ACTIVITY BRIEF

Dyes: Industrial scale up

The science at work

Only small quantities of dyes can be extracted or synthesised in the laboratory. However, scaling up to industrial scale presents various problems. Weighing small quantities of chemicals on an electronic balance is straightforward and quick. It can easily be tipped into a beaker or flask and other chemicals added. Imagine trying to measure out 100 kg of a chemical and transferring it to a reaction vessel big enough for it and the other chemicals needed.

Your brief

Earlier in this unit you will have extracted a natural dye and prepared a synthetic dye in the laboratory. Now you need to find out how various factors effect the scaling up of both processes to industrial scale, in particular:

costs of the raw materials	energy costs
size of reaction vessels	the percentage yield

Task 1 Industrial scale up

Before you start to work out the costs of making your natural dye and synthetic dye on an industrial scale, look at *Study sheet: Industrial scale up*. This shows how Sudan Orange R (an azo pigment used to colour oils, fats, waxes, shoe and floor polish) was manufactured and the costs involved. It will get you thinking about the factors that need to be considered in industrial scale up.

Task 2 Scaling up your preparations

Your reports on extracting a natural dye and preparing a synthetic dye should include *consideration of commercial manufacture*. You will gain the highest marks if your *calculations in relation to the scaling up for commercial manufacture (cost, percentage yield and size of reaction vessels) were complete for both dyes and are accurate in all respects.*

Read the first page of *Study Sheet: Scaling up your preparations*. Then complete the two tables: *Solution of natural dye* and *Synthetic dye*

This will provide evidence that you carried out calculations relating to the scaling up of your extraction method and preparative method for commercial manufacture (cost, percentage yield and size of reaction vessels).

STUDY SHEET

# Industrial scale up

Sudan Orange R

Sudan Orange R is an azo pigment. It is used to colour oils, fats, waxes, shoe and floor polish. Reading the following procedure will get you thinking abut the factors that need to be considered in industrial scale up. However, **do not make this pigment in the laboratory**. There is evidence it is carcinogenic.

Making Sudan Orange R in the laboratory

Dissolve 2.5 g phenylamine in 8 cm^3 concentrated hydrochloric acid and 8 cm^3 distilled water in a beaker or conical flask. Cool the solution in an ice bath. Add 10 cm^3 of chilled (0-5 ^{o}C) 20% sodium nitrite solution a little at a time. Make sure the temperature does not rise above 10 ^{o}C by adding a few grams of crushed ice if necessary.
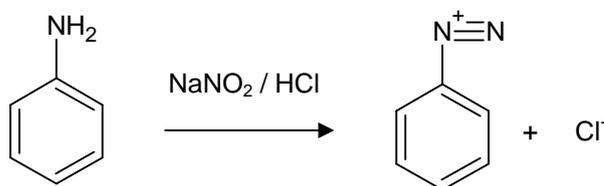
In a second beaker, dissolve 3.9 g 2-naphthol in 22.5 cm^3 2.5 mol dm^{-3} sodium hydroxide solution. Cool in an ice bath and add 10-15 g crushed ice to the solution to help the cooling.
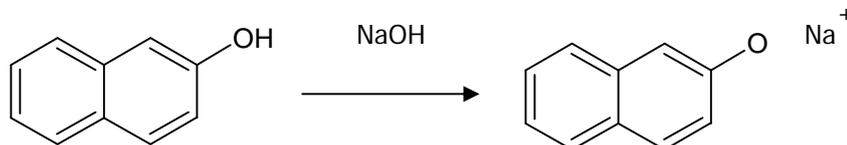
Stir the 2-naphthol solution vigorously, add the diazonium salt solution slowly and then cool the reaction mixture in an ice-bath with occasional stirring.
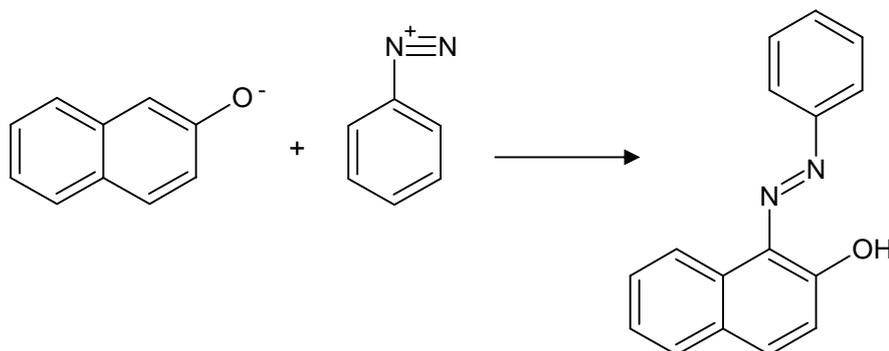
Filter the red dye that forms and wash well with water.

