



Translation for information purposes

Original: German

Fact Sheet and Current Situation: Classification of Azo Pigments in Water Hazard Classes

3rd version (status: 14 August 2017)

Background / Introduction

In October 2014 the Commission for the Evaluation of Water-Polluting Substances (KBwS) adopted the following decision:

„Azofarbstoffe/Azoverbindungen mit einer potentiell durch reduktive Azospaltungen freisetzbaren krebserzeugend einzustufenden (R45 bzw. H350) Aminkomponente“

(„Azo dyes/azo compounds with an amino component that can be potentially released due to reductive azo cleavage and needs to be classified as carcinogenic (R45 and H350, respectively“).

Such azo dyes/azo compounds are assigned the classification in water hazard class (WGK) 3. The status stated was “V: KBwS-Beschluss” (KBwS decision); date: 14 October 2014. Up until 10 August 2017, classifications with status V were only temporary.

This entry was found under identification no. 9001 in the Rigoletto database of the German Federal Environment Agency (UBA). The following pigments are explicitly named in this group entry:

- C.I. Pigment Yellow 12 (CAS no. 6358-85-6)
- C.I. Pigment Yellow 13 (CAS no. 5102-83-0)
- C.I. Pigment Yellow 14 (CAS no. 5468-75-7)
- C.I. Pigment Yellow 83 (CAS no. 5567-15-7)
- C.I. Pigment Yellow 174 (EC no. 911-715-0)
- C.I. Pigment Yellow 188 (CAS no. 72207-62-6)
- DCB-AAA-AAOT (CAS no. 68910-13-4)
- C.I. Pigment Orange 13 (CAS no. 3520-72-7)
- C.I. Pigment Orange 34 (CAS no. 15793-73-4)

The manufacturers of these azo pigments take the view that the above-mentioned azo pigments – unlike dyes – should not fall in this group entry. This can be scientifically substantiated with the very different properties of dyes and pigments, respectively.

For this reason, the manufacturers of azo pigments (represented by the VdMi) and the German Chemical Industry Association (VCI) jointly addressed the Federal Environment Agency (UBA) and the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (BMUB) – in order to present the expert arguments which show that the azo pigments should be deleted from the group entry, as classification in WGK 3 is not justified in scientific terms.

Here some of the core arguments:

Solubility / Bioavailability

Unlike dyes, it is an outstanding characteristic of pigments that they are insoluble in the respective application medium (like coatings, printing inks or plastics).

For example, the group entry explicitly names pigments manufactured on the basis of 3,3'-dichlorobenzidine. In contrast to dyes, which are based on unsubstituted benzidine, these pigments are ca. 10,000 times less soluble in water. Given their extremely low solubility in water (and also in n-octanol) and because of further physical-chemical properties, the impacted azo pigments can be deemed not bioavailable.

- LogPow <2,2
- No hydrolysis in aqueous solution
- No release of 3,3'-dichlorobenzidine after oral intake

Reductive cleavage of the azo-group

The possibility of a reductive cleavage of azo dyes, with a release of the respective aromatic amine on which they are based, was already examined in the 1990s within a revised version of the German Consumer Goods Ordinance (Bedarfsgegenständeverordnung). When using the method named in the Consumer Goods Ordinance, a reductive cleavage on the azo bond can be proven for dyes based on unsubstituted benzidine. Not least due to this behaviour, benzidine dyes were classified as carcinogenic in category 1A in the 90s of the last century.

By contrast, no such reductive cleavage is observed in the same conditions for pigments based on 3,3-dichlorobenzidine because of their extremely low solubility.

Toxicological behaviour of the impacted azo pigments

Based on the toxicological data submitted within REACH registrations, these points can be summed up for the impacted azo pigments based on 3,3'-dichlorobenzidine:

- No detection of 3,3'-dichlorobenzidine in toxicologically relevant quantities in toxicokinetic studies
- No toxic effect in studies on acute toxicity, irritant/corrosive effect, skin sensitising effect and toxicity after repeated dose
- Not carcinogenic
- Not mutagenic
- Not toxic to reproduction

The available toxicological assessments substantiate that the impacted pigments should not be classified as hazardous substances under the EU hazardous substances legislation.

Independent evaluations

Furthermore, evaluations by independent bodies (e.g. Advisory Committee on Existing Chemicals of Environmental Relevance/BUA, 1989) and the Canadian environmental agency (Environment Canada, 2014) conclude that the examined pigments based on 3,3'-dichlorobenzidine are not released in the environment in quantities that would constitute a danger for the environment or human health.

Based on the given data, the impacted azo pigments should be classified as “not water-polluting” (“nicht wassergefährdend/NWG) regarding the water hazard class.

WGK classification

In Germany, so far substances and also mixtures have been classified in water hazard classes (WGK) on the basis of the administrative provision on the classification of water-polluting substances (VwVws).

The ordinance on plants for the handling of water-polluting substances (Verordnung über Anlagen zum Umgang mit wassergefährdenden Stoffen / AwSV) was published on 21 April 2017 in the Federal Law Gazette (Bundesgesetzblatt) and fully entered into force on 1 August 2017. It replaces the earlier ordinances of the German federal states on plants for the handling of water-polluting substances (VAwS).

A list of all substances which were already classified before 1 August 2017 was published on 10 August 2017 in the Federal Gazette (Bundesanzeiger; BAnz AT 10.08.2017 B5). This included the entry with identification no. 9001 „Azofarbstoffe/Azoverbindungen mit einer potentiell durch reduktive Azospaltungen freisetzbaren krebserzeugend einzustufenden (H350) Aminkomponente“ („Azo dyes/azo compounds with an amino component that can be potentially released due to reductive azo cleavage and needs to be classified as carcinogenic (H350)”), which was only specified in the Rigoletto database prior to this.

Up until now, the arguments and presented data on extremely poor solubility, low bioavailability and absence of toxicity of the impacted azo pigments have not been accepted in the discussion with the German public authorities (and particularly with the UBA). The UBA points out that the sole criterion for whether azo pigments fall in this group entry or not is the hypothetical possibility that a reductive azo cleavage might potentially release a carcinogenic amine component.

The inclusion of azo pigments in the above group entry is derived from the MAK entry for azo dyes. For this reason, the VdMi contacted the MAK Commission – with the result that the review of the entry was officially announced on 1 July 2017 in the yellow pages of the MAK and BAT values list, where azo pigments are concerned. Manufacturers are expecting the review to bring clarification for azo pigments, as data are available to substantiate that they are different from dyes in their bioavailability. Thus, also the suspicion of a carcinogenic potential could be dispelled.