Acid dyes:- Introduction

Acid dyes are highly water soluble, and have better light fastness than basic dyes. The textile acid dyes are effective for protein fibers such as silk, wool, nylon and modified acrylics. They contain sulphonic acid groups, which are usually present as sodium sulphonate salts. These increase solubility in water, and give the dye molecules a negative charge. In an acidic solution, the -NH₂ functionalities of the fibres are protonated to give a positive charge: -NH₃+. This charge interacts with the negative dye charge, allowing the formation of ionic interactions. As well as this, Van-der-Waals bonds, dipolar bonds and hydrogen bonds are formed between dye and fibre. As a group, acid dyes can be divided into two sub-groups: acid-leveling or acid-milling.

Chemical structure of acid dyes

These dyes are normally very complex in structure but have large aromatic molecules, having a sulphonyl or amino group which makes them soluble in water. Most of the acid dyes belongs to following three main structural molecules,

1. Anthraquinon type
2. Azo dye type
3. Triphenylmethane type.

Different types of acid dyes

The basic dyes are classified into several groups, based on the leveling properties, economy of the dyeing and fastness properties, however generally these are classified into these three classes,

1. Neutral acid dyes :-
These are supra milling or fast acid dyes, having medium to good wet fastness properties, some of the dyes have poor light fastness in pale shades, many of the dyes are used as self shades only. These are applied to the fiber in a weakly acid or neutral pH.

2. Weak acid dyes
These dyes belongs to the milling class of dyes. These dyes have good fastness properties but light fastness is moderate to poor.

3. Strong acid dyes
These dyes are applied in a strongly acidic medium and also called leveling dyes, however there wet fastness properties is a limitation. These dyes are very good to produce the combination shades.

Classification according to dyeing characteristics

Acid dyes are commonly classified according to their dyeing behaviour, especially in relation to the dyeing pH, their migration ability during dyeing and their washing fastness. The molecular weight and the degree of sulphonation of the dye molecule determine these dyeing characteristics. The original classification of this type, based on their behaviour in wool dyeing, is as follows:

1. Level dyeing or equalising acid dyes;
2. Fast acid dyes;
3. Milling acid dyes;
4. Super-milling acid dyes.

Milling is the process in which a woollen material is treated, in weakly alkaline solution, with considerable mechanical action to promote felting. Dyes of good fastness to milling are essential to avoid colour bleeding during the process.

Properties of acid dyes
Since these are sold as a sodium salt, therefore these form a large anion in the aqueous medium.

The main properties of acid dyes are,

1. These dyes are anionic in nature.
2. These dyes are suitable for wool, silk, polyamide and modified acrylics.
3. These are applied from a strongly acidic to neutral pH bath.
4. These dyes have no affinity for cotton cellulose’s, hence not suitable for cellulosics.
5. These dyes combine with the fiber by hydrogen bonds, vander waals forces or through ionic linkages.

Mechanism of dyeing with acid dyes
Dissolution of dyes in aqueous solvent, produces a colored anion,

\[ \text{A-} \text{SO}_3\text{Na} + \text{H}_2\text{O} \rightarrow \text{A-} \text{SO}_3^- + \text{Na}^+ + \text{H}_3\text{O}^+ \]

The protein and polyamide fibers produce cationic sites in water under acidic conditions, as the acidity of the solution is increased more cationic sites are produced under these strongly acidic conditions. These cationic sites are thus available for the acid dye anions to combine with through hydrogen bonding, vander waals forces or ionic bonding. These linkages are strong enough to break, and thus dyeing produced are fast.

Application Parameters for Wool
Electrolyte in the acid dye bath acts as a retarding agent because of chlorides ions attracted by the positive sites at the fiber and in the competition between. Addition of acid acts as an exhausting agent, because strongly acidic conditions makes more cationic sites available and thus available dye anions got combined with these.

Dyeing temperature
The dyeing is generally carried out at boiling temperature for 30-60 minutes depending upon the depth of the shade and dyestuffs used.

Dyeing leveling agents
In the case dyeing with acid dyes, mainly cationic agents such as ethoxylated fatty amines are used as leveling agents.

