINS.

Polyesters can be defined as condensation polymers obtained by the esterification of polyols with polyacids. However, such a description is too restrictive since numerous other types of reactions exist which generate polyesters. Generally, a polyester is a polymer that contains ester functionality repeated in the polymer chain. Polyesters are linear if bifunctional molecules are used for the synthesis and are branched if at least one of the starting materials is at least trifunctional. For the nomenclature, the chemical term for the basic unit is used, as for example polyethyleneterephthalate or even poly (1,2 polypropylene adipate). When a polyester is synthesised from only two components, it may be considered as a homo-polyester whereas a co-polyester is obtained with at least two polyols or polyacids. The following structural units are characteristic of polyesters:



Research carried out by Carothers on linear polyesters (1928) and their synthesis enabled the general basis of polycondensation theory to be established and the relationship between the chemical structure and the properties of polyesters in the polymerised state. But, at the time these studies, linear polyesters had limited applications.

To obtain a good balance of the required properties, it is normal for the polyester to contain a mixture of aromatic and aliphatic diacids. Examples are adipic and terephthalic acid and a variation of triols in greater or lesser amounts in order slightly to increase the degree of branching of the polyester.

(i) Crystallisation.

A chemist working in the polyester field has a large range of raw materials at their disposal and one can imagine an infinite number of possible formulations. However, their selection must be able to meet the requirements of the paint formulator, who defines their needs in terms of application, mechanical properties etc. Therefore, before being able to produce a custom-built resin, the influence of the composition and the structure of the resin on the properties of the paint need to be known. This often remains the eternal problem to resolve. One of the critical characteristics of saturated polyesters, particularly of linear polyesters is their tendency towards crystallisation.

The crystalline state is not perfect and depending on the rate of crystallisation, different amorphous/crystalline ratios can be obtained. The crystalline form has a well-defined structure as shown by X-rays. For example, amorphous polyethylene terephthalate is soluble in phenols, cyelohexanone, dibutylphthalate and some polar or heterocyclic solvents; This brief description is useful for understanding polyester resins used in coatings.

A large number of low molecular weight linear and even branched polyesters crystallise at different rates ranging from a few minutes to a few months. The solution becomes cloudy and sometimes one can observe phase separation or the transformation of the resin solution into a hard non-transparent solid. Heating the crystallised resin, to 50-80°C, leads to a limpid solution. This propensity towards crystallisation is obviously an obstacle that needs studying in order 16-obviate it. Polyester resins with high melting points and glass transition temperatures, crystallise more readily, but many polyesters with soft consistency with a low melting point also display a distinct tendency to crystallise. Table 3-4 fists low molecular weight hydroxylated polyesters obtained from diols and diacids and their tendency towards crystallisation.

TABLE 3-4: TENDENCY OF SOME POLYESTERS BASED UPON DIFFERENT DIACIDS AND DIOLS TOWARDS CRYSTALLISATION.

Diols	**Diacid**	**Melting**	**Crystallisation**
Ethylene glycol	Terephthalic Acid	High T 260°C	Very rapid
Ethylene glycol	Isophthalic Acid	High T 240°C	slow
Ethylene glycol	Phthalic	Medium T 110°C	Very low
Ethylene glycol	Adipic Acid	Liquid	Rapid
1,2 Propylene glycol	Isophthalic Acid	Medium T	Very slow
1,2 Propylene glycol	Adipic Acid	Liquid	slow
1,5 Pentanedicil	Isophthalic Acid	Low T	Rapid
3 Methyl 1,5 Pentanediol	Isophthalic Acid	Low T	Absent
1,6 Hexanediol	Terephithalic Acid	Low T	Very rapid
1,6 Hexanediol	Isophthalic Acid	Low T	Absent
1,3 Propanediol	Terephthalic + Adipic acid	Low T	slow
1,3 Propanediol	Isophthalic + Adipic acid	Low T	Absent

Even a superficial examination of this table will show that crystallisation is favoured by a symmetrical structure. Hence to prevent this, it is necessary to break this symmetry by the use of a diol or a suitable diacid.

Here are a few rules resulting from practical studies carried out on polyester fibres.

The melting points of aromatic diacid polyesters are higher than those of aliphatic diacid polyesters. They decrease in the order:

Terephthalic > Isophthalic > Orthophthalic acid.

Aromatic diols have a similar influence on crystallisation. Cycloaliphatic structures have higher melting points than aliphatic structures. Dimethylolcyclohexane yields, for example, polyesters with higher melting points than those containing neopentylglycol.

(ii) Glass transition temperatures T_g.

Short aliphatic chains yield products with higher glass transition temperatures than long chains, and an even number of - CH_2 - groups in the diacid leads to higher melting points than those of products with an odd number of - CH_2 - groups.

The glass transition temperature (T_g changes in the same direction as the melting point. The T_g, is a characteristic property of a polymer. It is generally accepted that the melting point is 1.7 times greater than the T_g.

(iii) General properties.

The hydrolytic stability of aromatic diacid polyesters is higher than that of aliphatic diacid products. Moving from a diol to a triol, has minimal influence, but substitution in the chain has a favourable effect (as with NPG). Cycloaliphatic diols lead to polyesters with good resistance towards hydrolysis.
Chemical resistance is generally a function of the crosslinking density. Thermal stability is poor for long aliphatic chains. On the other hand, it is high for aromatic chains and increases when replacing Orthophthalic by terephthalic acid.
The mechanical properties are a function of the resin composition, its structure and its molecular weight. They can be predicted with rather good precision for polyesters with similar molecular weights and structures. The aliphatic constituents confer better flexibility, but hardness is reduced. Generally, high molecular weights lead to improved properties.

A polyester resin is characterised by its acid and hydroxyl values. The hydroxyl value enables one to calculate the quantity of crosslinking agent to use (such as a polyisocyanate for example).
Solubility in different solvents is a very important characteristic as well as their compatibility with crosslinking agents, such as melamine, formaldehyde resins. Polyesters are generally soluble in aromatic hydrocarbons and polar solvents. Their molecular weights and the molecular weight distribution are very important data since they enable one to know how the polymer was formed and to relate them to mechanical characteristics.

4. PREPARATION OF POLYESTER RESINS.

All of the known esterification methods can lead to the synthesis of polyesters. Some specified reactions that do not have an equivalent in simple ester chemistry can also be used for polyester synthesis.

(i) Direct esterification.

One of the most important routes goes via the direct esterification of diols and diacids. An excess of diol leads to linear polyesters of low molecular weight with hydroxyl functionality.

By varying the hydroxyl excess, the molecular weight of the polyester can be adjusted. When using equimolar quantities of reactants, a high molecular weight polyester can be obtained.

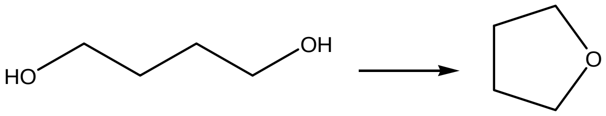
$$OH – R – OH + HOOC – R' – COOH \rightarrow HO – R – O – CO – R' – COOH + H_2O$$

The imbalance in the molar ratio due to inexact weighing and, above all, due to the loss of volatile components (such as neopentylglycol) leads to polyesters with terminal carboxylic or hydroxyl groups which, therefore, limit the molecular weight. If the synthesis is carried out in one step, it is difficult to control the molecular weight and, hence, the properties of the polyester. For example, in the synthesis of high molecular weight polyethyleneterephthalate, a two step technique is used. In the first step (the esterification), a di-hydroxyl-diester is obtained in the presence of a large excess of glycol.

$$2OH – R – OH + HOOC – R' – COOH \rightarrow HO – R – O – CO – R' – CO – R – OH + 2H_2O$$

The second step, alcoholysis, is carried out at high temperatures (280°C) with a high vacuum. This alcoholysis or esterification process enables one to obtain a high molecular weight polymer with the excess glycol being separated by distillation. One necessary condition for the reaction to proceed to completion is a volatile diol. The other method, which is acidolysis, (corresponding to an excess of diacids) is not applicable here since diacids are insufficiently volatile.

The direct esterification of polyols by polyacids (one or two step process) is a general method for the synthesis of polyesters, whether they are liquid or in powder form. In this type of synthesis all the diacids which can de-carboxylate are to be avoided as well as diols with tertiary hydroxyls which can dehydrate, diphenols of too low reactivity and some short chain diols which can crystallize (1,4 butanediol + isophthalic acid) or which can generate tetrahydrofuran. The formation of tetrahydrofuran from 1,4 butanediol can readily occur.



Theoretically, a reaction, between stable diols and diacids, only gives linear polyesters with terminal hydroxyl functions. However, there are secondary reactions and the choice of catalyst can be important in order to minimize these. The formation of a certain proportion of ether linkages depends upon the propensity of the diol to form this type of bond. Another secondary reaction consists of an anhydride formation within the chain leading to its rupture.

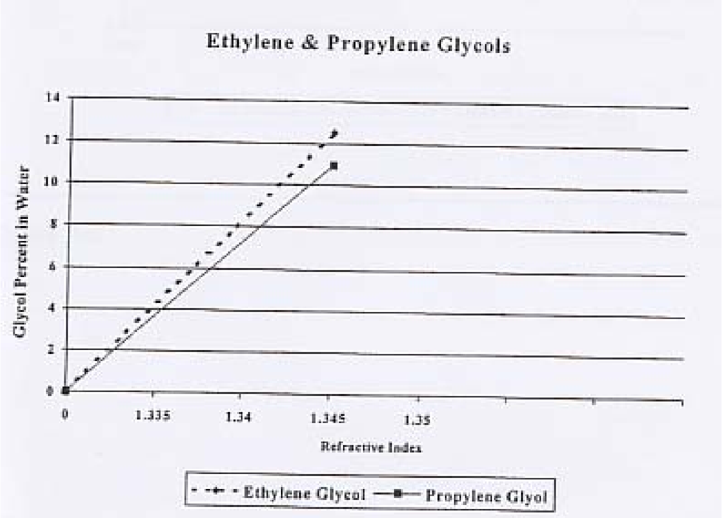
Some thermal decomposition is also inevitable and this leads to the formation of aceto-aldehydes in small quantities during the polycondensation reaction. Moreover at the same time cyclic polyesters are also formed (up to 1.5 % in polyethyleneterephthalate). These cyclic structures are also found in powder polyesters that are prepared from terephthalic acid and neopentylglycol. Such structures are formed between these two compounds, even in small quantities, and they are responsible for the undesirable blooming effect observed in powder coatings. In low molecular weight polyesters, the cyclic fraction can be significant, which lowers the hydroxyl value of the polyester and, hence, the solvent resistance of the film.

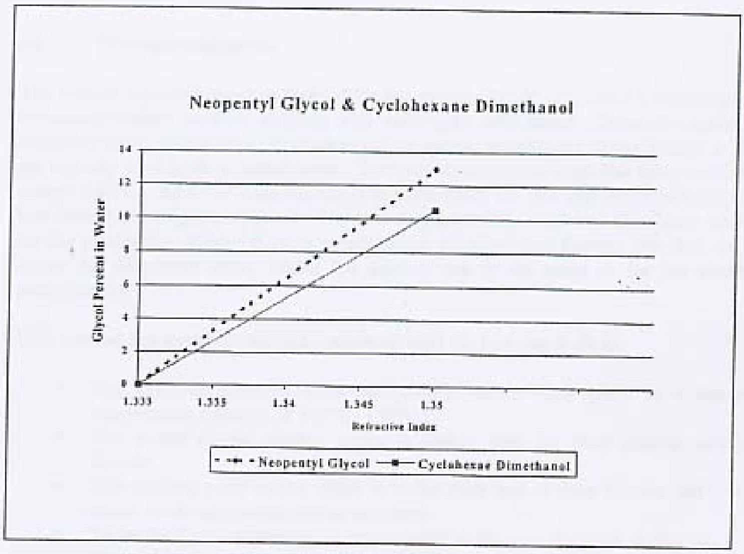
During the preparation of a Polyester using diols such as trimethylolpropane, and especially neopentylglycol, a significant loss of polyol can occur. This will disrupt the structure of the resin if the amount lost cannot be determined and compensation additions made. It is normal to use a packed column for maximum. Separation of the diol vapors that have been carried over with the water of reaction to minimize polyol losses, but there are losses all the same.

