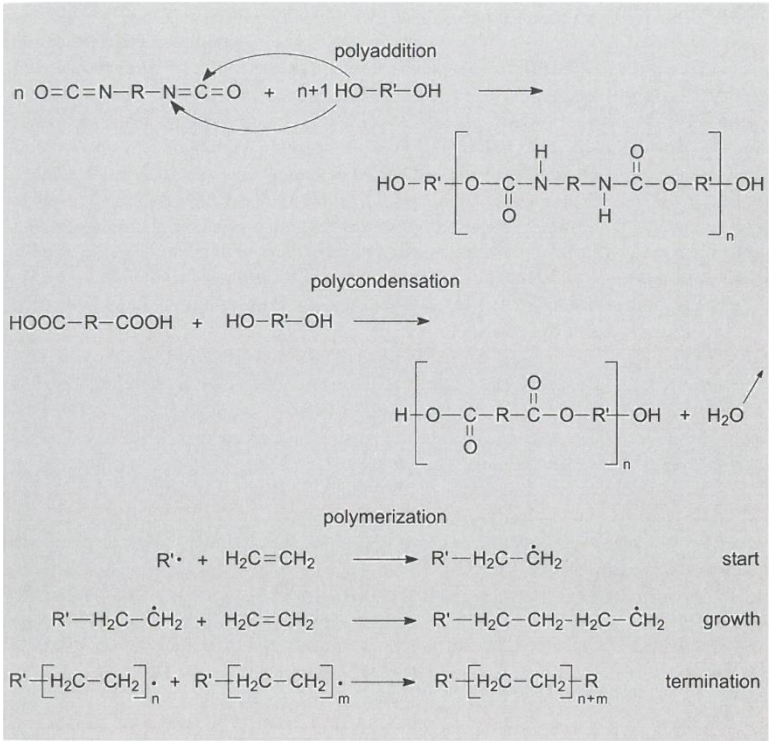
Chemistry of Coating Precursors and Curing Reactions

[Resin = Precursor] Chemistry

- Polycondensation reactions with release of byproducts (e.g. water, MeOH)
  - Step-growth (polycondensates)
- Polyaddition reactions
  - Step growth (polyadducts)
  - Chain growth (addition polymers)



Step-growth

–□– + –□– → –□–□– (dimer)

–□– + –□–□– → –□–□–□– (trimer)

–□– + –□–□–□– → –□–□–□–□– (tetramer)

–□–□– + –□–□– → –□–□–□–□– (tetramer)

–□– + –□–□–□–□– → –□–□–□–□–□– (pentamer)

–□–□– + –□–□–□– → –□–□–□–□–□– (pentamer)

etc. x-mer + y-mer → (x+y)-mer

Chain-growth

–□– + –□– → –□–□– + –□– → –□–□–□– + –□– → –□–□–□–□– + –□– → –□–□–□–□–□– + etc.

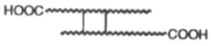
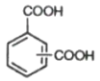
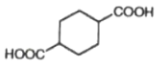
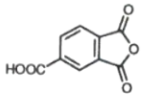
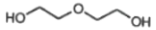
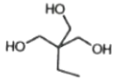
x-mer + monomer → (x+1)-mer

Resin Families

- Polycondensates
  - Polyesters resins (saturated, alkyds, unsaturated)
  - Amino resins (melamines)
  - Phenolics resins (resoles, novolacs)
- Polyadducts
  - Polyisocyanate resins (polyisocyanates, polyurethanes)
  - Epoxy resins
- (Free radical) Addition polymers
  - Polyacrylates

POLYCONDENSATES: POLYESTERS

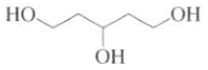
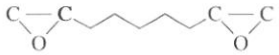
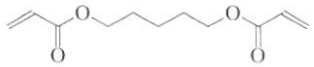
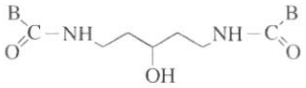
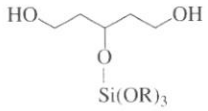
- Building blocks

Group	*Structure*	*Name*
'Soft' diacids	$HOOC-(CH_2)_n-COOH$	Alkanedioic Acids ($n = 0$–10)
	e.g. $HOOC-(CH_2)_4-COOH$	Adipic acid
		Dimerised fatty acid ($n = ca.\ 34$)
'Hard' diacids		1,2- = *o*-phthalic acid (anhydride)
		1,3- = isophthalic acid
		1,4- = terephthalic acid
		Cyclohexanedicarboxylic acid
Triacids		Trimellitic anhydride
Heterofunctional acids		Maleic anhydride
Diols	$HO-(CH_2)_n-OH$	Alkanediols ($n = 2$–10)
		Diethyleneglycol
		Neopentylglycol
Triols		Trimethylolpropane
		Glycerol
Tetrols		Pentaerythritol

SATURATED POLYESTERS

- Structure and functionality

- Versatile chemistry
- $10^3 < M_n < 3\ 10^4$ g mol^{-1}
- T_g < 0°C and > 100°C.
- Linear or branched.
- Customized functionality.
- Low functionality (often telechelic) may be a limitation to produce densely crosslinked materials after curing.
- Solid resins, solutions or dispersions.

Chemical structure	Polyester type	Molecular weight (g/mole)
	Linear, high molecular weight, hydroxyfunctional	10 – 30,000
	Linear, low molecular weight, hydroxyfunctional	1,500 – 6,000
	Branched, hydroxyfunctional	1,000 – 4,000
	Branched, carboxyfunctional	1,000 – 4,000
	Epoxy-modified	2,000 – 4,000
	Acrylate-modified	2,000 – 4,000
 H – B = blocking agent or 	Urethane-modified	2,000 – 7,000
	Silicone-modified	2,000 – 4,000

SATURATED POLYESTERS

- Crosslinking of saturated polyester binders with

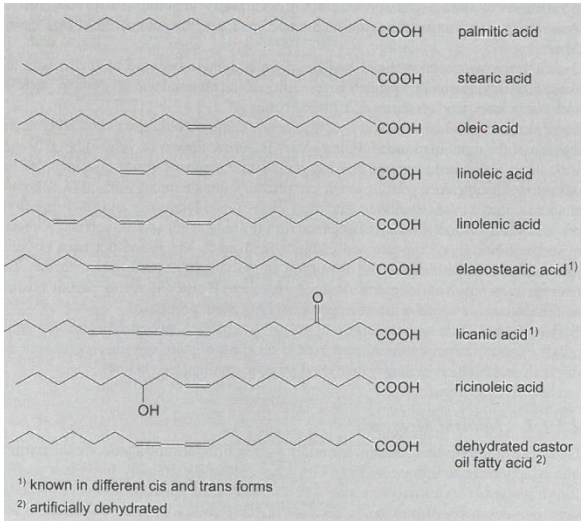
  - Amino resins (stoving)
  - Polyisocyanates (air- and forced-drying)
  - Blocked polyisocyanates (stoving, powder coatings)
  - Epoxy resins or epoxy crosslinkers (powder coatings)
  - Radiation curing

- PE binders can be formulated in any form (solventborne, high solids, waterborne, dispersions, radiation curing, powder).

