

Concerning the reduction of compounds to metal in electric furnaces, I have time to pick out only a few characteristic examples:

Boron is one of the rarest metals, but its compounds are abundant. It is made by bringing a volatile boron salt with hydrogen gas into an electric arc, where they are heated to a very high temperature. The salt is reduced by the hydrogen to metal, and the vapors produced are chilled before they have a chance to recombine. It is the same operating principle as is used in the fixation of atmospheric nitrogen in Norway. This boron is being put on the market for use in casting "conductivity" copper. This is one of the most recent productions of the electric furnace.

In Niagara Falls, Mr. Tone is reducing ordinary silica sand, SiO_2 , to metallic silicon. This gentleman once took me into the carborundum works at Niagara, showed me a barrel containing something, and told me to guess what it was. I made two or three vain guesses, and he finally told me that it was silicon, which, he said, "we can make for a few cents a pound." At that time metallic silicon was quoted in commercial price-lists at \$4 a gramme (\$18 a pound). He said he wanted to find some use for it. Silicon is somewhat volatile, and 25 per cent of that which he puts into his furnace goes up in smoke. He is now making silicon at Niagara Falls by the ton. Silica is mixed with carbon, put into a furnace heated by a carbon resistor, the mixture of silica and carbon being piled around the resistor, and the metal filters down around this resistor and runs out something like slag. It is being cast into vessels for use in chemical works. Thus is the most abundant element on earth now commercially available at a price of about six or seven cents a pound. One can only speculate as to the future uses of it; it is made from the cheapest materials; the reducing agent is cheap carbon; and you have metallic silica from the electric furnace.

The zinc industry is attracting a great deal of attention. It is, apparently, one of the least progressive of the metallurgical industries. Little bits of retorts are heated to a high temperature, a few shovelfuls of roasted ore mixed with carbon are put into each retort and left there for 24 hours. Everything is done in a very homeopathic way, and yet it is so difficult a metal to handle that it is only by holding fast the ground gained that it has reached its present status. The electric furnace zinc industry has been made suc-

cessful in Europe; there are works in profitable operation in Norway, Sweden, and Finland, while much skilful experimenting has been done in America. Last year 4,000 horse-power was being used in producing zinc in Scandinavia, and 7,000 horse-power has been added since then. The firms are very reticent about their methods; in fact, there is no reliable published data about their present type of furnace.

The manufacture of ferro-manganese, ferro-tungsten, etc., for making special steels, is done almost entirely in the electric furnace. The oxide of iron is mixed with the oxide of the metal to be reduced, with sufficient carbon for reduction. It takes about half a horse-power year to produce a ton of 50 per cent ferro-silicon, for instance. The chief seat of this industry is the Savoy, in France, but the industry is gaining ground in the United States and Canada, and imports are decreasing. Stassano, in Turin, was the first to make such alloys, using his arc-radiation furnace, but enormous furnaces (Helfenstein's) of 5,000 to 10,000 horse-power are now used in this industry, which thus led up to the electric furnace manufacture of pig-iron and pig-steel.

The manufacture of the cheapest metal we have from the cheapest ore we have by electrometallurgical process is, I suppose, one of the greatest triumphs of electrometallurgy. The electric current can really be used for doing what is now done in the blast, and it is possible under some circumstances to replace it by an electrometallurgical furnace; that is the last triumph of electrometallurgy.

In one little place in Sweden that I visited two years ago, charcoal was getting scarce, and they were importing coke from England to run their blast-furnaces, and the quality of the product was not that of iron made with charcoal. They were much interested in the electric furnace, because it requires only one-third as much fuel to make a ton of pig-iron as the blast-furnace. In their blast-furnaces, with the charcoal available, they could make 300,000 tons of pig-iron, but in the electric furnace they could make 900,000 tons with the same fuel; so that was one of the inducements to use the electric furnace. The Swedes spent a quarter of a million dollars before they had a successful working furnace. They did their work in a most scientific way all through, watched their temperatures and all the conditions, and knew exactly what they were doing all the time. As a net result, they

made pig-iron in the electric furnace as cheaply as they can in their blast-furnaces. The Jern Kontoret (Iron Masters' Society) bought the patents for the furnaces, so that they became the common property of all the ironmasters of Sweden, and they have been putting up furnaces pretty rapidly. The last one was designed for 12,000 horse-power. It has been running for nearly a year at from 6,000 horse-power to 8,000 horse-power, making 55 tons of pig-iron per day. If it were run at full capacity, I think they could make 100 tons a day, which is equal to the average capacity of one of their blast-furnaces.