It is possible to determine the amount of polyol lost by measuring how much is in the water obtained from the esterification reaction. This water is collected in a Dean and Stark receiver. By measuring the refractive index of the water polyol mixture, the amount of polyol present in the water can be estimated and, since the quantity of water recovered is known, the quantity of polyol lost can also be calculated. This should not exceed 10 % of the initial quantity (which means that the temperature at the top of the cooling column should never exceed 105°C) of polyol in the formula.

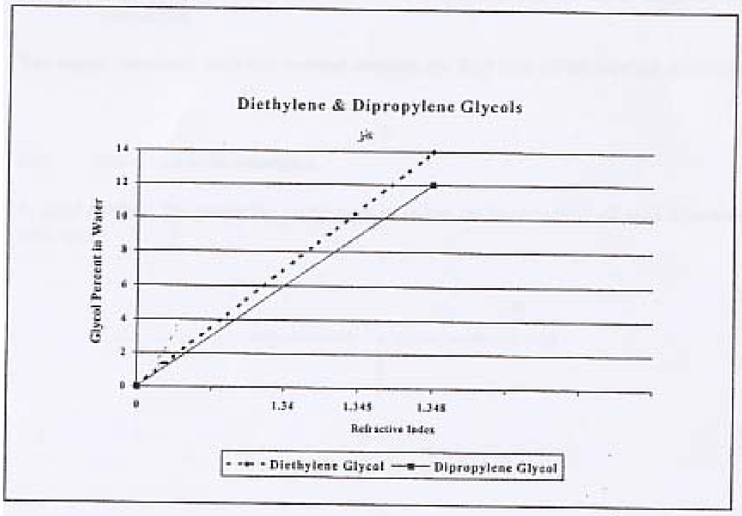
Levels above this mean that the plant is not suitable for the manufacture of polyester resins. Below this value, one can compensate during production by the addition of polyols. Tables and graphs of refractive indices for different polyol water mixtures are available. Figures 3-1 to 3-4 reproduced from the Amoco technical literature shows different refractive indices in water for different polyols. The common polyols that present most glycol loss problems include ethylene, propylene and neopentylglycol. Consider as an example neopentylglycol. If the refractive index of the water, glycol mixture in the receiver is 1.346, then it means that the water contains 6% NPG. If the total weight of water collected is known then the total amount of NPG lost is also known. For example, 100 kg of water containing NPG with a refractive index 1.346, means that 6 Kg of NPG has been lost. Depending upon the initial glycol excess used, it may be necessary to add a further 6Kg of NPG to compensate for these losses. It is much more difficult to estimate losses when a mixture of volatile polyols is used.

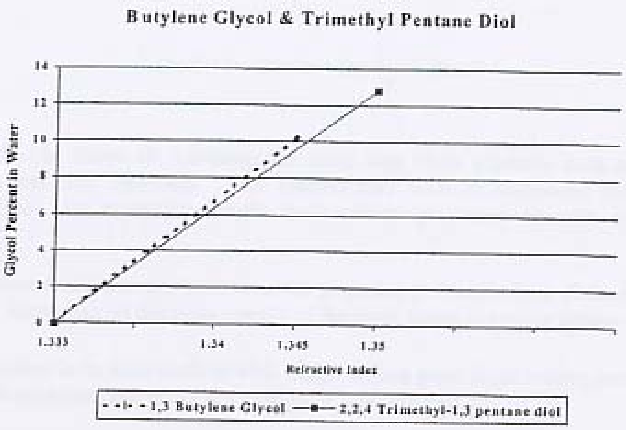
Figures 3-1 to 3-4, Refractive index of various polyols in water, in order to estimate glycol losses





Figures 3-2 & 3-3





(ii) Transesterification.

The second equally important method for the preparation of polyesters is based on a transesterification reaction of diols with carboxylic acid esters. Generally methyl esters are used. In the case of powder coating resins, terephthalic or isophthalic acid are directly used in their liquid form. The polycondensation reactions take place at around 280°C. As is the case for direct esterification, the one step reaction leads to low molecular weight polyesters. The two step process is exploited on a large scale for the production of polyethyleneterephthalate for fibres and sheets. The first step forms the dihydroxyl ester, whilst the second step is the same as for the direct esterification.

This method has some advantages compared with the first one such as:

- The reaction between diols and dialkyl esters takes place at a lower temperature (starting at 140°C-150°C).
- The purity of the methyl esters is higher than for their corresponding diacids.
- The melting point of the esters is lower than that of their diacids and it is easier to obtain homogeneous n-mixtures.
- There are fewer secondary reactions such as the etherification of polyols.
- Diols of low reactivity and of low stability can be used (such as phenols).
- Diols that are able to form cyclic structures can be used, such as 1,4 butanediol.

The major drawback with this method remains the high cost of the starting materials.

(iii) Diols and acid chiorides.

A third method for preparing polyesters is based on the reaction of acid chlorides with diols.

$$\mathrm{OH-R-OH} \;+\; \mathrm{ClOC-R'-COCl} \;\rightarrow\; \mathrm{HO-R-O-CO-R'-COCl} \;+\; \mathrm{HCl}$$

This method is, above all, advantageous when long chain aliphatic diols are used with low reactivity biphenols. This method also leads to sequenced polyesters starting from low molecular weight hydroxylated polyesters or even alternate polyesters.

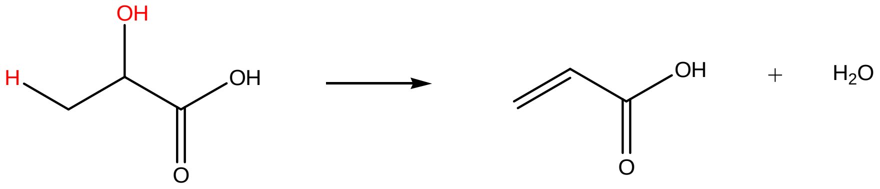
Various other techniques can be utilised for preparing polyesters from diols and acid chlorides, depending on the requirements of the resin. Some examples follow:

(a) Reaction in an inert medium with a high boiling point (high boiling point hydrocarbons) and under dry nitrogen to eliminate HCI.
(b) Reaction in an organic solvent in the presence of tertiary amines (pyridine or dimethylaniline) which absorb any acid generated.
(c) In some cases, an interfacial polycondensation can be used, for example diphenols in aqueous alkaline solution and diacid chlorides in solvents such as methylene chloride or toluene react rapidly at ambient temperature with vigorous agitation to convert the dispersion from the water immiscible phase into fine droplets.

Interfacial polycondensation also leads to polyamides (nylons). However, this technique is used for the preparation of special linear polyesters. The polycarbonates possess within the structure the carbonate group.

(iv) Self-esterification.

The self-esterification of hydroxyacids is a fourth method for the preparation of polyesters. This reaction requires a high temperature, up to 250'C, and is often carried out at reduced pressure. In many cases, this method cannot be used since dehydration or cyclisation problems interfere with the esterification reaction. Lactic acid, for example, can be transformed into acrylic acid.



Short chain hydroxyacids can easily cyclize forming lactones.

(v) Polyesters from lactones.

Lactones constitute the basis of a fifth method for the preparation of polyesters by a ring opening reaction of a lactone. These are reactions that are readily carried out in the presence of catalysts such as inorganic acids or Friedel Crafts complexes. The possibility of the lactone polymerising depends upon the number of carbons forming the ring.

Resins for powder coatings are manufactured at high temperatures in bulk without solvent. At the end of the synthesis, they are cooled and ground into flakes. Very often, terephthalic acid can be found as a major diacid due to its excellent mechanical properties. As a generalisation, formulations are similar to products in solution except that the final characteristics and the molecular weights are adapted for the relevant crosslinked systems mentioned above (high acid value, low OH value etc).

5. DIFFERENT POLYESTER CROSSLINKING MECHANISMS.

The formation of a paint film based on a polyester resin implies that it must be crosslinked or hardened with an external crosslinking agent. Indeed, polyester resins do not have sufficient film-forming properties except for thermoplastic polyesters. In the latter case, the general properties are rarely good enough for most applications.

The different chemical functions available within the polyester resin can be used as discussed below.

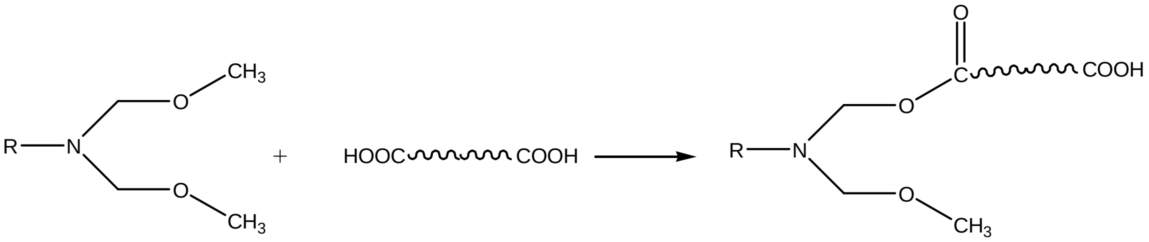
- Crosslinking through acid functionality.
- Crosslinking through hydroxyl functionality

(i) Crosslinking through carboxylic groups.

(a) With an etherified melamine formaldehyde resin.

A melamine formaldehyde resin is a member of the aminoplast family, which encompasses urea formaldehyde and benzoguanamine formaldehyde resins that act as crosslinking agent.

At a temperature above 120°C, the following reaction is observed:



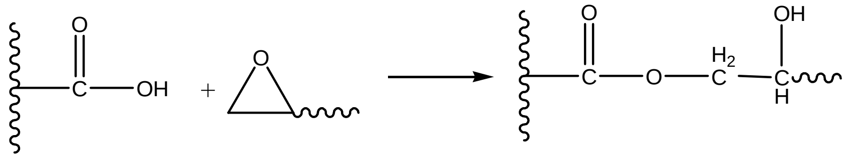
This reaction continues until a hard, completely crosslinked film is obtained. The ratios of polyesters and aminoplast resin vary within the range 60/40 to 80/20 depending upon temperature, nature of melamine resin and the final characteristics of the paint required. Resins of the hexamethoxymelamine type are used for temperatures starting from 150°C otherwise methylated, butylated or isobutylated formaldehyde resins can also be used.

It should be noted that normally this reaction is not designed into polyesters, with the more traditional hydroxyl aminoplast reactions predominating.

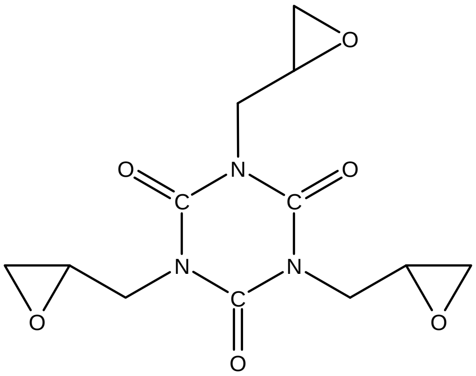
(b) With an epoxide resin.

This reaction is extensively used in powder coatings, more particularly in hybrid systems that are carboxyl functional polyester systems with epoxy resins, often of the type 3 variety, in ratios varying between 50\50 to 70\30.

The following reaction takes place:



By selecting suitable constituents so that they have, amongst other properties appropriate melting points, it is possible to produce powder coatings. The higher the acid value of die polyester resin, the greater the potential amount of epoxy resin in the polyester/epoxide mixture. A very well known epoxy hardener in powder coatings is TGIC (triglycidicisocyanuric acid ester).



