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Assessment of toxicity of textile dyes and chemicals via materials safety data sheets

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ABSTRACT

The textile industry has been condemned as being one of the world's worst offenders in terms of pollution. Chemical companies market a vast range of products such as dye formulations, colorants and finishing chemicals to the textile industry. This study was carried out in a textile mill. The research revealed that twenty two dyes and twenty five chemicals were used in the mill during twelve month period of the study. Thirty six Materials Safety Data Sheets (MSDSs) were collected from manufacturing companies/suppliers. Analysis of MSDSs together with the information provided on request by International Agency of Research on Cancer (IARC), France identified that various chemical substances used in the mill were harmful/toxic, carcinogenic, probably carcinogenic, and water polluting. Furthermore, it was identified that two out of three compounds classified as carcinogenic to humans were used in the mill either as chrome/metal/complex dye itself or as its mordants. It was therefore recommended to substitute chromium by hydrogen peroxide fixation. In addition, numerous problems with MSDSs and in occupational and safety practices on handling chemical substances in the mill were documented. The study consequently made several specific recommendations towards improvements.

KEYWORDS

Chemicals;
Dyes;
Material safety data sheet;
Textile;
Toxicity.

INTRODUCTION

In the entire world today there has been a growing awareness of the damage caused to the environment by the indiscriminate use of dyes and chemicals, some of which are very toxic and even carcinogenic.

Textile Industry and its impact on the Environment

The textile industry has been condemned as being one of the world's worst offenders in terms of pollution because it requires a great amount of two components: Chemicals - as many as 20,000 different chemical substances are used in the textile industry, from dyes to transfer agents. Vast amounts of water, a finite resource that is quickly becoming scarce, is used at every step of the textile wet processing. The processing water becomes saturated with chemical additives and is then expelled as wastewater; which in turn pollutes the environment by: the effluent's heat; its increased pH; and because it's saturated with dyes, de-formers, bleaches, detergents, optical brighteners, equalizers and many other potentially harmful compounds used in the textile wet processes[1].

Textile Mills discharge millions of litres of effluent each year, saturated with chemicals such as formaldehyde (HCHO), chlorine, heavy metals (such as lead and mercury) and others, which are significant sources of environmental degradation and human illnesses. Chlorine bleach is known to be extremely toxic to the environment and to consumers. Many textile manufacturers use dyes that release aromatic amines (e.g., benzidine, toluidine). Dye bath effluents may contain heavy metals, ammonia, alkali salts and large amounts of pigments - many of which are toxic. About 40 percent of globally used colorants contain organically bound chlorine, a known carcinogen. Natural dyes are rarely low - impact, depending on the specific dye and mordant used. Mordants (the substance used to "fix" the colour onto the fabric) such as chromium are very toxic and of high impact[2].

It is estimated that over 20,000 different dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide[3]. Unfortunately, most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration[4].

In addition, anti - microbial agents resistant to biological degradation are frequently used in the manufacture of textiles, particularly for natural fibers such as cotton and wool[5] The synthetic origin and complex aromatic structure of these agents make them resistant to biodegradation[6].

The textile industry consumes a substantial amount of water in its manufacturing processes mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition[7]. In addition, the effects caused by other pollutants in textile wastewater, and the presence of very small amounts of dyes (<1 mg/L for some dyes) in the water, which are nevertheless highly visible, seriously affects the aesthetic quality and transparency of water bodies such as lakes, rivers and others, leading to damage to the aquatic environment[8]. It is noteworthy that some dyes are highly toxic and mutagenic, and also decrease light penetration and photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation[9].

