

A Short History of Rubber Cables

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Discovery and Vulcanization of Rubber

In 1770 Joseph Priestley coined the word “rubber” for a gum-like substance which would erase pencil lines by rubbing. Natural rubber was collected from wild plants, principally the rubber tree, *Hevea brasiliensis*. Although natural rubber had been used by Native Americans long before discovery by Europeans and sporadic attempts had been made to develop commercial products from natural rubber, natural rubber could not be transformed into a substance with good flexibility in both hot and cold environments, without adhesiveness or tack. Charles Goodyear, a hardware merchant in Naugatuck, Connecticut, was able to accomplish this milestone in 1839 when he vulcanized natural rubber using sulfur and heat, for which he was granted a patent in 1844 [1]. The first major commercial application of vulcanized rubber was as a waterproofing agent for the Macintosh raincoat which did not get sticky in muggy London summers. By 1850, the Naugatuck Valley of Connecticut had become the rubber center of the world. By the time of Goodyear’s death in 1860, the rubber industry employed over 60,000 persons. Julius Day, Goodyear’s cousin, provided much of the investment that made all of this happen. Austin Goodyear Day, Julius’ son, worked with Goodyear and developed an improved rubber formulation. He later created a business empire supplying rubber to mills in the area that was based on the technology he developed for cleaning rubber. In 1853, A. G. Day cleaned 55,000 lbs of rubber, and in 1859, he cleaned and sold 500,000 lbs of rubber.

Application of Natural Rubber to Electrical Insulation

The use of natural rubber-based insulations for electrical wire dates from the earliest days of the electrical industry. Early manufacturers found that rubber benefits from the admixture of various compounding ingredients, such as mineral fillers and process aids, in addition to the vulcanization agents discovered by Charles Goodyear. Often rubber for electrical insulation was mixed with a product made by heating certain vegetable oils with sulfur in a reaction analogous to Goodyear’s vulcanization process and possibly spawned by that same idea. These materials are known variously as factice or pitch and are the source of the term “oil based rubber” often encountered as a description of old rubber compounds. In the early 1860s, A. G. Day started

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Rubber cables date back to the earliest electrical infrastructure, the telegraph, and have dominated industrial infrastructure to the present.

experiments aimed at improving rubber compounds while also lowering their cost. After 3,000 experiments, he developed “Kerite” (Table 1) [2], which may have been suggested by the Greek word, *Keros*, meaning wax. Natural rubber-based electrical insulation was the only polymeric material used as a wire and cable dielectric up to the 1930s, when the first suitable synthetics became available.

In the latter half of the 19th century, the transmission and distribution needs of telegraph, telephone, and electrical systems were the driving forces for the development of electrical insulation compounding technology. In 1837, Samuel Morse invented the telegraph, and the first (air-insulated) telegraph lines were strung between Washington, DC, and Baltimore in 1844 and between Baltimore and Philadelphia in 1846. Insulation of telegraph lines was problematic, especially where they had to be buried or placed underwater.

Table 1. Kerite Formulation, Circa 1860s.	
Coal Tar	25 lbs
Asphalt Heat together to 350°F for 1/2 hour, then add	15 lbs
Linseed oil Heat again to 350°F for 7 hours and let stand overnight. Heat to 240°F and add	70 lbs
Sulfur Heat to 320°F in 1/2 hour and add	10 lbs
Sulfur Heat again to 300°F and add	4 lbs
Talc Keep at same temperature for 1/2 to 3/4 hour, when vulcanization will have taken place and the mixture can be poured into molds or allowed to cool in mass.	56 lbs

A. G. Day had been looking for a new application for rubber, and the addition of Kerite to natural rubber provided the combination of ozone, moisture, and temperature resistance that allowed Kerite-insulated telegraph wires to provide reliable operation when placed overhead, buried, or submerged in either fresh or salt water. In combination with the superior performance of Kerite insulation, the invention of the crosshead extruder (Figure 1) by A. G. DeWolfe, Day’s plant superintendent, made Day a major supplier of telegraph cable. By 1868, over 200 Kerite-insulated telegraph cables had been installed in the United States, Canada, Panama, and Egypt. As Samuel Morse wrote of Kerite insulation in connection with the 1867 Paris Exposition:

“It appears to me that you have discovered the most perfect as yet of all insulating substances for submarine telegraph cables—the test to which it has been submitted and by which it has been approved to resist the deteriorating effects of the ozone of the atmosphere appear perfectly satisfactory, and I therefore most cheerfully and cordially join with those who have tested its efficiency in congratulating you on your success in introducing so valuable an aid to the telegraphic enterprises of the world.”

