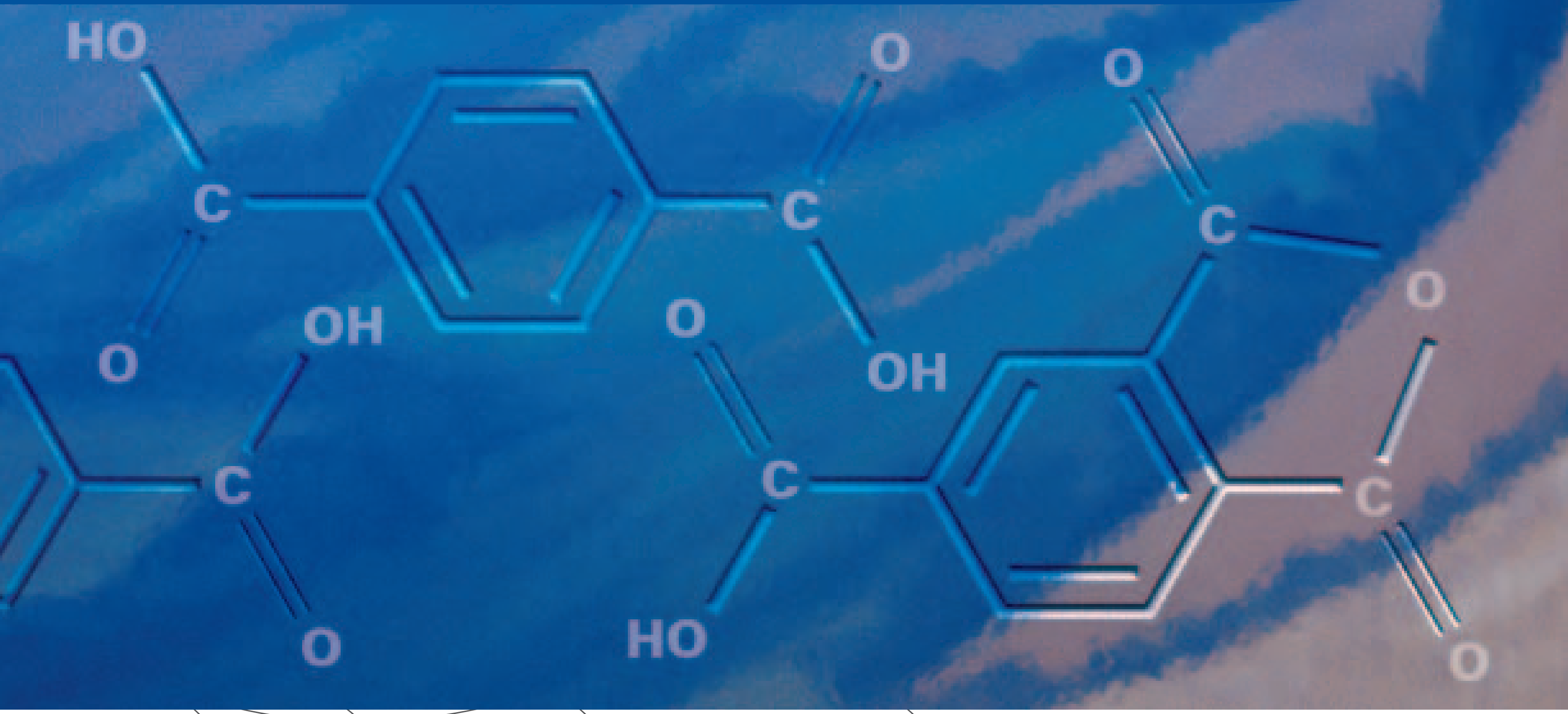
how to process better coating resins with BP PIA, TMA and TA



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Introduction

BP purified isophthalic acid, trimellitic anhydride and terephthalic acid are widely used to produce high quality polyester resins for coatings. The special advantages that these intermediates can provide are described in trade literature and in a number of other brochures published by BP.

Purified isophthalic acid (PIA) is used to produce resins with higher molecular weight, faster dry times, more flexibility, and greater resistance to weathering and chemical degradation than orthophthalate resins. Trimellitic anhydride (TMA) offers a unique route to making water soluble polyester resins with high aromatic content that can form films with performance equaling that of solvent reduced coatings. TMA also provides cross-linking sites through its carboxyl functionality in high performance powder coating resins. Terephthalic acid (TA) provides powder coating polymers with the required glass transition temperature for improved storage stability. Blends of PIA and TA are often used in saturated polyester polymers to yield improved polymer solubility characteristics.

BP also offers a new line of multifunctional aromatic acids that show promise for use in formulating high performance coatings polymers.
Ask your sales representative for technical information on BP's Fine Acids.

The special advantages of PIA, TMA and TA can be readily obtained in polyester resins. Although they are chemically similar to other aromatic acids and anhydrides, they must be properly incorporated into the resins to obtain the full end use advantages. This guide is an introduction to the processing techniques that BP's Chemical Intermediates Applications Laboratory finds useful when synthesizing resins based on PIA, TMA and TA.

This brochure includes basic or "textbook" chemistry and engineering information, as well as more specific material developed by our laboratories. Although the contents of this brochure may be elementary to the experienced resin formulator, this information is intended for use only by persons familiar with process safety and conventional resin processing techniques.

The topics covered include an outline of the chemical reactions that can occur during resin processing, equipment requirements, calculations that predict processing behavior, examples of the various ways PIA and TMA resins can be processed, techniques for increasing the rate of reaction and troubleshooting the abnormal synthesis.

About BP PIA, TMA and TA

PIA, TMA and TA are among the aromatic acids that are produced by BP's Mid-Century Oxidation Process. The chemical structures of these intermediates are illustrated below and their sales specifications are listed in Tables 1, 2 and 3.

BP PIA imparts outstanding adhesion and excellent chemical resistance to alkyd coatings. As compared to orthophthalates, PIA produces resins with faster dry times, more flexibility and greater weathering and chemical resistance. This highly pure, white crystalline powder is available from BP's plants in Joliet, Illinois, Geel, Belgium, and AGIC in Mizushima, Japan.

BP TMA offers high reactivity, trifunctionality and an acid-anhydride combination that are particularly valuable in water soluble coating resins. TMA is a solid, flaked product that hydrolyzes to trimellitic acid in the presence of moisture. To prevent hydrolysis, opened bags should be used promptly or the TMA should be repackaged and sealed.

Experience has shown that BP TA, used in modest amounts, improves certain characteristics such as solubility and pigment wetting without significantly changing physical properties of the finished resin.

Purified Isophthalic acid

PIA

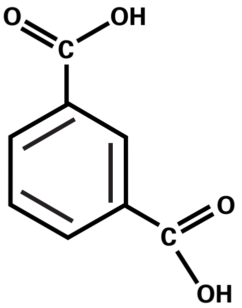


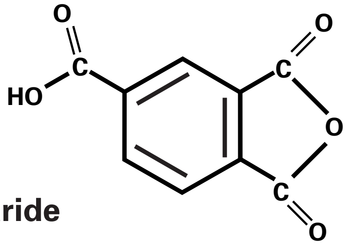
Table 1

Sales specifications of BP PIA*

Appearance	White crystalline powder
Acid number, mg KOH/g	675 ± 2
Moisture, wt. %	0.1 max.
Isophthalic acid, wt. %	99.8 min.
Ash, ppm	18 max.
Metals, ppm	
chromium	2 max
cobalt	1 max.
iron	1 max.
manganese	1 max.
molybdenum	1 max.
nickel	1 max.
titanium	1 max.

*Specifications subject to change without notice

TMA



Trimellitic anhydride

Table 2

Sales specifications of BP TMA*

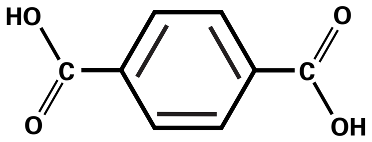
Appearance	White flakes
Trimellitic anhydride, wt. %	95.0 min.
Freezing point, °C (°F)	165 (329) min.
Color, ΔE	4.2 max.

*Specifications subject to change without notice.

TMA health and handling information

CAUTION! Improper handling of TMA may result in serious adverse health effects. This product should be handled in a well-ventilated fume hood, and the use of approved respiratory protection equipment is strongly recommended. This information is discussed in further detail in the Material Safety Data Sheet (MSDS) and in the BP Bulletin entitled *TMA Health and Safety Information*. We recommend that the MSDS and the brochure be reviewed before handling this product. This information is available upon request from your sales representative, or by writing the address shown on this brochure.

TA



Terephthalic acid

Table 3

Sales specifications of BP TA*

Moisture, wt. %	0.5 max.
Acid number, mg KOH/g	673 min. – 677 max.
Terephthalic acid, wt. %	98.5 min.
Ash, ppm	15 max.
Heavy metals, ppm	10 max.

*Specifications subject to change without notice.

PIA and TA health and handling information

CAUTION! Dust may produce mild eye irritation. Wear safety goggles if dust cannot be controlled. Store in a well-ventilated, dust-free area. Material Safety Data Sheets (MSDS) for PIA and TA are available upon request from your BP sales representative or by writing to BP at the address shown on this brochure. Always consult the Material Safety Data Sheet for products you consider using.

The chemistry of polyester coating resins

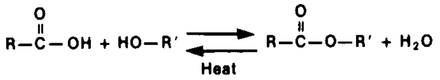
In common with other coating resins, polyesters must fulfill two roles. It must wet the pigment and disperse all paint components. If pigmentation is present, the resin must assist in pigment wetting. With further reaction, the resin becomes an insoluble film binding the paint solids to the substrate. The reactions that produce the relatively low molecular weight polyester are reviewed in this section followed by illustrations of the reactions that can convert the polyester into an insoluble film.

Polyester resins for coatings typically are made by condensation reactions between mono- and polybasic acids, anhydrides, polyols and esters. Contemporary coating resins are the reaction product of several raw materials with many chemical reactions happening simultaneously. To simplify, the common reactions occurring during resin synthesis are outlined below.

All polymers made by condensation reactions between acids and hydroxyls are termed polyesters. Polyesters made from long chain fatty esters, typically derived from vegetable oils, are called alkyds. While many coatings chemists tend to use the term polyester to describe only oil-free resins, in this discussion, polyester is meant to include oil-based alkyds.

Esterification

Esters can be formed by the reaction of a carboxylic acid and an alcohol when heated.

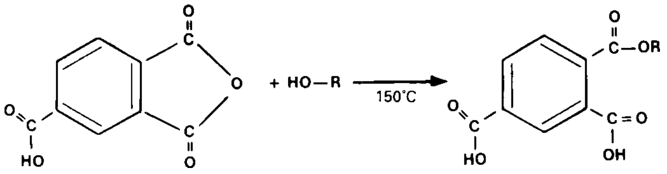


$$R{-}\overset{\overset{\large O}{\|}}{C}{-}OH + HO{-}R' \underset{\text{Heat}}{\rightleftharpoons} R{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}R' + H_2O$$

Acid Alcohol Ester Water

The rate of reaction depends on whether functional groups are primary, secondary or tertiary, on the concentration and proportions of reactants, on the solubility of the reactants, on the presence of catalysts, and on the temperature. Because the reaction is reversible, the removal of water is essential to prevent hydrolysis of the ester product.

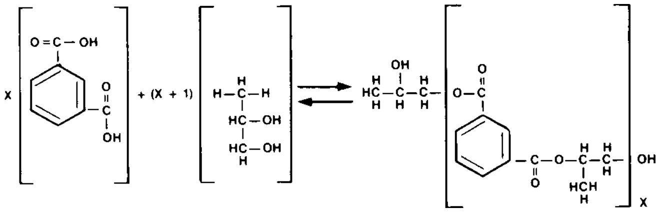
Anhydride groups react with alcohol to form an ester linkage and a free acid group. No water is evolved by this relatively low temperature (150°C) reaction.



TMA Alcohol TM Monoester

Polyesterification

When the reactant molecules each contain two or more functional groups, the reaction can be considered polyesterification.



