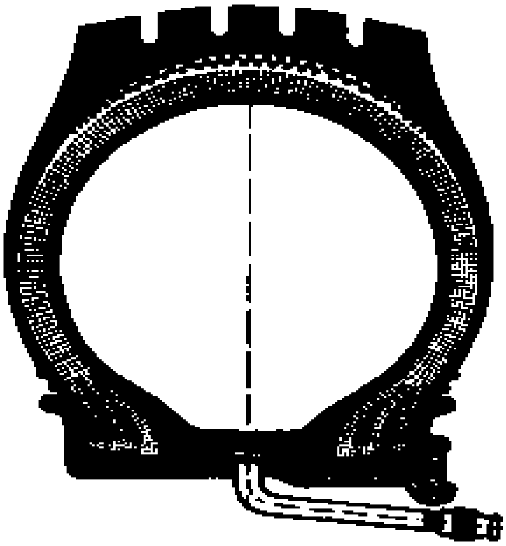
Tyres



The project was worked out by the students of the chemical technology class (third grade) of Masaryk secondary chemical school in Prague

Teacher : Jana Dudrová

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Enclosure

Introduction

By the end of the 20th century, humans are very probably moving around more on wheels than on their own feet. Each wheel has an indispensable part - a tyre. The number of cars, and hence the number of tyres, increases steadily.

Every item manufactured by humans has its own history. It is in fact a repository of experience and diligence of past generations, of materials and energy taken from nature. After a shorter or longer use, however, many things become an unpleasant and cumbersome waste.

We became acutely aware of the relationship between the manufacture and use of things and the build-up of waste when we visited a tyre-producing factory and, somewhat later, large-scale dumping grounds for worn-out tyres. From then on, the topic of the project was clear. We concentrated on the chemical side of rubber production and the methods for waste processing.

We cooperated with the following enterprises and institutions:

1. MITAS Prague - tyre production
2. KAUÈUK Kralupy nad Vltavou - production of styrene-butadiene rubber (SBR)
3. Czech Institute for Ecology Prague
4. KAC Uherský Brod - processing of used tyres
5. Pastròák Líbeznice Company - collection of used tyres

We all visited the production factory and the collection company while the subsequent tasks of further collection and processing of information were divided among the members of the team. The work of individual investigators partly overlapped since all of us wanted to have a first-hand personal contact with the technological part of the project - the manufacture and laboratory tests.

Group 1 - raw materials and preparation of rubber mixtures
Group 2 - production of SBR (styrene-butadiene rubber)
Group 3 - laboratory tests, economical information, history of the MITAS factory
Group 4 - environmental part - processing of used tyres

Acknowledgements

We visited the MITAS plant several times over a period of three months. Ing. Kamil Sosna and Mr. Pavel Kroupa, who graduated from our school, were very forthcoming and always ready to provide us with all the information we needed. Thanks to their willingness we learned many interesting details which we could have hardly found in textbooks. The situation in KAUÈUK was very similar, because the department of SBR was likewise headed by Ing. Jiøí Chyba, a former student of our school.

We should like to thank all three for the trouble they took to teach and instruct us.

Our thanks are also due to Ing. R. Skalík (KAC Corp.) and Mr. Pastiòák, who provided us with all the information about the operation of their companies. Both appreciated the fact that we, as students, were interested in environmental protection problems.

TECHNOLOGICAL PART

Corporation history and production programme

MITAS PRAGUE, joint stock company, was founded in 1934 under the name PNEUMICHELIN. 75 % of the stocks was owned by the French concern Michelin, 25 % stocks were state-owned. The production programme was tyres and tubes for cars, motor bikes and bicycles.

After World War II the corporation was renamed to MITAS Prague. The name was formed by joining of two renowned marks, Michelin and Veritas. The production programme gradually changed to the today´s production of both diagonal and radial tyres for trucks, agriculture and construction machinery, and special-use tyres. The largest tyre in production weighs 480 kg.

In 1985 the rubber compound preparation plant burned down. The tyre production went on but the mixtures had to be imported from other plants. The new compounding plant - one of the most modern plants of this type in central and east Europe - started its operation in 1993. The corporation has its own R&D facility.

The yearly production output is about 420 000 tyres, about 60 % of which is exported to advanced industrial countries. The production plant maintains the ISO 9001 quality standard.

Rubber compounds

The recipes for rubber compounds are manifold. The mixture composition depends on the envisioned service purpose. Different mixtures are used for tyre treads, others for tyre sidewalls. We were astonished to learn that, for some tyre types manufactured in the MITAS factory, up to 15 different mixtures are needed.

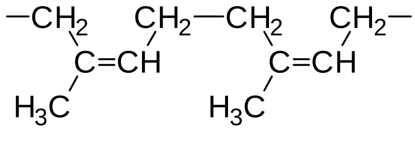
Rubber mixture components

1. Rubber

Rubbers are macromolecular substances belonging to elastomers. Following deformation, elastomers resume their original shape.

1.1. Natural rubber

Chemically, rubber is a polymer of 2-methyl-1,3-butadiene or isoprene, in fact a 1,4 cis isoprene.



Natural rubber is obtained from the rubber tree, especially of the species *Hevea brasiliensis.* Europeans first learned about the extraordinary flexible substance from Cristobal Colon after his return from his exploration of South America. Rubber trees grow in the tropical region of South America, South-East Asia and Africa. At the turn of the century, they have begun to be grown there on artificial plantations.

