

**Novel Ingredients for Coatings
Formulation**

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Introduction

Safety

In the nineties and certainly for the next millennium this word has been and will be in the forefront of everybody's mind. Safety for the employee, safety for the end-user, safety for the environment are all driving forces in the industrial environment at the moment.

In the coating's field two distinct areas of safety consciousness are becoming more and more prominent :

- *replacement of environmentally unfriendly products* : both in the emulsion polymerisation process and in the formulation of a final coating formulation alkylphenol alkoxyates are being replaced.
- *replacement of solvent by water as external carrier for the resin* : In an attempt to reduce the VOC - content of formulations and to reduce the overall solvent use in coating formulations resin manufacturers are turning to water. Two approaches are being followed :
 - reacting of a monomeric unit into the polymer thereby making it water compatible
 - emulsifying the unmodified resin in water

This paper will discuss three areas where Uniqema has been particularly active in over the last couple of years and will remain so in the future,

1. Replacement of nonylphenol ethoxylates in emulsion polymerisation reactions
2. Emulsification of resins in water.
3. Monomers that can be incorporated into certain water reducible resins so as to change their properties.

Nonylphenol ethoxylates replacement in emulsion polymerisation reaction

Emulsion polymerisation is a radical chain growth reaction of water - insoluble (co)monomers emulsified in an aqueous phase. The end - product is a submicron high MW (co)polymer dispersed in water ('a latex') and stabilised by surfactants. Latices are mainly used as film forming substances ('binder') in coatings and as thickeners/rheology modifiers.

Usually the surfactants used during the actual polymerisation process also give the final colloidal stability to the latex. In some cases extra surfactants are added at the end to increase the colloidal stability ('post-stabilisers'). The surfactants used can be of varying chemical nature but the most prominent nonionic surfactant in use is of the nonylphenol ethoxylate family.

Nonylphenol ethoxylates are very efficient products for the emulsion polymerisation process but unfortunately these products are considered as non-biodegradable. Some studies have also claimed bio-accumulation of its metabolites. This has lead formulators to look for alternatives.

Alkenyl Succinic Anhydride Condensates

Alkenyl succinic anhydride condensates, or ASACs for short, are a new class of chemistry that can be used as emulsifier / stabiliser in emulsion polymerisation reaction. The environmental profile of ASACs, is close to that alcohol ethoxylates and as such an improvement on the nonylphenol ethoxylates. Fig 1 shows a representation of an ASAC surfactant.

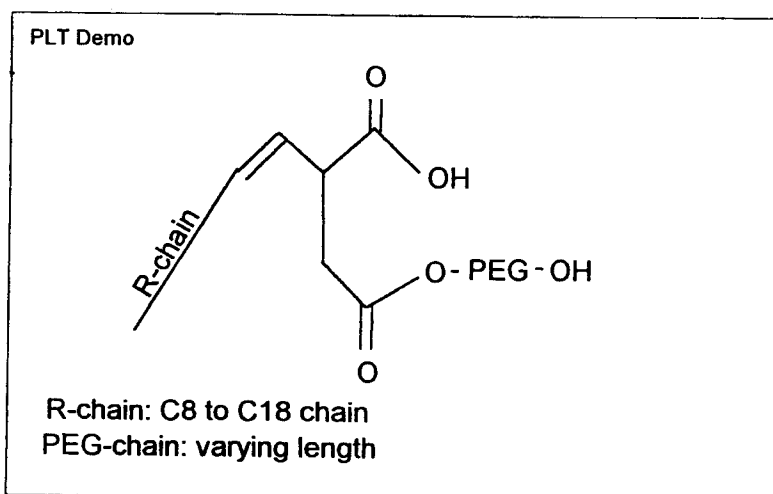


Fig.1 Schematic representation of an ASAC molecule

Experimental Results

Atpol E-5837 (C12 - ASA - PEG1800) was investigated for its emulsification / stabilisation behaviour in a vinylacetate / VeoVa 10 polymerisation reaction. Several latex and film parameters were investigated and compared to the same latex but which had been stabilised by a traditional nonylphenol based product. Table 1 reflects the formulation and the experimental results of a VeoVa 10 / VAc latex formulation with a nonylphenol - (20)POE and Atpol E - 5837 (C12 - ASA - PEG - 1800)