Isophthalic Acid Propylene Glycol Polyester

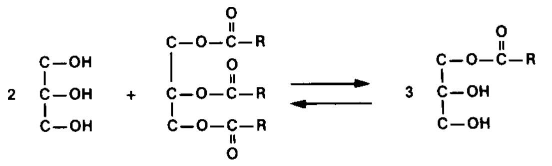
Polyesterification reaction rates are influenced by the same factors affecting simple esterification. With stoichiometric amounts of polyfunctional acids and hydroxyls, polyesterification can theoretically produce resins of almost infinite molecular weight. A major concern of coating resin producers is controlling molecular growth during polyesterification to produce a polymer of suitable viscosity. In the illustration, an excess of glycol results in a hydroxyl terminated polymer of finite size. Methods for controlling polymer growth will be covered in more detail in later sections of this brochure.

Ester exchange reactions

Esters can enter into exchange reactions with compounds containing hydroxyls (alcoholysis), carboxyls (acidolysis) and with other esters (ester interchange). Alcoholysis and acidolysis are useful reactions for increasing reactant solubility and dispersing oil unsaturation and pendant hydroxyls and carboxyls throughout the polymer.

Alcoholysis

Classic alcoholysis is used when preparing alkyds from triglyceride oils. Typically, the oil will be reacted with glycerol to form a mixture of mono-, di- and triglycerides. An idealized reaction is:

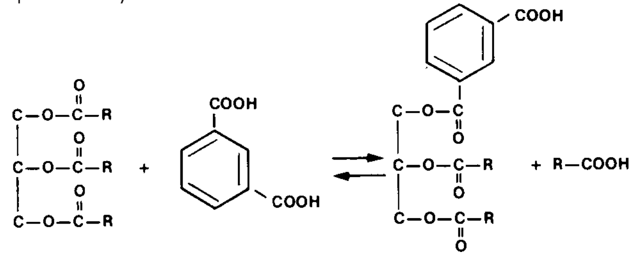


Glycerol Triglyceride Oil Monoglyceride

Typical alcoholysis is catalyzed by lithium hydroxide monohydrate or hydrated monobutyltin oxide. The partial esters formed by alcoholysis contribute to a more uniform distribution of functionality throughout the resin molecule.

Acidolysis

During acidolysis the acid portion of an ester is replaced by a new acid.

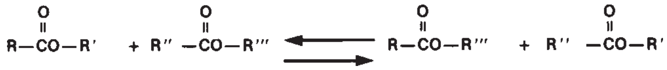


Triglyceride Oil
Isophthalic Acid
Acidolysate Product
Fatty Acid

This reaction has proven particularly valuable for rapidly introducing relatively insoluble acids to the reaction mixture. In the above example, PIA replaces one of the fatty esters on a triglyceride. The resultant half ester of PIA is considerably more soluble in the other reactants than PIA alone. This greater solubility and the presence of the coproduct fatty acid produces much faster reaction rates.

Ester interchange

As implied by the name, ester interchange involves the exchange of the functional groups adjacent to the ester linkages.



$$R{-}\overset{\overset{O}{\|}}{C}O{-}R' + R''{-}\overset{\overset{O}{\|}}{C}O{-}R''' \rightleftarrows R{-}\overset{\overset{O}{\|}}{C}O{-}R''' + R''{-}\overset{\overset{O}{\|}}{C}O{-}R'$$

Ester A
Ester B
Ester C
Ester D

It is believed that inter-ester exchanges occur during polyesterification, however, the extent and importance of this reaction is not well known. An example of ester interchange that does influence resin properties is the cyclization that can occur with orthophthalate polyesters, thus limiting molecular weight and impairing performance properties.

Side reactions during esterification

In the presence of heat and catalysts a variety of non-ester forming reactions can take place. Some side reactions that can effect resin structure and properties are discussed here.

Etherification

At typical resin processing temperatures of 210°C to 250°C, hydroxyl containing compounds can react to form ethers.

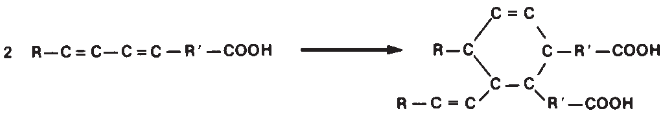
$$R{-}OH + R'{-}OH \xrightarrow[>210^{\circ}C]{} R{-}O{-}R' + H_2O\uparrow$$

Etherification tendencies are highest during alcoholysis when there is a substantial polyol excess and an alkaline catalyst. Etherification will introduce an undesired linkage to the polymer and reduce hydroxyl availability which may increase gelation tendencies.

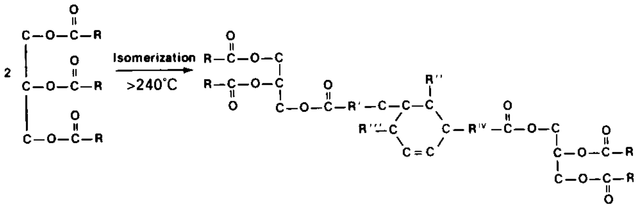
Addition reactions

The conjugated double bonds of drying oils and fatty acids can enter into free-radical and Diels-Alder reactions with themselves or with other unsaturated compounds such as vinyl modifiers or maleic anhydride.

Thermal polymerization of conjugated fatty acids or oils is sometimes called heat bodying.



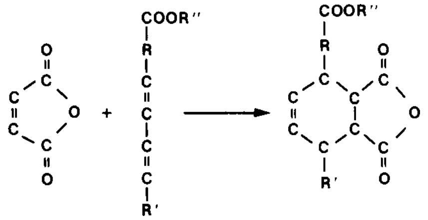
Conjugated Fatty Acid
Dimer Fatty Acid



Conjugated Triglyceride Oil
“Bodied” Oil

These reactions increase the molecular weight of the alkyd and reduce the available sites for curing. Heat bodying of certain fatty acids shortens dry hard time of paint films. Tung oil or tung fatty acid heat body so rapidly as to become mostly dimer acid of the type shown above. Avoiding temperatures over 240°C will minimize the rate of heat bodying.

Maleic anhydride or fumaric acid may be added to unsaturated materials to build molecular weight and provide harder coating films. For example, unsaturated fatty acid forms a trifunctional acid that can be used to produce coatings with harder films and faster dry times.



Maleic Anhydride
Conjugated Fatty Ester
Maleic Adduct

Reaction temperatures and rates

During resin synthesis, various reactions occur at different rates and in different temperature ranges. Heat-up rates and maximum temperatures at various stages are important determinants of final resin composition. To maintain batch-to-batch consistency when manufacturing resins, carefully monitor and duplicate all process variables.

The approximate rate of esterification at 232°C for some di- and tri-acids with triethylene glycol is shown in Figure 1. Because esterification occurs during the heating to 232°C, the chart is more properly an illustration of how rapidly the various acids reach complete reaction.

A further indication of reaction rate is given by the ionization constants of organic acids commonly used in esterification reactions. Because water solutions were used, anhydride materials were converted to the acid form; therefore, the first constant is not relevant to ester formation via anhydride opening.

Table 4

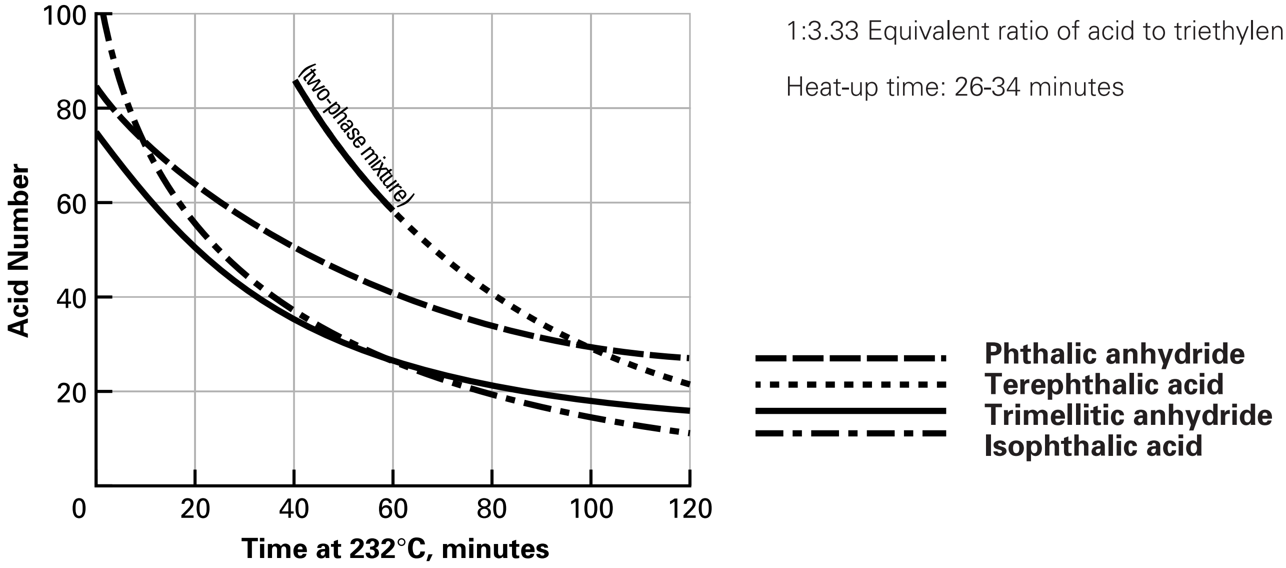
Ionization constants of organic acids in water*

Acid	K_1	K_2	K_3
Orthophthalic**	1.1x10^{-3}	3.8x10^{-6}	—
Isophthalic	2.4x10^{-4}	2.5x10^{-5}	—
Terephthalic	2.9x10^{-4}	3.5x10^{-5}	—
Trimellitic**	3.0x10^{-3}	1.4x10^{-4}	6.3x10^{-6}
Adipic	3.7x10^{-5}	3.9x10^{-6}	—
Maleic**	1.1x10^{-2}	6.0x10^{-7}	—

* Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed.
** Generally used as anhydrides, not acids.

Figure 1

Approximate esterification rates of aromatic acids and anhydrides



1:3.33 Equivalent ratio of acid to triethylene glycol

Heat-up time: 26-34 minutes

Transforming the liquid paint to insoluble film

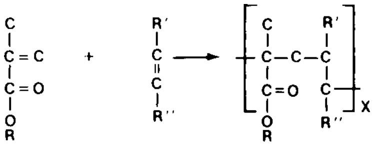
Mechanisms for film forming include solvent evaporation, internal cross-linking and cross-linking with an added reagent. Commercially useful polyesters are normally cross-linked using unsaturation, carboxyl or hydroxyl functionality built into the molecular structure.

Curing reactions

Curing through unsaturation

Conventional drying oil alkyds cure by oxygen-triggered cross-linking between the double bonds contributed by fatty acids in the resin formulation.

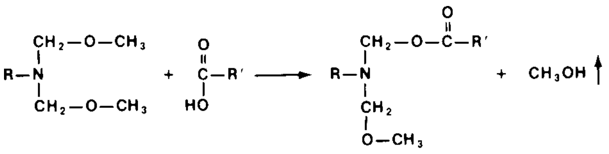
Paints can also be formulated with reactive vinyl compounds that will copolymerize and cross-link with isolated double bonds in the polymer structure. Typically, cure is initiated by catalyst with heat or radiation.



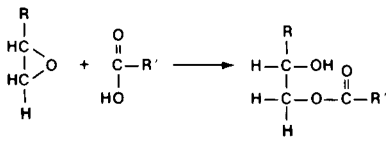
Vinyl Monomer
Unsaturated Alkyd Resin
Cured Resin

Curing through acid functionality

In addition to continued esterification, the carboxyl groups of a polyester can be used for curing with epoxies and melamines.



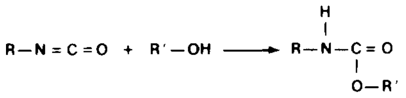
Methoxymethyl Functionality of Melamine
Carboxyl Functional Polyester
Cured Resin
Methanol



Epoxy Resin
Carboxyl Functional Polyester
Cured Resin

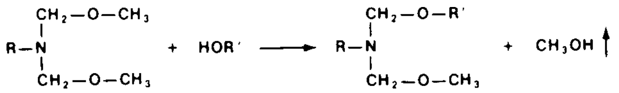
Curing through hydroxyl functionality

Many high performance alkyds are cured with isocyanates or amino resins such as melamines and urea-formaldehydes.