The polyester/TGIC mixture is in a ca. 95/5 to 93/7 ratio and curing is carried out between 30 minutes at 140°C to 10 minutes at 200°C. The coatings, prepared using this system, have excellent resistance to yellowing and weathering. This enables a long guarantee for exterior weathering.

There is a certain loss of elasticity over time, but with this system there is no loss of volatile organic compounds. TGIC is becoming subject to toxicological questions and its replacement is being urgently sought. This is also the case for economic reasons.

(ii) Reactions with the hydroxyl function.

(a) With an aminoplast (melamine formaldehyde or urea formaldehyde resins).

The hydroxyl functionality in a polyester resin can react with the ether linkages of the melamine resins through transetherification reactions that lead to the formation of volatile alcohols. This reaction is principally used in thermosetting liquid paints and is catalysed by acids such as para-toluene-sulphonic: acid. In water-dilutable polyesters there is a potential problem of interaction between neutralising amines and the acid used for catalysis. The neutralising agent may generate significant surface defects. For this reason special blocked catalysts have been developed - see Aminoplast book Vol. V p. 11 The Chemistry & Application of Amino-crosslinking Agents or Aminoplasts. SITA Technology, Edinburgh & London, 1998. ISBN 0471 978876.
The latter only unblock after the neutralising amine has evaporated, that is, normally above 120'C. For automobile primers, for example, for polyester crosslinking both a melamine resin, which may be a benzoguanamine, and a blocked polyisocyanate are used. This polyisocyanate is also capable of reacting with the melamine resin.

The curing temperatures range from 120°C to 160°C for polyester/melamine ratios varying between 60/40 to 90/10. These can be found in the majority of thermosetting liquid systems, particularly when their very good compromise between performance and cost price is considered.

(b) With a blocked polyisocyanate.

This system is particularly used in coil coating and automobile applications. It enables the hydroxyl functionality of a polyester to be crosslinked with a polyisocyanate using a single pack system. An example follows for a reaction in the range 140-180°C

Thereby, a polyurethane system. can be prepared which has storage stability and does not contain free polyisocyanate.
Crosslinking will only occur with a blocked polyisocyanate or with a mixed crosslinking system, such as melamine with a blocked polyisocyanate. The presence of urethane links enables the mechanical properties and exterior resistance to be improved when required. In liquid paints/coatings, the polyesters used have hydroxyl values of about 110 to 180 mg KOH/g, whereas in powder coatings, polyesters have a much lower hydroxyl content (ca. 40 to 110 mg KOH/g). The ratio of powder polyester / polyisocyanate varies from. 60/40 to 80/20 for temperatures of 20 minutes at 170°C to 10 minutes at 200°C. The blocked polyisocyanate are either:

- Blocked polyisocyanate, for example with caprolactam, which leads to the release during curing of this blocking agent.
- Uretidiones, which are in fact diisocyanate dimers (such as the dimer of IPDI), which in these cases does not lead to the release of volatile compounds.

(iii) With a polyisocyanate (two component system).

Today, two component polyurethanes are still made using polyester resins despite the ever increasing progress made in hydroxylated acrylic resins. The whole range of polyisocyanates described in the chapter on polyurethanes (Chapter 1, Volume III) can be used (Desmodur N, L, IL, BL, etc). The compounds obtained are called polyurethanes, although they contain more polyester linkages than urethanes

(iv) Use of a chelate.

This method of crosslinking involves the use of a pH sensitive chelate. When the pH falls during hardening, the chelate crosslinks the hydroxyl groups. This method is particularly applicable to water-dilutable polyesters using carboxylic groups for neutralisation and hence dilution in water. During the drying (film formation) phase, the neutralising amine evaporates and the pH falls drastically, thereby activating the chelate.

(v) Thermoplastic polyesters.

Finally, consider thermoplastic polyesters which do not possess a particular crosslinking system, but which form a film solely by physical drying due to their very high molecular weights. These very high molecular weights are obtained by significantly branching the resin during its production or by processing to very low hydroxyl and acid values, but the final film is not crosslinked by any of the methods described above. The mechanical properties are not normally as good and they cannot be exposed to too much light. Their adhesion to difficult substrates, such as on polystyrene or hi-fi's, can be very good. They remain difficult in terms of production because of their high viscosity and the processing required to obtain the necessary high molecular weights.

IV. EXAMPLES OF RESIN FORMULATIONS.

Example 3-1: POLYESTER FOR TWO COMPONENT POLYURETILANE PAINT FOR PLASTIC MATERIALS

Resin A:

Material	Weight %
Isophthalic acid	27.7
Adipic acid	24.3
Neopentylglycol	43.8
Trimethylolpropane	4.2
Total	100.0

Properties of resin

Water of reaction	11.8%
Acid value mg KOH/g	8
Hydroxyl value mg KOH/g	180
Gel acid value	75 mg KOH/g
Functionality	2.04
Patton Constant	1.178
Non-volatile content	70%
Gardner viscosity	E-F
Solvent	MEK - Ethylethoxypropionate 50/50
Gardner colour	< 1

Synthesis:
The synthesis is carried out by adding all the components at the start. The condensation is carried out at 230'C without azeotropic solvent.
The composition of the polyester uses two rather straightforward diols, to control the functionality which is near to 2 and, therefore, low, as well as isophthalic acid which will impart, as an aromatic diacid, the necessary chemical resistance and excellent mechanical properties (significantly better than those possible with Phthalic anhydride), whilst maintaining good UV resistance. On plastic it is important to have a coating which follows the deformations of the plastic. The high hydroxyl value gives high chemical resistance as well as a high exterior resistance. Generally, drying can be longer since it requires more crosslinking agent. Adipic acid is present to give the required balance between flexibility and hardness in the diacid components.

Example 3-2: POLYESTERS WITH HIGH NONVOLATILE CONTENT FOR THERMOSETTING STOVING FINISH TOPCOATS

(Taken from Amoco Chemical Company report N' IP47E)

Material	**Parts by weight**		
Polyesters	B	C	D
Isophthalic acid	23.6	27.7	24.6
Trimellitic anhydride	/	/	7.6
Adipic acid	20.7	24.3	21.6
Neopentylglycol	/	43.8	46.2
Trimethylpentanediol	52.1	/	/
Trimethylolpropane	3.6	4.2	/
Total	100.0	100.0	100.0

Equivalent acid ratios

Isophthalic acid	0.5	0.5	0.417
Trimellitic anhydride	\	\	0.166
Adipic acid	0.5	0.5	0.417

Equivalent polyol ratios

Neopentylglycol	/	0.9	1.0
Trimethylpentanediol	0.9	/	/
Trimethylolpropane	0.1	0.1	/

Properties of resins	A	B	C
Water of reaction	11.2	13.4	13.5
Acid value mg KOH/g	6.9	8.8	9.7
Hydroxyl value mg KOH/g	120.0	160.0	110.0
M_n	910.0		1210.0
Non-volatile content %	75.0	75.0	75.0
Solvent	MEK (50) pm - acetate (50)		
Gardner Viscosity	M-0	J-L	U-W
Gardner Color	2-3		

The principal difference between die three resins consists of the different addition of a trifunctional monomer. The first two formulations use TMP for this purpose whereas the latter uses trimellitic anhydride. This leads to an increase in the cyclic aromatic structures that increase the hardness and the general resistance of the paint film. Generally, the use of TAQ increases the viscosity of the final product compared with the use of TMA, but this must be compared to equal values of the resin parameters.

Example 3-3: WATER-DILUTABLE POLYESTER RESIN FOR STOVING FEMISH TOPCOATS

(Taken from Amoco Chemical Company report M TM 141)

Material	**Weight %**	
Resin	E	F
Neopentylglycol	34.0	21.1
Trimethylolpropane	7.3	/
Isophthalic acid	36.0	59.7
Adipic acid	15.8	/
Trimellitic anhydride	6.9	5.7
1,6 Hexanediol	/	13.5
Total	100.0	100.0

Properties of resin

Water losses	11.7%	12.9%
Acid mg KOH/g	35	33
Hydroxyl mg KOH/g	70	33
NonVolatile content%	90	70
Solvent	diethylene glycol	diethylene glycol
Gardner Viscosity	>Z 10	>Z 10
Functionality	2.122	2.037
Gel acid mg KOH/g	+ 11	+8
Patton Constant	0.977	0.983

Water dilutability

Resin	556	493
Dimethylethanolamine	13	14
Water	431	493

Properties of resin

Non-volatile content	49 – 51	34.5
pH	6 – 6.5	8 – 8.5

Synthesis:

1. Add NPG, TMP, Adipic and Isophthalic acid.
2. Heat to 230-240°C and keep at this temperature until the acid value < 3 mg KOH/g.
3. In both cases, add 0.5 g of Fascat 4100 at 120-140°C during this temperature rise.
4. Cool to 189°C, add TMA and heat to 200°C.
5. Maintain at this temperature until an acid value of < 19-20 mg KOH/g is obtained.
6. Neutralisation is carried out by adding the resin (which is maintained at 90-120°C) to the water + amine mixture. With vigorous agitation, maintain until a homogeneous dispersion is obtained.

It is normal practice to check the level of free TMA to ensure compliance with HSE and labelling requirements.
As it is a resin that will be thermally crosslinked, dimethylethanolamine, with its amine functionality, is used as the neutralisation amine. AMP 90 could also be used. For air drying resins a more volatile amine can be used, which in general is ammonia or even dilute soda lime. The neutralisation in general is carried out at 4050'C with the components, if possible, at the same temperature. The carboxylic functions can be neutralised with stoichiometric (100%), as well as below or above stoichiometric amounts. At 80% neutralisation, the sizes of the particles are reduced resulting in a slightly higher non-volatile content for the resin as supplied.

Example 34: POLYESTER RESIN FOR HYBRH) POWDER COATING SYSTEM
(Taken from Amoco report N' GTSR 108)

Material	**Weight %**
Resin G	
Neopentylglycol	35.9
terephthalic acid	53.0
Trimellitic anhydride	11.1
Total	100.0

Properties of resin

Water of reaction	11.5%
Acid value mg KOH/g	75-80
Viscosity ICI 200°C	35 - 40 Poises
Functionality	2.080
Patton Constant	0.890
Gel acid value rag KOH/g	+57
T_g, in °C	65-71
% unreacted TMA	<2%
Amount of internal catalyst	0.5%

Synthesis:

1. Add NPG and 50% of terephthalic acid.
2. Heat to 140°C, then as soon as the mixture can be stirred and add the rest of the terephthalic acid.
3. Heat to 240°C and maintain at this temperature until the acid value < 5 mg KOH/g and the viscosity is in the range 15-25 Poises at 200°C.
4. Cool to 180°C, add the TMA and heat to 210°C.
5. Maintain at 210°C until a viscosity of 15-25 Poises and acid value 75-80 rag KO1-Vg are attained. Add the catalyst and hold for 15 minutes at 2 1 TC. The catalyst is 2-methyl imidazole or benzyl trimethyl ammonium chloride.

In order to obtain very good mechanical properties, terephthalic acid is the major diacid. The functionality of the system is increased by using TMA which will not lead to a too high an increase in molecular weight or viscosity which remains an important factor for the appearance characteristics of the powder coating. The high acid value will enable large amounts of epoxide resins such as 50150. A priori, the higher the Tg, of the resin the better the stability during storage, because this reduces sintering or cold flow of the powder particles.