Alexander Graham Bell invented the telephone in 1876. The founder of The Okonite Company, John Haven Cheever, developed a moisture-resistant natural rubber-based insulation coined “Okonite” at about this same time (Table 2) [2]. The name was derived from the telegraph sign-off, “OK,” and “nite,” from the natural rubber compound called “vulcanite.” Shortly thereafter, in September 1878, Thomas Edison declared that he would light a half-mile radius of lower Manhattan with his new invention, the incandescent light bulb, which required four years, but in 1882 he flipped the switch at the first electric power station in America, on Pearl Street in New York City, which energized Okonite-insulated cables (Figure 2).

While Cheever pursued power applications for his Okonite-insulated cable, Kerite-insulated cable dominated electrical signal applications in the telegraph, telephone, and railroad industries. By 1889, Kerite-insulated cables operating at 1,100 V were delivered to the Seymour Electric Light Company. In 1898, a Kerite-insulated 1,000-kCM submarine cable was laid across the Gowanus Canal by the Coney Island and Brooklyn Railway.

Prior to 1925, rubber-insulated cables could support voltages up to about 7,500 V ac (Figure 3). The fundamental problems were the thermal aging characteristics of sulfur-cured natural rubber as well as the classic problems of contamination, dispersion, and agglomeration of compounding ingredients. Typical examples of inorganic mineral materials commonly used in high-grade rubber insulations were zinc oxide, litharge, whiting, colloidal clays, and talc. These were mixed with natural rubber (about 60% by volume), paraffin waxes, plasticizing oils, and resins. By 1931, 25-kV Okonite- and Kerite-insulated power cables were being supplied to a wide range of electric utilities.

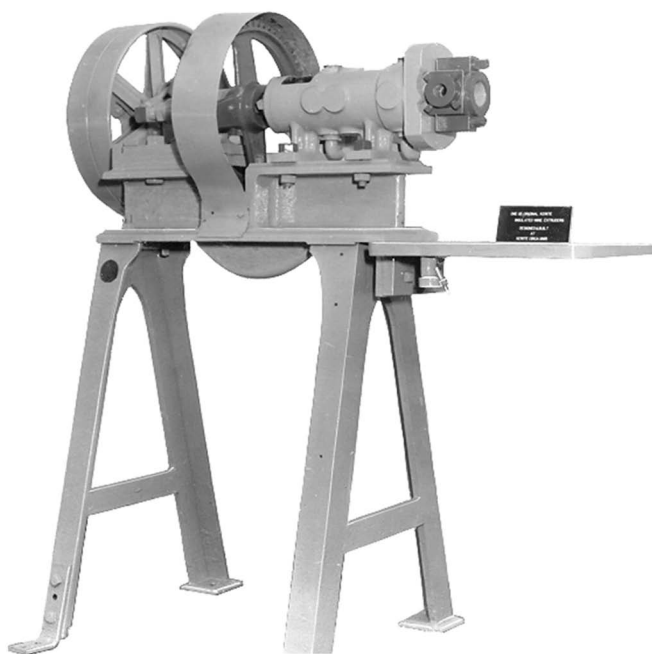


Figure 1. An early DeWolfe crosshead extruder from 1865.

Table 2. Okonite Formulation, Circa 1870s.	
India rubber	49.6%
Sulfur	5.3%
Lampblack	3.2%
Zinc oxide	15.5%
Litharge [lead(II) oxide]	26.3%
Silica	0.1%

