What is required from a Paint Coating

- Good Adhesion
- Flexibility
- Impact Resistance
- Resistance to environment
  - Chemical
  - Moisture
  - Sunlight / Rains

Types of Coatings

Conventional

- Lacquers, solutions of synthetic resins (vinyl chloride, rubber and acrylic)
- Water emulsion (latex) Coatings (acrylics and Vinyls)
- Oil based coatings
- Epoxy Coatings
- Coal tar Epoxy coatings
- Poly-urethanes
- Polyester and Vinyl ester coatings
- Organic Zn rich Coatings

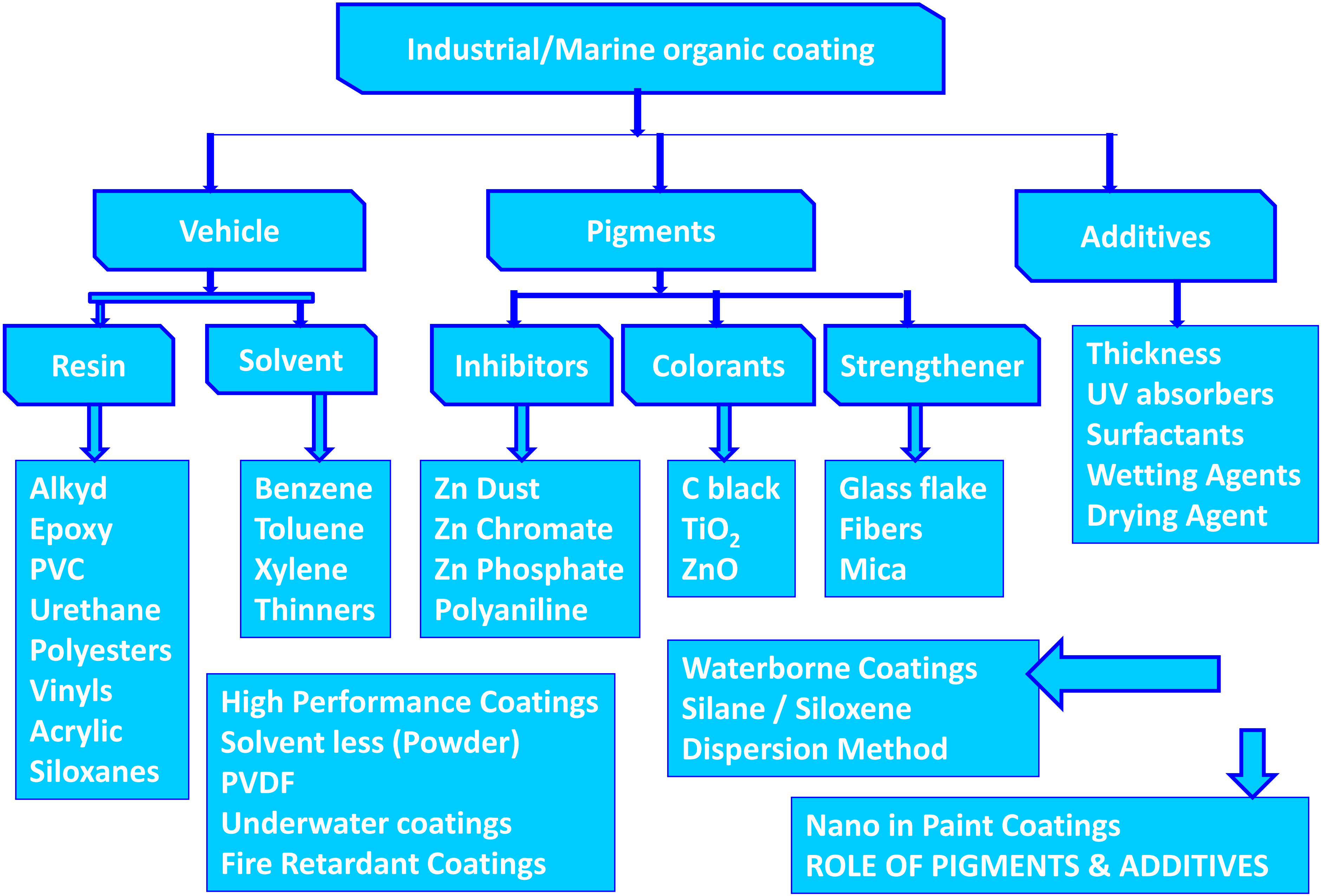
Special

- Solvent Less Coatings
- Fiber Reinforced coatings

Why we need Protective coating?

Corrosion protection

Functionalisation of the surface


Industrial/Marine organic coating
Vehicle
Pigments
Additives
Resin
Solvent
Inhibitors
Colorants
Strengthener
Thickness
UV absorbers
Surfactants
Wetting Agents
Drying Agent
Alkyd
Epoxy
PVC
Urethane
Polyesters
Vinyls
Acrylic
Siloxanes
Benzene
Toluene
Xylene
Thinners
Zn Dust
Zn Chromate
Zn Phosphate
Polyaniline
C black
TiO_2
ZnO
Glass flake
Fibers
Mica
Waterborne Coatings
Silane / Siloxene
Dispersion Method
High Performance Coatings
Solvent less (Powder)
PVDF
Underwater coatings
Fire Retardant Coatings
Nano in Paint Coatings
ROLE OF PIGMENTS & ADDITIVES

Coatings

Coatings → Chemistry → Binder used

Binder used → Epoxies, PU, Alkyd, Polyester, Polysiloxanes, Acrylics

Epoxies, PU, Alkyd, Polyester, Polysiloxanes, Acrylics →

- ✓Durability
- ✓Corrosion resistance
- ✓Mechanical properties

Other Desirable properties → ADDITIVES / PIGMENTS → Effectiveness

- ✓ Particle size
- ✓ Distribution/Dispersion
- ✓ Compatibility

Nano-sized additives provide more efficient properties than the conventional micron-sized (Lecture 10)

↓ Size decreases

↑ Effect increases

↑ Total surface area per volume increases

Galvanic series: Corrosion potentials

Difference of potential between two materials leads to one material dissolving protecting the other.

Potential (V)

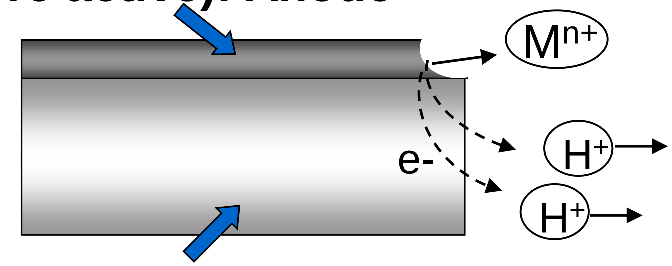
↑ Less active
More noble
(cathodic)

Sn	-0,14
Cu	-0,20
Si	-0,26
Fe	-0,67
Al	-0,85
Zn	-1,10
Mg	-1,73

More active
Less noble
(anodic) ↓

(i.e. NaCl plus 3 g/l H2O2 *at 25C.)*

Less noble material
(more active): Anode



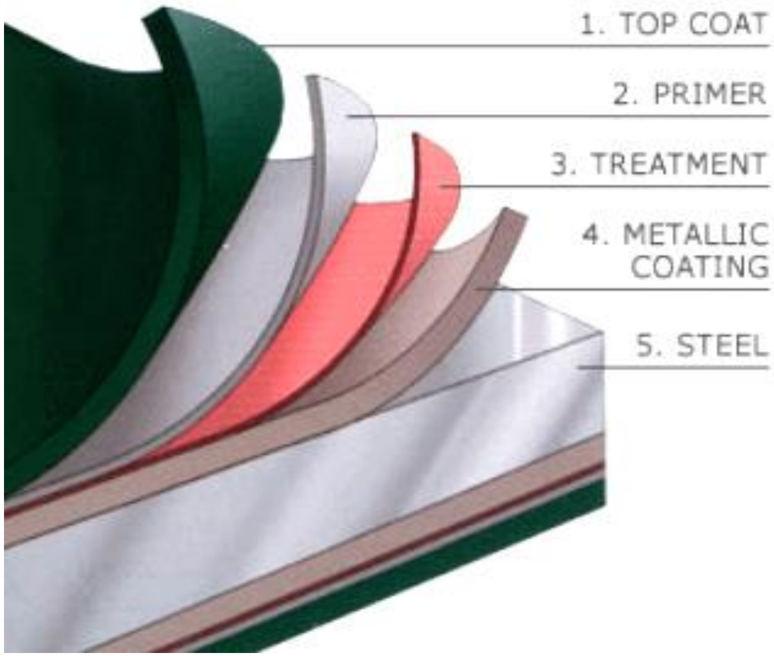
Noble material
(more resistant): Cathode

cathodic protection of steel
by zinc → HDG

Metallic coatings on steel are Zn based: GI, EZ, GA, Zn-Mg.

Organic coatings

1. Pretreatment: Adhesion
2. Primer: Corrosion & adhesion
3. **Topcoat:** Colour, gloss, UV stability & Scratch resistance

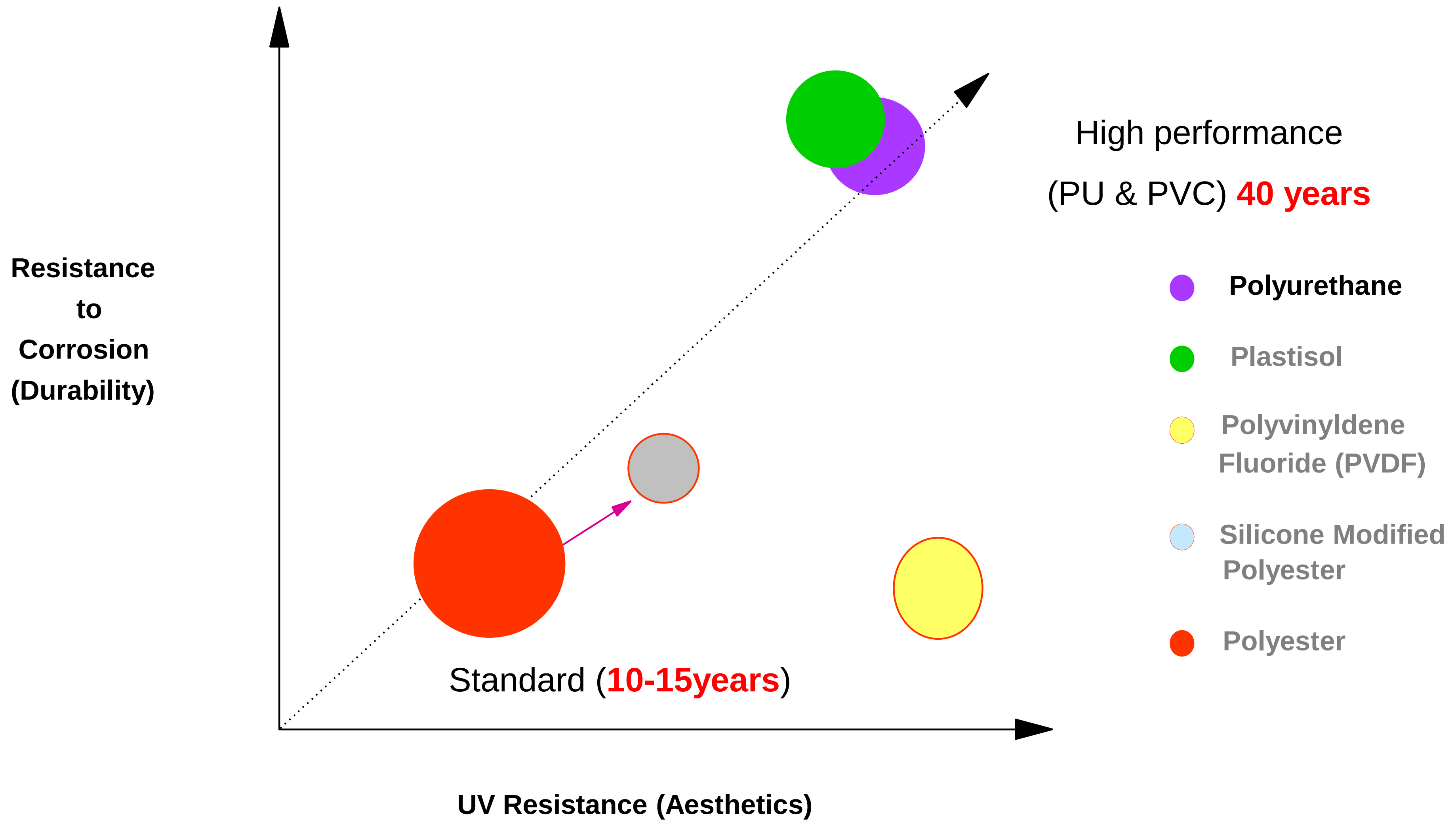


- Corrosion performance is the prime consideration (**Warranty**)

- Adhesion during roll forming and bending operations in order to avoid flaking and cracking

- Aesthetics will be more of a concern if the products is painted

Organic coatings: polymer vs performance



Basic Polymer Science

- Polymer: Large molecule with high molecular weight(mass) made up from a large number of similar small molecules

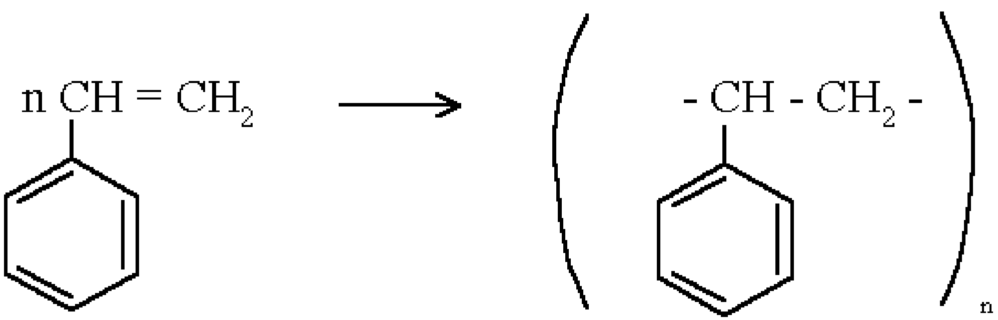
- Monomer: Small reactive molecule that bonds together with other similar ones to form a polymer

