

# Chemistry in your cupboard: Finish

## Introduction

Machine dishwashing is a complex process which has to rely on chemistry rather than manual effort to clean dishes. Dishwasher cleaning products contain a huge range of chemicals including surfactants or detergents, alkalis, bleaches, biosubstances and builders. Each of these has a distinct role in the cleaning of dishes but the difficulty is getting all these working together when they have different optimum conditions. Finish™ is a brand with a range of products available in different formulations but all based on the same broad principles.

## Links to the curriculum

This section contains information relevant to the following areas of your chemistry curriculum:

- Rates of reactions
- Group 7 elements
- Group 1 and 2 elements
- Biochemistry (proteins, fats and carbohydrates)
- Acids and bases

## FINISH

According to the Office of National Statistics, in 2008 almost 40% of homes in the UK had a dishwasher, up from around 25% in 1998. It is tempting to think of machine dishwashing as comparable to hand washing of dishes but in fact it is a much more complex process and involves a great deal more chemistry.

Hand dishwashing relies mostly on mechanical effort - continuing to brush or sponge (with the help of hot water and a detergent), until the dishes appear clean. With machine dishwashing, mechanical effort counts for less, and the chemistry has to do the cleaning. However, the conditions for machine washing can be both hotter and more alkaline that could be withstood by human hands.

Here we will look at some of the chemistry that goes on inside the dishwasher and relate it to chemistry that you already know. The science of dishwasher products is complex and we can only cover the basics here.

### Did you know?

Josephine Cochrane invented the modern dishwasher in 1886.

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Cochrane was a wealthy socialite whose servants kept chipping her fine china while hand washing it. She developed a rack and water jet system that was first demonstrated at the 1893 Chicago World Fair.



Figure 1: A product from the Finish range

### How does a dishwasher work? (1 of 2)

Before we consider the chemistry, we need to understand the mechanics of a dishwasher, Figure 2. This is essentially very simple.

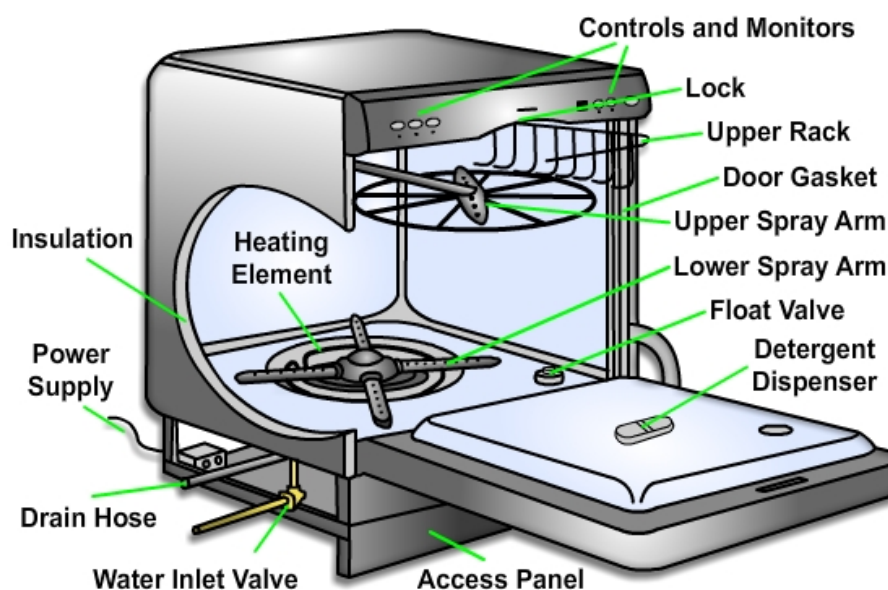


Figure 2: The basic layout of a dishwasher (courtesy of howstuffworks.com)

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A pump draws water through a water softener unit / ion exchanger and into the base of the machine. Here a heater heats the water to a suitable temperature and the dishwasher product dispenser opens so that the dishwasher tablet or powder containing a mix of chemicals falls into the water after approximately 5-10 minutes, when the water is still cold.

A pump then forces the water through two rotating spray arms which spray the water onto the dishes arranged in two baskets, Figure 3.

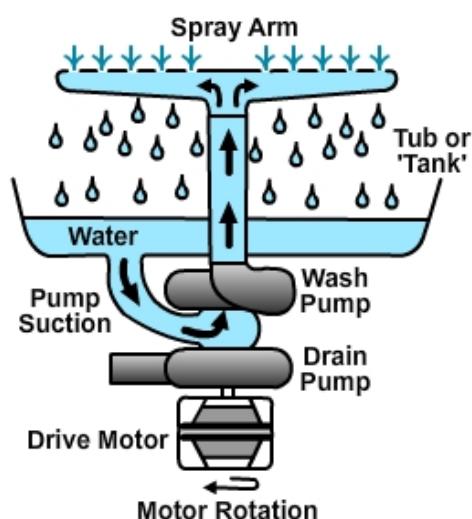


Figure 3: The washing cycle (courtesy of howstuffworks.com)

The dirty water is removed from the base of the machine, Figure 4.

