INTRODUCTION TO NATURAL AND SYNTHETIC RUBBERS

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Introduction

How many people realize the debt that transport owes to rubber? If we think of trains, aeroplanes, buses and coaches, motor cars and even the humble bicycle, all except trains are highly dependent on rubber. The modern car, for example, has more than 500 rubber parts. The tyres, of course, account for the bulk of the rubber involved—about 140 lb.—but there is still from 60 lb. to 120 lb. of fairly small rubber parts, used in electrical insulation, in seals round the doors and windows, in radiator hose, engine mountings, shock absorbers and fender guards, and if the cushions are of sponge rubber this will add considerably to the weight involved. The list could obviously be extended much further.

Perhaps railways are the part of transport where rubber plays its least obvious role. But even here train seats are sometimes of sponge rubber, doors and windows have rubber seals, and rubber flooring is quite common. One or two countries use rubber tyres for train wheels, rubber damping blocks between rails and bridge platforms, and pads between sleepers and rails. The moving parts of couplings and shock absorbers may also be of rubber. It has justly been said that rubber 'cushions' the modern traveller.

This is not the end of rubber's usefulness. In Britain some 54 per cent of all rubber production goes into tyres and tyre products. The next largest single outlet is in footwear, which consumes some 10 per cent of available rubber. Then comes foam or cellular rubber products with about 6 per cent, and wires and cables with 4 per cent. There follow a number of groups using about 1 per cent or 2 per cent each, and these include belting, hose, proofed goods such as rainwear, rubber thread, surgical goods, tiles and flooring, rings, seals and gaskets. Apart from these well-defined groups there are many products which do not fit into groups at all, and these are lumped together and called miscellaneous. This miscellaneous group is, however, the largest user of rubber, apart from tyres, and takes 15 per cent of all the rubber used in this country.

Even after this formidable list of rubber articles it is surprising that there are at least 40,000 different products based on rubber. This amazing versatility of rubber—it can be used with equal ease for elastic bands, pencil erasers and railway buffers—has caused it to be in great demand, and shortages have been felt acutely by everyone. Luckily in this country there have been few serious shortages, but other countries, notably Germany, have suffered both acute shortages and high prices, and in these periods strenuous efforts were made to produce a chemical substitute for rubber.

The extensive research that has gone into finding a substitute for rubber—in which Germany, France, America, Russia and Britain have all played a part—has produced a range of materials which are all like rubber in some degree or other, but which differ among themselves and often quite appreciably from rubber.

It has been agreed to call these materials 'Synthetic Rubbers', and rubber itself is usually referred to as 'Natural Rubber' because it is obtained not from the laboratory or factory, but from a tree. Although the original intention was to find a substitute for natural rubber, very few of these materials can really be called substitutes. Many of them have quite unique properties which enable them to be used where natural rubber cannot be used at all, for example, at high temperatures or where the material must come into contact with oil. Others have somewhat similar properties to natural rubber and can be used instead of it, for example, in making tyres.

The position of synthetic rubbers has only become established, however, since the end of the last war. Before this the synthetic rubber industry was the Cinderella industry. When a shortage of natural rubber occurred it was encouraged, when adequate and cheap supplies of natural rubber were available it was ignored. But since the end of the last war it has become generally accepted that synthetic rubber has a part to play in commerce alongside natural rubber.

Today synthetic rubber plants are springing up all over the world. Britain, after many years without a synthetic rubber industry of her own, has recently re-entered the field with a large plant at Hythe, near Southampton, and several smaller ones elsewhere.

The future is bright for synthetic rubber. More than 3,000,000 tons of rubber were consumed in 1959, of which synthetic rubber made up over a third. But with the expansion of the motor industry the demands for rubber are increasing every year, in all countries of the world. Stepping up the production of natural rubber is a slow business, as it takes seven years before a newly planted rubber tree is able to supply natural rubber regularly. Even if the newly developed high-yielding trees are planted extensively, most authorities are agreed that natural rubber production will not be able to keep up with the requirements.

