

## **DYEING AND FINISHING**

### **DETERGENTS, FABRIC SOFTENERS AND COMPLEXING AGENTS**

#### **3.14.1 Current criterion**

The current criterion is formulated as follows:

a) "Alkylphenoethoxylates (APEOs), bis(hydrogenated tallow alkyl) dimethyl ammonium chloride (DTDMAC), distearyl dimethyl ammonium chloride (DSDMAC), di(hardened tallow) dimethyl ammonium chloride (DHTDMAC) and ethylene diamine tetra acetate (EDTA) shall not be used and shall not be part of any preparations or formulations used.

b) At each wet-processing site, more than 95% by weight of the detergents, fabric softeners and complexing agents used shall be sufficiently degradable or eliminable in waste water treatment plants (as defined above in the criterion related to carding and spinning oils, waxes, finishes, lubricants and sizing).

*Test methods and thresholds as defined in the criterion above related to carding and spinning oils, waxes, finishes, lubricants and sizing. Test report required on application if appropriate (notably if sufficient information on the biodegradability or eliminability of the substances used is not available)."*

#### **3.14.2 Changes to the criterion**

Experiences from the Danish Competent Body show that the applicants often misinterpret this criterion, as the heading of the criterion mislead the applicant to believe that only detergents, fabric softeners and complexing agents are covered by this criterion. However the substances listed in 14 a '*...shall not be used and shall not be part of any preparations or formulations used*' according to the criterion. Furthermore, in the preface of the section (under the heading 'A2 Processes and Chemicals' before criterion 10) it is stated that '*...the criteria in this section apply, where appropriate, to all stages of production of the product...*' In order not to create confusion it is therefore suggested to split criterion 14 into two criteria with separate headings.

##### **3.14.2.1 Criterion 14 Auxiliary chemicals**

The first criterion is proposed to consist of a list of dangerous, hazardous and toxic components, which are not allowed for the production of textiles. In the current criterion 14a the following substances are listed: Alkylphenoethoxylates (APEOs), bis(hydrogenated tallow alkyl) dimethyl ammonium chloride (DTDMAC), distearyl dimethyl ammonium chloride (DSDMAC), di(hardened tallow) dimethyl ammonium chloride (DHTDMAC) and ethylene diamine tetra acetate (EDTA).

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During the first period of the project it was investigated, whether this list needs to include substances that are of equal concern in different phases of textile production, more specifically DTPA (diethylenetriamine pentaacetate), phosphonates, NTA (nitrilo triacetate) and LAS (Linear Alkylbenzene Sulfonates).

### *Toxicological and ecotoxicological properties of selected substances*

The draft IPPC reference document (IPPC (2001)) points to DTPA (diethylenetriamine pentaacetate) as being of equal concern as EDTA. Both compounds form very stable complexes with metals. They are poorly eliminable and may pass undegraded through common wastewater treatment systems and subsequently release the metals into the receiving effluent.

For phosphonate products, numerous studies have shown that little, if any, primary or ultimate biodegradation occurs in standard biodegradation tests such as the OECD screening test, BOD20 test, sapromat test and closed bottle test. As expected for highly water-soluble substances, the log Kow values for phosphonates are low.

The potential for bioaccumulation of phosphonates in aquatic organisms is therefore expected to be low as well. The aquatic toxicity of phosphonates to algae is complex to determine in bioassays, as the alga medium contains a precise level of micronutrients, which are held in solution by another chelator, EDTA.

Generally, the acute EC/LC50 values for phosphonates towards fish and invertebrates are well above 100 mg/l. One exception is the Eastern oyster for which acute LC50 values below 100 mg/l are found. The aquatic toxicity data obtained in long-term studies with fish are not markedly different from the data from short-term studies (96 hours). This indicates that phosphonates do not accumulate and that the maximum toxicity is obtained in short term tests. Phosphonates show a low oral and dermal toxicity and have not been shown to have carcinogenic, mutagenic or teratogenic properties (Madsen *et al.* (2001)).

The strong complexing capacity of NTA is expected to have adverse effects upon heavy metal removal during sewage treatment and upon mobilization of metals from sediments in receiving waters. Several investigations have shown that the presence of NTA in water/sediment systems increases the concentration of heavy metals in the water phase. NTA is known to be aerobically biodegradable by acclimated microorganisms. Biodegradability tests with NTA have been inconsistent; 90% degradation has been reported after 9 and 13 days in tests with activated sludge, while degradation attained only 20% in a CO2 evolution test after 28 days and did not occur in shake flask and BOD tests. Following a period of acclimatization, almost complete biodegradation has been reported for the activated sludge process when operated under optimum conditions. The toxicity of NTA towards algae, crustaceans and fish is low with EC/LC50 values well above 100 mg/l. The acute toxicity of NTA and its salts in animals is also relatively low. However, The International Agency for Research on Cancer (IARC) has evaluated that there is sufficient evidence for the carcinogenicity of NTA and its sodium salts in experimental animals, and the overall evaluation is that nitriloacetic acid and its

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salt are possibly carcinogenic to humans. IARC has placed NTA in Group 2B (Madsen *et al.* (2001)).

