Azo ban, eco-norms and testing

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Ecological aspects including azo ban enforced by Germany, Holland, Turkey, France and India; ban on certain chemicals employed in textile processing under eco-norms and containing with the pollution control; different eco-labelling schemes, like Okotex 100, MST, Clean Fashion, Steillmann and Indian Eco-label; and procedures currently employed to test the eco characteristics are discussed.

Keywords: Azo ban, Azo dyes, Arylamines, Eco-label, Eco-norms, Ecofriendly textiles

1 Introduction

Nearly 4000 commercial dyestuffs are manufactured by the major dyestuff industries in various countries including Germany, Switzerland, Italy, France, UK, USA, Japan, Russia, China and India. These dyestuffs include azo, anthraquinone, azine, oxazine, thiazine, stilbene, etc and the share of azo dye is highly significant. The chromophoric azo group (-N=N-) is found in many classes of dyes, viz. direct acid, acid mordant, disperse,azoic, reactive and metal complex dyes. A unique feature of azo dyes is that the nature does not produce analogous coloured substances.

Ecological aspects including azo ban enforced by Germany, Holland, Turkey, France and India; ban on certain chemicals employed in textile processing under eco-norms and containing with the pollution control; different eco-labelling schemes, like Okotex 100, MST, Clean Fashion, Steillmann and Indian eco-label; and procedures currently employed to test the eco characteristics are discussed in this paper.

2 Ecological Issues and Azo Ban in Germany

Ecological issues are becoming important factors in the marketing of consumer goods, including textiles, all over the world. The exporters of textile goods must, therefore, be in a position to adopt their products and processing techniques that comply with the new environmental regulations.

In a major study undertaken by the Ecological and Toxicological Association of the Dyestuff Manufacturing Industry (ETAD) to identify and assess the risks to health attributable to dyes and their intermediates, it was found that more than 90% of the over 4000 dyes tested in the survey had LD₅₀ values greater than 2×10⁵ mg/kg. The highest values for acute toxicity were found among the basic dyes and disazo direct dyes. Hatch reviewed the dermatological problems caused by textiles, dyes and other chemicals used in the textile industry with a focus on consumer rather than occupational exposure. He observed that nearly 31 dyes, mainly disperse with anthraquinone or azo structures, cause allergic contact dermatitis. Further, the studies have brought out the fact that dyes and chemicals which cause sensitization and possible incidence rate can only be deduced from studying the scattered reported incidence. Shenai dealt with the toxicity of dyes and intermediates and brought out the overview on the subject.

In September 1994, the German Government banned the use of azo dyes that yield, on reduction, any of the twenty arylamines, including benzidine and its disubstituted congeners. These amines are classified in Germany as substances that have been proved unequivocally to be carcinogenic. However, implementation of the above ban was effected from 1st April 1996. According to the German Legislation, “No articles of dress (textiles, leather, shoes) and bed linen can be put in trade, if these have been coloured with azo dyes that can release one of the twenty named amines”. The ban covers commodity goods that contain azo dyes which can form one of the following amines due to the reduction of one or more azo groups.

- The aromatic amines in question are classified into two groups, viz. MAK IIIA1 and MAK IIIA2.
- Under MAK IIIA1, benzidine, 4-aminobiphenyl, 2-naphthylamine and 4-chloro-o-toluidine,
which are definitely found to be carcinogenic, are listed. These amines could cause malignant tumours in humans.

Amines grouped under MAK III A2 are characterized as reasonably suspicious to be carcinogenic agents and also as materials, which were previously tested only on animals, and have proved to be clearly cancer-causing while testing the material that might cause health risks under conditions, which can be compared with a possible exposure of humans on their workplace or under similar circumstances. This group includes o-dianisidine, p-chloroaniline, o-toluidine, 3,3'-dichlorobenzidine, o-amino-azotoluene, 2-amino-4-nitrotoluene and m-toluene diamine.