Occupational hazards associated with textile dyes and chemicals

Some reactive dyes are recognised as respiratory sensitizers. Breathing in respiratory sensitizers can cause occupational asthma. Once a person is sensitised, re - exposure to even very small amounts of the same dye may result in allergic symptoms such as a runny or stuffy nose, watery or prickly eyes, wheezing, chest tightness and breathlessness. Some dyes can cause similar allergic skin reactions. Certain reactive, vat and disperse dyes are recognised skin sensitizers. A small number of dyes, based on the chemical Benzedrine, are thought to possibly cause cancer. Other dyes may also present hazards to health. Non - dyestuff chemicals can also be hazardous in a working environment: Fire hazards may arise from the use of flammable liquids which are easily ignited or oxidising agents which may make an existing fire more intense by fuelling it with oxygen. Corrosive chemicals can cause serious burns and may react dangerously with other chemicals. Violent reactions may be caused by substances which are dangerous when wet such as 'Hydros'. Hot liquids cause many blistering accidents. Perhaps the most prevalent health problems associated with dyeing and finishing processes arise from exposure to chemicals acting as irritants. They include formaldehyde - based resins, ammonia, acetic acid, some shrink - resist chemicals and optical whiteners, soda ash and bleach[10].

Exposure to hazardous materials can produce adverse health effects. These can be either acute or chronic, with many chemical substances capable of producing both. An acute health effect occurs soon after the initial exposure and usually related to a comparatively large, brief high - level exposure. These can include: eye irritation, nasal, throat and mucous membrane irritation, headaches and dermatitis or skin irritation and dizziness. A chronic health effect is often not noticed until long after the initial exposure. Effects may not be noticed for years, or even decades, after exposure. Generally, chronic health effects occur after repeated, low - level exposures. Examples of chronic health effects include, but are not limited to: cancer, extensive skin damage and chronic obstructive pulmonary disease among others[11].

Material safety data sheet (MSDS)

When confronted with a toxic substance on the job, workers should rely on the Material Safety Data Sheet (MSDS) to inform them of the substance's hazards. MSDS have origins in the 1970 Occupational Health and Safety Act, which established The Occupational Safety and Health Administration OSHA. In 1986, the agency introduced its first major regulatory policy, the Hazard Communication Standard (HCS) - also referred to as "Worker Right to Know." HCS requires chemical manufacturers and distributors to provide MSDS for every hazardous chemical to users to communicate information on these hazards. MSDS, Safety Data Sheet (SDS), or Product Safety Data Sheet (PSDS) is an important component of product stewardship and occupational safety and health. It is intended to provide workers and emergency personnel with procedures for handling or working with that substance in a safe manner, and includes information such as physical data (melting point, boiling point, flash point, etc.), composition, toxicity, health effects, first aid, reactivity, storage, disposal, permissible exposure limits and thresholds, personal protective equipment, and spill - handling procedures. MSDS formats can vary from source to source within a country depending on national requirements[12].

Although MSDS formats vary somewhat between countries and authors (an international MSDS format is documented in ANSI Standard Z400.1-1993), they generally outline the physical and chemical properties of the product, describe potential hazards associated with the substance (health, storage cautions, flammability, radioactivity, reactivity, etc.), prescribe emergency actions, and often include manufacturer identification, address, MSDS date, and emergency phone numbers[13].

In 2012, OSHA revised its Hazard Communication Standard to adopt the Globally Harmonized System for Classification and Labelling (GHS) – an international system used in many countries for determining the hazards of chemicals and to warn users of chemicals about those hazards through labels and data sheets. MSDSs will be replaced by Safety Data Sheets (SDSs) which have a consistent format and may include internationally recognized hazard symbols. This transition will be completed in stages and will be finished by June 2016[14].

SDSs are a widely used system for cataloguing information on chemicals, chemical compounds, and chemical mixtures. SDS information may include instructions for the safe use and potential hazards associated with a particular material or product. There is also a duty to properly label substances on the basis of physic - chemical, health and/or environmental risks. Labels can include hazard symbols such as the European Union standard black diagonal cross on an orange background, used to denote a harmful substance. An SDS for a substance is not primarily intended for use by the general consumer, focusing instead on the hazards of working with the material in an occupational setting. It is important to use an SDS specific to both country and supplier, as the same product (e.g. paints sold under identical brand names by the same company) can have different formulations in different countries. The formulation and hazard of a product using a generic name (e.g. *sugar soap*) may vary between manufacturers in the same country. [14]