Industrial manufacture of Sudan Orange R

Sudan Orange R is made in a batch process. Typically each batch is 500 kg. Quantities of materials per batch:

phenylamine	188 kg	2-naphthol	300 kg	30% w/w hydrochloric acid	520 kg
sodium nitrite	140 kg	ice	5000 kg	50% w/w sodium hydroxide	290 kg

It's a five stage process:

Stage 1: Raw materials dissolved in two mixing vessels

Stage 2: Solutions mixed and reaction takes place

Stage 3: Crystals of product formed in mixing vessel C are filtered off

Stage 4: Filtered product is dried either in a conventional over or a spray drier

Stage 5: Dried product is ground to a fine powder

Costs of industrial manufacture

(Adapted from *Industrial Chemistry*, CA Heaton, Blackie, 1986)

A **Materials costs** (to make a 500 kg batch of Sudan Orange R)

Chemical	Quantity	Cost
Phenylamine	188 kg	a
2-naphthol	300 kg	b
30% w/w hydrochloric acid	520 kg	c
50% w/w sodium hydroxide	290 kg	d
Sodium nitrite	140 kg	e

B **Manufacturing costs** (based on five batches (500 kg each) per five day week)

   (i) *Direct manufacturing costs*

Cost	Quantity	Cost
Labour	40 'man hours'	f
Steam	6×10^3 kg	g
Ice	5×10^3 kg	h
Electricity	60 kWh	i
Milling and testing		j
Depreciation		k
Maintenance		l

   (ii) *Manufacturing overheads*

   These are usually put in as an arbitrary factor (x) of the direct manufacturing costs.

Questions

1   What is the mole ratio of phenylamine to 2-naphthol in (a) the laboratory preparation, (b) the industrial manufacture?

2   What is the theoretical yield of Sudan Orange R in (a) the laboratory preparation, (b) the industrial manufacture?

3   Above 10 °C the diazonium salt hydrolyses (see right).

$$N \equiv N^{+} \quad + \quad H_2O \quad \rightarrow \quad OH \quad + \quad N_2 \quad + \quad H^{+}$$
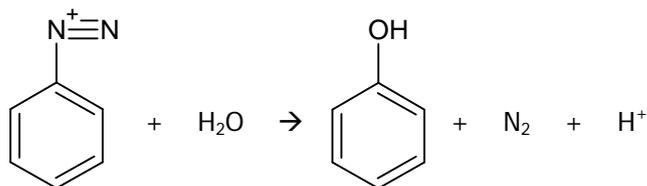
   a   Explain why the percentage yield is less if the reaction temperature is not controlled.