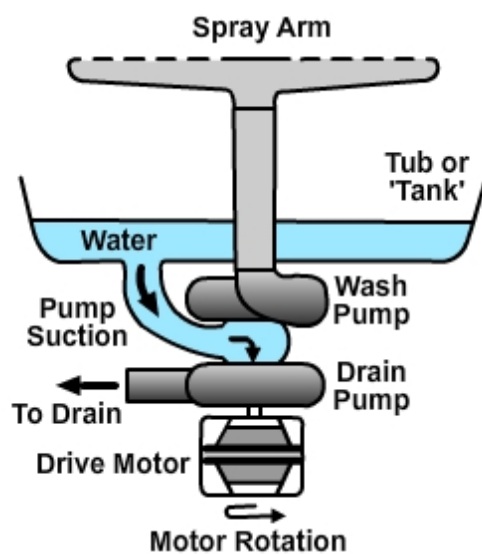


Figure 4: The draining cycle (courtesy of howstuffworks.com)

This is then refilled with clean water which is sprayed on the dishes to rinse them.

You can find more detail from the links below.

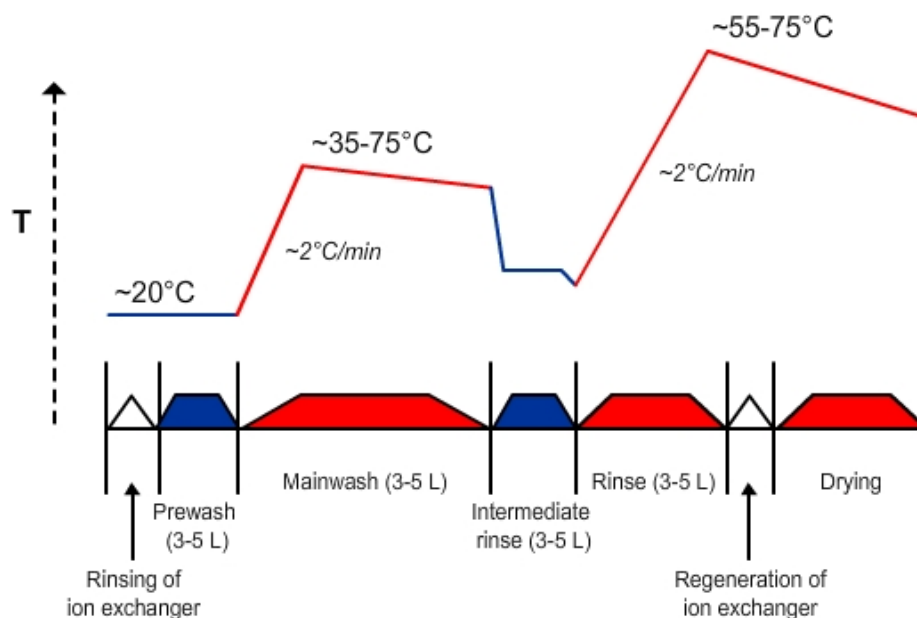
<http://home.howstuffworks.com/dishwasher.htm>

<http://www.dishwasher-care.org.uk/best.html>

### How does a dishwasher work? (2 of 2)

At various points in the cycle, the water is heated to a suitable temperature for the process taking place. The profile of a typical washing cycle is shown in Figure 5 in which temperature is plotted vertically and time horizontally.

Hot water is shown in red, cold (*ie* room temperature) in blue and sections involving the ion exchange resin in white.



**Figure 5: A typical dishwasher cleaning cycle. Only intensive programs use prewash cycles. Normal or Eco programs immediately start with the main cycle. The detergent is only dosed in the main wash.**

### Softening the water

The first chemical process in dishwashing is softening the water. Water in most areas of the UK contains significant levels of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (and in some cases  $\text{Fe}^{3+}$ ) ions.

These arise from the fact that in many areas water soaks through limestone rocks and dissolves some compounds containing these ions. This is assisted by the fact that rainwater is naturally acidic due to dissolved carbon dioxide. So tap water contains dissolved compounds such as calcium hydrogencarbonate and magnesium sulfate.

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**Figure 6: Hardness of water in the UK. The units are mg/l, ie  $\text{mg dm}^{-3}$ , of calcium carbonate equivalent (Courtesy of Caterchem UK)**

The map, Figure 6, indicates generally the hardness of water in various parts of the UK. These metal ions in hard water can interfere with a number of the chemical processes involved in dishwashing, which are explained below, and it is therefore better to remove them. They may also cause limescale to build up inside the machine. There are more details of the chemistry of hard water and its effect on cleaning processes in Calgon.

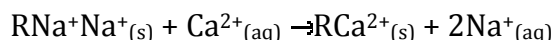
Dishwashers soften water by passing it through an **ion exchange resin** before it enters the machine itself. The resin is well-named – it literally exchanges doubly and triply positively-charged metal ions for singly positively-charged sodium ions which do not affect the washing processes.

### Question 1

**Explain why metals always form positive ions.**

This cannot go on forever, of course - the resin eventually runs out of sodium ions to exchange. To prevent this situation the resin is regenerated by flushing a concentrated solution of sodium chloride through it. This replaces the calcium and magnesium ions on the resin for sodium ions again and the calcium and magnesium ions are flushed away. From time to time, pure salt (sodium chloride) must be added to the reservoir in the dishwasher where the salt solution is made. Table salt should not be used, as most brands of this contain magnesium sulfate as an anti-caking agent - the last thing required in a water softener.

This process is essentially a reversible reaction and can be represented by an equation, where R represents the resin:



Although it is a reversible reaction, it never reaches equilibrium as in both softening and regeneration the water is constantly passing over the solid resin.