Heating rates
Heating rate is generally kept 1-30°C/Min

Washing off process
A typical dyeing cycle of nylon filament dyeing with acid dyes is shown in the above chart,
Method 1
At A set bath at 50° with:
4% Sulphuric Acid (96%)
5% Glaubers Salt anhydrous,
PH 2.5 to 3.5

At B add required amount to dyestuff.

Method 2
At A set bath at 50° with:
2% Formic Acid (85%)
5% Glaubers Salt anhydrous,
PH 3.5 to 4.5

At B add required amount of dye.

At C add 2% Sulphuric Acid (96%) or 2% Formic Acid (85%).

Thoroughly rinse after dyeing to remove loose colour.

**Fastness properties of acid dyes**
The wet and light fastness properties of the acid dyes varies from poor to excellent, depending upon the molecular structure of the dyes.

**The fastness properties as per the category are as follows**
Neutral acid dyes:-since these dyes have very good leveling and migration properties, and have a low affinity for the fiber, therefore the wet fastness properties of this class are generally poor.

Weak acid dyes or half milling dyes:-
These dyes have a medium to good affinity for the fiber and are generally applied in a weakly acidic bath, shows medium to good wet fastness properties. Strong acid dyes or super milling dyes:- These dyes have poor exhaustion properties, therefore applied under very strong acidic condition, exhibit good fastness properties.
DYEING AND PROCESSING- ACID DYES

What are acid dyes?
Acid dye class is a water soluble class of dyes with anionic properties. The textile acid dyes are effective for protein fibers such as silk, wool, nylon and modified acryllics. Acid dyes fix to the fibers by hydrogen bonding, vander waals forces and ionic linkages.

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Dyeing and Processing
Dyeing with Direct dyes
Dyeing Method With Direct Dyes

Direct Dyes

Direct Dyes are used in a wide range of dyeing applications such as on Cotton, Silk and Viscose Fabrics. Direct dyes are famous for their easy application, leveling property, good brightness and fastness. These dyes can be safely applied on Textiles and Leather.

PRE - TREATMENT

Good pre-treatment is essential if satisfactory dyeing is to be obtained. To get better depth and fair brightness, Grey Fabrics must be free from impurities like sizing materials and spinning oil by boiling the Grey with alkline or some times bleaching also carried out in case of pale shades.

METHOD OF DYEING

(1) DISSOLVING THE DYESTUFF

The dyestuff is pasted with cold water and dissolved by pouring 50 to 100 times its weight of Boiling water while stirring. The solution may be boiled to ensure complete dissolution. For certain dyes, which are dyes from and alkline dye bath, it is preferable to add half its weight of soda ash while pasting with water.

(2) YARN DYEING

Set the Dye Bath at 50°-60° C temperature with dyes solution, salt and soda ash. Run for 15 Minutes. Gradually raise Temperature to 90°-95° C. Run for 30 to 45 minutes. In order to overcome un level dyeing salt may be added in installments after about 15 minutes of initial dyeing prior to raising the dye bath temperature.

In the case of dyestuff which possess maximum affinity at temperature below boil, it is preferable to start dyeing at boil, dye for 15 to 20 minutes and then add salt in two installments to exhaust the bath and continue dyeing in a cooling bath (60° C) for 15 to 20 minutes.

JIGGER DYEING

The dyeing on the Jigger is carried out as follows:
First End : 1/2 quantity of Dyes solution, soda ash and 1/4 quantity of Salt at room Temperature. Second End : 1/2 quantity of Dyes solution, 1/4 quantity of Salt at 60°c, raised to 80°c. Third End : 1/4 quantity of Salt. Fourth End : 1/4 quantity of Salt.
The temperature is raised to boil and four ends are given at boil. Finally the dye-liquor is Drained and further two ends are given in cold water.

**AFTER TREATMENT**

Fastness to wet treatments can be improved by after treatment with 1-2% Cationic Dye Fixing Agents at 40-50° c for minutes. In case of some selected dyes, light fastness can be improved by after treatment with:-1-2% Copper Sulphate1-2% Actic (30%) at 80° c Temperature.