Basic Polymer Science – Addition Polymerisation

e.g. Polyethene

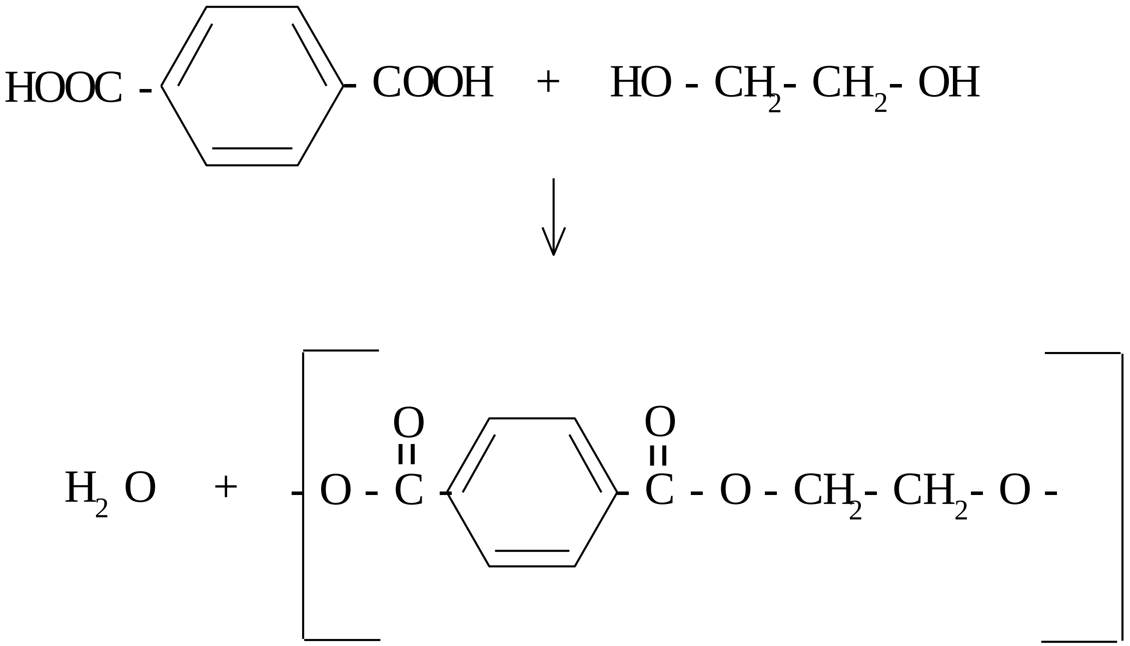
$$n\ CH_2 = CH_2 \longrightarrow (CH_2 - CH_2)_n$$

e.g. Polystyrene



Basic Polymer Science – Addition Polymerisation

Polyethylene terephthalate



Molecular Masses of Polymers

- Polymers are not pure materials

  They are a large number of molecules with different molecular masses

- The parameter chosen to represent characteristic is the Average Molecular Mass

- Molecular mass controls many of the macro properties of a polymeric system such as adhesion, elasticity, viscosity, brittleness, yieldability, hardness etc

Glass Transition Temperature

- Many of the physical properties of a polymer such as viscosity, elasticity, brittleness, hardness, yieldability, conductivity depend upon the temperature
- Over a particular temperature range polymers change from a glassy material into something more rubbery
- A specific point over this range is normally chosen to be representative and is termed the glass transition temperature

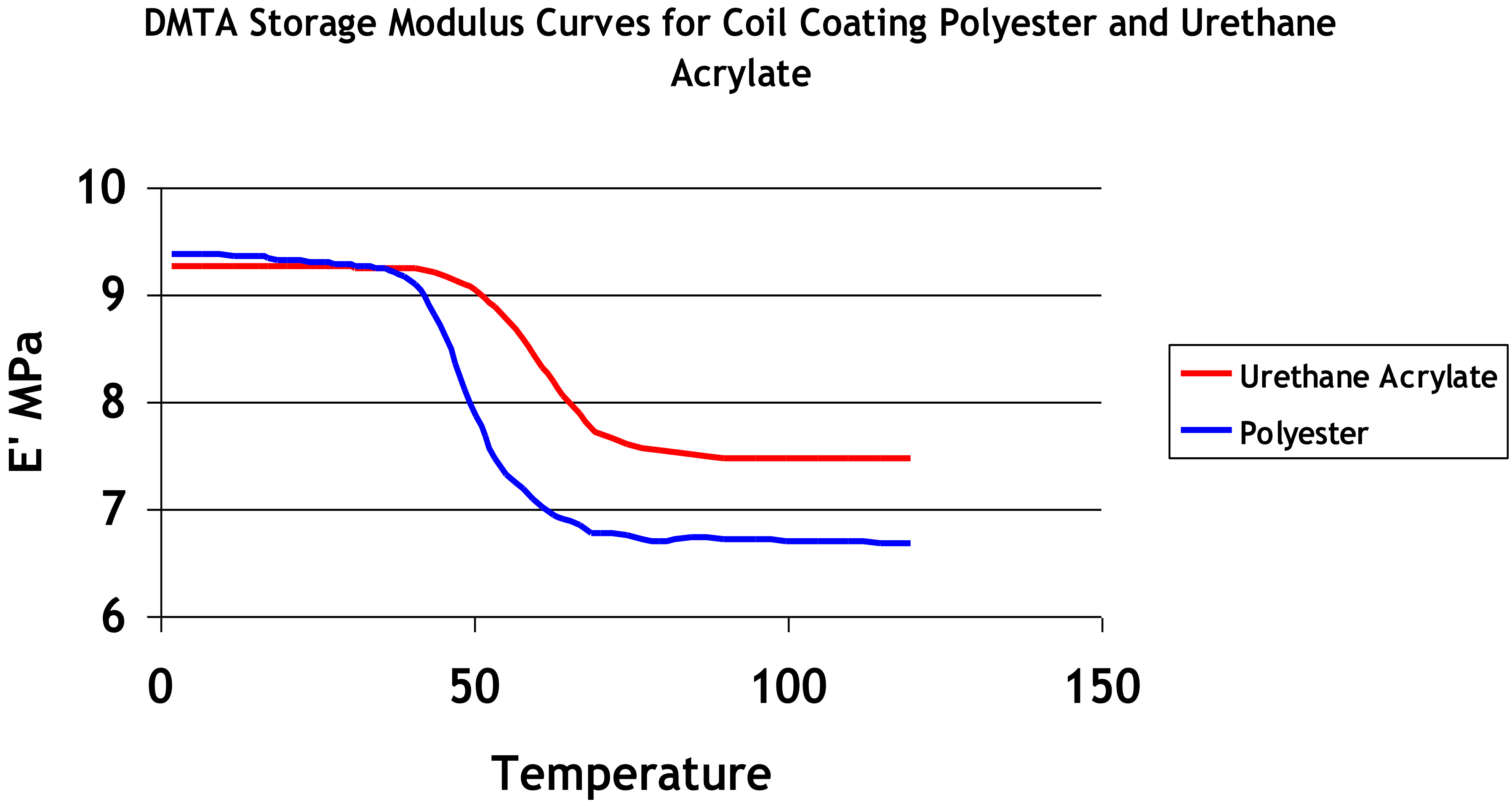
Glass Transition Temperature

- The glass transition temperature (Tg) is dependent upon the backbone of the polymer
- High Aromaticity: High Tg
- High Aliphaticity: Low Tg
- The range depends on molecular mass distribution, and the homogeneity of polymer

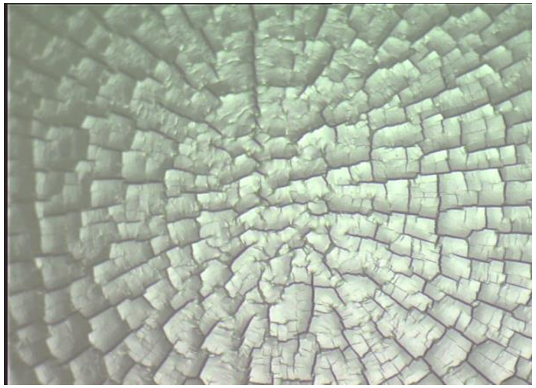
Types of Polymer

- Homopolymer: Single monomer used in preparation
- Copolymer: Two or more monomers used in preparation
- Condensation Polymer: Two or more monomers with different functional groups that react together to form the polymer and water
- **Thermoplastic**: Polymer that remains unchanged during a thermal cycle
- **Thermoset**: Polymer which changes properties during a thermal cycle

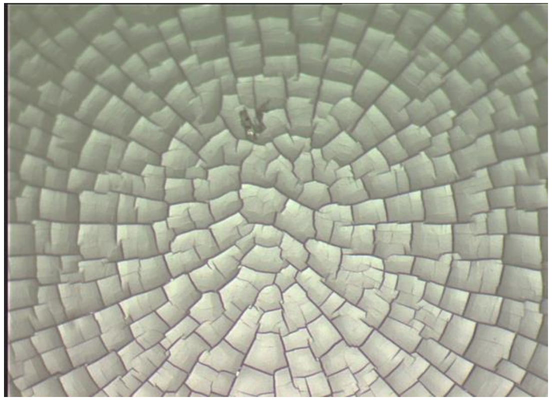
DMTA Comparison of Different Paints



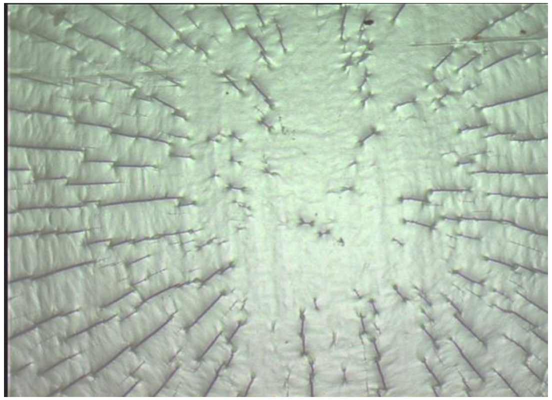
Erichsen Tests Under Controlled Humidity and Temperature



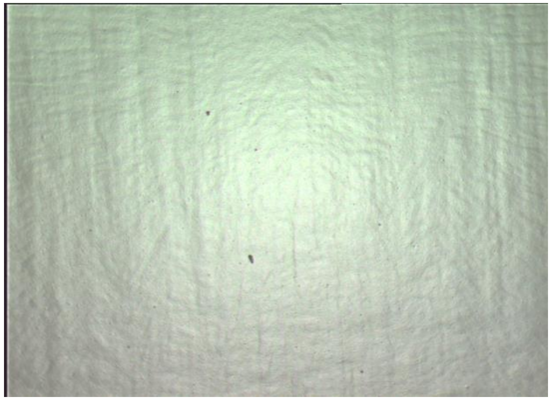
33C RH17



39C RH10



48C RH11



50C RH07

Water Emulsion Latex

Latex coatings are being successfully used to coat wood and masonry structures.

Relatively porous nature of structure allows water vapour to pass through them.

Advantages	Limitations
Reduced level of VOC	Limited Durability
Easy to apply, topcoat & repair	Poor chemical resist.
Fast to dry for recoating	Poor wetting of surface
Excellent Flexibility	Poor immersion service
Low Cost	Best cure above 50 C.

Oil Based Coatings

Coatings based upon drying oil (linseed oil, tung, soyabean, fish oil).

Cure by reaction with oxygen.

Though complete dry less than in one day, complete curing takes much longer.

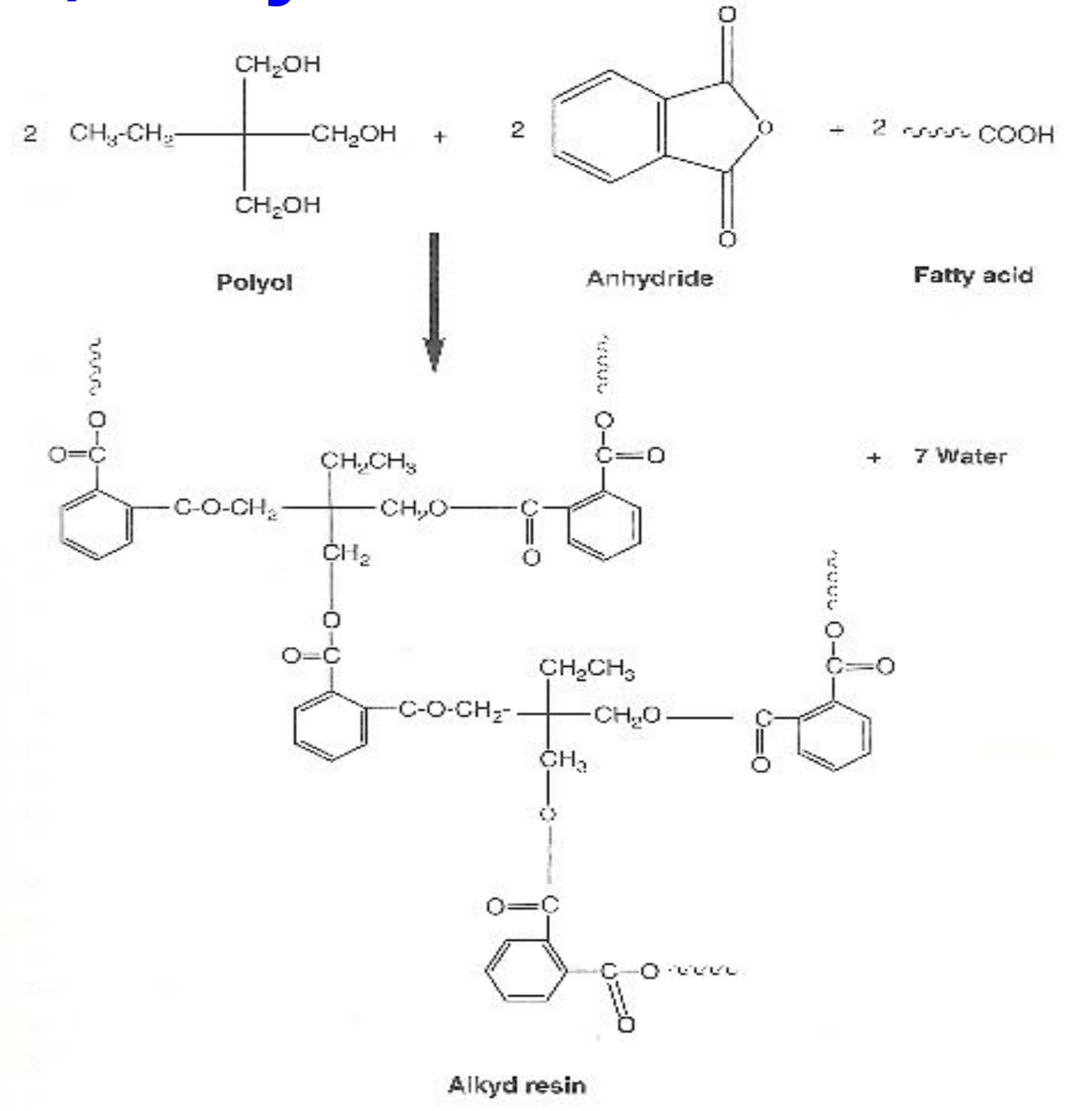
Alkyd coatings use resin formed by the reaction of polyhydric alcohols (glycerin) and polybasic acid (phthalic acid) followed by modification with drying oils. These cure much faster than unmodified alkyds..

Silicon alkyd coatings were developed by modifying alkyd resin with silicon (30%) to provide greater gloss retention.

Epoxy ester coatings are another modification of drying oils to improve performance, particularly chemical resistance.

Uralkyd coatings are formed with polyurethane. These coatings are hard.

