Ecological and toxicological properties of dyestuffs

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Introduction

IN recent years lot of awareness and concern has developed over the environmental issues of textile wet processing. The Pollution Control Board is also becoming more strict in the implementation of the pollution control act. This has brought a lot of environmental pressure on the textile processing industry. Dyes, especially, cause a lot of public concern, as even small concentrations (1 mg/1) are visible, unlike other chemicals. The Surat textile wet processing industry, comprising more than 240 process houses, roughly consumes 4500 MT/annum of mainly acid, disperse and direct dyes. An attempt has been made in this paper to assess the various ecological and toxicological properties of dyestuffs used in Surat and how they affect the environment. A database of these properties of dyes and chemicals can then be effectively utilized for waste minimization in a process house.

Toxicology of dyestuffs

The Ecological & Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) has been prominent in promoting research and building up of knowledge in all areas concerned with the field of Ecotox properties of dyestuffs over the years. Sandoz, Hoechst, ATUL, IDI are the only Indian members of ETAD from where Safety Data Sheets containing such information can be obtained.

1) *Acute toxicity*

This is a test carried out on animals (mainly rats) to ascertain the single oral dose of a dye which is required to kill 50% of a population of experimental animals within 14 days. This dose concentration is expressed in mg/kg of bodyweight and known as a lethal dose 50 (LD50).

Acute oral toxicity studies carried out by ETAD on rats of 4,461 commercial dyes show that 92% of these products have a low acute toxicity of LD50 exceeding 2000 mg/kg and only 1% (44 dyes) possessed LD50 less than 250 mg/kg. It was observed that basic dyes showed significantly higher toxicity (1).

On the basis of toxicity test results, the following grading of toxicity can be made. (refer table 1)

Thus most of the dyes fall under the less toxic group. Yet there are some dyes which have been specifically classified as toxic by ETAD as shown in the Table 2 (2).

2) *Chronic toxicity*

The possible chronic (long-term) effects of interest are carcinogenicity (cancer inducing), mutagenic (heredity modifying) and to a lesser extent, sensitization of the skin (allergic). These properties are of great importance to the Indian industry, as many known carcinogens like benzidine, & napthyl amine, which have been long since banned in USA and Europe, are still being used by our dyestuff manufacturers. The assessment of carcinogenicity requires huge financial and laboratory resources. Besides, it requires a lot of expertise in interpretation and relevance of dose - response relationship, when testing at the maximum tolerated dose, as most of the

Table 1

LD_{50} mg/kg	in classification	No. of dyes	%
Less than 25	Very poisonous		
25 to 200	Poisonous	44	1
200 to 2000	Harmful	314	7
> 2000	Not classified	4103	92
Total		4461	100

Table 2 - List of toxic dyes

C.I. Generic name	C.I. No.	LD50 Oral (mg/kg)
Acid Orange 156	26501	120 - 200
Acid Orange 165	28682	60
Basic Blue 3 •	51004	100
Basic Blue 7	42595	100
Basic Blue 81	42598	205
Basic Red 12	48070	25 - 31
Basic Violet 16 • +	48013	90
Basic Yellow 21 •	48060	171
Direct Orange 62	-	150
C.I. Azoic Diazo Component 20	37175	49
C.I. Azoic Diazo Component 24	37155	70
C.I. Azoic Diazo Component 41	37165	115

• Dyes used in the Surat Process Houses.; + LD_{50} (inhalation) 25 mg/m^3

Table 3

C.I. Generic name	C.I. number	Chemicals class	Diazo component
Direct Blue 6	22610	Azo	Benzidine
Direct Blue 14	23850	Azo	Tolidine
Direct Blue 15	24400	Azo	Dianisidine
Direct Blue 53	23860	Azo	Tolidine
Direct Orange 1		Azo	Benzidine
Direct Brown 2		Azo	Benzidine
Direct Brown 95	30145	Azo	Benzidine
Direct Black 38	30235	Azo	Benzidine
Acid Red 26	16150	Azo	Xylidine
Acid Red 85	22245	Azo	Benzidine
Acid Red 114	23635	Azo	Tolidine
Acid Violet 49	42640	Triphenyl methane	-
Basic Yellow 2	41000	Ketonimin	-
Basic Orange 14	46005	Acridine	-

dyes have low toxicity. Thus many of the dyes and chemicals used in our country have not been screened for carcinogenicity.

The list of dyes used in Surat and known to cause cancer in animals, (3,4) is given in table 3.

