NOVATEUR PUBLICATIONS
JournalNX- A Multidisciplinary Peer Reviewed Journal
ISSN No: 2581 - 4230
VOLUME 6, ISSUE 3, Mar. -2020

A STUDY OF DIFFERENT CLASSES OF DYES

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ABSTRACT:

The term dye is derived from old English word *daeg* or *daeh* meaning "colour". The archeological evidences have showed that dyeing was a widespread industrial enterprise in Egypt, India, and Mesopotamia in third millennium B.C. The basic dye substance was the plant juice revealed to people initially from stains of fruits, flowers and roots, left on the hands while picking them. Ever since the beginning of humankind, people have been using colorants for painting and dyeing of their surroundings, their skins and their clothes. Until the middle of the 19th century, all colorants applied were from natural origin. For example: insects (lac , cochineal and kermes) , fungi & lichens, Minerals like indigo for blue, gall black for black, orpiment for yellow. Ancient paintings discovered in caves in various parts of India provide ancient testimony of their application.

INTRODUCTION:

India since antiquity was known for excellent dye stuffs. India has been the largest dye producing country of the world in the past. Indigo dye (*nila*) presumed as indigenous Indian dye-drug was being used in Egypt for muslin dyeing in as early as 500 B.C. The history of Indian dyes appears to have started from vedic period. Vegetable substances like *manjistha* (madder), *maharanjana* (safflower), *haridra* (turmeric), *kala or askini* (possibly indicating indigo) were frequently used in vedic periods (1000 -500 B.C.).

In the pre vedic period a piece of purple colored cotton is available from the antiquities of Mohanjodaro (3000 B.C.) which from recent chemical examinations, suggested its coloration with madder (*rubia cordofolia*) (Marshal, 1931).

In post vedic period (500 B.C -3rd century A.D.) saffron *(kunkuma)*, indigo *(nila)* from plants, carbon black *(khanjana)* from minerals and *krimi* (dye producing insect) and *rocana* (yellow substance from cow's urine) were used for dyeing. The classical age upto the medieval period acknowledged the tinting capacity of a lot of substances from plants, minerals, and metals. Plants like *caesalpunia sappan, oldenlandia, malloutus phillipinensis ,indigofera tinctoria,piper longum*, Metals and minerals like iron *(ayas)*, iron sulphate *(kasisa)*, copper sulphate *(tuttha)* and antimony sulphate *(anjana)* were mainly used for dyeing. The medieval period was marked by the discovery of the colour fixation property and processes employed for the extraction of coloring principles from dye stuffs. By the late eighteenth century, applications of iron mordant for the fixation of colours like blue, green, and violet and aluminium mordant for fixation of red dye stuffs were used.

Synthetic dye manufacturing started in 1856, when the English chemist W.H. Perkin, In a classic case of serendipity, chanced upon his now famous 'Aniline Mauve' dye while he was attempting to synthesize quinine, the only cure for malaria. Perkin named this color Mauveine, after the French name of non-fast colour which was made of natural dyes. So "Mauve" (a basic dye) was the first synthetic dye stuff. Perkin, 18 years old, patented his invention and set up a production line. This concept of research and development was soon followed by others and new dyes began to appear on the market. Kékulé's discovery of the molecular structure of benzene in 1865 revolutionized the dyeing industry by producing lot of synthetic dyes.

Dyes are ionic organic compounds with structures including aryl rings which have delocalized electron systems. The colour of dye is due to presence of chromophore group. A chromophore has conjugated double bonds containing delocalized electrons. Other common chromophoric configurations include azo (-N=N-), carbonyl (-C-O), carbon (-C-C-), carbon-nitrogen (>C-NH or CH-N-), nitroso (-NO or N-OH), nitro (-NO2 or –NO-OH), and sulphur (C-S). The chromogen,which is a aromatic structure normally contains benzene ,naphthalene or anthracene rings, is a part of chromogen-chromophore structure along with a auxochrome. The presence of ionizing groups known as an auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Some common auxochrome groups are $–NH_3$, -COOH, $-HSO_3$, -OH, $-CH_3$, $-NO_2$, $-SO_3H$, -Br, -Cl, $-NH_2$.

