

**SYNTHESIS OF WATER -BORNE POLYESTERS:
EFFECT OF MOLECULAR WEIGHT ON PROPERTIES**

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TH 1151

**SUNITA SURYAKANT TANVADE
UNDER THE GUIDENCE OF
DR. S. P.VERNEKAR.**

**DIVISION OF POLYMER CHEMISTRY
NATIONAL CHEMICAL LABORATORY**

PUNE-411 008

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DEDICATED TO MY PERENTS

CERTIFICATE

Certified that the work incorporated in the thesis titled "Synthesis of water-borne polyesters: Effect of molecular weight on properties." Submitted by Miss Sunita Suryakant Tanvade was carried out by her under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.



(Dr. S. P. Vernekar)

Research Guide

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CHAPTER-1
SURFACE COATINGS

1.0 INTRODUCTION

Look around you, coatings are everywhere. If you are inside your house there is coating on the wall, refrigerator, cabinets, and furniture. Less obviously coatings are on the wire of electrical motors, printed circuits inside television sets, cassette tapes, videotapes and compact disks. If you are outside, coatings are on your house walls and car as well as inside your car on the vinyl sets under the hood and on components of the automotive stereo and computer system. Clearly the functional and decorative requirements of coatings span a very broad spectrum.

A surface coating fulfils two main purposes, to protect the object from destructive external attack and to give it an aesthetically attractive appearance.

The protective function includes interalia, resistance to air, water, organic liquids, and aggressive chemicals such as acids and alkalis together with improved superficial mechanical properties such as greater hardness and abrasion resistance. The decorative effect may be obtained through colour, gloss or texture or combination of these properties. It also serves functional purpose The low gloss paint on the ceiling of a room fills a decorative need, but it also has a function that it reflects and diffuses light to help provide even illumination. The coatings on the outside of automobile adds beauty to car and also helps to protect from rusting. The coating on the inside of a beverage can has little or no decorative value but it protects the beverage from the cans. In some cases the interior coating protects the cans from the beverage. Other coatings reduce the growth of alge and barrettes on ship bottom, protect optical fibers for telecommunications against abrasion, serves as the recording medium in audio-video tapes and so on. Coatings are important throughout the economy and they make essential contributions to most hi-tech fields.

1.1 Types of Coatings

Depending on the end use applications, coatings can be categorised into three types.

1.1.1 Architectural Coatings

It includes the familiar paints and varnishes (Transparent paint) used to decorate and protect buildings, outside and inside. They also include other paints and varnishes sold for use in the home and by small businesses for applications to such things such as cabinet, household furniture and the like. They are often called trade sales paint. Latex-based coatings comprise by far the largest fraction of architectural coatings.

1.1.2 Product Coatings

It is commonly called industrial coatings or industrial finishes and are applied in factories on products such as automobiles, appliances, magnet wire, furniture, metal cans, chewing gum, wrappers.... the list is almost endless. This market is often called the OEM market that is the original equipment manufacturer market. In most cases, the product coatings once designed for a particular customer manufacturing conditions and the performance requirements of its products. Thus the number of products in this category is much larger than in the others and the research and development requirements tend to be significantly higher.

1.1.3. Special Purpose Coatings

It is a catch all category for coatings that do not fit the other two. It includes coatings for cars and trucks that are applied outside the OEM factory, coatings for ships and aircraft and the familiar stripes of coating highways and parking lots. Coating for steel bridges, storage tanks, chemical factories and the like are classified as “Maintenance Coatings”.⁽¹⁾

1.2 Main Constituents of Paints, Varnishes and Lacquers

Paint consists of three main components: The binder, the pigment and the solvent.

1.2.1 Binder

The function of the binder is to provide the forces which hold the film together- cohesive forces and which hold film and substrate together - adhesive forces.

The binder is the most important of the three main components and is always present in a manufactured paint. Many of the properties of paints and related products, such as their mode of drying and the adhesive and mechanical properties of the films are determined in the first place by the nature of the binder. Hence, paints are often classified and may even be named according to the type of binder. Many types of binder are intrinsically brittle and have poor adhesion to the substrate. These deficiencies are corrected by the addition of plasticizers, which have as their primary function the improvement of the flexibility of the dried films such plasticisers must be non-volatile, so that they remain in the film at end of the drying process. The properties of the binder may also be improved by chemically incorporating certain groups of atoms into its molecular chain during its formation. This is known as internal plasticiser.

1.2.2 Pigment

The pigment is a fine powder whose function is to give the film it's desired colour and hiding properties. The pigment has a considerable influence on the consistency of the paint and hence on it's application properties. Pigments are also of importance for the resistance of the film to external attack in that they are partially responsible for such properties as hardness and resistance to abrasion and weathering.

1.2.3 Solvent

The solvent is a volatile liquid whose function is to dissolve such binders as would be solid or semi-solid at normal temperature, this is in the case of many resins and other binders. Such as

glue on the other hand, an oil paint containing a free flowing oil as binders requires no solvent, but solvent may nevertheless be used as a diluent, or thinner to obtain a suitable consistency for application. In many cases the same liquid fulfils the functions of solvent and diluent.

In addition to these three components, modern paints may contain additives of various kinds such as plasticizers, drier, wetting agents, flattening agents and emulsifiers or other stabilisers.

1.3 The Drying Process

A coating is generally applied on a surface in liquid form, which should form a solid film on the surface. The process is known as drying process.

A differentiation is made between physical and chemical drying according to the way in which film formation occurs.

1.3.1 Physical drying

A process in which film formation occurs solely as a result of the evaporation of the volatile constituents i.e. solvent and diluents of the paint or lacquer. As evaporation reaches near completion the molecules of the binder approach each other so closely that their secondary valence forces, which are only effective over short distances, come into play. Gel formation occurs at this stage resulting in the formation of a coherent film.

A film, which has been formed by physical drying, is held together, by weak secondary valence forces. Solvents may break these bonds again, and hence a film formed in this way is readily re-dissolved however old, it may be. A cellulose lacquer, as is well known, remains very sensitive to acetone, cellulose thinner and the like. French - polished surface will not stand alcohol. A glue-based paint contains a water-soluble binder and hence is not washable. Evaporation is normally a rapid process and physical drying takes place in quite a short time 5-15 min.

1.3.2 Chemical Drying

As the name implies it is a process in which the molecules of the binder undergo chemical reaction with each other and hence are bound together in the film by primary valences. These bonds are so strong that they cannot be broken by the action of solvents and a film formed by chemical drying is thus insoluble in solvents. If the material contains volatile components which is normally the case where synthetic binders are used, the chemical drying usually occurs only after the greater part of the volatile constituents has evaporated. There are two main types, of chemical drying and oxidative drying. In the process of oxidative drying the first stage is the uptake of oxygen from the air, the oxygenated molecules then react in ways which lead to chemical bonds between the molecules of the binder. Coatings containing drying oil such as linseed oil dry by oxidation. Oxidative drying is much less rapid than physical drying, but it may be accelerated by the addition of small amount of catalytically active substances known as dryers sometime called siccatives. The most common dryers are organic salts of lead, manganese and cobalt, which are soluble in the vehicle.

1.4 Curing

It may be defined as a process in which drying occurs by chemical reaction between the molecules of the binders not involving gaseous oxygen. If the reaction occurs at room temperature the products are described accurately as "Cold Curing Lacquers". If temperature of 70°C or higher is necessary to cause rapid reaction, the materials are known as stoving or baking coatings.

In view of the many different kinds of chemical reaction, which are now used to produce insoluble films the term convertible coating has been introduced. A convertible coating may be defined as one in which the binder in its final form in the film differs chemically from the binder in the form in which it is applied. The conversion of the one form to the other may be achieved by the action of some component of the atmosphere such as oxygen or water by

heat, by radiation, by the use of catalysts or by reaction between two or more binder components which are mixed shortly before application, or by a combination of two or more of these methods, where two different materials are mixed prior to application, the material is referred to as a two component coatings or as a reaction coatings. In general it may be said that sub-reaction coatings give films with higher hardness and chemical resistance than those obtained by oxidative drying.

When the drying process takes place during exposure to air at normal temperature it is called "Air Drying". If it is accelerated by the application of a moderate degree of heat it is termed "Forced drying" as distinct from stoving. According to British Standards 2015:1953 various stages in the drying of a paint or varnish film are distinguished by qualifying terms. ⁽²⁾

CHAPTER-2

WATER – BORNE COATINGS

2.0 INTRODUCTION

The progress of industrial development in most of the countries of the world has brought with it an increased pollution of the atmosphere with volatile organic substances. The causes are varied. Industrial production always results in concentrating and conglomerating traffic and industrial facilities as well as working and living people tied to increased waste and effluent quantities, emission of dusts and organic products. There are two chief human sources of organic emissions.

1. Industrial production facilities
2. Residential and recreational activities.

The following industrial activities play a significant role in the escape of organic emissions.

1. The coating industry
2. The chemical industry
3. Crude oil refining.
4. The printing and adhesive industry

With a contribution of approximately 20-25%, the coatings processing and manufacturing industry represents a quite significant source of organic emissions derived from human activities. It is in second place after vehicular traffic as a producer of atmospheric pollutants. Solvents from the coatings industry and other volatile products resulting from painting are considered to be organic emission. Because of the high contribution of solvents and in the context of a growing concern for the environment, it is the prerogative of the coatings manufacturer, the coating producer and the coatings processing industry to reduce drastically the solvent content of coatings system by any means possible. This resulted in the fact that the coating industry since then has concerned itself almost exclusively with the development and research of low solvent and solvent free coatings and the coatings producers are mainly pursuing new developments based on this new product group. In addition, major coatings

users such as the automotive and appliances industries are making corresponding demands on their paint suppliers to make low - solvent paint available.

Furthermore, there is increasing difficulty and expense of disposing of solvent containing wastes such as coatings residue and sludge's, that are considered hazardous waste. Today new investments in paint facilities are always made against a background of low solvent, and therefore more environment friendly coatings.

2.1 Problems with Solvents in Coatings-Occupational Hygiene and Ecology

All organic solvents are toxicants for organisms in the concentration in which they are employed in coatings. On human skin they cut to remove fat, they remove the protective layer and thus indirectly further the formation of skin redness, rashes and even inflammation by enabling the external influence of atmospheric agents chemical toxicants, bacteria or fungi. Inhaled solvent vapours affect in differing ways the circulatory system, the nervous system, the lungs and the liver depending on the type of solvent. Humans and the various animal species can thus react and be injured differently. Extrapolating the effect of toxicants from animal studies to their effect on humans is thus not always justified. Nevertheless, it is certainly beneficial from an occupational hygiene perspective to reduce the quantities of solvent used in coatings and to replace them whenever possible. Ecologically, solvent vapours are implicated in the formation of smog and the die off forests.

Upon entering the soil, most solvents are degraded by the micro bacteria and fungi that are present, so that pollution of the ground water usually need not be feared. In the case of transportation accidents and in the case of solvents that degrade with difficulty, a detrimental effect on the ground water is however a definite possibility.

The coatings wastes and residues formed by the manufacture and processing of coatings are hazardous waste and can only be stored in puncture proof form in special repositories. Preferably however, they are incinerated in strict compliance with official and legal guidelines. The premise here is that water dilutable coatings residues are also to be handled as hazardous wastes. The waste problem can in any case be partially solved by changing the coating system or preferably by developing new recycling process.

For these reasons, it is the interest of us all to concern ourselves with the development of low-solvent and solvent free alternatives.

2.2 ALTERNATIVES TO SOLVENT CONTAINING COATINGS SYSTEMS

In past years, numerous alternatives have been developed low solvent and solvent free coatings systems.

1. Water soluble coatings
2. Aqueous dispersions
3. Low-solvent high solids coatings
4. Powder coatings
5. Radiation - curing coatings.