**Direct Dyes**

Direct Dyes are molecules that adhere to the fabric molecules without help from other chemicals. Direct dyes are defined as anionic dyes with substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte, either sodium chloride (NaCl) or sodium sulfate (Na2SO4).. The dyeing process with direct dyes is very simple, Direct dyeing is normally carried out in a neutral or slight alkaline dyebath, at or near boiling point, but a separate aftertreatment such as cationic dye fixing, to enhance wet fastness has been necessary for most direct dyeing.

Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

Chemicals nature of direct dyes

Chemically they are salts of complex sulfonic acids.

Structure:-More than 75% of all direct dyes are unmetallised azo structures, great majority of them are disazo or polyazo types.

Ionic Nature:-Their ionic nature is anionic.

Solubility:-They are soluble in water.

Affinity:-They have an affinity for a wide variety of fibers such as cotton, viscose, silk jute, linen etc.. They do not make any permanent chemical bond with the cellulosic fibers but are attached to it via very week hydrogen bonding as well as vander waals forces. Their flat shape and their length enable them to lie along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds.

Types of direct dyes

The SDC classification of direct dyes is follows

(1) Class A – dyes that are self-levelling, i.e. dyes of good migration or leveling properties.

(2) Class B – dyes that are not self-levelling, but which can be controlled by addition of salt to give level results; they are described as salt-controllable.
Class C – dyes that are not self-levelling and which are highly sensitive to salt, the exhaustion of these dyes cannot adequately be controlled by addition of salt alone and they require additional control by temperature; they are described as temperature-controllable.

Application of Direct Dyes

Direct dyes are usually applied with the addition of electrolyte at or near the boil in the machines capable of running at atmospheric pressure. But in HTHP dyeing machines it is carried out at temperatures above the boil in case of pure as well as blended yarns.

An addition of alkali, usually sodium carbonate, may be made with acid-sensitive direct dyes and with hard water as well as to enhance the dye solubilisation. When cellulose is immersed in a solution of a direct dye it absorbs dye from the solution until equilibrium is attained, and at this stage most of the dye is taken up by the fibre. The rate of absorption and equilibrium exhaustion vary from dye to dye. The substantivity of the dye for cellulose is the proportion of the dye absorbed by the fibre compared with that remaining in the dyebath.

Dyeing Method

The color is pasted well and dissolved in boiling water to get a lump free solution. An addition of 0.5–2 g l−1 sodium carbonate may be advantageous when applying dyes of only moderate solubility in full depths.

The dyebath is set at 40°C,

Raise to the boil at 2 degC min−1.

Hold at the boil for 30–45 min,

During hold add 10–15 g l−1 of sodium chloride or calcined Glauber’s salt. Light shades are dyed without or lesser addition of salt.

Improved yields can be achieved when applying full depths by cooling to 80°C at the end of the period at the boil, adding a further 5 g l−1 salt and rising to the boil again.

Dye bath variables which must be considered for level dyeing,

1. Temperature of Dyeing and rate of heating

2. Electrolyte concentration and addition

3. Time

4. Dye solubility

5. Use of leveling agent
After treatment of Direct dyed material

The wet fastness properties (particularly washing, water and perspiration) of virtually all dyeing of direct dyes are inadequate for many end uses but notable improvements can be brought about by after treatments.

1. Diazotisation and development
2. Metal salt treatments
3. Cationic fixing agents
4. Formaldehyde treatment
5. Crosslinking agents and resin treatments

Stripping: Most direct dyes can be stripped of the use of stripping salts (Sodium Hydrosulphite) and/or by using a chlorine bleaching agent such as sodium hypochlorite, without harmful effects on the fibres.

Color fastness properties of Direct Dyed material: Generally these dyes are used where high wash fastness is not required.

Wash Fastness: poor unless treated with suitable dye fixing agent and/or fastness improving finishing agent.