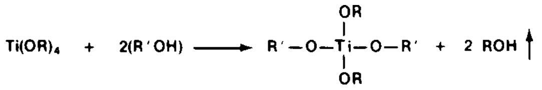
$R{-}N{=}C{=}O + R'{-}OH \longrightarrow R{-}\overset{H}{N}{-}\underset{O-R'}{C}{=}O$

Polyisocyanate
Hydroxyl Functional Polyester
Polyurethane



Methoxymethyl Functionality of Melamine
Hydroxyl Functional Polyester
Cured Resin
Methanol

Another method of cross-linking through the hydroxyl groups uses a pH sensitive chelate. When the pH drops during drying, the chelate cross-links the hydroxyls.



$Ti(OR)_4 + 2(R'OH) \longrightarrow R'{-}O{-}\underset{OR}{\overset{OR}{Ti}}{-}O{-}R' + 2\,ROH\uparrow$

Organic Titanate
Hydroxyl Functional Polyester
Cured Resin
Volatile Alcohol

This curing method is most applicable to water soluble polyesters solubilized through pendant carboxyls that are amine or ammonium hydroxide neutralized. Upon drying, the neutralizing base will volatilize, causing the pH of the system to drop, activating the chelate to cross-link the pendant hydroxyls.

Polyester resins containing residual carboxyl and hydroxyl functionality can also experience continued esterification during thermal cure until the free groups are sterically hindered.

Equipment for processing coating resins

The equipment needed to process a complete range of polyesters includes: a heated reactor with agitator, thermometers, inert gas sparge, reactant addition port and sampling port; an overhead system including a partial condenser for returning volatile polyols to the reactor, decanter traps for returning reflux solvents and total condenser for collecting reaction water; and a blending tank for thinning the finished resin.

CAUTION: Equipment must be designed and maintained to protect workers from unsafe exposure to esterification raw materials, the reaction mixture or evolved vapors. Processing equipment and procedures should be reviewed by qualified safety experts to ensure worker protection.

Reactors

Whether laboratory, pilot plant or commercial scale, the resin kettle must be constructed of material that will not corrode or contaminate the reaction mixture. At processing temperatures, organic acids, even fatty acids, can attack some metals. Stainless steel and glass are common materials for resin kettles. Type 316 SS is adequate for temperatures to 280°C.

Thorough agitation is essential to suspend solid part- icles, promote intimate contact of ingredients for faster reaction rates and to prevent hot spots which can lead to color formation. Turbine-blade agitators and vertical baffle plates are generally preferred to prevent the fluid from swirling (forming a vortex). BP's pilot plant reactors have the following equipment:

- Variable speed turbine blade agitators that maintain tip speeds of 200 to 1000 ft/min (1 to 5 meter/second).
- Mechanical foam breakers attached to top of agitators
- Baffles on the reactor wall that promote turbulence.

Figure 2a

Typical laboratory apparatus for fusion processing with glycol reflux

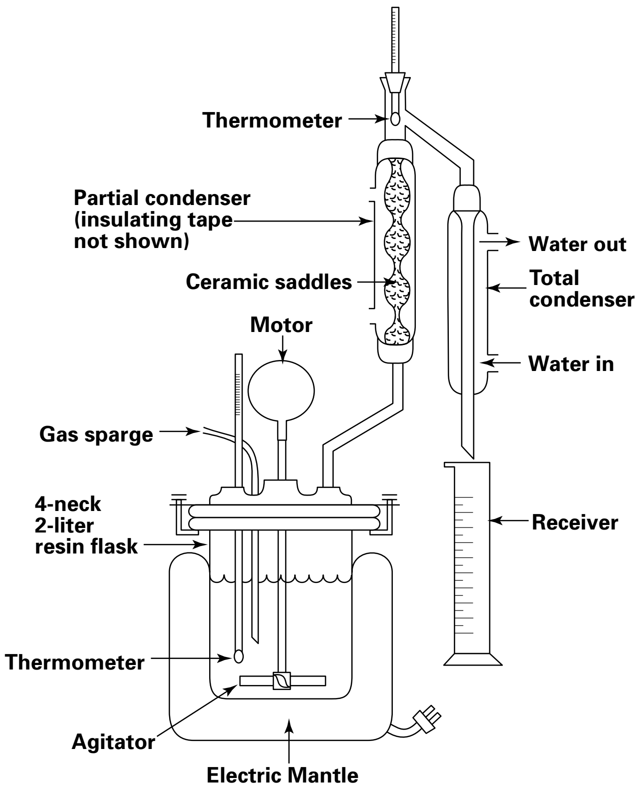
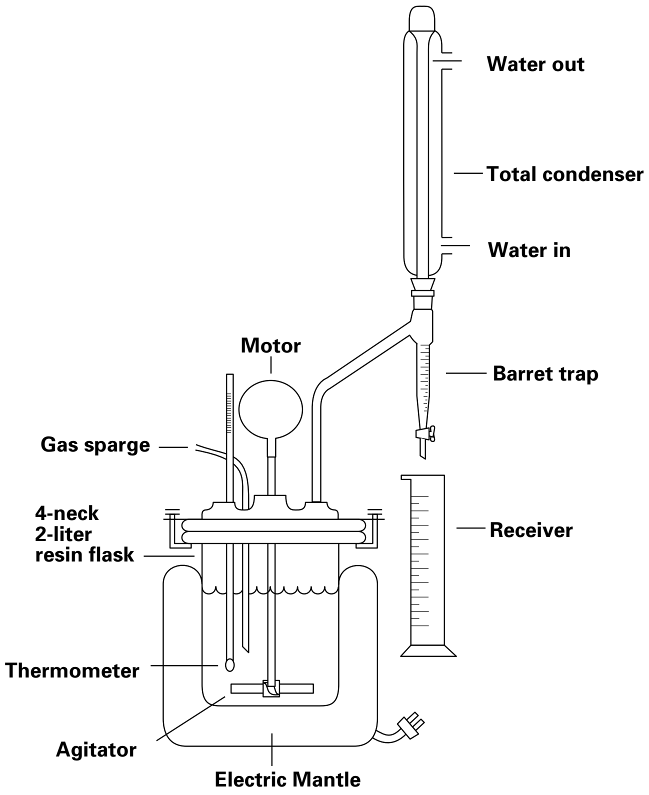


Figure 2b

Condenser system for solvent processing



To protect the resin from color formation, an inert gas sparge of nitrogen, carbon dioxide or combustion gases should blanket the reaction mixture during heat-up and finishing. Some processors rely on evolved water to blanket the reaction mixture. However, BP's experience indicates an inert gas sparge is required throughout processing to control color formation. The inert gas should contain less than 20 ppm (and preferably less than 10 ppm) oxygen. Sparge capacity should be adequate to blanket the charge within a convenient time, but slow enough that evolved vapors are thoroughly cooled in the condenser system. Near the end of the reaction, this sparge helps remove the last traces of water. The sparge rate typically used in our 60 gallon (230 liter) reactor is 0.1 to 0.3 scf/min (0.2 to 0.6 ml/sec air flow per liter of reactor capacity.

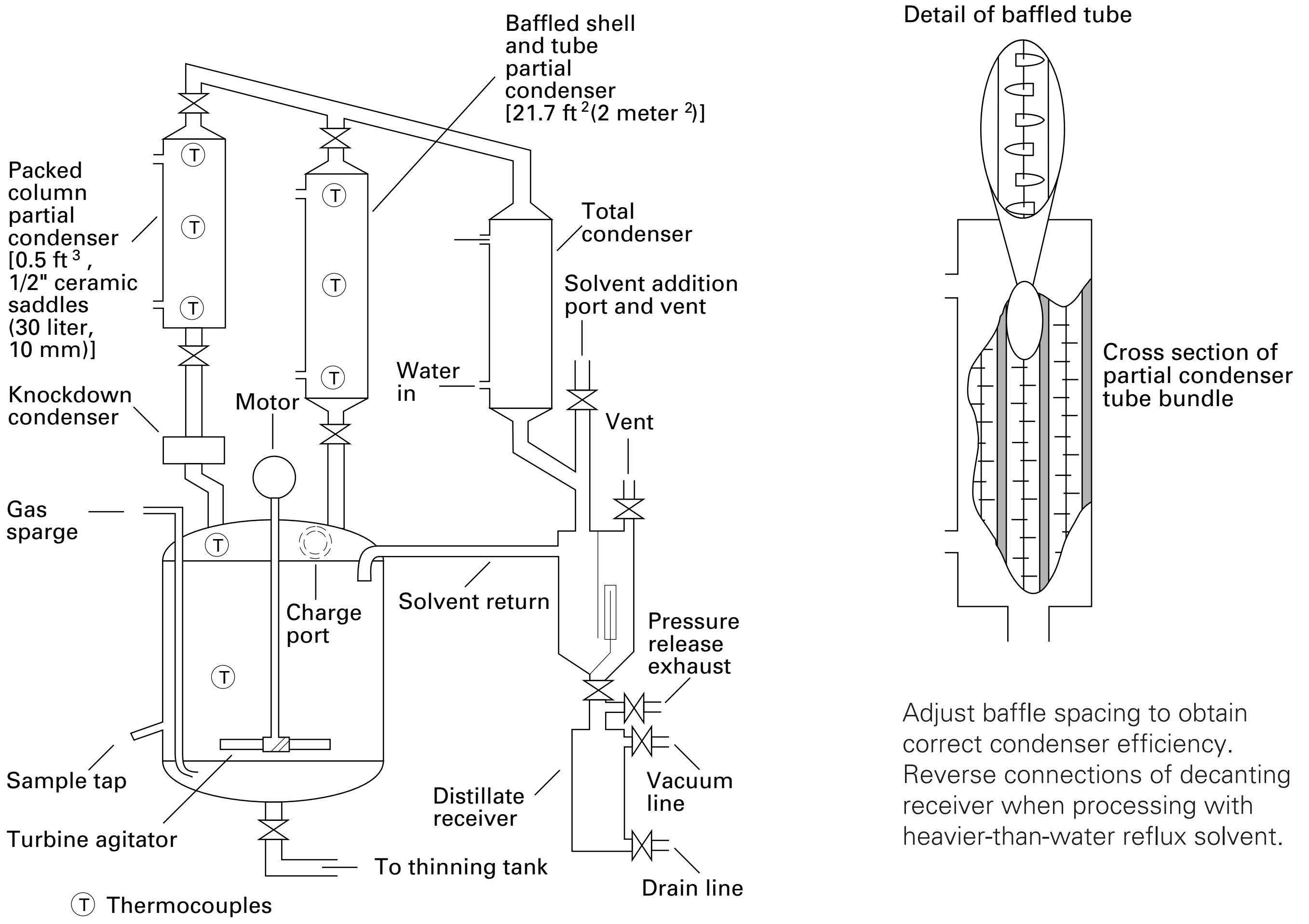
Fast water evolution during some stages of polyesterification can cause troublesome foaming. In an attempt to alleviate this problem, many larger scale reactors are equipped with mechanical foam breakers that rotate above the liquid level in the reactor.

Reactor heating should be of sufficient capacity to drive the esterification reaction vigorously. BP's reactor has a heating capacity of about 400 kJ/hour for each liter of charge (100 watt per liter). Indirect heating methods such as jacketing with steam or heat transfer fluids minimize hot spots and color formation compared with direct methods such as flame or electric coils. Jacketing can also be used to rapidly cool the reaction mixture. However, direct heating with gas, oil or electricity is less expensive.

Many coating resins are made by two- or three-stage reactions. Reactor design should allow convenient addition of liquid and solid reactants during processing without exposing the reaction mixture to the atmosphere or exposing operators to hazardous fumes. Provisions should also be made for sampling the resin during processing. Laboratory and small pilot plant reactors can be opened fairly quickly under a hood for sampling and reactant addition. Larger size reactors will need special access ports to avoid loss of volatiles, excessive heat loss, oxidation contamination and worker exposure to fumes. Sampling devices must be designed to obtain random, typical samples. Blind spots and dead ends must be avoided.

Figure 3

Typical pilot scale resin reactor



Adjust baffle spacing to obtain correct condenser efficiency. Reverse connections of decanting receiver when processing with heavier-than-water reflux solvent.

Accurate thermometers or thermocouples are necessary to follow the progress of the resin processing. At minimum, the temperature should be measured of the bulk of the reaction mixture and vapors at the top of the partial condenser. More useful is to have measuring devices from reactor vapor up through distillation head. The resultant temperature profile can predict fractionator flooding and help maintain higher reactor heating rates.