From the above overview, it is clear that many chemical substances used in the textile industry may be harmful, and therefore dangerous to handle unless proper safety precautions are used. Occupational safety and exposure during handling is therefore an equally important issue which needs to be managed just as closely as impacts on the external environment. OSHA has rules to limit workers' exposure to hundreds of chemicals. These limits are called Permissible Exposure Limits, or PELs. These are the exposure levels that OSHA can legally enforce. PELs are calculated based on an exposure for a full 8 - hour shift. This is called an 8 - hour Time -Weighted -Average, or TWA. Some chemicals are so dangerous that the exposure limits cannot be averaged over a full shift. Instead, the Short - Term Exposure Limits, or STELs, are based on 15- or 30 - minute periods. Other chemicals have Ceiling Limits. The Ceiling Limit must not be exceeded at any time during the work shift. Ceiling limits take precedence over all TWAs and STELs. The amount of a chemical a person is exposed to is usually measured in parts per million, or ppm. For every 1 million parts of air, there can be a certain number of parts of a chemical. One ppm is approximately equivalent to 1 teaspoon of water in a full bath tub. A material with a PEL of 100 ppm means that one could be exposed to 100 ppm for the entire 8-hour shift. Conversely, one could be exposed to 200 ppm for 4 hours, if one's exposure was 0 ppm for the remainder of the 8 - hour shift, as long as you have not exceeded the ceiling limit for the chemical[15].

This research attempted to address the above issues, as such, a study on toxicity of dyes and chemicals applied in the mill was undertaken, while MSDSs were used as a major instrument of the investigation. In addition examination into mill's occupational and safety practices on handling chemical substances by workers was undertaken.

MATERIALS AND METHODS

Entire record of dyes and chemicals used in the mill for 12 months period was conducted. The Manufacturing Companies/Suppliers of chemicals and dyes were visited /contacted and requested to provide Materials Safety Data Sheets (MSDSs) for each dye/chemical they supply. For specific dyes/chemicals where MSDSs were not available or data provided in MSDS was insufficient or incomplete, several International organizations were consulted, namely: International Register of Potentially Toxic Chemicals (IRPTC), Switzerland; International Agency for Research on Cancer (IARC), France and Ecological and Toxicological Association of Dyers and Organic Pigments Manufacturers (ETAD), Switzerland. Occupational and safety practices on handling chemicals in the mill's dyeing, scouring and finishing departments were observed for the same period. In - depth interviews and semi - structured questionnaire were used to gather the information from the Mill's management staff and machinery operators.

RESULTS

For the twelve month period of the study, twenty two dyes and twenty five chemicals were used in the mill. Out of these dyes, Disperse dyes for Polyester constituted 62.6%, Reactive dyes for Viscose Rayon - 13.1%, Metal/mordant dyes for Wool - 11%, Basic dyes for Acrylic - 7.7%, Sulphur dyes for Wool - 4.9% and Acid dyes for Wool - 0.7%. In addition to a dye, one or more of the following auxiliary chemicals were necessary for satisfactory dyeing: Acetic acid, dispersing agents, orthophenylphenol, and butylbenzoate carries - for Disperse dyes; Sodium chloride, sodium carbonate, sodium hydroxide, trisodium phosphate, and tetrasodium pyrophosphate - for Reactive dyes; Chromium, acetic acid, sodium sulphate, ammonium sulphate, penetrating agents, sulphuric or formic acid, and potassium or sodium dichromate - for Metal dyes; Acetic acid, tannic acid, formic acid, sodium sulphate, and sodium acetate - for Basic dyes; Sodium sulphide, sodium carbonate, sodium dichromate, acetic acid, hydrogen peroxide, sodium chloride, and copper sulphate - for Sulphur dyes; and Acetic acid, sulphuric acid, ammonium acetate, leveling agents, and ammonium phosphate – for Acid dyes.

Fibre and Fabric dyeing Department consumed (by weight) - 73% of Dyes and Chemicals, Fabric finishing Department consumed – 21%, and Wool scouring Department remaining consumed - 6%.

In the major consumer of dyes and chemicals - Fibre and Fabric dyeing Department, it was identified that consumption of Chemicals was at 89% (by weight) and 21% (by cost), and Dyes consumption was 11% and 74% respectively.

