This section contains an extract from an internal training manual which gives an introduction to the resin manufacturing process carried out at Dynea Ireland Ltd.
The Raw Materials

Aminoresins are polymeric condensation products of the reaction of aldehydes with compounds carrying aminic (containing an Amine group or NH₂ group - pertaining to or containing any of a group of organic compounds of nitrogen derived from ammonia) or amadic (containing an Amide, any of a large group of organic compounds containing the radical CONH₂ and, usually, a hydrocarbon) groups. Phenolic resins incorporate the aromatic alcohol phenol into their structure.

The raw materials for aminoplast resins are readily available and relatively cheap.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Chemical Structure</th>
<th>Properties</th>
</tr>
</thead>
</table>
| Methanol      | H₂C(OH)H           | - Bulk storage capacity on site 4,500m³  
- Clear, colourless, almost odourless liquid  
- Density - 0.7913g/cm³  
- Boiling Point - 64.7°C  
- Flash Point - 11°C |
| Formaldehyde  | H₂C=H              | - Colourless gas with a characteristic, pungent odour  
- Density - 0.815g/cm³  
- Boiling Point -19.5°C  
- Autoignition temperature - 300°C |
| Urea          | H₂N-C-NH₂          | - Secreted by humans 50g/day  
- Important fertiliser  
- White crystalline powder  
- Density - 1.32g/cm³  
- Melting Point - 133°C |
| Melamine      |                    | - Chemical name - 2,4,6-Triamino-1,3,5-Triazine  
- White Crystalline Powder  
- Very poor water solubility  
- Melting Point 354°C  
- Molecular Weight 126.12  
- Density 1.573g/cm³ |
| Phenol        | HO                 | - Aromatic alcohol  
- Almost colourless  
- Crystalline material  
- Dissolves very slightly in water to form a weak acidic solution |
Aminoplast Resin Manufacture and Use

Table 1: Resin Raw Materials

Resin Types

UF/MUF RESins (Aminoplasts)

- Work well with all wood species
- Cheap
- Easy to make
- Poor water toleration
- Formaldehyde emission issues

PF Resins

- Phenolic based reins
- More difficult to make
- Better water toleration

PMDi Resins

- Isocyanate based
- Better swell properties
- Better water toleration

Adhesive polymers are made by condensation polymerisation (the reaction releases H₂O and so is known as condensation)

\[
\begin{align*}
U + F & \rightleftharpoons UF + H_2O \\
UF + U & \rightleftharpoons UFU + H_2O \\
UFU + F & \rightleftharpoons UFUF + H_2O \\
UF + M & \rightleftharpoons UFM + H_2O \\
M + F & \rightleftharpoons MF + H_2O \text{ etc} \\
P + F & \rightarrow PF + H_2O \text{ etc}
\end{align*}
\]

Where U=Urea, F=Formaldehyde and M=Melamine.
Introduction to Urea-Formaldehyde Resins

The urea-formaldehyde resins (UF) are the most important and most used class of aminoresin adhesives. Formaldehyde is by far the primary aldehyde used. The advantage of UF adhesives are their

1. initial water solubility (this renders them eminently more suitable for bulk and relatively inexpensive production),
2. hardness,
3. non-flammability,
4. good thermal properties,
5. absence of colour in cured polymers, and
6. easy adaptability to a variety of curing conditions.

Thermosetting amino resins produced from urea are built up by condensation polymerisation.

Polymers are divided into two main classes, thermoplastic and thermosetting.

Thermoplastics soften and flow when heated and are normally shaped by heat and pressure. They will soften and flow again when re-heated.

Thermosetting plastics are moulded under heat and pressure. A chemical reaction occurs so that once moulded they do not soften when re-heated.

Urea is reacted with formaldehyde, which results in the formation of addition products such as methylol compounds (see below). Further reaction, and the concurrent elimination of addition water, leads to the formation of low molecular weight condensates which are still soluble. Higher molecular weight products, which are insoluble and infusible, are obtained by further condensing the low molecular weight condensates.

