The Saga of Indian Dyestuff Industry

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The dyestuff industry is the monitoring element of the development of chemical industry and technology as it covers almost all unit operations and processes in organic chemical synthesis and chemical engineering services equally. Thus, it provides major inputs to many other industries there by contributing in a large way to national economy. As major part of dyestuff industry's outputs are going into textile industry, where dyestuffs for cotton textiles are comparatively low and a phenomenal rise in demand for dyestuffs for synthetics.

The dyestuffs industry in the country is well developed. It is well equipped with sufficient capacities to meet the current demand for most of the dyestuffs in the country and overseas also. There are about 50 units in the organised sector at present having a total installed capacity of 55,000 tones per annum. There are also around 700* units in the small scale sector with having a total installed capacity of above 30,000 tones per annum. The data of small-scale sector is very scanty. However, the total current production of dyestuffs in the country may be around 85,000 tones per annum. The value of fixed capital of production of the industry exceeds Rs 500 crores.

Table 1: Indian Dyestuff Industry (Estimate)

1. No of units	
a. Organised	50
b. SSI	700
2. Fixed capital	Rs 500 crores
3. Production of finished Dyestuffs	85,000 tones per annum

The dyestuff industry in India is mainly located in Maharashtra and Gujarat. The dyestuff industry has undergone a process of restructuring since last 5 YEARS. Colour Chem Ltd. was the market leader before 5 years but has now opted to exit from dyestuff business and has entered into the manufacturing agreement with Dyestar (I) Ltd. where by Dyestar would be responsible for marketing and Colour Chem would be manufacturing dyes at its Thane factory Ciba India and IDI entered into a joint venture for production of cellulose and polyester dyes. IDI also tied up with Hindustan Ciba-Geigy for manufacturing and marketing of dyes and pigments. Atul products Ltd., a Lalbhai group company completed acquisition of Zeneca's 50% stakes in Atic industries Ltd. in 1995. It manufactures all ranges of dyes especially vat, sulphur and the reactive dyes. For cellulosic fabrics And going into the market by its own, after breaking of the tie with BASF Germany for marketing of vat dyes in global market before few years. The restructuring of Sandoz, following the merger of the company's life sciences business with Ciba led to creation of Clariant A.-G with the formation of Clariant India in the country which manufactures wide ranges of dyes and intermediates. BASF (I) Ltd. is manufacturing dyes for cellulosic, polyester, and leather dyes.

Dye classes which are being produced include acrylic fibre dyes, azo dyes, acid dyes, direct dyes, basic dyes, disperse dyes, ingrain dyes, fast colour bases, food dyes, naphthols, oil & spirit soluble dyes, optical brightners, organic pigments including pigments emulsions, reactive dyes, solublised vat dyes, stabilised azoics, sulphur dyes, vat dyes including indigoids.

The production of dyestuffs in organised sector reached a peak in past few decades but due to the demand recession coupled with cut-throat competition and uneconomic price realization saw it to decline little bit in recent years.

The production pattern of individual classes of dyestuffs, over the years indicates interesting trends. Azo dyes, acid dyes, direct dyes, basic dyes, food colours, ingrain dyes, naphthols and stabilised azoics saw a declining trend in production where as reactive dyes, vat dyes and particularly disperse dyes has increased considerably. The declining trend of azo dyes, basic dyes and naphthols could be attributed to the shift in production from organised sector to small sector. In case of ingrain dyes and stabilised azoics, the trend is declining due to technological obsolescence. Reactive and vat dye's production increased due to the growth in cotton fabrics coupled with their techno-economic superiority over other cotton dyes. In case of disperse dyes, increase is attributed to the ever rising demand for polyester fibre. The utilisation of capacity varies widely from one group to other. The capacity utilisation for acrylic fibre dyes, basic dyes, food dyes, fast colour bases and stabilised azoics was very poor. The capacity for naphthols, acid dyes, direct dyes, organic pigments, reactive dyes, vat dyes, sulphur dyes and specifically for disperse dyes has been well utilised.

