# DEVELOPMENTS IN THE RUBBER INDUSTRY: CHEMICAL ANALYSIS FOR STANDARDISATION

By

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## INTRODUCTION

Natural rubber (NR) has been known to man for a very long time. Of the many rubber bearing species only *Hevea brasiliensis* a forest tree native to South American has become the most important commercial source. Interest in the Guayule tree has not posed a serious threat to NR from *Hevea*. It is mentioned that Cristopher Columbus discovered rubber during his second voyage to the new world (1493 – 1496). In 1768, over 130 years later, a French Scientist made a pair of rubber riding boots for Fredrick the Great but they became sticky in hot weather and brittle in cold. In 1770, the name 'rubber' was coined by Priestly who found that it would rub off certain marks.

The invention of the masticator (1820) for mastication of rubber by the Englishman Thomas Hancock, may be regarded as the take off point for the industry. In 1823, the first water proof fabric was patented by Mackintosh, a Scotsman, who sandwitched a layer of rubber between two pieces of cloth. The events leading up to the discovery of vulcanization are attributed to a large extent to the American, Charles Goodyear. He made the great discovery that sulphur plus heat would make rubber stand changes in temperature. Overnight, rubber became useful for thousands of purposes.

The two inventions, namely mastication and vulcanization established the basis of modern rubber technology. A patent, describing the manufacture of the pneumatic tyre, taken in 1845 is attributed to R.W. Thompson, a Scotsman, but the first useful pneumatic tyre was made in 1888 by John Boyd Dunlop in England. Dunlop's tyre was specifically intended for the bicycle, and it was not until 1910 that a new era of motor cars and the automotion age arrived. Transport provides the main outlet for rubber and about 60 percent of all the natural and synthetic rubber consumed goes to manufacture of tyres of all kinds.

#### History of the plantation rubber industry

Preliminary studies on all the available Hevea species from the Amazon forest was carried out at the Kew gardens in England and a formative report on the feasibility of cultivating Hevea in Asia was prepared in 1872. Henry Wickham, in 1876, made a successful attempt in collecting about 70 000 Hevea seeds from Brazil. They were sent to the Kew gardens for germination and about 2000 seedlings were sent to Ceylon (now Sri Lanka) where they were successfully established. The oldest rubber trees to be planted in S.E. Asia are still alive and can be seen at the Henrathgoda Botanical Gardens at Gampaha. Simultaneously the Hevea tree was established in other parts of the Far East such as Malaya (Now Malaysia) and Netherlands East Indies (now Indonesia). By 1978 Hevea seedlings were quite widely distributed in the far east. In spite of Wickham's efforts up to 1900 the total area under cultivations in S.E. Asia was only 2500 Hectares, By 1938 a substantial quantity of NR was produced in South East Asia, About 97 per cent of the world NR supply was from Asia. The genesis of the sector car industry increased the world requirement for rubber by leaps and bounds. Brazil could satisfy only a limited demand. Rubber growers in the far east willingly disrupted supplies and this forced the large American Companies to establish plantations of their own elsewhere in the world. Firestone Tyre and Rubber Company established a large plantation in Liberia in 1923 and Goodyear Company established a similar plantation in the Philippines in 1928.

## History of the synthetic rubber industry

At the start of World War 2 very little synthetic rubber was produced anywhere in the World. Rubber is a polymer. It is formed by the union, in an orderly way, of a large number of monomers. In the rubber tree this synthesis takes place naturally and it is called biochemical synthesis. Industrial polymer synthesis by man was achieved in the 1930's due mainly to the excellent research work done by Nieuwland, Carothers, Seamon and others. At this time a massive research and development<sub>i</sub> programme was launched by the U.S. Government to prepare synthetic alternatives to NR. Styrene - Butadiene rubber (SBR) was the first to be manufactured. By 1945 production of SBR was running at about 1 million tonnes per year. By further improvements SBR could match NR in the principal applications in tyres. Synthetic polyisoprene, virtually a chemical replica of NR, was possible due to the startling discoveries of Ziegler and Natta. These discoveries have resulted in a serious challenge to the undisputed technical and commercial monopoly of NR.

Later, with the understanding of polymerization in more detail several other synthetic rubbers were produced. Those with polar groups could withstand hydrocarbon oils. Those with no double bonds in the main chain could withstand weathering. Then there was the development of silicone rubber which has very good retention of properties under extreme temperature conditions both low and high. They all come under special grades of synthetic rubber and they are very expensive.

To 'stretch' NR to perform under adverse conditions is a challenge faced by NR today, and it has been proved that NR can be chemically modified to meet at least part of this challenge.

### CHEMICAL ANALYSIS

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Chemical analysis is an important yardstick for quality assurance and standardisation and it is an essential tool for tracing impurities and defects in a product. It also gives valuable information about the composition of the product.

Chemical analysis in the rubber industry could be broadly classified under two headings, namely the analysis of raw rubber and the analysis of compounded and vulcanized rubber.

