ADVANCES IN THE SUBSTITUTION OF FORMALDEHYDE-BASED PRODUCTS

STUDIES TOWARDS THE SUBSTITUTION OF DECROLINE BASED PRODUCTS IN DISCHARGE PRINTING PROCESS

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1 PURPOSE OF THE STUDY

The purpose of this study is to devise alternatives for discharge printing products based on Decroline® [Zinc bis(hydroxymethanesulphinate)] as reducing agent. Substitutes should be based on products which do not release formaldehyde.

2 STRATEGY

The strategy employed in this substitution study is based in the following types of experiments:

- Technical experiments, aimed at preparing printed textile samples treated with discharge printing pastes made from different reducing agents.
- Quality measurements, to assess the properties of the printed samples prepared.
- Toxicity measurements, to establish the level of toxicity of the substitute substances under evaluation.

3 TEAMS INVOLVED IN THE STUDY

The alternative proposal study for Decroline base discharge printing pastes has been carried out by a team from the University of Santiago de Compostela, Spain (USC), led by Prof. F. Javier Sardina. This team was also in charge to compile the available information on the hazards (toxicity) posed by Decroline and the proposed substitutes.

Preparation of the required printed textile samples and the quality studies on the finished samples were carried out in cooperation with a team from Technical Advice, S. L. (Barcelona, Spain) led by Mr. Joan Roca.

Experimental toxicity measurements on the chemicals under evaluation were carried out by two teams from the University of Santiago de Compostela, Spain (USC), led by Profs. Laura Sánchez Piñón and M. Isabel Loza.

4 INTRODUCTION

Discharge printing is a finishing technique employed in textile fabrics. The procedure is carried out as follows: first, the fabric is dyed (with dyes that can be bleached with oxidising or reducing products) to obtain the ground coloration. After dyeing, the discharge printing paste is applied over the dyed fabric following some specific, desired patterns. Then the dye in the printed area is discharged after a steaming step. As a result of this process, a white discharge is produced in the printed area (white discharge). [1] The presence of discharge-resistant dyes (illuminating dye) in the discharge paste allows the preparation of coloured discharges, i. e. the pre-dyed background is bleached and the newly applied dye takes its place.

It should be noted that not all dyes are susceptible of undergoing the process described above. Azoic dyes can be easily discharged, but anthraquinone, phthalocyanine or triphenylmethane dyes can be sometimes resistant to degradation and therefore are not suitable for this type of finishing process.

4.1 Discharge printing agents

The most important components of the printing pastes employed for this process are the discharge agents. Oxidating or reducing agents can be employed for discharge printing, but the most important methods are based on reduction processes. Formaldehyde sulphoxylates are the most widely used agents in this technique; examples of this type of compounds are:[2]

- Zinc bis(hydroxymethanesulphinate) (CI Reducing agent 6, Decroline®).

1 Miles, C. and Leslie, W. Textile Printing, Revised 2nd Edn (Bradford: Society of Dyers and Colourists, 2010.
2 K Lacasse and W Baumann, Textile Chemicals: Environmental Data and Facts (Heidelberg, New York, NY: Springer Science & Business Media, Springer‐Verlag Berlin, 2004).

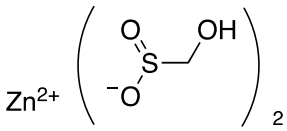
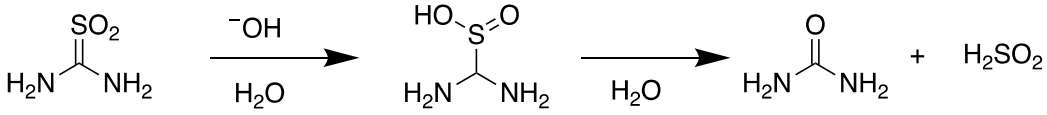


Figure 1. Zinc bis(hydroxymethanesulphinate)

- Sodium hydroxymethanesulfinate (CI Reducing Agent 2, Rongalit C®).
- Calcium bis(hydroxymethanesulphinate) (CI Reducing Agent 12, Rongalit H®).