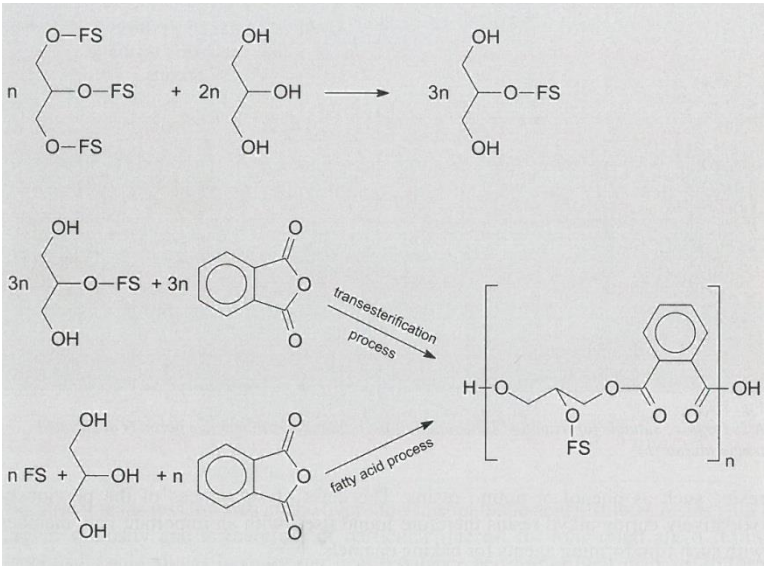
ALKYDS

Building blocks

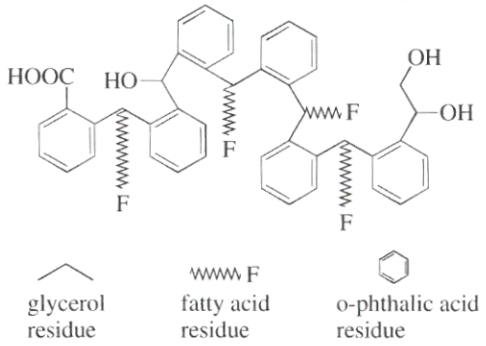
- Aromatic dicarboxylic acids (phtalic anhydride)
- Aliphatic dicarboxylic acids (e.g. adipic acid) for flexibility
- Polyols (glycerol, pentaerythritol, trimethylolpropane)
- Oils (e.g. vegetable)
- Examples of fatty acids:



Process



Simplified structure

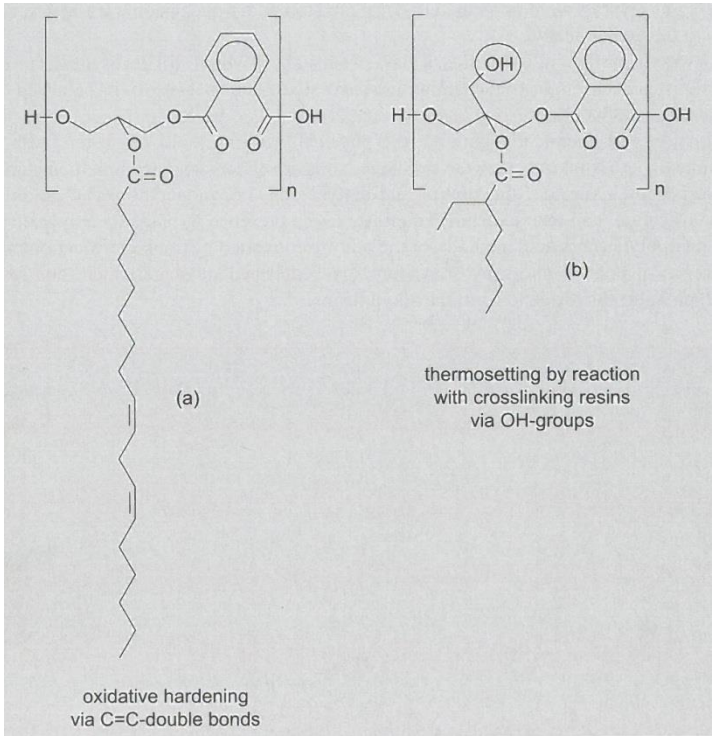


ALKYD RESINS

Classification

Drying or non-drying (depending on oil type and content)

Resin	Oil content
Short-oil	< 40%
Medium-oil	40-60%
Long-oil	>60 to 70%

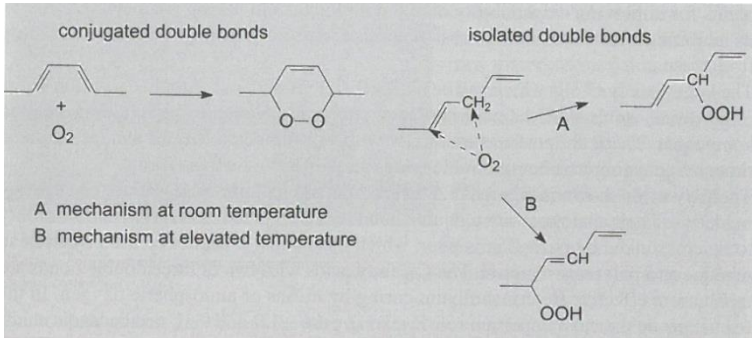


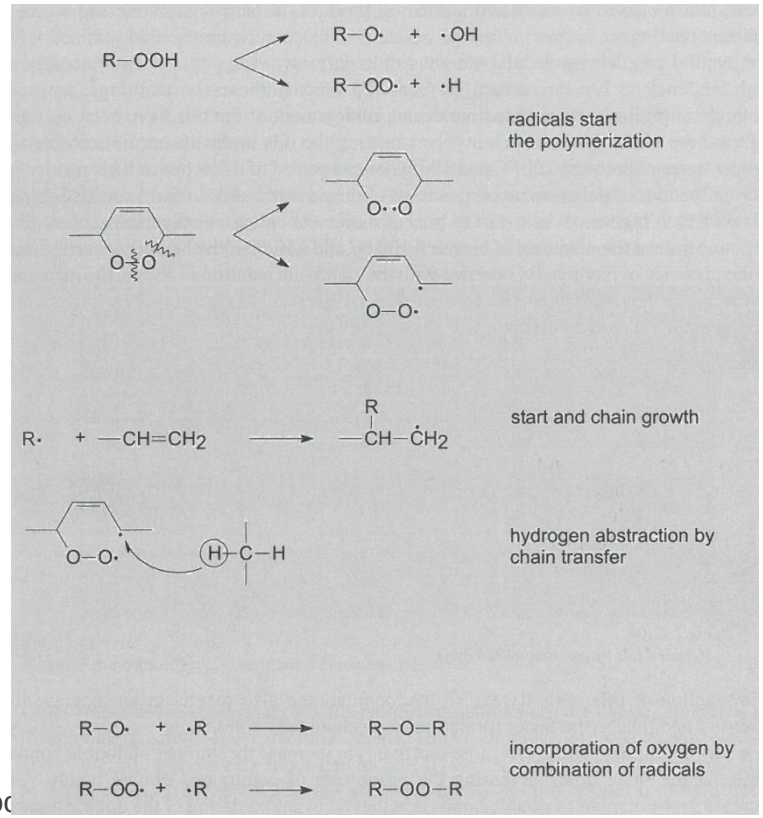
ALKYD « DRYING »

- Air drying
  - Long and medium-oil alkyds.
  - Oxidative and physical drying take place simultaneously during film formation.
  - Oxidative drying requires oxygen to initiate curing. Siccatives operate as accelerators.

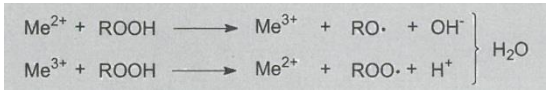
- Oven drying
  - Short-oil alkyds mostly combined with amino or polyisocyanate crosslinkers.

