Advance warning

The following items needed for activities in this unit may not already be in your school, and might take a little time to obtain.

Activity	Item(s)	Essential/Optional	Typical quantity per experiment
CD1	Ammonium vanadate(V) NH_4VO_3 Dry ice (can use a CO_2 generator)	Essential Optional	0.5 g (enough for 5–6 groups)
CD5	Cyclohexane Cyclohexene Methyl benzoate	Essential Essential Essential	2 cm ³ 2 cm ³ 2.5 cm ³
CD6	Phenylamine Ethyl 4-aminobenzoate (benzocaine) Methylphenol (cresol; any isomer) Naphthalen-2-ol (β-naphthol)	Essential Essential Essential Essential	1.5 cm ³ 2 g } few crystals
CD7.1	* White cotton cloth (untreated) * Durazol Red 2B * Procion Red MX-5B	Essential Essential Essential	0.2 g
CD7.2	 * White cotton, polyester and nylon, or a multifibre strip * Acid Blue 40 * Direct Red 23 * Disperse Yellow 7 	Essential Essential Essential Essential	0.4 g 0.2 g 0.1 g Enough for 10+ groups

* Current suppliers are listed on the Salters Advanced Chemistry Web Site.

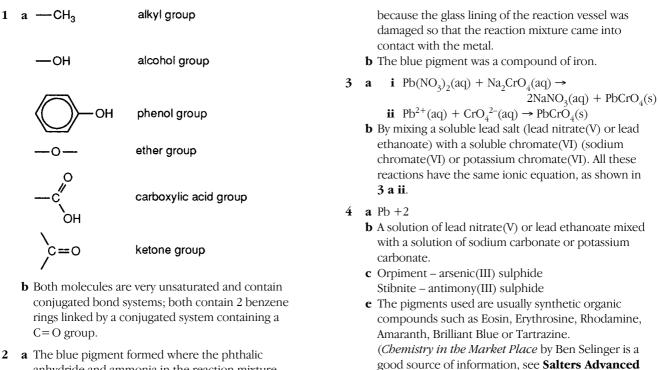
A special safety note

In each activity involving practical work, specific safety hazards are identified in the *list of requirements*. Further details can be found in books on safety, which have been listed on page 11. Nevertheless, you will need to be responsible, as in all laboratory work, for routine safety procedures.

The **Colour by Design** unit involves the use of a number of toxic or harmful chemicals such as phenylamine, naphthalen-2-ol and lead chromate(VI). *These compounds should be used in small quantities only, under strict supervision.*

Students should wear gloves when using dye solutions and should not handle the solid dyes. Technicians making up the dye solutions should use a fume cupboard. Eye protection should be worn as a matter of course whenever carrying out laboratory work.

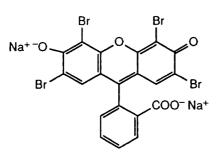
Storyline: answers to assignments



Chemistry Web Site.)

anhydride and ammonia in the reaction mixture reacted with the iron reaction vessel. This happened

eg Eosin



5 a The crystals of pure lead chromate(VI) shown in the first picture are mainly rod-shaped. Each rod is about 1 × 10⁻⁶ m to 2 × 10⁻⁶ m long. The pigment sample taken from a dark yellow area of the wheatfield is very similar, although it also contains a number of prisms. It is thought to be mainly Chrome Yellow. The pigment from the light yellow area of the wheatfield looks very different. There are some rods but also some smaller particles which are thought to be zinc oxide. (The larger particles are probably a mixture of lead chromate(VI) and lead sulphate.)

Note

Lead chromate(VI) can exist in two different forms, one monoclinic and the other orthorhombic. Many commercial Chrome Yellow pigments contain a mixture and different shades can be obtained by varying the proportions of each. The orthorhombic form is unstable and tends to change spontaneously into the monoclinic form. To prevent this happening, some pigment manufacturers would precipitate the lead chromate(VI) together with lead sulphate to give mixed crystals.