At Domnarfvet and Hagfors, in Sweden, the same thing is pending. At the latter works they calculate that with this large furnace there is a margin of \$2.50 per ton on the cost of pig-iron, to the advantage of the electrical furnace over their blast-furnaces, so that electric furnace pig-iron is being made at a profit and cheaper than it could be made in the blast-furnace in Sweden.

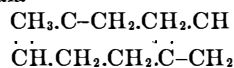
The possibility of making a product from this furnace which is not pig-iron, but which, as far as carbon content is concerned, will have to be classed as steel, has been proved. That product, with less than two per cent of carbon, is in reality impure steel, and not cast iron. It requires only a small amount of refining to bring it to pure steel. With the excess of iron ore present in the furnace you can make a low-carbon product. With electricity to furnish the heat, you can regulate the carbon so as to make a product with only two per cent of carbon. This is a possibility with an electric furnace; but it is not a possibility with the blast-furnace. We can thus make pig-steel, with less than two per cent carbon, which can be converted in the open-hearth furnace into pure steel in about half the time that the ordinary product of the blast-furnace takes. This will bring advantages with which the blast-furnace cannot possibly compete. In the case of the problem being worked out, pig-steel will replace pig-iron for the manufacture of steel; this opens up the possibility of the electric reduction of iron ore going into use in places where otherwise it would not go if the product were simply pig-iron. It may come into Canada or along our northern borders, where water-power can be obtained cheaply, for there is the large expenditure of 3,000 horse-power hours per ton of product to be reckoned with. This will be the next great advance in the electrometallurgy of iron and steel.

Artificial Production of Caoutchouc*

Considerations of Synthetic Production of an Elastic Colloidal Substance

By F. Willy Hinrichsen, of the Koenigliches National-Pruefungsamt, Berlin¹

THE question of the artificial production of rubber is a problem of the greatest commercial and scientific importance. The "synthetic rubber phantom" which for some time past greatly agitated the planters and all interested in the collection of wild and plantation rubber, is still so present in the memory of all, that it hardly seems necessary to dwell here upon the commercial importance of rubber synthesis. On the other hand, from a purely scientific viewpoint there was presented the problem of preparing for the first time, synthetically, a typical colloidal substance and to discover relations between chemical constitution and elastic properties. It is therefore evident that the above problem was eagerly approached from various angles of science and technology. While I am here giving a short review of the present state of this subject I must at the same time limit myself to several essential main points. Complete consideration of the subject is, of course, out of the question, since only a small portion of the work accomplished in the technical laboratories on this subject is made publicly available. After Harries², in his pioneer work of 1905, established that the chemical constitution of natural caoutchouc $\text{C}_{10}\text{H}_{16}$, as a 1.5-dimethyl-cyklooctadien of the formula



it was easier to approach the synthesis of the interesting hydrocarbon from the basis of the newly discovered knowledge. Several earlier observations had been made. Thus, Bouchardat³ had found that the hydrocarbon isoprene, C_5H_8 , resulting from the dry distillation of caoutchouc, and which had been previously discovered

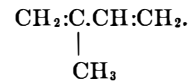
by Williams,⁴ was a colorless liquid which boiled easily and which could be converted into a rubber-like substance by polymerization in the presence of aqueous hydrochloric acid. Tilden⁵ had also found that, in the same way, isoprene which, in addition to being formed from caoutchouc, is produced by passing oil of turpentine through red hot tubes, was converted by hydrochloric acid or nitrosylchloride into caoutchouc. However, as in spite of many repetitions under varying conditions of experimentation by other investigators, and even by Tilden himself, it was no longer possible to obtain the same result; it was assumed that only a purely accidental observation had been made, and that the material obtained, which in the state of science then existing, could not be determined to be caoutchouc, was not really a caoutchouc and that the statements of Bouchardat and Tilden were based on errors.