Linear alkylbenzene sulfonates (LAS) have not yet been documented to biodegrade ultimately under anoxic conditions, and the known mechanisms that precede the aerobic mineralization require molecular oxygen. LAS can, however, be attacked and transformed by bacteria in the absence of molecular oxygen, which implies that LAS is not totally persistent in anoxic environments. Since LAS are generally not degraded under anoxic conditions, levels of LAS in the g/kg range can be found in sludge, which is applied to agricultural soil. The LAS in the sludge will normally biodegrade rapidly in well-aerated and aerobic soils. Aquatic sediments may contain LAS at mg/kg levels as shown by Danish monitoring of contaminants in coastal marine sediments. Most LAS have a low to moderate bioaccumulation potential with exception of the C13-2LAS that has a bioconcentration factor of more than 100.

In general, the homologues with the highest number of carbons in the alkyl chain are more toxic than those with shorter alkyl chains. LC50-values have been found in the range of 1-10 mg/l when *Daphnia Magna* were exposed to LAS homologues between C10 and C13. The same picture is seen for toxicity to fish, where LC50- 56 values below 1 mg/l have been found for C11.9, C13 and C14 in a study with rainbow trout. The toxicity of LAS bound in sediment is relatively low compared to LAS in solution. NOEC and LOEC values as high as 993 mg LAS/kg have been found, with a corresponding NOEC for LAS in solution being as low as 2.4 mg/kg.

The LD50-values found for oral and dermal administration have in general been higher than 400 mg/kg body weight, i.e. a relatively low toxicity to mammals, although rats appear to be more sensitive to LAS than mice. LAS have been classified as irritating to skin and eyes at concentrations above 20% and 5%, respectively.

No sub-chronic or long-term toxic effects have been reported. LAS was not mutagenic in Ames' test and studies show no evidence of carcinogenicity, teratogenic and embryotoxic effects. LAS are classified as Irritant (Xi) with the risk phrases R38 (Irritating to skin) and R41 (Risk of serious damage to eyes). LAS are not included in Annex I of the list of dangerous substances of Council Directive 67/548/EEC.

### *Discussions in the ad hoc Working Group*

With the above findings it was suggested at the third ahWG meeting in December 2001 to include DTPA, NTA and LAS in the list of substances that shall not be used and not be part of any preparations or formulations used. The main argument for including DTPA was the lack of biodegradability. For NTA its toxic properties towards human beings and its potential to mobilize metals in the aquatic environment are the main concerns. For LAS, the lacking degradation under anoxic conditions and the ecotoxic potential are the main concerns.

The discussion regarding this criterion at the ahWG meeting focused on NTA that was seen by the industry as a much needed chemical, where no relevant substitutes were

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available. This is especially the case for cellulose bleaching. ETAD remarked that no human exposure could be expected as the chemical would be emitted with the wastewater and undergo a fast biodegradation. The Danish EPA was concerned about the chemicals' ability to mobilize heavy metals, and the Swedish Competent Body mentioned that a Swedish certificate holder actually is processing today without the use of NTA, and that the problem is closely related to the hardness of the water.

Following the meeting, ETAD as well as TEGEWA underlined in their written comments to the proposal that a ban on especially NTA was problematic for some activities (dyeing of wool and/or polyamide fibers) as it cannot be replaced on short notice. The German Competent Body supported this view, a main argument being that the German Umwelt Bundesamt has recommended substituting EDTA by NTA for several years. TEGEWA further stated in their comments that LAS is readily biodegradable and do not show ecotoxicological properties that are different from other surfactants.

### *Proposal for a new criterion*

Based on the discussions in the ahWG and the comments received following the third meeting in the group, it was suggested to leave out the ban on NTA in the final suggestion for criteria. The proposed criterion is therefore formulated as follows:

“Alkylphenoethoxylates (APEOs), linear alkylbenzene sulfonates (LAS), bis(hydrogenated tallow alkyl) dimethyl ammonium chloride (DTDMAC), distearyl dimethyl ammonium chloride (DSDMAC), di(hardened tallow) dimethyl ammonium chloride (DHTDMAC) and ethylene diamine tetra acetate (EDTA) and 57 diethylene triamine penta acetate (DTPA) shall not be used and shall not be part of any preparations or formulations used.

*Assessment and verification: The applicant shall provide a declaration of nonuse.”*

### **3.14.2.2 Criterion 15 Detergents, fabric softeners and complexing agents**

The second criterion is proposed to deal with the biodegradability of detergents, fabric softeners and complexing agents. From the experiences gathered from the competent bodies it is known that many applicants - similar to criterion 10a – find this criterion difficult to comply with.

### *Proposal for a new criterion*

In order to specify the requirements more precisely, the following formulation was suggested at the third ahWG meeting in December 2001, along with a revised description of assessment and verification:

“Criterion 15. At each wet-processing site, at least 95% by weight of the detergents, at least 95% by weight of the fabric softeners and at least 95% by weight of the complexing agents used shall be sufficiently degradable or eliminable in wastewater treatment plants.