- **b** Emerald green absorbs in the infrared and so the trees appear dark. The Cobalt Blue and Zinc White used in the mountains reflect infrared light and appear bright. They cannot be distinguished from the sky because the sky also contains pigments which reflect infrared light.
- 6 **a** The energy of atoms is quantised and can have only fixed values. The frequency of radiation emitted by an excited atom is determined by the difference in energy between the excited electronic level and a lower electronic level.

$$E = bv$$

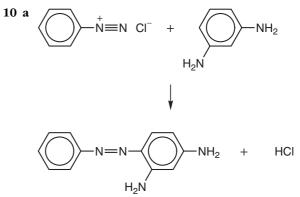
- **b** The spacing between the electronic energy levels is different for each atom, so the frequency of the radiation emitted is different.
- **c** Chemists compare the frequencies of lines in the LMA spectrum of a paint sample with the lines in reference spectra.
- 7 **a** $Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_{3}(s)$

A2 LEVEL

- **b** Complex formation. The Alizarin behaves as a bidentate ligand.
- **c** The aluminium ions hold the dye in the fibres by complexing both with –OH groups on the fibre and with the Alizarin molecules.
- **8 a** C₁₄H₁₀
 - **b** Isomers
 - c Structure B contains two very strained cyclobutenetype rings, in which the angles between carbon–carbon bonds in the ring are compressed to 90°.
 Both the structures A and C are stabilised by electron delocalisation which extends over the whole of the

molecules. In B, the two benzene ring systems behave independently, and the resulting stabilisation from electron delocalisation is lower.

- 9 a The two routes use different methods to introduce substituent groups into the anthraquinone molecule. Route I uses bromination; route II uses sulphonation.
 - **b** At the time, bromine was a comparatively rare chemical and too expensive for route I to be a commercial success. Bromine is now extracted on a large scale from sea water (see **From Minerals to Elements**) and is used widely in the manufacture of dyes and other organic chemicals.
 - **c** Electrophilic substitution.



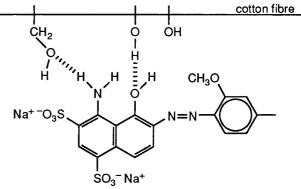
- **b** Diazonium compounds are unstable and start to decompose above about 5 °C. Diazotisation and coupling reactions have to be carried out in ice-cold solutions.
- \mathbf{c} –NH₂ group
- **11 a** The four ionic sulphonate groups, $-SO_3^-Na^+$, are mainly responsible for its solubility in water. The -OH and $-NH_2$ groups confer some solubility, but their effect is small by comparison.

Note

The $-SO_3^-$ groups contribute little to the colour of the molecule. Both the -OH and $-NH_2$ groups, however, have lone pairs of electrons which become involved with the delocalised electron system of the chromophore, and so both these groups affect the colour.

 \mathbf{b} –NH₂ and –OH groups

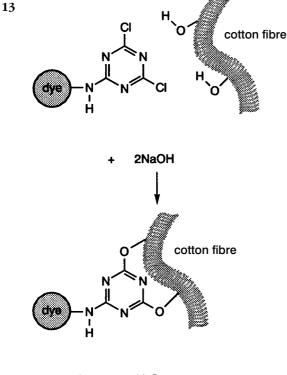


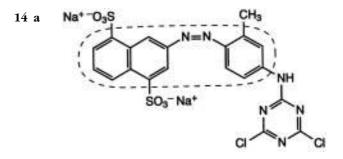


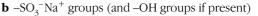
(Students should be aware that this representation of a cellulose fibre is highly simplified; the –OH groups on the fibre are not all in the same plane.)

CD ACTIVITIES: NOTES AND ANSWERS TO QUESTIONS

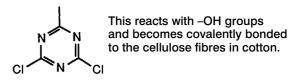
- **12 a** Some amino acids making up the protein chains in wool, -NH-CHR-CO-, contain free $-NH_2$ groups in the -R side-chain, eg lysine $-R = -(CH_2)_4 NH_2$.
 - **b** HCl
 - **c** The –NH₂ groups on the wool fibres would be in the unprotonated form. Also, alkali would react with the HCl formed and the position of equilibrium would move towards the products.
 - **d** Wool is a protein fibre. The protein tertiary structure can be denatured in alkaline solution. Also, some of the peptide linkages in the protein chains are hydrolysed. Cotton is a cellulose fibre made up of strings of glucose units and is more resistant to hydrolysis.