Formation of an Alkydresin from alcohol, fatty acid and a dibasic acid

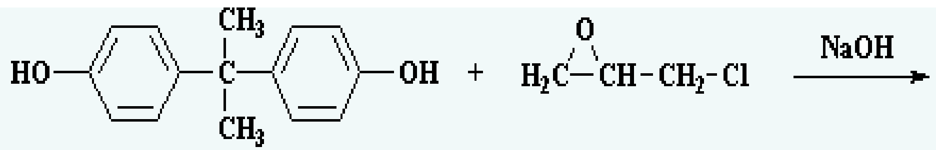


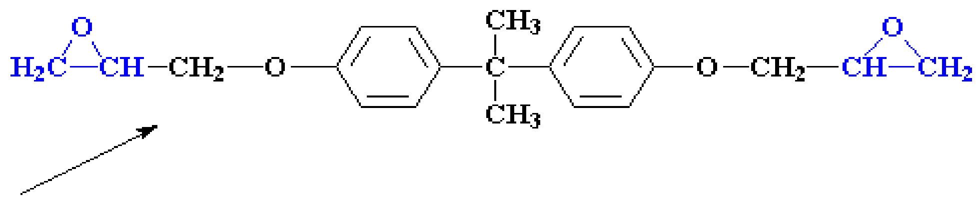
Epoxy Coatings

- The Most Common two component thermosetting product.
- An epoxy resin is based on a reaction product of phenols, commonly bisphenol F or Cresol with epichloridehydrin.
- Available in solvent free, with solvent or water containing formulations.
- The two components are called base and the curing agent. Latter is used to polymerise the epoxy resin which has major influence on the mechanical and chemical resistance properties. The most common curing agents are aliphatic amines, ketamines and polyamides.
- Epoxy coatings bond well to the abrasive cleaned steel and clean concrete.Their films are hard and relatively inflexible. They chalk in sunlight.

We make the prepolymer using bisphenol A and epichlorohydrin

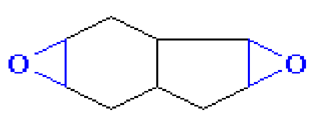
Bisphenol A   Epichlorohydrin

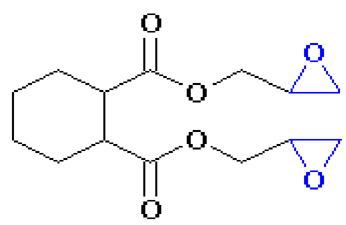




Diepoxy molecule

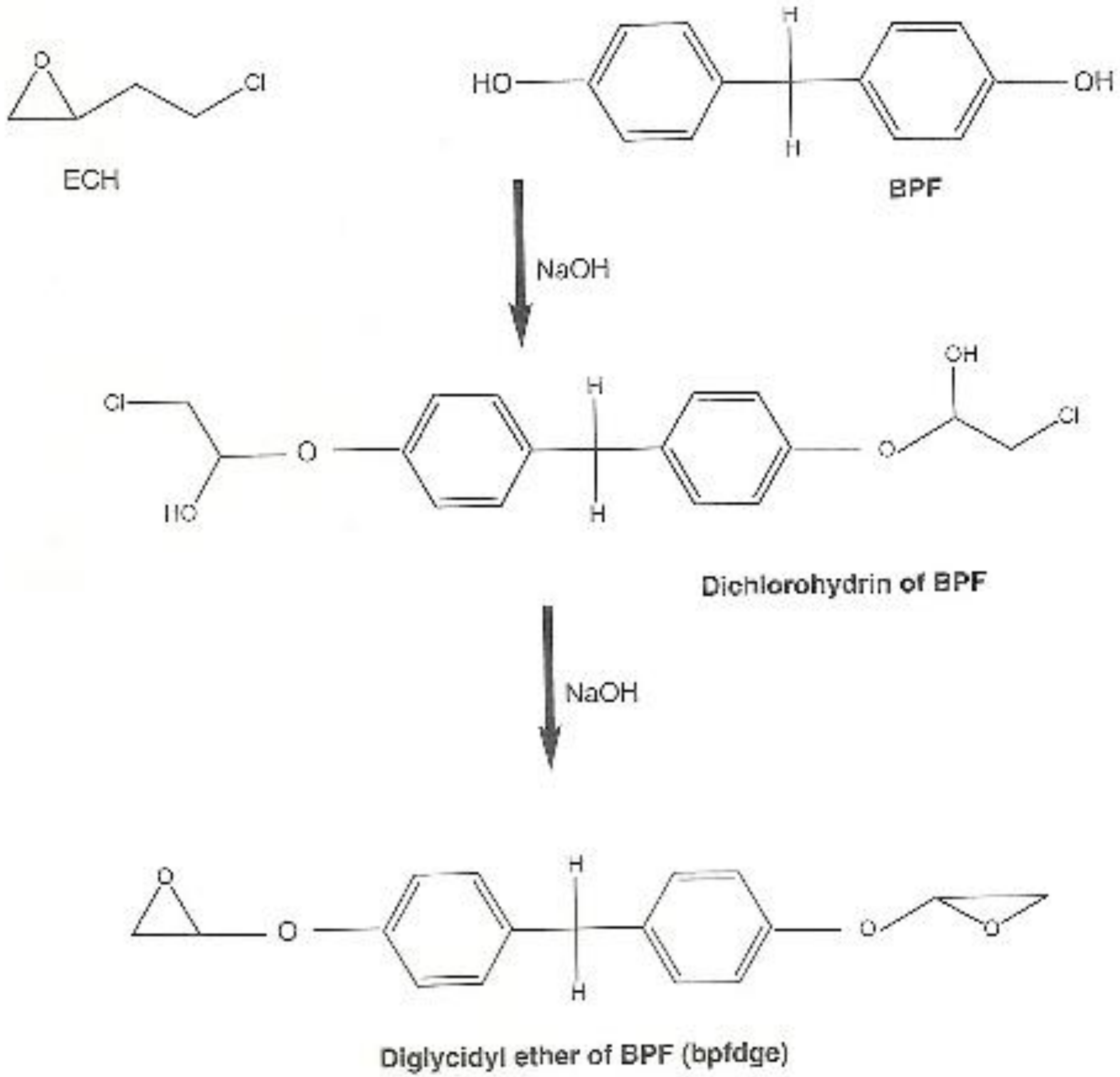
This is a small molecule diepoxy. You can think of it as the polymer shown above with a degree of polymerization of one. Some other diepoxy small molecules are shown below.



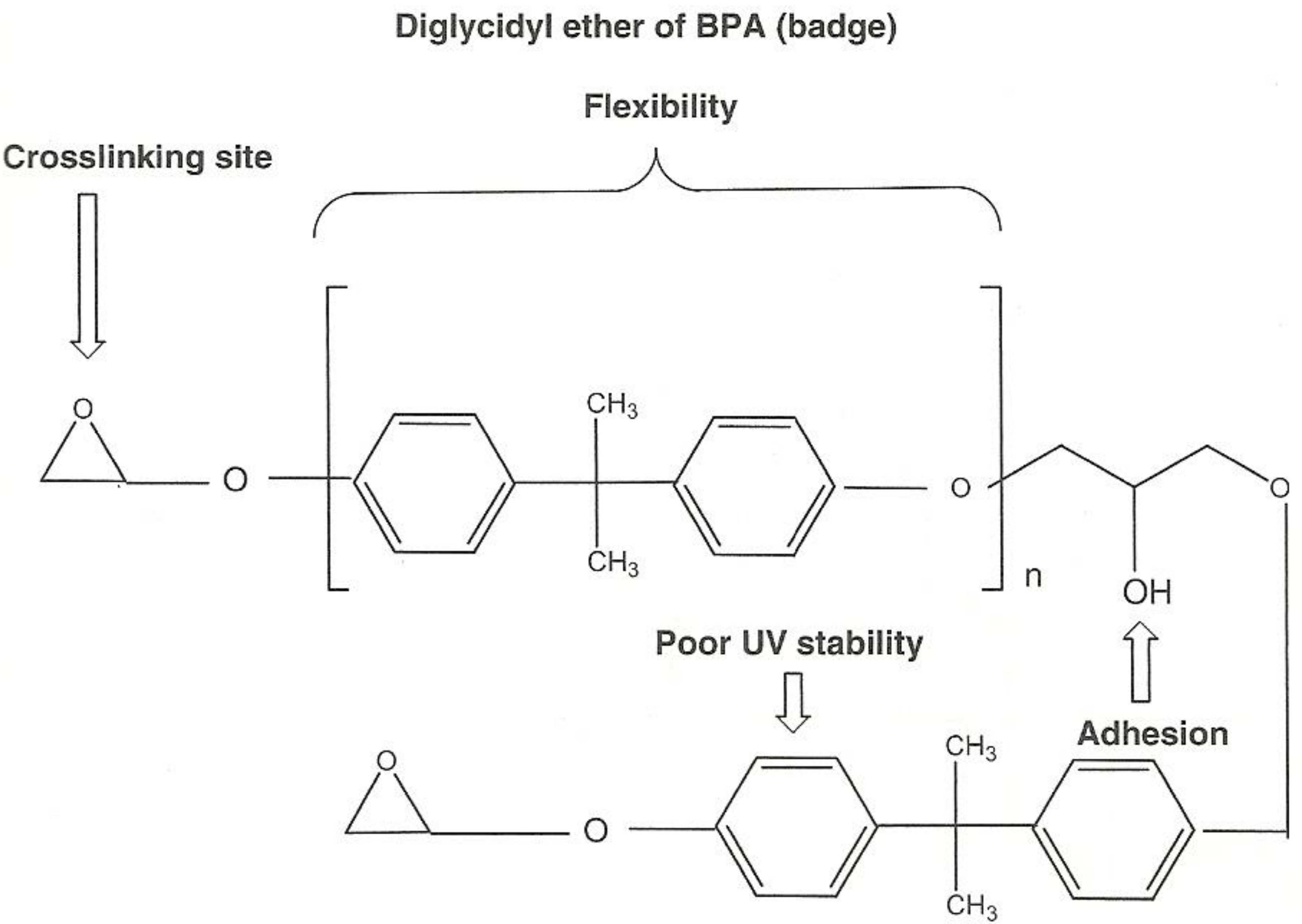


Epoxy Coatings

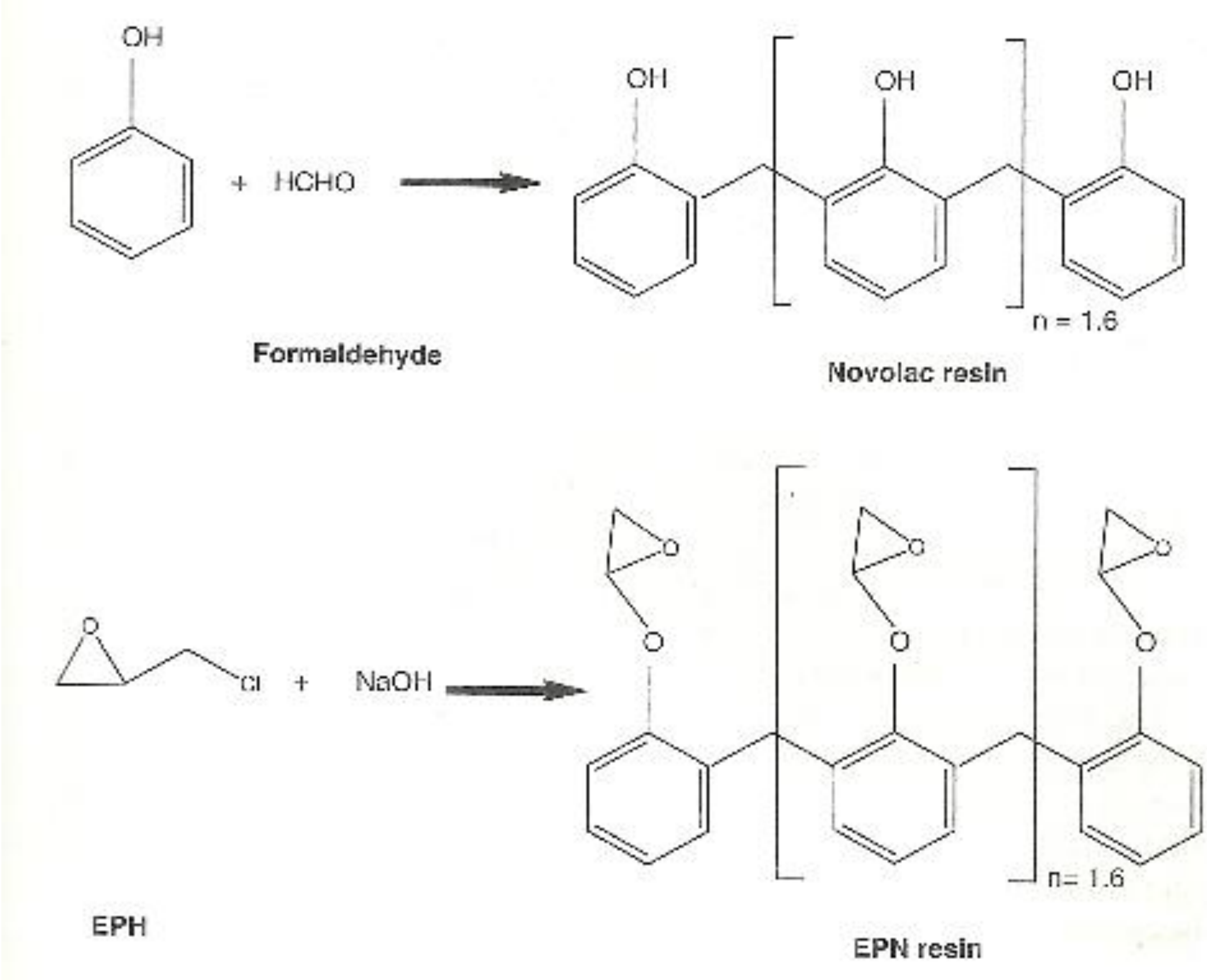
Epoxy Coatings



Epoxy Coatings



Epoxy Coatings



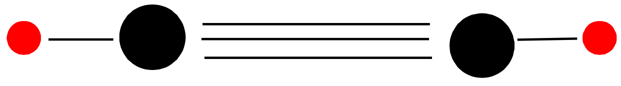
Formation of resin, which has three epoxide groups per monomer

Coil Coating Selection Criteria

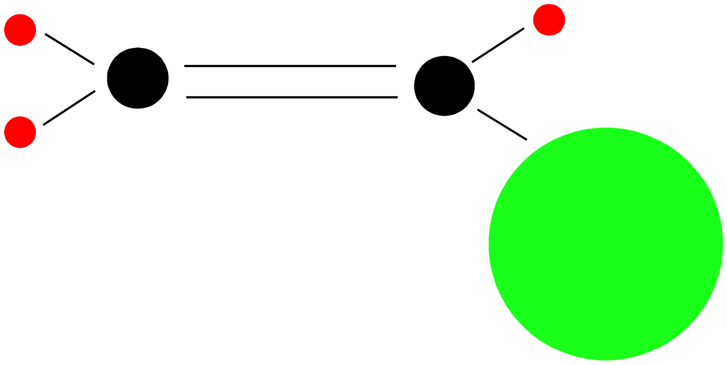
- Colour
- Cost
- Performance vs specification
  - Application technique
  - Drying/Cure
  - Adhesion
  - Mechanical properties – Impact resistance, formability, abrasion resistance
  - Corrosion resistance
  - Durability