In response to the German ban on the azo dyes with any one of the twenty amines or twenty-two (with the addition of another two) amines, the exporting countries and the manufacturers/exporters, including Govt./Support system organization and Industry Association in India, took a number of proactive initiatives. ETAD reviewed the content of the ban and observed that German regulation is hazard-based and not risk-based and the issue is to be addressed stepwise so that more focused approach to work out action points could be possible by all those concerned.

When Germany announced the ban in late 1994, a list of twenty banned amines along with a list of 48 dyes (prepared by F. Buyer A.G. and Lever Kusen) was circulated in India. Some of the dyes listed did not possess CI number and the structure of such dyes and hence the amines used in their preparation could not be found. However, Bayer indicated the amines based on which these dyes were put in the list.

Subsequently, Dyestar published a brochure on “German Legislation on Azo Dyes” in which the details of 113 dyes covering ten of the twenty listed aryl amines as compiled by the German Chemical Industry Association are given. The list also includes 30 dyes based on p-amino azobenzene and o-anisidine which are classified as category 2 carcinogens by the European Union.

A textile working group of the Federal Institute for Health Protection of Consumers and Veterinary Medicine intensively studied, without bias, the problems of health hazard. The team shared the opinion that none of the studies on chronic toxicity, carcinogenesis and metabolism of diaryl azo pigments based on 3,3'-dichlorobenzidine gave the evidence of azo splitting. In particular, they were also proved to be negative in the case of bio-monitoring studies conducted on test animals with oral application over a period of several weeks. However, only some of the azo pigments concerned were tested by means of this costly and sensitive method. Team inferred that given the stability of pigments and the instability of amines, exposure to such aromatic amines can practically be ignored. In the case of pure pigments, the conclusion may, therefore, be drawn that wearing of textiles which have been dyed with these pigments does not constitute a health risk given the lack of, or utmost, minimal exposure.

Though, azo ban on some of the twenty-two arylamines has been enforced recently, Case and Pearson reported in as early as 1954 that auramine causes occupational hazard among the workers employed in the manufacture of auramine. The hazard of benzidine was well known and by the end of 1960s, it was more or less accepted that benzidine was carcinogenic in nature. Dyestuff manufacturers in Germany, Japan, Italy and US voluntarily abandoned making benzidine.

3 Ban on Azo Dyes in Other Countries

After the Germany prohibited the import and marketing of textiles and allied articles containing azo dyes which, on reductive cleavage, release any of the twenty named amines, a few other countries too imposed similar restrictions. These include Holland (Netherlands), Turkey, France and India. However, the approach in enforcing ban varied from one to another.

3.1 Holland (Netherlands)

On 1 August 1996, Dutch regulations came into force, but the Dutch rules differ from the German regulations in the following way:

- The ban refers explicitly to azo dyestuffs only; azo pigments which are practically insoluble in the application medium are not affected.
- Garments, shoes, bedding, second hand articles, protective clothing, and items produced with recycled yarn containing banned azo dyestuffs to be phased out till December 1999.
- The Dutch regulations for determining banned azo dyestuffs in consumer goods are similar to the German method of detecting banned azo dyestuffs in textiles.
3.2 Turkey
Under the Turkish law, the following rules are effected from 1 March 1995.

- Dyestuffs based on MAK III A1 or MAK III A2 amines may not be used or imported into Turkey.
- MAK amines may not be used to produce dyestuffs in Turkey.
- Checks are made by analytical sampling of dyed textiles to ensure compliance with the regulations.

3.3 France
The French Government is planning to promulgate more extensive textile regulations. The most current draft (21 January 1997) includes among others, a ban on using azo dyestuffs which can cleave any of the 20 aromatic amines which is same as that of German ban.

