

CHAPTER II

TEXTILE DYES

Coloured objects acquire their true colour because they absorb a definite portion (complementary colour) of white light (visible portion of sunlight) and unaffacting the rest. Some chemical groups such as azo, keto, nitro, nitroso, ethylene and carbonyl which are responsible for the absorption of a portion of light are called chromophores and a compound containing a chromophore is called a chromogen. When a chromogen contains other groups called auxochromes like amino group the coloured compound acquires and additional property of getting bound to textile fibres. In other words, coloured compounds containing auxochromes become dyes.¹

Dyes can be grouped in accordance with 3 different principles:

1. Chemical structure of dye
2. Solubility of dyes
3. Application of dyes

¹ Shenai, V.A., Technology of textile processing : Technology of dyeing Vol. 6., 1st ed.(Bombay : Sevak publications,1977), p.1.

Classification of Dyes According to Chemical Structure

Dyes can be classified in seven groups² :

1. Azo dyes
2. Nitro and Nitroso dyes
3. Polymethine dyes
4. Aza (18) annulenes
5. Di-and Triarylcarbonium Dyes and their Aza Analogues
6. Sulphur Dyes
7. Carbonyl Dyes

1. Azo dyes

Azo dyes are compound containing azo groups (-N=N-) which are linked to sp^2 -hybridized carbon atoms. In accordance with the number of such groups the dyes are described as mono-, dis-, tris-, tetrakis- etc. azo dyes. The azo groups are mainly bound to benzene or naphthalene ring, but in some cases they are also attached to aromatic heterocycles or enolizable aliphatic groups. The azo compounds represent the largest group of industrial dyes, both in number and amount produced.

² Rys, P., and Zollinger, H., Fundamentals of the chemistry and application of dyes (London : Wilry-Interscience, 1972), pp. 42 - 158.

1.1 Anionic monoazo dyes

The presence of one, or more, water solubilizing ionizable substituents is characteristic of anionic monoazo dyes. They consist almost exclusively of sulphonic groups because these are readily accessible and because they are strong electrolytes and therefore almost completely dissociated in all activity ranges occurring in aqueous solutions.

These dyes are widely used for paper and leather and their heavy metal salts (Ba, Ca etc.) used as pigments. Their main application, as so-called acid dyes, is for dyeing protein and synthetic polyamide fibers.

The term "acid dye" denotes a large group of anionic dyes with a relatively low molecular weight that carry 1 to 3 sulphonic groups. They are mainly monoazo compounds, but also include disazo, nito, 1-amino-anthraquinone, triphenylcarbonium and other groups of compounds. The name "acid dye" is derived from the dyeing process; the dyes are applied to wool, silk and polyamides in weakly acid solution (pH 2-6)

1.2 Disperse azo dyes

Disperse dye are almost insoluble in water they can be applied to cellulose acetate fibers as well as most fully synthetic fiber from aqueous suspensions. Most yellow orange and red disperse dyes are azobenzene derivatives. In contrast to anionic monoazo dyes, benzene, not naphthalene, derivatives are the most important coupling components.

1.3 Azoic dyes

Azoic dyes are water-insoluble mono-, and (a few) disazo-, dyes for cellulose fibres, which are formed on the fibre by soaping a water-soluble

diazo compound with a water-soluble coupling component having affinity for cellulose

1.4 Complex-forming monoazo dyes

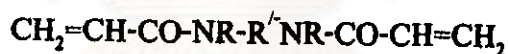
Metal complexes of monoazo compounds are principally used as chromium and cobalt complexes for dyeing protein and polyamide fibres as high-grade solvent dyes and as lakes

1.5 Direct dyes

Compounds which are able to dye cellulose fibres without the aid of mordants (tannin) are called direct or substantive dyes.

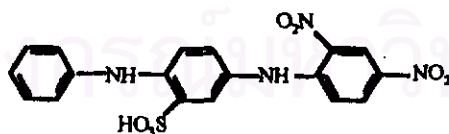
1.6 Reactive dyes

Reactive dyes are coloured compounds that react with textile fibres to form covalent bond e.g. Basazol dyes.



2. Nitro and nitroso dyes

This group comprises all those dye whose colour originates solely from the fact that an electron donor is conjugated with a nitro or nitroso group, in most case via a system of aromatic π -electrons, e.g.