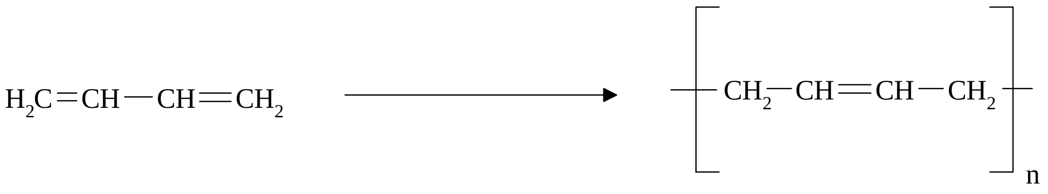
When the bark of the tree is cut, a white, milk-like liquid (called latex) flows out which contains 30 - 40 % of colloid rubber particles. Rubber is then precipitated by formic acid, washed with water and dried either by warm air (white crepe) or by smoke (brown crepe or smoked rubber). One tree yields 5 - 25 kg rubber. Natural rubber sufficed to cover all human needs for more than 100 years. Advances in the automobile industry, accompanied by increasing demands for rubber for tyre production, induced chemists to search for suitable replacements. Today, tens of different synthetic rubber types are being produced but the natural rubber is still in use since it imparts desirable properties to rubber mixtures. Its current price is also relatively advantageous. At the time of our visit, the MITAS factory processed rubber from Malaysia.

Prior to the actual preparation of the compound, natural rubber undergoes the so-called breakdown or mastication. The excessively long chains are split at the sites of double bonds by the action of air oxygen. The breakdown is achieved by passing the rubber through a masticating mill.

1.2 Synthetic rubbers

Here we give only those which we saw in the factory. The major type was styrene-butadiene rubber (SBR) produced in this country at the KAUÈUK Kralupy factory. We visited this enterprise and the production of SBR is therefore the subject of a separate chapter.

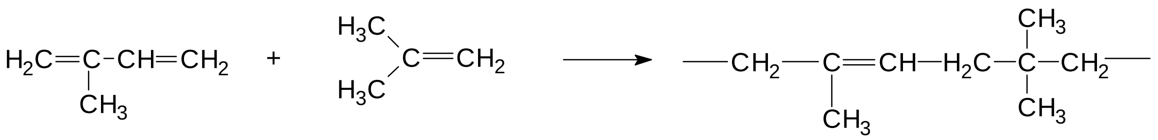
Polybutadiene rubber is imported from Russia.



$$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow \left[-CH_2{-}CH{=}CH{-}CH_2- \right]_n$$

Polyisoprene rubber, which is produced only in Russia, has structure and properties similar to those of natural rubber.

Isobutene-isoprene rubber - partially chlorinated, the major component of the polymer is isobutene, with about 3 % isoprene which makes vulcanization possible. It is used for the inner lining of tubeless tyres because it is gasproof.



$$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2 \; + \; (H_3C)_2C{=}CH_2 \longrightarrow -CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}H_2C{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2-$$

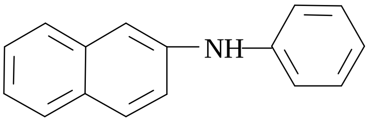
Note: The formulas do not show the composition of the polymer but only part of the chain containing both monomers.

2. Carbon black

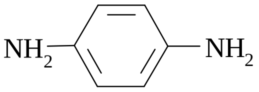
Carbon black - a defined type of soot - is used as filler. It provides rubber with strength and hardness, increases resistance against wear and heating. It gives the rubber a dark colour. Carbon black for the MITAS factory is supplied by DEZA Valašské Meziøíèí and is produced from coal tar. The carbon black has a specific surface area of 120 - 150 m^2/g. Tests are being carried out to replace carbon black for car tyres by modified SiO_2 and organic silans.

3. Antioxidants

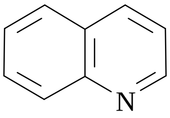
Even after vulcanization or curing the cross-linked polymer retains some of the double bonds which are attacked by oxygen and ozone. Although the content of ozone in air is not high, ozone is much more aggressive than oxygen. Its reaction with the double bonds gives rise to unstable peroxides or ozonides which undergo radical splitting and thereby cause cracks in the rubber structure - the aging of rubber. This process is markedly slowed down by substances called antioxidants such as 2-phenylnaphtylamine, which are imported from Slovakia or western Europe



The use of this substance rapidly declines owing to its carcinogenicity. The compounds used most at present are paraphenylenediamine (N-substituted by alkyl or aryl groups) and substituted quinoline.



paraphenylendiamine



quinoline

The mixture used for fabricating tyre sidewalls has to contain the highest levels of antioxidants.

4. Plasticisers

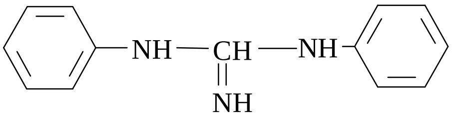
Plasticisers enhance the plasticity and thereby facilitate mechanical processing. Mineral oils are most often used for the purpose. The MITAS factory obtains these oils from PARAMO Pardubice.

5. Curing agents

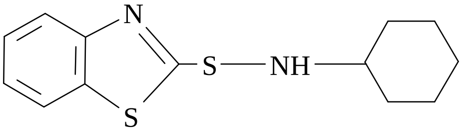
The agent used exclusively in MITAS is sulphur powder imported from Poland. The content of sulphur in the final product is 1 - 3 %. The higher sulphur level, the harder the rubber. Other curing agents are being tested, e.g. organic peroxides and curing resins.

