UNIT VIII

CHAPTER 8.1

Non-textile Uses of Dyes

The dye stuffs are mainly used for application on textile materials. However, they can also be used for colouring other substrates such as paper, leather, plastics, foods, drugs, cosmetics, etc. They also find application in colour photography. The dyes used for these substrates have chromophores and auxochromes similar to those in textile dyes. However, certain special properties may be required depending on the nature of the substrate. In some case, the higher fastness properties may be desired, whereas in other cases, brightness may become more important. Thus, an appropriate class of dye is necessary for a particular type of substrate. The dyeing conditions required for these substances will also be different.

8.1.1 Biomedical Uses of Dyes

A brief account of dyes having biological and medicinal applications is given below.

(a) Dyes Used in Formulations

The drugs either singly or in combination is administered in three formulations, i.e., tablets, capsules or syrups. The **basic objectives** of colouring these formulations are:

(i) To enhance the aesthetics of the tablets/capsules/syrups.

(ii) To help in the product identification.

(iii) The colour coating helps in maintaining the stability of tablet/capsule.

(iv) Helps to distinguish between the different formulations available in the market.

(v) It helps the illiterate patients to know which tablet/capsule should be taken when, on the basis of colour.

Tablets: Some inert materials like starch, chalk, etc. is mixed with the medicine along with a binder and compressed into a tablet. The tablets are of two types, i.e., coated and uncoated. Both of them can be coloured.

Capsules: There are two forms of capsules, i.e., hard shelled capsules and soft capsules. The capsules are used when the medicine has to be taken in the form of powder or granules. Both the types of capsules can be coloured by dyes or pigments. The white pigment like titanium dioxide makes the capsule opaque.

Syrups: These are thick liquids obtained by dissolving the drugs in alcohol, glycerol, sorbitol, etc. The syrups are coloured to make them attractive. The different syrups can be distinguished by their colours. In some cases, the colour is an indication of the flavouring essence added.

Syrup with orange flavour – yellow/orange dye

Syrup with lemon flavour – green/yellow dye

Syrup with mint flavour – white dye (TiO_2)

The dyes used to colour the tablets/capsules/syrups should meet the following conditions.

(i) They should be FDA/FSSAI approved colour.

(ii) The dyes used must be totally non-toxic.

(iii) They should not cause allergic reactions.

(iv) They should not interact with the drug.

(v) They should not have any physiolgical action themselves.

(vi) They should be pure and used in very minute amounts.

There are two types of dyes used for colouring tablets/capsules/syrups.

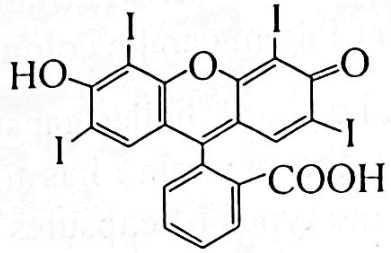
(1) Natural dyes or extracts can be used for colour coatings such as chlorophyll, anthocyanin, carotinoid, turmeric, saffron, etc.

(i) Natural colouring agents may give a dull, cloudy colour which may be uneven.

(ii) The herbal extracts may interact with the active drug.

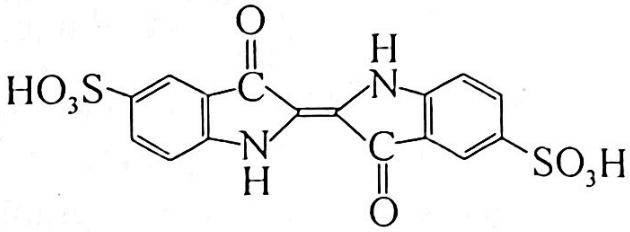
(2) Synthetic dyes: The FDA/FSSAI approved synthetic dyes are largely used to colour tablets/capsules/syrups

(i) Phthalein dyes



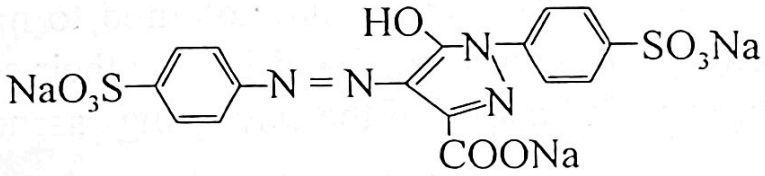
Erythrosin

(ii) Indigoid dyes



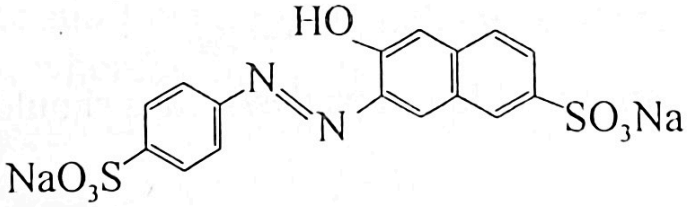
Indigo Caramine (Indigotin I)

(iii) Azo dyes



Tartrazine

(iv)

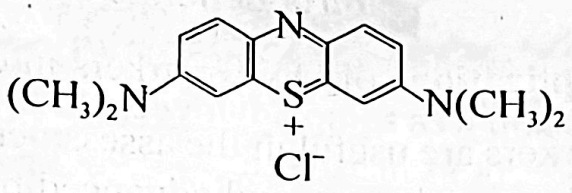


Sunset Yellow

(b) Biological Staining Agents

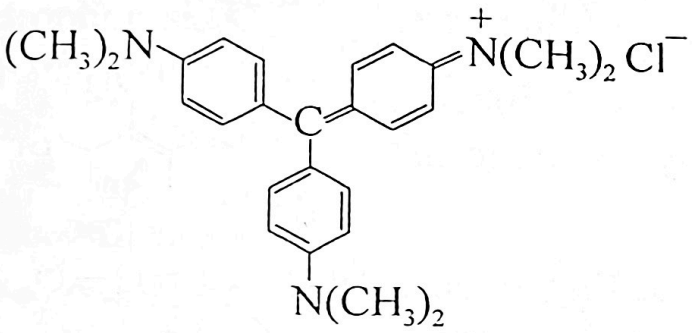
Many dyes belonging to azine, thiazone and triphenyl methane class are used as biological staining agents. Some of these dyes have the property of specifically staining certain microorganisms and hence they are useful in identifying and differentiating these microorganisms.

Methylene blue is the most commonly used stain in bacteriological techniques for examination of pathogenic organisms such as tuberculosis and cholera bacilli. Further, methylene blue is used to selectively stain the living tissues. For example, it deeply colours peripheral nervous system leaving other parts unstained.

