INTRODUCTION

Butyl rubber, introduced in 1942, is commercially produced by cationically copolymerizing isobutylene with small amounts of isoprene. The halogen derivatives, chloro- and bromo-, were introduced in the early 1960’s and have been commercially available since then. The halogenated derivatives of butyl rubber provide greater vulcanization flexibility and enhanced cure compatibility with other, more unsaturated general-purpose elastomers. Butyl polymers are among the most widely used synthetic elastomers in the world, ranking third in total synthetic elastomers consumed. As speciality elastomers, the butyl-based polymers have found their most important application in the tire industry although a host of other applications have evolved and continue to utilize their unique properties. There are two producers in the free world: Exxon Chemical Company, an affiliate of Exxon Corporation; and Polysar, Ltd., of Canada. The polymer is also produced in the USSR for internal consumption.

BUTYL RUBBER

Commercial butyl-rubber grades poly(methylpropene-co-2-methyl-1,3 butadiene) or poly(isobutylene-co-isoprene), are prepared by copolymerizing small amounts of isoprene. 1 to 3% of the monomer feed, with isobutylene, catalyzed by AlCl₃ dissolved in methyl chloride. The extremely rapid reaction is unique, proceeding via cationic polymerization at −100°C to completion in less than a second. Monomer purity is important to achieve the desired polymer molecular weights. The methyl chloride diluent and monomer feed must be carefully dried.

Historical

Butyl rubber had its origin in the work of the researchers, Gorianov and Butlerev (1870) and Otto (1927), who found that oily homopolymers of isobutylene...
could be produced in the presence of boron trifluoride. It wasn’t until the 1930’s that the I. G. Farben Company of Germany produced high-molecular-weight polyisobutlenes that possessed rubber-like properties but could not be vulcanized by normal methods because of their saturated hydrocarbon structure. These homopolymers are available today in a variety of molecular weights from Badischer of Germany and Exxon Chemical Company under the trade names OP-PANOL® and VISTANEX®, respectively. Their unique age-resistant properties have made them particularly suitable for uncured rubber sheeting, caulks and sealants, adhesives and chewing gum.

Subsequent research in the 1930’s led W. J. Sparks and R. M. Thomas of Exxon Research and Engineering Company (then known as the Standard Oil Development Company) to advance the state of the art of isobutylene polymerization, and in 1937 produced the first vulcanizable isobutylene-based elastomer by incorporating small amounts of a diolefin, and particularly isoprene, into the polymer molecule. This introduced the first concept of limited olefinic functionality for vulcanization in an otherwise saturated copolymer. Corresponding vulcanizates of these new copolymers (now known as “butyl rubber”) were found to possess a set of unique and desirable properties, e.g., low gas-permeability, high hysteresis, outstanding resistance to heat, ozone, chemical attack and tearing. Subsequent development to commercialization was spurred during World War II by the U.S. Government as part of its rubber-procurement program. Exxon built and operated the first butyl commercial facility in cooperation with the Government’s Rubber Reserve Board. In 1955, the commercial butyl plants were purchased by Exxon Chemical from the U.S. Government.

Butyl-rubber Manufacture

A schematic diagram of a typical butyl plant is shown in Fig. 10.1. The feed, which is a 25% solution of isobutylene (97–98%) and isoprene (2–3%) in methyl chloride, which is the diluent, is cooled to −100°C in a feed tank. At the same time, aluminum chloride is also being dissolved in methyl chloride. Both of these streams are then continuously injected into the reactor. Because the reaction is exothermic and is practically instantaneous, cooling is very important. To remove the heat of reaction, liquid ethylene is boiled continuously through the reactor cooling coils, keeping the reaction at −100°C. As the polymerization proceeds, a slurry of very small particles is formed in the reactor. This slurry overflows into a flash drum that contains copious quantities of hot water. Here the mixture is vigorously agitated, during which time the diluent and unreacted hydrocarbons are flashed off overhead.

At this point, an antioxidant and zinc stearate are introduced into the polymer. The antioxidant is added to prevent breakdown of the polymer in the subsequent finishing section. Zinc stearate is added to prevent the agglomeration,