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Synthetic Rubber for World War II and After

ABSTRACT

Synthetic rubber is essential for products used “at work, at home, at play, even [during] travel.”[1] Scientists began experiments to make synthetic rubber in the late 19th century, but they were not able to produce usable rubber until the mid-20th century. Japanese occupation of Malaysia early in World War II necessitated the U.S. government to launch massive synthetic-rubber development and production programs to produce rubber tires (and other rubber products) required for warfare. These developments formed the basis of that delivered the current synthetic-rubber industry. Following the end of World War II, the new synthetic rubber industry gave rise to political tensions in Great Britain and Southeast Asia. Chemists and chemical engineers have refined the synthetic rubber process such that production of synthetic rubber today exceeds that of natural rubber.

INTRODUCTION

The first half of the 20th century saw a remarkable increase in the need for synthetic rubber due to a booming motor-vehicle industry and because fluctuating natural-rubber prices destabilized the rubber market. At the turn of the 20th century, scientists had begun experimenting with polymers to develop synthetic rubbers suitable for motor-vehicle tires. However, early development was not successful until World War II when the United States established the American Synthetic Rubber Program that, for the first time, successfully organized the first large-scale synthetic rubber production. Synthetic rubber was a necessary

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[1] International Institute of Synthetic Rubber Producers, Inc., *Synthetic Rubber.* 13 April 2007. < http://www.iisrp.com/synthetic-rubber.html>

replacement for the United States war effort because the prevailing source of natural rubber, Malaysia, was occupied by the Japanese army. The American Synthetic Rubber Program was not only among the most "highly technical and complicated engineering jobs of all time,"[2] but also central to winning a "war, more than any war in history, [that was] a conflict of materials and resources, as well as a battle of men."[3]

BACKGROUND

Shortly before World War II, America was using one half of all rubber consumed in the world; 97% of that was imported from Malaysia, making rubber America's largest single import. The rubber industry, oft under-estimated, provides crucial support for numerous major industries that define the national economy. [4] 75% of all rubber produced was used for rubber-tired vehicles, airplanes, and tanks. Major industrial operations, such as manufacture of raincoats, shoes, hygiene products, and other consumer goods, required rubber not only in their products but also in the machinery that manufactured these products.[5] The importance of an adequate supply of rubber was recognized as early as the 1920's because natural rubber from British Malaysia was subject to large price fluctuations and export restrictions; the unpredictability of the natural rubber market stimulated the creation of several small, private American synthetic-rubber research programs.[6]

The threat of a rubber shortage was imminent in the late 1930's as international tensions increased. Shortly after the attack on Pearl Harbor in 1941, the Japanese exploited this "most

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[2] John L. Collyer. "Crisis in Rubber." *Proceedings of the Academy of Political Science,* Vol. 20, No. 2, Transportation in Wartime and the United Nations. (Jan., 1943), pp. 71-80.

[3] *Ibid.*

[4] R. P. Russell. "The Artificial Rubber Industry." *Proceeding of the Academy of Political Science*, Vol. 20, No. 1, Winning the War. (May 1942), pp. 72-78.

[5] Kurt Bloch. "Rubber Squeeze – Present and Future." *Far Eastern Survey*, Vol. 11, No. 2. (Jan. 26, 1942), pp. 26-29.

[6] American Chemical Society, "Beginnings," *United States Synthetic Rubber Program, 1939 -1945*, 2006, 14 Oct. 2006. <http://acswebcontent.acs.org/landmarks/landmarks/rbb/rbb_begin.html>

vulnerable spot" in the American economy by capturing much of Southeast Asia that produced 90% of the world's crude rubber supply.[7] Consequently, President Franklin D. Roosevelt appointed the Rubber Survey Committee, headed by financier Bernard M. Baruch, to "[get] the 'mostest rubber fastest'"[8] in the face of America's grim rubber shortage. [9]

The government initiated four plans to counter the rubber shortage: stockpile crude rubber via the Rubber Reserve Company established in 1940; develop natural-rubber production in South America; protect Far East rubber supplies with armed forces; and, most important, create large-capacity plants in the U.S. to manufacture synthetic rubber. The first two plans were of little help for solving the rubber problem because crude rubber suffers significant decrease in quality over time and because potential new rubber crops derived from rubber trees or guayule shrubs in South America cannot be produced with sufficient speed or abundance. The third plan of defending rubber supplies in the Far East was pursued unsuccessfully by the British and United States' armed forces beginning in 1942.[10] In January 1942 the Baruch committee asked President Roosevelt to issue an executive order authorizing the War Productions Board to assume 'full responsibility for the rubber program;' 700 million dollars were appropriated for the synthetic rubber industry; during World War II, the synthetic rubber industry grew from four plants [each controlled by one of the "big four" tire manufacturers, B.F. Goodrich, Goodyear, Firestone, and U.S. Rubber] to fifty-one plants operated by various chemical, oil, and rubber companies. This massive government stimulus to synthetic rubber production brought phenomenal growth: production grew from 8,000 long tons in 1941 to 495,000 long tons in 1944.