PVC Plastisol – The monomers
Coil coating

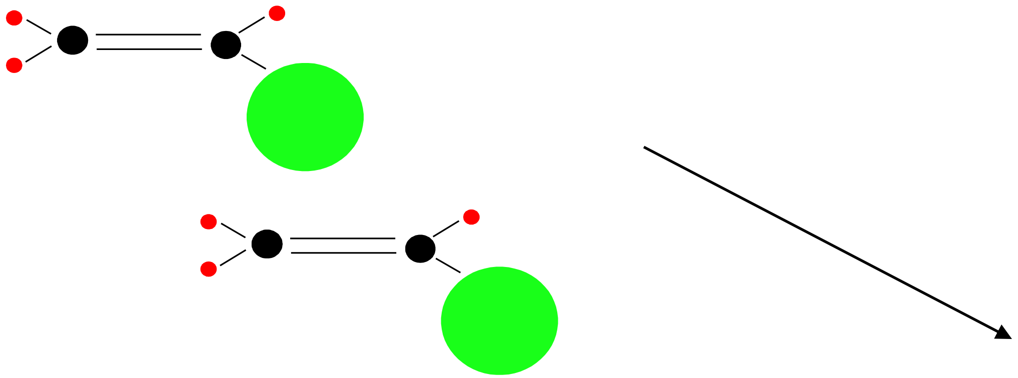
Acetylene



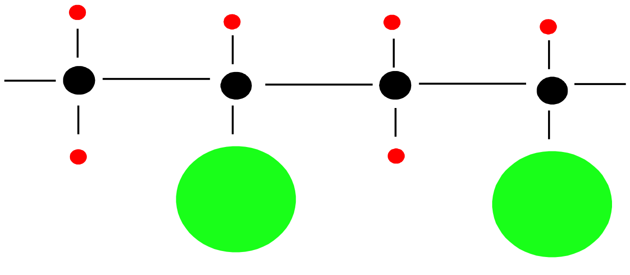
Vinyl Chloride



Polymerisation Process



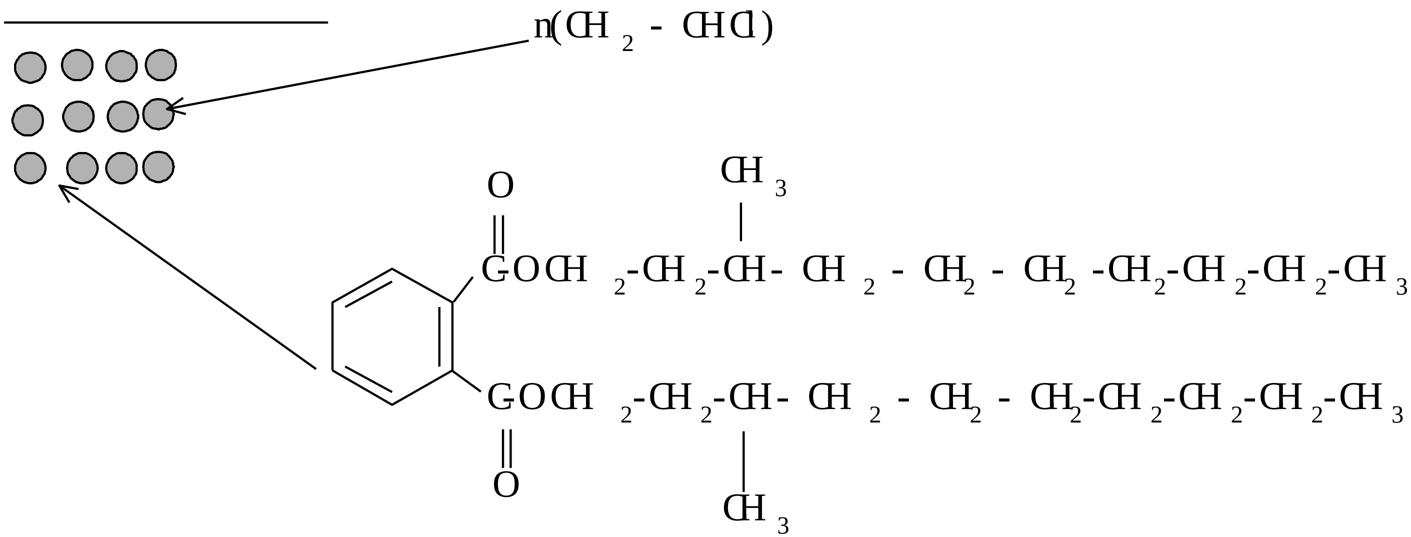
Polyvinyl Chloride



PVC Plastisol

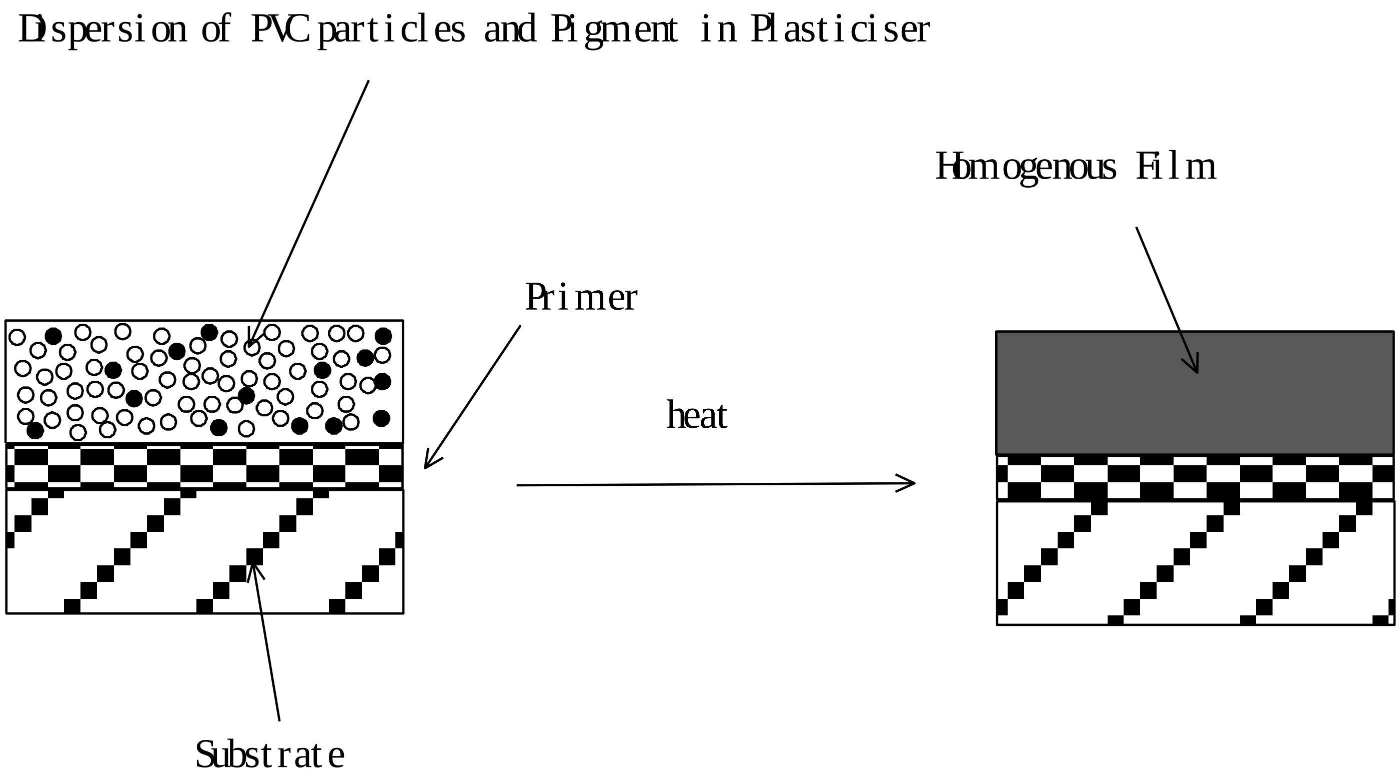
- Dispersion of PVC and Pigment Particles in a Plasticiser
- Liquid at Room Temperature
- PVC Soluble at Elevated Temperatures
- Cooling Results in Continuous Film

PVC Plastisol



DI ISODECYL PHTHALATE

PVC Plastisol



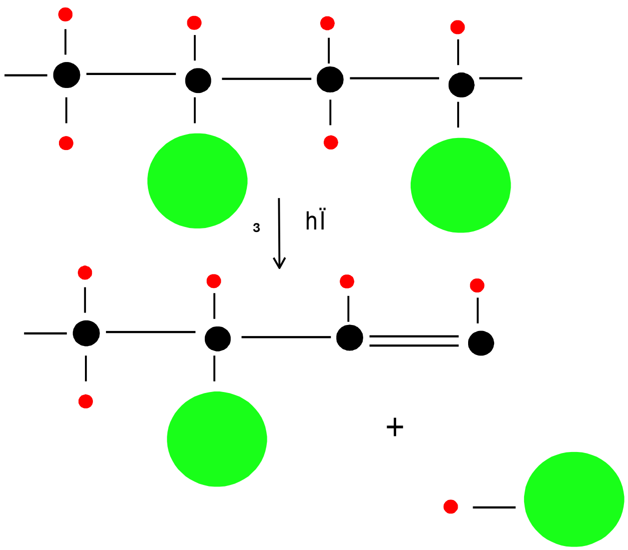
Properties of PVC Plastisol

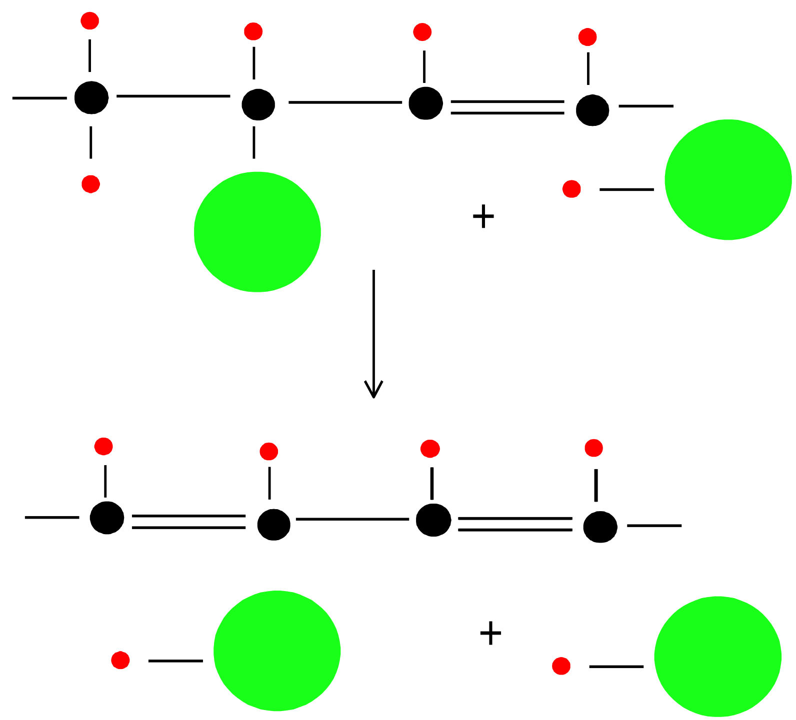
- Coil coating product
- Excellent mechanical properties
- Excellent corrosion resistance due to high film build
- Good durability
- **Main Application : Exterior facades and roofing of commercial and domestic buildings**

The Problem is….

- PVC is **not thermally stable**
  - The C-Cl bond breaks easily
- Plasticisers help stability but the system is heated strongly on the coil coating line
  - Heat stabilisers are necessary
- **Lead salts** were used in the first place but these are avoided by most people these days
  - **Di-butyl tin di-laurates** are common as are barium zinc soaps
- Basic fillers and small amounts of epoxy compounds are also common

Dehydrochlorination – Prince of Darkness





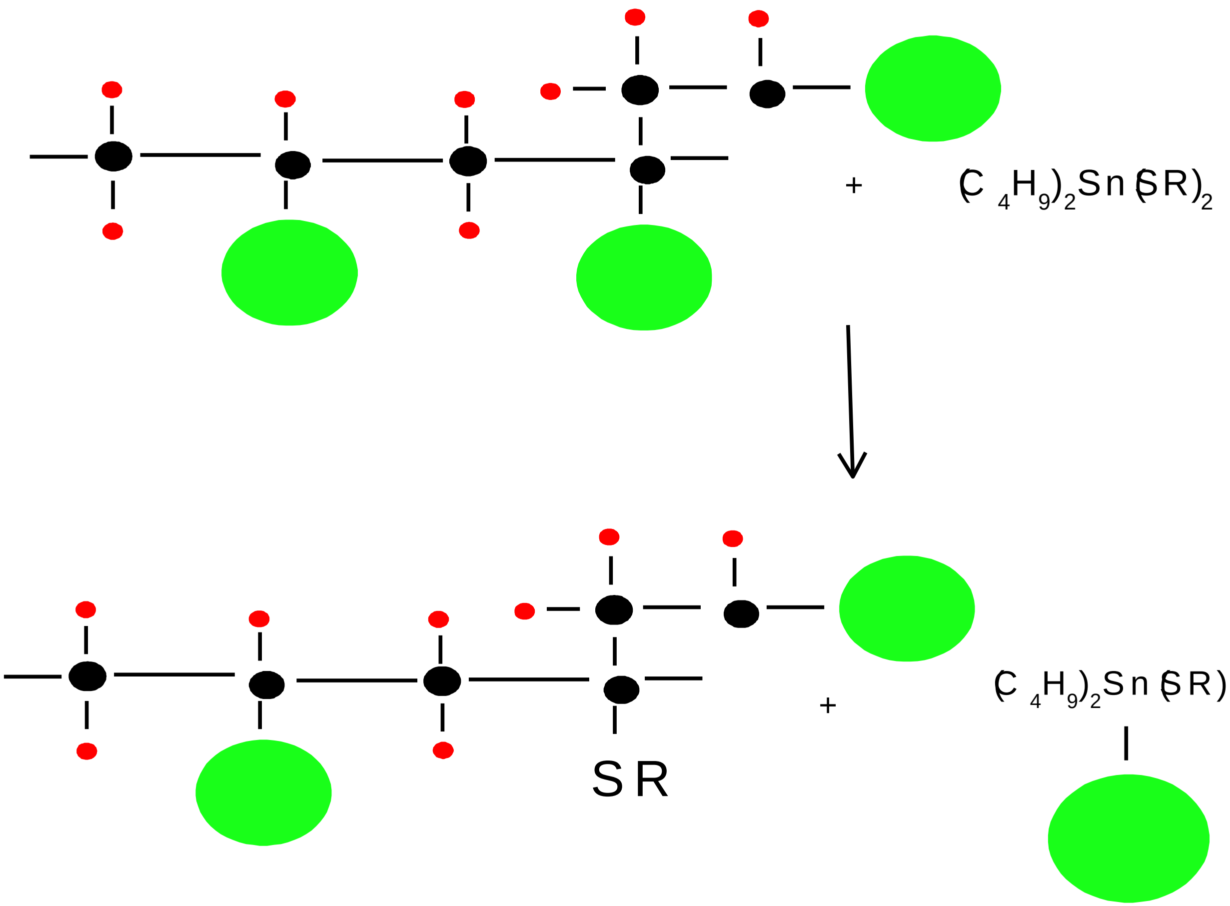
Lead led the Way to Stability

- Stabilisation requires
  - Rapid binding with HCl
  - An ability to replace labile chlorine atoms
  - Antioxidant action
  - Disruption of chromophoric groups
  - Inactivity of reaction products
- Lead compounds are good at this, particularly
  - Tribasic lead sulphate
  - Tetrabasic lead sulphate
  - Dibasic lead phosphite
  - Lead stearate