Light Fastness: Good

Rubbing Fastness: Moderate to Good

Chemical Wash Fastness: Poor

How to Identify a Direct Dye on a Substrate Dye class identification

How to test comparative strength of a cationic dye fixer

Azo Group A slide show

Chemistry of dyes

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Azo Group
A slide show

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Quick and level dyeing dyeing with Direct dyes
DYEING COTTON WITH SULPHUR DYES

• PREPARED BY THE ACTION OF SULPHUR AND CAUSTIC SODA UNDER THE INFLUENCE OF HEAT UPON VARIETY OF PHENOLS, AMINES AND NITRO COMPOUNDS

• FIRST SULPHUR DYE WAS PREPARED IN 1873 BY HEATING SAWDUST WITH SULPHUR AND CAUSTIC SODA

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CHARACTERISTICS

- CONTAIN SULPHUR S-S LINKAGES WITHIN THEIR MOLECULES
- INSOLUBLE IN WATER
- DISSOLVED IN PRESENCE OF Na2S AND SODA ASH
- Na2S ACTS AS REDUCING AGENT
- DYE.S-S.DYE +2H → DYE.SH +SH.DYE
- REDUCED DYE READILY OXIDIZE IN FIBRE TO ORIGINAL INSOLUBLE SULPHUR DYE WITH VERY GOOD FASTNESS PROPERTY
- DYE.SH + DYE.SH + O → D.E.S-S.DYE +H2O
- UNLIKE OTHER DYE CLASSES THE EXACT CHEMICAL STRUCTURE OF SULPHUR DYES IS NOT KNOWN.
SULPHUR DYSES

GENERAL PROPERTIES OF SULPHUR DYSES

• CHEAP AND EASY TO APPLY

• WET FASTNESS GOOD

• LIGHT FASTNESS SATISFACTORY

• CHEAP METHOD OF DYING COTTON WITH WET FASTNESS BETTER THAN DIRECT DYES

• ALL SULPHUR DYSES HAVE POOR FASTNESS TO CHLORINE

• DECOMPOSED BY ACID WITH THE LIBERATION OF SULPHUR
SULPHUR DYES

- DISSOLVING OF SULPHUR DYESTUFFS
- PASTE WITH COLD WATER
- ADD SODA ASH (EQUAL TO DYE)
- ADD Na2S (TWICE THE WEIGHT OF DYE)
- ADD BOILING WATER
- STIRR TILL DISSOLVED 10 MIN.
- FILTER BEFORE ADDING TO DYEBATH
- DYEING CARRIED OUT AT 60-80°C
- TIME 45-60 MIN.
- ADDITION OF COMMON SALT 20-30 g/l FACILITATE DYE EXHAUSTION
SULPHUR DYES

• DYEING
  • PREPARE THE BLANK BATH CONTAINING Na₂S (TWICE THE WEIGHT OF DYE) AND SODA ASH (EQUAL THE WEIGHT OF DYE)
  • RUN THE FABRIC THROUGH BLANK DYEBATH (ONE END)
  • ADD HALF THE QUANTITY OF REDUCED DYE
  • RUN ONE END
  • ADD SECOND HALF OF DYE
  • RUN ONE END
  • ADD COMMON SALT 20-30 g/l
  • RAISE THE TEMP. TO 60-80°C
  • RUN 6-8 ENDS (45-60 MIN)
  • RINSE WITH COLD WATER (ONE END)
  • OXIDIZE WITH H₂O₂ 2g/l AT 50°C (2ENDS)
  • RINSE
  • UNLOAD
  • DRY
SULPHUR DYES

- BRONZINESS OF SULPHUR BLACK
- SULPHUR BLACK HAS TENDENCY TO SHOW BRONZE APPEARANCE (DULL SHADE)
- MANY FACTORS RESPONSIBLE
  - EXCESSIVELY HEAVY DYEING RESULTING SURFACE DYE DEPOSITION
  - EXCESS USE OF COMMON SALT FOR EXHAUSTION
  - EXPOSURE OF FABRIC TO AIR WHILE DYEING (PREMATURE DYE OXIDATION)
  - FAILURE TO REMOVE EXCESS DYE DURING TREATMENTS AFTER DYEING
  - INSUFFICIENT Na2S IN DYEBATH
SULPHUR DYES

• REMOVL OF BONZINESS
  • AFTER-TREATMENT IN BATH CONTAINING DIL. Na2S SOLUTION (1-2 g/l) AT ROOM TEMP.

