

CARBORUNDUM: ITS HISTORY, MANUFACTURE
AND USES.

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For a number of years prior to 1890, I had been keeping a constant watch for anything that might suggest a method by which carbon could be crystallized. A realization of the importance of abrasive materials, in the industrial arts, together with the known superiority of crystalline carbons over all other substances, acted as a constant stimulus to continued exertion for the solution of the problem. In the year mentioned, having become associated with an electric light company, at Monongahela, Pa., I found myself in position to conduct experiments on a line which I had some years earlier formulated. The scheme was to cause carbon to be dissolved in melted silicate of alumina, or in the metals reduced therefrom, and by cooling the same to the point of solidification, cause the contained carbon to crystallize. You have heard that "fools rush in where angels fear to tread," and had I been a chemist, it is probable that such an experiment would not have been thought worthy of consideration, and certainly would not have been attempted. Be this as it may, the experiments were made with results more or less satisfactory.

The first experiment was with a furnace constructed of an iron bowl lined with carbon, in the central cavity of which was placed a mixture of carbon and clay; through the mixture was passed an electric current of sufficient amount to fuse the mass—a violent reaction following the fusion—the iron bowl, and a rod of carbon suspended in the centre of the mixture, forming the electrodes. After the mass had cooled, it was removed, broken and carefully examined, when a few bright crystals, blue in color and apparently very hard, were found to be in that part which immediately

surrounded the carbon electrodes. They were exceedingly small and only served to convince me that more and better arranged experiments would produce the desired results.

The iron bowl furnace was replaced with one constructed of refractory bricks, its interior dimensions being 10 inches in length by 4 inches wide and 4 inches deep. Into each end extended a carbon rod, so arranged as to be movable in the direction of its length, thus allowing of a variation of the distance through which the current would have to traverse the charging mixture. The electrical apparatus was arranged for supplying and regulating a current of from 100 to 200 ampères, and of an adjustable potential of from one to fifty volts. The current used was an alternating one, and the action and effects produced were thereby reduced to one of temperature, the probability of electrolytic effects not existing.

The first experiments were confined, more or less closely, to the original lines, as defined by the theory with which I commenced—carbon and clay forming the basis of operation. It was soon discovered that the crystals were not what I had expected to obtain—they were not pure carbon; in color they were usually blue, and their hardness was found to be sufficiently great to abrade the diamond. They seemed, however, to be exceedingly brittle, and it was only in the form of a very fine powder that they were capable of performing this work. Repeated attempts to charge the surface of a copper, or other metallic disc, were productive of failures, as compared with the results obtained with crushed diamond under similar conditions; the crystals being too brittle to withstand the pressure necessary to embed them, or in case of their being embedded, they would be broken and crushed when subjected to use in the manner of the well-known diamond saw.

At this point in the work the want of a name for the new product was felt. It had not been analyzed, and I was led to believe, from the materials used, together with the color, sapphire blue and ruby-red, hardness and general form, that the material was composed of carbon and alumina, and in this belief it was decided to construct the name of the new

material out of carbon and corundum, and it was named carborundum. The fitness of the name, in the eyes of the chemist, is, in view of the now known composition of the substance, doubtful, while in commerce, although phonetic and of pleasing effect in print, it is, perhaps, a trifle lengthy.

I had not continued my experiments long, before certain conditions and results obtained, led me to think the silica present in the furnace played a very prominent part in determining the quality and quantity of the carborundum; and with a view of determining whether or not this was the case, a mixture was made composed of carbon, silica and chloride of sodium; my former experiments having proven the presence of common salt to be beneficial, facili-