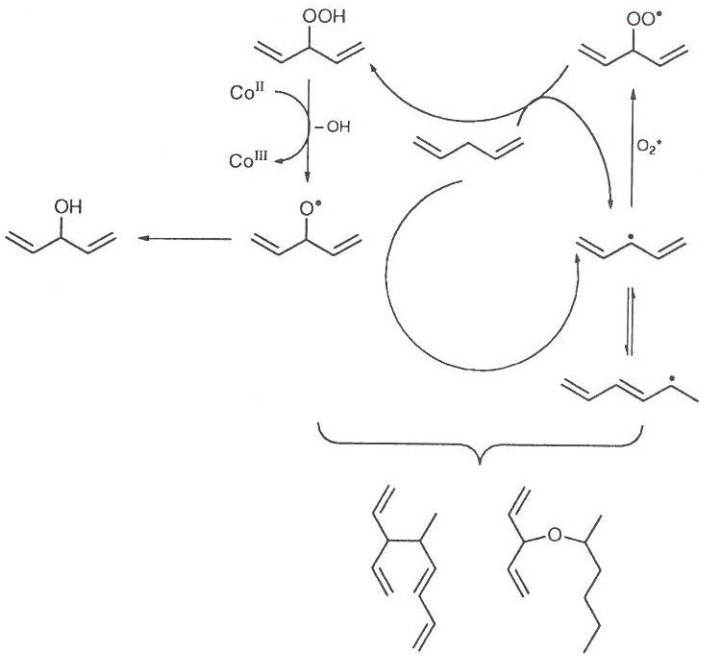
OXIDATIVE CURING





Acceleration of peroxide decomposition by siccatives

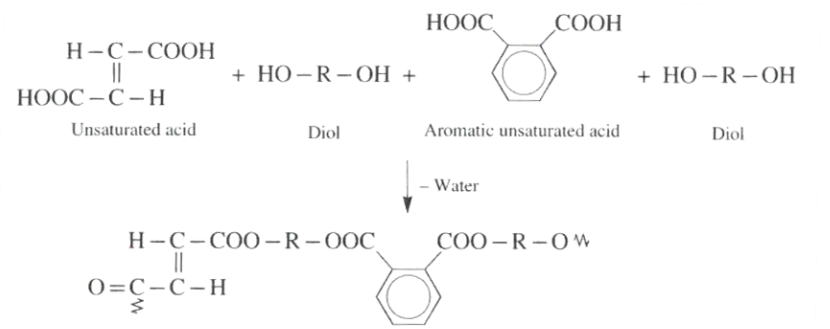




UNSATURATED POLYESTERS

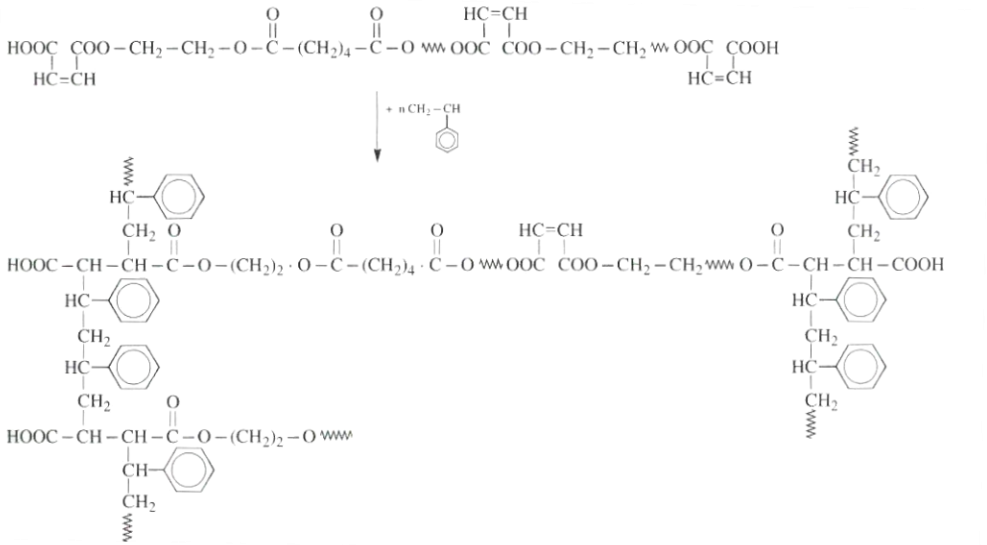
Building blocks

- Diacids: maleic/fumaric acid (anhydride), phtalic, iso and terephtalic acid.
- Diols: mono-, di-, triethylene or propylene glycol, neopentylglycol, butanediol.



Curing

- UP formulated with reactive diluents, usually styrene (cheap).
- Ambient or heat cure.
- Initiation with peroxides in combination with accelerators (photoinitiation is also an option).
- Inhibition by oxygen may lead to tacky surface.
- Styrene and maleic double bond forms alternating copolymers. Absence of homopolymers.
- Well-defined networks.



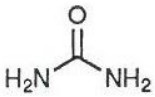
AMINO RESINS

- Amino-formaldehyde crosslinkers

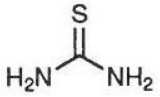
- The most important chemistry used in **stoved** coatings is based on optionally alkylated, amino-formaldehyde condensates (colorless!).

- Can be handled as 1-component systems with extended potlife.

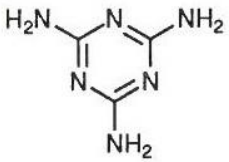
- Principal amino precursors are



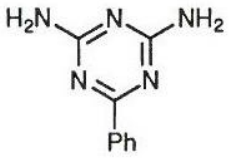
urea



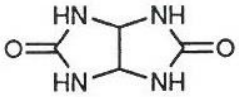
thiourea



melamine



benzoguanamine



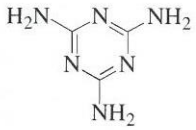
glycoluril

MELAMINE-FORMALDEHYDE

- Triazine

Triazine

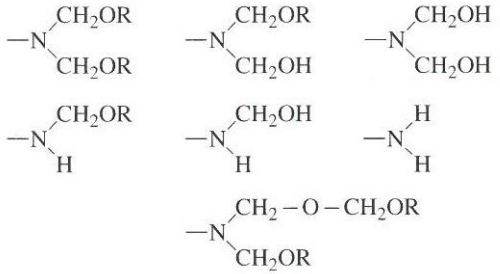
- Melamine



Melamine (2,4,6-Triamino-1,3,5-triazine)

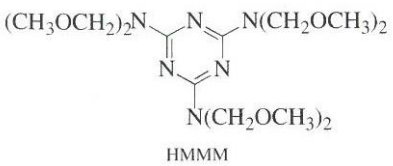
- Melamine is insoluble in most solvents.
- Methoxylation is not sufficient to achieve compatibility with binders. Additional etherification is required.

- Functional groups after hydroxymethylation (with formaldehyde) and etherification:



ALKYLATED MF RESINS

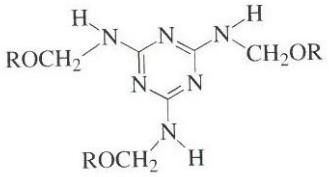
- Highly alkylated MF resin of methoxymethylmelamine (HMMM) type



HMMM

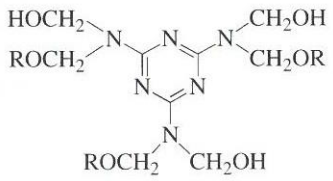
- Low reactivity.
- Strong acids required for co-condensation.
- Acid curing via carbocation formation (after loss of methanol).
- Little selfcondensation in absence of humidity (stable).

- Highly alkylated MF resin with high content of secondary amino groups



- Most reactive, weak acids used.
- Direct Schiff base formation without demethylolation (in acid conditions).
- Self-condensation takes place.

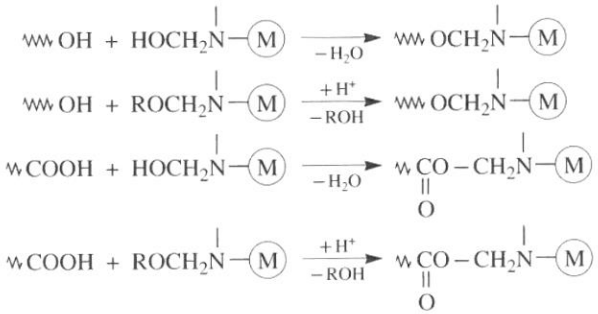
- Partially alkylated MF resin with high content of methylol groups



- Medium reactivity, curing using weak acids.
- Reactivity enhanced by Schiff base formation after demethylolation.
- Higher emission of formaldehyde.
- Self-condensation takes place.