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[7] William M. Tuttle, Jr. "The Birth of an Industry: The Synthetic Rubber 'Mess' in World War II." *Technology and Culture*, Vol. 22, No. 1. (Jan., 1981), pp. 35-67.

[8] Ibid.

[9] Vernon Herbert, *Synthetic Rubber – A Project that had to Succeed* (Westport, Conn.: Greenwood Press, 1985).

[10] Kurt Bloch. "Rubber Squeeze – Present and Future." *Far Eastern Survey*, Vol. 11, No. 2. (Jan. 26, 1942), pp. 26-29.

[11] In effect, the US Government launched not only an effort to preserve valuable rubber resources, but also a new multi-million synthetic-rubber industry.

HISTORY OF SYNTHETIC RUBBER

Chemists and chemical engineers were hard-pressed to develop artificial rubber. The race to develop synthetic rubber began in the mid-nineteenth century, largely in England and Germany. In 1860 English chemist Greville Williams was arguably the first to isolate and examine the properties of isoprene in rubber. William Tilden, an English chemistry professor at Mason College, Birmingham, was the first to find the chemical structure of isoprene in 1882. In the late 19th century, isoprene was polymerized using hydrochloric acid. In 1910, German chemist Carl Dietrich Harries discovered that isoprene could be polymerized faster by using sodium and that polymerized butadiene, in place of isoprene, yielded a similar rubber-like substance. Harries' discovery seeded not only the first commercially produced synthetic rubber (sodium-polybutadiene,) but also gave rise to the "Buna" rubbers of Germany.

I.G. Farbenindustrie, a conglomerate of German chemical companies, developed Buna rubbers [the first two letters taken from butadiene and the second two letters from "natrium," the German word for sodium] largely to wean Germany from natural, foreign rubber, a practice that was eventually integrated as a part of Germany's Four Year Plan of 1933 to maximize self-sufficiency by eliminating imports of food and chemicals.[12] To lower the costs of synthesizing rubber, I.G. Farbenindustrie switched from sodium polymerization to emulsion polymerization and replaced 25% of the butadiene with styrene. Thus, the Germans created Buna-Styrene (Buna-S,) a cheaper, more wear-resistant synthetic rubber.

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[11] P.T. Bauer. "The Prospects of Rubber." *Pacific Affairs*, Vol. 20, No. 4. (Dec. 1947), pp. 381-390.

[12] The Polymer Science Learning Center and Chemical Heritage Foundation, "Birth of Buna," *The Story of Rubber – A Self-Guided Polymer Expedition*, 2000, 16 Oct. 2006. < http://pslc.ws/macrog/exp/rubber/synth/buna.htm>

Buna-S eventually became the key synthetic rubber of the American Synthetic Rubber Program. America had access to German buna technology prior to World War II because I.G. Farbenindustrie and Esso (now Exxon) had agreed to share knowledge on petroleum products, including synthetic rubber. Although Esso had developed synthetic rubbers independently, namely butyl rubber, that rubbers did not exhibit sufficient resilience necessary for use in tires as SBR rubber, that is, styrene-butadiene rubber, has the necessary resilience.

CHEMICAL PROCESS

SBR accounted for 85% of the synthetic rubber produced during World War II.[13] SBR is a long-chain flexible polymer molecule that re-coils after it is uncoiled (stretched).

During the war, styrene-butadiene polymer was obtained via emulsion polymerization, at 41° Celsius. The most important ingredients are styrene and butadiene monomers. Styrene monomers are obtained by dehydrating the hyperoxide or alcohol that results from oxidizing ethylbenzene. Butadiene is derived by "dehydrogenation of ethylene, by dehydrogenation of butylenes in refineries, or by dehydrogenation of butanes from natural gas."[14] Surfactants necessary for emulsion polymerization are fatty-acid or rosin soaps.

