SYNTHESIS, DEVELOPMENT AND CHARACTERISATION OF DEHYDRATED CASTOR OIL POLY(GLYCERYL PHTHALATE) ALKYD RESINS

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R.S.A.

ABSTRACT

The dissertation studies the synthesis, formulation development, cross-linking and spectral characterisation of dehydrated castor oil poly(glyceryl phthalate) alkyd resins for use as air-dry surface coating vehicles.

Synthesis of alkyd resins involves simultaneous dehydration, alcoholysis and polyesterification reactions. Dehydration of castor oil is achieved *in situ* under phthalic anhydride catalysis. Alcoholysis of dehydrated castor oil by glycerol is also achieved *in situ* to form predominantly the monoglyceride. Polyesterification of the resultant mono- and diglycerides is realised through interaction with phthalic anhydride. The reaction is carried out at 280°C for 3 hours and at 225°C for 2 hours under azeotropic distillation with xylene. The parent poly(glyceryl phthalate) alkyd resin is synthesized by reaction of castor oil, glycerol and phthalic anhydride to a predetermined acid value.

Formulation development experiments were carried out to study the effect of variations in the dibasic acid to polyol/oil and polyol to oil ratios on alkyd resin properties. Model formulations exhibiting the best alkyd performance were developed. Predictive model formulation equations were derived from model formulation data and their limits of reliability and applicability established. The formulation of water soluble alkyd resins is modified to introduce pendant carboxylic acid groups along the polymer skeleton. Water solubility is achieved by neutralisation of the residual pendant carboxylic acid groups by 'fugitive' amines to yield water soluble alkyd soaps. The effect of variations in the nature and level of incorporation of amine is investigated. Alkyd resin solubilisation and resin acidity guide formulae were studied and developed.

Cross-linking chemistry of alkyd resins, both in the reactor (gelation) and on application (film formation) is investigated. Gelation manifested itself in two different forms, thermoplastic and thermosetting. An important alkyd constant, K, was established as an indispensable tool in control of premature gelation and in the prediction of resin drying characteristics. Autooxidation and solvent evaporation are the two competing curing mechanisms encountered in film formation. The nature and influence of each curing mechanism on the rate of cure and film characteristics is highlighted. Catalysis experiments were conducted with metallic driers (Co^{2+}, Mn^{2+} and Pb^{2+}) to bring the rate of drying of resin films to economically feasible limits and catalyst addition levels were established.

New spectral characterisation techniques based on Fourier Transform Infrared spectroscopy were investigated. An extensive study was carried out on FT IR spectral data to establish qualitative and quantitative relationships between transmission peak ratios and alkyd resin composition. Series dependent and series independent correlation equations, useful in quantifying alkyd resin components were derived. A new FT IR spectroanalytic characterisation method for dibasic acids is proposed. The method, if adopted, affords both qualitative and quantitative characterisation of the dibasic acid component in the alkyd resin matrix and it is envisaged the technique will supersede conventional methods in terms of speed and simplicity.

DECLARATION

I hereby declare that this is my own unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg, R.S.A. It has not been submitted before for any degree or examination in any other University.

ARNOLD NZERU

11TH day of FEBRUARY 1994.

JOHANNESBURG, R.S.A.

To my wife, Tendayi, and my family,
for their encouragement, support and patience,
during the many long hours I was unavailable
when they needed me most.

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1. LITERATURE REVIEW

1.1. INTRODUCTION

1.1.1. Historical Development

The formation of polyesters with resinous characteristics has long been known. Berzelius [1] in 1847, reported a resinous product from the reaction of tartaric acid with glycerol. Berthelot [2] in 1853, prepared a glyceryl ester of camphoric acid and von Bemmelen [3] in 1856, prepared glyceryl succinate and glyceryl citrate. Vorlander [4] in 1894, prepared glycol maleates. Watson Smith [5] in 1901, obtained a hard, brittle polymer by the reaction of glycerol with phthalic anhydride. In 1910 extensive investigations were begun at the General Electric Laboratories (U.S.A.) on the glycerol-phthalic anhydride reaction resulting in the development of resins which found limited use for bonding mica flake into sheet for electrical applications.

The work of Callahan [6], Friedberg [7], Arsem [8], Dawson [9] and Howell [10] showed that when part of the phthalic anhydride is replaced with monobasic acids, such as butyric or oleic acid, more flexible and more soluble resins result. In 1924, Kienle [11] (General Electric Co.) began an important series of investigations which culminated in 1933 in a patent covering the modification of polyesters with drying oils. Oil-modified polyesters, commonly referred to as alkyds , now account for approximately half of all the resins consumed in the protective coatings industry.

1.1.2. Nomenclature

Alkyd resins are resinous polyesters which are modified by incorporation of monobasic fatty acids. The term is derived from *al*cohol + a*cid* = *alcid*, but was changed to *alkyd* for euphony. Polyesters may be classed as heterochain macromolecular compounds that possess a plurality of carboxylate ester groups as components of their skeletal structures. By this definition there are distinguished from ester-containing polymers in which the carboxylate group form part of the substituent entities pendant from the backbone structure. The term polyester in its widest sense covers all polymeric products formed by the interaction of polyhydric alcohols with polybasic carboxylic acids.

1.1.3. Scope

A large number of polyesters are commercially available. These polymers are conveniently classified into the following types

Alkyds
Unsaturated polyesters
Poly(allyl ester)s
Poly(ethylene terephthalate)
Poly(butylene terephthalate)
Cyclohexylenedimethylene terephthalate polymers
Polyester thermoplastic elastomers
Polyarylates
Poly(p-hydroxybenzoate)s
Polyester plasticisers

1.2. CHEMISTRY

1.2.1. Reactivity and Mechanism

1.2.1.1. Chemical Reactions

The chemical reactions that occur during preparation of alkyd resins include (i) Condensation reactions among alkyd ingredients or alkyd modifiers, including esterification; ester, alcohol or acid exchanges; and etherification (ii) Addition reactions of unsaturated hydrocarbon portions of the monobasic fatty acids, including free radical or Diels-Alder reactions with other alkyd ingredients, modifiers or oxygen.
(iii) Addition reactions, especially free radical types, with other unsaturated alkyd ingredients.
(iv) Side reactions such as decarboxylation
Due to the complex composition of alkyds, an understanding of the chemistry of their behaviour is best derived by inference from the chemistry of simpler systems.

Esterification

The basic reaction involved in the preparation of alkyd resins is esterification. The reaction is reversible and the extent of the forward reaction is controlled by the rate at which the products are removed, hence in alkyd resin synthesis, water is continually removed during reaction.

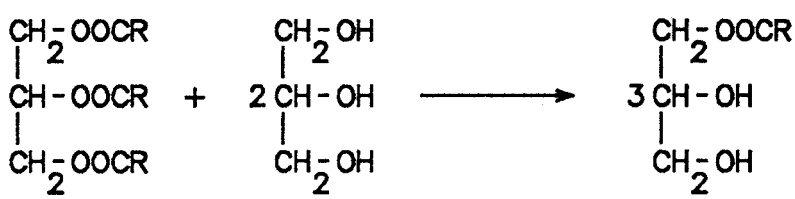
$$HOOC\text{-}R_1\text{-}COOH + HO\text{-}R_2\text{-}OH \text{ <-----> } HOO\text{-}R_1\text{-}COO\text{-}R_2\text{-}OH + H_2O$$

Ester Interchange Reactions

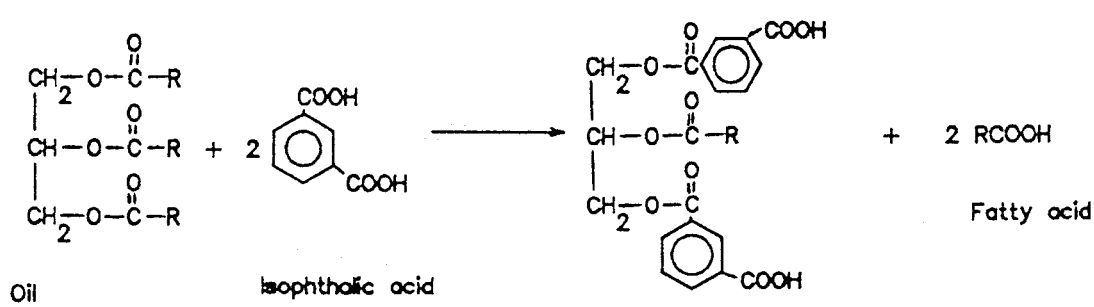
Ester interchange reactions encountered in alkyd resin reactions are alcoholysis and acidolysis. The reactions are special cases of esterification in the sense that only hydroxyl, carboxyl and ester groups are involved. These reactions are useful in increasing reactant solubility and dispersing

oil unsaturation and pendant hydroxyl (alcoholysis) and carboxyl (acidolysis) groups throughout the polymer. Both alcoholysis and acidolysis are reactions used in the preparation of alkyd resins from oils. If, for example a polyol and phthalic anhydride are added to the oil simultaneously, substantial amounts of insoluble polyol-phthalate form. The reactions are aimed at obtaining a partial ester best suited to produce linear polymers on subsequent polymerisation.

(i) Alcoholysis Reaction



(ii) Acidolysis Reaction

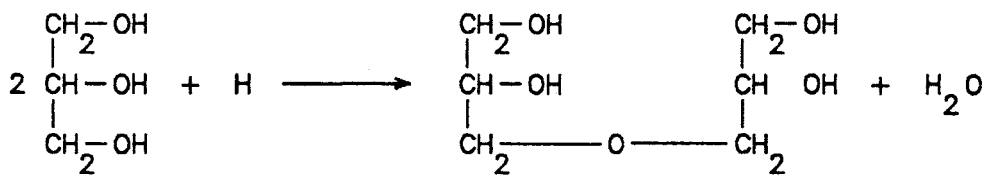


Etherification Reaction

At temperatures of alkyd processing, reactions other than esterification can occur with relative ease. Etherification of polyols may occur. At 280°C Brett [12] found as much as 27% etherification with glycerol as the polyol but this

was true when excess glycerol and alkaline catalyst were present.

At a more conventional temperature, 240°C, he reported less etherification, 8% with glycerol. Little etherification was reported with pentaerythritol at 240°C. Sorbitol is more prone to etherification than glycerol because it is capable of internal etherification.



glycerol

Reactions of Unsaturated Monobasic Fatty Acids

The non-carboxylic reactions of monobasic fatty acids that are pertinent to alkyd chemistry are dependent upon unsaturation in the fatty acid. Reactions in which there are single double bonds and conjugated pairs of double bonds can occur by both free radical or Diels-Alder mechanisms. The manner in which the reaction proceeds depends on the reagent, but may be related to the type of unsaturation in the fatty acid. Reactions with oxygen, for example, are free radical regardless of the type of fatty acid. During preparation, reaction of alkyds with oxygen is generally an undesirable side reaction.

Vinyl type modifiers can react by free radical addition. Other important Diels-Alder reactions in alkyd preparations include thermal polymerisation of unsaturated fatty acids and maleic anhydride addition.

Reactions with other Unsaturated Alkyd ingredients

Unsaturated alkyd ingredients, other than monobasic fatty acids, also serve as points for modification by both Diels-Alder and free radical addition reactions. Frequently unsaturated dibasic acids, such as maleic or fumaric, provide the reactive unsaturation for either free radical addition of vinyl type monomers or reaction with dienes such as rosin.

1.2.1.2. The Concept of Functionality and Gelation

Carothers [13], in 1929 showed the broad relationships of functionality to polymer formation and defined the conditions necessary for intermolecular condensation polymerisation of bifunctional monomers to produce linear, soluble and fusible polymers such as polyesters from glycols and dibasic acids.

Kienle and Hovey (1929-1930) [14] showed that although a bifunctional polymer such as glycol-phthalate polyester, is fusible and soluble even at the highest degree of esterification obtainable, the use of a trifunctional component as in glyceryl phthalate polyester leads to a gelled polymer long before completion of esterification.

When glycerol and phthalic anhydride are reacted in equivalent proportions, the acid value drops very rapidly at first, the dibasic acid reacts with primary hydroxyl groups of the glycerol to form rather short linear polyesters. As the reaction proceeds the secondary hydroxyls react with molecules of phthalic anhydride and connect short chains forming a complex branched or network structure. When approximately 80% esterification has taken place, the product becomes infusible and insoluble in common solvents (gelation).

The conditions necessary for gelation of such condensation has been treated mathematically by Carothers [15] and its application to the glycerol-phthalic anhydride reaction has been studied by Kienle and co-workers [16].

Carothers equation (simplified form) states that as the molecular weight becomes infinite at the gel point,

$$p = 2/f \qquad [1.1.]$$

where p = extent of reaction

f = average degree of functionality or average number of functional groups in the reacting molecules considering stoichiometric equivalents of interacting functional groups.

Carothers equation when applied to bifunctional reactants indicates that no gelation occurs even at 100% esterification. When applied to the reaction of equivalent quantities of glycerol and phthalic anhydride shows that gelation occurs at 83% esterification. The experimental results of Kienle and co-workers [16] using equivalent quantities showed gelation occurred at 79.5 - 79.6% reaction regardless of reaction temperature. Carothers equation assumes in effect that an indefinite number average molecular weight corresponds to gelation.

Flory [17] showed that in a system with average functionality of 3 and above, polymer growth does not place through chain growth followed by cross-linking. On the contrary, the growth appears to be random, with a great deal of branching to the point of gelation. Gelation occurs when a number of these irregular, relatively low molecular weight branched chains react with each other to form a 3-dimensional network.

Flory [18] introduced the application of probability statistics to the prediction of gelation as a logical refinement to explain the wide discrepancy in results.

Flory's equation is as follows

$$p^2 = 1/(f-1) \qquad [1.2.]$$

where p = extent of reaction at gelation

f= functionality of branching unit

Other investigators [19-21] have developed their theories of gelation. In practice, theoretical and actual gel points do not correspond despite numerous modifications and correction factors that have been applied to both Carothers and Flory equations.

Reaction of glycerol (3 hydroxyls) and phthalic anhydride (2 carboxyls) in equimolar proportions results in no gelation. Thus to achieve non-gelation, the average functionality must be approximately 2. The actual functionality of glycerol is limited to 2 since that is the number carboxyl groups available for reaction. If all the primary hydroxyl groups of glycerol react first, a linear polymer will result. Therefore, use of more glycerol than the stoichiometric quantity required by the hydroxyl groups present reduces functionality. Thus the use of excess polyol is an important method in reducing functionality.

Most alkyd formulations are such that glycerol has an actual functionality slightly more than 2.

$F_{OH}(actual) = F_{OH}(potential)/1+n$

where $F_{OH}(potential)$ = maximum functionality if all groups can react, n = decimal proportion of the polyol hydroxyl excess of carboxyl groups available.

An additional method for controlling functionality is the basis for the formation of oil-modified polyesters (alkyds).

Step 1 : Conversion of trifunctional polyol into bifunctional polyol (alcoholysis)

Step 2 : Conversion to a fatty acid-modified polyester (polyesterification)

1.2.1.3. Microgel Theory

The behaviour of alkyd resins often deviates from the theory of Flory [22]. To explain this, a mechanism of microgel formation by some of the alkyd molecules at a relatively early stage of the reaction was proposed [22]. The microgel particles are dispersed and stabilised by smaller molecules in the remaining reaction mixture. As polyesterification proceeds, more microgel particles are formed, until finally a point is reached where they can no longer be kept separated. The microgel particles flocculate or coalesce, phase inversion occurs, and the entire reaction mass gels. The drying capability of an alkyd resin comes primarily from the microgel fraction [22].

In a further elaboration [23,24] of the microgel theory, the formation of micelles as precursors of microgels was proposed. Thus, when some of the molecules have grown to reach certain fatty acid-polyester ratios, surface activity develops to form micelles. Polyesterification reactivity at the surface of the micelles is preferentially greater, which leads to eventual formation of microgels. Electron microscopy evidence indicated that the size of microgels increases with reaction time. Functional groups such as OH in the microgel structures are believed to be buried in the structure and not available for reactions. Unlike in polyesterification reactions without fatty acids, where at all stages of the reaction, up until the physical gelation of the reaction mixture, the hydroxyl values correspond with the calculated values. Furthermore, the oil-free systems show no sign of microgel formation under the electron microscope, and the reaction mixture

undergoes a sudden change from a soluble polymer to a gelled mass. The reaction temperature for alkyd systems observed [23,24] was kept at no more than 200°C, well short of what would normally be required for bodying of unsaturated oils in the absence of an oxidising agent.

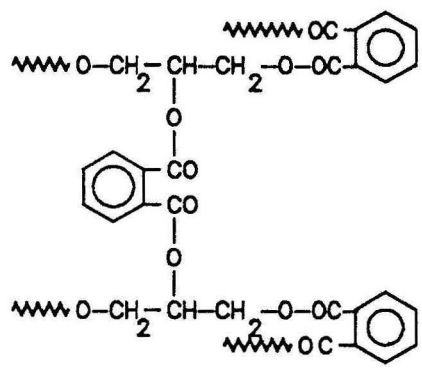
More recently, the formation of microgels was further confirmed by characterisation of fractions of alkyd resins from preparative gpc columns [25-28].

1.2.1.4. Kinetics

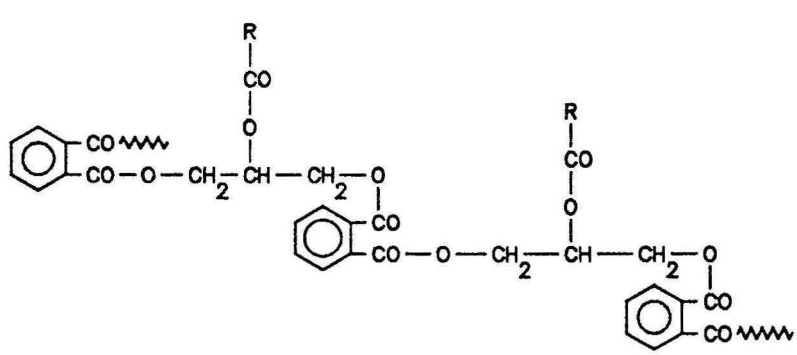
There is relatively little information on the kinetic process involved in alkyd reactions. One reason is that the innumerable possible reactions complicate the use of kinetics as a means of defining the mechanisms of reactions. Moore [29] suggests that the overall reaction rate is influenced by the rate of diffusion of water, especially in the latter stages. Moore also found that reaction order varied with small excesses of either reagent, but that at stoichiometric equivalence, the order of reaction was about 3 in the early stages of the reaction. Certainly, at least during the early reaction stage, the kinetics appear analogous to those of monofunctional esterification reactions.

1.2.2. Structure

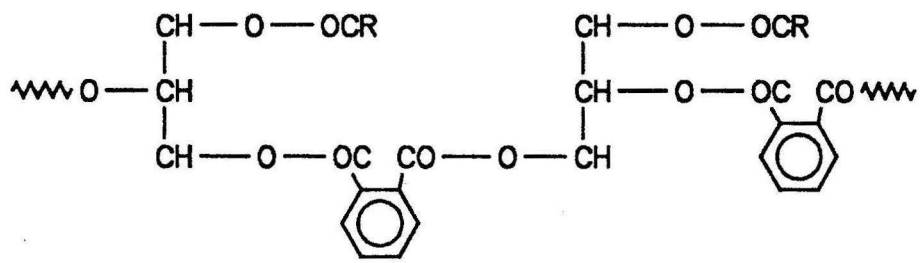
The structure of a resin obtained by simple esterification of glycerol with phthalic anhydride may be represented as follows



Poly(glyceryl phthalate) resins are brittle and of little practical use; however the incorporation of fatty acid residues into such a structure leads to highly successful surface coating vehicles. The detailed structure of the latter resins depends on the method of preparation. In the fatty acid process, the polyol, dibasic acid and fatty acids react simultaneously and it has been shown [30] that the primary hydroxyl groups of glycerol react more readily with phthalic carboxyl groups than with fatty acids whilst the reverse applies to the secondary hydroxyl groups. It is to be expected, therefore, that in an alkyd resin prepared by the fatty acid process the following type of structure would predominate.



In the alcoholysis process there is no fatty acid competing in the esterification reaction. Since alcoholysis generally results in a preponderance of α-monoglycerides, it is to be expected that in an alkyd resin prepared by this process the following structure would predominate:



A number of reactions other than esterification may occur during the production of alkyd resin and result in some deviation from the ideal structures shown above. For example, acid catalysed etherification may take place and esterification of this product would lead to a resin containing ether links.

1.2.3. Film formation

1.2.3.1. Autoxidation and Polymerisation

The mechanism by which an alkyd resin is converted from a liquid to a dry film is largely determined by the nature of the fatty acid residues present. When the fatty acid residues are derived from non-drying oils, the alkyd resin itself can not readily form dry films. When the fatty acid residues are derived from drying or semi-drying oils, the resin is itself is capable of forming dry films. The drying process involves attack by oxygen in the unsaturated regions of the fatty acid residues followed by cross-linking. The molecular weight of an alkyd resin is higher than that of an oil; consequently the number of cross-links needed to give a dry film is less and the drying time is reduced. Further, since relatively little cross-linking is required to dry

an alkyd film, the less unsaturated semi-drying oils can be used to prepare alkyd resins which dry readily.

The conversion of a drying or semi-drying oil alkyd resin to a solid film consists of two steps, namely aerial oxidation and cross-linking initiated by decomposition of the oxidation products. These processes are complex and the cross-linked systems are difficult to manipulate for analytical purposes. Marked differences in the behaviour of non-conjugated and conjugated unsaturated fatty acids and their esters towards oxidation have been observed.

Reactions of non-conjugated fatty acids and esters

Non-conjugated fatty acids and esters are susceptible to the general type of autooxidation. A methylene group adjacent to a double bond is particularly liable to lose a hydrogen atom since the resulting radical is resonance stabilised. The radical can react with oxygen to give a peroxidic radical which then abstracts hydrogen from a further α-methylene group to form a hydroperoxide and propagate the reaction.

The hydroperoxides formed may decompose in the following ways

$ROOH \text{ --------> } RO^{\cdot} + HO^{\cdot}$

$2ROOH \text{ ------> } RO^{\cdot} + ROO^{\cdot} + H_2O$

These reactions account for the first and second order which have been observed for the initial decomposition of some hydroperoxides. Subsequent to primary decomposition, induced decomposition may occur as follows :

$RO^{\cdot} + ROOH \text{ ------> } ROO^{\cdot} + ROH$

$ROO^{\cdot} + ROOH \text{ -----> } RO^{\cdot} + ROH + O_2$

$RO^{\cdot} + RH \text{ -----> } ROH + R^{\cdot}$

$HO^{\cdot} + RH \text{ -----> } H_2O + R^{\cdot}$

$R^{\cdot} + ROOH \text{ -----> } ROH + RO^{\cdot}$

Termination of the above reaction chain may occur by combinations of the following :

$RO^{\cdot} + RO^{\cdot} \text{ -----> } ROOR$

$ROO^{\cdot} + ROO^{\cdot} \text{ -----> } ROOR + O_2$

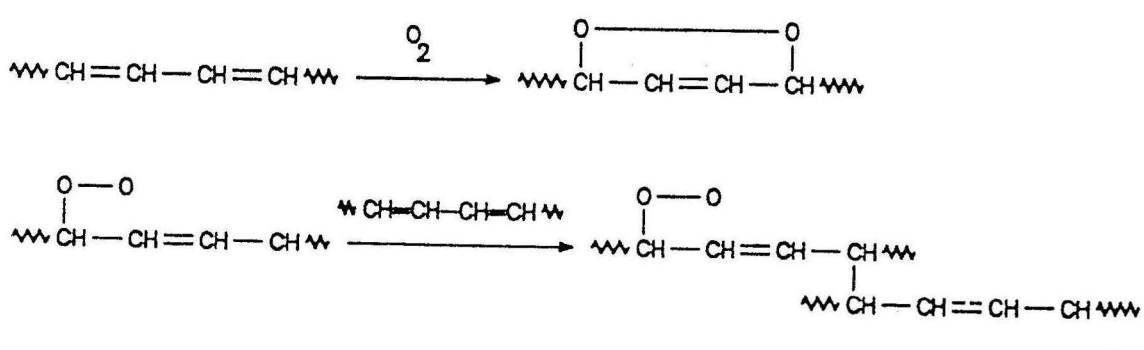
$R^{\cdot} + R^{\cdot} \text{ -----> } R\text{-}R$

$RO^{\cdot} + R^{\cdot} \text{ -----> } ROR$

$ROO^{\cdot} + R^{\cdot} \text{ -----> } ROOR$

Reactions of conjugated fatty acids and esters

Conjugated fatty acids and esters do not respond to aerial oxidation in the same manner as non-conjugated fatty acids and esters. In particular, cross-linked films derived from conjugated materials contain much more carbon-carbon bonding in the cross-links. It has been suggested that in these cases the initial product of oxidation is a 1,4-peroxide which initiates a diene-type polymerisation:



The steps involved in film formation can be summarised as:

(i) an induction period in which little visible change in chemical and physical properties occurs but oxygen is absorbed to destroy antioxidants.

(ii) a substantial increase in oxygen uptake with the appearance of hydroperoxides and conjugated dienes.

(iii) hydroperoxides form free radicals and the reaction becomes autocatalytic

(iv) onset of cleavage and polymerisation.

1.2.3.2. Rate of Drying and Film Hardness

D.T. Moore [31] investigated the quantitative relationships between film forming properties and fatty acid composition in alkyd resins using known mixtures of the various fatty acids present in drying and semi-drying oils. His work confirmed that the rate of drying is a function of polyunsaturated (polyenoic) acid content. The rate increases rapidly up to a polyenoic acid content of approximately 50% when a limiting value is gradually approached. The limiting value represents the point at which intermolecular polymerisation is largely completed and the polymer is of such a size that any additional polyunsaturates react intramolecularily.

Moore also found that the hardness of a film is proportional to the polyunsaturated acid content, and that at a constant polyunsaturated acid content, a change in the linoleic-linolenic ratio produces appreciable change in the ultimate hardness. He also showed that the presence of conjugated unsaturation up to a limit of about one half the total unsaturation has a beneficial effect on the drying time, however, the ultimate hardness of alkyd films is not appreciably affected by the ratio of conjugated to nonconjugated forms.

1.2.3.3. Colour Development

Colour development or after yellowing in white enamels is proportional to the polyunsaturated acid content, a change in the linoleic-linolenic ratio produces appreciable change in ultimate hardness.

The colour development conforms to the formula :

$$Y = A(L_1+5L_2)+B \qquad [1.3.]$$

where Y = degree of yellowing, L_1 = Linoleic acid, %

L_2 = Linolenic acid, %, A and B are constants.

The equation indicates that linolenic acid is five times as potent as linoleic acid in causing yellowing. Moore also studied the effect of adding various proportions of conjugated fatty acids derived from tung oil and dehydrated castor oil to the non conjugated acids derived from soya, cottonseed and linseed oils. The drying results showed that the presence of conjugated unsaturation up to a limit of about one half of the total unsaturation has a beneficial effect on the drying time. However, the ultimate hardness of alkyd films is not appreciably affected by the ratio of conjugated and non conjugated forms.

1.2.3.4. Driers or Catalysts

The formation of cross-linked films by various reactions described above is not rapid enough for practical purposes. Commercial surface coatings therefore contain driers which speed up the drying process.

Driers are materials that promote or accelerate the curing or hardening of film formers that contain oxidizable or drying oil components. Most commonly, driers are hydrocarbon-soluble salts (usually octoates, naphthenates and linoleates) of metals. The metallic driers may be divided

into primary (or participating) driers and promoter (or auxiliary) driers.

Primary driers

These include salts of cobalt and manganese and can by themselves catalyse the drying process. They have the highest catalytic activity and most pronounced accelerating effect on film formation. Primary driers are termed 'surface' or 'skin' driers since in oxidizable vehicles, cobalt or manganese, when used alone, will cause the surface of the film to rapidly set to a near solid while the underlying film does not reach this advanced state of oxidation. This uneven hardening will, in thick films, cause the defect known as 'wrinkling'.

Secondary driers

These include salts of lead, calcium, zinc and zirconium. While they possess a much lower level of catalytic activity, these metals, when used in combination with cobalt and/or manganese, give films that do not surface dry as rapidly and thus harden through more uniformly and are appropriately termed 'through' driers.

'Push and Pull' Mechanism of Drier Action

The detailed mechanism by which driers operate have not been elucidated although it is generally agreed that an important function of primary driers is to catalyse the decomposition of the hydroperoxides formed by the aerial oxidation of non-conjugated fatty acids and esters through the 'push and pull' action of the metal cation:

$ROOH + Co^{2+} \text{------>} RO^{\cdot} + OH^{-} + Co^{3+}$

$ROOH + Co^{3+} \text{------>} ROO^{\cdot} + H^{+} + Co^{2+}$

It has also been suggested that primary driers initiate the oxidation sequence by direct interaction of the metal ion with the fatty acid or ester as follows :

$RH + Co^{3+} \text{-----} > R^{\cdot} + Co^{2+} + H^{+}$

The mechanism of promoter driers is less clear. One suggestion is that they form salts with the acid groups present in an oil to give ionic cross-links which contribute to the initial drying of the film.

Enhanced drying efficiency in the presence of secondary driers has been assumed to be due to one of the following reasons or both : (a) they form coordination type complexes with hydroxyl groups on the polymers and thereby do not deactivate the primary driers and (b) they may act as strong bases eg calcium, which would preferentially neutralise acidic groups and thereby maintain the primary driers in the free state.

1.3. TECHNOLOGY

1.3.1. Raw materials

The principal raw materials involved in the preparation of alkyd resins are polyhydric alcohols (polyols), dibasic acids (or corresponding anhydrides) and modifying oils (or corresponding fatty acids).

1.3.1.1. Polyhydric alcohols

Resins have been made from many different polyhydric alcohols but by far the most important alcohol used commercially is glycerol. The alcohol component controls to a marked degree the physical properties of the resin obtained with phthalic anhydride.

Glycerol

Glycerol, propane-1,2,3-triol, a trihydric alcohol is a clear, water-white, viscous, hygroscopic liquid with a sweet taste at ordinary room temperatures above its melting point. Glycerol occurs naturally as triglycerides in all animal and vegetable fats and oils.

(i) Properties

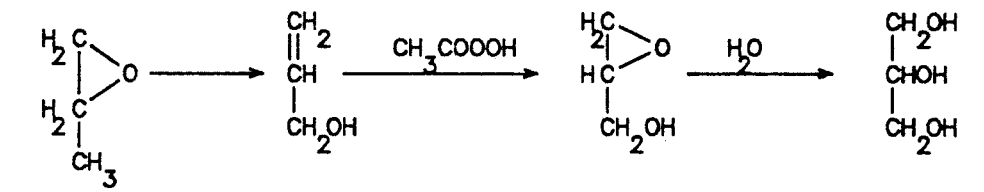
The physical properties of glycerol are m.p. 18.17°C, b.p. 290°C (101.3kPa), s.g.@ 25°C 1.2620 (100%), 1.2491 (95%), viscosity @ 25°C 1499 mPa.s. Glycerol is completely soluble in water and alcohol, lightly soluble in diethyl ether, ethyl acetate and dioxane and insoluble in hydrocarbons.

Glycerol is the preferred polyol for the preparation of alkyd resins due to its low cost and high boiling point (enables reactions to be carried out at high temperatures) and glycerol based alkyd resins have good solubility and compatibility characteristics and good film properties.

(ii) Source

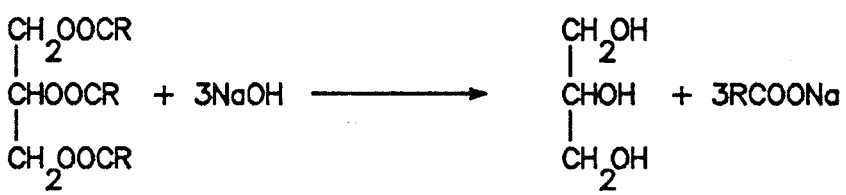
Glycerol is obtained both synthetically and as a by product in soap manufacture and fat splitting.

Propylene Oxide Route



Propylene oxide is isomerised to allyl alcohol by heating at 200-250°C in the presence of trilithium phosphate catalyst. The allyl alcohol is then epoxidised to glycidol with peracetic acid in ethyl acetate. The glycidol is then hydrolysed to glycerol.

By Product of Soap Manufacture

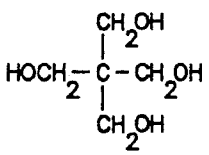


Oils or fats (glyceryl esters of fatty acids) are saponified by heating with aqueous sodium hydroxide. Sodium chloride is added to the reaction mixture to 'salt out' the soap which rises to the top of the liquid and the lower aqueous layer is run off, neutralised and evaporated. Salt is precipitated and filtered off to yield crude glycerol which is purified by

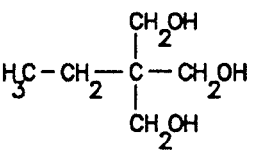
distillation under reduced pressure.

Other polyols

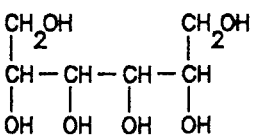
Other polyols are utilised to a lesser extent in the manufacture of alkyd resins to impart special properties. Such polyols include pentaerythritol, trimethylolpropane and sorbitol. Ethylene glycol and propylene glycol may be included to reduce cross-link intensity.



pentaerythritol



trimethylolpropane



sorbitol

1.3.1.2. Dibasic acids and anhydrides

Phthalic anhydride

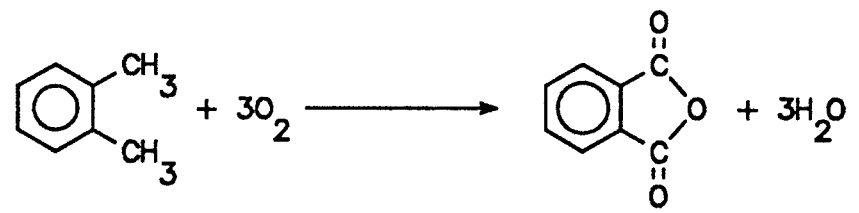
Phthalic anhydride is the difunctional acidic component most widely used in the manufacture of alkyd resins.

(i) Properties

Phthalic anhydride is a white crystalline solid, m.p. 131°C. Phthalic anhydride gives polyesters which are compatible with styrene and the cross-linked products are hard and rigid.

(ii) Synthesis

The anhydride is generally obtained by oxidation of o-xylene.

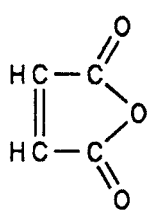


o–xylene phthalic anhydride

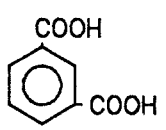
Reaction is carried out in the vapour phase by passing a mixture of o-xylene and air over a catalyst such as vanadium pentoxide supported on silica and promoted with titanium dioxide at about 400°C. The exit gases are cooled and phthalic anhydride is collected and purified by distillation under reduced pressure.

Other Dibasic Acids and Anhydrides

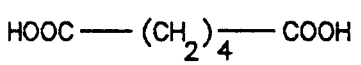
Other dibasic acids and anhydrides, which are used to a lesser extent include maleic anhydride, isophthalic acid, adipic acid and sebacic acid.



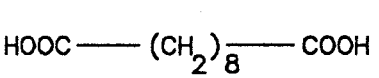
maleic anhydride



isophthalic acid



adipic acid



sebacic acid

1.3.1.3. Modifying oils and acids

The monobasic acid modifies the properties of alkyd resins in two ways, namely by its capacity to control functionality and so allow polymer growth and by the nature of its inherent physical and chemical properties. Oil-modification results in the resins being soluble in aliphatic solvents; atmospheric oxygen brings about rapid cross-linking of resin films and the cross-linked films are flexible and durable.

Vegetable Oils

(a) The Constitution of Vegetable Oils

Vegetable oils are fatty acid esters of glycerol (triglycerides). An array of glyceride oils and fatty acids of varying degrees of unsaturation and chain length are available. The properties of oils, both physical and chemical, are determined by the properties of the fatty acid component since this comprises 95% of the triglyceride molecule.

Oils have the general structure:

CH_2OCOR_1
|
$CH\text{-}OCOR_2$
|
CH_2OCOR_3

where R_1,R_2,R_3 represent fatty acid chains.

As glycerol is a trihydric alcohol, in each triglyceride molecule there are three esterified fatty acid molecules. The most common fatty acids present in glyceride oils are lauric, palmitic, stearic, oleic, linoleic, linolenic, eleostearic, ricinoleic and licanic acids.

(b) Classification of Oils

Oils are commonly designated as drying, nondrying and semi-drying depending on the effect of atmospheric oxygen on thin films of the oils. Rheineck and Austin [50] define them as follows : Drying oils, iodine value >140; semi-drying, 125-140 and nondrying, <125. Generally, films of drying oils become dry and insoluble after exposure for 2-6 days, films of semi-drying oils become tacky after 7 days and films of non-drying oils are still fluid after 20 days. Only drying and semi-drying oils are of importance in the manufacture of alkyd resins for surface coatings.

(c) Chemical Properties of Drying Oils

Unsaturated double bonds in the acyl glycerols (triglycerides) have some variable functionality depending on the reaction and conditions therein. Their functionality can be expressed as follows :

$$f = xy \qquad [1.4.]$$

where x = number of esterifiable hydroxyls,
y = average number of ethylene groups per acyl chain

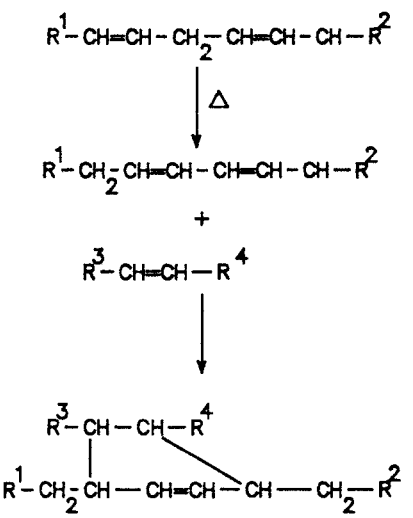
Functionality in drying oils is thus at best only a guide to behaviour since it varies with reaction and reaction conditions.

(i) Autoxidation and polymerisation

The degree and nature of unsaturation in the fatty acid groups dictates the susceptibility of a drying oil to absorb oxygen and cross-link to form a dry film. These reactions have already been discussed under Film formation [1.2.3.].

(ii) Thermal polymerisation

When heated in the absence of air, both conjugated and nonconjugated oils react to form polymeric products. If heating is carried out long enough, sufficient cross-linking results to form gels. Research has shown that, with the application of heat to the fatty acid chain, there is a migration of double bonds to the conjugated position subsequent to which the conjugated group so formed reacts with a double bond from a second fatty acid molecule by a Diels-Alder (1,4-addition) reaction. C-C polymers are formed in this manner, with the conjugated system formed by primary oxidation of an unsaturated diene or triene.



The resultant films have better alkali resistance than films formed by oxidation alone.

(d) Castor Oil

Castor oil is derived from the bean of the castor plant, *Ricinus Communis L.*, of the family *Eurphorbiaceae*. The castor plant occurs in practically all tropical and subtropical countries, either wild or cultivated. Oil content of castor seed is between 48-53%.

(i) Chemical Composition

Castor oil is unique in that it contains 87-90% ricinoleic acid, cis-12-hydroxyoctadec-9-enoic acid, a rare source of an eighteen carbon hydroxylated fatty acid with one double bond. It is one of the few naturally occurring glycerides that approaches a pure compound.

The average fatty acid composition of castor oil is as follows ricinoleic acid (89.5%), dihydroxystearic acid (0.7%), palmitic acid (1.0%), stearic acid (1.0%), oleic acid (3.0%), linoleic acid (4.2%), linolenic acid (0.30%) and eicosanoic acid (0.30).

(ii) Properties

Castor oil has the following properties :

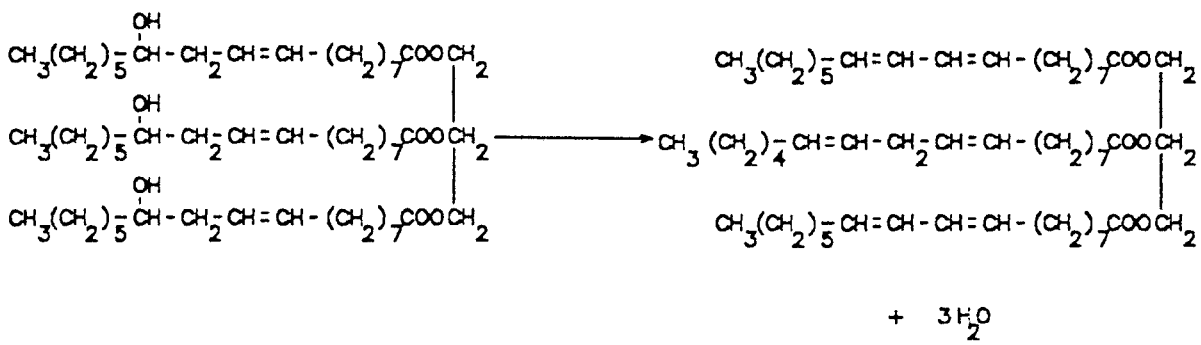
acid value - 2 (max), clarity - clear, colour (Gardner) - 2, hydroxyl value - 160-168, refractive index @ 25°C - 1.4764-1.4778, saponification value - 176-184, solubility in alcohol - complete, specific gravity @ 25°C - 0.957-0.961, unsaponifiable matter - 0.70% (max), viscosity @ 25, cm^2/s (stokes) - 6.5-8.0 and iodine value - 84-88.

The oil is distinguished from other triglycerides by its high specific gravity, viscosity and hydroxyl value. A unique feature is its solubility in alcohol, 1 volume oil is soluble in 2 volumes of 95% ethanol at room temperature and is miscible in all proportions with absolute alcohol. The oil is typically soluble in polar organic solvents and less soluble in aliphatic hydrocarbon solvents. Its slight solubility in petroleum ether is a characteristic which distinguishes it from other oils.

(iii) Dehydration of Castor Oil

Catalytic dehydration converts castor oil into an excellent drying oil. Dehydrated castor oil (D.C.O.) is used extensively in the coating industry in the manufacture of alkyd resins. Organic and inorganic acids were found effective for the dehydration of castor oil and these include acetic, phthalic, rosin and fatty acids and some of their anhydrides, sulphuric, sulphonic, phosphoric, silico-tungstic acids and their salts.

Mechanism of Dehydration



Dehydration occurs by esterification and pyrolytic cleavage to give an unsaturated bond. The released acid re-esterifies another hydroxyl group and cleavage is repeated. In the dehydration the 12-hydroxyl group is removed with a nearby hydrogen atom to form a new double bond and water. The reaction is first order with an activation energy of about 188 J/mol (43 cal/mol). Dehydration forms nonconjugated as well as conjugated diene structures in the dehydrated esters. One major side reaction is esterification to give a polyester.

(iv) Properties of D.C.O.

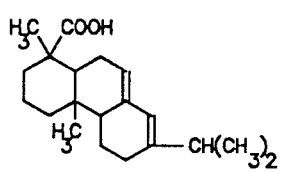
D.C.O. is well known for its non-yellowing film formation, outstanding colour retention, flexibility and adhesion in protective coatings.

Specifications for D.C.O.

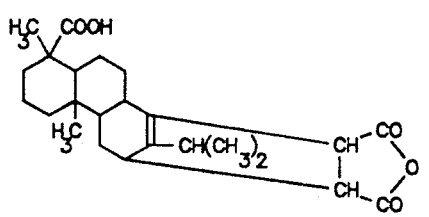
Property	Unbodied	Bodied
Viscosity @ 25°C	F to I	Z2 to Z4
Specific gravity @ 25°C	0.926-0.937	0.944-0.966
Acid value	6	6
Saponification value	188-195	188-195
Iodine value (Wijs)	125-145	100 minimum
Colour (Gardner)	6	7
Gel time @ 315°C, min	145	63
Set to touch time, h	2.5	1.4
Refractive index @ 25°C	1.4805-1.4825	1.4860-1.4890

Other Oils and Acids

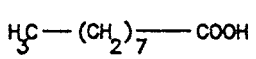
Naturally occurring and synthetic acids are also used in the manufacture of alkyd resins. These include rosin, the adduct of rosin and maleic anhydride, synthetic fatty acids such as pelargonic acid and isooctanoic acid.



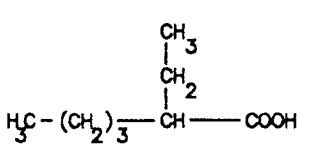
rosin



adduct of rosin and maleic anhydride



pelargonic acid



isooctanoic acid

1.3.2. Modifications

Alkyds, as a group, are characterised by rapid drying, good adhesion, flexibility, mar resistance and durability. Their principal weakness is the ease with which the ester groups, which form so large a part of the molecules, are hydrolysed under alkaline conditions. It is possible to produce alkyds with greatly improved resistance to hydrolysis by use of special polyols, or acids containing sterically hindered carboxyl groups.

The wide spectrum of alkyds is broadened by modifications with a wide array of polymeric and reactive functional materials to impart improved and/or special film forming properties. Modifying materials include nitrocellulose, urea-formaldehyde resins, melamine-formaldehyde resins, silicones, phenolic resins, chlorinated rubber, synthetic latexes, vinyl resins, reactive monomers, cellulose acetobutyrate, phenolic varnishes, polyamides, natural resins and monobasic aromatic acids. The modifying materials may be present in physical or chemical combination.

In general, compatibility of alkyd resins depends upon polarity and it is inversely proportional to the degree of polymerisation. In a long-oil resin, the large number of long chain fatty acid groups impart a non-polar character to the molecule. In short-oil alkyds, the high proportion of hydroxyl groups imparts not only polarity, but acts as centres of potential reactivity with a host of hydroxyl reactive materials. Undoubtedly, the aromatic ring in phthalic anhydride and the ester linkages contribute polarity. Moreover unsaturation in the fatty acid chain allows interpolymerisation with many vinyl monomers, epoxidation and other reactions typical of the double bond.

1.3.2.1. Physical modifications

The materials which are blended with alkyd resins to bring about specific improvements include cellulose nitrate (which confers fast drying characteristics and toughness) and chlorinated rubber (which imparts fire-resistance and toughness).

1.3.2.2. Chemical modifications

Chemically modifying materials react with suitable formulated alkyd resins and are usually incorporated during the preparation of the alkyd resin.

(a) Water Soluble Alkyd Resins

Formulation of water-soluble alkyd resins is modified to introduce pendant carboxylic acid groups along the polymer backbone. These pendant acid groups can be neutralised with basic compounds to produce water soluble soaps of the alkyd polymer. Most water soluble alkyds in commercial use have an acid value of 40-65 (on resin solids).