Condenser systems

Fractionating columns or partial condensers are essential equipment for removing water and reducing loss of glycol, polyol and high boiling solvents during processing. To provide greater flexibility for synthesizing a variety of resins, the condenser system should be equipped for water removal and return of glycols, polyols, and water-immiscible solvents of high and low density. Figures 2 and 3 outline BP’s overhead systems for laboratory and pilot plant reactors.

BP’s 2-liter laboratory reactors are equipped with 25x400mm condenser tubes filled with enough 6-mm ceramic saddles to displace 35cm^3. The condenser tubes can be wrapped with insulation tape to reduce heat loss. Condensers for other size glassware reactors are scaled to keep equipment volume ratio constant.

BP’s pilot scale reactors use either baffled tube and shell condensers with a cooling jacket or packed columns. The jacket is designed for use with either water or steam. The heat transfer area of the partial condenser is about 10m^2/m^3 of kettle capacity. For safe pressure processing, the jacket of the partial condenser should be rated at the same pressure as the reactor.

The correct operating conditions for the partial condenser change as the reaction progresses. Early in the reaction the vapors consist mostly of superheated glycol. For efficient glycol recovery, the partial condenser should be run with a high reflux ratio (but not enough to cause flooding). Near the end of the reaction, the vapors consist mostly of water (i.e., low pressure steam). Efficient water removal requires less reflux and less cooling (or perhaps even steam heat).

Thinning tanks

Pilot plant and commercial reactors are equipped with thinning tanks so that capacity will not be reduced by the space allowance in the reactor for solvent addition. The thinning tank also has the advantage of reducing reactor residence time. Thinning tanks should have twice the capacity of the associated reactors.

If the tank is very far from the reactor, the connecting line may need to be heat traced. Enclosed systems for pumping resin and solvent into the tank are essential for controlling vapor emission. The agitator for a thinning tank must be able to handle fairly viscous materials, but does not need the same power as the reactor agitator. Hot and cold fluid jacketing of the tank can be useful both for maintaining heat to aid solubility and to cool a hot resin solution to packaging temperature.

Calculations that predict resin processing outcome

The calculations suggested in this section serve several purposes. Given a finished formulation, the calculations can help determine the theoretical end properties of the resin, the amount of reaction water which will be evolved, the probable risk of gelation and the amount of cross-linker required to cure the resin. The calculations also offer help when reformulating resins to modify certain properties and when using basic principles to formulate new resins.

BP offers a free copy of our computer program, *Polycalc,* which calculates polyester and alkyd characterization data on most IBM-compatible personal computers. Contact your BP sales representative for a copy.

Importance of equivalent weights

A prerequisite for using the formulation calculations is a knowledge of the equivalent weight of each reactant.

The equivalent weight (Eq. Wt.) of a material is its molecular weight (MW) divided by its theoretical functionality (F) and can be directly calculated for known materials:

$$\text{(1)} \quad \text{Eq. Wt.} = \frac{\text{MW}}{\text{F}}$$

For example, PIA [HOOC (C_6H_4) COOH] has a molecular weight of 166 and two functional groups; therefore, its equivalent weight is 83. Similarly, TMA [O_3C_2 (C_6H_3) COOH] has molecular weight of 192 and three functional groups (the anhydride formation reacts as two functional groups); therefore, TMA has an equivalent weight of 64.

Implicit in the term "equivalent weight" is the type of functionality. When a material contains more than one type of reactive functionality, the equivalent weight term must be explicitly modified by the functionality type. For materials of unknown or mixed composition, the equivalent weight can be calculated from the experimentally determined acid number (AN) or hydroxyl number (OHN) (ASTM Methods D1639 and D1957). The units of these numbers are mg KOH/g of resin solids. This factor of 56,100 (which is the mole weight of KOH multiplied by 1,000) becomes the numerator in calculations 2 and 3.

$$\text{(2)} \quad \text{Acid Eq. Wt.} = \frac{56{,}100}{\text{AN}}$$

$$\text{(3)} \quad \text{Hydroxyl Eq. Wt.} = \frac{56{,}100}{\text{OHN}}$$

Equivalent weight can also be calculated from the weight percent hydroxyl (Wt. % OH) if it is known. The numerator is derived from the mole weight of hydroxyl functionality, multiplied by 100.

$$\text{(4)} \quad \text{Hydroxyl Eq. Wt.} = \frac{1{,}700}{\text{Wt. \% OH}}$$

The equivalent weights of many common raw materials are listed in the Appendix.

Water of esterification and resin yield

The basic reaction producing polyesters is the esterification reaction. Ideally, this is the reaction of an equivalent number of acid groups and hydroxyl groups, yielding a polyester and water.

For reasons that are discussed below and in other sections, virtually all polyester coating resins are formulated with an excess of hydroxyl groups. Consequently, if the polyesterification reaction goes to completion, the amount of water evolved relates directly to the equivalents of acid and acid-anhydride charged to the reactor.

Calculation 5 sums the weight of water contributed by each source of carboxyl functionality. Each carboxyl equivalence yields a mole of water. Each mole of TMA (functionality of 3) contributes 2 moles of water. Each anhydride mole (functionality of 2) yields a mole of water.

$$\text{(5)} \quad H_2O \text{ off} = \text{Weight of } H_2O \text{ off at completion}$$

$$H_2O \text{ off} = 18 \text{ (Eq acids)} + 12 \text{ (Eq TMA)} + 9 \text{ (Eq anhydrides)}$$

The calculation of water evolved is useful both as a tool for following the course of the esterification reaction as distillate is collected, and to find the difference between charge weight and yield (Y).

$$\text{(6)} \quad Y = \text{Charge Wt.} - H_2O \text{ off (from Eq. 5)}$$

Many water soluble resins are formulated to contain pendant carboxyls that can be neutralized to provide water solubility. Such resins will display fairly high acid numbers (AN) and evolve less reaction water than is calculated by Equation 6. A correction factor for high acid number resins is given by the expression

$$\frac{18 \text{ (AN)}}{56{,}100}$$

The yield in Equation 6 is divided by one minus this factor to calculate the yield of higher acid number resins (Y').

(7)
$$Y' = \frac{\text{Charge Wt.} - H_2O \text{ off}}{1 - \frac{18\,(AN)}{56{,}100}}$$

A more accurate calculation for water evolved can be derived from the corrected yield of Equation 7.

(8)
$$H_2O \text{ off (corrected)} = \text{Charge Wt.} - Y' \text{ (from Eq. 7)}$$

Equations 5 and 8 are equivalent for very low acid number resins.

Oil length and fatty acids

Traditional alkyds are formulated with significant drying oil or fatty acid content. Alkyds containing oil are typically described as having a given "oil length" which relates to the weight percent of oil in the formulation. By convention, these designators are:

Oil length	**% Oil**
Short	< 45
Medium	45-55
Long	55-70
Very long	> 70

If a resin is formulated with triglyceride oil, the calculation of percent oil is simply the charge weight of oil divided by the total yield and multiplied by 100

(9)
$$\%\text{ Oil} = \frac{(\text{Wt. Oil})\,100}{Y'}$$

When formulating to a target oil length, the charge weight of oil can be calculated using Equation 10. High final acid numbers may give rise to small differences between target oil length and final percent oil. This is because Equation 10 uses the theoretical water off (Eq. 5), not the somewhat lower, corrected water off (Eq. 8).

(10)
$$\text{Wt. Oil} = \frac{(\text{Charge Wt.} - H_2O \text{ off})\ \%\text{ Oil}}{100}$$

Many alkyds are formulated using fatty acids with various trifunctional polyols in place of oil. To calculate the percent oil or oil length of a resin formulated with fatty acid, the weight of fatty acid plus the polyol (PO) required to esterify the acid less the esterification water is divided by total yield. The equivalents of fatty acid and polyol are, of course, equal; therefore, the equation uses the known equivalents of fatty acid times polyol equivalent weight to calculate polyol weight.

(11)
$$\%\text{ Oil} = \frac{\text{Wt. FA} + \text{Eq. FA}\,(\text{Eq. Wt. PO} - 18)}{Y'} \times 100$$

Percent oil can be converted to percent fatty acid using Equation 12.

(12)
$$\%\text{ FA} = \frac{\%\text{ Oil}}{1 + \frac{\text{Eq. Wt. PO} - 18}{\text{Eq. Wt. FA}}}$$

The charge weight of fatty acid needed to obtain a given percent fatty acid may be determined using Equation 13.

(13)
$$\text{Wt. FA} = \frac{\%\text{FA}\,(\text{Wt. Carboxyl Material except FA} + \text{Wt. PO} - \text{Wt. } H_2O}{100 - \%\text{ FA}\left(1 + \frac{\text{Eq. Wt. PO} - 18}{\text{Eq. Wt. FA}}\right)}$$

A useful rule of thumb when using fatty acids is to charge 5 percent less fatty acid than oil and add the corresponding equivalence of polyol. While this estimation is based on glycerol, other triols typically used in such formulations have relatively low equivalent weight; therefore, changing the triol does not significantly change the calculated oil length.

Hydroxyl excess and formulating to avoid gelation

As polyesterification occurs between polyfunctional carboxyl- and hydroxyl-containing molecules, the result can be ever-increasing chain length. Monomers that have three or more functional groups particularly contribute to rapid polymer growth.

For practical purposes, coatings polymers must be limited in molecular size until they are applied and cured. Various alternatives are available for limiting the polyesterification reaction. Traditional resins based on drying oils contain monofunctional fatty esters that act as chain terminators and effectively limit polymer growth to practical viscosity ranges.

At the other end of the spectrum are totally synthetic or oil-free resins, based entirely on di- and trifunctional materials (see Resin Formulation 5, page 24). Chain growth in such resins can be controlled by the use of an excess of polyol which tends to produce relatively low molecular weight polymers that are hydroxyl terminated when all the acid groups are reacted.

Traditional resin formulators have developed rules of thumb dictating increased hydroxyl excesses as oil length is shortened. Because these traditional alkyds were oil-based, the excess hydroxyl has been defined as the added polyol divided by the polyol required to esterify the synthetic acids or anhydrides. The polyol required for esterification is, of course, equal to the equivalents of carboxyl in the reaction.

(14)
$$\%\text{ Ex. OH in Charge} = \frac{(\text{Eq. PO} - \text{Eq. Carboxyl})}{\text{Eq. Carboxyl}}\,100 = \left(\frac{\text{Eq. PO}}{\text{Eq. Carboxyl}} - 1\right)100$$

To maintain the traditional definition, when determining percent excess hydroxyl in the charge for alkyds based on fatty acids, the fatty acid equivalents and polyol required for their esterification are excluded from this calculation.

When designing contemporary high performance coating resins, many formulators prefer to use an hydroxyl excess calculation based on total polyol charge or finished resin basis. This expression resembles Equation 14, except that the equivalents of fatty acid and all the triol are included in the calculation. When oil is used, its carboxyl and hydroxyl equivalents must also be included for this expression.

$$(15)\quad \text{\% Ex. OH in Resin} = \left(\frac{\text{Eq. Hydroxyl Material}}{\text{Eq. Carboxyl Material}} - 1\right)100$$

This calculation can be further modified to find the amount of polyol needed when a target hydroxyl excess is given.

$$(16)\quad \text{Wt. PO} = (\text{Eq. Carboxyl})\left(\text{Eq. Wt. PO}\left[1+\frac{\text{\% Ex. OH in Charge}}{100}\right]\right)$$

Patton’s gelation constant

A useful analytical tool that verifies the required level of hydroxyl excess and provides a guide to the gelation tendencies of various formulations is Patton’s K value or alkyd constant (see Bibliography).

$$(17)\quad K = \frac{\text{Moles Hydroxyl Material} + \text{Moles Carboxyl Material}}{\text{Eq. Carboxyl Material}}$$

Although the derivation of this calculation is beyond the scope of this brochure, there is considerable empirical evidence that certain K values are associated with good polymer growth, low acid number and avoidance of gelation during processing.

Use of the K value offers a logical approach to accounting for the various methods of controlling polymer size: hydroxyl excess, high final acid number, monofunctional acids, reduction of hydroxyl polyfunctionality, etc.

The K value helps predict the probability that the resin may gel during processing as the target acid number is approached. The actual gelation tendency of a resin will vary somewhat depending on equipment and glycol loss during processing. Consequently, the target K value is not universally applicable; rather, each resin processing plant should determine the target K values for their equipment and formulate new resins to match these target values.