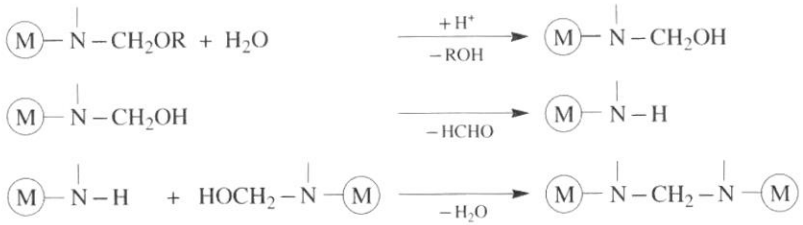
CURING (CO- AND SELF-CONDENSATION)

External crosslinking:



Self-crosslinking:

or

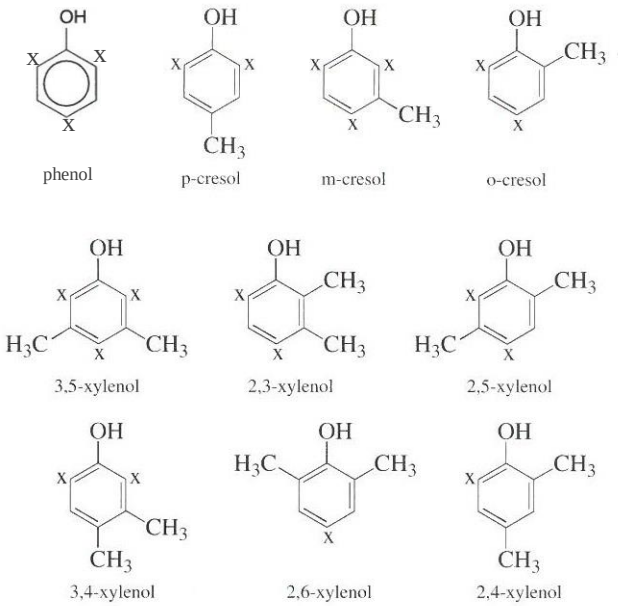


M = melamine resin segment

PHENOLIC RESINS

- Phenol-formaldehyde (PF) resins

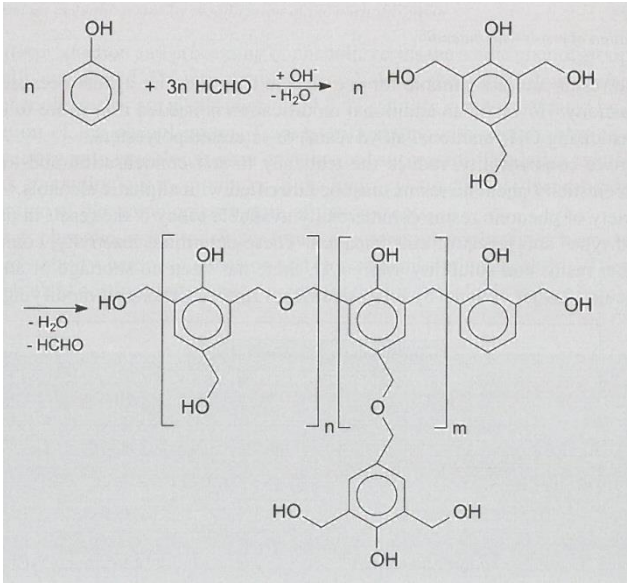
- Synthetic resins obtained by condensation of phenols and formaldehyde.
- Resistant to chemicals and heat. Excellent mechanical properties.
- Drawback is the intrinsic colour and yellowing tendency (aromatic).
- Precursors other than phenol: cresol, xylenol, alkylphenol, Bisϕ A.



Synthesis of PF Resins

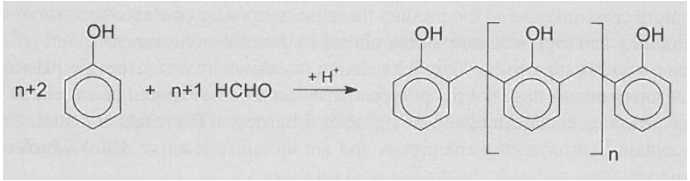
Resole resins

- Reaction of formaldehyde with (substituted) phenols.
- Synthesis in basic conditions using an excess of formaldehyde.
- Self-crosslinkable.



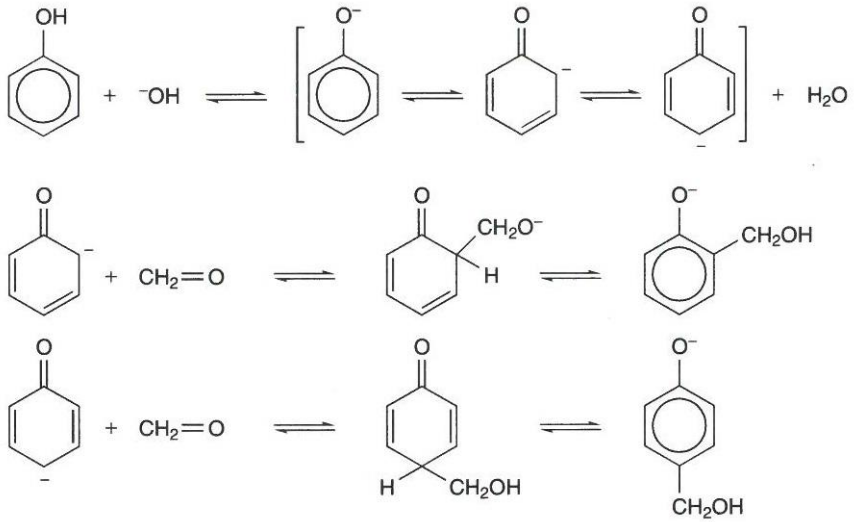
Novolac resins

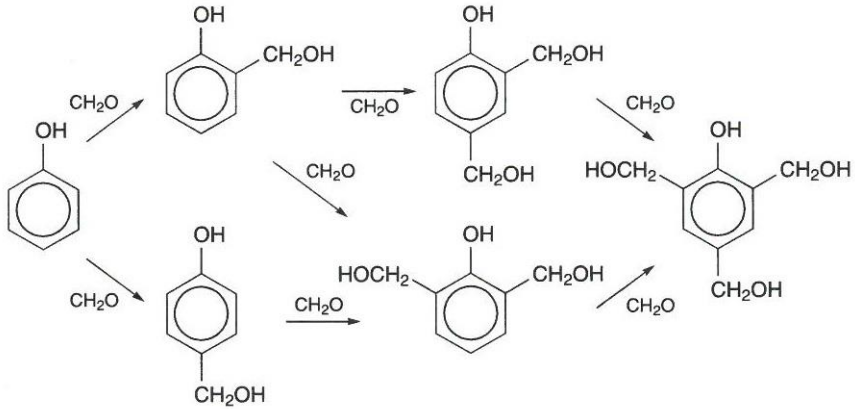
- Reaction of formaldehyde with (substituted) phenols.
- Synthesis in acidic conditions using an excess of phenol.