The pendant acid groups can be incorporated into the polymer backbone in different ways:

(i) Method 1

The method involves initially preparing a hydroxy rich prepolymer of low acid value, usually below 10. The prepolymer (partial alkyd) is made by reacting suitable quantities of vegetable oils or fatty acids with dibasic acids or anhydrides and polyols. Normal alkyd processing techniques and temperatures are used to make this prepolymer. When the desired acid value has been reached, more di- or tri-basic acid or anhydride is added. The reaction mixture is then processed at temperatures in the vicinity of 170-200°C down to an acid value of 40-65. Materials such as phthalic or trimellitic anhydrides are typical of the acids or anhydrides used in the second stage.

(ii) Method 2

The method involves initially preparing a maleinized oil. This is achieved by reacting maleic anhydride or fumaric acid with an oil or fatty acid containing conjugated unsaturation. Usually this is carried out at temperatures of 210-240°C. The maleinized oil is then reacted with a dibasic acid and a polyol. This is then processed in a similar manner to conventional alkyds down to an acid value of 40-65 at temperatures between 175-200°C. The second stage of this process involves the reaction of the unreacted anhydride groups and the polyols. The reaction occurs at temperatures slightly above 150°C. The true acid polyol condensation reaction, except for fatty acids, does not generally occur to any significant degree at temperatures below 200°C. Controlling the temperature during this stage ensures that there will be sufficient free carboxylic acid groups available for neutralisation and solubilisation in water.

(b) Aminoresins

Melamine and urea-formaldehyde resins confer improved hardness, durability and alkali resistance. The reactions involved are those of alkyd resin hydroxyl groups with the amino methylol groups as well as self-condensation of the amino methylol groups. The reaction is faster when some free acid is present, and often these are added as catalysts, such as para-toluene sulphonic acid. Some common cross-linking reactions are

Amino--NCH_2OR + HO--Alkyd ------> Amino--NCH_2-O--Alkyd + ROH

Amino--$N(CH_2OH)_2$ + 2 HO--Alkyd ---> Amino--$N(CH_2$-O--Alkyd$)_2$ + $2H_2O$

The properties of the resultant film will depend very much on the ratio of amino to alkyd resin used. The usual range is from 10-40% amino resin to the total alkyd resin solids content. The higher the levels give harder and better colour stability at the expense of flexibility and adhesion.

(b) Phenolic resins

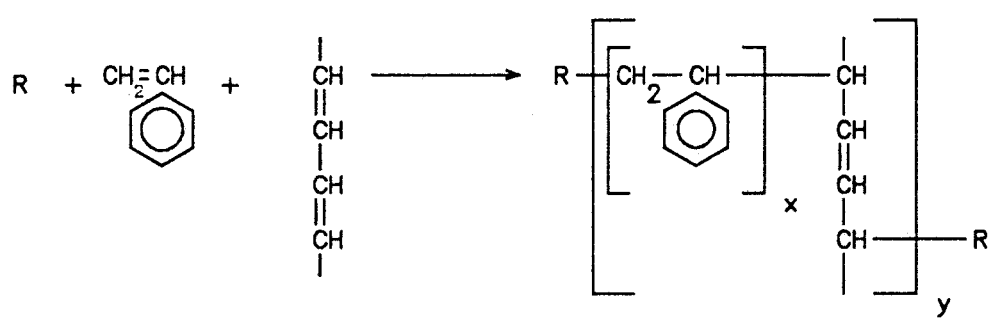
Phenolic resins impart fast drying characteristics, superior water resistance, gloss and hardness as well as improved alkali, grease and oil resistance. The reaction occurs between the phenolic methylol groups and the alkyd hydroxyl group.

$$Ph\text{--}CH_2OH + HO\text{--}Alkyd \longrightarrow Ph\text{--}CH_2\text{-}O\text{--}Alkyd + H_2O$$

(c) Reactive monomers

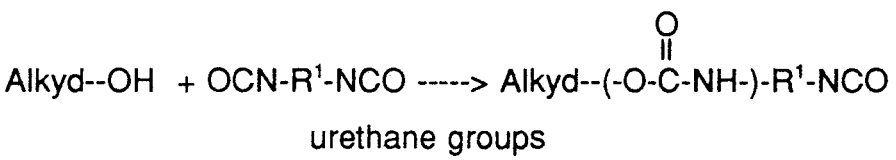
Chemically-modified alkyd resins may also be prepared by the use of vinyl-type monomers such as styrene, vinyltoluene, methyl methacrylate and acrylonitrile, of which styrene is the most commonly used.

Styrenation is achieved by the reaction of styrene and the preformed alkyd resin. Styrenated alkyd resins give finishes with good colour retention and alkali resistance but with reduced solvent resistance.The styrenation of conjugated alkyds probably involves 1,4 addition as follows:



(d) Urethane alkyds

The free hydroxyl groups of alkyds react with polyisocyanates to form urethane linkages. The products dry faster and have improved chemical and abrasion resistance.



(e) Silicone resins

Reactive silicone intermediates react with hydroxyl groups in long-oil drying alkyds to give copolymers with greatly improved durability, gloss retention and increased heat resistance.

1.3.2. Resin Formulation

1.3.2.1. Formulation Tools

Carothers [13] stated that as the molecular weight becomes infinite at gel point, $p = 2/f$ where p = extent of reaction, f= average degree of functionality.

Deviations from theory found in actual synthesis of alkyds and reasons for these deviations received the attention of a number of investigators who proposed numerous modifications and correction factors to the Carothers equation. Even with these modifications, the theoretical and actual gel points do not correspond. The equations are of limited value in designing an alkyd resin from theoretical considerations alone.

The possible reasons for the lack of agreement between theoretical and practical gel points are

(i) Intramolecular esterification reactions that result in ring closure [14] are terminating

(ii) Side reactions can increase functionality without loss of carboxyl groups. Two common examples are etherification of polyol [32] and reaction of unsaturated dibasic acids such as maleic anhydride with an unsaturated fatty acid (Diels-Alder condensation)

(iii) There is some thermal dimerisation of polyunsaturated fatty acids [20].

(iv) The proposed equations assume all groups are equally reactive and available. Solomon and Hopwood [24] have shown that this is incorrect.

(v) The calculated gel points correspond with the initial formation of branched or cross-linked polymer, whereas the actual gel points represent significant amounts of three dimensional structure [33].

In alkyd formulations, the polymer chemist generally seeks to prepare a resin with the highest molecular weight at low acid values without encountering gelation.

Patton's alkyd constant, K.

Patton [34] derived an alkyd constant based on the adaptation of Carothers [35] functionality equation.

$$K = m_o/e_A = 1 \qquad [1.4.]$$

where m_o = total number of acid or hydroxyl bearing molecules in a given alkyd composition at the beginning of condensation between carboxyl and hydroxyl groups

e_A = total number of acid equivalents in the reaction.

Patton studied a group of alkyd formulations reported in literature. The m_o/e_A ratio was computed for each formulation and the mean value for the ratio was 1.022 + or - 0.023; the small difference from unity is explained by the fact that the 1.00 is theoretically derived for the ratio m_o/e_A and pertains to completion of condensation at incipient gelation. However, formulating close to gelation presents the danger of product loss. Accordingly, experience dictates that a margin of safety in processing be provided. The deviation of the alkyd constant from unity is also due to the previously mentioned factors that account for the lack of agreement between theoretical and actual gel points.

Patton's analysis of a large number of formulations revealed that those alkyds based on phthalic anhydride tend to have low m_o/e_A values whereas those based on isophthalic acid tend to have higher values. Experimentally determined alkyd constants were found to be 1.005 + or - 0.014 for phthalic anhydride resins and 1.05 + or - 0.008 for isophthalic acid based resins.

A m_o/e_A value which is 0.05 unit from the above values indicates a probability of encountering premature gelation short of a 100% reaction. A m_o/e_A value that is greater than the above values, indicates deficient

reactive functionality from an excess of hydroxyl groups.

Formulation tools are available in the form of alkyd constants. The alkyd constants provides the resin chemist with a tool of assessing the feasibility of preparing a given alkyd formulation. Although alkyd constants provide valuable data on reactant proportions, the choice of raw materials must be carefully evaluated in view of the wide variety of available polyols, polybasic and monobasic acids. The use of alkyd constants represents a good starting point in formulation and will reduce the number of experiments necessary for developing and evaluating alkyd resins.

1.3.2.2. Classification of Alkyd Resins

Classification of alkyd resins is based on the nature of the fatty acid and the oil length.

(i) Drying vs Non-drying, and the Specific Source of Fatty Acid

Alkyd resins can be broadly classified into drying and non-drying types depending on the ability of their films to dry by air oxidation. The drying ability is derived from the polyunsaturated fatty acids in the resin composition. More frequently, an alkyd is classified by the source of fatty acid, e.g. a linseed alkyd, a tung oil modified soya alkyd, or a coconut alkyd.

(ii) Classification by Oil Length or Fatty Acid Content

The amount of fatty acid modification in the polyester structure of an alkyd resin prescribes such properties as solubility, compatibility, and film hardness of the resin. Therefore, this is the most frequently encountered way of classifying alkyd resins.

The oil length of an alkyd resin is defined as the weight percent of oil or triglyceride equivalent, or alternatively, as the weight percent of fatty acids in the finished resin. Since the overwhelming majority of alkyd resins is based on phthalic anhydride, it is customary to describe an alkyd in terms of its phthalic anhydride content in percentage based on the finished resin.

Alkyd resins are classified into four classes by oil length.

Resin Class	Oil, %	Fatty Acid,%	Phthalic Anhydride, %
Very long	>70	>68	<20
Long	56-70	53-68	20-30
Medium	46-55	46-55	30-35
Short	<45	<42	>35

These demarcations are arbitrary and the boundaries are usually not clear cut . More frequently, alkyd resins are described by a combined classification in terms of their oil length, type of fatty acids, and any unusual ingredients. Such descriptions as a an isophthalic, very long tall oil alkyd; a medium oil dehydrated castor - PE alkyd; or a short oil lauric-benzoic alkyd, immediately project the general properties of the resin.

1.3.2.3. Effect of Degree of Fatty Acid Modification

The degree of fatty acid modification of alkyd resins greatly affects the properties of the resin as reflected in the following table:

Property	Fatty acid modification, %				
	30	40	50	60	70
aromaticity of solvent	aromatic				aliphatic
pet spirits tolerance	---------->				
solubility	---------->				
viscosity	<----------				
set time	<----------				
air-dry time	<----------				---------->
baking speed	<----------				
hardness	<----------				
brushing ease	---------->				
tendency toward flow, sagging and grinding ease	---------->				
initial gloss	<----------				
gloss retention	<----------				
colour retention	<----------				
exterior durability	---------->				<----------
storage stability	---------->				
water permeability	---------->				<----------

1.4. MANUFACTURE

Alkyd resins can be processed directly from fatty acids, but it is economical to use vegetable oils (triglycerides) as the starting materials. The oils are incorporated into the alkyd resin by first carrying out an ester interchange reaction with compounds containing hydroxyl or carboxyl groups. On completion of alcoholysis (or acidolysis), the alkyd is processed to completion by either fusion or azeotropic technique.

1.4.1. Alcoholysis Process (Monoglyceride)

The oil is heated with the polyol at about 240°C in the presence of a basic catalyst to achieve alcoholysis. Due to ester interchange reactions the fatty acids rearrange themselves among the excess hydroxyl groups and the goal is convert the oil into a monoglyceride. Typically the oil is treated with glycerol using a molar ratio of 1:2 and the principal product is the monoglyceride. In practice molar ratios higher than 1:2 are used, giving an excess of hydroxyl groups in the alcoholysis product.

The α-monoglyceride predominates over the ß-monoglyceride due to the fact that primary attached groups are constantly being removed, but only occasionally returned and that primary hydroxyls not only predominate 1:2, but are also easily reacted. The alcholysis reaction is monitored by alcohol solubility.

After the monoglyceride is formed, the dibasic acid is added and the mixture is treated either by the fusion or azeotropic process.

1.4.2. Acidolysis Process

Acidolysis is an alternative to alcoholysis, but generally requires a higher temperature and is seldom used. Nevertheless, it does provide a convenient means of incorporating relatively insoluble acids such as isophthalic and terephthalic. Acidolysis is carried out at about 280°C and the reaction is

generally complete within an hour when the reaction mix clears.

1.4.3. Fatty Acid Process

The oil is first hydrolysed to give free fatty acids which are then heated at 200-240°C with a mixture of polyol and dibasic acid. Simultaneous condensation of the polyol, dibasic acid and fatty acids thereby occurs and the latter become incorporated into the polymer structure. The process is conducted either by the fusion or the aeotropic process.

1.4.4. Comparison of Fatty Acid and Alcoholysis Processes

(i) Cost : The fatty acid process is more expensive than the alcoholysis process. Fatty acids and glycerol, or other polyhydric alcohols, are all much dearer than drying oils, and moreover a greater weight of glycerol is required.

(ii) Ease of Operation : The fatty acid process is much simpler to operate, particularly for alkyds containing very reactive oils.

(iii) Colour : Drying oil fatty acids darken during storage, so that the alcoholysis process usually gives paler resins.

(iv) Versatility : The use of fatty acid process permits greater variation in formulation. In the alcoholysis process, even if polyhydric alcohols other than glycerol are used, that portion esterified in the oil is glycerol, so that of the mixed polyhydric alcohols present one must be glycerol. In the fatty acid process the glycerol can be totally excluded if desired. The same can be said of the modifying fatty acid. Using a drying oil in the monoglyceride process all the component fatty acids of the drying oil are necessarily present, whereas the fatty acid process allows the use of purer fatty acids (obtained by distillation or segregation).

Generally, alkyds made by the fatty acid process have lower viscosity than similar alkyds made by the alcoholysis process. The water resistance of the former resins is superior.

1.4.4. Esterification

The esterification stage of alkyd resin manufacture is a condensation reaction and evolved water should be removed to shift the reaction equilibrium forward. Two techniques are normally employed to remove the water, viz. Fusion (solventless) and the Azeotrope (solvent) processes.

1.4.4.1. Fusion Process

The process involves fusion of the components at an elevated temperature. The reaction mixture in the reactor is continually and vigorously sparged with an inert gas (normally nitrogen or carbon dioxide). The inert gas has two effects : the hot reaction mixture is protected from attack by oxygen and the evolved water vapour is continually removed from the reactor.

1.4.4.2. Azeotrope Process

Azeotrope processing involves the addition of small quantities of a hydrocarbon solvent (xylene or toluene) to the reaction mixture. At elevated temperatures, a water/solvent azeotrope is formed which is condensed externally to the reactor. The water and solvent are separated, the solvent being returned to the reactor and the water run to waste.

1.4.4.3. Comparison of Fusion and Azeotropic Processes

(a) Fusion Process

The advantages of the process include

(i) Lower capital cost due to simple equipment

(ii) The reactor temperature can be controlled independently of the loaded components.

(iii) The bubbling action of the inert gas improves agitation.

(iv) The sublimation effect can be advantageous in certain instances where removal of one of the reactants may be desirable.

The disadvantages of the process include

(i) The use of inert gas can cause problems with loss of components by sublimation and physical entrainment.

(ii) Scaling from one reactor to another of different size or shape may require reformulation because of variations in component losses.

(b) Azeotropic Process

The advantages of the process include

(i) Loss of components is minimal and often superior resin quality is achieved as the refluxing solvent continually cleans resin from the sides of the reactor and enables a more uniform product to be prepared that is free from gel particles.

(ii) Scaling from one reactor to another of different size or shape presents fewer problems.

(iii) The presence of solvent reduces the viscosity of the alkyd enabling better agitation and this facilitates better water removal and heat distribution.

The disadvantages of the process include

(i) Higher capital costs due to complex condensation and separation equipment.

(ii) The reactor temperature is controlled by the quantity of refluxing solvent.

(iii) The solvent may be difficult to remove completely if it is not required in the final product.

1.4.4.4. Control of Esterification

The esterification reaction is normally controlled by viscosity increase and acid value decrease. Samples are taken from the batch at pre-determined intervals after processing temperature has been reached. The samples for viscosity measurements are diluted with solvent, which is usually the same solvent and in the same ratio that the batch is to be finally manufactured. The viscosity is usually determined by the Gardner-Holdt method and acid value by titration with alcoholic potassium hydroxide solution.

An important aid to controlling batches is to plot viscosity against time on semi-logarithmic graph paper. A batch processing normally appears as a straight line, and by extrapolation, it is possible to judge whether the processing temperature should be increased for slow-bodying, or reduced for fast bodying batches.

1.5. APPLICATIONS

1.5.1. Very Long Oil Alkyds : 75 percent and above

The use of very long alkyds is restricted to the printing ink industry. Since they rely solely on the oil to effect drying, true drying oils are used, linseed being the most common. Alkyds of this type are frequently used as modifiers for heat-set and quick-set inks where they improve pigment wetting and scruff resistance. They are also used as binders for metal decorating inks. Vinylated, very long oil alkyds are also used in printing inks, where they show improved resistance to emulsification in lithographic inks.

Very long non-drying oil based alkyds find limited use as plasticisers; castor is the preferred oil. Since flexibility is the main requirement, straight chain dibasic acids are used in their formulation. Plasticisers of this type are mainly used with ethyl cellulose and nitrocellulose where they show excellent compatibility and retain flexibility at low temperatures.

1.5.2. Long Oil Alkyds : 60 to 75 percent

Long oil length alkyds are almost always prepared from drying and semi-drying oils, with pentaerythritol being the preferred polyol. The most common oils used are linseed and the semi-drying oils, soya, safflower, sunflower and tall oil.

All the resins in this range are soluble in low odour aliphatic solvents, permitting excellent brushing properties with good flow characteristics and easy brush cleaning. Their main use is in architecture and maintenance as brushing enamels, undercoats and primers and also marine paints. Their slowness to dry and lack of response to force drying has prevented their use in industrial finishes.

In these resins, linseed oil gives the best drying properties, but is prone to yellowing away from direct sunlight; their main use, therefore, is restricted to primers and exterior finishing coats and in dark colours.

Most architectural high gloss enamels for the consumer market are formulated on long oil soya based alkyds. Safflower-oil based alkyds give slightly better drying and non-yellowing properties. Sunflower-oil-based alkyds have properties in between those of soya and safflower. Tall-oil based alkyds give good non-yellowing properties with reasonable drying time.

Topside marine paints are generally based on enamels similar to architectural high gloss materials, but additional oil is frequently added to undercoats to ensure adequate flexibility. Also, as marine paints, these alkyds may be fortified with chlorinated rubber.

Siliconised long oil alkyds have improved resistance to chalking. They are somewhat prone to checking on long term exposure, but this can be overcome , provided properly formulated undercoats are used. Because of their high cost, they have only found limited acceptance in high performance areas.

Rosin additions are not normally made to long oil alkyds since gloss and colour retention are downgraded. These alkyds do give better flow and speed of set and rosin modified alkyds are used in architectural undercoats. In these cases, if the undercoat is to be used externally, it is advisable to add linseed oil to improve flexibility.

Long oil alkyds modified with polyamide resins are used to produce thixotropic architectural paints. These resins are also used in fairly high proportions in some undercoats, where they show excellent non-penetrating

properties and ease of brushing. Polyamide modified long oil alkyds are frequently blended at lower levels into a variety of paints to produce a slight degree of thixotropy, thereby improving antisettling and application properties.

1.5.3. Medium Oil Alkyds : 45 to 60 percent

Products in this range are probably the most versatile of all alkyds. In general, all round durability is better than among their longer or shorter relations. They still maintain solubility in low boiling aliphatic solvents, enabling brushing paints to be prepared, but they can also be produced in faster evaporating solvents for industrial spray applications.

The most commonly used unmodified medium oil length alkyds are based on linseed oil. Colour retention is not a problem since they are generally used in exterior situations. Alkyds of this type are extensively used in anti-corrosive primers and in general maintenance painting applications.

Medium oil linseed and soya alkyds are used in automotive refinishing and implement enamels. In these cases they are frequently modified with shorter oil alkyds, the extent depending on the individual applications. If durability is the prime requirement, then the extent of modification is usually small; where some loss of durability can be tolerated, then higher levels are used with resultant faster drying properties. Medium oil length alkyds for these applications are sometimes chain-stopped to achieve faster drying set times without significant loss of durability. A specific application for medium oil alkyds is in flat wall paints. These are highly polymerised products cut in hydrocarbon solvents of low solvency power. Under these conditions, the formation of a large number of resin aggregates leads to products with excellent non-penetrating properties over a variety of porous surfaces.

Medium oil length alkyds dissolved in toluol are used in conjunction with

chlorinated rubber for road marking paints. Rosin and phenolic modifications are frequently made to medium oil length oil alkyds, to give them excellent hard drying properties, with improved resistance to abrasion, water and alkali. They are extensively used in maintenance paints, industrial primers and some marine primers. They form the basis of conventional paving paints.

Some non-drying medium oil length alkyds are produced in the range 45-50% for use in exterior nitrocellulose lacquers.

1.5.4. Short Oil Alkyds : Less than 45%

Unmodified short drying oil alkyds are typically made of linseed, soya or dehydrated castor oils. The linseed-based alkyds are used in automotive refinishing and in general purpose industrial air drying enamels. They also perform well in force dry and low bake situations. Soya and dehydrated castor oils can be used in air drying systems, but they tend to be slow drying for most applications. They perform well in force drying and baking systems, either with metal driers or when modified with amino resins. In these cases they have good baking properties with excellent film characteristics; their colour retention is only fair and they are not used in light coloured paints that are liable to be overbaked. Low-rosin-containing tall oil alkyds have good colour retention on baking with amino resins and are used as the basis for most industrial baking enamels where high durability is not required.

Non-drying, short oil alkyds are generally based on castor or coconut oils. Coconut oil alkyds give the best exterior durability; castor oil lacquers have the best film properties. In combination with melamine formaldehyde resins, these alkyds give baking enamels with excellent resistance to yellowing and good exterior durability. Both the semi-drying and non-drying short oil alkyds can be used with urea-formaldehyde resins for acid catalysed room

temperature curing enamels and lacquers. When they are modified with nitrocellulose and have weak acid catalysts, they can be supplied as one component finishes. These acid catalysed finishes are used in clear and pigmented systems for timber furniture.

Rosin and phenolic modification of short drying oil alkyds is frequently carried out. These modifications considerably speed up drying, improve hardness and adhesion and impart aliphatic solvent solubility. They find extensive use in general purpose, air drying industrial enamels, drum paints and shop primers. They show good compatibility with medium oil alkyds and are used in blends to speed drying.

Most styrenated alkyds fall into the category of short oil alkyds. They are extremely fast drying with excellent toughness. Their poor re-coating properties and only fair durability limit their applications. They are mainly used as one coat finishes for small articles. Modifications with acrylic monomers improve durability at the expense of toughness and drying properties. These find limited applications as automotive refinishing enamels. Acrylated and styrenated short oil alkyds are used in baking systems as metal decorating enamels. Chain stopping of alkyds is also carried out. They have better durability than other fast drying alkyds, but like vinylated alkyds, have re-coating problems.

2. EXPERIMENTAL

2.1. MATERIALS

2.1.1. Phthalic Anhydride : $C_6H_4.CO.O.CO.$

Phthalic anhydride is a white crystalline solid. It is the difunctional acidic component used in the synthesis of alkyd resins in the study.
MW = 148.12, m.p. = 131 - 134°C, b.p. = 284°C, Assay = 98%

2.1.2. Glycerol : $C_3H_5(OH)_3$

Glycerol is a clear water-white, viscous, hygroscopic liquid. It is completely soluble in water and alcohol. Glycerol is the polyol component used in the synthesis of alkyd resins in the study.
MW = 92.10, m.p. = 20°C, b.p. = 290°C, density = 1.261 g/ml,
Assay = 99.5%

2.1.3. Castor Oil : $C_3H_5[CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COO]_3$

Castor oil is a clear pale yellow, viscous liquid. It is completely soluble in alcohol. Castor oil is the oil component used in the synthesis of alkyd resins in the study.
MW = 932, density = 0.9600 g/ml

2.1.4. Bases

2.1.4.1. Ethanolamine : $H_2NCH_2CH_2OH$

MW = 61.08, density = 1.02 g/ml, Assay = 98%

2.1.4.2. Diethanolamine : $NH(CH_2CH_20H)_2$

MW = 105.14, density = 1.10 g/ml, Assay = 98%

2.1.4.3. Triethanolamine : $N(CH_2CH_20H)_3$

MW = 149.19, density = 1.12 g/ml, Assay = 98%

2.1.4.4. Ammonia Hydroxide : NH_4OH

MW = 35.05, Assay (NH_3) = 25%

2.1.5. Solvents

2.1.5.1. Xylene : $C_6H_4(CH_3)_2$

MW = 106.17, density = 0.87 g/ml, b.p. = 180°C, boiling range 5°C

2.1.5.2. Distilled Water : H_2O

MW = 18, b.p. = 100°C

2.1.6. Catalysts

2.1.6.1. Cobalt Naphthenate

Assay approx. 8% Co

2.1.6.2. Manganese Octoate

Assay approx. 9% Mn

2.1.6.3. Lead Octoate

Assay approx. 36% Pb

2.1.6.3. Miscellaneous Chemicals

2.1.6.3.1. Potassium Hydroxide : KOH

MW = 56.11, Assay = 84%

2.1.6.3.2. Ethanol : C_2H_5OH

MW = 46.07, density = 0.7893 g/ml @ 20°C, b.p. = 78.5°C

2.1.6.3.3. Methanol : CH_3OH

MW = 32.04, density @ 15°C = 0.7961 g/ml, b.p. = 64.5°C

2.1.6.3.4. Hydrochloric Acid : HCl

MW = 36.46, density = 1.16 g/ml, Assay = 32%

2.2. RESIN SYNTHESIS

2.2.1. Synthesis Route

Resins were synthesized by a single stage synthesis route in which dehydration, alcoholysis and polyesterification reactions proceed simultaneously. The route was preferred to an alternative three stage route in which dehydration, alcoholysis and polyesterification reactions are realised separately due to shorter cycle times and the autocatalytric nature of the system at the reaction temperature.

2.2.2. Synthesis Processes

Two synthesis processes were utilised in the study, an azeotrope process and a fusion process under an inert atmosphere. The azeotrope process was used in the synthesis of base formulations and the fusion process was used in formulation modification in the production of water soluble resins.

The azeotrope is preferred in base formulations due to a cleaner process in which no sublimatioon of phthalic anhydride is encountered. The fusion process is preferred in modified formulations since it does not introduce any solvent into the resin which affects solubilisation of resin on completion of synthesis. Both processes aid water removal and protect the resin from atmospheric oxidation.

2.3.3. Synthesis Procedures

Resins containing different proportions of phthalic anhydride, glycerol and castor oil were prepared according to the proportions given in Table 1.1. and 1.2. [Appendix]. The resins were prepared according to the following procedures.

(i) Base Formulations

Phthalic anhydride, glycerol and castor oil were charged into a flat bottomed glass reactor equipped with a Dean and Stark Apparatus, a thermometer, heating facilities and a magnetic stirrer. Xylene (10%) was then added to aid azeotropic distillation of water produced in the reactions. The reaction mixture was then heated rapidly to 280°C (<1hr) and the temperature maintained constant for 3 hours under continous mechanical stirring. The reaction temperature was then reduced to 225°C and reaction continued for another 2 hours. Water and xylene were distilled as the reaction proceeded. Xylene was returned back into the reactor and water is decanted to control the amount of refluxing solvent in the reactor. At the end of the reaction, the resin was purged with nitrogen to remove the solvent.

Periodic acid value determinations were carried out for series 1 resins [Table 3.1.] to study the reaction profiles [Figures 1.1.-1.5.]. Acid value determinations were done on all resins at the completion of the reaction [Table 3.2.]. The resins were processed to an acid value less than 20.

(ii) Modified Formulations

Phthalic anhydride (PA_1), glycerol and castor oil were charged into a flat bottomed glass reactor equipped with a gas inlet, thermometer, heating facilities and a magnetic stirrer. The reaction mixture was heated rapidly to 280°C (<1hr) and the temperature maintained for 3 hours under continous mechanical stirring and nitrogen atmosphere. The reaction temperature was then lowered to 225°C and the reaction continued for another 2 hours. The reaction mixture is then allowed to cool to below 100°C under a nitrogen atmosphere. The remainder of phthalic anhydride (PA_2) is then added and the temperature raised to between 170-200°C for 3 hours. The acid value of the resin should be between 40-65 based on resin solids.

2.3. TESTING METHODS

2.3.1. Acid Value

Acid value is a measure of the degree of esterification and is the number of mg of KOH required to neutralise 1 g of alkyd resin or oil. Acid values of resins are given in Tables 3.1. and 3.2. [Appendix].

Reagents : Alcoholic potassium hydroxide (stndardised)
Solvent mixture - 2 parts xylene : 1 part alcohol
Phenolpthalein indicator

Procedure : 1 - 2 g of resin is weighed and dissolved in neutralised 50ml of solvent mixture. Titrate against alcoholic potassium hydroxide solution using 5 drops of phenolpthalein as indicator to a pink end point which lasts for 30 seconds.

$$\text{Acid Value} = \frac{\text{Titre} * \text{Molarity} * 56.1}{\text{Sample weight (g)}}$$

2.3.2. Gel Time

Gel time is a measure of the degree of polymerisation and is the time taken for the resin to be converted from a liquid to a gel. Gel times are given in Table 4 [Appendix].

Procedure : A minute drop of the alkyd is placed on a hot plate at 200°C. The alkyd is spread out with a spatula. The film is stroked lightly with the spatula until marks develop and remain and the time is recorded as the gel time.

2.3.3. Drying Time

Drying time is a measure of the rate of autooxidation and solvent evaporation during film formation and is the time taken for resin film to be converted from a liquid to a solid film. Drying times are given in Tables 5.1., 5.2. and 5.3. [Appendix].

Procedure : Catalysed and uncatalysed resin solutions (50%) were prepared. A spatula is used to apply thin resin films on aluminium metal strips and the strips are placed in an incubator with air circulation at a controlled temperature of 25°C. The state of the applied film is tested either by spatula or by hand.

2.3.4. Fourier Transform Infrared Analysis

Instrument : JASCO 5000 FT IR machine.

Procedure : The uncured resin was placed as a smear between 2 NaCl cells. The amount of sample was kept approximately constant so that the spectra are comparable. Good spectra were collected when the transmission of the reference peak (methylene at 1460 cm^{-1}) was between 9-20%. The reference peak was therefore used to control the amount of sample for analysis. The spectra were scanned between 4300 - 400 cm^{-1}. For solid samples, a KBr disc was prepared. The collected spectra are given in Appendix.

3. DISCUSSION

3.1. FORMULATION DEVELOPMENT

3.1.1. Introduction

Surface coatings fall generally into two broad classes. One class comprises of trade-sales coatings and the other industrial coatings. The coatings belonging to each group differ from the point of view of property requirements and end applications. Trade-sales coatings are mainly used for decorative purposes whereas industrial coatings are used mainly for protective purposes.

The basic principles governing formulation design are curing mechanism, end use properties and raw materials. The primary objective of the study was to develop air dry D.C.O. alkyd resins for use as surface coating vehicles in both trade-sales and industrial formulations. The application dictates resin property requirements. The raw material list was screened based on considerations of material cost and availability.

The nature of alkyd resins demand careful formulation in order to have rates of reaction capable of control to yield non-gelled products with good drying characteristics. Predictive equations aimed at optimising formulations for alkyd resins [36-38] provide only a first approximation of starting formula because of the complexities of alkyd resin systems. The development of predictive formulation equations applicable to D.C.O. alkyd resins was investigated. Formulation of solvent-borne as well as water-borne resins was achieved in conformance with environmental legislation. Replacing

solvent borne coatings with water borne coatings not only reduces solvent vapour emission, but also improves the safety against fire and health hazards of organic solvents, as well as reducing cost.

3.1.2. Base Formulations

3.1.2.1. Formulation Aids

Formulation aids were used in formulation development to cut down on formulation time and minimise premature gelation by weeding out bad formulations. Formulation aids are available in the form of alkyd constants. Alkyd constants of formulations are given in Table 2 [Appendix]. Alkyd constants provide valuable information on the feasibility of processing a given alkyd formulation and the final resin cure characteristics. The theoretically derived alkyd constant at incipient gelation is unit. Alkyd constants below unit indicate a high incidence of encountering premature gelation from a deficiency of hydroxyl groups. To avoid premature gelation, the average functionality of the alkyd formulation must be no more than 2 [14]. In reality deviations are evident due to the non-ideality of alkyd resin reactions. Alkyd constants above unit indicate an excess of hydroxyl groups. In air dry alkyds, high hydroxyl values slows drying, acting as gel peptisers as in the alkyd reactor. Several investigators have shown that excessive hydroxyl values impart unsatisfactory alkyd performance manifested in slower drying, decreased durability and decreased water resistance [39,40].

3.1.2.2. Experimental Formulations

Formulation Scanning

A statistical formulation scan was carried out on a large population of experimental formulations. Attention was focused on the development of base formulations for both convertible and non-convertible coatings which are applicable as is or after modifications to suit specific applications. Four series of formulations were proposed for synthesis. The composition of the resins was designed so as to encompass the whole composition spectrum of air dry alkyd resin systems. The proposed experimental formulations had the same basic qualitative composition, but variations in quantitative composition.

Forty (40) experimental formulations, ten (10) in each series, were proposed for synthesis. The oil to polyol ratio was maintained constant in each series, but variations were effected across different series. In each series, variations in the dibasic acid to polyol/oil ratio was effected down the series. The composition of the resins is given in Table 1.1. [Appendix].

Formulation Screening

The criteria used in the screening of the experimental formulations was (i) drying characteristics and (ii) gelation incidence during processing. In formulation development, only formulations with the potential to cross link and form dry films are useful and were investigated. However, the study seeks to develop new spectral characterisation techniques, hence a large set of data was required. Therefore, formulations rejected in formulation development, were nevertheless processed for the development of spectral characterisation techniques. Other screening criteria like viscosity were considered minor during formulation development since they can easily be addressed during formulation of the final coating.

Screening was achieved in two stages, two different techniques being adopted, a molecular as well as a synthetic approach.

(i) The Molecular Approach

The molecular approach is a preliminary screening technique which was implemented to select stable experimental formulations with promising drying characteristics. The technique is purely theoretical and utilises alkyd constants. The basic premise of this approach is that when the total number of moles of polyol is equal or slightly larger than that of the dibasic acid, and the hydroxyl groups are present in excess, the probability of gelation is very small.

Alkyd constants (K), were calculated for each experimental formulation. The calculated alkyd constants obtained ranged from 0.72 to 8.88. Alkyd resins with alkyd constants in the neighbourhood of the theoretically derived gelation point of unit were chosen, that is, formulations with K values between 1.00 - 2.00. Formulations with K values above 2.00 were deemed to have excessive hydroxyl values, and those with K values less than 1.00, insufficient hydroxyl component to prevent premature gelation.

The molecular approach, however, is inherent with shortcomings as a result of the complexities of alkyd resin reactions resulting in deviations from the ideal, and hence further screening was inevitable.

(ii) The Synthetic Approach

The synthetic approach is a practical technique which was used to determine the feasibility of processing a given experimental formulation. The test is pragmatic and final in the sense that no matter how attractive a formulation may appear on paper, if it can not be processed, then it is useless and should be rejected outright. This technique weeded out four (4) formulations, one in each series, which resulted in premature gelation.

Despite differences in composition, all the gelled formulations had approximately the same alkyd constants (1.02 - 1.05) [Table 2]. The approach thus tests the predictions of its predecessor and therefore ascertains the reliability of alkyd constants in predicting gelation incidence in D.C.O. alkyd resin processing.

Shortcomings in the approach are apparent due to the limitations imposed by the length of the screening process and the fact that, no definite information on the drying properties can be extracted, except from resin viscosity, which is vague anyway.

A general trend between resin properties and alkyd constants is evident from both the molecular and synthetic approaches. The higher the K value, the lower the gelation incidence and the poor the resin drying characteristics, and the reverse is true. The final formulation selected should therefore be consistent with the requirements of the two parallel approaches. The K value should be as low as possible while at the same time, the formulation should retain its immunity from gelation during processing. A compromise is therefore struck between the two extremes.

Test Formulations

The relationship (within defined limits) between alkyd constants, gelation incidence and drying characteristics having been established, the findings were used to develop test formulations. Test formulations were developed within set composition confines of the developed model formulations. The test formulations were carefully tailored in order that their compositions were exactly in between series already processed. This was done so that resins are representative of any variations that may be observed to the trends already established. Alkyd constants of the formulations were calculated and test formulations (5.0. , 6.0. and 7.0.) with values approximating those of the model resins were selected and processed [Table 1.1.]. The chosen

formulations proved to have both good drying properties and low gelation incidence.

3.1.2.3. Formulation Processing

Synthesis Route

Experimental formulations were processed by the single stage monoglyceride azeotrope process, in which dehydration, alcoholysis and esterification reactions take place simultaneously. The route is preferred to the three stage synthesis route due shorter cycle times and the autocatalytic nature of the system.

Reaction Control

Alkyd formulations were processed to a point short of completion, that is, a point where the reaction mixture still shows a finite acid number. Formulations were processed to an acid number less than 20, though the theoretical acid number at complete esterification is zero for all the formulations. One reason for this practice is that esterification reaction rate becomes very slow as the concentration of carboxyl groups becomes small, and it would be time consuming to wait for the last residual carboxyl group to react. The trend is reflected in reaction profile graphs, Figures 1.1.-1.5. [Appendix].

Formulations were also processed to a point short of completion to guard against premature gelation. The molecular chain length is a function of the extent of reaction as shown in the following equation

$$x_n = 1/(1-p) \qquad [3.1.]$$

where x_n = average degree of polymerisation

p = fractional extent of reaction

The esterification of phthalic anhydride is slower and shows a higher temperature dependence (higher activation energy), than that of fatty acids [41-43]. Therefore it is assumed that residual acidity is from unreacted dibasic acid and this contributes to the limiting chain growth.
In the study, premature gelation is minimised through functionality control. Functionality was kept under check through a molar excess of polyol over dibasic acids in the alkyd formulation. If the molar ratio between the polyol and dibasic acid is *r*, equation [3.1.] may be rewritten as :

$$x_n = (1+1/r)/[(2/r)(1-p)+1-1/r] \qquad [3.2.]$$

which indicates that a fractional increment in *r* and/or a fractional reduction in *p* would give a substantial reduction in x_n. The best formulations developed had an excess hydroxyl of 45-81% and hence an *r* value of 1.45-1.81.

Process Scale-up

The standard batch size used in processing all the formulations was 100.00g. In the conversion of laboratory syntheses into commercially viable operations, several problems are anticipated due to the differences in batch sizes. The changes in the reaction environments create technical problems of great magnitude.

Dehydration, alcoholysis and polyesterification reactions all contribute towards the production of a quality product. The extent of individual reactions is largely determined by the time taken to achieve reaction temperature. The heating pattern is dependent on the heating source and batch size. The attainable extents of individual reactions are interrelated and therefore an equilibrium position exists at which all reactions proceed to acceptable limits.

Reaction temperature has to be achieved rapidly, within an hour. If rapid heating is not achieved, the polyesterification reaction, which commences at much lower temperatures (170°C) than dehydration (265°C) and alcoholysis (280°C) results in the following (i) a decrease in phthalic anhydride levels (ii) a decrease in glycerol levels and (iii) an increase in the resin molecular weight. Depletion in phthalic anhydride levels results in poor dehydration due to reduced catalysis. Reduction in glycerol levels result in poor alcoholysis of the oil. A high resin molecular weight implies limited accessibility of hydroxyl groups (ricinoleic fatty acid chain) for cleavage due to steric hindrance. The end result is a product with poor film forming properties. Fortunately, esterification reactions are reversible and dehydration is not. Reversible reactions, according to *Le Chatelier's Principle*, can have their equilibrium position shifted in either direction by manipulation of reaction conditions. Dehydration is least affected. The reaction data acquired will afford reaction tailoring to ensure satisfactory reaction extents in all resin synthesis reactions. Research is therefore necessary in chemical kinetics, reaction engineering and process modelling in order to develop a synthesis process independent of the restrictions imposed by the batch size, indirectly through reaction time. Process scale-up techniques are beyond the scope of the study.

3.1.2.4. Formula Development

Model Formulations

Formulations exhibiting the best alkyd performance were chosen as models for the study and development of qualitative and quantitative relationships between alkyd resin parameters of composition, gelation incidence and drying characteristics. Analysis of the model formulations (7) resulted in the realisation that all the formulations have common parameters. The model formulations have approximately the same alkyd constants (1.15 - 1.19) and

an excess hydroxyl value between 45-81%. Therefore, it was possible to derive mathematical functions relating different alkyd resin components and alkyd parameters, which all model formulations should satisfy and which can thus be used in formulation development.

The following data, extracted from Table 1.1. [Appendix] was used in the mathematical derivations.

Let phthalic anhydride content = X_m , X_p
Let glycerol content = Y_m , Y_p
Let castor oil content = Z_m , Z_p
m = moles, p = parts

Resin	X_m	X_p	Y_m	Y_p	Z_m	Z_p	K
1.5.	0.1688	25.00	0.1629	15.00	0.0644	60.00	1.17
2.6.	0.2025	30.00	0.2280	21.00	0.0526	49.00	1.19
3.7.	0.2363	35.00	0.2823	26.00	0.0418	39.00	1.19
4.8.	0.2701	40.00	0.3257	30.00	0.0322	30.00	1.16
5.0.	0.1857	27.50	0.1968	18.125	0.0583	54.375	1.19
6.0.	0.2194	32.50	0.2565	23.625	0.0471	43.875	1.19
7.0	0.2532	37.50	0.3054	28.125	0.0369	34.375	1.18

Model Formulation Equations

Mathematical functions of the model formulations relating X, Y, and Z variables were derived using a computer.

$$Y_m = 1.6075X_m - 0.1016 \qquad [3.3.]$$

$$Y_p = X_p - 9.3750 \qquad [3.4.]$$

$Z_m = 0.1173 - 0.3177X_m$ [3.5.]

$Z_p = 109.3750 - 2.0000X_p$ [3.6.]

Equations 3.3., 3.4., 3.5. and 3.6. describe linear functions with correlation coefficients, $r_{3.3.} = 0.9962$, $r_{3.4.} = 0.9963$, $r_{3.5.} = 0.9990$ and $r_{3.6.} = 0.9991$. The equations are valid in the $Y_m = 0.1688 - 0.2701$ and $Y_p = 25.00 - 40.00$ domains. Graphic relationships of the equations are illustrated in Figures 2.1.-2.4. [Appendix].

Reliability and Applicability of Formulation Equations

Good correlations were obtained between alkyd resin components and constants as reflected by the correlation coefficients, and hence either the molar or part composition functions can be used in formulation development.

The validity of the model formulation equations was determined by both the molecular and the synthetic approach. Test formulations were computed from the derived equations and processed. Calculation of K values for each computed formulation gave values within or very close to the established 1.16 - 1.19 region. As expected, no premature gelation was encountered in the test formulations and good drying properties were achieved, in consistency with the predictions of equations.

3.1.3. Formulation Modification

The solvent-borne film-forming alkyds (base formulations) are too hydrophobic to form solutions in water. Water-soluble versions of these solvent borne polymer types were produced by introducing specific functional groups along the polymer backbone through modification in formulation. These functional groups are hydrophillic or can be modified to produce hydrophillic groups.

3.1.3.1. Formulation Aids

Resin acidity is an important alkyd parameter in the manufacture of water-soluble polymers. Acid number is a measure of the ionic character of the alkyd expressed as carboxylic acid groups. Neutralisation of these carboxyl groups result in the formation of hydrophillic alkyd soaps which are water-soluble. Water-soluble alkyd resins have an acid value between 40 to 65 (resin solids). Acid values below this range indicates poor solubility due to insufficient solubilising groups. Acid values above this range implies low alkyd molecular weight due to insufficient reaction or excessive dibasic acid and imparts unsatisfactory alkyd performance.

3.1.3.2. Experimental Formulations

Formulation Scanning

Base formulations exhibiting the best alkyd performance were selected for modification. Formulation modification was effected in the model base formulations with a view of achieving a final acid value of 40 - 65 (solids). Several bases were investigated to determine their suitability as neutralising agents in the solubilisation process.

In formulation modification, unlike in base formulations where extensive formulation scanning was carried out due to lack of D.C.O. formulation literature, intensive use of water solubilisation literature is made. The work

of other researchers' is used in the selection of neutralising bases and incorporation levels.

Nature of Amine

Fugitive bases were preferred to non-fugitive bases. Non-fugitive bases, such as caustic soda, leave the salt in the coating film and damage its water and corrosion resistance. Organic as well as inorganic fugitive bases were investigated for their solubilising properties and these include ammonia, monoethanolamine (M.E.A.), diethanolamine (D.E.A.) and triethanolamine (T.E.A.).

Variation of Amine Levels

The amine level introduced in a formulation significantly affects resin drying properties, viscosity and viscosity drying curves, stability of resin. Other work has shown that as the degree of neutralisation approaches and exceeds 100%, the viscosity variation may not be as significant. The work proved that it is usually necessary to have amine levels just above 100% neutralisation to give adequate storage stability. The amine addition level of 105% neutralisation was found to be satisfactory and was used in all solubilisation experiments.

As a rule, drying times will increase with increasing amine levels. Loss of amine, or insufficient amine, leads to precipitation of the polymer from aqueous solution on storage. Excessive amine levels promotes hydrolytic decomposition of alkyds due to ester hydrolysis. Variation of pH (amine level) has a significant effect on the gloss of the dried film.

Formulation Screening

The criteria used in the screening process was (i) resin solubility in water (ii) resin drying properties and (iii) emulsion stability.

Gelation incidence was considered low since the formulations are modified

versions of stable base formulations. Like in base formulations, the other properties of viscosity characteristics, gloss, foam control are considered minor and can be conveniently addressed during formulation of the coating system. The main aim is to solubilise the polymer while at the same time maintaining its drying properties. The offshoots of formulation modification mentioned above were therefore not given much weight during the investigation since these can be conveniently addressed during formulation of the coating system.

Choice of Amine

All the bases investigated had good solubilising properties. Variations were observed in their drying characteristics and emulsion stability. The variations are due to differences in molecular weight which determines amine volatility. Drying characteristics deteriorated with increasing molecular weight, while the reverse trend was true for emulsion stability.

Ammonia gave the best drying speed. However, its poor emulsion stability due to high volatility, greatly affects the shelf life of the developed product. Another setback is due to the fact that formulations neutralised with ammonia are neither consumer nor atmosphere friendly, due to the fouling noxious odours characteristic of such formulations.

Drying time in the ethanolamines increased with increased molecular weight due to lower volatility. Emulsion stability was good in all three bases, though minor variations were observed due to differences in molecular weight. The variations were considered minor in comparison to drying characteristics. Monoethanolamine was found to be the most suitable neutralising agent among the ethanolamines. The ethanolamines are free from any offending odours.

