K.T.S.P. Mandal's

Categories of Organic Pigments Hutatma

Rajguru Mahavidyalaya, Rajgurunagar

Department of Chemistry

T.Y.B.Sc. Sem-V

Industrial chemistry paper CH-505

Associate Prof. Kolekar S.S.

As per new revised choicebased credit system syllabus w.e.f. June 2021

Dyes and Pigments

Dyes- Introduction, good qualities of dyes Chromophore, Auxochrome, Classification of dyes, pigment- Introduction, Classification of Pigments, Categories of Organic Pigments

Introduction

A dye is coloured substance that has affinity to the substrate to which it is being applied. The dye is generally a substance which is capable of colouring fabric in such manner that colour can not be removed by rubbing or washing. All colourd substances are not dye. For example. Azo-benzene is of orange red colour but it is not dye because it is not capable of colouring the fibre. The dye can be used for imparting colour to paper, plastic, leather.

Qualities of a Good dye

1. It must have a suitable and attractive colour.

2. It must be able to attach itself to material (e.g. cloth) from solution or to be capable of fixed on it. For example, azobenzene is a coloured but cannot fix itself to a fabric. Therefore, azobenzene is not a dye. Picric acid is able to dye silk or wool, a permanent yellow colour but not cotton. Hence dye must form a chemical union with the substrate to be dyed or it may get associated with the substrate by an intimate physical union.

3 Dye must be soluble in water or in a suitable solvent and should form a stable dispersion in water and good

4. The substrate to be dyed must have a natural affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion.

5. When a dye is fixed to a substrate, it must be fast to washing, dry cleaning, light, heat and other agencies. It must be resistant to chemicals like soap, washing soda detergents, acids or alkalies There is probably no dye which can be guaranteed not to alter shade under all conditions

Chromophore, Auxochrome

Various theories have been put forward to establish a relation between colour and constitution. Some of the important theories are Witt's theory, quinonoid theory, resonance theory and molecular orbital theory O. N. Witt (1876), pointed out that all coloured organic compounds contain certain

A compound containing a chromophore, is called chromogen If a chromogen has one or more auxochromes, the resulting substance is called a dye.

Dye = Chromogen + Auxochrome

Types of Chromophores

1) Independent chromophores - When a single chromophore is sufficient to impart colour to the compound. For example, azo group (-N-N-), nitroso group (-N- O) and ortho and para quinonoid group etc.

2) Dependent Chromophores - More than one chromophore is required to produce colour in the chromogen. For example, >C-0. group, >CC< group etc. Acetone having one ketonic group is colourless, where as diacetyl, having two ketonic groups is yellow, and triketopentane (having three ketonic groups) is orange. Colourless Acetone, Yellow is Diacetyl

Dyes are basically ionizing and aromatic compounds, they have chromophores (an isolated function group capable of absorbing UV radiations e g $-NO_2$, -C=N, -C=C-, -C=S etc.) present in them.

Chromophores act by making energy changes in the delocalized election cloud of dye This alteration invariably results in the compound absorbing radiation within the visible range of colours and not outside it than eyes det this absorption, and responds to the colour.

How can the colour of the Dyes be altered? The colour of the dyes are altered by the Modifiers. The colour modifiers of methyl or ethyl groups are responsible for any alteration in the dyes, they alter the energy in delocalised electrons. e.g. Methyl Violet Series.

Auxochrome

Auxochrome the only substance responsible for providing solubility and cohesiveness to dyes. An auxochrome is a group of atoms attach to the chromophore which modifies the ability of that chromophore to absorb light to a longer wavelength. these groups are called as auxochromes. Some of the auxochromes are-OH-OCH-NH, etc.

Benzene is chromophore, λmax. Value is 255nm

Phenol has λmax. Value is 270 nm

If chromogen has one or more auxochrome, the resulting substance is called a dye.

Dye is Chromogen+ Auxochrome

Important functions of Auxochrome are

They increase the intensity of colour for e.g. (1) Nitrobenzene is pale yellow, as-NO_2, group is a chromophore.