Opacity, Staining and Toxicity

- Many lead salts are opacifying and so can not be used in transparent applications
- Sulphide staining is a particular problem
- Toxicity of lead salts has precluded their use for a long time

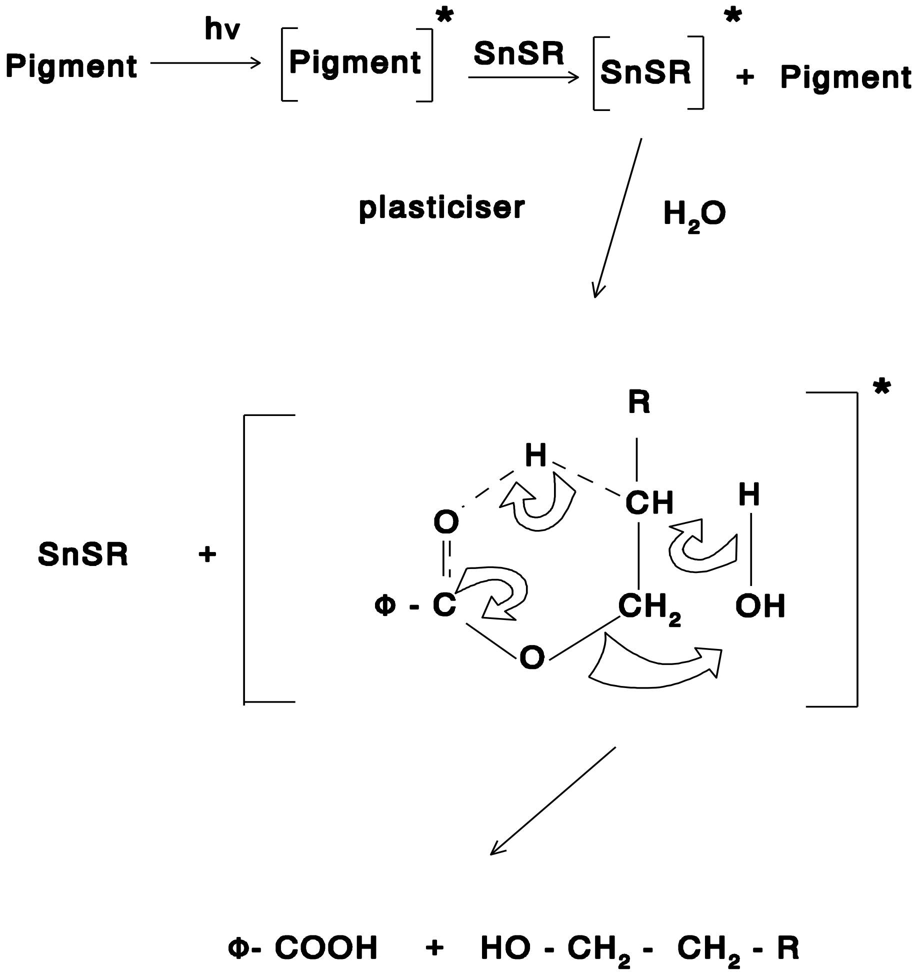
Di-butyl tin di-laurates to the Rescue



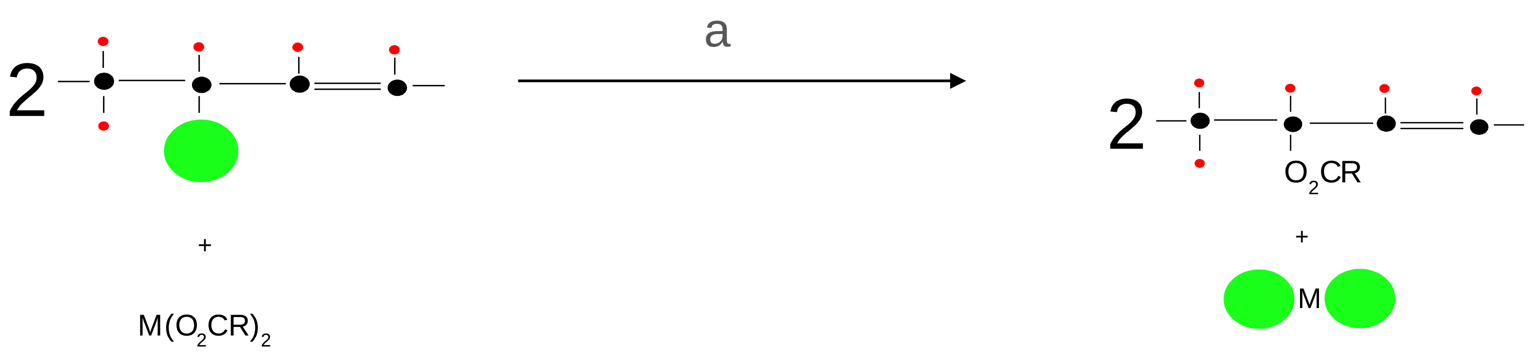
Tin can be a problem too!

- Some colours containing red pigments have poor durability if tin stabilisers are used
- **The degradation of tin containing plastisols must involve:**
  - the absorption of light by the pigment
  - the transfer of the energy to the tin mercaptide
  - the formation of an excited state between the tin mercaptide and either water or the plasticiser
  - the hydrolysis of the ester linkage

The Tin terminator



Soaps Clean Up!



b

$$ZnCl_2 + Ba(O_2CR)_2 \longrightarrow Zn\,(O_2CR)_2 + Ba\,Cl_2$$

If M = Zn a is rapid but $ZnCl_2$ encourages dehydrochlorination

If M = Cd a is again rapid but $CdCl_2$ also encourages dehydrochlorination but less rapidly

If M = Ba or Ca first reaction a is slow but reaction b is fast

$BaCl_2$ and $CaCl_2$ are unreactive towards dehydrochlorination

But Undesirable Reactions Occur!

- The degradation of BaZn containing plastisols must involve:
  - oxidation of PVC
  - radical attack on aliphatic backbone at active site
  - cleavage of backbone to produce lower molecular weight phthalate homologue

General Comments

- PVC has a greater tendency to oxidise than de-hydrochlorinate under aerobic conditions
- Tin stabilised systems are more likely to delaminate
- Reds and browns are more prone to degradation because the pigments involved absorb blue light
- TiO_2 strongly absorbs UV light which may account for the sensitivity of whites

PVDF

- Suspension of Particles of Polyvinyldifluoride and pigment

$$(-CH_2 - CF_2-)_n$$

- Solution of acrylic resin in Isophorone
- Dissolution of PVdF occurs at elevated temperature
- Solvent evaporates leaving an inter-penetrating network

PVDF

- Highly durable coating system
- Low film weight - limited corrosion resistance
- Limited colour range due to need for opacifying pigmentation
- Facades and roofing of buildings requiring excellent weather resistance

Chemistry of Polyesters

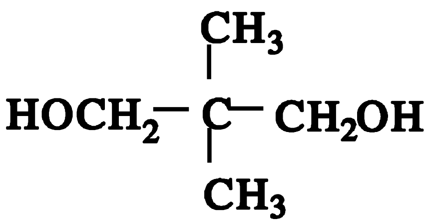
Esterification Reactions

$$R'-COOH + R-OH \xrightarrow[\text{or } OH^{-}]{H^{+}} R'-\overset{O}{\overset{||}{C}}-O-R + H_2O$$

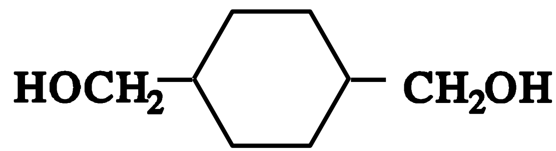
$$HOO-C-R'-COOH + HO-R-OH \longrightarrow HOOC-R'-\overset{O}{\overset{||}{C}}-O-R-OH + H_2O$$

Chemistry of Polyesters

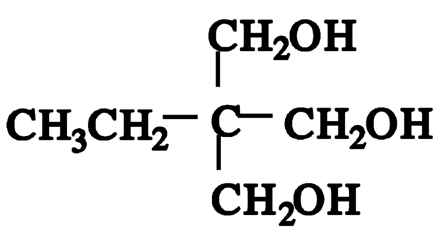
COMMON POLYOLS



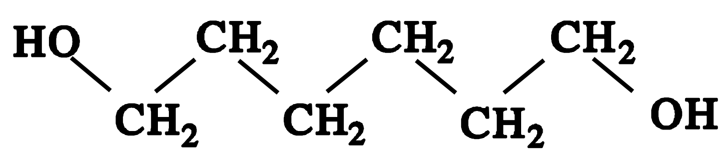
Neopentyl glycol (NPG)



Cyclohexanedimethanol (CHDM)



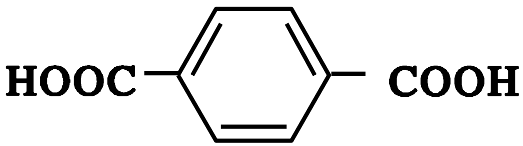
Trimethylolpropane (TMP)



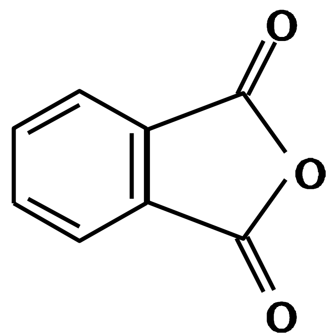
1,6 Hexanediol (HD)

Chemistry of Polyesters

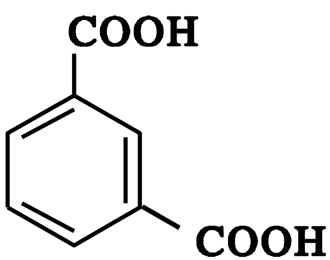
AROMATIC ACIDS and ANHYDRIDES



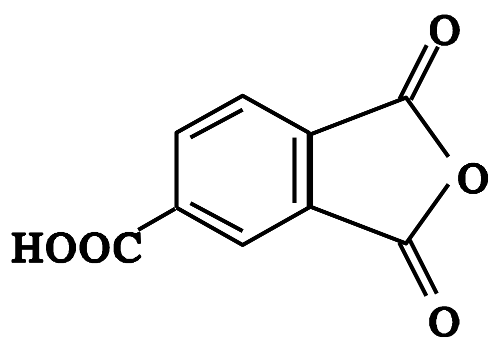
Terephthalic Acid (TA)



Orthophthalic Anhydride (PA)



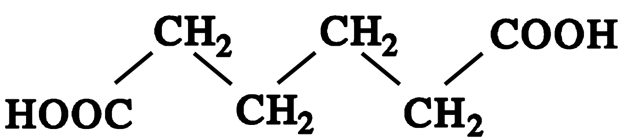
Isophthalic Acid (IA)



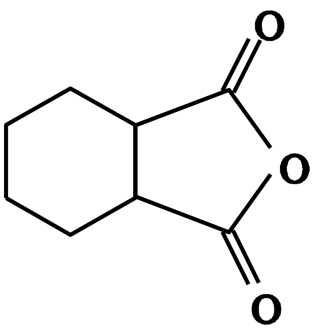
Trimellitic Anhydride (TM

Chemistry of Polyesters

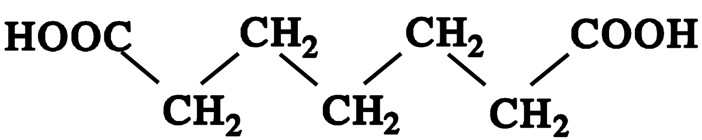
ALIPHATIC ACIDS



Adipic acid (AA)



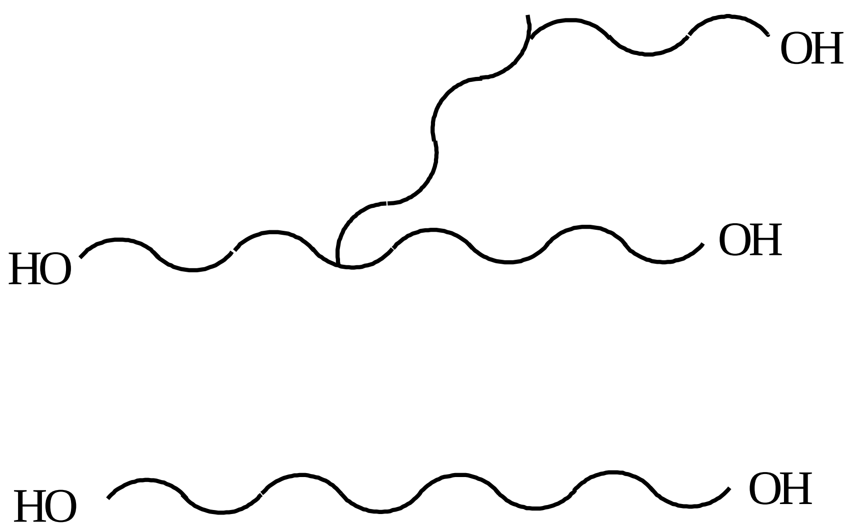
Hexahydrophthalic anhydride (HHPA)



Azelaic acid (AZA)