С



- **d** The main difference is that Procion Brilliant Red 2BS has an –OH functional group substituted in the chromophore. This group has a lone pair of electrons which can become involved in the delocalised electron system. This changes the electronic energy levels in the molecule and affects the colour.
- **15 a** All possible decomposition products have –SO₂OH groups so that they will be soluble in water.
 - **b** If all the -SO₂OH groups were replaced by -COOH groups the large dye molecule would become insoluble in the ink solvent.

+ 2NaCl + $2H_2O$

Activities: notes and answers to questions.

CD1 Changing colours chemically

Safety note Ammonium vanadate(V) is toxic and an irritant. Concentrated sulphuric acid is extremely corrosive. (**CARE** Avoid skin contact). Lead compounds are toxic and should be handled with care. Wear heavy gloves when handling dry ice. Full information about other hazardous chemicals is given on the activity sheet.

Comments

A unit on colour may be started in many ways. This activity provides a series of investigations involving colour changes with different causes. Students need not carry out all the investigations. It may be best to work in pairs or small groups and divide up the reactions between the members of the group. Alternatively, the investigations could be set up in a circus arrangement. The activity could also include an exhibition of coloured substances and materials.

Making an alkaline solution of glucose

A2 LEVEL

Dissolve 10 g NaOH or KOH (**CARE** Corrosive) in 500 cm^3 water. Add 10 g glucose to the cooled solution. (*Quantities enough for 5 groups*)

The alkaline solution of glucose should be made up beforehand. It is best to make it up the same day as it gradually turns yellow-brown.

Making an acidified solution of ammonium vanadate(V) (ammonium metavanadate NH_4VO_3)

Put $\overset{4}{0.5}$ g $\overset{5}{0}$ mmonium vanadate(V) NH₄VO₃ (**CARE** Toxic, irritant) into a conical flask and add about 50 cm³ 1.0 mol dm⁻³ sulphuric acid (**CARE** Irritant). Carefully add about 10 cm³ concentrated sulphuric acid (**CARE** Extremely corrosive; avoid skin contact) and swirl the flask until you obtain a clear yellow solution. (*Quantities enough for 5–6 groups.*)

1 The first disappearance of the blue colour may take up to 30 minutes. Subsequently, the intervals are much shorter.

Methylene Blue (MB) is a redox indicator. It is blue in its oxidised form, and colourless in its reduced form. It acts as a catalyst in the reaction of glucose with oxygen. Shaking the mixture aerates the solution. The process continues until either the glucose or the oxygen in the solution is used up.

$$\begin{array}{l} O_2(g)\rightleftharpoons O_2(aq)\\ MB(colourless) + O_2(aq)\rightleftharpoons MB \ (blue) + OH^-(aq)\\ MB \ (blue) + alkaline \rightarrow MB \ (colourless) + other\\ glucose \qquad products \end{array}$$

Note

Indigo Carmine is another redox indicator which can be used in place of Methylene Blue. It gives colour changes of yellow \rightarrow red \rightarrow green.

- 2 Granulated zinc reacts rather slowly, whereas the metal powder reacts too quickly for all the colour changes to be distinguished. Better results will be obtained using zinc wool or swarf, if this is available. An explanation of the redox reactions involved can be found in **Activity SS5.1**.
- **3** Zinc oxide is *polymorphic* and exists in two solid forms with different structures and colours.
- The crystals of lead nitrate(V) (CARE Toxic) and potassium iodide should be ground beforehand. Use a separate pestle and mortar for each compound. (CARE Do not breathe in the dust.)
 There is a slow reaction in the solid state. The reaction takes place instantaneously on mixing the solutions.
- 5 All the colour changes in this section are the result of exchanging ions or ligands.