(ii) p-nitroaniline is dark yellow, as-NO_2, group is chromophore and-NH_2 group acts as auxochrome

(iii) Auxochromes make the chromogen a dye by fixing to the fibre due to the formation of chemical bond between the fibre and auxochrome e.g. Benzene (colourless) Azobenzene (coloured, but not a dye) p-amino benzene hydrochloride (a dye, aniline yellow) as a dye because it contains -N=N chromophore and -$NH_3^+Cl^-$ is auxochrome which formed the bond with fiber. Auxochrome has the ability to intensify colours. Auxochromes are of two types positively charged or negatively charged

Types of Auxochromes

1) Batho chromic group-Those groups which deepen the colour of the chromogen, called bathochromic groups. For example, primary, secondary or tertiary amino groups increase the colour of the chromogen. Conjugation of double bond with a second one or with a triple bond, carbonyl, carboxyl or nitro group gives rise to high intensity bands in the region 2000-2300 A representing a bathochromic displacement of 150-450 A* with respect to ethylene.

2) Hypochromic groups- Those groups which lighten the colour of a chromogen are called hypochromic group, for example, acetylation of - OH or -NH_2 groups, structural changes that increase intensity of absorption are said to be hyperchromic, while those decreasing the intensity are hypochromic.

Classification of Dyes

Dyes are classified from both the chemical and the application viewpoints. Classification of dyes according to their mode of application is concerned mainly with the various different methods of dyeing to various fibres with the different dyes.

Classification of dyes according to their application

1) Acid dyes: Acid dyes are usually the sodium salts of sulphonic acid or phenolic compounds. The colour of an acid dye is in its negative ion. Such anionic dyes are attached to the positively charged amine groups in the fibre. Wool-$NH_2H_2SO_4$. + Dye acid gives Wool-NH_2 dye acid + H_2SO_4. Examples of acid dyes are Martius yellow, naphthol yellow. Process Fabric is stirred in the hot solution of the dyes in the presence of either an acid or salt till it is uniformly dyed. Then it is removed and dried Uses Acid dyes are of great importance in wool and silk dyeing

2) Basic dyes: These are mostly amino or substituted amino derivatives or the salts of coloured bases with HCl or $ZnCl_2$ Examples: Methyl violet, magenta. Process(1) Cotton is first mordanted with tannin or fatty acid salt of ammonia. (1) The colour is then developed by heating the mordanted cotton in a bath of basic dye at about 60°C(ii) Then it is removed and dried

Uses

(1) These are mostly applied to paper, cotton and silk

(2) Solvent basic dyes have also been used in writing and painting inks.

3) Direct (Substantive) dyes: These dyes are also called salt dyes, because of the fact that dyeing is usually carried out in presence of common salt.

Examples Congo red, direct black etc.

Process:

(1) The dye is applied to the fabric in a hot boiling solution and then removing and drying the fibre.

(ii) Addition of common salts deceases the solubility of the dye and hence cause better exhaustion of it from the dyeing solution

(iii) Substantive dyes probably become fixed on the fibre by hydrogen bonding

Uses - Direct dyes are used to dye animal fibres as well as cotton or the vegetable fibres. (without mordant) directly.

4) Mordant or Adjective dyes: Mordant dyes contain -OH or -COOH radicals frequently attached to azo anthracene complex. These dyes cannot dye animal and vegetable fibres directly, but require a presence of a medium of a third substance, called mordant. Mordant dyeing consists in cotton in such a manner as to affix to it either acidic or basic group. If the dye is acidic in nature, the mordant must be basic and vice versa.

Example

(1) Basic moderents used for acidic dyes are metallic hydroxides of Cr, Al, Sn and Fe.

(2) Acidic mordant used for basic dyes is usually tannin or tannic acid.

Process:

(1) The mordant dyeing is really a metallic salt or lake formed in the fibre.

2)The sulphonated castor oil dipped into the solution of metallic salt. (aluminium sulphate), and finally streamed.