Formulation modification can therefore be achieved with either ammonia or monoethanolamine. In order to have a formulation with good drying characteristics and emulsion stability, both bases are incorporated in the formulation, the proportions being determined by the property which is considered most important in the particular formulation.

Hydrolytic stability of water-soluble alkyds

As expected, water reducible alkyds suffer from limited hydrolytic stability. Steric shielding and avoidance of neighbouring nucleophiles to the ester groups in the resin are two of the conditions for the attainment of maximum hydrolysis resistance for polymer ester groups [44].

Glycerol gives resins with poor hydrolytic stability [45], therefore polyols such as trimethylol propane, trimethylol ethane, neopentyl glycol and 1,4 cyclohexanedimethanol with primary hydroxyl groups are preferred for the preparation of water soluble alkyd resins. Primary hydroxyl groups generally react with acids and anhydrides more readily than secondary hydroxyl groups.

Due to the nature of the synthesis route adopted (monoglyceride process), the oil molecules exist as triglycerides and therefore have glycerol in their molecular structure. Glycerol can not therefore be totally excluded from the system as long as the synthesis route is via the monoglyceride process. The research was done primarily for the benefit of a commercial organisation and hence limitations were imposed on both raw materials and synthesis route.

To improve on hydrolytic stability, polyols with primary hydroxyls can be used. The synthesis route will also have to be altered to eliminate glycerol. Castor oil is hydrolysed to yield glycerol and fatty acids. Alkyd resins are then synthesized by the fatty acid process using recommended polyols.

3.1.3.5. Formulation Processing

Synthesis Route

The processing procedure used is a modification of the one used in processing base formulations. Formulations were processed by a two stage monoglyceride fusion process under a nitrogen atmosphere. The fusion process replaces the azeotrope process since the solvent (xylene), is difficult to remove completely at the end of processing, making solubilisation of the polymer difficult. The disadvantage of the process is the loss of phthalic anhydride through sublimation.

Reaction Profile

In the first stage, the formulations are processed to an acid value below 10. The first stage is important to build as high a resin molecular weight as possible. In the second stage, more phthalic anhydride is added and the reaction temperature reduced so that pendant residual carboxylic acid groups are introduced along the polymer backbone. The second stage is to build the ionic character of the polymer. At lower temperatures (170-200°C), only anhydride groups react to form half-esters, leaving carboxylic groups unreacted and free for neutralisation. The alkyd resins were processed to an acid value between 40 - 65 based on resin solids.

The gelation incidence in formulations was very low, due to changes in processing techniques. In stage 1, there is an abundance of hydroxyl groups to guard against premature gelation. In stage 2, the temperature is reduced to control the reactivity of the dibasic acid. The formulations are less prone to gelation due a higher final resin acid value and therefore lower degree of polymerisation.

3.1.3.4. Formula Development

Resin Acidity Guide Formula

Formulation modification to impart water-solubility requires that the dibasic acid be added in two separate stages. A simple formula based on theoretical considerations was used for calculating the amount of dibasic acid required in stage 2 in order to achieve the required acid value.

Let final batch size = X
Let final acid value = Y
Acid value of PA (theoretical) = 757.49
Total PA required in formulation = PA_T
(As per model base formulation)
PA required in Stage 2 = PA_2
PA required in Stage 1 = PA_1
= $PA_T - PA_2$

$$Y = (757.49 * PA_2)/2X$$

$$Y = (378.75 * PA_2)/X \qquad [3.7.]$$

Phthalic anhydride has a functionality of 2. In Stage 2, the reaction conditions are such that ideally one anhydride group reacts, leaving an unreacted carboxylic group on each phthalic anhydride molecule. Therefore, the effective functionality of phthalic anhydride under the prescribed reaction conditions is one. The required amount of phthalic anhydride has to be multiplied by a factor of 2 to maintain the desired acidity or the acid value has to be divided by 2. The value of Y is established already at 40-65 (resin solids).

Solubilisation Formula

To make a water-soluble coating, the polymer must be adequately solubilized to achieve water-solubility. The following equation was used to calculate the amount of amine necessary to neutralize the polymer.

$$W = [A * E * S * D]/56100 \qquad [3.8.]$$

where W = mass of amine to be used

A = acid value (solids) of the polymer

E = equivalent weight of amine

S = solid content of resin

D = degree of neutralisation required

3.1.4. Conclusion

Alkyd resin formulation design is a complex subject in which no rigid rules apply. The subject is made relatively easier through a systematic theoretical as well practical approach in formulation experimentation. Trial and error methods of formulation can not be afforded due to the danger of product loss either through premature gelation or formation of non-drying products, and the sheer length of formulation time required. The study culminated in limited but useful generalisations.

Formulation Aids

Alkyd constants (K) proved to be invaluable assets in formulation development. The constant was established to be a reliable indicator of the probability of premature gelation during formulation processing and in prediction of the drying characteristics of resins. Resin acidity was the workhorse in formulation of water soluble resins.

Formula Development

Air dry D.C.O. alkyd resin model formulations were developed. Formulations were made available in two versions, solvent-borne and water-borne systems. Predictive formulation equations unique to D.C.O. poly(glyceryl phthalate) alkyd resins were developed. Model formulation equations which optimise formulations through drastic cuts in formulation time, increased gelation immunity and guaranteed drying characteristics were developed. The equations had good correlations and their limits of applicability and reliability were established. Excellent test formulations were developed from the equations which required very little or no fine tuning. Simple formulation equations for solubilisation and resin acidity were also developed for water-based resins.

Formulation Processing

The method and duration of processing was found to contribute greatly towards resin properties. Therefore standard synthetic procedures were adopted for all formulations processed in the study, and hence all trends or relationships deduced or apparent are within the defined experimental conditions. The sensitivity of formulations to reaction conditions is best seen in formulation modification, in which the same basic recipe can result in resins with totally different properties.

3.2. CROSS-LINKING

3.2.1. Introduction

Resin cross-linking during formulation processing, manifested in premature gelation, is an undesirable phenomenon, that, paradoxically, is companion to a desired property, film formation. A balance is therefore struck in resin formulation to produce stable formulations which can be processed without the danger of product loss, but still retaining the ability to cross-link on application.

Alkyd resins do not remain thermoplastic in their ultimate applications. The film integrity is largely derived after resin molecules have been cross-linked through unsaturation functionalities on their fatty acid chains. Solvent evaporation is also the other mode of film formation encountered in the study. The term curing mechanism is used loosely to imply cross-linking or film formation with or without accompanying chemical reactions. The curing mechanism and the type of resin system selected for each coating system vary depending on the base criteria. The film characteristics and consequently its end applications are dependent on the cure mechanism. In general, it will be seen that non-convertible resins are restricted to decorative formulations (trade sales) whereas convertible resins are useful in both decorative and protective formulations (industrial). The developed formulations, however, exhibit both curing mechanisms, though to varying extents. The curing mechanism of fundamental importance in the study is the autooxidation process.

The structural influence of curing mechanism, resin type and rate of cure on film properties is important in surface coatings. A knowledge of these underlying principles is essential in order to design an optimum coating system for a particular end application.

3.2.2. Curing Mechanisms

Cross-linking of alkyd resins in premature gelation and film formation is due to two different chemical processes which result in the same physical state, gelation. The extent of gelation is however different. Gelation in the reactor is universal and converts the whole reaction mass into a solid whilst gelation in film formation is localised to the film surface. The two processes are also distinguishable from the differences in the temperatures at which reactions commence. In order to differentiate between the two processes, curing in the reactor is termed gelation and curing on application is termed film formation.

3.2.2.1. Gelation

Cross-linking Reactions

In premature gelation, cross-linking is a result of reactions between functional groups present in the alkyd resin ingredients. The reactions that are causative to the gelation process are : esterification, which increases the molecular weight of the resin, etherification of polyols, which increases the chances of gelation by forming higher functionality materials and reducing the number of hydroxyl groups available for esterification; cross-linking between unsaturated groups especially conjugated double bonds; and the phenomenon of microgel theory.

Gelation can also be accelerated by autooxidative and thermal polymerisation, but the exclusion of air from the reaction system by the azeotrope (base formulations) and nitrogen (formulation modification) and the controlled reaction temperatures make their contribution insignificant.

Reaction Control

Gelation incidence during synthesis can be monitored by carrying out gel tests on the resin. The probability of encountering premature gelation is minimal at the beginning of the reaction and increases as the molecular weight increases. Gelation in the reactor is always a threat, due either to completion of polyesterification, or due to the occurrence of side reactions. Should gelation begin, its progress is extremely rapid and almost impossible to arrest. Therefore during manufacture, extrapolation of plots, is routinely done for predicting the end point in order to terminate the reaction in time to prevent gelation. However, gel times were not used as process control aids since formulations were processed until gelation in order to determine the exact gelation point. The information is useful in the prediction of gelation points through empirically derived alkyd constants and excess hydroxyls.

Nature of Gelation

Gelation manifested itself in two different forms, thermoplastic and thermosetting gelation. However, the major contribution to gelation in the study remain cross-linking reactions. In thermoplastic gelation, the high resin viscosity is due to the formation of high molecular weight linear polymers and three dimensional structures are minimal. This type of gelation occurs when both polyol and dibasic acid contents are high (high polyester content) and the oil content is low. Thermoplastic gelation can not be detected by gelation tests since the molecules are effectively linear and are fluid at the test temperature.

In thermosetting gelation, high resin viscosity is due to the formation of three dimensional structures. This type of gelation occurs when the formulation has a hydroxyl deficiency. Gelation in the study was realised due to both processes, though their contribution is variable. Thermosetting gelation predominates at high oil levels and at high polyester levels the

contribution of thermoplastic gelation becomes pronounced. Thermosetting gelation is detectable by the gelation test as the concentration of three dimensional structures is high and the resin gels.

Gelation Tests

The gelation test is a simple and fast method of assessing resin stability towards gelation during manufacture and also gives an insight into the film formation characteristics. Gel times are a function of the degree of fatty acid content, type of oil or fatty acid, molar ratio of reactants, method of processing, extent of reaction and reaction temperature [46]. The test is subjective but good duplication of results can be achieved with experience.

Gel times increase with a decrease in fatty acid content. In accelerated gel times (200°C), the resin film is converted into a gelled mass by both intramolecular alkyd resin reactions and autooxidation reactions, though the latter reaction is dominant. The rate at which phase inversion occurs indicates the degree of polymerisation. Gel times generally increased from series 1 to 4 as expected, due to a decrease in the fatty acid content. In series 1 and 2 the gel times are almost the same. This is due to the fact that gel times are not only dependent on oil content, but are also dependent on degree of polymerisation, which is governed by the polyester content. Therefore in series 1 and 2, the ratios between fatty acid/polyester content balance each other and hence the gel times are almost equal.

Gel times are indicative of the degree of polymerisation and the curing time of the resin films. The shorter the gel time, the closer the alkyd resin is to gelation and determination of gel times is a valuable adjunct in attaining uniformity and eliminating premature gelation. Gel times were determined for resins selected in formulation development only and these are given in Table 4 [Appendix].

Excess Hydroxyl and Gelation

The model formulations developed have an excess hydroxyl of between 45-81%. The excess hydroxyl required in order to process stable formulations increases across the series as the fatty acid content decreases/polyester content increases [Table 2]. The unexpected increase in gelation incidence across the series at the same excess hydroxyl can be explained by the new understanding that some of the hydroxyl groups are buried in the microgel structures [23-29] as outlined in the microgel theory. Due to increasing polyester concentration across the series, the molecules grow to reach the minimum fatty acid-polyester ratios required for micelle formation more rapidly and hydroxyl groups are buried in the microgel structures making them unavailable for reaction. The non-availability of the hydroxyl groups upsets the functionality of the system and hence gelation occurs at higher hydroxyl values.

3.2.2.2. Film Formation

(a) Nature of Film Formation

The nature of the curing mechanism dictates the resin properties and film characteristics. The curing mechanisms in air dry alkyd systems developed are of two types, a chemical convertible (autooxidation) process and a physical non-convertible (solvent evaporation) process. Both mechanisms have specific advantages and by combining the two mechanisms in one coating, a hybrid coating with superior properties is envisaged than if curing was the sole result of a single mechanism. The effect of variations in the contribution of each mechanism towards film formation is highlighted.

(i) Autooxidation Reactions

Film formation in this process is through autooxidation reactions which convert an alkyd resin from a liquid to a dry film through aerial oxidation and cross-linking initiated by the decomposition of the oxidation products. This type of curing mechanism forms the basis of film formation in the study. Autooxidation is an *in situ* curing process in which the carbon to carbon unsaturation in the fatty acid acts as cross-linking agents. The curing mechanism is an important measure in reducing the resin viscosity and high molecular weights are not a prerequisite to film formation. In resins 1.5. and 2.6., where autooxidation is the dominant film formation mechanism, the viscosity of the resin is lower than in resins 3.7. and 4.8. where autooxidation reactions are much reduced.

Film Characteristics

Autooxidation reactions have a substantial influence on the final properties of the coating films. The degree of cross-linking affects the surface hardness and mechanical properties of the films. Surface hardness increases across the series from resin 1.5. (series 1) to resin 4.8. (series 4). This is due to an increase in the polyester content as the fatty acid content decreases. An increase in the degree of flexibility is realised across the series for the same reason as in film hardness.

The film mechanical properties may be deceptive due to solvent retention. Highly polymerised resins (3.7. and 4.8.) exhibit strong solvent retention. Retention of the solvent may give false impressions of flexibility, adhesion and tensile strength of a film. Interesting facts on the subject of solvent retention have been recorded by Bogin and Wampner. They have found that when flow of lacquer film ceases, it may still contain as much as 25% of the volatiles. When the film is dry to touch as much as 13% of volatiles may still be present. 5-8% of volatiles may be present after one week's drying [47].

Chemical resistance, as expected, decreases across the series with a decrease in cross-link intensity. Alkyd resins, despite their good adhesion, durability, flexibility and mar resistance are characterised by poor alkali resistance due to ester hydrolysis. Therefore, the increase in ester content across the series aggravates the susceptibility of resins to hydrolysis.

Cross-linking reactions convert alkyd resins into an infusible insoluble film. The films are less affected by service temperatures. Solvent resistance (xylene) decreases across the series, from resin 1.5. to 4.8. as cross-linking intensity decreases. Films formed by the autooxidation process are suitable for both protective and decorative applications due to the film qualities outlined above.

Evidence of Curing Mechanism

Autooxidation reactions convert the alkyd resin into a thermosetting insoluble film. Film insolubility is therefore an indication of a sufficiently high degree of cross-linking reactions to render the film insoluble. The cured films were tested for their solubility in the diluting solvent (xylene) and the results are given in Table 6 [Appendix]. Resins with good drying properties (1.5.,2.6.,3.7. and 4.8.) proved insoluble whereas resins with poor drying properties proved soluble.

(ii) Solvent Evaporation

Film formation in this process relies entirely on solvent evaporation. On application, the solvent molecules evaporate from the resin solution or emulsion (water soluble systems) leaving the resin molecules to crystallize and coalesce thus forming a solid film. Solvent evaporation in this study is treated as a physical cross-linking process, in which the physical entanglement of resin molecules as the solvent evaporates results in film formation. The curing mechanism is more rapid than the autooxidation process.

High molecular weights (high resin viscosities) are a prerequisite for film formation in this mechanism. This is evident from the drying times of uncatalysed model resins. Resins 1.3. and 2.6. were still wet after 24 hours whereas resins 3.7. and 4.8. dried within 3 hours. The results are given in Table 5.1. [Appendix]. High molecular weights are required to ensure both drying and film durability since no chemical reactions take place.

Film Characteristics

As there are no chemical reactions in this process, the film remains thermoplastic after drying. Due to their thermoplasticity, the films have a high degree of flexibility.

Chemical resistance is poor as three dimensional cross-links are minimal. Films resulting from this process alone are restricted to decorative coatings where service conditions are less demanding than in protective coatings. Nevertheless, formulated resins exhibit both mechanisms in varying proportions and hence can be applied in both instances.

Evidence of Curing Mechanism

The presence of this curing mechanism is supported by solubility tests on resin films of uncatalysed systems after 24 hours. The solubility test results are given in Table 6 [Appendix]. Drying is attributed to solvent evaporation since autooxidation reactions proceed much slower under the specified test conditions. The resin films, both dry and wet, proved soluble in xylene despite their different physical states, implying that their chemical composition was similar and hence no chemical reactions had taken place during film formation.

(b) Rate of Film Formation

Influence of Formulation Variables

In formulation development, it is evident that a compromise between two opposing property requirements is always necessary in order to obtain suitable air-dry resins. The property requirements considered are maximum cross-linking potential determined by fatty acid content and maximum resin durability determined by the polyester content of the resin.

(i) Influence of Oil Type

The cure rate is very dependent on the degree and nature of unsaturation in the fatty acids. Alkyd resins depend on drying oils for autooxidative film formation. Catalytic dehydration converts castor oil, a non-drying oil, into an excellent drying oil. Film formation of castor oil alkyd resins is therefore determined by the degree of unsaturation in the ricinoleic fatty acid chain. Dehydration of castor oil results in the formation of non-conjugated and conjugated dienes through the elimination of the 12-hydroxyl group and an adjacent hydrogen atom with the subsequent introduction of a double bond. The increased unsaturation in the fatty acid chain increases reactivity of the alkyd resin during autooxidation and polymerisation reactions.

The fundamental premise in D.C.O. alkyd resin synthesis is that sufficient dehydration is realised to ensure good resin drying characteristics. Insufficient dehydration results in non-drying alkyd resins, which are of limited use in surface coating chemistry. Dehydration levels could not be quantified by conventional dehydration methods, due to the nature of the synthesis procedure adopted. However, by inference, the fact that some formulations exhibited good drying properties was considered an indication of sufficient dehydration in all resins, since all formulations were processed

by the same standard synthesis procedure. Nevertheless, minor variations in dehydration levels are expected due differences in formulation composition and minor fluctuations in reaction conditions and as a result drying is affected.

(ii) Influence of Oil Content

The fatty acid content of the resin determines the maximum cross-linking potential at the expense of resin durability. Autooxidation reactions are the dominant curing mechanism at high oil levels and hence the poor drying properties of uncatalysed resins 1.5. and 2.6. As the fatty acid content decreases, autooxidation reactions are reduced, and solvent evaporation appears as a competing curing mechanism. At low fatty acid/high polyester content, solvent evaporation becomes the dominant curing mechanism, as seen in relatively fast drying in uncatalysed resin systems 3.7. and 4.8. [Table 5.1.].

The fatty acid content also influences the film appearance. Resins with high oil levels depend solely on autooxidation reactions for film formation and are more prone to wrinkling than films of resins with low oil levels. Wrinkling tendency is highest in series 1 (resin 1.5.) and decreases across the series, with series 4 (resin 4.8.) having the least wrinkling tendency.

(iii) Influence of Catalysts

Film formation through oxidative mechanisms requires the presence of metallic salts in order to bring drying time within economically feasible limits. Catalysis of the autooxidation process of alkyd resins was achieved by use of drier blends, comprising of both primary and secondary driers in order to achieve synergistic properties. The primary driers, cobalt naphthenate and manganese octoate, both function as true catalysts with lowering the activation energy of the autooxidation process. Cobalt is an effective catalyst for hydroperoxide formation, whereas manganese favours the

breakdown of oxygenated products. The secondary drier, lead octoate, functions by modification of the polymerisation process of autooxidation accelerated by cobalt and manganese cations.

Optimum Catalyst Levels

The technology of the use of driers is an empirical art rather than a science, since different oils respond to the catalytic activity of metals in different ways. The optimum catalyst concentrations to achieve the best film forming properties were determined by a series of experiments, using recommended catalyst concentration in literature as starting guidelines. The catalysts were added to resin formulations individually in order to ascertain their catalysis properties. The sequence of addition was in decreasing order of reactivity.

Cobalt has the highest catalytic activity in promoting autooxidation. Recommended addition levels are 0.02 - 0.08% by mass of metal based on vehicle solids. An optimum concentration was determined by experiment. Rapid surface drying with little through dry was observed on using cobalt alone and this resulted in wrinkled films.

Manganese has surface drying activity with some through-drying properties. Berry and Mueller have proposed that manganese favours breakdown of oxygenated products. Further it is claimed that manganese gives more rapid drying when alkyd resin has passed through the induction stage of drying. Manganese is used at 0.02-0.06% metal content based on the vehicle solids. Introduction of manganese reduced degree of wrinkling in resin films. Manganese could not be used alone because of its lower catalytic activity.

Lead has good 'through drying' properties and is added at 0.50-1.00% based on vehicle solids. The through dry properties are ascribed to its ability to cause polymerisation after the induction period of the drying process has begun. Addition of the lead drier reduced wrinkling considerably. Wrinkling

is difficult to eliminate completely especially if thick films are used. Resin 1.5. exhibited the highest wrinkling tendency due to its high oil content. Wrinkling was less prevalent in other model resins though the film thickness played a part. Wrinkling is normally treated as a film defect, but is exploited in the manufacture of wrinkled alkyd paints.

The experimentally determined catalyst incorporation levels, based on resin solids, are as follows :

Solvent based resin systems :
Cobalt Naphthenate (8% Co) - 2.00%
Manganese Octoate (9% Mn) - 2.00%
Lead Octoate (36% Pb) - 7.00%

Water based resin systems :
Cobalt Napthenate (8% Co) - 2.00%
Manganese Octoate (9% Mn) - 1.00%

The effect of excess driers was also investigated. Threshold catalyst concentrations were determined for individual catalysts. Further increases of driers above the threshold values show no advantages and excessive levels result in retardation of drying process.

(iv) Influence of Solvent Type

The evaporation rate of a solvent is technically important because it affects the rate of deposition of a film from solution, which in turn controls the structure of the film. If the evaporation rate is too rapid, the film may lack homogeneity, and moisture will be simultaneously deposited from the ambient atmosphere. Too low an evaporation rate will result in long uneconomical drying rates.

Xylene was found to be a suitable diluting solvent for the resins, satisfying both properties of resin solution stability and good drying rates. Investigations were concerned only with finding a suitable diluting solvent, other solvents used to impart special properties e.g. flow properties, can easily be investigated in formulation of the surface coating.

Water soluble versions proved to have longer drying times than their solvent counterparts [Table 5.3.]. The differences in drying times are due to the differences in solvent polarity. Water, a polar solvent, has a very high degree of H-bonding and therefore its volatility is very low. On the other hand, xylene is a non polar solvent, with a higher boiling point than water, but has a much lower degree of H-bonding and therefore much greater volatility.

Influence of Curing Conditions

(i) Temperature

The curing temperature greatly affects the rate of film formation and film properties. As expected, high temperatures accelerate the degree of cure and low temperatures retard cure rate. Curing was therefore carried at a standard temperature of 25°C which approximates ambient temperatures.

(ii) Humidity Levels

High humidity levels retard the rate of drying. Drying under increased humidity restricts the evaporation rate. Resins applied under humid conditions had prolonged drying times than those applied under normal dry conditions, all other variables being the same. Retardation is observed in both solvent based and water based, but is more pronounced in the latter. The retardation effect of high humidity levels is both physical and chemical in nature. High humidity levels result in saturation of atmospheric air, which helps in water evaporation, and hence the amount of water picked up from

the wet resin film is low.

The high moisture content also affects the activity of the driers. It has been shown [48,49] that the drying rate is very dependent on the coordination number of the metal ion. All ligands capable of forming complexes with the metal ion retard the efficiency of these driers. The hydroxyl group of water is no exception.

Drying Times

The drying time of a resin can be defined as the time taken for the conversion of a wet resin film into a dry solid film.

The drying test, like the gelation test, is a subjective test, however, reproducible results are obtained with experience.

(i) Uncatalysed Solvent Based Resin Systems

Drying in uncatalysed solvent based resin systems is due to solvent evaporation only, autooxidation reactions proceed very slowly without catalysis. Drying was realised in 3 hours for resins 3.7. and 4.8. and poor drying properties were evident in resins 1.5. and 2.6. The drying rate increased across the series with an increase in polyester content. Drying times are given in Table 5.1. [Appendix].

(ii) Catalysed Solvent Based Resin Systems

Drying in catalysed solvent based resin systems is due to both autooxidative and solvent evaporation mechanisms. The drying rate increased across the series. This trend is due to the dominance of solvent evaporation in the initial stages of film formation. Solvent evaporation is a faster drying process than autooxidation. The drying rate due to autooxidation decreases across the series due to a decrease in the fatty acid content. However, it is not possible to exclude solvent evaporation in film formation so as to determine the different rates of autooxidation, though it is possible to exclude

autooxidation reactions (uncatalysed systems). The rates of autooxidation are therefore extracted from gelation tests of undiluted and uncatalysed resins. Gelation is due solely to autooxidation as no solvent is present. Considering the autooxidation mechanism alone, there is a direct relationship between gel times and drying times. The shorter the gel time, the shorter the drying time. The drying times of catalysed resin systems are given in Table 5.2. [Appendix].

(iii) Catalysed Water Based Systems

Drying in water-based resin systems is due to autooxidation and solvent evaporation, though the contribution of the latter is much less than in solvent based systems due to lower molecular weights and lower evaporation rates of water. The drying rate is reduced and drying times are given in Table 5.3. [Appendix]. Water based systems are modified versions of solvent based systems and due to the nature of the synthesis procedure, the molecular weights are lower at the same dibasic acid content. Therefore for the best alkyd performance, resins with dibasic acid contents greater than 20% in stage 1 are preferred.

3.2.3. Conclusion

The ultimate coating applications of alkyds have the implicit requirement that the alkyd resin be capable of gelation. However, such gelation is desired only after the coating vehicle has been applied to the substrate. Cross-linking to the point of gelation before application is undesirable because such insoluble, infusible resins are intractable.

Gelation

Premature gelation in the reactor is a direct result of alkyd resin intramolecular reactions of polyesterification and side reactions of etherification, cross-linking of unsaturation functionalities and the microgel phenomenon. Autooxidative polymerisation is excluded by the nature of the processing procedure.

Two forms of gelation are evident from the study, a physical gelation process, thermoplastic in nature and a chemical gelation process, thermosetting in nature. The two processes, are however inseparable and they occur simultaneously either in the reactor or after application though to different extents. Thermosetting gelation is responsible for film formation in the autooxidative mechanism and thermoplastic gelation is responsible for film formation in the solvent evaporation mechanism.

Gel times are indicative of the degree of polymerisation and drying times of resin films. Short gel times are characteristic of high molecular weights and short dry times. Resins with good drying properties had gel times less than 2 minutes. Too short a gel time affects the storage stability of the resin, though drying properties will be excellent. Gel times are also useful as process control aids in premature gelation prevention.

Contrary to expectations, gelation incidence increased across the series at constant excess hydroxyls. This anomaly was explained by the microgel theory in which the hydroxyl groups are buried in the microgel structures thus upsetting the functionality of the system. The fatty acid/polyester ratios plays an important part in the microgel theory. High gelation incidence at high excess hydroxyls is also attributed to thermoplastic gelation as a result of high polyester concentrations.

Film Formation

The mechanism of film formation contributed greatly towards film characteristics. Film formation was the direct result of two different processes. The autooxidation mechanism proved to have important film attributes of mechanical and chemical resistance. The mechanism predominates at high oil levels. High wrinkling tendency at high oil levels proved to be a setback. The solvent evaporation mechanism complimented the former process by increased drying speed, reduced wrinkling tendency and increased flexibility. Setbacks of the latter mechanism include poor mechanical and chemical properties. The mechanism predominated at high polyester contents.

In solvent evaporation drying times are directly related to polyester content. A high polyester content corresponds to a short drying time. In autooxidation, drying times are directly related to fatty acid content (up to a limiting value) through gel times. At low fatty acid contents, the relationship remains the same but is masked by the interference of solvent evaporation which upsets the trend. Water borne coatings proved to have longer drying times than their solvent based counterparts.

The rate of film formation is influenced by formulation variables and the ratios between the variables. Castor oil, unless subjected to catalytic dehydration, forms non-drying resins. The degree of dehydration therefore played an important role, though it could not be quantified by conventional methods. The oil content, as highlighted under the nature of film formation, dictates the predominating curing mechanism and therefore the rate of film formation. High oil contents resulted in longer drying times.

Catalysis was effected to speed up the drying process. At low oil levels, drying could be achieved without catalysis at the expense of mechanical and chemical resistance. Drier blends of primary (cobalt) and secondary (manganese and lead) driers were used to ensure good drying characteristics. Addition levels were determined experimentally for both solvent and water based systems.

3.3. FOURIER TRANSFORM INFRARED CHARACTERISATION

3.3.1. Introduction

Alkyd resins represent the largest single quantity of resins produced for use in the surface coatings industry. Despite their widespread usage and simple composition, a scan of literature revealed no simple and fast method for the complete analysis of the composition of such resins.

Conventional alkyd resin analysis methods are incomplete and fairly cumbersome techniques and each technique concentrates on a specific functional group in the resin and no all round technique for both qualitative and quantitative characterisation is available. The physical characterisation techniques of specific gravity, viscosity, solubility etc are vague analytical tools to quantify or qualify chemical composition of alkyd resins. Conventional chemical characterisation techniques, though much useful than physical methods also have their deficiencies. The chemical methods e.g. acid value for analysis of acidic components, may also be deceptive and offer little insight into the total composition of the resin.

An attempt is made to derive an all round qualitative and quantitative spectral characterisation technique of the dibasic acid, polyol and oil components of the resin, in which all the information is extracted from the resin spectrum. The study deals with a characterisation technique of alkyd resins based on FT IR spectroscopy in which no chemical derivations are required and identification is obtained from transmission peaks and peak ratios in a single spectrum. A spectral characterisation technique based on the same principles can also be investigated for ^{13}C-NMR, but the FT IR method is preferred due to simplicity and availability.

3.3.2. Qualitative Analysis

3.3.2.1. Alkyd Resin Group Frequencies

Group frequencies are vibrations associated with certain structural units. The approximate constancy of group frequencies has been well established and forms the basis of structural analysis of compounds. Not all vibrations are good group frequencies, and some group frequencies which maintain a fairly constant position for most compounds may suddenly appear at new frequencies for certain other compounds as a result of the differences in the chemical environment of the structural unit.

Correlation tables provided in literature were used to assign different peaks present in the resin spectra. The resins' spectra collected have the same characteristic peaks though intensity variations are observed due to differences in concentration of absorbing species. In some spectra, especially at the beginning of each series (1.1. , 2.1. , 3.1. and 4.1.), some characteristic groups (e.g. phthalic at 745) were not detected due to low concentrations and hence masking by stronger peaks. Minor shifts in spectral positions were also observed as a result of the changing chemical environments. The correlation tables and peak assignments are given in Tables 7 and 8 respectively [Appendix].

The spectra of D.C.O. poly(glyceryl phthalate) alkyd resins reflect the presence of a multiplicity of characteristic functional groups, both active and non-active in alkyd resin synthesis and cross-linking reactions. Characteristic functional groups were chosen for the FT IR study of both qualitative and quantitative analysis of alkyd resin composition. The functional groups of interest include hydroxyl, carboxyl, ester (aliphatic and aromatic) , C=C double bonds, methylene, carbonyl and methyl groups. The spectra of both raw materials and synthesized alkyd resins are given in spectra 1-27 [Appendix].

3.3.2.2. The Dibasic Acid Component

Benzene Derivatives

Characteristic group frequencies in the 950-650 cm^{-1} are related to the substitution on the benzene ring. Phthalic anhydride is 1,2-disubstituted and the peaks observed in the 770-735 cm^{-1} are assigned to this group. The peak observed at 745 cm^{-1} is an excellent group frequency for the phthalic anhydride component.

Interference in this group can result from the methylene rock at 734-720 cm^{-1}. However, the peak's sensitivity to quantitative variations in the phthalic anhydride content further confirm the assignment.

Aromatic CH Stretch

CH stretching frequencies of the aromatic ring of the phthalic component appear near 3030 cm^{-1}. The aromatic CH stretch is a band of medium to weak intensity depending on the concentration of the phthalic component in the resin. Since this is in the region of the olefinic CH stretch, the aromatic CH vibration is indistinguishable from the olefinic CH stretch. The group is therefore unreliable in qualitative detection of the dibasic acid component.

Aromatic Ring Frequencies

One of the best series of group frequencies for recognising the presence of aromatic ring structures occurs in the 1600-1450 cm^{-1} region. The characteristic peaks at 1600 and 1580 cm^{-1} of resins are assigned to this group. The peaks are quite sharp and unmistakable, though small.

The region is close to CH_3 and CH_2 vibrations at 1460 but the groups are clearly distinguishable in the spectra in terms of both position and intensity, and hence no interference is observed.

Benzene Ring Vibrations in the 1225-950 cm^{-1}

While a number of characteristic group frequencies of aromatic compounds can appear in the 1225-950 cm^{-1} region, their weak intensity and variability of position make them only fair group frequencies. Also, this region contains a large number of bands in addition to those found for aromatic compounds. Because of these factors, this region is not as useful as the 2000-1660 cm^{-1}, 1600-1450 cm^{-1}, and 950-650 cm^{-1} regions for recognizing aromatic ring frequencies which identify the phthalic component.

3.3.2.3. The Polyol Component

The Hydroxyl Group

The structural unit, C-O-H, which is present in glycerol has a group frequency which is clearly distinguishable at 859 cm^{-1}. The O-H stretching frequency, which is useful in recognising the presence of the C-O-H structural unit, has a very broad peak at the 3500 cm^{-1} region.

The OH signals are not solely due to the polyol component. The residual OH from the ricinoleic fatty acid interferes with the 859 cm^{-1} peak and water from both dehydration and polyesterification also contribute to the 3500 cm^{-1} peak, though both contributions are minimal. The synthesis route employed seeks to eliminate all hydroxyl groups from castor oil and the azeotrope mops up the water produced. This is only an ideal situation which is difficult to achieve due to practical limitations. Nevertheless, despite interferences, the major contribution is from glycerol.

Interference of the OH peak at 3500cm^{-1} is possible from the CH peaks of both polyol, oil and aromatic ring of phthalic anhydride. From the spectra, the peaks are clearly distinguishable and hence unmistakable. The hydroxyl group provides the best characteristic group for the qualitative detection of the polyol in the alkyd resin matrix. The OH peaks at 3500 and 859 cm^{-1} are satisfactory peaks in qualitative analysis of the polyol component.

Methylene Groups

The methylene groups present in glycerol have peaks clearly recognisable at 1460 cm^{-1} (due to the CH_2 scissors vibration) and at 2928 and 2858 cm^{-1} (due to the CH olefinic stretch) spectral regions. Methylene species are also present in other alkyd species and hence are not attributable to glycerol alone. The group cannot therefore be used for qualitative detection of the polyol component in the alkyd resin matrix.

Interference in the methylene signal is encountered from methyl groups (oil) at 1470 cm^{-1} and the CH, both olefinic (methyl groups) and aromatic stretch (dibasic acid) at 2928 and 2858 cm^{-1}.

3.3.2.4. The Oil Component

Aliphatic Ester

The aliphatic ester is present in the oil molecules which exist predominantly as triglycerides. The ester group frequency has an intense peak in the 1475-1460 cm^{-1} and 742-734 cm^{-1}. The aliphatic ester group is unique to the oil component only. The aliphatic ester is the best group for detection of the oil component in the alkyd resin matrix. Interference is observed from the aromatic ester and carbonyl groups of phthalic anhydride. The group between 742-734 cm^{-1} is masked by the more intense peaks from the phthalic component and therefore is unreliable.

The ester group is identified through the carbonyl peak, which unfortunately is also present in the phthalic component. The C=O structural unit has a stretching vibration which is an excellent group frequency. It generally results in a very intense and sharp band, appearing in the 1850-1650 cm^{-1} region for most compounds.

The carbonyl group frequency appears in more than one chemical species in the alkyd resin (aliphatic ester, aromatic ester, anhydride and carboxylic groups). This group is therefore unreliable in both qualitative and quantitative analysis of alkyd resin composition.

Methyl Groups

The methyl groups are unique to the oil component and can therefore be used to identify the oil component. However, the CH_3 and CH_2 asymmetric stretch at 2930 cm^{-1}, the CH_3 and CH_2 symmetric stretch at 2858 cm^{-1} and the CH_3 and CH_2 symmetric scissors at 1460 cm^{-1} are indistinguishable. The CH_3 is therefore an unreliable group for the identification of the oil.

C=C Unsaturation

The C=C aliphatic double bonds are present in the oil molecules alone. As dehydration takes place the C=C unsaturation increases and a distinguishable peak becomes apparent at 970 cm^{-1}. This characteristic peak can be used for the qualitative identification of the oil component. However the group is unreliable since it is very sensitive to the degree of dehydration and is not detected at all in some alkyd resins.

3.3.3. Quantitative Analysis

3.3.3.1. Reference Functional Group

The CH_2 functional group was found to be the best group representative of a reference. A reference functional group should be basically inert in alkyd resin reactions and be at relatively high concentrations in all samples as to give a sharp and intense peak. The methylene group is of such high concentration in both oil and polyol, hence its absorption peak at 1460 cm^{-1} is sharp and intense and is unmistakable in all synthesized alkyd resins.

The reference functional group was used as the standard in the calculation of peak ratios and also as a guide in determining the sample thickness. Good spectra were obtained when the reference peak was between 9-20% transmission. The best correlations between peak ratios and resin parameters were obtained using the 1460 cm^{-1} methylene peak as the reference point.

3.3.3.2. Correlation Equations

Characteristic peak intensities of the reliable characteristic groups collected were expressed as peak ratios of the reference peak. The peak intensities (%) were expressed as peak ratios in order to have comparable intensities. Peak ratios account for the differences in peak intensity due to sample thickness as opposed to concentration differences of the absorbing species in the sample matrix. The % transmission of the peaks are recorded by the instrument, but in certain instances, some peaks were skipped and had to be measured manually. For broad peaks, e.g. the hydroxyl peak, the transmission had to be measured manually since the instrument did not record transmission at the centre of the peak. Peak intensities (%T) and peak ratios are given in Tables 8.1.-8.4. [Appendix].

Correlations are investigated in the confines of the Beer-Lambert's law. Differences in peak ratios due to deviations from the above law are beyond the scope of the study and all efforts are made to ensure that the sample thickness does not vary significantly. This is achieved by maintaining the transmission peak of the reference functional group approximately in the same range (9-20%).

Correlation equations were then derived using a computer. Two sets of equations were derived for peak ratios versus composition of alkyd resin component.

Let phthalic anhydride content = X_{mn} , X_{pn}
Let glycerol content = Y_{mn} , Y_{pn}
Let castor oil content = Z_{mn} , Z_{pn}
Let transmission peak ratios = T_n
m = moles, p = parts and n = resin series

Series Dependent Correlation Equations

(i) The Dibasic Acid Component

The phthalic anhydride peak at 745 cm^{-1} provided the best correlations between peak ratios and dibasic acid. The peak is sensitive to quantitative variations in the dibasic acid. The peak ratios decreased with increased phthalic anhydride levels due to lower transmissions (higher absorption).

Correlation equations were derived for peak ratios (T_n) versus dibasic acid content (X_m, X_p) at constant polyol/oil ratios.

$$T_1 = 2.0299 - 3.9982X_{m1} \qquad [3.9.]$$

$$T_1 = 2.0300 - 0.0270X_{p1} \qquad [3.10.]$$

$T_2 = 2.4122 - 7.4671X_{m2}$ [3.11.]

$T_2 = 2.4120 - 0.0504X_{p2}$ [3.12.]

$T_3 = 1.9641 - 4.6816X_{m3}$ [3.13.]

$T_3 = 1.9640 - 0.0316X_{p3}$ [3.14.]

$T_4 = 2.0128 - 5.1973X_{m4}$ [3.15.]

$T_4 = 2.0128 - 0.0660X_{p4}$ [3.16.]

The equations describe linear functions with correlation coefficients $r_{3.9.} = 0.9475$, $r_{3.10.} = 0.9434$, $r_{3.11.} = r_{3.12} = 0.9949$, $r_{3.13.} = 0.9716$, $r_{3.14.} = 0.9715$, $r_{3.15.} = r_{3.16.} = 0.9880$. Graphic relationships of the equations are illustrated in Figures 3.1.-3.8. [Appendix].

(ii) The Polyol Component

The polyol component is characterised by the abundance of hydroxyl groups as part of its molecular composition. Due to a preponderance of hydroxyl species in glycerol, castor oil, water (from dehydration and esterification) and phthalic acid, the contribution and origin of the individual hydroxyl groups to the peak intensity cannot be ascertained. The interference of OH species from other chemical species apart from glycerol is non uniform, and its effect is erratic and therefore as a result no good correlations are obtained.

The hydroxyl peak ratios do not provide good correlations, though a general trend is apparent. There is a general increase in peak ratios due to decreased polyol content as well as increased reaction with phthalic anhydride.

The polyol component can be related directly to the phthalic anhydride, since these are the reacting chemical species. Phthalic anhydride reacts with polyol to form the polyester. An inverse relationship therefore exists between phthalic anhydride peak ratio and the polyol component. A high polyol component effectively mops up the dibasic acid and hence low peak ratios. Correlations can therefore be derived between the phthalic anhydride peak ratios at 745 cm^{-1} and the polyol component.

Correlation equations were derived for peak ratios (T_n) versus polyol content (Y_m, Y_p) at constant polyol/oil ratios.

$$T_1 = 12.4600Y_{m1} - 0.6747 \qquad [3.17.]$$

$$T_1 = 0.1350Y_{p1} - 0.6700 \qquad [3.18.]$$

$$T_2 = 15.4600Y_{m2} - 2.3729 \qquad [3.19.]$$

$$T_2 = 0.1680Y_{p2} - 2.6280 \qquad [3.20.]$$

$$T_3 = 7.2709Y_{m3} - 1.1942 \qquad [3.21.]$$

$$T_3 = 0.0790Y_{p3} - 1.3540 \qquad [3.22.]$$

$$T_4 = 6.4624Y_{m4} - 1.4957 \qquad [3.23.]$$

$$T_4 = 0.0702Y_{p4} - 1.4958 \qquad [3.24.]$$

The equations describe linear functions with correlation coefficients $r_{3.17.} = 0.9481$, $r_{3.18.} = 0.9434$, $r_{3.19.} = r_{3.20.} = 0.9949$, $r_{3.21.} = r_{3.22.} = 0.9715$, $r_{3.23.} = r_{3.24.} = 0.9880$. Graphic relationships of the equations are illustrated in Figures 3.9-3.16. [Appendix].

(iii) The Oil Component

The methyl group and the aliphatic ester are the only groups that are characteristic to the oil component only. As mentioned earlier under qualitative analysis, the methyl groups are indistinguishable from methylene species at 1460 cm^{-1} and the aromatic CH stretch at 2928-2932 and 2858 cm^{-1}. The aliphatic ester is detected through the C=O and therefore unreliable since the C=O signal is due to several different chemical species. The oil component is therefore quantified indirectly through the dibasic acid component.

In resin synthesis, the polyol/oil ratio is maintained constant in each series. The oil provides a template for the attachment of the polyol hydroxyl groups in the alcoholysis reaction. An indirect relationship (third party) therefore exists between the oil component and the dibasic acid through the polyol. Since no reliable direct correlations are available for the oil component, use is made of the phthalic component. Correlations between phthalic peak ratios and the oil content are derived.

Correlation equations were derived for peak ratios (T_n) versus oil component (Z_m, Z_p) at constant polyol/oil ratios.

$$T_1 = 31.3953Z_{m1} - 0.6747 \qquad [3.25.]$$

$$T_1 = 0.0337Z_{p1} - 0.6700 \qquad [3.26.]$$

$$T_2 = 53.7461Z_{m2} - 1.8755 \qquad [3.27.]$$

$$T_2 = 0.0574Z_{p2} - 1.8630 \qquad [3.28.]$$

$T_3 = 49.3750Z_{m3} - 1.2108$ [3.29.]

$T_3 = 0.0702Z_{p3} - 1.1960$ [3.30.]

$T_4 = 65.5620Z_{m4} - 1.5030$ [3.31.]

$T_1 = 0.0702Z_{p4} - 1.4958$ [3.32.]

The equations describe linear functions with correlation coefficients $r_{3.25.} = r_{3.26.} = 0.9476$, $r_{3.27.} = 0.9950$, $r_{3.28.} = 0.9949$, $r_{3.29.} = r_{3.30.} = 0.9715$, $r_{3.31.} = 0.9885$ and $r_{3.32.} = 0.9800$. Graphic relationships of the equations are illustrated in Figures 3.17-3.24 [Appendix].

In all the series dependent equations, good correlations were obtained between peak ratios and dibasic acid, polyol and oil content in each series. However, the characterisation technique breaks down since the derived correlation equations are series dependent and can not be used without the polyol/oil ratio, which is unavailable from spectral methods. The polyol/oil ratio may be obtained by other methods which are beyond the scope of the study.

(iv) The Polyol/Oil Ratio

The series dependent correlation equations derived are, however, useless if the polyol/oil ratio is not established. The four series have different polyol/oil ratios and given a sample of unknown composition, it will be difficult to determine which set of equations to use. Spectral methods were therefore investigated to determine the polyol/oil ratios.

The polyol/oil ratio is constant for each series. It is therefore envisaged that for a chosen characteristic group frequency common to both polyol and oil (methylene group), the peak ratio will remain constant in a given series. A methylene peak at 706 cm^{-1} was chosen (apart from the methylene peak at 1460 cm^{-1}) and peak ratios were computed against the reference peak. The results showed a decrease in peak ratios down the series, contrary to expectations in which a constant peak ratio is anticipated. Overlapping of peak ratios between series further compounded the problem. The trend is attributed to interference of the methylene rock by the phthalic component at 745 cm^{-1}. Other peaks were also investigated, but the non-constancy of the peak ratios was a setback. Therefore no spectral methods of determining the polyol/oil ratio could be found and all series dependent correlations were abandoned. Other methods for the determination of the polyol/oil ratio, apart from spectral methods, were not investigated since they are beyond the scope of the study. The characterisation techniques of interest are those that are derived using resin spectral details only.

Series Independent Correlation Equations

Analysis of the peak ratios of different series at constant dibasic acid content resulted in the realisation that the ratios are almost equal. Therefore it was possible to derive mathematical functions which relate peak ratios and dibasic acid content which are independent of the polyol/oil ratio. The phthalic peak at 745 cm^{-1} is due to the aromatic ring of the phthalic component and therefore should ideally be the same for all series (different polyol/oil ratios) at constant dibasic acid content. Minor variations are anticipated due to the non-constancy of the reference peak in different series.

The following data extracted from Tables 8.1.-8.4. [Appendix] was used in the derivation of the mathematical functions.