As a result of the enormous increases of the prices of rubber during the last few years and also because of the zealous scientific attention to the caoutchouc problem, particularly by Harries, the attention of a large circle of people, particularly in the industries, was drawn to the problem of the synthetic production of caoutchouc. The result was, that Fritz Hofmann and Carl Coutelle,⁶ chemists of the Elberfeld Farbenfabriken vorm. Bayer & Co., succeeded in 1909 in converting absolutely pure isoprene, which they obtained by a new method, into caoutchouc, by simply heating it in a closed tube, either by itself or in the presence of certain other substances. A sample of this caoutchouc was sent to Harries, who proved with certainty by chemical tests that in this case caoutchouc actually resulted. Since the process by which Hofmann and Coutelle worked was not yet known, Harries also took up the experiments on the conversion of isoprene into caoutchouc, and in March 1910 he re-

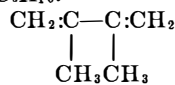
ported in a lecture in Vienna⁷ on his observations, stating that it is possible to convert isoprene into caoutchouc by heating it in a closed tube in the presence of glacial acetic acid. Harries deserves the credit for being the first to publish a process which could be repeated, for converting isoprene into caoutchouc.

After the ball had once been started rolling investigations were also begun by others attacking the problem. Particular credit should also be accorded especially in the technical interpretation of the problem in addition to the Elberfeld Farbenfabriken, to numerous individual native and foreign investigators, and of industrial establishments, the Badische Anilin und Sodafabrik of Ludwigshafen.

Even in the original patent specifications of the Elberfeld Farbenfabriken the raw material was not limited to isoprene, but a series of hydrocarbons of related constitution was included in the scope of the observation. Isoprene itself has the formula



It contains two neighboring double bonds, a so-called system of "conjugated double bonds." Other compounds with conjugated double bonds, as was recognized by Hofmann and Coutelle from the start, also possessed as does isoprene the same property of polymerizing into caoutchouc-like substances. Among these we have for example, erythrene, C_4H_6 : $\text{CH}_2:\text{CH}:\text{CH}:\text{CH}_2$; further dimethylbutadiene, C_6H_{10} :



and many other similarly constructed substances.

Aside from the fact that because of the varied natures of the raw materials there was possibility of obtaining a whole series of different caoutchoucs, which of course must differ from each other because of their chemical

* *Zeitschrift des Vereins deutscher Ingenieure*, 1915, vol. 59, p. 16.

¹ See also Hinrichsen and Memmler: *Der Kautschuk und seine Pruefung*, published by S. Hirzel, Leipzig 1910; pp. 20 et seq. Ditmar: *Die Synthese des Kautschuks*, published by Th. Steinkopf, Dresden 1912.

² *Ber.*, 1904, vol. 37, p. 2,708; 1905, vol. 38, p. 1,195.

³ *Compt. rend.*, 1875, vol. 80, p. 1,446; 1879, vol. 89, p. 1,117.

⁴ *Proc. Royal Soc., London*, 1860, vol. 10, p. 516.

⁵ *Chem. News*, 1882, vol. 46, p. 120.

⁶ German Patent Applications F. 28,390. Class 39b Group 1. September 11th, 1909. German patent 235,423, September 30th, 1909. German Patent 235,686, December 28th, 1909.

⁷ *Gummi Ztg.*, 1910, vol. 24, p. 850.

constitution, it was also noticed that the process of polymerization itself was susceptible of variation and that caoutchoucs prepared in various ways from the same raw material would differ from each other.

Harries⁸, and independently of him the English investigators Mathews and Strange⁹, simultaneously observed that the polymerization in the presence of metallic sodium took place with great velocity, but that the caoutchouc obtained was different from that obtained by beating alone. Furthermore, the chemists of the Badische Anilin und Sodafabrik found that the results were different when the polymerization with sodium was carried out in a carbon dioxide atmosphere. Another process which was developed in the Badische Anilin und Sodafabrik depends on the use of ozonids or peroxids as catalyzers.

According to the kind of raw material and the method of polymerizing, rubbers are obtained which vary from one another totally in their properties. The following summary gives, according to Holt's¹⁰ statements, a brief

of which would have to very greatly exceed that of the present rubber plantations. From all these processes there will result such large quantities of by-products, that their removal would give rise to even more difficult problems than that of producing the caoutchouc itself.¹¹

Even in spite of the last named difficulties the question of price would not be the controlling one if the previously mentioned objects were accomplished and if it were possible to produce by the proper choice of working conditions caoutchouc-like materials specially adapted for certain purposes. It can be imagined that certain synthetic caoutchoucs designed for definite purposes, embodying a combination of certain favorable properties may surpass natural caoutchouc and may be sold at a higher price. This has not yet been achieved.