	NP - formulation (parts per thousand)	ASAC- formulation (parts per thousand)
Formulation		
<i>IRC</i>		
water	311.60	311.60
NaDBS (10%)	15.50	15.50
Potassium pasulphate	0.51	0.51
Borax	2.59	2.59
Cellosize QP 300	10.30	10.30
<i>Monomer solution</i>		
vinyl acetate	362.00	362.00
VeoVa 10	155.00	155.00
nonylphenol - 20 EO	10.30	-
Atpol E-5837	-	10.30
water	69.00	69.00
<i>Initiator solution</i>		
water	62.00	62.00
potassium persulfate	1.20	1.20
Latex properties		
coagulum (%)	< 0.1	< 0.1
non volatiles (%)	53.6	53.6
viscosity (mPa.s)	880	1100
average particle size (nm)	381	337
electrolyte stability	>0.45M C ₂ Cl ₂	>0.45M C ₂ Cl ₂
freeze- thaw stability	fails at -20/+23C	> 5 cycles -20/+23C
shear stability	PS increase	no PS increase
Film properties		
water spot resistance	7	2
water uptake (%)	164	65

Table 1. Comparison of ASAC and NPE stabilised VAc/VeoVa 10 latex

Direct replacement of nonylphenol ethoxylates by an ASAC type molecule has resulted, for this formulation, in :

- a process of similar performance (coagulum levels are the same)
- a smaller particle size which should lead to a better storage stability performance
- a similar electrolyte stability of the latex
- a better freeze - thaw stability with the ASAC based formulation staying stable after 5 cycles of - 20 deg C / +23 deg C.
- a better resistance to shear. No particle size increase was observed for the ASAC based formulation.
- a deterioration of the water spot resistance as blooming was more evident on the ASAC based latex film.
- a vast improvement on the water uptake of the ASAC based latex film

Emulsification of resins in water

Producing an emulsion (a heterogeneous system of two immiscible liquid phases, with one of the phases dispersed into the other phase as fine droplets) is another way of moving towards aqueous based formulations. In this case the dispersed phase is the resin and the continuous phase is water. To produce stable resin emulsions some key aspects must be taken into consideration : (1) emulsification method, (2) emulsifier selection for specific resins.

Emulsification method

Two methods are used extensively : the direct emulsification method and the emulsion inversion technique or indirect emulsification method.

In the direct emulsification method, the water soluble emulsifiers are dissolved in the water phase and the oil soluble ones in the oil phase. Both phases are heated to a temperature 5-15C above the softening point of the resins. The oil phase is subsequently slowly added to the water phase under continuous stirring.

Using the emulsion inversion point technique we again prepare both phases but put all surfactants in the oil phase and heat to 5-15C above the softening point of the resin. Now we add the water phase to the oil phase under continuous stirring. To start with we will produce a W/O-emulsion. As more water phase is added the viscosity of the emulsion will increase.

At the inversion point the viscosity of the emulsion will be at its maximum. Further addition of waterphase will result in the inversion of the emulsion from a W/O to a O/W-emulsion. Subsequently further addition of the water phase will further reduce the viscosity of the formulation.

The big advantage of the emulsion inversion technique is the fact that it results in a more homogeneous distribution and a smaller particle size. Typically inversion techniques will give mean particle size values below 250nm while this is usually round 1µm for emulsions made using the direct method. Other advantages of the invert technique are less foam generation and better long term stability.

Uniqema has been active mainly in the development of suitable emulsifiers that allow the emulsification of alkyd resins, tackifier resins and epoxy resins.

Alkyd resins

Alkyd resin emulsions are being evaluated as a way to reduce the amount of organic solvent in the coating. Main negative aspects of the solvents are :

- negative influence on the environment (ozone depletion)
- negative influence on health (Organo Psycho Syndrome)
- flammability

Balance is key to successful alkyd resin emulsification, balance between particle size and paint properties. As we decrease the particle size of the alkyd resin emulsion the stability of the emulsion increases but also a number of paint properties improve : gloss, water resistance, viscosity, pigment binding capacity. At the same time a number of paint properties will be impaired : drying time, vapour transmission, brushability. Finding the right balance is critical to the development of a successful paint formulation.