### What does a dishwasher cleaning agent contain?

The purpose of a dishwasher cleaning agent is to remove dirt (often called 'soil') from the articles inside by dissolving it or making it into a suspension in the washing water. It must also prevent its re-deposition on the articles so that the soil can be carried away by the washing water.

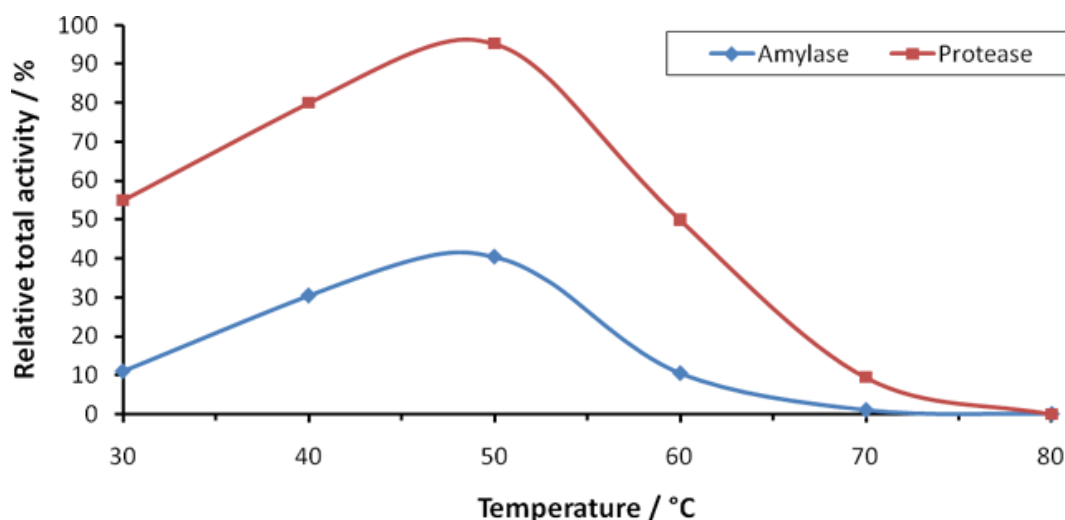
It must be chemically compatible with all the materials being washed and also with the materials from which the dishwasher itself is made.

Dishwasher tablets and powders contain a surprising mix of chemicals, far more than just the detergent you might expect.

These are as follows:

- **Surfactants (detergents)** - these promote mixing between oil- and fat-based soil and water.
- **Alkalis** - these emulsify grease and adjust the pH of the water to the optimum for the other components to work
- **Bleaches** - these oxidise coloured substances to colourless ones
- **Biosubstances** - these are enzymes that break down starch- and protein-based soils
- **Builders** - these help to soften water and trap metal ions that would interfere with the cleaning process and hold dirt in solution
- **Auxiliaries** - these include substances used to make and disintegrate the tablet as well as colours and perfumes

One problem that may be encountered is getting all these different ingredients to work together when they have different optimum conditions. Enzymes, for example, work best at moderate temperatures around 50 °C - see Figure 7. They are denatured and will no longer work if they have been exposed to temperatures much above this for any length of time.



**Figure 7: The temperature dependence of enzyme activity. Proteases decompose proteins and amylases decompose starch-based soils**

On the other hand, grease removal will work best at high temperatures when fats melt to oils making them easier to remove. And, of course, all chemical reactions go faster at higher temperatures - twice as fast for every 10 °C rise is a useful rule of thumb.

There is a similar issue with pH. Cleaning takes place best at alkaline pHs but the optimum pH for most enzymes is neutral to mildly alkaline - they are denatured in strongly acidic or alkaline environments. The optimum pH for the bleach, however, is around 10.

One further complication for the designers of dishwashers and their associated cleaning products is to do with user behaviour; it is usual to wash together a large variety of materials *e.g.* glass, porcelain, plastics, and different metals. This is in contrast with clothes washing, where users seem prepared to separate out different types of material - wool, synthetics, cotton *etc.* The optimum conditions for many of the materials in the dishwasher will differ.

### Surfactants or detergents (1 of 2)

Greasy stains do not mix with water because the main interactions between water molecules are hydrogen bonding and those between molecules of oils and fats (which constitute grease) are van der Waals forces.

To get water and grease to mix we use molecules called surfactants or detergents. These two terms refer to essentially the same thing - molecules that are 'tadpole shaped' in that they have a non-polar 'tail' and a polar or ionic 'head'. The 'tail' can form van der Waals bonds with non-polar grease molecules whilst the 'head' can form hydrogen bonds with water, Figure 8. This is an example of the 'like dissolves like' rule.

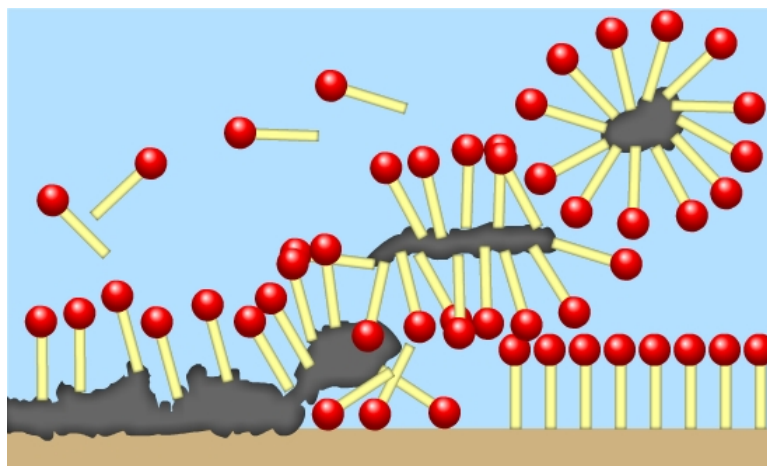


Figure 8: The non-polar tails (in yellow) of 'tadpole shaped' detergent molecules mix with grease, while the polar heads (in red) mix with water, thus forcing the grease and water to mix

There are essentially three types of surfactants – anionic, cationic and non-ionic.