Dibasic Acid Content		*T_1	T_2	T_3	T_4	$T_{av.}$
Parts	Moles					
10	0.0675	1.71	2.01	1.72	1.72	1.82
15	0.1013	1.71	1.53	1.41	1.46	1.47
20	0.1350	1.47	1.38	1.29	1.30	1.32
25	0.1688	1.34	1.17	1.21	1.07	1.15
30	0.2025	-	0.93	1.03	0.94	0.97
35	0.2363	-	-	-	0.85	0.85

Correlation equations were derived for the average peak ratios ($T_{av.}$) and dibasic acid content (X_m, X_p).

$$T = 2.1017 - 5.5190X_m \qquad [3.33.]$$

$$T = 2.1016 - 3.7257X_p \qquad [3.34.]$$

The equations describe linear functions with correlation coefficients $r_{3.33.} = r_{3.34.} = 0.9853$. Graphic relationships of the equations are illustrated in Figures 4.1. and 4.2 [Appendix].

*Higher peak ratio values were obtained for series 1 and hence these were not used in the derivation of the correlation equations. The differences are attributed to experimental variations in the synthesis of alkyd resins. It should be noted that in the synthesis of series 1 resins, especially at high dibasic acid contents, violent bumping was observed and a significant amount of dibasic acid was lost to the refluxing solvent. This is evident from the whitish colour assumed by the solvent as the reaction commences.

Ideally all the refluxing solvent should return to the reaction vessel, but unfortunately not all is returned since the water produced by the reaction is not enough to displace all the solvent in the trap. The amount of the dibasic acid in the reactor is therefore less than that on the formulation and this is more so in series 1 than any other series. Series 1 resins have therefore, as expected, higher transmittance (lower absorption) than other resin series. Bumping of the reaction mix is dependent on the polyol/oil ratios and decreases with an increase in polyol content. Bumping is very reduced in series 2, 3 and 4.

Theoretically the peak ratio values should be the same. The phthalic peak at 745 cm^{-1} is independent of the state of the dibasic acid hence both monomeric and polymeric forms have peaks at the same wavelength. A large set of data may be necessary to eradicate the discrepancies. However, even if the high peak values of series 1 resins are substituted in the characterisation equations, the maximum error realised in the dibasic acid content is 5%. The derived equations are applicable to all resin series and are free of the restrictions imposed by the polyol/oil ratios in previous equations.

3.3.3.3.Instrumental Dependence of Correlation Equations

The spectral data of the resins used in the derivation of the correlation equations is dependent on the resolution of the instrument. Variations in resin spectral details is therefore expected when two different machines are used. The effect is however minimised by the use of peak ratios which account for intensity differences in peak signals and also cancel out instrumental factors.

The possibility of instrumental dependence of correlation equations cannot be dismissed. Instrument calibrated correlation equations can therefore be derived for each instrument. Several resins with different compositions in

terms of both dibasic acid, polyol and polyol/oil contents are synthesized and their spectra collected. Peak ratios are then calculated and correlation equations are derived as before based on the new data.

3.3.3.4. Further Research

The spectral characterisation techniques derived are unique to the phthalic anhydride component in D.C.O. poly(glyceryl phthalate) alkyd resins. The applicability of the method under varying chemical environments was not investigated, although the underlying principles on which the method is based remain the same. New characterisation correlation equations have to be derived for alkyd resins with different dibasic acid, polyol and oil composition to the one studied. The same principles are used in the derivations though the reference and analyte peaks may vary. Further research is therefore necessary to ascertain the effect of variations in chemical environments on transmission peak ratios. Alkyd resins with different composition to those studied are beyond the scope of the study.

3.3.4. Conclusion

Qualitative Analysis

Identification of the alkyd resin components of dibasic acid and polyol components was achieved by a study of the resin spectra. The dibasic acid component was identified through the aromatic groups at 745, 1580 and 1600 cm^{-1}. The polyol component was identified through the hydroxyl groups at 859 and 3500 cm^{-1}. No reliable characteristic group could be found for the oil component. The methyl, methylene and aliphatic ester groups are not reliable characteristic groups due to interferences.

Quantitative Analysis

Good correlations were obtained between peak ratios and alkyd resin composition. Both series dependent and series independent correlation equations were derived. The series dependent correlation equations could not be used for characterisation due to the non-availability of the polyol/oil ratios from spectral methods. Series independent equations overcame the need to determine the polyol/oil ratio and are therefore applicable to all resins and free from the restrictions imposed by the polyol/oil ratios. The instrumental dependence of the correlation equations can not be dismissed and instrument calibrated equations can be derived.

The FT IR quantitative study of D.C.O. poly(glyceryl phthalate) alkyd resins culminated in the derivation of a new spectral characterisation technique for dibasic acid component in the alkyd resin matrix. The method is not a highly accurate measure of the quantitative composition of alkyds, but is nevertheless, a quick convenient which is of great commercial rather than academic interest.

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Table 1.1. : Base Formulations Composition

Resin	Phthalic Anhydride		Glycerol		Castor Oil	
	Parts	Moles	Parts	Moles	Parts	Moles
1.1.	5.00	0.0338	19.00	0.2063	76.00	0.0815
1.2.	10.00	0.0675	18.00	0.1954	72.00	0.0773
1.3.	15.00	0.1013	17.00	0.1846	68.00	0.0730
1.4.	20.00	0.1350	16.00	0.1737	64.00	0.0687
1.5.	25.00	0.1688	15.00	0.1629	60.00	0.0644
1.6.	30.00	0.2025	14.00	0.1520	56.00	0.0601
2.1.	5.00	0.0338	28.50	0.2932	66.50	0.0714
2.2.	10.00	0.0675	27.00	0.2769	63.00	0.0676
2.3.	15.00	0.1013	25.50	0.2606	59.50	0.0638
2.4.	20.00	0.1350	24.00	0.2443	56.00	0.0601
2.5.	25.00	0.1688	22.50	0.2280	52.50	0.0563
2.6.	30.00	0.2025	21.00	0.2117	49.00	0.0526
2.7.	35.00	0.2363	19.50	0.1954	45.50	0.0488
3.1.	5.00	0.0338	38.00	0.4126	57.00	0.0612
3.2.	10.00	0.0675	36.00	0.3909	54.00	0.0579
3.3.	15.00	0.1013	34.00	0.3692	51.00	0.0547
3.4.	20.00	0.1350	32.00	0.3474	48.00	0.0515
3.5.	25.00	0.1688	30.00	0.3257	45.00	0.0483
3.6.	30.00	0.2025	28.00	0.3040	42.00	0.0451
3.7.	35.00	0.2363	26.00	0.2823	39.00	0.0418
3.8.	40.00	0.2701	24.00	0.2606	36.00	0.0386
4.1.	5.00	0.0338	47.50	0.5157	47.50	0.0510
4.2.	10.00	0.0675	45.00	0.4886	45.00	0.0483
4.3.	15.00	0.1013	42.50	0.4615	42.50	0.0456
4.4.	20.00	0.1350	40.00	0.4343	40.00	0.0429
4.5.	25.00	0.1688	37.50	0.4072	37.50	0.0402
4.6.	30.00	0.2025	35.00	0.3800	35.00	0.0376
4.7.	35.00	0.2363	32.50	0.3529	32.50	0.0349
4.8.	40.00	0.2701	30.00	0.3257	30.00	0.0322
4.9.	45.00	0.3038	27.50	0.2986	27.50	0.0295
5.0.	27.50	0.1857	18.125	0.1968	54.375	0.0583
6.0.	32.50	0.2194	23.625	0.2565	43.875	0.0471
7.0.	37.50	0.2532	28.125	0.3054	34.375	0.0369

Table 1.2. : Modified Formulations Composition

Resin	PA1		PA2		Glycerol		Castor oil	
	Parts	Moles	Parts	Moles	Parts	Moles	Parts	Moles
1.5.1.	11.14	0.0752	13.86	0.0936	15.00	0.1629	60.00	0.0644
2.6.1.	16.14	0.1090	13.86	0.0936	21.00	0.2280	49.00	0.0526
3.7.1.	21.14	0.1427	13.86	0.0936	26.00	0.2823	39.00	0.0418
4.8.1.	26.14	0.1765	13.86	0.0936	30.00	0.3257	30.00	0.0322
5.0.1.	13.64	0.0921	13.86	0.0936	18.125	0.1968	54.375	0.0583
6.0.1.	18.64	0.1258	13.86	0.0936	23.625	0.2565	43.875	0.0471
7.0.1.	23.64	0.1596	13.86	0.0936	28.125	0.3054	34.375	0.0369

Table 5.3. : Drying Times of Catalysed Water-based Resins

Resin	Assignment (4hrs)	Assessment
1.5.1	Dry	Satisfactory
2.6.1.	Dry	Satisfactory
3.7.1.	Dry	Good
4.8.1.	Dry	Good
5.0.1.	Dry	Satisfactory
6.0.1.	Dry	Satisfactory
7.0.1.	Dry	Good

Table 2. : Excess Hydroxyl (%), Alkyd Constants and Gelation Incidence

Resin	Excess Hydroxyl	Alkyd Constant, K	Gelation Incidence
1.1.	816.89	4.75	None
1.2.	334.22	2.52	None
1.3.	173.48	1.77	None
1.4.	93.00	1.40	None
1.5.	44.80	1.17	None
1.6.	12.59	1.02	Gelation (<4hrs)
2.1.	1203.11	5.89	None
2.2.	515.33	3.05	None
2.3.	286.07	2.10	None
2.4.	171.44	1.63	None
2.5.	102.66	1.34	None
2.6.	56.81	1.15	None
2.7.	24.06	1.02	Gelation (<3hrs)
3.1.	1733.78	7.50	None
3.2.	768.67	3.82	None
3.3.	446.96	2.59	None
3.4.	286.00	1.98	None
3.5.	189.51	1.61	None
3.6.	125.19	1.36	None
3.7.	79.24	1.19	None
3.8.	44.70	1.05	Gelation (<3hrs)
4.1.	2192.00	8.88	None
4.2.	985.78	4.48	None
4.3.	583.70	3.02	None
4.4.	382.56	2.27	None
4.5.	261.96	1.83	None
4.6.	181.48	1.53	None
4.7.	130.41	1.32	None
4.8.	80.84	1.16	None
4.9.	47.46	1.04	Gelation (<3hrs)
5.0.	58.97	1.19	None
6.0.	75.32	1.19	None
7.0.	80.92	1.18	None

Table 3.1. : Reaction Profile Data for Series 1 Resins

Resin Number	Reaction Time (hrs)	Acid Value (mg KOH)
1.3.	0	114.96
	1	5.76
	2	3.08
	3	2.22
	4	1.83
	5	1.65
1.4.	0	152.77
	1	7.70
	2	4.26
	3	3.12
	4	2.71
	5	2.30
1.5.	0	190.57
	1	11.97
	2	9.82
	3	8.18
	4	6.90
	5	6.01
1.6.	0	192.10
	1	22.60
	2	19.50
	3	18.72
	4	17.98*

Table 3.2. : Acid Values

Resin	Acid Value (mg KOH)
1.1.	0.76
1.2.	0.96
1.3.	1.65
1.4.	2.30
1.5.	6.01
2.1.	0.69
2.2.	0.81
2.3.	1.35
2.4.	2.73
2.5.	3.20
2.6.	3.43
3.1.	0.65
3.2.	0.71
3.3.	1.00
3.4.	1.04
3.5.	1.40
3.6.	1.75
3.7.	2.90
4.1.	0.70
4.2.	0.95
4.3.	1.15
4.4.	1.27
4.5.	1.20
4.6.	1.30
4.7.	1.48
4.8.	1.77
4.9.	2.25

Table 4 : Gel Times of Uncatalysed Resins @ 200°C

Resin	Gel Time (s)
1.3.	534
1.4.	271
1.5.	95
2.4.	486
2.5.	225
2.6.	85
3.4.	>600
3.5.	>600
3.6.	462
3.7.	120
4.5	>600
4.6.	>600
4.7.	515
4.8.	151
5.0.	93
6.0.	101
7.0.	140

Table 5.1. : Drying Times of Uncatalysed Solvent-based Resins

Resin	Assignment (3hrs)	Assessment
1.3.	Wet	Poor
1.4.	Wet	Poor
1.5.	Tacky	Poor
2.4.	Wet	Poor
2.5.	Wet	Poor
2.6.	Tacky	Poor
3.4.	Wet	Poor
3.5.	Tacky	Poor
3.6.	Touch dry	Satisfactory
3.7.	Dry	Good
4.5.	Wet	Poor
4.6.	Tacky	Poor
4.7.	Touch dry	Satisfactory
4.8.	Dry	Good
5.0.	Tacky	Poor
6.0.	Touch dry	Satisfactory
7.0.	Dry	Good

Table 5.2. : Drying Times of Catalysed Solvent-based Resins

Resin	Assignment (3hrs)	Assessment
1.3.	Wet	Poor
1.4.	Tacky	Satisfactory
1.5.	Dry	Good
2.4.	Wet	Poor
2.5.	Tacky	Satisfactory
2.6.	Dry	Good
3.4.	Wet	Poor
3.5.	Wet	Poor
3.6.	Tacky	Satisfactory
3.7.	Dry	Good
4.5.	Wet	Poor
4.6.	Wet	Poor
4.7.	Tacky	Satisfactory
4.8.	Dry	Good
5.0.	Dry	Good
6.0.	Dry	Good
7.0.	Dry	Good

Table 6 : Solvent Resistance of Solvent-based Resin Films (24hrs)

Resin	Catalysed Films	Uncatalysed Films
1.3.	Soluble	Soluble
1.4.	Soluble	Soluble
1.5.	Insoluble	Soluble
2.4.	Soluble	Soluble
2.5.	Soluble	Soluble
2.6.	Insoluble	Soluble
3.4.	Soluble	Soluble
3.5.	Soluble	Soluble
3.6.	Soluble	Soluble
3.7.	Insoluble	Soluble
4.5.	Soluble	Soluble
4.6.	Soluble	Soluble
4.7.	Soluble	Soluble
4.8.	Insoluble	Soluble
5.0.	Insoluble	Soluble
6.0.	Insoluble	Soluble
7.0.	Insoluble	Soluble

Table 7 : FT IR Peak Assignments

Peak cm-1	Assignment
3500	Free OH - glycerol, castor oil (undehydrated) and water
2928	Aromatic (phthalic) and olefinic (methyl and methylene) CH stretch
2858	Olefinic CH stretch - methyl and methylene groups
1734	C=O stretch - aromatic (phthalic) and aliphatic (oil) ester and anhydride (phthalic)
1600	Aromatic ring (phthalic component)
1580	Aromatic ring (phthalic component) anhydride
1460	Olefinic CH stretch - methylene and methyl groups
1280	C=O stretch - aliphatic (oil) and aromatic (phthalic) ester and anhydride (phthalic)
1073	Phthalic component
970	C=C unsaturation - castor oil
859	C-OH - glycerol and undehydrated castor oil
745	Ortho disubstituted aromatic ring (phthalic)
706	CH stretch - olefinic (methyl and methylene) and aromatic (phthalic)

Table 8.1. : Alkyd Resin Transmission Peaks (%T)

RESIN	1460	745	1600	1580	3500	859	1280
1.1.	11.2	-	-	-	8.7	24.8	9.8
1.2.	14.2	24.3	26.9	27.1	12.8	29.3	9.9
1.3.	10.3	17.6	20.1	20.3	10.9	24.2	5.5
1.4.	15.1	22.2	22.3	22.4	15.4	29.7	7.9
1.5.	9.7	13.0	17.5	17.2	13.3	25.3	2.6
2.1.	18.6	-	-	-	9.8	32.9	16.9
2.2.	9.9	19.9	31.8	32.2	4.8	26.7	4.0
2.3.	17.3	26.4	33.2	33.7	11.3	35.5	6.7
2.4.	12.0	16.5	23.5	23.6	11.2	28.5	3.7
2.5.	13.0	15.2	21.2	21.1	14.8	26.6	4.9
2.6.	13.3	12.4	24.9	24.5	18.6	34.7	2.1
3.1.	9.4	-	-	-	4.6	20.2	7.6
3.2.	11.0	18.9	24.4	25.1	5.3	23.6	7.6
3.3.	19.3	27.3	32.8	33.1	11.2	35.2	9.4
3.4.	12.0	15.5	26.3	26.8	5.2	29.0	2.5
3.5.	12.1	14.7	21.8	22.0	8.0	27.1	2.8
3.6.	11.5	11.8	18.5	18.5	10.1	25.9	2.6
4.1.	-	-	-	-	-	-	-
4.2.	12.5	-	30.8	31.5	3.7	27.0	5.8
4.3.	15.0	21.9	31.8	32.3	6.0	30.9	5.1
4.4.	11.6	15.1	26.3	26.8	5.7	28.6	1.6
4.5.	11.9	12.7	22.1	22.6	6.5	25.5	3.3
4.6.	9.7	9.1	17.7	18.2	4.3	23.7	1.7
4.7.	9.5	8.1	15.0	15.1	6.2	21.3	1.1

Table 8.2 : Alkyd Resin Transmission Peaks (%T)

RESIN	1073	1125	1742	2930	2858	986	706
1.1.	11.5	10.6	6.5	4.9	5.9	-	-
1.2.	13.4	12.1	6.4	5.2	7.4	-	-
1.3.	9.0	7.5	3.1	2.5	4.3	-	-
1.4.	13.0	11.0	4.7	4.9	7.8	-	-
1.5.	6.0	4.4	1.1	1.7	3.8	14.9	19.7
2.1.	16.1	17.0	11.8	8.1	10.2	-	-
2.2.	6.5	6.0	1.7	0.9	2.7	-	20.9
2.3.	11.7	10.8	3.8	3.2	6.9	-	-
2.4.	7.4	6.2	2.2	2.7	5.5	18.2	22.4
2.5.	8.4	7.2	3.3	4.8	7.7	17.5	20.8
2.6.	5.3	3.8	1.2	2.6	5.8	20.1	21.9
3.1.	6.3	-	5.3	3.5	5.3	-	-
3.2.	9.2	8.8	5.4	3.8	5.4	-	-
3.3.	14.2	13.4	6.3	5.5	9.8	-	-
3.4.	5.9	5.3	1.5	2.1	5.0	19.2	20.5
3.5.	6.1	5.5	2.0	3.2	6.3	18.1	20.2
3.6.	5.3	4.6	1.7	3.5	6.4	16.2	18.0
4.1.	-	-	-	-	-	-	-
4.2.	6.8	6.9	3.6	2.1	4.7	-	-
4.3.	7.5	7.7	3.7	3.6	7.2	-	24.1
4.4.	4.0	3.4	1.0	1.6	4.3	17.5	20.6
4.5.	5.9	5.7	2.8	4.6	7.8	16.9	17.4
4.6.	3.6	3.3	1.2	2.5	5.3	14.8	14.4
4.7.	3.4	3.0	0.8	3.3	6.5	13.7	13.3

Table 8.3. : Peak Ratios

RESIN	REF PEAK 1460	745	1600	1580	3500	859	1280
1.1.	11.2	-	-	-	0.78	2.21	0.88
1.2.	14.2	1.71	1.89	1.91	0.90	2.06	0.70
1.3.	10.3	1.71	1.95	1.15	1.06	2.35	0.53
1.4.	15.1	1.47	1.48	1.48	1.02	1.97	0.52
1.5.	9.7	1.34	1.80	1.77	1.37	2.61	0.27
2.1.	18.6	-	-	-	0.53	1.77	0.91
2.2.	9.9	2.01	3.21	3.25	0.48	2.70	0.40
2.3.	17.3	1.53	1.92	1.95	0.65	2.05	0.39
2.4.	12.0	1.38	1.96	1.97	0.93	2.38	0.31
2.5.	13.0	1.17	1.63	1.62	1.11	2.05	0.38
2.6.	13.3	0.93	1.87	1.84	1.40	2.61	0.16
3.1.	9.4	-	-	-	0.49	2.15	0.67
3.2.	11.0	1.72	2.22	2.28	0.48	2.15	0.69
3.3.	19.3	1.41	1.70	1.72	0.58	1.82	0.49
3.4.	12.0	1.29	2.19	2.23	0.43	2.42	0.21
3.5.	12.1	1.21	1.80	1.82	0.66	2.24	0.23
3.6.	11.5	1.03	1.61	1.61	0.88	2.25	0.23
4.1.	-	-	-	-	-	-	-
4.2.	12.5	1.72	2.46	2.52	0.30	2.16	0.46
4.3.	15.0	1.46	2.12	2.15	0.40	2.06	0.34
4.4.	11.6	1.30	2.26	2.31	0.49	2.47	0.14
4.5.	11.9	1.07	1.86	1.90	0.55	2.14	0.28
4.6.	9.7	0.94	1.82	1.88	0.44	2.44	0.18
4.7.	9.5	0.85	1.58	1.59	0.65	2.24	0.12

Table 8.4. : Peak Ratios

RESIN	REF PEAK 1460	1073	1125	1742	2928	2858	986	706
1.1.	11.2	1.03	0.95	0.58	0.45	0.53	-	-
1.2.	14.2	0.94	0.85	0.45	0.37	0.52	-	-
1.3.	10.3	0.87	0.73	0.30	0.24	0.42	-	-
1.4.	15.1	0.86	0.73	0.31	0.32	0.52	-	-
1.5.	9.7	0.62	0.45	0.11	0.18	0.39	1.54	2.03
2.1.	18.6	0.87	0.91	0.63	0.44	0.55	-	-
2.2.	9.9	0.66	0.60	0.17	0.09	0.27	-	-
2.3.	17.3	0.68	0.62	0.22	0.18	0.40	-	-
2.4.	12.0	0.62	0.52	0.18	0.23	0.46	1.52	1.87
2.5.	13.0	0.65	0.55	0.25	0.37	0.59	1.35	1.60
2.6.	13.3	0.39	0.29	0.09	0.20	0.44	1.51	1.65
3.1.	9.4	0.67	-	0.56	0.37	0.56	-	-
3.2.	11.0	0.84	0.80	0.49	0.35	0.49	-	-
3.3.	19.3	0.74	0.69	0.33	0.28	0.51	-	-
3.4.	12.0	0.49	0.44	0.13	0.18	0.42	1.60	1.71
3.5.	12.1	0.50	0.45	0.17	0.26	0.52	1.50	1.66
3.6.	11.5	0.46	0.40	0.15	0.30	0.56	1.41	1.57
4.1.	-	-	-	-	-	-	-	-
4.2.	12.5	0.54	0.55	0.29	0.17	0.38	-	-
4.3.	15.0	0.50	0.51	0.25	0.24	0.48	-	1.61
4.4.	11.6	0.34	0.29	0.09	0.14	0.37	1.51	1.78
4.5.	11.9	0.50	0.48	0.24	0.39	0.66	1.42	1.46
4.6.	9.7	0.37	0.34	0.12	0.26	0.55	1.53	1.48
4.7.	9.5	0.36	0.32	0.08	0.38	0.68	1.44	1.40

Figure 1.1. : Resin 1.3. Reaction Profile

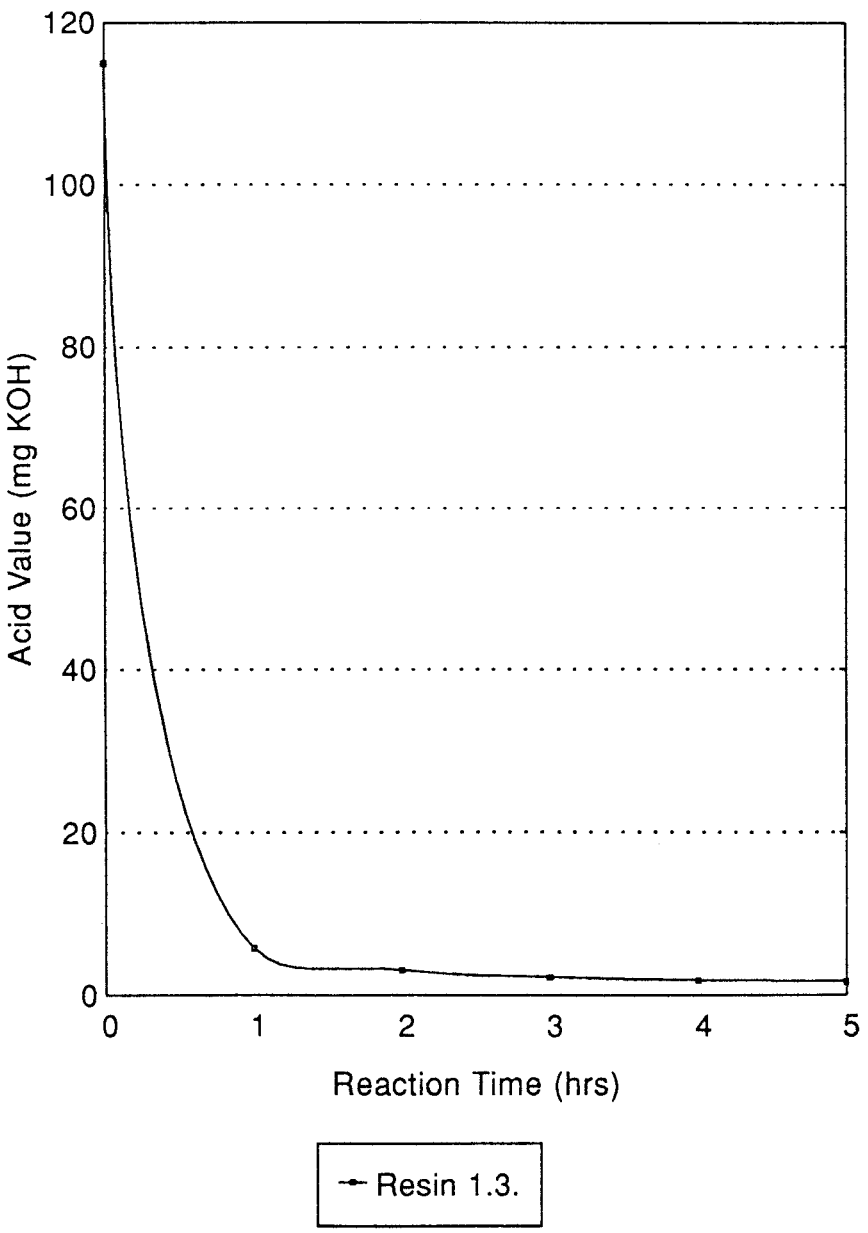


Figure 1.2. : Resin 1.4. Reaction Profile

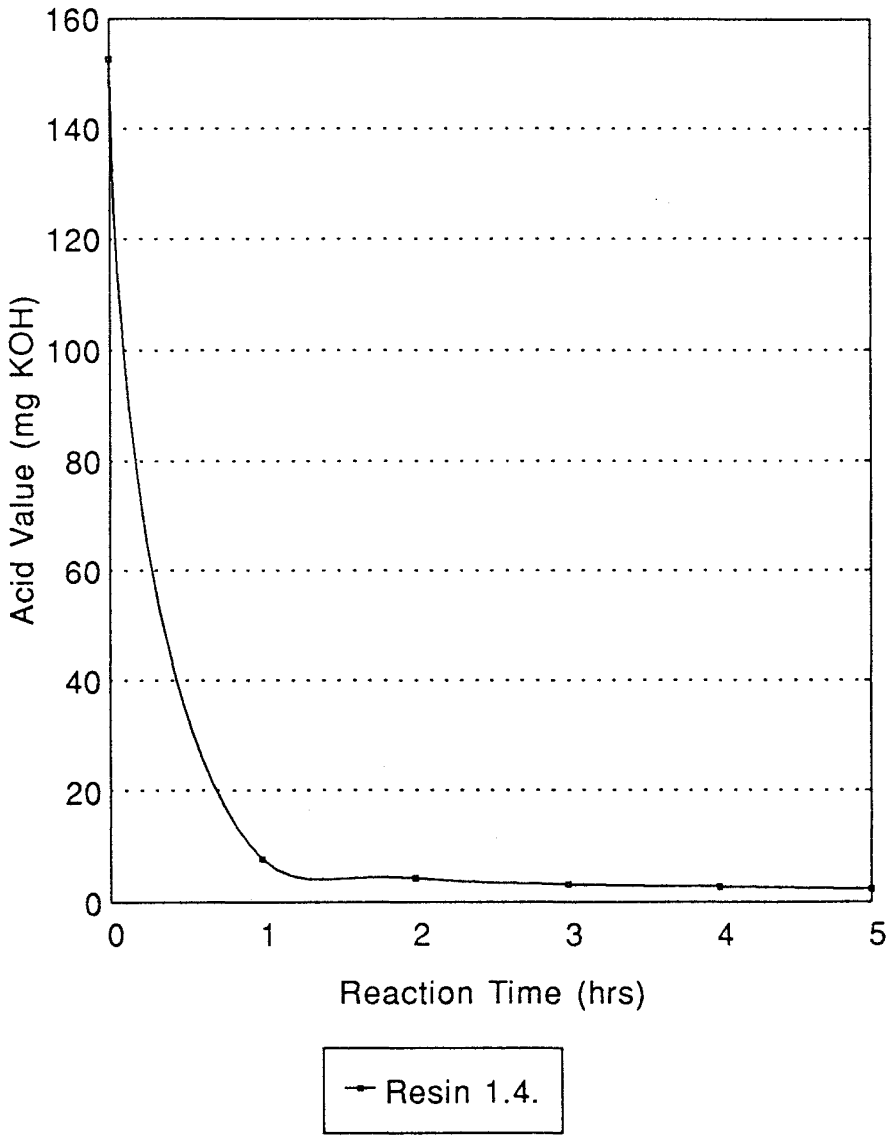


Figure 1.3. : Resin 1.5. Reaction Profile

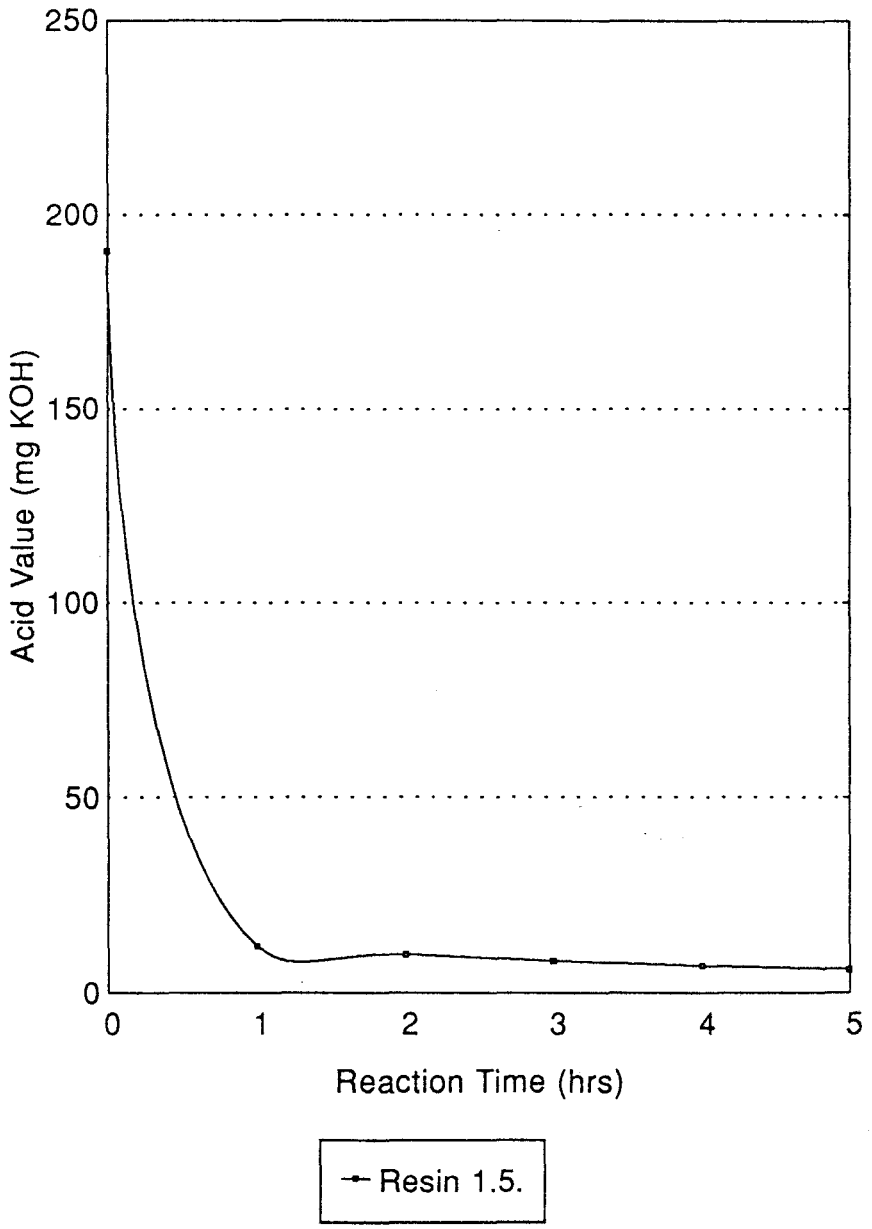


Figure 1.4. : Resin 1.6 Reaction Profile

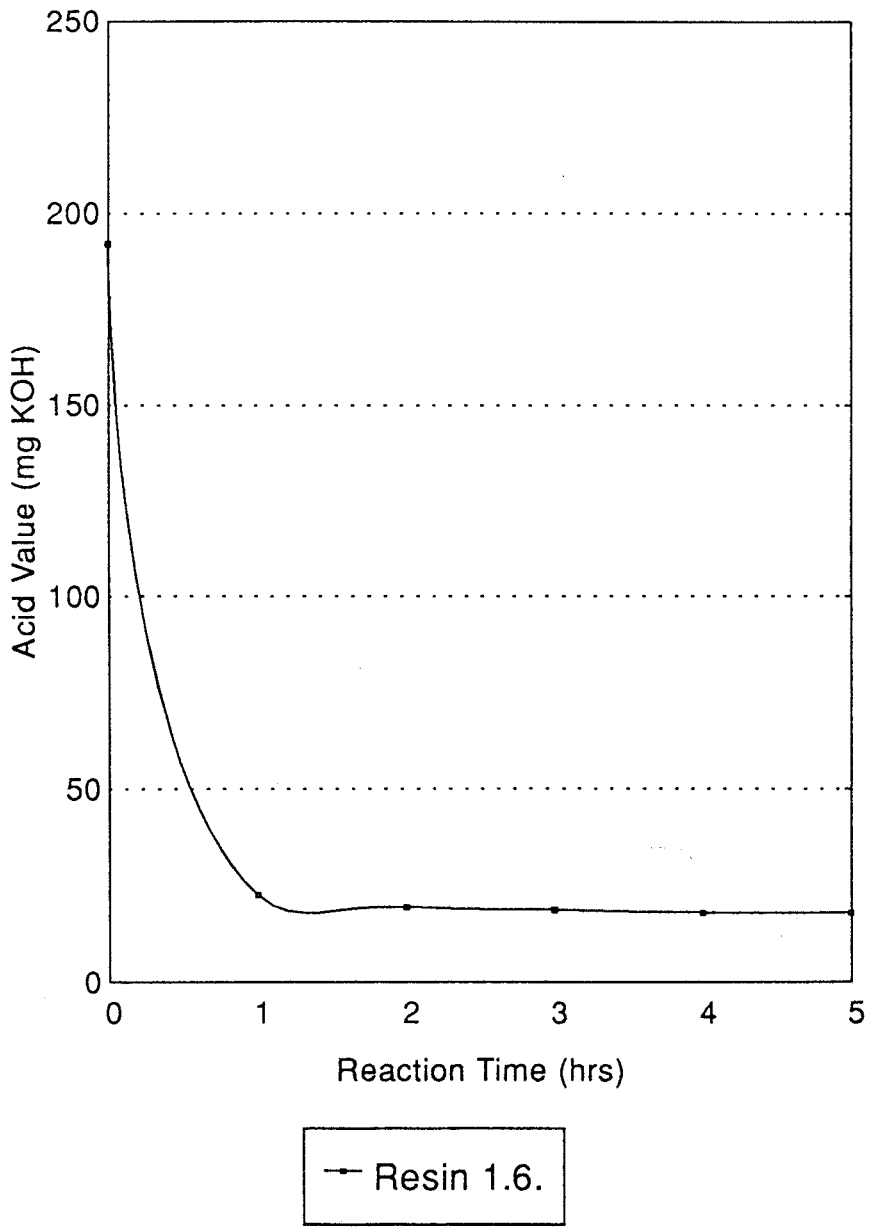
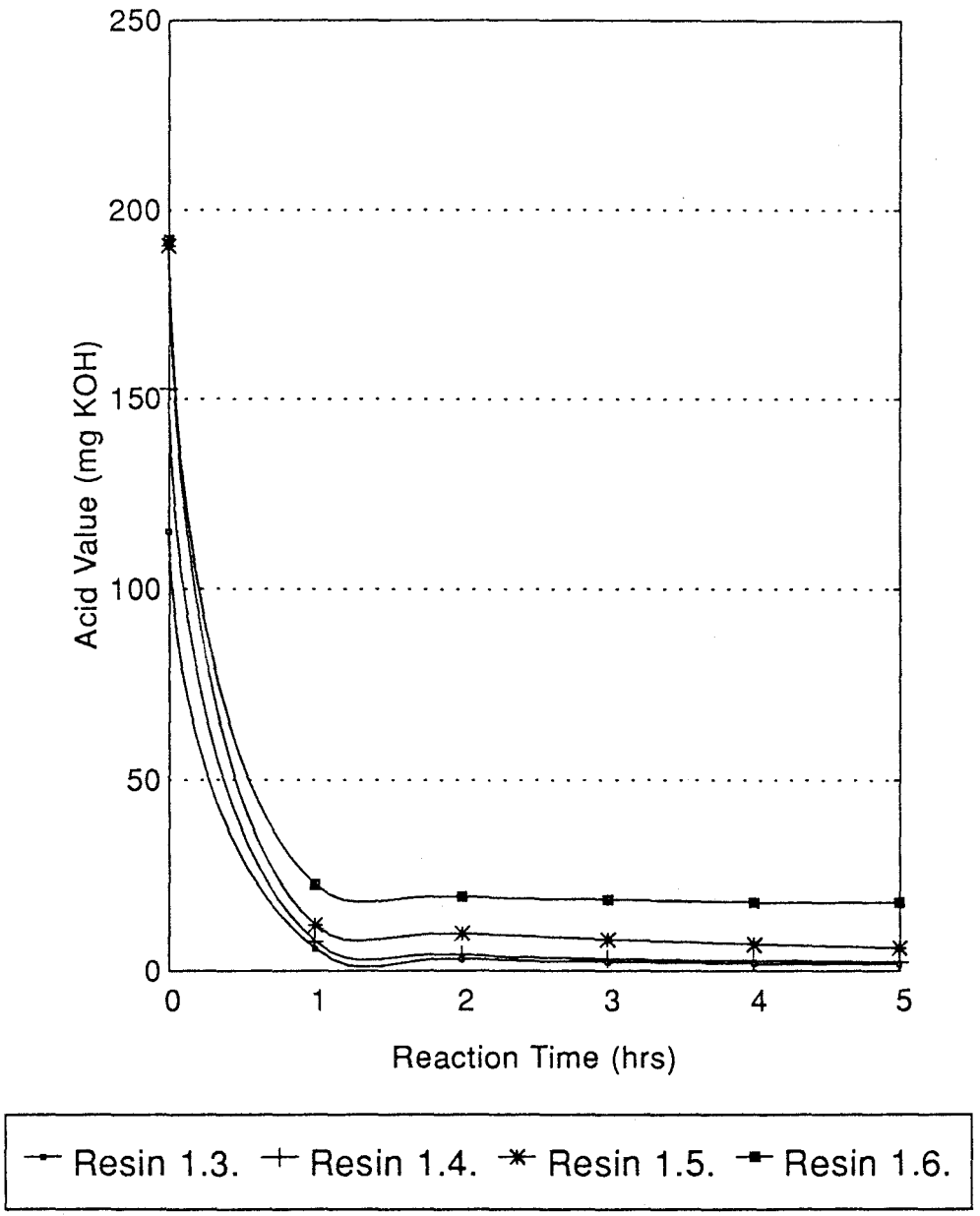


Figure 1.5. : Series 1 Resins Reaction Profiles



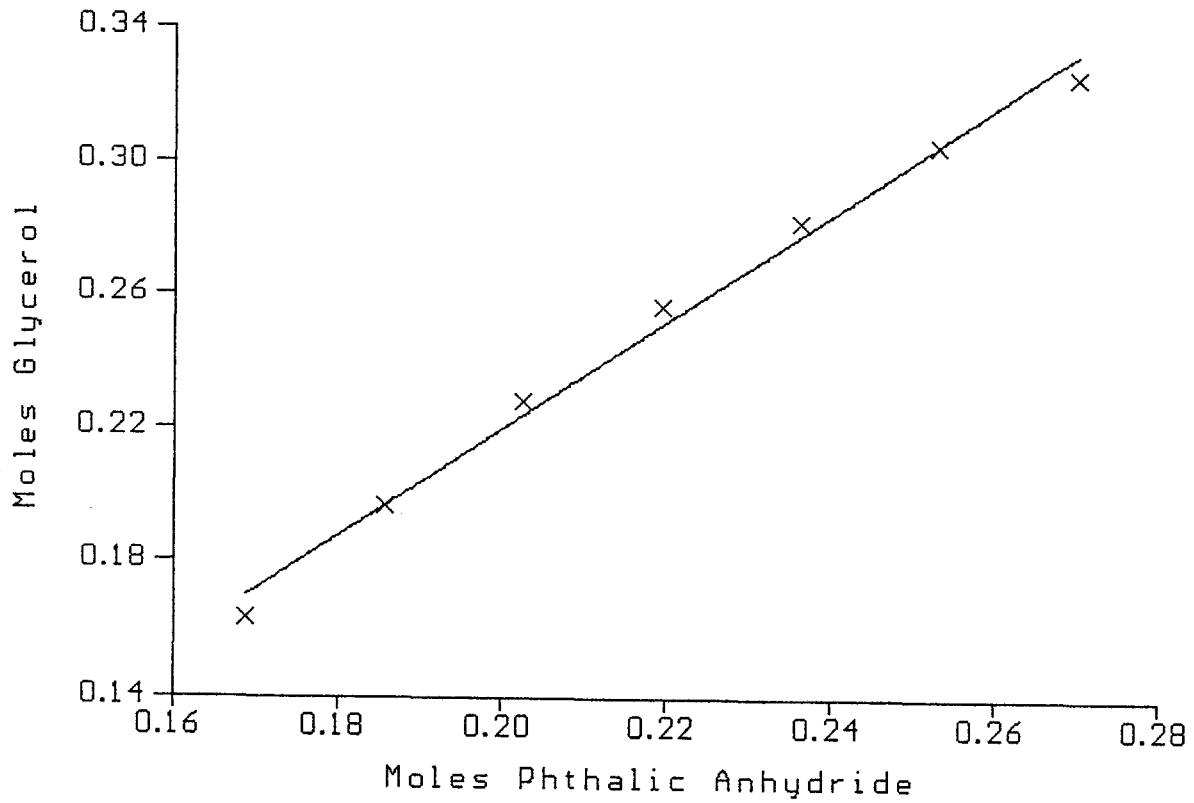


Figure 2.1. : Model Formulation Equation 3.3. - Moles Glycerol (Y_m) versus Moles Phthalic Anhydride (X_m).

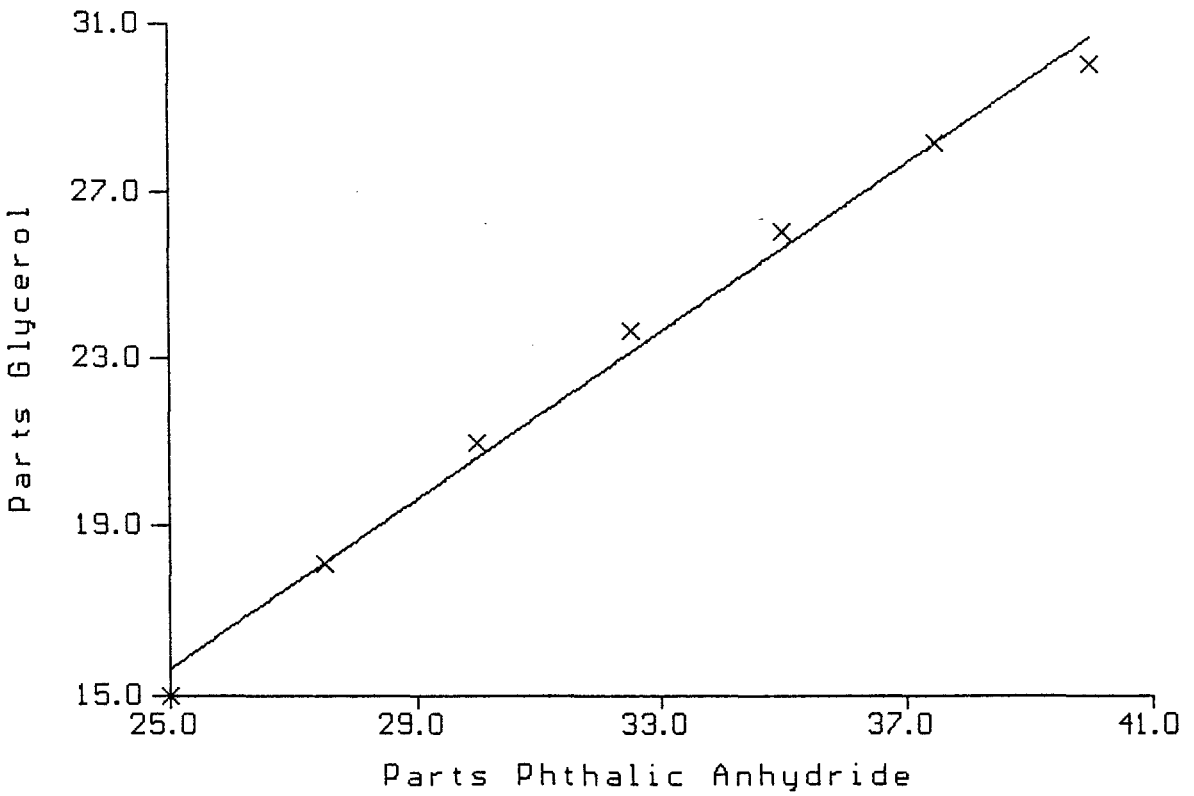


Figure 2.2. : Model Formulation Equation 3.4. - Parts Glycerol (Y_p) versus Parts Phthalic Anhydride (X_p).