Three surfactants are specifically useful for the emulsification of alkyd resins

- '**Atsurf**' 3969 : . mixture of nonionic surfactant
. can be used alone or in combination with the anionic surfactant '**Atsurf**' 3300B
- '**Atlas**' G-5000 : . EO/PE block copolymer on a short chain alcohol
. can be use in combination with '**Atsurf**' 3300B
- '**Atsurf**' 3300B : . alkyl aryl sulfphonate

Table 2 and 3 give some examples of alkyd resins emulsions

	Ingredients (% w/w)	
Tall oil alkyd	50	50
'Atsurf' 3969	5	-
'Atlas' G-5000	-	3.4
'Atsurf' 3300B	-	1.6
Demineralised water	up to 100	up to 100
Average particle size (nm)	245	193

Table 2 : emulsification results for a long oil tall oil alkyd resins
(oil length : approx 74% acid number : < 10 mg KOH/g)
(inversion emulsion technique at 60 deg C)

	Ingredients (% w/w)
Soybean oil alkyd	50
'Atsurf' 3969	3.5
demineralised water	up to 100
Av. particle size (µm)	1.04
Storage stability	> 6 mths in range +5C to +40C

Table 3. Formulation and evaluation results for a long oil soybean oil alkyd resin emulsion (oil length: approx 65%, phthalic anhydride: approx 24%)
(inversion emulsion technique at 8%)

Tackifier resins

Tackifier resins are the viscous component of a pressure sensitive adhesive while an elastomer provides the elastic component. The tackifying resin determines the visco-elastic behaviour and final properties of the adhesive.

There are two major classes of tackifier resins : (1) Rosins derivatives which includes rosins, modified rosins, rosin esters and other rosin derivatives and (2) hydrocarbon resins which are low molecular weight thermoplastic polymers derived from cracked petroleum distillates, terpene fractions, coal tar and a variety of monomers.

Rosin is a thermoplastic acidic resin obtained from pine trees. It is a mixture of organic acids called rosin acids. Rosin itself is unsuited for use in general because it is subject to oxidation and crystallisation. Because of this, most rosins have been subjected to a series of reactions to

form modified rosins and rosin derivatives. These are base raw materials for the production of adhesives.

Hydrocarbon tackifiers resins are true low molecular weight polymers derived from monomers obtained from petroleum, wood or coal. Their performance characteristics are determined by the monomer composition, polymerisation method and the molecular weight of the final product.

Tackifier resin emulsification is best done using the emulsion inversion point method. Emulsification temperatures can be as high as 95C as some resins have softening points above 90C. To facilitate emulsification thought can be given to reducing the softening point by blending with low softening point resins or the addition of a solvent

For the emulsification of tackifiers resins the use of phosphate esters has proved to be particularly effective :

- 'Atphos' 3205-E : nonylphenol - 9EO - phosphate ester acid
- 'Atphos' 3202 : nonylphenol - 6EO - phosphate ester acid

Table 4 and 5 give some examples of tackifiers resin emulsifications.

Ingredients (% w/w)		
Rosin resin	50	
'Atphos' 3205-E	4	
Triethanolamine	0.5 to 1.7	
Demineralised water	up to 100	
pH	Mean particle size (nm)	Width (nm)
8	160	84
7.8	161	94
7.5	161	71
6.8	198	268
3.6	208	247

Table 4. Formulation and particle size change verses pH for a stabilised rosin ester-emulsion (softening point : approx 78C, acid value : < 10 mg KOH/g) (Emulsion inversion technique at 95C)

	Ingredients (% w/w)			
	50	50	50	50
modified aliphatic hydrocarbon resin	50	50	50	50
'Atphos' 3202	4.5	-	4.5	-
'Atphos' 3205-E	-	4.5	-	4.5
Triethanol amine	1.7	1.7	1.1	1.1
demineralised water	up to 100	up to 100	up to 100	up to 100
pH	7.5	7.5	6.4	6.4
mean particle size (nm)	180	172	207	177
width particle size (nm)	194	51	268	104

Table 5 Formulation and evaluation results for a modified aliphatic hydrocarbon resin emulsion (softening point : approx 85C; acid value : < 10 mg KOH/g) (emulsion inversion technique at 95C)

Epoxy resins

Most epoxy resins are reaction products of epichlorhydrine and Bisphenol A. EEW or Epoxide Equivalent Weight is a characteristic value used to classify epoxy resins. EEW is defined as the amount (gr) of resin needed to provide 1M equivalent of epoxide.

Epoxy resins with low EEW are cured by reaction of the epoxy group via the use of amine functional hardners. These resins tend to be used in ambient - cured applications.

Epoxy resins with high EEW are cured by reaction with the hydroxyl group. These resins tend to be used in heat-cured applications.