**Anionic surfactants** have a negatively charged head. Common types include soaps, Figure 9, and alkylbenzene sulfonates, Figure 10.

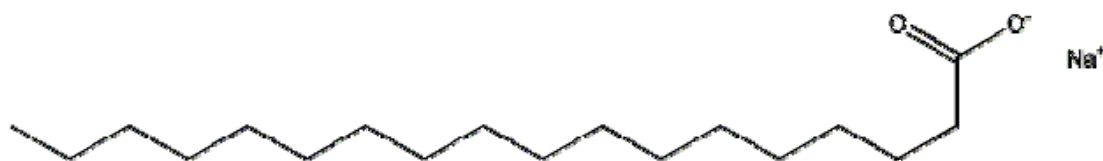


Figure 9: Sodium stearate (a soap) – an anionic surfactant

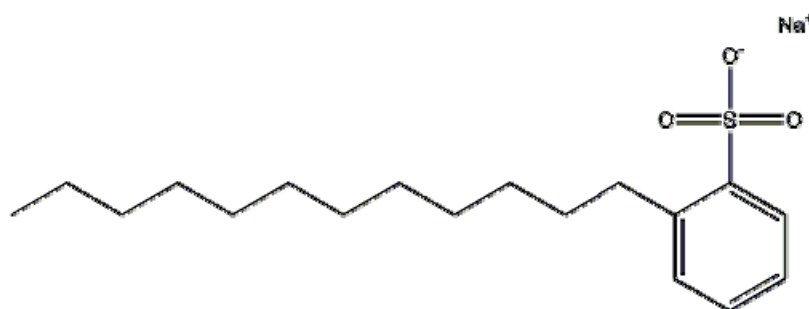


Figure 10: Sodium dodecylbenzene sulfonate – an anionic surfactant

**Cationic surfactants** have a positively charged head. Common types include alkyl ammonium chlorides, Figure 11.



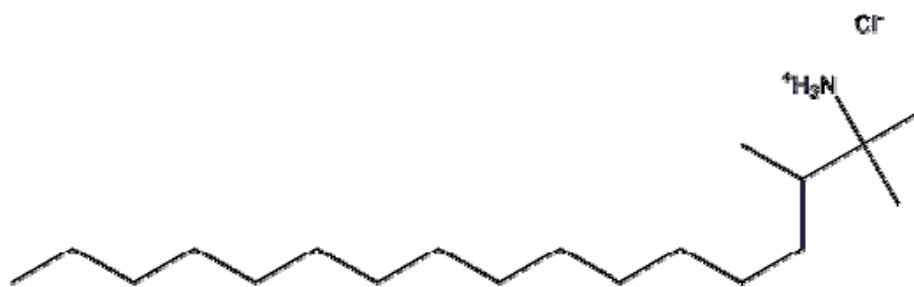


Figure 11: Trimethylhexadecyl ammonium chloride – a cationic surfactant

**Non ionic surfactants** have a polar, but uncharged, head. Common types include polyethylene ethoxylates, Figure 12.



Figure 12: A polyethylene ethoxylate – a nonionic detergent

### Surfactants or detergents (2 of 2)

Surfactants are probably the ingredients one expects in a dishwasher product - we often call the product simply a dishwasher detergent. However, they play a relatively minor role in the product. Non-ionic polyethylene ethoxylates are chosen as the main surfactants in Finish as they produce relatively little foam.

Their main function is to enable greasy soils to mix with water. Much of the soil on dishes is held there by grease. Greases and oils are chemically similar; they consist largely of esters of fatty acids - long chain carboxylic acids - with glycerol, see Figure 13. These contain long hydrocarbon chains which are essentially non-polar, and therefore do not form hydrogen bonds or dipole-dipole bonds with water molecules.

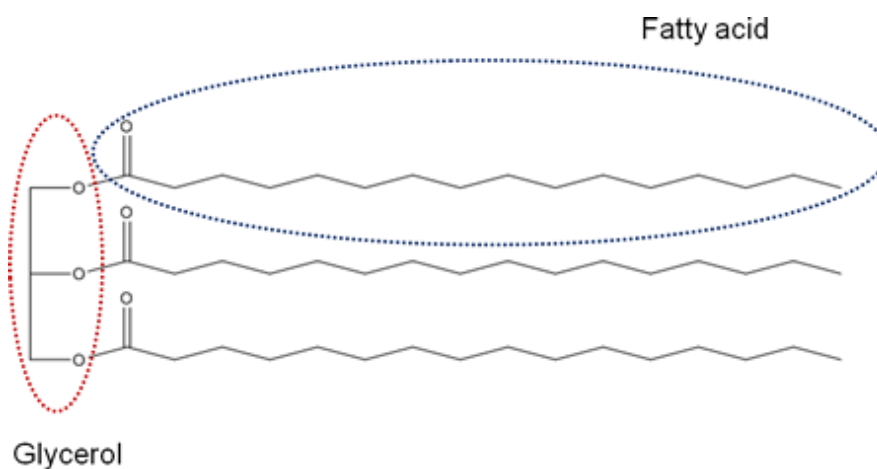


Figure 13: A typical fat or oil - which it is depends on the chain lengths of the three fatty acids and whether or not their hydrocarbon chains are branched

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When dissolved in water, surfactants tend to cluster at the surface (hence the name), so that their non-polar tails can stick out of the water. Surfactant molecules can form structures called micelles: these are small spheres made of surfactant that trap oil molecules and enable them to dissolve in the water.