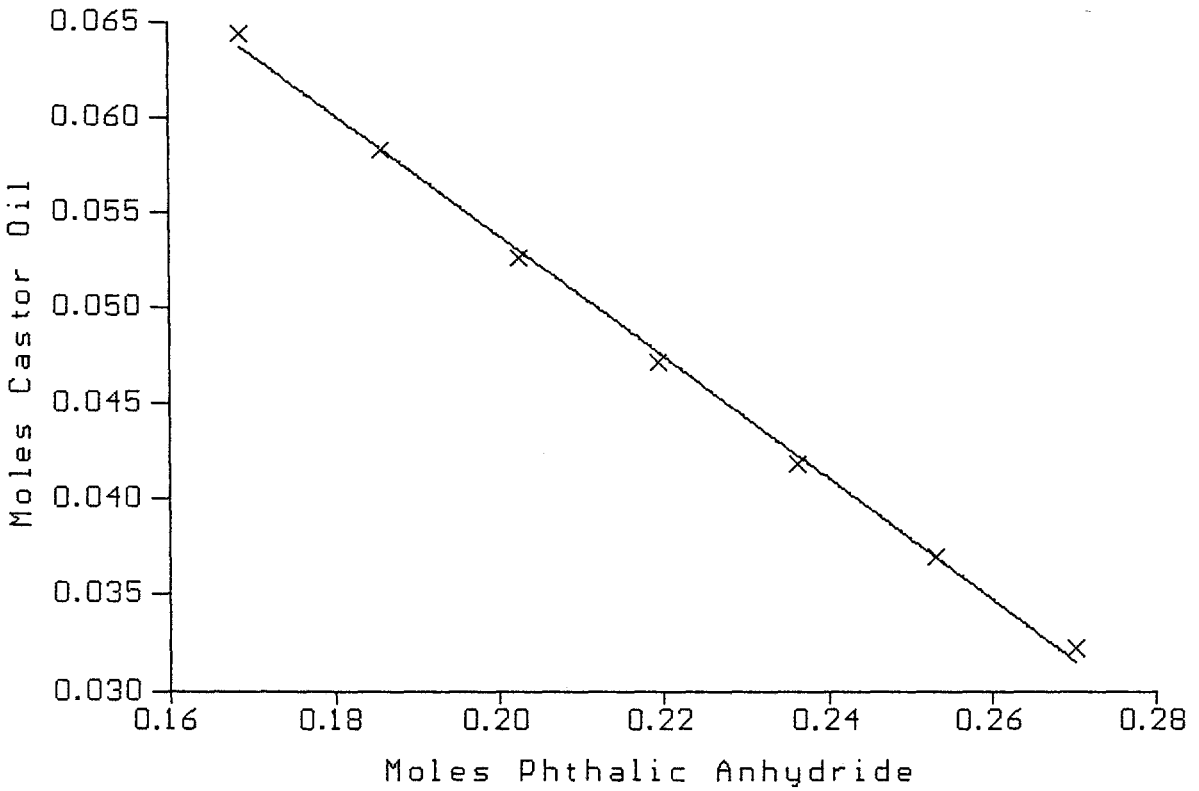


Figure 2.3. : Model Formulation Equation 3.5. - Moles Castor Oil (Z_m) versus Moles Phthalic Anhydride (X_m).

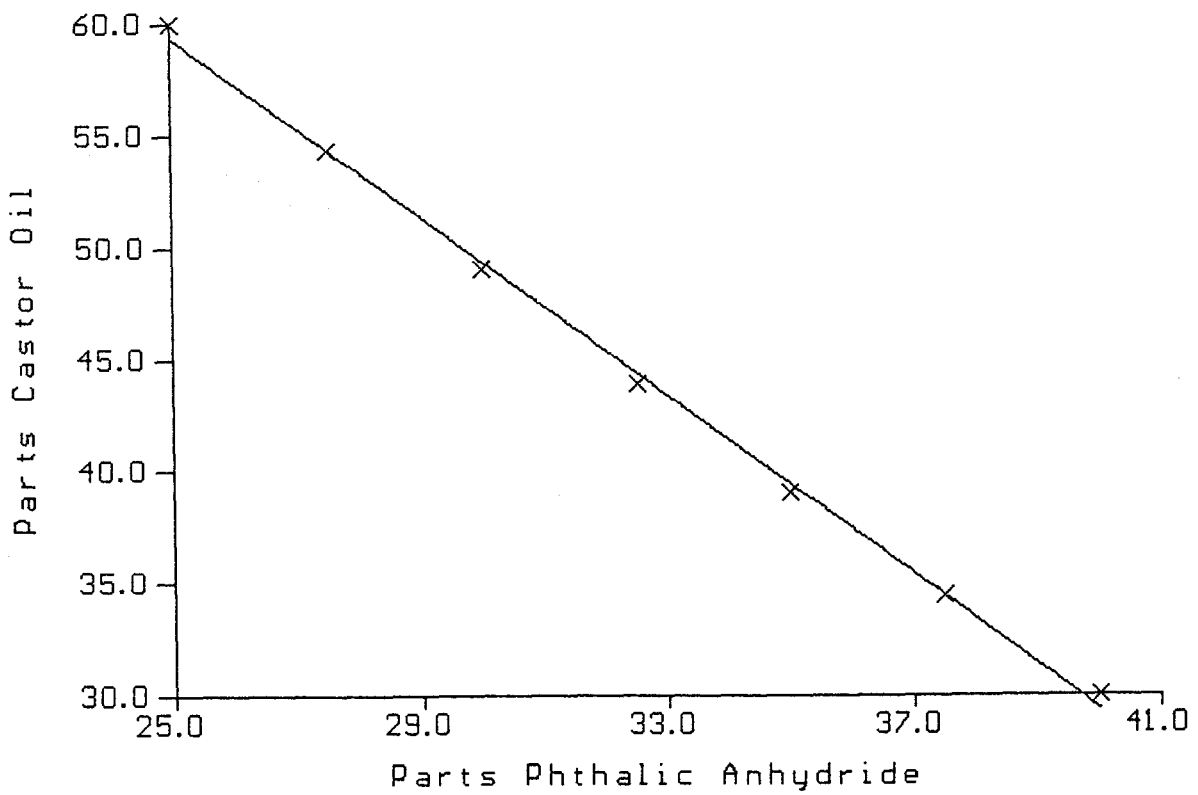


Figure 2.4. : Model Formulation Equation 3.6. - Parts Castor Oil (Z_p) versus Parts Phthalic Anhydride (X_p).

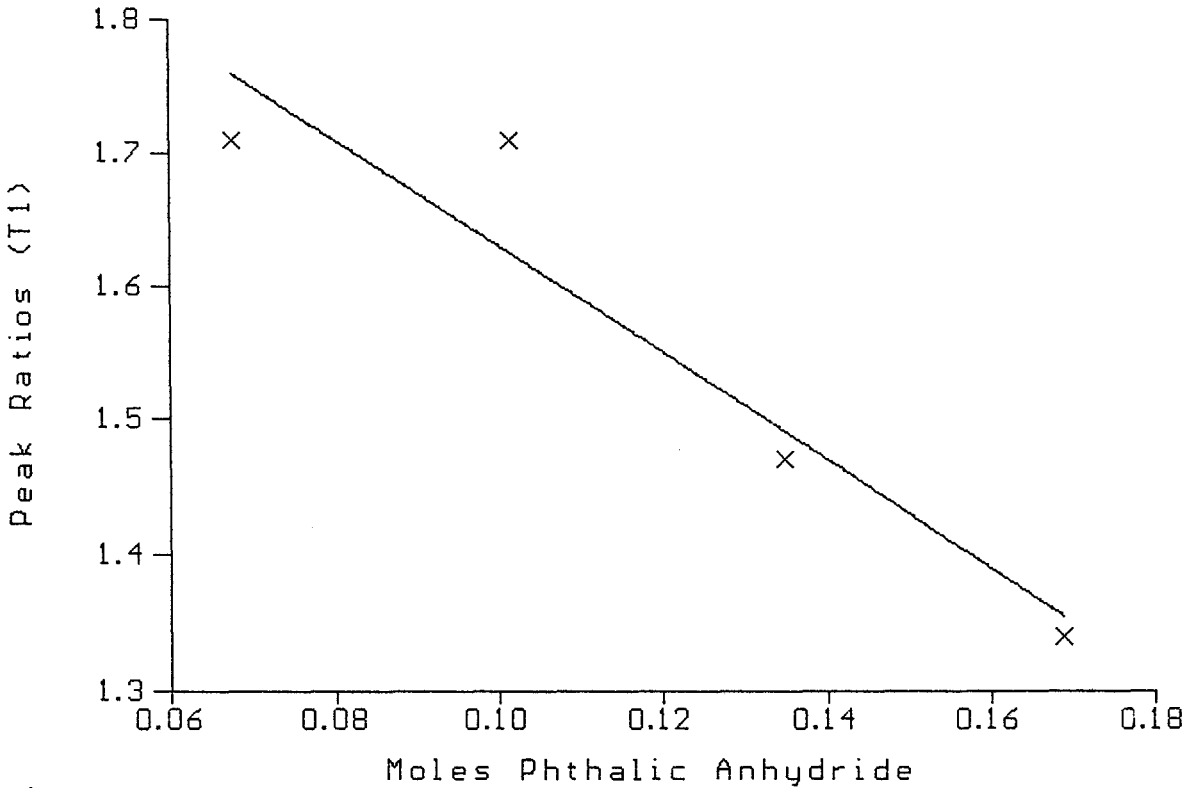


Figure 3.1. : Series 1 Series Dependent Correlation Equation 3.9. Peak Ratios (T_1) versus Moles Phthalic Anhydride (X_{m1}).

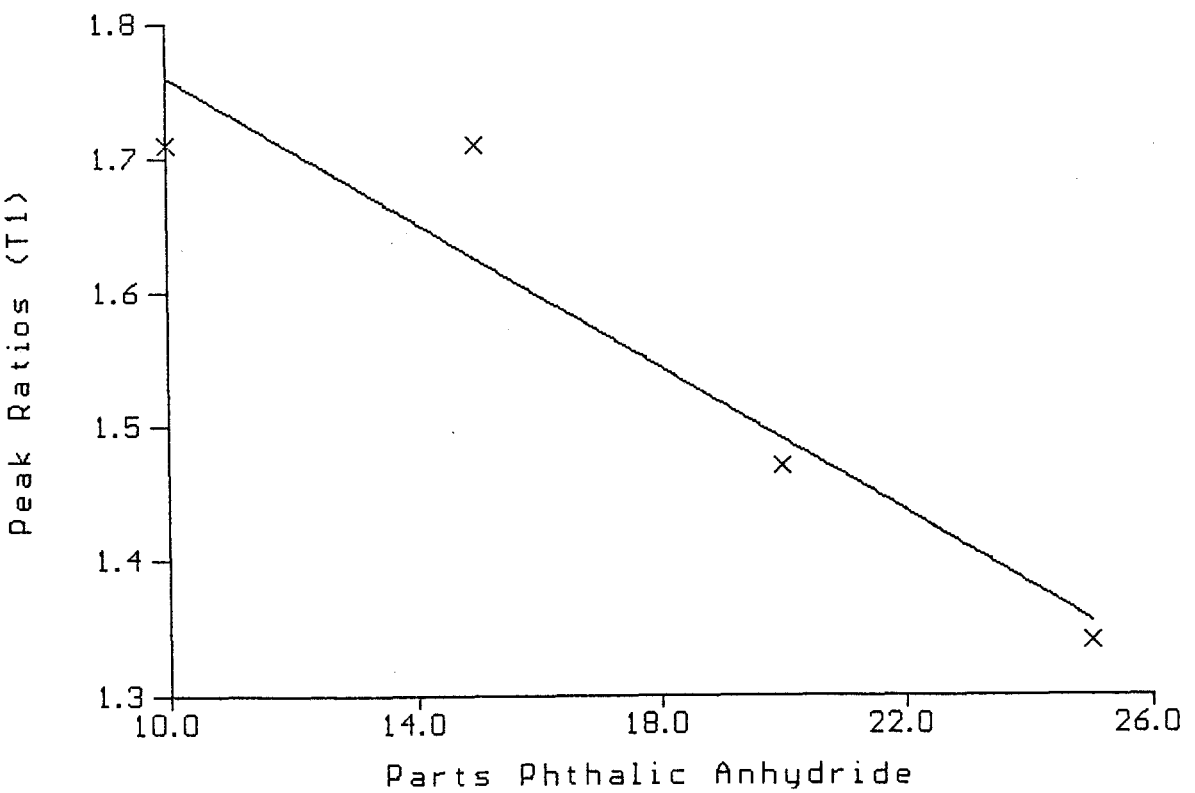


Figure 3.2. : Series 1 Series Dependent Correlation Equation 3.10, Peak Ratios (T_1) versus Parts Phthalic Anhydride (X_{p1}).

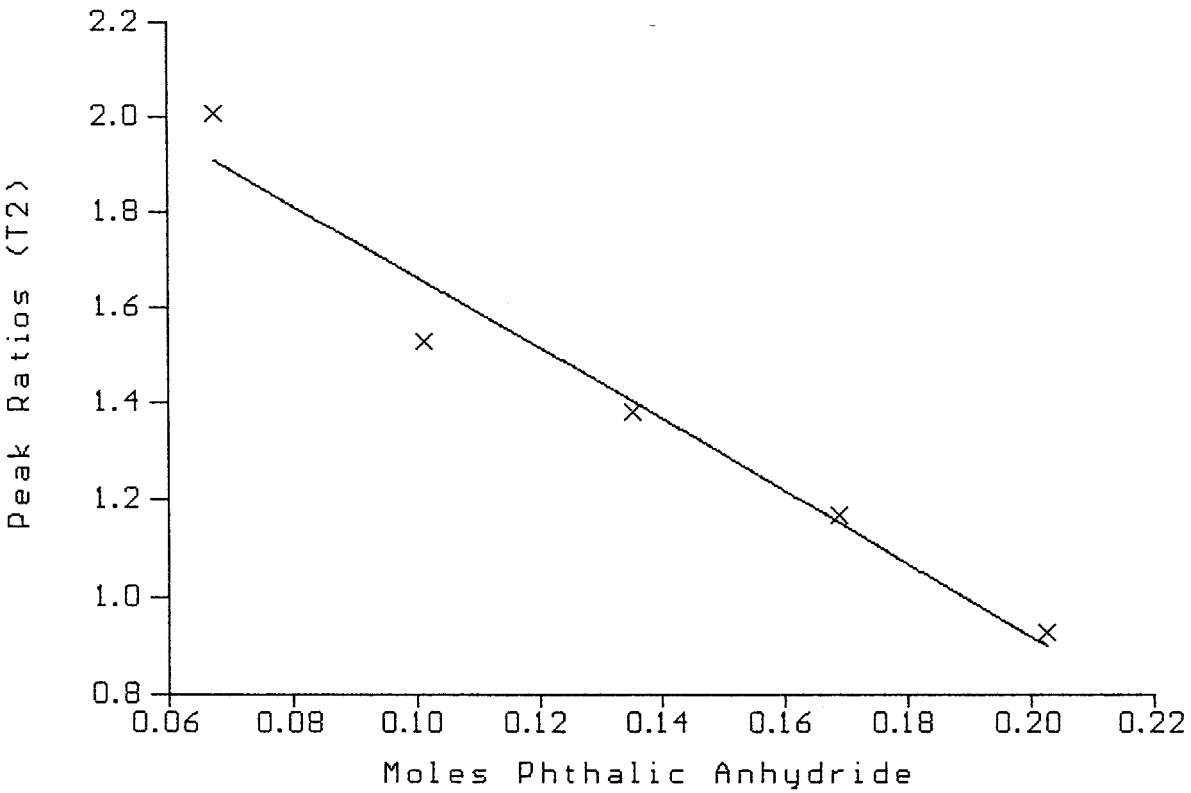


Figure 3.3. : Series 2 Series Dependent Correlation Equation 3.11. Peak Ratios (T_2) versus Moles Phthalic Anhydride (X_{m2}).

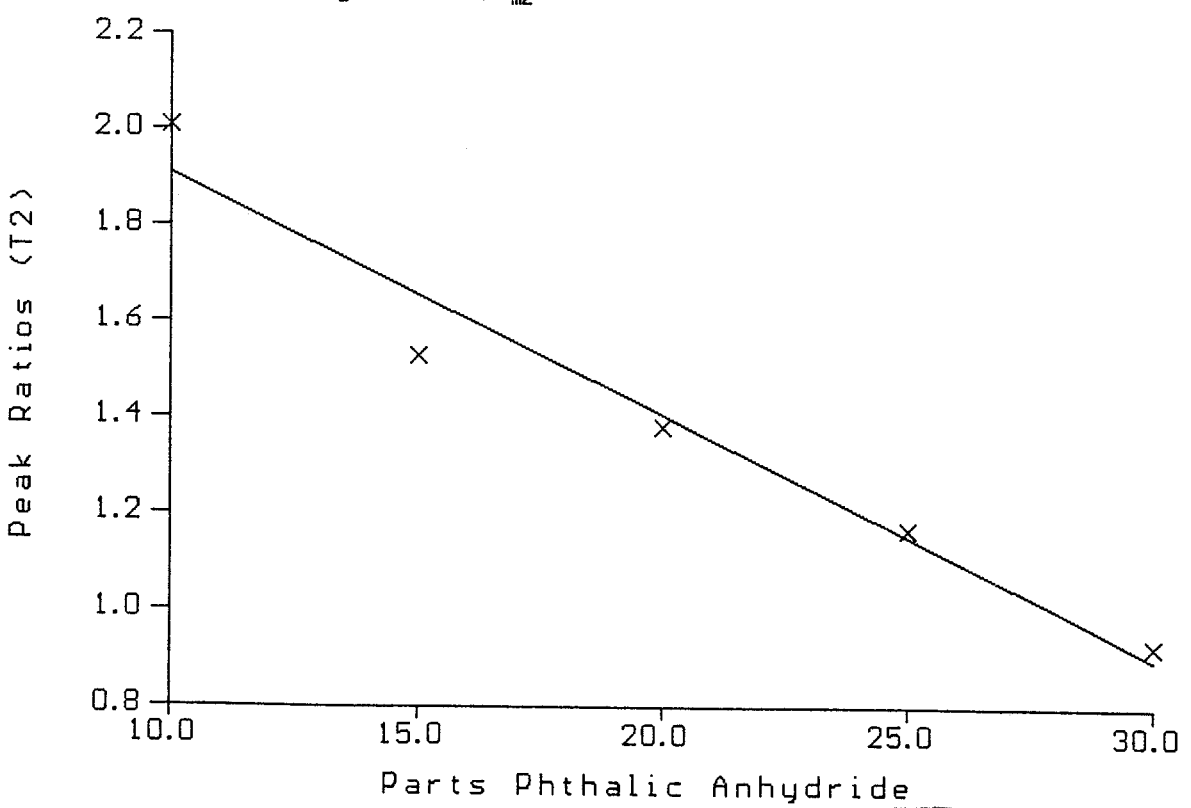


Figure 3.4. : Series 2 Series Dependent Correlation Equation 3.12. Peak Ratios (T_2) versus Parts Phthalic Anhydride (X_{p2}).

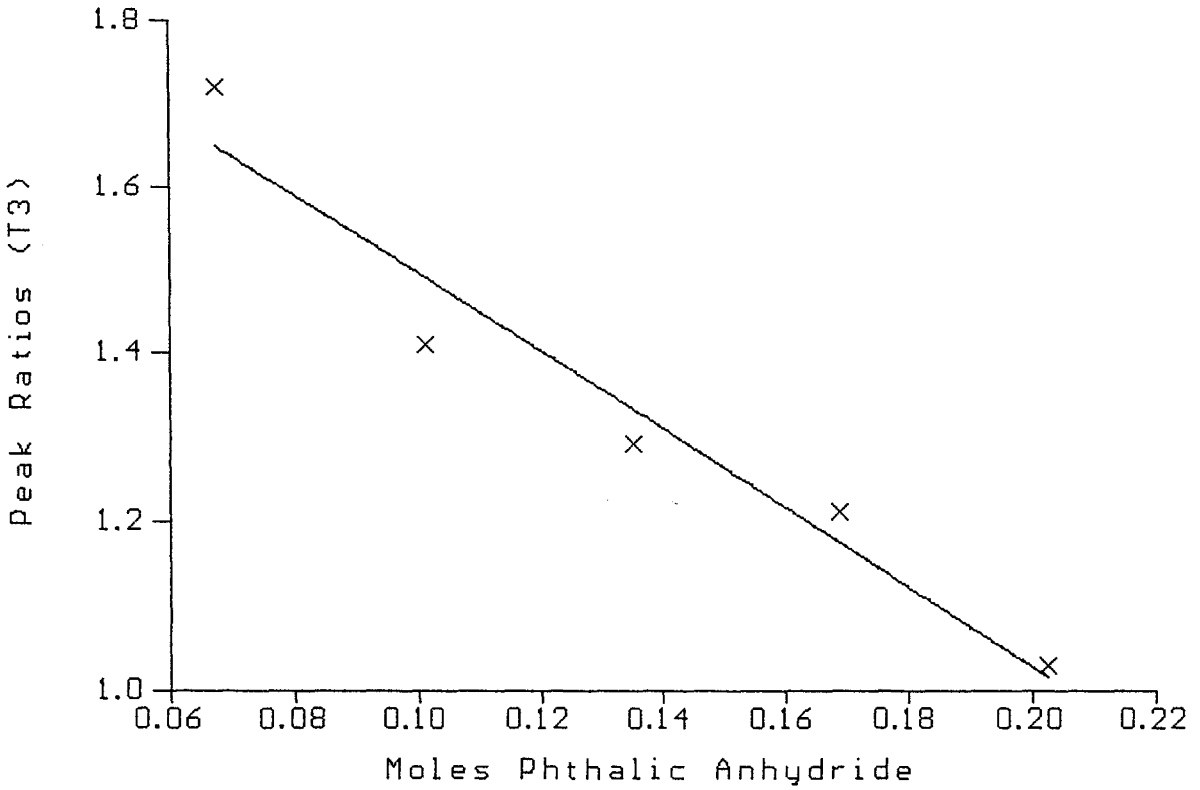


Figure 3.5. : Series 3 Series Dependent Correlation Equation 3.13. Peak Ratios (T_3) versus Moles Phthalic Anhydride (X_{m3}).

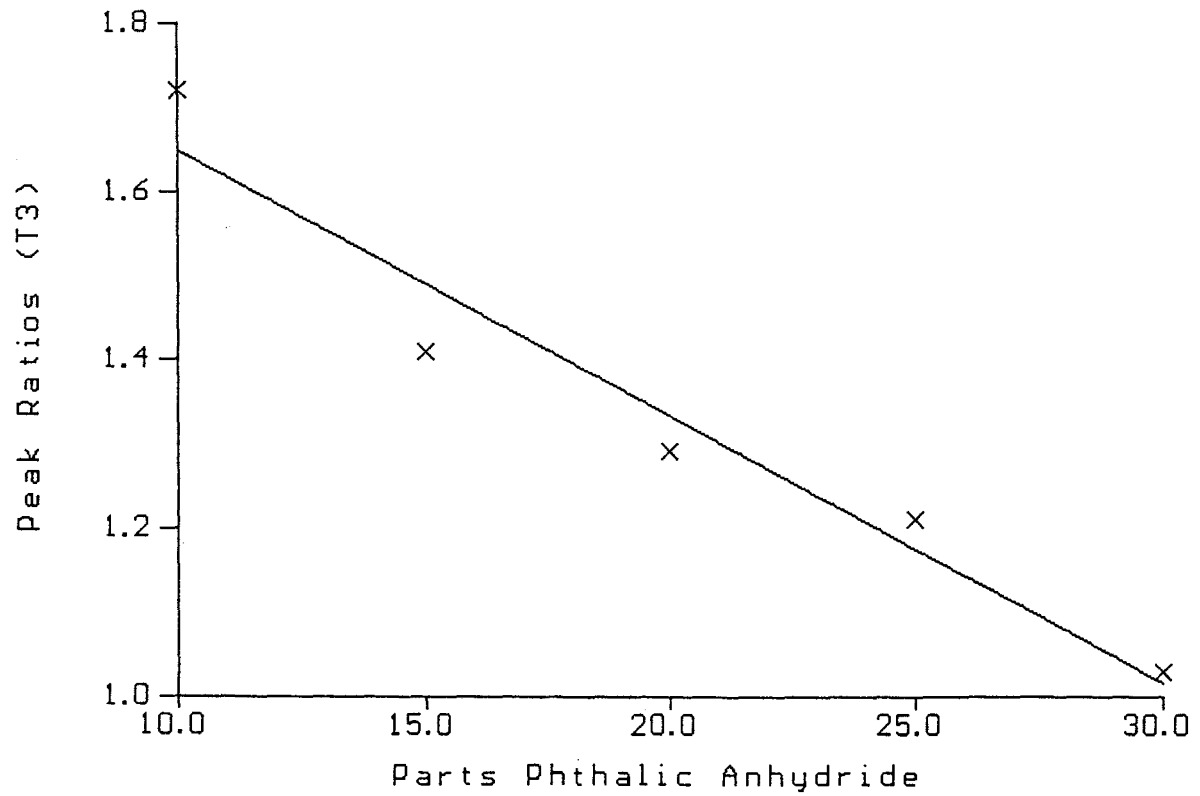


Figure 3.6. : Series 3 Series Dependent Correlation Equation 3.14. Peak Ratios (T_3) versus Parts Phthalic Anhydride (X_{p1}).

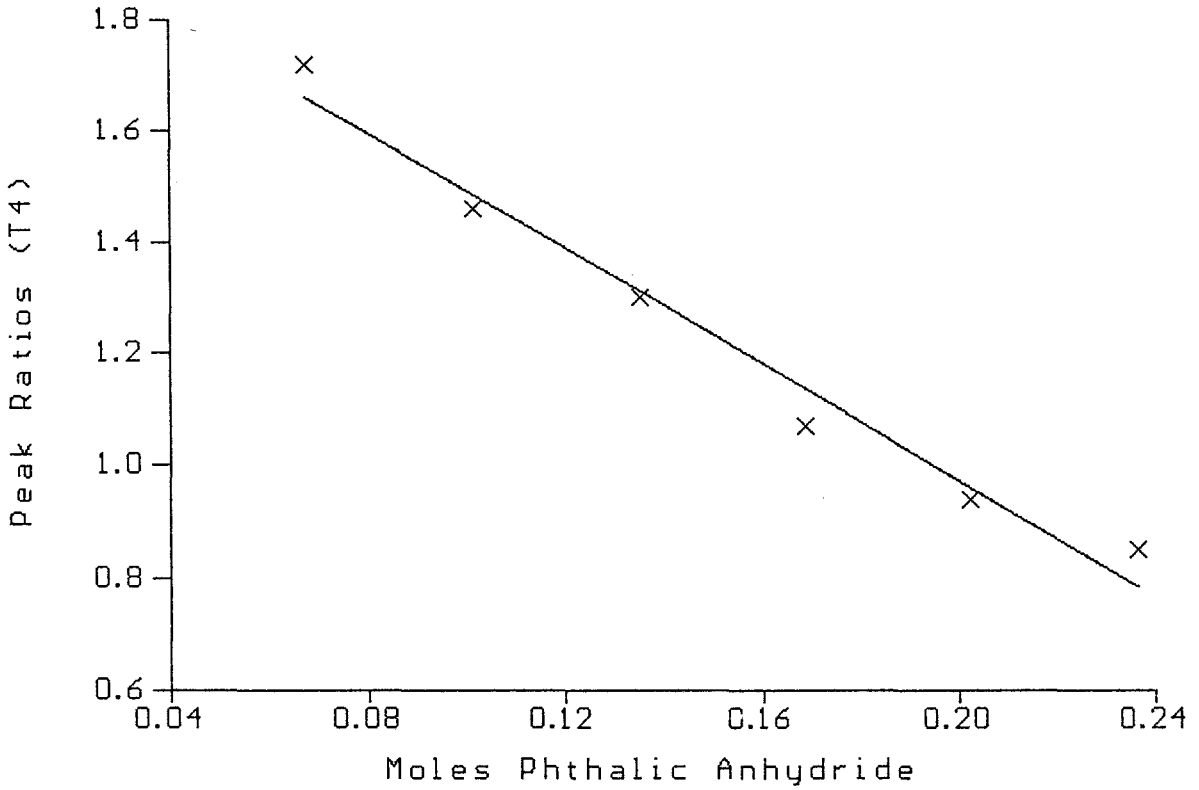


Figure 3.7. : Series 4 Series Dependent Correlation Equation 3.15. Peak Ratios (T_4) versus Moles Phthalic Anhydride (X_{m4}).

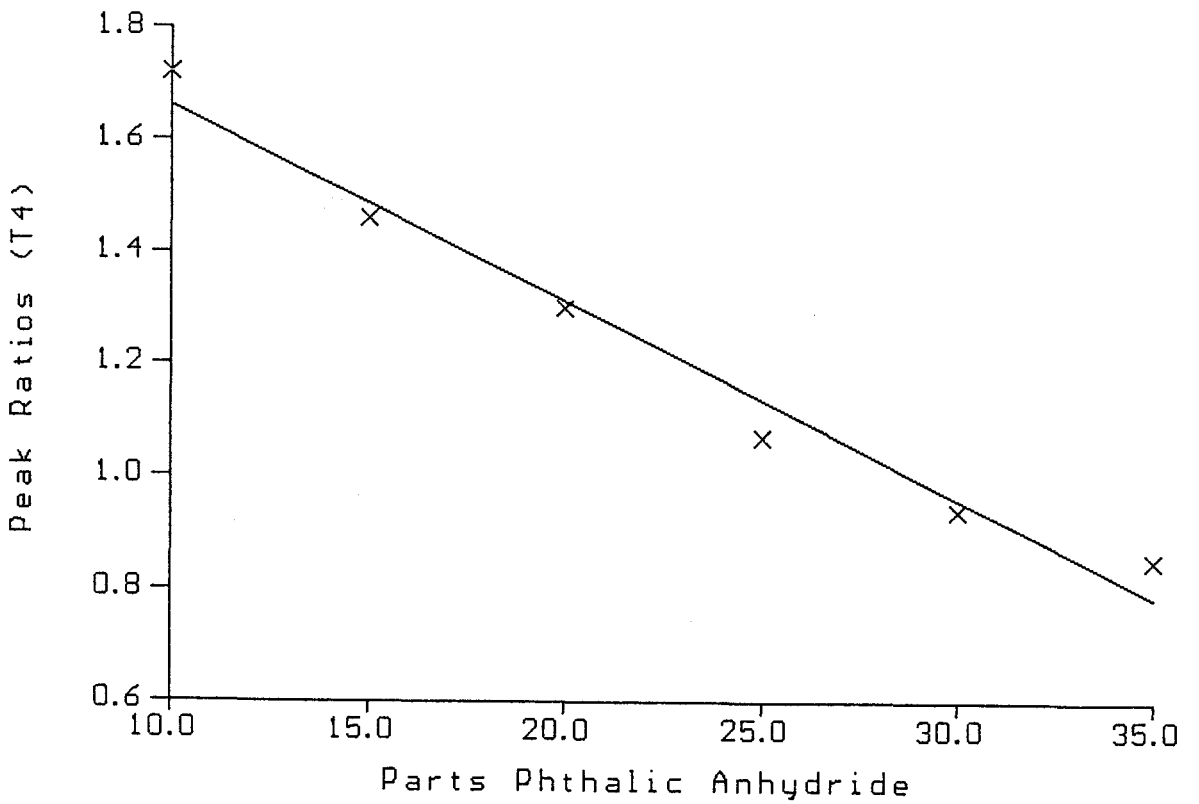


Figure 3.8. : Series 4 Series Dependent Correlation Equation 3.16. Peak Ratios (T_4) versus Parts Phthalic Anhydride (X_{p4}).

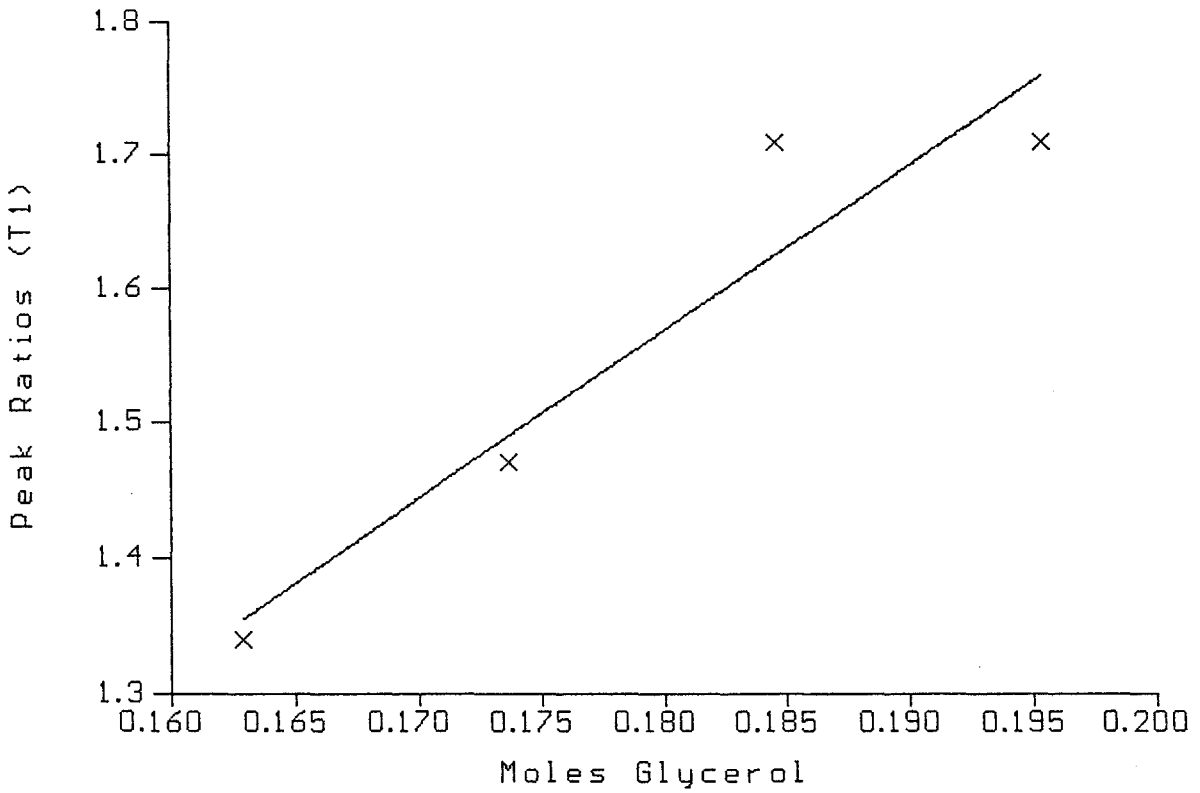


Figure 3.9. : Series 1 Series Dependent Correlation Equation 3.17. Peak Ratios (T_1) versus Moles Glycerol (Y_{m1}).

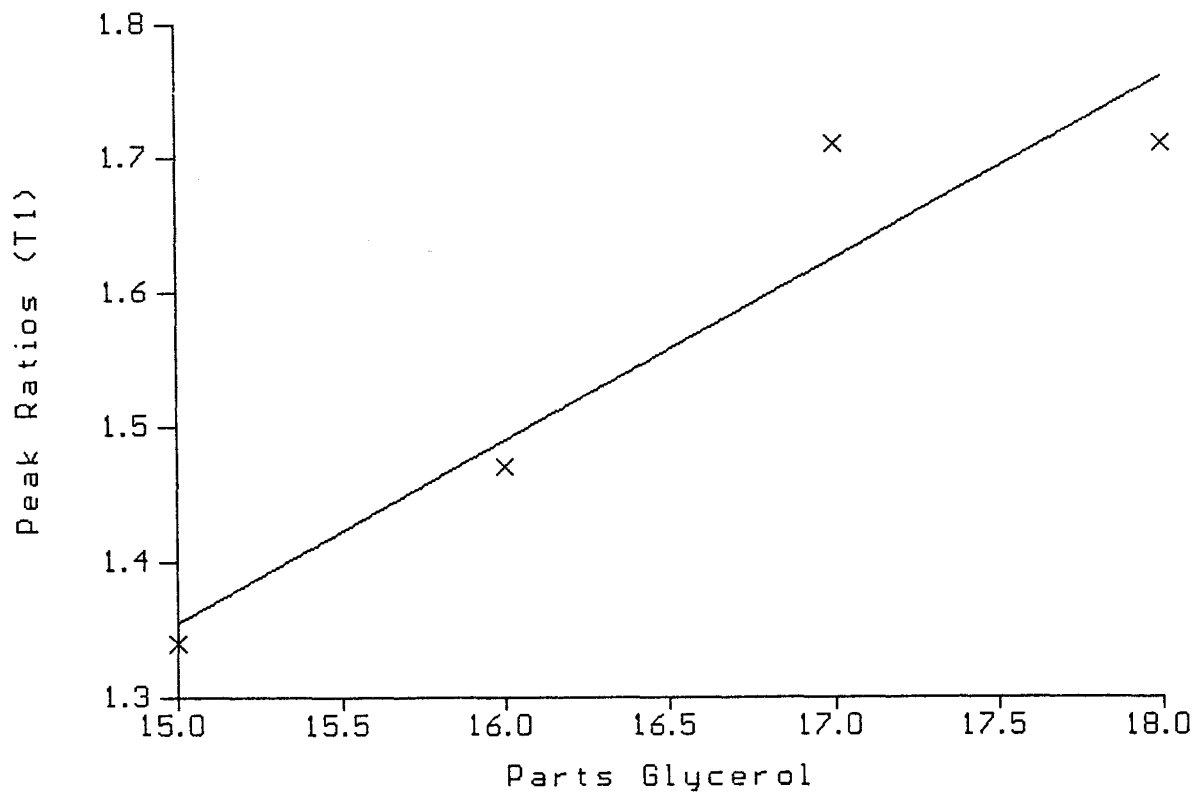


Figure 3.10. : Series 1 Series Dependent Correlation Equation 3.18. Peak Ratios (T_1) versus Parts Glycerol (Y_{p1}).

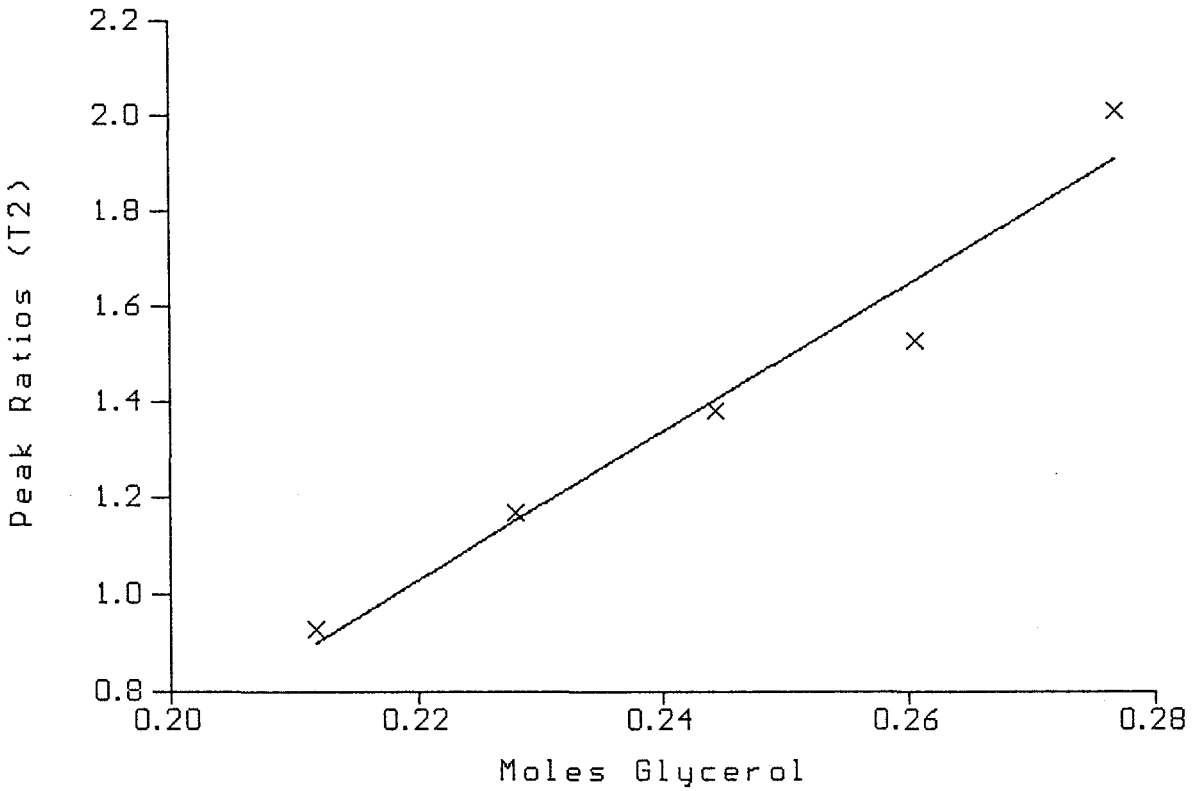


Figure 3.11. : Series 2 Series Dependent Correlation Equation 3.19. Peak Ratios (T_2) versus Moles Glycerol (Y_{m2}).

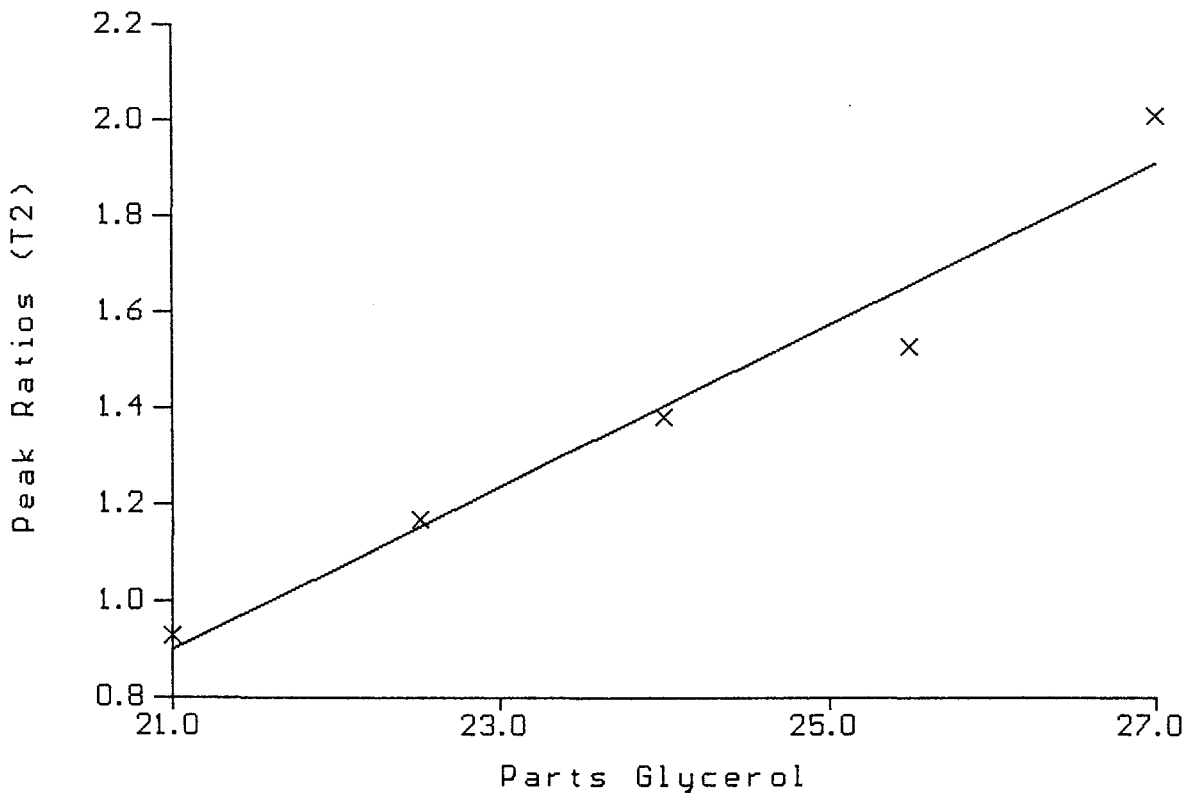


Figure 3.12. : Series 2 Series Dependent Correlation Equation 3.20. Peak Ratios (T_2) versus Parts Glycerol (Y_{p2}).

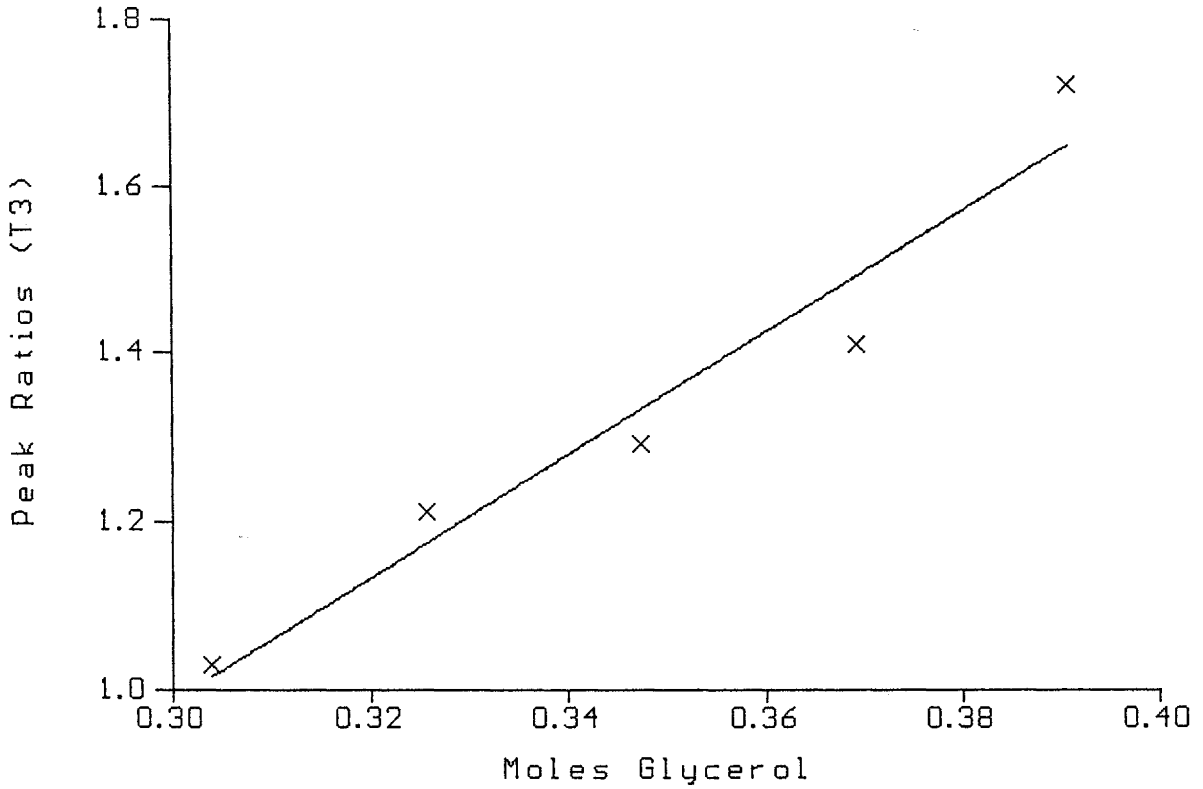


Figure 3.13. : Series 3 Series Dependent Correlation Equation 3.21. Peak Ratios (T_3) versus Moles Glycerol (Y_{m3}).