6. Curing accelerators

These substances shorten the curing period from hours to minutes, lower the vulcanization temperature and slow down rubber aging. Their molecules contain nitrogen and sulphur. The magnitude of their effect varies; a so-called slow accelerator is diphenylguanidine.



Faster accelerators are N-sulphenamides.



The efficiency of accelerators is increased by the so-called activator, viz. zinc oxide (imported from Poland or Austria). A small amount of stearic acid, which is also added to the mixture, forms with zinc oxide zinc stearate. Starting raw materials, especially ZnO, are checked for the presence of heavy metals (Cu, Mn, Cr, Fe) which act as rubber poisons, forming in the rubber a variety of complex compounds which tend to disturb the structure of the macromolecular chains.

An approximate composition of the mixture per 100 weight parts of rubber is as follows:

35	parts of carbon black
2.5	parts of sulphur
0.75	parts of an accelerator
4	parts of an activator
0.5	parts of stearic acid
0.7	parts of antioxidants
2	parts of a plasticiser

Compounding plant

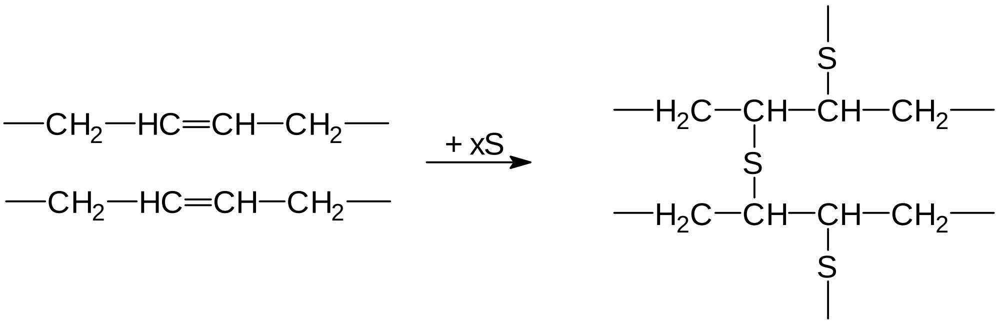
Compounding plant is a new modern part of the factory. The upper storey houses storage tanks with different kinds of rubber which are brought into the plant in the form of rectangular blocks or bales weighing 30 - 33 kg, wrapped in polyethylene foil. These are brought on electric cars to an automatic balance. Depending on the particular recipe, the appropriate number of synthetic rubber bales is placed on the balance, and antioxidants in polyethylene bags are added together with processed natural rubber (natural rubber makes up about 60 - 70 % of all rubbers by weight). After the processing by breaking, natural rubber is in the form of belts about 80 cm wide and 1.5 - 2 cm thick. The charge weight is automatically adjusted to 220 kg by chopping off parts of these natural rubber belts and the raw materials are poured into a blender which is situated one floor down. Other components that come into the blender are carbon black (by a special pipeline from a storage tank), stearic acid and mineral oil. The mixture is blended about 3 minutes and is concomitantly heated to 150 - 170 °C. The temperature must not exceed 200 °C since then the mixture could ignite. At this temperature, the polyethylene foil melts and blends with the other components.The compound leaving the first blender has the form of black belts of the same size as those of the natural rubber. These belts are suspended from frames and sprayed by aqueous solution of potassium soap to cool down.

Before the compound enters the next blender, it is supplemented with sulphur powder, curing accelerators and zinc oxide. These admixtures are added unpackaged because at the temperature in the blender, i.e. 120 °C, the polyethylene foil would not melt. The temperature during the second blending must not exceed this value to preclude the start of vulcanization. The homogenized final compound than comes into a large production hall called the tyre building bay, where it is layered onto polyamide textiles. In this hall, different compounds are used to build tyres of the required kind. The plant produces only a small part of steel wire cord tyres. This type of cord is used for tyres exposed to high speeds, i.e. mostly for passenger cars or buses. The tyre bead contains a steel wire reinforcing it. We noticed that the steel wires of which the steel rope is made look golden since they are covered with a brass layer. The reason is that brass adheres better to rubber than steel.

Vulcanization

The principle of vulcanization

Vulcanization or curing is a physico-chemical process during which the curing agent or energy cause structural changes in the elastomer. An elastomer (rubber) with linear structure of macromolecules is converted into rubber with spatial macromolecular structure. During vulcanization, linkages or cross-bridges are formed between the linear chains and this brings about cross-linking of the structure.



Depending on the curing agent used, these cross-bridges can be simple chemical bonds, e.g. bonds between the carbon atoms of individual chains or one or more sulphur atoms, or they may be represented by the bulky chains of a phenol-formaldehyde resin.

The properties of the vulcanizate depend on the concentration of the cross-bridges, the regularity of their distribution and their stability. Depending on their chemical nature, the stability of the cross-bridges decreases in the sequence:

$$C-C > C-O-C > C-N-C > C-S-C > C-S_X-C$$

Beneficial effects of vulcanization

The main reason for vulcanizing or curing rubber is a considerable improvement of its mechanical and physico-chemical properties. The improvement of mechanical properties includes increase in tensile strength, tear resistance, wear resistance and elasticity but, at the same time, decrease in elongation. In contrast to uncured rubber which dissolves in some organic solvents, vulcanized rubber only swells when exposed to them. Vulcanized rubber is also less sensitive to temperature changes and retains its flexibility and rigidity over a broad temperature range.

How is vulcanization done?

Vulcanization is the last step in the technological process of rubber production.