The solution lies in making greater use of synthetic rubber. In this country synthetic rubber has been imported since about 1944, but the volume has not been very large. In the early days the quality was markedly inferior to that of natural rubber. Today the position has changed. British manufacturers have adequate home-produced supplies of a range of the latest synthetic rubbers available, and their properties and qualities are a great improvement upon earlier varieties.

The object of this book is to explain what these various rubbers are, how they behave, and why they behave as they do. As synthetic rubbers are now being made in this country and will play an important part in the future of the rubber industry, most of this book is devoted to them. How they are made and how they compare with natural rubber is discussed in the appropriate place.

To enable a reasonable comparison to be made between natural rubber and the various synthetic rubbers the subject has been treated from a scientific standpoint, and to keep the size of the book between reasonable limits much technological information has been omitted. Because of the comparison between natural and synthetic rubbers the first section of this book is devoted to natural rubber. In this section the fundamentals of rubber science are introduced, to be developed later in connection with the synthetic rubbers.

This book is intended as an introduction to a complex subject, and as a survey or report for non-technical readers who wish to know something about rubber. The reader who requires further information on a particular point or topic should consult the bibliography at the end of the book.

PART ONE

Natural Rubber

1

The story of natural rubber

The early history

Although the widespread use and development of natural rubber is comparatively modern, rubber was known in very early times. There is some evidence, for example, that rubber was used—notably for play-balls—in Ethiopia, and from there a ball game spread to Egypt. The use of rubber never became widespread in Europe, however, until the nineteenth century, and this may be connected with the distribution of rubber-bearing plants.

Natural rubber is a product of many trees and plants. But it can only be obtained reasonably easily, and in large enough quantities to make its use worth while, from a few types of tree. These trees were not very common in the Old World, but they occurred much more frequently in the New. It is not very surprising, therefore, that rubber has been known and used by the natives of South America for a very long time.

Columbus is usually given credit for having been the first of the modern Europeans to see natural rubber, and it is said that he brought back rubber play-balls which he obtained from the natives of Haiti on his second voyage in 1493–6. This information comes from early Spanish records of about 1535; and most of the early information on rubber comes from Spanish or Portuguese authors describing the wonders of the New World. It is reported that Cortez, the Spanish conqueror of South America, watched a ball game at the court of the Aztec king Montezuma II. According to Captain Fernandez de Oriedo, the official historian of the Indies, writing in

1535, the game was called 'Batey'. It was played between teams of ten or more in a high-walled court with a line across the middle like a tennis net. The object of the game seemed to be to knock the ball—three or four inches in diameter and solid rubber—through stone rings set vertically in the court walls at each end of the line. This scored a goal. There appeared to be a certain amount of religious significance attached to the game, though heavy betting on the result was not unknown.

The historian makes particular reference to the rubber balls, which 'bounce much higher than our balloons'. This is presumably a reference to European balls, which would be of leather and inflated. The Indian ball, if dropped from the hand, bounced up again nearly to the height of the hand. To the early Spanish explorers this must have seemed wonderful, for there was no material known then—and there are very few now—which can approach natural rubber in its ball-bouncing qualities.

A few years later F. J. de Torquemada wrote of a tree which exuded a white liquid when its trunk was struck with a hatchet. The South American Indians collected this liquid in vessels, or, if they had no vessel handy, allowed it to run over them and dry out. On drying out the liquid left a clear brownish film of the tough elastic substance we now call natural rubber. The Indians peeled the pieces off, boiled them in water, and shaped the rubber into balls or other articles. The liquid itself—usually now referred to as latex—could be smeared onto cloth, and the resulting film of rubber made the cloth waterproof.

The Spanish, records de Torquemada, used rubber to wax their cloaks against the rain. 'They were impervious to water, but the sun ruined them.' This is an early reference to one of the grave disadvantages of untreated natural rubber—raw rubber as it is usually called. In the hot sun raw rubber eventually goes sticky and smells badly. Nevertheless, the Spaniards in South America made good use of rubber. They solved the problem of transporting the liquid metal mercury by using hemp or linen bags insulated with rubber, the bags having the additional advantage of being flexible. They impregnated a great many different materials with rubber and made small cloaks, boots, shoes, carriage-tops and outside coverings for many articles.