i $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$ green precipitate

ii $\operatorname{NH}_3(\operatorname{aq}) + \operatorname{H}_2\operatorname{O}(l) \rightleftharpoons \operatorname{NH}_4^+(\operatorname{aq}) + \operatorname{OH}^-(\operatorname{aq})$ $\operatorname{Cu}^{2+}(\operatorname{aq}) + 2\operatorname{OH}^-(\operatorname{aq}) \rightleftharpoons \operatorname{Cu}(\operatorname{OH})_2(s)$ pale blue precipitate

Then, when excess ammonia is added, the pale blue precipitate dissolves and a deep blue solution forms.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

deep blue solution

iv $4\text{Fe}^{3+}(aq) + 3[\text{Fe}(\text{CN})_6]^{4-}(aq) \rightleftharpoons \text{Fe}^{(\text{III})}_4[\text{Fe}^{(\text{II})}(\text{CN})_6]_3(s)$ deep blue precipitate (Prussian Blue)

(Prussian Blue is used as a pigment. It was once used for colouring Prussian military uniforms and for making the original 'blue prints' prepared by engineering designers.)

- $\mathbf{v} \quad [Fe(H_2O)_6]^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons \\ [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l) \\ deep red$
- **6** Universal Indicator is a mixture of acid–base indicators and shows a range of colours depending on the pH of the solution.

7
$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

In the second part of the experiment the chromate(VI) ion is first converted into a dichromate(VI) ion:

$$2 \operatorname{CrO}_{4}^{2-}(aq) + 2\mathrm{H}^{+}(aq) \rightleftharpoons \operatorname{Cr}_{2}\mathrm{O}_{7}^{2-}(aq) + \mathrm{H}_{2}\mathrm{O}(l)$$

Lead chromate(VI) is precipitated, the equilibrium above being displaced to the left as the lead ions are added.



Summary of types of changes

Reaction	Type of change
1	redox reactions
2	redox reactions
3	polymorphic change
4	ionic precipitation reaction
5 i	ionic precipitation reaction
5 ii	ionic precipitation reaction followed by ligand exchange reaction
5 iii	ligand exchange reaction
5 iv	ionic precipitation reaction
5 v	ligand exchange reaction
6	acid-base reaction
7	ionic precipitation reaction

CD3 Seeing colours

Safety note Information about hazardous chemicals is given on the activity sheet.

An alternative arrangement which works well is to place the solution in a Petri dish on top of an OHP.

A hand-held direct vision spectroscope or a diffraction grating can be used to analyse the light. A finely ruled diffraction grating (300 line) gives good results.

- **a** A spectroscope separates the colours in white light to give a continuous spectrum.
- b The continuous spectrum is replaced by a series of coloured lines or bands against a dark background.
 Coloured solutions absorb some wavelengths of visible light. The light *not* absorbed passes through the solution and reaches the eye.
- **c** Pigments on the surface of a painting absorb some wavelengths of the visible radiation falling on them. The wavelengths *not* absorbed are reflected from the surface and reach the eye. It is a mixture of these colours that we see.

CD4.1 Using reflectance spectra to identify pigments

- **a** Area A contains Azurite. Area B contains Natural Ultramarine.
- **b** Azurite is $2CuCO_3.Cu(OH)_2$.

Natural Ultramarine is a sodium aluminium silicate containing sulphur. (Ultramarine was a much prized pigment at that time. It was more expensive than the gold that was often used to gild large areas of paintings in the early Renaissance.)

- **c** Azurite reflects blue and green light and is a turquoiseblue colour. Ultramarine reflects a significant amount of red light in addition to blue. This makes the pigment appear a deeper, more purple blue. It is richer and warmer than Azurite which has a very low red reflectance.
- **d** Area A was in the blue-green of the ceiling. Area B was in the rich blue mantle of the Apostle on the extreme left of the group.
- **e** It is a way of recording the place from where the spectrum was obtained. This is very important if the work is part of a research programme to measure the reflectance spectrum of precisely the same spot after a period of years.

f The fading of individual pigments can be monitored. Advice can then be given on the best type of lighting to reduce the rate of fading. The lighting should be low in the wavelength absorbed by the most vulnerable pigments.