Mechanism of Resole Synthesis

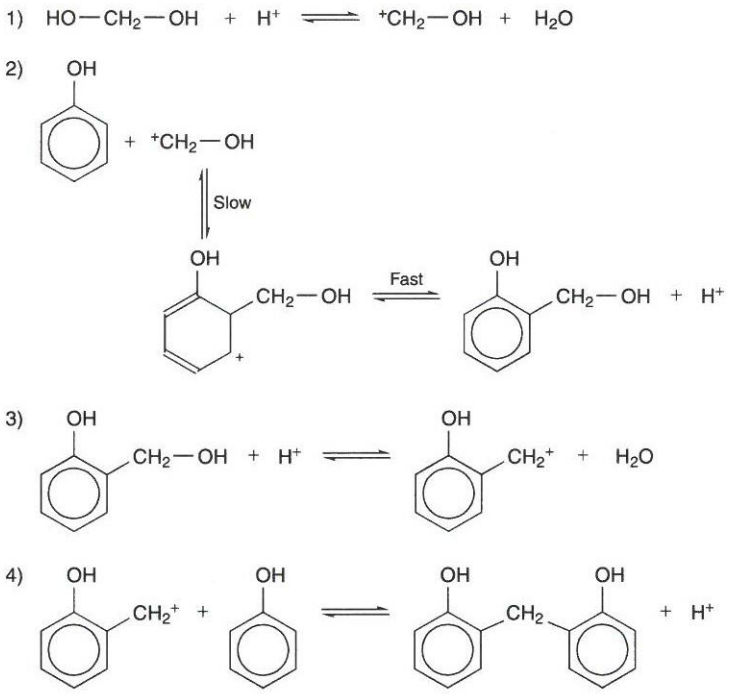
- Alkaline conditions





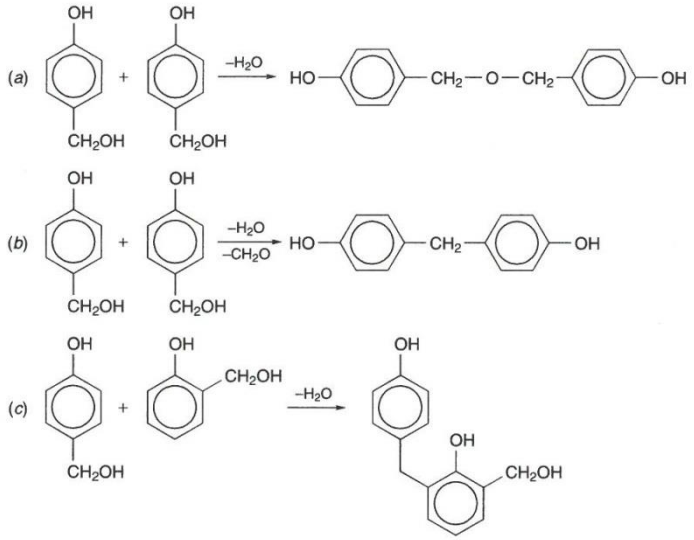
MECHANISM OF NOVOLAC SYNTHESIS

- Electrophilic aromatic substitution in acid condition

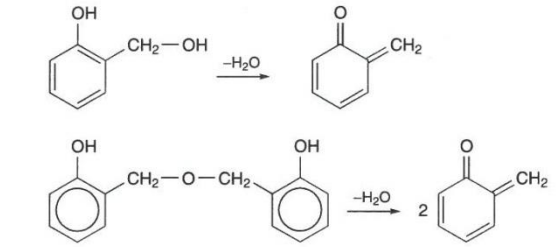


CROSS-LINKING OF RESOLES

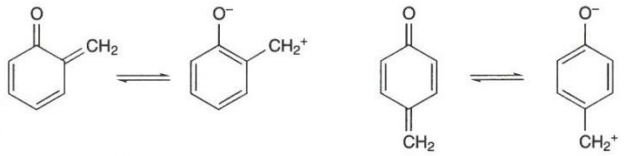
- **Inter**molecular condensation of hydromethyl substituents eliminate water to form ether linkages (< 130°C) or eliminate both water and formaldehyde to form methylene linkages (> 130°C).



- **Intra**molecular condensation (dehydration) of hydromethylgroup or dimethylether linkages to form quinone methides. Quinone methides are key intermediates in both resole synthesis and crosslinking reactions.



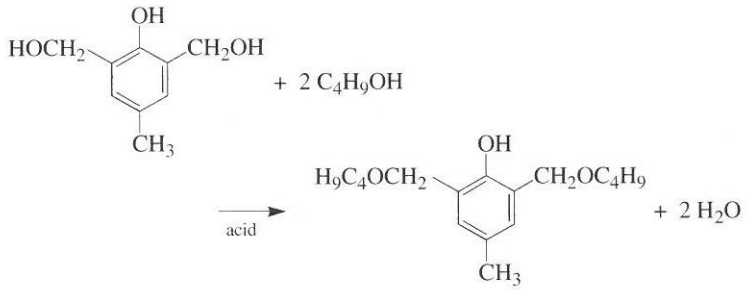
Dehydration of methylols or benzylic ethers to form quinone methides.



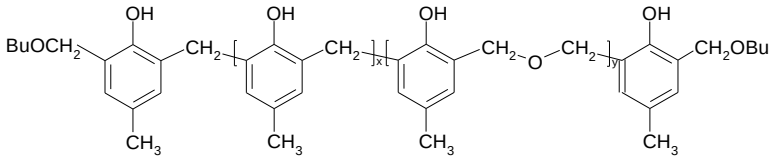
Resonance of quinone methides.

ETHERIFIED PHENOLIC RESINS

- Example: Butylation of resoles



- Increases solubility in less polar solvents and other polymers.
- Properties such as adhesion, elasticity, and levelling are improved.
- A sizeable increase in flexibility and resistance properties is achieved by mixing butylated resoles with epoxy resins.
- Drawback is the loss in reactivity.
- Example: Butylated p-cresol resole



PF Crosslinker Formulations

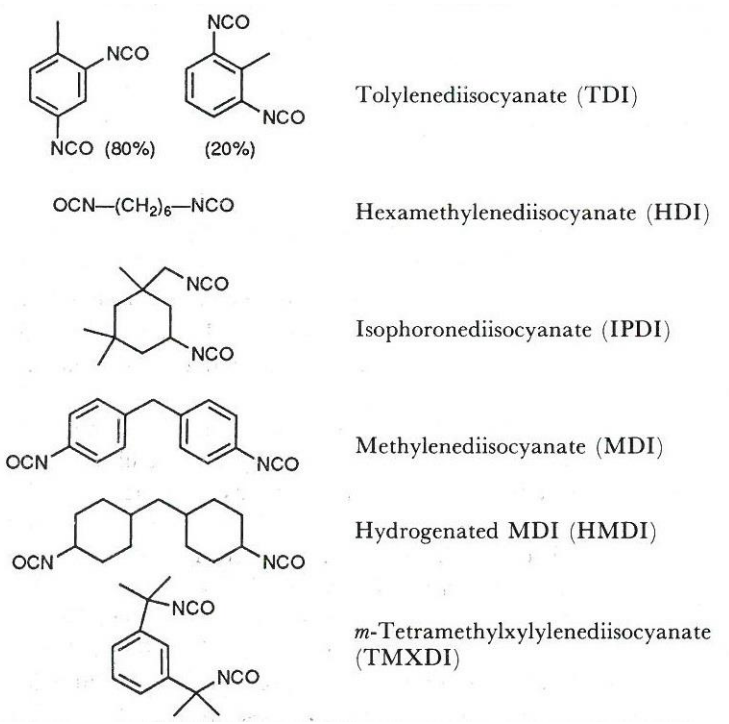
- Phenolic resins as crosslinkers

  - Hydroxyl functional resins based on e.g. epoxy or polyester resins are crosslinked with reactive phenolic-based resins (resoles).
  - Optimal properties achieved with binder in excess.
  - Curing usually in acid conditions.
  - Network buildup fairly complex.

POLYADDUCTS: POLYISOCYANATE RESINS

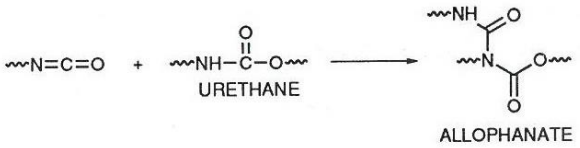
- Difunctional isocyanates as the core building blocks

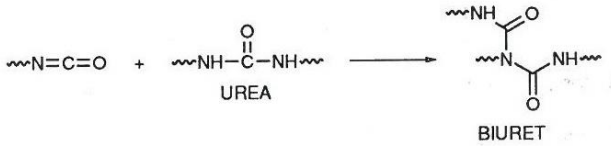
- High reactivity of NCO with activated hydrogen.
- Reactivity aromatic > aliphatic isocyanates.
- Aromaticity causes absorption of ultraviolet (UV) radiation which triggers numerous oxidative side reactions and form moieties which cause a discoloration to yellow or brown.

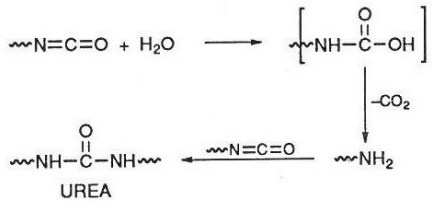


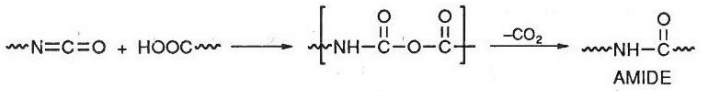
ISOCYANATE CHEMISTRY

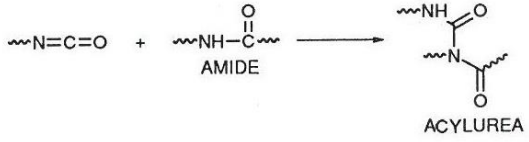
- Isocyanate reactions with activated hydrogens



