

Duffield

WOOL DYEING WITH ENVIRONMENTALLY ACCEPTABLE LEVELS  
OF CHROMIUM IN EFFLUENT

P.A. Duffield, J.M. Wimbush, P.F.A. Demot

IWS Development Centre, Valley Drive, Ilkley LS29 8PB  
West Yorkshire, England

SYNOPSIS

Chromium compounds are just one of the many groups of chemicals subject to environmental regulations and this is of concern to many industries, including the wool textile processing industry. Approximately seventy percent of wool textile dyeing is currently carried out with chromium containing or chrome dyestuffs. The relevant legislation and the likely impact of these controls on wool textile dyeing processes are briefly discussed. Methods to reduce chromium residues from wool dyeing are presented for the different dye classes involved, with an indication of the benefits which can be achieved.

INTRODUCTION

Effluents from a wide range of industries may contain chromium, usually as chromates or dichromates. The dyeing of wool textiles may be a significant source of chromium in the aquatic environment, particularly in those geographical areas where the wool textile dyeing industry is concentrated. Three classes of wool textile dyes contain chromium or are applied with chromium; chrome dyes are used in approximately 30% of wool textile dyeing, 2:1 metal complex dyes in about 35% and 1:1 metal complex dyes in only 4%

Residues are discharged from exhausted dyebaths to sewage treatment works (STW), or direct to surface waters. Passage through STW removes much chromium, but significant concentrations can be detected in the STW effluent and in the receiving surface waters. Deposition of chromium in STW sludge may result in detectable concentrations of the metal when the sludge is disposed to agricultural land.

Two oxidation states of chromium, (III and VI), determine the chemical activity and toxicity of its compounds. In addition to these two forms of free chromium, the metal may also be present as a complex with organic molecules, for example pre-metallised dyes. Environmental concentrations are usually reported as total chromium irrespective of the chemical state of the metal.

#### LEGISLATION GOVERNING THE INDUSTRIAL DISCHARGE OF CHROMIUM

Legislation to control the concentrations of chromium in industrial discharges and surface waters has been enacted in most industrialised countries and an EEC directive is in preparation<sup>1</sup>,<sup>3</sup>,<sup>4</sup>,<sup>5</sup>,<sup>6</sup>. For sewage sludge disposed to land an EEC limit of 50 mg chromium per kilogram of treated agricultural soil is in force<sup>2</sup>.

The current UK river quality standards differ between coarse fish rivers and other surface waters. They can usually be met by the textile dyeing industry, as the rivers in the regions where the industry is concentrated are mainly classified as coarse fish rivers and can therefore tolerate higher concentrations of chromium than the more sensitive salmon rivers (150 ug chromium per litre annual average for coarse fish rivers of low water hardness).

In the Federal Republic of Germany (FRG), charges for each "pollution unit" above a "pollution threshold", are imposed on dischargers of chromium. Above the pollution thresholds of 50 ug chromium per litre and 2.5 Kg chromium per annum, a charge of DM 40 is made for every pollution unit of 500g chromium (total) discharged<sup>4</sup>. Several Federal states specify upper limits for chromium discharges (0.2 mg/l and 8 g/hr) which may only be exceeded with special permission.

In the USA, environmental quality standards (EQS) are imposed for "recoverable chromium". The twenty-four hour and maximum permitted EQS of 0.3 ug/l and 21 ug/l, respectively, are very strict and effectively restricts chrome dyeing in the United States. Premetallised dyes are however widely used without apparently

exceeding the standards, presumably because these dyes do not give positive results in the specified test.

TABLE I Proposed EEC Environmental Quality Standards for Chromium

Medium	Concentration of chromium	
	Total	Dissolved
Inland surface water	15 ug/l	10 ug/l
Internal coastal and sea water	5 ug/L	3 ug/l
River sediments (ex. estuaries)	200 mg/Kg- (dry weight)	

The proposed EEC environmental quality standards for chromium (Table I) are more stringent than current UK and Federal German regulations and may restrict the discharge of pre-metallised dyestuffs, as well as chrome dyes.

#### OPTIMISED DYEING TECHNIQUES

In response to the increasingly severe restrictions on the discharge of chromium in effluents dyestuff manufacturers and IWS, in conjunction with research institutes, have continued to develop techniques to minimise chromium discharges in dyehouse effluent, since for many applications, only chrome containing dyes can provide the required shade and colour fastness.

