Guidance for the User Industry on the Environmental Hazard Labelling of Dyestuffs

This guidance is a simplified user manual referring in particular to dyes and is not legally binding.

ECOLOGICAL AND TOXICOLOGICAL ASSOCIATION OF DYES AND ORGANIC PIGMENTS MANUFACTURERS
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1. PURPOSE OF THE GUIDANCE DOCUMENT

This guidance is designed to assist those persons responsible for environmental safety with respect to the use of dyes in the leather, paper, and textile industries. In addition to the existing physical and health hazards the revised Preparations Directive makes the classification and labelling requirement “dangerous for the environment” applicable to dye preparations.

The information provided in this document should enable the plant manager to understand the concept of this new piece of legislation and to take the necessary measures to use dyes in a responsible way, i.e. to ensure that the application process does not present an unjustifiable risk to the environment (see also ETAD Information Notice No.4).

2. GENERAL INTRODUCTION

A fundamental aspect of EU chemical control legislation is the hazard assessment of dangerous substances and preparations. This leads to testing requirements (for the notification of new substances) and classification criteria which should enable harmonised labelling and the issue of adequate Safety Data Sheets. Labelling and Safety Data Sheets form the basis of hazard communication and they provide advice on appropriate exposure controls for the safe handling of chemicals. Hazard and exposure are the integral parts of Risk Assessment. Correct evaluation and the control of risks arising from the use of chemicals can only be achieved by performing a risk assessment. This guidance document illustrates how preparations of dyestuffs are classified in terms of environmental hazards which form the basis of pollution prevention.

3. LEGISLATION BACKGROUND

Hazard Assessment is a prerequisite for the classification and labelling of substances and preparations. In the case of new substances, a base set of data must be submitted as a notification to the authorities of an EU member state. Hazard classification criteria, labelling and packaging requirements are laid down in the “Dangerous Substances Directive” as last amended by the 7th Amendment (92/32/EEC) and in the “Dangerous Preparations Directive” (99/45/EC). The evaluation and control of risks from existing substances is covered by the “Restrictions on the Marketing and Use of certain Dangerous Substances and Preparations” (76/769/EEC). The most stringent laws on risk management are those which prohibit or severely restrict the use of certain products. In the EU it is the Council Directive (76/769/EEC) which prescribes such risk reduction measures.

3.1 The new hazard label

Hazard classifications for substances are officially determined and listed by the Commission of the European Communities in Annex I of Directive 67/548/EEC. Preparations are mixtures of substances. Dangerous preparations must also be classified and labelled.

Manufacturers and suppliers are required by law to classify and label hazardous substances.

The classification of hazardous substances is based on the available data.

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“Restrictions on the marketing and use of certain dangerous Substances and Preparations” prescribes such risk reduction measures.
The classification and labelling of hazardous preparations is based on either available data, component (i.e. substance) data or the % proportion of hazardous substances contained in the preparation.

The hazard classification “dangerous for the environment” has been in use for some time in the case of substances. Due to the revision of the EU Dangerous Substances Directive the hazard classification “dangerous for the environment” has now been extended to include preparations. Preparations are preparations and for the first time they must be labelled for supply if they are “dangerous for the environment”. In order to carry out a hazard assessment, data must be generated. The absence of hazard labelling cannot be taken to mean that a product is not hazardous. It may mean that the required data are not available.

ETAD member companies in complying with the ETAD Code of Ethics, are committed to provide sufficient data for an initial hazard assessment. ETAD members, however, complying with the ETAD Code of Ethics and the Responsible Care® programme, are committed to provide sufficient data for an initial hazard assessment thus ensuring correct labelling, if necessary.

In the case of preparations (i.e. mixtures of substances) the Preparations Directive allows three alternatives for making an assessment which may or may not lead to a hazard classification:

- based on given concentration limits of hazardous components
- by calculation from known data on the components
- based on test data for the preparation itself

The majority of dyes have been tested as the final standardised products and these data have priority over limits or calculation methods. Thus the actual classification is essentially the same procedure as that used for substances. Classifications such as “irritant”, “harmful”, “corrosive” are well known for both substances and preparations within the dye user industry. Less well known is the classification “dangerous for the environment”. Although already in use for some time in the case of substances this classification has now been newly introduced for preparations. As dyes are preparations this means that the end-users will be encountering this labelling for the first time. The example below shows a typical labelling used for a product classified as “dangerous for the environment”:

A comprehensive hazard assessment based on ecological and ecotoxicological data includes parameters such as the acute toxicity to aquatic organisms (tested on three species: fish, daphnia and algae), biodegradability, elimination by physical processes (e.g. flocculation or adsorption), bioconcentration, solubility, partition coefficient and chronic or long-term ecotoxicity. Not all these data are available for every product and the hazard assessment is normally based on the data quoted in the safety data sheet. Thus products which are not labelled as “dangerous for the environment” must be viewed within the context of the stated data because the full data package may not be available e.g. tests may not have been carried out on each of the three major species: fish, daphnia and algae. This is also true in the case of the better known toxicological and physical-chemical hazards. It cannot be assumed that a product is not hazardous because it is not labelled as hazardous unless all the test data cited in the legislation are available. A complete data set is not required by law for substances unless these are “notified substances” and even then the data package required is determined according to the sales volume. ETAD members, however, complying with the ETAD Code of Ethics and the Responsible Care® programme, are committed to provide sufficient data for an initial hazard assessment.