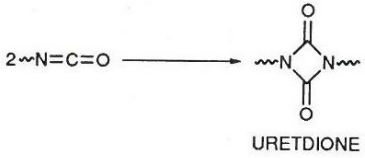




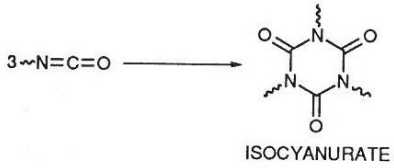




Dimerization



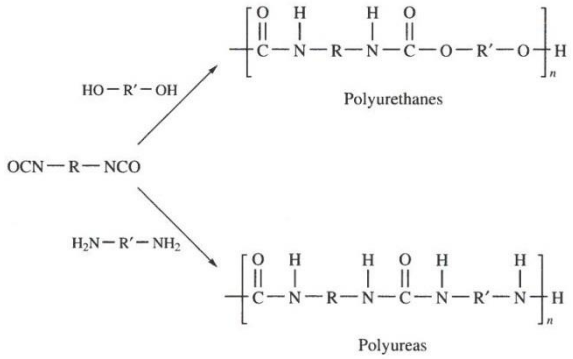
Trimerization

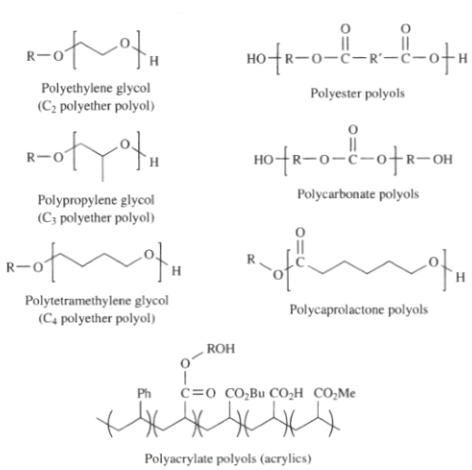


POLYURETHANE RESINS

Building blocks

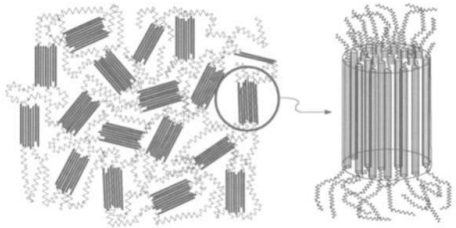
- Diols based on polyesters, polyethers, polycarbonates, etc…
- Diols are linked together by diisocyanates (in excess).
- Endcapping of -NCO is an option to introduce new functionalities (e.g. acrylates).
- Chain extension with diamines leads to formation of hard urea linkages.





Structure and functionality

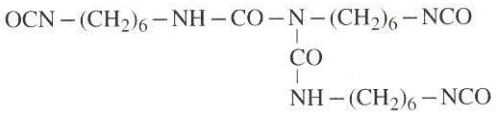
- Versatile chemistry
- $10^3 < M_n < 10^5$ g mol^{-1}
- Large T_g spectrum.
- Linear or branched.
- Customized functionality.
- Low functionality (often 2).
- Solutions or dispersions.
- Microphase separation possible with hard domains (crystalline/amorphous) in soft amorphous matrix.



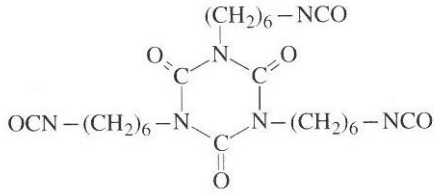
POLYISOCYANATE RESINS

- Polyisocyanate crosslinkers

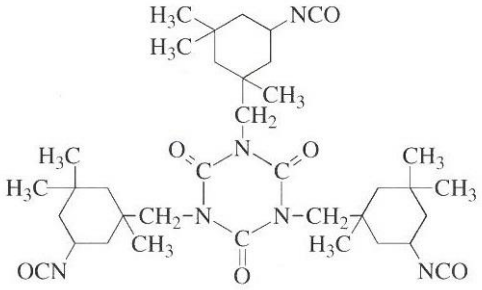
- Biuret of HDI



- HDI isocyanurate trimer



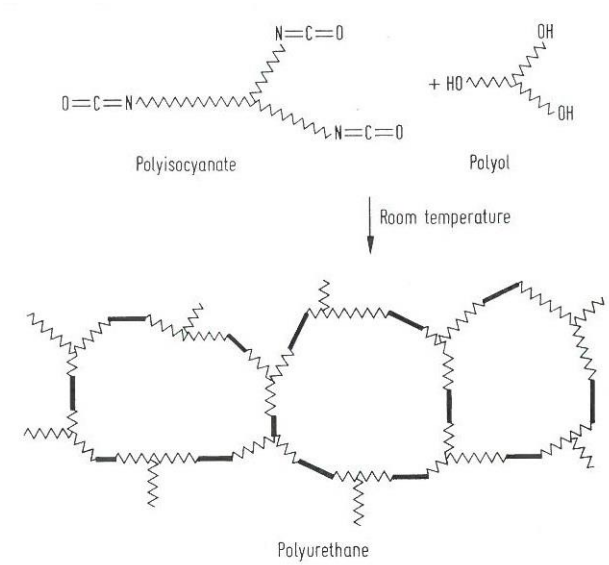
- IPDI isocyanurate trimer



2K-PUR

- Two-pack polyurethane (PUR) structure

- Acrylic or saturated (oil-free) polyester polyols crosslinked with polyisocyanates.
- Ambient cure (optionally slightly forced) using Lewis acids (e.g. tin compounds) or bases as catalyst (tertiary amines).
- Limited potlife.

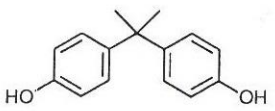


EPOXY RESINS

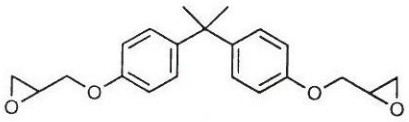
- Organic compounds with more than one epoxide group per molecule used to obtain polymers.

- Most important family for coatings are glycidyl ethers of bisphenol A (or F).

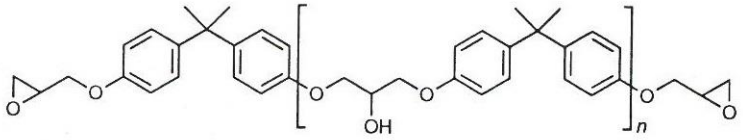
Bisphenol A — BisϕA: M_w 228 g/mol



Diglycidyl ether of bisphenol A — DGEBA: M_w 340 g/mol

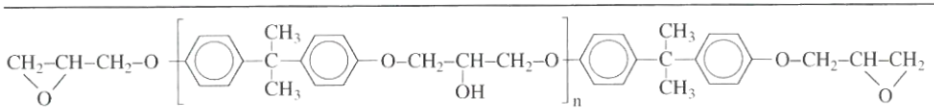


Epoxy resin



- Epoxy resins are usually combined with suitable crosslinkers or hardeners in a matched functional ratio.

EPOXY RESINS



Type	Epoxide content mmol/g	Epoxide equivalent (g/Equ)	Molecular weight	Softening temperature to DIN 51920 (°C)	Viscosity at 25 °C to DIN 53015 (mPa · s)
liquid, low viscosity	5.25 to 5.70	175 to 190	~ 350	–	7,000 to 10,000
liquid medium viscosity	5.10 to 5.40	185 to 195	~ 370	–	10,000 to 16,000
semi-solid	3.70 to 4.35	230 to 270	~ 450	–	450 to 700 [1]
solid, type 1	1.80 to 2.25	450 to 550	~ 900	70 to 80	160 to 250 [2]
solid, type 2	1.45 to 1.80	550 to 700	~ 1,100	80 to 90	280 to 350 [2]
solid, type 4	1.05 to 1.25	800 to 950	~ 1,500	95 to 105	450 to 600 [2]
solid, type 7	0.40 to 0.62	1,600 to 2,500	~ 3,000	120 to 140	1,500 to 3,000 [2]
solid, type 9	0.25 to 0.40	2,500 to 4,000	~ 4,000	140 to 160	3,500 to 10,000 [2]
solid, type 10	0.16 to 0.25	4,000 to 6,000	~ 5,000	150 to 180	5,000 to 40,000 [2]
high-molecular, dissolved 40% in MEK	<0.05	> 20,000	~20,000	–	>1,000
phenoxy resins	<0.01	>100,000	>30,000	>200	2,500 to 7,500 [3]

1) 70% in butyl diglycol (diethylenglycolmonobutylether)
2) 40% in butyl diglycol
3) 20% in acetone/toluene 1:1