  • AFTER-TREATMENT IN A LIQUOR CONTAINING SOAP AND OLIVE OIL. 1-2 g/l
  • TEMP 60 C, TIME 30 MIN.
  • DRY WITHOUT RINSING
  • TREATMENT WITH 2 g/l AMMONIA AND 2-3 g/L TRO
SULPHUR DYES

TENDERING

• SULPHUR DYES PARTICULARLY SULPHUR BLACK SHADES ARE LIABLE TO CAUSE TENDERING OF DYED FABRIC ON STORAGE
• CAUSE: GRADUAL OXIDATION OF SULPHUR TO H2SO4

PREVENTION

• 1. TREATMENT OF DYED FABRIC WITH SODIUM ACETATE
• DRYING WITHOUT RINSING
• PRESENCE OF SODIUM ACETATE ON DYED FABRIC CONVERTS HARMFUL H2SO4 TO HARMLESS ACETIC ACID
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CHARACTERISTICS

- Contain sulphur S-S linkages within their molecules
- Insoluble in water
- Dissolved in presence of Na2S and soda ash
- Na2S acts as reducing agent
- Reduced dye readily oxidize in fibre to original insoluble sulphur dye with very good fastness property
- Dye.SH + Dye.SH + O → DE.S-S.Dye +H2O
- Unlike other dye classes the exact chemical structure of sulphur dyes is not known.
SULPHUR DYES

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• PRESENCE OF SODIUM ACETATE ON DYED FABRIC CONVERTS HARMFUL H₂SO₄ TO HARMLESS ACETIC ACID
ACCELERATED TENDERING TEST

- SUBJECT DYED AND UNDYED FABRIC TO 140°C FOR 1 hr.
- CONDITION FOR 12 hrs.
- REPEAT HEAT TREATMENT
- CONDITION FOR 12 hrs.
- CHECK THE TENSILE STRENGTH OF DYED AND UNDYED FABRICS.
- IF SULPHUR DYE HAS TENDERING PROPERTY, THERE WOULD HEAVY LOSS IN TENSILE STRENGTH COMPARED TO UNDYED FABRIC.
Dyeing of Cotton with Vat dye

Vat dye

Vat dye is one of the oldest types of dye. It is mainly suitable for cellulosic fibre for best overall fastness properties. Because of the popularity of blue jeans, indigo is still one of the most important dye in the world in the present time..

Why called vat dye :

The word vat means “vessel”. They are water insoluble. So it is reduced by fermentation in wooden vessel. The vat dyes are naturally obtained coloring materials from the ancient time and kept into wooden vat and make soluble in vat by the process of fermentation- so it is called vat dyes. They can’t be used directly & requires vatting. They are insoluble in water but become soluble from by vatting process. The process of converting insoluble vat dye by strong reducing agent in called vatting process. This converted, water soluble pigment is called leuco from & they have substantivity for cotton.

Properties

1. Vat dye are insoluble & can’t be directly applied to textile material. Before dyeing they need vatting.
2. Vat dyes are insoluble in water, solubilised by treatment with caustic soda and reducing agent, usually hyposulphite, the resulting leuco compounds have affinity for textile fiber, on exposure to air leuco compound impregnated fiber re-oxidises to the insoluble parent dye.
3. Vat dyes mainly belong to indigoid and anthraquinoid classes and are characterized by high fastness, specially anthraquinoids.
4. Mainly used or cellulosic fibre but for protein fibre pH should be control properly.
5. Most valuable for dyeing and printing cotton, wool and silk.
6. After dyeing, the dyes are entrapped inside the fibre & can’t come out during soaping & other treatment. So wet fastness is very good around 4-5.
7. Most of the vat dye are extremely fast to light. So used in curtain.
9. Rubbing fastness is not good.
10. Various shade is found
11. Dyeing process is difficult & different such as sulphure or indigo dyeing process.
12. Costly
13. Particle size is very small. So poor rubbing fastness.