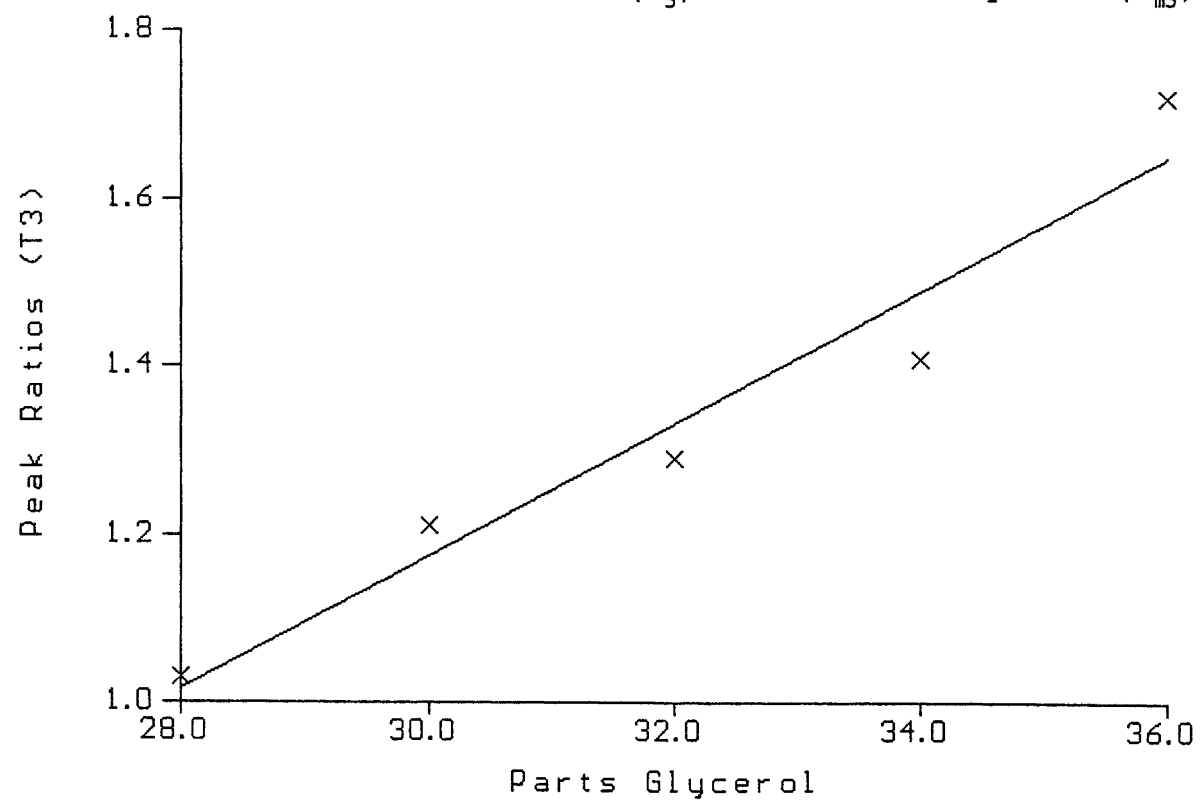


Figure 3.14. : Series 3 Series Dependent Correlation Equation 3.22. Peak Ratios (T_3) versus Parts Glycerol (Y_{p1}).

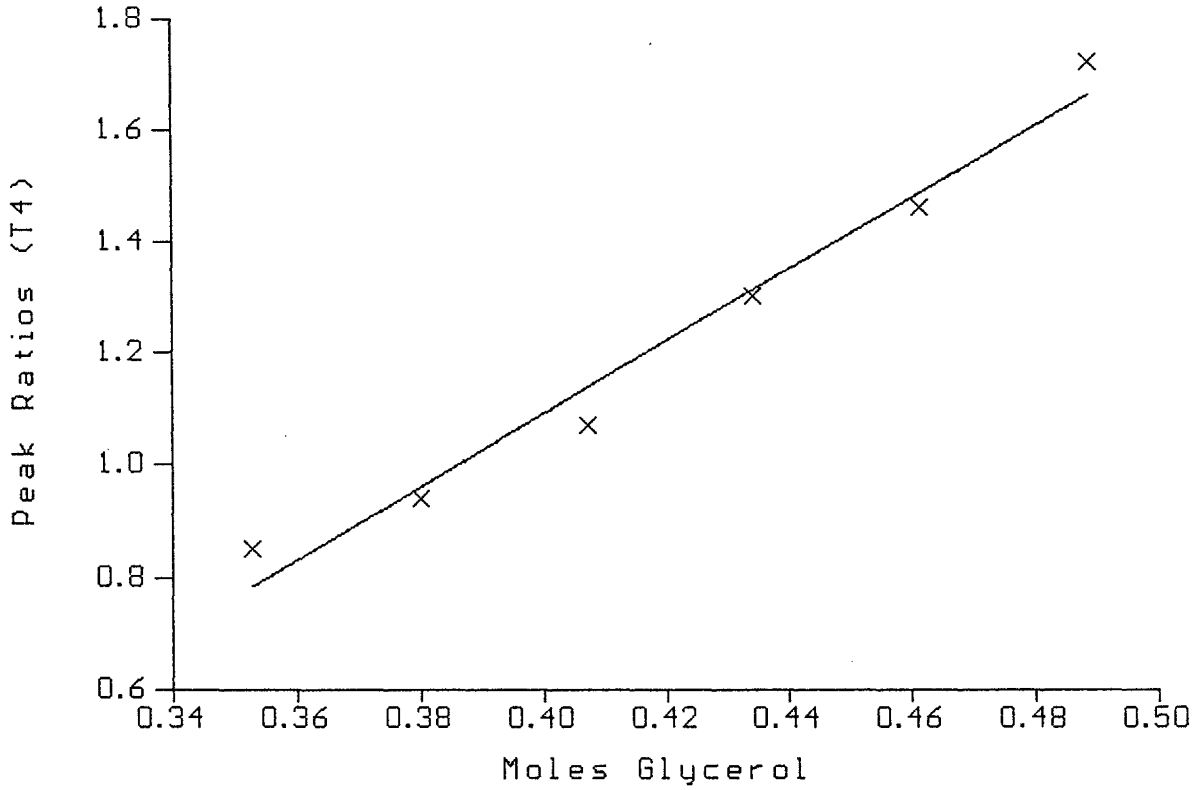


Figure 3.15. : Series 4 Series Dependent Correlation Equation 3.23. Peak Ratios (T_4) versus Moles Glycerol (Y_{m4}).

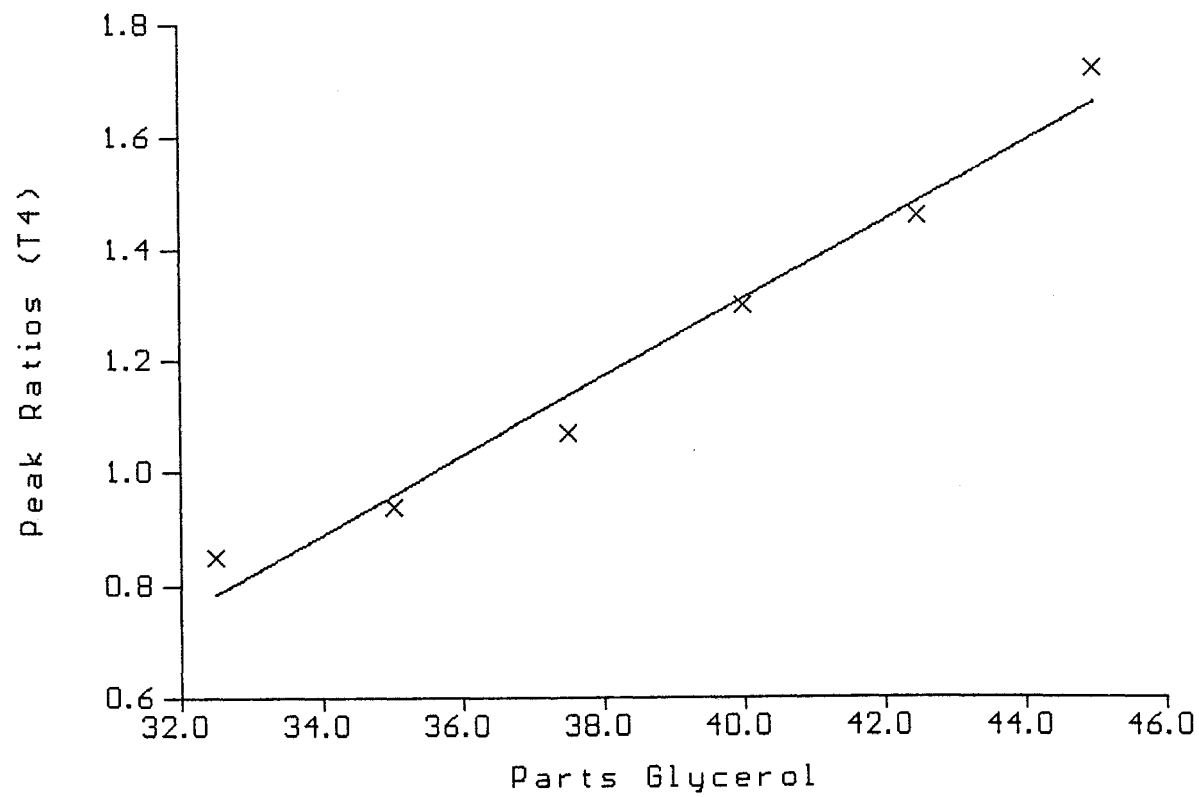


Figure 3.16. : Series 4 Series Dependent Correlation Equation 3.24. Peak Ratios (T_4) versus Parts Glycerol (Y_{p4}).

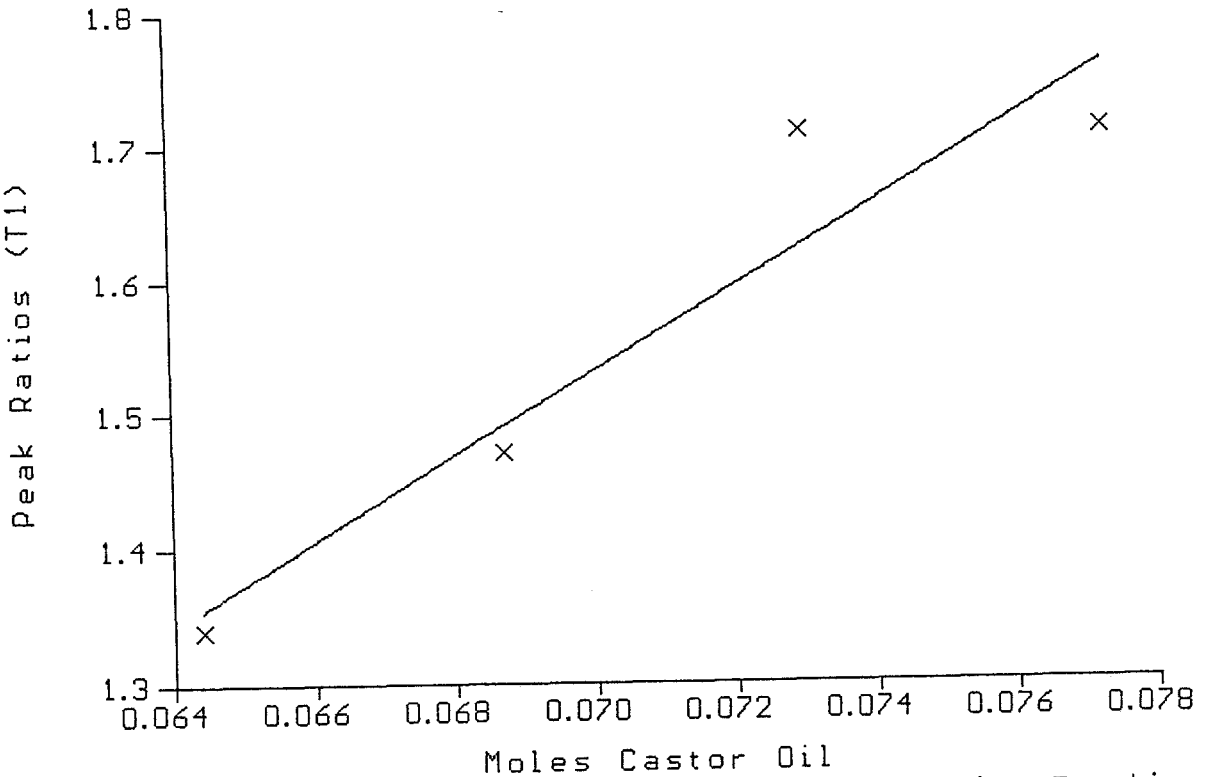


Figure 3.17. : Series 1 Series Dependent Correlation Equation 3.25. Peak Ratios (T_1) versus Moles Castor Oil (Z_{m1}).

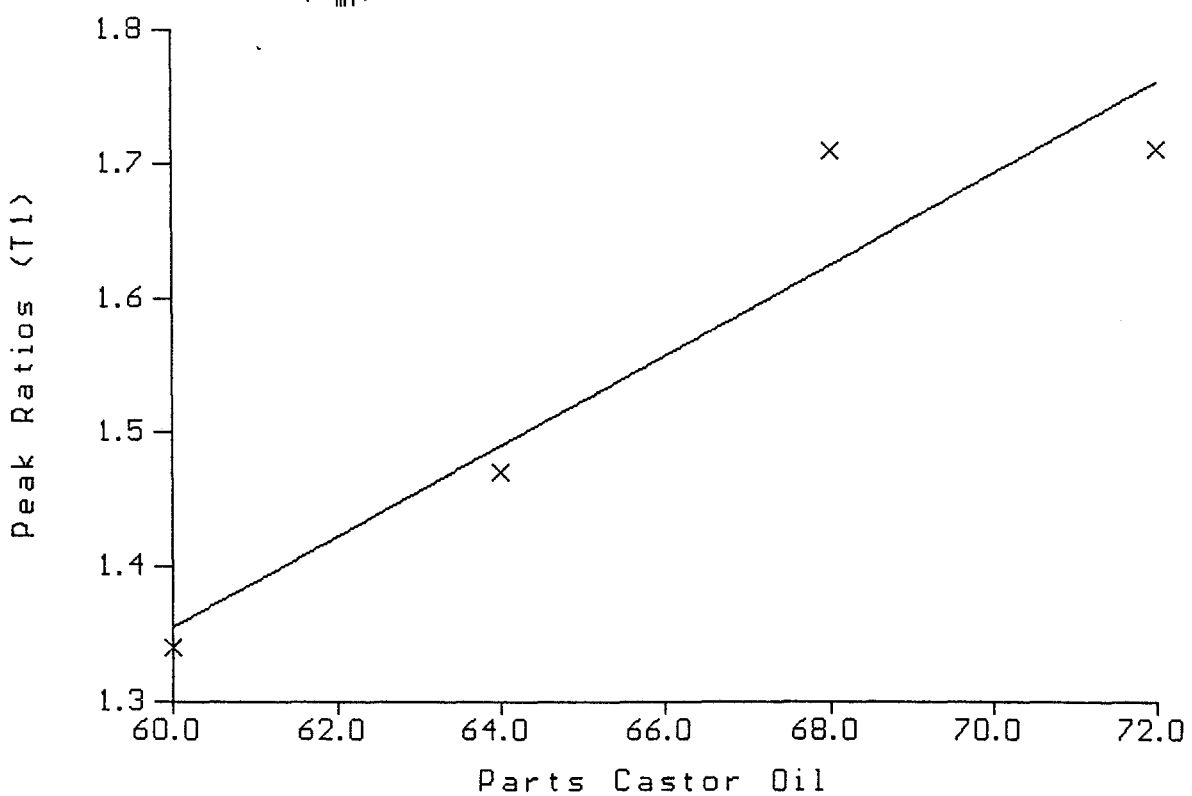


Figure 3.18. : Series 1 Series Dependent Correlation Equation 3.26. Peak Ratios (T_1) versus Parts Castor Oil (Z_{p1}).

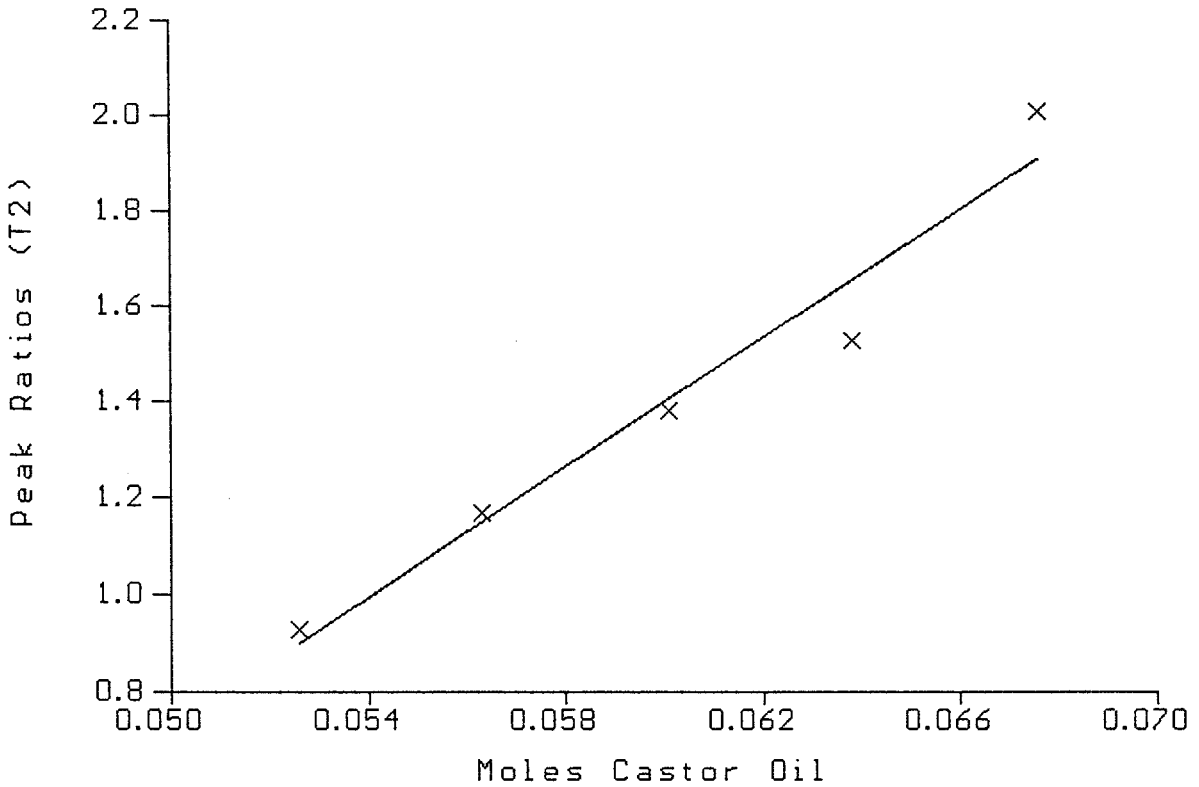


Figure 3.19. : Series 2 Series Dependent Correlation Equation 3.27. Peak Ratios (T_2) versus Moles Castor Oil (Z_{m2}).

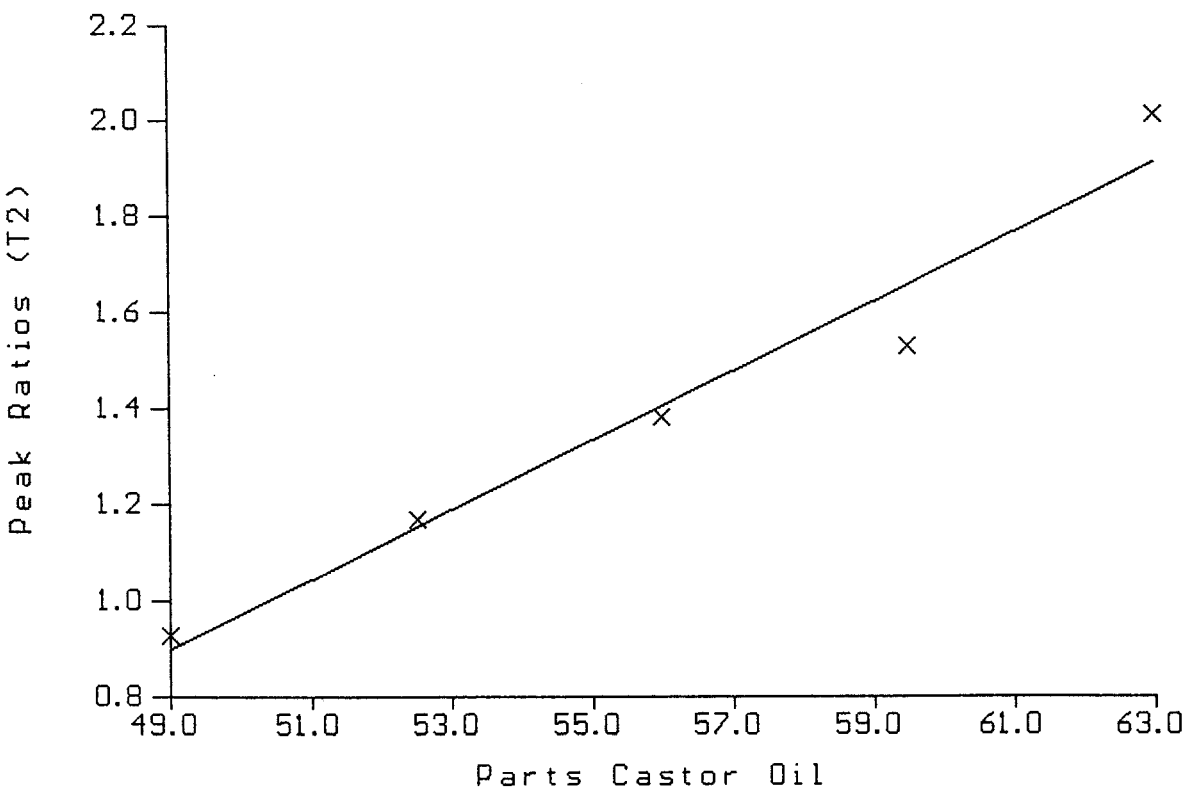


Figure 3.20. : Series 2 Series Dependent Correlation Equation 3.28. Peak Ratios (T_2) versus Parts Castor Oil (Z_{p2}).

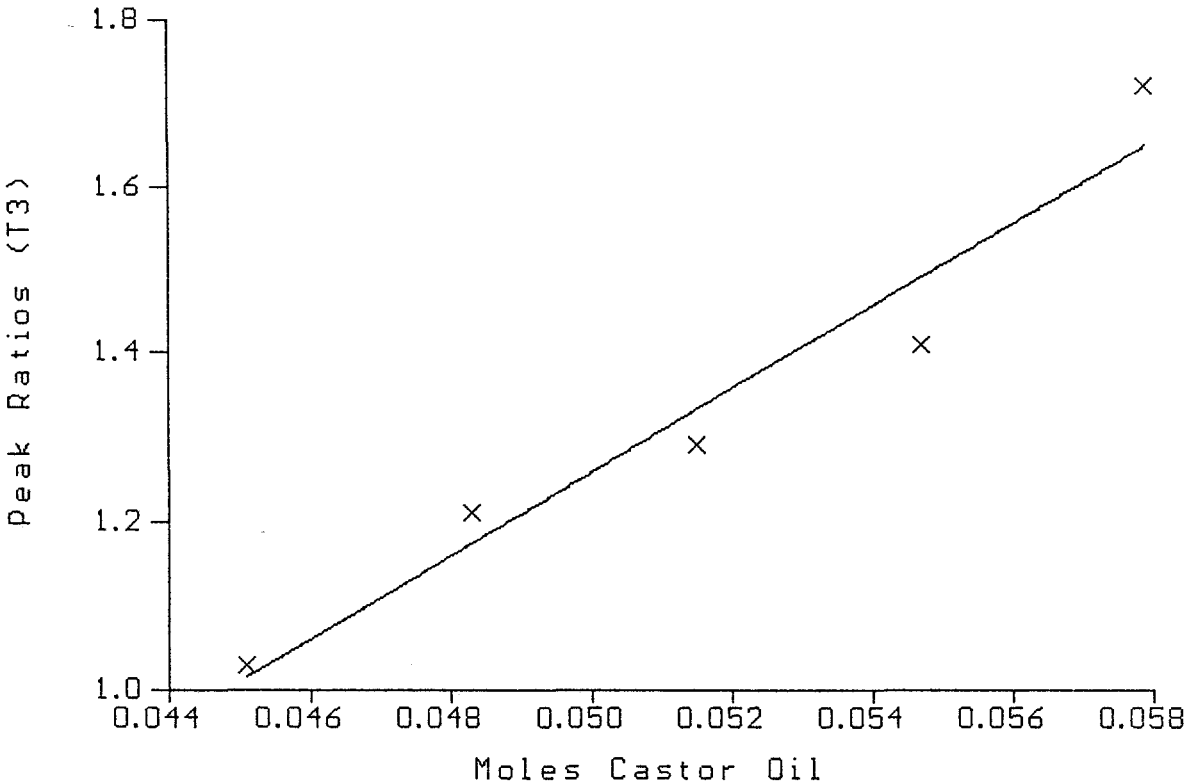


Figure 3.21. : Series 3 Series Dependent Correlation Equation 3.29. Peak Ratios (T_3) versus Moles Castor Oil (Z_{m3}).

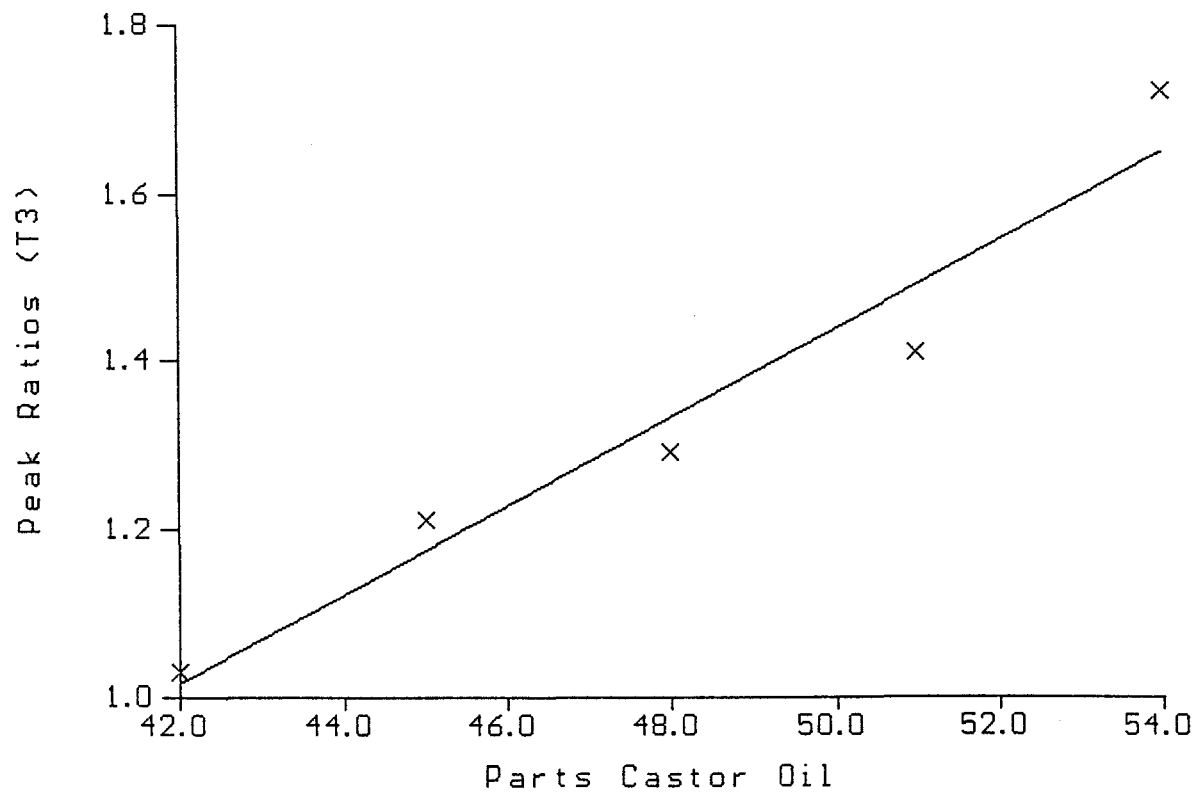


Figure 3.22. : Series 3 Series Dependent Correlation Equation 3.30. Peak Ratios (T_3) versus Parts Castor Oil (Z_{p1}).

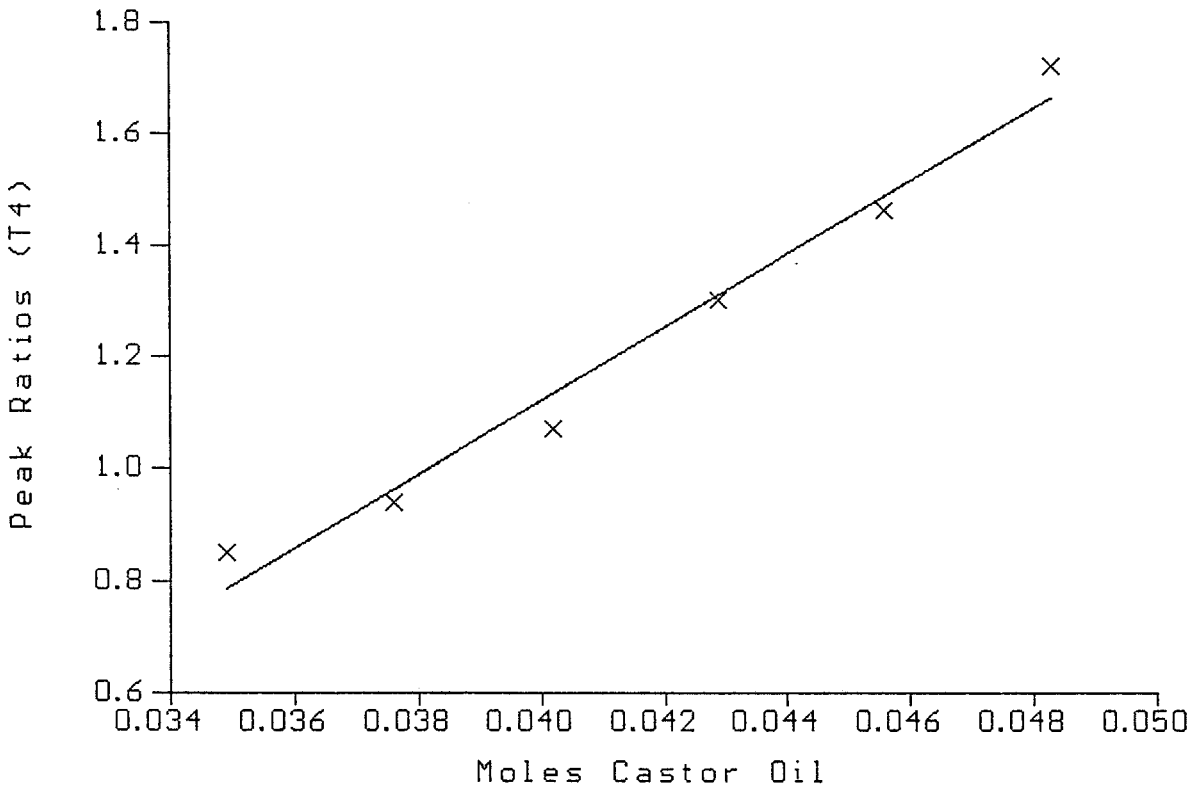


Figure 3.23. : Series 4 Series Dependent Correlation Equation 3.31. Peak Ratios (T_4) versus Moles Castor Oil (Z_{m4}).

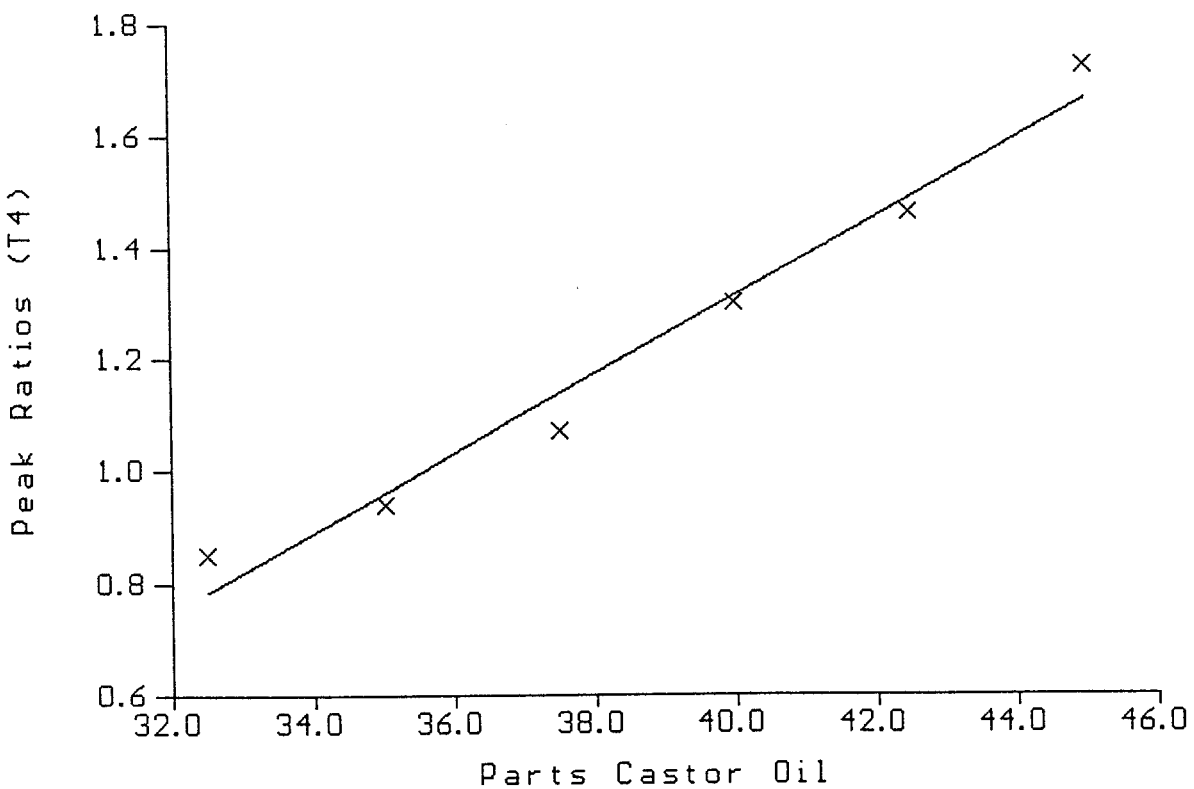


Figure 3.24. : Series 4 Series Dependent Correlation Equation 3.32. Peak Ratios (T_4) versus Parts Castor Oil (Z_{p4}).

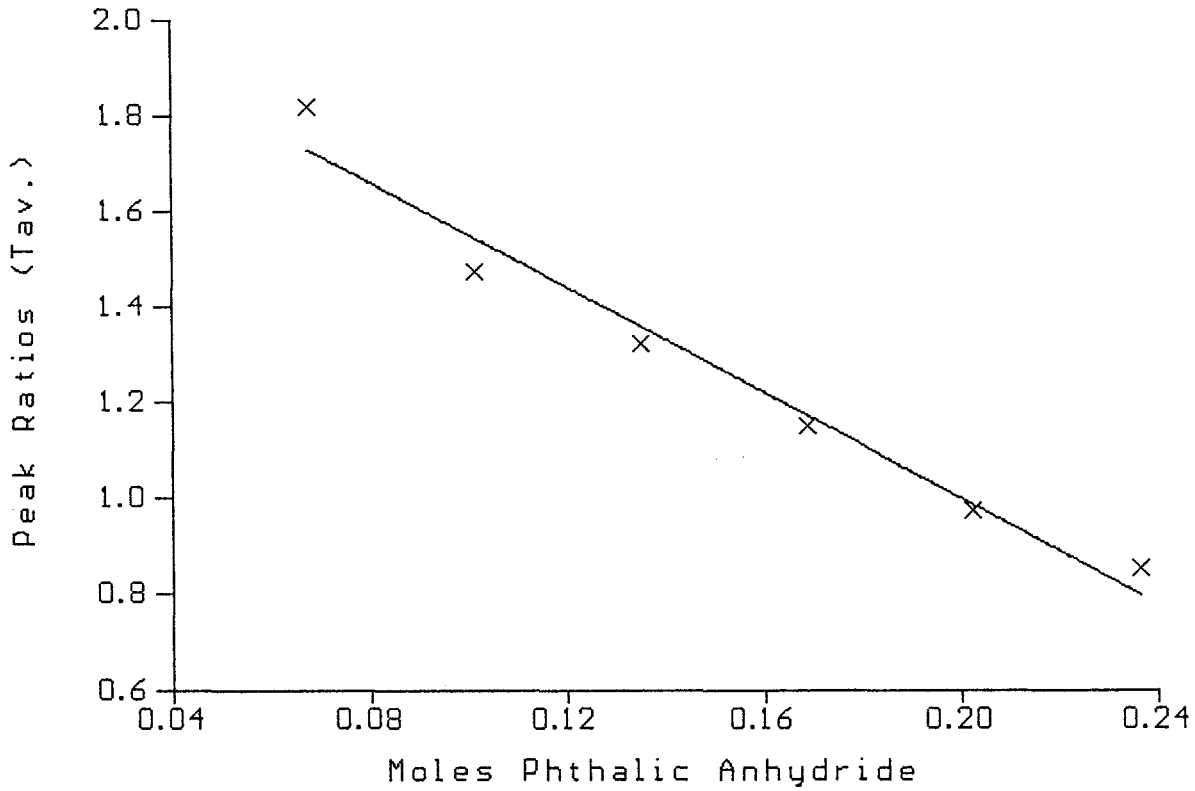


Figure 4.1. : Series Independent Correlation Equation 3.33. Peak Ratios ($T_{av.}$) versus Moles Phthalic Anhydride (Y_m).

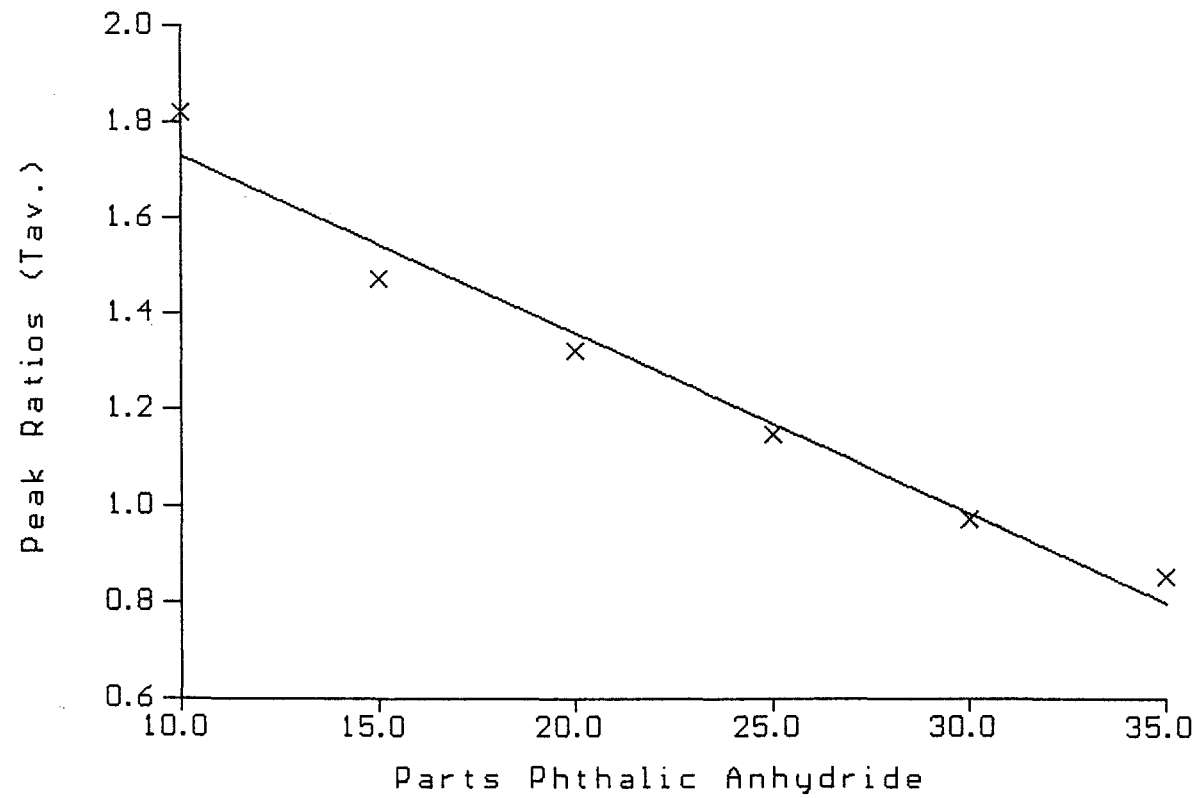
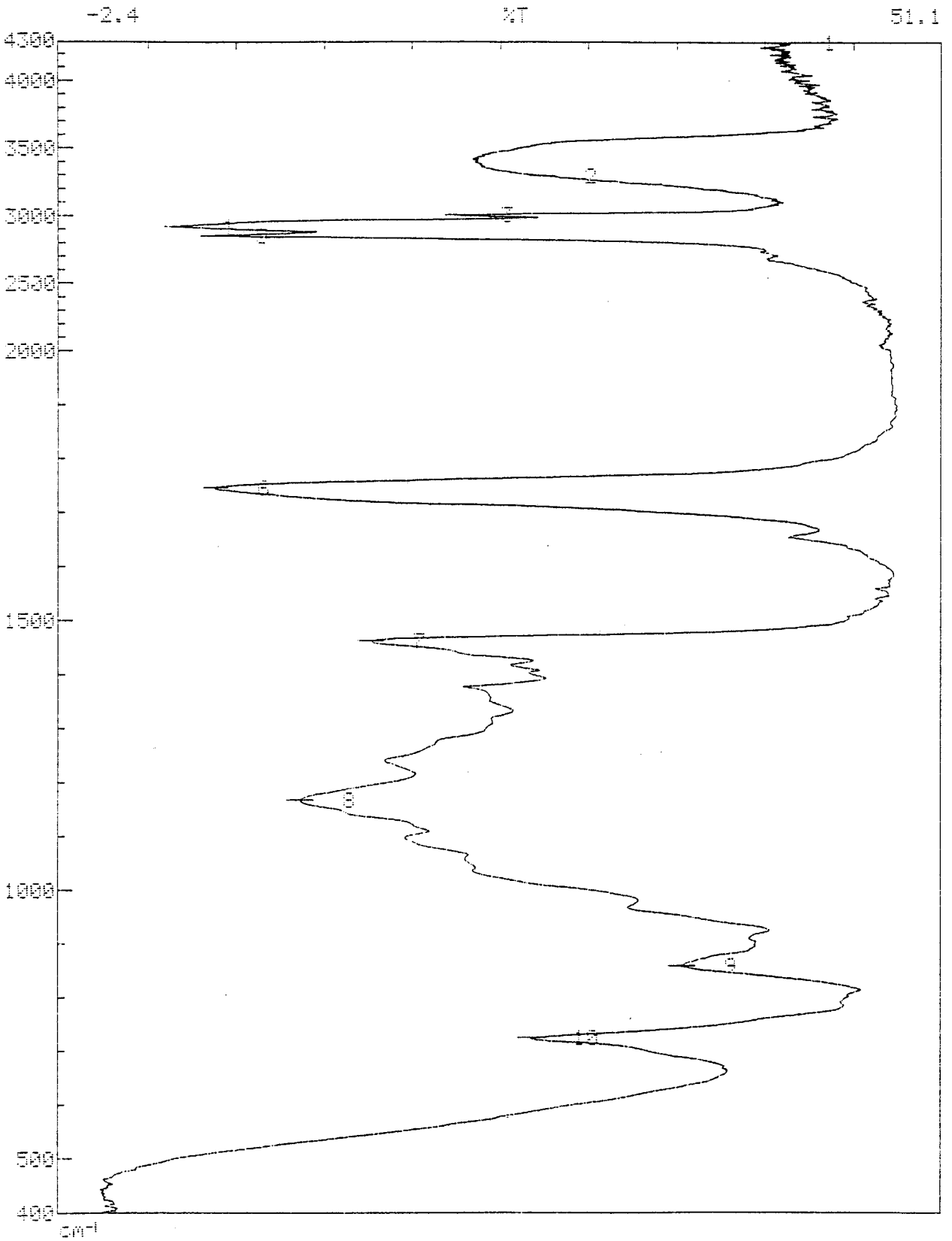
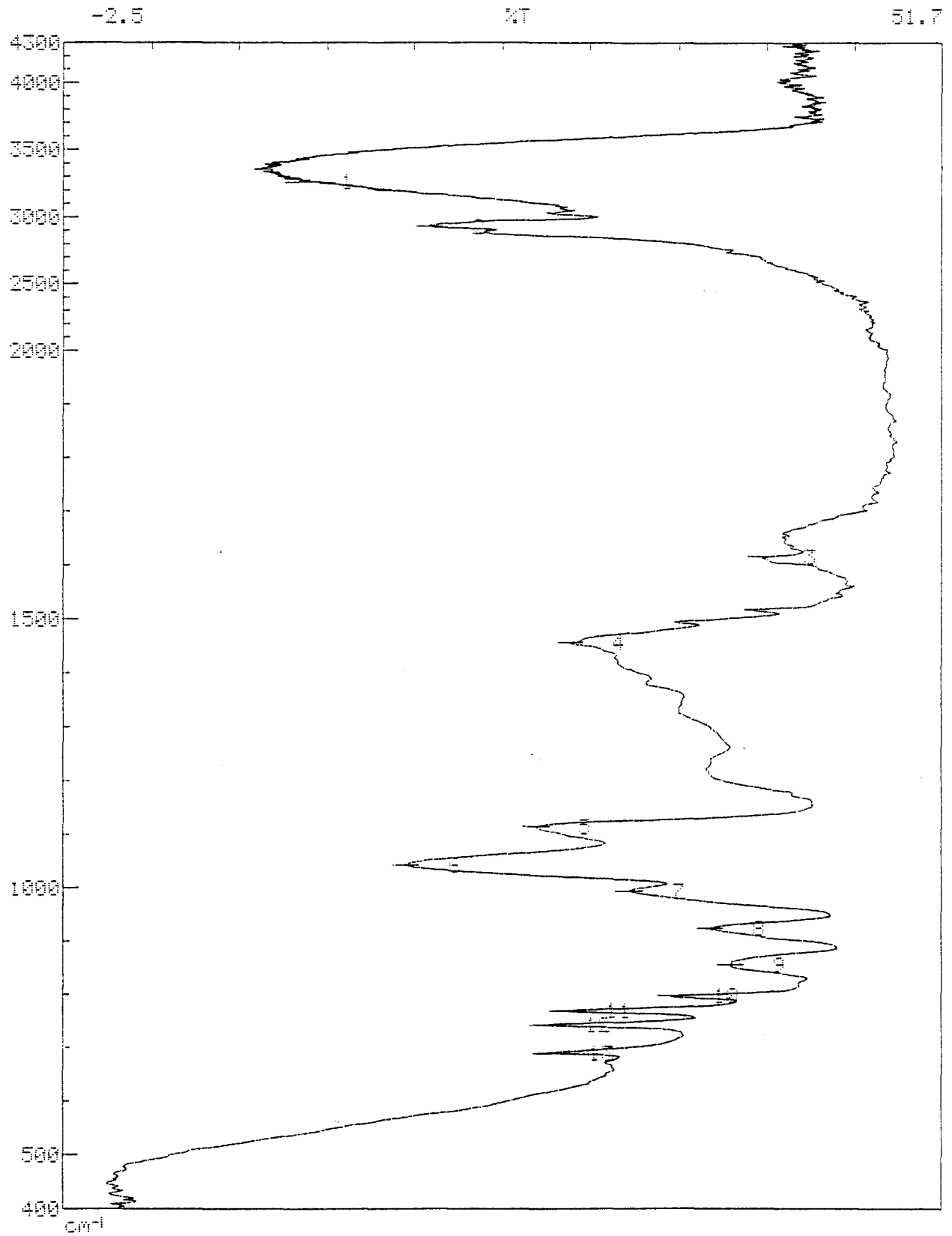


Figure 4.2. : Series Independent Correlation Equation 3.34. Peak Ratios ($T_{av.}$) versus Parts Phthalic Anhydride (Y_p).