EPOXY CURING IN COATINGS

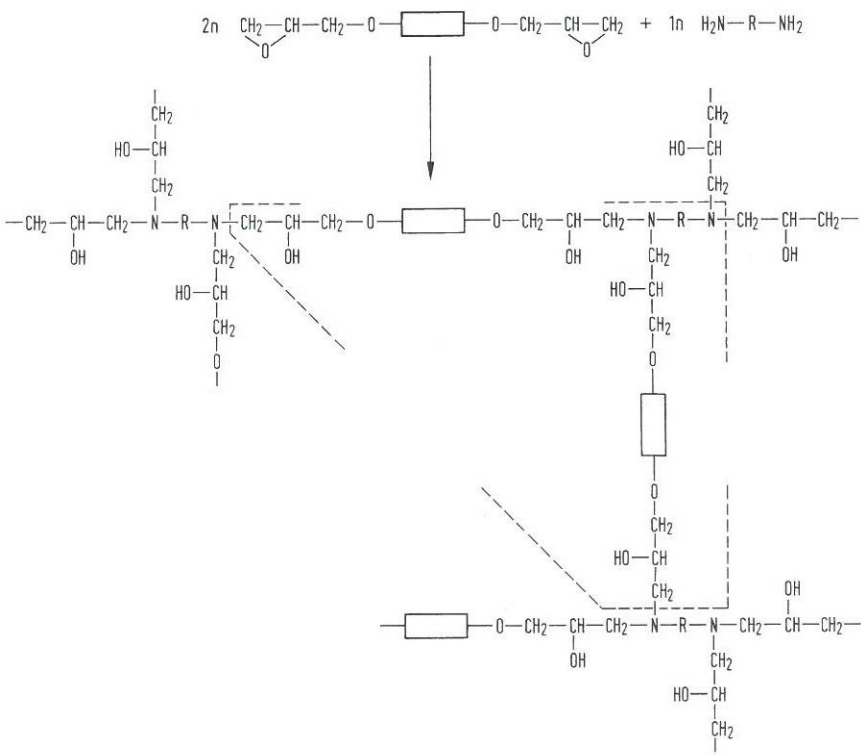
- Epoxy groups can react with amines (most common), phenols, isocyanates, acids, thiols.

Epoxy resin/curing-agent combinations and their applications

	Curing agent type	Main curing mechanism	Resin type	Molecular mass	Typical application
Ambient cure	Amines and polyamidoamines	Polyaddition via the epoxide group	liquid	≤400	2-component systems for havy corrosion protection and floor coverings. Building blocks for chemical modification
	Polyamidoamines and amine adducts	Polyaddition via the epoxide group	solid, type 1 solid, type 2	about 900 about 1,100	refiniching paints marine paints
Powder baking	Latent amines, polyesters, OH-terminated epoxy resins	Polyaddition via the epoxide group	solid, type 3 solid, type 4	about 1,300 about 1,500	powder coatings
Enamel stoving	Phenolic resins, amino resins, polyanhydride	Polycondensation via OH-groups, polyaddition via epoxide/OH	solid, type 6 solid, type 7 solid, type 8	about 3,000	can coatings coil coatings
	Phenolic resins, amino resins	Polycondensation via OH groups	solid, type 9 solid, type 10	about 4,000 about 5,000	can coatings tube coatings
Ambient cure	Isocyanates	Polyaddition via OH groups	solid, type 9, thermoplastic epoxy resins	about 4,000 about 20,000	2-component PU coatings, e.g. primers
	Air drying	Air oxydative polymerization of epoxy resin fatty acid esters	solid, type 4	about 1,500	tube coatings, external primers, one coat paints

AMINE CURING OF EPOXY RESINS

- Epoxy groups react with primary and secondary amines.
- Reactivity aliphatic > aromatic amines.
- Hydroxy groups act as catalyst resulting in an autocatalytic reaction process.
- Absence of side reactions when [epoxy]≈[amine] → « model » networks.
- When [epoxy]>[amine] (or low-reactive amine), epoxy-hydroxy reactions start to compete.



Chemical name	Usual abbreviation	Molecular mass	Active H^+ equivalent weight
Ethylenediamine	EDA	60	15
Diethylenetriamine	DETA	103	21
Triethylenetetramine	TETA	146	24
Tetraethylenepentamine	TEPA	189	27
Pentaethylenehexamine	PEHA	232	29
1,3-Pentanediamine	DAMP	102	25
2-Methylpentamethylenediamine	MPMDA	116	29
Dipropylenetriamine	DPTA	131	26
Diethylaminopropyleneamine	DEAPA	130	26 to 42*
Trimethylhexamethylenediamine	TMD	158	40
Polyoxypropylenediamine	JEFFAMINE D 230	230	57
Polyoxypropylenetriamine	JEFFAMINE T 400	400	100
Diaminodiphenylmethane	DDM	198	50
Diethylaminodiphenylmethane	DEDDM	234	59
Diaminodiphenylsulfone	DDS	248	62
Diethyltoluenediamine	DETDA	178	44
Benzylaminoproylamine	BAPA	150	50
m-Xylylenediamine	MXDA	136	34
Diaminocylohexane	DAC	114	28
Bis-(aminomethyl)cyclohexane	BAC	142	35
Isophoronediamine	IPD	170	43
Cyclohexylaminopropylamine	NAPCHA	156	52
Diaminodicyclohexylmethane	PACM	210	53
Dimethyldiamino-dicyclohexylmethane		238	60
Bis-aminomethyl-dicylopentadiene	TCD-Diamin	194	49
N-Aminoethylpiperazine	NAEP	129	22 to 32*
Dicyandiamide	DICY	84	12 to 21*

* contain catalytic nitrogen – an exact active H^+ equivalent weight cannot therefore be specified

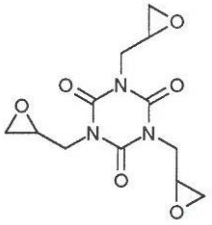
POWDER COATINGS

- Hybrid powders: acid-functional unsaturated polyester (f=2-3) and *epoxy resins* (f=2)

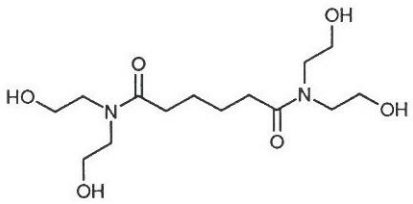
  - Resins are mixed in equivalent functional ratio. Carboxylic groups react with epoxy groups but also with the secondary hydroxyl groups!
  - Stoving temperature between 140 and 200°C using a catalyst (phosphines, phsosphonium or amonium salts).

- Polyester powders: acid-functional unsaturated polyester (f=2) and *hardener* (low equivalent weight crosslinker f>2)

  - Epoxy hardeners: TGIC (triglycidyl isocyanurate; f=3, toxic) or di- or tri-glycidyl esters of terephthalic and isophthalic acid, tetrahydrophthalic acid and trimellitic acid (such as “Araldite PT 910”, non-toxic).



  - Hydroxy hardeners: multifunctional hydroxyalkylamides (e.g. Primid XL552; f=4)



ADDITION POLYMERS: ACRYLIC BINDERS (CHAIN GROWTH)