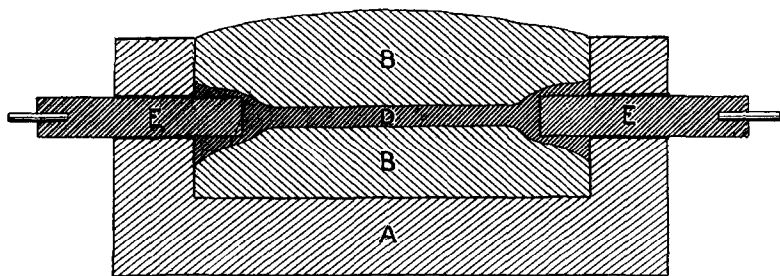


FIG. 1.—Longitudinal section of furnace.

tating the fusion, and to some extent protecting the mass in the furnace from oxidation by air contact. The carbon used was obtained from the carbon rods used in arc lamps, they having been reduced to a powder. These carbons had been made from the coke residue obtained in the distillation of petroleum. The silica was of a good grade of glass sand, its composition not being known. The salt was a good average quality. These materials were mixed in the proportion of forty per cent. each, of carbon and sand, and twenty per cent. of salt, and the mixture was placed in the furnace.

I had met with considerable trouble in operating the furnace from the difficulty in starting the fusion of the mixture, and the continual changes that occurred in the

internal resistance; the contacts, or connection between the electrodes and mixture, were also very difficult to maintain. To obviate or reduce these objectionable features, the connections and chargings were made in the manner shown in the diagram, where *A* represents the walls of the furnace, *B B* the mixture of carbon, salt and sand, *E E* the carbon rods or electrodes, and *D* a core of granular carbon, this core being enlarged at its extremities and made to surround the ends of the electrodes.

The furnace having been prepared in this manner, the electric current was made to pass. The value of this current was never constant, thus: on starting it would have a value of about forty ampères, with a potential of about fifty volts; the ampères would immediately increase, the potential being kept constant until the limit of the apparatus, or 200 ampères, had been reached, at which point the regulation of the potential would begin, finally stopping at about twenty-five volts, the ampères remaining at 200. These changes were produced, on the part of the current quantity, by a reduction in the resistance of the furnace due to the increasing temperature of the core and mixture, fusing of the salt, and eventually to the formation of a black material, consisting of a mixture of carborundum and free carbon, this material having a high conductivity. The reduction of the potential was produced by the ordinary methods of regulation, and was made to prevent the continued increase of the ampères and consequent burning out of the generating apparatus.

An experiment was made with the mixture, arrangements of charge and current as stated, the time required being about four hours. The mass heated slowly, the first outward indication of the internal heat and reactions being the appearance of monoxide of carbon, which was lighted and continued to burn during the remainder of the experiment; later, occasional bursts of white vapors of chloride of sodium would occur, and these would be followed by a flow of melted chloride of sodium, forming miniature volcanic craters.

The action was continued until there was a cessation of

these disturbances, until the blue flames of burning monoxide of carbon became tinged with a deep yellow from the sodium, and until the reduction of the potential indicated a low resistance, resulting from the formation of the black substance above referred to; the current was then stopped, and the furnace permitted to cool and opened.

A representation of the cross-section of the furnace when opened is shown in *Fig. 2*, where *A* represents the walls of the furnace; *B*, the mixture of carbon, sand and salt, now a solid cemented mass consisting of sand and carbon held together with the fused salt; *D*, the carbon core, and *G C* and *W*, zones of portions of the original mixture *B*, now transformed into materials of variable composition.

The results obtained from the first experiments with a

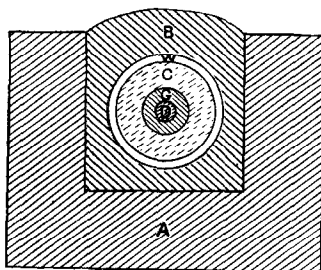


FIG. 2.—Cross-section of furnace.

mixture containing silica, instead of silicate of alumina, were so much superior to the results formerly secured, that the use of clay was abandoned.

Such is a brief sketch of the first manufacture of carborundum. Its further development and present manufacture form a large portion of the history of the Carborundum Company.