The difference between fats and oils is one of melting point - at room temperature fats are solid and oils are liquid due to their shorter hydrocarbon chains. Solid greases adhere to surfaces better than liquid oils which just tend to roll off. So a high temperature which turns fats into oils is helpful for cleaning.

## Alkalis

Many cleaning products act best in somewhat alkaline solution.

This is because alkalis

- emulsify grease by reacting with insoluble fatty acids to form ionic salts which are soluble
- protect the metal of washing machines and dishwashers from acid corrosion
- help to reduce re-deposition of dirt that has been removed, by coating particles of it with negatively charged hydroxide ions – this means the dirt particles repel each other and remain in suspension rather than clumping together to form large aggregates which would tend to precipitate out onto dishes
- percarbonate-based bleaches work best in somewhat alkaline solution

The dishwasher water is kept at about pH 10 – significantly alkaline. At the high temperature of the wash, hydroxide ions react with the molecules of grease and break them up into salts of fatty acids and glycerol. This is the main mechanism for removing grease.

The reaction is shown in Figure 14 and is the same as that for making soap from fats and oils – saponification.

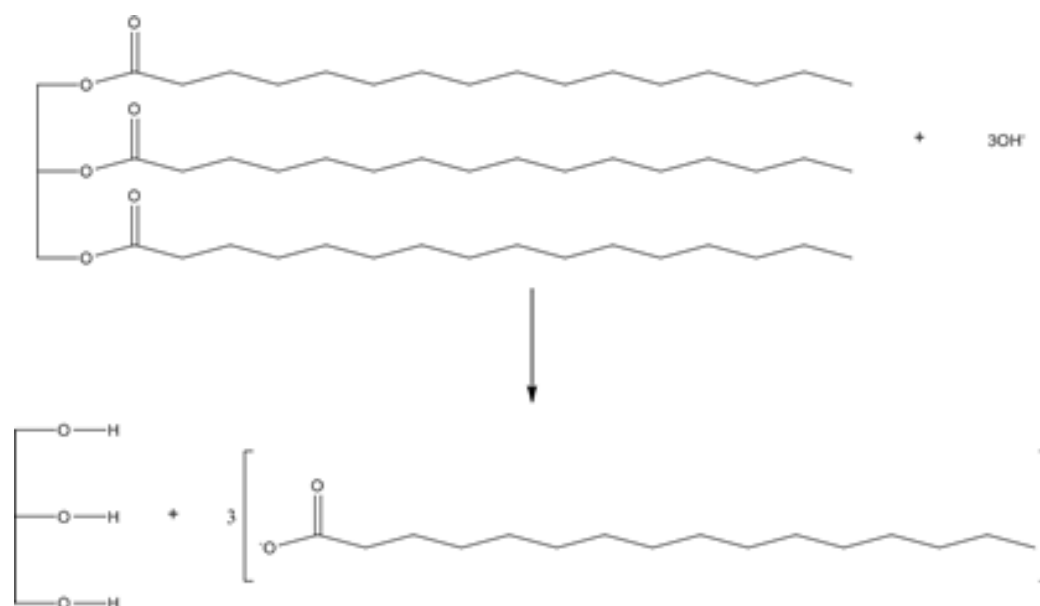


Figure 14: The saponification of grease

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**Question 2**

- a) Explain why the products of the above reaction are more soluble than the original fat molecules.  
 b) Give the systematic name of glycerol.

Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is used in the dishwasher product to make the solution alkaline. It is the salt of a strong alkali (sodium hydroxide) and a weak acid (carbonic acid) and is therefore alkaline. It dissociates in solution to form carbonate ions,  $\text{CO}_3^{2-}$ , which help to maintain the pH of the washing water at around 10.

**Question 3**

Explain how the carbonate ion can make an aqueous solution alkaline.

**Bleaches (1 of 2)**

Bleaches are used to oxidise coloured substances to colourless ones.

The bleach used is sodium percarbonate. This is a white granular powder of formula  $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .

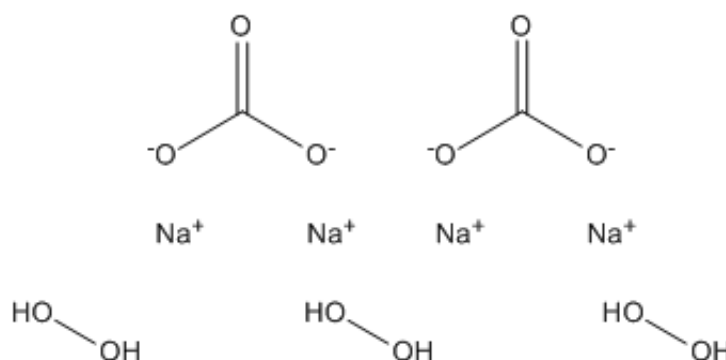
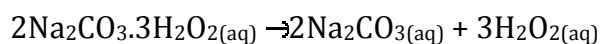


Figure 15: Structure of sodium percarbonate

In water it breaks down into sodium carbonate and hydrogen peroxide.



