

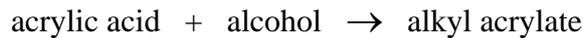
ACRYLICS

Acrylics are polyesters based on acrylic acid (propenoic acid - $\text{CH}_2=\text{CHCO}_2\text{H}$) formed from the polymerisation of an alkyl acrylate ester. They are widely used in the surface coatings industry (e.g. in paints) as well as being used in sheet form because of the exceptional clarity and durability of the sheets.

They are produced in a two step process.

Step 1 - Production of the monomer

The monomer is formed from the reaction between acrylic acid and an alcohol as follows:



Step 2 - Polymerisation

A radical (i.e. a molecule with an odd number of electrons) then adds to one end of the double bond of the alkyl acrylate forming a radical monomer which then polymerises.

The properties of the resulting acrylics vary depending on the nature of the alkyl groups both on the alcohol and the acrylic acid.

This process is potentially environmentally harmful so gaseous emissions and liquid wastes are treated on site to ensure that they meet local body specifications. In addition, the reaction is carried out in water rather than a hydrocarbon solvent to minimise the environmental impact.

INTRODUCTION

Acrylics are esters of acrylic acids, that is they are the products formed by the reaction of an acrylic acid¹ and alcohol. The esters of acrylic acid polymerise readily to form exceptionally clear plastics. These are widely used in applications requiring clear durable surfaces, e.g. in the aircraft and automobile industries. In more common use are surface coatings involving acrylics (see articles). The physical properties of the acrylics (such as gloss, hardness, adhesion and flexibility) can be modified by altering the composition of the monomer mixture used in the polymerisation process.

Uses of acrylics

Acrylics are used in a wide range of industries, and the list below is simply a selection of some of the more common examples:

- Adhesives
- The textile industry (e.g. making the sponge fill used in padded jackets)
- Paper coatings
- The paint industry (particularly in paints used for road markings)
- Cement modifiers

¹Acrylic acid is the common name of propenoic acid ($\text{CH}_2=\text{CHCOOH}$). 'Acrylic acids' are derivatives of acrylic acid and have the general formula $\text{CH}_2=\text{CRCOOH}$.

Some of these uses are mentioned in other relevant articles as well.

Polymerisation methods

The polymerisation process proceeds readily in the presence of catalysts and may be carried out in any one of four different ways: in emulsion, in bulk, in solution or in suspension.

- *Emulsion polymerisation* occurs in a water / monomer emulsion using a water-soluble catalyst. Emulsion polymerisation is the main process used in NZ for the production of acrylic polymers and is the process described in detail in this article.
- *Bulk polymerisation* is carried out in the absence of any solvent. The catalyst is mixed in with the monomer and the polymerisation is then left to occur with time. This is the method commonly used to manufacture acrylic sheets.
- *Solution polymerisation* is carried out in a solvent in which both the monomer and subsequent polymer are soluble. Only low molecular weight polymers can be manufactured by this process, as high molecular weight polymers cause very high viscosities.
- *Suspension polymerisation* is carried out in the presence of a solvent (usually water) in which the monomer is insoluble and in which it is suspended by agitation. To prevent the droplets of monomer from coalescing and also to prevent the polymer from coagulating, protective colloids are added. Suitable colloids include bentonite, starch, polyvinyl alcohol and magnesium silicate. In contrast to emulsion polymerisation the catalyst is monomer-soluble and is dissolved in the suspended droplets.

THE MANUFACTURING PROCESS

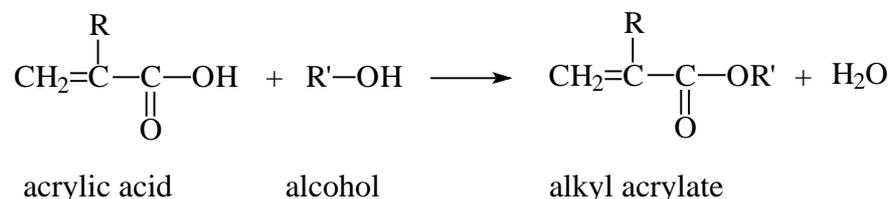
The polymers are manufactured from monomers that are formed from the reactions of acrylic acids with alcohols. These are then polymerised using a radical initiator in a water emulsion.

Raw materials

The following components are needed for the reaction.

Monomer

Monomers are prepared by a reversible reaction between an acrylic acid and an alcohol:



The major monomers used are ethyl acrylate, methyl methacrylate and butyl acrylate, as well as non-acrylic monomers such as vinyl acetate and styrene which behave similarly. No acrylic polymers of simply one monomer (e.g. perspex - polymethylmethacrylate) are made in New Zealand. However, a wide range of copolymers² are produced, and by varying the

²A copolymer is a polymer of the formAAAAAABBBBBBAAAAAABBBBBB...., i.e one which consists of alternating short strings of monomer A and monomer B.

ratio of their monomers a series of polymers with a wide range of glass transition temperatures can be produced.