The results obtained were so promising that it was thought a lucrative business could be made of the manufacture and marketing of carborundum, and acting on this belief, a company was organized for these purposes. The processes of manufacturing carborundum and the working of it up into marketable form, were elaborated, and up to the present time are undergoing changes and improvements.

One of the first acts of the company was the equipment of a chemical laboratory, and the engagement of Dr. Otto Mulhaeuser, who entered at once into an exhaustive analytical study of carborundum. The results of his labors might be briefly stated as follows:

A sample of carborundum, as originally made from carbon, clay and salt, and having, to the unassisted eye, a blue-black color, but under the microscope exhibiting a few crystals of a yellow-green color, some black, some white, with the majority blue, had the following composition:

Si,	60.51
C,	30.09
Al ₂ O ₃ ,	4.78
CaO,17
MgO,18
O,	4.27
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	100.00

A sample of carborundum, made from carbon, sand and salt, having a clear light-green color, gave as its composition:

Si,	69.19
C,	29.71
Al ₂ O ₃ and Fe ₂ O ₃ ,39
CaO,19
MgO,06
O,47
	<hr/>
	100.00

From these figures we learn that what we have called carborundum is, in a pure state, carbide of silicon, responding to the formula SiC, the other substances being impurities. The carbon used in the manufacture of the last sample—the one from sand—was obtained from the coke of bituminous coal, and by it the iron was introduced which we find in the analysis.

The great difficulty met with in obtaining a complete combustion of the carbon, necessitated the reduction of the sample to the finest powder; the samples used for analysis being obtained by floating in water for some minutes, thus

permitting the coarser particles to fall down and be separated from the finer. This latter portion, remaining in suspension in the water, was decanted into another vessel and permitted to settle for some longer period. The degree of fineness of the powder is then indicated by the number of minutes it stood in the first vessel. The necessity for this minute subdivision is shown by the following percentages of carbon as determined from powders of different degrees of fineness, all of them forming part of one original sample :

	<i>Per Cent. C.</i>
Crushed crystals,	24·82
One minute,	25·08
Two minutes,	27·06
Three minutes,	28·04
Four minutes,	29·71

The wonderful permanency of carborundum, when exposed to a high temperature, is also shown by the fact that clean and pure powder heated to bright redness in a current of oxygen for a period of one hour lost only ·41 per cent.; this same quality is also shown in the following determination of silica (SiO_2) formed by the ignition of carborundum (SiC) crystals in the open air in a platinum crucible at a bright red heat for ten hours :

	<i>Grs.</i>
Weight of crucible,	28·5315
Weight of crucible and SiC ,	29·0362
Weight of crucible and SiC after ignition,	29·0220
Loss,	·0142
Weight after ignition,	29·0220
Weight after treating with HF and H_2SO_4 ,	29·0082
SiO_2 ,	·0138
Total loss,	·0276
Weight of SiC at first,	·5047
	<i>Per Cent.</i>
Total loss,	5·5
Loss per hour,	·55

While the effort is always made to produce carborundum as nearly pure as possible, the conditions of its manufacture are such as to cause a larger or smaller percentage of

impurities to be present. It is, of course, impossible to use a mixture of carbon and silicon as represented in the composition of carborundum, an excess of carbon must be present at the beginning of the process to take up the oxygen present and that entering from the air. It has been found that a very good proportion for the mixture is twenty parts carbon, twenty-five parts sand and ten parts salt (by weight). A sample of carborundum made from this mixture was tested for silica (SiO_2) and a treatment for eight days with hydrofluoric acid (HF) showed the amount present to be 1.56 per cent.

Before entering upon a consideration of the commercial features of carborundum, I will present the following condensed report of the investigations of Dr. Mulhaeuser, as prepared by him at my request for this paper.

The structure and chemical composition of the mass after the reaction was found to be as follows, reference being made to the diagram, *Fig. 2*.

D represents the path of the current, the core of carbon connecting the terminals forming with the latter the resistance by which the electrical energy is transformed into heat energy. This core shows—after the reaction—no change.

