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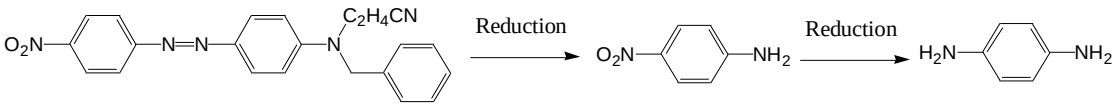
ETAD Information Notice on false positives for paraphenylenediamine in polyester articles (October 2023)

Background

ETAD member companies have reported of findings of para-phenylenediamine (PPD, CAS 106-50-3) in textile articles dyed with disperse dyes, analysed according to the method ISO/EN 14362. This method is a globally used reference for compliance to textiles RSL, and PPD is listed/monitored in some of these RSLs as an amine of concern. When determining compliance to these standards, findings of PPD above the limit of 20 mg/Kg will cause the article to fail.

Evaluation of available information

By checking the structures of the dyes used in the reported cases of affected textile articles, companies found that **in no case disperse dyes were used which could release PPD under reductive cleavage**[1]**.** In all cases, however, at least one of the disperse dyes used to colour the article could **potentially cleave to paranitroaniline** (CAS 100-01-6).
This observation provides an explanation to the reported PPD findings: Paranitroaniline, after being released in the reductive cleavage step of method ISO/EN 14362, is further reduced to PPD, which is then determined together with the amines from the direct azo reduction (see example below).



Double reduction of a para-nitroaniline-based azo dye

This side-reaction is favoured by the fact that ISO/EN 14362 prescribes the use of a large excess of sodium hydrosulfite. Under the method conditions (pH 6 at 70° C), two different aspects will play a role: on one hand, the reduction potential of sodium hydrosulfite is very high, and it will easily reduce the nitro group to an amino group. On the other hand, the stability of sodium hydrosulfite diminishes by acidic pH and when increasing the temperature. After the first reduction step has taken place, the quantity of sodium hydrosulfite available for the second step may vary notably, which would cause, in turn, the variable results observed in the reported cases even by the same fabric. This is in accordance with the assumption that the found PPD is not coming from the primary reduction step.

It must also be noted that the detection of PPD could theoretically be related to the presence of aminoazobenzene. However, a specific identification method for this amine is a standard procedure described in part 3 of ISO/EN 14362 and, **as a very important difference to the paranitroaniline case, in the case of aminoazobenzene aniline should also be found**. Thus, the absence of aniline in presence of PPD can be used as an indication of the possible double reduction mechanism shown above.

[1] At least in the EU, there currently are no market-relevant disperse dyes which could reductively cleave to PPD.

The actual presence of a specific dye cleaving to PPD can then be confirmed, if necessary, in the textile extract according to ISO/EN 14362 before applying the reductive step.

Recommendations for the value chain

It is clear that this is a false positive result depending on the analytical method; this aspect should therefore be taken into account to avoid incorrect declaration of article failures.

We recommend to the **manufacturers of dyes** reportedly or potentially affected to refer to this document and provide beforehand the information that a certain product might cause false positives for PPD. This information could be accompanied by the indication of a direct contact person at the company who can provide further details and assistance if needed.

Except for the case of aminoazobenzene, analytical laboratories should consider all cases of findings of PPD as false positives, particularly by textile articles which can be dyed with disperse dyes, (dark shades of polyester have been especially reported as affected). Following such a finding, we advise to gather information on the dyes used and check whether they can cleave to paranitroaniline.
As mentioned above, the information on the dyes could be already available in advance as part of the product information, but **a direct communication between the analytical service providers and the dye manufacturer should take place by any unclear finding of PPD**. This for different reasons:

- The dye manufacturers may already have own results on the dye;
- The dye manufacturer can provide a dye sample to use as a reference for the direct identification;
- In some cases, information on the dye might still be CBI, which could be only shared under confidentiality agreement.