Example 3-5: POLYESTER RESIN COATING FOR COIL COATING

(Taken from Eastman report PA11CNcP)

Material	**Weight %**	
Neopentylglycol	22.4	20.1
Cyclohexanedimethylol	20.8	18.5
1,6 Hexane diol		4.2
Adipic acid	5.0	1
Isophthalic acid	11.3	1.1.2
Terephthalic acid	11.3	11.2
Cyclohexane dicarboxylic	29.2	34.8
Total	100.0	1000

Properties of resin

Water or reaction	12%	12.1%
Acid value mg KOH/g	4	4
Hydroxyl value mg KOH/g	36	31
Mw	10720	12980
Mn	4270	4630
Viscosity at 200°C (ICI Poises)	33	29
Gardner viscosity	Z 5	Z 4
T, °C	23	23
Functionality	2	2
Patton Constant	2.028	2.024
Non-volatile content %	60	60

Synthesis:

1. Add all the polyols and then the polyacids.
2. Heat to 200°C for 2 to 3 hours.
3. Maintain at 200°C until an acid value of 1 mg KOH/g is obtained.
4. Establish reflux with Solvesso 150, which is the azeotropic solvent.
5. Cool to 140°C and add CHDA.
6. Heat to 240°C and maintain until an acid value < 25 mg KOH/g is obtained.
7. Cool to 140°C and then dilute the products with Solvesso 150.

In this coil coating application, resins with excellent shaping mechanical properties are required. The use of aromatic diacids for imparting hardness and chemical resistance is carried out uniquely with terephthalic and also isophthalic acids. Hexanediol is the best suited linear diol, imparting good flexibility but it should also be used sparingly due to its poor hardness. The use of CHDM and CHDA improves hardness compared to aliphatic compounds and also chemical resistance. Of the two formulations the second is the more expensive but should also be the best.

Example 3-6: POLYESTER RESIN FOR TWO CONTONENT POLYURETHANE
(Taken from Eastman report N* N - 196)

Material	**Weight %**	
	A	B
2,2,4Trimethylpentanediolglycol (TNTD)	38.0	/
Neopentylglycol	/	36.5
Trimethylolpropane	15.0	8.3
Isophthalic acid	29.7	47.0
Adipic acid	17.3	8.2
Total	100.0	100.0

Properties of resin

Water of reaction	10.7%	12.2%
Acid value mg KOH/g	2	3
Hydroxyl value mg KOH/g	125	117
Gardner Viscosity	Z6	> Z6
Non-volatile content %	90	90
Molecular weight	1700	1760
Gardner colour	3-4	1
Reaction time	13 hr	8.5 hr

Synthesis:
The synthesis is carried out in a one step process with toluene (5%) as an azeotropic solvent. The process is carried out at 215 'C with the temperature rising to 215'C within 3 hours. 50 ppm of DBTL is used as catalyst.

90% dilution with the following mixture (complying with rule 66): - .
Toluene (20%) + Butyl acetate (35%) + Cyclohexanone (10%) + EKTASOLVE EE (15%) + MEK (20%)

The polyester based on TMPD enables the viscosity to be lower and hence a higher non-volatile paint content, good durability, humidity resistance as well as intermediate hardness. The polyester based on NPG will have impact resistance, good exterior resistance, adhesion, gloss and good hardness.

Example 3-7: POLYESTER RESINS FOR COIL COATING

Material	**Weight %**	
Resin	**C1**	**D1**
Neopentylglycol	22.4	20.1
CI-IDM	20.8	18.5
Adipic acid	5.0	/
1-6 Hexanediol	/	4.2
Isophthalic acid	11.3	11.2
Terephthalic acid	11.3	11.2
CHDA	29.2	34.8
Total	100.0	100.0

Ratio CHDM/NPG = 40/60
10 mol% diols or diacids are hexanediol or adipic

Synthesis:

1. Add all the components except CHDA.
2. Heat at 200°C for 2 hours.
3. Maintain at this temperature until the acid value is <1 mg KOH/g.
4. Cool to 140°C and add CHDA.
5. Heat to 230°C and maintain until the acid value < 25 mg KOH/g.
6. Cool to 140°C, add the esterification catalyst and heat to 230°C with azeotropic removal of the water of reaction by Solvesso 150 at 230°C.

The flexible nature of the resin is attributed to the combination of CHDA/CHDM that provides a compromise between hardness, flexibility and exterior resistance. It is, however, necessary to use isophthalic and terephthalic acids in order to obtain the chemical resistance required by these coil systems and also to provide a minimum hardness. Adipic or hexanediol act as flexibilising components, but they are only present in small amounts.

As can be seen, merely by changing the ratios of hard or soft polyols and polyacids and their wide variety, a whole range of polyester resins can be formed. However, when the requirements of each class of polyester and their field of application are considered, some parameters are already pre-imposed and represent restrictions or guidelines for the formulator. For example, a polyester resin for a hybrid powder system must have a certain acid value and a certain T. value. However, each formulator needs to have his/her own formulation routines and each time there is the need to develop a polyester resin, they should know the impact of certain raw materials on the properties of the resin on the resulting paint. By simply changing the ratios of five or six raw materials and the production process, it is possible to formulate excellent polyesters.

Example 3-8: POLYESTER RESIN WITH EXCELLENT EXTERIOR DURABILITY

Material	**Weight %**
Water	3.0
Neopentylglycol	24.0
Trimethylolpropane	5.0
Isophthalic acid	18.0
Terephthalic: acid	9.0
Adipic acid	11.0
Solvent (xylene)	30.0
Total	100.0

Properties of resin

Non-volatile content	64 – 66%
Acid value	< 10 mg KOH/g

Process:

1. Charge items 1 & 2
2. Heat to about 100°C and add items 3-6.
3. Heat to 200°C as fast as possible, whilst keeping the head temperature below about 103°C to minimize glycol losses.
4. On reaching 200°C, check water of reaction for glycol losses by measuring refractive index. If necessary cool to about 150°C and make, glycol correction
5. Hold at 210-220°C until acid value < 10 mg KOH/g
6. Cool and discharge into solvent.
7. Check solids and adjust if necessary.
8. Cool and filter

This is a traditional and typical formulation for a polyester. The mixture of isophthalic and terephthalic acids is typical being about 2 parts of isophthalic to 1 part of terephthalic acid. This minimises crystallinity problems. Adipic acid imparts some degree of flexibility and further reduces crystallinity of the resin. Trimethylolpropane being trifunctional gives the necessary degree of branching for a good crosslinked network to be formed.

Modified polyester resins

Example 3-9: DUVIER ACID MODIFIED POLYESTER

(from Unichema International literature)

Material	**Weight %**
Pripol 1022 dimer acid	15.8
Trimethylolpropane	7.9
Neopentylglycol	16.0
Propylene glycol	4.4
Phthalic anhydride	23.0
Maleic anhydride	3.8
Xylene	0.7
Solvesso 100	28.4
Total	100.0

Properties of resin

Non-volatile content	64 – 66%
Viscosity	45 – 55 Poises @ 21°C
Acid value	< mg KOH/g

Process:

1. Charge items 1-3 and heat to 100°C
2. At 100°C, add items 4-7
3. Increase temperature to 200°C at a heating rate to keep the head temperature below 103°C (to minimise glycol losses).
4. Monitor refractive index of water of reaction and make glycol correction if necessary
5. Hold at 200-205°C until acid value < 10 mg/KOH/g
6. Cool and discharge whilst hot into solvent (item. 8)
7. Adjust for solids and filter

This type of polyester resin does not use the more expensive isophthalic and terephthalic acids, partly because the incorporation of dimer acid and end use of the resin doesn't justify the extra cost. The properties obtained by using Phthalic are different and approach those of an alkyd. These resins would be crosslinked by aminoplasts between 100 – 130°C, depending upon the reactivity of the aminoplast and cure time. This type of modified resin has found usage in flexible coil coatings and general industrial applications, where colour is unimportant.

Siliconised Polyesters

The incorporation of silicone imparts excellent heat resistance to polyesters. Therefore, it is not surprising that siliconised polyesters are used in cookware applications. The polyester acts as a 'carrier' for the silicone. Various levels of silicone can be used. The higher is the level, the better is the heat resistance, but the more expensive is the resin.

Another major application of siliconised polyesters is coil coated architectural claddings. In this application, the siliconisation imparts good external durability. However the base polyester must contain suitable acid and polyol components. If the base polyester has poor exterior durability characteristics, siliconisation will not give top of the range exterior durability.

The normal process for siliconisation is first to prepare a base polyester. The organosilicone compound is then added with suitable a catalyst. Reaction times and temperatures will vary according to the amount of siliconisation required and the type of organosilicone being added. Suppliers of organosilicone materials offer good advice.

For cookware applications this could be relatively straightforward, being based upon isophthalic - or terephthalic acids or a mixture with a tri- and possibly di-functional polyol.
The greater the proportion of terephthalic acid, die harder the resulting film, all other parameters being equal

THE USE OF MONOFUNCTIONAL EPOXY RESINS AS MODIFIERS

Normally the reaction of a monofunctional epoxy resin without any other functionality like ethylenic unsaturation, removes the epoxy group. However, the hnkages so formed and the incorporation of the molecule attached to the epoxy group can in some circumstances confer desirable advantages. One such material is Cardura E-10. Shell publish some excellent technical information on the usage of Cardura E-10 and the properties of coatings prepared from Cardura E-10 modified resins. Some of this will be reproduced here to illustrate options available to both resin and coating formulators.

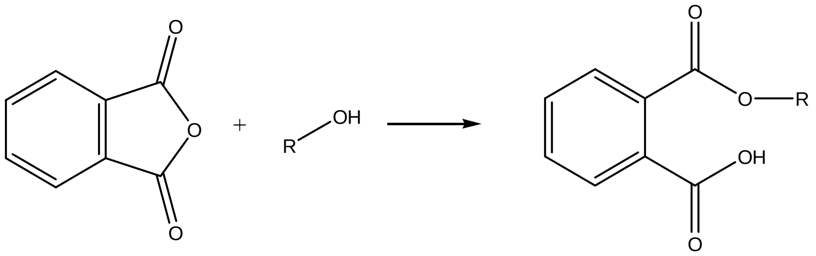
Cardura E-10 is branched and saturated and assuming that it has been incorporated through the reaction of its epoxy group it can only normally contribute to crosslinking in systems with co-curing resins. For ambient temperature or air drying systems some further modifications are required. As a general rule, in stoving enamels Cardura E-10 contributes the following:

- Exterior durability
- Very good gloss and build
- High hardness
- Good adhesion
- Excellent colour retention
- Excellent gloss retention on overbake
- Very good chemical resistance

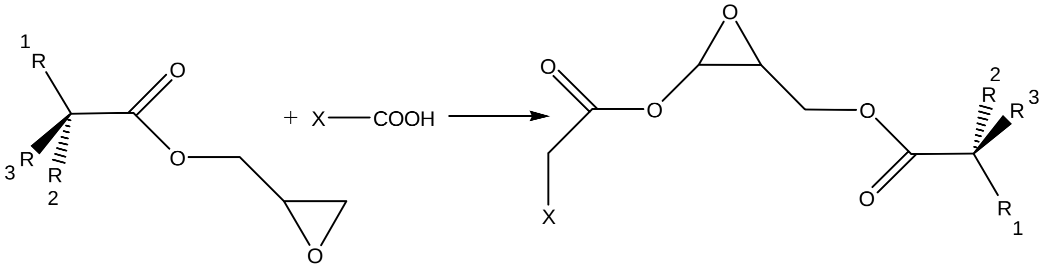
The branched structure of versatic acid (Cardura E-10 is the glycidyl ether of versatic acid) reduces the reactivity of its carboxylic acid group. Whilst this gives improved chemical resistance in the films, it creates problems in incorporating it into a polyester or alkyd. Long reaction times and high temperatures are required. However the use of the epoxy modified versatic acid (Cardura E-10) overcomes many of these problems.

The branched versatic structure can be readily incorporated into a polyester giving a relatively narrow molecular weight distribution resin. This can enable high solids paints to be formulated.