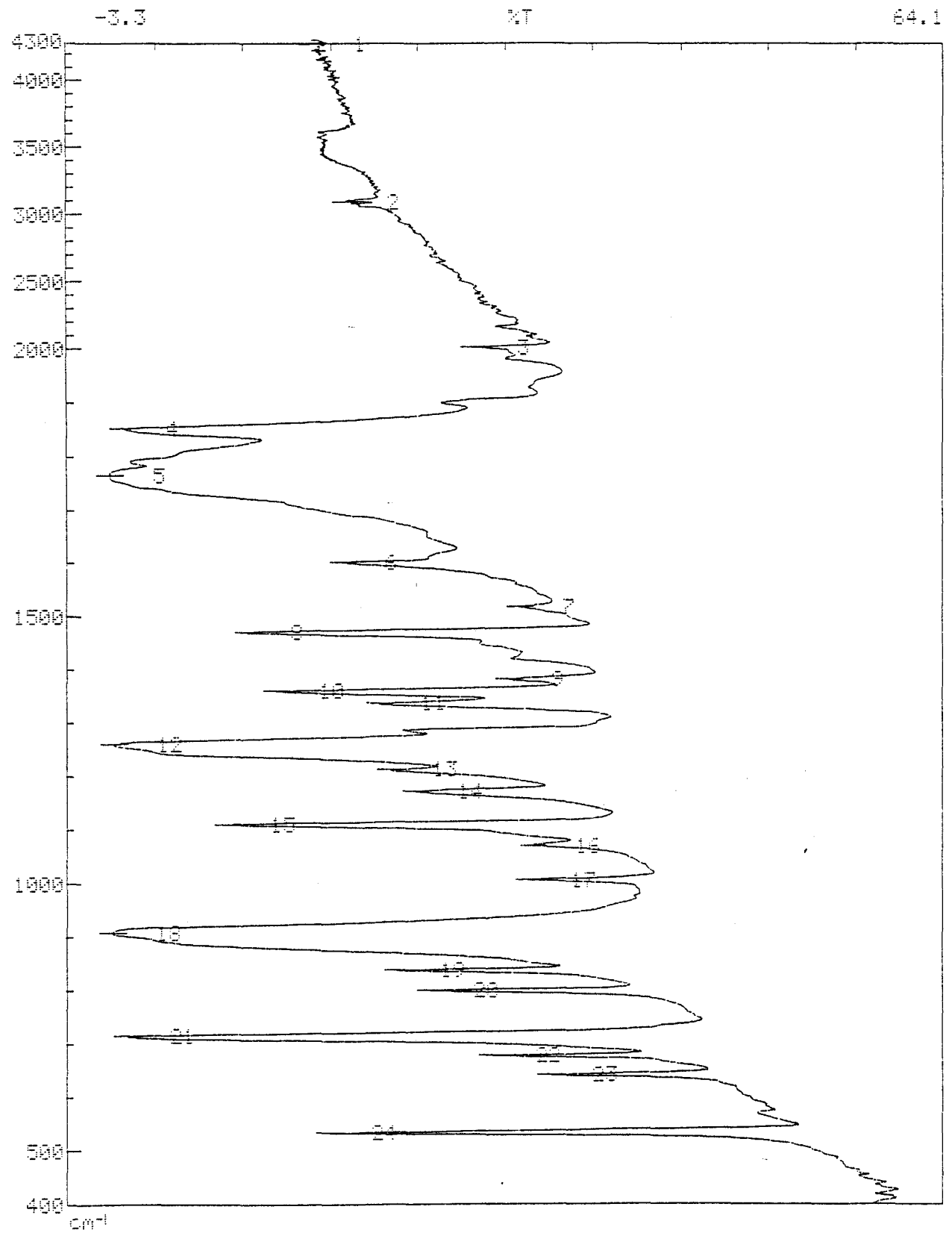
Spectrum 1 : Castor oil



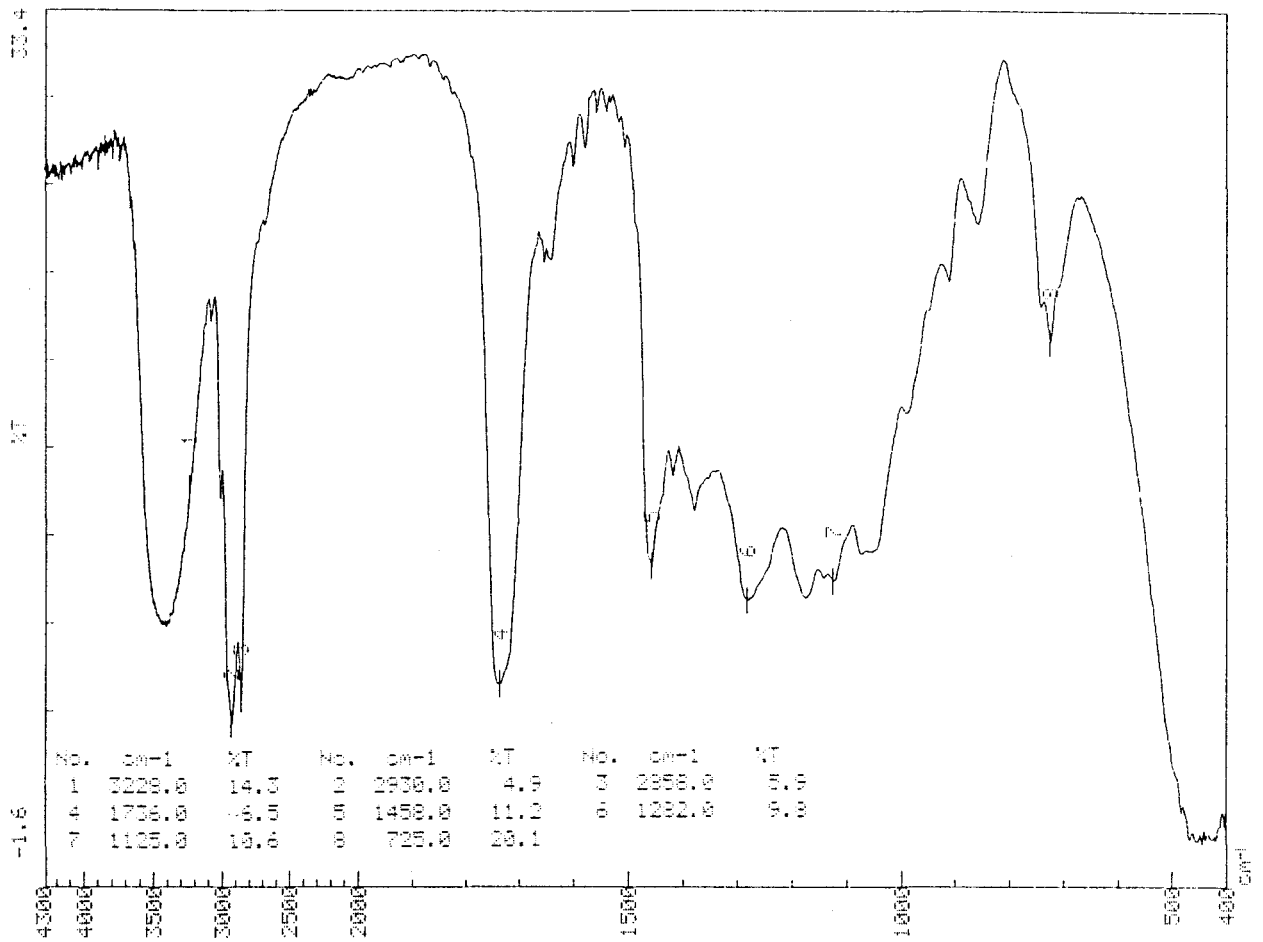
Spectrum 2 : Glycerol



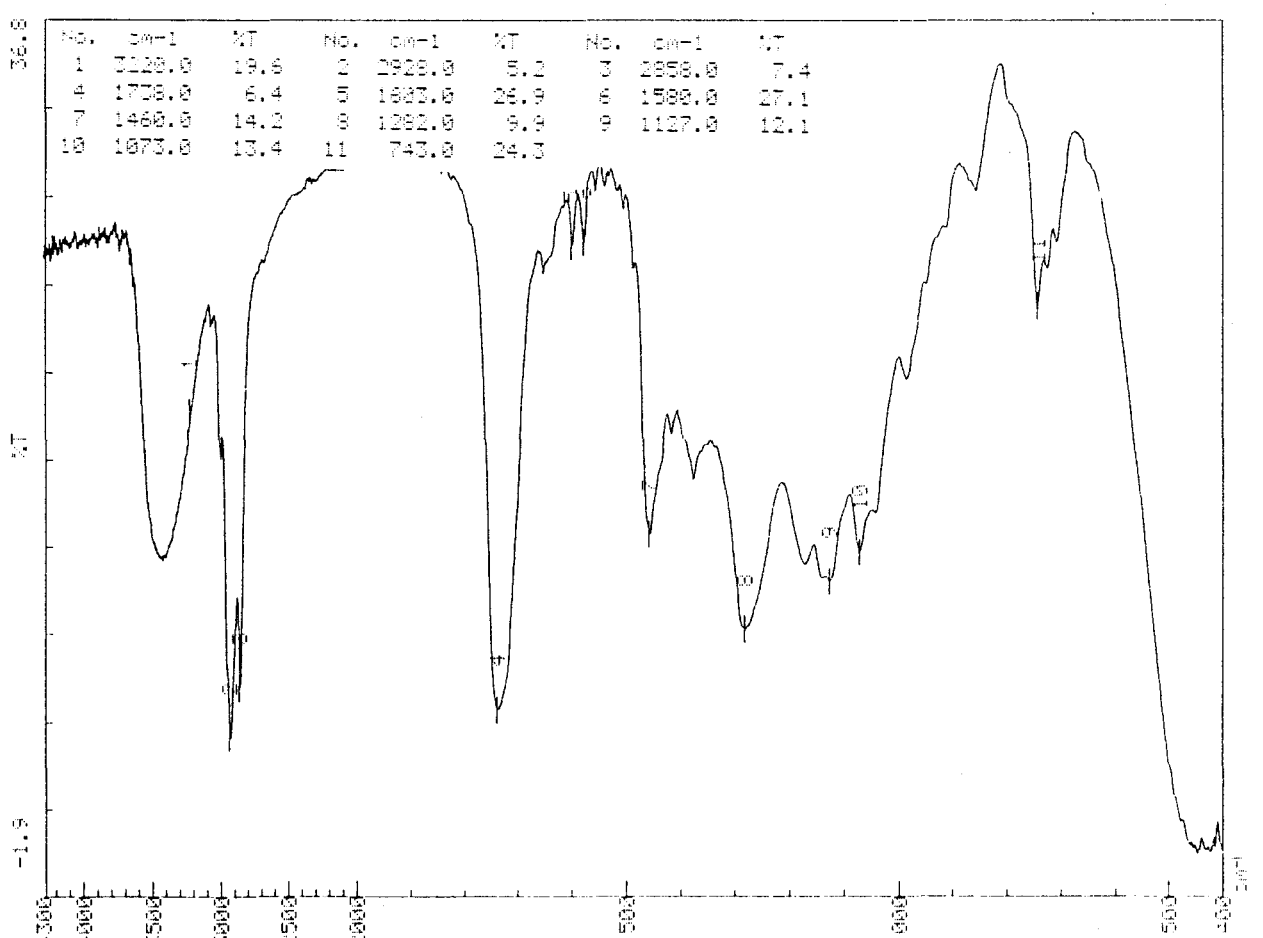
Spectrum 3 : Phthalic anhydride



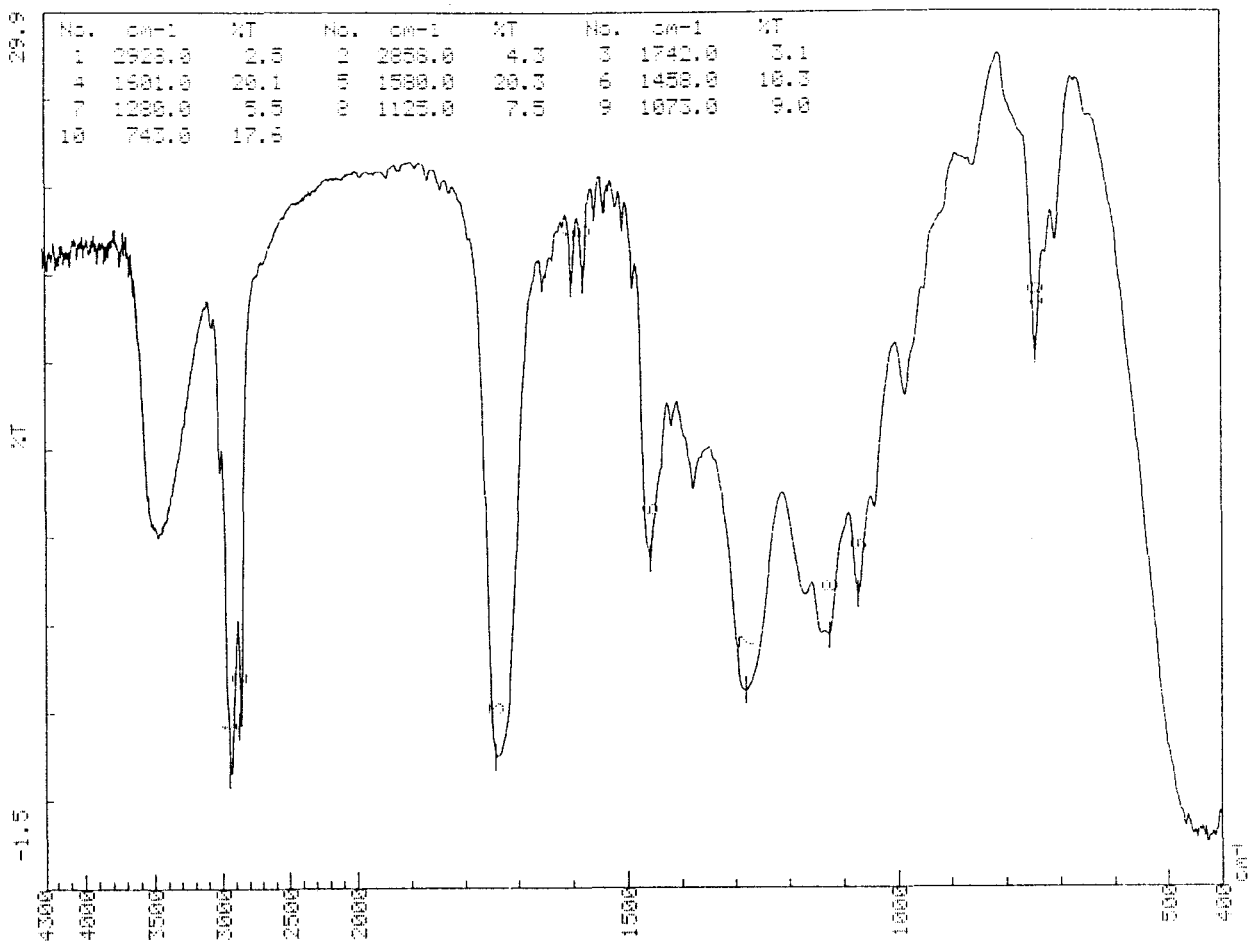
Spectrum 4 : Alkyd resin 1.1.



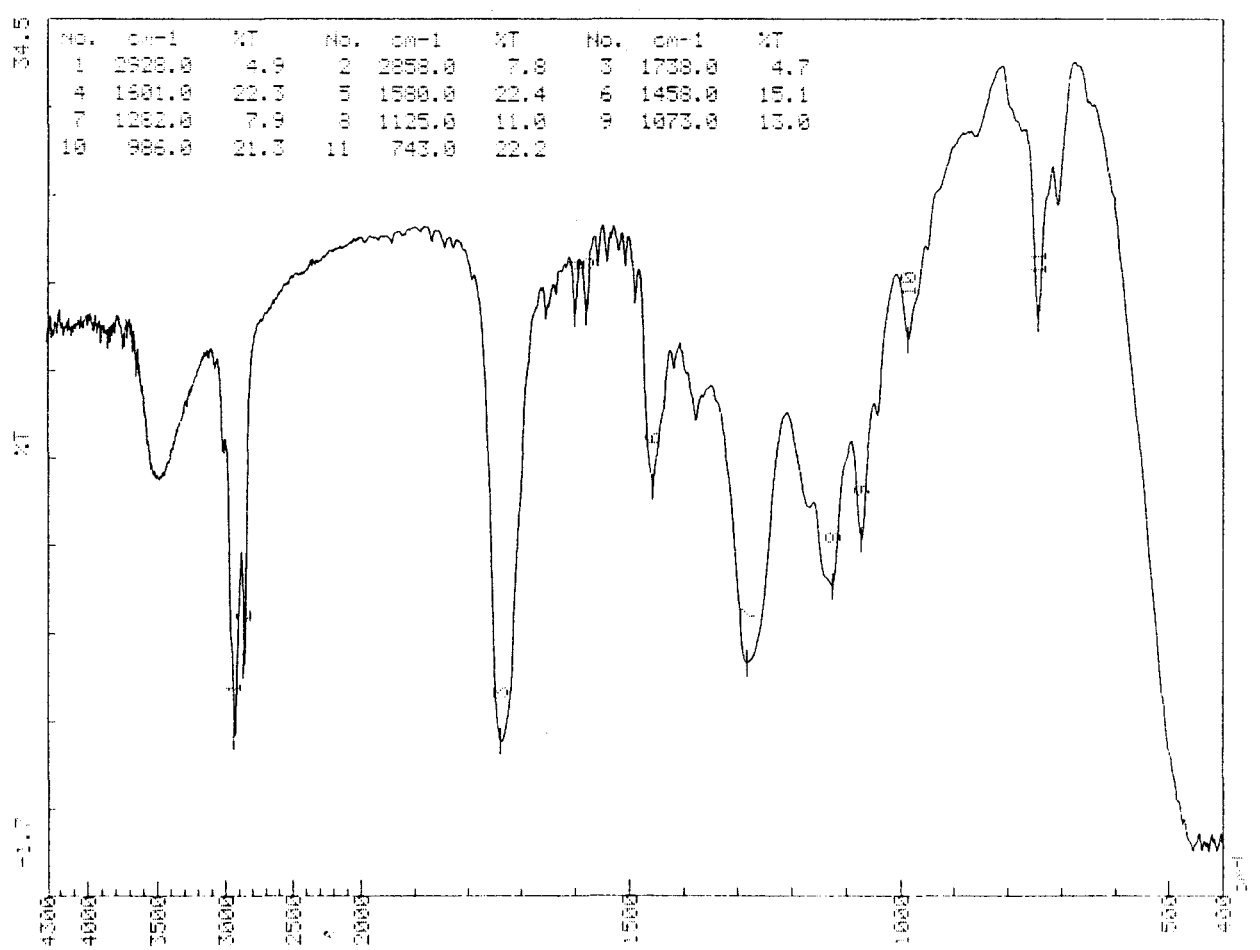
Spectrum 5 : Alkyd resin 1.2.



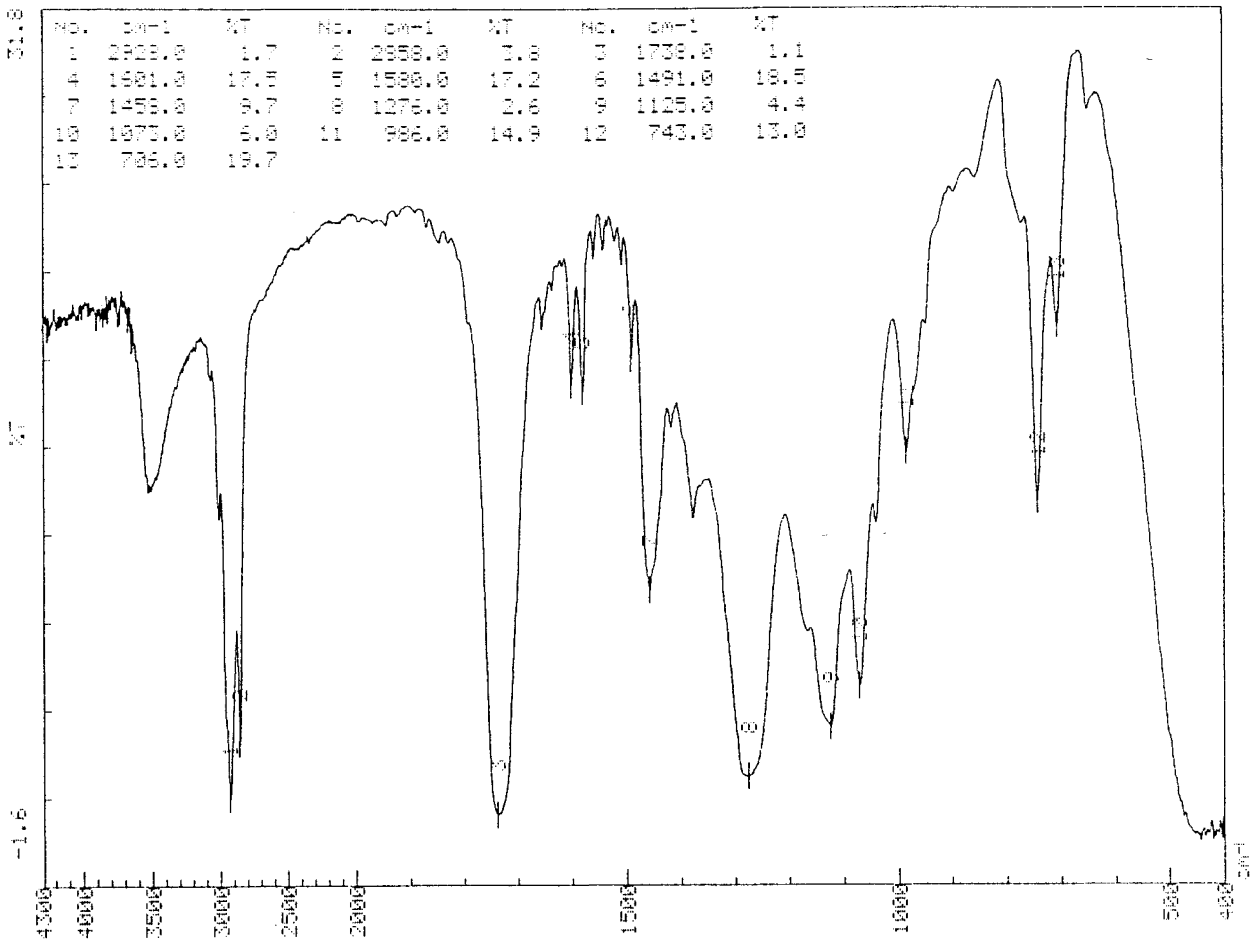
Spectrum 6 : Alkyd resin 1.3.



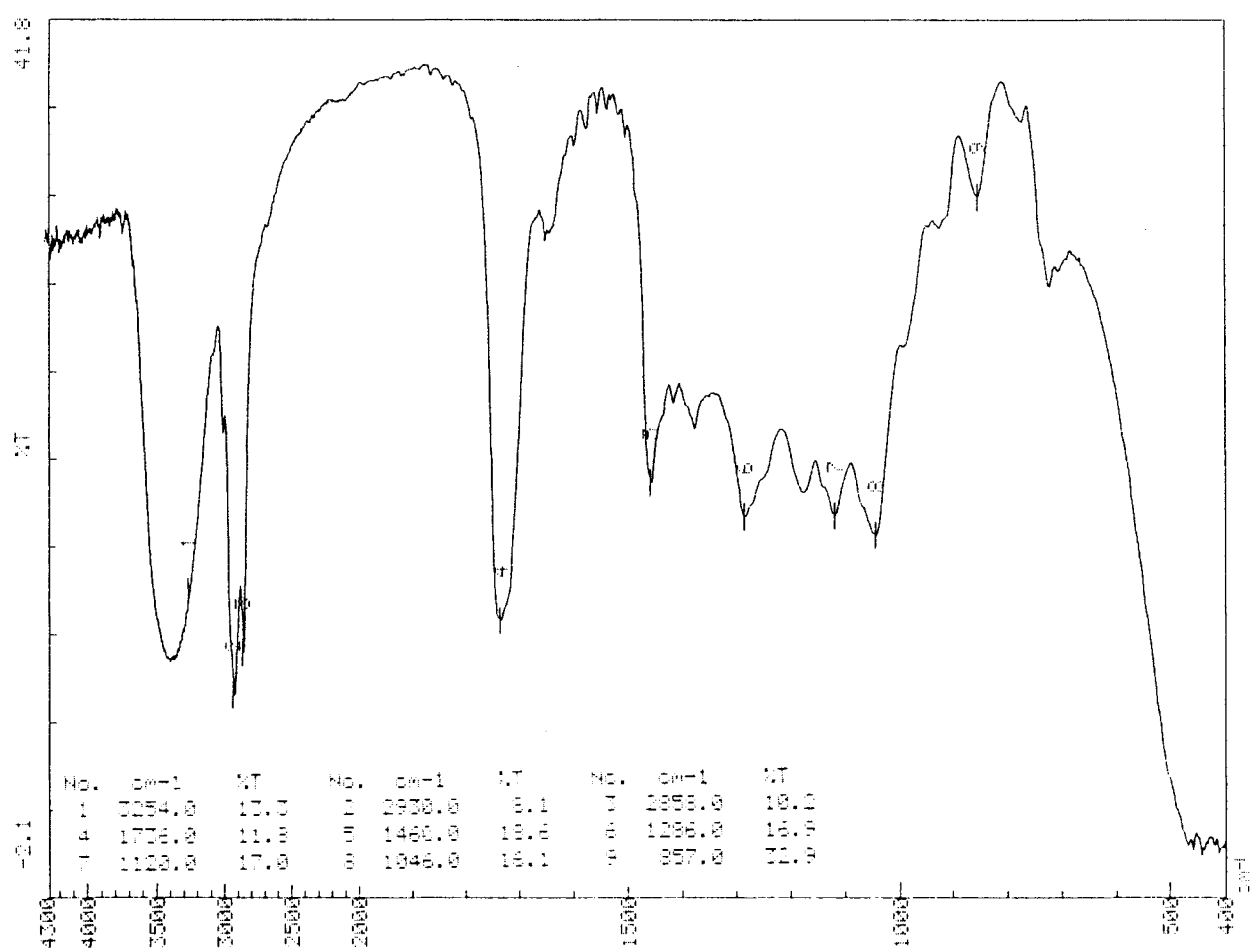
Spectrum 7 : Alkyd resin 1.4.



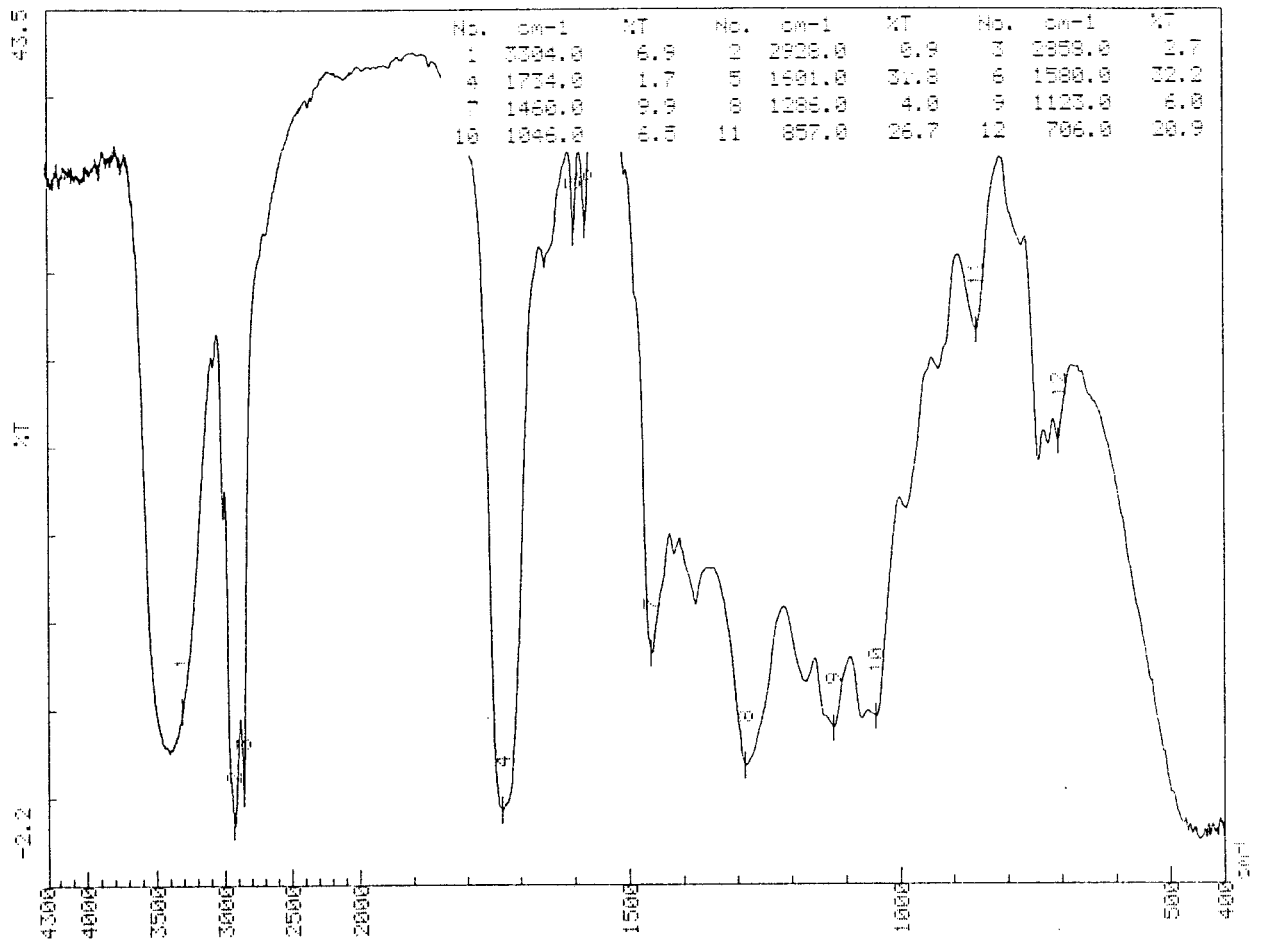
Spectrum 8 : Alkyd resin 1.5.



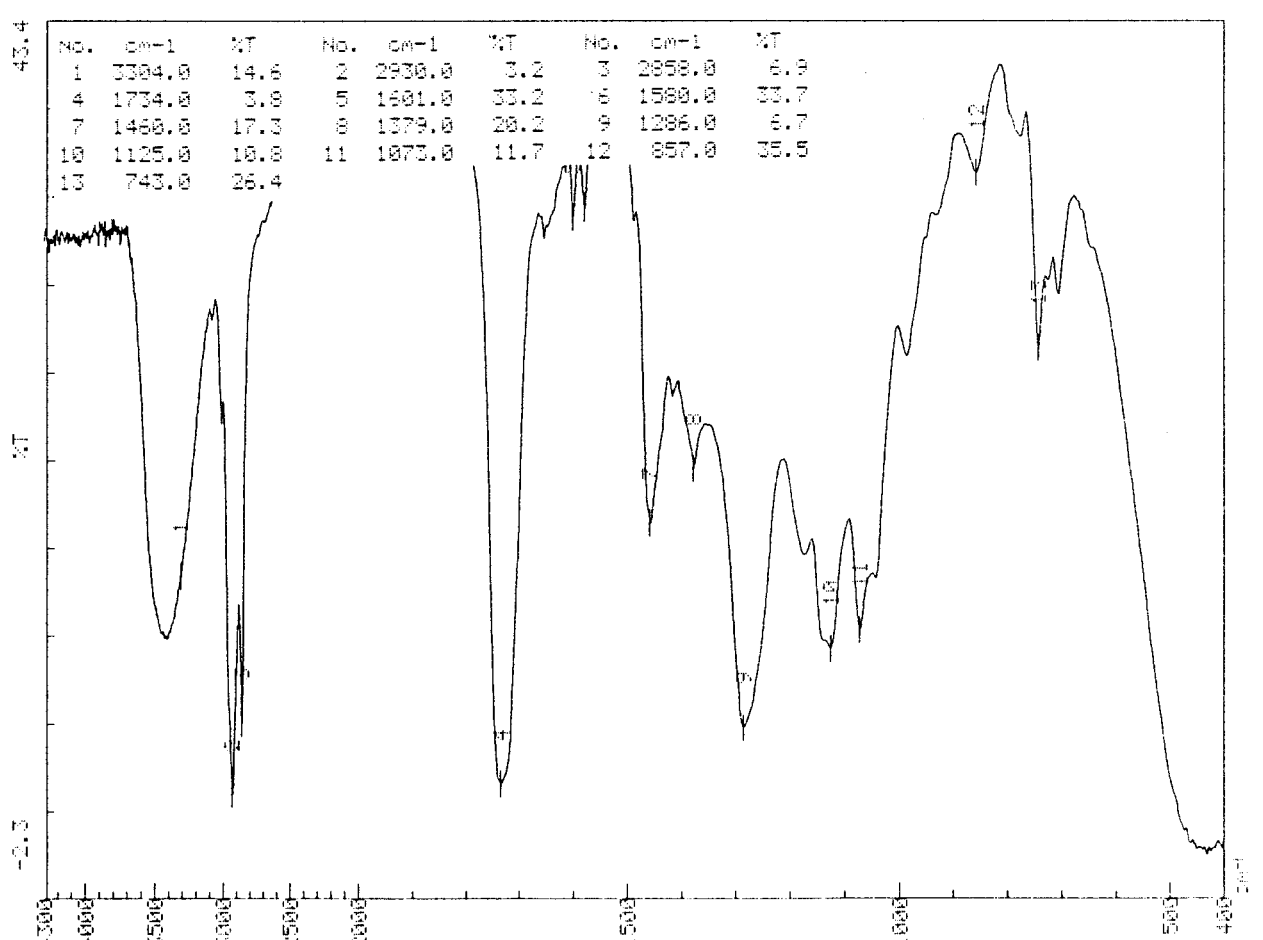
Spectrum 9 : Alkyd resin 2.1.



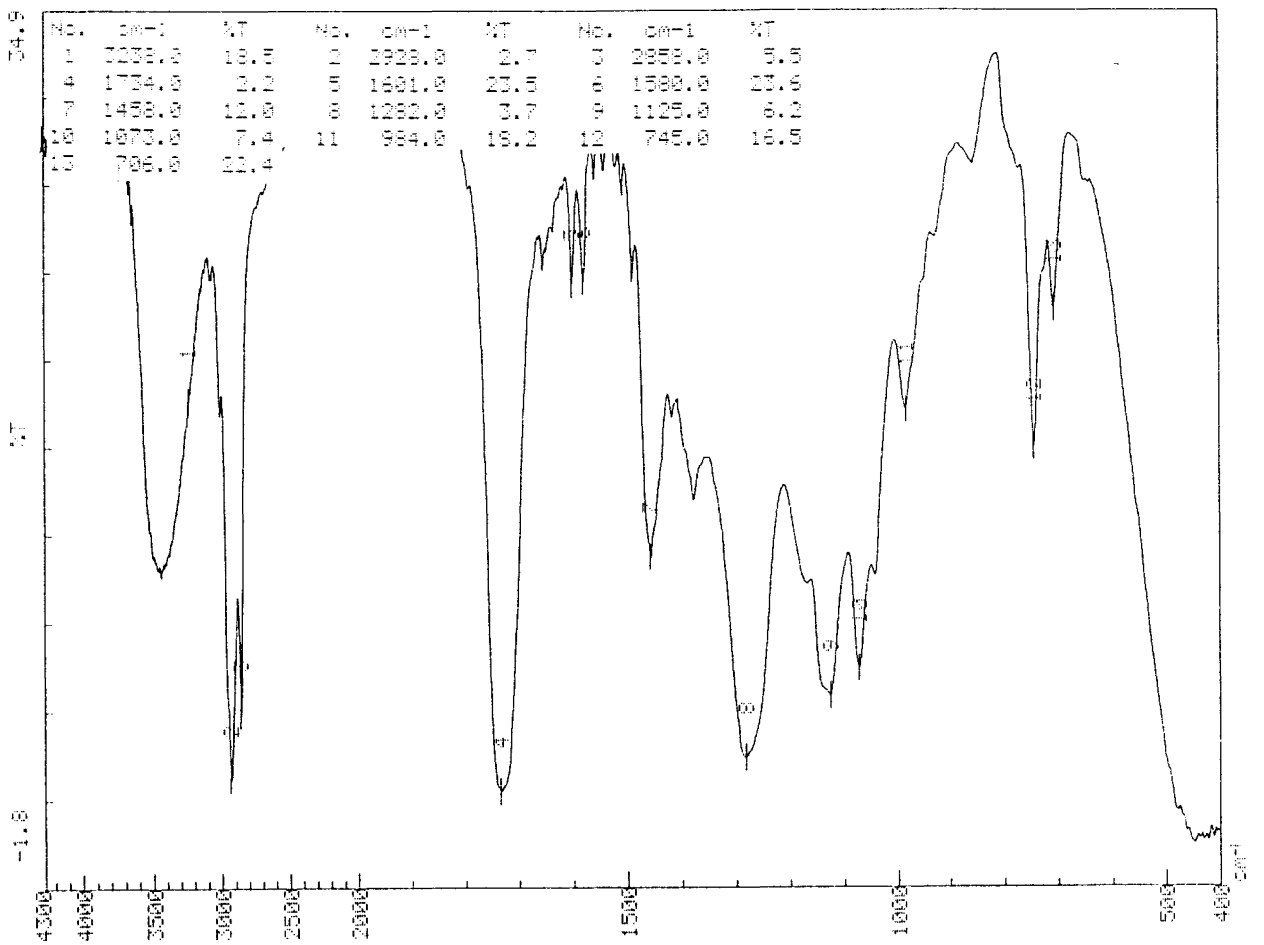
Spectrum 10 : Alkyd resin 2.2.



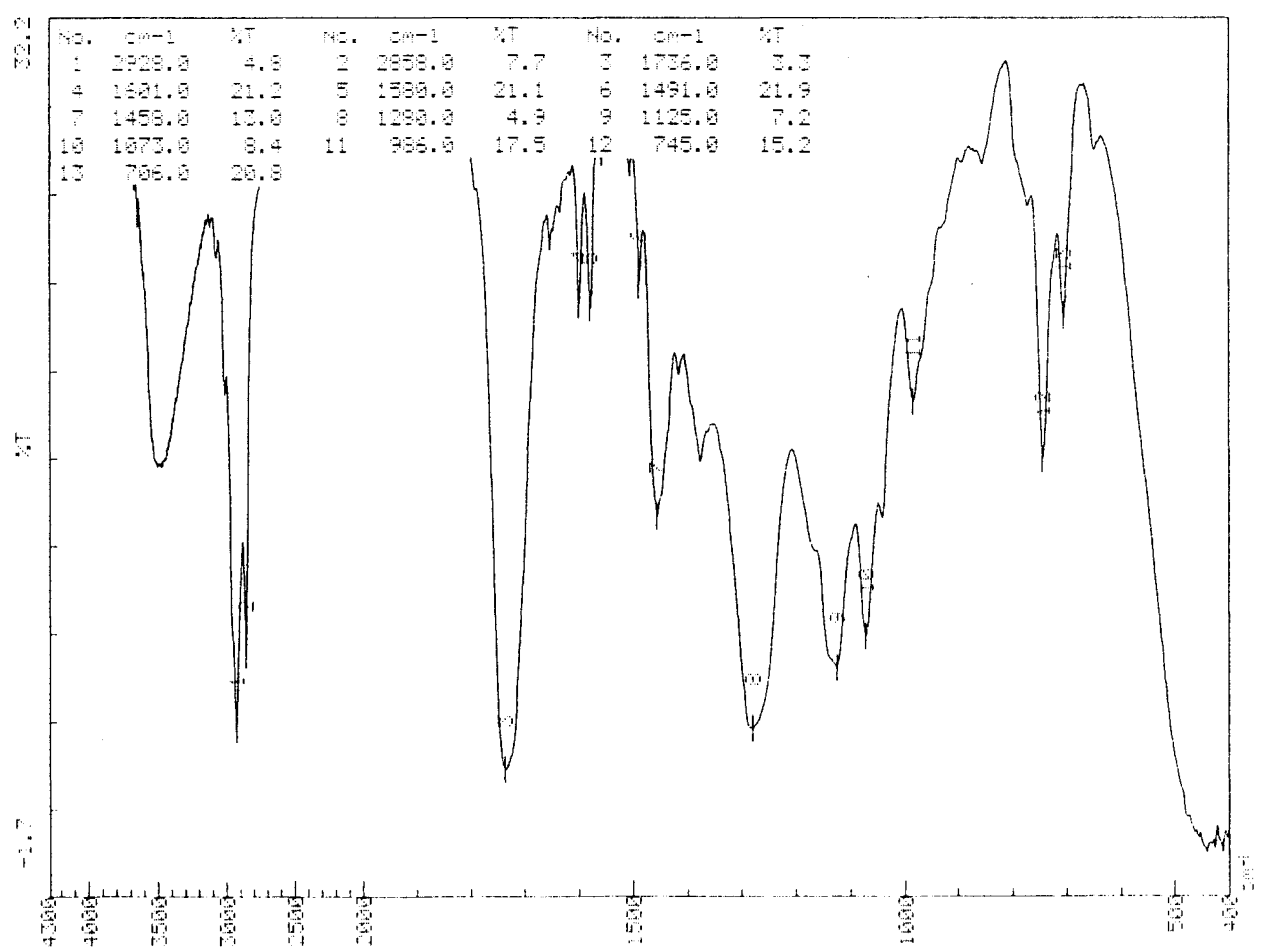
Spectrum 11 : Alkyd resin 2.3.



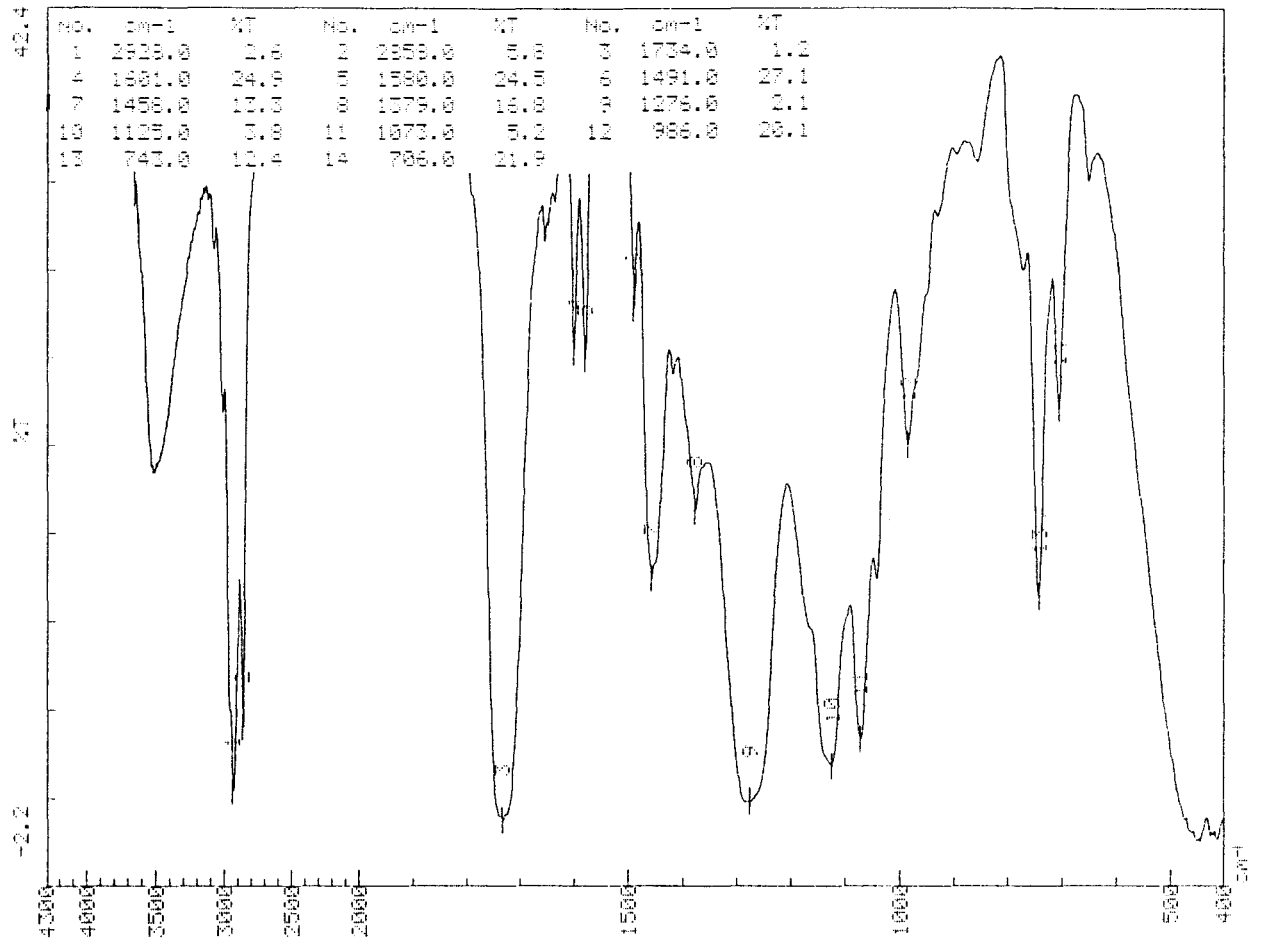
Spectrum 12 : Alkyd resin 2.4.