Surfactant

A surfactant is a substance composed of mutually repellent polar and non-polar ends. The surfactant surrounds each monomer droplet with a layer of surfactant with the polar tails oriented towards the surrounding water thus forming a micelle.

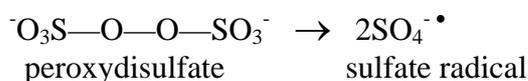
Water

Water is used as the medium to disperse these micelles. During the process the water acts as a solvent for the surfactants and initiators, as well as as a heat transfer medium.

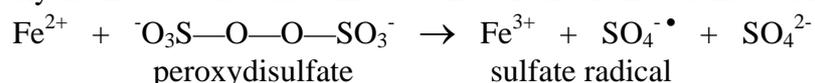
Initiator

The initiators (catalysts) usually used are water soluble peroxidic salts such as ammonium or sodium peroxydisulfate. The reaction can be initiated either by thermal or redox initiation.

In thermal initiation the peroxydisulfate dissociates to give two $\text{SO}_4^{\cdot-}$ radicals



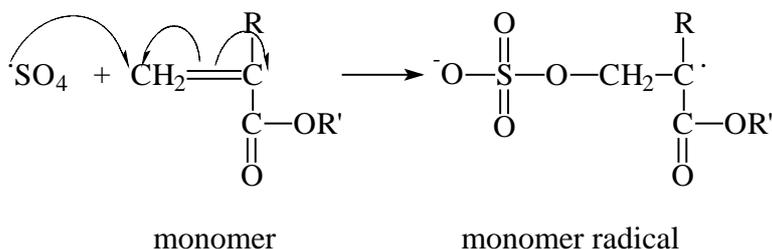
In redox initiation a reducing agent (usually Fe^{2+} or Ag^+) is used to provide one electron, causing the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion:

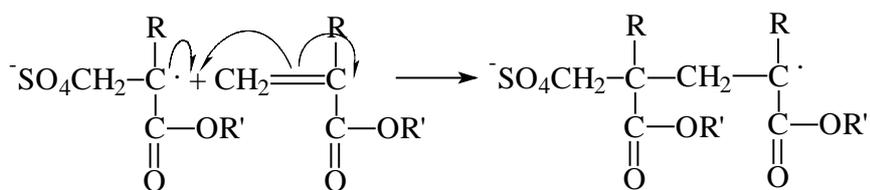


Polymerisation

The emulsion polymerisation process is carried out in a reaction kettle, which is fitted with a jacket for heating and cooling to allow control of temperature during the reaction.

Surfactant and water are first charged into the kettle. The monomer emulsion and initiator solution (containing redox agents to split the persulphate into sulphate radicals) is then transferred from the monomer feed tank into the kettle at a controlled rate. The mixture in the kettle is constantly agitated while the monomer is being added. During this time the monomer polymerises in accordance with the reactions given below.





monomer radical

dimer radical

etc.

Once the reaction has proceeded far enough to use up all the available polymerisation sites, the contents of the kettle are transferred to the stainless steel blend tank. The batch is then cooled, adjusted and transferred to holding tanks for storage and subsequent packing.

UTILITIES

A significant number of utilities are needed to carry out a series of ancillary processes. These include:

- A steam boiler to supply steam to the kettle for heating, and a water cooling system to cool the kettle.
- A treatment unit to remove fumes from the air exhausted from process vessels.
- Electric power for monitoring systems and feed pumps.
- Nitrogen gas under pressure for the sparging of the kettle prior to the dissociation of the initiator.

ROLE OF THE LABORATORY

The quality of the final product depends on the control exercised during the production process. Routine quality control checks of the following properties are carried out throughout the manufacturing process:

- | | |
|------------------|-------------------------|
| • Solids content | • Residual monomer |
| • pH | • Mechanical stability |
| • Viscosity | • Freeze/thaw stability |
| • Gel levels | • Compatibility |

One of the most important tests of the finished polymer is determining its 'glass transition temperature', which is a measure of its toughness. This is done by heating the polymer at a constant rate and measuring its temperature. When a graph of time against polymer temperature is plotted, there will be points where the graph is flat, i.e. the polymer is being heated but it is not getting hotter. At these points the plastic is undergoing some sort of phase change between two different solid phases, and the heat energy is being used to rearrange the structure of the material rather than to simply heat it. Where these transitions occur and how many there are effects the toughness of the plastic.

ENVIRONMENTAL IMPLICATIONS

Since the emulsion process takes place in water problems associated with solvent use are avoided. All fumes from process vessels are passed through a treatment unit before discharge to the atmosphere. Water used for cooling is recycled through the cooling towers to reduce waste and process water is thoroughly treated to comply with local body regulations. Rohm and Haas are a company dedicated to the production of high quality products, and are the holders of several international environmental awards.

Compiled by Roger Glanville (Unitec Auckland) following an interview with Bobby Kanji (Rohm and Haas New Zealand). Edited by Heather Wansbrough following further communication with Bobby Kanji.