

## How was the first artificial dye made? **Answers**

### *Perkin's patent*

- For example:
  - Mix aniline and another organic substance, eg toluidine.
  - Add bichromate.
  - Leave to stand.
  - Filter.
  - Dry the residue.
  - Extract the residue with coal tar naphtha.
  - Evaporate off the naphtha.
  - Dissolve the residue in methylated spirits.
- See text - aniline, sulfate of toluidine, solution of xylidine, bichromate, coal-tar naphtha, methylated spirit
- aniline - phenylamine; toluidine – 1-amino-2-methylbenzene or 2-amino-1-methylbenzene; xylidine - dimethylaminobenzene; coal tar naphtha - the same name is used today. Coal tar naphtha is a mixture of varying percentages of aromatic hydrocarbons including toluene, xylene and benzene; methylated spirit - 95% ethanol, 5% methanol; by 'bichromate' Perkin probably meant sodium (or potassium) dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ ).
- Black powder – a compound produced between the oxidised aniline and oxidised other organic material
  - brown substance - this is most likely mauveine sulfate
  - mauveine sulfate + ethanol → mauveine ethanoate + sulfate ions
- Potential difficulties to solve include: obtaining and transporting the raw materials; transferring large quantities of liquids between vessels; checking temperatures; filtering large quantities of liquids; health and safety hazards, such as flammability and toxicity.

### *The modern process*

- For example:
  - Add reagents to a conical vial with a spin vane in place.
  - Add 30 mg of potassium dichromate in 160 cm<sup>3</sup> of water.
  - Stir for 2 hours.
  - Draw off the liquid.
  - Place the solid on filter paper.
  - Apply suction filtration.
  - Wash with distilled water.
  - Dry at 110 °C for 30 minutes.
  - Wash with petroleum ether.
  - Dry at 110 °C for 10 minutes
  - Wash with 25% methanol / water solution.
  - Evaporate to 5 cm<sup>3</sup> volume.
  - Transfer to a conical flask.
  - Add 300 mm<sup>3</sup> of methanol to the solid.
  - Draw off the liquid into a 3 cm<sup>3</sup> flask.
  - Evaporate liquid to 30 mm<sup>3</sup> volume.
- See text
- Aniline - phenylamine; o-toluidine – 1-amino-2-methylbenzene or 2-amino-1-methylbenzene; p-toluidine – 1-amino-4-methylbenzene or 1-methyl-4-aminobenzene; petroleum ether is a general organic solvent comprising a mixture of hydrocarbons with  $M_r$  values between 87-114, including benzene. It is also called 'petroleum naphtha' or 'petroleum spirits' and is similar to the 'coal tar naphtha' described in the Perkin instructions.

4.
  - a. '2N' = 2 mol dm<sup>-3</sup> in modern units
  - b. 0.052 ml
  - c. a microscale version of a magnetic stirrer
  - d. The black solid is the organic product generated between the oxidised aniline and oxidised toluidine.
  - e. The raw product is being 'cleaned' of reagent molecules that have not reacted.
5. Measuring small quantities of chemicals accurately.

*Compare the procedures*

1. The modern procedure is longer with more washings of the product; the modern procedure names discrete chemicals; the amounts are more accurate; wider range of techniques.
2. Suction filtration; spin vane (stirring and heating of small quantities); measuring small quantities
3. The modern process: the greater precision and more extensive washings will contribute to this.
4. Examples - Periodic Table exists now, also naming of chemicals, understanding of structures and reaction processes; safety procedures, waste disposal, new techniques, better measurement. Essentially, Perkin knew the process but not the chemistry behind it.