C.I. Acid Orange 3

3. Polymethine dyes

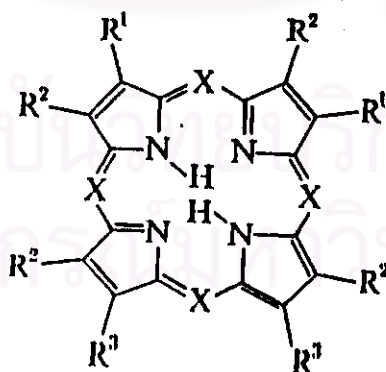
Polymethine dyes comprise a large group of coloured compounds, which in a simplified form, can be described by means of the mesomeric system.



The groups X and Y are linked by a conjugated chain with an odd number of methine groups, one acts as electron acceptor, the other as electron donor.

4. Aza [18] annulenes

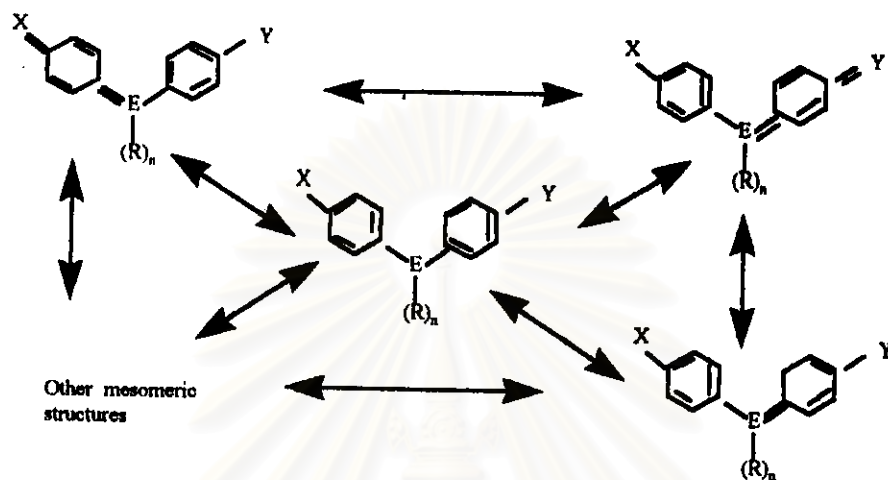
The chromophore of the dyes of the [18] annulene series of ring system is a cyclic system of conjugated double bonds, with 18 π -electron. Their best-known representatives are the biologically important colouring matter of blood (haemin : Fe³⁺ complex of (1.4.1) : X = H, R¹ = H = CH₂); R² = CH₃; R³ = CH₂ = CH₂COOH), and the synthetic phthalocyanine ; the former are derivative of porphin (1.4.1); X = H; R¹ = R² = R³ = H).



(1.4.1)

1.5 Di- and Triarylcarbonium Dyes and their Aza Analogues

This group is a group of aryloque poly (aza) methine dyes, which can be regarded as resonance hybrids of several mesomeric structures.

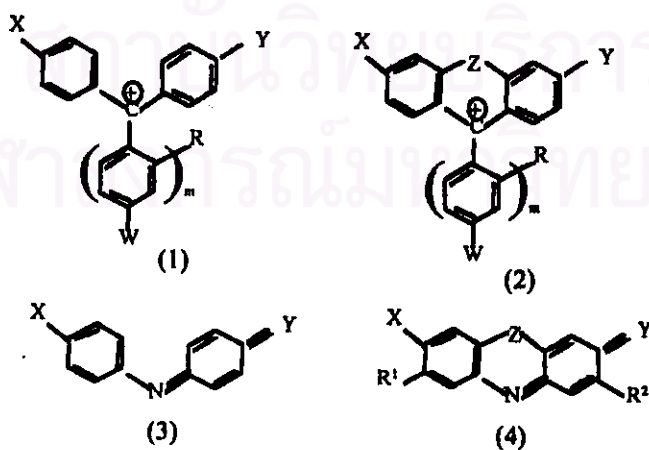


E : sp^2 C atom : $n = 1$

E : N atom : $n = 0$

The total charge q can be positive, negative or zero. X, Y and E are groups, at least two of which can be considered to be electron donors, in accordance with the mesomeric expression.

This class of dyes can be derived from the structures.