3) The soaked fire was then dipped into solution dye

(4) The colloidal metal hydroxide adheres to the fire and molecule metallic mordant form complex salt or take by means of chelation. The thus formed is fast washing

(5) The colour be varied by using the other method Aluminium suitable for dyeing painting cotton alizarin

5) Vat dyes: Vat dyes are insoluble water, their reduced form soluble solution and as result leuco base obtained if fabric immersed in alkaline solution of reduced dye (vat), the leuco compound obtained and withdrawal and exposure air, oxidised to the which remain fixed the dye which remain fixed the cloth. Examples Indigo and anthraquinone vat dyes

Process

(i)Vat dyeing is carried out by continuous process in which cotton cloth

from a roll is conveyed over system of rollers into solution of reduced dye.

(ii) The cloth then conveyed into a chamber, where leuca compound to fabric carried by steaming process. (iii) The fabric next passed oxidizing bath, containing chromate and finally the soaping rinsing and baths. (iv) Cellulosic fiber the form yarn is placed in stationary compartment of dyeing apparatus. Then the caustic hydrosulphite of the dye is pumped through the material

Uses

(1) vat dye widely applied to cotton.

(2) These dyes are applied wool and silk as these fibers are sensitive to alkalies.

6) Sulphur dyes: These are complex substances containing Sulphur, which are water, soluble in cold alkaline solution sodium sulphide (Na_2S) and give leuco compound (reduced dye). Example Sulphur block,

Process The cotton fibre dipped in solution air which oxidizes the leuco compound to insoluble dye. Sulphur dyes are usually dark colour, expensive and fast.

Uses: Sulphur dyes are used to for dyeing cotton fibric

PIGMENTS

Introduction

Pigments are various organic and inorganic insoluble substances, which are widely bed in surface coating They are also used in ink, plastic, rubber, ceramic industries to impart colour. Pigments are generally added into paints to affect properties associated with a appearance such as colour, opacity, glass, metallic look depth. In addition, pigments are commonly used to protect the substrate against corrosion attack by microbes and retard flammability in old days, white lead [$2PCO_3$), $Pb(OH)_2$]. zine oxide (ZnO) principle white pigments used. Coloured pigments consisted of Pussian blue, lead, chromates, various iron oxides Now, Titanium dioxide (TiO_2) is one of the most important of white pigments Carbon black, graphite and lamp black are the chief black pigments Strontium chromate and barium chromate are yellow pigments

Classification of Pigments

The most satisfactory way to classify a pigment is according to its source Inorganic Pigments: They are of the type mineral-earth but generally are metallic oxides or synthetic Pigments that are of the type mineral-earth are very simple and naturally occurring colored substances. The preparation process is also simple and consists of the steps of washing drying, pulverizing and mixing into a formulation Examples of inorganic pigments can be materials like lead oxide, cobalt blue, chromium oxide, cadmium yellow, molybdate. or and nickel titanate (2) Organic Pigments: Organic pigments are not usually found in nature. Majority of the pigments comes with relatively low levels of toxicity, not providing any major environmental concern. Raw materials include coal tar and petroleum distillates that a transformed into insoluble precipitates. Organic pigments are used as mass colorants. They are popular in plastics, synthetic fibers and as surface coatings - paints and inks.

Categories of Organic Pigments are - Mono azo pigments, Diazo pigments, Acid and base dye pigments and other poly cycle pigments Characteristics of Organic Pigments

(1) Very good stability to solvents, light, heat and weathering

2) Good strength

3) Cost effectiveness

4) Consistency and unique shades

5) Completely non-toxic

6) Very bright and rich colours

7) Organic pigment show good colour strength

(ii) Metallic Pigments Today metallic pigments are very popular category of pigments. They are of two types aluminium and zinc.

(a) Aluminium Pigments: These are further divided into two categories namely leafing grade and non-leafing grade. The aluminium pigments are produced from aluminium has purity in the range of 99.3 to 99.97 %. As corrosion protection coats, roof coatings, highly heat-resistance paints, chrome effective paints.