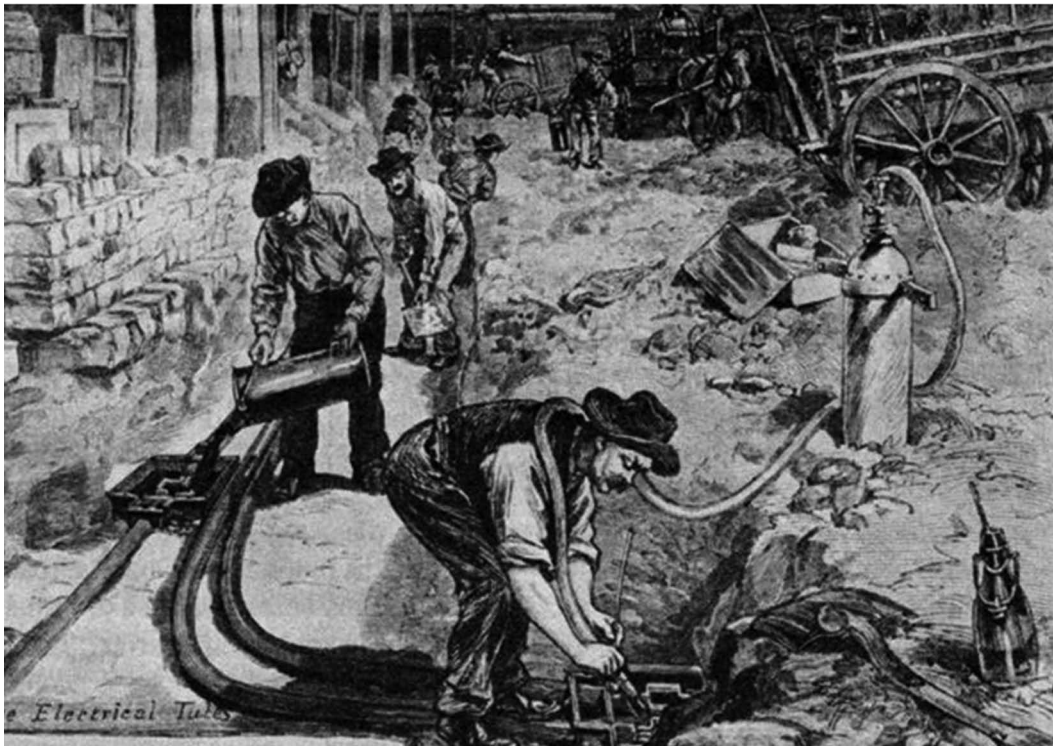


Figure 2. Installation of rubber-insulated electric cables by the Edison company. A worker can be seen pouring tar into a splice box.

Synthetic Alternatives to Natural Rubber

Butadiene Polymers

The search for synthetic alternatives to natural rubber is about as old as the rubber industry itself. The first good

alternative to natural rubber was not discovered until 1933, when the idea of copolymerizing styrene with butadiene was conceived by Walter Bock and Edward Tschunkur at I.G. Farben in Germany [3]. Polybutadiene was invented a few years earlier, but its physical properties were inadequate as a replacement



Figure 3. The first underground residential distribution (URD) cable system was based on rubber cable operating at 5 kV (Fishers Island, NY.)

for natural rubber. The copolymerization of some styrene with butadiene improved the strength and wear properties greatly. Soon thereafter, Standard Oil acquired this technology through a technology exchange agreement with I.G. Farben. This styrene butadiene copolymer was called “Buna-S” in Germany. In the United States, it was called “GRS,” which stood for Government Rubber-Styrene, since the earliest production was under the auspices of the Rubber Reserve Program during WWII. Later the more descriptive term, “SBR,” was applied to styrene butadiene rubber. Styrene butadiene rubber was used extensively as wire insulation from the 1940s through the 1960s. Although the use of SBR in wire and cable has declined, SBR remains the largest volume synthetic rubber produced today.

Butyl Rubber

Another interesting chemical reaction, also discovered at I.G. Farben and later acquired by Standard Oil, was the polymerization of isobutylene to make polyisobutylene [4]. Standard Oil further developed the process, copolymerizing a small amount of isoprene with the isobutylene, to make another useful rubber known as butyl rubber, which was commercialized in 1944, after about 10 years of unsuccessful attempts to produce a vulcanizable polyisobutylene. William Sparks and Robert Thomas share credit for the invention of butyl rubber, which has several advantages over SBR and natural rubber as an electrical insulation. The nearly fully saturated backbone of butyl rubber provides greatly improved resistance to oxidation from heat, ozone, or exposure to UV light. In addition, the barrier properties of butyl rubber are outstanding, which accounts for its use in the tire industry for liners and inner tubes. The greater stability of butyl rubber motivated improved insulation formulations based on ingredients such as calcined kaolin, which improved water resistance and the dielectric properties. Butyl rubber compounds could be rated for 85°C and 15-kV applications. Although a significant improvement over natural rubber and SBR, the quirky processing characteristics of butyl rubber ensured continued search for improved polymers.

Ethylene Propylene Rubber (EPR)

In 1955, the discovery by General Electric of dialkyl peroxides as cross-linking agents for various polymers was a major step forward in the development of still better rubber insulations [5]. Peroxides can be dissociated with heat into very reactive species, known as free radicals, which have sufficient energy to develop cross-links between saturated polymers, thereby eliminating the need for double bonds in the polymer. Though first applied to cross-linking polyethylene, the technology was a natural fit for EPR, which was developed a few years later following the catalyst development by Carl Ziegler and Giulio Natta [6].

Initially, the coordination catalyst of Carl Ziegler provided a novel route to polyethylene; however, Giulio Natta extended its application significantly, polymerizing and copolymerizing other monomers. This class of catalysts was revolutionary in facilitating the development of many poly olefins and other polymers. The 1955 Nobel Prize in chemistry was awarded jointly to Carl Ziegler and Giulio Natta for their work.