In the MITAS plant the half-finished rubber products are cured as follows: The half-finished product is placed into a vulcanizing press where it is exposed to pressurized steam of 140 - 180 ^{o}C. This brings about moulding of the product into the desired shape and, at the same time, the curing agent causes its vulcanization. Product shaping and vulcanization are thus performed in a single step. To prevent the product from sticking to the mould, the mould is sprayed with emulsions of separating agents.

Plant laboratories

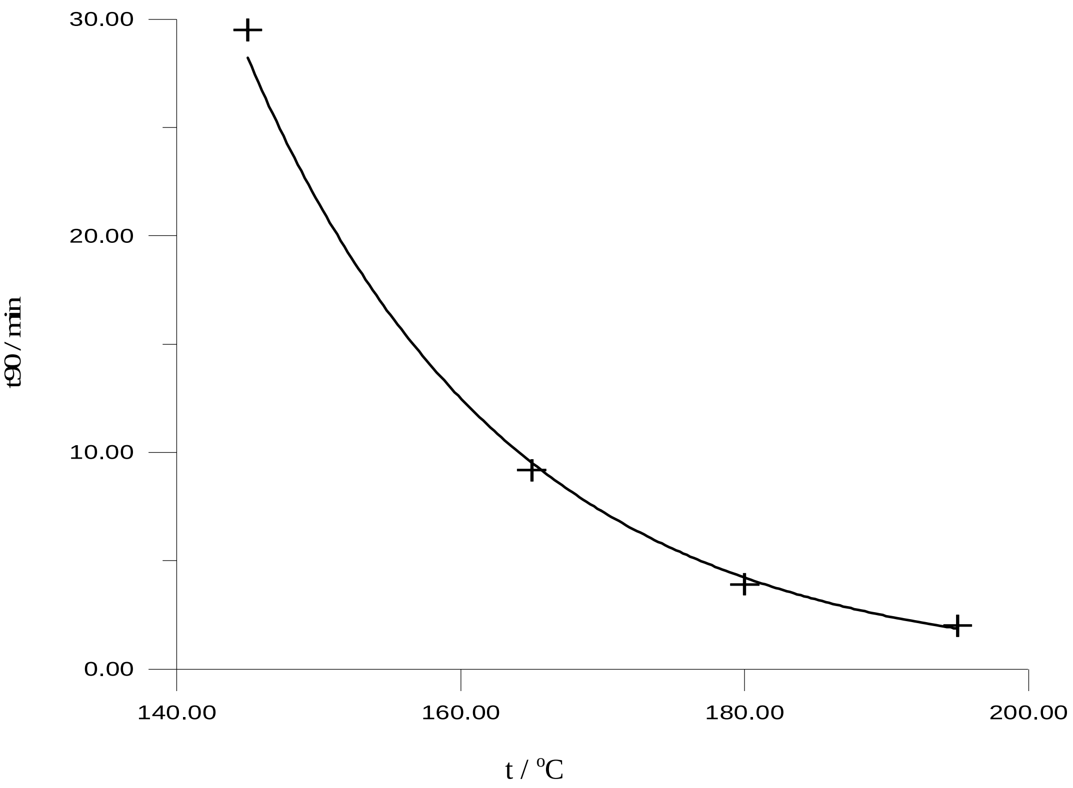
Laboratories for measurement of physical and mechanical properties

If the rubber compound has been prepared according to the recipe and well-homogenized, its samples have to exhibit certain properties. The samples are collected automatically in the production hall and are brought to the laboratory by pneumatic mail. The properties to be tested include density, viscosity, tensile strength, rigidity and other properties. We saw all the tests and familiarized ourselves with their principles. We were then given the opportunity to work on the device in which the time necessary for curing is determined. The sample is placed on a metal stand which rotates, the direction of the rotation changing with a set frequency. The sample is enclosed in a metal press and is heated to the desired temperature. Heating makes the rubber plastic. The resistance which the rubber offers against the rotary motion is recorded over a time as the so-called vulcanization curve. The parameter to be measured is in fact the torque (in N.m) necessary to cause sliding of the rotating stand within the tested material.

The start of vulcanization is demonstrated by a resistance increase on the curve. The measurement is controlled by a programme which determines t_{max}, i.e. the time interval during which the maximum number of sulphidic bonds is formed (maximum cross-linking). Other parameters are printed out at the same time. One of these, t_{90}, represents the time interval necessary for a 90 % cross-linking. This parameter is taken to be a characteristic parameter of a rubber. We drew a graph of its temperature dependence.

A table of values read from vulcanization curves 1 to 4 (samples of the same compound)

t / °C	145	165	180	195
t_{90} / min	29,5	9,18	3,91	2,00



Temperature dependence of parameter t_{90}

Vulcanization of rubber products is never conducted for the t_{max} interval but for a shorter period of time. The heated product has a certain heat inertia and the vulcanization therefore proceeds even after the heat supply has been switched off. Large-size tyres are usually cured for an interval equal to t_{30}. Products consisting of a thin rubber layer can be cured for t_{90}. The reason is that if the actual vulcanization period exceeds t_{max}, the spatial structure may sooner or later become degraded and the sulphide bonds may disappear. This situation is clearly documented on the time course of the vulcanization curve 5 (sample from another compound) at 195 °C which illustrates a rapid drop of the resistance.

Vulcanization curve 6 describes the time course of vulcanization involving the use of a slow accelerator whereas curve 7 shows the process with the use of a faster accelerator at the same temperature. The difference in t_{90} is 0.58 min, and the t_{90} in the latter case is therefore 28 % shorter.