3.4 India

- As per the Indian regulations, since 1993 the manufacture, processing, storage, consumption and sale of benzidine-based dyestuffs are prohibited. These regulations refer to 42 named benzidine dyestuffs (generic types).
- A corresponding ban was imposed from 26 June 1997 on 70 azo dyes which can release carcinogenic arylamines including o-anisidine and p-amine azobenzene on reductive cleavage.
- The names of the banned amines are not given in the regulations. In all, 112 dyes are banned under the azo ban.

4 Recent Developments Following the Azo Ban
The European Union is preparing to ban around 300 textile dyes containing chemicals known to increase the risk of cancer. These dyes are likely to be banned as reported by Motschi and Clarke. According to ETAD, the consumer exposure to these dyes is very small. However, it encourages its members to seek safer alternatives and does not want to continue to support the marketing of carcinogens. Further, the planned legislation would cover the textiles and leather goods having more than temporary contact with the skin, including clothing, bedding, gloves and chair covers.

5 Ecofriendly Textiles and Eco-norms
To manage quality and ecological features of textile products and processing, one needs to introduce the concept of ecofriendly textiles. Towards ecofriendliness of textiles, one has to address the product evaluation, process evaluation, appropriate measures for correction, and finally validation of the textile products for their ecofriendly features, i.e., eco-labelling. To ascertain the above, testing of textiles on physical, chemical and eco characteristics becomes necessary. The process involves identification of the ecofriendly features. If any inadequacy is found, it is to be corrected/modified and finally the ecofriendly features are to be validated for accreditation.

Some of the measures to manage the ban on certain azo dyes and a few toxic chemicals used in the manufacture of various textile goods is to avoid their usage completely. These toxic materials are being used in the cotton cultivation, sheep culture, sericulture, sizing, bleaching, dyeing and finishing. It is estimated that around 8000 different chemicals are used by the industry and a possible remedy is given below:

<table>
<thead>
<tr>
<th>Textile process</th>
<th>Toxic substances to be avoided</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton growing</td>
<td>Banned pesticides such as DDT, Dieldrin, Aldrin</td>
</tr>
<tr>
<td>Wool storing</td>
<td>Banned insecticides</td>
</tr>
<tr>
<td>Silk worm culture</td>
<td>Banned pesticides</td>
</tr>
<tr>
<td>Sizing</td>
<td>PCP as preservative</td>
</tr>
<tr>
<td>Scouring</td>
<td>Chlorinated products</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Chlorine bleaching</td>
</tr>
<tr>
<td>Dyeing and printing</td>
<td>Azo dyes releasing harmful amines</td>
</tr>
<tr>
<td></td>
<td>Dyes containing traces of heavy metals</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde as a mordant</td>
</tr>
<tr>
<td>Finishing</td>
<td>Formaldehyde as a finishing agent</td>
</tr>
<tr>
<td>Garment manufacture</td>
<td>Stain removers containing chlorinated products</td>
</tr>
</tbody>
</table>

The industry and trade have to start using alternate dyes and textiles auxiliaries in the place of the conventional ones which contain the above listed toxic materials that are carcinogenic in character and allergic by nature. In other words, the industry may have to adopt a "cradle to grave approach" for the manufacture of ecofriendly textiles, i.e., the industry should start applying eco prescription right from the stage of cultivation/production of fibres and also during spinning, weaving, chemical processing, garment manufacture and even packaging.

6 Eco Standards and Eco-labels with Special Reference to European Countries
To promote the concept of ecofriendly textiles, a comprehensive system of eco-labels is advocated by European countries. For the purpose of issuing eco-
labels, certain norms/criteria are stipulated in respect of textile product, on the basis of Cradle-to-Grave approach. These criteria have been developed on analyzing the products during entire life cycle commencing with extraction of raw material, processing through the stages of production, distribution and utilization, and disposal after use. The norms are also referred to as eco standards. By and large, these standards are voluntary in nature.

While formulating eco-norms for the issuance of eco-labels, at present the use of seven different classes of chemicals in textile production and processing are taken into consideration. These are: (i) formaldehyde, (ii) toxic pesticides, (iii) pentachlorophenol (PCP), (iv) heavy metal traces, (v) azo dyes which release carcinogenic amines, (vi) halogen carriers, and (vii) chlorine bleaching.

