

**STUDIES TOWARDS THE ELIMINATION OF DIARYLIDE
BASED PIGMENTS IN THE TEXTILE MANUFACTURING
PROCESS**

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1 PURPOSE OF THE STUDY

The purpose of this study is to evaluate the elimination of the use of diarylide based pigments in textile printing.

2 STRATEGY

The strategy employed in this study has been:

- Literature and technical revision on diarylide based pigments
- Study of the decomposition of diarylide based pigments under printing conditions to release banned diamines
- Study of the toxicological classification of the released diamines
- Recommendation of the non-use of diarylide based pigments.

3 TEAMS INVOLVED IN THE STUDY

This study has been carried out by a scientific team of the University of Santiago de Compostela, Spain (USC), led by Prof. F. Javier Sardina.

4 INTRODUCTION

4.1 Diarylide pigments

One of the most important group of organic pigments with yellow/orange shades are the diarylide pigments.¹ These pigments are bisazo compounds synthesized by a double diazocoupling of a benzidine derivative, usually 3,3'-dichlorobenzidine,

¹ Herbst, W.; Hunger, K. *Industrial Organic Pigments: Production, Properties, Applications*, 3rd ed.; Wiley-VCH: Weinheim, 2004

with acetoacetarylides or 1-aryl-5-pyrazolone. Diarylide yellow pigments, which display excellent color strength, are usually disazoacetoacetanilides, while diarylide orange pigments are disazopyrazolones. Figure 1 shows the general structures of this group of pigments.

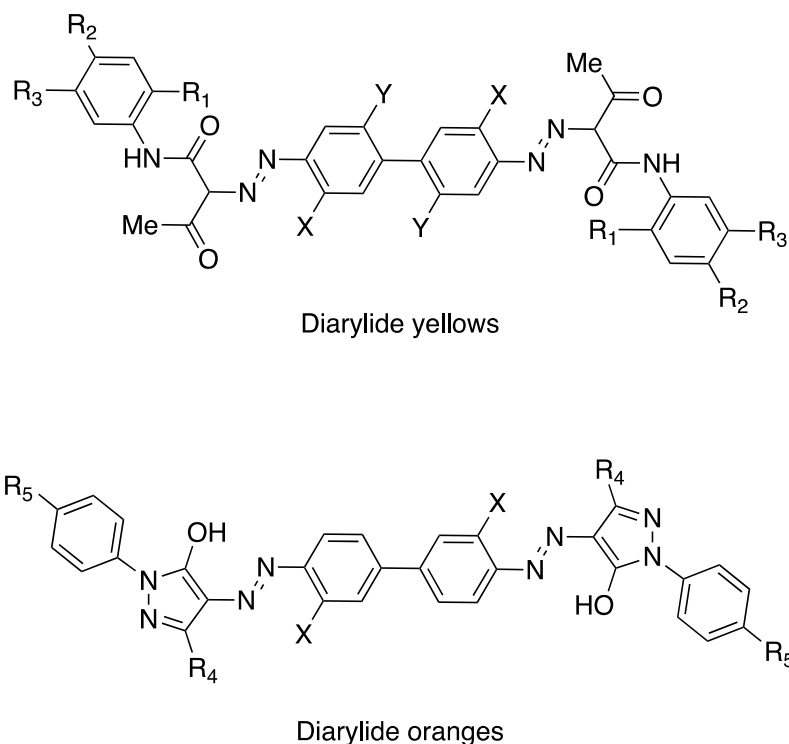


Figure 1. General structure of diarylide pigments

Among others, important examples of these pigments are C.I. Pigments Yellow 12, 13, 17, 83, and 176; and C.I. Pigments Orange 13 and 34, which incorporate 3,3'-dichlorobenzidine in their molecules. There are also examples of pigments derived from 3,3'-dimethylbenzidine, such as C.I. Pigment Yellow 16.

4.2 Release of banned arylamines from diarylide pigments

According to the information revised, the diarylide pigments are susceptible to thermal breakdown at temperatures above 200°C.² This decomposition has been described initially in polymers where diarylide pigments had been employed for mass coloration (masterbatches). The thermal decomposition can release soluble monoazo dyes or even the aromatic diamines (e.g. 3,3'-dichlorobenzidine) themselves, with the subsequent concern.³

In addition to this decomposition at high temperatures, it is also important to consider the formation 3,3'-dichlorobenzidine-releasing substances when diarylide pigments based on C.I. Pigment Orange 13 or 34 are used in combination with black pigments based on C.I. Pigment Black 7. This decomposition/solubilisation could result in the release of 3,3'-dichlorobenzidine during the process of textile printing. This fact has been contemplated by several chemical companies that recommend to avoid the use of mixtures of the mentioned pigments for textile printing (e.g. BASF or Dystar, among others).

² a) Christie, R. M.; Howie, B. D., *Dyes and Pigments*, **2009**, *80*, 245–253; b) Harris, R. M. *Coloring Technology for plastics*, Plastics Design Library, 1999.

³ Az, R.; Dewald, B.; Schnaitmann, D., *Dyes and Pigments*, **1991**, *15*, 1-14.

5 TOXICOLOGICAL CLASSIFICATION OF 3,3'-DICHLOROBENZIDINE AND 3,3'-DIMETHYLBENZIDINE

The following table summarizes the health and environmental hazards associated with 3,3'-dichlorobenzidine and 3,3'-dimethylbenzidine, which can be released from the decomposition of diarylide pigments. Hazards have been assigned considering the Table 3.1 of Annex VI of the CLP Regulation [(EC) No. 1272/2008].⁴

Table 1. Health and environmental hazards associated to 4-chloroaniline

Entry	Substances	CAS No.	Hazards
1	3,3'-Dichlorobenzidine	91-94-1	Carc. 1B
			Skin Sens. 1
			Aquatic Acute 1
			Aquatic Chronic 1
			Acute Tox 4
2	3,3'-Dimethylbenzidine	119-93-7	Carc. 1B
			Aquatic Chronic 2
			Acute Tox 4

6 PROPOSAL OF SUBSTITUTION OF DIARYLIDE BASED PIGMENTS

Considering that:

- I. diarylide pigments can undergo decomposition under printing conditions to release banned arylamines,

⁴ European Regulation on Classification, Labelling and Packaging of Substances and Mixtures

- II. the toxicological classification of the releasable 3,3'-dichlorobenzidine and 3,3'-dimethylbenzidine, which are banned arylamines in textile and leather articles, and
- III. the existence of commercial alternatives to diarylide pigments, e.g. monoazo pigments or disazo pigments not-based on banned diamines.

Inditex puts forward the need for the replacement of printing pastes based on diarylide pigments that include in their structure banned arylamines, including but not limited to: CI Pigments yellow 12, 13, 14, 16, 17 and 83; and CI Pigments Orange 13 and 34.