Hydrogen peroxide is the active oxidising agent as it in turn breaks down to oxygen and water. The beauty of this system is that the starting material is a relatively stable powder (although it obviously must be kept dry) and the by-products (sodium carbonate and water) are innocuous.

**Question 4**

- a) Write an equation for hydrogen peroxide decomposing to oxygen and water  
 b) Use this and the equation above to work out how many moles of oxygen can be obtained from 2 moles of sodium percarbonate.

c) Now work out these quantities in terms of grams of sodium percarbonate and oxygen.

d) One commercial specification for sodium percarbonate guarantees 'not less than 13% active oxygen. From your calculation above, is this realistic?

### Bleaches (2 of 2)

Activators are added to help the bleaches work. These are essentially, and act similarly to, catalysts. They speed up the reaction so that it can take place effectively at lower temperatures than without the activator. However, activators are consumed stoichiometrically whilst catalysts are not.

The use of activators makes the bleaches more compatible with the enzymes in the dishwasher formulation.

### Question 5

Explain the phrase 'This makes the bleaches more compatible with the enzymes.'

Figure 16 show bleach activity and enzyme activity at different stages of the wash cycle.

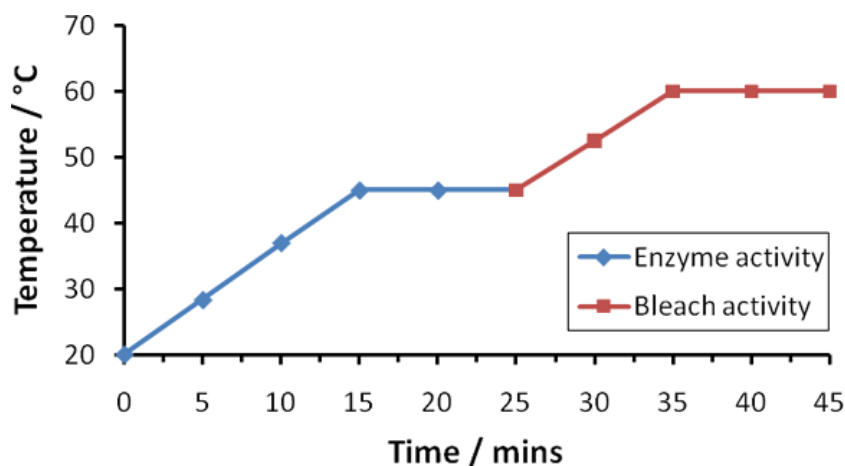


Figure 16: Enzyme activity (blue) and bleach activity (red) at different stages of the wash cycle

### Biosubstances

Essentially, these are enzymes –

- proteases (to help break down proteins)
- amylases (to help break down starches)

### Question 6

Suggest foods that are based on

- proteins
- starches

Proteases decompose big, water-insoluble protein molecules into small soluble units.

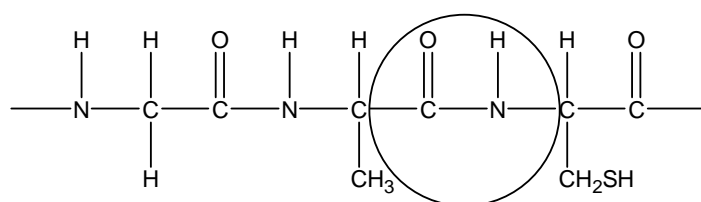


Figure 17: Part of a protein molecule

Amylases decompose big, water-insoluble starch molecules into small soluble units.

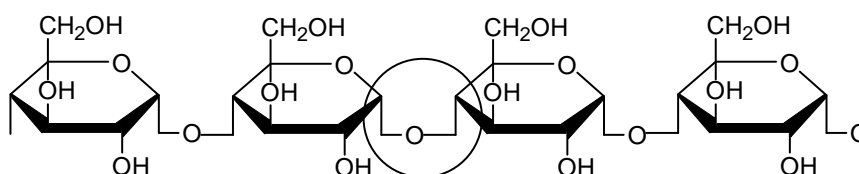


Figure 18: Part of a starch molecule

### Question 7

Suggest what are the 'small soluble units' produced by the breakdown of

- proteins
- starches

In both cases, the breakdown process is a hydrolysis reaction (reaction with water).

### Question 8

a) Look at the structures in Figures 17 and 18. Each has one of the linkages where hydrolysis takes place circled.

Draw the products after hydrolysis has taken place for part of a protein molecule

b) Look at the structures in Figures 17 and 18. Each has one of the linkages where hydrolysis takes place circled.

Draw the products after hydrolysis has taken place for part of a starch molecule

As indicated previously, enzymes have optimum pHs and temperatures, so this has to be built into the design of the washing cycle. Enzymes will be denatured and cease to function after the main wash cycle of the dishwasher program.

### Builders

Builders have a number of functions including softening, buffering and emulsifying.

$\text{Ca}^{2+}$  ions have largely been removed from the starting washing water by the ion exchange resin in the dishwasher but more may originate from the soil itself. These can be dealt with by the builder.