For the emulsification of epoxy resins ethylene oxide / propylene oxide copolymers are very useful :

- 'Synperonic' PE/F108 : EO/PO block copolymer

to be used alone or in combination with another EO/PO block copolymer like 'Synperonic' PE/F68, 'Synperonic' PE/F87, 'Synperonic' PE/F88, 'Synperonic' PE/F127

- 'Synperonic' T707 : EO/PO block copolymer on an ethylene diamine backbone
to be used alone or in combination with 'Synperonic' PE/F108

Table 7 and 8 give some examples of epoxy resin emulsions

	Ingredients (% w/w)	
	Epikote 1001	55
'Synperonic' PE/F 108	5.5	3.3
'Synperonic' T707	-	2.2
Demineralised water	up to 100	up to 100
Average particle size (nm)	0.86	0.8

Table 7 Formulation and evaluation of epoxy resin emulsion
(EEW : 476, melting range : 50-62 C)
(emulsion inversion technique at 80C)

	Ingredients % (w/w)	
	Dow Der 671	55
'Synperonic' PE/F 108	5.5	3.3
'Synperonic' T707	-	2.2
Demineralised water	up to 100	up to 100
average particle size (nm)	0.9	0.8

Table 8 Formulation and evaluation of a low molecular weight solid resins for two package coating systems and tape adhesives
(EEW = 475-550, 100% solids, softening point : 70-80C)
(emulsion inversion technique at 85C)

Monomers for water reducible resins

As water reducible resins are being developed new technologies for monomer building blocks are also progressing. These monomers are included in the formulation to improve certain aspects of the polymer behaviour. Two different types of monomer building blocks will be discussed : (1) dimer acids and (2) bisphenol A alkoxyates.

Dimer acids

Dimer fatty acids are prepared by a complex oligomerisation reaction of unsaturated fatty acids (predominantly C18 types). The dimerisation yields a mixture of mono-, di- and tri-carboxylic acids. The monocarboxylic acids are distilled from the polyfunctional acids resulting in "crude" dimer fatty acid. This consists of dicarboxylic "dimer" and tricarboxylic "trimer" in a ratio of 80/20. This grade of dimer fatty acid can be used as such, or hydrogenated to yield products with lighter colour and oxidation stability.

The mixture can also be further purified into pure dimer and trimer by molecular distillation. By hydrogenation of the purified dicarboxylic acid a very light coloured polymer grade dimer acid is obtained, which is applied as a building block in high molecular weight polymers such as polyamides, polyesters and polyurethanes.

Further hydrogenation of the polymer grade dimer acid yields a pure C36-dimerdiol which is used to design high quality esters, polyesters and polyurethanes.

Fig 2 illustrates the polymerisation and purification scheme of triglycerides.

During the dimerisation process a wide range of isomers of difunctional and trifunctional fatty acids is created. Dimer fatty acid is commonly recognised to be a mix of the following isomers : linear (7%); cyclic (65%) and aromatic dimer (18%) ,as can be seen in Fig 3.