The water soluble coatings contain binders that, either because of their strongly polar structure are intrinsically soluble or at best swell-in water, or which after chemical reaction usually with the formation of binder salts, pass into the water soluble state. The binders that are water soluble due to their structure remain in principle water-soluble even after drying is a disadvantage, which must be compensated by combining with other binders or resins through chemical reaction with hardeners or by supplemental protection of the coating.

Water soluble binder salts can result from the reaction of binders having acid groups with amines or the reaction of binders containing basic groups with acids. Volatile bases or acids should always be used as the neutralising components. These are capable of escaping during the drying of the coatings with the reconstruction of the water insoluble acidic or basic binder. Such binders can also be cross-linked at their reactive groups at room temperature or at elevated temperature which further improves their water resistance properties. Stability to dampness and water is an important condition for corrosion protection coatings.

Low solvent coatings, so called medium- solid or high solid coatings can be manufactured in two ways.

- a. The selection of the solvent to be used not upon price, but upon the ability to dissolve the binder with low viscosity and high solids content.
- b. Development of low molecular weight binders with better solubility in solvents.

Solvent selection can be empirical or based on calculation using the solubility parameters of the solvents and binders. Fundamentally, the solubility parameters a thermodynamic values which give a quantitative prediction of the type and strength of molecular interaction between solution viscosity based on the solubility parameters is possible.

The development of low molecular weight binders cans result from physically and chemically drying binders. In both cases, there are natural limits to the venture. The molecular weight of the physically drying binders cannot reach values that are too low or the coatings may become susceptible to dirt or even tacky as well as lose their mechanical properties of hardness and elasticity. In the case of chemically drying binders, the functionality increases rapidly with decreasing molecular weight, the binders become very polar and moisture sensitive. In addition the use of large quantities of hardeners is required, which often results in a strong cross-linking, associated with increased brittleness of the coating.

Low solvent coatings, powder coatings and radiation curing coatings are speciality coatings having limited use in special applications.

In certain application water-borne coatings are preferred and there is a trend to replace solvent based coatings with water- borne coatings. In water-borne coatings water is a main solvent. Properties of water are different than other organic solvents generally

used in coatings. It is necessary to understand the difference between properties of water and other organic solvents before formulating water-borne coatings.

2.3 Properties of Water

In water borne coatings, water serves as solvent and dispersion medium compared with other solvent, water has decidedly different properties.

1. Water freezes at 0°C as a rule; water-borne coatings should therefore be stored above the freeze point. It must be checked in every case, whether the freezing process changes the coatings technical properties such as stability, processing or surface properties.
2. Water boils at 100°C and vaporises as homogeneous substances with a relatively low volatility compared with solvents. In solvent containing coatings solvent mixture are present that provide for a time-wise extended, uniform vaporisation and therefore the development of a smooth coatings surface. In the case of water borne coatings, difficulties with the optical surface quality of the coating must be anticipated for this reason. To counter this auxiliary solvents and film-building agents are used in water borne solvents. The use of additives and the correct selection of binders must be contributed to mastering surface problem.
3. Water has a decidedly higher surface tension than organic solvents. This leads to a poorer wetting of the substrate to be coated. Addition of auxiliary solvents serves to reduce the surface tension of the water
4. Water has a higher enthalpy of vaporisation compared with solvents. The drying of water borne coating therefore requires the addition of greater amount of energy and also requires a more time.

5. Water is not flammable, an advantage that can affect the cost of insurance premiums for insurance and is also of significance in terms of handling storage and shipping.
6. Water has totally different solubility parameters than organic solvents. It is definitely polar and forms significantly stronger hydrogen bonds, than those known for organic solvents. As a result, the interaction between binder and water molecules is also of a different quality and quantity than in the case of solvent containing coating.
7. The electrical and thermal conductivity of water is of a different magnitude than those of organic solvents. In contrast with solvents, water used in coatings is not an insulator. This is the reason for the problems to be anticipated in conceptualising electrostatically sprayed water-borne coatings.
8. Water is non-toxic, non-flammable, non-hazardous solvent with least effluent problem.
9. It is low cost solvent. ⁽³⁾

2.4 Types of Aqueous Coatings System

There are three general types of aqueous coating.

1. Water-soluble
2. Water dispersible
3. Water reducible.

All have one thing in common that they contain water as the principle volatile component or reducer. The advantages of water for this purpose are its nominal cost, non-flammability, true odour lessness and non-toxicity. Along with these advantages there are certain disadvantages or limitation to the use of water in coatings. It is more difficult to adjust wetting, flow drying and other characteristic of coatings containing water. In solvent type coatings solvents and diluents may be selected from a great assortment of materials available in a variety of composition and boiling ranges in order to adjust application properties.

2.4.1 Water-soluble

In water-soluble coatings the vehicle or binder is dissolved in water. Since binder is soluble in water, it will remain water sensitive unless converted to an insoluble form by some means such as polymerisation. For this reason many coatings based on water soluble resins are of the baking type. Water-soluble coatings have the following general properties.

Advantages

1. Simple formulas:- Pigment, vehicle and water with which catalyst and defomers are necessary in some cases.
2. Ease of manufacture: - It can be handled the same as conventional solvent type paints with the pigment being ground directly into the vehicle.
2. Good film continuity: - Continuous film similar to conventional solvent system.
4. Gloss: - Possible to produce coatings of high gloss.

2.4.2 Water Dispersible:-

In water dispersible type of coatings the vehicle consists of small particles of binder distributed in water medium. The size of these particles ranges from 0.1 to 10 microns.

Advantages

1. High Molecular Weight: -- It is possible to use high molecular weight polymer with outstanding properties such as colour retention, water resistance, chemical resistance, good chemical strength.
2. Air-drying: - Superior coatings are obtained on air-drying
3. Good holdout: - On all types of surfaces including porous substrates

2.4.3 Water Reducible:-

Water reducible materials can be produced in which conventional solvent materials are used along with surfactant. For application these can be reduced with water. Properties are somewhat intermediate between solvent and water-based paints. If enough water is present, the liquid paint will not burn if it exposed to a flame even though it contains some inflammable solvent. ⁽⁴⁾

2.5 Binders

Binders play important role in coatings. They are polymeric materials capable of forming films. Properties of a coatings and method of processing are governed by properties of binder to a larger extent. Various types of binders are used depending on properties desired from a coating for particular application. Some of the binders used for coatings are described below.

- (1) Acrylics:
- (2) Amino resins
- (3) Bituminous:
- (4) Cellulose's:
- (5) Drying Oils:
- (6) Epoxies:
- (7) Chlorinated Polyethers:
- (8) Fluorocarbons:
- (9) Hydrocarbons:
- (10) Phenolics:
- (11) Polyamides:
- (12) Polyethylene:
- (13) Rubbers:
- (14) Polystyrene:
- (15) Polyurethane and polyisocyanates
- (16) Alkyds

2.6 ALKYDS AND POLYESTERS AS BINDERS FOR WATER-BORNE COATING

2.6.1 Alkyds

Alkyds are a group of resins, which can be called “oil - modified polyester resins”. They are polymers formed by the reaction of polybasic acids, polyhydric alcohols and fatty acids. The polybasic acid may be phthalic anhydride, maleic anhydride etc. the polyhydric alcohol may be glycerine, pentaerythritol etc and the fatty acids of soya, linseed, dehydrated castor oil, etc. Alkyd resins are formed by a condensation reaction with the elimination of water. The greater the oil contents of an alkyd the greater the flexibility. Alkyds have good adhesion and good compatibility with other resins in emulsion form. Alkyds sometimes show loss of water and dry on prolonged storage. The incorporation of a polyethylene glycol into an alkyd resin produces a resin that is easily dispersed in water.

Alkyds can be produced in a water-soluble form by formulating a molecular weight. One method of producing a water- soluble alkyd is to incorporate a tri functional acid such as trimellitic anhydride or dimethylol propionic acid. Water solubility can be achieved by stopping the processing of the resin at light acid value and neutralising with an amine or ammonia to produce a water- soluble salt.

Alkyd resin are very versatile materials and they are used in combination with many other resins.

2.6.1.1 Use of alkyds in coatings

Alkyds and saturated polyester-based coatings have wide applications. Variations in the kind and proportions of the ingredients and in the method of manufacture lead to alkyds of widely varying properties and this is reflected in the large number of alkyds which resin manufacturers make available to the coatings industry as standard products for different application.

In addition to the wide variety of alkyds, the number of different binders in which they are used is greatly increased by the excellent compatibility with other binders which alkyds display. They may be used in conjunction with drying oils, phenolic resin, amino resin, nitro-cellulose, rosin derivatives, maleic resins, chlorinated rubbers, cyclized rubbers etc.

As a group rapid drying, good adhesion, elasticity, marproofness and durability distinguish the alkyds. Their principal weakness resides in the ease with which the ester groups, which form so large a part of the molecules, are hydrolysed, particularly under alkaline conditions. Even in this respect it is possible to produce alkyds with greatly improved resistance to hydrolysis, by the use of polyols or by the use of acids containing sterically hindered carboxyl groups.

The alkyds achieved their first success in stoving coatings, where their use led to the solution of a number of problems which had proved largely insoluble with oleoresins lacquers. Stoving schedules could be speeded up and temperatures lowered with completely satisfactory results. In combination with urea and later with melamine resins even greater production flexibility and result of higher quality were obtainable. For the industries making cars, refrigerators, washing machines and many others goods the advantage of alkyd resins was the start of a revolution in finishing methods.

2.6.2 Polyesters

Polyesters are a class of polymers containing carboxylate ester groups in the polymer back-bone.

By this definition they are distinguished from other ester containing polymers in which carboxylate groups form part of the pendant substituents on the polymer chain such as in cellulose acetate, poly (acrylate) and poly (vinyl ester). Water –soluble saturated polyesters are used in industrial baking e.g. in combination with melamine formaldehyde resin. They display good properties relative to elasticity, surface hardness, wear resistance, gloss, weathering resistance and scratch resistance and often parallel corresponding short oil alkyd resin. It has wide application in coil coatings, office equipment and in the automobile supply industry. These coatings are easy to process. Thus polyesters as a class has wide application in different fields.

2.6.2.1 Synthesis of polyesters

Some of the synthetic routes for preparation of polyesters are listed below:

1. Direct esterification: It involves reaction of a diacid with a dihydroxyl compound.
2. Alcoholysis: It consists of reacting a diol with dicarboxylic acid diester.
3. Acidolysis: By reacting diol diester and dicarboxylic acid.
4. Double ester exchange: By reacting diol diester with dicarboxylic acid diesters.
5. By reacting acid chloride of dicarboxylic acid with diols
6. By ring opening polymerization of cyclic esters.

The chemical structure of the polyester can be manipulated by proper selection of monomer. A control of molecular weight may be achieved by the use of mono carboxylic acid, which terminates the growing chain.

Polyesterification is a step growth reaction; it is essential to use the reactants close to their stoichiometric proportions. Any imbalance in the stoichiometry results in a lowering of the

molecular weight. ^(5,6) This phenomenon can be used as a tool to control the number average molecular weight of the polyester.

Most of the polyester based coatings presently used are solvent based. There is need to develop water borne polyester coatings. There has been an effort to develop water borne polyesters, which is reviewed below.

2.7 Water- Borne Polyesters

Water-soluble polyesters are prepared by introducing hydrophilic groups into the polymer chain or inside chains. These polyesters are supplied in water or the diluted with water on site. They are frequently combined with neutralising or salt forming agents and water miscible co-solvents. Water-soluble polyesters are usually converted to water insoluble form after application and water evaporation. Low molecular weight polyesters are converted into high molecular weight and the hydrophilic groups are converted into hydrophobic form by condensation with water dispersed co reactants such as urea, phenol, melamine formaldehyde resins.

The monomer used in the preparation of water soluble polyesters are usually the same as those used in polyesters and alkyds except the minor amounts of special intermediates e.g. dimethylol, propionic acid or trimellitic anhydride to confer the water solubility. The properties and performance of these polymers are excellent than those of the parent polyesters.

