Dry cleaning and Green Chemistry

The purpose of this activity is to look at the effect that applying the principles of Green Chemistry (see The twelve principles of Green Chemistry) can have on the environmental impact of a well known process: dry cleaning. Students first examine what happens in 'ordinary' cleaning and consider a simple explanation of how a detergent works. They then look at dry cleaning and the impact the solvents used in this process can have on the environment. Finally, the 'greening' of this process through the use of liquid carbon dioxide as a solvent is discussed.

This material is aimed at 14–16 year olds. A more advanced version is available at http://www.chemsoc.org/networks/learnnet/green/co2/index.htm.

Background information – surface tension

Water molecules hold on to each other tightly and create a surface tension. In order to use water to clean grease from an item, the surface tension has to be reduced to allow the water to wet the thing you are trying to clean. Surface tension is the force that makes a blob of water stay together and not spread out. It allows pond skaters and other insects to walk across water and also enables a pin to float.

If you look closely at drops of water you can see that they try to form spheres. Gravity stretches out drops that cling to an eye dropper or a tap. However, when the drops fall, they become spherical. The shape of a water drop is a result of surface tension. Water is composed of molecules each consisting of two hydrogen atoms and one oxygen atom. These molecules are attracted to each other. In the middle of a drop of water, each molecule is surrounded by other molecules on all sides so it is pulled equally in all directions by these attractive forces. On the surface, however, the molecules only experience attractive forces in certain directions: across the surface and inward. This causes the water to try to form a shape with the smallest possible surface area – a sphere. Gravity causes water drops resting on a surface, to flatten out as shown in Figure 1.

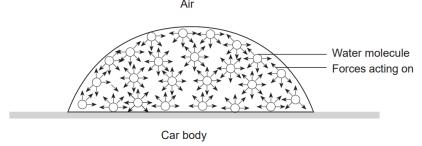


Figure 1 A water drop on a surface

The molecules at the surface of a body of water behave like an elastic membrane. You can easily see the elastic membrane effect if you float a needle on the surface of a glass of water. Lower the needle gently onto the water surface with a pair of tweezers, let go and examine the water near the needle. You will see that the water surface is depressed slightly as though it were a thin sheet of rubber.

The addition of a surfactant like liquid soap or washing up liquid to water reduces its surface tension. Water molecules do not bond as strongly with soap molecules as they do with each other. Therefore, the force that enables the molecules to behave like an elastic membrane is weaker if soap is present. If you put a drop of liquid soap in the glass of water with the needle the surface tension is greatly reduced and the needle quickly sinks.



Part 1 Practical work

Equipment required – normal cleaning

- Test-tubes
- Oil in plastic dropper bottles or with pipettes
- Washing up liquid in plastic dropper bottles or with pipettes
- Access to water
- Bungs.

Emphasise to students the need to mix the oil and water without shaking so hard that a lot of foam is formed.

Equipment required - how detergents work

- A few clean 2p coins
- Plastic dropping pipettes
- Paper towels
- Washing up liquid
- Solid soap
- Cooking oil
- Paraffin wax
- Sugar
- A soft lead pencil (the 'lead' is actually graphite).

Emphasise to students the need to make sure the 2p coin is cleaned properly after each test. If there is any trace of washing up liquid or soap on the coin when another substance is being tested the results could be inconclusive.

Answers - Part 1

- 1. Water alone will not remove the oil because oil and water do not mix.
- 2. Water and washing up liquid may remove the oil because the washing up liquid helps the water and oil to mix. This allows the oil to be washed away in the water.
- 3. The water forms a curved or bulging shape on the top of the coin as shown in Figure 2.



Figure 2 Water on top of the coin

- 4. The washing-up liquid and soap made the number of drops that would fit onto the coin decrease.
- 5. The oils made the number of drops of water that would fit on the coin increase.
- 6. Adding a detergent to the water enables the oil and water to mix together. The oil will be held in the water by the detergent molecules, which act as a bridge between the oil and water molecules. This allows the oil and grease to be washed away in the water and the dishes become clean.