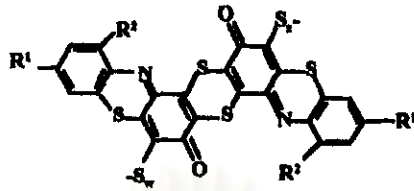
- A. Diphenylmethane dye (1 : m = 0)
- B. Triphenylmethane dye (1 : m = 1)
1. Malachite Gree type (1 : m = 1; X = Y = NR¹R² W = H)
 2. Crystal Violet type (1 : m = 1; X = Y = W = NR¹R²)
 3. Phenolphthaleine type (1 : m = 1; X = Y = OH)
- C. Acridine (2 : m = 0 or 1, Z = NR¹)
- D. (Thio) Xanthene (2 : m = 0 or 1; Z = O or S)
- E. Quinoneimine (3)
1. The indamine type (3 : x = NR¹R², Y = NR³R⁴)
 2. The indoaniline type (3 : x = NR¹R², Y = O)
 3. The indophenol type (3 : x = OH, Y = O)
- F. Azine (4 : Z = NR)
- G. Oxazine (4 : Z = O)
- H. Thiazine (4 ; Z = S)

They are principally used for dyeing silk, wool, paper, office stationery, cosmetics.

6. Sulphur dyes

The sulphur dyes are a class of water-insoluble, macromolecular, coloured compounds obtained by treating aromatic amines, phenols and aminophenols with sulphur and/or sodium polysulphide. By the action of sodium sulphide, these dyes are converted during the dyeing process into water-soluble derivatives which are

adsorbed by cellulose fibres and are subsequently insolubilized by atmospheric oxidation.



C.I. Sulphur Blue 13: $R^1 = \text{phenylamino}$, $R^2 = \text{H}$, $w = 0-3$

7. Carbonyl dyes

All dyes with at least two conjugated carbonyl groups are classified as carbonyl dyes. These include indigo, anthraquinone, higher anellated and other carbonyl compounds.

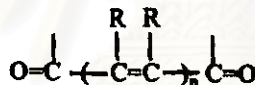


Figure 2.7.1 Conjugated carbonyl groups

All indigo dyes contain the group in Fig. 2. 7.2 as the parent system, which is responsible for the colour.

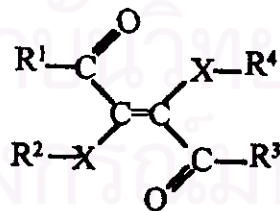


Figure 2. 7.2 Group as the parent system of indigo dyes

X = electron donor

$R^1, R^2, R^3, R^4 = \text{H}$ for simplest structure

Anthraquinone (Fig.2.7.3), the basic system of carbonyl dyes, has a faintly yellow colour; the edge of its long wave UV. band ($\lambda_{\max}=327$ nm, in CH_2Cl_2) extends into the visible spectrum. It is not itself a dye. The introduction of relative simple electron donors gives anthraquinone compounds which, according to the strength of the electron donors, absorb in any desired region of the visible spectrum.

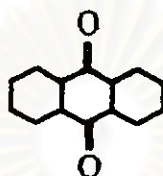


Figure 2.7.3 Anthraquinone

Classification of Dyes According to Solubility

Dyes can be classified in two groups³:

1. Water-soluble dyes

Water-solubility is conferred on many dyes by the presence of at least one salt-forming group. The commonest of these are sulphonic acid group and carboxylic acid group. Dyes solubilized by either of these groups are generally isolated as their sodium salts. They are described as anionic dyes since it is anion that is coloured. Dyes containing basic groups form water soluble salts with acids, and these are cationic dyes, since the coloured ion is positively charged.

³ Allen, R.L.M., Colour chemistry (Great Britain : Nelson, 1971), pp. 11 - 13.

2. Water-insoluble dyes

The dyes concerned may be classified as follows:

2.1 Dyes soluble in the substrate

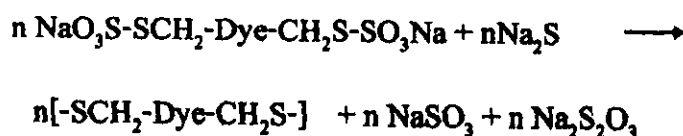
These include disperse dyes, which are prepared as finely divided aqueous dispersions for application to synthetic fibres, and also solvent-soluble dyes. In this context the term includes organic solvents of all types, and the dyes are applied in the media such as spirit and oil stains, varnishes, transparent lacquers, printing inks, waxes, polishes, soaps, cosmetics and petrol.

