

INDUSTRIAL RESINS

An industrial resin is a synthetic polymer which has adhesive, film-forming or useful reactive properties. Many such polymers are made commercially in New Zealand and the following selection of these are described in this article.

Unsaturated polyester resins

These are formed from the reaction of a diol (a molecule containing several hydroxyl groups) and an unsaturated diprotic acid. The resulting polyester chains are dissolved in a reactive solvent. The chains crosslink to form a hard, strong resin which is used in making the hulls of boats and in the production of "synthetic marble".

Alkyd resins

Alkyd resins are used in many solvent-based paint systems and are a type of polyester made from polyols, acids and vegetable oils.

Emulsion polymers

These are emulsions of monomers in water. As the water evaporates, the monomers polymerise to form a thermosetting film. These are widely used as adhesives (e.g. PVA) and in water-based paints.

Amino resins for surface coatings

When molecules containing amino groups are reacted with formaldehyde an amino resin is formed. Their primary use is as a crosslinking agent and as such they are used in paints in conjunction with other polymers such as alkyds.

Polyurethane resins

Polyurethanes result from the reaction of a polyalcohol and an organic di-isocyanate. They can be used as surface coatings, to make furniture and footwear and in foam form, for packaging.

Polyamide-epichlorohydrin resins

These are formed in two steps. The first step involves reacting a polyfunctional amine with a diprotic acid to form a polyaminoamide resin. This is then crosslinked with an epichlorohydrin monomer. The resultant resin is used to coat paper fibres, increasing the strength of the wet paper from less than 2% to around 30% of its dry strength.

Formaldehyde resins

Formaldehyde resins are made by reacting formaldehyde with any of a variety of substances such as urea and phenol. The reagents are mixed to form a thermosetting cross-linked polymer used in reconstituted wood (e.g. plywood) and timber adhesives.

INTRODUCTION

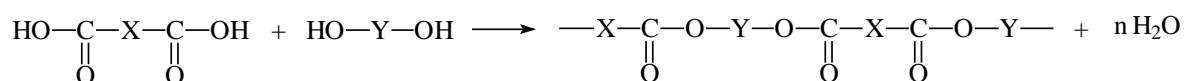
The term "industrial resins" refers to any synthetic polymer resin made for commercial use. As such it includes many substances that, chemically, have very little in common and thus have a wide variety of applications. Industrial resins are used in New Zealand for anything from synthetic leather to paint binders to imitation marble vanity tops and the adhesives used to hold plywood together.

RESINS COMMONLY MADE IN NEW ZEALAND

The following section listed some resins commonly made in New Zealand, briefly describes the process by which they are manufactured and the uses for which they are produced. For some of the resins, such as polyester resins, a great variety of different ingredients can be used in varying proportions to produce different results. Where this is the case the types of variation that can occur are described.

Unsaturated polyester resins

In general, polyester resins result from the condensation reaction between a diprotic acid and a polyhydric alcohol, e.g.



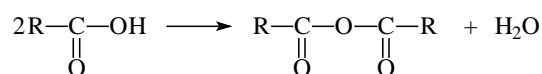
Any change in type or proportion of reactants results in a change in properties of the polymeric product so an infinite number of polyesters is theoretically possible.

Possible variations in formulations

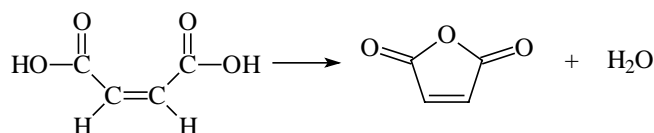
Unsaturated polyesters are produced from a glycol¹ and maleic anhydride², which is faster reacting than maleic acid and produces less water. Some specialised resins that need high chemical resistance use fumaric acid³ instead of maleic anhydride because it copolymerises better.

¹A glycol is a diprotic alcohol. Propylene glycol (propane-1,2-diol) is commonly used.

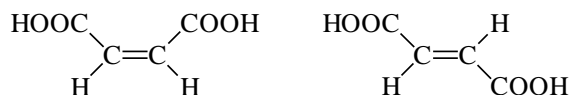
²An acid anhydride (such as maleic anhydride) is what you would get if you reacted two moles of a particular carboxylic acid together and lost one mole of water, i.e.

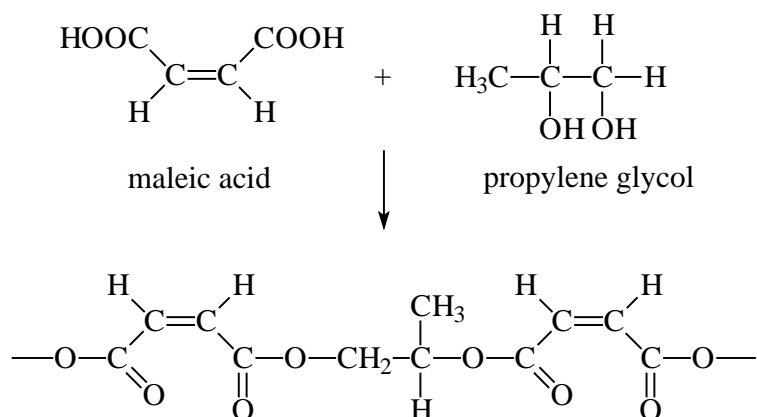


Maleic acid is a diprotic carboxylic acid (i.e. it has two carboxylic acid groups) so in this case the two carboxylic acid groups of the same acid molecule react together to give the five membered ring of maleic anhydride as follows:

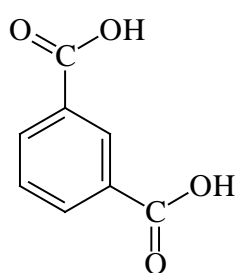


³Maleic acid and fumaric acid are respectively the *cis* and *trans* forms of butenedioic acid:

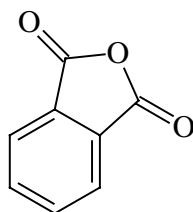




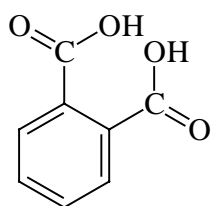
Other acids are used in conjunction with the unsaturated maleic type to prevent the resin from being too reactive. *Ortho*-phthalic anhydride is the most common and is used in "general purpose" formulations (used in boat building, some cast sanitary-ware etc.). Isophthalic acid is used where better chemical resistance is required (e.g. in oil storage tanks). Adipic acid is used where flexibility is required (e.g. in resins for autopatch compounds). Halogenated acids (e.g. tetrabromophthalic anhydride) can be used to produce reduced flammability in mouldings.



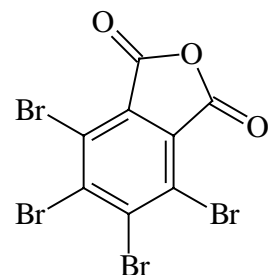
isophthalic acid



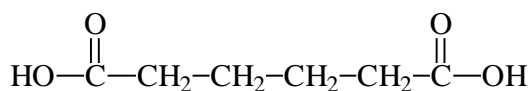
o-phthalic anhydride



o-phthalic acid

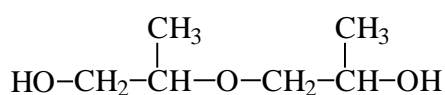


tetrabromophthalic anhydride

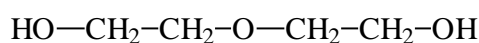


adipic acid

Other glycols can be used, e.g. dipropylene glycol and diethylene glycol give some degree of flexibility and neopentyl glycol offers better chemical resistance.

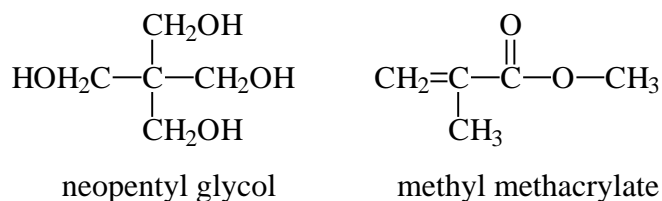


dipropylene glycol



diethylene glycol

Methyl methacrylate can be used as a part replacement for styrene in the monomer portion of the resin. This offers better resistance to yellowing on exposure to UV radiation and is most commonly used in resins intended for manufacture of translucent fibreglass sheeting.



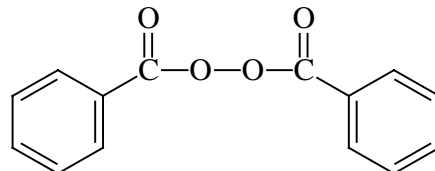
The manufacturing process

The resin is manufactured in a batch process using 1500 - 5000 L stainless steel kettles fully equipped for heating, cooling, pressure, vacuum refluxing and distillation. The mixture is cooked at up to 220°C for between 14 and 40 hours. Samples of the reaction mixture are taken from time to time and their acidity and viscosity measured to assess the progress of the reaction. After cooking the polymer is cooled and dissolved into styrene, a polymerisable solvent (i.e. one that can copolymerise with the polyester).

Heating of highly flammable reactants and solvents poses practical problems. Hot water or super-heated steam are produced in a room detached from the kettles and circulated in jackets around the kettles. Thus, all likelihood of spark or flame ignition in the processing area is eliminated.

Removal of water from the reaction mixture to obtain maximum yields is accomplished in one of two ways:

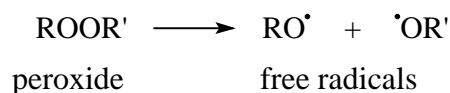
- Sparging. Nitrogen gas is bubbled through the mixture to increase the surface area. The water evaporates and is carried out of the mixture and condensed.
- By refluxing with a water absorbing solvent such as toluene⁴ or xylene⁵.