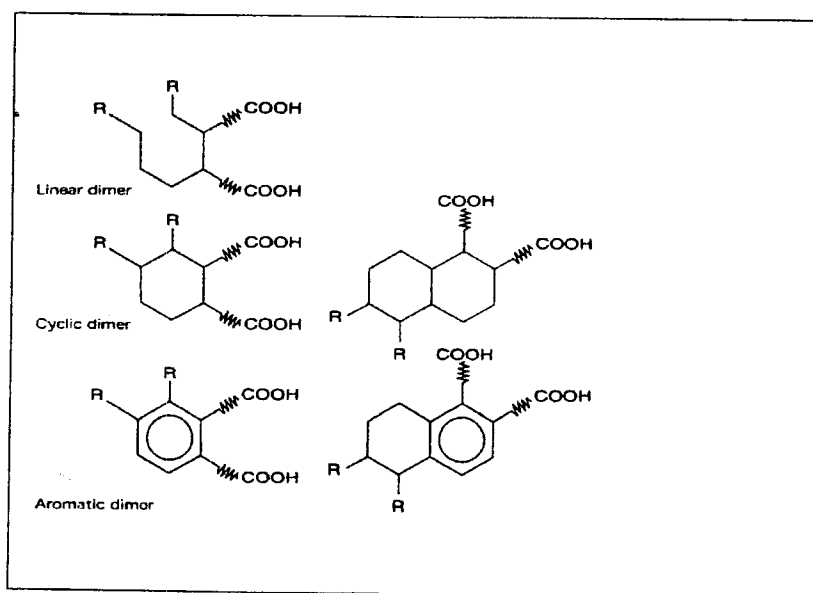


Fig 3 : Schematic representation of dimer acid isomers

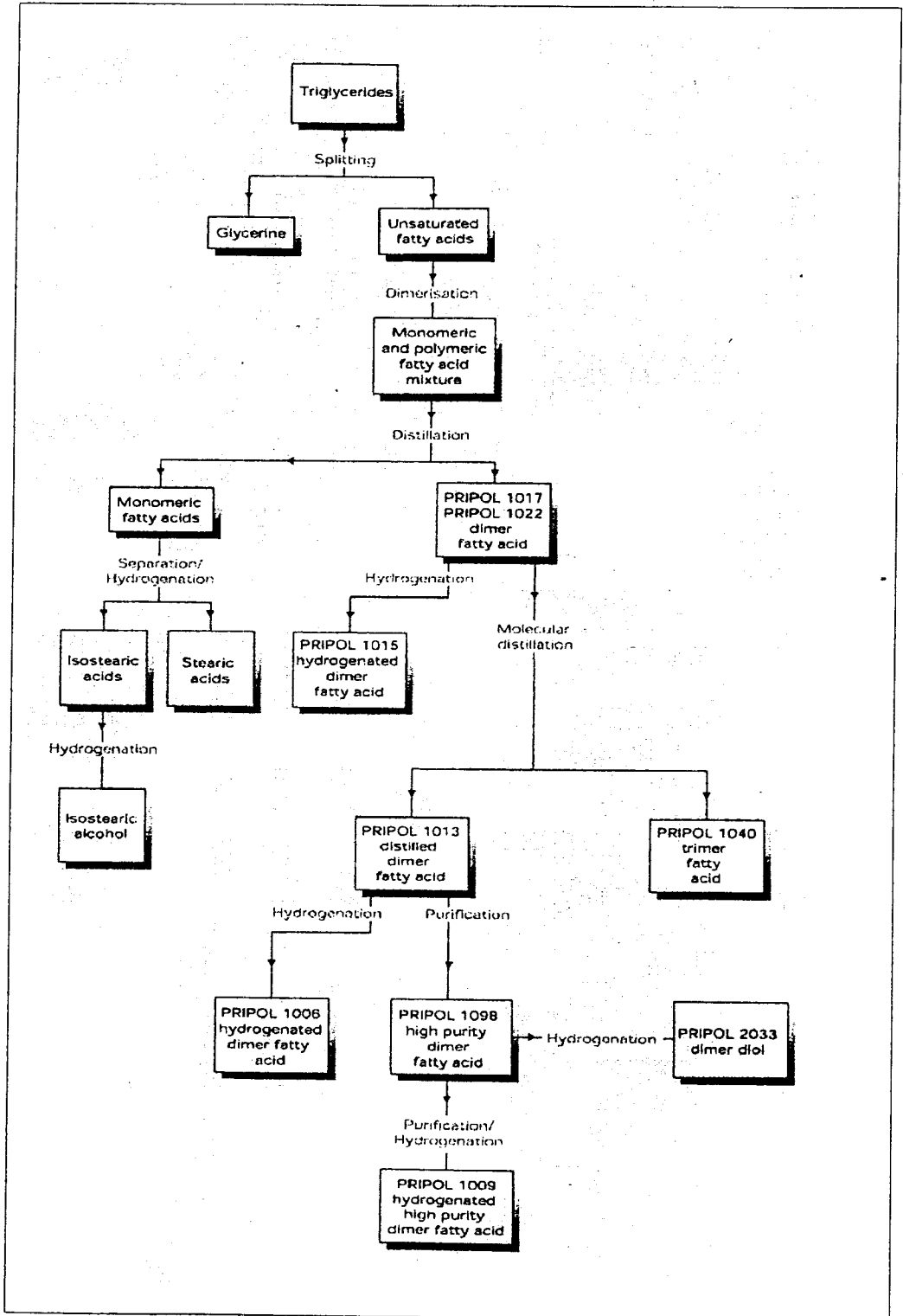


Fig 2 : Polymerisation and purification scheme of triglycerides

Two examples of the effects of the use of dimer fatty acids as monomer building blocks will be discussed.

* Branched polyester / melamine system

Prior to the baking process all the water and co-solvents should have evaporated completely. This ensures a smooth and defect-free paint film. By the incorporation of the dimer fatty acid shorter flash off times can be achieved for waterborne system. Fig 4 illustrates the basic principle for a polyester / melamine waterbased system.