The greatest disadvantage of the amino resins is their bond deterioration, caused by water and moisture. This is due to the hydrolysis of the aminomethylenic bond. Therefore, UF resins are used only for interior applications.

Methyl and amino groups cannot be isolated on their own as they are unstable and thus highly reactive.

A methyl group consists of a carbon with three hydrogens attached: \( \text{CH}_3 \) this is what is referred to as Me when writing the shorthand for methanol – \( \text{MeOH} \). Thus methanol consists of a methyl group (Me) attached to an alcohol, or \( \text{OH}_2 \), group – \( \text{CH}_2\text{OH} \).

An amino group consists of a Nitrogen with two hydrogens attached – \( \text{NH}_2 \) These groups can be seen in Table 1 above to be present in both urea and melamine.

The reaction between urea and formaldehyde is complex. The combination of these two chemical compounds results in both linear and branched polymers, as well as tridimensional networks, in the cured resin. This is due to a functionality of 4 in urea (due to the presence of 4 replaceable hydrogen atoms – in reality only trifunctional due to hindrance) and a functionality of 2 in formaldehyde.
Aminoplast Resin Manufacture and Use

The most important factors determining the properties of the reaction products are

1. the relative molar proportion of the reaction products
2. the reaction temperature, and
3. the various pH values at which condensation takes place.
4. the purity of the raw materials used.

These factors influence the increase of the molecular weight of the resin. Therefore, the characteristics of the reaction products differ considerably when lower and higher condensation stages are compared, especially solubility, viscosity, water retention, and curing of the adhesive. They all depend to a large extent on molecular weights.

pH is a measure of the acidity/alkalinity of a material. Examples of items and their pHs are given below.

- distilled water (7.0)
- milk (6.6)
- coffee (5.0)
- beer (4.4)
- orange juice (3.7)
- fruit vinegar (3.2)
- cola beverages (2.8)

When measuring acids we are measuring the H⁺ concentration, e.g. H₂SO₄ = sulphuric acid is the acid created when ammonium sulphate and formaldehyde react.

When measuring bases we are measuring the OH⁻ concentration, e.g. NaOH = caustic soda.

Sulphuric acid would be a strong acid and therefore have a very low pH while caustic soda solutions would be strong bases (or strongly alkaline) and therefore have high pHs.
The reaction between urea and formaldehyde is divided into two stages. The first is the acid condensation to form mono-, di- and trimethylolures (tetramethylolurea has never been isolated). This stage of the process is known as methylolation. The reaction at this point is speeded up by the use of elevated temperatures (in the order of 90-95°C). The methylolation reaction is exothermic and temperatures increase up to about 80°C without the necessity to add any further heat.

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O}^+ & \rightarrow \text{HCO}^+ \text{OH} + \text{H}_2\text{O} \\
\text{formaldehyde} & \quad \text{Carbenium ion} \\
\text{HCO}^+ \text{OH} + \text{H}_2\text{N}^+ \text{C}^- \text{NH}_2 & \rightarrow \text{HCO}^- \text{NH}^+ \text{C}^- \text{NH}_2 + \text{H}^+
\end{align*}
\]

So in short

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{N}^+ \text{C}^- \text{NH}_2 & \rightarrow \text{HCO}^- \text{NH}^+ \text{C}^- \text{NH}_2 \\
\text{formaldehyde} & \quad \text{urea} \\
\text{Monomethylolurea}
\end{align*}
\]

Further reaction at this point produces di- and trimethylolurea.

\[
\begin{align*}
\text{HCO}^- \text{NH}^+ \text{C}^- \text{NH}_2 + \text{HCHO} & \rightarrow \text{HCO}^- \text{NH}^+ \text{C}^- \text{NH}_2 \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{Dimethylolurea} & \quad \text{Monomethylolurea} \\
\text{formaldehyde} & \quad \text{urea}
\end{align*}
\]

\[
\begin{align*}
\text{HCO}^- \text{NH}^+ \text{C}^- \text{NH}_2 \text{CH}_2 + \text{HCHO} & \rightarrow \text{HCO}^- \text{N}^+ \text{C}^- \text{NH}^- \text{CH}_2 \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{Trimethylolurea} & \quad \text{Dimethylolurea} \\
\text{formaldehyde} & \quad \text{Monomethylolurea}
\end{align*}
\]

Etc.