No sufficient technical data have yet been made public regarding the technical adaptability of synthetic caoutchouc. As far as known observations on this subject go, it is evident that synthetic caoutchouc has not approached the properties, especially the stability of natural

| CAOUTCHOUCS FROM BUTADIENE, C ₄ H ₆ . | | | |
|--|---|--|--|
| Normal caoutchouc (by heating): easily soluble, elastic, vulcanizable. | Ozonid caoutchouc: insoluble, swells up greatly, very elastic, unvulcanizable. | Carbon dioxide caoutchouc: insoluble, does not swell up, moderately elastic, unvulcanizable. | Sodium caoutchouc: easily soluble, elastic, vulcanizable. |
| CAOUTCHOUCS FROM ISOPRENE, C ₅ H ₈ . | | | |
| Normal caoutchouc: easily soluble, elastic, vulcanizable. | Ozonid caoutchouc: swells up greatly, only soluble after rolling, elastic, vulcanizable. | Carbon dioxide caoutchouc: insoluble, does not swell up, elastic, vulcanizable. | Sodium caoutchouc: easily soluble, not elastic, difficultly and incompletely vulcanizable. |
| CAOUTCHOUCS FROM DIMETHYLBUTADIENE, C ₆ H ₁₀ . | | | |
| Normal caoutchouc: easily soluble, not elastic, can only be vulcanized to hard rubber. | Ozonid caoutchouc: swells up, only soluble after rolling, not elastic, can only be vulcanized to hard rubber. | Carbon dioxide caoutchouc: insoluble, does not swell up, not elastic, difficultly vulcanizable, easily oxidizable. | Sodium caoutchouc: soluble and insoluble modification, not elastic, unvulcanizable. |

review of a series of such varying caoutchouc-like substances.

The scientific significance of the above-mentioned facts is obvious. It was the first time that elastic colloidal materials were synthetically prepared. The possibility of obtaining materials having changing properties by changing the raw material and the polymerization process, that is, by choice of the experimentation conditions, led to the hope that it must be possible, as in the field of dyestuffs and odoriferous substances, arbitrarily to obtain materials of definite properties by means of slight changes which would be particularly suitable for definite purposes. Just as we are able, in the case of dyestuffs to change the tone of the dyestuff at will by the addition of certain groups, etc., so it should also be possible in a similar way to arbitrarily change the elastic and solidity qualities of caoutchouc.

It is entirely different as regards the economic importance of the synthesis of caoutchouc. Should artificial rubber become a serious rival of natural rubber it must equal it in two respects: price and technical adaptability. It is not necessary, however, to conceive of the complete replacement of natural rubber by artificial, as in the case of indigo, alizarin, etc.

As regards the price of synthetic caoutchouc, this is first of all governed by the cost of preparing the hydrocarbons of the isoprene series which serve as the raw materials. In this respect great progress has undoubtedly been made in the most recent times. A process of the Badische Anilin und Sodafabrik which depends on certain fractions of petroleum seems to promise special success.

Additional raw materials are among others, starch, amyl alcohol, oil of turpentine, acetylene, etc. In spite of the great pains that have been taken in order to increase the yields of the various processes, it must be said that the desired goal has not yet been reached. As regards the price of a serious competition of the artificial with plantation rubber is not yet to be thought of. In addition also the amount of oil of turpentine which would be required, is limited and its price would soar with an increasing demand. In order to secure the starch necessary for the world's demand of rubber, which already amounts to more than 100,000 metric tons yearly, fields of corn or potatoes would have to be planted, the extent

Cost in Cement Manufacture

THE cost of power required in the manufacture of Portland cement reaches a higher percentage of the total cost of production than in most any other industry; and investigations seem to show that, when properly operated, there is little difference in the power required by different types of machines used in the processes. It is therefore evident that any reduction in the costs must be in the direction of the power used, and it is believed that the application of electric power can be made to materially reduce the expense of manufacture.

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⁸ Ann., 1911, vol. 383, p. 188.
⁹ Compare Harries: Z. angew. Chem., 1912, vol. 25, p. 1,458.
¹⁰ Z. angew. Chem., 1914, vol. 27, p. 153.
¹¹ Compare F. Hoffmann: Z. angew. Chem., 1912, vol. 25, p. 1,462.
¹² Ber., 1914, vol. 47, p. 350. See also Harries, *ibid.* p., 573. Steimmig, *ibid.*, p. 852.