LIFE / FIT FOR REACH

Substitution of formaldehyde in wood adhesives

This case study aims to illustrate a chemical substitution process. It is based on publicly available information on company's experience as well as on substance hazards, alternatives to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1. Case description

Formaldehyde is dangerous to human health. Production of wood adhesives used to make plywood is a dominant end use for this chemical. Comprehensive studies have been done on substitution and alternatives that have been applied successfuly do exist (E.g. Soy-based resin).

Formaldehyde's readiness to polymerize makes it ideal for the production of resins that are durable, even in wet environments. Plywood that is "exterior-grade" or needs to withstand wet conditions is usually made with the dark red phenolformaldehyde resin. Hardwood plywood, often used for making furniture and cabinetry, is made with less expensive and higher-emitting ureaformaldehyde resins.

1.1 Hazards of Formaldehyde

Formaldehyde has the following hazards according to C&L Inventory:

- Acute Toxicity 3; by ingestion, skin contact and inhalation.
- Skin Corrosion 1B; severe skin burn and eye damage.
- Skin Sensitisation 1; allergic skin reaction.
- Mutagenic 2; suspected of causing genetic defects.
- Carcinogenic 1B; may cause cancer.


Skin Corrosion 1B


Carcinogenic 1B
Mutagenic 2
Skin Sensitisation 1


Acute Toxicity 3

Because formaldehyde is highly reactive, water soluble and rapidly metabolized, people may experience its toxic, irritating and sensitizing effects at the site of contact, such as the upper respiratory tract, the eyes and the skin.

1.2 Regulatory status

REACH status: Formaldehyde is in the CoRAP list of ECHA and has been evaluated for chemical safety assessment, undertaken as part of the REACH registration process and Registered under REACH. In EU there is no common defined OEL (Occupational Exposure Limit) yet. But in 2008 the European Union Scientific Committee on Occupational Exposure Limit Values (SCOEL) proposed an eight hour exposure limit of 0.2 ppm and short term exposure limit (STEL) of 0.4 ppm. According to the harmonised European standard EN 13986 (2008) for wood-based panels, formaldehyde emission limit for plywood is 0.1 ppm.

There are STEL values set by EU member states individually for each state. In the UK, STEL value for 8 hour exposure period is 2 ppm. In France, this value is 1 ppm.

2 Substitution process

2.1 Substitution incentives

Company decided to substitute formaldehyde in their Hardwood Plywood adhesives due to concerns from consumers and workers. Chief executive of the company decided to improve the public image of the products and decrease the health risk by substitution.

2.2 The substitution project

2.2.1 Initial research and orientation in the field

The initial research quickly revealed that there are formaldehyde-free alternatives already available and in use. The company had no previous experience in substitution, hence searched for help on the internet. This search came up with an alternatives assessment framework, which they decided to implement. The framework included economic, technical performance, human health hazard, environmental hazard assessments.

2.2.2 Identification of alternatives

The company found out that "soy-based resin mixed with polyamide-epichlorohydrin (PAE) resin" and "Polyvinyl acrylate (PVA)" are two possible chemical alternatives. Company gathered data for the assessment of each alternative with a help of standard methods defined by regulation. The results are as follows:

Tabel 1. Hazard characteristics of soy-based resin, epichlorohydrin (component of PAE) and PVA

	Soy based resin	**Epichlorohydrin (CAS 106-89-8)**	**PVA (CAS 9003-20-7)**
Highly toxic	No	Acute tox. 3: H331, H311, H301	No
Skin/Eye irritation	Slightly toxic in case of skin/eye contact	Skin Corr. 1B	May cause irritation in respiratory tract and eyes
Carcinogenicity	Not listed in CLP, IARC	Cat. 2A, Carc. 1B	Not listed in IARC, CLP and ESIS

	or ESIS		
Mutagenicity	Not listed	No data	Not listed
Reprotoxicity	Not listed	No	Not listed
Endocrine disruption	Not listed	Cat. 1	Not listed
Respiratory/skin sensitization	Not listed	Skin sens. 1	Not listed
Neurotoxicity	Not listed	Not listed	Not listed
Aquatic toxicity	No	No data in CLP. Toxicity to aquatic organisms in other sources	No
Bioaccumulation	No	Uncertain. Bio-concentration in aquatic organisms is low	No
Persistence	No	No	Not biodegradable
Greenhouse gas formation potential	Not listed	Not listed	Not listed
Ozone depletion potential	Not listed	Not listed	Not listed