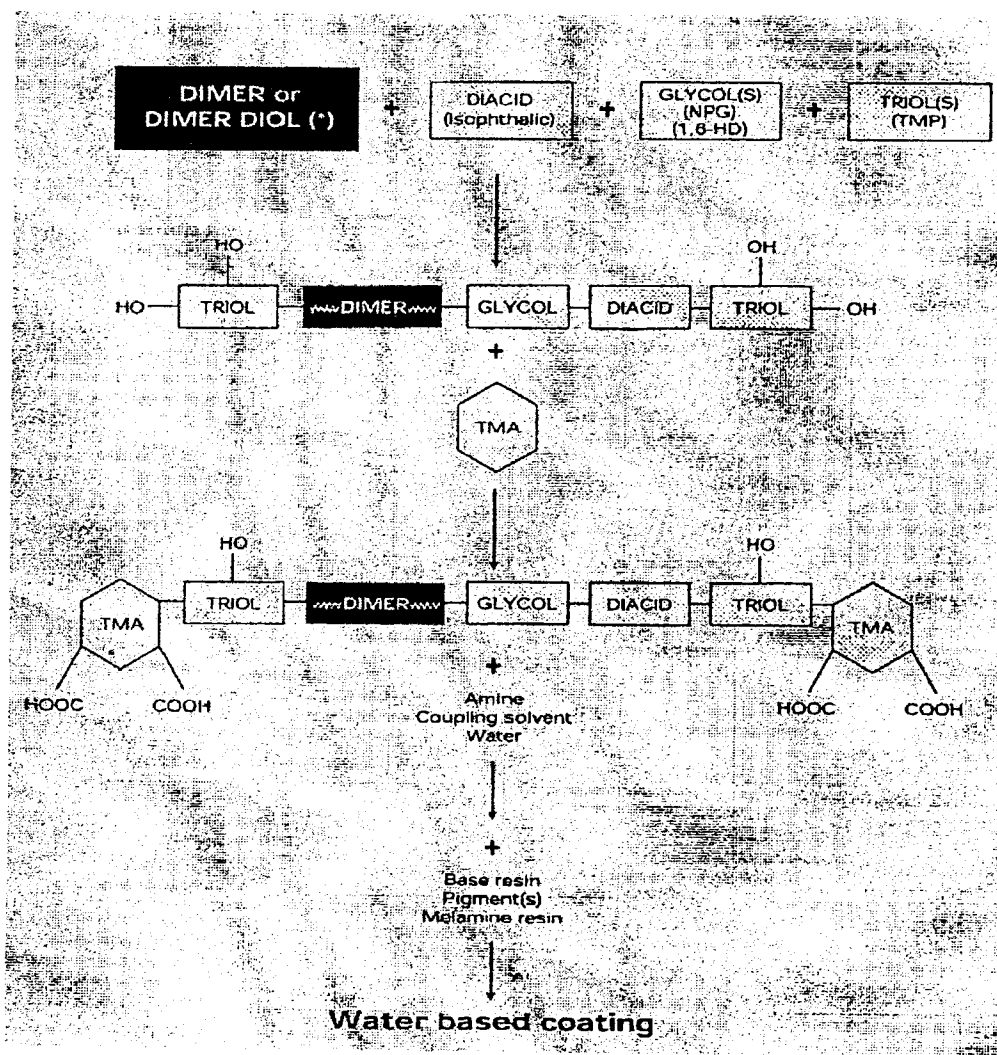


Fig 4 Basic principle for branched polyester / Melamine water based coating

An example of a water based branched polyester formulation can be formed in Table 9. Subsequently Table 10 shows the performance of this resin in a white enamel formulation.

Formulation *		
1	PRIPOL 2033	40
	Neopentyl glycol	358
	trimethylol propane	85
	Isophthalic acid	407
	Esterification catalyst	0.5
	Adipic acid	158
2	Trimellitic anhydride	79

Table 9 Example of branched polyester resins
(* parts by weight)

Material	parts by weight
Polyester resin (80%)	25.5
Dimethylethanoamine	1.8
Water	39.6
Cymel 303 ^(TM)	4.6
Tioxide TR 90 ^(M)	28
Performance	
20 min. mill 100 µm Wet film on steel 10 min. at 160 [°] C	
Erichsen cupping (mm)	7.4
Adhesion (cross-cut)	GT 1-2
Impact (Kg-cm)	
direct at 100 cm	excellent
reverse at 100 cm	excellent
Gloss (< 20°/60°)	63% / 78%
Pencil hardness (no cut)	2 H
K ¹⁵ ig hardness (sec.)	160
Chemical resistance	
NaOH 10%	excellent
Acetic acid 10%	excellent
Sulphuric acid 10%	excellent
Petrol	excellent

* Polyurethane system

Water based polyurethane systems suffer from long flash-off times and poor hydrolytic stability. Hydrolytic stability can be improved by the incorporation of polycarbonate

polyols but these tend to be expensive. By the inclusion of dimer fatty acids into the polymer (Fig 5) good hydrolytic stability can be achieved leading to excellent shelf life stability, flash-off times become short and very good adhesion is observed on various substrates. Table 11 gives an example of a water based polyurethane formulation.