The reaction of Cardura E-10 with Phthalic anhydride produces an interesting intermediate that as of yet has not been fully exploited. Cardura E-10 is monofunctional with respect to epoxy, but in the anhydride or acid - epoxy reaction hydroxyl group is formed making this a latent difunctional material. Being monofunctional with respect to epoxide greatly reduces the risks of gelation that would be present if a di epoxide were used. Cardura E- 10 is in its own right an invaluable raw material giving resins with good gloss and topcoat appearance. Once the anhydride ring has been opened as shown below, the reaction with Cardura E- 10 can then proceed through the epoxy - acid reaction, producing another hydroxyl group in the process that is also shown below.



Second stage reaction of Cardura E- 10 with Phthalic anhydride:



Where X is the half ester of Phthalic anhydride.

Shell publish details of preparing a range of Cardura modified resins. Some of the techniques used are different to those commonly encountered in resin chemistry, thus they will be considered further.

As a general rule the incorporation of Cardura E-10 into a polyester or alkyd will give the equivalent of a polyester (or alkyd) with a fatty acid content between 30 - 45 weight %. These would be classified as short oil alkyds or polyesters (consult the alkyd chapter for further details).
It is possible to react all the components in an 'all in one' process. Whilst gloss, colour retention and chemical resistance are good, mechanical properties may suffer. In a two stage process the mechanical properties are generally unproved whilst retaining the other benefits, provided the Phthalic anhydride and glycerol are not replaced by alterative and that the resin is used in a stoving system

In addition to the simplest, Phthalic anhydride, glycerol, Cardura E- 10 reactants, it is possible to substitute, wholly or partially, alternative dibasic acids and polyols. The partial replacement (25 mole %) of Phthalic anhydride by some Adipic acid will give a highly flexible resin film However, the final properties are not influenced by whether a one or two stage process is used, therefore a single stage reaction at 240°C is used.

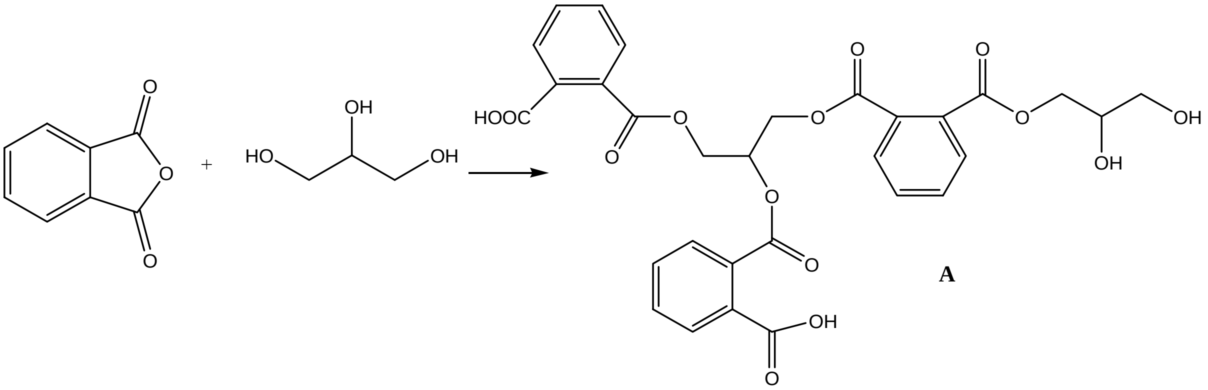
A single stage reaction may also be used if no anhydride were present for example a isophthalic or terephthalic acid reaction with Cardura E-10 and a polyol to give high hydroxyl content resins suitable for isocyanate curing. Many of the Cardura E-10 modified resins intended for non-stoving applications can be made by a single stage process. High hydroxyl value resins suitable for isocyanate cured systems can be made from isophthalic acid or Phthalic anhydride with trimethylolpropane and Cardura E-10. A one stage process would be used with a maximum reaction temperature of 240°C.

There are various ways of preparing the Cardura modified resins in a two stage process. These have been termed conventional and reverse cooking.
The conventional method involves preparing a hydroxyl functional resin from the reaction of Phthalic anhydride and glycerol and then reacting this intermediate with further Phthalic anhydride and Cardura E-10. The anhydride ring is opened by reaction with a polyol to give a hydroxyl rich resin, This is then reacted with further Phthalic anhydride and Cardura E-10.

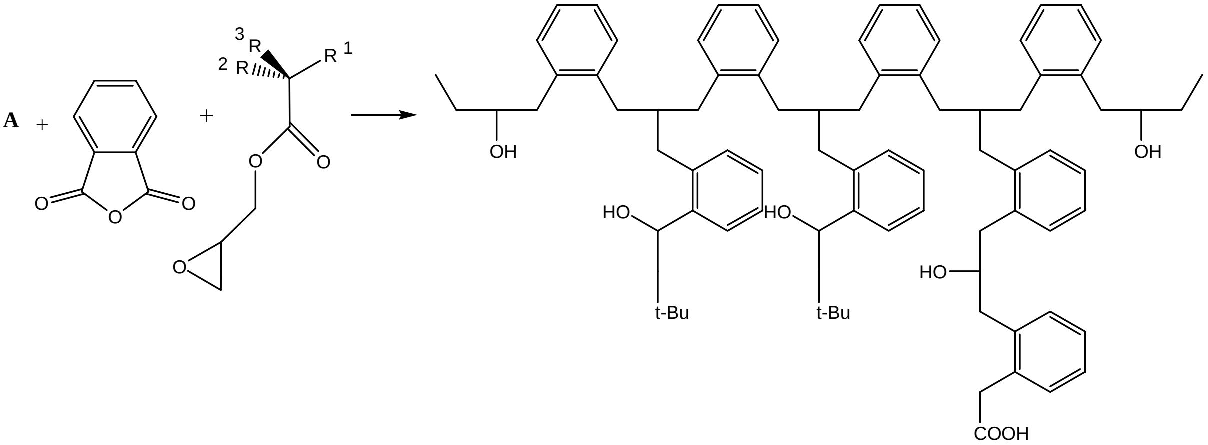
This procedure gives the correct steric arrangements for E-10 units for optimisation of properties.

A reaction scheme for a conventional two stage reaction is shown in below. Typical formulations and processes are discussed later.

First stage:



Second stage:



For a conventional two stage reaction with Phthalic anhydride and glycerol being initially reacted in the first stage, the reaction temperature is about 240°C. The second stage where further Phthalic anhydride and Cardura E- 10 are incorporated is carried out at about 150°C At this temperature the anhydride ring is opened rapidly by reaction with hydroxyl groups, but the rate of reaction of the resulting carboxylic acid group with hydroxyls is slow compared to the much faster epoxy - acid reaction.

The viscosity of the first stage intermediate determines the viscosity of the resulting resin. Water must be removed before the second Phthalic anhydride addition otherwise the anhydride ring will be preferentially opened by water forming Phthalic acid which will react with Cardura E-10 giving a low molecular weight adduct rather than being chemically bonded to the resin structure through the anhydride group. Glycerol is available m different grades and some can have an adverse affect on colour For example synthetic glycerol gives better colour products than natural glycerol.

The reactions are not restricted to Phthalic anhydride and succinic anhydride can be used as a total replacement and with trimethylolpropane it can give a resin suitable for high solids applications with a viscosity of L1-1.35 Pas @ 25T @ 80 % non-volatile content.

A further variation is the use of one or two reactors for the conventional two stage reactions. In a one-reactor formulation the initial charge can be less than 20% of the final reactor volume. Rather than use two reactors it is possible to reformulate so that up to 35% of the Cardura E-10 can be incorporated into the first stage without loss of resin performance. As this represents about 60% of the final volume of the resin, a single reactor can be used. In essence this is a hybrid approach. As a comparison a simple phthalic anhydride, glycerol, Cardura E-10 based resin suitable for general purpose stoving enamels or nitrocellulose lacquers prepared by a one and two reactor route is given below. Consult the Shell literature for further details.

Cardura E-10 modified general-purpose stoving enamel resin, two stage, two reactor conventional process.

Component	**Weight %**
Phthalic Anhydride	8.52
Glycerol	6.99
Xylene (azeotropic Solvent)	2.00

Charge the above and process as a polyester using xylene as an azeotroping solvent after reaching processing temperature of 240°C. Hold for viscosity acid value. Cool to 200°C and discharge into the second reactor containing a slurry of the following.

Phthalic Anhydride	23.35
Cardura E 10	43.26

Carefully heat to 120°C and then to 150°C and hold at 150°C until an acid value of 4-8 mg KOH/g is reached. Cool and dilute with xylene.

Xilene (thinning solvent)	18.00
Total	104.12

The water of reaction (4.12%) is based upon half the number of equivalents of Phthalic anhydride that is in excess.

Properties of resin

Non-volatile conteút	80±1%
Viscosity @, 25°C	25 Pas
Acid value	4 - 8 mg KOH/g
Colour	1 - 2 Gardner

The fatty acid content is 40% of the final resin

The first stage is 18% of the total weight of resin produced.

Example 3-10 Cardura E-10 modified resin for general-purpose stoving (120 -150°C) enamels prepared by a conventional two stage single reactor process.

Component	**Weight %**
Phthahc anhydride	21.39
Cardura E- 10	21.68
Glycerol	6.56
Xylene (azeotrope solvent)	3.00

Charge items 1-3 and heat to 190°C. Increase to 240°C and hold until acid value is < 3 mg KOH/g but > 1 mg KOH/g. Use azeotropic solvent if required. Cool to 200°C and add Cardura E- 10 and then phthalic anhydride.

Phthalic Anhydride	23.35
Cardura E 10	43.26

Raise the temperature to 150°C and hold until acid value is 4-8 mg KOH/g. Cool and dilute with xylene.

* Note that adding the Cardura before the Phthalic anhydride gives a lower viscosity product

Properties of resin

Non-volatile content	80 ± 1%
Viscosity @ 25°C	25 Pas
Acid value	4 - 8 mg KOH/g
Colour	1-2 Gardner

First stage represents 59% of the total weight of resin.

It should be noted that any free water in the second stage reaction will result in an increased rate of reaction, but will give a resin with a low viscosity and poor mechanical properties.

In the two reactor process the first stage represents only 18% of the total resin, whereas in the one reactor process the first stage-represents 59% of the total resin weight.

The other technique involves preparing a Phthalic anhydride Cardura E-10 adduct and then reacting it with glycerol as shown below. Note that the anhydride, ring is opened by an initiating polyol and a small amount of glycerol is present as the initiating hydroxyl By adding the bulk of the glycerol after the epoxy Phthalic reaction, superior properties are obtained compared to an 'all-in! process. Note that no water is formed during the first stage. The anhydride ring is opened by the glycerol, without the formation of water, and the reaction of Cardura E-10 with acid groups does not produce water of reaction.
The second stage involving the condensation of glycerol with the Phthalic epoxy adduct produces water and primary hydroxyl groups.

The reaction of epoxy with acid yields secondary hydroxyl groups. The presence of the primary hydroxyl groups (from the residual glycerol hydroxyls) winch are not sterically hindered compared to those from. a conventional two stage process gives a resin with enhanced reactivity during crosslinking. This enables lower stoving temperature finishes to be formulated. This technique has been referred to as reverse cooking.

A possible formulation for this type of reverse cooked resin taken from, the Shell literature follows. This should be compared to the two formulations and processes given earlier for the conventional one or two reactor product. This resin is suitable for use m general purpose stoving enamels with stoving temperatures in the region of 100-120°C. Note that although the formulations are similar the product prepared by the reverse process is suitable for lower stoving temperatures.

It should be noted that the initial reactor charge is about 93% of the resin weight, thus there is no need for a two reactor process for reversed cooked resins.

Example 3-11 Phthalic anhydride Cardura E-10 modified polyester for low bake (100-120°C) automotive finishes, reverse cooking process.