Part 2 Dry cleaning

This section of the work emphasises the environmental impact of the usual dry cleaning process at the moment to help students understand why it might need to be changed. Students will need a copy of The twelve principles of Green Chemistry.



Before students begin this section, carry out two demonstrations. First, demonstrate how dry cleaning works. Put some oil into a test-tube and show that it can be dissolved in organic solvents. Explain that the process does not need a detergent because the oil or grease dissolves in this kind of solvent without it.

Next, demonstrate how carbon dioxide can be made to form a liquid. Students should already know about carbon dioxide gas and they may have seen dry ice (solid carbon dioxide) but they will probably be unfamiliar with the idea that it can form a liquid too. Either do the demonstration detailed below or show the video clip of this demonstration found at http://www.nottingham.ac.uk/~pczctg/Video Clips Menu.htm (accessed January 2006).

Equipment required for the carbon dioxide demonstration

- Eye protection
- Tongs or gloves
- One disposable plastic pipette
- One zip-sealing plastic sandwich bag
- A pair of pliers
- A few small pieces of dry ice.

Health and safety

Wear eye protection.

Read our standard health and safety guidance at https://rsc.li/3us7Hae

Wear gloves and handle the dry ice with care – prolonged contact with the skin can cause frostbite.

What to do



Figure 3 Preparing a pipette for the demonstration

- 1. Cut the tip end off a plastic pipette as shown in Figure 3. Put 4–5 small pieces of dry ice into the pipette. Slip the pipette into a zip-sealing sandwich bag, allowing only the tip end to protrude. Partially zip the bag closed. Use a pair of pliers to clamp the open end of the pipette so that it is sealed. It may be helpful to fold the tip end once or twice to help shut the opening and ensure that no gas escapes.
- 2. Once the carbon dioxide has liquefied, loosen your grip on the pliers to release the pressure.
- 3. Reseal the pipette with the pliers and repeat the process of building up and releasing pressure to observe several changes of state.

Answers – Part 2

1. PERC is the solvent, oil or grease the solute and the resulting mixture of PERC and grease is the solution.



- 2. PERC can cause problems to humans and animals when it is breathed in. If too much is inhaled it can cause dizziness and confusion. If it gets into drinking water and animals and humans drink it then the liver and kidneys can be damaged. It will stay in fatty tissue in the body. If it is released into the air and there are other polluting chemicals present then PERC can contribute to photochemical smog.
- 3. Chemists are keen to find an alternative to PERC because it can cause so many problems. It can be a particular problem to people who work in the dry cleaning industry and are exposed to PERC regularly.
- 4. If carbon dioxide is released into the environment it will become a gas and gets blown away.
- 5. This is better for the environment because it does not cause liver and kidney damage to animals and does not play a part in causing photochemical smog.
- 6. This is worse for the environment because it will contribute to the rising levels of CO₂ in the atmosphere, which may be causing global warming. However, it should be emphasised that much of the CO₂ used for dry cleaning is the byproduct of other industrial processes; if it were not used in dry cleaning, it would be released into the environment anyway. The quantities on an industrial scale are relatively small.
- 7. The answer is the students' own response to what they have read. Most will probably conclude that CO₂ is less harmful than PERC. They may decide they need further information on some aspect of the subject, eg whether using CO₂ will require detergents and what effect those detergents might have on the environment.

Answers – Part 3

- 1. You do not need to use a detergent with PERC because the PERC dissolves grease without one. A detergent is not required to make the grease stay in the solvent as it would be with water.
- 2. After the oil and water were mixed, they separated again.
- 3. When a detergent was added, the oil stayed in the water and the substances remained mixed.
- 4. When carbon dioxide and oils are mixed they separate again if they are left to stand because they do not dissolve each other.
- 5. This would not help in cleaning clothes because the grease would not mix with the carbon dioxide but would stay on the clothes.
- 6. This process uses a solvent that is renewable, relatively inexpensive and can be recycled. (It also uses less energy overall but students are unlikely to realise this unless they do extra research on the process.)