Bis(hydroxymethanesulphinate) based products are very effective from the technical point of view, but from the point of view of sustainability, the use of this substance has a serious drawback, namely that free **formaldehyde** is released in wastewaters as a by-product of the use of Decroline or Rongalit. Even the printed products could contain non-compliant levels of formaldehyde.

Thiourea dioxide is another reducing agent that can also be employed for discharge printing. When this chemical is heated in presence of water and alkali, diaminomethanesulfinic acid is formed. The decomposition of this intermediate would afford sulphoxylic acid, which is the actual reducing agent.



Scheme 1. Thiourea dioxide as reducing agent

One of the advantages of discharge pastes based on this chemical is that it does not contain nor it releases formaldehyde, which makes it a good candidate to substitute the formaldehyde-based sulphoxylates as active reducing agents in discharge printing. However, the use of thiourea dioxide has some performance problems associated, for example, its strong reducing character may induce the alteration of the pigments employed as iluminants under certain circunstances.

5 TECHNICAL EXPERIMENTS

The first stage of this study was the comparison of the performance of several discharge printing pastes following the steps listed below:

- Selection of the discharge printing pastes
- Preparation of the corresponding textile samples
- Evaluation of the samples prepared

5.1 Selection of the discharge printing pastes

According to the available technical and commercial information, in this study we have compared the performance of bis(hydroxymethanesulphinate) and thiourea dioxide based printing pastes. The following table shows the commercial products selected.

Table 1. Commercial discharge printing products selected for the study

Brand Name	Zinc bis(hydroxymethanesulphinate) based	Thiourea dioxide based
ASUTEX	Reductor DC	Reductor H113
ACHITEX-MINERVA	Reducing agent Z	Reducing agent ECO
CHT	N/A	Redulit F
ARCHROMA	Rongalit D	N/A

5.2 Preparation of the textile samples

In progress. Projected completion date: July 2018.

5.3 Evaluation of the prepared samples

Once the samples prepared by discharge printing have been obtained, the quality and the properties, including formaldehyde contain will studied.

6 QUALITY MEASUREMENTS AND PROPERTIES

6.1 Evaluation of textiles obtained by discharge printing

In progress. Projected completion date: July-August 2018.

6.2 Summary of performance results and relative cost of the discharge printing pastes

In progress. Projected completion date: August 2018.

6.3 Conclusions of the technical studies

To be completed. Projected completion date: August 2018.

7 TOXICOLOGICAL CLASSIFICATION OF HYDROXYMETHANESULFINATE SALTS AND THIOUREA DIOXIDE ACCORDING TO THE EUROPEAN REGULATION EC NO. 1272/2008 (CLP)

7.1 Zinc bis(hydroxymethanesulfinate)

Zinc bis(hydroxymethanesulfinate), also known as Decroline® (CAS 24887-06-7; EC Number: 246-515-6), is NOT currently covered by the CLP Harmonized Classification and Labelling (Table 3.1 of Annex VI of the CLP).

Additional information on the toxicological classification of this substance can be obtained on the website of the ECHA (European Chemicals Agency), such as Notifications. Notifications are comprised of preliminary information on the toxicity or hazardousness of chemical substances, voluntarily submitted by the companies that wish to manufacture or distribute those substances. As such, Notifications contain information which has bot been yet subjected to the rigourous vetting process used by ECHA to produce a Harmonized Classification.