The largest consumers of water-soluble polyesters are the surface coatings and related industries. The use of other water soluble alkyds increased in coatings for automotive parts, machinery and other metal and glass applications, water soluble polyesters and alkyds also find use in paints, stains coil and wire coatings and appliance and electrodeposition top coats. Aqueous systems are less hazardous and can be less expensive.

Depending upon the chemical composition and configuration unsaturated polyester can be made to exhibit high chemical resistance a low degree of flammability, high resistance to weathering and excellent electrical properties. These properties are not always obtainable from polyester; thus the large variety of unsaturated polyester which are used for construction, machine, housing electrical insulator, tanks, pipes, boats and furniture parts.

2.7.1 Water- Dispersible Oils and Alkyds

Numerous water-soluble paints systems are based on resinous or drying oil compositions emulsified with natural colloids. Emulsions of oils or alkyds with soaps of ammoniated fatty acids ⁽⁷⁾ and anionic or non-ionic emulsifiers and colloids met with limited acceptance because of poor stability, low water resistance and slow drying properties. Attempts to introduce hydrophilic emulsifying agents into the polymer to improve stability led to water-soluble, oil based polyesters.

These esters are prepared by shifting esterification equilibrium at high temperature by removing the water produced. ⁽⁸⁾ The ester groups are sensitive to hydrolysis. The polyester are dispersed and stored in an aqueous solution.

2.7.2 Water-soluble Polyester Compositions

These polyesters can be divided in to two types according to whether the ester linkages are in the side chains (I) or in the main chain (II).

In type (I) the ester groups are on the short side chains and are for the most part, derived from rosin and triglyceride oils or their component as opposed to acrylic or vinyl acetate type polymers. Type (II) represents the conventional polyesters and alkyd structure prepared from polyol and polyacids when the ester group is part of the polymer chain as well as side chain.

2.7.2.1 Type- (I) polyesters

2.7.2.2 Maleic anhydride Treated Polyesters

The reaction of unsaturated oils with maleic anhydride gives a water- soluble product after neutralisation with base. ⁽⁹⁾ The salt formation allows polymer dispersion under low shear conditions in to particles smaller than emulsion, stabilised by a dipole layer on the surfaces. With a conjugated unsaturation such as that found in tung oil on it's derived acids, the maleic anhydride reaction mechanism is of the Diels- Alder type. ⁽¹⁰⁾

High acidity (80-160%) is needed to supply sufficient neutralisation sites. 2- butoxyethanol is a useful co solvent. Its surface- active balance of hydrophobic and hydrophilic portion of the molecule helps in particle formation by the emulsion action of the maleic residue salt groups attached to the oil. ^(11,12) Lower boiling alcohols are used when fast evaporation is needed. ^(13,14) Surface active co solvents ⁽¹⁵⁾ are frequently used to stabilise particle dispersions ⁽¹⁶⁾ and minimise polymer acidity requirements. The sizes of the particle or micelles indicated above are frequently less than what wavelength of light, giving clear dispersion.

2.7.2.3 Rosin Esters Treated with Maleic Anhydride

Similar to type –I water soluble polyesters are rosin esters treated with maleic anhydride or fumaric acid. The reaction with the maleic anhydride may be conducted on the rosin esters. Alternatively, the rosin acid may react with maleic anhydride or fumaric acid and esterified with the polyol, to give a similar carboxyl – functional polyester. They find extensive use in water- soluble inks.

2.7.2.4 Epoxy or Styrene- Allyl Alcohol Co- Polymer Esters

Oil paints treated with maleic anhydride are sufficiently stable in dip primer applications. But electrodepositions is more demanding because of its sensitivity to the acidic components resulting from hydrolysis of a polyester. ⁽¹⁷⁾ Furthermore these oils provide little corrosion

protection because of poor hydrolysis resistance. By replacing the glycerol with the polyol such as an epoxy resin, the resulting fatty acid ester groups are spaced farther apart with the hard non-saponified resin. ⁽⁵⁾ The fatty acids of these polyesters may then be treated with maleic anhydride to supply carboxyls for neutralisation and water solubility. ⁽¹⁸⁾ Alternatively unreacted hydroxyl may react with anhydrides, such as succinic, to give solubilizing carboxyls.

2.7.3 Type -II polyesters

In type -II polyesters the sequence of ester groups is repeated in the continuing polymer chain. The hydrophilic sites needed for water solubility determine the preparation methods and the solution properties.

2.7.3.1 Alkyds Modified With Poly (Ethylene Oxide)

Water -soluble polyesters can be prepared having high concentration of hydrophilic non-ionic groups such as hydroxyls along the polymer chain. ⁽¹⁹⁾ These polyesters are readily hydrolysed and their use is limited to a few melamine-formaldehyde thermosetting systems. The reaction of alkyd resins with polyethylene oxide (molecular weight 200-5000) introduces a hydrophilic segment on the polymer chains, which act as an emulsifier to aid the formation of hydrophobic particles shielding the polyester chain from hydrolysis. ⁽²⁰⁾

Although these water- soluble alkyds are used as polymer binders for architectural paints or stains, water sensitivity, tackiness, blocking and low drying rates create problems. They are blended in minor proportions with latex-based paints to improve the chalkiness and adhesion of weathered paint surfaces. These alkyds are also used in textile finishes, ⁽²¹⁾ particularly when cured with melamine or urea formaldehyde resins.

2.7.3.2 Polyesters or Alkyds Modified by Trimellitic Anhydride

In the 1970s interest in water- soluble, low oil alkyds increased because hardness developed rapidly and corrosion resistance on metal- finishing assembly lines employing oxidative

curing was good. High aromatic acid content promotes hardness and corrosion resistance; trimellitic anhydride offered a convenient source of carboxyls for neutralisation.

Maleic anhydride treatment was less desirable in these low oil alkyds because of the tendency to consume unsaturation from the fatty acids needed for oxidative cross-linking.

The three potential carboxyls of TMA are convenient for placing a carboxyl at intervals along the polyester chain promoting water solubility at low acid contents. The anhydride groups react with pendent hydroxyls to place the residual carboxyls along or at the end of a performed polyester chain. For imparting corrosion resistance and hydrolytic stability, trimellitic anhydride and isophthalic acid are preferred over phthalic anhydride. ^(8,16) Low hydroxyl content promotes hydrolytic stability and water resistance. The product is diluted with 2-butoxyethanol to 70% non volatile. These water-soluble alkyd solutions in co solvent are frequently used as pigment dispersion media before further dilution with dryers, neutralising amines, and water to suitable viscosities. ⁽²²⁻²³⁾

2.7.3.3 Oil- Free Thermosetting Polyesters

Compositions for curing with hexmethoxymethylol melamine resins through their hydroxyl and carboxyl groups can be prepared with formulations. For lower cost formulations, trimellitic anhydride is frequently replaced by adipic or isophthalic acid, and glycol content is reduced. Such water-soluble polyesters are used in electrodeposited, topcoat- quality paints, frequently in combination with acrylic resins. Similar coatings are used in exterior can coatings. ^(24,25)

2.7.3.4 Dimethylolpropionic Acid Polyesters

Water- soluble polyesters or alkyds prepared with dimethylolpropionic acid (DMPA) polyol exhibit improved hydrolytic stability. The carboxyl group does not participate in the reaction, but the two-hydroxyl groups link with the polyester chain. However, because of its high price DMPA is little used in water-soluble polyesters and alkyds. It is used, however in water-

soluble urethane ⁽²⁶⁾ or urethane oils, ⁽²⁷⁾ where it increases solubility. The polyester is neutralised with dimethylethanolamine and diluted to 35% nonvolatiles with water.

2.7.3.5 Sulfoisophthalic Acid Polyesters

Patents have been issued on the preparation and use of sulfonated water-soluble esters ⁽²⁸⁾ for textile sizing and treatment, and on phosphate ester ionic groups ⁽²⁹⁾ in corrosion-resistant, water-soluble polyesters. The sodium salt of 5-sulfoisophthalic acid, as well as hydroxyl functional sulfonic acids, has also been patented. ⁽³⁰⁾ The strong acids apparently increase the adhesion of the polyester to the base polyester fiber and improve washability, dye reception, and fabric feels. They are also useful in adhesives. ⁽³¹⁾

2.7.3.6 Polyesterimides and Polyesteramides

Water-soluble polyesters and alkyds for wire coating have been patented ⁽³²⁾ as well as inclusion of primary amine and diamine residues along the polymer chain for improved wire-enamel resistance. ⁽³³⁾ Polyesterimides are also described for use in water-soluble polyester adhesives. ⁽³⁴⁾

Thus various types of water-borne polyesters are known. However present trend is to develop polyesters containing solubilizing groups to improve shelf life of coating. Disadvantages of water-borne polyester coating are their sensitivity to hydrolysis. Polyester is prone to hydrolysis. However sensitivity to hydrolysis depends on structure of polyesters. Structures of both diacids and polyols determine the stability of polyester towards hydrolysis

2.8 SELECTION OF MONOMERS FOR POLYESTERS

2.8.1 Selection of Polyol

Polyols are selected on the basis of cost, rate of esterification, stability during high temperature processing i.e. minimum decomposition and discoloration ease of separation from water during processing. Viscosity of ester at equal molecular weight and functionality, effect on Tg, rate of cross-linking with melamine formaldehyde resin (MF) and the hydrolytic stability of their ester. The most widely used diol is neopentyle glycol (NPG) and triol is tri methylol propionic acid (TMP) both have the neopently type structure. They are relatively difficult to esterify. It is fair but not always accurate generalisation that the slower the rate of esterification the greater the resistance of the ester to hydrolysis. The hydrolytic stability of the ester of NPG is significantly better than those from less hindered glycol like ethylene glycol or propylene glycol. Neopentyl glycol (B.P.-213°C) is volatile at esterification temperature so that well designed fractionating and condensing equipment is needed to permit the removal of water with a minimum loss of glycol during processing at 220 to 240°C. NPG has no beta hydrogen and therefore, imparts stability to heat, hydrolysis and weathering to polyester. It imparts chemical resistance as well.

2.8.2 Selection of Polyacids

Most polyesters contain a mixture of aromatic to aliphatic acid is the major factor that controls the Tg of the resin. Aromatic acid ester hydrolyse more slowly than aliphatic ester, unless there is an anchimeric affect. Sterically hindered carboxylic acid groups esterify more slowly and their ester are generally more stable to hydrolysis.

The processing cost advantage of phthalic anhydride (PA) results from it's lower melting point (131°C) it can be handled as a molten liquid it is readily soluble in the reaction mixture and it's reactive anhydride structure rapidly forms mono esters at about 160°C on the other hand isophthalic anhydride (IPA) (MP>300°C) is more difficult to process because it

dissolves slowly in the reaction medium and its lower reactivity slows the processing. These problems are even more acute with terephthalic acid. Due to the required longer time at high temperature volatilisation losses and acid catalysed side reactions e.g. etherification or dehydration of polyols are more serious problems than with PA.

Adipic acid is probably the most widely used aliphatic dibasic acid. Succinic and glutaric acids give esters with inferior hydrolytic stability presumably due to the anchimeric effect longer chain acids such as azelaic and sebacic acids may give somewhat better hydrolytic stability and greater reduction of Tg as compared with adipic acid but are more expensive.

The PA and IPA is used because of their ease of handling, good balance of properties and economy IPA is typically used as a total replacement for PA when a tougher, more flexible faster drying and more chemical and fume - resistance coating is required.

2.8.3 Trimellitic Anhydride

The ester group of partially esterified TMA is particularly subject to hydrolysis because of the anchimeric effect of the adjacent carboxylic acid group. Hydrolysis of the TMA partial ester will result in removing of the solubilizing carboxyl groups and thereby, destabilise the resin dispersion. The film properties may also be adversely affected. In addition, the use of primary alcohol as a solvent is recommended. Primary alcohols have been found to esterify carboxylic acid groups and transesterify groups during the thinning at 160°C and at a slow but appreciable rate, during storage of the resin. TMA promote chain branching and provide carboxyl groups along the polyester chain, which can be utilised in making water-soluble resins.