Very little rubber seemed to filter across to Europe, and most people, including scientists, remained in ignorance of the new material. A start was made in remedying this situation in 1736, when the French Academy of Science sent a survey party to Peru. The object of the survey was to measure an arc of the meridian at the Equator, and the expedition was led by Charles de la Condamine, a noted astronomer. La Condamine was also a keen naturalist, and from Quito in Equador he sent back some samples of rubber to the French Academy. He also wrote a covering note describing how the Indians reported collecting the white syrup of various trees and drying it over fires. Smoking rubber is a process which is still carried out today.

La Condamine also made what must have been an extremely hazardous journey for those days. From Quito on the west coast of South America he crossed the Andes and followed the Amazon down to Para near the mouth of the river on the east coast, a journey of well over 2,000 miles. From Para, la Condamine travelled north along the coast to Cayenne in French Guiana, and there he made the acquaintance of François Fresneau, an engineer employed by King Louis XV of France. Fresneau was also a keen naturalist and interested in rubber. He had seen many samples of natural rubber, brought by Indians from the interior, but he had never seen a tree that produced it. In fact, few Europeans had, for rubber trees were thinly scattered and grew deep in the jungle.

Fresneau spent 14 years looking for the source of natural rubber, patiently searching out and examining many trees before finding the one he was looking for. He carefully noted a description of the tree, and made a pair of boots from its rubber. Then he wrote to la Condamine and the latter read his report to the French Academy. Fresneau's work also gave the first indication that several kinds of trees produced rubber and, later, rubber-bearing plants were found as far afield as Africa and Madagascar. He also reported that freshly dried rubber, or even a freshly cut surface, tended to stick to itself, the joint being quite as strong as the rest of the rubber.

Thus he stumbled across a very important property of rubber, the property of tackiness or 'tack' as it is usually called. In the early days it was more often a disadvantage than an advantage; but later, use was made of it, and today it would be very difficult to build a tyre without it.

Fresneau made another very important contribution to the knowledge of rubber, and thereby assisted in the birth of the rubber industry. At that time rubber usually reached Europe in the form of rubber balls or boots and shoes, and they were exceedingly inconvenient for fashioning into other articles. The milky sap from the tree, latex, was difficult to transport as it quickly fermented if left exposed to the air. A solvent was needed which would dissolve the rubber. The rubber solution could then be applied directly to cloth, or poured into a mould, or even on to a flat surface, so that when the solvent evaporated an easily manipulated film of rubber would be obtained.

There were very few suitable solvents available, and Fresneau discovered that turpentine was the best. The result was not completely satisfactory, as the film of rubber it left after evaporation tended to become very sticky when hot, and hard and brittle when cold. But it was better than nothing, and Fresneau duly sent off a report to his senior minister in the Government service. Within two months, however, two French chemists had reported similar findings.

The beginnings of the rubber industry

With the discovery of a solvent for rubber the way was open for rubber manufacturing to begin. There were still many difficulties to overcome, probably not the least being the popularization of a rather unprepossessing-looking material, and it needed men of foresight and technical skill to develop it. The adventurous French balloonists began to use rubber to cover their balloon fabrics, and in 1803 a small factory was erected near Paris to manufacture elastic bands.

Interest was awakening in the new substance on this side of the Channel. Up to this time rubber was known by a variety of names of which 'gum elastic' was probably the most common. In 1770 Joseph Priestley, the discoverer of oxygen, remarked that gum elastic would rub out pencil-marks from paper, and so the name 'rubber' was born. Probably the first impetus to the rubber industry in Britain came with the beginning of gas lighting in this country. In 1815 there were 4,000 gas lamps in London, and gas undertakings were springing up in each large town. In 1819 Charles Mackintosh, a dye manufacturer of Glasgow, decided to buy the coal-tar by-products of the Glasgow gas works. He was able to sell the pitch, and to obtain this he had to distil off the lighter oil. This lighter oil, called coal-tar naphtha, proved to be an excellent solvent for rubber. Not only that, it gave a much less sticky rubber on evaporation than did turpentine. The film of rubber after evaporation was still a little sticky, but Mackintosh got over that by laying down a film of rubber on some woollen cloth and covering the sticky surface with another layer of cloth.