First, soap is dissolved in water until the critical micelle concentration is reached. Second, styrene and butadiene monomers are added with a water-soluble free-radical initiator, such as potassium peroxydisulfate or dodecyl mercaptan. Peroxydisulfate requires high heat, 50°C, to initiate radicals. Propagation occurs in the monomer-swollen micelle (micellular nucleation.):[15,16]

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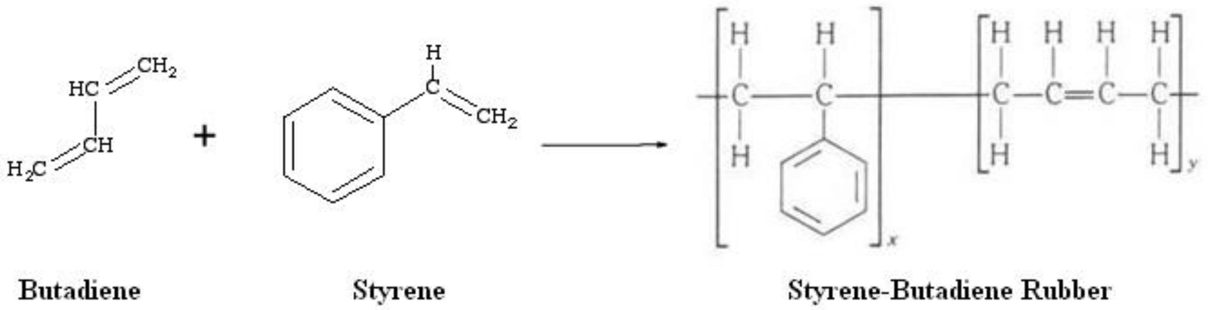
[13] American Chemical Society, "Beginnings," *United States Synthetic Rubber Program, 1939 -1945*, 2006, 14 Oct. 2006. <http://acswebcontent.acs.org/landmarks/landmarks/rbb/rbb_begin.html>

[14] Stephen T. Semegen. "Rubber, Synthetic." Encyclopedia of Physical Science and Technology. San Diego: Academic Press, 2002.

[15] The Chemical Thesaurus. "Sort and Find Chemical Entities." 1 Feb 2007. <http://www.chemthes.com/find.php>

[16] Faculty of Engineering, Kasetsart University. "Styrene Butadiene Rubber." 1 Feb 2007. <http://www.eng.ku.ac.th/~mat/MatDB/MatDB/SOURCE/Struc/polymers/synrub/synrub.htm>



Propagation ends when there are no more monomer droplets and the reaction rate drops suddenly.

Termination occurs with a “shortstop” – a dilute solution of hydroquinone – that chemically reduces initiating species (thus halting free-radical creation), and that traps and neutralizes the free radicals already generated. The emulsion-polymerization process yields a monomer-to-polymer conversion of about 60%.[17] The resulting compound is composed of polymer particles suspended in water (a latex.)

The resulting polymer can be strengthened during emulsion polymerization through vulcanization, which cross-links macromolecular chains. Vulcanization requires sulfur, as well as stearic acid, an accelerator, and zinc oxide, which activates the accelerator.[18]

The shortstopped latex, is transferred to a large holding tank called “blowdown tank.” Remaining gaseous butadiene monomers are released when the latex is degassed using vacuum flashing in a series of horizontal “flash tanks.” Residual styrene monomers are removed at the top of a vertical plate column via steam distillation when latex runs countercurrent to pumped steam.[19]

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[17] “Styrene-Butadiene Rubber." Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons, Inc, 1992.

[18] “Elastomers, Synthetic." Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons, Inc, 1992.

[19] U.S. Environmental Protection Agency. “Chapter 6: Organic Chemical Process Industry - Synthetic Rubber.” *AP 42*, Fifth Edition, Volume I. 10 Jan. 2006. <http://www.epa.gov/ttn/chief/ap42/ch06/index.html>

Latex is reacts with antioxidants, usually an amine or a phenol-type molecule, because double bonds in the latex are vulnerable to degradation by heat, light, and oxygen. The latex is also reinforced with carbon black or silica, and extended with clay and chalk. The product then undergoes a 2-stage coagulation process where dilute sulfuric acid and sodium chloride solution are added in an open-air tank. Coagulation breaks the emulsion and results in rubber crumb. The crumb is then water-washed, reground, filtered, and dried. The dried crumbs are then hydraulically packaged into standard 80-lb bales, bagged or film wrapped, and then boxed for shipment. [20,21]

Regardless of the impressive advances in synthetic-rubber research programs during World War II, synthetic rubber, at that time, was neither cost-nor quality-competitive with natural rubber[22] Although SBR exhibits high resilience and can absorb large amounts of petroleum oil without a significant decline in performance, SBR exhibits low resistance to heat and is usually blended with natural rubber when used in tire treads. [23,24] Regardless of the inferiority of synthetic rubbers, Baruch explained “a bad process which will give us rubber now is better than a perfect process which will not give us rubber until too late.”[25]

POST-WAR TENSIONS:

In the early post-war year, U.S. chemical engineers significantly improved the synthetic-rubber process’ efficiency and product quality.

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[20] “Styrene-Butadiene Rubber." Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons, Inc, 1992.