   b   Explain why the percentage yield in the industrial process may be less than that obtained in a laboratory preparation.
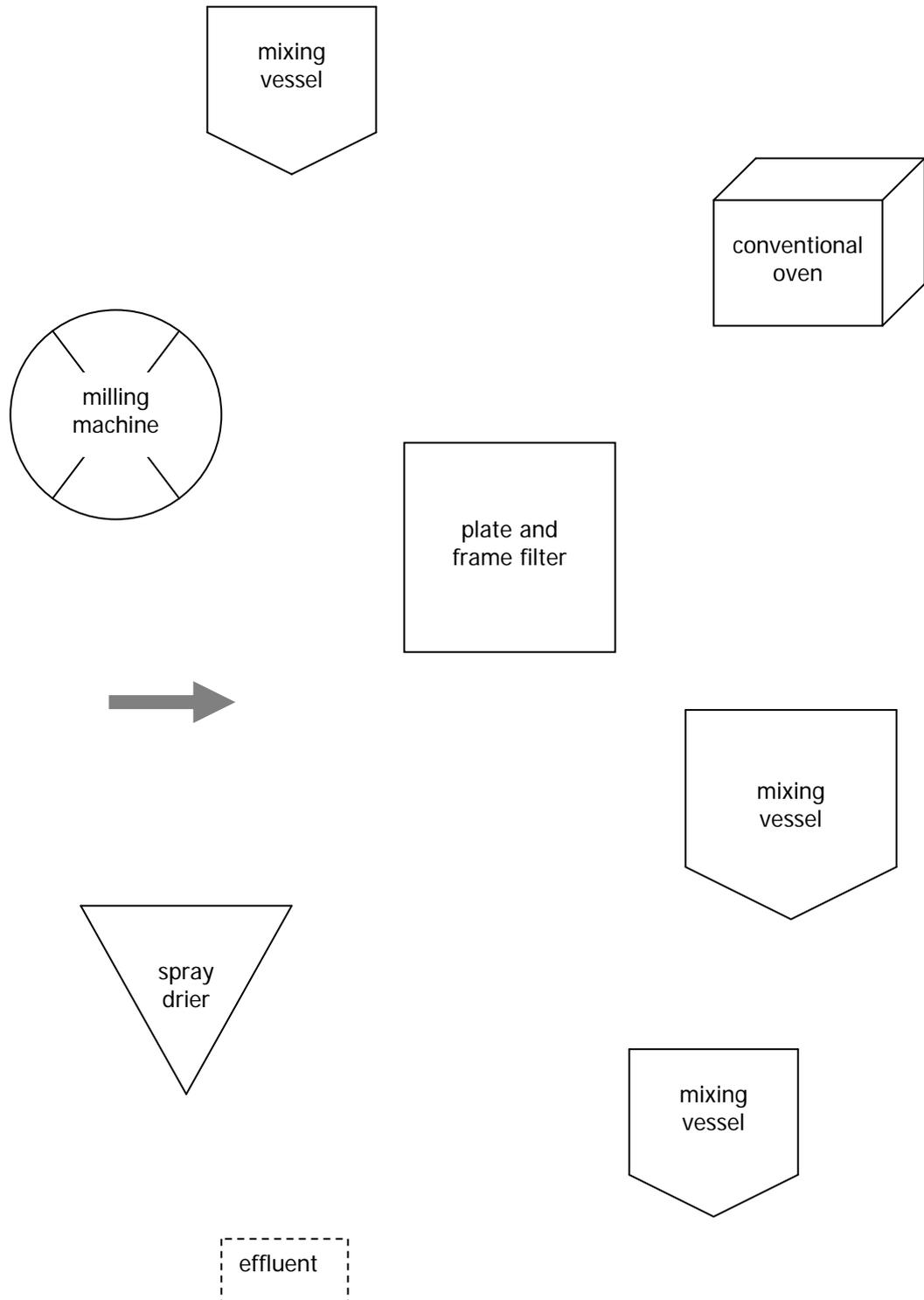
4   How many times greater is the scale of industrial manufacture of Sudan Orange R compared with the laboratory synthesis?

5   From the selection of industrial vessels shown below, decide which would be needed for (a) the diazonium salt solution, (b) the 2-naphthol solution, (c) the coupling reaction. Explain your choice.

Small vessels	Medium-sized vessels
Capacities available (dm^3)	Capacities available (dm^3)
63	
100	1000
160	1600
250	2500
400	4000
630	6300
	8000
	10 000

6   Use the symbols on the next page to draw a flow diagram for the manufacturing process. Label your flow diagram to show which materials are present at each stage of the process.

7   Write an expression for the total cost of making a 500 kg batch of Sudan Orange R using information provided in **Industrial manufacture of Sudan Orange R.**

mixing
vessel

conventional
oven

milling
machine

plate and
frame filter

mixing
vessel

spray
drier

mixing
vessel

effluent

STUDY SHEET

Scaling up you preparations

Natural plant dye

Write down the name of the dye you extracted, together with the starting materials you used and a <u>brief</u> summary of the method.

Dye _____

Starting materials _____

_____

Summary of method

_____

_____

_____

_____

_____

_____

_____

_____

Synthetic dye

Write down the name of the dye you synthesised, together with the starting materials you used and a <u>brief</u> summary of the method.