Alkyds based on PIA seem to be optimally formulated when the K value is approximately 1.04. This target should be modified in some cases. Free acid groups in the finished polymer can act as chain terminators; therefore, the K value of high acid value resins should be reduced. An experimentally determined value for reducing the target K value is:

$$0.0025\,(\text{AN} - 8)$$

The third hydroxyl of trimethylolethane or trimethylol propane is slightly more reactive than that of glycerol, therefore, the target K value should be increased by an additional 0.01 when glycerol is used.

Because oils contain equivalent amounts of carboxyl and hydroxyl in the forms of fatty acid and glycerol, three moles of fatty acid and one mole of triol must be included for each mole of oil when calculating the K of oil-based alkyds.

Molecular weight and equivalent weight of finished resin

The calculated molecular weight (Equation 18) of a formulation is a guide to its probable viscosity and the consequent need for thinning solvents to obtain desired handling characteristics. If calculation of the denominator in Equation 18 yields a negative number, review the parameters to insure they are valid.

$$(18)\quad \text{MW} = \frac{Y'}{\text{Moles Carboxyl} + \text{Moles Hydroxyl} + \dfrac{(\text{AN})\,Y'}{56{,}100} - \text{Eq. Carboxyl}}$$

Residual hydroxyl functionality in the finished resin is often used to cure the resin through cross-linkers such as amino resins. The optimal amount of cross-linker is directly related to the available hydroxyls. Too much cross-linker can plasticize the film, while too little leaves unreacted hydroxyls leading to poor stain resistance. The hydroxyl equivalent weight of the polyester resin can be calculated from an experimentally determined hydroxyl number (ASTM D1957), Equation 19.

$$(19)\quad \text{Hydroxyl Eq. Wt.} = \frac{56{,}100}{\text{OHN}}$$

The theoretical OH number may be calculated from the original charge of materials, Equation 20.

$$(20)\quad \text{OHN} = \frac{(\text{Eq. Hydroxyl Material} - \text{Eq. Carboxyl Material})\,56{,}100}{Y'} + \text{AN}$$

Determining lost glycol

An analysis of the gelation constant calculation (Patton's K value) indicates that diol excesses are more efficient than triol excesses in reducing gelation tendency. However, many diols or glycols have fairly low boiling or sublimation points and high water solubility. Consequently, some glycol is usually carried into the distillate during esterification.

Even a minor loss of glycol can lower the K value enough to make gelation likely as a low acid number is approached. Although careful selection of efficient partial condensers (see Equipment Section, page 8) will minimize glycol loss, some loss should be expected whenever low boiling glycols are used.

Methods to correct glycol loss rely on a determination of glycol in the distillate. Some formulators use the excess of distillate collected beyond the theoretical water of reaction as an indication of glycol loss. In our experience, this method lacks sufficient precision, particularly with high acid number resins. Also, the reaction must be nearly complete before glycol is known. This may be too late to prevent gelation.

BP's preferred method for determining glycol in the distillate is to use the refractive index of the collected distillate. The figures on page 15 show the change in refractive index for water solutions of various glycols. The calculation of total glycol loss is the percent glycol determined to be in the distillate times expected water of reaction as calculated by Equation 8.

$$\text{(21)} \quad \text{Lost glycol} = (\text{\% glycol in distillate})\ (\text{Charge Wt.} - Y')$$

If a mixture of glycols is used, mostly the lower boiling one will be lost to the distillate. The impact of reflux solvents on distillate refractive indices has not been evaluated in our laboratories.

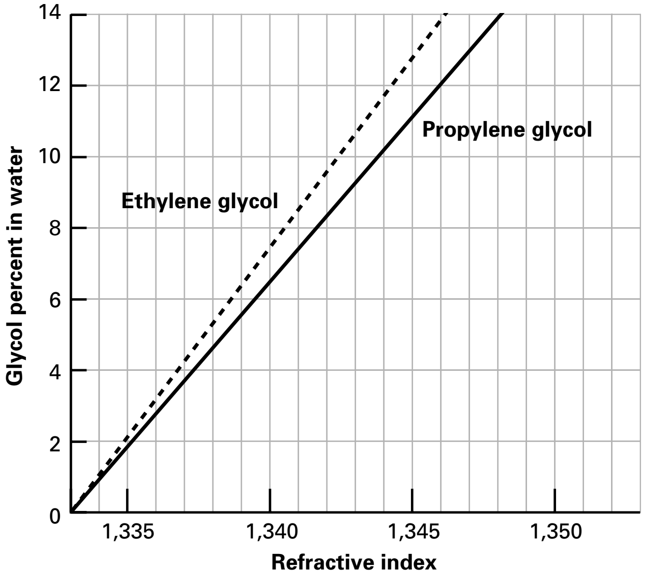
Lost glycol compensation

Because refractive index is rapidly determined, glycol loss rate can be determined at the mid-point of the reaction (as determined by volume of collected distillate) and make-up glycol charged while there is sufficient time for it to be reacted and before there is any gelation danger.

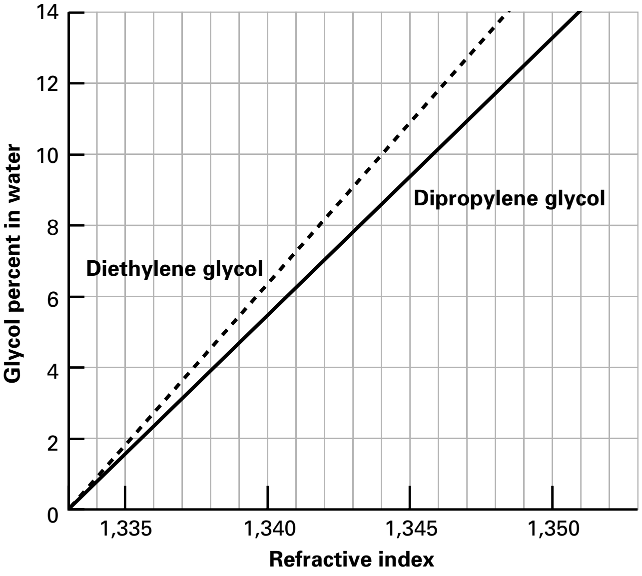
When similar types of resins are produced in a particular reactor, a history of typical glycol loss can be developed. In BP's experience, predictions of glycol loss with particular condensers and glycol type are quite reliable and can be the basis for charging a glycol excess in anticipation of the loss. By this second method, refractive index determinations should be made to confirm the expected rate of glycol loss.

Determining glycol content of distillate water using refractive index

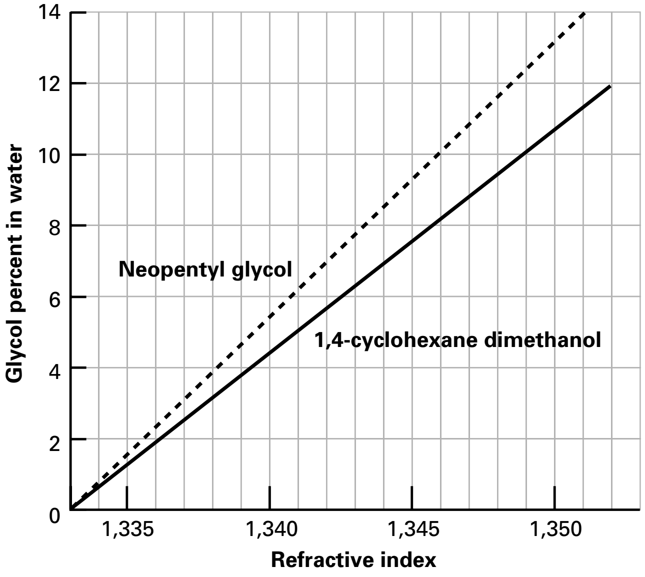
Ethylene and propylene glycols



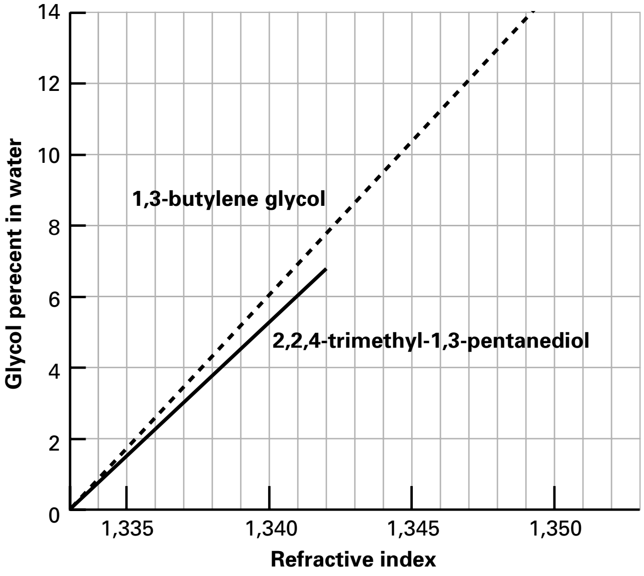
Diethylene and dipropylene glycols



Neopentyl glycol and cyclohexane dimethanol



Butylene glycol and trimethyl pentanediol



Calculation example 1

Formulate an oil-free polyester based on a 9:2:3 molar ratio of PIA:TMA:adipic acid with a target acid number of 5 using neopentyl glycol. Formulate with excess hydroxyl to use for melamine cure.

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	9	18	83	1494	—
TMA	2	6	64	384	—
AA	3	6	73	438	—
NPG	—	—	52	—	—
H_2O off (corrected)				—	—
Yield				—	1000

Calculate weight of polyol needed with 30 percent excess hydroxyl.

$$(16)\quad \text{Wt. PO} = (18+6+6)\left(52\left[1+\frac{30}{100}\right]\right) = 2028$$

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	9	18	83	1494	—
TMA	2	6	64	384	—
AA	3	6	73	438	—
NPG	19.5	39	52	2028	—
H_2O off (corrected)				—	—
Yield				—	1000

Check for K value (target K = 1.04).

$$(17)\qquad K = \frac{19.5+9+2+3}{18+6+6} = 1.117$$

This indicates the resin will have too many low molecular weight fractions and will not cure readily. Reformulate to lower K by using 15 percent excess hydroxyl.

$$(16)\quad \text{Wt. PO} = (18+6+6)\left(52\left[1+\frac{15}{100}\right]\right) = 1794$$

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	9	18	83	1494	—
TMA	2	6	64	384	—
AA	3	6	73	438	—
NPG	17.25	34.5	52	1794	—
H2O off (corrected)				—	—
Yield				—	1000

The new K matches the target.

$$(17)\qquad K = \frac{17.5+9+2+3}{18+6+6} = 1.04$$

Calculate water of esterification,

$$(5)\qquad H_2O\ \text{off} = 18\ (18+6)+12\ (6) = 504$$

theoretical yield,

$$(7) \qquad Y' = \frac{4{,}110 - 504}{1 - \frac{18\ (5)}{56{,}100}} = 3{,}612$$

and correct water of esterification.

$$(8) \qquad H_2O \text{ off (corrected)} = 4110 - 3612 = 498$$

Multiply all weights by the factor $\frac{1000}{Y}$ to obtain charge weights for 1000 part yield.

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	9	18	83	1494	413.6
TMA	2	6	64	384	106.3
AA	3	6	73	438	121.3
NPG	17.25	34.5	52	1794	496.7
H_2O off (corrected)				498	137.9
Yield				3612	1000.0

Calculate percent excess hydroxyl,

$$(15) \quad \%\ \text{Ex. OH} = \left(\frac{34.5}{30} - 1\right) 100 = 15\%$$

hydroxyl number,

$$(20) \quad \text{OHN} = \frac{(34.5 - 30)\ 56{,}100}{3612} + 5 = 75$$

and molecular weight.

$$(18) \quad \text{MW} = \frac{3612}{14 + 17.25 + \left(\frac{(5)\ 3612}{56{,}100}\right) - 30} = 2298$$

This polyester is Resin Formulation 5 in the processing examples section.

Calculation example 2

Formulate a water soluble polyester based on PIA and TMA (3.5:1 molar ratio) using trimethylol propane and tall oil fatty acid, aiming for 51 percent oil and acid number of 55.

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	3.5	7	83	581	—
TMA	1	3	64	192	—
TMP	—	—	45	—	—
TOFA	—	—	289	—	—
H_2O off (corrected)				—	—
Yield					1000

Calculate weight of polyol necessary to esterify PIA and TMA.