Laboratory of analytical chemistry

Determination of sulphur content in rubber (the Grote-Krekeler method)

Principle: A sample of rubber is quantitatively combusted and the resulting sulphur dioxide is oxidized by hydrogen peroxide to sulphuric acid which is determined alkalimetrically.

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$
$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$

The equations imply that 1 mole NaOH corresponds to 0.5 mole SO_2, i.e. also to 0.5 mole S.

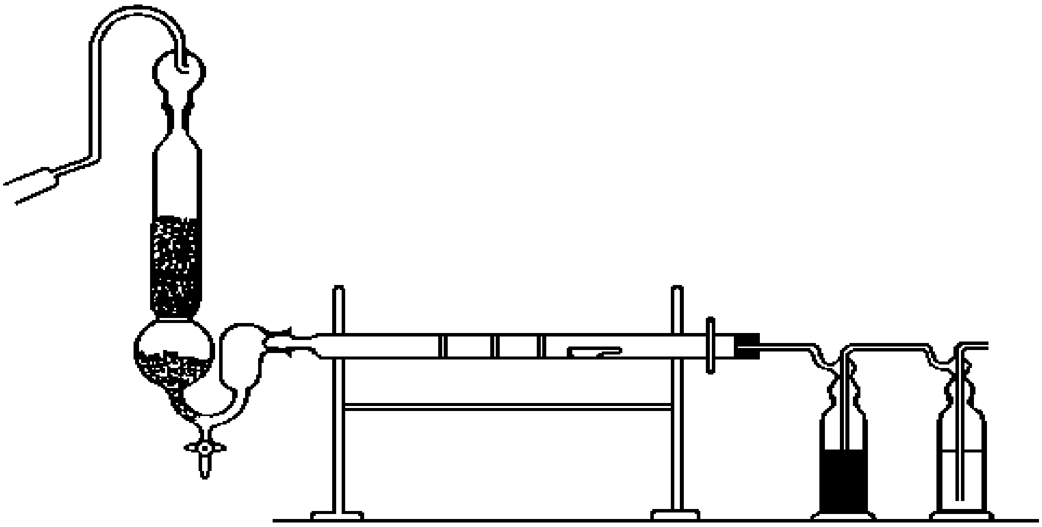
Chemicals: 10 % aqueous solution of H_2O_2

about 0.1 $mol.dm^3$ NaOH, its exact concentration being determined by oxalic acid titration with methyl orange or methyl red as indicators.

Procedure:

An exact amount of 0.2 - 0.5 g sample is weighed into a porcelain weighing boat. The boat is slid into a silica combustion tube preheated to a red glow. The tube is connected via a ground silica joint to a receiver into which about 50 cm^3 of 10 % H_2O_2 is placed. The other end of the tube is connected to two washing bottles the first of which contains 10 % KOH solution for absorption of acid fumes from the air, the second glass wool. The setup is connected to a pump which, when switched on, draws air into the tube. Heat is supplied by an electric furnace which travels along the tube in the direction towards the weighing boat so that the whole sample is incinerated. After incineration the furnace is switched off, the pump is disconnected and the contents of the receiver are quantitatively transferred into a titration flask by distilled water washes.

sample weight	$m = 0.2025$ g
concentration of volumetric NaOH solution	$c = 0.1012\ mol.dm^3$
consumption of the volumetric solution	$V = 1.30\ cm^3 = 1.30.10^3\ dm^3$
molar weight of sulphur	$M(S) = 32.064\ g.mol^{-1}$
the amount of sulphur	n(S)
weight fraction of sulphur	w(S)



The apparatus for determination of sulphur content

Calculation of the sulphur content in the sample:

$$n_S = \frac{n_{NaOH}}{2} = \frac{c \cdot V}{2}$$

$$m_S = n_S \cdot M_S = \frac{c \cdot V \cdot M_S}{2}$$

$$w_S = \frac{m_S}{m} = \frac{c \cdot V \cdot M_S}{2 \cdot m}$$

Insertion of actual values:

$$w_S = \frac{0{,}1012\, mol \cdot dm^{-3} \cdot 1{,}30 \cdot 10^{-3}\, dm^3 \cdot 32{,}064\, g \cdot mol^{-1}}{2 \cdot 0{,}2025\, g}$$

$$w_S = 1{,}04\ \%$$

Our rubber sample contained 1.04 % sulphur by weight.

Manufacture of styrene-butadiene rubber (SBR)

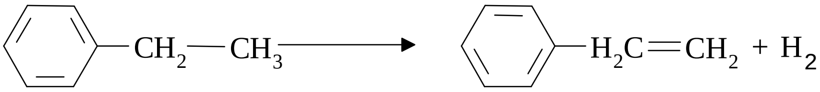
On one freezing winter day we visited the KAUÈUK plant at Kralupy nad Vltavou, about 30 km from Prague. The plant produces both monomers necessary for the subsequent manufacture of SBR, viz. polystyrene, acrylonitrilebutadiene styrene, methyl-tert-butylester, which is consumed by the crude oil refinery next door, and other products.

We had the opportunity to become acquainted to considerable detail with the SBR manufacture plant. The plant produces six SBR types differing in the degree of polymerization, oil content, types of the emulsifier or antioxidant used. The major product is SBR 1500 which is readily processable in rubber industry.