A survey of UK industry on one river system, which has a high concentration of wool dyehouses, has indicated that, unless optimised dyeing techniques are adopted, the proposed EEC limit for chromium in surface water will be exceeded.

Techniques for minimising residual dyebath chromium levels are available for both chrome and metal complex dyes and are outlined below:

## Chrome Dyes

There are several parameters in chrome dyeing which, when optimised, can reduce chromium residues.

If the dyebath exhaustion is incomplete before chroming, then residual dye in the liquor will be chromed and remain in the liquor to add to the discharged chromium. Optimum results will be obtained by draining the dye liquor and chroming in a fresh bath.

There is an optimum pH region for ensuring maximum dye chroming, and therefore minimum residual chromium levels. The range is from pH 3.5 to 3.8 and should be attained with formic acid, since some other acids may reduce the efficiency of chroming.

It is also essential, for maximum chroming efficiency, to eliminate chemicals from the chroming bath which will inhibit the chromium/dye interaction, such as sequestering agents. Sulphate ions also inhibit the exhaustion of the dichromate anion.

There is an obvious relationship between the amount of dichromate added to the chroming bath and residual levels of chromium. By optimising the parameters as described above it has been possible to reduce the levels of dichromate additions without adversely affecting the shade or colour fastness performance of chrome dyes.

### Optimised Chroming Procedures

A range of optimised chroming conditions are available to ensure minimum chromium effluent as follows:

- 1) IWS has developed a low temperature chrome dyeing method at 90°C using sodium thiosulphate in chroming, which offers advantages of reduced fibre damage, energy savings and reduced chromium effluent. This technique is a straightforward, low cost technology and is becoming the standard application technique for chrome dyes (Fig 1).

## LOW TEMPERATURE CHROME DYEING

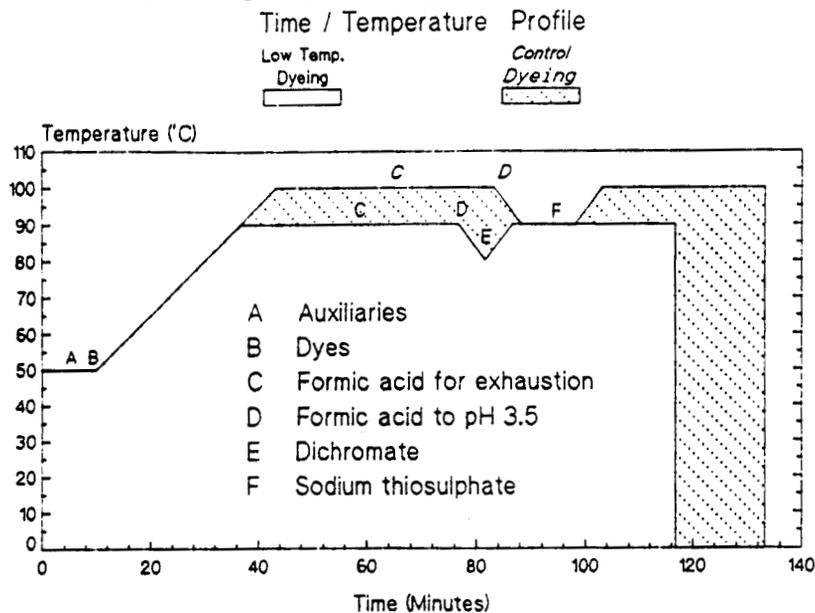


Figure 1 Low Temperature Chrome Dyeing Method with Thiosulphate

It is necessary to add sodium thiosulphate after chroming at 90°C for 10 minutes. The quantities of thiosulphate to be used are calculated by multiplying the level of dichromate by 1.7. The technique can of course be used at 98-100°C to give similar or even lower chromium residues.

ii) The Bayer method uses minimum dichromate levels, calculated from factors published for the range of Diamond dyes<sup>7</sup>. The dyeing procedure requires that sodium sulphate (7.5% anhydrous) is added on reaching maximum temperature during chroming. Although it was previously stated that sulphate must be excluded, in this case it is necessary to ensure level chroming when using minimum levels of dichromate.

iii) The Ciba-Geigy recommendations for chrome dyeing do not rely on individual factors for each dye in order to calculate the quantity of dichromate required. Instead, a general calculation is applied to all recipes.

