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Guidelines for the Reduction of Dyes Released from Pulp and Paper Mills

Environment Canada

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Foreword

1. In developing the annexed Guidelines, representatives of the federal and provincial governments, environmental non-government organizations and industry were consulted regarding control strategies for reducing the levels of MAPBAP acetate released from pulp and paper mills.
2. The Minister of the Environment recommends that the appropriate regulatory agency adopt the annexed Guidelines as baseline standards for the levels of dyes released from pulp and paper mills. However, local conditions, such as density of industrial development, topography and other environmental considerations, may necessitate the adoption of more stringent requirements than those suggested in these Guidelines. Ongoing advances in reduction strategies and in technology should also be taken into account.

Definitions

3. The following definitions apply in these Guidelines:

“MAPBAP acetate”: means a cationic dye (basic) with the chemical name Methylum, [4-(dimethylamino)phenyl]bis[4-(ethylamino)-3-methylphenyl]- (MAPBAP acetate), Chemical Abstracts Service (CAS) Registry Number 72102-55-7.

“Mill”: means a plant that produces pulp, paper, paperboard, hardboard, insulating or building board¹.

“Operator”: means a person who operates, has control or custody of or is in charge of a mill².

“Paper product”: means paper, coated paper, paperboard, hardboard, boxboard, linerboard, insulating board, building board, corrugating medium, tissue, moulded cellulose product and any other product directly derived from pulp².

“Primary treatment”: means the settlement tanks that partly remove solid and organic material from a pulp and paper mill wastewater and produce outputs in the form of primary sludge and scum.

“Pulp”: means processed cellulose fibres that are derived from wood, other plant material or recycled paper products².

“Retention”: means the percentage (%) by mass of the MAPBAP acetate bonded to pulp or paper products.

Scope

4. These Guidelines apply to the operator of a pulp and paper mill that uses one or more of the dyes listed in Appendix 1. They lay out certain limits that should not be exceeded and good practices to observe in order to limit dye quantities released in the final effluent.

¹ *Pulp and Paper Mill Defoamer and Wood Chip Regulations* (<http://laws-lois.justice.gc.ca/PDF/SOR-92-268.pdf>)

² *Pulp and Paper Effluent Regulations* (<http://laws-lois.justice.gc.ca/PDF/SOR-92-269.pdf>)

5. The limits and good practices presented in these Guidelines may be respected using existing industry methods and technologies.

Performance guidelines

6. The retention of dyes used in the pulp and paper process and that are subject to these Guidelines should respect the limits specified in Appendix 1.
7. The removal of solids in the primary wastewater treatment, which allows for dye removal by adsorption, should respect the limits specified in Appendix 1.
8. A containment plan should be in place to prevent the release of dyes into the environment or the sewer system during dye storage (for example, fixed supply tank, tote, drum or any other container), handling and disposal.

8.1. A secondary containment³ should be configured with capacity equal to or greater than:

- 110% of the capacity of the tank if there is only one tank; or
- 100% of the capacity of the largest tank plus 10% of the aggregate capacity of all other tanks.

8.2. During the purge of dye from the equipment, piping or tank containing dyes, operational measures for its collection or recirculation should be in place to prevent dye releases to water.

Declaration

9. The operator of a mill that is subject to these Guidelines should indicate in writing to the Minister of the Environment (no later than six months after final publication of the Guidelines or six months after starting to use a dye) its intention to implement the Guidelines. The Minister of the Environment should be notified in writing if the mill permanently ceases to use the dye.

³ *Guidelines for Secondary Containment for Above Ground Storage Tanks*, Industrial Waste and Wastewater Branch, Alberta Environmental Protection, May 16, 1997

Monitoring

10. The operator of a mill that is subject to these Guidelines should, at least once a year, verify that activities are carried out in compliance with the limits specified in Appendix 1 and record the quantity of the dye released to the environment or to a sewer system during its storage, handling or disposal.

Report

11. The operator of a mill that is subject to the Guidelines should provide a report to the Minister of the Environment that includes the following:
 - The name and address of the mill.
 - The technical contact person, telephone and fax numbers, and email address.
 - The quantity of the dye subject to these Guidelines purchased or used during the previous calendar year.
 - Results of the tests referred to in the Monitoring section, the date of testing, and the method for determining dye retention, if different from those proposed in Appendix 3.
 - The quantity of the dye subject to these Guidelines released to the environment or to a sewer system as a result of its storage, handling or disposal.

The operator should provide the first report to the Minister of the Environment three years after the final publication of these Guidelines. An annual report would subsequently only be sent if the limits of Appendix 1 were not respected or if at least one of the dyes subject to these Guidelines were released to the environment or to a sewer system as a result of storage, handling or disposal.