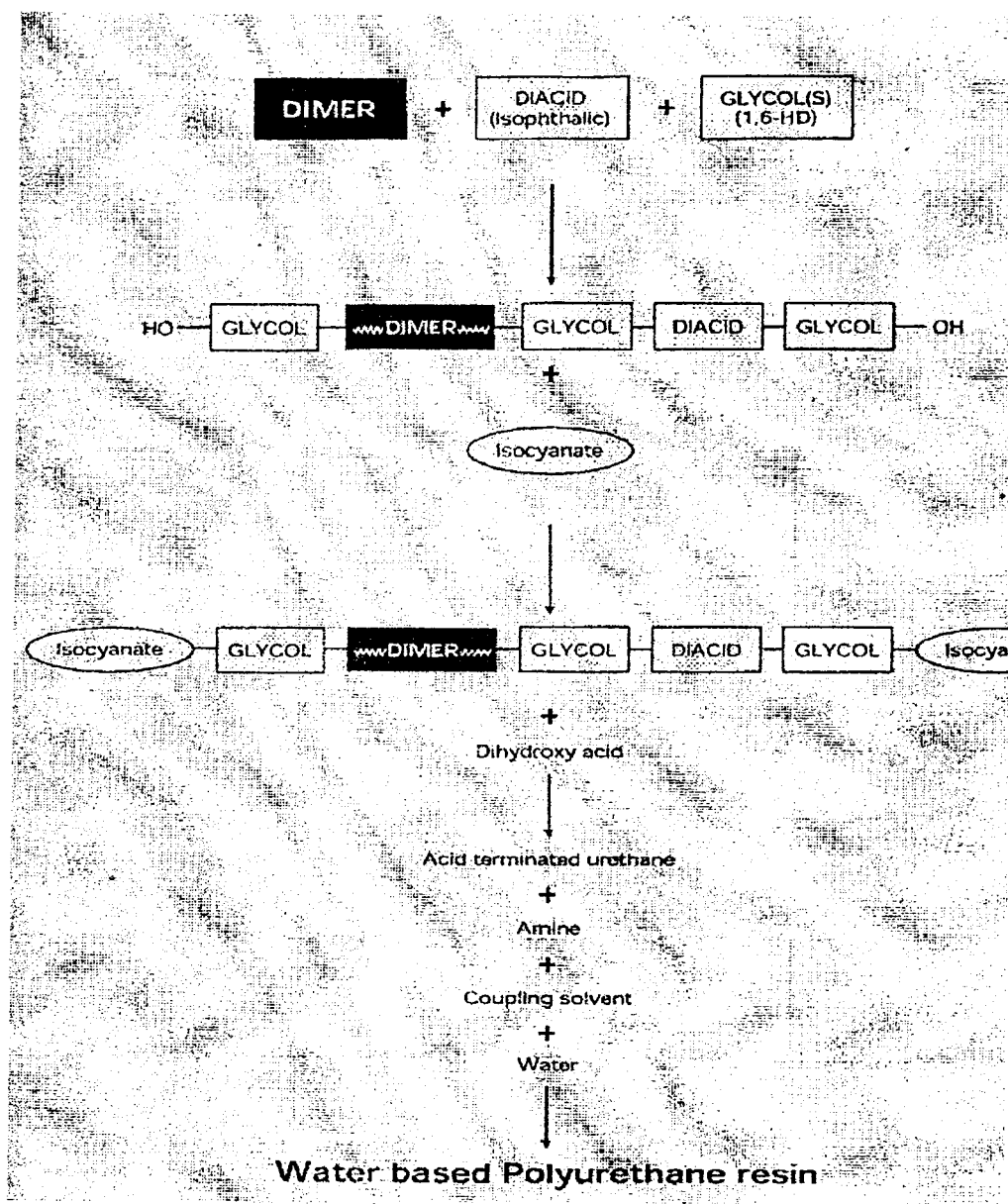


Fig 5 Reaction pathway for the preparation of waterbased polyurethane resins.