(16) Wt. PO = (7 + 3) (45) = 450

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	3.5	7	83	581	—
TMA	1	3	64	192	—
TMP	3.3	10	45	450	—
TOFA	—	—	289	—	—
H_2O off (corrected)				—	—
Yield				—	1000

Calculate water of esterification at complete reaction.

(5) H_2O off = 18 (7) + 12 (3) = 162

Change percent oil to percent fatty acid,

$$(12)\quad \%\ \text{FA} = \frac{51}{1 + \frac{45 - 18}{289}} = 46.6$$

and calculate weight of fatty acid.

$$(13)\quad \text{Wt. FA} = \frac{46.6\ (581 + 192 + 450 - 162)}{100 - 46.6\ \left(1 + \frac{45 - 18}{289}\right)} = 1008$$

Determine equivalents of fatty acid from weight, then increase polyol charge to account for fatty acid esterification. (Additional 3.5 equivalents or 158 parts polyol.)

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	3.5	7	83	581	—
TMA	1	3	64	192	—
TMP	4.5	13.5	45	608	—
TOFA	3.5	3.5	289	1008	—
H_2O off (corrected)				—	—
Yield				—	1000

Check K value.

Target K = 1.04 – (55 – 8) 0.0025 = 0.923

Calculated K approximates target.

$$(17)\quad K = \frac{4.5 + 3.5 + 1 + 3.5}{13.5} = 0.926$$

Amend water of esterification for fatty acid esterification,

$$(5)\quad H_2O \text{ off} = 18\,(7 + 3.5) + 12\,(3) = 225$$

calculate yield,

$$(7)\quad Y' = \frac{2389 - 225}{1 - \frac{18\,(55)}{56{,}100}} = 2203$$

correct water of esterification for acid number,

$$(8)\quad H_2O \text{ off (corrected)} = 2389 - 2203 = 186$$

and multiply all weights by $\frac{1000}{Y}$ to obtain charge weights for 1000 part yield.

	Moles	**Equivalents**	**Equivalent weight**	**Weight**	**Charge for 1000 part yield**
PIA	3.5	7	83	581	263.7
TMA	1	3	64	192	87.1
TMP	4.5	13.5	45	608	276.0
TOFA	3.5	3.5	289	1008	457.6
H_2O off (corrected)				186	84.4
Yield				2203	1000.0

Calculate percent excess hydroxyl,

$$(15)\quad \%\ \text{Ex. OH} = \left(\frac{13.5}{13.5} - 1\right) 100 = 0$$

hydroxyl number,

$$(20)\quad \text{OHN} = \frac{(13.5 - 13.5)\ 56{,}100}{2203} + 55 = 55$$

percent oil,

$$(11)\quad \%\ \text{Oil} = \frac{1008 + 3.5\,(45 - 18)}{2203} \times 100 = 50$$

and molecular weight.

$$(18)\quad MW = \frac{2203}{8 + 4.5 + \left(\frac{(55)\ 2203}{56{,}100}\right) - 13.5} = 1899$$

This alkyd is Resin Formulation 4 of the processing examples section.

Examples of processing PIA coatings resins

This section illustrates the processing of five resins based on PIA to help bring together the concepts of reaction dynamics, equipment selection and formula calculations. The equivalent ratios of ingredients for these resins are shown in Table 5. These and similar resins are shown in suggested paint formulations in other brochures published by BP Chemical Formulators wishing to investigate the applications of these resins can obtain literature through their BP sales representative.

Table 5

Summary of resins used as processing examples

	Equivalent ratios				
Resin formulation	**1**	**2**	**3**	**4**	**5**
Isophthalic acid	4.5	4.6	5.0	5.0	3.0
Trimellitic anhydride	—	—	—	2.2	1.0
Adipic acid	—	—	—	—	1.0
Fatty acid	1.0	—	—	2.5	—
Triglyceride oil	—	1.0	6.1	—	—
Benzoic acid	1.1	1.1	—	—	—
Trimethylol ethane	7.5	6.6	—	—	—
Trimethylol propane	—	—	5.9	9.7	—
Neopentyl glycol	—	—	—	—	5.7
Properties					
Target acid number	10 – 15	10 – 15	10 – 15	55 – 60	5
Hydroxyl excess, wt. %	14	14	9	1	15
Gelation tendency, Patton K	1.04	1.04	1.14	0.93	1.04
Theoretical molecular wt.	2050	2000	1160	1800	2340
Oil content, %	30	30	75	50	0
Paint application areas					
	Traffic paints and Wood coatings	Traffic paints and Wood coatings	Printing inks	General purpose, Maintenance and Implement enamels	Appliance, Automotive, and Coil coatings
BP bulletins describing similar resins					
				TM-139 TM-140	TM-134 TM-141

Fusion processing of long oil isophthalic alkyds

Resin Formulation 1, shown in Table 6, is an example of the simple fusion processing procedure for a long oil isophthalic alkyd resin. The condenser configuration for fusion processing consists of a steam heated partial condenser to reduce glycol loss and a total condenser to remove water generated during the reaction and to control emissions (see equipment diagram on page 8).

Process the alkyd by charging the reactor with the oil and the glycol and heat until alcoholysis is complete. In this example, the soybean oil and glycerine were heated to 250°C for approximately 1 hour at which time alcoholysis was complete. After cooling the reactants to 160°C, PIA was added. The mixture was then heated to 230°C and maintained.

Esterification is continued to a peak reactor temperature of 260°C. Evolving water will keep the temperature below 260°C until the reaction nears completion. As water evolution slows, begin monitoring the acid number, viscosity and any other parameters, such as cure time, that are specified for the resin application.

As the target properties are approached, fade the kettle heat to slow the reaction and avoid overshooting the desired end point. Cool to 140°C, then thin with mineral spirits pumped in slowly below the surface or by adding the resin slowly to cool mineral spirits. Solvent added to the resin above the solvent's boiling point will help cool the resin.

CAUTION: Care must be exercised to avoid explosive boiling of the solvent or excessive evaporation loss.

Solvent reflux processing of isophthalic alkyds

Toluene and xylene, the common reflux solvents for alkyds, do not seem to reduce PIA solubility in esterification vapors and may induce PIA carry-over into the condenser system.

BP has investigated two routes to circumvent this unsuitability of aromatic solvents for reflux processing with isophthalic alkyds. One route is to substitute solvents that will wash PIA back into the reactor. We have had success using methyl isobutyl ketone (MIBK) as a reflux solvent during the heat-up portion of the esterification reaction. An example of this process is shown below with Resin Formulation 1.

When the peak esterification temperature can be attained, PIA half ester formation is essentially complete and conventional solvents such as xylene and toluene can be used.

Solvent refluxes of either type offer the advantages of improved stripping of the last water of reaction, a more mobile reaction mixture with more easily controlled temperature and viscosity, and cleaner equipment after processing.

Table 6

Resin Formulation 1
Long oil PIA alkyd

Ingredients	**Parts by weight**	**Equivalents**
BP PIA	302	3.63
Soybean oil	630	2.15
Glycerine	132	4.30
Total charge	1064	
less water of reaction	– 64	
Yield	1000	
Reflux solvent, MIBK	30-40	
Catalyst*	0.31	

Properties	**Fusion processed**	**Solvent reflux processed**
Acid number	8.0	9.0
Viscosity, Gardner-Holdt	Z_2+	Z_9+
Non-volatile material, %	70	70
Solvent	Mineral spirits	
Calculations		
Hydroxyl excess, %	18	18
Gelation index, Patton's K	1.06	1.06
Theoretical molecular wt	2031	2031
Oil content, %	63	63

* Hydrated monobutyltin oxide, Fascat 4100, Atochem, Inc.

This resin demonstrates good hardness and resistance properties in wood coatings.

Example of solvent processing a long oil isophthalic alkyd

Resin Formulation 1 can be processed using the solvent reflux technique. The condenser system for this technique includes a steam-heated partial condenser and split shell decanting receiver for returning the organic solvent to the reactor (see equipment diagrams on page 8). Soybean oil and glycerine were charged and heated to 204°C, then the catalyst was added. The reaction was heated to 250°C and maintained for approximately 1 hour to allow alcholysis to occur. After cooling the reactor to 140°C, PIA and MIBK were added.

After adding all reagents to the reactor, the partial condenser was shut and the total condenser opened, returning the MIBK to the kettle. The reaction was maintained at 250°C until reaching an acid number of 9. Then, MIBK was removed via distillation. After cooling the reaction to 140°C, the resin was thinned to 70% NVM with mineral spirits. All precautions previously described for fusion processing were taken.

Processing isophthalic alkyds using triglyceride oil

When isophthalic alkyds are made with oil instead of fatty acids, certain procedures are necessary to break up the oil and distribute its components randomly through the polymer structure. These procedures are basically two types of ester exchange: alcoholysis and acidolysis.

During alcoholysis the oil undergoes exchange reaction with additional polyol. The ideal result of an alcoholysis exchange is to convert all triglyceride to mono- and diglyceride.

In acidolysis, a diacid such as PIA replaces a fatty acid on the triol backbone. The generation of free fatty acid and formation of isophthalate half esters encourages much faster subsequent reaction.

Alcoholysis can be used with any oil-containing alkyd. However, acidolysis is only suitable for longer oil lengths because there must be sufficient oil to have a one to one molecular ratio of oil to acid.

Resin Formulation 2 is an example of a first-stage alcoholysis followed by a reflux azeotropic esterification using MIBK. Oil-based Resin Formulation 2 is also interesting for its similarity to the fatty acid-based Resin Formulation 1.

Resin Formulation 3 is an example of an acidolysis process. The resin is a very long oil alkyd processed by a two-stage reaction in which PIA and the oil undergo an ester exchange followed by fusion esterification with added triol.

Alcoholysis of medium oil length PIA alkyd with solvent reflux finish

The ideal alcoholysis reaction occurs between twice as many moles of triol as oil. The theoretical outcome is a one to one distribution of fatty acids among the triol molecules. An excess of triol can accelerate the reaction and facilitate handling.

The oil and trimethylol ethane were charged to a reactor equipped with a solvent reflux condenser system. The mixture was heated to 170°C with nitrogen sparge and agitation. Lithium hydroxide monohydrate alcoholysis catalyst was added and heating continued to 238°C. The alcoholysis reaction was continued until the reaction product formed a clear 20 percent solution in methanol, indicating the absence of triglyceride oil in the mixture. The aromatic acids were then added and the reactor closed. MIBK was added through the receiver trap and allowed to flow into the kettle. Reflux esterification proceeded with a maximum temperature of 232°C until the theoretical water was collected. The reflux solvent was drained from the trap and the resin held for a 30-second cure time.* The reaction was cooled to 215 – 220°C, held for final properties, then thinned to 50 percent solids with toluene.

* Cure is the time required for a drop of polymer to change from liquid to gelatinous state on a 200°C hot plate.

Table 7

Resin Formulation 2
Oil-based short oil PIA alkyd

Ingredients	Parts by weight	Equivalents
BP PIA	385	4.64
Alkali refined soya oil	298	1.017
Trimethylolethane	276	6.73
Benzoic acid	142	1.165
Total charge	1101	
less water of reaction	–101	
Yield	1000	
Reflux solvent	30	
Lithium hydroxide monohydrate catalyst	0.1	
Properties		
Acid number	14.1	
Viscosity, Gardner-Holdt	V-	
Non-volatile material, %	50	
Solvent	Toluene	
Calculations		
Hydroxyl excess, %	14	
Gelation index, Patton's K	1.04	
Theoretical molecular wt.	1940	
Oil content, %	30	

Acidolysis with long oil PIA alkyd

In the first stage of the reaction for Resin Formulation 3, the linseed oil and PIA are subjected to an ester exchange reaction with the goal of replacing one fatty acid on each triglyceride with PIA to make PIA half esters. Nearly complete conversion to the half ester form is apparent when the reaction mixture becomes clear. The acidolysis proceeds quite rapidly (generally completed within 1 hour at 280°C or 10 minutes at 300°C) and the acidolysate product is much easier to esterify with the added triols. Color formation and the possible corrosion of stainless steel at 300°C may necessitate using the lower acidolysis temperature in some cases.