2.8.4 Dimethylol Propionic Acid

An alternative approach that provide somewhat better but still limited hydrolytic stability is to use 2,2-Dimethyl propionic acid as one of the diol component. The carboxylic acid group of this monomer is highly hindered by being located on a tertiary carbon. The resulting

differential reactivity makes it possible to esterify the hydroxyl groups while leaving most of the acid groups unreacted. While they are too hindered to esterify readily the acid groups are accessible to proton and readily form salt.

2.8.5 Neutralisation Agents

The most important method for converting classical coatings resins into water-reducible form is salt formation. With this the carboxyl groups present in the anionic resin are neutralised with ammonia, amines or amine derivatives. The acid number of such resins is normally higher than that of the usual systems. The influence of the neutralisation agents used is important for the stability of the resulting water-soluble resin and its technical applications properties.

The background for the great significance that the correct selection of the neutralisation agent has, is the viscosity anomaly of water-reducible resins. The neutralisation agent has a significant effect on this. The neutralisation should be as complete as possible. An insufficient dose results in a greater viscosity peak because of the slight polarity and thus solubility of the resin molecules. An over dose has no direct effect on the viscosity peak. The base strength of the amine used is obviously unimportant. Not only the neutralising effect and salt formation of the amine, but also its effect as a solubility promoter play an important role. The amine influences the storage stability pH value, viscosity.

As already mentioned, amines or their derivatives are used as neutralisation components. Triethyl amine (TEA) is frequently used. Ammonia is indicated as a less toxic substitute product, but is also not totally tried from a purely technical view has the disadvantage of hardly possessing auxiliary solvent properties. Good results are obtained with mixtures of amino alcohol, and ammonia or triethyl amine.

2.9 CROSS LINKING REACTIONS

Amongst all reaction in polymer chemistry, a cross-linking reaction is by far the most useful industrially. Bridging formed between linear polymer chains, leading to a three dimensional network structure, are know as “Cross-Links”.

The cross-links between polymer molecules can be either through regular covalent bonds or through secondary valence type linking such as hydrogen bonds. The former types called chemical cross-linking or irreversible cross-linking and the latter, the physical or reversible cross-linking, in fact plays a vital role in polymer crystallisation. The intermolecular connections effected through secondary valance bonds, such as hydrogen bonds, are undoubtedly weaker compared to the regular covalent bonds, and hence can be removed with much ease such as by dissolving the polymer in appropriate solvents or by simply heating the polymer above it's T_m . A chemically cross-linked polymer can neither be melted by heating nor dissolved in a solvent. Prolonged or drastic heating will lead to the degradation of the polymer.

Polyesters used for water-borne coatings have low molecular weight and as such they can not form a film. These polyester are cross-linked with multifunctional resins such as melamine formaldehyde, phenol formaldehyde and urea formaldehyde. Generally melamine formaldehyde resin with high functionality are preferred.

2.9.1 Melamine Formaldehyde

Melamine formaldehyde resin is used because of their greater functionality, have significantly different properties to urea formaldehyde resins having better chemical resistance, colour retention at elevated temperature, better exterior durability, and shorter baking schedules. When in combination with hydroxyl resin it should be noted that their reactivity might be less than that expected for steric reason. They are more expensive.

UF resins are very satisfactory, however, for general purpose industrial finishes and the extensively used in acid catalysed room temperature cured wood finishes.

Alkylated melamine resins are chosen by their reactivity where high reactivity may mean high viscosity and rapid cure but low mineral spirit tolerance and hence poorer compatibility with alkyd resins. While the generally used resins are butylated, other alcohols are used. Secondary and tertiary alcohol modified resins are generally slower curing but may result in harder film.

2.9.2 Application Process

The methods adopted depend on the market in which the paint is used, each type of paint being formulated to meet the needs of the application method. Spreading by brush or hand-held roller is the main method for applying decorative / architectural paints and the maintenance of structural steel work and buildings generally. It is also important in marine maintenance.

Application by spraying is the most widely applicable method. It is used for painting motor cars in the factory and by re-finishers following accident damage. It is used in the wood finishing industry and in general industrial paints. Electrode position as method of painting has become growth area during the last two decades. It has become established as the main method of priming the steel body shells of motor cars. The total process, which involves degreasing phosphate treatment electro deposition of primer & then sprays application of surface and finishing coats has raised the standards corrosion resistance and general appearance considerably during this period. Electro deposition may take place with the car body acting as either the anode or cathode. In recent years it has been claimed that cathodic forms of electro paint give the better corrosion protection.

The main requirement for these types of finishes are appearance, durability and corrosion protection Automotive finishes comprise mainly of an under coat or a primer and topcoat.

Topcoats are usually formulated to impart high gloss. The most important single performance parameter for automotive coatings is excellence of appearance. Other properties play an important role in the selection of suitable automotive coating systems are mechanical properties of films and their durability on outdoor exposure. Mechanical properties include mainly film adhesion to substrates intercoat adhesion of system components, film hardness and retention of film integrity under deformation on bending stretching sharp impact or stress developed by sudden thermal shock. Durability, on the other hand mainly includes blister resistance or resistance to gloss loss during exposure to humidity and condensation. These are usually applied in the film thickness of 7.5-25 μ .

2.10 OBJECTIVE OF WORK

From the forgoing description, it is evident that saturated polyesters based on adipic acid, neopentyl glycol and trimellitic anhydride has good hydrolytic stability, a property desired for water-borne polyester similarly introduction of aromatic acids improves properties of polyesters but lowers water solubility. A balance can be achieved by partial replacement of aliphatic diacids with aromatic acids. Trimellitic anhydride serves as a partial substitute for aliphatic diacids and it also provides free acid for water solubilisation. It has wide applications in different fields. However much work is not reported on this subject. Hence the present work was undertaken to study water-borne polyesters based on adipic acid, neopentylglycol and TMA.

In a polydispersed system, containing both low and high molecular weight components, low molecular weight component get fully solvated to start with and then they diffuse out forming a solution, while higher molecular weight components remain still in the mode of progressive salvation. When ΔH is negative, the high molecular weight components also get fully solvated with time and go into solution. The higher the molecular weight, the longer the time taken for dissolution since the number of segments to be solvated is larger on the other hand when ΔH is positive. The point of equilibrium may be reached before the high molecular weight component also gets fully solvated. At the point of equilibrium $T.\Delta.S$ become equal to $+\Delta H$ and therefore, molecules with a molecular weight below a certain critical value will be in solution and those above it will be in a swollen state. ⁽³⁵⁾

Thus molecular weight also influences solubility and properties of cross-linked coatings. Low molecular weight polyesters give higher cross-link density rendering coating brittle, while high molecular weight polymers may pose difficulties in solubility. Thus proper balance of molecular weight of polyester is essential for optimum properties.

Thus present work describes the synthesis and characterisation of acid and hydroxyl value of adipic acid neopentyl glycol and TMA based polyesters of five different molecular weight of 500 to 5000 by varying the ratio of NPG: adipic acid mole ratio. It also describes preparation of water borne polyesters and their characterisation by determining abrasion resistance, scratch resistance, impact resistance, film thickness, adhesion, water resistance, solvent resistance.

CHAPTER-3
EXPERIMENTAL

3.1 Chemicals

1.	Neopentyl Glycol (NPG), L.R. Grade S.D. Fine Chemicals, (Mumbai)
2.	Adipic Acid (AA), L.R. Grade S.D. Fine Chemicals, (Mumbai)
3.	Trimellitic anhydride (TMA) Alderich Chemical Company, INC.
4.	Melamine Formaldehyde resins (MF), Pidilite Industries, Mumbai.
5.	Triethyl amine (TEA), M/s (Ranbaxy Laboratory, India)
6.	Acetic anhydride, L.R. Grade S.D. Fine Chemicals, (Mumbai)
7.	Pyridine, M/s (Ranbaxy Laboratory, India)
8.	2-butoxy ethanol, L.R. Grade S.D. Fine Chemicals, (Mumbai)
9.	Xylene, M/s (Ranbaxy Laboratory, India)
*	All chemicals were used without further purification.

3.2 Preparation Of Water Borne Polyester

3.2.1 Experimental Set Up

The polyesterification reaction was carried out in a 500 ml four- neck round bottom flask, equipped with a mechanical stirrer, gas bubbler, thermowell and Dean-Stark assembly. The schematic diagram of the reactor is shown in diagram of polyesterification reaction.

500-ml capacity heating mantle was used for heating. Gas bubbler was used to purge the nitrogen gas in order to maintain inert atmosphere over the reaction mixture. A thermometer was inserted into the thermowell. Dean-Stark apparatus was used to remove the water of reaction azeotropically.

3.2.2 Preparation of polyester No -1

In one litre capacity four neck round bottom flask equipped with mechanical stirrer, thermowell, gas bubbler and dean- stark apparatus, 189.0045 g of AA, 218.9110 g NPG, 0.25 g of DBTO and 15 g of xylene were charged and the flask was heated in one litre capacity heating mantle to 110°C.

At this stage stirring and gas purging started. At about 110° C water of condensation started coming out and getting collected in dean- stark apparatus as temperature of the flask went on increasing. The rate of heating was controlled in such a way that temperature increased 10° C / hr. At this rate the flask was heated till the temperature reached to 220° C. The flask was maintained at 220°C till acid value reached less than one and the desired hydroxyl value was obtained. The amount of water collected in the first stage was 46 ml. After obtaining the desired hydroxyl value, flask was cooled and required quantity of TMA was added at room temperature. Again flask was heated slowly to 170° C in about 2h time and maintained at 170°C till the remaining water of condensation (14ml.) was collected.

The polyester was cooled to room temperature. The polyester was transparent liquid in appearance.

3.2.3 Quaternisation with TEA

In a 100 ml three neck round bottom flask, equipped with mechanical stirrer, dropping funnel and thermowell, 50 gm of above polyester and 5 ml of 2- butoxy ethanol were taken. The mixture was stirred and 9.0017 ml TEA was added dropwise to this mixture in 15 minutes While stirring. The temperature rises to around 55⁰ C.

3.2.4 Preparation of water-borne polyester

Above polyester solution was added to 12.14ml (for 70 % solid) water content in a 500 ml beaker at ambient temperature with vigorous stirring. The stirring was continued for ½ h to obtained transparent, clear water-borne polyester.

