A Ranking System for the Health Risks of Epoxy Products

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Introduction

Epoxy products are widely applied in the construction industry. They have excellent adhesive characteristics on various surfaces, they are resistant to most chemicals and they do not rot. Contrary to reactive polyesters and acrylates, epoxy's hardly shrink after application. These qualities make the use of epoxy's extremely popular. Technically speaking however, epoxy's also have disadvantages. Especially the discolourisation under the influence of sunlight can be disadvantageous in certain applications.

Some applications of epoxy's are:
- rehabilitation of rotten wood, by removing deteriorated parts and replacement by epoxy mass
- repair of affected concrete, in a comparable way
- chemically resistant floor finishing
- reinforcement of cement based floor finishing to achieve a higher mechanical resistance
- rust prevention coating on metal
- as an adhesive in many applications, varying from anchors for concrete to restoration activities

In most cases, epoxy's consist of two components, a resin and a hardener. The resin consists of a polycondensation product of epichlorohydrine and bisphenol. The hardener is an amine.
Sometimes there is a third component, for instance in thick epoxy floor finishing layers. Generally, this third component is a filler.

Fully hardened epoxy products are inert and after hardening, little or no harm to health is to be expected. However, the individual components and products that are not fully hardened can be harmful to health. The resin, based on bisphenol A or bisphenol F, or mixtures of these two, is a skin aller-

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gen. Hardeners consists of amines that can affect the skin. The legal classification varies from 'irritating' to 'corrosive'. Furthermore, many hardeners are skin allergens. In practice, about one out of every five epoxy workers develops a skin allergy. This can be so serious, that they have to leave the profession and a profession without exposure to epoxy's must be chosen instead.
Furthermore, free epichlorohydrine can remain in the resin after production of the resin. Epichlorohydrine is a carcinogen. The content of free epichlorohydrine can be reduced to less than 3 parts per million (ppm) through optimisation of the production process.
Certain amines are also carcinogens. Aromatic amines are still applied, especially with concrete injection.
The allergenicity of epoxy products can be reduced by applying larger molecules. Prereacted products or prepolymers are then applied. In the hardener a higher molecular weight amine can be chosen, or a polyamino amide. However, disadvantages are a higher viscosity on application and a slower hardening. Above certain molecular weights, no hardening occurs at room temperature. This does not mean a necessary disadvantage in industrial situations, when products can be heated. But in the construction industry hardening at room temperature is indispensable.
The wide range of required characteristics makes that especially among hardeners there is a large choice. The composition of the resin is less variable, this is an oligomer of bisphenol A or bisphenol F with epichlorohydrine. In general the molecular weight is below 700.

Ranking of epoxy's

In conclusion, the harmfulness of epoxy's varies strongly, and depends among other things on the desired characteristics. This offers the possibility to classify epoxy's according to their harmfulness. In general, this type of classification has two objectives:
- to inform the user about the harmfulness of epoxy's with comparable applications,
- to stimulate investigation into less harmful products.

An ideal classification system should be based on information that is easily accessible, should not be too complex, should be controllable and, above all should be discriminating.
Preferably, for each type of application, there should be products available in more than one class. The system should stimulate improvement of products, in order to create a dynamic situation.
For the reason of accessibility of information, most existing classification systems are based on the information provided in the Material Safety Data Sheet (MSDS). This has some major advantages:
- a MSDS must be set up for all epoxy products, so that the information is accessible without further procedures
- the information must be delivered according to a standard format, so that it can be found quickly and simply
- the information is composed in accordance with legal criteria, so it should be uniform for all types of products.

There are also some major disadvantages:
- only relatively large quantities, sometimes 20%, of the individual components must be specified. This disadvantage will disappear when the new Preparations Directive will come into force
- the MSDS is based on a 'hazard' approach. Components are classified regardless of the chance of exposure.
- We have explored the possibilities for an alternative classification system, that not only takes the hazard, but also the chance of exposure into consideration. But the prerequisite that information must be easily accessible, remains.

Basis of the classification system

Because not only the hazard but also the chance of exposure is taken into consideration, the system is based on a relatively large amount of criteria. The criteria consist of two major groups:
- toxicity data, as a measure for the hazard. These data can be found on the MSDS
- physical-chemical data, as a measure for the chance of exposure. These can partly be found on the MSDS, partly in handbooks.