Table 2: Production in the organised sector ('000 MT)

Dyestuff	Installed Capacity	Production
Azo Dyes	5.0	2.2
Azo Direct Dyes	1.0	0.3
Disperse Dyes	4.1	4.9
Fast Colour Bases	1.2	0.2
Ingrain Dyes	0.3	0.05
Oil Soluble Dyes	0.2	0.4
Optical Brightners	1.5	1.2
Organic Pigments	12.8	9.9
Pigment Emulsions	6.5	4.1
Reactive Dyes	8.0	6.2
Sulphur Black	4.2	2.7
Vat Dyes	2.7	2.5
Soluble vat Dyes	0.3	0.06
Food Colours	0.2	0.05
Naphthols	2.1	0.9
Other Dyes	7.5	6.9
Total	**57.6**	**42.56**

Source: Chemical Industry Digest May-June 1999

In India, cotton still enjoys a very prominent place as 75% cotton and 25% synthetic is assumed the consumption pattern. Hence it seems that inspite of the trend towards synthetics, cotton will retain its dominance for years to come and hence the dyes used for cotton also enjoy its demand.

Table 3: Cloth pattern in 1999-2000

Material	M. meters	% break-up
Cotton	13200	60
Blended	4400	20
Synthetics	4400	20

Source: Chemical Industry Digest May-June 1999

Among synthetics, the growth rate will be highest for polyester followed by nylon & acrylics.

The growth rate is very modest for azo, naphthols, basic and fast colour bases. The azo dyes based on benzidine and other banned amines have been withdrawn because of their health hazards. Similar considerations are likely to keep the demand for food dyes static throughout the period. Latest trend shows the usage of high cost but high quality vat dyes from textile industry. There has been a considerable shift in consumption to the relatively cheaper reactive and sulphur dyes.

The progressive orientation towards synthetics and particularly polyester based textiles has resulted in a phenomenal rise in the consumption of disperse dyes. Although cotton dyes as a whole dominate Indian scene, disperse dyes holds the biggest growth potential in domestic and international market.

Table 4: Share of individual dyestuffs in total exports (%)

Direct dyes	4.1
Basic	3.7
Reactive	40.1
Pigments	18.2
Disperse	5.1
Acid/mordant	13.2
Vat	2.8
Naphthols	7.0
Optical brightners	1.0
Others	4.8

Source: Chemical Industry Digest May-June 1999

In recent years because of strict global norms, many dye intermediates are banned due to their carcinogenic nature. Thus, azo dyes from these intermediates are now eliminated from the manufacturing unit's entire list. There are all together 21 banned amines including benzidine, which are carcinogenic. Therefore azo dyes obtained from these banned amines cannot be exported & marketed in the global market. All dyes with the dye effluents such as colour, metal, salt etc., are bad due to stringent environmental regulations.

Vat dyes whose raw material and manufacturing costs are very high and hence are very expensive. Therefore, only organised sector can afford to produce these dyes. Dyes with poor or with moderate fastness properties, as some direct, basic dyes would strip off easily and fade upon exposure to light and chemical environment. Hence dyes with superior properties, wide range of colours and Eco-friendly are of great importance for the years to come apart from being economically viable.

General Properties of Dyeing

Dyeing of textile fibres and fabrics was practiced in very early ages in China and in India as early as 2500 B.C, by colouring silk. Until the middle of last century, all dyes were obtained from natural sources. Most of these colours of natural origin used those days were not capable of producing permanent colours on textiles and hence 'Mordants' are used to impregnate with metallic oxides, which bite the dye and hold it on the fibre. Until 1884, all the synthetic dyes which had appeared were not substances to cotton but from then onwards much development had taken place in dye classes to get better shades with supremely good fastness characteristics on to the substrate.