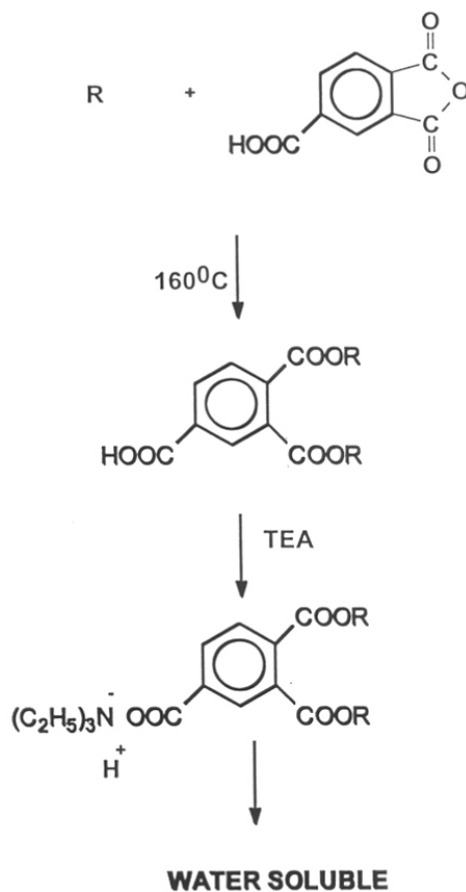
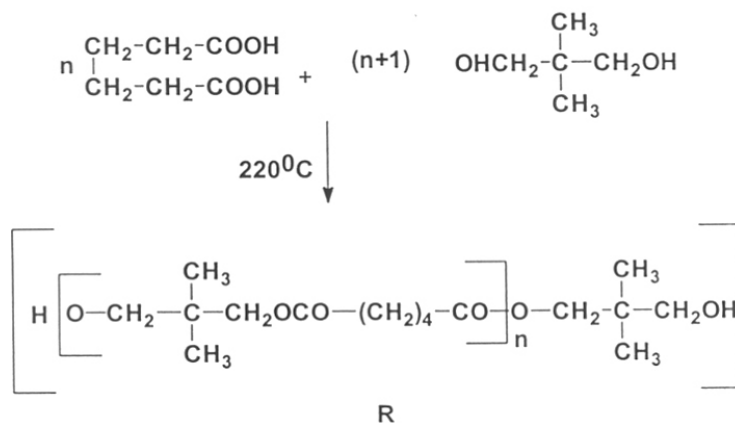
3.2.5 Preparation of coating

10 gm of above solution was taken in 100-ml beaker to which 2 gm melamine formaldehyde resin was added and stirred with a glass rod for 10 minutes to get a homogeneous solution. To this 0.6gm of PTSA solution in water 0.6gm of F.C. 430 (levelling agent) was added and stirred by glass rod for 5 minutes.

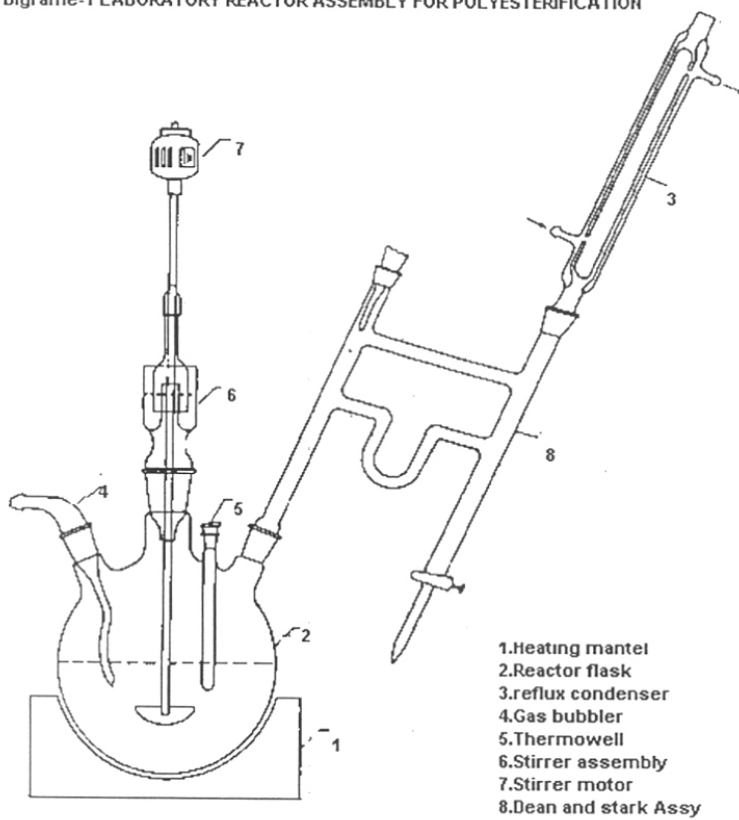
Glass and aluminium plate cleaned with acetone was coated with above solution using brush No- 4 to give coating of thickness ~ 1.5 mile the plates after levelling was placed in a levelled oven maintained at 160^oc for 30 minutes.

Coatings of all other polyesters were prepared by similar procedure. However quantity of 2-butoxy ethanol was added depending on the viscosity of the polyesters.

SYNTHESIS OF POLYESTER



Digrame-1 LABORATORY REACTOR ASSEMBLY FOR POLYESTERIFICATION



3.3 CHARACTERISATION TECHNIQUES

3.3.1 Determination Of Acid Number

Definition

Acid value is a numerical measurement of the quantity of free acids (both organic and inorganic) in a substance. It is quoted as the number of milligrams of potassium hydroxide, which are required to neutralise the free acid in one gm of the substances.

Standard: ASTM D-4662 (1990)

Apparatus: Measuring cylinder, 100 ml conical flask with stopper, micro-burette (0.02 ml)

Reagents and chemical :

0.1N alcoholic KOH, bromothymol blue indicator, distilled toluene and ethyl alcohol

Procedure:

About one gram sample was accurately weighed in 100-ml conical flask. It was dissolved in 25 ml 1:1 solution of toluene: ethyl alcohol mixture. It was shaken till all the material dissolved. Five drops of bromothymol blue indicator were added to the flask and the content titrated against 0.1N alcoholic KOH with stirring. End point was yellow to green to blue. A blank was also run at the same time.

Calculation: Acid number = $\frac{(S-B) \times N \times 56.1}{W}$

W

Where S = Volume of alcoholic KOH required for sample titration.

B = Blank titration volume of alcoholic KOH.

N = Exact normality of alcoholic KOH.

W = Weight of sample taken.

Analysis time: One Hour.

3.3.2 Determination Hydroxyl Value

Definition:

It is numerical measure of the content of free hydroxyl groups in organic substances. It is expressed as the number of milligram of potassium hydroxide equivalent to the hydroxyl contents in one gram of the substance.

Standard:

ASTM E-222 (1990)

Apparatus:

250-ml conical flask with standard F -19 joint condenser, M-19 joints. Hot plate with variable resistance for temperature control, burette of 50-ml capacity with 0.1ml reading. Acetic anhydride (AR grade) distilled pyridine (99.5%), phenolphthalein indicator, 0.5 N alcoholic KOH.

Acetylating reagent :

Acetylating reagent was prepared by taking 10ml of acetic anhydride in a 100ml measuring cylinder and diluting it to 100ml by the addition of dry pyridine. The fresh reagent was used for estimation.

Procedure:

About one gm of sample was weighed accurately to the nearest milligram in a 250-ml conical flask and 10ml of acetylating reagent was added to it with pipette. The flask was connected to refluxing condenser and heated on a hot plate at reflux temperature for one hr. Reaction mixture was cooled to room temperature and refluxed again for 15 min. after the addition of 25ml distilled water. The mixture was cooled at room temperature and condenser washed

with 2ml water to wash adhering reagent and condensed vapours in to the flask.

The mixture was titrated with 0.5 N alcoholic KOH using phenolphthalein as an indicator to a faint pink end point. Two blanks were also run at the same time. At least three readings were taken for each sample.

Calculation :

$$\text{Hydroxyl Number} = \frac{[A-B] \times N \times 56.1}{W}$$

Where

A = Ml of Alcoholic KOH required for the titration of Blank.

B = Ml of the Alcoholic KOH required for the titration of the sample.

N = Normality of Alcoholic KOH

W = Weight of sample taken.

Analysis Time: Four to five hour.

3.3.3 Abrasion Resistance

Abrasion:

The removal of surface material from any solid through the frictional act of another solids, liquid or a gas or combination there of or by chemical degradation.

ASTM - D – 4060

A widely used test is the Taber Abrader. Two rotating abrasive wheels roll on a panel creating a circular wear path. The test is continued until the coating is worn through and the results are reported in numbers of rotations required to wear through one mil (25µm) at coating.

(Load) Weight= 1000 Gm (1Kg.)

Wheel = CS 17

Cycles = 1000

3.3.4 Scratch Hardness

ASTM - D5178

ASTM - D2197

An important requirement is that a film of a coating within a reasonable time of applications shall reach a degree of hardness suited to the purpose, which the object is to fulfil. This is represented by the force, which must be applied to a hard more or less pointed object in order that it shall cause a scratch in the film.

3.3.5 Film Thickness Measure (Digital)

ISO 2178 and 2360

In the protection of steel by the use of anti corrosive paint systems it is of vital importance that the paints are applied at adequate film thickness. The rather uncertain results, which have been obtained to date, indicate within certain limits a roughly linear relationship between film thickness and the protective properties of the painting system.

The quantity of primer, which is necessary to give a certain film thickness, is strongly dependent on the roughness of the metal surface. On the basis of experience it is usually recommend that the minimum thickness of dry primer coat on a smooth surface should be Ca - $40\mu\text{m}$ (15 mil). A short blasted surface where the irregularities may be over $50\mu\text{m}$ will require greater quantities of paint per unit area. In corrosive atmosphere it is usual to recommend a film thickness, of primer and finish together of about $150\mu\text{m}$. $1\text{ mil} = 25.4\mu\text{m}$.

3.3.6 Bending Test - Mandrel Test

ASTM - D-522-41

This test is carried out by bending a metal panel on which the coating has been applied round cylindrical mandrels of varying diameter the film being on the outside of the bend. The smaller the diameter of mandrel at which cracks appear in the film the better is the flexibility of the film.

On common type of flexibility is a mandrel bend test in which a coated panel is bent around a rod or cone used as a support around which to bend a coated panel. The panel is bent with the coated site away from the mandrel. Any crack in the coating on the bend is reported as a failure.

3.3.7 Impact Resistance

ASTM D 2794-93

1.8 Kg weight 40" Tube,

Impact tests evaluate the ability of the coating to withstand extension without cracking when the determination is applied rapidly. A weight is dropped down a guide tube onto a hemispherical indenter that rests on the coated panel. An opening, opposite the indenter in the base support, on which the panel rests, permits deformation of the panel. If the coated side is up that is it is directly hit by the indenter, the test is called a direct impact test. If the back of the panel is up, the test is called a reverse impact test. The weight is dropped from greater and greater heights until the coating and panel cracks.

3.3.8 Chemical Resistance

ASTM - C - 581-68

Solvent resistance test is one of the properties that must be balanced with Mechanical properties for much application. It is also appropriate because resistance to swelling of crosslinked films is directly related to XLD (cross-linked density) which also affects many mechanical properties.

The most common test is the Methyl Ethyl Keton (MEK) double rub test. This can be done with a tissue soaked with MEK rubbed on the panel but is more conveniently done with a felt tip marker pen filled with solvent. The test can be mechanised so that there is one stroke back and forth (one double rub) on the film each second and a timer can be used as a counter. A soft thermoplastic coating will rub off with very few rubs. In the case of thermosetting coating the number of rubs. The coating will stand increase as the degree of reaction increases. The tests are sensitive to the development of low cross-link density gets higher. Usually the test is stepped after 200 double rubs. Therefore, a series of highly crosslinked

coatings may be reported to give 200 + double rub resistance even though there are difference in the extent of cross-linking.

3.3.9 Viscosity Determination

Standard: ASTM – 4878

Viscosity:

When a force is applied at the liquid surface of area A, it undergoes deformation or shearing. Tendency of the liquid to resist this deformation is called viscosity. It is the ratio of shear stress and shear rate D,

The internal resistance to flow possessed by a liquid. It is determined by measuring the force required shearing the liquid. i.e. to move one layer over another in orderly flow without turbulence at a defined rate.

Rotating disk viscometer, such as a Brookfield viscometer have a motor that can rotate a disk in a liquid at a range of revolution per minute. The resulting torque is measured. The instrument must be calibrated with standards. The measurements should be made in a container of the same dimensions as that in which the standardisation was carried out since the distance of the disk below the surface of the liquid, above the bottom of the container and from the sidewalls can affect the response. Rotating disk viscometers can detect whether a system is shear thinning or shear thickening by measurements. Carried out at different rpm settings. They can detect thixotropy by a change in response over time at the same rpm setting. They cannot provide absolute viscosity data as a function of shear rate.

The effect of temperature on viscosity is important. Viscosity almost decreases as temperature increase.