2.2 Temporary solubilized dyes

These dyes are converted into a water-soluble form by chemical modification, applied to suitable fibres from aqueous solution, then re-converted into insoluble form within the fibre. The Vat and Sulphur dyes are applied by means of this principle

2.3 Polycondensation dyes

Condense dyes defined as 'dyes the molecules of which during or after application react covalently with each other or with molecules of another compound (other than the substrate) to form molecules of much increased size'. The first commercial dyes of this type were the Inthion(FH), which are said to form polymeric disulphides on the fibre by reaction of thiosulphuric acid groups with sodium sulphide:



2.4 Dyes formed within the fibre

The Azoic (or Insoluble Azo) dyes are produced by applying coupling and diazo components to cellulosic fibres either in succession or together so that azo pigment particles are formed in cavities within the fibre structure. The particles are caused to aggregate by a subsequent hot soaping, so that they become firmly fixed and are resistant to wet treatments.

Phthalocyanine dyes can be produced on the fibre by applying a precursor such as aminoiminoisoindole with a copper or nickel salt and a reducing agent and then baking or steaming.

Mordant dyes of the alizarin type and basic dyes applied to cotton mordanted with tannic acid or a synthetic agent are properly included in this group since they are converted into insoluble derivatives within fibre.

2.4 Pigments

Pigments differ from dyes in that they have no affinity for fibres or other substrates, but since pigments are used for colouring synthetic fibres it is necessary to include them in the present classification. Water-soluble dyes formed upon the fibre are pigments in specialized applications.

Classification of Dyes According to Application⁴

1. Sulphur dyes

Sulphur dyes are mainly used for cellulosic fibres, dyeing having moderate all-round fastness. They are applied from a sodium sulphide bath, the dyes being

⁴ Abrahart, E.N., Dyes and their intermediates (Oxford : Pergamon Press, 1968), pp. 34 - 39.

reduced to a water-soluble form, reoxidation to shade occurring on the fibre by contact with air.

2. Azoic dyes

The term describes a system of producing an insoluble azo dye *in situ*, i.e. on the fibre, one intermediate (coupling component) having affinity for cellulosic fibres being padded onto the material, i.e. the cloth is passed in full width through a bath containing a solution of component and is squeezed dry by being passed through rollers. The impregnated material is then brought into contact with a solution of the second intermediate (diazo component) where upon the insoluble dye is formed. The major application is the dyeing and printing of cellulosic fibres especially cotton, giving shades of a high standard of fastness to light and wet processing.

3. Ingrain dyes

The term ingrain is applied to all types of dyes form *in situ* on the substrate by the development or coupling of intermediate compounds which are not themselves true finished dyes. The group thus includes Azoic and Oxidation dyes, but C.I. limits the ingrain section to those developed "from growing knowledge of phthalocyanines".

4. Vat dyes

This large and very important group comprises:

4.1 Indigoid and thioindigoid dyes

4.2 Anthraquinonoid dyes

They are applied from aqueous medium as leuco compounds(vat) obtained by alkaline reduction using sodium hydrosulphite (hydros), subsequent

oxidation reforming the original insoluble dye on the substrate. Water-soluble *leuco esters* are valuable for producing pale shades, or for colouring materials that are difficult to penetrate. The original dye is regenerated by simultaneous hydrolysis and oxidation. The major application is the dyeing and printing of cotton.

5. Acid dyes

Acid dyes find their main application in the textile field on wool, but are also used on silk, polyamide, acrylic and regenerated protein fibres, also paper and leather: they are normally applied from a dye liquor containing sulphuric, formic, or acetic acids; neutral and even slightly alkaline dye baths are occasionally used. Chemical types involved are azo, anthraquinone, triarylmethane, azine, xanthene, ketonimine, nitro and nitroso compounds. They include dyes giving very bright hues and have a wide range of fastness properties from very poor to very good.

6. Mordant dyes

In the C.I. the group cover "dyes sold by their makers under such names as mordant dyes, chrome dyes, metachrome dyes, afterchrome dyes, chrome printing colour". It does not include the basic dyes which are dyed on tannin-antimony mordanted cotton, a mordant being a substance, e.g. tannic acid, with which cloth (cotton) must be treated before being dyed, the dye otherwise having no affinity for the fibre. Certain types of acid dyes can form complexes with metals, in particular chromium, the lake formed on the fibre conferring better wet fastness than that of the acid dye itself.