A major determining factor involved in the environmental classification is the ready biodegradability. Dyes in general are not readily biodegradable in standard tests which allows the following simplified table of criteria. The table assumes that data are available for the product itself and that the product has not been classified on the basis of component data.

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3.2 The safety data sheet (SDS)

In addition to the hazard labelling the supplier of a hazardous product must by law provide a Safety Data Sheet. In 1975 the member companies of “ETAD” (The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers) introduced, on a voluntary basis, a safety data sheet containing a recommended minimum set of data. It was – and remains – recommended that SDSs should be available for all products even if these are not classified as hazardous. The ETAD SDS preceded the present legislation by many years and was one of the first standardised SDSs. It was adopted by many other branches of the chemical industry.

A relatively new piece of legislation in the European Union is Directive 91/155/EEC; better known as the Safety Data Sheet Directive. The introduction of this Directive was used by ETAD member companies to expand the data base for products and to make the data more understandable.

ETAD member companies have attempted in the change to the EU SDS to supply the user with data in a more understandable form.

An idealized example of such a safety data sheet is given below. The content shown is limited to the ecological data.

**The data given can be summarized as follows:**

- The product is a dye and therefore it can be assumed to be not readily biodegradable. This is reflected in the ratio of the BOD5 and COD which is less than 0.5. The product is only partially eliminated by adsorption onto effluent treatment sludge as shown in a test for inherent biodegradation (OECD 302B). Thus some product can be expected to enter surface waters. It is not harmful or toxic to waste water treatment organisms. As the fish toxicity is greater than 1mg/l but less than 10mg/l and the product is not readily biodegradable it must be classified as “toxic to aquatic organisms” (N, R51/33) and be labelled accordingly. Due to the high water solubility no bioconcentration is expected. Emissions to the aqueous environment are a point source i.e. localized and not diffuse such as those originating from numerous or public sources.

**BIOLOGICAL DATA**

- **Bioelimination:** 40-50 %, DOC analysis OECD 302B
- **Mobility:** On application – point source into the aquatic environment
- **Bioconcentration:** Due to the high water solubility, not expected to bioconcentrate

**ECOTOXICOLOGICAL DATA**

- **Bacterial toxicity** IC50 > 300mg/l
- **Fish toxicity** LC50 3.2
- **Daphnia toxicity** EC50 30mg/l
- **Algae toxicity** EC50 no data
- **Behaviour in treatment plants** no adverse effects are to be expected

**ADDITIONAL ECOLOGY DATA**

- **BOD5** 0 mg
- **O2/g COD** T200
- **mgO2/g TOC** 32 %

3.3 Special cases

In this section two special cases are described:

- a) the algal toxicity test with respect to water soluble dyes with intense colour properties
- b) dyes that are poorly water-soluble

- a) water soluble dyes with intense colour properties

One of the tests required for the environmental classification of dyes is the algae growth toxicity study. Algae, which are unicellular aquatic plants, need light in order to grow (photosynthesis). Under the conditions of the standard OECD test, intensely coloured substances prevent the passage of light to the algae which inhibits the growth and gives the impression that the dye has produced a toxic effect. In reality the observed inhibition of growth is normally not a result of the chemical’s inherent toxicity, but a function of its light reducing capacity. Even if the acute toxicity results in other species show no toxicity, classification would be made on the basis of this erroneous algal toxicity result. Recent developments include an additional test method that compensates to some degree for light absorption.
4. METHODS OF CLASSIFICATION

b) dyes that are poorly water-soluble

Three areas are critical for the assessment of poorly water-soluble dyes.

i) testing for acute toxicity effects

As previously mentioned water-soluble dyes are classified almost entirely on the basis of the acute toxicity results. However, for poorly water-soluble dyes e.g. disperse dyes, it is difficult to test them at the concentrations recommended in the OECD guidelines. Under these circumstances the acute tests are carried out up to the limit of solubility in the test media. If a toxic effect is observed then a true result can be quoted. However, if no toxic effect is seen and because testing at high concentrations is not possible then the only conclusion that can be reached is that the dye is not toxic up to the limit of solubility. Alternatively, the test can be carried out, despite the insolubility, at a nominal concentration e.g. 100 mg/l test substance and any toxic effects observed.