Component	Weight %	Equivalent
1. Phthalic anhydride	31.98	0.4322
2. CarduraE-10	35.21	0.1408
3. Glycerol	1.35	

Charge 1-3 and heat to 150°C under nitrogen sparge. Hold at 150°C for 30 minutes before raising the temperature to 180°C. Hold until an epoxy group content of 140-200 is obtained and then cool to 130-140°C.

Glycerol	5.35
Xylene (reflux solvent)	5.00

Charge 4 and part of 5 and heat to 190-200°C over 1 hour. Water will distil. Heat to 230-240°C and hold keeping a constant reflux using further xylene (remainder of 5) if necessary until the acid value is < 12 mg KOH/g. Cool and add xylene (6) to 70% solids.

Xylene (thinning solvent)	25.00
Total	103.89

The water of reaction is calculated from the number of equivalents of phthalic anhydride and Cardura E-10. Phthalic anhydride is in excess (0.4322 cf 0.1408), thus consider only phthalic anhydride which liberates only half its equivalent weight of water because the first reaction is anhydride ring opening - (0.43212 x 18 = 3.89 wt%)

Properties of resin

Non-volatile content	70 ± 1%
Viscosity @ 25°C	38 - 54 Poises
Acid value	10 - 12 mg KOH/g
Colour	

It is possible to use an acid initiated rather than a polyol initiated reverse cooking technique. Here a fatty acid such as dehydrated castor oil fatty acid is the initiator. Azelaic acid or other dibasic acids can also be used for initiating the reaction. Here the acid functionality reacts with the epoxy group forming a hydroxyl group that can open the phthalic anhydride ring.

This technique can give low bake resins for automotive finishes which will cure at 80°C compared to 100-120°C for a polyol initiated formulation, due to their higher reactivity from the presence of primary hydroxyl groups. Both of these stoving temperatures are lower than the conventional two stage process resin that requires 120-150°C stoving temperatures.

The use of DCOFA gives an air drying enamel for retouching, when acid catalysed. It can also give low bake 80°C stoving enamels. Resins for high solid coatings can be formulated using a dibasic acid initiated reverse cook and they can give a high degree of flexibility in the resin. An example of a high solids resin taken from the Shell literature follows;

Example 3-12 High solids coating based on Cardura E-10, reverse cooked, acid initiated.

Component	**Weight %**	**Equivalent**
Phthalic anhydride	27.53	0.3720
DCOFA	10.32	0.0360
Cardura E-10	23.32	0.0933

Charge the above and heat to 135'C. Allow exotherm to raise temperature to 200°C. Hold until EGC is 140-200°C. Cool to 180°C. Then add;

Trimethylolpropane	22.82
Xylene (azeotropic solvent)	3.00

Raise the temperature over 1-2 hours to 240°C and hold until the acid value < 12 mg KOH/g. Cool and thin with xylene.

Xylene (thinning solvent)	17.00
Total	103.89

theoretical amount of water. As before the phthalic anhydride is in excess, but the DCFOA has to be considered. Use half the number of equivalents of phthalic plus those for DCOFA thus;

(0.372012 + 0.0360) x 18 = 0.2175 x 18 = 3.99%

Properties of resin

Non-volatile content	80±1%
Viscosity @ 25°C	4.5 - 7.8 Pa.s
Acid value mg KOH/g	< 12

The important factors for obtaining a low viscosity at high solids with this type of resin is the use of excess polyol and the termination of the reaction at a relatively high acid value. The use of trimethylolpropane at about half the number of hydroxyl equivalents to trimethylolpropane will give a low bake resin suitable for stoving at 80°C.
Substitution of Azelaic acid for dimerised fatty acid gives similar properties except that with Azelaic acid being saturated, the resulting resin is not suitable for air dry applications.

The properties of stoving enamels based on Cardura E-10 modified resins mainly depend upon the type, reactivity and ratio of the ammo resin and the stoving schedule. None of this is surprising. Most of the resins described above are suitable for general industrial finishing and some can be used for automotive topcoats. For details of the properties of Cardura E- 10 modified resins and stoved finishes based upon them consult the Shell literature.

An example of a Cardura E-10 modified polyester designed to be crosslinked with melamine or urea formaldehyde resins for use in coil coatings taken from the Shell literature follows:

Example 3-13 Cardura E-10 modified polyester for coil coating for dadding

Component	**Weight**
Isophthalic acid	23.42
Terephthalic acid	4.11
Azelaic acid	7.80
Cardura E-10	25.90

Charge 1-4 and raise the temperature to 175°C under nitrogen sparge. Hold at 175°C until an epoxy group content of 140 - 200 is reached, normally after 30 - 45 minutes. Cool to 130°C and add the following.

Neopentylglycol	8.63
Trimethylolpropane	5.54
Xylene (azeotropic solvent)	5.00

Raise the temperature to 175 – 180°C and hold for 1 hour.
Raise the temperature to 220 – 230°C over 2 hours. Once the NPG is fixed use xylene as an azeotropic solvent, if required.
Hold at 220 – 230°C until the acid value < 10 mg KOH/g. Cool and dilute to 70% solids in xylene.

Xylene (thinning solvent)	25.00
Total	105.40

Theoretical amount of water. Assume that epoxy only reacts with acid and that all remaining acid reacts with hydroxyl. Number of acid equivalent is 0.415. Number of epoxy equivalents (on acid epoxy reaction only) is 0.113.
Weight of water liberated is: (0.415 - 0.113) x 18 = 5.4%

Properties of resin

Non-volatile content	70±1%
Viscosity @ 25°C	27 - 49 Poises
Acid value mg KOH/g	10 – 12

A packed column would be used to minimise, the loss of neopentylglycol. The refluxing water and glycol is fractionally distilled on the theoretical plates with the higher boiling glycol being returned to the reaction vessel. In the theoretical calculations no allowance has been made for glycol losses. A two stage process is used to maximise the benefits of incorporating Cardura E-10. Good durability, which is essential for external coil coated cladding, is provided by the choice of reactants.
This is an example of a reverse cooked, acid initiated process. Although a dibasic acid initiator (in thus case Azelaic acid) is not required for reaction because the isophthalic acid will both initiate and react, a polyester of similar characteristics to a reverse cooked polyester is obtained when Azelaic acid is present initially. This gives the resin its flexibility. Substitution by Adipic acid will give a lower cost resin, albeit with some loss of flexibility.
Some of the modified resins can be used with nitrocellulose to give air-drying finishes or high hydroxyl value variants can be used for incorporation in isocyanate cured systems.

V EXAMPLES OF PAINT FORMULATIONS.

Example 3-14: metallised basecoat with linear polyester for wet on wet coverage by a coating varnish

Material	weight %
Stapa mobilux 161 or R 167	5.0
Xylene	6.0
Whilst stirring make into a paste	
Vialkyd AN 950 or Dynapol H 700	15.0
CAB 381/18% butyl acetate	55.0
Resamine HF 480	2.5
Maprenal MF 590	4.7
Aerosil 200	0.9
Butylglycol	5.0
Butyl acetate / Xylene	5.9
Total	100.0

Paint characteristics

Viscosity DIN 4	13 – 15 s
Drying condition	Air + 30’120°C at 20’ 150°C
Varnish coating	After 3 to 5 min air drying

The polyester resin AN 950 (or Dynapol) imparts the basic mechanical properties to this metallised base, which has to endure significant mechanical constraints such as gritting. It is a relatively linear polyester, but yet has no crystallisation problems. The crosslinking agent (MF590) is a melamine formaldehyde resin, which is very reactive. It imparts hardness and chemical resistance and also rapid film hardness. It can only be used with rather flexible resins, because it gives rather hard and brittle film and the use of a plasticizer is necessary.
Resamine HF 480 acts as the latter and can plasticize the system whilst being involved in crosslinking (it is a urea formaldehyde resin) which avoids having surface cratering. CAB imparts physical drying to the system that is indispensable for this type of paint that must also partially dry physically.

Example 3-15: Two component satin varnish with rapid drying, high elasticity and good interlayer adhesion

Material	**Weight %**
Vialkyd AN 950/70X	17.0
Nitrocellulose chips H24 / 20%	60.0
Palatinol O (dimethylglycolphthalate)	3.6
Cridust 3620 (PE wax)	1.0
Matting agent OK 412	1.0
Solvent mixture *	15.4
Baysilon OL / 1 % (silicon oil)	2.0
Total	100.0

- Solvent mixture: Ethyl acetate (20) + Butyl acetate (40) + Xylene (25) + MEK (10)
- Nitrocellulose Solution: H24 (30) + Ethyl acetate(25) + Butyl acetate(25) + MiBK(20)

Paint characteristics

Viscosity DIN 4	Ca. 65 s
Dry to touch	Ca. 10 – 15 min

In this two component varnish, a rather flexible polyester is used. It is of low functionality with a rather high hydroxyl value (160 mg KOH/g) in order to plasticize a system based on nitrocellulose and also to impart greater chemical resistance to the film after crosslinking with the polyisocyanate. The use of a phthalate once again ensures flexibility. The matting agent OK 412 is a precipitated silica, often used for matting varnishes. Baysilon enables the wetting of the film to be improved.

The use of a poly ethylene wax imparts a certain resistance towards scratching and also a matting effect. As the drying is in air, the solvent fraction needs to be rather volatile, with a small amount of a less volatile solvent to avoid problems in appearance due to too rapid evaporation. The use of xylene and butyl acetate allow the evaporation of other solvents to be controlled which are a lot more volatile.

This varnish displays good solvent and scratch resistance. It is used as an open pore varnish for kitchen furniture.

Example 3-16: Two component white paint for PVC

Materials	Weight %
Vialkyd AN 950/70X	50.0
Kronos 2059	30.0
Bentone 34 10%	1.0
Calcium octoate 4%	0.1
Methyl glycol acetate	17.4
Baysilon OL 1%	1.0
Zinc octoate 8% / 10%	0.3
Additol XL 121	0.2
Total	100.0

Paint characteristics

Viscosity DIN 4 20°C	60 s
Dry to touch	
At room temperature	3-4 hours
At 80 – 100°C	30 minutes

This white paint has good U.V. resistance due to the standard titanium dioxide (2059) and cycloaliphatic polyisocyanate used. The use of a Bentone gel imparts a little thixotropy (non-drip quality) to the paint that will be applied by a spray gun without drastically reducing the gloss. It is also possible to use the same basic urethane modified polyester (SCA type) in order to have a more pronounced varnish anti-run effect, without a negative effect on gloss. The zinc derivative here acts as a catalyst for the hydroxyl-isocyanate reaction. The calcium derivative is a good wetting agent.

Example 3-17: Automobile one component primer

Materials	Weight %
Vialkyd AN 927/70	32.00
Kronos 2310	8.67
Micronised Barytes	18.45
Special black 10	0.05
Aerosil R 972	0.31
Ircogel 905	039
Butyldiglycol	2.08
Byk 358	0.58
Additol VXL 6212	0.23
NTA	2.11
Exxal 13	2.46
Solvesso 100	10.51
Additol XL 433/60	16.80
Maprenal UT 980/62	5»55
Additol XL 480	0.20

Total	100.00

Paint characteristics

Paint non volatile content	ca. 63%
Pigment Binder ratio	0.75 / 1
Curing temperature	20’ to 140°C – 150°C

The basic resin of this automobile sealer is a moderately functionalised polyester with a hydroxyl value of ca. 140 mg KOH/g. It has standard mechanical properties and only crosslinking with melamine resin, MF 980 resin (benzoguanamine), or one of even greater reactivity, would be insufficient in terms of gritting or interlayer adhesion. This type of paint must have full interlayer adhesion of the complete automobile paint system as well as the required mechanical properties.
That is, cationic Electrodeposition + primer + metallised base + varnish. The number of coats applied, with some coats sometimes being applied twice, can create problems in terms of lack of cohesion and adhesion.