Chemistry of Polyesters

Idealised Structure of a Polyester



Chemistry of Polyesters

Parameters of Coil Coating Polyesters

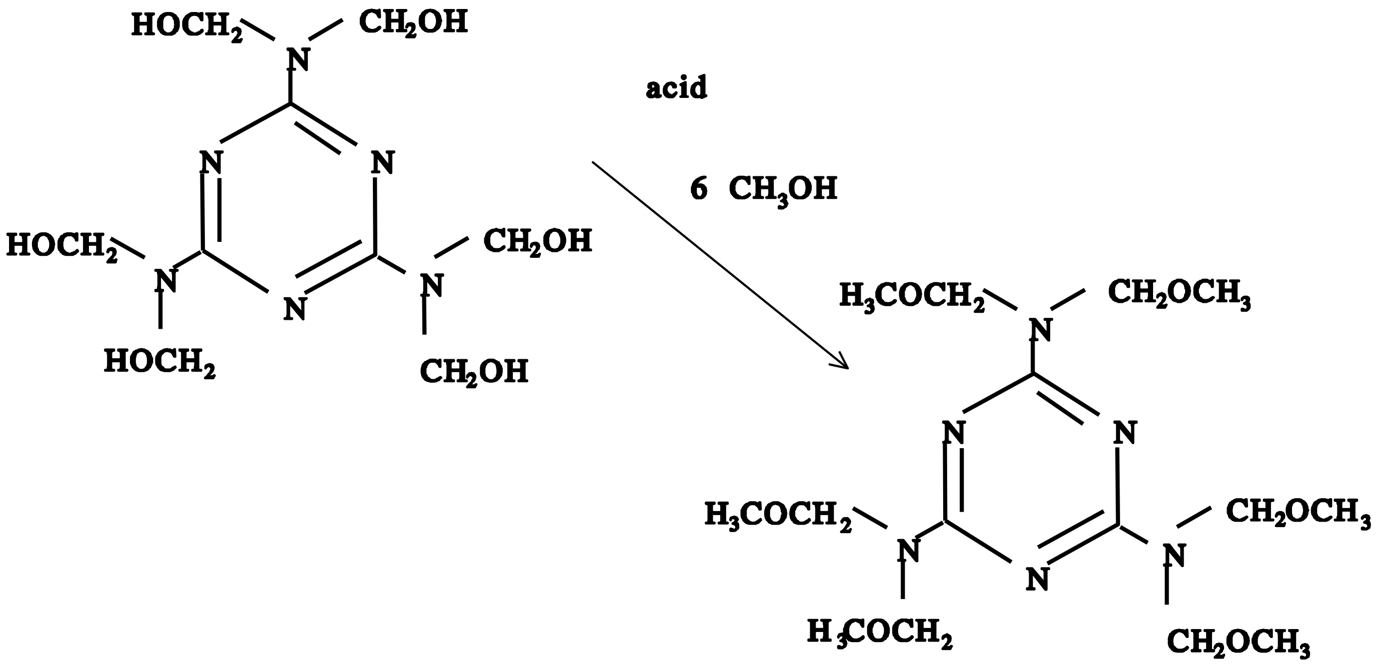
Parameter	Control	Consequence
Tg	Monomers Backbone	High Tg High Aromatic Good Moisture Resistance Low Tg High Aliphatic Good Flexibility
Molecular Weight	Processing	Mechanical Properties
OH Content	Monomers(amount of TMP) Molecular Weight	Crosslink Density

Most Primer Resins are high Tg, high mol wgt(>15000), low hydoxyl value(5-10)

Most Topcoat Resins have Tg around ambient, modest mol wgt(3500-5000), modest hydroxyl value(35-50)