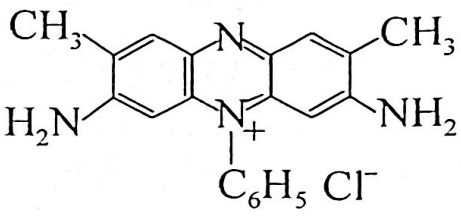


Methylene blue

Christian Gram devised Gram staining method to classify bacteria into two types. In this method, the fixed bacterial smear is treated with a solution of crystal violet and then with iodine solution which reacts with the dye and the cell constituents. The smear is then washed with alcohol (decolourising agent) and counterstain such as Safranine-T (red dye) is added. The bacteria which retain the colour of crystal violet are called Gram positive bacteria. But those which lose the violet colour and get counterstained red by Safranine-T, are called Gram-negative bacteria.



Crystal violet



Safranine-T

Tetraiodo and tetrabromo phenolphthalein are used as stains in the X-ray examination of gall blader and liver respectively. 3-iodo and 4-iodo alizarine are opaque to X-rays and hence used in X-ray visualization.

(c) DNA Markers

The special characteristics of any object or living tissue which can be easily identified are called markers. DNA markers also known as genetic markers are defined as follows:

(i) Any genetic element such as location, DNA sequence or chromosome feature, which can be readily detected by molecular techniques and used to follow chromosome or its segment during genetic analysis is called DNA marker.

(ii) Any unique DNA sequence having known location and associated with a particular trait and used in restriction mapping experiments to identify that sequence is called DNA marker.

Important Applications of DNA markers in crop improvement:

(i) DNA markers are useful in the assessment of genetic diversity in germplasm, cultivars, and advanced breeding material.

(ii) DNA markers can be used for constructing genetic linkage maps.

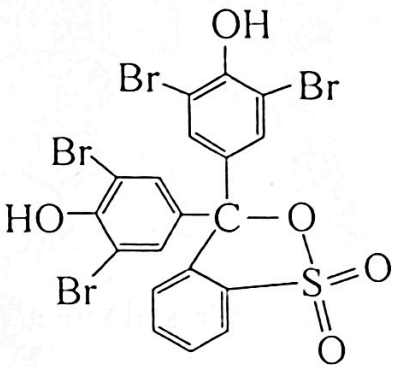
(iii) DNA markers are useful in identification of new useful alleles in the germplasm and wild species of crop plants.

(iv) DNA markers are used in marker assisted selection which has several advantages over straight selection.

(v) DNA markers are useful in study of crop evolution.

Several dyes are used in the DNA markers.

1. Bromophenol blue: This is a triphenyl methane dye, which is structurally related to the indicator phenolphthalein.

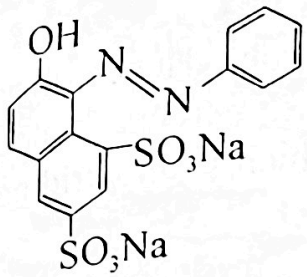


It is prepared by slowly adding excess bromine to hot solution of phenolphthalein in glacial acetic acid. Bromophenol blue is used as follows.

(i) As acid base indicator, its useful range lies between 3.0 (yellow) to 4.6 (blue).

(ii) Colour marker: It can also be used as a colour marker to monitor the process of agarose gel or polyacrylamide gel electrophoresis. Since bromophenol blue carries a slight negative charge at moderate pH, it will migrate in the same direction as DNA or protein in a gel. The rate at which it migrates varies with the gel density and buffer composition. In a typical 1% agarose gel in a TBE buffer, bromophenol blue migrates at the same rate as DNA fragment of about 300 base pairs.

(iii) As a dye: At neutral pH, the dye absorbs red light strongly and solution appears blue. At low pH, the dye absorbs U.V. and blue light strongly and solution appears yellow. In the middle of the range at pH 3.6, the indicator has green-red colour which shifts depending on concentration and/or path length through which the solution is observed and this phenomenon is called dichromatic colour. Kraft's dichromaticity index is the extent of change in colour hue when the thickness or concentration of observed sample is changed. Bromophenol blue has the highest value of this index, i.e., 10.



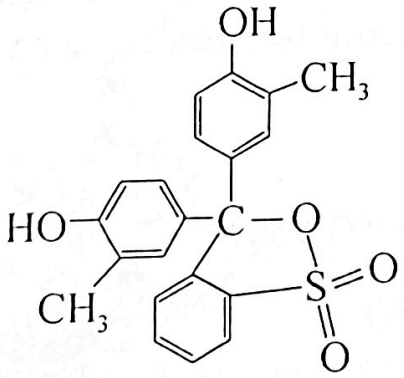
(ii) Orange G: Orange Gleb or acid orange 10 is an azo dye which comes as a disodium salt in the form of orange crystals. It can be used as follows:

(i) As a staining agent: It is used in histology in many staining formulations. For example, Orange G is in the papanicolaou stain to stain keratin. It is also a major component of the Alexander test for pollen staining. It is often combined with other yellow dyes and used to stain erythrocytes in trichrome methods.

(ii) Colour marker: Orange G can be used as a colour marker to monitor the process of agarose gel as well as polyacrylamide gel electrophoresis, running approximately at the size of 50 base pairs (bp) DNA molecule. The size of the DNA to be scanned for a particular dye depends on the concentration of gel and the buffer system used.

Even though it has two ionizable groups, it shows only two colours in aqueous solution; brilliant orange in neutral and acid pH or red in pH greater than 9.

3. Cresol Red: It is triphenyl methane dye. It is used as pH indicator in the range 7.2 to 8.8. It is frequently used for monitoring the pH in aquaria.

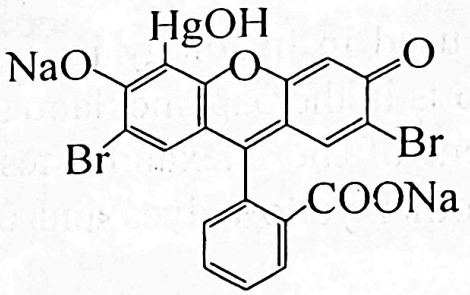


(i) In molecular biology: Cresol Red can also be used in many common molecular biology reactions as loading dyes. Cresol Red inhibits Taq polymerase to different degree compared to other loading dyes.