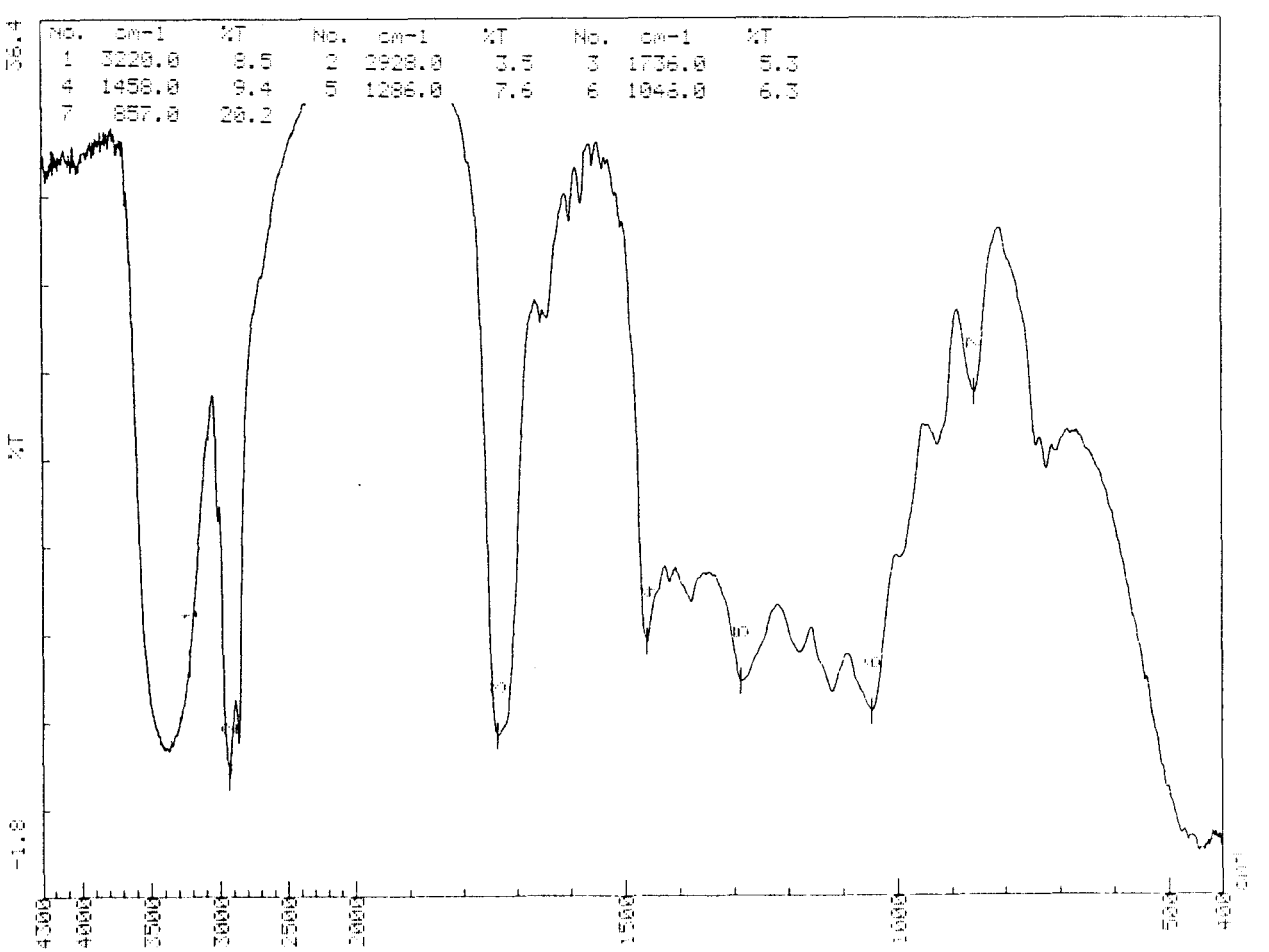
Spectrum 13 : Alkyd resin 2.5.



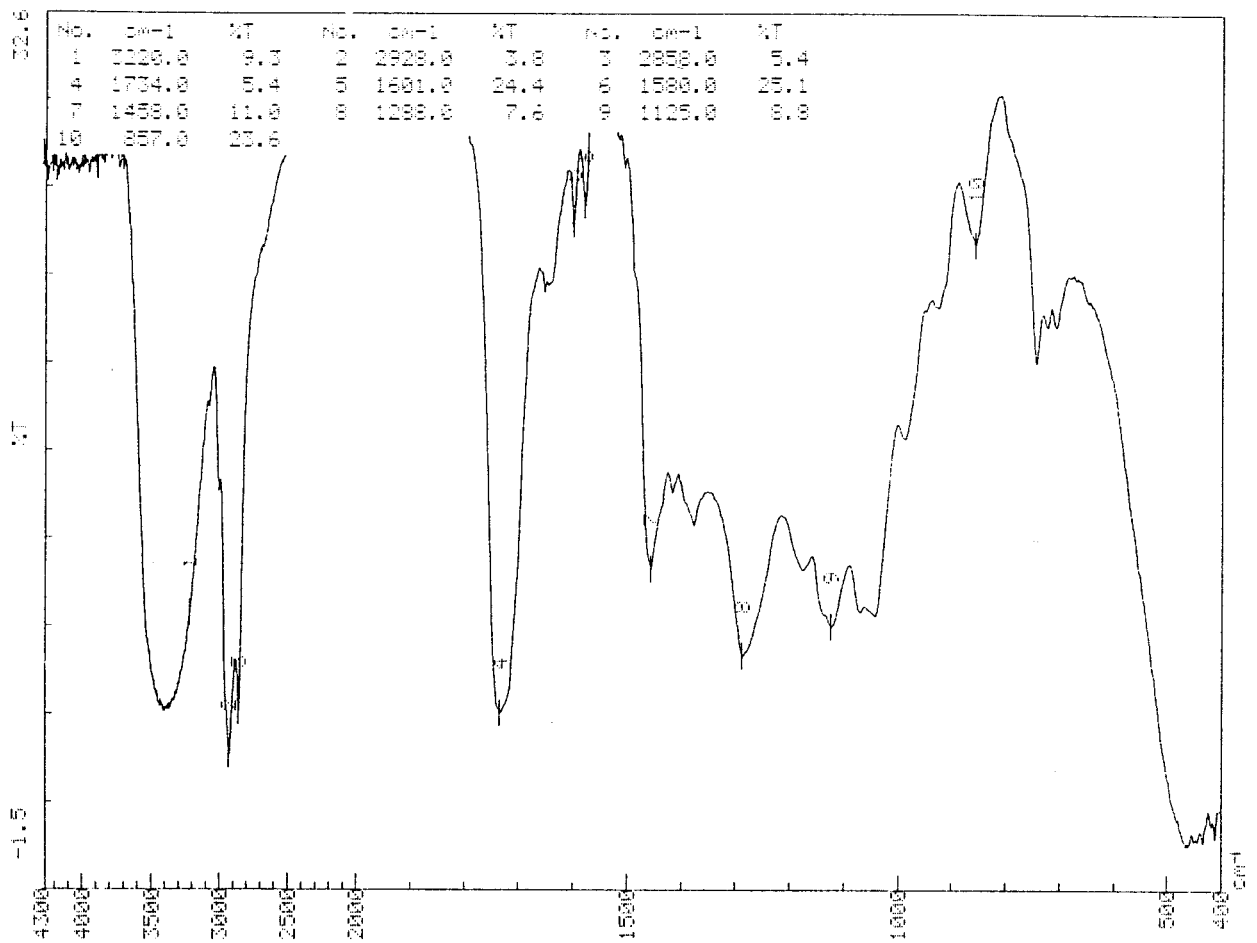
Spectrum 14 : Alkyd resin 2.6.



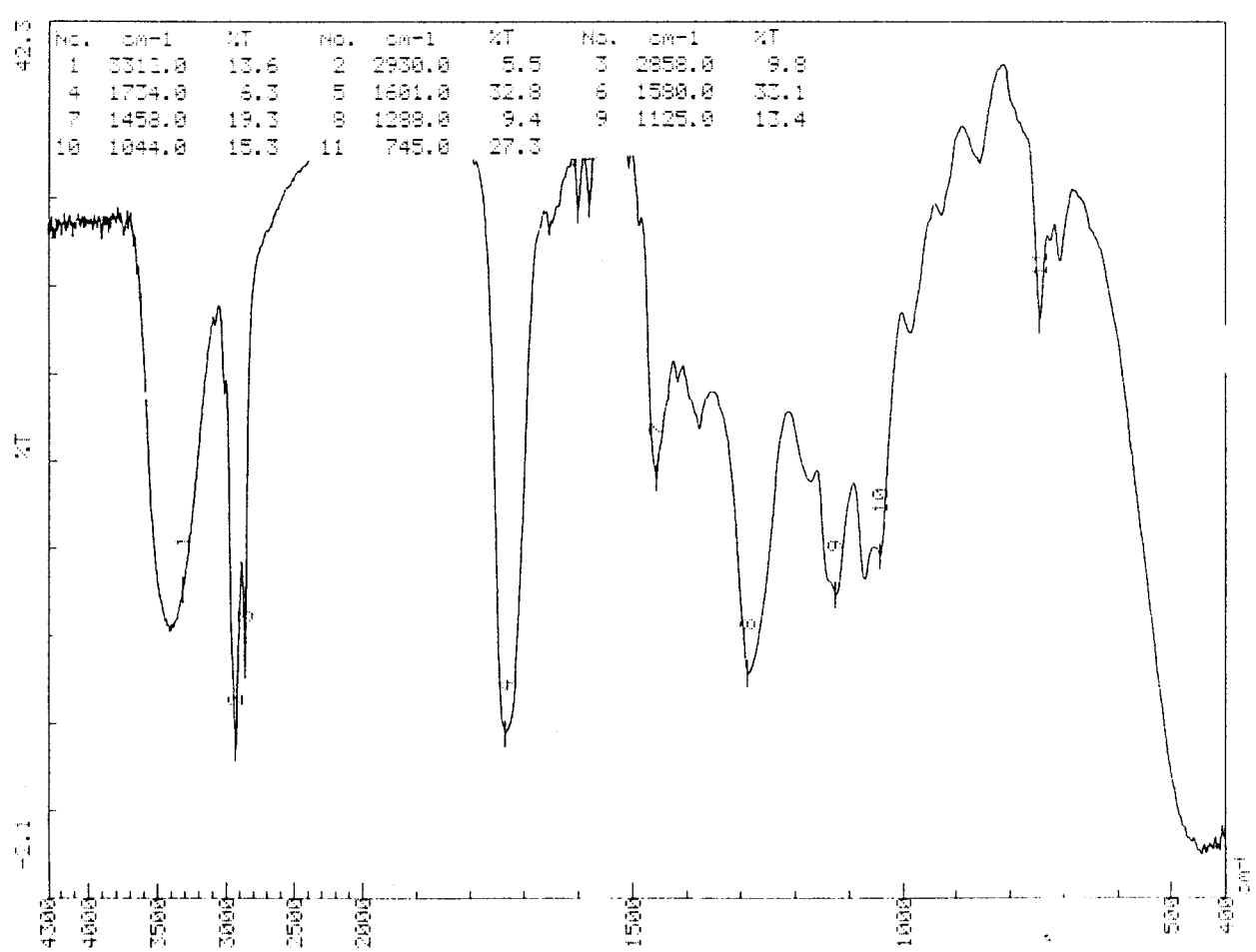
Spectrum 15 : Alkyd resin 3.1.



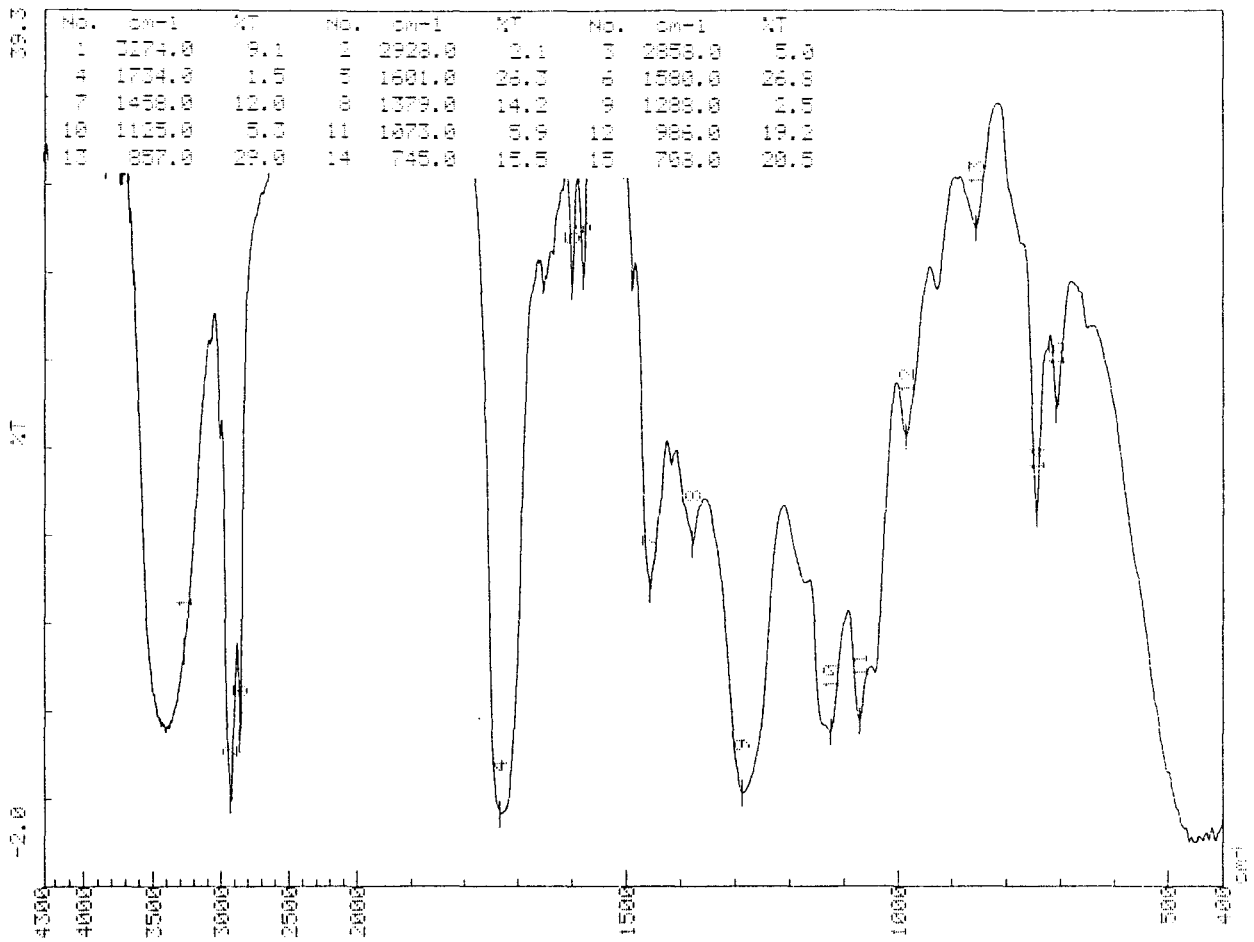
Spectrum 16 : Alkyd resin 3.2.



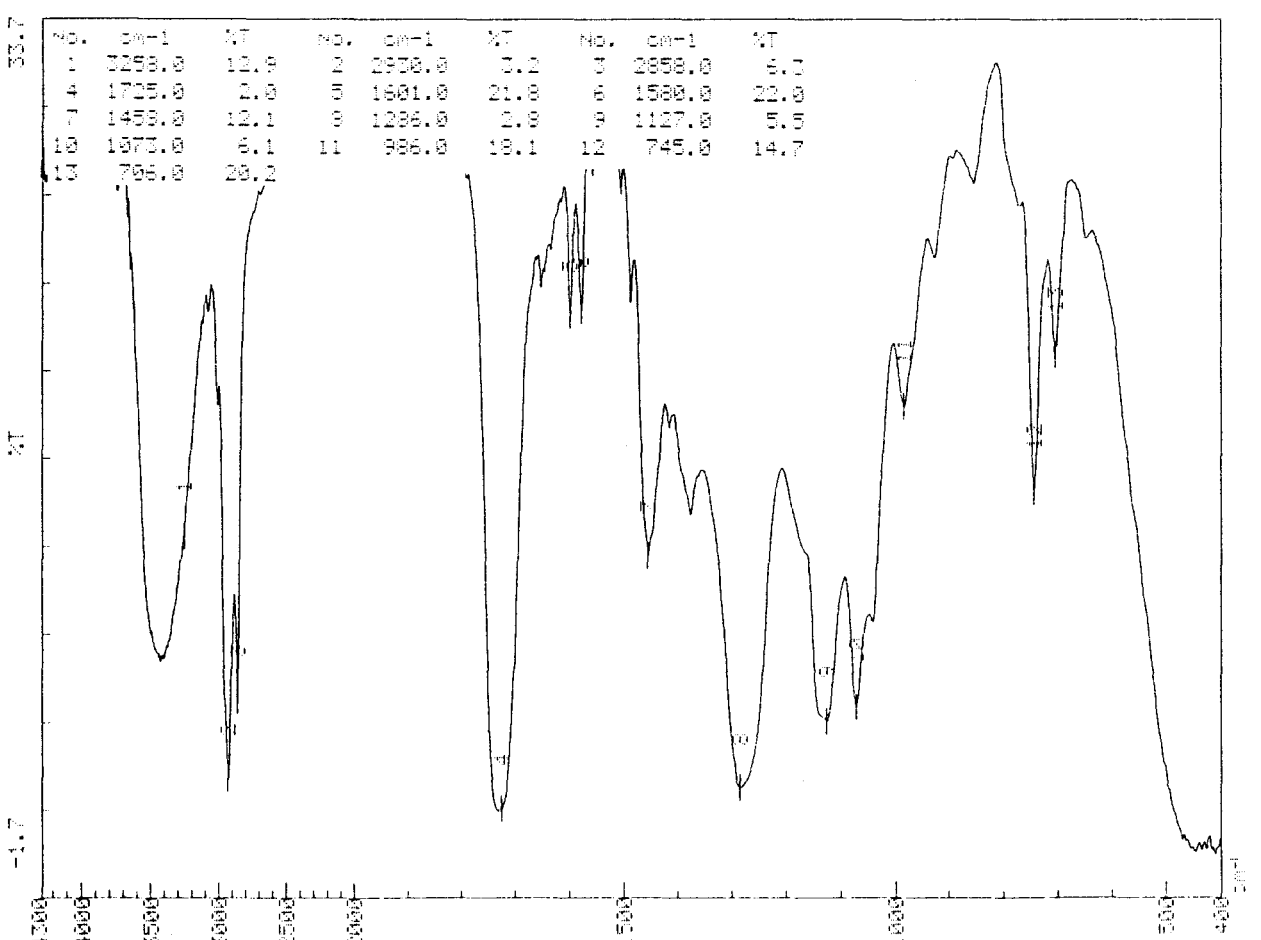
Spectrum 17 : Alkyd resin 3.3.



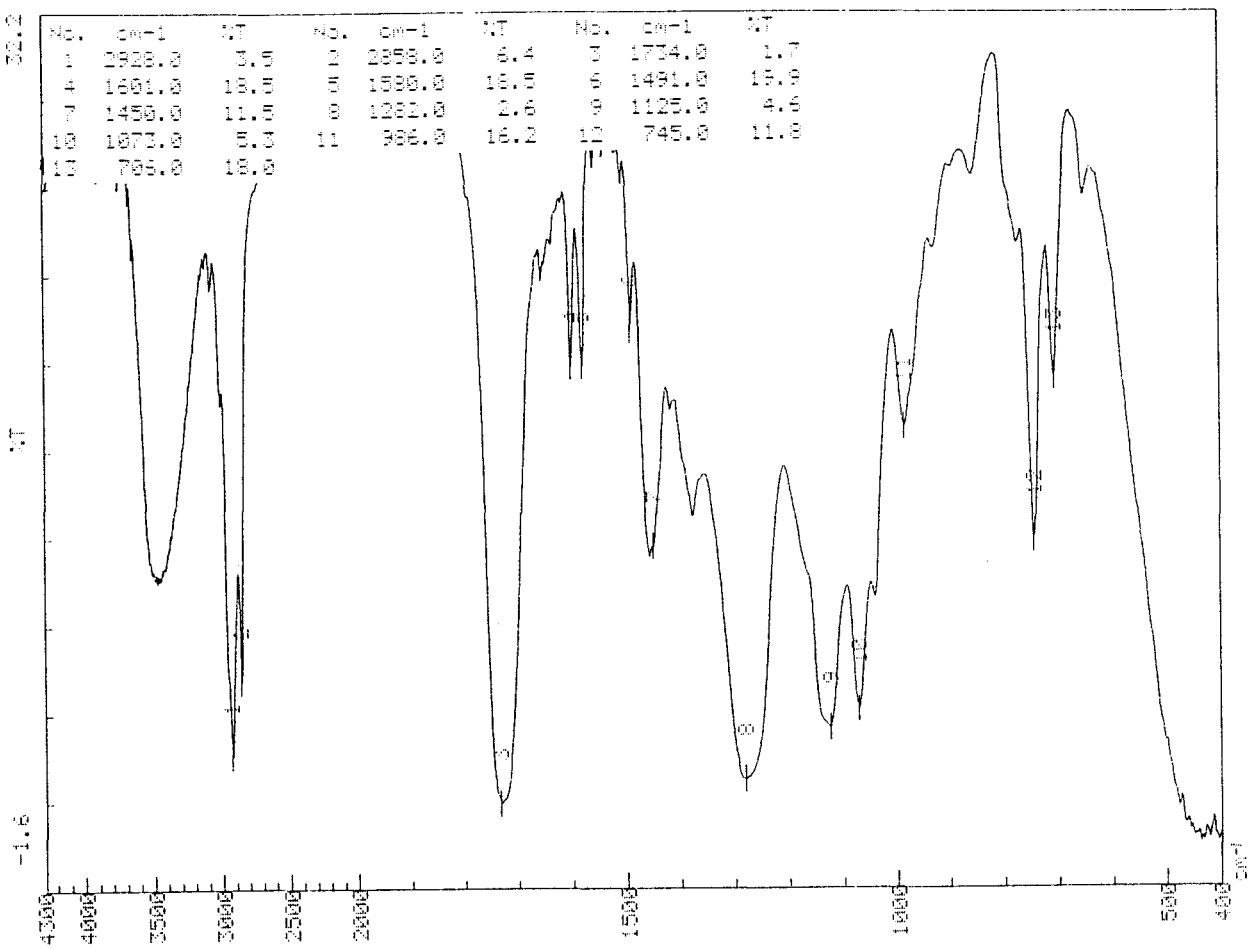
Spectrum 18 : Alkyd resin 3.4.



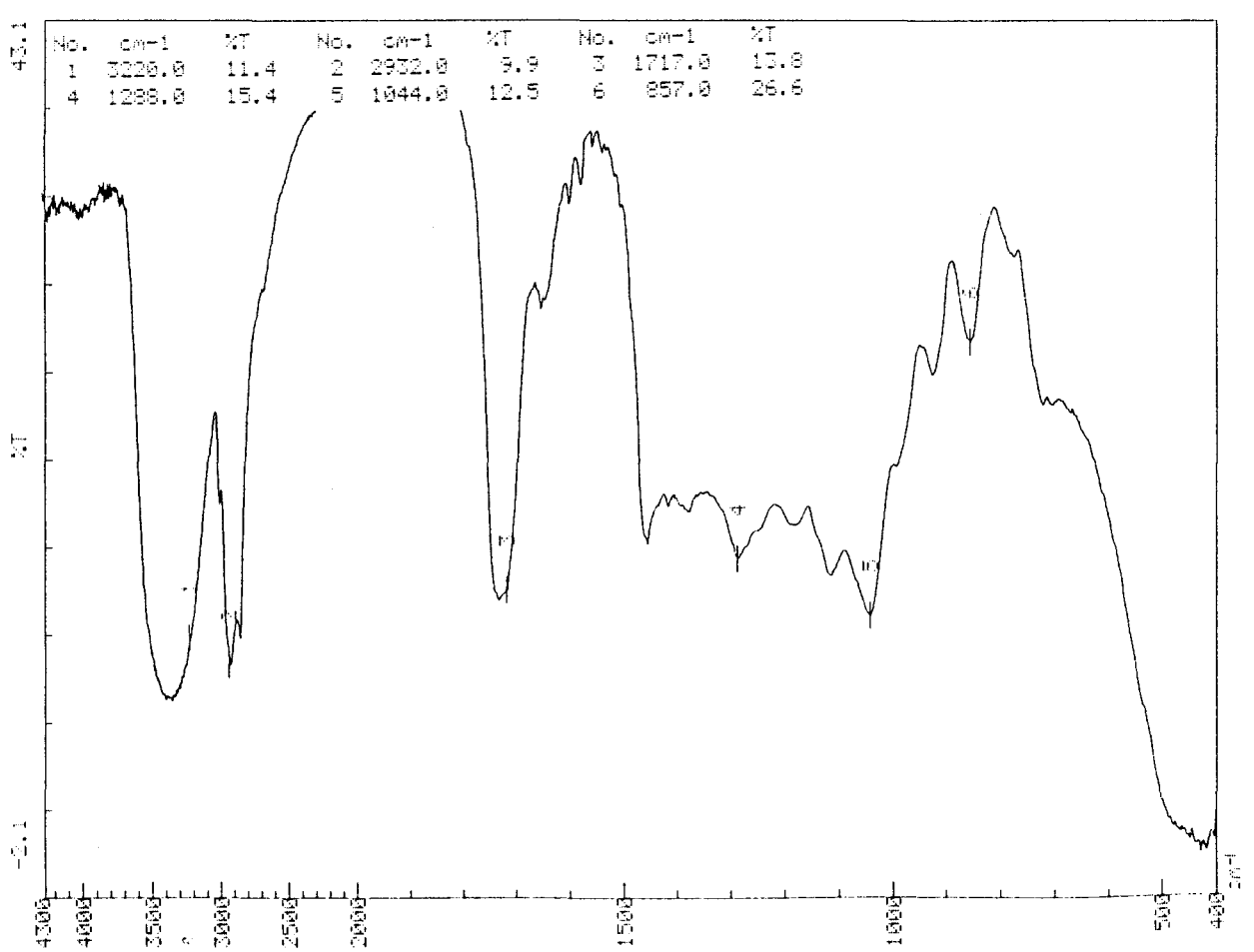
Spectrum 19 : Alkyd resin 3.5.



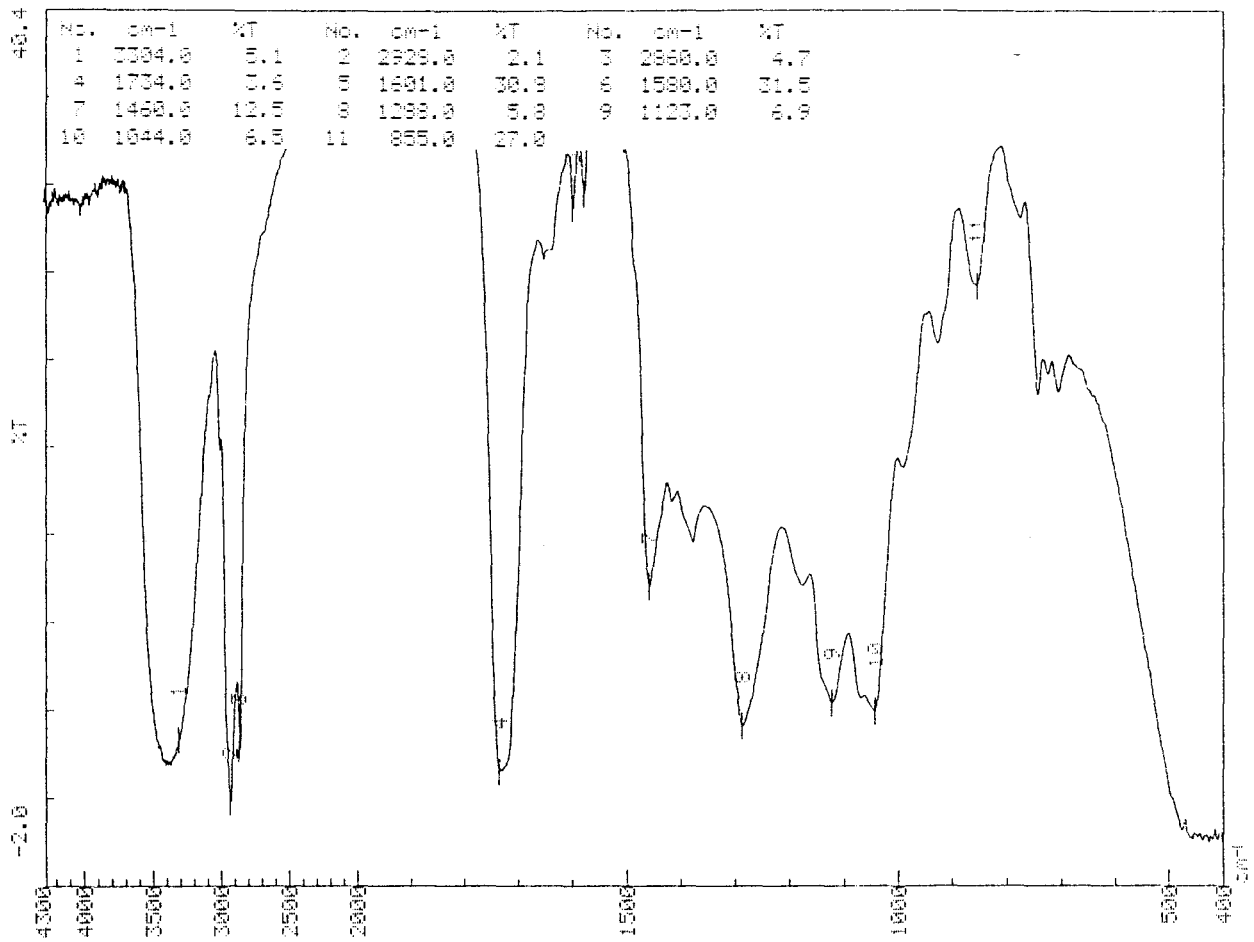
Spectrum 20 : Alkyd resin 3.6.



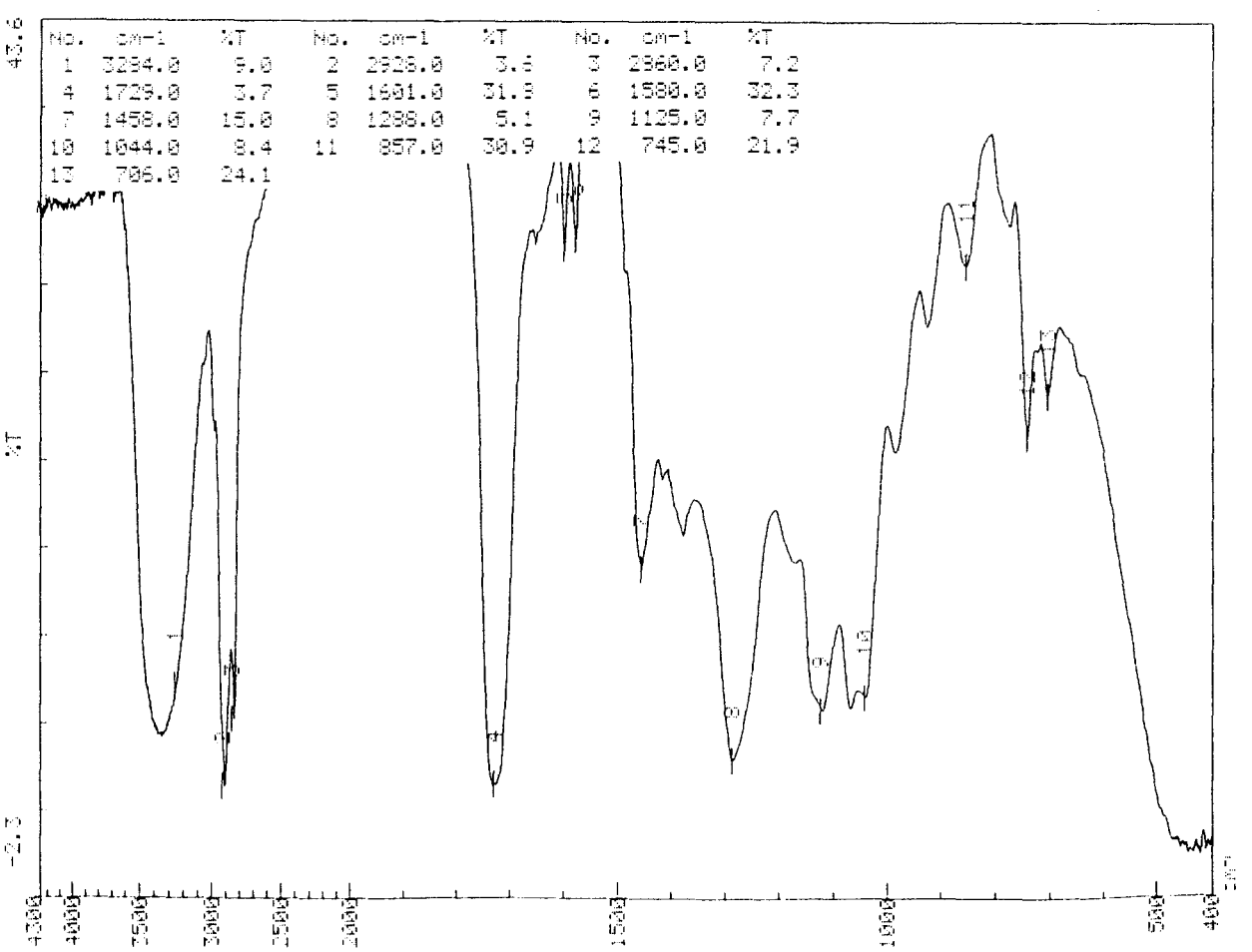
Spectrum 21 : Alkyd resin 4.1.



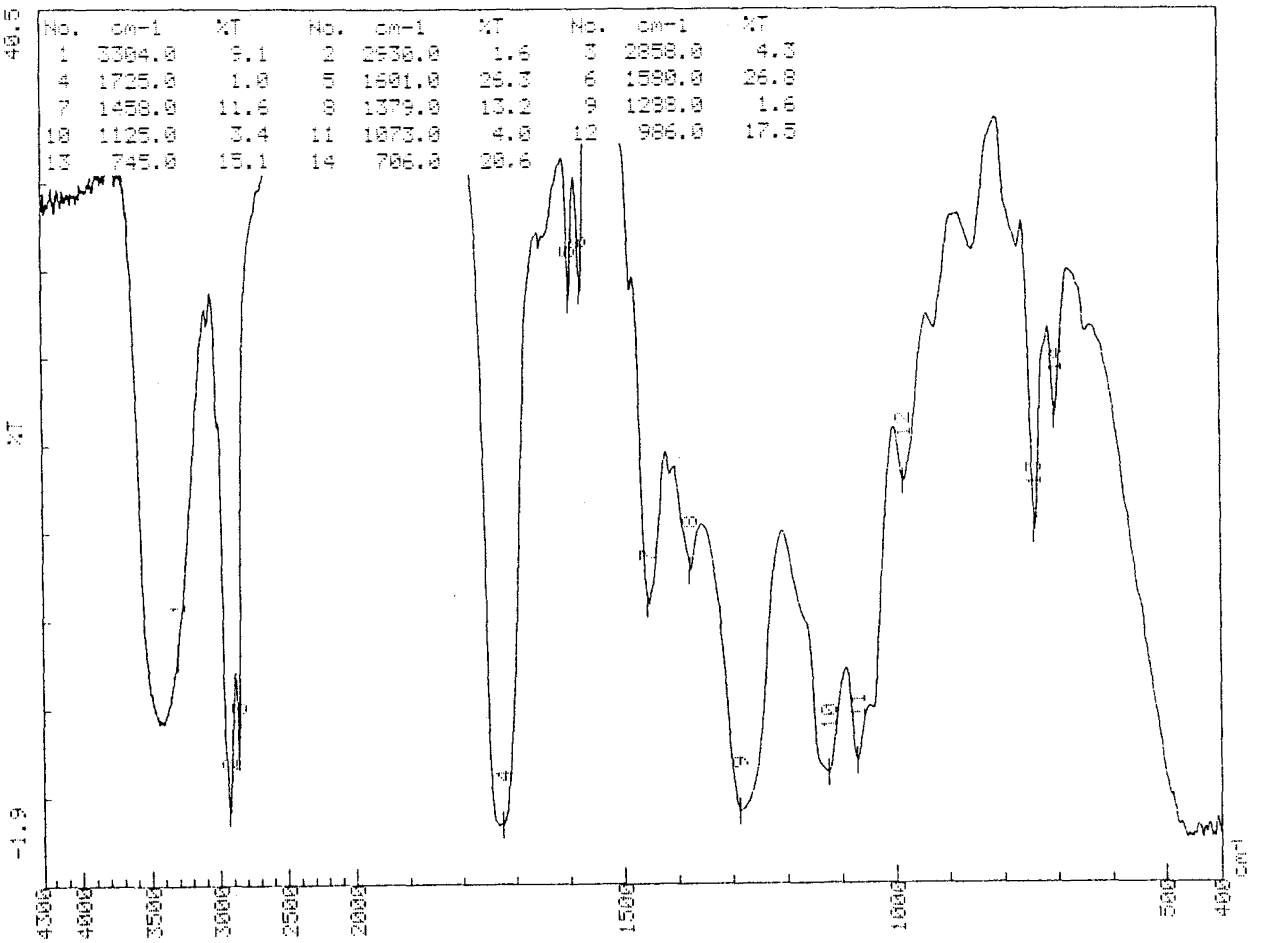
Spectrum 22 : Alkyd resin 4.2.



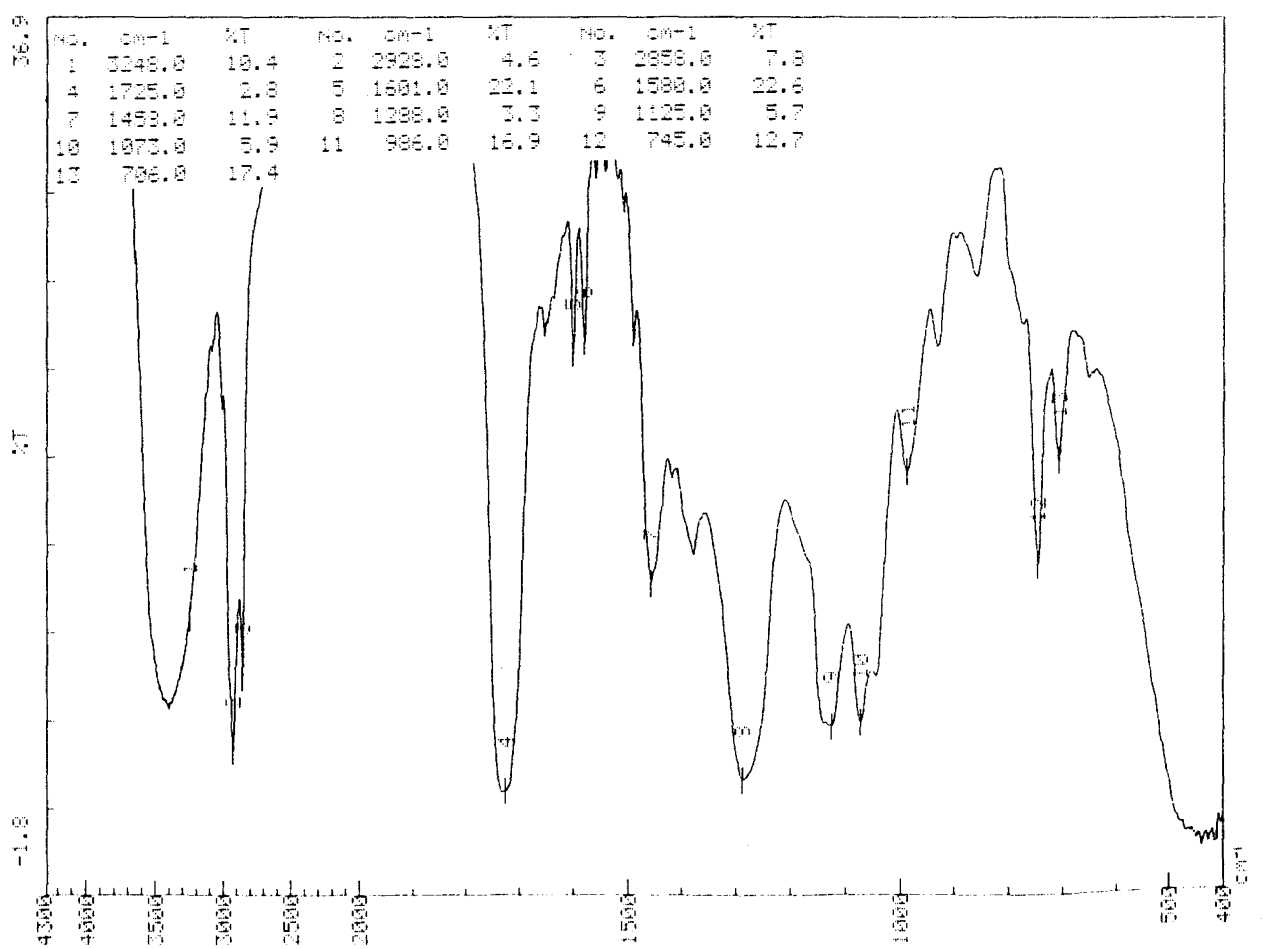
Spectrum 23 : Alkyd resin 4.3.



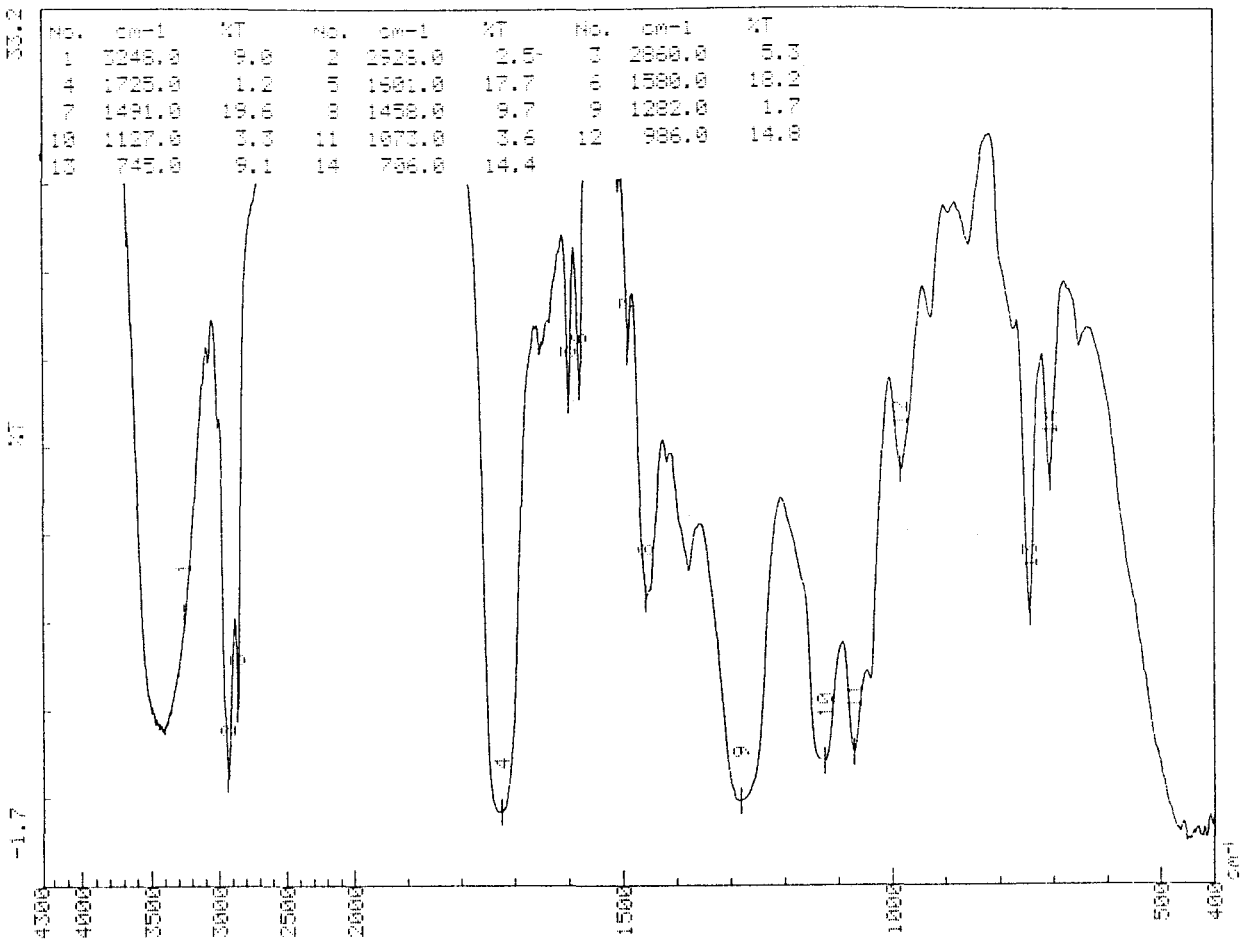
Spectrum 24 : Alkyd resin 4.4.



Spectrum 25 : Alkyd resin 4.5.



Spectrum 26 : Alkyd resin 4.6.



Spectrum 27 : Alkyd resin 4.7.