The twelve principles of Green Chemistry

1. Prevention

Try not to make waste, then you do not have to clean it up.

2. Atom economy

The final product should aim to contain all the atoms used in the process.

3. Less hazardous chemical synthesis

Wherever it is possible, production methods should be designed to make substances that are less toxic to people or the environment.

4. Designing safer chemicals

Chemical products should be designed to do their job with minimum harm to people or the environment.

5. Safer solvents

When making materials try not to use solvents or other unnecessary chemicals. If they are needed, then they should not be harmful to the environment in any way.

6. Design for energy efficiency

The energy needed to carry out a reaction should be minimized to reduce environmental and economic impact. If possible, processes should be carried out at ambient temperatures and pressures.

7. Use of renewable feedstocks

A raw material should be renewable wherever possible.

8. Reduce derivatives.

Try not to have too many steps in the reaction because this means more reagents are needed and more waste is made.

9. Catalysis

Reactions that are catalysed are more efficient than uncatalysed reactions.

10. Design for degradation

When chemical products are finished with, they should break down into substances that are not toxic and do not stay in the environment.

11. Real-time analysis for pollution prevention

Methods need to be developed so that harmful products are detected before they are made.

12. Inherently safer chemistry for accident prevention

Substances used in a chemical process should be chosen to minimise the risk of chemical accidents, including explosions and fire.



Dry cleaning and Green Chemistry - part 1

This activity is about:

- How 'normal' cleaning works
- What dry cleaning is
- How dry cleaning can be made 'greener' by chemists.

Normal cleaning

You will need

- 2 test-tubes
- Oil
- Washing up liquid
- 2 bungs.

What to do

- Fill the test-tubes about 1/4 full with water and pour about 1/2 cm oil on top. Put the bung in the top of one of the tubes and mix the oil and water by turning the test-tube upside down a few times. Do not shake it. Watch what happens when you leave the mixture to stand.
- Add a few drops of washing up liquid to the other test-tube. Mix the contents in the same way as you did with the first test tube. Do not shake it hard or you will just make lots of foam. Watch what happens when you leave the mixture to stand.
- Record your observations carefully.

Observations

1.	If you drop oil on your shirt while you are cooking, will water on its own remove it? Why?
2.	If you put water and washing up liquid on your shirt, will that remove the oil? Why?



Washing up liquid is a type of substance known as a detergent. This experiment has shown that detergents help to break up oil into smaller droplets so that it can mix with water, which makes it easier to get things clean. The next experiment will help you understand how detergents work.

How detergents work

You will need

- A few clean 2p coins
- Plastic dropping pipettes
- Paper towels
- Washing up liquid
- Solid soap
- Cooking oil
- Paraffin wax
- Sugar
- A soft lead pencil (the 'lead' is actually graphite).

Test substances

What to do

- Using a pipette, put water onto a 2p coin one drop at a time. Count how many drops you can get to balance on the coin. Dry the coin carefully and repeat the test twice.
- Do the same experiment again, but this time rub the coin with one of the test substances before you drop water onto it.
- Record your results in a table.
- 3. What shape does the water make on the coin just before it falls off? Draw what you saw.

4.	have on the number of drops you could balance on the coin?
5.	Oil and wax are substances we might want to remove when we clean something. What effect did these substances have on the number of drops of water you could balance on the coin?

Water drops hold together very well, which allows them to form the round shape you saw on the coin. They prefer to hold on to each other than to grease and oil. Water does not mix



with oils unless we add something else. Detergents contain molecules that act as a 'bridge' between oil and water. One end of the detergent molecule can dissolve in water; we call it hydrophilic ('hydro' means water and 'philic' means loving). The other end of the detergent molecule can dissolve in oil; we call it lipophilic ('lipo' means oil).



The 'bridge' formed by a detergent between oil and water allows them to mix so the dirt and grease can be washed away with the water.