The main supplier of the dyes and chemicals was Ciba-Geigy of Germany through their Kenyan agents in Nairobi. Thirty six MSDSs were collected from the above suppliers in the course of the study. Several MSDSs did not contain information on all the chemicals present, including those known to be serious sensitizers or carcinogens. In two instances MSDSs were prepared by third party and not by the manufacturing company or supplier. In the mill MSDSs were available for only very few compounds, for some chemicals only Chemicals Safety Manual existed. From the MSDSs analysis it was identified that 56% of the chemicals and 90.9% of the dyes used by the mill were supplied under Trade names. For several compounds MSDSs were either not available or the data in MSDSs was incomplete. Accuracy and completeness of MSDSs were found to be relatively poor.

Critical analysis of MSDSs showed that: Four dyes (disperse, metal complex/chrome/mordant and basic groups) namely respectively: Maxilon Red GRL; Terasil Red 3BL-01; Lanaset Orange RN and Terasil Blue BGE-01 were classified as harmful to humans. Two dyes (all disperse group) namely: 0203 Serilen Black LCB and 0225 Serilen Black R-FSN were harmful to fish. Four dyes (all disperse group) namely: 0373 Serilene Black BNFS; 0233 Serilene Yellow 4RL200; 0242 Serilene Red BR-LS and 0203 Serilene Black LCB were not readily biodegradable. All dyes of disperse group, with exception of Terasil Blue BGE-01, were classified as slightly water polluting. Four dyes (all disperse group) namely: 0373 Serilene Black BNFS; 0233 Serilene Yellow 4RL200; 0242 Serilene Red BR-LS and 0225 Serilene Black R-FSN were not classified as hazardous to health. However, 0225 Serilene Black R-FSN is harmful if swallowed; 0242 Serilene Red BR-LS causes sensitization by skin contact and 0373 Serilene Black BNFS is irritant to skin.

Regarding chemicals, it was identified that Univadene DIF was classified as harmful to humans if swallowed and can cause sensitization by skin contact, Invadine LUN was classified as serious irritant to skin and can cause risk of damage to eyes and Ultratex EMJ and Albegal Set can be considered as not harmful to humans and they are non - irritant to skin and eyes (tested on rabbits). Three chemical compounds, namely: Chromium compounds, Potassium dichromate (Cr^{+6}) and Potassium dichromate (Cr^{+3}) were classified as carcinogenic to humans with sufficient evidence on their status for both humans and animals. Formaldehyde was classified as probably carcinogenic to humans with limited evidence on its carcinogenic status to humans, but sufficient information that they are carcinogenic to animals. Hydrogen peroxide was not classified as carcinogenic to humans.

Additional information on carcinogenic status of selected dyes and chemicals applied in mill was requested from the three International organizations; out of these the reply was received from IARC, France.

To examine the occupational practices on handling chemicals, forty five questioners were distributed and interviews were conducted. Out of these thirty seven questionnaires were returned fully completed, six questionnaires were returned incomplete and two questionnaires were misplaced by responders, and therefore the latter were not included for the evaluation. It was noticed that operating staff indicated that some technical terminology used in MSDSs were very difficult for them to understand, leading either to confusion or complete misinterpretation of the meaning.

DISCUSSION AND RECOMMENDATIONS

A large portion of dyes/chemicals used in the mill were identified as potentially hazardous/toxic and exposure to some of these chemicals has been regulated by International authorities (e.g. OSHA's permissible exposure limit (PEL) etc). In addition some chemicals have been allocated threshold limit values (TLV) and short term exposure limits (STEL) e.g. by the American Conference of Governmental Industrial Hygienists.

The study recommends that exposure to such chemicals should be kept below the applicable TLV and STEL levels. In addition, if necessary, suitable respiratory and other protective equipment should be provided at the mill. Atmospheric analysis of the chemicals store should be carried out periodically. Another recommendation is to substitute harmful/toxic compound(s) by less harmful/toxic one(s). Specifically, in the mill, two out of three compounds classified as carcinogenic to humans were used in either chrome/metal complex/ mordant dyes itself or as their mordants. It is therefore recommended to substitute chromium fixation by hydrogen peroxide according to Veldhuisen, 1991[16].