With regards to Zinc bis(hydroxymethanesulfinate), Notifications have been submitted by 100 Notifiers. The hazards associated with Zinc bis(hydroxymethanesulfinate) included in these Notifications are the following:

- Health Hazards:
  - Acute Toxicity 4 (oral)
  - Eye Irritant 2
  - Mutagenic 2
- Environment Hazards:
  - Aquatic Chronic 3

7.2 Sodium hydroxymethanesulfinate

Sodium hydroxymethanesulfinate, also known as Rongalit C® (CAS 149-44-0; EC Number: 205-739-4), is NOT currently covered by the CLP Harmonized Classification and Labeling (Table 3.1 of Annex VI of the CLP).

Additional information on the toxicological classification of this substance can be reviewed on the website of the ECHA (European Chemicals Agency). Registration Dossier and Notifications collect the classification of the substance provided by manufacturers and importers.

A. Notifications

According to the Notifications (66 Notifiers), the hazards associated with Sodium hydroxymethanesulfinate are the following:

- Health Hazards:
  - Mutagenic 2.
  - Toxic for Reproduction 2.

The remaining notifiers (140) have considered the substance as "Not classified" on the ECHA website.

B. Registration Dossier

According to the Registration Dossier (40 Registrants), the hazards associated with Sodium hydroxymethanesulfinate are the following:

- Health Hazards:

- Mutagenic 2
- Toxic for Reproduction 2

C. Additional Information

The Community Rolling Action Plan (https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan) has included the Sodium hydroxymethanesulfinate in the CoRAP List, in order to clarify the initial concern that the manufacture and use of this substance could pose to human health or the environment in relation to endocrine disruption.

The Member State responsible for carrying out the evaluation in 2019 will be The Netherlands.

7.3 Thiourea dioxide

Thiourea dioxide (CAS 1758-73-2; EC Number: 217-157-8), is NOT currently covered by the CLP Harmonized Classification and Labelling (Table 3.1 of Annex VI of the CLP).

Additional information on the toxicological classification of this substance can be reviewed on the website of the ECHA (European Chemicals Agency). Registration Dossier and Notifications collect the classification of the substance provided by manufacturers and importers.

A. Notifications

According to the Notifications (30 Notifiers), the hazards associated with thiourea dioxide are the following

- Health Hazards:
  - Acute Toxicity 4 (oral)
  - Skin Irritant 2
  - Eye Irritant 2

  - Specific Target Organ Toxicity-Single Exposure 3 (STOT SE 3) (respiratory irritation)
- Physical Hazards:
  - Self-heating substance 1

B. Registration Dossier

According to the Registration Dossier (40 Registrants), the hazards associated with Sodium hydroxymethanesulfinate are the following:

- Health Hazards:
  - Acute Toxicity 4 (oral and inhalation).
  - Skin Irritant 2.
  - Eye Damage 1.
  - Specific Target Organ Toxicity-Repeated Exposure 2 (STOT RE 2) (effect on blood-oral).
  - Specific Target Organ Toxicity-Single Exposure 3 (STOT SE 3) (respiratory irritation).
- Physical Hazards:
  - Self-reactive substance Type G.
  - Self-heating substance 1.

7.4 Conclusions about the current toxicological classification of the substances evaluated

After a revision of the current classification according to the European Regulation EC No. 1272/2008 (CLP) of the zinc bis(hydroxymethanesulphinate), sodium hydroxymethanesulfinate and the thiourea dioxide, it was found that the substances are not classified. However, the information related to the Registration and/or Notifications shows that these substances are suspected to bear properties that could pose a risk to human health and/or environment.

Therefore, in order to verify these intrinsic properties, Inditex has decided to carry out toxicological tests on these substances in several experimental models.

8 TOXICITY MEASUREMENTS

In progress. Projected completion date: July 2018.

8.1 Test conditions

In progress. Projected completion date: July 2018.

8.2 Methodology

In progress. Projected completion date: July 2018.

8.3 Toxicity studies of the commercial formulations used for textiles

In progress. Projected completion date: July-August 2018.

9 CONCLUSIONS OF THE TECHNICAL AND TOXICITY STUDIES

In progress. Projected completion date: August-September 2018.