U.	greasy dishes.

Dry cleaning and Green Chemistry - part 2

Dry cleaning

Some clothes are made of fabrics that would be damaged if they were washed in water. They may shrink or stretch or be damaged in some other way. These clothes need to be 'dry cleaned.' Dry cleaning is not really dry at all, it just uses solvents other than water to do the cleaning. One of the most common solvents used in dry cleaning is 1,1,2,2 tetrachloroethene (sometimes called perchloroethene or PERC).

PERC

Below is some information about PERC from the US Environmental Protection Agency. PERC is a colourless, non-flammable liquid. The largest user of PERC is the dry cleaning industry. It accounts for 80 to 85 % of all dry cleaning fluid used. Exposure to PERC can occur in the workplace or in the environment following releases into air, water, land, or groundwater.

PERC enters the body when it is breathed in with contaminated air or when it is consumed with contaminated food or water. It is less likely to be absorbed through skin contact. Once in the body PERC can remain there and is stored in fat tissue. It dissolves only slightly when mixed with water. Most direct releases of PERC to the environment are to air. Once in the air, PERC breaks down to other chemicals over several weeks. Plants and animals living in environments contaminated with PERC can store small amounts of the chemical. Laboratory studies show that PERC causes kidney and liver damage and can cause cancer in animals regularly exposed to it by breathing and by mouth.

Effects of PERC on human health and the environment depend on the amount of PERC present and the length and frequency of exposure. People who work with PERC on a regular basis will suffer the most effects. Effects also depend on the health of a person or the condition of the environment when exposure occurs. Breathing PERC over longer periods of time can cause liver and kidney damage in humans. Workers exposed repeatedly to large amounts of PERC in air can also experience memory loss and confusion.

PERC by itself is not likely to cause environmental harm at levels normally found in the environment. PERC can contribute to the formation of photochemical smog when it reacts with other substances in air. These reactions tend to remove PERC before it reaches the upper atmosphere, where it would damage the ozone layer.

Chemicals in the Environment: Perchloroethylene (CAS No. 127-18-4), Office of Pollution Prevention and Toxics, US Environmental Protection Agency 1994 (see http://www.epa.gov.chemfact/f perchl.txt)



Que	stions
1.	When PERC is used in dry cleaning to remove oil or grease, what are the solute, the solvent and the solution?
2.	What problems might PERC cause if it is released into the environment?
3.	Why are chemists keen to find an alternative to using PERC for dry cleaning?
New v	vays of dry cleaning are being developed. One of these methods uses liquid carbon
4.	If carbon dioxide is released during the dry cleaning process, what will happen to it and where will it go?
5.	In what ways is this better for the environment than if PERC is released?
6.	In what ways is this worse for the environment?
7.	Overall, do you think it is a good idea to try to replace PERC with carbon dioxide? Can you decide now or do you need more information? What else might you want to know before making a decision?



Dry cleaning and Green Chemistry - part 3

A new dry cleaning process

An advantage of using a solvent such as PERC for dry cleaning is that you do not need to use a detergent as well.

1.	Why is a detergent not needed when dry cleaning with PERC?
	carbon dioxide dissolves small molecules, but not large molecules like oils and e. Think back to your experiment with water and oil.
2.	What happened when two substances which cannot dissolve each other (oil and water) were mixed?
3.	What changed when a detergent was added to the mixture?
4.	What would you expect to happen when liquid carbon dioxide and oils are mixed?
5.	Would this be any help in cleaning clothes? Why?

Adding a detergent to a mixture of carbon dioxide and oil has no effect at all. The lipophilic end of the detergent molecule dissolves in the oil but the hydrophilic end is designed to dissolve in water and will not dissolve in carbon dioxide. The detergent cannot act as a bridge between oil and carbon dioxide.

What is needed is a molecule that can form a bridge between oil and carbon dioxide. As before, one end needs to be lipophilic, but now the other end needs to be 'carbon dioxide-philic' so that it can dissolve in the carbon dioxide. A chemist called Dr Joseph DeSimone has recently managed to make such a molecule. He has now set up a dry cleaning company which uses this newer technology. This is an example of 'Green Chemistry.'



Ο.	principles of Green Chemistry to help you answer the question.