**VAT DYES ARE COMMONLY USED FOR**

1. Superior Quality Shirting Material
2. Military Uniforms
3. Furnishings
4. Curtain,
5. Toweling
6. Denim Etc.

**Classification:**

**According to their application process:**

Vat dyeing conditions can vary widely in terms of temperature and the amount of salt and alkali required, depending on the nature of the dye applied. Based on temperature, amount of caustic soda, hydrosulphite and salt, used in dyeing, vat dyes can be classified into 3 main groups

**1. The 1N (indanthrene normal) group**

i. IN dyes (N = normal) are highly substantive
ii. vatting temperatures (60°C) and dyeing temperatures (60°C).
iii. no salt is added to the dyebath
iv. because of the high substantivity of the leuco dyes for cotton;

**2. The IW (indanthrene Warm) group**

i. IW dyes (W = warm) have higher affinity
ii. requires the use of moderate concentrated NaOH and
iii. lower vatting (50°C) and dyeing temperatures (50°C).
iv. the leuco forms of these dyes have moderate substantivity for cotton
v. some addition of salt is needed during dyeing to aid exhaustion;
3. The IK group

i. IK dyes (I = Indanthren, K = cold) have low affinity,

ii. only need a low concentration of NaOH with

iii. low vatting (40°C) and dyeing temperatures (20°C).

iv. these dyes have low substantivity for cotton and

v. need considerable salt for good dyebath exhaustion.

Some have amide groups that would be hydrolyzed under the vatting and dyeing conditions used for IN and IW dyes. There are special processes for some black vat dyes that require an oxidative aftertreatment to develop the full black colour.

Table compares the characteristics of these three types of vat dye. The required concentrations of hydrose, caustic soda and salt increase with increasing amounts of dye in the bath and with increasing liquor ratio.

**On basis on chemical structure:**

On the basis of chemical structure vat dyes are 2 types.

1. anthraquinonoid

2. indigoid vat dyes.

**Anthraquinonoid:**

In anthraquinonoid, one or more quinine (\(>\text{C}=\text{O}\)) groups act as chromophores & groups such as hydroxy (\(-\text{OH}\)) alkylamino (\(-\text{NHR} \text{ or } \text{NR}_2\)) benzamido etc are auxochromes.

**Indigoid:**

Indigoid dyes contain \((-\text{C}=\text{C})\) as the chromophore & \((-\text{NH}, -\text{S})\) as auxochromes. They can be further divided into 4 sub class

1. Indigo & its derivatives & homologues
Dyeing of cotton with vat dye

Vat dyes are water insoluble pigment. So vatting is done for making it solubilized form. Its application inverts reduction to water soluble leuco compound, then dyeing is done & after that re-oxidation of leuco dye in the fibre to soluble pigments. There are basic 4 steps for vat dyeing. They are——

1. Vatting

The step in which the reduction of the dyestuff into its leuco-form takes place is called vatting. It is the process of converting insoluble dye to soluble vat dye. They are reduced to soluble leuco compound & this process is called vatting.

Vat dyes are generally more difficult to reduce than sulphur dyes. Various reducing agents are used. Sodium dithionite (hydrosulphite) is still the most widely employed for vatting.

In this stage insoluble vat dye is reduced to produce weak acidic leuco from. A strong reducing agent dihydro sulphite, \( \text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \) or hydros is used for vatting. Vatting is carried out in strong alkali condition.

Decomposition of hydros occurs rapidly in acidic solution. So during dyeing material should not be over exposed to air.
2. **Dyeing:**
Absorption of *leuco* compound by the cotton during dyeing. The vatted dye (*leuco* form) are substantive to the cellulose material. Dyeing is carried out at lower temperature. To achieve adequate exhaustion an electrolyte is added to the dye liquor & temperature may be increased from 20-60°C & agitated for 15 min the goods are totally immersed to prevent premature oxidation.