Builders used include phosphates, citrates and polycarboxylates, Figure 19. Notice that each one has oxygen atoms with a negative charge. These can form complexes with  $\text{Ca}^{2+}$  ions and effectively remove them from solution.

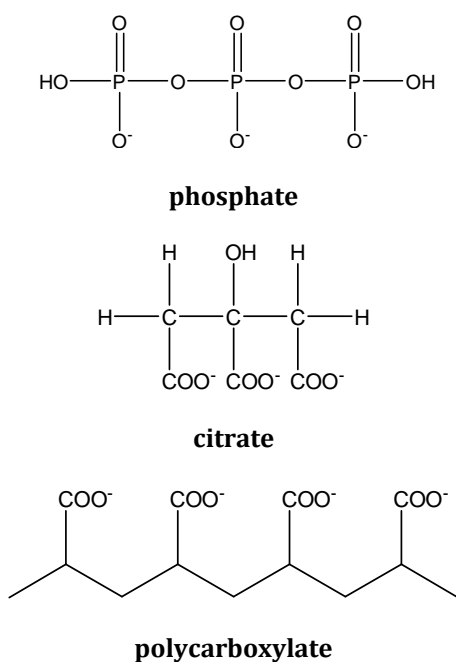


Figure 19: Structures of some common builders

### Question 9

- What feature do the oxygen atoms have which enables them to form a bond with  $\text{Ca}^{2+}$  ions?
- What name is given to this type of bonding?

The  $\text{COO}^-$  groups can accept protons from acidic water and keep it alkaline.

It is often thought that phosphates are no longer used in household products because they can get into watercourses and cause eutrophication - the overgrowth of plants caused by the fertilising effect of phosphates. In fact there is no such blanket ban and phosphates are still used in dishwashing products as the contribution to the total P-load is less than 5%. The main quantity is coming from agricultural land, human metabolism and industrial waste water.

### Rinse aid

The final part of the washing cycle is a rinse with clean water that has been softened by the ion exchange resin. In most machines it is possible to add a rinse aid to this cycle from a separate compartment to the main dishwashing product.

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Rinse aid is a surfactant that reduces the surface tension of water. Surface tension is the 'skin' effect on the surface of water that makes it 'curl up' into droplets on clean surfaces, see Figure 20, rather than spread in a thin layer over the whole surface.



Figure 20: The surface tension of water causes the formation of droplets

Surface tension is caused by hydrogen bonds between water molecules at the surface of liquid water. Surfactant molecules cluster at the surface of a water droplet because their 'tails' do not form hydrogen bonds with water and the surface is the only place where this can occur. This disrupts the hydrogen bonding, lowering the surface tension and allowing the water to spread out, leaving a greater surface area which speeds evaporation and hence drying.

It also allows the water to drain more easily from the surfaces of the dishes as shown below.

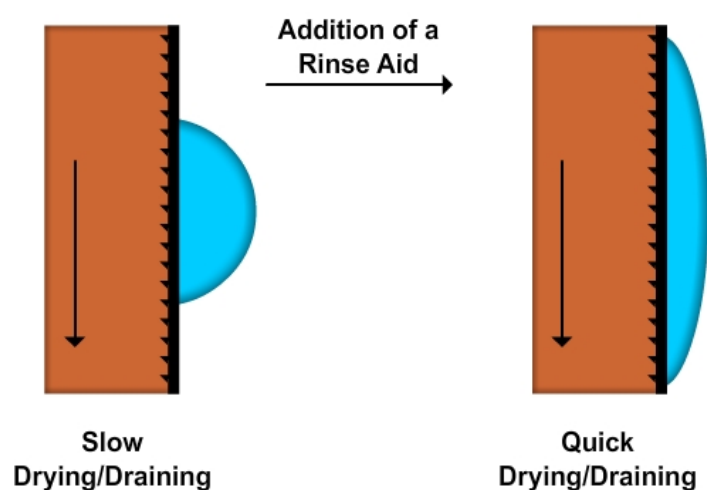


Figure 21: Rinse aid produces droplets with a greater surface area to speed drying and draining

## Recent developments

Dishwasher technology continues to improve; newer machines may have sensors which can be used to determine the best program for a wash. These include:

- determination of the amount of soil in the washing water
- measurement of water hardness
- determination of dish load

### Question 10

**Suggest how the hardness of the water entering a dishwasher might be measured. Remember the result must be obtained quickly and 'electronically' so that it can be fed back to control the machine, so a titration, for example, would not do. Hint, hardness is caused by aqueous  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.**

For example the amount of soil in the water can be measured by shining a light through a sample of water and noting how much is absorbed – the more light absorbed, the dirtier the water.



Figure 22: Dishwashing in action (courtesy of howstuffworks.com)

## Different formulations

Finish branded products are sold in a number of forms with different formulations, Figure 23.





Figure 23: Different forms and formulations of Finish

The ingredients of just one formulation, Finish Powerball classic tablets regular, are listed in Figure 24.

Ingredients:
PENTASODIUM TRIPHOSPHATE
SODIUM CARBONATE
SODIUM CARBONATE PEROXIDE
PEG-130 - PEG-150
AQUA
PEG-30 - PEG-40
SODIUM SILICATE
TAED
CELLULOSE
CITRIC ACID
FATTY ALCOHOL ALKOXYLATE
SODIUM POLYACRYLATE
SUCROSE
GLYCEROL
ORYZA SATIVA STARCH
BENZOTRIAZOLE
TETRASODIUM ETIDRONATE
PARFUM (LIMONENE)
PROTEASE
COLORANT
MAGNESIUM STEARATE
AMYLASE

Figure 24: Ingredients found in Finish Powerball classic tablets regular

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Some of these have been discussed above but there are a number of others that are beyond the scope of this piece. All of them contribute to the final product in some way.