G represents a shell of a brilliant black mass which surrounds the carbon core; it consists of crystalline-like aggregates, which are arranged radially to the axis of the core. The part near the core consists of pure carbon, those parts more distant from the axis of the core are more or less mixed with carborundum crystals. A sample of that part gave, for instance, the following analytical results:

	<i>Per Cent.</i>
Free carbon,	66.29
Carborundum,	33.71

The free carbon has all the properties of graphite, it blackens the fingers, etc. The carborundum found in this zone *G* gave the following numbers:

	<i>Per Cent.</i>
C,	30.49
Si,	68.26
Fe_2O_3 ,	0.77
CaO ,	0.48

To separate the carbon from the carborundum the mass is heated with hot oxygen. The crystals obtained in this way, though they possess generally the properties of carborundum, seem to differ a little in their optical qualities. They show, after having been freed from carbon, all the colors of the spectrum; especially brilliant are the red and violet rays.

C represents the chief product of the reaction, the zone of the carborundum, chemically spoken of as crystallized carbide of silicon. The zone of carborundum surrounds the graphite zone. The crystals are arranged radially to the axis of the core, and form in general a bright green shell. For the purpose of analysis, a sample of that shell was reduced to a powder of the proper fineness and gave the following figures:

	<i>Per Cent.</i>
Si,	62.70
Fe ₂ O ₃ and Al ₂ O ₃ ,	0.93
MgO,	0.11
C,	36.26

This analysis showed clearly that carborundum consists essentially of carbon and silicon associated together in the proportion of one atom each. In order to clean the product, to free it from iron, aluminum, etc., the powder was treated in the following manner: First with hydrochloric acid, then with dilute caustic soda and water, then the powder was put in a combustion tube, heated to dark redness and a current of oxygen passed over it for about one hour. All free carbon and perhaps a little of the combined carbon is burned off and a powder obtained, which contains now only silica, acid, traces of magnesia, alumina and iron, besides the carbide of silicon. By treating the powder with hydrofluoric acid, the carbide of silicon is obtained nearly pure. One of the many samples cleaned in this way, gave the following results:

	<i>Per Cent.</i>
Si,	69.10
C,	30.20
Al ₂ O ₃ and Fe ₂ O ₃ ,	0.49
CaO,	0.15

A compound having the formula SiC contains seventy per cent. Si and thirty per cent. C.

If pure carbon and pure silicic acid be taken the carborundum crystals will be white; if these materials contain iron, the crystals show a greenish-yellow color.

The crystals are not dissolved either by hydrofluoric acid or by any other acid; they are slightly attacked by dilute caustic and carbonated alkalis; and they are decomposed by caustic or carbonate of soda by fusion. The carbon is separated and silicon is transformed in silicic acid, the whole mass becomes black, then after some time the carbon burns off.

When reduced to a very fine powder and floated in water, carborundum does not settle, even after a period of months. It behaves like a colloidal substance, for instance metallic silver. By adding an acid or a salt, the extremely fine powder settles.

W represents a white or gray-greenish looking shell, surrounding the zone of carborundum crystals. The mass consists of small pieces of the size of the original sand grains. These pieces are soft and may be reduced very easily to a fine powder. The qualitative analysis showed that the powder had the same constituents as the carborundum crystals, and the powder was, therefore, cleaned in the same manner as in the case of those crystals. The white-green shell was crushed and alternately heated with hydrochloric acid, caustic soda, water, hot oxygen and hydrofluoric acid. The resulting powder had the following composition:

	<i>Per Cent.</i>
C,	27.93
Si,	65.42
Fe ₂ O ₃ and Al ₂ O ₃ ,	5.09
CaO,	0.33
MgO,	0.21

We may say then, that the powder consists essentially of carbide of silicon. But this carbide of silicon is different from the other one in that it forms no crystals, is amorphous and very soft, and of no value as an abrasive. It has been obtained at a comparatively low temperature—far distant from the core—and is identical with the product recently obtained by I. Schützenberger.

[*To be continued.*]