Building blocks

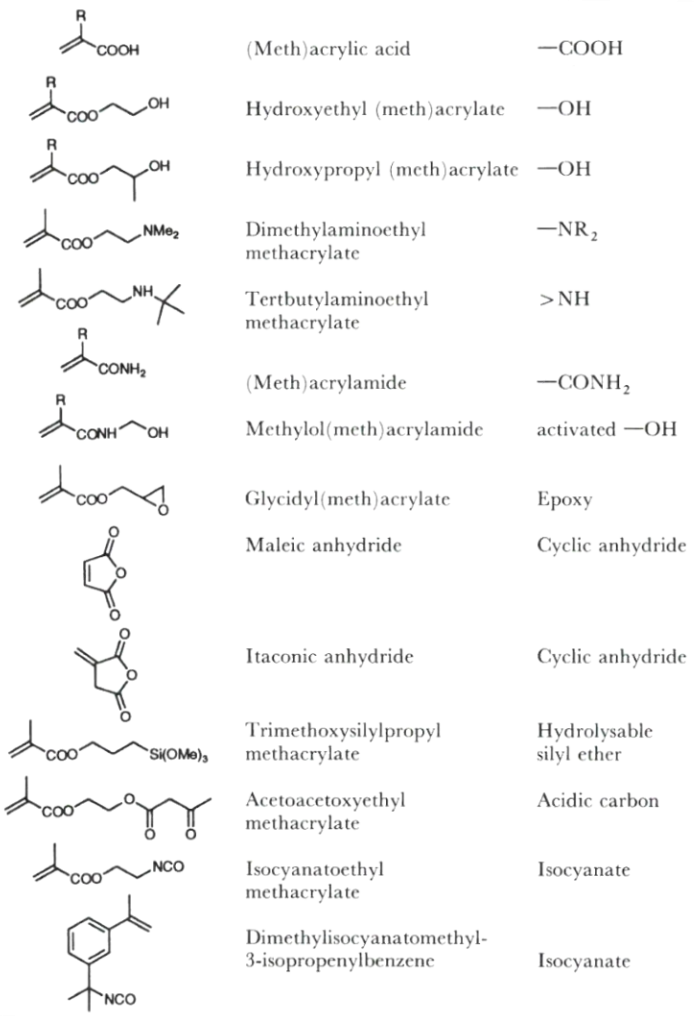
- T_g controlling monomers
  - Hard: Methyl methacrylate, styrene
  - Soft: Butyl acrylate, 2-ethylhexyl acrylate
- Functional monomers

Structure and functionality

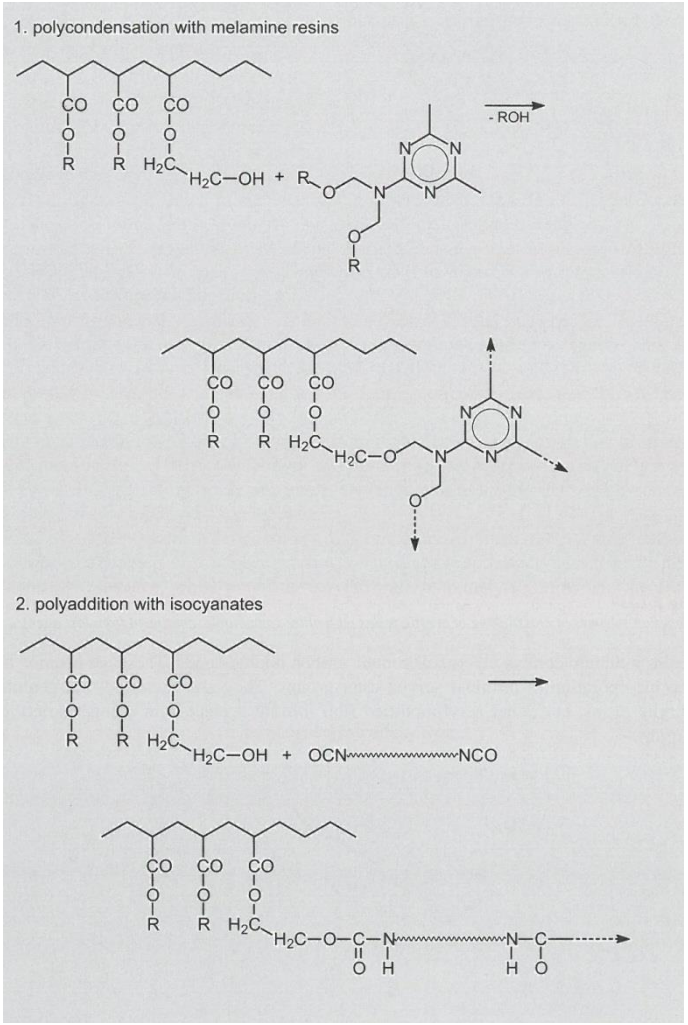
- Versatile chemistry
- $10^3 < M_n < 10^6$ g mol^{-1}
- T_g < 0°C and > 100°C.
- Linear or branched.
- Customized functionality.
- High **lateral** functionality (> 4) leading to densely crosslinked materials after curing.
- Solutions or dispersions.

Process

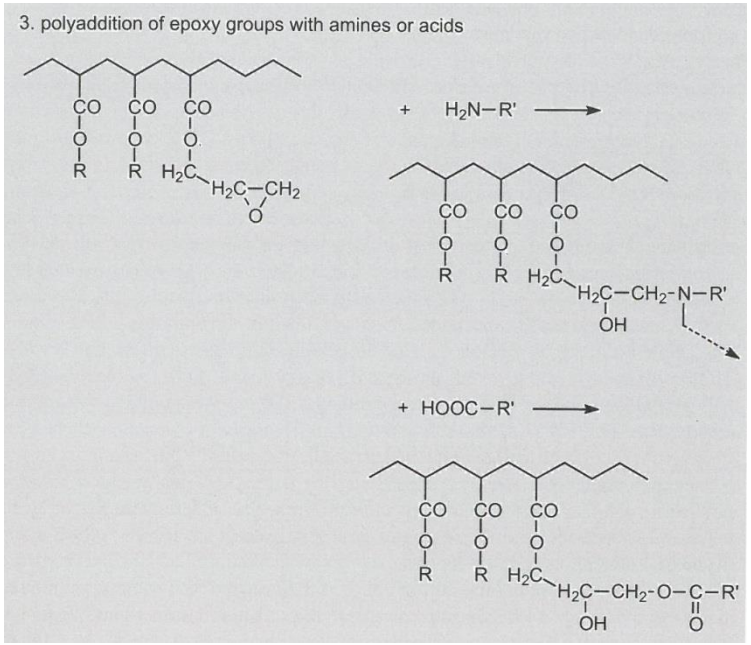
- Bulk polymerization
- Solution polymerization
- Emulsion polymerization



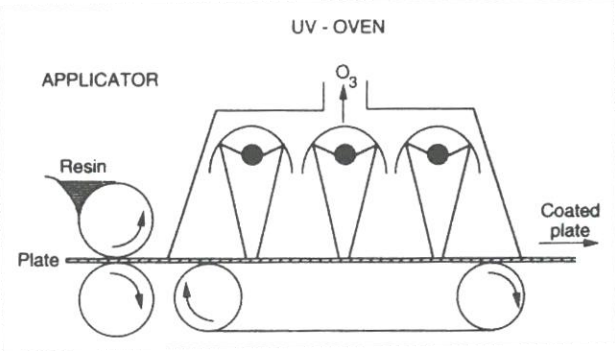
CURING OF ACRYLIC BINDERS



- Thermal curing (1K)
  - Stoving of hydroxy, epoxy or carboxylic functional acrylic resin with urea or melamine resins, or block isocyanates.
- Ambient cure (2K)
  - Hydroxyl functional polyacrylates can be crosslinked with polyisocyanates.
  - Metal complexes for carboxylic resins.



ULTRAVIOLET CURING



- Free-radical polymerization
  - Acrylates
  - Thiol-ene
  - Unsaturated polyesters
- Cationic polymerization
  - Epoxides

Ultraviolet Curable Resins

Oligomers

- Polyesteracrylates (EB800)
- Polyetheracrylates
- Polyurethane acrylates
- Epoxyacrylates (EB600? 604, 605)

Photoinitiators

- α cleavable (Norrish Type I)
- H-abstraction (Norrish Type II)

Reactive Diluents

- Monoacrylates (IBoA, THFA, MMA, Phenoxyethylacrylate, Cardura acrylate, …)
- Diacrylate (HDDA, TPGDA, DPGDA, NGPDA, …)
- Triacrylate (TMPTA, PETIA, GPTA, …)
- Tetracryalate (PETRA, diTMPTRA, …)

Accelerators

- Amino acrylates
- Thiols

Additives

- Resin stabilizers
- Adhesion promoters
- Wetting and flow agents
- Fillers
- Pigments

MONOGRAPHS

- Resins for Coatings, D. Stoye and W. Freitag, Hanser
- BASF Handbook on Basics of Coating Technology, A. Goldschmidt and H.-J. Streitberger, Vincentz Network
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- UV Coatings, R. Schwalm, Elsevier
- The Chemistry and Physics of Coatings, A. Marrion, RSC publications
- Radiation Curing in Polymer Science and Technology, J.-P. Fouassier and J. Rabek, Elsevier
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