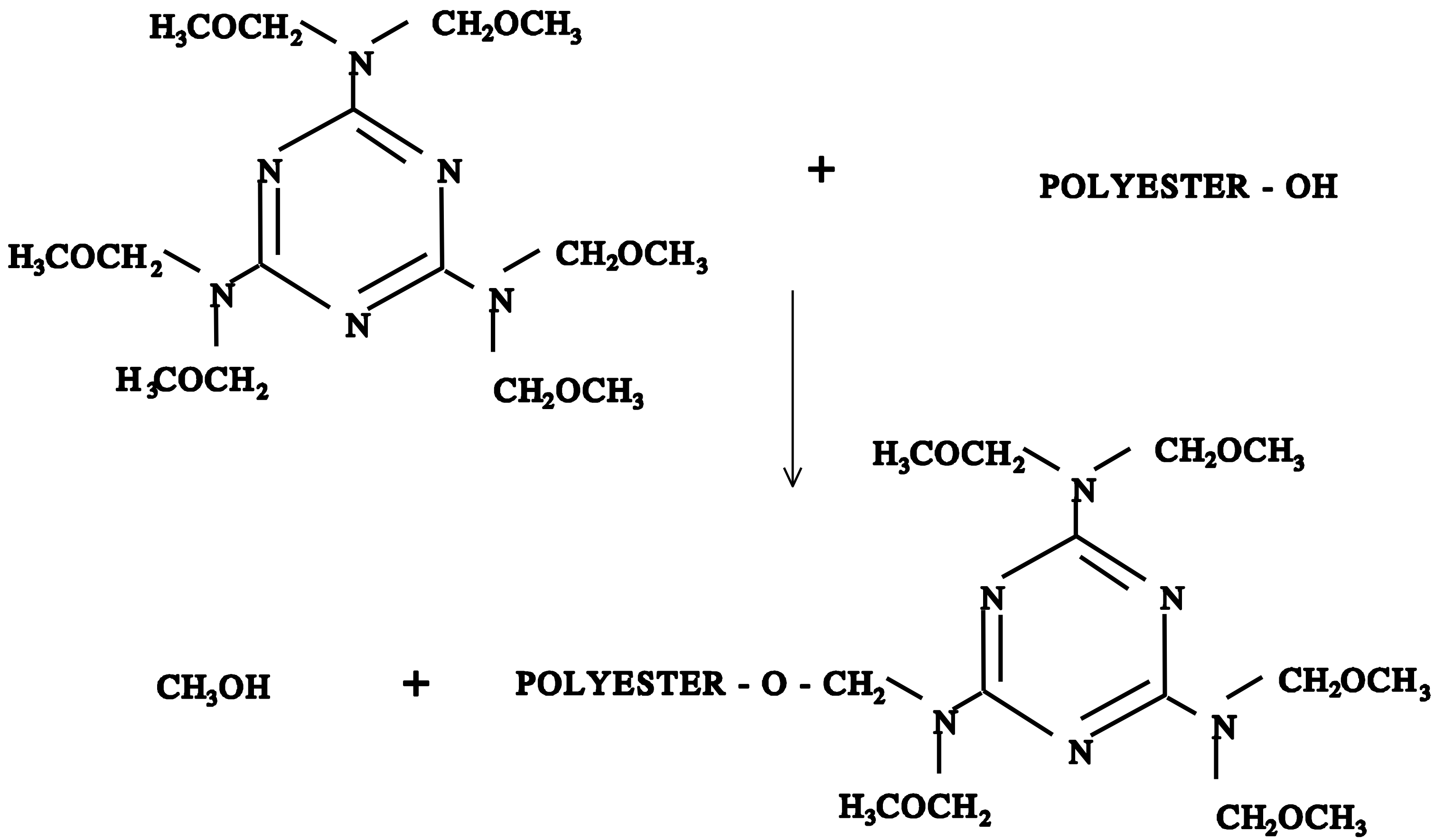
Chemistry of Polyesters

PREPARATION OF MELAMINE-FORMALDEHYDE RESINS

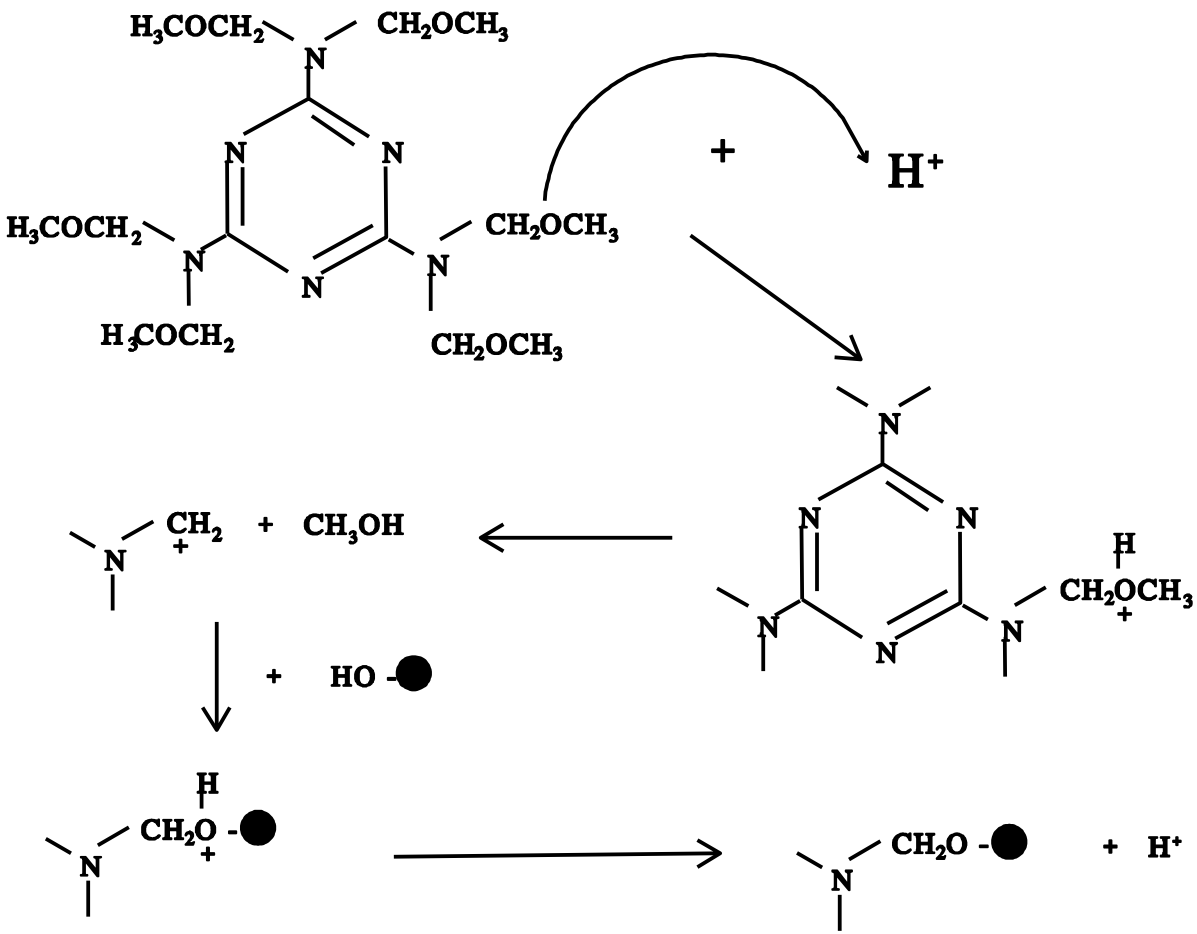


Chemistry of Polyesters

TRANSETHERIFICATION CURE REACTION

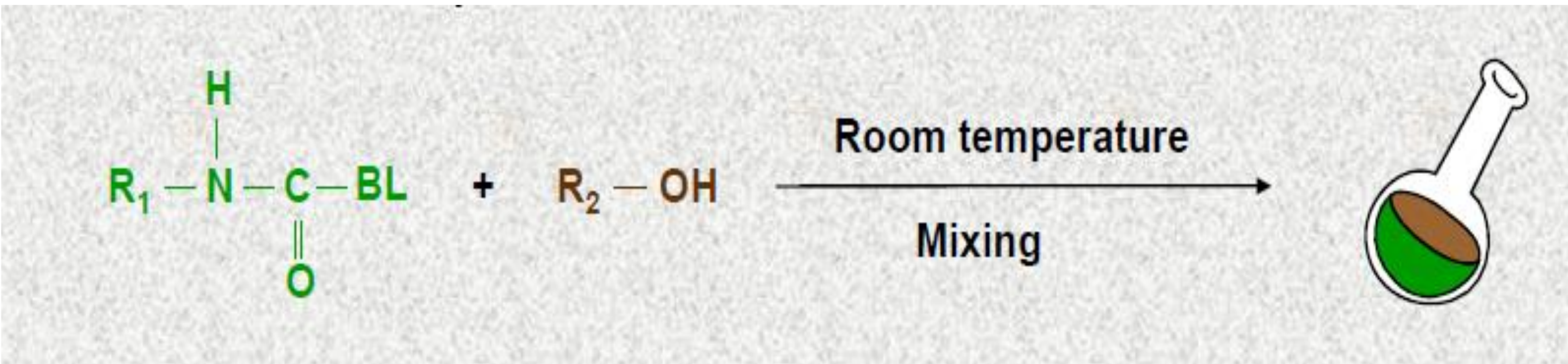


Chemistry of Polyesters Mechanism

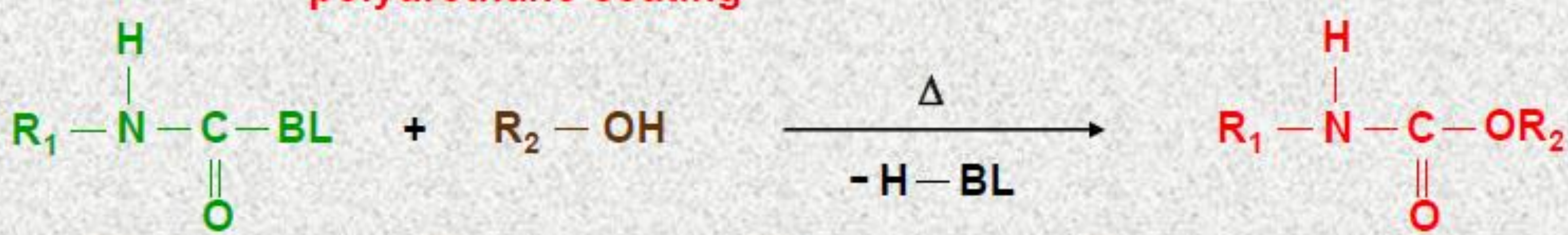


Chemistry of Polyurethanes

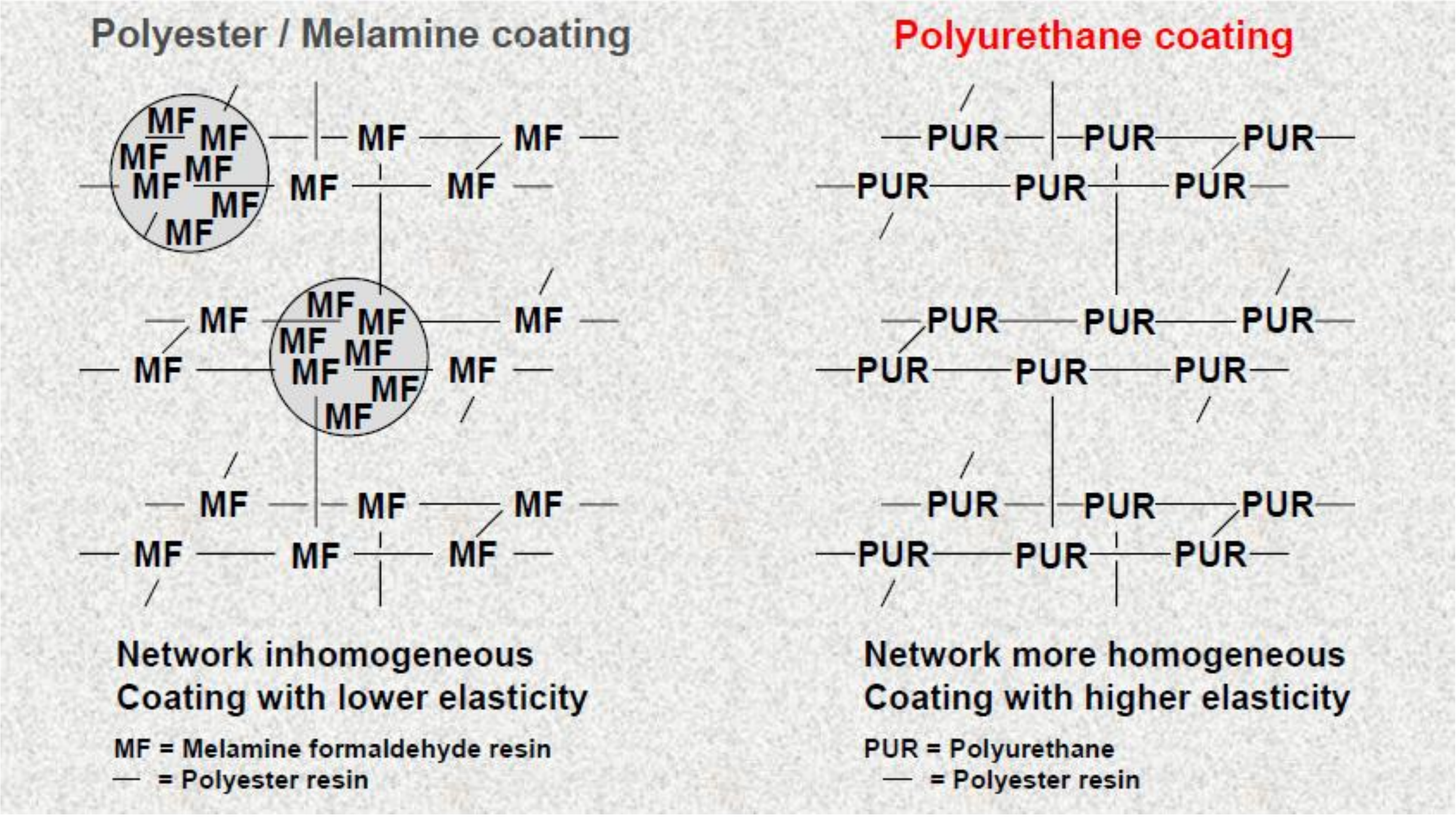
Chemical: OH functional polymer (Polyol) and blocked Isocyanates are mixed at RT



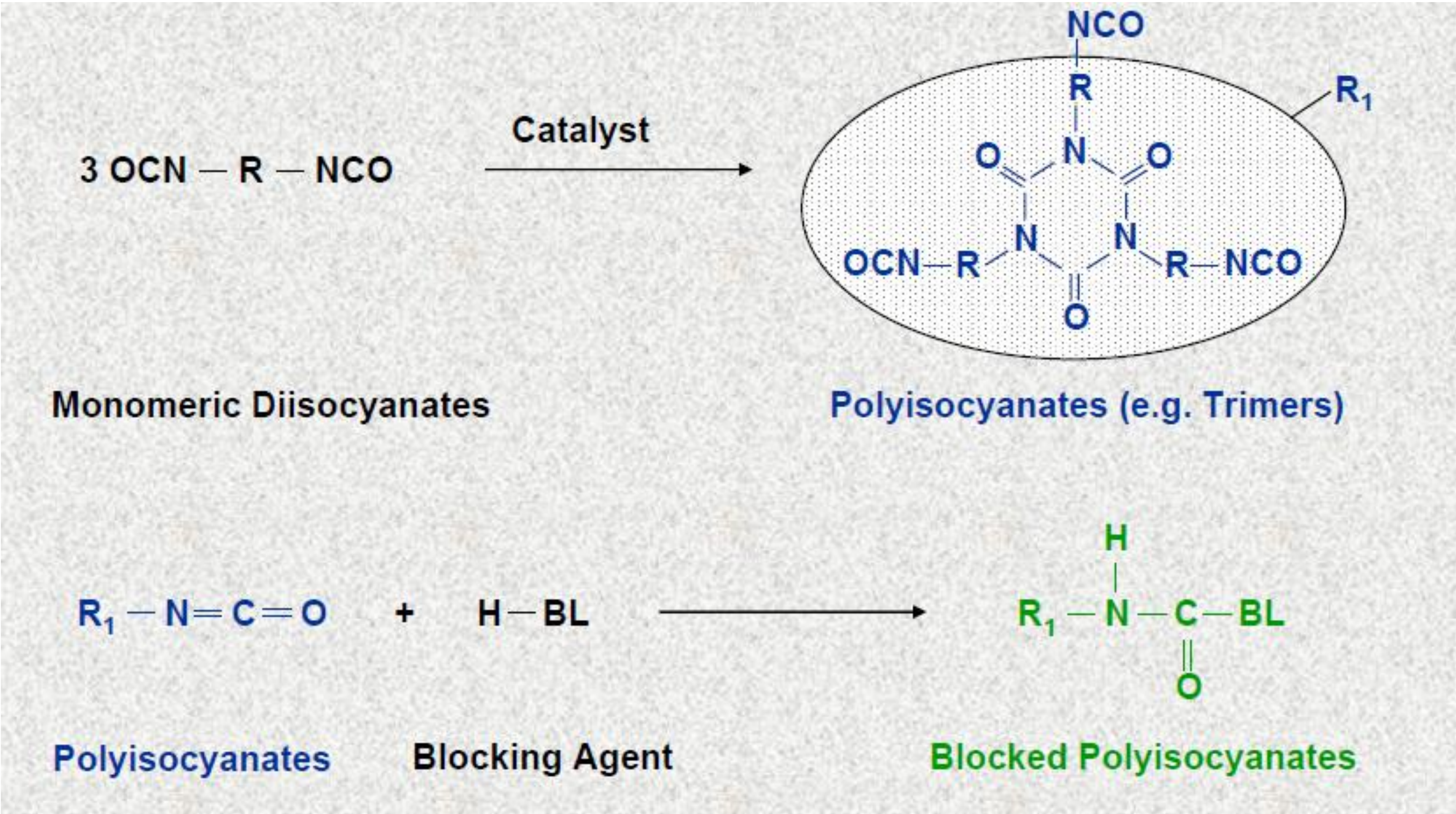
Stoving process: During the stoving process the blocking agent (H-BL) splits of under formation of a a high molecular weight polyurethane coating



Ideal 1K PU network



Blocked Polyisocyanate



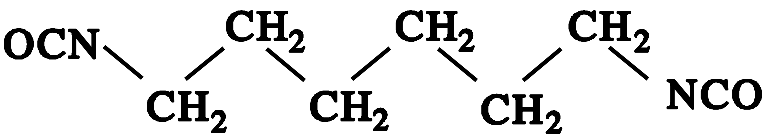
Blocked Polyisocyanate
Relationship Structure & Properties

Typical properties of blocked polyisocyanates (e.g. trimers) depend on:

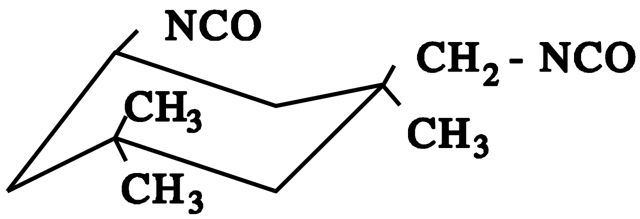
- Type of monomeric diisocyanate
  - → Influence on flexibility
  - → Influence on viscosity
  - → Influence on chemical resistance
- Type of blocking agent
  - → Influence on reactivity (depending on deblocking temperature)
  - → Additional influence of catalyst on deblocking temperature (e.g. DBTL)

Chemistry of Polyurethanes

ISOCYANATES AVAILABLE FOR COIL COATINGS



HEXAMETHYLENE DI-ISOCYANATE

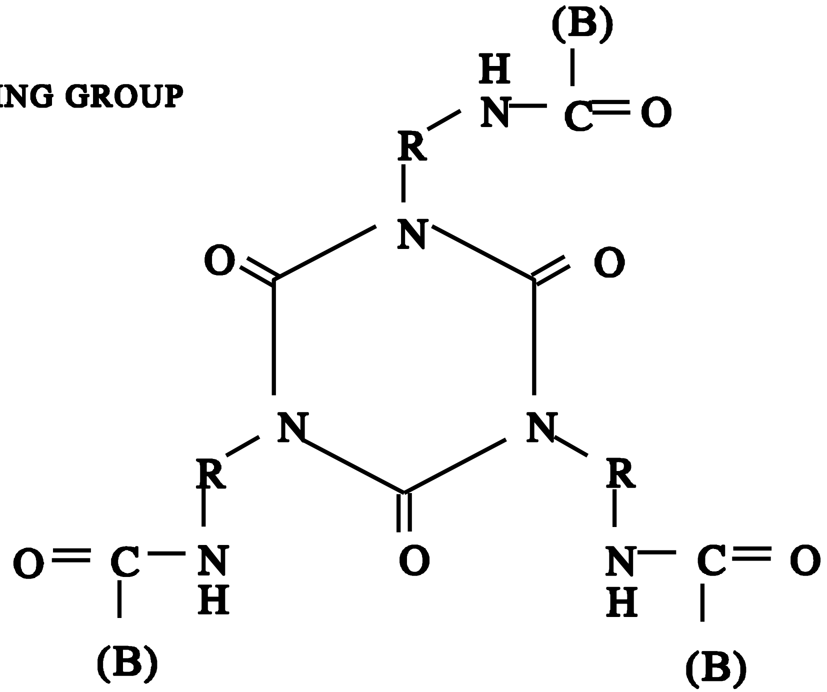


ISOPHORONE DI-ISOCYANATE

Chemistry of Polyurethanes

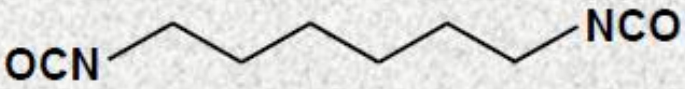
STRUCTURE OF A TRIS ISOCYANURATE

B = BLOCKING GROUP

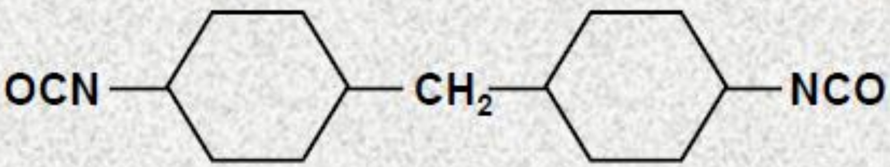


R = ISOPHORONE or HEXAMETHYLENE

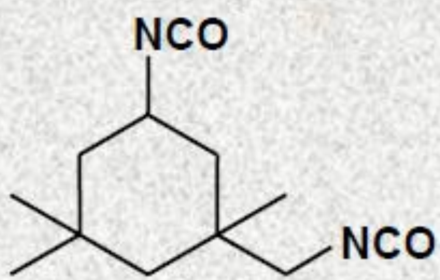
Important Aliphatic Diisocyanates



Hexamethylene diisocyanate (HDI)



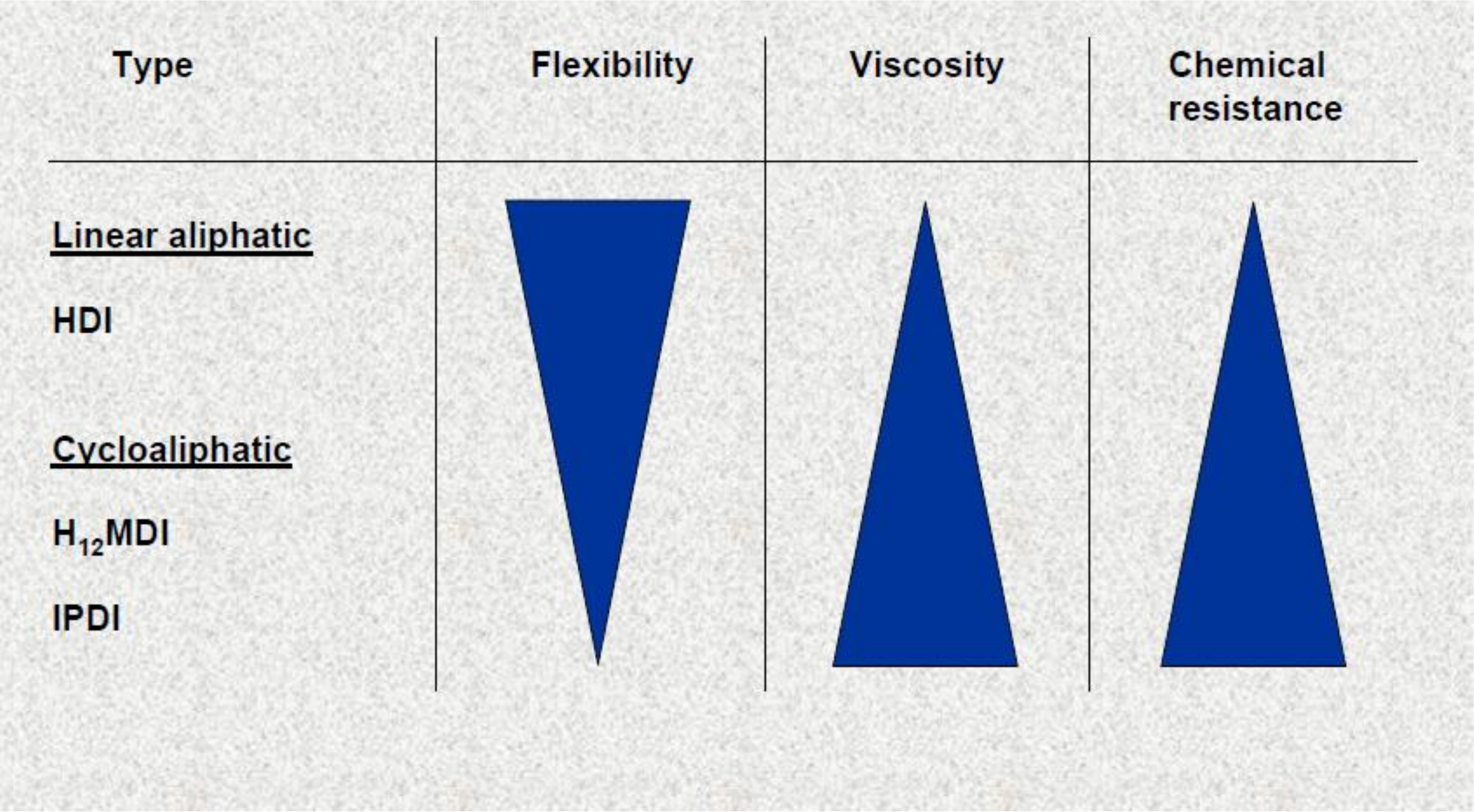
Bis-(4-isocyanatocyclohexyl)methane ($H_{12}MDI$)



Isophorone diisocyanate (IPDI)

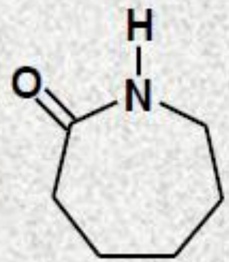
(3-Isocyanatomethyl-3,5,5-trimethylcycloxexylisocyanate)