Record keeping

12. The operator of a mill that is subject to these Guidelines should retain all relevant records for at least five years beginning on the date of their creation and make them available to the Minister of the Environment upon request.

Appendix 1: Limits

Substance	Minimum retention in paper products ⁽¹⁾	Solids removal efficiency by the primary treatment ⁽²⁾
MAPBAP acetate (CAS 72102-55-7)	90%	75%

(1) A method for determining dye retention on fibres is shown in Appendix 3.

(2) The calculation of the solids removal efficiency by the primary treatment is shown in Appendix 2.

Appendix 2: Calculation of solids removal efficiency by the primary wastewater treatment

$$ESS = \left(1 - \frac{SS_o}{SS_i}\right) \times 100\%$$

Where

ESS = solids removal efficiency (%)

SS_o = solids concentration at the outlet of the primary treatment system (mg/L)

SS_i = solids concentration at the inlet of the primary treatment system (mg/L)

Note: The sampling should be conducted while the primary treatment system is stable and the mill is in operation.

Appendix 3: Proposed method for measuring dye retention on fibres⁴

Equipment

- Spectrophotometer
- Fibreglass filter paper (1.5- μm nominal porosity).
- Deionized water
- Büchner vacuum flask
- Stirrer hot plate
- Beakers
- Graduated cylinder
- Analytical balance measuring to at least four decimal places
- Pipettes
- pH meter
- Conductivity meter

Products

- Dye to be tested
- Fresh, undyed (never dried) pulp

Procedure

1. Preparation of dye solution
 - a. Dilute the dye to 0.2 g/L (**C_i**) with deionized water.
2. Use the spectrophotometer to determine the maximum absorption wavelength and develop a “concentration-absorbance” curve using that value. Establish the minimum dye concentration that can be measured with this instrument (minimum

⁴ The method was reviewed and tested by a laboratory associated with the University of British Columbia.

measurable value).

3. Pulp retention measure

- a. Dilute 2.00 g of dry pulp in deionized water until you achieve a 1% consistency.
- b. Agitate at 50°C for 2 minutes or until no fibre flocs remain.
- c. Filter with the Büchner and filter paper and keep the filtrate in a beaker.
- d. Measure the filtrate absorbance (**A int**) at the wavelength established in Step 2 in order to estimate the interference caused by suspended solids and the filtrate colour.
- e. Measure the quantity of dry pulp on the filter paper.
- f. Calculate the pulp retention. A 99% minimum value is required to minimize interference with the absorption measure. For lower retention, increase the quantity of pulp or use a lower-porosity fibreglass filter.

4. Dye retention measure

- a. Weigh 2.00 g of dry pulp.
- b. Add 180 mL of deionized water.
- c. Add 20 mL of the dye solution (**V_i**) to the pulp to obtain a concentration of 0.002 g pure dye/g dry pulp.
 - The final consistency of the pulp should be 1%.
- d. Agitate at 50°C for 2 minutes or until no fibre flocs remain.
- e. Filter with the Büchner and filter paper.
- f. Measure the filtrate volume (**V_f**).
- g. Measure the filtrate absorbance (**A_f**).
- h. Calculate the corrected absorbance (**A corr**) = **A_f** – **A int** (from Step 3-d).
- i. Calculate the dye concentration in the filtrate (**C_f**) with the “concentration-absorbance” curve (Step 2), using the corrected absorbance (**A corr**).
- j. Calculate the quantity of (pure) dye in the filtrate (**D_f**) = **V_f** x **C_f** [g].
- k. Calculate the initial quantity of (pure) dye (**D_i**) = **V_i** x **C_i** [g].
- l. Measure the pH and conductivity of the filtrate (for reference only).

- m. Calculate the dye retention = $(D_i - D_f) / D_i \times 100\%$.
- n. Repeat Step 4 twice. Record the mean retention, pH and conductivity.

Notes

- a. The initial dye quantity per gram of pulp used is based on the hypothesis that the lowest value the spectrophotometer can measure in the filtrate is 1 ppm of dye and that the dye retention is approximately 90%. The quantity of dye may need to be adjusted should these hypotheses not apply.
- b. Instruments used should be calibrated.
- c. Results should be presented to the appropriate significant decimal places.
- d. The minimum measurable value of the instruments should be determined.
- e. If a measurement falls below the minimum measurable value for an instrument, then the minimum measurable value should be used or reported.
- f. Factors that may affect dye retention include: conductivity (salts), temperature, pH, quantity of anionic trash in water, pulp type, dye type, pulp consistency, and initial concentration.