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*Assessment and verification: “sufficiently biodegradable or eliminable” is as defined above in the criterion related to auxiliaries and finishing agents for fibers and yarns. The applicant shall provide appropriate documentation, safety data sheets, test reports and/or declarations, indicating the test methods and results as above, and showing compliance with this criterion for all detergents, fabric softeners and complexing agents used.”*

The working group did not have any comments to the proposed wording of the criterion.

### 3.14.3 Future revisions

As described above, the work in the ahWG was much focused on formulating a criterion regarding auxiliary chemicals that could be accepted by all stakeholders. Future directions were not discussed, but it is obvious from the many comments that there is a need to make an in-depth assessment of the use of NTA. This is currently being done in relation to the eco-label criteria for household detergents, and it is suggested that the knowledge and experiences from this work are utilized in a future revision.

## HALOGENATED CARRIERS

### 3.23.1 Current criterion

The current criterion is formulated as follows: “Halogenated carriers shall not be used”

### 3.23.2 Changes to the criterion

The criterion has not been challenged or subject to alternative proposals, but the heading is changed making it clear that the criterion applies to polyester. In the proposal for a new criterion, the following assessment and verification procedure has been added for clarification:

*“Assessment and verification: The applicant shall provide a declaration of nonuse.”*

## FORMALDEHYDE

### 3.25.1 Current criterion

The current criterion is formulated as follows:

“The amount of free and partly hydrolysable formaldehyde in the final fabric shall not exceed 30 ppm for products intended for infants of less than 2 years of age, 75 ppm for products that come into direct contact with the skin, and 300 ppm for all other products.

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*Test method: Japan Law 112, PRENISO 14184-1 or Finnish standard SFS 4996.*

*Test report required on application (except for yarns)."*

### 3.25.2 Changes to the criterion

At the first ahWG it was suggested that the criterion could be put in line with the Nordic Swan Label regarding same limits for all textiles in direct contact with skin (indoor clothes and bed linen).

Some interested parties have questioned the reason for having such low limits on formaldehyde. The reason is that formaldehyde is considered carcinogenic (Carc3, R40), toxic (R23/24/25), sensitizing (R43) and corrosive (R34).

Test method should be changed to EN ISO 14184-1.

The present criterion does not require a test report for yarns. Normally formaldehyde releasing substances are used on fabric, but formaldehyde releasing dye fastness improvers are sometimes used, which means that they could be used in connection with yarn dyeing as well. This in turn means that the exception should be removed.

The ahWG meeting in May 2001 was predominantly in favor of the revised criterion. Comments received since the meeting varies, some are in favor and wants to precise that bed linen should be considered 'close to skin', and others are against a stricter criterion. At the haw meeting December 2001 the criterion was not questioned, thus the formulation is now:

"The amount of free and partly hydrolysable formaldehyde in the final fabric shall not exceed 30 paps for products that come into direct contact with the skin, and 300 paps for all other products.

*Assessment and verification: The applicant shall either provide a declaration that formaldehyde containing products have not been applied or provide a test report using the following test method: EN ISO 14184-1."*

A test, however, is to be preferred.

## WASTE WATER DISCHARGES FROM WET-PROCESSING

### 3.26.1 Current criterion

a) Waste water from wet-processing sites (except greasy wool scouring sites) shall, when discharged to surface waters after treatment (whether on-site or off-site), have a COD content of less than 25g/kg.

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b) If the effluent is treated on site and discharged directly to surface waters, it shall also have a pH between 6 and 9 (unless the pH of the receiving water is outside this range) and a temperature of less than 40°C (unless the t° of the receiving water is above this value).

*Test method: ISO 6060. Test report and appropriate data required on application.*

### 3.26.2 Changes to the criterion

PARCOM 97/1 has a limit of 160 mg/l COD. Given the following examples of water consumption, a discharge value in g/kg textile produced can be calculated:

100 l/kg corresponds to 16 g/kg COD

200 l/kg corresponds to 32 g/kg COD.

This means, that the existing criterion in relation to the PARCOM-limit corresponds to a water consumption of 156 l/kg. As PARCOM has a limit between 100 and 150 l/kg depending on the type a factory, it indicates that the eco-label criterion can be tightened a bit.

No further information has been received regarding possible changes to the limits in this criterion. It was therefore suggested to leave the criterion unchanged, apart from making an exception regarding flax retting in the same way as for wool scouring. Flax retting is covered by criterion 4. Also the assessment and verification part has been revised, and the complete criterion now is formulated as follows:

(a) Waste water from wet-processing sites (except greasy wool scouring sites and flax retting sites) shall, when discharged to surface waters after treatment (whether on-site or off-site), have a COD content of less than 25 g/kg, expressed as an annual average.

*Assessment and verification: The applicant shall provide detailed documentation and test reports, using ISO 6060, showing compliance with this criterion, together with a declaration of compliance.*

(b) If the effluent is treated on site and discharged directly to surface waters, it shall also have a pH between 6 and 9 (unless the pH of the receiving water is outside this range) and a temperature of less than 40°C (unless the temperature of the receiving water is above this value).

*Assessment and verification: The applicant shall provide documentation and test reports showing compliance with this criterion, together with a declaration of compliance.”*