Crosslinking with a blocked polyisocyanate of the IPDI type or trimer of HDI gives a polyurethane structure with good resistance to gritting and adhesion. The level of barium sulphate can be varied between 75/25 to 25/75 compared with titanium dioxide depending on the tint of the primer, since the tint of the latter is adapted to that of the finish in order to have a cosmetic finish.

In the case of grit impact, the bottom layer is also important. The filler also reduces cost. Whatever die ratio, the impact on gritting resistance is not high. Thixotropy is obtained by using a pyrogenic silica, Aerosil. The solvent fraction is very important for the film appearance and its surface tension that will significantly affect the final paint quality on the vehicle. The use of a small amount of low volatility solvent (Exxal 13 or BDG) is important, for the appearance and flow of the film.

This primer can be crosslinked at temperatures between 40°C and 165°C. it can be sanded very rapidly. Sometimes epoxy resins are used to improve interlayer adhesion, when it is deemed necessary. The black pigment is a carbon black of standard quality.

Example 3-18: Stoving finish primer for coil coating

Materials	**Weight %**
Vialkyd AN 927/70	33.1
Aerosil 200	0.2
Kronos 2310	25.8
Disperbyk 182	1.0
Butyldiglycol	7.8
Additol XL 433	16.5
Solvesso 200 S	15.3
Byk 322	0.3
Total	100.0

Paint characteristics

Viscosity Ford #4 @, 23°C	100 s
Non-volatile component 1g 1h at 120°C	61%
Thickness of dry film	5-10 µm
Polyester blocked isocyanate ratio	70/30
Pigment Binder ratio	0.78/1
Curing conditions	< 30 s at 220-250°C

In this coil formulation, a titanium derivative with excellent exterior resistance and with a dispersing wetting additive, which is normally recommended for water dilutable systems, is used. In this system, it assists in improving gloss. Byk 322 is a polysiloxane and as well as helping in terms of surface tension and flow it also helps in wetting the substrate. It has anti-cratering properties. In this type of application, the solvent fraction is of rather low volatility, notably with an aromatic fraction with a high boiling point. Additol XL 433 is a polyisocyanate adduct based on EPDI which improves the flexibility of the system compared with crosslinking only with a melamine formaldehyde resin.

Table 3-7 contains a comparison of formulation characteristics upon changing the polyester / blocked isocyanate ratio

TABLE 3-7: COMPARISON OF THE EFFECTS ON PROPERTIES BY VARYING THE POLYESTER, BLOCKED ISOCYANATE RATIO.

Ratio PE/ blocked PU	**85/15**	**80/20**	**75/25**	**70/30**
AN 927	81.00	76.22	71.46	66.70
Aerosil 200	0.40	0.40	0.40	0.40
Kronos 2310	52.00	52.00	52.0	52.0
Disperbyk 182	2.00	2.00	2.00	2.00
Butyldiglycol	15.60	52.00	52.00	52.00
XL 433	16.70	22.23	27.79	33.35
Solvesso 200	31.75	38.80	36.90	30.70
Byk 322	0.80	0.83	0.82	0.80
Viscosity (s)	97.00	96.00	92.00	98.00
Non-volatile content %	61.90	61.60	61.00	61.30
Curing time	27s	27s	27s	27s
Thickness	12 µm	14 µm	12 µm	21 µm
Gloss 20°	53	50	44	57
Gloss 60°	87	85	83	61
Kónig hardness (s)	20	24	45	90
Adhesion	1-2	1-2	1-2	2
Reverse impact	> 100 cm	> 100 cm	> 100 cm	> 100cm

Example 3-19: Single coat white, with good adhesion on galvanised steel

Material	**Weight %**
Vialkyd AN 950/70	37.0
Maprenal MF 915/75	8.4
Kronos 2310	34.0
Epikote 1001/75	5.0
Byk 358	0.5
Butylglycol acetate	4.5
Xylene/Butanol (80/20)	10.6
Total	100.0

Paint characteristics

Pigment Binder ratio	0.95/1
Polyester Melamine ratio	80/20
Non volatile content	69%
Viscosity Ford #4	90S
Adhesion on metal sheet senzimir	(20’ 160°C) GT 0
240 h climatic enclosure (20’ 160°C)	Good
Buchhohlz hardness	100
Erichsen	7 mm
Waxing mark 1 nun	Good
Weathering: 2000 hr Xenotest: gloss loss at 60°	From 90% to 70%

The use of a chorine treated titanium pigment gives excellent exterior resistance. The use of epoxy resin in small amounts improves adhesion on this difficult substrate. The use of a methylated melamine resin imparts greater build to the paint as well as improved exterior resistance when compared with butylated derivatives. The amino resin used in this formulation is of average reactivity. The surface tension additive is Byk 358 that is a somewhat polar polyacrylate suitable for this type of formulation.

Example 3-20: Two component finishing paint for inorganic substrates such as concrete

Material	**Weight %**		
	A	B	C
		Mineral Effect	Structured Paint
Desmophen 651/67%	31.2	23.6	18.7
NTA	5.1	5.0	14.6
Methoxybutyl acetate	3.0	4.3	3.2
Thixatrol GSV anti drip	/	1.5	1 '3
Desmorapid PP 10% catalyst	1.2	0.8	0.7
Acronal with 10% degasser	0.2	0.2	0.1
U02 RKB4	31.8	11.4	18.8
10 % Bentone 3ì2'	2.1	3.0	2.2
Tinuvin 292 (anti UV)	0.4	0.3	0.3
Miox AS Micaceous iron oxide	/	29.9	/
Mistrofll' (talc)	/	/	24.9
Desmodur N 75	25.0	20.0	15.2

Total	100.0	100.0	100 n

Paint characteristics

Stoichiometry	100%	110%	100%
Pigment / binder ratio	1/0.8	1/1.4	1/1.8
Application time	8 h	8 h	8 h

Formulation A has high gloss.

Formulation B is a satin paint whose colour tends towards grey.

These paints are diluted at a nozzle flow rate of 4 nun at 80-120 s for a roller or spray gun application. It is possible to apply film weights of 130 to 150 g/m^2. The viscosity will be lowered for a spray gun or airless application.

Formulation C with the amount of hardener has the necessary viscosity for a direct airless or roller application. The significant load factor leads to the structured effect due to the use of a talc, which is absent in die other two formulations.

The substrate should be pre-treated with a prime coat layer such as a base coat.

Example 3-21: Two component polyurethane paints for plastic mat. using polyester A

Material	**Weight %**		
	i	Ii	iii
Polyester 70%	50.810	50.511	52.673
Titanium dioxíde	3.810	3.816	3.835
Special Black 4'	0.200	0.198	0.203
Byk 358'	1.200	1.200	1.200
Ethyl 3 ethoxypionate	14.900	19.778	20.929
Dibutyl tin dilaurate	0.060	0.057	0.058
Desmodur N 75'	29.020	/	/
Desmodur N 33903	/	24.440	/
Desmodur N 3200'	/	/	21.102
Total	100.000	100.000	100.000

Paint characteristics

Degree of crosslinking	110%	110%	110%
Pigment / binder ratio	0.0711	0.0711	0.0711
Ratio TiO_2 / black	95/5	95/5	95/5
Viscosity Ford # 4	28s	24s	22s
VOC g/l	369	375	368

Adhesion (Crosshatch)

Xenoy	100	100	100

ABS	100	100	100

*Xenoy is a high impact engineering thermoplastic designed for exterior automotive components, such as bumpers and fenders.

MEK resistance double rubs

Xenoy	100	100	100
ABS	100	85	69

Gloss 60°

Xenoy	91.7	91.4	92
ABS	91.7	91.2	91

Water immersion
24 h at 43°C

Adhesion in %			
Xenoy	100	100	100
ABS	100	100	100
Change in gloss			
Xenoy	-0.55	-1.2	-0.03
ABS	-1.31	-1.64	0

Resistance to 0. 1 N HCI
2 hours

- No discoloration on the two substrates.
- No softening on the two substrates.
- No appearance change.

Chemical resistance
(24 hr exposure)

ABS			
Ink	10	10	10
Mustard	2	2	2
Cola	10	10	10
Coffee	8	9	7
Detergent	10	10	10
Lipstick	9	10	8
lodine tint	3	2	3

10 = no change 5 = moderate 4 = considerable 2 = severe

Pencil hardness

Xenoy	F	F	3H
ABS	B – HB	B – HB	HB

Elongation % 90% 79% 96.6%

Resistance to UV Loss of gloss

250 h	81	90	81
500 h	81	88	81
750 h	62	78	59
1000 h	15	71	16

Yellowing value

Initial	-2.7	-2.3	-4.3
250 h	-1.8	-0.2	-3.1
500 h	-2.0	-0.4	-3.5
750 h	-2.7	-0.6	-4.2
1000 h	-2.7	-0.8	-4.2

The use of three different crosslinking agents in the above formulations gives an indication of the changes in film properties that can be achieved by only changing the crosslinking agent. Desmodur N75 and N3200 are HDI derivatives. N3200 has a higher viscosity and molecular weight N3390 is a trimer of HDI that leads to improvements in the performances of these systems especially in terms of exterior resistance, gloss and yellowing resistance.

Example 3-22: One component automobile assembly primer

Material	**weight %**
Desmodur BL 3175/75	9.14
Alkynol 1665/65%	22.52
Desmophen 670/80%'	7.47
Maprenal NT 980/62	8.68
Blanc Fixe	20.51
Mixture of pigments RAL 7000	6.83
Antiterra U	0.17
Aerosi1 paste	3.42
Byk 354	0.17
% DBTL	0.34
MPA/Butyl acetate/Xylene 1: 1: 1	20.75
Total	100.00

Aerosil paste

Alkynol 1665	60
Aerosil R 972	10
MPA	30

Paint characteristics

Mechanical tests

Erichsen in mm	10
Impact test ASTM D 2794	60 inch/pound
Kónig pendulum hardness	135 s
Persoz hardness	290 s

The basic polyester in this formulation is Alkynol 1665 that is a traditional polyester for this application, which has standard mechanical properties. These are significantly improved by Desmophen 670, which is a very flexible polyester which improves gritting resistance, whilst giving film build due to its high non-volatile content. The crosslinking is carried out with a benzoguanamine formaldehyde resin, which not only imparts chemical resistance properties, but also improves appearance. The other crosslinking agent is a polyisocyanate (BL 3175) based on the trimer of HDI which leads to a high level of gritting resistance, especially after several coats of paint have been applied and with impacts at large angles (90'). Here, as with the formulation based on AN 927, a titanium derivative (Kronos 2059) is complemented by micro fixed white in order to extend the tint, whilst re

economically viable. Bentone gel is practically no longer used in these types of primer and Aerosil paste is used to impart high thixotropy, which is useful during electrostatic mini bowl application. This paint is brought to a cut viscosity of 30 s for application. It is certainly necessary to use a few percent of a low volatility solvent in order to give a good appearance. Optimum curing can be achieved at 140-150°C for 30'. In this temperature range, polyisocyanates blocked with MEKO will unblock.

Example 3-23: One component white finishing paint with high non-volatile content based on polyesters resins

These formulations use polyester resins B, C and D described in Example 3-2.