The eco standards were stipulated by (i) MST, the German Textile Association, (ii) OTN 100, the OEKOTEX Institute from Austria, (iii) Clean Fashion, and (iv) Steillmann. The last two private eco-label issuing organizations in Germany are popular in European countries. In addition to the above four eco-labels, a number of private and national eco-labels are operating in Europe. In some cases, these labels are used solely as a marketing instrument and have little factual and technical substance. In the face of the proliferation of eco-labels, the Coordination Committee for the Textiles Industries in the EEC (COMITEXTIL) supports a single European label. Further, it is learnt that the European Union is finalizing the criteria for common European Community Eco-label (EC Eco-label) after taking into consideration the criteria specified by other eco-labels.

The Government of India has also evolved eco standards for the eco-labelling of the textile items in consultation with the Indian Textile Trade and Industry. The criteria for the environment-friendly textiles, including cotton, woolen, man-made, jute and silk products, were notified in the Gazette of 8 October 1996 by the Ministry of Environment and Forests. The eco-labelling of textiles notified in the Gazette is a voluntary scheme. This scheme aims at distinguishing, through the agency of Eco-mark, any product which is made, used or disposed of in a way that significantly reduces the adverse effect it would otherwise have on the environment. The earthen pot is being used as the logo of this scheme.

The norms/criteria stipulated for eco parameters in the popular eco-labels operating in Europe and in the Indian Eco Mark Scheme for textiles are shown in Table 1.

### 7 Testing of Eco Parameters

Though the testing methods are stipulated under the German ban, the process of standardization is still to be accomplished. The eco testing laboratories, set up at different centres with the state-of-the-art chromatographic and spectroscopic equipments and accessories for the testing of different eco parameters, have adopted the following sample preparation procedures and the instrumental analysis for the different eco parameters.

#### 7.1 Banned Amines

Germany has evolved a test method to detect the use of azo colourants banned by the ordinance on commodities in textiles. The method is applicable to detect banned amines used in the manufacture and treatment of coloured textiles made of cellulose and protein fibres, such as cotton, viscose, wool and silk. The detection of banned azo colourants used in synthetic fibres (polyester and polyacrylate) requires additional steps such as the extraction of the sample using an appropriate organic solvent. The solvent used may be formic acid in case of nylon, dimethylformamide in case of polyacrylate and xylene in the case of polyester.

Banned azo colourants are those which on cleavage of their azo group form any of the 20 amines banned by German Ordinance. According to the current state of scientific knowledge, the evidence of the use of banned azo colourants in the preparation and treatment of textile articles is said to exist, where the coloured textile article or part thereof yields, on cleavage under the conditions of this procedure, one of the 20 banned amines and the determined level of any of these amines exceeds 30 mg/kg (ppm). However, the Indian norms are stipulated as <50 mg/kg (ppm).

As per this method, the textile specimen is treated with sodium dithionite in a citrate buffered aqueous solution of pH 6 at 70°C in a closed vessel. The amines released in the process of reductive cleavage are transferred to t-butyl methyl ether phase by means of liquid-liquid extraction. The butyl methyl ether extract is then concentrated under mild conditions in an evaporator and the residue is dissolved in methanol/ethyl acetate, depending on the equipment used for subsequent analysis. Three types of evaporators, viz. rotary vacuum evaporator,
Table I—A comparison of the norms/criteria stipulated for eco-labelling of textiles\(^{6,11,12,14,15}\)