Mutagenicity

The above mentioned limitations for carrying out expensive long-term testing, prompted and intensive search for simpler tests for determining the carcinogenic effects of chemicals. Most short-term tests thus developed for identifying potential carcinogens depend on the determination of a mutagenic effect, i.e., their ability to react with the genetic material. Testing of mutagenicity is mainly done by the Salmonella Microsome assay developed by Ames.

Some Azo compounds which were found to be mutagenic using the Salmonella assay are listed in Table 4 (5):

Table 4 - List of mutagenic dyes

Acid Red 2
Basic Orange 2
Pigment Orange 5
Pigment Red 1
Pigment Red 40
Direct Black 19

Skin Sensitization

According to Hatch and Malibach, some disperse dyes were found to cause allergic contact eczema. Potentially allergic dyes are listed in Table 5(3).

Potentially allergic dyes

Table 5

Chemical class	C.I. generic name
Anthraquinone	Disperse Red 11, 15
	Disperse Blue 1, 3, 7, 26, 35
Azo	Disperse Red 1, 17
	Disperse Blue 102, 124
	Disperse Orange 1, 3, 76
Nitro	Disperse Yellow 1, 9
Methine	Disperse Yellow 39, 49
Quinoline	Disperse Yellow 54, 64
Triphenyl Methane	Acid Violet 17

3) *Heavy metals*

Discharge consents for heavy metals are extremely stringent as they can be highly toxic to the animals and aquatic life in general. The toxicity would depend upon the physico-chemical form. For example copper ions are very toxic, whereas copper bound to organic matter is not harmful. Unfortunately this is not widely acknowledged in setting the limits in consent conditions, which, in the above example, would in all probability relate to the total copper and not the part that is "available". Metal complex dyes contain chelated chromium, cobalt, copper and nikel. Some cationic dyes are marketed as zinc salts, where the zinc content could be of the order of 2-3%. Besides, traces of more hazardous metals like mercury, cadmium and arsenic are found as impurities from intermediates in very low concentrations of less than 1 ppm.

Ecological properties

4) *Biodegradability*

Dyes have high stability towards a multitude of physical and chemical influences and hence, not surprisingly, they show a similar stability against breakdown by many microorganisms. Most of the dyes do not biodegrade under the short aerobic biological treatments of municipal sewage plants. But many dyes, especially the important azo dyes, are degraded substantially under the anaerobic digestion process in municipal sewage treatment works, and in anaerobic sediments and soils (6,7,8). The split aromatic amines undergo fairly ready degradation under aerobic conditions (9). Thus the aerobic conditions of rivers and lakes should degrade traces of aromatic amines formed from the biodegradation of azo dyes if these should accumulate in the river sediments.

5) *Aquatic toxicity*

Aquatic toxicity is expressed by LC_{50} which is a concentration expressed in mg/litre of a product, which, when administered by the respiratory route, is expected to kill 50% of the population of experimental fishes during an exposure of 48 hrs. Aquatic toxicity is another important issue for the Surat textile industry, as it is situated on the banks of the Tapi river and the Gujarat Pollution Control Board insists on LC_{10} i.e. 90% survival of fishes in 100% effluent, in areas where the effluent is discharged into waters used for fishing. Tests carried out by ETAD members on 3000 dyes in common use, 98% have an LC_{50} value in excess of 1 mg/1. In only 27 cases (16 of them basic dyes of those 10 triphenyl methane structures) is the LC_{50} of the order of 0.05 mg/1. Fish toxicity results are summarized in Table 6(10).

Table 6
Fish toxicity level of dyes in common use

LC50 value (mg/l)	Proportion of dyes (%)
< 1	2
1 - 10	1
10 - 100	27
100 - 500	31
> 500	28

Thus, dyes with few exceptions, are toxic only at levels which are orders of magnitude greater than levels which would be highly visible in rivers. Dyes can be visible at as low concentrations like 0.1 to 1 mg/1. Thus provided there is no "visual pollution" in the rivers, dyes are unlikely to have adverse acute effects on aquatic life. A list of toxicity of some common dyes used in Surat is shown in Table 7. Toxicity of some other products are also listed for the sake of comparison (12, 13).