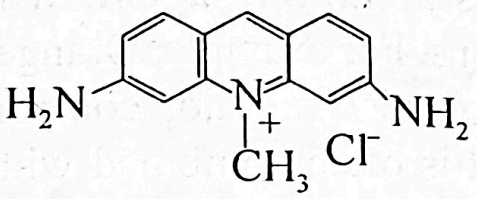
(ii) Colour marker: The process of agarose gel or polyacrylamide gel electrophoresis can be monitored using Cresol Red as a colour marker. DNA molecule of bigger size of upto 125 base pair can be run in a 1% agarose gel.

(d) Dyes Used as Therapeutics

Certain dyes have curative or therapeutic properties. Hence, they are more useful as medicines rather than as dyes. Thus, mercurochrome which is a derivative of fluorescein and acriflavin which is an acridine dye, both have antiseptic properties.

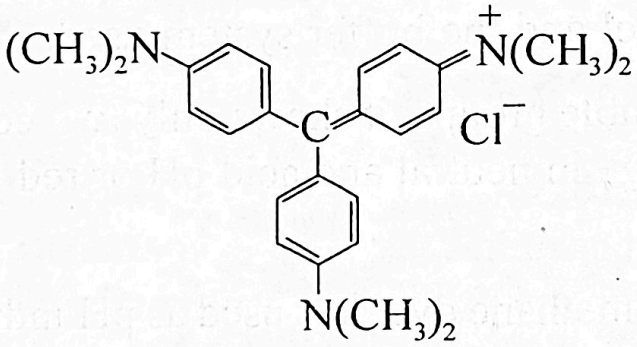


Mercurochrome (Merbromin)

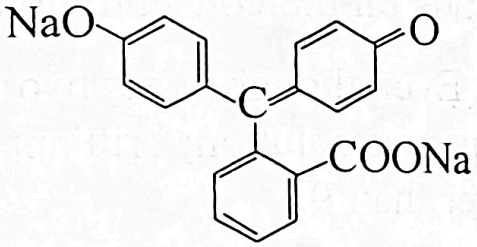


Acriflavin

Crystal violet, methyl violet, etc. are effective against skin diseases. Phenolphthalein is used as a mild laxative.

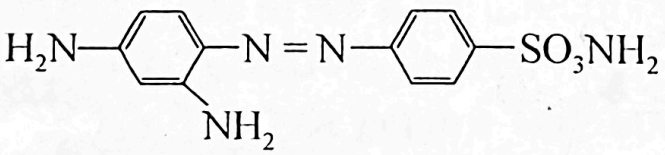


Crystal violet

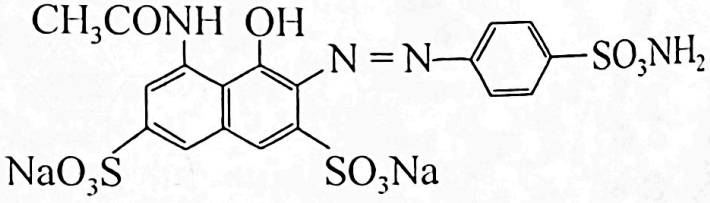


Phenolphthalein

Protonsil and neoprotonsil are used in treatment of trypanosomiasis (sleeping sickness). Neoprotonsil has higher solubility and bactericidal activity than protonsil.



Protonsil



Neoprotonsil

The medicinal dyes should also satisfy the conditions applicable to mainly food colours. They should be non-toxic and should not interact with other components of the medicinal preparation.

8.1.2 Dyes Used in Food and Cosmetics

(A) Food colours

The foodstuffs like sweet meats, jams, toffees, etc. are coloured, mainly to make them attractive and increase their appeal. The most important consideration in the choice of these dyes is that the dye should be non-toxic and completely harmless to human being. Thus, many synthetic dyes cannot be used as they may be toxic. Some natural dyes like turmeric, saffron, etc. are used to limited extent. But they are largely replaced by synthetic dyes as they have low cost and many shades are available.

The food colours should have following general chracteristcs:

(i) They should be non-toxic and completely harmless to human beings.

(ii) They should have aesthetically suitable colour.

(iii) They should be highly soluble in water, alcohol or edible oil.

(iv) They should not react with the flavouring materials and preservatives, etc. Thus, the taste and flavour should not be affected.

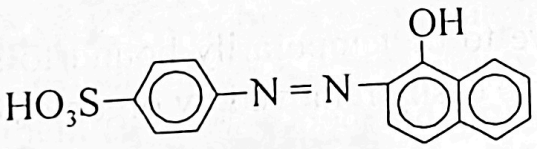
(v) They should be stable to heat and light.

(vi) They should not be attacked by microorganisms.

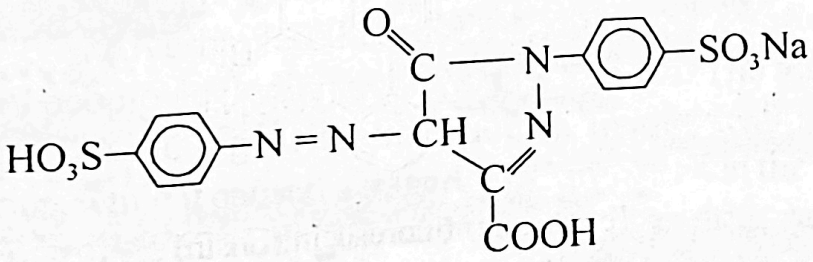
(vii) They should be highly pure and should not contain heavy metal impurities.

Examples of food colours

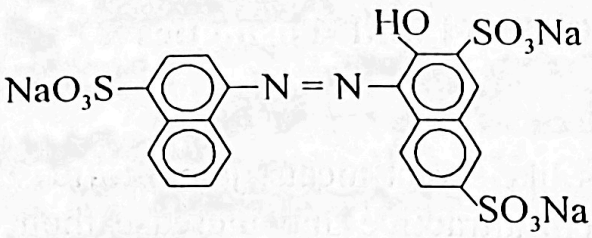
The following monoazo dyes are used as food colours:



Orange I

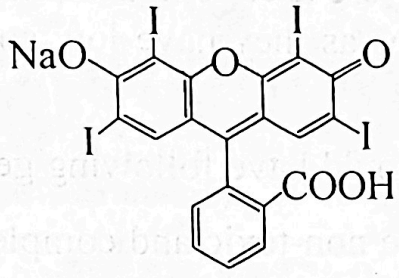


Tartazine



Amaranth

Some phthalein dyes which are halogenated derivatives of fluorescein are used as food colours.



Erythrosine

(B) Dyes used in Cosmetics

A number of dyes are used in the preparations of various cosmetics (beauty aids) such as face powders, lipsticks, nail polishes, etc. The fastness properties are not important for these dyes.

