Bio-based 5-HMF as an economically and ecologically interesting substitute in formaldehyde resins

The formaldehyde-based resin manufacturing industry is facing a growing challenge. Formaldehyde, a carcinogen which also has further adverse effects on human health, is increasingly encountering public and political criticism. Similarly, the use of petro-based phenol for producing PF (Phenol-Formaldehyde) resins has also led to an intensified search for more sustainable, bio-based alternatives for this sector.

On 6 June 2014, the EU published the 6th Adaptation to Technical and Scientific Progress of the CLP (Classification, Labelling and Packaging) Regulation in the Official Journal. The classification of formaldehyde in this Adaptation as carcinogenic and mutagenic has far-reaching and, in part, immediate consequences for businesses. The Commission Regulation (EU) 605/2014 amends the Commission Regulation (EU) 1272/2008 with respect to the classification, labelling and packaging of substances and mixtures (CLP Regulation), for the purpose of adaptation to technical and scientific progress. Amongst other things, the list of hazardous substances in Annexe VI of the CLP Regulation was amended. Of greatest relevance to many businesses is the new categorisation of formaldehyde as carcinogenic (Category 1B) and mutagenic (Category 2), and the future requirement to label it as such.

The new substance classification and labelling requirements generally apply from 1 April 2015. Substances which were classified, labelled and packaged as well as marketed before 1 December 2014, must only be re-labelled and re-packaged by 1 December 2016. The new labelling and packaging requirements only apply to mixtures from 1 June 2017. For other areas of law, the amended Regulation, which comes into force on the twentieth day following its publication in the Official Journal on 6 June 2014, that is on 26 June 2014, will have immediate and far-reaching consequences, which also affect the use of formaldehyde.
The key issues include, amongst others:

- health and safety protection for workers in industry, trades and commerce via the Carcinogens Directive (in Germany, implemented by the GefStV or Hazardous Substances Act)
- production safety via the Production Safety Directive, which requires that products should not pose any dangers (in Germany, implemented by the ProdSG or Law Concerning the Supply of Products to the Market)
- plant construction law via the TA Luft or Federal Air Pollution Control Act and the 31st BImSchV or Federal Emissions Control Act, in particular for numerous thermic processes (combustion plants, engines, biogas usage, drying processes)
- specific legislation relating to construction products, cosmetics, fuels (E 10), toys, consumer goods which come into contact with foodstuffs, textiles, all with implications for the domestic market, as well as for construction law including tenancy law
- guidelines for the award of environmental certification such as the German Blue Angel
- adaptation of numerous safety data sheets, product information requirements in accordance with Art. 33 of the REACH Regulation
- prohibitions on putting into circulation or using for substances and mixtures in accordance with Annexe XVII, no. 28 - 30 REACH Regulation

In addition, the corresponding classification of formaldehyde in Annexe VI of the CLP Regulation will, in the medium term, lead to its inclusion in Annexe XIV of the REACH Regulation, which will mean that use of the substance will require prior permission.

5-HMF as a substitute for formaldehyde

5-hydroxymethylfurfural (5-HMF) is being researched as a possible substitute for formaldehyde in a range of studies on the synthesis of phenolic resins (PF), melamine resins (MF) and urea resins (UF). The aim of all these studies is to partially or fully replace formaldehyde in the relevant materials, in order to reduce or entirely eliminate the continuous release of formaldehyde. Although the majority of the formaldehyde is used up during production of the relevant resin (by reaction with urea, melamine or phenol), a certain proportion still remains in the end product and can therefore still be slowly out-gassed. Formaldehyde is also out-gassed by the end product during slow hydrolysis of the relevant resin. Partially replacing formaldehyde with 5-HMF in these products can in part drastically reduce the release of formaldehyde by means of cross-linking. Full replacement with 5-HMF would naturally lead to no more formaldehyde emissions.