CD4.2 What factors affect the drying potential of an oil?

Students will probably need help in working out the chemistry of the drying process. The chemistry is complex, and the details are not fully understood, but it should be possible to discuss the *types of reactions* likely to occur.

- **a** The drying oils have the highest iodine numbers.
- **b** ICl reacts with C=C bonds in an electrophilic addition reaction.

$$-CH=CH- + ICI \rightarrow -CHI-CHCI$$

- c C=C groups (Drying oils have a high proportion of triesters based on carboxylic acids containing 1, 2 or 3 C=C bonds.)
- **d** Oxygen. Linseed oil increases in mass as it hardens in air. This does not happen in an atmosphere of nitrogen.

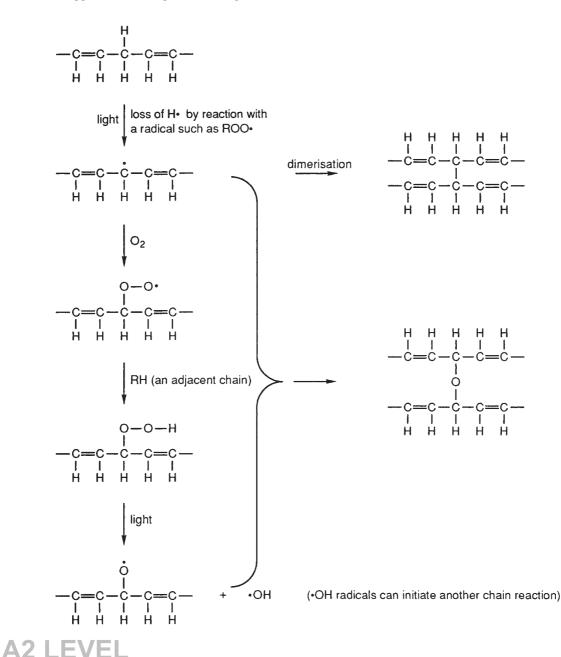
Note

Figure 2 in the activity shows that linseed oil absorbs almost 20% of its own mass of oxygen. Students can calculate that this corresponds to the uptake of about five or six molecules of oxygen for each triester.

e The drying process involves reaction of the unsaturated chains with oxygen, followed by a polymerisation reaction in which cross-linking takes place between the chains of the triesters. The reactions take place more readily in the presence of light and probably involve radicals. The result is a vast interlocking network of triesters joined by C–C, C–O–C and C–O–O–C bridges.

Some thickening takes place when linseed oil is boiled in the absence of air, suggesting that other types of polymerisation, not involving oxidation, can also take place.

An example of the sort of reactions which can occur in the presence of light and oxygen is shown below. The chains containing double bonds form relatively stable radicals.



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- **f** For example, repeat the experiment with linseed oil using pure O_2 in place of air; hydrolyse the triesters in the hardened oil and examine the liberated acids spectroscopically.
- **g** When a water-based paint dries, the water evaporates leaving behind the pigments. When an oil paint 'dries', there is no loss of solvent. Instead, there is a slow chemical reaction in which the oil reacts with oxygen and then polymerises into a 3-dimensional cross-linked network. This traps the pigment particles in a hard protective coating.

CD4.3 Investigating paint media

medium	palmitate : stearate ratio	
poppy seed oil linseed oil walnut oil egg tempera	5.4:1 1.3:1 2.5:1 1.5:1	

- **a** The palmitate : stearate ratio in the sample from Cima's painting is 1.28 : 1, showing the medium was linseed oil. (This fits in well with information provided by art historians about techniques in use at that time.)
- **b** Palmitic acid and stearic acids are saturated acids present in all drying oils. Their ratio is unchanged by the drying process and is characteristic of the oil.
- **c** Intermolecular forces must be overcome when a liquid boils. The intermolecular forces between acid molecules are stronger than those between ester molecules, because there is hydrogen bonding between acid molecules, but not between ester molecules.
- **d** Heat under reflux with methanol in the presence of concentrated sulphuric acid as catalyst.

$$CH_{3}$$
 - OH + H - O - C - (CH_{2})_{14}CH_{3}
 \downarrow
 CH_{3} - O - C - (CH_{2})_{14}CH_{3} + H_{2}O

CD4.4 Identifying a pigment

The pigment is mainly yellow Orpiment with a little orange Realgar. Both are sulphides of arsenic. The Cima is a very early example of the use of Orpiment and Realgar together.