The copolymerization of propylene and ethylene yielded EPR, which demonstrated several unique and valuable attributes. Commercial interest in EPR was quite intense since it promised a rubber with tremendous environmental stability at low cost. By the early 1960s, two manufacturers in Europe and three in the United States had begun production. Wire and cable producers were quick to recognize the advantages of EPR and were offering EPR-insulated cables by 1962 [7]–[9].

The Evolution of Properties and Molecular Structure

The properties of polymers are the result of molecular composition and structure. Compositionally, EPR is a hydrocarbon, having an unsaturated carbon backbone (no carbon-carbon double bonds), dominated by linear -CH₂- and branched -CH- units, which are relatively stable and flexible building blocks for a polymer. The branches off of the main polymer chain, which can be long or short, also have a similar composition. While many types of unsaturated hydrocarbon polymers have very similar compositions in terms of their relative content of carbon and hydrogen (e.g., polyethylenes, polypropylenes, and EPR polymers), their structures vary widely and account for significant differences in physical properties.

The structure, or architecture, of a polymer refers to the regularity of the repeating units and branching points as well as the length of the main chain and branches. Polymers with highly regular structures, those having repeating patterns of similar backbone units, allow the polymer chains to organize, or pack, more efficiently into relatively tight groupings; these polymers are referred to as more crystalline. Polymers that have a more random distribution of differing backbone units and/or branching points do not allow the polymer chains to organize very efficiently. Since these poorly organized polymer chains do not pack very efficiently (i.e., higher free volume), they have more freedom of movement in the polymer network and are referred to as amorphous.

Linear polymers that have only one type of backbone unit and no branching, such as found in some polyethylenes and polypropylenes, can organize much more easily. Their crystallinity leads to more rigid polymer networks, which is demonstrated by their physical properties such as high hardness, high modulus, and high tensile strength.

Carbon-carbon double bonds, commonly referred to as “unsaturation,” are less stable than carbon-carbon single bonds and have a more rigid, planar geometry. Due to the latent reactivity associated with the large number of double bonds in the polymer backbones of both natural rubber and SBR, these polymers demonstrate relatively poor stability to heat, ozone, and UV radiation. In contrast, butyl rubber has a nearly saturated backbone, which affords greatly improved thermal aging and weathering properties, and a dense packing of methyl groups around the polymer backbone, which results in little free volume and accounts for the very low gas permeability of butyl rubbers. All of these rubbers are hydrocarbons and thus are good dielectrics with excellent water resistance.

Ethylene propylene rubber is a generic term for a wide range of polymers based on copolymers of ethylene and propylene. Ethylene propylene rubber polymers with highly tailored properties can be fine tuned to particular applications and processing conditions by varying the ratio of these two monomers, the average molecular weight (i.e., the length of polymer chain), the molecular weight distribution (i.e., the distribution of chain lengths), the degree of side branching, and other such parameters. For example, EPR polymer chains can have widely varying degrees of crystalline and amorphous character. While all EPR polymers have at least some degree of amorphous character, they may have no crystalline character or only a moderate level of crystalline character. In EPR, crystallinity is largely associated with ethylene monomer content, where incorporation of more ethylene leads to higher crystallinity.

A compounder of wire and cable dielectrics can select from a wide range of electrical-grade EPR polymers to emphasize such finished properties as ultimate tensile strength, flexibility, resilience, aging performance, or hardness. In addition,



Figure 4. Examples of power cables insulated with ethylene propylene rubber-based insulations.

properties that can affect processing, such as viscosity, extrudate appearance, speed of curing, green strength, and so on, can be varied through modifications of the molecular structure of EPR. Balancing these properties requires finesse on the part of the rubber chemist but also provides the means to develop materials with properties targeted for the specific use or set of conditions. Properly formulated, an EPR compound will exhibit excellent electrical properties, excellent high temperature performance, low water permeability, as well as resistance to water trees, acids, bases, ozone, and UV.

Conclusion

Ethylene propylene rubber polymers are inherently more expensive than polyethylene, and the highly refined fillers used in EPR-based insulations cost about the same as the polymer on a volume basis. Cables which employ EPR-based insulations are therefore inherently somewhat more costly to manufacture than cables insulated with polyethylene and tend to be used where reliability is important. Ethylene propylene rubber-based power cables dominate industrial applications, have a substantial market share in the utility sector, and are applied at transmission voltages up to 138 kV (Figure 4). The primary advantages of such cable include flexibility and an inherent resistance to failure caused by electrochemical degradation (i.e., water treeing). As a result, EPR-based insulations do not require protection from moisture even at 138 kV, a voltage at which other insulations are normally protected by a metallic moisture barrier.

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