benzoyl peroxide

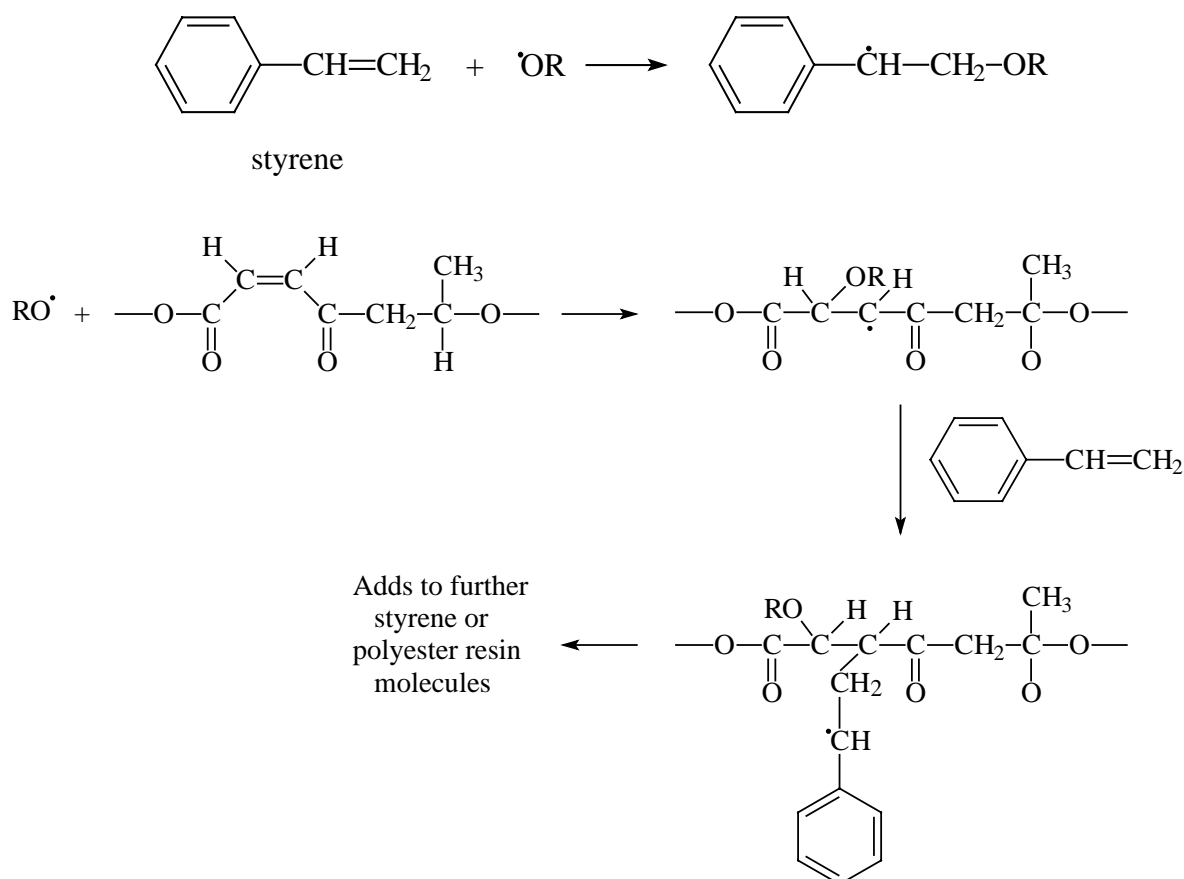
Uses of unsaturated polyester resins

The polymer resin product is used by the fibre-glass industry for building boats and car bodies, for encapsulating electrical components, for coating concrete to give a smooth sterile surface in food-manufacturing plants and for the production of "synthetic marble". In all of these applications the polyester-styrene mixture is poured into a mould and a free radical initiator such as MEKP (methyl ethyl ketone peroxide) or benzoyl peroxide added to initiate crosslinking.



⁴ monomethylbenzene. Also called toluol.

⁵ a mixture of the three dimethylbenzenes. Also called xylol.



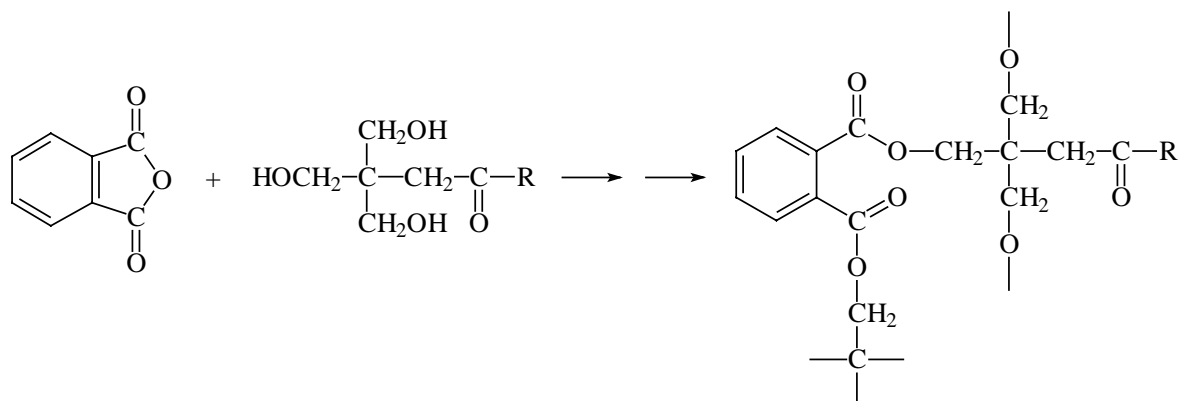
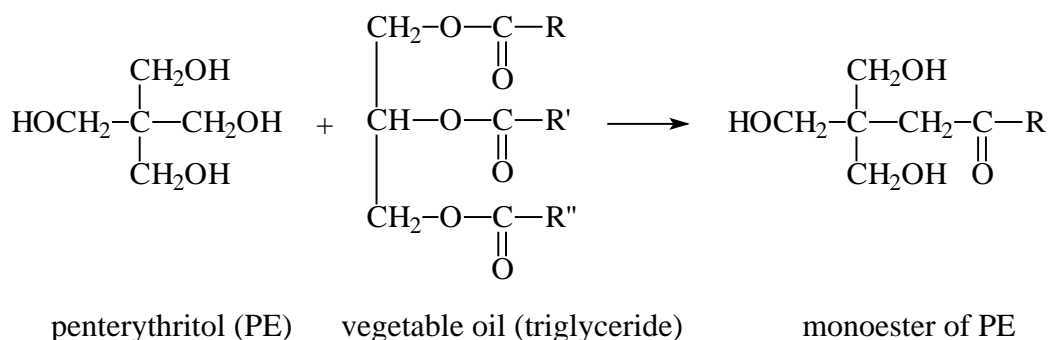
Thus polyester chains are linked together by polystyrene bridges. Polyesters can be easily moulded (by simply pouring the solution into a mould) and the resulting end product is resistant to attack and long-lasting.