The LMA spectrum indicates that the pigment is a compound of arsenic. The yellow colour of the pigment suggests that it is mostly Orpiment, but specks of orange Realgar can be seen in the photomicrograph.

This is supported by the historical evidence. Orpiment, though rare in western oil paintings generally, was commonly used in Venetian paintings in the 16th century.

CD4.5 Finding a perfect match

Manganese Blue Monastral Blue Prussian Blue

low red reflectance



high red reflectance

From the reflectance spectra, the best match for Azurite used in the blue-green areas of the ceiling is Manganese Blue. The best match for the genuine Ultramarine used in the mantle of the Apostle on the extreme left of the group is synthetic French Ultramarine.

CD5 Comparing bydrocarbons

Safety note Cyclohexane, cyclohexene, and methylbenzene are highly flammable liquids and produce harmful vapours. Only a few drops should be used in each reaction. If very small quantities are used, it should not be necessary for the work to be carried out in a fume cupboard. Full information about hazardous chemicals is given on the activity sheet.

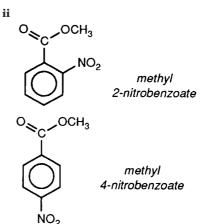
Making a solution of Br_2 in cyclohexane

This must be done in a fume cupboard. Bromine liquid produces an irritant vapour which is very toxic. The liquid causes severe burns. Wear heavy gloves, a lab coat and a face shield. A beaker of approx. 1 mol dm⁻³ sodium thiosulphate solution should be available to treat spillages. The bromine solution is best measured out by students using a marked teat pipette. Check that this is in good condition before the start of the experiment. Keep the bromine solution out of direct sunlight.

Comments

The nitration of methyl benzoate only works well with *fresh* concentrated sulphuric acid. Students should use **Chemical Ideas** Chapter 12 and a textbook where necessary to explain their results in this activity.

- 1 Reaction with bromine Methylbenzene is an activated arene and reacts to give substitution products with bromine in hexane without addition of FeBr₃. It does not react with bromine water.
- 2 Reaction with potassium manganate(VII) The white crystals formed from the oxidation of methylbenzene are benzoic acid. The methyl side-chain only has been oxidised. The benzene ring itself is very resistant to oxidation.
- **a** Simple hydrocarbons such as ethane and ethene are gases.
- **b** To mix the organic and aqueous phases.
- **c** No reaction. This would involve breaking up the stable delocalised ring system of benzene.
- d i Cooled in ice. Temperature kept below $10 \,^{\circ}$ C



iii Recrystallise (using hot ethanol) and take a mp. Pure methyl 3-nitrobenzoate melts at 77.5 °C. (Could also use t.l.c and compare your crystals with a standard sample.)

CD6 Making azo dyes

Safety note Phenylamine is toxic and harmful by inhalation, skin absorption and ingestion. Benzocaine can be an irritant. The coupling agents are toxic and corrosive, or harmful. The azo dyes produced may have carcinogenic properties. **It is essential the safety advice given in the activity is followed**. Students should measure out the phenylamine in a fume cupboard. Gloves must be worn throughout the experiment. Full information about hazardous chemicals is given on the activity sheet.

The colours produced will vary from yellow, through orange, to red. Students should be able to pick out chromophores and discuss the effects of functional groups.

- **b** Diazonium salts are unstable and decompose above 5 °C.
- c Sodium phenoxide



The negative charge is delocalised over the benzene ring. This means that the ring is more electron-rich than usual and reacts readily with the electrophilic diazonium ion.