Chroming is then carried out as normal, but reducing the pH to 3.5-3.8 after 10 minutes at maximum temperature. This delay in reducing the dyebath pH ensures level chroming. As a consequence of optimising chroming conditions, it has been possible with most dyes, to dye and chrome at 92°C with no loss in fastness properties.

iv) The Sandoz method uses minimum dichromate levels, calculated from factors for each dye<sup>8</sup> and the addition of a proprietary product, Lyocol CR, 5 minutes after reaching chroming temperature. By using this technique it is possible to dye at 90°C and chrome at 95°C with all Sandoz chrome dyes.

The benefits of optimised chrome dyeing are illustrated in figure 2 for one UK dyehouse.

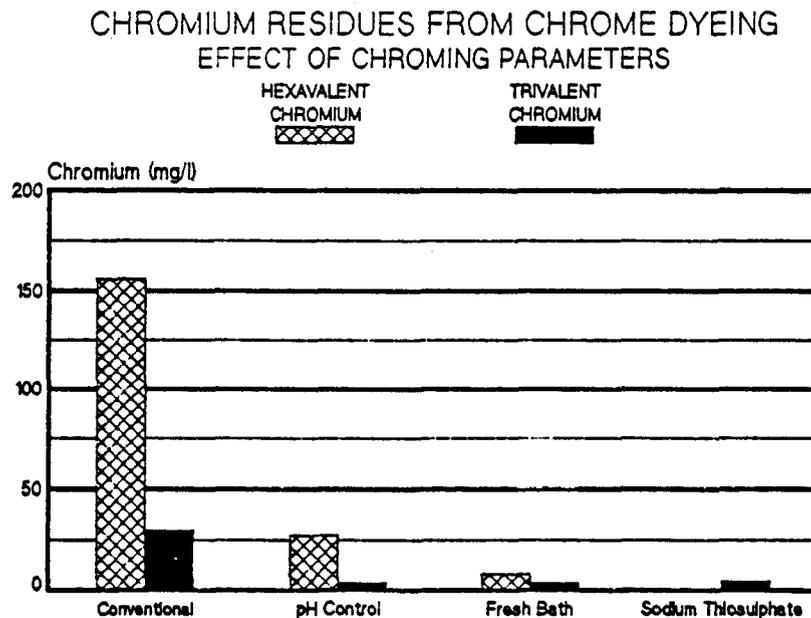


Figure 2 Effect of Chroming Parameters on Chromium Residues

Further data on the benefits of two optimised chroming methods are given in Table II, and indicate the low chromium levels which were achieved in a normal production environment. Additional benefits arising from reduced fibre damage were realised from the low temperature dyeing process with thiosulphate.

TABLE II Dyebath Chromium Residues with Optimised Chroming

Chroming Methods	Residual Chromium (mg/l)
Control dyeing Black	66.00
Control dyeing Navy	83.00
Black 98°C, Lyocol CR (Sandoz)	1.68 - 3.50
Navy, 98°C, Lyocol CR (Sandoz)	1.00 - 4.30
Black 90°C, thiosulphate	3.00 - 6.00
Navy, 90°C, thiosulphate	2.50 - 3.50

#### Metal Complex Dyes

In order to reduce residual chromium levels from metal complex dyes it is necessary to ensure maximum dyebath exhaustion.

#### 1:1 Metal Complex Dyes

These dyes are commonly used on piece goods and yarn where level dyeing performance is critical. A consequence of their excellent migration properties is that a significant quantity of dyestuff remains in the exhausted dyebath. The dyes have traditionally been applied with up to 8.0% sulphuric acid, in order to promote migration however two developments should be noted:

1) The new Neolan P range of dyes from Ciba-Geigy are modified 1:1 metal complex dyes, which can be applied at pH 3.5-4.0 with a specific dyeing auxiliary, Albegal PLUS<sup>9</sup>. This has the effect of giving good dyebath exhaustion, shade reproducibility and reduced fibre damage, when compared with the traditional sulphuric acid method. The benefits of Neolan P dyes on residual chromium levels are illustrated below.