Raw materials

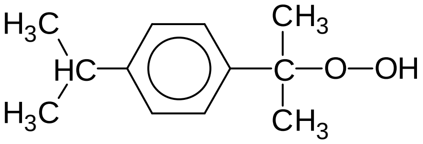
Under normal conditions, 1,4-butadiene is a colourless gas with low solubility in water (the boiling point is -4.4 °C). It is obtained by extractive distillation from the hydrocarbon C_4 fraction which contains, in addition to butadiene, also butenes and small amounts of C_3 and C_5 hydrocarbons.

Styrene (vinylbenzene) is a toxic colourless fluid with a characteristic smell (boiling point 145.2 °C). It is produced in-house by catalytic dehydrogenation of ethylbenzene which is imported from CHEMOPETROL Litvínov.



Initiators

Radical-induced polymerations are performed with the use of inorganic or organic peroxides. In the KAUÈUK plant this is diisopropylbenzenehydroperoxide. The degradation of the peroxide is activated by Fe^{2+} compounds.



Emulsifiers

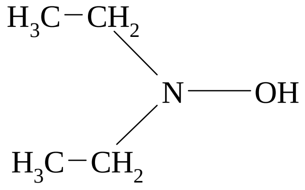
Emulsifiers are compounds which render possible the formation of a stable emulsion. The plant uses for the purpose mostly saponified rosin, sometimes potassium palmitate or stearate ($C_{15}H_{31}COOK$, $C_{17}H_{35}COOK$).

Regulators of chain elongation

These are R-SH thiols of higher molecular weight.

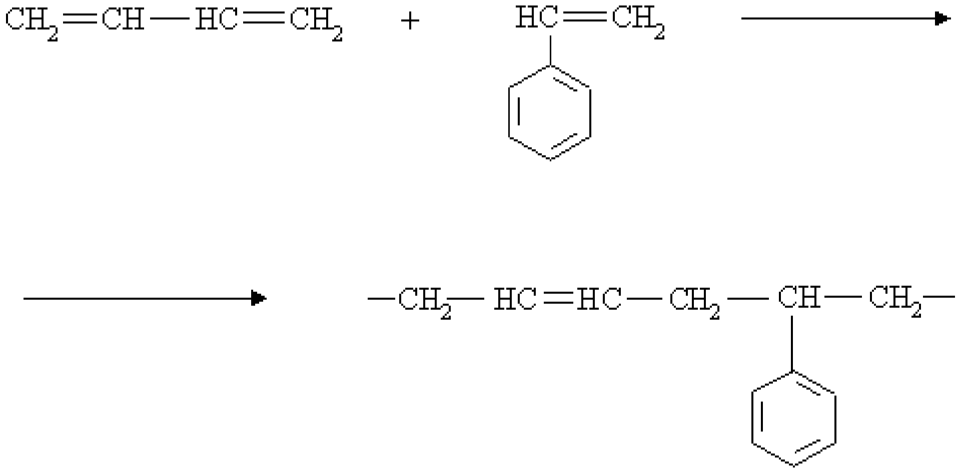
Chain elongation stoppers (shortstoppers)

These substances bind free radicals and thereby stop chain elongation. The compound used as shortstopper is N,N-diethylhydroxylamine.



SBR production

The actual SBR manufacture is based on emulsion copolymeration. The butadiene/styrene ratio is 76 %: 24 %.



The polymeration is carried out at 5 - 10 °C continuously in cascade-arrayed reactors. A 6 - 10 % conversion is achieved in each of them. The polymeration is interrupted at a 60 - 70 % conversion. A higher conversion degree is undesirable since then the chains would have irregular structure and would be excessively branched. The reaction is exothermic and the reactors are cooled by salt brine. The first reactor is supplied with both monomers, an aqueous emulsifier solution and the initiator is added.

We noted in the production bay that warning signs for radioactive emitters were situated near the individual reactors. We were told that the density of the reaction mixture, and thereby the degree of conversion, is determined via the absorption of radioactive radiation. Formerly, samples had to be taken every two hours to determine the reaction mixture density in the laboratory. The effluent from the last reactor is latex which contains still unreacted monomers. It is therefore transported to a two-stage demonomerization step. In the first stage the latex is steam-heated to 40 °C which results in the removal of butadiene. The second stage is performed under reduced pressure at 75 °C and involves the removal of styrene. Both monomers are returned to the production phase. The demonomerized latex is taken into a storage tank where it is homogenized by stirring so that the final product has a uniform quality. The next step is latex coagulation through the action of salt brine ($CaCl_2$ solution) and H_2SO_4 at pH 2.5 - 3. The salt brine concentration was substantially reduced by the use of auxiliary coagulants based on polymeric amines. The rubber is stabilized by the addition of antioxidants (see above in the section „Rubber compounds“). SBR is much more oxidation-resistant than natural rubber. The resulting rubber granulate is then washed with hot water, dewatered by means of rollers, and dried in a hot-air dryer. The dried product is pressed into 33 kg bales and packaged into polyethylene foil. Part of the production is shipped to domestic rubber plants and the rest is exported into many countries all over the world.

Environmental protection

We were interested in what was being done in the polymeration plant for environmental improvement. The following measures had been implemented:

1. Lowering of waste water salinity
2. Introduction of antioxidants which are nor carcinogenic and do not give rise to nitrosoamines
3. Substantial reduction of styrene air pollution

Even after demonomerization, a certain amount of styrene remains in the rubber granulate. This styrene used to contaminate the air in the dryer and hence the ambient atmosphere. This contamination amounted to about 900 tons of styrene every year. At present, the air from the dryer is mixed with natural gas and is subjected to catalytic combustion.