The dyes and pigments used in cosmetics require to have the following properties:

(i) They should have brightness and attractiveness.

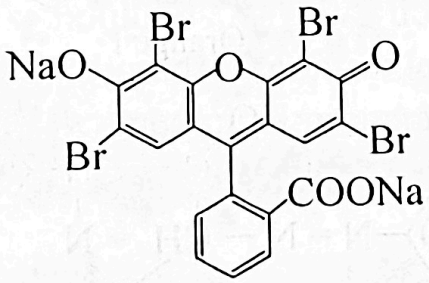
(ii) They should have resistance to perspiration.

(iii) They should be non-toxic.

(iv) They should be water soluble or oil soluble.

(v) They should not affect skin.

(vi) They have to be temporarily bound to skin or nails, so that they can be easily removed by organic solvents like acetone.



Tetrabromo fluorescein (Eosin)

Face powders and lipsticks are coloured with organic or mineral pigments.

The dyes used for nailpolish and lipstick are derivatives of fluorescein. Tetra bromo derivative of fluorescein, i.e., Eosin dispersed in oil is used as nail polish. Eosin also gives coloured lakes with transition metal salts which are oil soluble and are used in lipsticks.

(C) Introduction to FDA and FSSAI

Food and, to a lesser extent, drugs are primary to our lives. The foods and drugs go from procurement/production, processing, storage, packaging, transport to retailing. Thus, they go through so many stages that we are not sure about their source and its final contents. Hence, there is a need for government regulatory authority at every stage, such as FSSAI and FDA.

FSSAI stands for Food Safety and Standards Authority of India. It was set up by Ministry of Health and Family Welfare, Governemnt of India, in August 2011, having jurisdiction all over India. The main purpose of FSSAI is public safety and health. FSSAI is a multiregulatory agency to oversee the manufacture, storage, distribution, sale and import of food products and drugs, to ensure that they are safe for human consumption. Before FSSAI, there were numerous agencies and departments that were to oversee different aspects of food production, transport and safety. However, these, were often stuck in bureaucratic hurdles, when interacting with each other. Therefore, the Food Safety and Standards Act, 2006 was passed which consolidated all these services into one and thus FSSAI was set up.

FDA stands for Food and Drug Aministration, was set up under department of health and human services by federal government of USA, in June 1906. Thus, FDA is a very huge organisation having a broad regulatory authority all over America. FDA's responsibility are closely related to those of other government agencies. Food and Drug Act of 1906 was one of the world's most comprehensive and effective public health networks covering more than 200 laws. Then there were many amendments. The FD&C Act completely overhauled the public health system, after a toxic elixir killed several people, including children, in America. The vigilance of FDA prevented the marketing of thalidomide (a medicine for morning sickness) in America, while it caused a tragedy in Europe. Then the Kefauver Harris Amendments of 1962 strengthened the rules for drug safety. The medicinal device amendments of 1976, followed a US senate finding that faulty medicinal devices had caused injuries and even some deaths.

Comparison of FSSAI and FDA

Thus, both FSSAI and FDA are government regulatory agencies which have same basic purpose, i.e., public health and safety. But they operate in different regions; FDA in USA and FSSAI in India. FDA is a larger agency having wider scope than FSSAI. Further, FDA was established much earlier (1906) compared to FSSAI which is relatively new (2011). Both the agencies are responsible for ensuring that foods and drugs are manufactured safely and no undesirable things (adultrants) are added. Thus, safety, efficacy and security of human and veternary foods and drugs, biological products, cosmetics and medical devices including those which emit radiations, is ensured.

Duties and Responsibilities of FDA and FSSAI

(i) Foods: They lay down science-based standards and limits for articles of food for their manufacture, storage, transport, retailing and import. This includes foods from animal origin like meat, fish, fowl, eggs and also veternary food.

(ii) Drugs: They formulate stringent rules and regulations for manufacture or import of drugs by imposing GMP (Good Manufacturing Practices) and GLP (Good Laboratory Practices). This includes biological products like vaccines, blood, blood products, tissues, stem cells, etc.

(iii) Packaging: The foods and drugs should be packaged using suitable non-toxic and stable materials so as to preserve the quality of the product till it reaches the consumer. There should not be any leaching of colour or metal residues into the food or drug.

(iv) Labelling is equally important. It should indicate the manufacturer, its address, batch number, name of product, ingredients and their percentages, date of manufacture, expiry date and MRP. Indicators to show whether it is purely vegetable product (green dot) or includes animal products (brown dot).

(v) Medical Devices: They have to lay down exact specification and their limits for medical devices such as stents, pace makers, dental devices, dializers, surgical instruments, implants, intraoccular lens and prosthetics.

(vi) Advertising: The governmnet trade commission regulates the advertising for foods, including veternary, drugs and cosmetics. It helps to protect consumer by stopping unfair, deceptive or fraudulent practices in the marketplace.

(vii) Information: The right information regarding the rules, regulations, standards enforced by FDA and FSSAI must be brought to the notice of consumer through notifications, newspapers, media, seminars, etc. Also there should be opening for consumer complaints and suggestions.

(viii) Approval: Only those products which follow all the rules and standards are called FSSAI or FDA approved and they are allowed to display the logo *fssai* or FDA. The products and the companies which do not adhere to the above regulations set by FDA/FSSAI can be fined. If they refuse to conform to the regulations, they may be banned from selling the products in the market.

8.1.3 Paper and Leather Dyes

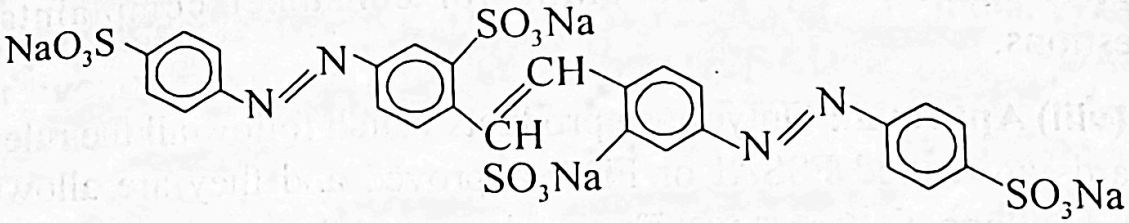
(a) (i) Structure of paper: Wood, which is the source of paper, consists of long cellulosic fibers held together by lignin. Paper is made from wood pulp from which lignin is removed. Thus, paper is made up of short cellulosic fibers which are bound by glue and other adhesives. Some additives like waste cotton are added to increase the strength of paper and glazing agents to prevent spreading of ink on paper. Due to high molecular weight, the cellulose present in paper is insoluble in water.