Raw rubber includes both natural and synthetic rubber. There are different grades of natural rubber (NR) but they all belong to the class, cis-poly isoprene. The building block or monomer is cis-isoprene. Raw NR contains in addition to cis-polyisoprene: (about 92%) other non rubber ingredients such as proteins, phospholipids, carotenoids, sugars, mineral substances and naturally occuring antioxidants and activators. In RSS, due to the method of manufacture there are phenolic substances deposited on the sheet such as, O-cresol, 2,6 dimethyl phenol.

In pale crepe most of the non-rubber constituents, specially the carotenoids, are either removed as a first fraction or bleached by the addition of a bleaching agent during the process of manufacture. The age old practice is to grade NR by visual examination. The new method of presentation of NR as Technically Specified Rubber (TSR) mainly in block form requires both chemical and physical analysis of raw rubber.

The synthetic rubbers are of many varieties where the building blocks vary in chemical composition from one type to another. In the same type there can be variations as well, but the buildings units are the same. Among the many types of synthetic rubbers are included, styrene-butadiene rubber (SBR). As the name indicates the building block of SBR consists of two monomers, styrene and butadiene. They are called heteropolymers. To this group belongs nitrile rubber (NBR), which is a polymer of acrylonitrile and butadiene and butyl rubber (IIR) which is a polymer of isoprene and isobutylene. Among the more important synthetic homopolymers are polybutadiene (PB) synthetic poly cis-isoprene (IR), poly chloroprene (CR) and silicone rubber (SR).

# Identification of the polymer.

In the case of the raw polymer, a special extraction procedure is not required. Lassaignes sodium fusion test is quite a useful test for the detection of nitrogen and chlorine in nitrile rubber and chloroprene rubber, respectively. Nitrogen may also be spotted in NR but nitrile rubber can be easily differentiated from natural rubber by the colour intensity.

A more accurate identification of the raw polymer can be done by Infra Red (IR) analytical techniques.

The identification of raw polymer in a vulcanized rubber product is more complicated. A compound or vulcanized rubber is an extremely complex system containing a large number of components. A generalised formulation is indicated in Table 1.

# Table 1. Vulcanized rubber

Polymer Carbon black Inorganic filler Zinc Oxide Processing aids Protective agents Vulcanization residues Non-rubber (from NR)

# Sulphur

In the case of vulcanized rubber the first stage in the analysis is invariably solvent extraction using solvents such as methyl ethyl ketone (MEK), acetone, chloroform and benzene. This is conventionally carried out in a soxhlet extractor. The components shown on the right hand column of Table 1 will be contained in the soluble fraction, whereas those in the left hand column are insoluble. Elemental sulphur will be distributed in the two fractions depending upon the extent of vulcanization. The insoluble and solubler fraction will now be further discussed.

# Insoluble fraction:

The main components of the insoluble fraction are polymer and filler. This is pyrolised at about 400 - 450°C in a stream of nitrogen. The pyrolysate is collected in a water cooled U-tube and is examined by IR spectroscopy for the base polymer. The pyrolised residue is then heated in oxygen at about 900°C until all combustible material, essentially carbon black has been removed. The ash that is left over which is mainly metal oxides can be further analysed after separating into acid :soluble and acid insoluble fractions. By complexometric titration, elements such as calcium, magnesium, zinc, iron, titanium and aluminium can be detected. Silica in the soluble portion can be detected by conversion to silicon tetra fluoride using hydrogen fluoride..

Atomic absorbtion spectroscopy and elemental analysis, using the elemental analyser, are also useful equipment to detect metals. Pyrolysis gas chromatography is a very useful method to identify the base polymer in extremely small samples. The technique involves rapid pyrolysis of the sample and the separation of the volatile products in the column of the apparatus.

# Soluble fraction

Analysis of the complex mixture present in the soluble fraction is carried out by thin layer chromatography (TLC). High performance liquid chromatography (HPLC) is currently used and is a more precise method of estimation.

In TLC a small sample is applied to a thin layer of absorbent, usually supported on a glass plate and a solvent allowed to diffuse up the plate. The various components, in the sample migrate in the solvent at rates determined by their chemical structure. By this means the constituents in the soluble fraction may be separated as a series of spots and subsequently identified by reference to their individual migration rates and the colours developed after spraying with a specific reagent. In order to achieve a complete analysis of the soluble fraction a number of different solvent systems may have to be employed together with a range of spray reagents.

# Analysis performed on the total sample ·

In order to establish details of the type of vulcanizing system used and the state of vulcanization it is essential to analyse the sulphur content of the sample in a number of different ways.

Thus the total sulphur, free elemental sulphur and sulphidic sulphur contents together with the sulphur remaining after solvent extraction can be determined by standard chemical procedures.

# **Conclusions**:

The value of all the information which can be obtained by the application of these chemical analytical procedures cannot be underestimated.

The analytical procedure is an essential prerequisite to the development of quality control methods of a chemical nature for use in rubber factories.

The rapid deterioration of an article in service may be due to an omission of antidegradant, contamination by trace metals such as copper and manganese and faults in the vulcanizing system. All these can be detected by a full chemical analysis.