Dye _____

Starting materials _____

_____

Summary of method

_____

_____

_____

_____

_____

_____

_____

_____

This activity is about industrial scale up. Most dyes are made by a batch process. Explain the difference between a batch process and a continuous process.

_____

_____

_____

In your calculations, assume that you need to make:

▪ a batch of 500 dm^3 of natural dye solution

▪ a batch of 500 kg of the synthetic dye.

Complete the two tables (*Solution of natural dye* and *Synthetic dye* on pages 9 and 10) to provide evidence that you carried out calculations relating to the scaling up of your extraction method and preparative method for commercial manufacture (cost, percentage yield and size of reaction vessels).

Things to consider:

Costs of raw materials

Look at how the price per kilogram of chemicals is lower the larger the quantity bought.

Percentage yield

Percentage yield may depend on:

a the position of equilibrium (ratio of products:reactants) for a reversible reaction in equilibrium

b competing reactions; in other words, other products are formed

   (Note: a and b depend on reaction conditions such as temperature, pressure and time)

c mechanical losses during material handling, e.g. transferring materials, may be reduced in a larger scale extraction/preparation.

With this in mind, can you assume the percentage yield will be the same when the dye is made on industrial scale as it was in the laboratory?

Size of reaction vessels

Suppose a 250 cm^3 beaker was used in the laboratory to make 10 g of product. You might argue that each gram of product needs 25 cm^3 and so a 25000 cm^3 (25 dm^3) reaction vessel is needed for 1 kg (1000 g). Do you think there are other factors to consider?

Energy costs relating to manufacture

Suppose that in the laboratory the temperature of 100 cm^3 (0.1 dm^3) of aqueous reaction mixture was raised from 20 ^{o}C to 80 ^{o}C. Using

heat change = mass of solution x specific heat capacity of solution x temperature change

the energy required = (100 x 4.2 x 60) = 25200 J = 25.2 kJ (assuming the specific heat capacity of the aqueous solution is approximately the same as water)

Imagine the industrial process requires 1000 dm^3 to be heated 20 ^{o}C to 80 ^{o}C. This would require

25.2 x $\frac{1000}{0.1}$ = 252 000 kJ

Energy is usually bought in kilowatt hours (kWh). The cost can be calculated by looking up industrial tariffs for electricity or gas and using the relationship 3.6×10^6 J = 1 kWh.

Other operations also require energy. For example, mixing and stirring the reaction mixture, moving chemicals around using rotary pumps for liquids or vacuum pumps for solids.

Further, there are overheads such as lighting, heating or air-conditioning, and extraction units to keep the air clean in the manufacturing area.

Solution of natural dye

	Starting materials	Laboratory scale	Industrial scale	Calculation of approximate cost to manufacture a 500 kg batch
Size of reactor				
Materials Remember to base your calculations on ▪ the quantities of raw materials needed (buying in bulk is cheaper) ▪ an estimate of the percentage yield	Names	Quantities	Percentage yield Quantities	
Energy List the operations that consume energy. Where possible, calculate the energy required, e.g. to heat the reaction mixture.	Energy for	Estimate energy used	Estimate energy required	

Synthetic dye

	Starting materials	Laboratory scale	Industrial scale	Calculation of approximate cost to manufacture a 500 kg batch
Size of reactor				
Materials Remember to base your calculations on ▪ the quantities of raw materials needed (buying in bulk is cheaper) ▪ an estimate of the percentage yield	Names	Quantities	Percentage yield Quantities	
Energy List the operations that consume energy. Where possible, calculate the energy required, e.g. to heat the reaction mixture.	Energy for	Estimate energy used	Estimate energy required	

Teacher notes

From the assessment evidence grid for AQA A2 Unit 13 Colour chemistry:

You need to produce a portfolio of evidence containing:

A. a report detailing the extraction of a natural (plant) dye together with details of its application to three different fabrics

B. a report detailing the preparation of a synthetic dye together with details of its application to three different fabrics

These reports must include consideration of commercial manufacture, in particular:

- costs of the raw materials for each dye

- the percentage yield

- size of reaction vessels

- energy costs relating to the manufacture of each dye.