Data Sources: European Commission, CLP, ESIS, OECD, SIN list, Vela et al. 2003, Kyoto Protocol Annex A, Montreal protocol, ECHA registered substances, SDSC, IARC, EU Endocrine disruptor database, SIGMA Aldrich safety data sheet, Environment Canada, EU EDC DB, Toxnet/HSDB, U.S. EPA.

The company searched for a supplier and obtained Safety Data Sheets for components of the two products.

1) Soy-based resin product is comprised of soy flour "blended with a very small amount of proprietary resin". Using it a "soy-based plywood" is made by glueing sheets of hardwood together with the resin product. The company found out that polyamide-epichlorohydrin (PAE) included in this resin is hazardous, however, material safety data sheet (MSDS) of this proprietary resin reports no hazardous

ingredients. The manufacturer of the soy-based resin reports that the addition to and mixing of the PAE with the soy flour is a closed process and that manufacturing workers do not have contact with the PAE or the mixed PAE-soy resin.

The company recognizes the need to think about the chemicals used in the production of the product components as well, and not only focus on the product itself. The understands that it is important to consider that the PAE chemical is manufactured with epichlorohydrin, which is hazardous to human health and a probable human and confirmed animal carcinogen. According to the manufacturer and the national authorities, epichlorohydrin is completely consumed in the batch manufacturing process used to make the resin. There are no emissions from this process and no residual or "free" epichlorohydrin remain in the PAE, where it is irreversibly transformed in the polymer matrix. Because of this, there is apparently no potential for worker, consumer or environmental exposure to epichlorohydrin during the hardwood plywood manufacture, use or disposal.

2) Having reasearched the second alternative - PVA, the company recognised that the persistence of PVA in the environment due to its non biodegradable nature is a concern.

After gathering the information from environmental, economic and performance assessments, the company prepared the following comparison table to help with the decision:

	Bioresins	**PVA**
Health aspects	PROS: no hazardous substances (tannins, lignins) CONS: bioresins contains Epichlorohydrin (Classified by IARC group 2A). According to US EPA (1984) it is completely consumed in the batch manufacturing process used to make the resin. Other bioresins intended for industrial production contains also small amount of dangerous substances.	CONS: some PVA glues include an isocyanate catalyst (isocyanates are sensitisers and can cause asthma and dermatitis)
Environmental aspects	PROS: readily biodegradable; natural product	CONS: No information
Performance aspects	PROS: performance aspects similar to formaldehyde-based plywood CONS: most of the bioresins are still in the stage of development	PROS: excellent performance characteristics for interior (TURI, 2006) CONS: PVA is not

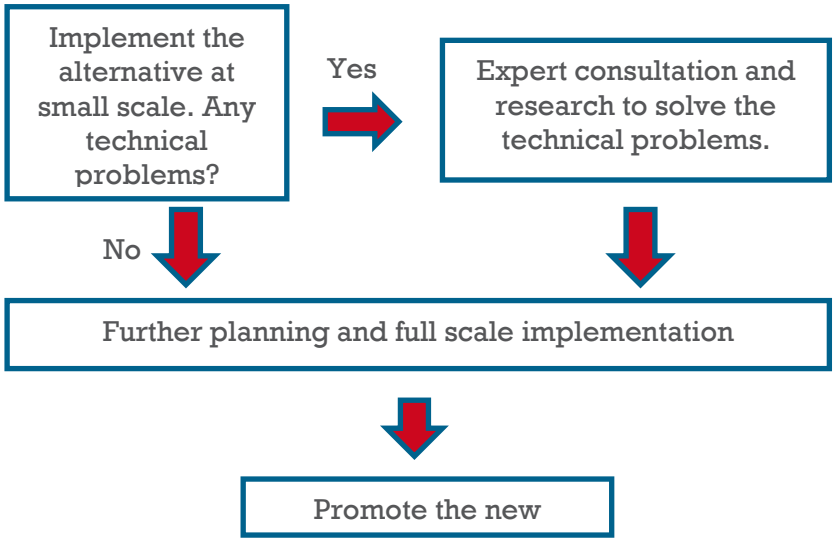
		waterresistant and can substitute Formaldehyde only in a small range (cabinetry)
Cost aspects	PROS: currently available at a similar cost to formaldehyde-based plywood	No information