7. Metal complex

These dyes, though formally related to the chromium lakes formed *in situ* and referred to above, are produced as metal complexes of o, o' dihydroxy-azo dyes in

bulk for use by the dyer as acid dyes mainly for wool; they also find application on silk and polyamide fibres. The dyes are of two kinds:

7.1 Acid dyeing premetallized dyes (1 metal atom, usually chromium, combined with one molecule of azo dye) known as 1:1 dyes and introduced in 1919. The chief use is in wool dyeing, but the large amount of sulphuric acid needed in the dyebath is often a disadvantage.

7.2 Neutral-dyeing premetallized dyes, introduced in 1951, are much the more important type. They are 1:2 complexes (1 metal atom, chromium or cobalt, combined with two molecules of azo dye) dyed from a neutral or slightly acid bath. They give dyeing of very high all-round fastness properties, and they possess particularly good leveling properties.

8. Disperse dyes

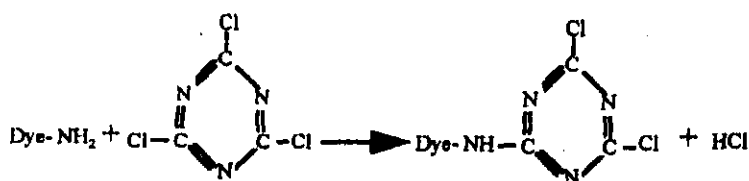
The IC (1953) definition was "a class of water-insoluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous dispersion". Recent work has shown that such dyes do, however, dissolve to a very slight extent in water and the degree of solubility influences the dyeing and leveling properties. They belong to three main classes, viz. nitroarylamine, azo and anthraquinone. Almost all contain amino- or substituted amino groups, but do not contain solubilizing groups such as sulphonic acid groups. They are usually ground in a mill to fine particle sizes (1-10 μ) in an aqueous medium containing a dispersing agent. The latter normally stabilizes the dye suspension and acts as a restraining and retarding agent. The principal use are the dyeing of cellulose acetate, nylon, polyester and polyacrylonitrile fibres. The mechanism in each case is believed to be one of solution in the fibre, no specific electrically charged dye sites being needed for dyeing to take place.

9. Solvent dyes

Solvent dyes, as the name implies, are those soluble in organic solvents. The range of solvents is a fairly wide one from the simpler aliphatic alcohols, esters, ketones, methylated glycols, aliphatic and aromatic hydrocarbons to oils, fats and waxes. The chief chromophoric system employed are: Azo including premetallized azo dyes, Anthraquinone and triarylmethane, Nigrosine and certain azo dyes. Among the many uses for solvent dyes are the manufacture of stains, varnishes, transparent lacquers, inks, copying papers, typewriter ribbons and for the coloration of candles, sealing waxes, polishes and surface finishes. They are also used for the mass coloration of molding powders, synthetic polymer compositions and for colouring soap, cosmetics, petrol, fuel oils, and the preparation of signaling smokes.

10. Reactive dyes

Reactive dye may be defined as a dye which, under the conditions of application, enters into chemical combination with the substrate, a covalent link being formed. The reactive dyes were originally developed for the direct dyeing of cotton and cellulosic fibres. Their outstanding properties, however, have led to great research activity in a search for dyes applicable not only to cotton but also to wool, silk and polyamides. Water-insoluble disperse dyes having reactive groups have been introduced principally for the dyeing of polyamide fibres on which they show improved washing and heat-fixation fastness. More than half the commercially available reactive dyes are chlorotriazinyl derivatives. These dyes were made by condensing and amino derivative of a suitable dye with cyanuric chloride:



Environmental considerations play an increasingly important role in textile processing. For exhaust air and waste water, there are numerous criteria that must be observed. For textiles, limits on the particular substance have been and are being laid down either by law or as a result of the demands of clothing manufacturers.⁵

Pollutants in Dyeing Waste Water

In general, the pollutants in waste water from a dyeing factory are described below.⁶

1. Colouring due to dyes
2. pH variation
3. BOD demand : large amounts of starch, proteins, and organic acids used during the textile weaving process are included in waste water from dyeing factories, increase the BOD significantly.
4. COD demand : detergent and compound adhesives that are used in dyeing factories, increase the COD.
5. Suspended solid demand : large amounts of pollutants, such as fibrous waste and polymer oligomer.
6. Others : residual chlorine common salts, foul odors, foam, etc.