6) *Bioaccumulation* is defined as the factor Ca/Ce, where Ca is the concentration of the dye or chemical in the animal species and Ce that for the environment . The possibility of bioaccumulation in fishes has, therefore, to be considered. The partition coefficient in n-octanol/water mixture (Pow) is used as a measure of bioaccumulation. If Pow is less than 1000 it can be predicted that bioaccumulation factor in fish (BF) is less than 100, at which levels no problems of bioaccumulation are foreseen (12). It has been observed that water soluble dyes do not bioaccumulate. Water insoluble dyes like disperse with Pow above 1000 still show no evidence of bioaccumulation, and neither do pigments.

Table 7: Fish toxicity of some dyes and chemicals.

Dyes/Substance	LC50
Acid Yellow 17	180
Acid Orange 7	165
Acid Red 52	> 500
Acid Red 119	> 500
Acid Blue 7	1 - 100
Acid Blue 113	10
Acid Black 52	7
Acid Black 1	180
Disperse Yellow 3	> 180
Disperse Scarlet 54	100 - 500
Disperse Red 167	100 - 500
Disperse Blue 79	> 100
Nonyl phenol ethoxylate (9.5 mole)	10
Copper sulfate	1.8
DDT	0.006

Environmental dye levels

The approximate environmental levels in the receiving waters of a particular dyestuff used at 1000kg/year in a dyeing house can be calculated as shown in table 8.

Another similar calculation may be used to calculate the total levels of dyestuff from a dyeing and printing house (refer table 9).

An individual process house will have access to virtually all the data in the above calculations. It should be noted that for the above hypothetical printing house effluent dye concentration calculation (10 mg/litre) represents a small fraction as compared to other discharged chemicals, surfactants, fabric sizes and impurities. Besides, the river flow quoted in both the examples corresponds to a small stream of approxi-

Table 8

Dye used	1000 kg/year
Number of days used	100 days
Amount used/day	10 kgs
Amount discharged (if exhaustion rate 90%)	1 kg/day
Mean concentration in sewage from 2 lakh people (100 liters/head)	0.25 mg/litre
Mean concentration in treated sewage effluent (50% removal)	0.1 mg/litre
Mean concentration in receiving water (flow 4 * 10 m³/day)	1 µg/litre

Table 9

Weight of fabric processed	600 tonnes/year
Total dyes used (at 2%)	12 tonnes/year
Dyes discharged in the effluent (if exhaustion rate is 90%)	1.2 tonnes/year
Volume of effluent (200 liters/kg for dyeing & printing)	1,20,000 m³/year
Total dyestuff concentration in untreated effluent	10 mg/litre
Mean concentration in sewage from 2 lakh people (100 liters/head)	2 mg/litre
Mean concentration in treated sewage effluent (50% removal)	1 mg/litre
Mean concentration in receiving water (flow 4 * 10m³/day)	10 µg/litre

mately 4 m wide and 82m deep flowing at a speed of 2 km/hr. (13)

Summary

In relation to the growing awareness and concern for the environment, ecology and work-place hygiene, corresponding care must also be taken by the textile processors as well as the dyestuff and auxiliaries manufacturers. The processors should voluntarily renunciate unsafe dyes, especially carcinogenic dyes, if the manufacturers do not take this step themselves. Processors can minimize exposure to workers by providing well ventilated dyes storerooms, protective clothing, dust masks, etc. and by informing and training workers for safe handling of dyes and chemicals. Low dusting, granular dyes if developed by our manufacturers, can solve lot of dusting-related health hazards. Dyestuff manufacturers can contribute immensely by supplying Safety Data Sheets containing the above-described ecological and toxicological properties which can then be effectively used by processors for waste minimization techniques.

References:

1) R.Anliker, JSDC Sep. 1979,317- 326
2) R.Anliker, JSDC May 1988, 223-225.
3) R.Moll, Melliand, 10/1991, 836 - 840.
4) E. Longstaff, Dyes & Pigments, 4/1983, 243 - 304.
5) ETAD Information Notice - "Azo Colorants. An overview of their unique characteristics & the requirements for their safe handling & use".
6) D. Brown, Chemosphere, Vol. 12,3,1983,397 - 404.
7) D. Brown, Chemosphere, Vol.15,4,1986, 479 -491.
8) D. Brown, Chemosphere, Vol.16,7,1987, 1539 - 1553.
9) D. Brown, Chemosphere, 3, 1983, 405 - 414.
10) Ecological Aspects of colour chemistry - I. Holme
11) Sandoz Safety Data Sheets.
12) I.G. Laing, Rev. Prog. Coloration 21, 1991,56 - 71.
13) D. Brown, Ecotoxicological & Environmental Safety, 13, 1987, 139 - 147.