(b) Zinc Pigments: Zinc pigments come in two forms of powder and dust. Usually the zinc dust is finer as compared to powder and is spherical in shape. The dust also has a light coating of zinc oxide

(iv) Industrial Pigments

Though every pigment has industrial application, a few popular industrial pigments have been given below that have very wide use. e.g CLC pigments DPP pigments, Effect pigments

General Physical Properties of Pigments

There are two important physical properties of pigments --

(1) Refractive index and (ii) Binder stability.

Categories of Organic Pigments are - Mono azo pigments, Diazo pigments, Acid and basic dye pigments, Phthalocyanine pigments, Quinacridone pigments, other poly cycle pigments Characteristics of Organic Pigments

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There are two important physical properties of pigments - (1) Refractive index and (ii) Binder stability.

Inorganic pigment – Zinc oxide pigment

Raw Materials: For the industrial synthesis of ZnO pigments, formerly zinc ores or metal from zinc producers were used, Today zinc residues and secondary zinc are preferred. The production processes of ZnO are modified from time to time

Production of Zinc oxide Pigment

1) Direct process (American process)

It is the most simple, cost effective and energy saving route for the manufacture of zinc oxide pigments. It consists of two steps:

(1) $ZnO+C \rightarrow Zn + CO$

The carbon monoxide acts as a reducing agent. It further reacts with ZnO and CO, is generated

$ZnO + CO \rightarrow Zn + CO_2$

This reaction takes place at the exit of the furnace by oxygen present in

the kilns.

Uses: Zinc cade pigments are mainly used in paints, coatings and artists colors, a additives in exterior paints for wood preservation, in antifouling and anticorrosion paints, to improve film formation and durability of cured films, as avoidance of mildew, in industry (as an activator for vulcanization accelerators in synthetic and natural rubber materials), in the pharmaceutical industries because of their antibacterial properties, in the formation of dental cements, in glasses, ceramics and enamels, as a w material for chromates, phosphates, bromates, ferrites and organic as additive in animal food , Iron oxide pigments

Properties

Iron oxide pigments show wide variety of colours ranging from yellow, orange, red, brown to black. They are chemically stable and nontoxic and relatively low production cost. Iron oxide pigments are classified into natural and synthetic iron oxide type e.g. Natural iron oxide pigments are of the following types:

Alpha -FeOOH colour change with increasing particle size from green-yellow yellow.

Gamma -FeCOOH-colour change with increasing particle size from yellow to orange.

Natural iron oxide pigments are mainly used in inexpensive marine coatings or in coatings with a glue, oil or lime base, the colouring of cement, artificial stone, wallpaper, drawing pastles and chalks.

Synthetic iron oxide pigments show higher and more iron oxide contents. Synthetic iron oxide pigments are more important because they have pure colour. Chemically pure FeO, FeOO11 are mainly produced for red, yellow, orange and black pigments Production of iron oxide

pigment

Following are various processes used for the production of highquality iron oxide pigments. For such production it is essential to control the particle size, particle size distribution, particle shape and composition. Following processes are usually followed

1) Solid state processes for red, black, brown pigments

2) Precipitation processes for yellow, red, orange and black pigments

3) Lux process for black, yellow and red pigments. Out of these three processes we are going to study only the precipitation process.

Raw materials

Raw materials used for these processes are mainly byproducts from other industrial processes especially iron (II) sulphate and iron (III) chloride from the steel industry and iron scrap from the metal working industry. Precipitation process. The production of alpha-FeOOH, alpha-FeO, and FeO. pigments can be carried by combined precipitation-oxidation processes and using air as the oxidizing agent. The starting material used for this process is iron (II) sulphate solutions. In order to achieve soft pigments with a pure bright colour, appropriate reaction conditions are useful, the production of the yellow alpha -FeOOH is done with FeSO4 7H2O as the source. Alternatively, solutions from iron and steel pickling can be used. The presence of other metal ions should be avoided in order to get good colour of the final iron oxide pigment.

Reference:- According to the new revised syllabus of Savitribai Phule Pune University from June 2021 Text book of Industrial chemistry for T.Y. B.Sc. course (CH- 505), Sem-v Manali Publication, Nirali Publication and google images