![Reduction of Indigo](image)

3. **Re oxidation of vat:**
After absorption by the fibre, the dye in its soluble *leuco* form is converted to the original pigment by oxidation. This process is carried out in the course of wet treatment (washing) by addition of oxidants such as hydrogen peroxide, perborate to the liquor or exposed to open air.

![Re oxidation of Vat](image)
4. After-treatment

In this stage unfixed dye deposited on the surface are washed off. The material in weakly alkaline liquor with a detergent at boiling temperature. This soap treatment is not only aimed at removing pigment particles, but also allows the crystallisation of amorphous dye particles, which gives the material the final shade and the fastness properties typical of vat dyes.

5. Recipe

Vat dye  1%
Wetting agent  1.5 g/L
Sequestering agent  0.75 g/L
Caustic  4%
Hydrose  3%
Salt  20 g/L
M:L  1:10
Temp  60-100°C
A Presentation on...

REACTIVE DYE

1. Introduction & Discussion

Definition, naming, history, characteristics, classification, trade name etc
Definition

- A dye, which is capable of reacting chemically with a substrate to form a covalent dye substrate linkage, is known as reactive dye.
- Here the dye contains a reactive group and this reactive group makes covalent bond with the fiber polymer and act as an integral part of fiber.
Reaction

\[
D-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-O SO}_3\text{Na} + \text{HO- cell} \rightarrow \\
D-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-O-cell} + \text{NaHSO}_3
\]

\[
D-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-O SO}_3\text{Na} + \text{NH}_2\text{- wool} \rightarrow \\
D-\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-NH-Wool} + \text{NaHSO}_3
\]

Here, \(D\) = dye part.

\text{Wool} = \text{wool polymer.}

\text{Cell} = \text{cellulosic polymer.}

Reasons for so named

- Reactive dyes are so called because this is the only type of dye, which has reactive group, and that reactive group reacts chemically with fiber polymer molecules and form covalent bond.
Properties of reactive dye

1. Reactive dyes are cationic dyes, which are used for dyeing cellulose, protein and polyamide fibres.
2. Reactive dyes are found in powder, liquid and print paste form.
3. During dyeing the reactive group of this dye forms covalent bond with fibre polymer and becomes an integral part of the fibre.
4. Reactive dyes are soluble in water.
5. They have very good light fastness with rating about 6.
6. Textile materials dyed with reactive dyes have very good wash fastness with rating about 4-5 due to strong covalent bonds formed between fibre polymer and reactive group of dye.
7. Reactive dye gives brighter shades and has moderate rubbing fastness.
8. Dyeing method of reactive dyes is easy.
9. It requires less time and low temperature for dyeing.

History

The first three reactive dyes were:
- PROCION YELLOW R
- PROCION BRILLIANT RED 2B
- PROCION BLUE 3G

Two chemists of ICI company (UK) named Stephen and Rattee invent a new dye in 1956.

They were awarded gold medal of the society of dyes and colorists for the year 1960.
Reason of Popularity

- Ability to produce bright shades of wide range.
- High leveling quality.
- Good washing fastness.
- Good light fastness.
- Simple dyeing method therefore one stage dyeing.
- Low temperature dyeing (below 100°C)
- Lower cost, i.e. cheaper.

Classification

On the basis of reactive group:
1. Halogen derivatives
   - Triazine group
   - Pyrimidine group
   - Quinoxaline dyes
2. Activated vinyl compound

On the basis of temperature:
1. Hot Brand
2. Cold Brand

On the basis of reactivity:
1. Highly reactive
2. Moderate reactive
3. Lower reactive
## Trade Name

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Manufacturer</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procion</td>
<td>I.C.I</td>
<td>U.K</td>
</tr>
<tr>
<td>Cibacron</td>
<td>Ciba</td>
<td>Switzerland</td>
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<tr>
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<td>Primazin</td>
<td>BASF</td>
<td>Germany</td>
</tr>
<tr>
<td>Drimarine</td>
<td>Sandoz</td>
<td>Switzerland</td>
</tr>
</tbody>
</table>
Characteristics of reactive group of reactive dye:

- Reactive groups do not contribute to the color of dye. Chromogen group imparts it.
- The reactivity of vinyl sulphone group is less than that of halogen group.
- If no of reactive group increases, binding also increases.
- Reactive dye absorb up to 90%.
- Molecular weight of reactive group 69-211gm/mole.
- If the molecular weight of reactive group increases, reactivity increases.
- Chlorine imparts medium reactivity, but it is cheap.
- Reactivity of fluorine is the least and its rate hydrolysis is also less.
- Reactivity of vinyl sulphone group increases with increasing temperature and pH.
- Sulphone group has more solubility but it is not stable.
- Generally low molecular weight dyes are of hot brand.
- Less affinity dyes are used for pad method.

Assistants used for dyeing with reactive dyes

- Salt:
  - It neutralizes the electro negativity of fibre surface when immersed in solution.
  - It puts extra energy to push the dye inside the fibre polymer i.e. increase absorption of dye.
- Alkali:
  - to maintain proper pH in dye bath and thus to create alkaline condition.
  - Alkali is used as a dye-fixing agent.
- Urea: It helps to get required shade of dye.
- Soaping:
  - Extra color is removed from fibre surface. Thus washing fastness is improved. Soaping increases the brightness and stability of the dye.
Dyeing mechanism of reactive dye

- Exhaustion of dye in presence of electrolyte or dye absorption.
- Fixation under the influence of alkali.
- Wash-off the unfixed dye from material surface.

3 Application & Practices

Factors, Application methods, stripping, hydrolysis, faults & remedies
1) pH of the dye bath
2) Amount of alkali
3) Dyeing temperature
4) Electrolyte concentration
5) Time of dyeing
6) Liquor ratio

Different methods of reactive dye application

• Pad-batch method.
• Pad batch processes are of two types-
  – Pad (alkali)-batch (cold) process.
  – Pad (alkali)-batch (warm or hot) process.
• Pad dry method
• Pad steam method.
Cold Pad Batch

Steps:
1) The fabric is first padded in a padding mangle with reactive dye in presence of an alkali.
2) The padded fabric is rolled in a batch and the batches are wrapped by polyethylene sheets and stored in wet condition for 1-24 hours at 200-300°C in a room.
3) During the storage period, the rolls may be kept slowly rotating to prevent seepage of the dye liquor.
4) After storing time is finished fabric is washed in a rope washing machine to remove the unfixed dye from fabric surface.

![Diagram of Pad-Wash Method](image-url)
Stripping becomes necessary when uneven dyeing occurs. By stripping azo group (~N=N~) from the dye is removed.

**Partial stripping:**
- Acetic acid: 5-10 parts
- Water: 1000 parts
- Or
- Formic acid: 2.5 to 10 parts
- With water: 1000 parts
- Temperature: 70 - 100°C
- Time: until desired shade is obtained.

**Full stripping:**
- Na-hypochlorite: 1%
- at room temperature
- Na-hydrosulphite: 1% at boil.
- Time: 30 min

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**Hydrolysis of reactive dye**

Reaction of dye with water is hydrolysis of reactive dye

1. Hydrolysis of halogen containing reactive dye,

\[
D-R-\text{Cl} + \text{H-OH} \rightarrow D-R-\text{OH} + \text{H-Cl}
\]

1. Hydrolysis of activated vinyl compound containing dye,

\[
D-F-\text{CH}_2-\text{CH}_2-\text{OSO}_3\text{H} + \text{H-OH} \rightarrow D-F-\text{CH}_2-\text{CH}_2-\text{OH} + \text{H}_2\text{SO}_4
\]
Prevention of Hydrolysis

- As hydrolysis increases with increasing temperature during dissolving and application temperature should not be more than 40°C.
- Dye and alkali solution are prepared separately and mixed just before using.
- Dye and alkali should not be kept for long time after mixing.

Dyeing Faults

- Uneven Dyeing
- Batch to Batch Shade variation
- Patchy dyeing effect
- Roll to roll variation or Meter to Meter variation
- Crease mark
- Dye spot
- Wrinkle mark
- Softener Mark
Conclusion

Thank you