Alkyd resins

The introduction of a vegetable oil into the polyester reaction gives a product called an alkyd resin. Raw materials are commonly phthalic anhydride imported from the U.S.A., U.K. or Japan; pentaerythritol imported from Canada and soya bean or linseed oil produced locally or imported from Europe. The reaction is usually catalysed by an oxide, hydroxide or organic salt of calcium or one of the alkali (group I) metals.

The manufacturing process

The manufacture of the alkyds proceeds in two stages. Pentaerythritol and vegetable oil are first heated with the catalyst for about two hours at 270°C. The vegetable oil is an ester of glycerol and long chain unsaturated fatty acids, and the reaction is a trans esterification, the fatty acids forming an ester with the polyhydroxy-alcohol pentaerythritol. Di- and tri- esters of PE and di- and monoglycerides are also presumably formed. After cooling the mixture to 150°C, a slight excess of phthalic anhydride is added and the mixture is reheated to 240°C where it is held for several hours while the polyester alkyd resin is formed:



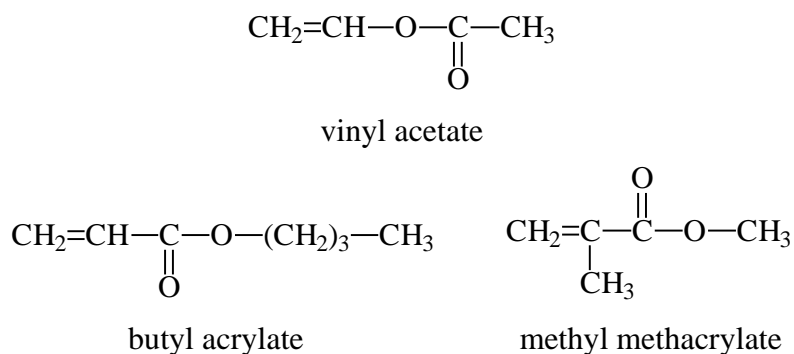
The reaction is monitored by acidity and viscosity measurements. Water is removed by evaporating with the solvent xylol which is recycled. The unsaturated fatty acid residues react with oxygen to give further polymerisation in the drying of the paint or curing of the resin. By changing oil, acid or alcohol, a wide range of alkyd resins can be made.

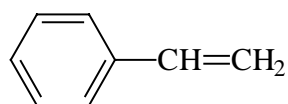
Uses of alkyd resins

Alkyd resins are used in solvent-based paints. These paints incorporate driers (e.g. cobalt naphthenate) which cause the alkyd to crosslink with itself using atmospheric oxygen as the solvent evaporates, resulting in a polymer that is no longer soluble in the original solvent. Alkyds are also used in stoving enamels where they are crosslinked with amino resins (see below).

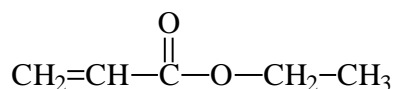
Emulsion polymers

These are emulsions of monomers in water that polymerise as the water evaporates. Examples of common monomers are given below.





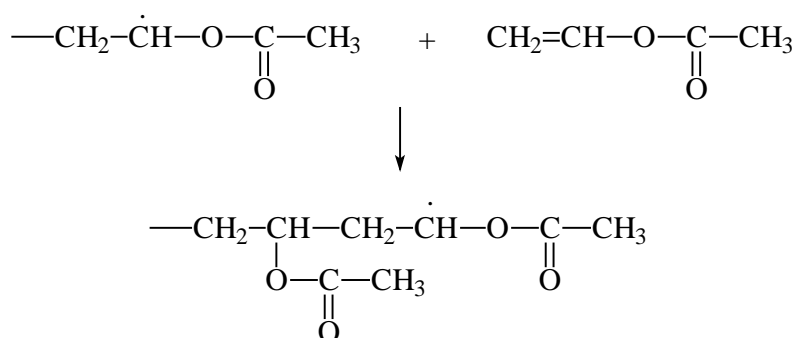
styrene



ethyl acrylate

A typical manufacturing process

PVA (polyvinyl acetate) glue is probably the best known emulsion polymer. It is manufactured by free radical addition copolymerisation⁶ of an aqueous emulsion of vinyl acetate and butyl acrylate. As the reaction is an exothermic chain reaction, the reaction vessel and conditions are different from the kettles previously described. The reaction is initiated by ammonium or potassium persulphate and bisulphite which react together to give free radicals which add to the vinyl monomer to initiate the free radical chain reaction:



A section of the vinyl acetate portion of the copolymer

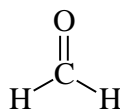
The reactants are fed into the reaction vessel continuously as reaction proceeds, and excess heat produced is removed by cooling water. Acrylic emulsions from acrylic acid and its esters are made in a similar way and used for wall-paper coatings.