ii) bioconcentration potential

The partition coefficient is a measure of the tendency of a substance to dissolve preferentially in either water or n-octanol. n-Octanol is considered a surrogate for fat tissue. The Partition Coefficient is usually expressed as its logarithm (log P). If the log P is ≥3 then the substance prefers to dissolve in octanol and a potential to bioconcentrate is assumed. If the log P is < 3 then bioconcentration is extremely unlikely to be significant. In the former case a bioconcentration test can be carried out to confirm the predicted behaviour. Bioconcentration is the tendency of a substance to be stored in living tissue and thus to enter the food chain. Poorly water-soluble substances often have a high n-octanol-water partition coefficient. The fact remains, however, that the majority of dyes that have been tested in a fish bioconcentration test did not show any tendency to bioconcentrate.

Overall effect:
Considering all three parameters, a poorly water-soluble dye showing the following properties is labelled R53 – “may cause long-term adverse effects in the aquatic environment.” No symbol is required.

- a water solubility of < 1 mg/l
- no acute toxicity up to the limit of solubility
- partition coefficient (log Pow) greater or equal 3
- not readily biodegradable

Long term toxicity studies can be used to further investigate and possibly allay the need to classify a product as “dangerous for the environment.” However, these tests are time-consuming, expensive and not routinely required by the majority of the world’s regulatory authorities and are thus not generally carried out. The poorly water-soluble dyes thus remain classified and labelled on the basis of their water solubility and partition coefficient rather than on any known toxicity or bioconcentration.

The evaluation of the health and environmental hazards of a preparation can be assessed either by a calculation method based on the concentration(s) in the preparation of any component(s) that are hazardous or based on tests carried out on the preparation itself. If test results are available for the preparation then the hazard classification based on these results has priority over calculation methods.
6. ENVIRONMENTAL RISK ASSESSMENT

The objective of the legislator in the EU is, by means of the enactment of Directives and Guidelines, to achieve a comprehensive control over hazardous chemicals and to harmonise the requirements within the single market. Strategically this objective can only be achieved stepwise. A legislative basis for the process already exists although the implementation and enactment especially with respect to differing product classes e.g. for substances and preparations, are in differing stages of development. In general the legislation controlling substances is developed faster than that for preparations. The classification “dangerous for the environment” was introduced for substances well before being introduced for preparations.

The final step is risk-management achieved by (in order of severity) reporting of import and export quantities, special use conditions, user restrictions, product safety data sheets and application data. The risk is assessed separately and includes the exposure data. If PEC : PNEC = < 1 the greater the probability of no adverse effects in the aquatic environment. If PEC : PNEC = > 1 the greater the probability of adverse effects in the aquatic environment.

The concept of classifying and labelling preparations as environmentally hazardous is not new. In many cases the products have already been identified and labelled for transport by major manufacturers and these labels have been seen by end-users.

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Examples of risk assessment

The first example below shows that a dye classified as “hazardous for the environment” does not pose a high priority risk when assessed by a screening calculation. The second example shows a dye which is not classified as “hazardous for the environment” but which nevertheless presents a risk. These case studies illustrate that the hazard classification may not predetermine the need or otherwise for risk management measures.

A constant problem is that risk management is introduced by many local authorities based on the hazard assessment and not on a risk assessment. A hazard assessment considers only product specific properties and not the actual risk or total effluent load. Based on these considerations a less hazardous product can pose a higher risk than a more hazardous product.

The following table demonstrates the parameters with an impact on the environmental classification, and hence the labelling of dyes, and the parameters with an impact on the environmental risk assessment.

Parameters used for determining environmental concentrations and thus the risk, include the quantity and frequency of use, use patterns, degree of exhaustion and fixation onto the substrate, elimination and/or biodegradation in effluent treatment plants, adsorption-desorption data and the degree of dilution. These parameters vary depending on dye types, application methods, waste water treatment flows and river sizes. The dye manufacturer, in the absence of local data, can normally make only generalised assumptions on the actual risk by using standard models to provide the factors described above.

If the “Predicted Environmental Concentration (PEC)” in the environment is higher than the “Predicted No Effect Concentration (PNEC)” under realistic and typical conditions or using default values the manufacturer is obliged to address the potential risk. For instance additional data could be generated in order to reduce the assessment factor and/or the factors used in the standard model calculation of the predicted environmental concentration can be made more realistic by basing these on actual conditions in practice (e.g. parameters for a major user). In extreme cases field measurements may be necessary. By calculation or measurement the certainty must be assured that the concentration in the environment is below the predicted no effect concentration. If this proves unattainable then risk-management must be introduced.

The parameters for calculating environmental concentrations e.g. quantities, application methods, process and effluent treatment flow volumes, river flow volumes and frequency data differ significantly according to user and region. Thus the manufacturer initially starts with a screening calculation based on “worst case” conditions.