The dyes have little affinity for cellulosic fibres but they have some affinity towards the binding materials present in paper. The dyeing of paper may be carried out by: (i) adding dye to wood pulp itself, (ii) dipping paper in the dye solution, or (iii) impregnating the dye into the matrix of paper.

(a) (ii) Requirements of dyes used for paper:

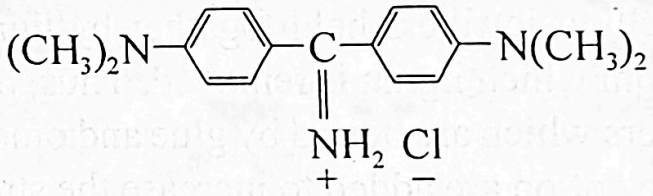
1. They should have fastness towards acid, chlorine, etc. when used for writing paper where acidic glues and inks are used.
2. Dyes in coloured sheets used in plastic laminates must have fastness to light as they are always exposed to light.
3. They must have resistance to ink eradicators and wet rubbing.
4. They must have fastness towards alkali as paper may contain alkaline adhesives or when the paper is used to package alkaline materials like soap.
5. Dyes used for paper napkins, towels, facial tissues or when the paper is used for packaging wet materials, it must be fast to bleeding in water.

(a) (iii) Dyes used for paper: Direct dyes are widely used for dyeing of paper. For example, the bisazo dye, chrysophenine-G is a direct dye which has good affinity to paper and resistant to bleeding in water.

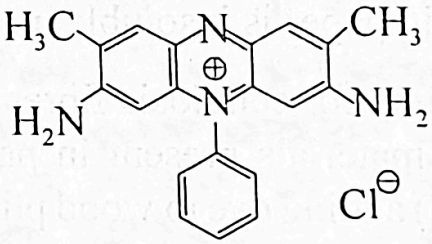


Chrysophenine G

Although basic dyes have no affinity for pure cellulosic fibers, they have affinity toward binding materials and degradation products of cellulose present in paper. Hence, the following basic dyes are used for dyeing paper.

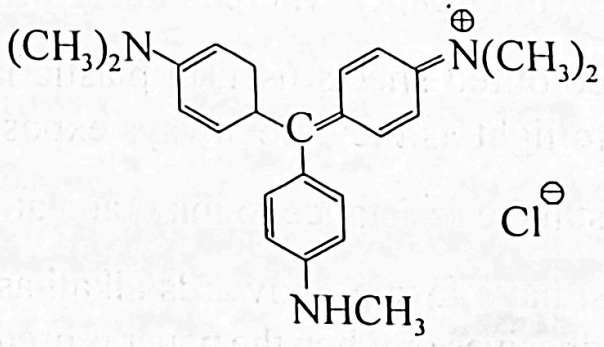


Auramine-O



Safranine-T

Carbon papers are made by coating the paper with waxes, carbon black and a small amount of a blue dye soluble in oil. The blue dye is used to counteract the slight reddish tone of carbon black.



Methyl violet 10 BNS

(b) (i) Structure of leather: The source of leather is animal skins and hides. Tanning involves chemical treatment of skins and hides of animals to produce leather. Leather is made up of fibrous protein called collegen and it has rough and uneven structure.

Before tanning process, skins and hides are dehaired by Na_2S solution, degreased, desalted and soaked in water upto two days. Tanning is carried out by using acidic compounds like tanin obtained from plant source or using formic acid. This is followed by surface coating or finishing. Nowadays, tanning is carried by using Chromium (III) salt solutions, to produce superior chrome leather.

Tanning makes the leather more durable and chemically stable and prevents it decomposition. Leather has rough and uneven structure. After tanning, it becomes soft and uniform.

(b) (ii) Requirements of leather dyes

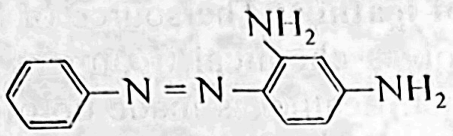
1. Although it is a surface dyeing, some penetration is needed to make up for the lack of affinity between dye and leather. The compact structure of leather makes penetration difficult but it is improved by the presence of sulphonic acid groups ($-SO_3H$) in the dye.
2. The dye should not be sensitive to the variations in the structure of the leather and should produce uniform dyeing (levelling effect).
3. They should be resistant to abrasion and perspiration.
4. The light fastness is not very important for leather dyes. However, the lack of light fastness causes reddening of deep shades which is called **bronzing**.

(b) (iii) Dyes used for leather

The natural dyes were used earlier for leather along with mordants like iron, aluminium, chromium, etc. For example, haematin produced a rich black colour with iron. However, with the knowledge about the stucture of leather, many synthetic dyes were developed.

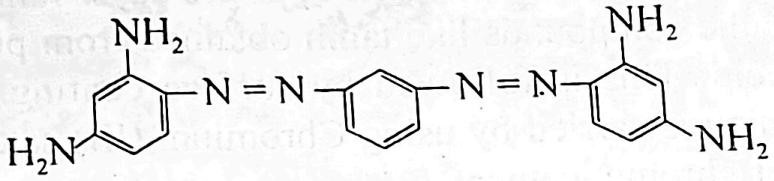
The chemical class of dyes used is mostly azo dyes. Basic dyes produce deep and rich shades. They are resistant to perspiration. So, leather dyed with these dyes are used for making gloves and clothing.

e.g., Chrysoidine Y is basic monoazo dye used for dyeing leather.



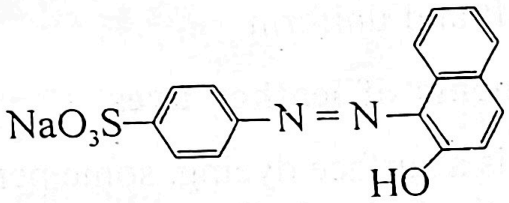
Chrysoidine Y

Bismark Brown is basic bisazo dye.



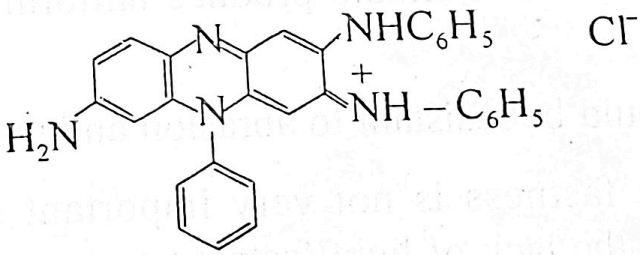
Bismark Brown

Orange II is acid mono azodye used for dyeing leather.