CD7.1 Dyeing with a direct dye and a reactive dye

This and the following activity can be done at the same time with some students doing **CD 7.1** and others **CD 7.2**.

Safety note Procion dyes are reactive chemicals and cases of respiratory allergy have occurred among people who handle them on a regular basis. (Procion Yellow, in particular, has caused problems, so it is important not to change the colour and to use the red dye recommended.) Avoid generating and breathing the dust, mist or droplets during handling. The very small amounts of dyes used in the activity should present no problem if normal safety procedures for handling chemicals are followed. (If symptoms similar to hay fever or asthma do develop, the person should seek medical attention.)

To make the dye solutions

These should be made up beforehand in a fume cupboard. Gloves must be worn when handling dye powders and solutions. Students should not handle the powdered dyes.

Direct dye Each dyebath requires 0.2 g Durazol Red 2B dissolved in 250 cm³ water.

Fibre reactive dye Each dyebath requires 0.3 g Procion Red MX-5B dissolved in 200 cm³ water at room temperature.

Comments

White cotton bandage is a convenient source of white untreated cotton. Cotton dyed with the direct dye is a duller red and is less fast to washing. (The dyed samples will probably appear little different after one washing, but it should be possible to see a difference in the wash water.)

The dyeing process for the fibre reactive dye is more complex and takes longer. It requires sodium carbonate and larger quantities of salt. Some dye is lost through hydrolysis. However, it can be carried out at room temperature, whereas the dye bath for the direct dye must be boiled.

A2 LEVEL

CD7.2 Different dyes for different fibres

This and the previous activity can be done at the same time with some students doing **CD 7.1** and others **CD 7.2**.

Safety note The solid dyes should be handled with care. Avoid breathing in fine particles of the solid dye and wear gloves and use a fume cupboard when making up the solution. The solid dyes should not be handled by students. Full information about hazardous chemicals is given on the activity sheet.

Making up a solution of the dye mixture

Dissolve the following quantities of dyes in 140 cm^3 water.

Acid Blue 40	0.4 g
Direct Red 23	0.2 g
Disperse Yellow 7	0.1g
Citric acid	0.015-0.020 g

Comments

Direct Red 23 dyes cotton; Disperse Yellow dyes polyester; both Disperse Yellow and Acid Blue 40 dye nylon, so the result is a dark green fabric. (Some Direct Red 23 may also attach itself to the nylon fibres to give an overall green/brown colour.)

Direct Red 23 has structure Z. It dyes cotton well and does not move on the chromatogram because it binds strongly to cellulose fibres. The long dye molecules align with the cellulose fibres, and induced dipole forces and hydrogen bonds bind the dye molecules to the fibres. The –OH and –NH groups on the Direct Red 23 molecule can hydrogen bond with the –OH groups on the glucose units in the fibre. (The –SO₃⁻Na⁺ groups are present to increase the solubility of the dye in water. These groups may cause the dye to bind to the free –NH₃⁺ groups in nylon to some extent.)

Acid Blue 40 has structure Y. It dyes nylon well and moves some way on the chromatogram. It has little affinity for polyester but some affinity for cotton. The molecules contain $-SO_3^-$ groups which form ionic attractions with free $-NH_3^+$ groups in nylon fibres. (Nylon has $-NH_3^+$ groups only at the end of the chains.) The dye molecules can also form hydrogen bonds with the polyamide fibres.

Disperse Yellow 7 (dye X) dyes nylon and polyester but not cotton. It moves a long way on the chromatogram since it has little affinity for cellulose. Its molecules are small with no ionic groups and only limited opportunity for hydrogen bonding. Polyester and nylon fibres are relatively non-polar. The dye molecules are attracted to the fibres by instantaneous dipole–induced dipole forces.

Possible uses

A dye mixture of this type could be used to dye fabrics woven from different fibres (e.g. union fabrics made from separate wool and cotton yarns) or blended yarns spun from two types of fibre (e.g. polyester–cotton). The dye mixture can be used to give the different fibres the same or different colours.