CHAPTER-4
RESULT AND DISCUSSION

4.1 RESULT AND DISCUSSION

As mentioned in chapter-2, the main objective of this work was to study the effect of molecular weight on properties of water- borne polyesters coating based on adipic acid, neopentyl glycol and trimellitic anhydride (TMA). In this context five hydroxyl terminated polyesters of different molecular weights namely 500, 1000, 1500,2000,2500 were synthesised by reacting adipic acid and neopentyl glycol as described in experimental part. Determining acid value after different time interval monitored reaction and the reaction was stopped when expected acid value was obtained (Table-2 & 3). At this time these polyesters were characterised by determining hydroxyl value as described in experimental part. Both acid and hydroxyl values of polyesters decreases with increase in molecular weight.

Number average molecular weight of this polyester was calculated from their hydroxyl values. These values are very close to that of expected molecular weights (Table- 2 & 3). IR spectrum of representative sample (Polyester -2) shows characteristic absorption of ester group at 1750 cm^{-1} and OH group at 3500 cm^{-1} (Figure-1). Thus after confirming the structure of polyesters by IR and confirming molecular weight by hydroxyl values, desired quantities of TMA was added to maintain polyester: TMA ratio of 2:1 so that hydroxyl terminated polyester containing one TMA unit in each polyester moiety was obtained. It is known that the solubility of polyester in water depends on acid value of the polyesters. Because quaternary salt of the acid group with triethyl amine is responsible for the solubility of the polyester in water. Reduction in acid value beyond a certain limit reduces its solubility and increases the viscosity. So polyesters of only up to ~ 2500 molecular weight were prepared by this method.

TABLE: 1**COMPOSITION FOR WATER- BORNE POLYESTER**

POLYESTER NO./ MW	NPG	AA	TMA	XYLENE	DBTO
P-No.-1-500	43.7822	37.8009	15.5297	3	0.05
P-No.-2-1000	42.0240	47.1735	7.7523	3	0.05
P-No.-3-1500	41.5471	49.9776	5.4750	3	0.05
P-No.-4-2000	41.2772	51.4919	4.2307	3	0.05
P-No.-5-2500	41.0772	52.2419	3.6146	3	0.05
P-No.-6-3000	38.6627	50.1014	8.2358	3	0.05
P-No.-7-3500	38.4060	50.3218	8.2720	3	0.05
P-No.-8-4000	38.2121	50.4884	8.2994	3	0.05
P-No.-9-4500	38.1585	50.7641	8.1935	3	0.05
P-No.-10-5000	38.0418	50.9773	7.9808	3	0.05

TABLE - 2

THEROTICAL HYDROXYL AND CARBOXYL VALUE OF
POLYESTERS

Experiment No.	Hydroxyl Value (mg KOH/g)	Acid Value (mg KOH/g)	Molecular weight	% solid
P.No.1	200	99.99671	561.00	97
P.No.2	102.4506	51.2126	1095.00	97
P.No.3	71.2174	35.5953	1575	97
P.No.4	56.5662	28.2831	1983	97
P.No.5	48.3800	24.2222	2319.00	97
P.No.6	36.61	54.9014	3065.00	97
P.No.7.	31.5429	55.1761	3557.00	97
P.No.8	27.6967	55.3900	4051.00	97
P.No.9	24.2191	54.2000	4634.44	97
P.No.10	21.3344	53.2950	5259.11	97

TABLE - 3

CHRECTERIZATION OF POLYESTER

Experiment No.	Appearance	Hydroxyl Value (mg KOH/g)	Carboxyl Value (mg KOH/g)	Molecular weight
P.No.1	Transparent	185.46	86.65	604.98
P.No.2	Transparent	105.10	51.9619	1067.55
P.No.3	Transparent	64.82	35.1453	1726.15
P.No.4	Transparent	51.11	25.4600	2195.26
P.No.5	Transparent	46.87	26.3953	2393.85
P.No.6	Transparent	26.44	43.22	4243.57
P.No.7.	Transparent	32.86	51.8561	3414.48
P.No.8	Transparent	27.56	54.6689	4071.11
P.No.9	Transparent	26.00	47.27	4315.38
P.No.10	Transparent	23.98	50.86	4680.85

It was observed that higher molecular weight polyesters with lower than ~ 20-carboxyl values are not easily soluble in water. In present work polyester up to ~ 2500 molecular weight were found to soluble in water to give clear transparent solution. Hence higher molecular weight polyesters were not synthesised by this method. Thus polyester P-No-1 to P-No-5 were prepared by this technique. However second set of higher molecular weight polyesters were prepared by adding higher quantities of TMA so that the polyesters have acid values of ~ 54 where as hydroxyl values are low. Ratio of adipic acid : neopentyl glycol : trimellitic anhydride were so adjusted that the acid values of all these polyesters is ~ 54. Where the molecular weight was determined by hydroxyl value, vary between 3000-5000 (P-No-6 to P-N0-10). Since in all these polyesters carboxyl values are high these polyesters on quaternisation with an amine are easily soluble in water giving low viscosity transparent clear solution. Thus as a part of this work we synthesised ten polyesters in two sets of five polyesters each. These polyesters were charecterized by IR, and determination of acid and hydroxyl values. Molecular weight of these polyesters was calculated from hydroxyl values. Water-borne coatings of these polyesters were prepared by reacting polyester with triethyl amine to prepare quaternary salt of acid group followed by dissolution in 2-butoxy ethanol and subsequent dilution with water as described in experimental part. Brookfield viscosities of some of these solutions were determined at 25°C to study the trend (Table- 4). As expected viscosities increase with increase in molecular weight of polymers in first set of polyesters. However in second set of polyesters there is not much change in viscosities, probably due to their similar acid values. Thus probably viscosity and solubility are determined by acid value of the polyesters.

Water- borne polyesters thus prepared was cross-linked by adding appropriate quantities of melamine formaldehyde resin. Hexa functional methylated melamine formaldehyde resin

pidifix – 330 obtained from Dr. Beck and Co, Pune was used for cross- linking water borne polyesters. Curing of water borne polyester was effected by heating the polyester with melamine formaldehyde resin at 160⁰C for 30 minutes. These conditions were kept constant for all polyesters. Quantity of the melamine formaldehyde resin for optimum cure was determined by trial and error method using different quantities of curing agent and testing the cured film for clarity, strength and tackiness. Generally addition of 5 to 30 % of melamine formaldehyde resin is recommended. However in our present work 20-25 % melamine formaldehyde resin was found to give optimum properties. Thus in case of coating based on 500 molecular weight polyester, 20% MF gives optimum cure. Where as coating based on 1000 to 2500 molecular weight gives an optimum cure at 25 % melamine formaldehyde.

After determining the required quantities of curing agent for optimum properties cured films of these polyesters were prepared on a glass and aluminium plate by brushing technique. The plates after coating were cured at 160⁰C for 30 minute in an oven. These films were tested for abrasion resistance, scratch hardness resistance, impact strength, adhesion water and chemical resistance. Abrasion resistance is an important property of a coating material. A coating with high abrasion resistance is preferred. Abrasion resistance of cured film on aluminium plate was determined with 1Kg load for 1000 cycles.

Except for coating based on P-No-1 (molecular wt. 500) polyester, coatings based on all other polyester showed excellent abrasion resistance. No weight loss or marks were observed up to 1000 cycles. (Table – 4) in fact polyurethane coating based on same polyesters showed considerable abrasion after 500 cycles. These results reveal that all polyesters above 500 molecular weight give coating with high abrasion resistance.

Scratch resistance of these coating was determined as per ASTM standard D 5178 on scratch hardness tester. Scratch hardness increases with increase in molecular weight of polyester. Highest scratch resistance was observed for polyester coating based on polyester of molecular

weight ~ 2500 (P-No-5). However scratch resistance of second set of polyester of higher acid value is low though molecular weight are aromatic moiety of TMA in these polymer is more than that of first set of polyesters. These results are contradictory. Probably carboxyl groups play role in determining scratch resistance. However it could not be proved.

TABLE: 4

FILM PROPERTIES

Experiment	Abrasion	Scratch	Impact	Adhesion	Thickness	Viscosity
No	Resistance	Hardness	Resistance	1/8" Mandrel	(mile)	(cps)
P-NO-1	2.48	1.800	1Kg Passes	Passes	1.68	30
P-NO-2	No. Wt loss.	2.400	1Kg Passes	Passes	2.26	40
P-NO-3	No. Wt loss.	3.000	1 Kg Passes	Passes	1.71	70
P-NO-4	No. Wt loss.	3.000	1 Kg Passes	Passes	1.18	85
P-NO-5	No. Wt loss.	3.200	1 Kg Passes	Passes	1.71	100
P-NO-6	No. Wt loss.	1.700	1 Kg Passes	Passes	2.73	30
P-NO-7	No. Wt loss.	2.500	1 Kg Passes	Passes	1.80	10
P-NO-8	No. Wt loss.	1000	1 Kg Passes	Passes	1.99	10.5
P-NO-9	No. Wt loss.	1.200	1 Kg Passes	Passes	1.89	10
P-NO-10	No. Wt loss.	1.400	1 Kg Passes	Passes	1.34	12.5

TABLE: 5

SOLVENT RESISTANCE (a)

Experiment No.	MEK Double Rubs	Toluene Double Rubs
P.No-1	40	290
P.No-2	280	700
P.No-3	430	1000
P.No-4	90	281
P.No-5	200	500
P.No-6	1900	2000
P.No-7	2000	2000
P.No-8	550	500
P.No-9	600	500
P.No-10	70	500

SOLVENT RESISTANCE (b)

Experiment No.	15 % HCl (one week)	2 % NaOH (one week)
P-No.1	Poor adhesion Brittle No strength	Poor adhesion No strength
P-No.2	Poor adhesion Slightly hezy	Poor adhesion Blistering
P-No.3	Good adhesion and strength Strong film	Good adhesion and film is strong
P-No.4	Poor adhesion Hey, White	Good adhesion Slightly blisters
P-No.5	Good adhesion White, soft, Blisters	Good adhesion
P-No.6	Poor adhesion, brittle No strength	Poor adhesion No strength
P-No.7	Poor adhesion No strength	Poor adhesion No strength
P-No.8	Poor adhesion, White	Poor adhesion No strength
P-No.9	Poor adhesion, white Brittle	Poor adhesion No strength
P-No.10	Poor adhesion, brittle No strength	Poor adhesion No strength

Impact resistance of the coating was determined by dropping a weight of 1.8 Kg on the coated film. Generally a coating film is supposed to pass this test if it withstands a dropping weight of 1.8 Kg without any crack. All the samples pass this test. Adhesion of the coating to metal was tested by a coating an aluminium plate of 2mm thickness. A piece of 1cm width is cut from this plate. This piece was bent suddenly. The film is detached from the metal strip if adhesion is not good. All polyester coatings pass these test.

Water resistance is another important test for a coating material. Since water borne polyester are soluble in water they are likely to have hydrophilicity even after curing and coating may be affected by cold or hot water. A good water resistance is desired for a coating material. Water resistance was tested by immersing coated glass or metal plate in water for a week at room temperature and in boiling water for 30 minutes. Observation of this test is tabulated in Table – 6. It was observed that low molecular weight polyester (P-1 & P-2) give a film of poor water resistance. Water resistance improves as molecular weight is increased. In fact polyester of ~ 2500 gives a film with excellent water resistance for hot and cold water. However no particular trend was observed for second set of polyesters. Probably distribution of hydrophilic acid salt group plays a role in determining water resistance.

Solvent resistance is another important property of a coating material. Solvent resistance of the film was determined by double rub test in MEK and toluene solvents. As described in experimental part. A definite trend could not be observed though solvent resistance improved with increase in molecular weight up to a certain molecular weight. Probably this property is dependent on cross- link density and hydrophilic groups. However polyesters based coatings has good solvent resistance.