We became convinced that the chemical industry need not be environmentally harmful. Of course, every measure taken for environmental protection results in higher costs. But - cleaner air and water are worth it, aren´t they?

Environmental part

The yearly number of worn-out tyres produced worldwide is about 1 billion. We obtained an overview of the possibilities of utilization of worn-out tyres at the Czech Institute for Ecology in Prague 4, where we also performed a computer-aided literature survey of journals in this field. Our study of the literature showed that both the tyre material and its energy content can be recycled or reclamined. We divided the possibilities into the following classes:

- tyre retreading
- production of a regenerate
- use as fuel
- chemical processing
- mechanical and physical processing

1. Retreading

If it were not for tyre aging, retreading would represent an environmentally ideal recycling process. Owing to spontaneous degradation processes, even a completely unused tyre becomes unusable after 6 - 7 years because of inherent security risks. Currently, retreading is performed mostly in truck tyres which are in a daily heavy duty. Since their wear is therefore relatively rapid, the aging processes have no time to take place to any considerable extent. The tyre life-time is naturally affected by the service type, the technical condition of the vehicle, and the driving style.

2. Production of a regenerate

Soon after the discovery of vulcanization, attempts were made to regenerate or reclaim old rubber. These yielded a number of procedures for processing old rubber to a regenerate.

The terms regeneration and regenerate are not entirely correct since the process does not retrieve rubber. The oldest process was a purely mechanical milling to a fine dust which was then added to new mixtures. The process is still in use to a small extent - it represents the only method of utilizing hard rubber. Other regeneration processes included heat and chemical treatments (steaming, action of alkalies, salt solutions, organic solvents or oils). Oils are added in all cases as plasticisers and the regeneration is carried out in an autoclave.

The regeneration involves breaking of the cross-linking bonds, shortening of polymer chains and the formation of new bonds. This permits a new vulcanization. In order to obtain a high-quality regenerate, the rubber has to be freed of its textile components.

At present, the rubber processing industry uses an addition of about 10 % regenerate referred to the quantity of new rubber.

3. Use as fuel

The heating value of tyre waste is relatively high (cca 30 MJ.kg^{-1}). Some countries such as Great Britain and Germany operate electric and heating power plants using this waste as fuel. Most often, the waste is used as an auxiliary fuel in cement producing furnaces, e.g. at the Czech cement production plants at Mokrá near Brno and in Èížkovice. The sulphur content (1 - 2 %) presents no problems since the resulting SO_2 binds to the alkaline cement components. The heat value of the waste is high but one should not forget that large amounts of energy are consumed during tyre production. The use as energy source is therefore not optimal and, in addition, it in fact leads to an irreversible annihilation of a chemical raw material.

4. Chemical processing

The literature gives the following possibilities of utilization:

- Pyrolysis can provide a mixture of hydrocarbons and utilizable carbon black. Some processes make use of pyrolysis with hydrogenation, which yields a mixture of saturated hydrocarbons. The sulphur is converted into H_2S.
- Japanese scientists elaborated a new method in which the tyres are exposed to 40 % NaOH solution at 400 ^{o}C and a pressure of 4 MPa. Under these conditions the tyres are dissolved within 15 min to yield an oily mixture of long-chain hydrocarbons.
- A new biotechnological method of utilization of rubber waste is being tested in the USA. The waste from worn-out tyres is mixed with microorganisms of the *Sulfobolus* species at low pH and a temperature of about 70 ^{o}C. The microorganisms cleave the C-S bonds and provide material for new utilization. The research goal is to use this method for utilizing about 20 % of old tyres.

5. Mechanical and physical processing

We present this method last because we had the opportunity to contact the KAC corporation in Uherský Brod which buys off tyres and reclaims the rubber. Because of the large distance from Prague, the contact was only by correspondence but, upon our request, the ditrector of the corporation sent us a detailed description of both technology and the corporate plans. In his accompanying letter, he complimented the school on awakening in the students interest in problems associated with waste processing.

The biggest problem in any tyre scrap recycling process is the multicomponent nature of the waste. The corporation buying old tyres has to separate these components, i.e. rubber, textiles and steel. This separation can be done by two methods.

5.1 Cryogenic method

The tyres are chilled to -80 ^{o}C with liquid nitrogen. At this low temperature they become brittle and can be relatively easily chopped up by a chopping mill. The resulting granulate has a high production cost and the original properties of the rubber are considerably changed. The consumption of nitrogen is 0.6 kg per 1 kg tyres.

5.2 Multiple milling at room temperature (used by the KAC)

The tyres are first chopped to pieces of about 60 x 60 mm. Large truck tyres are first longitudinally cut to halves and the steel wire belts are torn out of the beads, to avoid fast wear and tear to the chopper mill. Along with steel parts from other tyres, the steel wires are collected and sent to steel mills for further processing.

The chopper mills are followed by recycling lines which include mills and separators. The lines fulfil two functions:
- a gradual grinding to fine-fraction granulate
- separation of steel and textiles.

The end products are packaged granulate with different grain size, steel and textiles. A high-purity granulate is used for producing reclaimed rubber or regenerate (ECO BARUM Otrokovice). This process saves valuable raw materials in the rubber industry.

Another use consists in blending of the granulate with various binders (rubber, polyurethanes, etc.). The resulting products are used for sports floor surfacing, playground surfacing, carpets, heat-isolating mats, soundproofing wall lining, shock-absorbing elements for train or tram tracks, motorway milestones, etc. This production line is not yet currently established in the factory but its introduction is planned. We saw with interest some of these products in MITAS, though coming from other producers.