They gain the highest marks for this part of the assessment if:

- *Calculations in relation to the scaling up for commercial manufacture (cost, percentage yield and size of reaction vessels) were complete for both dyes and are accurate in all respects.*

This part of the specification is flawed. Industrial manufacture of dyes from plants is negligible and likely to remain so (information supplied by the Society of Dyers and Colourists). Even when dyeing using plant extracts was common, solid dyes were not isolated. Rather, the solution of extracted dye was used, containing, as it did, other substances also extracted from the plant. There has been recent interest in resurrecting indigo production from suitable plants, but this will not contribute significantly to meeting the huge demand for indigo.

Therefore, calculation of scale up for dyes the students have made is of limited value, perhaps. But scale up is vital in the chemical industry, so we suggest a preliminary exercise where students compare a laboratory preparation with its industrial equivalent.
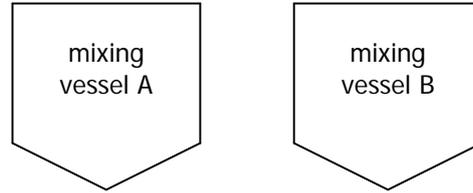
The Society of Dyers and Colourists have reservations about using the synthesis of Sudan Orange R. There is evidence that this pigment is carcinogenic. It is listed as a carcinogen in "Sax's Dangerous Properties of Industrial Materials" 10th edition and has a rating of 3 which is the worst rating in terms of toxicity and reactivity. Further, this product is not used as a textile dye. However, it is a solvent colorant and as such used in the colouration of oils, fats, waxes, shoe and floor polish.

Despite this, the example is included because the structures of reactants are fairly simple and the chemistry straightforward. However, **it is strongly advised that students do not carry out the laboratory preparation**.
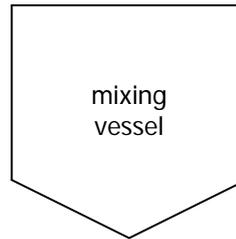
Answers to questions in *Industrial scale up*:

1 (a) 0.02688:0.2708 = 1.007, (b) 2022:2083 = 1.030

2 (a) 6.667 g, (b) 501.5 kg

3 (a) Any diazonium salt hydrolyses cannot make the azo dye, (b) Temperature control is more difficult on a large scale

4 75,200 times

5 (a) the diazonium salt solution: 188 kg phenylamine, 502 kg hydrochloric acid, 140 kg sodium nitrite (700 dm^3 if added as 20% w/w solution), anything up to, say, 500 kg ice (roughly 1000 kg is available for the complete process). So this is about 1800 kg. Allow space agitation etc. Suitable vessel: probably 4000 dm^3.

   (b) the 2-naphthol solution: 300 kg 2-naphthol; 290 kg 50% w/w sodium hydroxide, anything up to 300 kg ice. So this is 1000 kg. Allow space agitation etc. Suitable vessel: probably 2500 dm^3.

   (c) the coupling reaction. Minimum of 2800 kg of material from two vessels. Allow space agitation etc. Suitable vessel: probably 6300 dm^3.

6 Flow diagram (see next page).

7 Materials costs for one batch = a + b + c + d + e = *A*

   Direct manufacturing costs for five batches (1 week) = f + g + h + i + j + k + l = *B* ;Direct manufacturing costs for one batch = 0.2*B*; Manufacturing overheads = 0.2*B* x *x*
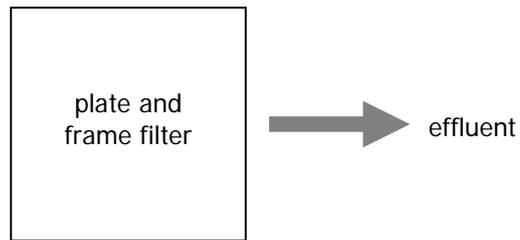
   Total cost to make one batch = *A* + 0.2*Bx*

Stage 1
Raw materials dissolved in two mixing vessels

mixing vessel A

mixing vessel B

Stage 2
Solutions mixed and reaction takes place

mixing vessel

Stage 3
Crystals of product formed in mixing vessel C are filtered off

plate and frame filter

→ effluent

Stage 4
Filtered product is dried either in a conventional over or a spray drier

conventional oven

spray drier

milling machine