This was the original Mackintosh waterproof fabric. The result was by no means perfect. The rubber still smelled rather badly in hot weather, tended to become hard and brittle when cold and never lasted very long; but it was a great improvement on anything that had gone before. Mackintosh took out a patent in 1823 and established a factory in Manchester.

One of the first people to apply for a licence to use Mackintosh's discovery was Thomas Hancock. Hancock and Mackintosh probably started their careers in rubber at about the same time. Hancock was a coach-builder in London when he became interested in rubber, and in 1820 he opened a small shop for making elastic tops for gloves, waist-bands and pockets ('to prevent their being picked'). He cut the rubber into thin strips for sewing into the material and thereby collected a lot of waste pieces. Trying to find a way of utilizing them, he too found that newly cut rubber was tacky, and he was able to stick small pieces together. This suggested a solution to his problem. If he could tear the rubber up small enough he might possibly make a flat sheet. There was an obvious need here for a machine, and Hancock promptly designed one.

Hancock's machine, which is the forerunner of the modern

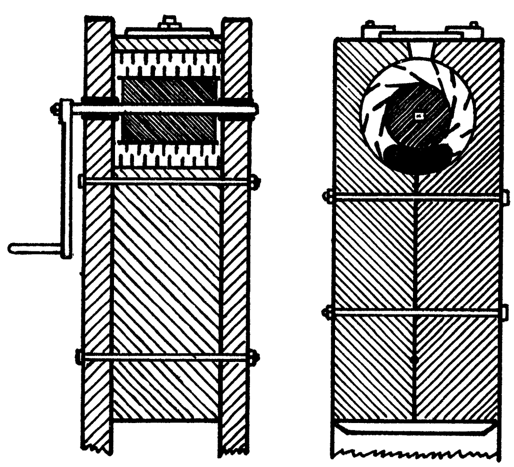

FIG. 1. Hancock's 'Pickle'

internal mixer, was called the 'pickle' to keep the idea secret from competitors (Fig. 1). The machine consisted of a hollow drum lined with teeth. Inside this was a cylinder, also equipped with teeth, which could be revolved by means of a handle. Hancock's idea was to put in a charge of rubber and tear it into small pieces by means of the revolving teeth. He found, however, that it required a great deal more power to turn the handle than he had expected, and the rubber got very hot in the process. When he took it out he found that instead of being in pieces the rubber had turned into a soft plastic ball.

This process is now known as mastication. When the rubber is in this soft and dough-like condition solid powders and even liquids may be mixed into it quite easily. Hancock himself mixed pitch, tar and various other materials into rubber to improve its qualities. This discovery of Hancock's is the basis of the modern rubber industry, for not only does mastication allow various substances to be mixed into rubber, but in the plastic state rubber can be moulded into any desired shape.

Goodyear and vulcanization

Although Hancock and his contemporaries were making great strides in the manufacture of rubber articles, they were not blind to the disadvantages of their raw material. It was very adversely affected by changes of temperature, and in continuous use quickly lost its strength and elasticity.

Many of the early pioneers believed that the root of the trouble lay in the choice of solvent. There was probably more than a grain of truth in this idea, for it seems that the early disasters of the young rubber industry in America may be directly attributed to the use of turpentine, which was almost the only solvent used there. The first rubber boom unfortunately coincided with hot weather; many of the products were ruined, and many newly formed rubber companies went bankrupt.

A company which survived the early troubles was the Roxbury India Rubber Company, begun in 1833 by Edwin M. Chaffee. Chaffee was one of the pioneers of rubber, not because he improved the substance very much, but because he invented two of the most important machines now used in rubber processing. Independently of Hancock he invented a machine which would masticate rubber. It was simply two steam-heated rollers, revolving at different speeds.

Rubber inserted between the rollers was squeezed and torn at the same time and was soon reduced to a thin plastic sheet on one of the rollers. Chaffee found that masticated rubber dissolved in solvents much more easily than rubber which had not been masticated, and he was able to keep his turpentine down to the minimum.