Uses of emulsion polymers

Emulsion polymers are used in two industries: the paints industry and the adhesives industry. In the paints industry they form the basis of water-thinnable paints, and they are used in the adhesives industry for wood and cardboard glues. They are also used to coat wall and printing papers and used in inks.

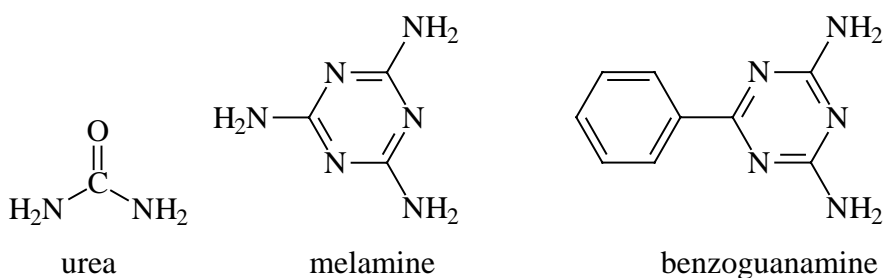
Amino resins for surface coatings

Amino resins are produced by reactions involving formaldehyde with amine functional compounds such as urea, melamine and benzoguanamine.



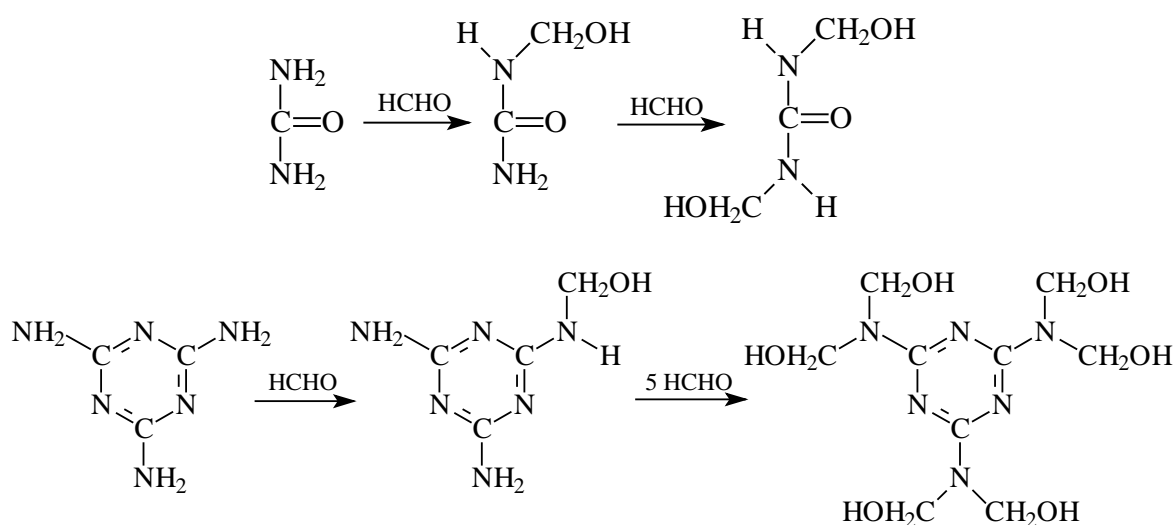
formaldehyde

⁶A copolymer is a polymer of the formAAAAAABBBBBBBBAAAAAABBBBBBBB...., i.e. one which consists of alternating short strings of monomer A and monomer B.

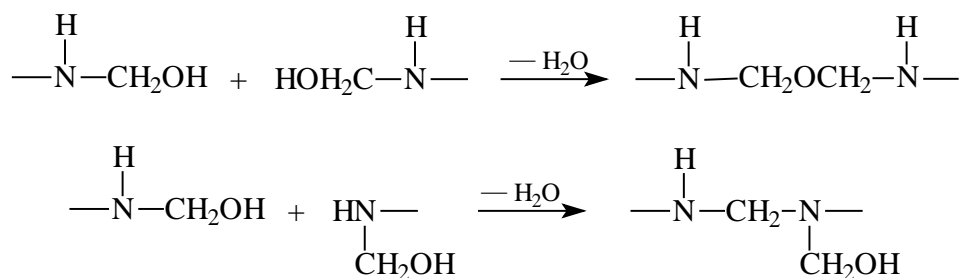


The manufacturing process

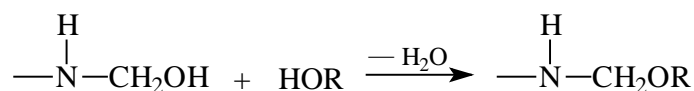
The first step in the reaction involves addition of the formaldehyde to the amine groups to form methylol compounds (methyl groups with one hydrogen replaced by a hydroxy group) by effectively adding N—H across the C=O of the formaldehyde.