The forces, which direct dye molecules to textile fibres are complex and the process consists of three stages which, are

(1) Migration of dye from the solution to the interface,

(2) Diffusion of the dye from the surface towards the centre of the fibre.

(3) The anchoring of the dye molecules by covalent or hydrogen bonds, or other forces of a physical nature.

The dye molecules at the fibre surface are governed by

(1) Electro-potential forces

(2) Temperature and

(3) Agitation.

All fibres when immersed in water or aqueous solutions acquire an electric potential called Zeta potential.

The entry of dye molecule into the fibre from interfacial layer is extremely rapid and high concentration, high agitation and increase in temperature can bring about a much greater decrease of the time of half dyeing. Diffusion of dye molecules within the fibre from outside layers into the interior of the fibre can be given by Ficke's law. The chemical attachment is through formation of a covalent bond, ionic bond, hydrogen bond, Vander Waal's force, induced polarity, dispersion forces, hydrophobic interactions. Now initially the free energy of the solution is greater than that of the fiber phase. This difference in free energy is the driving force, which will bring about the transfer of dye on to the fiber until equilibrium is reached, hence during dyeing, heat is given out.

Fastness Classification: All dyes are seldom equally fast to all the influences and it is possible to a have to have good fastness in one respects like washing but may have poor fastness in other respects like light. All the properties except light are measured on 1-5 scale where the numbers corresponding to the following graduations;

(a) Alternation of shade during testing:

Grade 5 -Shade Unaltered

Grade 4 - Very slight loss depth or alteration

Grade 3 - Appreciable loss or alteration

Grade 2 - Direct loss or alteration

Grade 1 - Great loss or much altered

(b) Staining of adjacent materials

Grade 5 - No staining of adjacent white

Grade 4 - Very slight staining of adjacent white

Grade 3 - Appreciable staining of adjacent white

Grade 2 - Deep staining of adjacent white

Grade 1 - Adjacent white dyed deeply.

(c) Light fastness measured in a scale of 1-8:

Grade 8 - Max fastness

Grade 7 -Excellent fastness

Grade 6 -Very good fastness

Grade 5 - Good fastness

Grade 4 - Fair fastness

Grade 3 - Moderate fastness

Grade 2 - Slight fastness

Grade 1 - Poor fastness

Various dye classes, which are used to colour textile fibres and their properties, are listed below;

(a) Basic dyes: These dyes are brilliant and posses high intensity of their colours. When a basic dye is treated with an alkali, it is decomposed with the liberation of the dye base, which is colourless. Basic dyes are of poor fastness to light and vary with regard to washing fastness from poor to moderate. Table 5 provides general conception of their fastness on wool.

Table 5

DYE	FASTNESS PROPERTIES	
	LIGHT	WASHING
(1) Auramine	1-2	1-2
(2) Rhodamine 6GB	1-2	1-2
(3) Methyl Violet	1-2	1-2
(4) Crystal Violet	1-2	1-2

On treatment with reducing agents, most basic dyes are converted to colourless compounds with comparative ease.

(b) Acid dyes: Most of acid dyes are sulphonic acid salts, but few of them are containing carboxyl groups. These dyes have direct affinity towards protein fibres and are main class used for wool dyeing. Polyamide fibres also have affinity for acid dyes. Most of the level dyeing acid dyes generally give 1-2 grading for wet fastness.

(c) Direct dyes: The direct dyes are also known as substantive colours and majority of these dyes are sulphonated azo compounds which are very similar to acid dyes and differentiation of acid and direct dyes is hair line thin. Most of these dyes lack wet fastness property, which is a disadvantage. To improve their wash fastness property, many methods have been used to increase molecular weight of the dye, after it has been absorbed by the fibre, to incorporate less solubility in water.

The molecule containing a primary amino group directly attached to an aromatic nucleus can be diazotized when the dye is on the fibre and then coupled with various phenols or aromatic amines to form new azo dyes 'in situ' on the fibre with improved wet fastness. As another chromophore is included, shade of the dye on the fabric will change.