### Further information

Several varieties of Finish™ are sold in the UK by Reckitt Benckiser (<http://www.finish.co.uk/>). There are other branded products which work in a similar way.

Teachers and students who are interested in more details about household products might wish to consult the following book:

G. Wagner *et al*, *Household Cleaning, Care and Maintenance - Products-Chemistry, Application, Ecology and Consumer Safety*, Verlag für chemische Industrie  
ISBN 3-87846-241-7

### Acknowledgements

The Royal Society of Chemistry wishes to thank Chris Jones, Alexandra Hary and Gunnar Noeding of Reckitt Benckiser for help in preparing this material.

The Royal Society of Chemistry gratefully acknowledges that this project was initially supported by Reckitt Benckiser in 2007. Reckitt Benckiser conducted a final review in 2013 so please note that certain information may be out of date.

## QUESTIONS AND ANSWERS

### Question 1

**Explain why metals always form positive ions.**

Metals all have one, two or three electrons in their outer shells. It is easier to lose these to attain a full outer shell of electrons (a noble gas arrangement) than to gain electrons. Loss of negatively-charged electrons produces positive ions.

### Question 2

**a) Explain why the products of the above reaction are more soluble than the original fat molecules.**

One product is a negative ion which can interact with water molecules better than a neutral molecule. The other is a small molecule with a high proportion of -OH groups that can hydrogen bond with water.

**b) Give the systematic name of glycerol.**

Propane-1,2,3-triol.

### Question 3

**Explain how the carbonate ion can make an aqueous solution alkaline.**

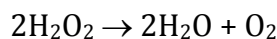
It can accept protons ( $\text{H}^+$  ions) from the solution to form  $\text{HCO}_3^-$ , leaving an excess of  $\text{OH}^-$  ions.

### Question 4

**a) Write an equation for hydrogen peroxide decomposing to oxygen and water**

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**b) Use this and the equation above to work out how many moles of oxygen can be obtained from 2 moles of sodium percarbonate.**

2 mol sodium percarbonate produces 3 mol hydrogen peroxide, which would produce 1.5 mol oxygen molecules.

**c) Now work out these quantities in terms of grams of sodium percarbonate and oxygen.**

2 mol sodium percarbonate has a mass of 314 g

1.5 mol oxygen molecules has a mass of 48 g

**d) One commercial specification for sodium percarbonate guarantees 'not less than 13% active oxygen. From your calculation above, is this realistic?**

$(48 / 314) \times 100 = 15.3\%$ , so the specification is realistic.

### Question 5

**Explain the phrase 'This makes the bleaches more compatible with the enzymes.'**

Enzymes have their optimum temperature at around 50 °C. Above this temperature the proteins from which they are made denature. The bleaching reaction, on the other hand, will continue to work faster as the temperature increases and so, ideally, a higher temperature than 50 °C would be better.

### Question 6

**Suggest foods that are based on**

**a) proteins**

Meats, cheese, egg *etc*

**b) starches**

Bread, pasta, rice *etc*

### Question 7

**Suggest what are the 'small soluble units' produced by the breakdown of**

**a) proteins**

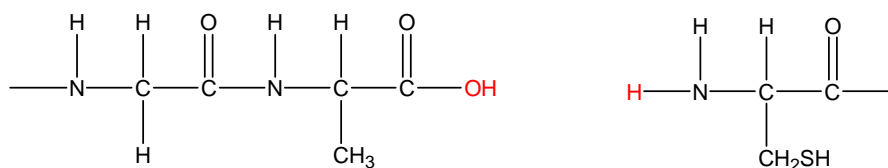
Amino acids

**b) starches**

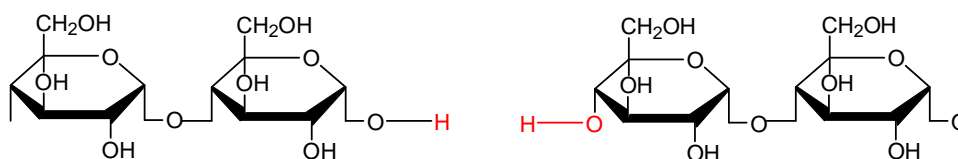
Sugars

### Question 8

**a) Look at the structures in Figures 17 and 18. Each has one of the linkages where hydrolysis takes place circled. Draw the products after hydrolysis has taken place for part of a protein molecule**



b) Look at the structures in Figures 17 and 18. Each has one of the linkages where hydrolysis takes place circled. Draw the products after hydrolysis has taken place for part of a starch molecule



### Question 9

a) What feature do the oxygen atoms have which enables them to form a bond with  $\text{Ca}^{2+}$  ions?

Lone pairs of electrons.

b) What name is given to this type of bonding?

Dative or co-ordinate bonding.

### Question 10

Suggest how the hardness of the water entering a dishwasher might be measured. Remember the result must be obtained quickly and 'electronically' so that it can be fed back to control the machine, so a titration, for example, would not do.

Hint, hardness is caused by aqueous  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

Water hardness could be determined by measuring the electrical conductivity of the water – the harder the water, the more ions and the higher the conductivity. (Other suggestions are possible)