Based on colour, structure and application methods in color index, there are 14 different classes.

a) Acid dyes:

This is the largest class of dyes consisting of more than 2300 dyes. These dyes are anionic compounds used for nitrogen containing fabrics like wool, silk, polyamide, and modified acryl. They bind to the cationic Nh4+ ions of these fibers. The adjective 'acid' refers to the pH in acid dye dye baths rather than the presence of acid groups (sulphonate ,carboxy) in the molecular structure of these dyes.

b) Reactive dyes:

These dyes have reactive groups that form covalent bonds OH-, NH-, SH-groups in fibers (cotton, wool, silk, nylon). The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride. Most of the reactive dyes are azo or metal complex azo compounds.

c) Direct dyes:

These are relatively large molecules with high affinity with cellulose fibers. They bind to fibers because of van der wall forces. Direct dyes are mostly azo dyes with more than one azo bond phthalocynine, stilbene or oxazine compounds.

d) Basic dyes:

These dyes are mainly cationic compounds used in dyeing of acid group containing fibers like synthetic polyacryl. Most basic dyes are diarylmethane, triarylmethane , anthraquinone. They bind to acid groups of the fibers.

e) Mordant dye:

These dyes are fixed to fabric by the addition of mordant, a chemical that combine the dye with the fibers. This method of dyeing is the oldest method, nowadays this method is used less frequently. Most of the mordant dyes are oxazine or triarylmethane, azo compounds. Mordants used are mostly dichromates and chromium complexes. These dyes are used with leather, silk, wool, and modified cellulose fibers.

f) Disperse dyes:

These dyes are very less soluble dyes. They can penetrate synthetic fibers like polyester, cellulose acetate, acryl, polyamide etc only in dye baths having temperature of more than 120 degree Celsius or chemical softeners. These dyes diffuse when fibres are swelled in dye bath with fine disperse solution of these dyes. These dyes are mostly anthraquinones or metal complex azo compounds, nitro or small azo compounds.

g) Pigment dyes:

These dyes are mostly azo or metal complex phthalocynines and also quinacridone and anthroquinones. These insoluble, non-ionic compounds retain their crystalline or particulate structure throughout their application. Pigment dyeing is achieved from a dispersed aqueous solution and therefore requires the dispersing agents. Pigments are usually used together with thickeners in print pastes for printing diverse fabrics.

h) Vat dyes:

These dyes have been used since last 5000 years and Indigo dye is the most famous dye in this group. 'Vat' refers to the vats used for reduction of Indigo plants through fermentation. These are water insoluble dyes and are used in dyeing of cellulose fibers. The dyeing method is based on the solubility of vat dyes in reduced form. Reduced with sodium dithionite, the soluble reduced dye impregnates the fabric. Next, oxidation is applied to bring back the dye in insoluble form. Almost all the vat dyes are anthraquinones or indigoids.

i) Anionic dyes & Ingrain dyes:

These dyes are the insoluble products of a reaction between a coupling component and a diazotized aromatic amine. This reaction is carried out on fiber. The coupling agents are usually napthols, phenols, or acetoacetylamides.

j) Fluorescent brighteners:

Chemically there are different classes of brighteners like coumarin derivatives, pyrazolines, stilbene derivatives, napthalamides, 1, 2- ethane derivatives and heterocyclic and aromatic compounds. Fluorescent dyes in usual sense are not dyes because they lack intense colour. They mask the yellowish tint of natural fibers by absorbing UV light and weakly emitting visible blue light.

k) Sulphur dyes:

These are complex polymeric aromatics with heterocyclic S-containing rings. These dyes are used in dyeing of cellulose fibers. The method of dyeing involves reduction and oxidation similar to that of vat dyes.

l) Solvent dyes:

These are the non-ionic dyes that are used in dyeing of substrates in which they can dissolve, e.g – waxes, varnish, fats, plastic and inks. Solvent dyes are mostly diazo compounds that underwent some molecular rearrangement. Triarylmethane, anthraquinone, phthalocynanine are also used as solvent dyes.

m) Food dyes:

This class of dyes describes the role of dyes, rather than their mode of use. Food dyes can be mordant, direct and vat dyes, their use are strictly controlled via legislation. As the food dyes are used as food additives they are manufactured to a higher standard than industrial dyes. Most of the food dyes are azo dyes, although anthraquinone and triphenylmethane are used for colours such as green and blue.

n) Other dye classes:

A number of other classes have been established , including – oxidation bases for hair and fur, leather dyes for leather, carbine dyes for coloring multiple substrates, laser dyes and contrast dyes for magnetic resonance imaging.