For example: A dye Primulene is greenish yellow and when diazotized and coupled with

(a) Phenol, hue changed to reddish yellow

(b) β-Naphthol, hue changed to red

(c) m-Phenylenediamine, hue changed to dull red.

The effect of this on fastness properties is given in table 6.

Table 6

DEVELOPER	WASH FASTNESS	LIGHT FASTNESS
Undeveloped primuline	2	1
Developed with phenol	4	1
Developed with β-Naphthol	4	1
Developed with m-PDA	4	1
Developed with PMP	4	3

Amongst the developers, which are commonly used to couple with diazotized, dyes are:

β-Naphthol, m-PDA, Phenol, Resorcinol, m-Toluylediamine, Phenyl methylpyrazole, N-Phenyl phenyl phenylenediamine, Toulene,2,4 diamine.

By this method exact matching of shade is not easy because of the change of colour brought about by coupling. Thus they don't find extensive use for exact colour matching applications but are commonly used for dyeing darker shades of moderate fastness at a low cost.

Table 7

DYE C.I. NO	WASH FASTNESS (before)	WASH FASTNESS (after)
Direct yellow 64	3	4
Direct red 126	3	4
Direct blue 2	2	3
Direct blue 20	4	4

Another method to improve fastness is to after treat with formaldehyde. The improvement in fastness is of the order of one in the scale of ISO wash test. It is evident that unless direct dyes have been after treated, stripping of dyes is inevitable in many cases. The colour can be removed easily by boiling with sodium hydrosulphite or by bleaching. Hence the colour can be stripped off from the fabric due to its inherent nature of poor fastness property but not due to the activity of detergent.

Modern dyes are used very extensively for wool and polyamide fibres. They have very good wet-fastness and satisfactory light fastness properties.

Table 8

DYE C.I. NO	WASH FASTNESS ISO 3	LIGHT FASTNESS ISO TEST
Mordant yellow 30	5	6
Mordant red 9	5	6-7
Mordant black 11	5	7
Mordant blue 1	5	4

Azoic dyes are extensively used widely for cellulosic fabrics. Cotton yarns dyed with azoic colour lack rubbing fastness and can cause staining of adjacent areas during wet processing and washing operations. During washing wit detergent, due to rubbing the insoluble pigment deposited on the surface of the fibre strips out. Thus Azoic colours, which have poor rubbing fastness bleed, colour on rubbing and not due to detergent application, which is misunderstood as due to formers application.

Sulfur dyes are deep and easy to apply. Their wet fastness is good and light fastness is satisfactory and hence these provide cheap method of dyeing with better-wet fastness than direct dyes.

Vat dyes are important class of dyes by which cellulosic fibers can be dyed The light fastness of few dyes would be rated as moderate and depending upon their properties the purpose for end use can be selected.

Table 9

DYE C I NO.	LIGHT	CAUSTIC	BLEACH
Vat yellow 1	5-6	3-4	5
Vat yellow 2	4	5	5
Vat orange 1	6-7	3-4	5
Vat red 24	6-7	5	4-5
Vat blue 6	7-8	5	3-4

Disperse dyes are used for cellulosic acetate, polyester fibers etc, have quite good light and washing properties, but some blue anthraquinone pigments suffer from gas fading.

Table 10

DYE C.I. NO	LIGHT S D C	WASH (ISO 3 ALTERATION)
Disperse yellow 1	4-5	2
Disperse red 9	5	3
Disperse violet 1	6	3-4
Disperse blue 1	3-4	4

Reactive dyes are the most used dyes for dyeing cellulosic fibres and they possess extremely good light and wash fastness properties but have poor hypochlorite bleaching in many cases.

