THE DEVELOPMENT AND USE OF SYNTHETIC RUBBER IN THE U.S.A.

BY

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When the oral invitation of Dr. Baptiste to talk in Colombo was given me in November, 1957, at the B. F. Goodrich Research Center in Brecksville, Ohio, it was agreed that my remarks would cover the development, production, and use of synthetic rubber in the U.S.A. But, as the Director has recently chosen to have the talk presented before a larger group than the Board of Directors of the Rubber Research Institute of Ceylon, the scope of the subject matter has been enlarged to include mention of certain researches as the foundation stones upon which a new industry has been designed and built.

Prelude.—Michael Faraday, the pioneer scientist and progenitor of the electrical industry, made an analysis of "India rubber" in 1826 at the request of his friend Thomas Hancock, pioneer of the rubber industry in England. This noteworthy analysis of Faraday established rubber as a hydrocarbon $(C_5H_8)\times$.

Interlude.—William Tilden, teacher of organic chemistry, reviewing earlier work by French and German scientists became convinced (1882-1886) that isoprene C_5H_8, boiling at 30°C was the molecular unit from which the chemist could make rubber. He pried into this corner of the unknown on a test-tube scale, was rewarded when specimens of isoprene set aside in a well-lighted place were observed to have changed to a solid jelly with properties resembling rubber. He let his observations be known in lectures and in papers. It was a subject that was soon to be involved in international jealousy between scientists in France, Germany and England, each group trying to establish priority for its own nationals in the realm of discovery of "synthetic" rubber, a quest in which not a single one of these scientists proved to be successful.

Before 1914 two companies working in the U.S.A. (Hood Rubber Company, Watertown, Massachusetts, and Diamond Rubber Company, Akron, Ohio) made and built articles of synthetic rubbers derived from isoprene, butadiene and dimethylbutadiene, and the I. G. Farben, Germany, had tires made and cured from a rubber of the dimethylbutadiene type derived from acetone. None of these ventures were commercial successes, and they served mainly to emphasize that in research, as in love, the true path never runs smooth.

Interval between World Wars.—Dr. Duisberg, I. G. Farben founder, with unsupported pride in German progress, had the Kaiser's car equipped with tires of W rubber (based upon acetone). The idea of making W rubber compete with natural rubber proved fantastic and was abandoned, but Dr. Duisberg, with indomitable belief in German superiority, in 1924 organized anew the search by the I. G. scientists for a workable synthetic rubber, a quest that led later to the Buna rubbers.

It was also in 1924 that the Du Pont Company started research in the U.S.A. toward a synthesis of rubber with an appropriation of a half million dollars to support it.

In 1926, The B. F. Goodrich Company employed Dr. Waldo Semon, a research scientist to hunt systematically for a novel method of making chemical rubbers.

During the decade 1930-40 these three independent projects succeeded in producing new chemical rubbers and in developing their syntheses past the pilot plant stage into commercial production.

Du Pont's Neoprene, a polymer of 2-chlor-butadiene was the first diene synthetic rubber stemming from these post-War I researches to be made commercially. Acetylene and hydrochloric acid are the source materials. Wallace Carothers of Nylon fame was one of the inventors of Neoprene.

The Buna Rubbers and Ameripol.—The studies in Germany by I. G. Farben and those in Akron by B. F. Goodrich originated copolymers that were made by joining simpler chemicals (monomers) in a water emulsion. The resulting latex had to be coagulated with significant deviations from the steps followed in natural latex coagulation to yield the solid form of synthetic rubber. The formation of a latex from a water emulsion of chemicals gave marked chemical engineering advantages over previous methods, *viz.* the handling of liquids with proportioning pumps and meters, the precise control of temperature, and the maintenance of a delicate heat balance since the rubber formation is a heat-producing step, and unless heat is bled off the product is inferior.

The predominant monomer used (usually 70-75%) to make general purpose rubber was butadiene. The choice of secondary monomers and the control of operating conditions determined the types of synthetic rubber produced. In Germany the "lettered" Bunas, Buna N, Buna S, etc. and Perbunan were sold by the I. G. Farben to the rubber consumers to be fabricated into articles. In Akron 1940, synthetic rubber appeared dramatically on the market as the "Ameripol" tire, all of the steps in both synthesis and article manufacture being performed within The B. F. Goodrich Company.