2.3 Selected alternative and justification

The company decided to proceed with the soy-based alternative for their water tolerant hardwood plywood product.

2.4 Implementation

Implementation plan



State of play

Small scale implementation revealed that some minor adjustments should be done for the machinery to optimise the process. The company has managed to manufacture a product that has the desired properties as revealed by technical performance tests in wet conditions under load bearings.

2.5 Communication of substitution

Company promoted its product as a formaldehyde-free hardwood plywood.

2.6 Costs and savings

The costs of research, testing and small scale implementation phase is expected to pay off. The company predicts an increased demand after the promotion of the formaldehyde-free plywood.

2.7 Evaluation

Overall, the substitution has been successful.

3 References

APA- The Engineered Wood Association. 2016. *EN 13986 : 2004 +A1:2015. Wood-based panels for use in construction – Characteristics, evaluation of conformity and marking.* Available at: *http://apawood-europe.org/official-guidelines/european-standards/individual-standards/en-13986/ (viewed in September 2016).*

Cayman Chemical Company. 2012. Safety Data Sheet. *Formaldehyde Assay Standard.* Available at: https://www.caymanchem.com/msdss/700384m.pdf (viewed in September 2016).

CHIMAR. 2008. *Update on the formaldehyde release from wood-based panels.* Available at: http://www.chimarhellas.com/wp-content/uploads/2008/07/formaldehyde_2008.pdf (viewed in September 2016).

ECHA.2008. *Recommendation from the Scientific Committee on Occupational Exposure Limits for Formaldehyde*. Available at: http://ec.europa.eu/social/BlobServlet?docId=3863&langId=en (viewed in September 2016).

ECHA. 2016. *Formaldehyde*. Available at: http://echa.europa.eu/en/registration-dossier/-/registered-dossier/15858 (viewed in September 2016).

ECHA. 2016. *Substance information. Formaldehyde*. Available at: http://echa.europa.eu/en/substance-information/-/substanceinfo/100.000.002 (viewed in September 2016).

Health and Safety Executive. 2011. *EH40/2005 Workplace exposure limits*. Available at: http://www.hse.gov.uk/pUbns/priced/eh40.pdf

J. M. Loveridge Ltd. 2002. *Formaldehyde safety data sheet*. Available at: http://www.jmloveridge.com/cosh/Formaldehyde.pdf (viewed in September 2016).

OSHA, United States Department of Labor. 2016. *Toxic and Hazardous Substances. Formaldehyde.* Available at: https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=10075&p_table=STANDARDS (viewed in September 2016).

Spectrum Chemical MFG Corp. 2012. *Material Safety Data Sheet. Polyvinyl Acetate*. Available at: https://www.spectrumchemical.com/MSDS/ZQ446.pdf (viewed in September 2016).

SUBSPORT. 2013. *SUBSPORT Specific Substances. Alternative Assessment – Formaldehyde*. Available at: http://www.subsport.eu/wp-content/uploads/data/formaldehyde.pdf (viewed in September 2016).

TURI, University of Massachusetts Lowell. 2006. *Five Chemicals Alternatives Assessment Study*. Available at: http://www.turi.org/TURI_Publications/TURI_Methods_Policy_Reports/Five_Chemicals_Alternatives_Assessment_Study._2006/Full_Report (viewed in September 2016).

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