Majority of chemicals and dyes were coming from the manufacturer/supplier under Trade name because there was no legal requirement or predisposition for the manufacturing company to disclose the complete chemical composition/formulation to its customers. Trade

TABLE 1: Carcinogenic status of selected textile dyes and chemicals used in the mill

Name	Effect on human beings	Effect on animals	Group	Use
Formaldehyde	L	S	2A	Finishing agent
Hydrogen Peroxide	I	L	3	Bleaching agent
Chromium compounds	S	S	1	Chrome dye
Potasium dichromate Cr^{+6}	S	S	1	Chrome dye
Potasium dichromate Cr^{+3}	S	S	1	Wool preservative

name equals "business secret". In addition to business secret there was a disturbing issue of Identity Card for newly introduced chemical compounds. The International Dangerous Substances Directive of 1996 obliges all manufacturers or importers of new chemical compounds to carry out a study which examines the possible risks for man and the environment presented by such compound before the product is introduced. For the textile auxiliary producer, this means that any modification to dyes, reducing agents, finishers, etc, must be tested and registered before the modified product can be marketed, even if the new substance accounts for only 0.1% of the existing formulae. In order to comply with these safety requirements the company incurs considerable expenditure with registration, also there was a time implication. Registration can take up to two years; depending on the country. This issue of ID was often avoided under the cover of trade names. All the above individually or in combination made the full identification of associated to those chemicals/ dyes risks more difficult. In addition, in most cases some of these products served the same purpose in wet processing and can therefore cause confusion leading to purchasing more than one product for the same job. This consequently can bring about unnecessary expenses for the mill.

In the regard of trade names it was recommended, that textile companies should request and be provided by chemical/dye manufacturing companies with complete information/formulation on these chemicals/dyes regarding their toxicity, handling precautions etc. In addition a list of products available and suitable for the same job should be attached for customer's consideration.

Analysis of questionnaires reveals that the chemicals that have immediate harmful effect on contact with human body were recognized by the mill's chemicals/ dyes handling staff to be harmful/toxic. Examples are acetic acid, hydrogen peroxide, sodium hydrosulphite and caustic soda. Other chemicals have been noted by the manufacturers as having harmful effects on repeated exposure, but these had been assumed by the staff as harmless. Examples are sodium carbonate, ammonium sulphate, trisodiumphosphate and various other functional chemicals that come in trade names.

To increase the level of understanding on potential dangers when handling chemical substances the study advised introducing a systematic training program on occupational safety for workers handling chemical substances in the mill. The study recommended that with corrosives like some alkalis and acids, care should be taken to prevent skin contact by the provision of appropriate protective clothing, including approved eye protection. Also emergency showers including eye washers should be provided where there is a risk of serious or substantial contact with corrosive substances. Some powdered chemicals are susceptible to spontaneous combustion, while others are combustible on contact with small amounts of water, these materials should be kept in suitable metal container with sealed lids. Oxidizing agents, though not combustible, may in fire conditions increase the danger and should not be stored with flammable liquids.

Study of the questionnaires assessing worker comprehension of MSDS have found that workers reported difficulty in reading and understanding significant parts of technical information in the MSDSs. MSDSs were particularly difficult to understand for workers with limited English proficiency, and there was no requirement to provide non - English speakers with information in their native language, such as Kiswahili or vernacular language.

The study recommended whenever possible using the standardized hazard symbols instead of highly technical terminology in MSDSs. On using third party in preparation of MSDSs workers in the mill should use third party MSDSs with care as the manufacturer may choose not to reveal their formulation to a third party.