The key chemicals involved in the synthesis of rubber are the dienes. Charted by formulas, they are these:

$CH_2=CH\text{-}CH=CH_2.$	Butadiene.
$CH_2=\overset{CH_3}{C}\text{-}CH=CH_2.$	Isoprene, 2-methylbutadiene.
$CH_2=\overset{Cl}{C}\text{-}CH=CH_2.$	Chloroprene, 2-chlor-butadiene.

These compounds are all diolefines which is another way of saying they contain at least four carbon atoms, and the same arrangement of double

$$\underset{1}{C}=\underset{2}{C}\text{-}\underset{3}{C}=\underset{4}{C}$$

bonds, which to the chemist indicates (1) the possibility of this molecule reacting in at least four different ways, and (2) the release of a definite quantity of energy as heat for each type of reaction initiated. Of the four types of reaction possible (neglecting others as less probable), one is preferred and the other three are to be avoided if possible. The properties of the resulting rubbers depend on how well the chemists and chemical engineers have been able to divert the chemical step (polymer formation) into the precise path that it should follow. Fortunately, researches have cleared up most of the obscurities which formerly surrounded the polymer forming step so that scientists and engineers can set up and adhere to rigid specifications of both process and product.

Isoprene, which Tilden had favored as the source of a chemical rubber, is not readily or cheaply available even in the modern chemical industry, although petroleum can be made to furnish isoprene by off-beat methods of manufacture. Chloroprene is the product of a special chemical reaction not likely to be in demand for purposes other than making Neoprene. Its cost, like that of isoprene, seemed destined to be fairly high. But butadiene of high purity at low cost can be made abundantly by fractional purification from cracked petroleum. Hence, butadiene became the preferred member of the diene family for rubber synthesis.

Butyl Rubber.— In 1940 the Standard Oil Company of New Jersey announced the discovery of Butyl rubber, properly termed a petroleum rubber since over 95% of its weight is derived from isobutylene, a cracked petroleum fraction, and less than 5% from isoprene. This, depicted in broad strokes and with minor omissions, is the status of synthetic rubber research and development at the time the Japanese invaded South-East Asia and cut off 90% or more of the world's natural rubber.

The Standard Oil Company of New Jersey had acquired from Germany the right to license others to make the Buna rubbers developed by I. G. Farben. By 1942 at least two of the large rubber companies had small plants erected to make Buna rubber. Together with the Du Pont plant to make Neoprene and the B. F. Goodrich plant to make the Ameripol and the Hycar-type synthetic rubbers, the total capacity of the country was limited to a production of only a few thousand long tons a year of synthetic rubber.

The individual companies who faced the need to manufacture synthetic rubber after the start of World War II were unable to command enough capital to do the whole job. Congress was asked to empower the Government to build large plants in the interest of national security. The officials appointed to formulate plans could not decide just how large the plants should be. After a lapse of two years with nothing done, the Japanese blew up Pearl Harbor and invaded South-East Asia.

Magnitude of the Problem after Pearl Harbor.—

(1) The rubber requirements of the U.S.A. and her allies were ca. a million tons a year.

(2) The raw materials for synthetic rubber had to come from sources in great demand for other purposes in the war period; for example, aviation fuels, foodstuffs, etc.

(3) The course followed had to equip the country, although at war, with both Germany and Japan, to make the rubber and to convert it by mass production methods into fabricated articles at a rate double that of any period in the previous decade.

(4) The work of the Baruch Committee, consisting of two scientists and a philanthropist, gave us the blueprint and the schedule that had to be followed. The plan which proved workable within the dates set by the committee included:

(*a*) The appointment of a "rubber czar," initially William Jeffers, served to mobilize the brains and the vast resources needed to get on with the job.

(*b*) The immediate increase of facilities for making reclaimed rubber which helped a great deal, especially during the first year of rubber famine.