Orange II

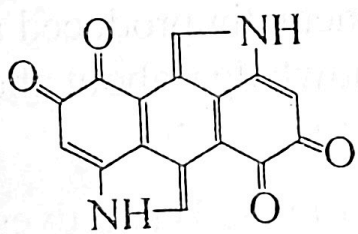
Some aniline and acridines are also used for leather. Nigrosine-C is water soluble black dye obtained by oxidation of aniline hydrochloride with nitrobenzene in the presence of ferric chloride. The dye is used in boot polishes.



Nigrosine-C

8.1.4 Miscellaneous Dyes

(A) Hair Dyes

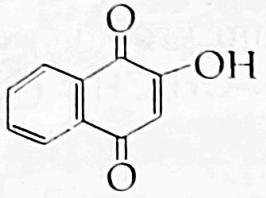


Melanin

The colour of the hair is due to a coloured pigment called melanin which is produced in the body. Due to ageing and/or pollution, production of melanin is reduced resulting in grey hair.

Hair dye is used for cosmetic purposes which when applied externally masks the grey hair, resulting in a uniform black or brown colour.

Natural hair dyes: Henna is most commonly used natural hair colour which is of deposit-only type, giving temporary orange-reddish colour.



Lawsone (2-Hydroxy naphthaquinone)

Henna plant (Lawsonia innermis-L) contains the active component called lawsone (10^4 ppm) in the form of a glycoside.

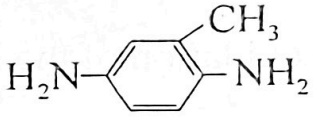
The active component, lawsone binds with keratin which is the protein present in hair. It also contains 1,4-naphthoquinone, gallic acid and tannin (10^5 ppm). When henna is mixed with indigo plant (*Indigofera Tinctoria*), brown/black shades are obtained. But when mixed with pyrogallol, a dark purple colour is obtained. The mixture of henna, black walnut powder and dried gooseberry gives black colour. But henna needs repeated applications and also does not give uniformity in colour.

Synthetic hair dyes have largely replaced natural hair dyes. The permanent synthetic hair colours are made up of three components:

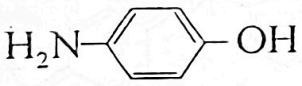
(i) Primary intermediates (or precursors)

The most common precursor used is 1,4-diamino benzene or para phenylene diamine (PPD). Currently, other *para*-disubstituted compounds used as precursors are also given below:

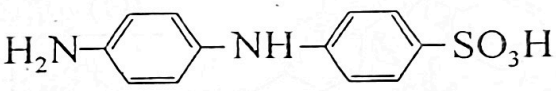
PPD



2, 5-Diamino toluene

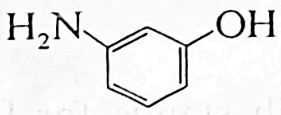


p-Amino phenol



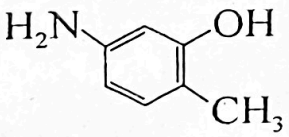
p-Amino diphenyl amine sulphonic acid

(ii) Coupling Agents: These are *meta*-disubstituted compounds which couple with precursor to give an intermediate compound.



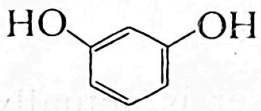
m-Amino phenol

(A)



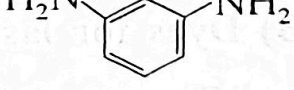
4-Amino-2-hydroxy toluene

(B)



Resorcinol

(C)



m-Phenylene diamine

(D)

The final colour of the hair dye depends on the coupler used.

PPD + A or B ⟶ Red shade

PPD + C ⟶ Green-yellow

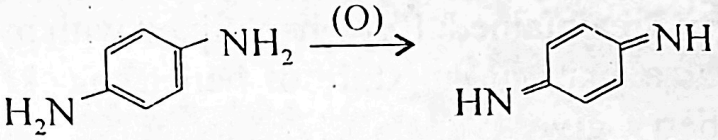
PPD + D ⟶ Blue shade

2,5-Diamino toluene + A ⟶ Magenta brown

(iii) An oxidant, usually H_2O_2 in alkaline medium provided by ammonia. Instead of ammonia, mono ethanol amine (H_2N-CH_2CH_2–OH) can be used as a milder alkaline medium.

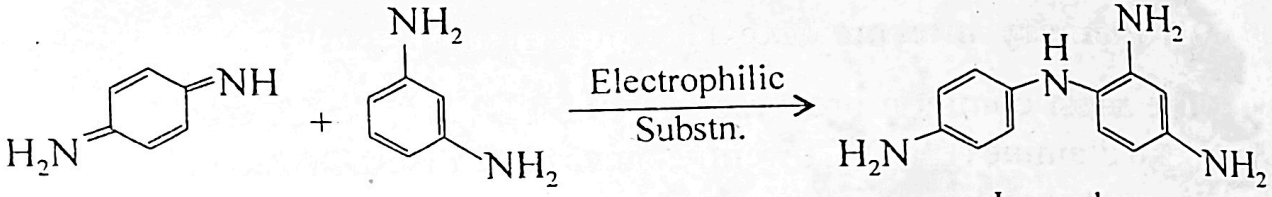
The chemical process of hair dyeing takes place according to following mechanism:

Step (1) *Para*-phenylene diamine is oxidised into quinone diimine.



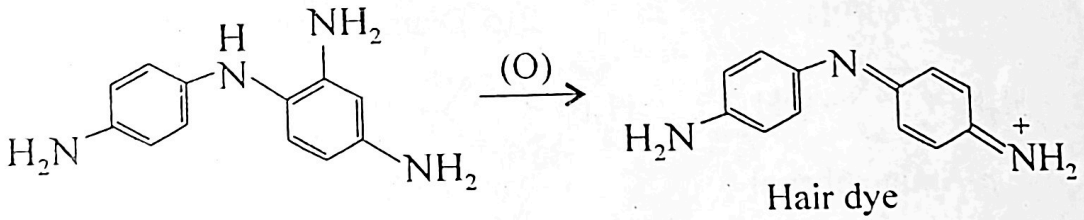
Quinone diimine

Step (2) The oxidised product combines with the coupling agent to form the leuco base (colourless compound).



Coupler Leuco base

Step (3) The oxidation of the leuco base results in the final hair dye.