India produces 64,000 tonnes of dyes, 2 per cent of which 7,040 tonnes are directly discharged into the environment. With the Indian dyestuff industry growing by over 50 per cent during the last decade, India is now the second largest producer of dyes and intermediaries in Asia. The production is estimated to be around 60,000 tonnes or about 6.6 per cent of the world production. There are around 700 varieties of dyes and dye intermediaries produced in India. In India only a third of the dyestuff producing industries are in organised sector. The rest come from the unregulated small-scale sector, which produces more than half of India's aggregate volumes. This sector pays no heed to environmental concerns. The domestic textile industry, which consumes up to 80 per cent of the dyestuffs produced, looks for manageable costs rather than consistent quality. So the bulk of its demand for dyes is met by the small- scale sector. The small-scale sector's substantially lower investment in pollution control measures also makes it more economical. Dyes are carcinogenic, skin irritant and these can cause allergic dermatitis and mutation (Namasivayam et al, 1996). Mathur et al (2005) carried out Ames *Salmonella*/microsome mutagenicity assay to study Mutagenicity assessment of effluents from textile/dye industries of Sanganer, Jaipur (India). They reported high mutagenic activity in the underground water as well as surface water in the area.

The textile industry which extensively uses dyes has been condemned as being one of the world's worst offenders in terms of pollution because of two reasons:

Chemicals:

As many as 2,000 different chemicals are used in the textile industry, from dyes to transfer agents; the typical textile dye wastewater composition is quite complex. These waste streams contain dyeing process auxiliaries that may include xylenes, phenols, buffers, bleaches and scouring agents, water softeners, surfactants, enzymes, caustic compounds and acids. Traditionally produced fabrics contain residuals of chemicals used during their manufacture—chemicals that evaporate into the air we breathe or are absorbed through our skin. Some of the chemicals are carcinogenic or may cause harm to children even before birth, while others may trigger allergic reactions in some people. According to a survey the population that is allergic to chemicals will grow to 60 percent by the year 2020. Such chemicals also add to food chain by various means and became a major reason of malignancies in humans. Many textile manufacturers use dyes that release aromatic amines (e.g., benzidine, toluidine). Dyebath effluents may contain heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments - many of which are toxic. About 40 percent of globally used colorants contain organically bound chlorine, a known carcinogen.

Water:

Although water is abundant on Earth, since almost 97% of the water contains salt, it is not suitable for drinking or for the various industrial purposes. Of the remaining 3%, two thirds is in the form of ice and snow leaving only about 1% of the total water as fresh water. Of this fresh water, ground water accounts for about 98% and the surface water is only about 2%. Thus of the total amount of water present on Earth, only about 0.02% is available in the lakes and streams. Global consumption of fresh water is doubling every 20 years. Therefore such a limited resource of water is very precious and needs conservation.

The textile industry is one of the most chemically intensive industries on earth, and the leading polluter of clean water (after agriculture). A finite resource like water is quickly becoming scarce, and is used at every step in textile dyeing industry both to convey the chemicals used during that step and to wash them out before beginning of next step.

The water becomes full of chemical additives and is then expelled as wastewater; which in turn pollutes the environment by the effluent's heat, increased pH, saturated with dyes, de-foamers, bleaches, detergents, optical brighteners, equalizers and many other chemicals used during the process. The textile industry is a water intensive industry with water being used in every stage of wet processing from sizing, desizing, scouring and bleaching of fibers to the dyeing, finishing and printing of fabrics. Every textile plant requires large volumes of water and produces high volumes of effluent wastewater. Due to the federal, state and local regulations, textile manufacturers must limit the discharge of color from their plants. The ability to economically eliminate or lower the amount of color in textile wastewater will have a major influence on the continued viability of many textile-manufacturing industries. Dye manufacturing, distilleries, textile, paper and pulp mills, tanneries, electroplating and food processing industries discharge colored wastewater into the environment.

The colored effluents after mixing with surface and ground water system also contaminate the drinking water. Color is a visible pollutant and the water contaminated with colors is neither suitable for drinking purpose nor it is fit for agricultural use because it inhibits photosynthetic process in plants.

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