(5) Congress empowered the Government to build and run 52 plants which cost over $700 million to make GR-S (Government rubber-styrene type), butyl, Neoprene, and minimal amounts of rubber of other types. By the end of 1943 all plants were operating. A million tons of rubber were made in 1945.

(6) Technical information from all sources were pooled under the "rubber czar" and extensive research studies were organized, *de novo*, under Government direction to support the project and to anticipate improvements. Improvements in both process and product were not slow in coming and continued steadily.

(7) Government spent up to $5 million a year on research and brought scientists from universities, from industry, and from research institutes to apply joint efforts to the problems.

(8) Patents were pooled for the duration of the emergency under orderly provisions set up promptly by Government agencies.

It would have been very easy in 1943 to take a pessimistic view of the whole program of Government rubber, with three-fourths of a billion dollars spent, and the copolymer plants turning out increasing tonnages of a product that the rubber technologists did not know how to use. Fortunately, the pessimism concerning our efforts in America was confined to Germany where their rubber scientists assured the Wehrmacht that our efforts were doomed to disaster, and the Baruch plan could not possibly be made to work. After all, the composition of the Baruch Committee with two college presidents and a philanthropist lent some credence to this viewpoint.

However, in our country there was no occasion for gloom. We recognized the competence of Dr. Conant and Dr. Compton as trained research investigators who had consulted the best sources of information and had omitted no detail in their study. We knew that as they had planned our work and scheduled the goals precisely, that we had to work the plan and meet the deadlines set.

Interlude on Latex.—Mention has been made of the emulsion process synthetic rubbers (GR-S, Buna S, Buna N, the Hycars, etc.) in which the rubber is derived in the form of a latex. Significant is the small size of the latex globules in these copolymer rubbers (less than one-tenth the diameter of the particles in natural latex). Adsorbed on the surface of the fine synthetic rubber particles are non-rubber ingredients (soap predominantly) in much higher amounts than in Hevea latex. These impurities occasioned special problems in handling the latex and standardizing the quality of the rubber in the Government plants.

Now, if you will pardon a digression, there are a few personal observations that I should like to make pertaining to best methods of conducting researches. The best way to solve difficult problems is to have gifted scientists who have made fundamental studies long enough ahead of time to be prepared for the challenge when it becomes necessary to meet it. "Then," to quote Milton, "if virtue feeble were, Heaven itself would stoop to her."

The B. F. Goodrich Company after 1926 had a continuous interest in rubber latex. After 1933 they maintained the Malayan research laboratory at Kuala Lumpur under Edwin Newton to study rubber at the source. Incidentally, Edwin Newton helped develop the Anode Process for making articles from natural latex and it is not without point that he was a pioneer in the emulsion polymer field of the vinyls.

Associated with Mr. Newton at Kuala Lumpur were Edward Willson, colloidal chemist, and W. D. Stewart, biochemist. It is not the purpose of this discussion to relate the story of the Malayan adventures of these research men beyond mention of their acquaintance with rubber at the tree, a curious admixture of hydrocarbon, protein, enzymes, catalases, sugars and mineral impurities. But based on the plantation speaking acquaintance with Hevea, Willson and Stewart were destined to make strategic contributions to the synthetic rubber program in the U.S.A. Willson's work related to cleaning up the impurities on the minute synthetic latex particles, and it was done promptly and unobtrusively in the shakedown runs of the polymer plants. It would be oversimplification to say that if you want to remove salts, more salt should be added, but in actual operation it seemed almost that simple.

The invention of cold rubber by W. D. Stewart was suggested by his knowledge of tree rubber, where the rubber never exceeds 38°C in temperature. Stewart was prompted to look for catalysts that functioned in synthesis more nearly like enzymes in living systems. "Cold rubber" patents, the property of The B. F. Goodrich Company turned over to the Government in wartime, were the basis on which millions of tons of "cold rubber" were made in the GR-S plants. Cold rubber gave advantages over GR-S in both the uncured and cured state. It was the sustained extra effort of talented research scientists like those just mentioned that made the synthetic rubber produced a little better than seemed necessary.