Each criterion leads to the assignment of penalty points to the product. The more penalty points, the more harmful the product is. The total amount of penalty points leads to classification into a limited number of classes. The criteria are mentioned in Table 1.
The system is inspired on, but not equal to, the system that is in use in Germany to rank the harmfulness of substances and preparations for the water ecosystem, the so-called 'Wassergefährdungsklasse'. This system also works with penalty points per substance.
During the development of the classification system, there have been five meetings with the suppliers in which an intensive exchange of information and points of view has taken place.

Generally, the amount of free epichlorohydrine is not specified on the MSDS. The concentration is below the legal limit

Table 1: criteria for attribution of penalty points to epoxy products on the basis of individual components

1. amount of free epichlorohydrine in the resin and in the reactive diluent
2. presence of components with a T or T^+ symbol
3. presence of components that are carcinogenic, mutagenic, reprotoxic, or sensitisers for the respiratory tract (based on R-phrases)
4. presence of hardeners with R43, R34 or R 35
5. amount of reactive diluent in the resin
6. amount of VOC (volatile organic compounds)
7. lack of product information
8. boiling point of the amines in the hardener
9. boiling point of reactive diluents
10. molecular weight of the amines in the hardener
11. molecular weight of reactive diluents
12. amount of free amine in the hardener.

for specification. The members of the Association of Plastic Manufacturers in Europe (APME) have agreed upon a concentration limit of 5 ppm in unmodified resins and of 20 ppm in reactive diluents.

For the looking up of physical constants, the identity of the substance must be known. It will be impossible to find these when the information on the MSDS is limited to the specification of substance groups.
The classification with the corresponding penalty points is presented in Table 2

Results of a test-classification

It is important that the classification system discriminates *within* groups of products. When for instance all putties come into a certain category and all coatings come into another, we can find out whether putties or coatings are more harmful. But within these groups of products it is impossible to discriminate.
As a test, we have performed the classification of a group of epoxy coatings. We have retrieved the data of 17 coatings from six suppliers. These coatings were solvent-based, solvent

Table 2: Summary of criteria and corresponding penalty points.

Criterion	Specification	Penalty points
1.Amount of free epichlorohydrine in resin and/or reactive diluent	• [ECH] > APME- limit	25
	[ECH] unknown	25
2. Presence of substances with symbol T or T^+	• *Per* component with T^+ > 0,1%	10
	• *Per* component with T > 1%	10
	• *Per* component with T^+ > 1%	20
3. Presence of carcinogenic, mutagenic, respiratory tract-sensitising and reprotoxic compounds	• *Per* compound with one ore more of the R-phrases: 39,45,46,48,49,60, 61 > 0,1%, or 40, 42, 62, 63, 64 > 1%	10
4. Presence of corrosive and/or sensitising hardener components	• Hardener component(s) with R34, 35 of 43	15
5. Amount of sensitising reactive diluent in the resin	• *Per* reactive diluent in the amount of:	
	o < 2,5%	2
	o 2,5-10%	5
	o 10-25%	10
	o > 25%	15
6. Amount of Volatile Organic Compounds	• > 100 g/l for metal coatings	10
	• > 60 g/l for other epoxy products	10
7. Lack of product information	• Classification not possible due to lack of information	150*
8. Boiling point of the hardener(s)	• *Per* hardener (amine) with a boiling point < 250°C	5
9. Boiling point of the reactive diluent(s)	• *Per* reactive diluent with boiling point <250°C	5
10. Molecular weight of the hardener(s)	• *Per* hardener with molecular weight:	
	o < 200	10
	o 200-400	5
	o > 400	0
11. Molecular weight of the reactive diluent(s)	• *Per* reactive diluent with molecular weight:	
	o < 200	10
	o 200-300	5
	o > 300	0
12. Amount of free amine in the hardener	• *Per* free amine in an amount of:	
	o < 2,5%	2
	o 2,5-10%	5
	o 10-25%	10
	o > 25%	15

** About the maximum number of penalty points*

Table 3: Results of the test classification of epoxy coatings.