Hair dye

The alkaline medium provided by ammonia open the pores in the shafts of hair. The large dye molecules enter the pores in the hair shafts and get locked in.

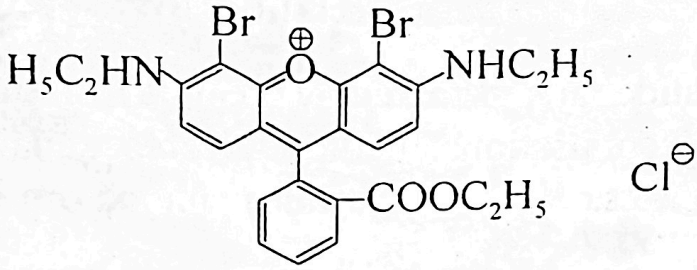
(B) Dyes for lasers

The word laser is actually an acronym which stands for Light Amplification by stimulated Emission of Radiation. Lasers are used for a variety of applications in medicine, e.g., for eye surgery, therapy for Carpel Tunnel Syndrome and for photocoagulation. Laser light is monochromatic, directional and coherent. While ordinary white light is a combination of many colours of light, emitted in many directions away from the source. Lasers consist of a lasing medium which is either gaseous or liquid or

solid. Sometimes, semi-conducting material is also used as laser medium. Organic dyes, from Rhodamine or coumarin or polymethine class are also used as dye lasers may be in liquid solution or in suspension form. They are tunable over a broad range of wavelengths. Dye lasers, in which complex organic dyes in solution are the lasing material, can be tuned to produce light of any chosen wavelength over a range of the visible spectrum.

Example:

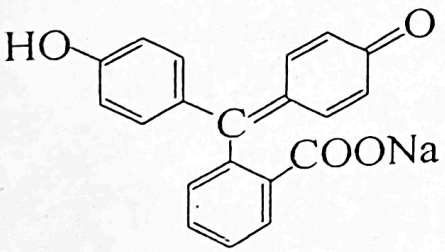
Xanthene dyes: Rhodamine 6G is used as laser dye.



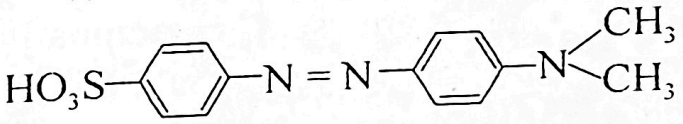
Rhodamine 6G

(C) Dyes used as Indicators

There are many dyes which change colour at different pH of the medium. These can be used as indicators in acid-base titrations. For example, phenolphthalein, methyl orange, methyl red, congo red, etc.

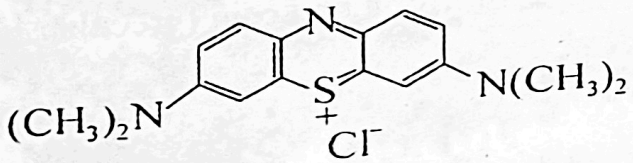


Phenolphthalein

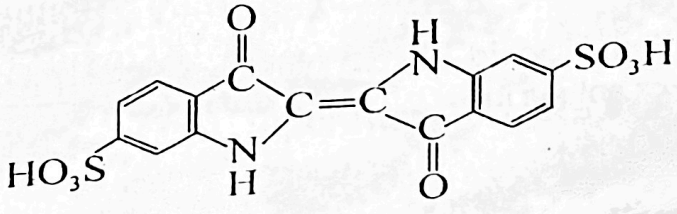


Methyl Orange

Certain dyes change colour when in contact with inorganic salt solutions when they undergo a change in their redox state. Such dyes are used as indicators in redox titrations. For example, methylene blue and indigo caramine are redox indicators.

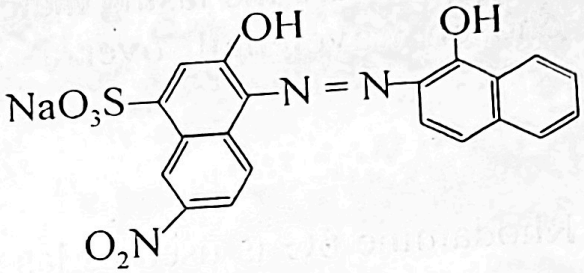


Methylene blue



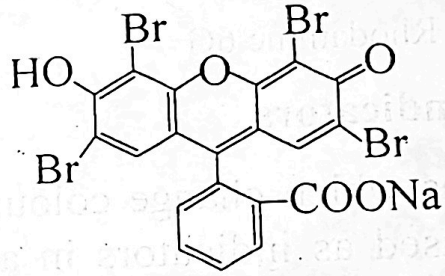
Indigo caramine

In complexometric titrations using EDTA solution zinc, magnesium, copper salts can be estimated by using the dye eriochrome black T as the indicator. The end point is indicated by a change of colour from wine-red to blue.



Eriochrome black T (EBT)

The soluble halides are estimated by precipitation titration with silver nitrate solution. In such titrations, dichloro fluorescein and eosin are used as adsorption indicators.



Eosin

Certain dyes are used as precipitating agents in estimation of metals. For example, naphthol yellow is used for estimation of Co, Hg, K, Rb and Orange IV for Zn and Hg.

Formation of phenolphthalein indicator (pink colour) in phthalein test can be used to detect phthalic acid/andhydride or phenol.

$$\text{Phthalic acid or anhydride} + \text{Phenol} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \xrightarrow{NaOH} \text{Phenolphthalein (pink colour)}$$

Formation of indicator fluorescein (greenish yellow fluorescence) in phthalein test can be used to detect phthalic acid or anhydride or resorcinol.

$$\text{Phthalic acid or anhydride} + \text{Resorcinol} \xrightarrow[\Delta]{\text{Conc } H_2SO_4} \xrightarrow{NaOH} \text{Fluorescein (greenish yellow fluorescence)}$$

(D) Security Inks

The writings in ordinary inks can be tampered with and altered. Hence, the need for security inks for printing documents of importance such as cheques, passports, security labels and secure documents. Previously, ultraviolet ink was used for security printing, as it was invisible in normal light but fluorescent under U.V. light. However, as they are visible under U.V. light the original marking can be located and altered using fluorescent dyes which are readily available.

The current security inks can be applied on substrates such as paper, cardboard, fabric, plastic, glass, etc. The security ink consists of two components:

(i) The first marking fluid which on applying and drying is invisible in visible or U.V. light. It may contain phthalates or quinazoles whose molecular structure do not allow the absorption of U.V.