The KAC has also other plans, e.g. scrap textile processing.

Other possibilities of application of reclaimed granulate are the production of macadam mixtures for road surfacing. Roads with these surfaces have been successfully constructed in Austria and Sweden (a test section Vienna - Linz).

We were most impressed by the patent-protected product called PETRO-EX manufactured by the company. It is a very fine granulate fraction with a particular particle structure. Under a microscope it is seen as fine fibres which have the capacity to envelop or occlude microscopic droplets of oil, crude oil, petrol and other nonpolar substances. PETRO-EX can therefore be used for absorbing these substances that have leaked out during environmental pollution accidents, both on land and in water. PETRO-EX is not volatilized and has a high sorption capacity - 10 kg PETRO-EX can absorb 38 l petrol, 34 l crude oil or 30 l engine oil. For comparison - current materials used for the purpose absorb about 8 l oil per 10 kg. PETRO-EX absorbs the leaked substance immediately, is nontoxic, floats on the water surface, and its surface after application is not slippery. It can be used preventively in filter mats in wastewater treatment facilities and industrial plants. Upon use, it can be burned in high-temperature furnaces.

In conclusion we should like to explain why we did not visit any of such plants near Prague. Such facility indeed exists near Prague, but its recycling lines stand idle because the corporation went bankrupt. In our country, operation of these plants is highly risky and we are therefor worried by the thought that old tyres will again be found discarded in the woods.

Economy

The production process and its economics are closely intertwined. We therefore tried to obtain information also about the economics of the rubber-producing enterprises. We gathered data on the prices of raw materials and products, the total production, export of products and import of raw materials.

The MITAS factory

We found out that in 1996 the MITAS factory produced 380 000 tyres of all types. The plan for 1997 is 440 0000 tyres which should be shipped to customers both within our country and abroad. The whole 1997 production has been sold in advance. The enterprise exports 65 - 75 % of its production to other countries, especially to Italy, Spain, Germany and France.

In order to keep its competitive edge on foreign markets, the enterprise has to continuously lower the production costs. The yearly inflation rate in the EU countries is about 3 % whereas in the Czech Republic it is some 10 %. The enterprise therefore cannot compensate the cost increase solely by increasing the product price but it has to increase labour productivity and introduce modern technologies. We realized the importance of testing, in the R&D laboratory, possible ways of shortening the curing time even by a mere 1 - 2 min. The outcome is simply a higher daily production. At present, the enterprise has to repay a credit that it had to take in order to build the new compounding plant.

The actual approximate daily production costs of the MITAS plant include:

25 tons of natural rubber	about 1 000 000 Kè
20 tons of synthetic rubbers	about 1 000 000 Kè

Natural rubber is imported from South-East Asia, mostly from Malaysia, Vietnam, Thailand and Cambodia. The price of natural rubber, which is set daily at the London Commodity Exchange, is approximately 40 000 Kè per ton. The above values imply that the synthetic rubber is more expensive than the natural one, although it is not imported from distant countries. (The majority of synthetic rubber is due to SBR which is produced in this country). The high price of synthetic rubber reflects its high production costs since it is produced by complex processes from the basic raw material - crude oil. The natural rubber is „manufactured“ by the nature. The prices of the products include also costs of other necessary raw materials, energy, labor costs, overheads, etc. The largest, so-called giant tyres manufactured in the plant are sold for approximately 45 000 Kè apiece.

The Pastròák Líbeznice Company - collection of used tyres

For taking worn-out tyres for recycling, the corporation collects the following payments (per 1 tyre):

passenger cars	15 Kè
trucks and lorries	65 Kè
tractors	165 Kè
caterpillars, etc.	up to 1000 Kè

Most tyres are sold to two cement-producing plants to which the corporation pays per piece:

passenger cars	10 Kè
trucks	20 Kè
other	25 Kè

The difference between these prices is the company´s profit.

Conclusion

During the work on the project, we collected a large body of information and numerous literature sources - textbooks, monographs on subjects from the field, corporate brochures and leaflets. We learned how to search for essential information, how to take up contacts with the personnel in the production plants and enterprises, and, last but not least, how to cooperate mutually. Another art we learned was how to set up a text on a certain subject. We carried out the editing of the text quite independently on school computers or at home.

Our report on the results of our investigation into the fates of the tyre was based mostly on our direct observations and notes we made in the factories. We did not expect to learn so much about an everyday simple thing such as tyre. On the other hand, it became quite clear that, in terms of knowledge of the subject, we just scratched the surface. We discovered unexpected connections and acquired new pieces of information. This kind of learning and training was very interesting.

In autumn we want to present our project at the Students´ Technical Conference in our school. At present, other students from other classes work on various topics from the field of chemistry and environmental protection. We shall invite to the Conference representatives of different enterprises, of education authorities, our schoolmates and our parents. Presenting our results there will give us the opportunity to popularize chemistry and to talk on the particular topic in front of a large audience.

Most of us will probably decide to study chemistry at the university, and some may specialize in the study of the chemistry of polymers. We took inspiration also from the fact that we saw former students of our school working in responsible positions in the various enterprises.

Our work on the project was coordinated by our teacher Mgr. Jana Dudrová.

The following students participated in the project:

Jaroslav Bauer
Tomáš Koèí
Tomáš Minaøík
Radek Pernica
Jakub Pilaø
Tomáš Svoboda
Pavel Tužina
Vojtìch Vojík

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