Information for Candidates

1. This leaflet contains an article, which is needed in preparation for Question 5 in the externally assessed examination F332.

2. You will need to read the article carefully and also have covered the learning outcomes for unit F332 (Chemistry of Natural Resources).

3. You will be expected to apply your knowledge and understanding of the work covered in the unit to answer this question. There are 20 marks available on the paper for this question.

4. You can seek advice from your teacher about the content of the article and you can discuss it with others in your class. You may also investigate the topic yourself using any resources available to you.

5. You will not be able to bring your copy of the article, or other materials, into the examination. The examination paper will contain a fresh copy of the article as an insert.

6. You will not have time to read this article for the first time in the examination if you are to complete the examination paper within the specified time. However, you should refer to the article when answering the questions.
Next time you are out on a mountain bike, in a car or even an aeroplane, stop and think about the chemistry involved in the tyres you are travelling on. Those tyres are pneumatic tyres containing compressed air and, on your vehicle, they perform a variety of functions. Since the Scotsman, Robert William Thompson, filed the first patent for a pneumatic tyre in 1845, tyre technology has developed a huge amount – and many of these improvements are due to chemistry.

Typically, a rubber tyre is composed of rubbers (both natural and synthetic), carbon black, oils and resins, curing agents and anti-ageing chemicals. No tyre is complete without all of these components and each one has a varied and interesting chemistry.

**Natural rubber** Natural rubber can be obtained from bushes from many parts of the world (e.g. Brazil, Sri Lanka and Malaysia). However, by far the best and most widely used source is the *Hevea brasilienensis* tree originating from South America. The rubber is obtained as latex, a colloidal dispersion of nanoscale rubber particles in water. At the beginning of the twentieth century, C. D. Harries showed that natural rubber consists of repeating units. It was initially believed that the structural units were joined to form rings, but it was soon established that they are joined in long chains. These chains have the structure shown in Fig. 1 – and can be produced synthetically by joining isoprene (2-methylbuta-1,3-diene) units to give a polymer structure.

In natural rubber, the configuration across the double bond is 98% cis. This cis arrangement gives rise to rubber’s property of increasing in strength when stretched, by allowing the chains to form **crystalline regions**. Notice that the addition polymerisation of natural rubber is not a simple reaction, such as happens when ethene polymerises. Two double bonds in isoprene open to form a polymer that contains **only one** double bond in its repeating unit. Natural rubber has many limitations. It cannot be used on its own to make tyres due to its thermoplastic nature. It would become very hard in the winter and during the summer it would melt into a sticky, smelly mess. Imagine riding a bicycle that would stick to the road in summer! Fortunately the problem of its thermoplastic nature is overcome by ‘curing’ natural rubber by heating with sulfur, as described in a later paragraph.

**Synthetic rubber** Synthetic rubber was first produced by carrying out the polymerisation of dienes (alkenes containing two double bonds) in the laboratory. Since it is impossible to recreate the exact conditions for natural rubber synthesis, the laboratory-based syntheses initially gave poor quality products. For example, early attempts at polymerising isoprene in the laboratory gave synthetic rubber as a mixture of *cis* and *trans* isomers. The best synthetic rubber is a **co-polymer**, obtained by combining a diene and an alkene. Thus polymerisation of butadiene with phenylethene (styrene) gives the copolymer, styrene-butadiene rubber (SBR), Fig. 2.

To produce this ‘natural-like’ synthetic rubber, a process called emulsion polymerisation is used. In this process, butadiene and styrene are polymerised in water with a surfactant to give a colloidal dispersion of the polymer in water. This process is often done at 5 °C (rather than above 50 °C, as is more normal for an emulsion polymerisation) to give the desired rubber properties. Another variety of synthetic rubber is known as butyl rubber and is produced by polymerising...
2-methylpropene. The polymer in this case is a saturated hydrocarbon. Nowadays, many types of synthetic rubber are available for use in tyres.

Fig. 2 Structures of monomeric building blocks

Curing agents In 1839, Charles Goodyear discovered, accidentally, that heating rubber and sulfur together produced a new version of rubber that did not flow or become sticky at higher temperatures. This process of sulfur curing is called vulcanisation after Vulcan, the Roman God of fire. The chemical process of vulcanisation is called cross-linking and it changes the property of rubber to the hard, durable material we associate with car and bike tyres. Fig. 3 shows a schematic diagram of cross-linking.

Fig. 3 Sulfur

This produces a more rigid structure, which limits the movement of polymer chains. Unfortunately, vulcanisation with sulfur is a slow process, taking about 8 hours for the rubber to cure. A typical car tyre is cured for 15 minutes at 150 °C. However, the time can be reduced by the addition of accelerators such as those shown in Fig. 4.

Fig. 4 Accelerator molecules

Accelerators increase the rate of cure by catalysing the addition of sulfur chains to the rubber molecules.

Anti-ageing chemicals A tyre is subjected to quite harsh operating conditions. Factors such as heat, fatigue, weathering and exposure to ultraviolet light all reduce the life of a tyre. You will probably be aware of the effect sunlight has on a rubber band. Therefore, various chemicals are added to prevent tyre degradation.

Tyred out! Tyres are very important in all our lives and it is likely that they will continue to be so for the foreseeable future. An important question is ‘where do all the used tyres go?’ Tyres are inherently strong and this makes them almost impossible to destroy after use. In the USA, 250 million used tyres are produced each year and at the moment most (about 75%) are simply buried in landfill. But this and other methods of disposal can have a serious impact on the environment. Some tyres are recycled to make products such as cushioned surfaces for children’s playgrounds. An exciting project for chemists of the future would be to develop an environmentally friendly tyre.
Information for Teachers

1 This Advance Notice material should be issued to candidates on or after the date shown on the front cover of the candidate instructions sheet at the discretion and convenience of the Centre. Candidates can be given the material at any point, but it is suggested that this should be at least four weeks before the examination date.

2 Candidates will need to read the article carefully. Time can be built into the teaching programme to introduce the article content. Candidates should be able to discuss the article freely and be given support and advice in the interpretation of the content so that they are able to answer the question based on the article in the externally assessed examination. Candidates should also be encouraged to investigate the topics covered in the article for themselves.

3 Candidates will be expected to apply their knowledge and understanding of unit F332 to the question based on the article. There are 20 marks available on the paper for this question.

4 The Advance Notice material must not be taken into the examination. The examination paper will contain a fresh copy of the article, as an insert to the paper. Candidates should be reminded that they do not have sufficient time during the examination to read the article for the first time. They should, however, refer to the article printed in the insert in the examination paper to help them to answer the questions.

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