Nr.	Type	Penalty Points	Penalty Points without lack of information on amount of ECH	Remarks
1	Water based	45	20	
2	Solvent free	70	45	
3	Solvent based	95	70	
4	Solvent free	240	215	Addition of 150 pts. due to lack of information about reactive diluents
5	Solvent based	85	60	
6	Water based	175	150	Addition of 150 pts. due to lack of information about reactive diluents
7	Water based	175	150	Addition of 150 pts. due to lack of information about reactive diluents
8	Water based	100	75	
9	Solvent free	80	55	
10	Water based	185	160	Addition of 150 pts. due to lack of information about reactive diluents
11	Solvent free	245	220	Addition of 150 pts. due to lack of information about reactive diluents
12	Water based	55	30	-
13	Solvent free	115	90	-
14	Water based	77	77	-
15	Water based	52	52	-
16	Solvent free	100	100	Diluent with R42 (allergen to resp. tract)
17	Solvent free	80	80	-

free and water based coatings. The results of the test are summarized in Table 3.

Not all suppliers delivered the full set of data, not even after a reminder. For five products, the identity of the reactive diluents was unknown. For 13 products, information about the amount of free epichlorohydrine was missing. At this moment we assume that the raw material suppliers will be able to provide the data about the amount of free epichlorohydrine. In the discussion we assume that all products meet the APME-criteria.
Eight products were water based. The total amount of penalty points varied from 20 to 160. In three cases, 150 penalty points were added due to lack of information about the reactive diluents. When those products are not taken into consideration, there are five water based coatings with 20 to 77 penalty points.
Seven products were solvent-free, the amount of penalty points varied from 45 to 220. In two cases the identity of the reactive diluents was missing, so we also added 150 penalty points., Without those two products, five products remained with penalty points varying between 45 to 100 points.
Finally, two products were solvent based. The number of penalty points amounted to 60 and 70.

The system appears to be well discriminating. The amount of penalty points varied from 20 to 100.
Notably, not one group of products is better than another . The range of penalty points is lower for water based coatings than for solvent based and solvent free coatings, but two water based coatings score more penalty points than solvent based coatings. And, there are also two solvent free coatings that score lower than the water based coatings with the highest amount of penalty points.

Although the system discriminates, this does not mean that it discriminates in the right way. To conclude, we need a more thorough investigation into the field of application of the different coatings.

Division into classes

The discussion about division into different classes can become obscured by political motives. It is tempting of course for a supplier to propose a limit in the classification so that his product ends up into a favourable class, or that of a competitor into an unfavourable one. For instance: a limit of 25 or 30 points can be favourable for one supplier and very unfavourable for another supplier. Therefore, we agreed with the suppliers to classify a larger sample of products and to add other products than coatings. The limit for the best 20% will then become class one, between 21 and 40% is class two, and so on until class 5. This division is of course very arbitrary, because there is no clear rationale behind these limits. However, it is impossible to draw limits on the basis of health effects, because there is such a large amount of parameters under consideration. Moreover, some parameters are only indirectly related to health effects. And for the moment, there is no allergen-free epoxy product. As a matter of fact, one can doubt whether there will ever be one. Hence, we would say that the division is arbitrary, but pragmatic.
The results of ranking the twelve epoxy coatings into four classes are presented in Table 4.

The first two classes include about 25 points, the other two about 20. Water based coatings show up in the first two classes, solvent free products in all classes except class 3. We just have two solvent based products, which is insufficient to draw conclusions.

Table 4 division of products into classes based on equal size of the groups

Class	Points	Type (W = water based, F = solvent free, S = solvent based)
1	20 – 46	2W, 1F
2	46 – 69	1W, 1F, 1S
3	70 – 79	2W, 1S
4	79 - 100	3F

Conclusions

A first test with the classification system shows that within the group of coatings the system discriminates well. The amount of attributed penalty points ranges from 20 to 100, which is a factor of five difference. There is also discrimination within the various types of coatings, for water based coatings the difference is a factor of almost four and for solvent free coatings a factor of more than two.
The system offers sufficient room for variation by varying the amount of penalty points per property. Should we for instance want to give more weight to allergenic properties of a compound, then the amount of penalty points for the amount of sensitising components can be raised.
The fact that it is not easy to obtain all information from the suppliers can be considered a problem. This originates in part from the fact that formulators must get their information from the suppliers of raw material. This pertains for instance to the amount of free epichlorohydrine in the resin. A more international approach would therefore help tremendously.