#### Chromium Residues 1:1 Metal Complex Dyes (Navy Shade)

	<u>Residual Chromium Level (mg/l)</u>
Conventional 1:1 metal complex	5.47
Neolan P recipe	1.33

ii) Sulphamic acid has the property of decomposing in hot aqueous solutions thereby causing the pH to rise. When used to replace sulphuric acid for applying 1:1 metal complex dyes, the initial pH (2.0-2.5) ensures good migration, whilst the increase to pH 3.0-3.5, as the dyebath temperature increases, gives good dyebath exhaustion. An additional benefit is the significant reduction in fibre damage. To ensure maximum migration and levelness, a specific dye levelling agent, Uniperol 5700, is available from BASF. This method has been shown in industrial trials to give improved dyebath exhaustion, with improved wool fibre properties.

#### 1:2 Metal Complex Dyes

Recent developments in new dyestuff ranges based on monosulphonated metal complex/milling dyes enable application at pH 4.5-5.0 with specific auxiliaries, to produce good dyestuff exhaustion and minimum fibre damage. The application techniques for disulphonated 1:2 metal complex dyes are normally associated with high dyebath exhaustion levels.

New application techniques are currently under evaluation at IWS to improve dyestuff exhaustion and minimise chromium levels with 1:2 metal complex dyes. These include:

- Application with low temperature dyeing auxiliaries
- Colourex acid dosing and temperature control
- Dyeing at temperatures above the boil
- Isolac S-I acid dosing at constant 80°C.

Of these methods the acid dosing techniques are still under evaluation, but initial results are promising.

The application with low temperature dyeing auxiliaries has concentrated mainly on two products, Baylan NT (Bayer) and Lanasan LT (Sandoz), which are normally used for dyeing at 85 or 90°C. It was felt however from the nature of the products, that they would improve dyebath exhaustion at the boil. Investigations have confirmed this, indicated in Table III.

TABLE III Effect of Low Temperature Dyeing Auxiliaries on Dyebath Exhaustion of 2:1 Metal Complex Dyes

Shade No	Total Dyestuff (%)	Dyestuff Exhaustion (%)		
		Control	Baylan NT	
1	1.32	95.0	98.9	3.9
2	0.75	93.6	98.9	5.3
3	1.48	94.5	96.8	2.3/3.8
Shade No	Total Dyestuff (%)	Control	Lanasan LT	
1	1.32	90.4	96.3	5.9
2	0.90	85.7	96.9	11.2
3	2.52	87.6	96.5	8.9

3/26.0/8.9  
20

Dyeing at temperatures above the boil led not to a reduction in dyebath exhaustion levels but an increase. This increase in residual dyestuff can be attributed to the greater degree of dye migration as the dyebath temperature is raised above the boil.

#### CONCLUSIONS

That restrictions on discharges of chromium in textile waste waters will become more severe in almost every country is certain. It is equally certain that in some areas the industry will not meet the new requirements unless dyeing methods are improved. However, techniques are available which will permit wool dyers to significantly reduce the quantities of discharged chromium from both chrome and metal complex dyeings. It is essential that these are promoted if the environmentally friendly image of the wool fibre is to be maintained. Equally important is that the development of new dyeing techniques continues in anticipation of even more stringent controls.

REFERENCES

- (1) Proposed Environmental Quality Standards for List II substances in water: Chromium. WRC Technical Report TR-207. June 1984.
- (2) The use of sewage sludge on agricultural land, Booklet 2409, ADAS Soil Scientist's Pollution and Waste Products Group, revised 1987.
- (3) Gesetz uber Abgaben fur das Einleiten von Abwasser in Gewasser (Abwasserabgabengesetz-AbwAG) - Law on taxes for the discharge of waste water into stretches of water (Waste water tax law-AbwAG). Bonn. 5 March 1987.
- (4) Verordnung uber die Genehmigungspflicht fur das Einleiten wassergefahrdender Stoffe in Sammelkanalisationen und ihre Uberwachung (VGS). Bavarian law and official gazette No.21/1985. 27th September 1985.
- (5) Ambient water quality criteria: chromium. EPA 440/5-80-035. October 1980.
- (6) Draft Daughter Directive COM (85) 733 final. Proposal for a Council Directive on water quality objectives for chromium. 18th December 1985. Amended as COM (88) 29 Final. 3rd February 1988.
- (7) Bayer Pattern Card No Sp.521.
- (8) Sandoz Pattern Card No PM2/1/81.
- (9) Ciba-Geigy Pattern Card No WO 3370.