Resin Formulation 3 was processed by charging the oil to the reactor and heating to 150°C with nitrogen sparge and agitation. The PIA was then added and heating continued to 280°C. The mixture was held at 280°C for one hour, then cooled to 225°C and the polyol added. The mixture was reheated to 232°C and fusion esterified to final properties. The target cooling temperature after acidolysis will depend on the polyol to be added. For glycerol or trimethylols, cool to 215 to 225°C, for pentaerithrytol, cool to 230 to 250°C.

Acidolysis is a useful technique only for formulations containing a minimum of one mole of oil per mole of acid. The difficulty of suspending large concentrations of PIA in certain oils may further limit the range of applicable formulations. The temperature required for acidolysis will heat body certain oils. Therefore, resins may need to be formulated to higher K values with extra hydroxyl functionality to avoid gelation. The high vapor pressure and sublimation rate of phthalic anhydride preclude its use in an acidolysis reaction without special equipment.

Table 8

Resin Formulation 3
Very long oil PIA alkyd

Materials	**Parts by weight**	**Equivalents**
Alkali refined linseed oil	750	2.56
Trimethylolpropane	113	2.51
BP PIA	175	2.11
Total charge	1038	
less water of reaction	– 38	
Yield	1000	
Properties		
Acid number	12.5	
Viscosity, Gardner-Holdt	Z_1	
Non-volatile material, %	100	
Calculations		
Hydroxyl excess, %	9	
Gelation index, Patton’s K	1.14	
Theoretical molecular wt.	1167	
Oil content, %	75	

This alkyd is designed to be a printing ink vehicle. Although similar formulations are outstanding resins for applications such as house paints, the K value of this example probably precludes its use in conventional paints.

Processing with TMA

TMA can be used either as the primary source of pendant unreacted carboxyl groups to provide water solubility or as a source of polymer branching in place of trifunctional glycols.

CAUTION: When exposed to moisture, TMA will convert to the triacid form quickly. Esterification of free carboxyl requires much higher temperature than is required for anhydride opening and also produces water of reaction.

Resin Formulations 4 and 5 illustrate the two roles that TMA may play in a coatings resin. In Resin Formulation 4, the temperature is held to no more than 180°C after TMA is added. In Resin Formulation 5, TMA is added with the other ingredients and is reacted at the maximum temperature of 232°C. Theoretically, in Resin Formulation 4 only 1 to 1.2 carboxyl groups of TMA per mole of TMA have been reacted, while in Resin Formulation 5, all three carboxyl groups have been reacted. If both functions are desired in the same resin, the results can be obtained by splitting the TMA charge between a first stage processed at a normal peak esterification temperature and a second stage held at 180 to 200°C for desired extent of reaction of TMA.

Processing a water-borne TMA/PIA alkyd

Resin Formulation 4 is processed by a two-stage fusion esterification. The fatty acid, polyol and PIA were charged to a normal fusion esterification reactor, heated with agitation and inert gas sparge to 249°C, and held for an acid number of 10. Then the resin was cooled to 180°C, and the TMA was dispersed into the resin. The mixture was held at 175 to 180°C for a 60 acid number. The resin was then cooled to 160°C and thinned in the appropriate ether glycol solvent. This resin offers outstanding performance in water soluble industrial and maintenance primers and enamels.

Table 9

Resin Formulation 4
TMA-based water soluble alkyd

Materials	**Parts by weight**	**Equivalents**
BP PIA	264	3.18
BP TMA	87	1.36
Tall oil fatty acid*	456	1.58
Trimethylolpropane	277	6.16
Total charge	1084	
less water of reaction	– 84	
Yield	1000	
Properties		
Acid number	55-60	
Viscosity, Gardner-Holdt	Z_7	
Non-volatile material, %	80	
Solvent	Ether glycol**	
Calculations		
Hydroxyl excess, %	1	
Gelation index, Patton's K	0.928	
Theoretical molecular wt.	1860	
Oil content, %	50	

* Equivalent weight of 289 determined by manufacturer.
**Dowanol® PM (Dow Chemical Co.) for air dry paints; butoxyethanol for baking enamels.

Processing an oil-free TMA/PIA polyester

When TMA is to be fully reacted as the primary source of branching, the resin formulation will normally use only diol sources of hydroxyl functionality. Consequently, the reaction is a glycol reflux esterification and an efficient partial condenser is required.

To process Resin Formulation 5, all the ingredients were charged to a reactor equipped with an inert gas sparge and heated. Agitation was started as soon as the materials began to melt. Catalyst was added at 140°C and heating continued with glycol reflux to 232°C. The heat input was controlled to minimize glycol loss. The reaction mixture was held at 232°C until the overhead vapor temperature dropped. The fractionation column was then by-passed and processing continued for final properties.

Alternatively, the resin could be finished using solvent reflux as described in the next section which discusses techniques to shorten processing time. With melamine cure, this resin offers outstanding weathering and stain resistance for appliance and other metal finishing applications.

Table 10

Resin Formulation 5
Oil-free polyester

Materials	**Parts by weight**	**Equivalents**
BP PIA	413	4.98
BP TMA	107	1.67
Neopentyl glycol	496	9.54
Adipic acid	122	1.67
Total charge	1138	
less water of reaction	–138	
Yield	1000	
Esterification catalyst*	0.57	
Properties		
Acid number	4.9	
Viscosity	Y-Z	
Non-volatile material, %	60	
Solvent	Xylene	
Calculations		
Hydroxyl excess, %	15	
Gelation index, Patton's K	1.04	
Theoretical molecular wt.	2364	
Oil content, %	0	

* Hydrated monobutyltin oxide, Fascat® 4100, Atochem, Inc.

Processing a Powder Coating Polyester with TA

PTA is used primarily to increase the Tg and improve the mechanical properties of powder coatings resins. Resin formulation 6 found in Table 11 illustrates such a system based on BP's terephthalic acid (TA), trimellitic anhydride (TMA), and purified isophthalic acid (PIA). The TA content provides for optimum flexibility, Tg, and storage stability, while the PIA content provides a source of residual carboxyl functionality for crosslinking. TMA is incorporated as a source of trifunctionality for polymer branching and contributes to improved hardness and resistance properties.

In the processing of Resin Formulation 6, the neopentyl glycol and half of the first stage terephthalic acid were added to a reactor, heated with agitation and inert gas sparge, to 140°C to achieve a slurry of ingredients. Then the remaining half of the terephthalic acid and the trimellitic anhydride were added along with the esterification catalyst. Heating was continued to 238°C and held for a prepolymer acid number of 10 or less. The reaction temperature was reduced to 193°C and purified isophthalic acid was added as part of the second reaction stage. Once the targeted acid number was achieved, the reaction mixture was discharged from the reactor, cooled, and flaked or grinded. This resin can be used in powder coatings that are crosslinked with tetra-functional hydroxyalkylamide, Primid XL-552. Polymers of this type may also find utility in TGIC, triglycidylisocyanurate, cured powder coating systems or with epoxy resins in 70/30 polyester/epoxy hybrid powder coatings.

Table 11

Resin Formulation 6 TA-based powder coating polyester*

Materials	**Parts by weight**	**Equivalents**
BP TA	1475	17.77
BP TMA	62	0.97
Neopentyl Glycol	1079	20.75
BP PIA	246	2.96
Total Charge	2862	
less water of reaction	-362	
Yield	2500	
Esterification Catalyst [1]	1.43	
Properties		
Acid number, mg KOH/g		
Prepolymer	9 - 10	
Final	34 - 36	
ICI viscosity @ 200°C, poise		
Prepolymer	9 - 11	
Final	37 - 39	
Glass transition temperature, Tg, °C		63 - 70
Unreacted TMA in polymer, wt. %		<0.03

1. Hydrated monobutyl tin oxide, Fascat 4100, Elf Atochem North America, Inc.

* *Reference:* GTSR-91A -- Experimental Carboxyl Functional Polyesters for Powder Coatings

Techniques to shorten processing time

The primary determinants of esterification rate with any given resin formulation are reaction temperature, intimacy of contact among the reactants, presence of catalysts and hydroxyl excess at various stages. This section offers suggestions that can help speed the processing of isopolyester coating resins. Not all of the suggestions are universally applicable, but often two or more can be used in combination to obtain excellent processing times.

Achieving higher temperatures

Limitations on maximum reaction temperature include color formation, reactor heating capacity and decomposition tendencies of certain reactants. The most common temperature limitation is the boiling point of reactants such as lightweight polyols.

Because glycols such as propylene glycol reflux during esterification, they hold the kettle temperature at their boiling point until late in the reaction. If reformulation with higher boiling polyols is not desired, the reaction temperature may be raised by using greater than atmospheric pressure.

CAUTION: Pressure processing should not be attempted without careful review of equipment and procedures by qualified safety officials.

Pressure processing is, of course, limited to reactors rated for holding moderate, positive pressures. BP's work has shown significantly shortened reaction time at gauge pressures of about 350 kPa (50 psig). To minimize excessive glycol loss during pressure processing, uniform pressure should be maintained throughout the reactor, partial condenser, total condenser and receiver system.

It is particularly important to maintain the correct temperature and a high heat transfer capacity on the partial condenser. The theoretically optimum partial condenser is jacketed with super-heated water at the same pressure as the reactor pressure. The boiling point of the jacket coolant will thus equal the temperature at which water of reaction is carried through the partial condenser. Simultaneously, the heat of vaporization of the jacket water offers a very high heat absorption capacity to efficiently return the glycol to the reactor. Pressure should be built and maintained with an inert gas sparge to minimize glycol loss as pressure is released.

CAUTION: Always release pressure slowly, allowing the mass of resin to cool below the boiling point of water for that pressure to avoid the possibility of severe condenser flooding and resin carry-over.

Improving reactant intimacy

The initial reaction mixture for producing PIA-based alkyds generally includes incompatible or insoluble reactant phases. Reactions are thus restricted to the materials at the interfacial boundaries. Techniques that increase the interfacial area or increase the solubility of the reactants can dramatically decrease total process time.

The acidolysis reaction scheme is a technique for increasing reactant solubility. Transesterification of PIA with triglyceride oil converts the acid to the more soluble half ester which will readily react with the other ingredients of the formulation. The acidolysis reaction is, of course, only applicable for medium to long oil length formulations.

In formulations where acidolysis is not feasible, BP has found that a polymer charge technique offers substantial processing time savings.

Introducing about five percent of some linear polyester with the initial charge apparently greatly increases reactant intimacy. In a process study, the resin shown below was processed with a polymer charge and a solvent reflux finish in 30 percent less total reactor time than was the conventionally processed resin.

Materials	**Equivalent ratio**
Isophthalic acid	1.00
Adipic acid	0.43
Propylene glycol	1.46
Pentaerythritol	0.11

Accelerated processing

The standard processing technique is to heat the polyols and adipic acid to 90°C, charge the PIA, then react with glycol reflux at a maximum temperature of 232°C until the desired acid value and/or viscosity is achieved. The resin is then cooled and diluted with solvent.

To accelerate processing, charge five percent of finished resin with the polyols and adipic acid. Add PIA during heat-up when the reaction mixture reaches 90°C. Heat to 232°C until the overhead temperature drops to 90°C. When the overhead temperature begins to drop, add sufficient xylene to maintain continuous reflux using an automatic decanting receiver. Continue reflux processing to the target acid number.

The theory of this technique is that the polymer will act as a solvent for the PIA causing more intimate contact between the otherwise insoluble acid and polyol.

The accelerated processing associated with solvent reflux is due both to the partial pressure of the reflux solvent which aids water evolution at lower temperatures and to improved reactant solubility.

Paints formulated with the resins from the four process variations provided generally equivalent properties. Resins processed with reflux finishing offered slightly better flow and resistance to accelerated weathering. The resin processed by the reflux finish method was not expected to finish so soon; therefore, its end point was passed, resulting in lower acid number and higher molecular weight.

BP recommends using fairly linear polymers with low residual functionality as charge polymers. Polymers with excessive branching and functionality may cause rapid viscosity build and premature gelation. At the 5 percent level, the polymer charge technique does not significantly reduce reactor capacity.

Catalysts

In limited evaluations with oil-free isopolyesters, hydrated monobutyltin oxide, butyl stannoic acid, tetrabutyl titanate, stannous oxalate and dibutyltin oxide have provided measurably faster esterification rates. The resultant polymers have approximately the same viscosity, acid value and hydroxyl value as the same formulation processed without catalyst.