(ii) The second marking fluid contains novolac resins, bisphenols or hydroxy benzoates. It reacts with the first fluid and activates it. The original marking remains invisible in normal light but the product of reaction between two fluids can absorb U.V. light and becomes fluorescent.

Thus, there are two levels of security as the original marking must be activated and then viewed under U.V. The two marking fluids can be applied in solvent vehicles such as alcohol, acetone or ethyl methyl ketone. Alternatively, they can be applied as micronised particles in aqueous solution with a binder.

Chemical A: 3, 3-Bis (4-Dimethyl (amino phenyl)-6-dimethyl amino phthalide OR quinazoline dye.

Compound B contains Benzyl-4-hydroxybenzoate/4,4-isopropylidene diphenol resin/modified alkyl phenol polymer.

Types of Security Inks:

(i) **Reactive Ink:** is solvent sensitive and any attempt to alter the markings can be easily detected.

(ii) **Thermochromic Ink:** is sensitive to temperature changes due to which the colour appears or disappears.

(iii) **Optically Variable Ink (OVI):** has tiny flakes of metallic films which change in colour when viewed from different angles. It is usually seen in currency notes in which colour varies from blue green or red → purple at different angles.

(iv) **Invisible Ink:** is mainly used for purpose of document protection or cheque printing. The markings cannot be seen in visible light but becomes visible under U.V. Light.

(v) **Water-based Fugitive Ink:** We can easily detect any attempt to alter the markings made by this ink using water or other solvent as the ink runs.

(vi) **Magnetic Ink:** is used in printing MICR code on the cheque, which contains sensitive information about account number, sort code, cheque number, etc. This ink contains tiny magnetic flakes which communicate with the electronic reader to verify the information.

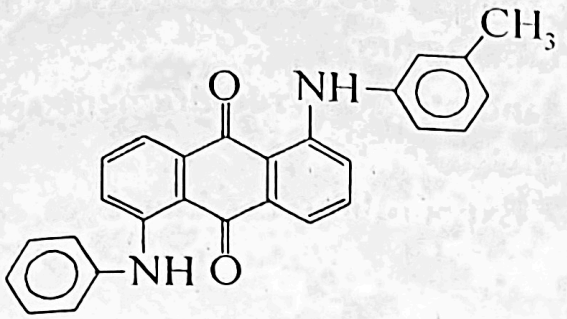
(vii) **Secondary Fluorescent Ink:** The fluorescent inks become visible under U.V. light. But only when some alteration is attempted in the original printing, this ink will glow with green colour having a red shade.

(viii) **Biometric Ink:** Contains DNA tags which a machine can read or they may react to a particular solvent. Biometric ink works best for verification of the authenticity of a genuine product.

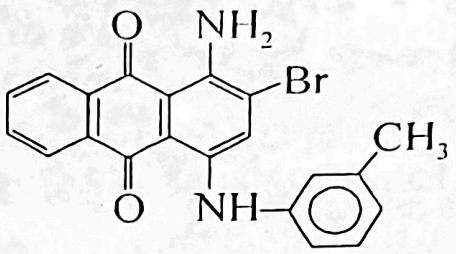
Indelible Ink which is also called lunar caustic is used in elections in India. Indelible ink is used to put a semi-permanent mark on the finger to prevent that person from voting multiple times. Mysore Paints and Varnishes Limited is the only company in India which is authorised to produce indelible ink. Indelible ink comes as a inky black solution which mainly contains silver nitrate solution along with some violet dye in alcohol. When it is applied on skin, it is absorbed and decomposes to produce microscopic particles of silver which causes brownish-black stain. Since the stain is absorbed by the skin, it remains for nearly a month on the finger.

(E) Coloured Smokes and Camouflage Colours

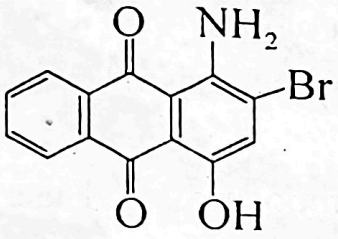
The coloured smokes are used as signals for passing information during war times. The pigments used for the purpose must have a deep colour, thermal stability and volatility. The coloured smoke is produced by igniting a mixture of the pigments, potassium chlorate and sugar. Different pigments produce different coloured smokes thus giving different signals. The following pigments are generally used.



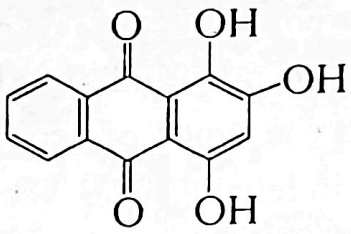
(Violet pigment)



(Blue pigment)

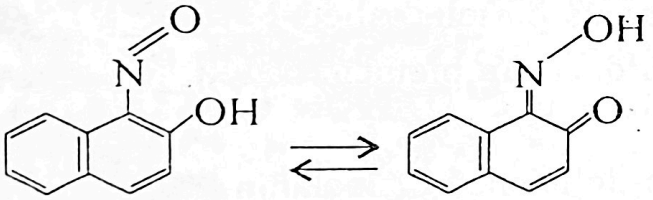


(Wine red pigment)

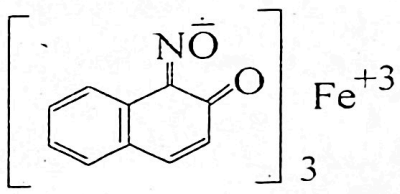


Purpurin (Brown pigment)

Camouflage colours are dyes which absorb infrared rays and hence cannot be detected by infrared photography. Thus, a dispersion of phthalocyanins and pigment green (Fe complex of 1-Nitroso-2-naphthol) is sprayed on the important installations. Hence, during the war times, these targets can be protected by avoiding detection by infrared photography.



1-Nitroso-2-naphthol



Fe^{+3} complex

Questions

1. What is the objective of colouring the formulations? What are their requirements?
2. Draw the structures of:
   (i) Indigo caramine (ii) Tartrazine (iii) Sunset yellow
3. What is meant by biological staining? Give two examples with structure.
4. What are DNA markers? Give applications of DNA markers.
5. Draw the structures and uses of the following as colour markers:
   (i) Bromophenol blue (ii) Orange G (iii) Cresol Red
6. Give two examples of dyes having therapeutic action. Give their use.
7. What are the requirements of dyes used as food colours? Give two examples with structure.
8. Explain the following terms giving their importance:
   (i) FDA (ii) FSSAI
9. Compare FDA and FSSAI. What are their duties and responsibilities?