This machine of Chaffee's was the forerunner of the modern mixing mill, and it had the rollers placed horizontally. Chaffee also tried putting the rollers on top of each other, and found that he could coat fabric with rubber in this way. This machine was the forerunner of the modern coating machine or Calender. Chaffee's machine actually had four rollers and weighed nearly 30 tons. It was referred to as the 'Mammoth'.

Chaffee's inventive genius enabled his company to survive many of the early disasters which overtook his competitors, but the company did not prosper. In 1836 the Roxbury Company was approached by an inventor called Charles Goodyear, who suggested a new type of valve for an air cushion. Goodyear had been interested in rubber for some years, but it seems that this was his first contact with the grim realities of the rubber situation. He became interested in the problems of rubber and set out to try and solve them.

Goodyear and Hancock must be considered the two outstanding figures in the history of natural rubber, yet the contrast between them is astonishing. Hancock was industrious and phlegmatic. As each problem presented itself he set to work to solve it carefully and systematically. When he had made his discoveries he patented them, taking great care that they were not easily infringed. He was a good business man and steadily built up his own business, collaborating with Mackintosh when necessary and eventually going into partnership with him.

Goodyear was a visionary. Originally he wanted to enter the Ministry, but was dissuaded from this course by his father who sent him into business in Philadelphia. But Goodyear was never a success in business, and throughout his life trailed a succession of debts behind him. At times he conducted his experiments in prison. Yet in spite of all this and constant ill-health, he retained a conviction that rubber could be 'cured' of the effects of temperature, stickiness and its other adverse properties.

Goodyear realized that improved mechanical treatment of rubber would not solve the problem, and a better choice of solvent was only a partial answer. It seemed that some sort of chemical treatment was the only solution. Goodyear tried mixing into rubber, therefore, everything that he could possibly think of. After many trials, magnesia seemed to give good results, but a spell of hot weather quickly disposed of this theory. Later, boiling rubber with lime seemed to have solved his problem, but once again he was quickly disappointed. At one stage in his experiments he used nitric acid to remove some bronze powder from rubber, and discovered that the acid left the rubber surface hard, leathery and definitely not sticky. Goodyear was convinced that this was the treatment he had been looking for, and he took out a patent for his 'acid gas' process.

Unfortunately the acid gas process did not stand the test of time, because the treatment only took place at the surface of the material and the acid did not penetrate. Nevertheless Goodyear managed to sell some licences for his patent. He sold one to the Roxbury Company and thereby came into contact with a certain Nathaniel Hayward, who was working with the company and who had a patent for mixing sulphur with rubber and exposing it to the sun. Goodyear became interested in this idea, bought the patent, and with Hayward began experimenting and manufacturing. But the effects of the acid gas process and the sulphur treatment proved to be only temporary, and soon they were faced with failure. Unfortunately Goodyear had undertaken the production of a large quantity of mailbags for the United States Government, and the failure of his processes led him into debt again.

After his despair came success. One of his experimental samples, in which sulphur had been mixed with rubber, was accidentally left on a hot stove all night. The rubber charred, instead of melting as ordinary rubber would have done, and Goodyear noticed that it had certain leathery properties. Heat, he reasoned, might be the answer. If he could heat his rubber-sulphur mixture for just the right length of time it might give the change he was looking for. After more experiments Goodyear found that it did—and he was surprised by the extent of the change. He had begun with raw rubber which, though it had a certain amount of elasticity, was generally poor in physical properties. His sulphur and heat treatment converted it into a much stronger material, with much more elasticity, and, more important as far as he was concerned, it remained largely unaffected by changes of temperature and did not become sticky.

Having discovered the secret of changing or 'curing' rubber, he could make no one believe him, and for some reason best known to himself Goodyear did not patent the discovery until five years after he had made it. His patent was issued in 1844.

In about 1842 Hancock received some pieces of rubber which had been treated by an unknown process. The rubber was impervious to heat, did not become sticky and was not much affected by solvents. The pieces were brought from America by the agent of the inventor, who was, it must be assumed, Goodyear.