Formulation *	
PRIPOL 1006 modified polyester (N)	214
N-methylpyrrolidone	97
Dimethylol propionic acid (DMPA)	15
Isophorone diisocyanate (IPDI)	71
Dibutyl tin dilaurate (DBTL)	0.2
Triethylene amine (TEA)	11.3
Water / Ethylene diamine (10:1)	50
Water	600

Table 11 Example of waterbased polyurethane resins.
(* parts by weight)

Bisphenol A alkoxyates

Bisphenol A is a main ingredient in epoxy resins where it provides many of the final resin characteristics e.g. toughness, durability, adhesion, corrosion resistance and chemical resistance. It is also responsible, due to the molecular build-up of the molecule, for the rigidity / brittleness of the polymer.

The combination of polymer chemistry and surfactant chemistry has resulted in the development of a range of products that incorporate all the positive aspects of bisphenol A but overcome some of the negative aspects. By the reaction of bisphenol A with ethylene oxide or propylene oxide a more flexible molecule has been developed that finds applications in both solvent and waterbased system. Table 12 lists the products available from Uniqema.

Product Name	Alkoxyate
'Atlas' G-1672	2.2 ethoxyate
'Atlas' G-389	6.0 ethoxyate
'Atlas' G-1652A	2.0 propoxyate
'Atlas' G-1652	2.2 propoxyate
'Atlas' G-1653	3.0 propoxyate
'Atlas' G-1666	16.0 propoxyate

Table 12 Bisphenol A alkoxyates from Uniqema.

Applications for bisphenol A alkoxylates have been found in :

* Epoxy resins

If you list the main properties of epoxy resins as (1) tough, durable, (2) excellent adhesion, (3) corrosion resistance, (4) high level of resistance to attack by a wide range of chemicals and (5) very rigid/ brittle with low mechanical properties and resistance to deforming. The first four properties are imparted by the presence of bisphenol A in the polymer. The brittleness and rigidity is also imparted by the bisphenol A as it doesn't allow flexibility in the polymer backbone.

To incorporate flexibility into the resin you can :

1. use flexible hardeners (typically polyamide type hardeners where flexibility is enhanced by the use of Uniqema's Pripol dimer fatty acids)
2. increase the spacing between the aromatic rings of the bisphenol A molecule by substitution them by bisphenol A alkoxylates.

* Alkyd resins / Polyester resins

Bisphenol A Alkoxylates can be used in solvent and water based polyester and alkyd resin manufacture. Partial replacement of the polyol by the bisphenol A Alkoxylate allows some of the beneficial properties like better adhesion, corrosion resistance to be incorporated into this type of polymer.

The use of BPAA's has been shown to have improved the colour stability and colour development in coating systems.

* Polyethers

In poly-(phenylene sulfone) - type polymers BPAs are used to lower the glass transition temperature (T_g) from more than 500 degC to a manageable 190 degC (=poly(ether sulfone)-type polymers). Replacement of the BPA by BPAA will further reduce the T_g as BPAA's give the polymer even more flexibility.

* Polyurethanes

In polyurethane, the BPAA products may be used as chain extenders in pre-polymers to impart flexibility, or in the manufacture of polyesterols, particularly the adipates. Polyurethanes, based on these polyesterols, are characterised by resistance to hydrolysis, high mechanical stability, low glass transition temperatures (when compared to other polyesterols), and fast

crystallisation. The overall performance characteristics of the BPAA based products are far above most competing products. In addition, BPAAs offer the ability to develop a wide range of tailor-made products for various standard and speciality applications.

* Diacrylates

The BPAA products are also used as intermediates for the production of bifunctional diacrylates. The monomer may be used in conjunction with other acrylated polymer and as a reactive diluent for use in radiation curable systems for printing inks and decorative coatings.

* Adhesives

For adhesive applications, polyols formulated with BPAAs provide faster crystallisation and better tack properties. Excellent heat and corrosion resistance are exhibited for adhesive compounds based on BPAAs

* Other Applications

As a flexible building block, BPAAs are incorporated into the production of various other components for use as sizing agents, surfactants, photographic stabilisers, polymer thickeners, plasticisers for PVC, polycarbonate elastomers, and air freshners.

Conclusion

Though by no means complete the coatings industry now has at its disposal a series of products and processes that can allow it to migrate away from solvent based products towards water based products. Water based products / processes still represent a major challenge but by close cooperation between resin manufacturers, coating producers and auxiliary producers like surfactant companies these can be and will be overcome.