The methylol compounds can react together by a condensation reaction mechanism to give polymers. Reactions can take place between two methylol groups or between one methylol group and active hydrogen atoms.



This is similar to the reactions used in production of urea formaldehyde resins for use in production of particleboard and medium density fibre board (see below). The products of these reactions have limited solubility in water, are insoluble in solvents and are unstable. For use in surface coatings the polymers are modified by reaction with alcohols.



The effect of the ether grouping is to improve the stability, modify the solubility and increase compatibility with other polymeric compounds. A variety of different alcohols can be used depending upon the properties required from the resin.

Uses of amino resins in surface coatings

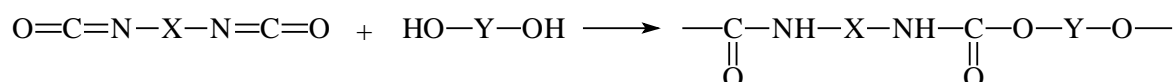
Amino resins are used as crosslinkers in stoved paint systems in combination with other polymeric materials including alkyds, acrylics, epoxies and saturated polyesters. They are used in paints in a wide variety of applications including automotive, domestic appliances, coil coating, metal decorating and general industrial finishes.

Butylated urea-formaldehyde resins can be used in conjunction with alkyd resins in acid catalysed furniture lacquers which dry and cure at room temperature.

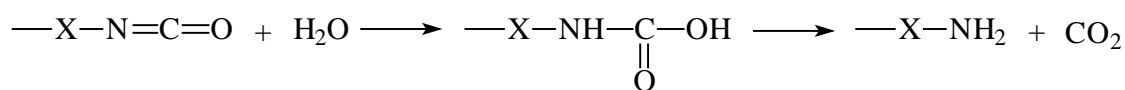
Polyurethane resins

Polyurethane coating resins and varnishes offer advantages over alkyd resin systems in speed of drying, hardness of the film and resistance to wear. Types made in New Zealand include urethane oils, urethane alkyds, moisture curing polyurethanes and foams.

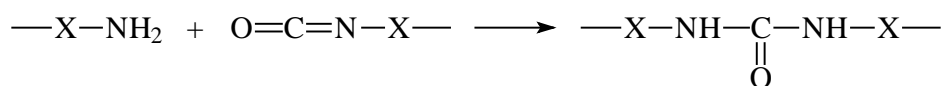
A polyurethane is formed by the reaction of a polyalcohol and an organic di-isocyanate:



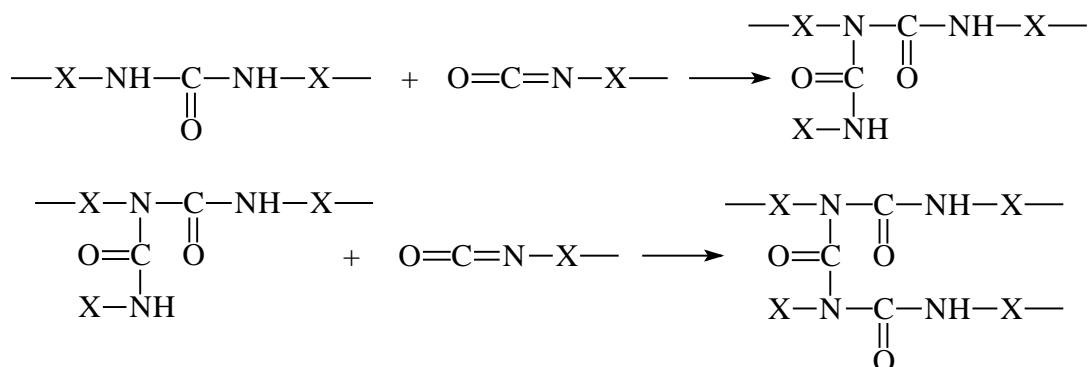
When isocyanates react with water, amines and carbon dioxide are produced:



The amine can then react with the isocyanate to form a "disubstituted urea":