When the exotherm subsides (usually after 15-30 minutes), the methylol compounds have formed, and the reaction is completed under reflux by adding a trace of acid to decrease the pH to the polymer-building stage (pH 5.0 to 5.3).
The rate of this reaction is directly proportional to the concentration of hydrogen ions (in other words, the more acid the reaction mixture, the faster the reaction proceeds).

The rate of reaction in the methylation step (1:1 formaldehyde/urea molar ratio) is 3 times faster than the condensation step (2:1 molar ratio). As can be seen below, the rate of the condensation reaction increases both with temperature and pH.
Acid is not used directly in the process but rather it is created by the reaction of formaldehyde and ammonium sulphate as follows:

\[ 6 \text{H}_2\text{C}=\text{O} + 2(\text{NH}_4)_2\text{SO}_4 \rightleftharpoons 2\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \]

\[ \text{Hexamethylenetetramine} \]

When the acid is added, the second stage of the resin reaction, which is known as condensation (due to release of water), begins.

As soon as the right viscosity is reached, the pH is increased to stop polymers building and the resin solution is cooled to about 50°C. More urea (called second urea) is added to consume the excess of formaldehyde, until the molar ratio or formaldehyde to urea is in the order of 1.1:1. Depending on the resin type, excess water elimination may be necessary and the resin may be subject to vacuum distillation to achieve the final solids of 63-66%. Increasing second or further urea additions tends to improve bond quality, especially at low formaldehyde/urea ratios (as the formaldehyde is not fully reacted into the polymer and is available for bonding?).

After production, the resin will have a reasonably wide molecular weight distribution with the monomer still being the predominant single species and the various increasing molecular weight branches being present to greater or lesser degrees (see Figure 1 below).
Figure 1: GPC analysis of typical UF resin. DMSO is the solvent used.
**Introduction to Melamine-Urea-Formaldehyde Resins**

Melamine-Formaldehyde (MF) and Melamine-Urea-Formaldehyde (mUF and MUF) resins are among the most used adhesives for exterior and semiexterior wood panels and for the preparation and bonding of both low- and high-pressure paper laminates and overlays. Their much higher resistance to water attack (greater when more melamine) is their main distinguishing characteristic from urea-formaldehyde (UF) resins. Melamine is an expensive raw material so its use is controlled as much as possible and it tends to only be added where there is a proven need in the application.

The condensation reaction of melamine with formaldehyde is similar to but different from the reaction of formaldehyde with urea. As for urea, formaldehyde first attacks the amino groups of melamine, forming methylol compounds. However, formaldehyde addition to melamine occurs more easily and completely than does addition to urea. The amino group in melamine accepts up to two molecules of formaldehyde. Thus complete methylolation of melamine is possible, which is not the case with urea. Up to six molecules of formaldehyde are attached to a molecule of melamine.

For MF resins:

![Chemical structure of MF resins](image1.png)

And for MUF resins:

![Chemical structure of MUF resins](image2.png)

In final curing, melamine based resins tend to form less methylene bridges than UF resins and so liberate considerably less formaldehyde than UF resins at this stage.
Due to the heavily cross-linked structure which results when they cure completely, MF resins have a characteristic rigidity and brittleness. When these resins are used for impregnated paper overlays, small amounts of modifying compound, typically 3-5%, are often co-polymerised with the MF resin during its preparation to give better flexibility to the finished product. Caprolactam would have been used in Cork for this purpose. Diethylene Glycol is also used for this purpose.

MF (and MUF) adhesive resins for plywood and particleboard must be prepared to quite different characteristics than those for paper impregnation. The latter must have lower viscosity but still high resin solids content because they need to penetrate the paper substrate to a high resin load, to be dried without losing adhesive capability, and only later to be able to bond strongly to a substrate. MUF resins for board applications are generally more condensed, to obtain lower penetrability of the wood substrate (otherwise some of the adhesive is lost by overpenetration into the substrate).