TABLE: 6

WATER RESISTANCE

Experiment No.	Water Resistance for one week at Room Temperature	Water Resistance in Boiling water for 30 Min.
P.No.1	Slightly white poor adhesion soft.	Very Poor adhesion removed from glass.
P.No. 2	Slightly hezy, blister	Soft Film, Poor Adhesion
P.No.3	Clear Transparent, good adhesion	Very Good Adhesion
P.No.4	Clear Transparent good adhesion	Slightly white film, after drying it's become clear good adhesion.
P.No.5	White Soft Good adhesion	Slightly white after drying it in clear, good adhesion.
P.No.6	White, Very soft	Poor adhesion, Film is brittle and hezy after drying, it is clear
P.No. 7	Slightly hezy and soft	Very Poor Adhesive, hezy
P.No.8	White good adhesion	Hezy film and good adhesion
P.No.9	White, Hezy, Good Adhesion	Good adhesion, film is soft and brittle
P.No.10	Slightly white, good adhesion	Good adhesion, Film is Soft and Brittle.

These films have low resistance to 15% HCl and 2% NaOH solution at ambient temperature.

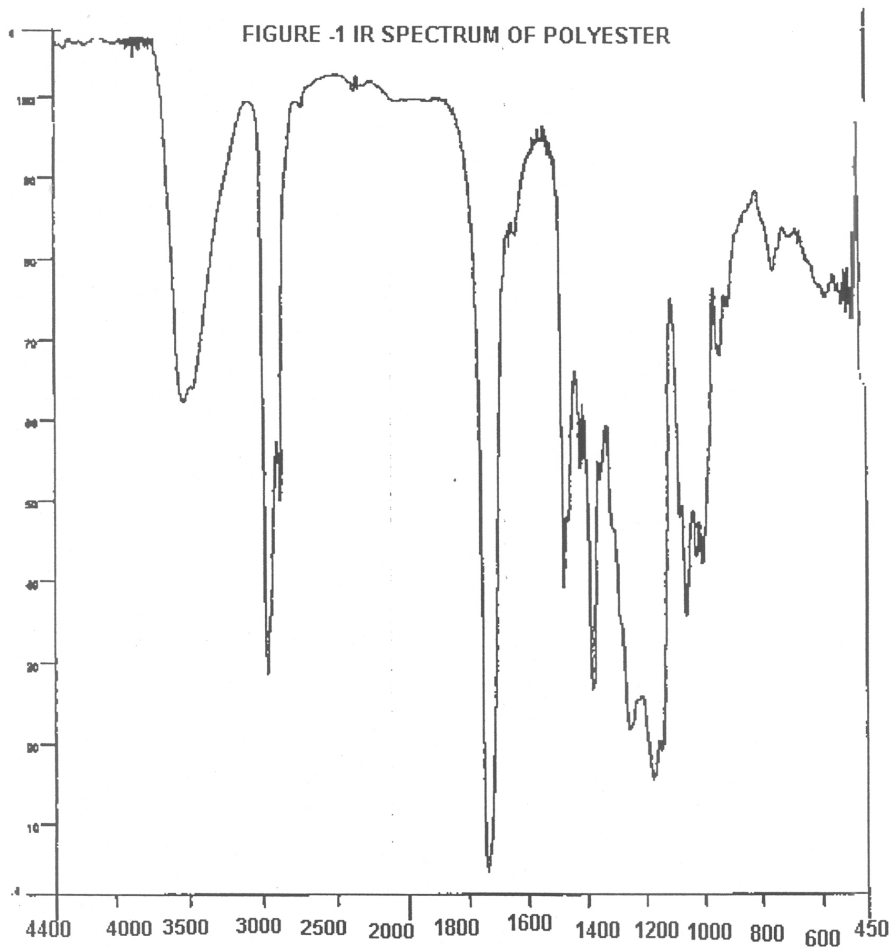
Thermal stability is another important property of a coating. Thermal stability of a coating is influenced by the structure of the binder. In the present work thermal stability of a coating was studied by thermogravimetric analysis by TGA-7, PERKIN ELMER. Film obtained after evaporation of solvent and cross-linked at 160°C for 10 min. was used for thermal analysis. Thermal analysis was carried out in nitrogen atmosphere with increasing temperature rate of 10°C / min. Typical thermograms of coating material obtained from polyesters of five different molecular weights are shown Table -7.

Initial decomposition temperature and maximum decomposition temperature (T_{max}) are shown in Table-7. In the present work it has been observed that the molecular weight of the polyesters influences initial decomposition temperature of the coating. The coating based on polyester of 500 molecular weight has lowest. Initial decomposition temperature of 300° C where coating based on 2500 molecular weight polyester has higher initial decomposition temperature of 365.399° C. Thus initial decomposition temperature of coating increases with increase in molecular weight of polyester.

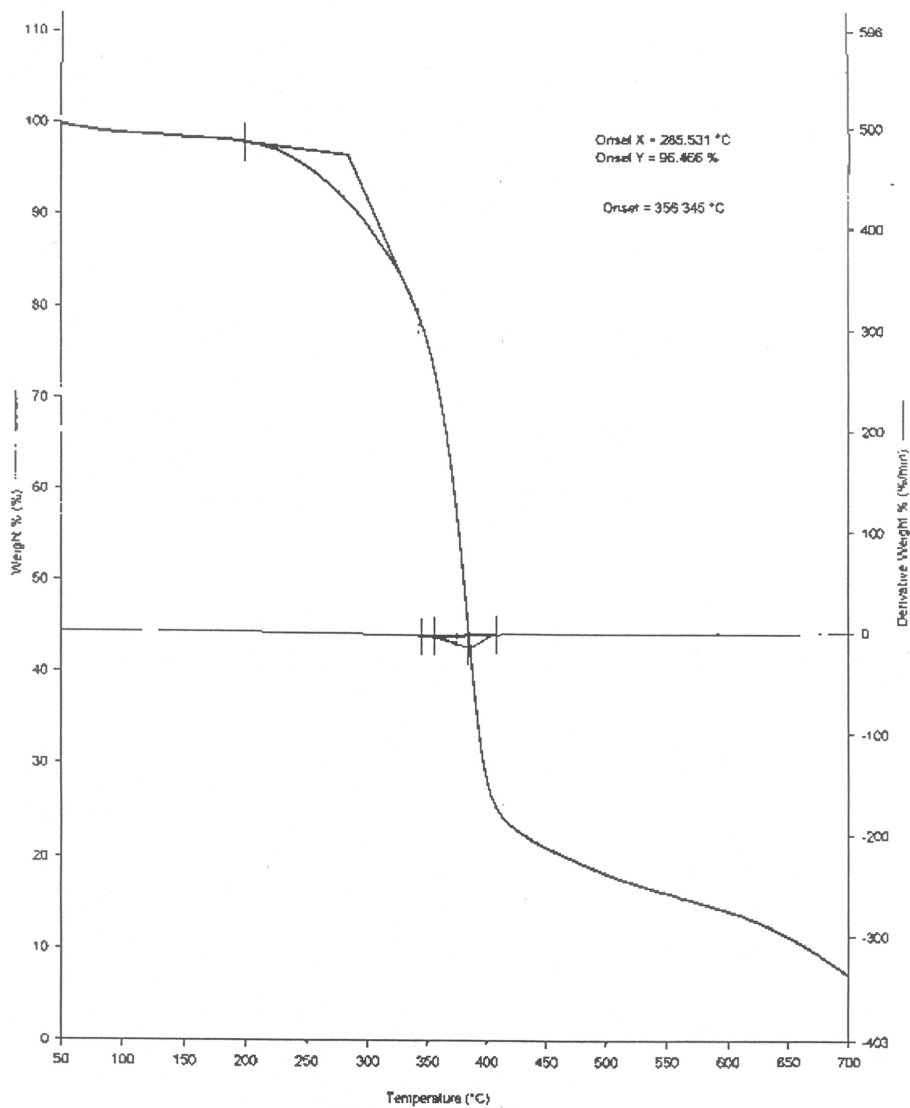
Maximum decomposition temperature T_{max} of the coating varies between 356°C to 407°C. Maximum decomposition temperature will depend on structure of the polymer backbone and cross-link density. It has been observed that initially T_{max} increases with increase in molecular weight of polyester. Thus T_{max} of coating based on polyester of molecular weight 500 was 356°C. Which increase to 407°C for coating based on polyester of 1500 molecular weight. However with further increase in molecular weight of polyester the T_{max} decreases. Thus coating based on polyester of 1500 molecular weight has optimum T_{max} .

TABLE: 7**THERMOGRAVIMETRIC ANALYSIS**

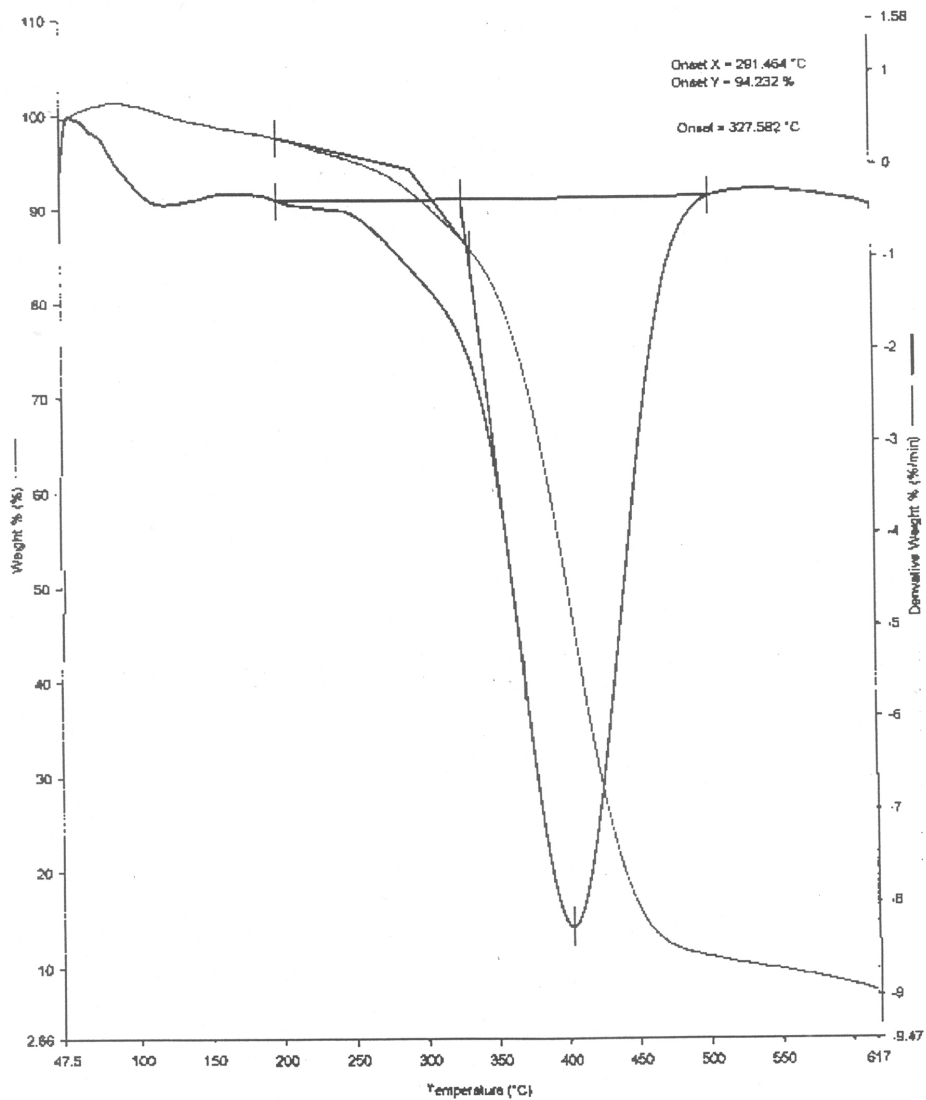
Polyester no/Mw	Initial decomposition	Final decomposition
P-1 (500)	285.531	356.345
P-2 (1000)	291.464	327.582
P-3 (1500)	305.187	417.510
P-4 (2000)	310.057	383.411
P-5 (2500)	365.399	375.464