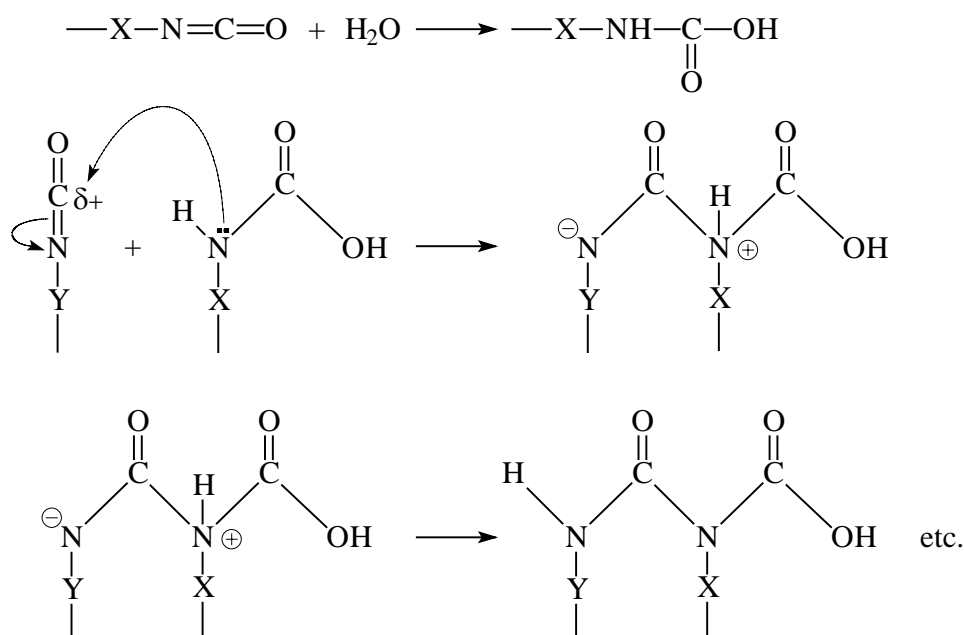
This can then react with further isocyanate to give crosslinks between the polyurethane chains, giving a durable resin:



The manufacture of condensed polyurethanes

Urethane oils can be formed by the addition of vegetable oil to the polyurethane. Urethane alkyds can be formed by reacting isocyanates with alkyds. They cure in the same way as alkyds, that is, by oxidative crosslinking of the unsaturated groups in the fatty acid portions of the molecule.

Moisture curing polyurethanes are produced by reaction of isocyanates with polyether or polyester polyols. Unreacted isocyanate groups are present and these react with atmospheric moisture to cure the resins by forming crosslinked polyurea polyurethane structures.



The manufacture of polyurethane foam

The basic ingredients of polyurethane (the polyol and the isocyanate) are mixed together in a mould in the presence of a catalyst. A highly exothermic reaction occurs, producing sufficient heat to vapourise a liquid "blowing agent". A blowing agent is used in the production of polyurethane foams to cause the polyurethane to expand out so that it sets as a foam. In its absence a solid resin forms. Depending on the various reagents used the density of the polyurethane formed can vary between 6 and 1200 kg m⁻³.

Uses of polyurethane resins

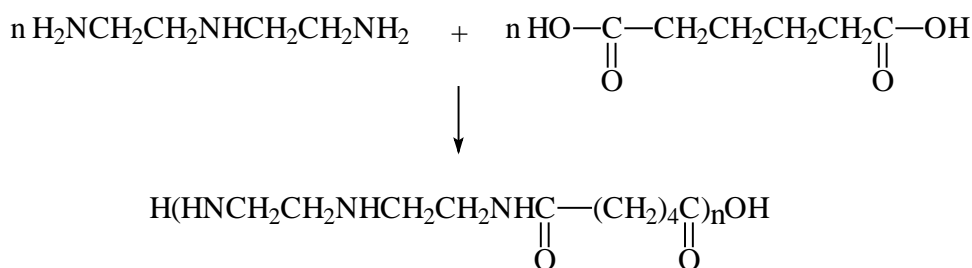
Urethane oils are used instead of conventional drying oils in some applications as they are faster-drying and give a harder finish. Polyurethane alkyds and moisture curing polyurethanes are used in elastomers, paints, adhesives and as thermoplastics in a variety of applications. Polyurethane foams have a variety of different uses depending of the density of foam produced. Low density foams are used in packaging and insulation and high density in moulded furniture. Microcellular foams are used in shoe soles, car bumpers and synthetic leathers.

Polyamide-epichlorohydrin resins

These are polymeric materials which are used in the manufacture of certain grades of paper which require additional strength when wet (e.g. kitchen towelling).

The manufacturing process

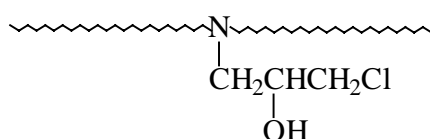
The resins are made in two stages. First a polyaminoamide resin is made by reaction of a polyfunctional amine such as diethylene triamine with a difunctional acid such as adipic acid.



In the second stage the polymer formed as described is reacted with epichlorohydrin



which reacts with available amine groups forming the amino chlorohydrin



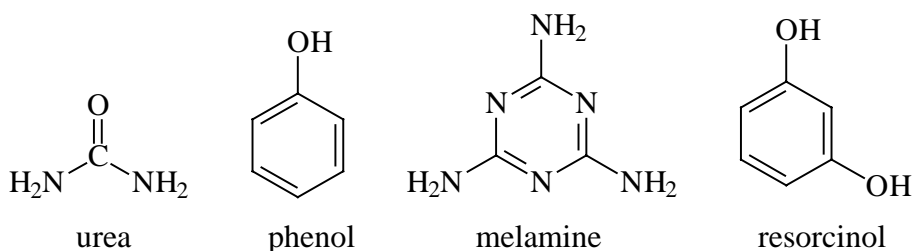
which can further react by crosslinking between polymer chains or stabilise by forming a cyclic structure.

The uses of polyamide-epichlorohydrin resins

As stated above, the major use of these resins is in papermaking. The resins are supplied as dilute aqueous solutions and are injected into the papermaking stock shortly before it reaches the papermaking machine. 0.5-1% solid resin (on dry fibre) can allow wet paper to retain over 30% of its dry strength while without the resin, the strength retention would be 0-2% when wet. This is used for papers that need to remain strong when wet, such as hamburger wrappers.