Table 11

DYE C.I. No.	LIGHT	WASH	BLEACH (Hypochlorite)
Reactive yellow 7	6	5	4-5
Reactive orange 14	5	5	1
Reactive red 8	4-5	4-5	2
Reactive blue 5	6-7	5	3
Reactive blue HSR	6-7	5	1

Dyeing of Synthetic Fibers

Disperse dyes on nylon fibers have good light fastness ranges from 4-6 and wash fastness varies from 2-4, and they are not satisfactory in very heavy shades. Direct cotton dyes used for polyamides have shown light fastness of the order 5-6 and wash fastness between 4-5. Acid dyes on polyamides show high light fastness property ranging from 6-7 and wash fastness properties from 4-5.

Soap is a metallic salt of a saturated or an unsaturated higher fatty acid, like Lead, Calcium, Magnesium or other metal salts. In practice sodium or potassium salts are used as detergents. Molecules of soap can be looked upon as being composed of hydrophilic or water seeking, heads and hydrophobic or water avoiding tails. Soap is a surface-active compound, which tends to lower surface tension at boundaries between water and air or oily substances. Oil is the nastiest dirt, which has to be removed from the textile fabric using detergent. Oil and water always separates into two layers. If soap is added the paraffin tail seeks the oil and hydrophilic heads remain in water. Soap reduces the surface tension and allows the oil to form a comparatively stable emulsion in water.

Synthetic detergents or surfactants which have replaced soap in domestic use and in industrial field to a great extent. Their Calcium and Magnesium compounds are not insoluble in water. They can be in the form of powders, liquid detergents (light and heavy duty), paste, solid detergents (light and heavy duty). Heavy-duty household washing powders normally contain 57-58% light soda ash and optical brightners/ bleaching agents 0.1-2.0% with various other ingredients. Liquid detergents are used for heavy duty washing both by hand and for washing machines for washing wool and silk. Synthetic detergents are not affected by hard water and retain properties at all conditions. They may cause harm to the textile fabric if their alkalinity level is more, by causing fiber deformation or stripping of the dye or decomposition of the dye. If this factor is taken care of by keeping the alkalinity level in the prescribed limit then detergents are not responsible for the removal of colour from the coloured fabrics upon washing.

It can be noted that dyes, which are having low light, wash, and rubbing fastness properties give up colour and shade naturally, on exposure to light or by washing. This phenomenon has nothing to do with the type of detergent used. Thus detergent is not the only factor by which colour strips off but it is the inherent fastness properties, nature of fibre, compatibility of the dye on the fibre etc. are important factors which govern stripping of the colour from fabric rather than the detergent.

Table 12: Status of Dye industry in India

Market Size 1995= 1575.41 Crores.	% Share
1. Indian Dyestuff Industries	17.65%
2. Atul Products	10.00%
3. Atic Industries	9.10%
4. Jaysynth Dyechem	7.5%
5. Mardia Chemicals	7.2%
6. Colour Chem	6.9%
7. Sudarshan Chemical Industries	6.7%
8. Others	35.00%

Source: Colourage

	In Crores of Rupees			
Dyes & Intermediates	1995-96	1996-97	19997-98	1998 April
Exports	1545.8	1944.8	2228.0	1792.42
Market Value	2576.33	3241.33	3713.33	2987.3667

Source: Ministry of Commerce

Prouct	Quantity in Kg	Value in Rs.
Disperse	2847465	697815892
Acid, Mordant	12514757	2372107516
Basic	2627454	425078643
Direct	3095627	627324975
Vat, Sol. Vat	1930895	1646765613
Reactive	2620396	5178656113
Pigment	10455827	288490263
Azoic	39590	9563142
Sulphur, Solvent	171614	30563006
Food, Other classes	5737387	1263173891
Optical Whiteners	1741506	271629273
Misc. Classes	4076543	819957844