Urea resins are thermosetting plastics from the amino plastics group. They are manufactured by poly-condensation of urea and formaldehyde. They are mostly processed together with fillers (e.g. wood flour, short-fibre α-cellulose and textile fibres) into white moulding compounds which are light-fast, odour- and tasteless and which are barely affected by ether, alcohol, petrol, aromatic hydrocarbons, esters and chlorinated hydrocarbons. Urea moulding compounds are used above all for light-coloured moulded parts in electrical, radio and television technology, for furniture fittings, and also for the manufacture of kitchen equipment and other consumer articles. However, such products
are not as water- and temperature-resistant as products made from phenoplastics and melamine resins; in addition, the subsequent release of formaldehyde from the finished product is problematic.

Condensation products made from urea resin and formaldehyde have achieved major importance as glue components for the particle board industry (HF-glue). Non-elastic urea resin foams are manufactured on larger scales e.g. for thermal insulation. A urea-formaldehyde solution is introduced into a foam produced by the vigorous agitation of water and emulsifier and polycondensated in this form. They are also used in the area of textile auxiliary agents. For example, crease-resistant fabrics, fabric stiffeners and the satin finishes for artificial silk are manufactured by impregnating these materials with a watery solution of urea resin and then subsequently hardening them. The condensation of urea with formaldehyde in the presence of alcohols, e.g. butanol, leads to exceptional coating resins with a high gloss and good scratch- and water-resistance, which are compatible to a good degree with cellulose nitrate and alkyd resins and are used in particular for solvent-resistant, non-yellowing baking varnish. Urea and formaldehyde condensation products are also employed for soil improvement, in particular for high-value cultures in greenhouses. Approximately 100 million tonnes of urea resin are produced annually.

Melamine resin or melamine-formaldehyde is likewise a thermosetting plastic material composed of melamine and formaldehyde, which is manufactured by polymerisation. Melamine resin is the main component in high-pressure laminates and laminate flooring. Melamine resin wall tile sections can also be used as panels. Melamine-formaldehyde is also employed in plastic laminates and overlay materials. Formaldehyde is more tightly bound in MF than in urea-formaldehyde, thus emissions are lower.

Phenol-formaldehyde resins (PF) are obtained through the reaction of phenol or substituted phenol with formaldehyde. The so-called novolacs obtained via acid condensation are mainly used for the purposes of varnishing and waterproofing, for the manufacture of floor coverings and, in combination with fillers and hexamethylenetetramine, as hardening agents for moulding compounds. The phenolic resins obtained via alkaline condensation are used to a limited extent as casting resins and synthetic resins. Resin in the resol stage is poured into forms and hardened by slow warming into translucent or, with certain additives, dramatically coloured objects, e.g. handles. In order to improve its mechanical qualities, the majority of phenolic resin is processed together with up to 50 % fillers, such as cotton, cellulose, stone marl, sawdust, magnesium oxide and magnesium stearate. Resols or resitols are pressed together with fillers to produce finished parts, such as buttons, holders, handles, radio and camera housings or to produce semi-finished products, such as panels, profiles or blocks, which can subsequently be mechanically finished. Wood panels and lengths of fabric and paper are turned into exceptionally resistant laminates by the addition of resitol as a binding agent.

Bio-based 5-HMF is an economically interesting and highly promising substitute for formaldehyde in PF resins and its numerous applications.
About AVA Biochem

Swiss-based AVA Biochem is the global leader in the industrial production of bio-based platform chemical 5-Hydroxymethylfurfural (5-HMF, CAS 67-47-0). AVA Biochem developed, patented and piloted a breakthrough Hydro Thermal Processing technology (HTP) for the conversion of fructose to 5-HMF. This efficient, robust, water based and scalable process offers the best economic yield of 5-HMF.

5-Hydroxymethylfurfural derived from sugars is the link between biomass and furan-based chemicals. With its various functional groups and associated reaction sites, this small molecule opens the door to a wide range of chemical modifications, which makes 5-HMF a versatile renewable building block.

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