[21] “Elastomers, Synthetic." Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons, Inc, 1992.

[22] R. P. Russel. “The Artificial Rubber Industry.” *Proceeding of the Academy of Political Science*, Vol. 20, No. 1, Winning the War. (May, 1942), pp. 72-78.

[23] Robert Solo. “The New Threat of Synthetic to Natural Rubber.” *Southern Economic Journal,* Vol. 22, No. 1. (Jul., 1955), pp. 55-64.

[24] Stephen T. Semegen. "Rubber, Synthetic." Encyclopedia of Physical Science and Technology. San Diego: Academic Press, 2002.

[25] William M. Tuttle, Jr. “The Birth of an Industry: The Synthetic Rubber ‘Mess’ in World War II.” *Technology and Culture,* Vol. 22, No. 1. (Jan., 1981), pp. 35-67.

Synthetic rubber gave rise to post-war international tensions. The synthetic rubber industry, a growing commercial American enterprise, threatened the international natural-rubber arena. A threat to the Southeast Asian natural-rubber industry was not only a threat to large British investments in rubber plantations and the "economic future of the British empire itself,"[26] but also an economic threat to underdeveloped Southeast Asian rubber-exporting countries where rubber exports encompass a large portion of annual revenue. When the Southeast Asian rubber-exporting countries lost the US natural-rubber market to synthetic rubber, they were pressed to trade with Communist countries, rather than America, and that had a significant effect on foreign policies of the US and Southeast Asia in the 1950's and 60's.[27]

POST-WAR SYNTHETIC RUBBER:

Chemical engineers continued to refine synthetic-rubber processes after World War II. Notably, German scientists discovered a method of cold (rather than hot) emulsion polymerization, a process that is more easily controlled and is slower to develop undesired gels within the latex. Chemical engineers have also streamlined the two-step coagulation process by replacing the sodium chloride brine through increasing the amount of polyamine coagulants, giving a product with less ash residue. Consumption of synthetic rubbers has surpassed that of natural rubber. Today, SBR is the most widely used synthetic polymer, followed by polyethylene, polypropylene, polyester, and polystyrene.[28] Styrene-butadiene rubber is the largest volume synthetic rubber produced – the world-wide production capacity of emulsion

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[26] Kurt Bloch. "Rubber Squeeze – Present and Future." *Far Eastern Survey*, Vol. 11, No. 2. (Jan. 26, 1942), pp. 26-29.

[27] Ibid.

[28] "Styrene-Butadiene Rubber." Kirk-Othmer Encyclopedia of Chemical Technology. New York: John Wiley & Sons, Inc, 1992.

polymerized SBR rubber alone is 2,457,000 metric tons.[29] The second largest volume of synthetic rubber is polybutadiene rubber (BR). In 1999, world-wide consumption of polybutadiene rubber was 1,953,000 metric tons.[30]

CONCLUSION

Early in World War II, the Japanese blockade of America's natural rubber supplies from Southeast Asia gave rise to the American Synthetic Rubber Program, that – in a remarkably short time – manufactured huge quantities of synthetic rubber to supply Allied forces. Although some efforts to make synthetic rubber date back to the mid nineteenth century, the American Synthetic Rubber program of the 1940's produced a huge surge in synthetic-rubber technology. This surge, due to World War II, represents one of the greatest achievements of chemical technology. The Synthetic Rubber Program was not only an engineering breakthrough, but also key to the Allies' success in World War II: lack of "rubber could [have] cost us the war."[31]

The success of the American synthetic-rubber industry caused international tensions after the war because it threatening to replace production of natural rubber in other countries. Because chemical engineers continued to refine synthetic-rubber production, natural rubber has now been essentially replaced by synthetic rubber for numerous products (especially automobiles and truck tires) and industrial processes. The synthetic-rubber industry, born from the necessities of warfare, is now a major part of the world's economy.

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[29] U.S. International Trade Commission, "Certain Emulsion Styrene-Butadiene Rubber From Brazil, Korea, and Mexico," *News Release* 99-060, Invs. Nos. 731-TA-794-796 (F.) (April 1999) 13 April 2007. <http://www.usitc.gov/ext_relations/news_release/1999/ER0429W2.HTM>

[30] International Institute of Synthetic Rubber Producers, Inc, "Polybutadiene Rubber (BR,)" *Synthetic Rubber*. 13 April 2007. <http://www.iisrp.com/WebPolymers/01FinalPolybutadieneVer2.pdf>

[31] John L. Collyer. "Crisis in Rubber." *Proceedings of the Academy of Political Science*, Vol. 20, No. 2, Transportation in Wartime and the United Nations. (Jan., 1943), pp. 71-80.