Moreover, it was identified that Fibre and Fabric Dyeing Department was a major consumer of dyes and chemicals among the wet processes in the mill. In particular, dyes incur the majority of the cost accounting for 74%, in contrast to 11% of their weight for the same in that department. This reveals that even a small saving in consumption of dyes can lead to a corresponding greater saving in total cost for chemicals and dyes in this department and hence the need to reduce dye wastages is clear. A partial hydrolysis, or decomposition, of the dye during dyeing results in dye remaining on the surface of the fabric which must be removed /washed away. This unfixed dye, with amounts ranging from 5 to 40% then becomes present in dyehouse effluents. According to Cooper P. (2000), the percentage of unfixed dyes is within the following ranges: disperse group (10 - 20%), reactive group (10 - 40%), mordant/chrome/ metal complex (5 - 25%), basic (5 - 30%), sulphur (20 - 40%) and acid (5 - 20%). One of the most difficult tasks confronted by the wastewater treatment plants of textile industries is the removal of the colour of these compounds, mainly because dyes and pigments are designed to resist biodegradation, such that they remain in the environment for a long period of time. For example, the half - life of the hydrolyzed dye Reactive Blue 19 is about 46 years at pH 7 and 25°C. Carneiro *et al*., 2010 designed and optimized an accurate and sensitive analytical method for monitoring the dyes C.I. Disperse Blue 373 (DB373), C.I. Disperse Orange 37 (DO37) and C.I. Disperse Violet 93 (DV93) in environmental samples. This investigation showed that DB373, DO37 and DV93 were present in both untreated river water and drinking water, indicating that the effluent treatment (pre - chlorination, flocculation, coagulation and flotation) generally used by drinking water treatment plants, was not entirely effective in removing these dyes. This study was confirmed by the mutagenic activity detected in these wastewaters.

In this context, to conserve textile dyes and chemicals and to reduce their environmental impacts on the environment, the study recommends installing a Vacuum Suction system and Automatic dyes/chemicals dispersing system at the mill. It is estimated that the vacuum suction system installed at Chieng Sang Industry Co. Ltd. Thailand has led to a 25% saving in dyes and chemicals (http://www.emcentre.com/unepweb). Automation, on the other hand, offers faster delivery times, better laboratory – to - dye house correlation, a wider variety of styles and higher quality. Handling of some chemicals is hazardous so an automated system also minimizes the chances of worker injury.

Moreover, to promote Global "Green textiles" movement, Eco - labelling should be introduced for textile end - products in the mill. Such labelling would state, for example, that the textile content of the product was manufactured at an accredited factory and would contain information about the product`s biodegradability, and also on toxicity of the dyes/colorants used. For example "no toxic dyes/chemicals were used to produce this textile product". Consumers would be better informed in making purchasing decisions, and would be better able to weigh up the trade - offs, since helping to secure environmental benefits unavoidably means paying the higher product prices resulting from manufacturer's increased "environmental spend". At present, a larger number of producers in the country see no marketing advantage in proclaiming "environmental soundness" of their products and processes. This attitude hopefully will change with increasing consumer awareness and concern in Kenya.

CONCLUSION

MSDSs are vital ingredient for providing reliable information on toxicity of chemical compounds and associated precautions on handling such compounds. MSDSs were the only form of mandated public disclosure of chemical's toxicity in the mil. Therefore they should be readily available to the staff handling chemicals; in addition, to make MSDSs more understandable some technical terminology in MSDSs should be substituted by self - explanatory standardized label elements assigned by hazard class and category such as internationally recognized hazard symbols.

Accurate and full disclosure of toxic ingredients is an important step towards improving health outcomes for workers in the industry. Accurate disclosure is a foundation. Particularly in the arena of chemical substances management and regulation - where so little information on toxicity and enforcement exists - disclosure mechanisms provide an important lever to create political and economic incentives for industry change towards healthier and "Green" manufacturing.

Considering the fact that the textile wet processes are recognized as one of the most environmentally unfriendly industrial processes, it is of extreme importance to find alternative, eco-friendly methods and substances.

SOURCE

IARC, France, 2012

KEYS:

I – inadequate evidence

S – Sufficient information that they are carcinogenic

L – Limited evidence on their carcinogenic status

Group 1 - agent is carcinogenic to human beings

2A - agent is probably carcinogenic to humans

2B - agent is possibly carcinogenic to humans
3 - agent is not classifiable as to carcinogenic to humans

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