Hancock was interested in the rubber and he began experimenting. He says that the pieces he examined smelled slightly of sulphur and presumably he used sulphur in his experiments. He also found, as Goodyear had done, that the last decisive step—that of using sufficient heat—was the most difficult to discover. But after many experiments he did discover it, and by immersing rubber in molten sulphur he was able to reproduce the change effected by Goodyear. He also noticed that some of his pieces of rubber, which were left

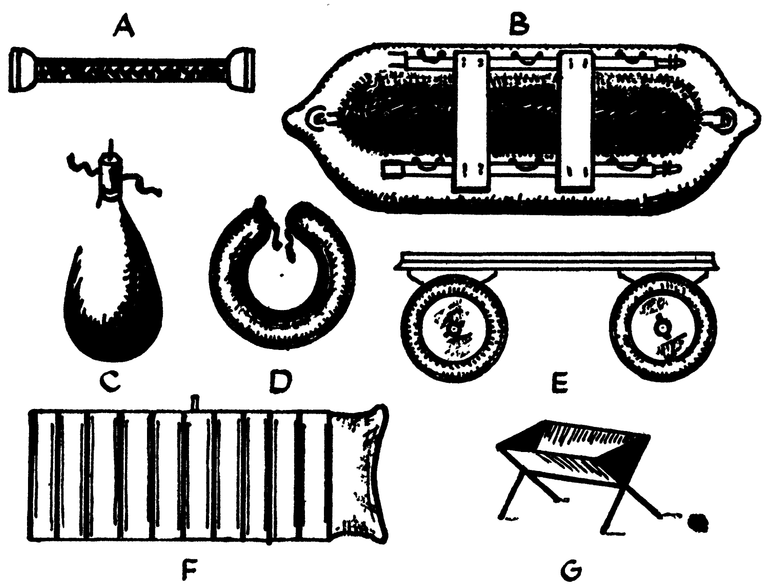

FIG. 2. Some articles described by Goodyear and Hancock
A. Chest expander. B. Inflatable boat. C. Rubber buoy. D. Life jacket. E. Noiseless railway-truck wheels (these were actually adopted by British railway companies in the 1930's). F. Inflatable mattress. Hancock invented the system of division into compartments (reeding) still in use. G. Child's bath (this model was marketed as the latest and best about 1935). A, C, D and G are from Goodyear (1855), B, E and F from Hancock (1857)

longer in the molten sulphur and nearer the bottom of the pot—that is nearer the fire—became hard and brittle. Thus he discovered what is now known as Ebonite. Hancock's patent was issued in 1843. The process was called 'vulcanization' by one of Hancock's colleagues, and the name was adopted generally.

It is clear that Goodyear first discovered vulcanization, but Hancock secured the English patent rights to it, and so Goodyear lost financially and in recognition. Goodyear's story after this is but a continuation of what went before. He patented over 200 applications of rubber and died in 1860, in New York, leaving his widow debts of over 200,000 dollars. The great rubber company which bears his name, the Goodyear Tire and Rubber Company, was formed 38 years after he died.

Hancock, on the other hand, died in 1865 a comparatively wealthy man. He, too, had a long list of patents and inventions to his credit. Between them these two men discovered an astonishing number of uses for rubber. Many of them are still in use today, and many are being rediscovered.

Plantation rubber

In the time of Goodyear and Hancock rubber came mainly from South America, although Goodyear reported receiving supplies of rubber from Java, Penang, Singapore and Assam. It was steadily becoming obvious, however, that though rubber could be obtained from quite a number of trees and plants, the best rubber came from one type of tree only. This tree grew in South America, and its botanical name is *Hevea braziliensis.*

The supply of rubber was often in the form of shoes, fashioned by the natives of the Amazon, and these were actually worn in the United States. The supply to Europe was usually a mixed bag of shoes, rubber balls and many other articles, which were usually used only as raw material. Apart from the unsatisfactory way the raw material was shipped abroad, the difficult and often disorganized collection of the latex made a few far-sighted people wonder whether rubber trees could be systematically cultivated. Hancock was one of these, and as early as 1835 he suggested cultivating the best type of rubber tree in the East and West Indies. Nothing very much was done about it then, but in 1855 we find him corresponding with Sir James Hooker, Director of Kew Gardens, London. Hooker eventually managed to interest an assistant secretary at the India Office in