Important monomeric Diisocyanates

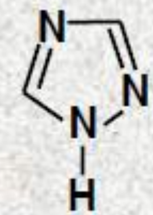


Important Blocking agents

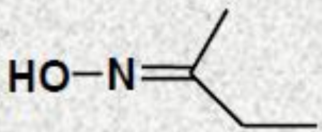
ε-Caprolactam
(ε-CAP)



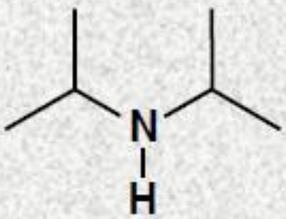
1,2,4-Triazole
(TRIA)



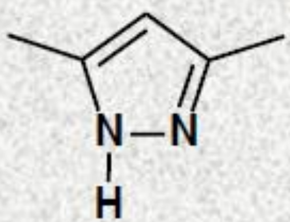
Methyl ethyl ketoxime
(MEKO)



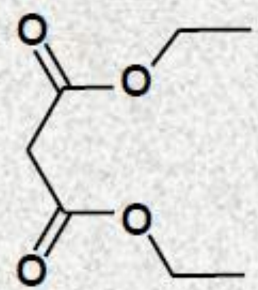
Diisopropylamine
(DIPA)



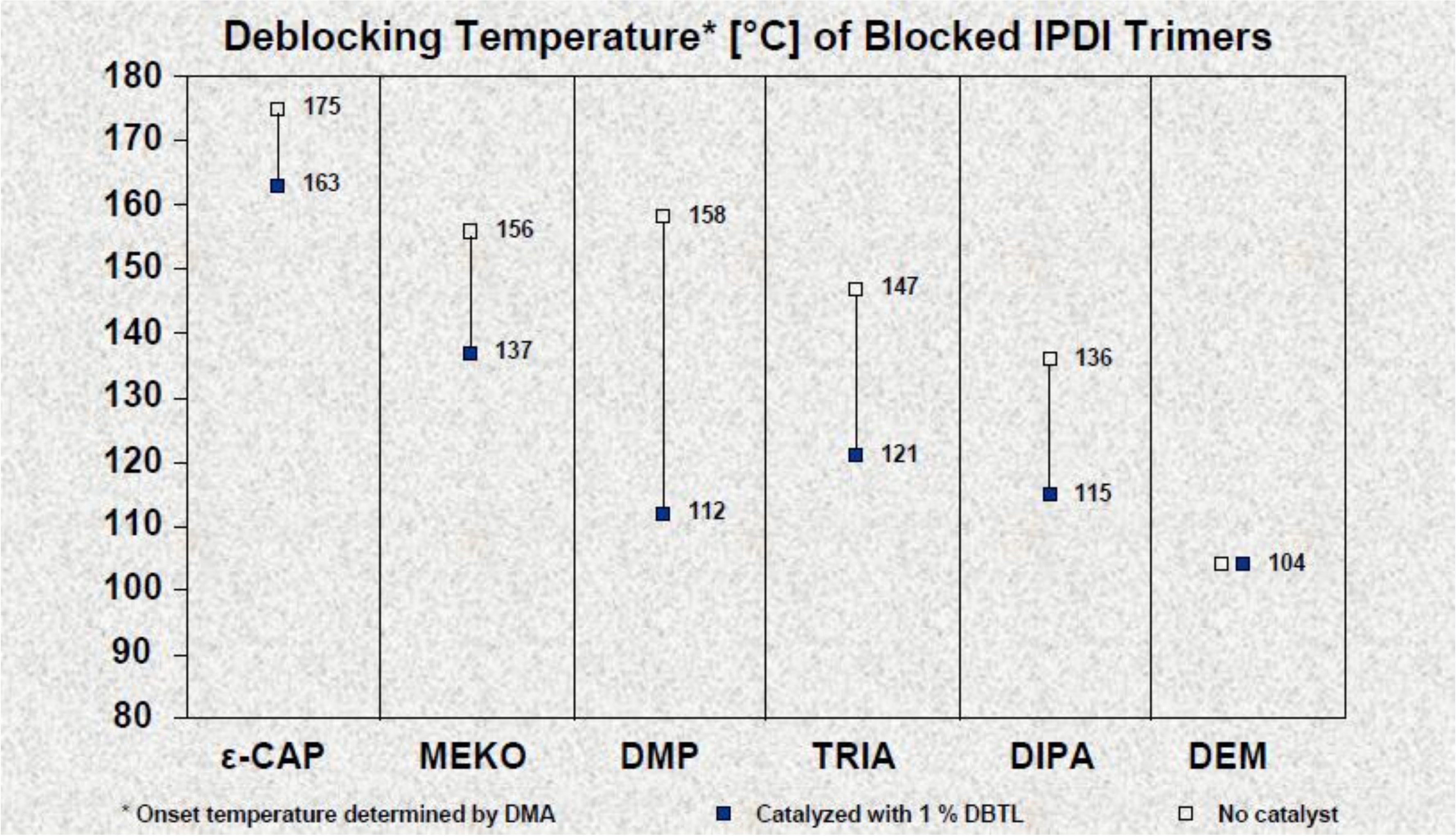
3,5-Dimethylpyrazole
(DMP)



Diethyl malonate
(DEM)



Influence of Blocking agents



Chemistry of Polyurethanes
Durability

HYDROLYSIS OF MELAMINE CROSSLINK

$$>N - CH_2 - 0 - R \; + \; H_2O \longrightarrow >N - CH_2 - 0H \; + \; HOR$$

ELSEVIER

Progress in Organic Coatings 43 (2001) 131–140

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Multistep chemistry in thin films; the challenges of blocked isocyanates

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Received 11 September 2000; received in revised form 18 April 2001; accepted 2 May 2001

Solvents

- Nearly half of the organic solvents sold are consumed by the paint industry
- Dissolve/dilute resin
- Control/substrate wetting
- Adjust viscosity to suit application method
- Aid coalescence of polymeric particles in waterbased systems

Solvents - Categories

Hydrocarbons: Aliphatic, Aromatic

Oxygenated: Alcohols, Ketones, Esters, Glycol Ethers, Ethers

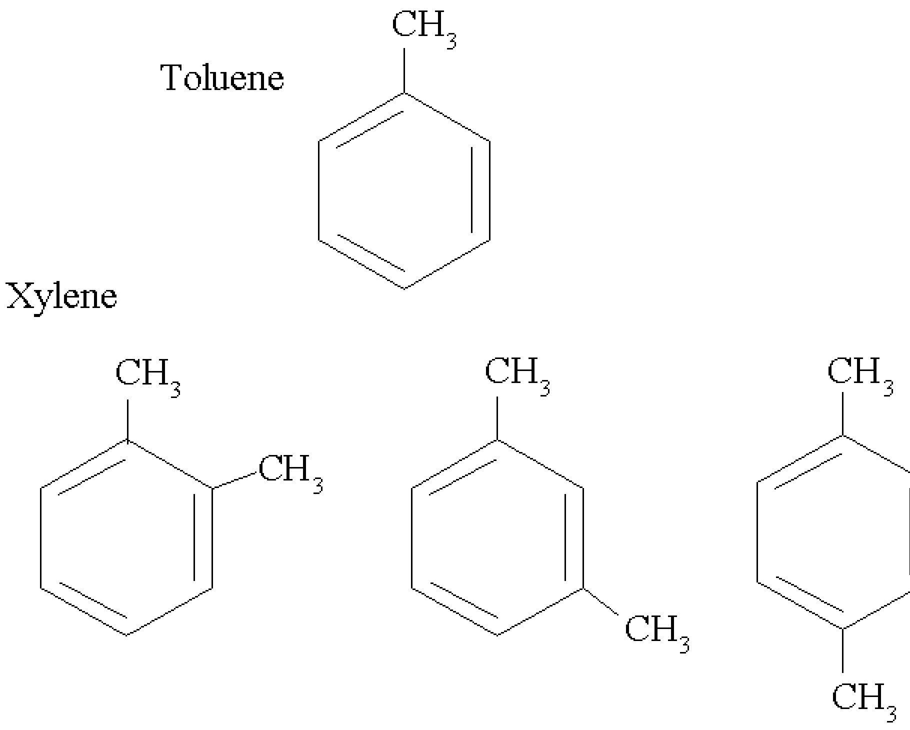
Fast, Slow, Low Flash, High Flash

Aliphatic Hydrocarbon Solvents

- Octane: Linear
- Iso-octane: Branched
- Cyclohexane: Cyclic

Aromatic Hydrocarbon Solvents

Aromatics have higher solvent power than aliphatics but they generally require hazard labels.



Hydrocarbon Blends

	Aromatic Content	Boiling Range	Flash Point
White Spirit	<17	155-195°C	40°C
'Solvesso 100' type	100%	165-180°C	47°C
'Solvesso 150' type	100%	190-210°C	65°C

Ketone Solvents

Solvent	Structure	Boiling Point	Flash Point
Acetone	CH_3 CO CH_3	56	-6
Methyl Ethyl Ketone	CH_3 CH_2 CO CH_3	80	-4
Methyl Isobutyl Ketone	$(CH_3)_2$ CH CH_2 CO CH_3	117	13
Cyclohexanone		157	44
Isophorone		215	88
Diacetone alcohol	HO $C(CH_3)_2$ CH_2 $COCH_3$	168	49

- Ketones are strong solvents, Isophorone is restricted by air pollution regulations.

Alcohol Solvents

Solvent	Structure	Boiling Point	Flash Point
Methanol	$CH_3\ OH$	65	10
Ethanol	$CH_3\ CH_2\ OH$	78	12
n-Propanol	$CH_3\ CH_2\ CH_2\ OH$	97	23
Iso Propanol	$CH_3\ CH\ OH\ CH_3$	82	12
n-Butanol	$CH_3\ CH_2\ CH_2\ CH_2$ -OH	118	36
Iso Butanol	$(CH_3)_2\ CH\ CH_2\ OH$	108	30

- **Methanol is toxic**
- **Not suitable for isocyanates**

Ester Solvents

Solvent	**Structure**	**Boiling Point**	**Flash Point**
Ethyl Acetate	$CH_3\ COO\ CH_2\ CH_3$	77	-5
n-Butyl Acetate	$CH_3\ COO\ (CH_2)_3\ CH_3$	126	28
Dibasic Ester	$CH_3\ OOC\ (CH_2)_n\ COO\ CH_3$	196-212	100
Texanol	$(CH_3)_2\ CH\ COO\ CH_2\ C(CH_3)_2\ CH\ OH\ CH\ (CH_3)_2$	245	120

- **Dibasic Ester is a mixture of n = 2, 3 + 4**
- **Strong odour but strong solvents**

Glycol Ethers

Solvent	Common Name	Structure	BPt	Flsh Pt
Ethylene Glycol Monoethyl Ether	Methyl Cellosolve	CH_3 O $(CH_2)_2$ OH	125	49
Ethylene Glycol Mono Ethyl Ether	Cellosolve	CH_3 CH_2 $O(CH_2)_2$ OH	134-136	6
Propylene Glycol Mono Methyl Ether	Dowanol PM	CH_3 O CH_2 CH (CH_3) OH	120	32

- **Ethyl Ethers restricted due to toxicity,**
- **Glycol Esters have low evaporation rates, can keep film open during cure**

Glycol Ether Esters

Solvent	Common Name	Structure	BPt	Flsh Pt
Propylene Glycol Mono Methyl Ether Acetate	Dowanol PMA	CH_3 O CH_2 CH (CH_3) OOC.CH_3	140	47

Solvent Selection

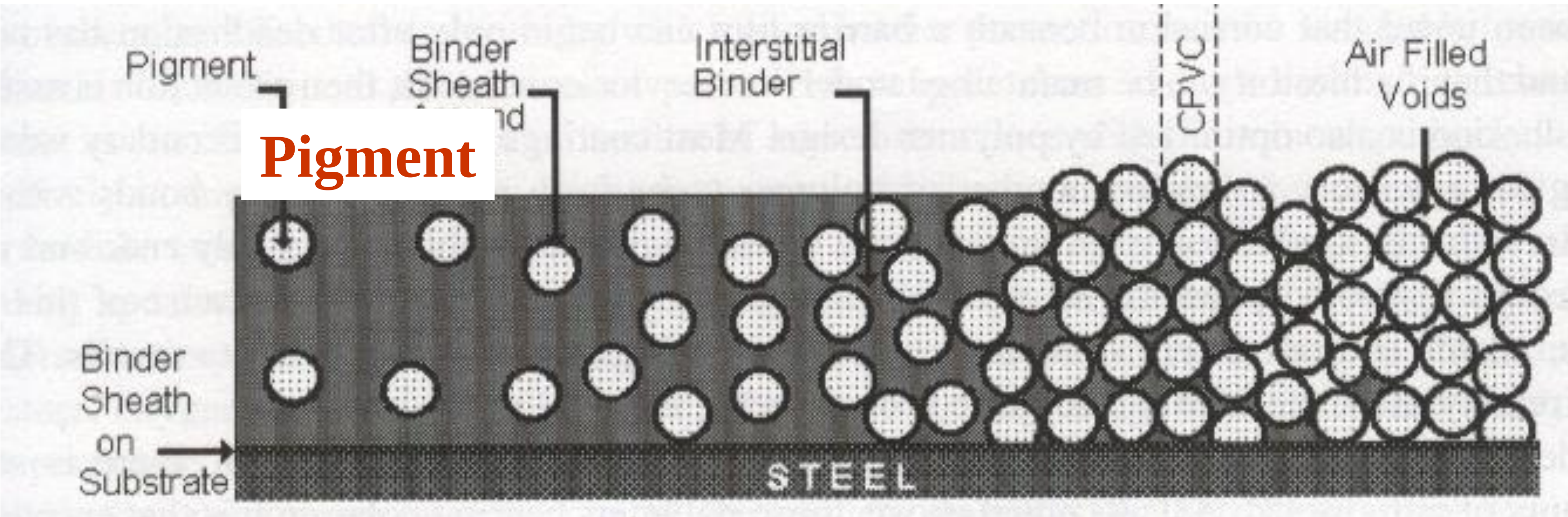
- Air Drying: Fast
- Oven Drying: Slow (mixture)
- Solvency: Some true solvent is required

- Coil Coatings are heated rapidly in an oven
- Some reaction products are volatile
- The film needs to stay ‘open’ for as long as possible
- Use solvents with high boiling ranges

\- Polar resins like polar solvents

\- Non-polar resins prefer non-polar solvents

Role of Pigments



Barrier Coating

Inhibitive Primer

Organic Rich Coatings

Inorganic rich coating

Summary & Conclusions

- Basic understanding of polymer choice important.
- Paint Coating is one of the most effective and known methods of corrosion protection at the surface.
- To get an excellent corrosion protection, several factors which include, proper surface preparation, correct application technique and suitable environmental conditions.
- Paint selection is very important. Depending upon the environment, a suitable system is selected.

Thank you