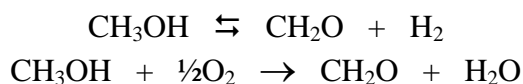
Formaldehyde resins

Formaldehyde resins are formed by the reaction of formaldehyde with urea, phenol, melamine or resorcinol, and are used as adhesives.



The manufacturing process

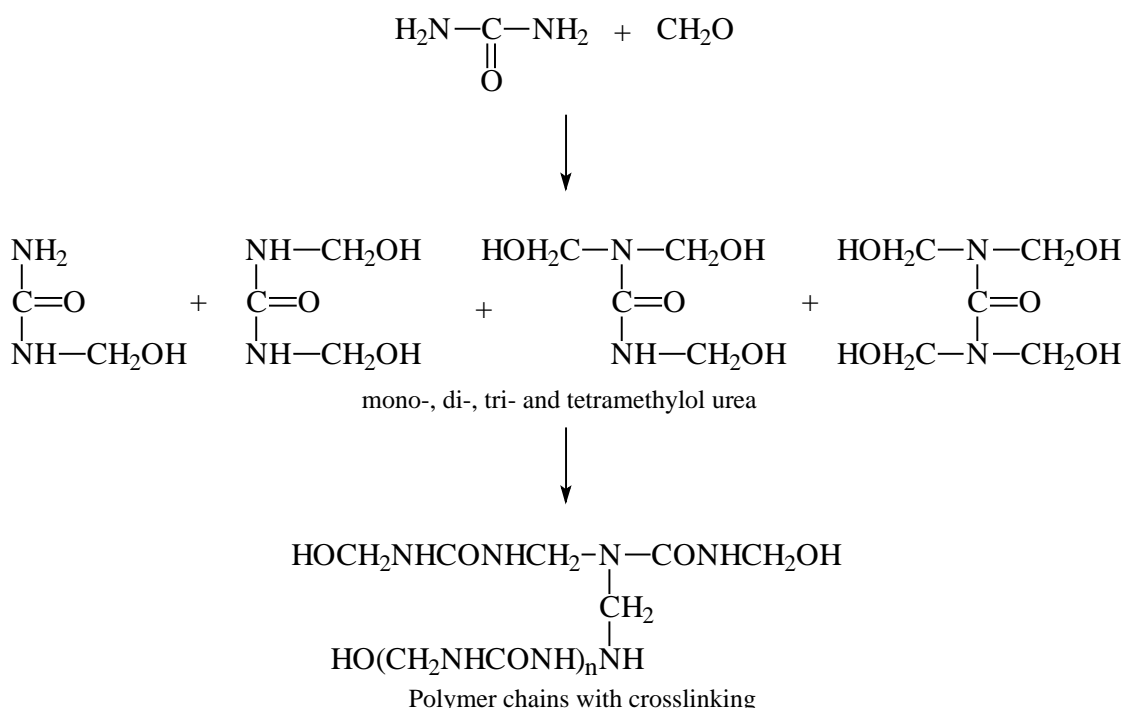
The formaldehyde is produced by ICI Resins by silver-catalysed methanol oxidation:



The methanol is vapourised and blown across a silver catalyst. The formaldehyde gas formed is absorbed into water and removed continuously as a 45 - 50% solution.

The resin is now produced in a batch process. The formaldehyde is fed into the reactor and heated to 60°C. Alkali is added and then urea (produced in Taranaki - see article), during which time the mixture falls to 40°C. Finally the mixture is adjusted to pH 5 and heated to 90°C and left until sufficient polymerisation has taken place (this will depend on the desired end use of the resin). The reaction is then quenched with alkali and cooled.

The reactions occurring are complex and imperfectly understood, but it is known that chains are formed in accordance with the following reaction scheme:



Uses of urea formaldehyde resins

The major use of these resins is in adhesives, and as such they are used in the production of reconstituted woods such as particleboard and plywood as well as in laminated wood. They are also used for a variety of other purposes including textile treatments, paints and enamels, glass fibre insulation binders and in the pulp and paper industry.

ROLE OF THE LABORATORY

In all of the resins described above the end product can be substantially altered by changing the proportions of reactants used, the pH or the temperature. Because of this, these factors are monitored by the laboratory at the plant to ensure consistent quality. The final product is also tested using four types of routine tests:

- Viscosity
- acid value (i.e. the amount of acid present)
- non-volatiles content
- pH (only useful for some polymers, such as emulsion polymers and some formaldehydes)

The results of these tests do not give the composition of the final product, but they do identify whether the product is the same as has been produced before. In the production of industrial resins it is enough to know that a consistent product is being produced, and it is not essential to know its exact composition.

Written by R. Biddle (Henderson High School) and John Packer, with the help of Dr. A. Thompson (A.C. Hatrick Limited). Updated for this edition by Heather Wansbrough following correspondence with John Blanchard (A.C. Hatrick Limited) and with reference to:

- The ICI fact sheets on polyurethane and urea formaldehyde
- *The McGraw-Hill Encyclopedia of Science and Technology*; McGraw-Hill, Inc.; 1992