Source: Ministry of Commerce

Company	Production 1996-97 (tonnes)	Production 1997-98 (tonnes)	Sales 1996-97 (crores)	Sales 1997-98 (crores)
Atul	9272	8360	287.05	284.34
IDI	7896	6898	280.55	279.30
Jaysynth Dyechem	8401	9540	179.45	207.07
Sudarshan Chemicals Industries	8095	9461	137.87	159.76
Colour Chem	123345	313991	154.71	158.65
Metro Chem	4971	6148	122.92	116.53
Ciba Speciality Chemicals	5111	7480	62.31	98.30
Clariant (I)	596	376	44.30	87.17
Pidilite Industries	669	976	93.45	82.57
Indokem Ltd.	466*	715*	58.32	69.63
Vanavil Dyes & Chemicals	1339	1555	26.42	45.91
Amar Dyechem	239	315	31.34	42.06
Amal Products	985	1190	41.59	41.59
Jasynth Dyestuff(I)	3269	3269	23.75	40.28
Deepak Nitrite	1253	2182	37.32	37.32
Serene Industries	1183	1099	27.77	31.46
Plastiblends India	3553	1978	81.73	30.47
Ultramafine & Pigments	4000	5352	23.48	29.41
Poddar Pigments	4736	4505	24.50	27.44
**=Others(Sales)	--	--	20.54**	27.19**
Total for 76 Companies	1257	1653	1759.37	1896.42
*='000 Litres/	466	715	---------	---------
Tonnes / (Rs.)	229254	411700	217052	219.92

Item Code	1996-97	1997-98
Export Quality (Tonnes)	13300	17418
Export Value (Rs)	1514.5	1733.9
Import Quality (Tonnes)	35335	33951
Import Value (Rs)	468.3	527.9
Sales Value (Rs)	2170.5	2197.9
Market Size (Rs)	2694.5	2638.8
Domestic Consumption (Rs)	1124.3	992

Status of dye Industry in India (and other Asian countries) - The Market of Dyes in India

Descriptor	Value
· Market Value (Rs. Crores) = 3713.	Please mention source and year Economic Intelligence Service CMIE Aug. 1999. & Ministry of Commerce Annual Report 1998. 1997-98

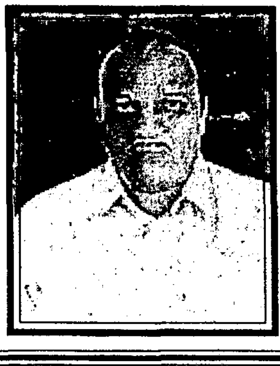
Major Manufacturers	Major Brands	Value (Rs. Crores)	% of total
1. Indian Dyestuff	Navinon, Navisol,	382	10.3
2. Atul	Naviline,	386	10.4
3. Jaysynth Dyechem	Tulacid, Tuladir Novatic, Tulaster on	282 217	7.6 5.8
4. Sudarshan Chemic all Industires.			
5. Colour Chem	Arylamide, Toluidine Reds,	159	4.3
6. Metro Chem	Colorin	134	3.6
7. Ciba Speciality Chemicals		119	3.2
8. Clariant	Cibacron	111	3
9. Others	Dimarine, Solar	1923	51.8

• Rate of growth (%) • 14.6 (for year 1996-1997-98) • 25.8 (for year 1995-1996-97)	Ministry of Commerce annual reports (1995 to 1998)

Trends in Market Shares (in %)

Company	1996-97	1997-98	Growth
Atul	10.85	10.43	-3.8
I.D.I	10.63	10.25	-3.6
Jaysynth Dye Chem	6.80	7.60	11.7
Sudarshan Chem. Ind.	5.22	5.86	12.3
Mardia Chemicals	5.86	5.82	-0.7
Colour Chem	4.66	4.28	8.1
Metro Chem Industies	2.36	3.61	53
Ciba Speciality Chemicals(I)	1.65	3.20	98
Clariant (I)	3.54	3.03	-14.4
Pidilite Industries Ltd	2.21	2.55	15.4
Total of these companies	53.85	56.62	5.1

Economic Intelligence Service CMIE Aug. 1999



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