<table>
<thead>
<tr>
<th>Eco parameter</th>
<th>Criteria/norms stipulated, ppm</th>
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<tbody>
<tr>
<td></td>
<td>M.S.T</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td></td>
</tr>
<tr>
<td>Baby clothing</td>
<td>20</td>
</tr>
<tr>
<td>Close to skin</td>
<td>75</td>
</tr>
<tr>
<td>Outer wear</td>
<td>300</td>
</tr>
<tr>
<td>Toxic pesticides</td>
<td>1</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>0.5</td>
</tr>
<tr>
<td>Heavy metals</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>Azo dyes containing carcinogenic amines</td>
<td>Ban</td>
</tr>
<tr>
<td>Halogen carriers</td>
<td>Ban</td>
</tr>
<tr>
<td>Chlorine bleaching</td>
<td>—</td>
</tr>
</tbody>
</table>

Further, it is also observed under German ban that the carcinogenic amines must be estimated by means of at least two different methods in order to avoid any possible misinterpretation caused by interfering substances\(^{14,16}\). If any of the banned amines is present, its qualification may be done using only HPLC with DAD.

7.2 Testing of Heavy Metals

The heavy metals present in the textile product are extracted by artificial acid sweat solution. Alternatively, the textile sample is digested using conc. nitric acid over a hot plate or by using sophisticated digestion systems such as microwave furnace or microwave digestion system. This extract or the digested solution is analysed by using either atomic absorption spectrometer (with flame and graphite furnace) or inductively coupled plasma emission spectrometer.
While operating with the atomic absorption spectrometer (AAS), a hollow cathode lamp (the cathode of which is coated with the element of interest) is used for the analysis of each element. Consequently, different lamps are required for the analysis of a maximum of 3 elements. Thus, this technique is not preferable for the simultaneous analysis of 4 or more elements. In such cases, inductively coupled plasma emission spectrometer is used. However, in most of the cases, the level of accuracy and minimum detection limit are better with AAS.

While using atomic absorption spectrometer, the extract is introduced into the flame or graphite furnace. Due to the very high temperature in the flame/furnace, the chemical bonds of the sample are broken and it is completely atomized. Radiation emitted by a hollow cathode lamp, the cathode of which is coated with the metal to be analysed, are made to pass through the vapour layer of atoms. The detector measures the decrease in the light intensity of radiation emitted by the lamp, which is a measure of the quantity of the tested metal.

7.3 Testing of Formaldehyde

Three different methods are adopted for testing this parameter as given below:

(i) Japanese Test Method 112-1973—In this method, formaldehyde is extracted from the fabric at 40°C and is made to react with acetyl acetone. The extract is cooled to room temperature and then its extinction is measured at 412 nm using uv-visual spectrometer. The quantity of formaldehyde present in the textile product is determined.

(ii) BS:6806—In this method, chromotropic acid is used for colour development and the absorption is measured at 585 nm using uv-visual spectrometer.

(iii) AATCC Method 112-1993—The formaldehyde evolved from textiles under the accelerated storage conditions is determined by this method. This method is suitable in case of textile samples which when extracted as per Japanese Law 112, give a coloured solution. In this method also, the absorbency of the extract is measured at 412 nm.

7.4 Testing of PCP

The sample is extracted with methanol in a soxhlet assembly. The extract is subjected to a multi-step cleaning operation in order to eliminate the contaminants which are co-extracted from the sample. It is then acetylated with acetic anhydride. The acetylated phenols in the extract are separated by capillary column in the gas chromatograph (GC) and are then detected and quantified by electron capture detector (ECD).

7.5 Testing of Pesticides

The sample is extracted with a suitable solvent or mixture of solvents. The residue is cleaned up over gel permeation chromatography (GPC) to eliminate interfering matrix compounds of higher molecular weight. It is then analysed by the GC with electron capture detector (ECD) or mass spectrometer (MS).

7.6 Testing of Other Quality Characteristics

Colour fastness properties of dye, though do not form part of eco character, have a direct bearing on the eco-norms as the bleeding of colour due to washing, perspiration, exposure to sunlight, rubbing, etc. can contribute for hazardous features. These quality parameters need to be tested as per standard methods of testing, viz. AATCC, BS, ISO, IS and other specific standards.¹ ³ ⁴

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