Material	**Weight %**			
Formulation N°	**1**	**2**	**3**	**4**
Polyester resin B/75	40.05	/	/	/
Polyester resin C/75	/	37.65	37.65	/
Polyester resin D/75	/	/	/	37.64
Títanium Kronos 21901	36.05	36.29	36.29	33.86
Cymel 303 2	10.01	12.09	12.09	9.41
FC 4303	3.86	3.86	3.86	3.86
MEK + Pr-Glycol-Ac	8.43	8.51	8.51	13.72
Nacure 5225 30%	/	/	1.60	/
Para- Toluene sulphonic acid	1.60	1.60	/	1.51

Total	100.00	100.00	100.00	100.00

Paint characteristics:

Pigment binder ratio	0.9/1			
Resin melamine, ratio	75/25	70/30	70/30	75/25
Non volatile content%	80	79	79	74
VOC in g/l	290	310	310	360
Viscosity Ford #4 in s	35 – 40	37 – 44	32 – 37	35 – 40

Curing = 10 minutes at 82°C + 20 ' at 120°C on Bonderite 37

Thickness in µm	30 – 38			
Pencil Hardness	2H	2 – 3H	H – 2H	3H
Direct impact/lb	120	110	160	140
Reverse impact/lb	130	100	160	120
% Adhesion	100	100	100	100

Salt spray 250 hours

Corrosion change(mm)	<1 (1/32)	<1 (1/32)	<1 (1/32)	<1 (1/32)
Adhesion loss in (mm)	4 (5/32)	4 (5/32)	1.5 (1/16)	5 (3/16)

Resistance to humidity 256 hours

Initial loss	95	94	94	94
Final loss	81	79	92	74
Blistering	8D	7D	None	8D

8 = small blister 1-2 significantly attacked
F,M, MD and D designate progressively greater blister density.

24 hour resistance covered spot

Lipstick	8	9	9	10
Mustard	9	9	8	10
Ink	10	10	9	10
Iodine tint	7	7	7	7
MEK double rubs	> 100	> 100	> 100	> 100

In this formulation the use of a good quality titanium, derivative gives a good exterior resistance. The high non-volatile content is provided by polyesters with 75% non-volatile content as well as by a hexamethoxylated melamine that has a non-volatile content of 100%. The VOC levels are very high. MEK is a solvent with good 'cutting power', which enables paint to be diluted efficiently although the high volatility of MEK can adversely affect the appearance of the film. A fluorinated surface tension agent (Fluorad) enables the surface tension to be significantly altered and the solvent based on propylene glycol is a low volatility solvent, which also improves surface tension whilst displaying interesting solvent properties.
The use of an acid, either p-toluene sulphonic acid or Nacure 5225, catalyses the Hydroxyl/melamine reaction, which is very important at a temperature of 1200C, the curing temperature for these coatings. Generally, Para toluene sulphonic acid is used, although there can be difficulties with paint storage stability notably with a change in viscosity. Nacure is a blocked acid catalyst which improves storage stability. These should, however, be used

sparingly because their presence could lead to water sensitivity and affect the water resistance of the paint film.
It can be clearly seen that the use of Nacure enables one to improve crosslinking of the system, whilst improving the stability of the paint at 50°C as well as at ambient temperature. Hardness is improved as well as water and corrosion resistance. Conversely, chemical resistance is slightly reduced although it still remains excellent.

The polyester resin with the lowest viscosity (Resin B - Example 3-2) enables one to prepare paints with the highest non-volatile content. Despite only a 25% Cymel content, it displays the lowest VOC.

The coating based on the TMA resin displays a better corrosion resistance.

Example 3-24: water-dilutable white stoving finish paint with good storage stability

Material	**weight %**
Polyester resin E/49%	43.95
Dimethylethanolamine	0.57
Water	28.48
Cymel 303	5.37
FC 430	0.15
Kronos 2190	21.48
Total	100.00

Paint characteristics

Pigment binder ratio	0.9/1
Resin melamine, ratio	80/20
Amount of cosolvent	5%
Non volatile content	49%
VOC lb/gal	1.4
pH	8.15
Viscosity Zahn #2	25 s

Curing:	5 min flash (to eliminate water) + 20 minutes at 175°C
Thickness of the film:	30–38µm

	Initial		**After 4 weeks at 50°**	
	CRS	**Bonderite 37**	**CRS**	**Bonderite 37**
Gloss at 60°	93	91	89	87
Pencil Hardness	3H	3H	3H	4H
Impact resistance				
Direct	150	160	160	110
Reverse	110	120	100	90
MEK double rubs	> 100	> 100	> 100	> 100

CRS: Cold rolled steel (Q panels)

Salt spray	**CRS**	**CRS**	**B 37**	**CRS**	**B 37**
	96 h	**240 h**	**240 h**	**96 h**	**240 h**
Corrosion start in mm	< 1	1 – 1.5	0.5 – 1	< 1	1
Adhesion loss in mm	11	13	3	10	2 – 3

Resistance Q UV (4 h 60°C + 4 h Condensation 60°C)

Initial gloss	93
167 hr	85
260	85
572	55
670	46
860	34
1016	32

Stability upon storage:

	pH	**Viscosity**
Initial	8.15	25 s
1 week	7.62	22 s
2 week	7.40	19 s
3 week	7.27	17 s
4 week	7.24	16 s

DMEA is used to adjust the pH if evaporation has taken place. Titane 2190 is well suited for water-dilutable systems. Crosslinking is by a hexamethoxylated melamine formaldehyde resin, which is readily compatible with water-based resins. As a surface tension modifier, a rather efficient fluorinated additive is used which destroys foam

Example 3-25: Highly flexible water-dilutable white stoving finish
This paint formulation uses resin F described in Example 3-3.

Material	**Weight %**
Resin F 134.5%	68.03
Water	8.11
Cymel 303'	2.61
Kronos 2190'	20.86
33% FC 4303	0.39
Total	100.00

Paint characteristics

Pigment binder ratio	0.8/1
Resin melamine ratio	90/10
Non-volatile content	47%
Viscosity Ford #4	37s
pH	8.40

Curing 10 minutes at 80°C + 20 minutes at 175°C
Thickness: 30-38 µm

Substrate	**CRS**	**BD 37**	**BD 1000**
Pencil Hardness	H	H	H
Impact resistance			
Direct	160	160	160
Inverse	160	160	160
Salt spray	100 h	240 h	240 h
Corrosion in mm	3116	1/16	1/16
Loss of adhesion	3/16	1/16	1116
Appearance	Blistering	Loss of gloss	Loss of gloss and start of corrosion

Chemical resistance on CRS

Lipstick	9
Mustard	8
Iodine tint	7
Waxing	6

Humidity resistance (Gloss 60°)

Initial	88
168 hr	85
240 hr	85
240 hr + 24 hr covered with watch glass	80

W O M (Gloss 60°)

Initial	83
100 hr	80
300 hr	69 (film cracking)
500 hr	62

In order to improve the flexibility, the melamine content is reduced using resin F. If even more flexibility is required, Cymel 370 can be used.

Example 3-26: White powder coating formulation – hybrid system

This powder coating formulation uses resin G, described in Example 3-4.

Material	**Weight %**
Carboxylated polyester resin G	35.62
Epoxy Epon 2002	32.48
Resiflow P672	1.00
Benzoin	0.50
Kronos 2190	31.00

Total	100.00

Preparation

1. Mix all components except titanium and stir at 2000 rev/min over 60 s.
2. Add titanium and stir once again at 2000 rev/min.
3. Place in extruder at 300 rev/min with mix zones at 85°C – 105°C.
4. Grind after cooling.

Characteristics of powder coating

Curing 20’ 180°C

Substrate	B1000	B-37	CRS
Thickness	38 – 50 µm		
Gloss 20°	96	96.5	96.5
MEK double rubs	Small loss of gloss and slight softening		
Adhesion	5B	5B	5B
Direct í2gct	140	140	160
Revers ct	140	120	160

Salt spray

	CRS	**CRS**
	100 h	**250 h**
Start of corrosion	1 mm	1 – 3 mm
Loss of adhesion	1 – 2 mm	5 – 6 mm

CRS ZINC PHOSPHATE		
	500 h	**1000 h**
Start of corrosion	1 – 2	1 – 2
Loss of adhesion	none	none

Humidity resistance

Initial gloss	98.8	98.5
Br. After 500 h	98.2	97.4
Blistering	none	none

Chemical resistance

Mustard	10	10
Lipstick	10	10
Iodine tint	7 – 8	7
Waxing	6	6

A type '2' epoxy resin is used to crosslink the carboxyl functionality of the polyester resin. Benzoin is a useful degassing additive during crosslinking that enables the surface to remain open to allow any volatile reaction component to escape from the film. However, this type of additive can lead to yellowing. The flow of the film is improved by the use of Resiflow that can be replaced by Modaflow 3.

Example 3-27: Coil coating

This formulation uses either resin C1or D1 described in Example 3-7.

Material	**Weight %**
Polyester resin CI or DIV 60%	56.3
Cymel 301	3.6
Kronos 2310	25.0
Blocked dinonyl naphthalene sulphonic acid	1.9
Byk 358	0.6
Solvent cut	12.6
Total	100.0

Characteristics of paint:

Pigment binder ratio	40/60
Polyester melamine ratio	90/10

Resin	**C1**	**D1**
Gloss 20°	78	73
Gloss 60°	90	86
NEK double rubs	90	80
Initial hardness	2hr	2hr
After 30’ boiling water		
Covered	15 min	30 nu«n
Adhesion	100	100

Chemical resistance:

Mustard after 24 h	3/4	2/4
Lipstick 24 h	4/5	3/4
Ink 24 h	4/4	4/3
Grape juice 24 h	5/5	5/5
50 % Sulphuric acid 24 h	5/5	5/5

Detergent resistance 5 days / 10 days at 165°C:

% Gloss at 60°	96/69	98/95
% Gloss at 20°	74/24	84/63

This coating is extremely flexible due to the polyester structure and also because of the low content of melamine formaldehyde resin. The titanium dioxide used for this coil application has class A weathering resistance. The paint is adjusted to 50% by volume with the solvent action and applied to pre-treated 721 Bonderite. Curing is for 30s at 313'C which gives a peak metal temperature (pma) of 216°C.

These two resins contain CHDA and CHDM and the properties obtained from cured films containing them demonstrate their ability to combine good mechanical properties and hardness whilst still achieving good flexibility. The components of the polyesters giving flexibility are Adipic acid or hexane diol. They are only about 5 %. When hexanediol is used instead of the Adipic acid the characteristics are slightly better. NPG remains one of the major diols since it contributes greatly to the performance of the coil coating.

IV CONCLUSION

As seen throughout this chapter on polyester resins, through their components and applications, it cannot be denied that they represent an important category of resins. The scope of polyester resins as such is rather broad and becomes even broader if all of the resins used in the polyurethane industry are included. The powder field remains an important area and this will certainly remain the case for many years to come.

The diversity of the monomers that can be used for the preparation of polyesters remains a prime asset for the progression of these products and to guarantee their presence for many years to come on the paint market. Polyester resins manage to compete with the new products which are being developed and which are environmentally friendly. They can be found in water reducible coatings, in powder coatings and in UV crosslinking systems.

Today, the expression; saturated polyester is synonymous with flexibility. Their extreme flexibility and perfect compatibility enables them to be used in blends with acrylic resins in cases where impact resistance or elongation is necessary.

Polyester development will continue as long as there is progression in new basic polyols and polyacids, which will enable improvements in the properties of resins, such as exterior resistance, non-volatile content, yellowing or even the use of FDA approved products.

The Tg, of a polyester resin is similar to that of an acrylic resin and can be adjusted over a very wide and very practical range. Polyesters can be amorphous, crystalline, semi-crystalline, branched, linear, thermoset and thermoplastic as well as flexible/elastic and hard/brittle.

Polyesters are heat, moisture and oxygen resistant as well as being resistant to many other substances. In the powder sector, they are completely dominant (with epoxies) and they give excellent results. In the case of polyurethanes, they are often adjusted in order to be the flexible part of the final product which after crosslinking retains some degree of flexibility.

There is also an analogy between polyesters for paints and fibres, which are not always of the same type in terms of their high crystallinity and extreme flexibility. It is clear that this sector involves a very large volume for polyester resins, which are also found in polyurethane fibres. After 100 years of existence, polyester resins have a technical connotation and enter, dynamically into the third millennium.