The Use of Synthetic Rubber.—Now we come to the little known and unheralded story, the use of synthetic rubber. GR-S, the main purpose Government rubber which issued in volume from these polymer plants, was a commodity unknown to 95% of the factory compounders in 1943. It seemed not at all suitable to serve as a basis for military and civilian goods needed to win the war.

GR-S had poor building tack. It took more time on the mill. The batches did not knit well together. The building plies required cementing. The union with tire cords upon curing was defective. GR-S carried more fatty acids initially than crude rubber, so the helpful addition of more stearic acid or lauric acid, as in previous practice, to effect cure was not permitted. It took only two-thirds as much sulfur as natural rubber had required and all recipes, all mixing specifications, all building instructions, and all curing procedures had to be revised promptly and in the face of inadequate information. As if the devil himself had a hand in it, it was mandatory in the same period to swing over the cords of 90% of the tires from cotton to high tenacity rayon. It was found unsound to blend synthetic with natural rubber, so the crippled compounder could not limp along on that crutch. He had to solve one after another of these burdensome problems with little help from anyone. So, that is what he did!

It was soon discovered that the handling of GR-S stocks in internal mixers operated at higher temperatures with 20% more material and at speeds a third higher than for natural rubber batches gave stocks that handled well. Resorcinol-formaldehyde latex treatment of the cords gave uniform bonding. The cleanliness of the rubber in the bale led to fewer carcass defects, and the tread wear of tires with GR-S was brought to a level as good as or better than with natural rubber. A structural carbon black later originated by the petroleum companies bettered tread wear by another 15%.

In the manufacture of rubber articles during World War II, there was voluntary exchange of technical information between rubber manufacturers. This exchange was promoted by technologists appointed by the rubber czar, but not even the rubber czar had the authority to order this action by the competing rubber companies. The voluntary exchange basis proved highly effective as an educational step to all parties involved.

Patents and research information in the field of synthetic rubber manufacture were made available to the Government under separate contracts with those who supplied the starting hydrocarbons (the petroleum industry) and with those who operated the rubber plants (the rubber industry). These contracts had dates of termination which were scrupulously observed. All the plants have been sold back to private business after roughly a dozen years' operation by the Government, in which profit was earned, $50 million in one year. The sale netted the Government 96.3% of the fair evaluation set upon these plants in 1955. The fair valuation was about half-way between the book value of the plants fully depreciated, and that value without any depreciation.

The use of general purpose synthetic rubber over fifteen years in our country and its acceptance on a quality basis make it probable that we shall never base as much as 50% of our nation's rubber requirements on natural rubber, even with a constantly increasing demand for natural rubber. Especially in the form of latex, this demand promises to be brisk.

Natural rubber, regardless of origin, is destined in the future to compete with butadiene rubbers. Butadiene stripped out of cracked petroleum is the basic economic unit of general purpose rubbers made by synthesis. A fair average price for butadiene of 12 cents a pound enables the producer of GR-S to sell this rubber at 24 cents. Some day, it is reasonable to expect that cheaper hydrocarbons than butadienes may be fashioned into rubbers that will undersell those derived from butadiene.

Research has recently been able to duplicate the molecule of natural rubber by starting with isoprene and reacting it with contact catalysts. It is the identical molecule that nature produces in at least two thousand living plants, but in no instance more effectively than in Hevea Brasiliensis. The laboratory product is a bit cleaner than natural rubber and free from non-rubber impurities. But it seems reasonable to suppose that it will always be higher in price than the rubbers based upon butadiene, and perhaps in the price range of Neoprene. Scientists place this discovery in the front rank of chemical achievements. As a citizen of a country which has consistently supported the United Nations, I hail this achievement as having removed one more possible threat to world peace. The world can never again be cut off by military occupation from 93% of its supply of rubber as a raw material.

To you in Ceylon who are interested in the future growth and health of rubber production, I congratulate you upon your faith in and support of research. Whatever course the rubber growers may face in the future, there can be no question that the results of scientific studies will give the information that you need to solve your problems. There is no royal road to success, no crystal ball gazers, no advertising ballyhoo artist who can benefit you. Place your trust in the truth and in scientific inquiry which invariably leads to it.