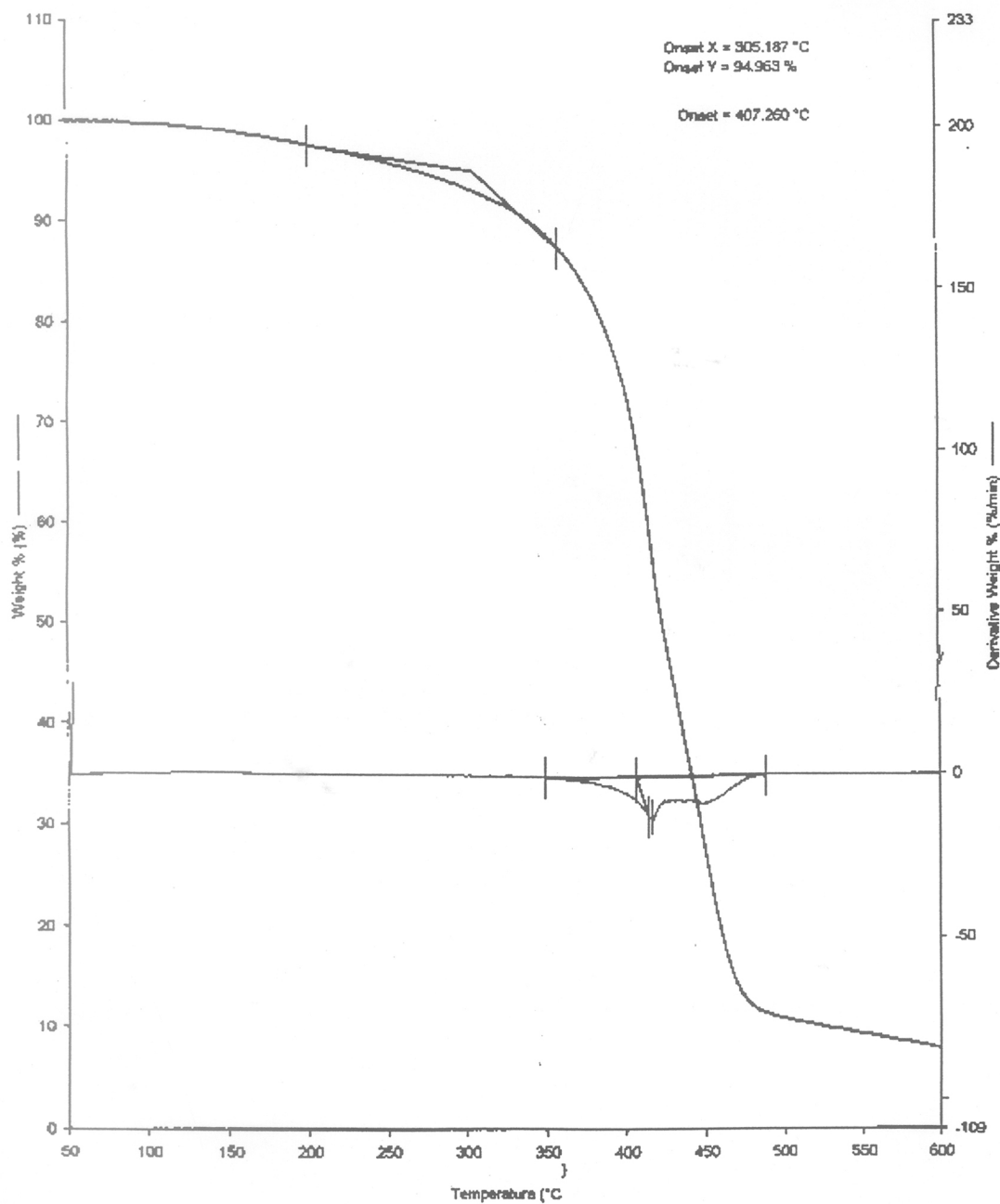
THERMOGRAM OF COATING BASED ON P-NO-1



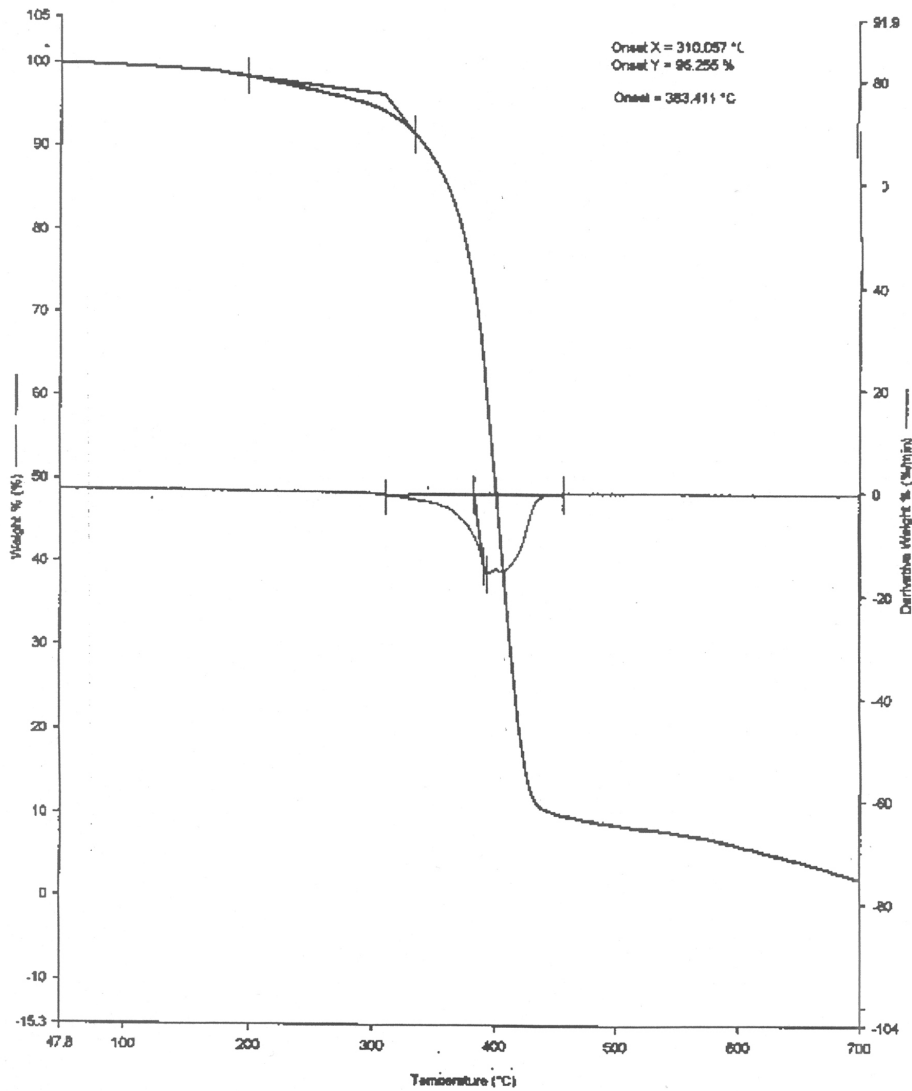
THERMOGRAM OF COATING BASED ON P-N0-2



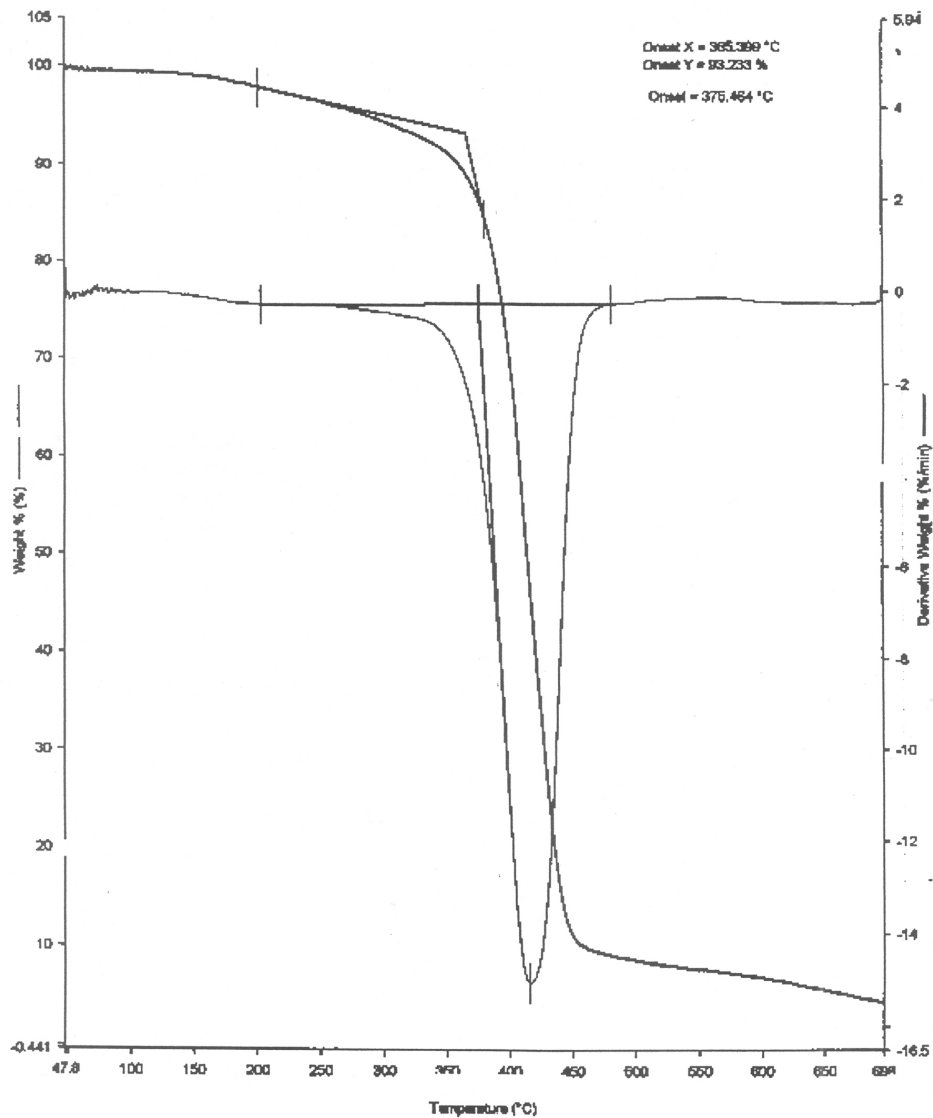
THERMOGRAM OF COATING BASED ON P-N0-3



THERMOGRAM OF COATING BASED ON P-NO-4



THERMOGRAM OF COATING BASED ON P-NO-5



4.2 CONCLUSION

1. Polyesters of five different molecular weight namely ~ 500, ~1000, ~1500,~2000 and ~ 2500 were based on adipic acid, neopentyl glycol and TMA were synthesised. Higher molecular polymer of ~ 3000 to 5000 were synthesised using higher quantities of TMA so that acid values of these polymers are around 55.
2. These polymers were characterised by IR spectroscopy and determination of hydroxyl and carboxyl values.
3. Water borne polyester coatings was prepared using these polymers by standard procedure. These coatings are stable at ambient temperature. Cross-link films obtained by curing of this polyester with melamine formaldehyde resin are clear and transparent. Water borne polyester coating has good film forming properties.
4. Effect of molecular weight of polyesters on properties of film was studied by determining abrasion resistance, scratch resistance, impact resistance, water and solvent resistance. Scratch resistance, impact resistance, water and solvent resistance improves with increasing molecular weight. A polyester of molecular weight ~ 2000 gives stable water borne polyester coating material with having best overall properties. Higher molecular weight than ~ 2500 polyester have low solubility in water and higher viscosity and low stability.
5. Initial decomposition temperature of the coating was increases with increase in molecular weight of polyester.

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