The catalyzed resins have slightly larger molecular size (by gel permeation chromatography). As a consequence of shorter reaction time, the catalyzed resins seem to experience lower glycol loss during processing. The effect of catalysts on finished coating properties must be thoroughly evaluated before using a catalyst in commercial situations.

Hydroxyl excess

An excess of hydroxyl functionality helps the acid groups react faster, as predicted by classical physical chemistry theory. Obviously the total polyol charge is determined by factors which preclude an excess increase simply to accelerate processing. However, formulations containing acids with different reaction rates can often be processed more quickly by a two-stage method.

In the first stage, all the hydroxyl-containing material is charged with only the slow reacting acids. When the reaction mixture clears (an indication of near complete half ester formation) the faster reacting acids can be added and the resin finished to the normal end point. This technique has the added advantage of ensuring a more random distribution of aromatic acid through the polymer chain.

Table 12

Time savings with polymer charge and solvent reflux finishing

Processing method	Reactor residence	Acid value	Hydroxyl number	Molecular weight, VPO	Distillate glycol, %
Standard	14-1/2 hr.	17.8	49.1	1755	1.9
Reflux finish	12-1/4 hr.	5.5	47.4	2223	1.4
Polymer charge	12-3/4 hr.	21.5	33.4	1661	2.5
Polymer charge with reflux finish	10 hr.	22.0	25.7	1698	2.4

Troubleshooting guide

Poor resin color

Possible cause	Suggested remedies
Low quality inert gas	Inert gas sparge must contain less than 20 ppm oxygen, and preferably less than 10 ppm. Many oxygen determining devices are not sensitive to this low level of oxygen contamination.
Poor agitation	With some formulations, the initial charge may form a thick slurry, which easily collects on the baffles or high side walls of the kettle. If this slurry remains on the walls, it may char during rapid heat-up. To control this problem, improve agitation and/or modify baffles of the reactor. Consider use of water to aid the slurry of ingredients.
Hot spots	A reaction kettle with localized hot spots may cause resin discoloration, especially when combined with poor agitation. To control this problem, eliminate hot spots and improve agitation.
Contaminants	Protect raw materials from contamination by utilizing proper storage and transferring facilities. Raw material suppliers can provide additional recommendations.

Processing time too long

See page 25 "Techniques to shorten process times."

Possible cause	Suggested remedies
Inadequate heat supply	Inadequate heat supply may cause excessively long heat-up periods, especially with stepwise or multi-stage processing techniques. Establish an adequate heat supply.
Poor agitation or inadequate inert gas sparge rate	Improve agitation and/or increase the rate of the inert gas sparge to aid removal of the water of esterification. Water of esterification remaining in the resin can hinder progress of the reaction.
Poor solubility	Since PIA is generally insoluble in the initial reaction mixture of polyesters or alkyds, techniques that increase solubility of the reactants can dramatically decrease process time. Acidolysis and alcoholysis are examples of these techniques. See page 4.
Inadequate partial condenser	For fusion processing, make sure that the partial condenser is designed to accommodate the additional water of esterification produced when processing PIA-based polymers. Inadequate condenser capacity can cause high glycol losses and may retard removal of water. Slow water removal, in turn, lowers the reaction rate.
Inadequate cooling	Cooling time has a significant effect on total processing time. Use cooling coils instead of a cooling jacket as they provide a larger surface area for heat transfer. If the coils are equipped to operate with both water and steam, they may also be used in the initial heating of the batch.
Too much hydroxyl excess	Formulations with too high an excess exhibit rapid acid number decrease, but lengthy process times may be required to achieve the desired viscosity. Reduce the glycol excess to reduce processing time.
Too little hydroxyl excess	Formulations with too low an excess exhibit a rapid viscosity increase and an extremely low acid number decrease. For these, the desired acid number may be unattainable within the desired viscosity range. Increase the glycol excess to reduce processing time.

Hazy resin

Possible cause	Suggested remedies
Resin contamination during storage	Various polyester resins are not compatible with each other. Storage of incompatible resins in the same tank can result in haze. You should clean finished resin storage facilities between batches or investigate the compatibility of different resins before storage.
Excess use of lithium hydroxide catalyst	Alkyds processed via alcoholysis may have a residual haze due to the formation of lithium salts of PIA.
Incomplete reaction of polymer ingredients	Unreacted PIA may lead to a hazy resin.
Haze from crystallinity of polymer	Saturated polyesters based on high levels of PIA may tend toward insolubility and appear hazy from polymer crystallinity. Avoid this by using blends of TA with the PIA. This phenomenon may be reversible with application of low heat (50 to 60°C) to the polymer solution.

Low acid number

Possible cause	Suggested remedies
Too much glycol excess	A low acid number usually results when the formulation contains too much hydroxyl excess. To control this problem, decrease glycol excess until you obtain an acid number in the proper range.

Low viscosity

Possible cause	Suggested remedies
Too much glycol excess	Insufficient viscosity build-up can result from too much glycol excess. Usual signs of this problem are low viscosity and extremely low acid number. Check the polymer formulation and decrease glycol excess to increase molecular weight and polymer viscosity.
Incomplete reaction	If the reaction is too slow, review the remedies under "Processing Time Too Long."

High acid number

Possible cause	Suggested remedies
Insufficient glycol excess	A high acid number may result when the formulation contains insufficient glycol excess. This may be corrected by increasing the hydroxyl excess of the formula. CAUTION: You must be careful not to obtain a lower acid number at the expense of significantly increasing the hydroxyl number and lowering the molecular weight of the finished polymer.
High glycol loss	Loss of a significant portion of the glycol may result in an unusually high acid number at the desired viscosity. Review the remedies under "High Glycol Losses."
Incomplete reaction	A polyester resin which has not been processed to its required endpoint will have a high acid number. If the reaction is slow, review the remedies under "Processing Time Too Long."

High glycol losses

See page 14 "Determining Lost Glycol" and "Lost Glycol Compensation."

Possible cause	Suggested remedies
Inefficient partial condenser	See page 10 "Condenser Systems."
Sparge rate too high	Excess gas flow through the reactor will draw off glycol. Adjust the sparge rate so that it does not exceed 0.6 ml/sec gas flow per liter reactor volume.
Temperature too high	Too high of a reactor temperature may increase glycol loss. Reduce the heat applied to remedy.

High hydroxyl number

Possible cause	Suggested remedies
Too much glycol excess	A high glycol excess tends to yield resins with a high hydroxyl number. It is important to choose a glycol excess that will yield the desired hydroxyl number range when the polymer is processed to the desired endpoint.
Incomplete reaction	A polyester resin which has not been processed to its required endpoint will have a high hydroxyl number (and a high acid number). If the reaction is slow, see remedies under "Processing Time Too Long."

Foaming

Possible cause	Suggested remedies
Vapors in reaction mixture	The vapor constituent of foam is usually sparge gas, evolved volatile by products from the esterification reaction, or boiling reflux solvent. The safest remedy is to reduce the sparge rate, reduce heat input, and decrease agitation. Judicious use of chemical defoamers may be effective; however, they must be thoroughly evaluated for their possible effects on the finished paint even at low levels. The use of a mechanical foam breaker in the reactor is recommended.

Condenser flooding

Possible cause	Suggested remedies
Inadequate partial condenser	The lack of heat transfer capacity of the partial condenser and its limited surface area is the normal culprit (see page 10). Intermittent use of a cold water jacketed knockdown below the partial condenser can correct flooding when it occurs. Reduction of heat input to the reactor is another remedy.
Excessive inert gas sparge	Reduce gas sparge rate.

Resin gelation

Early signs of gelation are a tail in the viscosity tube bubble and gel particles in resin samples. If the resin starts to climb the agitator shaft, severe gelation is occurring. This may also be indicated by an increase in power to the agitator.

When early signs are detected, several steps can be taken to prevent gelation. The remedies are to stop molecular chain growth and solvate the resin. Rapid cooling or polyol addition will slow esterification and chain growth. The intended cosolvent for the resin may be added to the reactor if the temperature is sufficiently low, or triglyceride oil can act like a solvent and be used to dilute the resin.

If these steps appear ineffective or if severe gelation is occurring, a solution of triethylene glycol or other high boiling glycol, a glycol ether, such as diethylene glycol n-butyl ether, and triethanol amine may be added to the resin. This step is a last resort and will ruin the batch through de-esterification and solvent contamination, but will avoid the major clean-up expense associated with a resin setting-up in the reactor.

A very common gelation problem occurs while the resin is being drained from the reactor. Some resins will hang up in the reactor and gel through residual heat. This gelled resin is most easily removed by saponifying with hot water and caustic. The saponification can be aided by a solvent which softens the gelled polymer.

Possible cause	Suggested remedies
Improper ratio of raw materials	Run formulation through *Polycalc* (see GTSR-74), review results for proper ratios of reactants and alkyd constant. Double check batch weights of materials as charged to the reactor.
Glycol loss	Check the refractive index of the distillate for glycol loss. See page 14, "Determining Lost Glycol" and "Lost Glycol Compensation"

Appendix

Equivalent weights of commonly used materials

Acids-Anhydrides

Monofunctional

Benzoic acid	122
p-t-Butyl benzoic acid	178
Capric acid	172
Caproic Acid	116
Castor fatty acid	297
Castor fatty acid, dehydrated	280
Coconut fatty acid	216
Cottonseed fatty acid	280
Dimethylol propionic acid	134
2-Ethyl butyric acid	116
2-Ethyl hexoic acid	144
Lauric acid	200
Linseed fatty acid	280
Myristic acid	228
Oleic acid	282
Pelargonic acid	160
Soya fatty acid	280
Stearic acid	284
Tall oil fatty acid	280

Difunctional

Adipic acid	73
Azelaic acid	94
Cyclohexanedicarboxylic acid	86
Dimethyl glutarate	80
Fumaric acid	58
Isophthalic acid	83
Maleic anhydride	49
Phthalic anhydride	74
Sebacic acid	101
Succinic anhydride	50
Terephthalic acid	83

Trifunctional

Citric acid	64
Trimellitic anhydride	64
Trimesic acid	70

Tetrafunctional

Pyromellitic dianhydride	55

Alcohols

Monofunctional

Amyl alcohol	88
Benzyl alcohol	108
Butyl alcohol	74
Cetyl alcohol (Hexadecanol)	242
Ethyl alcohol	46
2-Ethyl hexyl alcohol	130
Hexyl alcohol	102
Isobutyl alcohol	74
Isopropyl alcohol	60
Methyl alcohol	32
Octyl alcohol	130
Pentyl alcohol	88
Propyl alcohol	60

Difunctional

Butanediol	45
Cyclohexanedimethanol	72
Diethylene glycol	53
Dimethylol propionic acid	67
Dipropylene glycol	67
Ethylene glycol	31
Esterdiol - 204	102
1, 6 - Hexanediol	59
Hexylene glycol	59
Neopentyl glycol	52
1, 5 - Pentanediol	52
Propylene glycol	38
Tetraethylene glycol	97
Triethylene glycol	75
Trimethylene glycol	38
Trimethyl pentanediol	73

Trifunctional

Glycerine, 99%	31
Trimethylol ethane	41
Trimethylol propane	45
Tris (hydroxyethyl) isocyanurate	87

Tetrafunctional

Pentaerythritol	36

Oils

Castor	310
Coconut	229
Corn	293
Cottonseed	293
Dehydrated castor	293
Linseed	293
Safflower	293
Soya	293
Tung	293

Glossary of terms used in calculations

AN	acid number (ASTM D1639)
Charge wt.	charge weight of reactants
Eq.	number of equivalents
Eq. acid	equivalents of acid (excluding anhydrides)
Eq. carboxyl	equivalents of carboxyl (acids and anhydrides including fatty acids)
Eq. carboxyl material	total equivalents of carboxyl functionality (including fatty acid equivalents from oil)
Eq. hydroxyl material	total equivalents of hydroxyl functionality (including glycerol equivalents from oil)
Eq. Wt.	equivalent weight
F	theoretical functionality
FA	fatty acid
H_2O off	theoretical water of reaction
K	Patton’s alkyd constant
MW	molecular weight
OHN	hydroxyl number (ASTM D1957)
% Ex. OH	percent excess hydroxyl
PO	polyol
Wt. % OH	weight percent hydroxyl
Y	yield
Y’	corrected yield of high acid number resins

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