⁵ Grund, N., " Environmental considerations of textile printing products", *JSDC* 111 (January/February 1995) : 7 - 10.

⁶ Oshima, H., " Textile dyeing and finishing : waste water treatment technology " Paper presented at the Improving of efficient environment for textile industry, Bangkok, Thailand, 17 - 18 December 1996.

Colour Removal Process

Colour removal process include the following:⁷

1. Chlorination

Chlorination using chlorine, hypochlorites or chlorine dioxide is a very effective treatment, but suffers from the possibility that organic halocarbons might be produced in the decolorisation process. Stringent safety precautions are associated with use of chlorine gas.

2. Ozone treatment

Ozone treatment on-site is generally expensive. Ozone is also toxic and precaution in its use and generation must be observed.

3. Adsorption

Absorption onto carbon is very effective for colour removal, but unfortunately the adsorption process is non-specific and large quantities of carbon can be required. Carbon is not available in a regenerable form and the treatment tends to be expensive.

4. Precipitation

Most of dyes can be satisfactorily precipitated using lime, alum or iron salts, followed by flocculation and settlement or separation by filtration. This method is extensively employed at present, but safe and inexpensive disposal of the settled sludge is becoming increasingly difficult. Simple pH control can also be an effective treatment for colour removal.

⁷ James Robinson Ltd., " Sulphur dyes and the environment ", *ISDC* 111 (June 1995) : 172 - 175.

5. Reduction

Water companies are investigating the treatment of dye waste by bacterial anaerobic reduction of the effluent. This has been proven as an effective colour removal treatment, but the reductive cleavage of azo dyes results in aromatic amines that may be carcinogenic, promoting caution in the use of this process. This process has not been complete degradable dye molecule.⁸

6. Electrochemical treatment

The process involves the use of a sacrificial iron electrode. When a direct current is passed through the cell, Fe(OH)_2 is produced. It is hypothesized that the large surface area of Fe(OH)_2 can adsorb organic compounds and that this adsorption is pathway for dye removal.⁹

7. Membrane filtration

Membrane processes are filtration processes in which the pore size of the membrane is of molecular dimensions. The molecular separation characteristic make membranes can be used to reduce or eliminate salt toxicity and color from dyehouse effluent containing fiber reactive dyes.¹⁰

The German Federal Council (Bundesrat) passed the 2nd and 3rd ordinance to amend the German physiological-contact ordinance. According to these ordinances, from 1 July 1995, azo dyes that can form any of 20 listed carcinogenic amines through cleavage of one or more azo groups may no longer be used in the manufacture of

⁸ Morimoto, K., "Decoloring waste water in textile industry" Paper presented at the Improving of efficient environment for textile industry, Bangkok, Thailand, 17 - 18 December 1996.

⁹ Kiener, L.V., and Uhrich, K.D., "Electrochemical removal of color from dye-laden waste-water" Water and pollution control association of South Carolina Fall, Conference, 1987.

¹⁰ Douglas, L.W., Leonard, T.F., and William, D.H., "Use of membrane filtration for water recycling in fiber reactive dyeing" Cotton Incorporated: research report, November 1993. (Mimeographed).

articles, whose contact with the human body is intended to be not merely of a temporary nature. These articles include fabrics for clothing and bedclothes. From 1 January 1996, no textile products that have been dyed or printed with such dyes may be offered for sale in Germany. Prohibits the use of azo dyes that can be form any of the following aromatic amines through of one or more azo groups.

4- Aminodiphenyl

Benzidine

4- Chloro- o -toluidine

2-Naphthylamine

o- Aminoazotoluene

2- Amino-4- nitrotoluene

p- Chloraniline

2,4- Diaminoanisole

4,4' - Diaminodiphenylmethane

3,3' - Dichlorbenzidine

3,3' - Dimethoxybenzidine

3,3' - Dimethylbenzidine

3,3' - Dimethyl-4,4' - diaminodiphenylmethane

p- Cresidine

4,4' - Methylene-bis-(2-chloraniline)

4,4' - Oxydianiline

4,4' - Thiodianiline

o- Toluidine

2,4- Toluylenediamine

2,4,5- Trimethylaniline