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CARBONIZING METALS

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My invention relates to a process of coating metal surfaces with an adherent layer of carbon and more particularly to a process of carbonizing nickel, iron, steel and other metals which are used as electrodes in electron discharge devices.

The usual methods of carbonizing metals by heating in an atmosphere of hydrocarbon gas have many disadvantages in preparing electrodes for electron discharge devices. Carbon bearing atmospheres, such as gasoline vapor, or natural gas, usually do not deposit a gas-free and adherent coating on the metal. When the firing temperature is high the resulting coating is fluffy and can be easily rubbed off, and if the temperature is low the residue is tarry and is unsuited for radio tube uses. Iron is particularly hard to carbonize in a hydrocarbon atmosphere because few of the commercial gases or vapors will decompose and deposit carbon at a temperature below the carburizing and hardening temperature of the iron.

An object of my invention is to carbonize metals, especially metals of the ferrous group, in such a manner that a uniform adherent coating is produced on the metal.

Another object of my invention is a process of carbonizing metal which is fast, and economical, and which produces a gas-free and adherent coating at temperatures below the hardening temperature of the metal.

The characteristic features of my invention are defined with particularity in the appended claims and preferred embodiments thereof are described in the following specification. I have discovered a mixture of commercial gases which when heated within a specified range of temperatures will rapidly deposit on metal surfaces an adherent black coating of carbon. The gases comprise a hydrocarbon, which will decompose at a relatively low temperature, mixed in various proportions with carbon dioxide. The carbon dioxide apparently is not inert, in the same sense that nitrogen is inert, during the heating of the gas and the deposition of carbon. Tests having shown that nitrogen added to the hydrocarbon gas functions merely as a diluent.

According to one feature of my invention the metal to be carbonized is heated to a relatively low temperature, preferably below about 650° C. in the mixed gaseous atmosphere composed essentially of one part of hydrocarbon gas and between .75 and 2.0 parts of carbon dioxide. The heating is continued for one-half to two minutes, whereupon the metal is cooled, out of contact with air, to below the oxidizing temperature of the

metal in air. This process is particularly useful in carbonizing iron which heretofore could not be coated with an adherent layer of carbon without some case carburization and hardening of the iron. Apparently carbonizing processes heretofore in use required firing temperatures so high that the deposited carbon entered into the iron and formed carbides. Firing temperatures below 650° C. in an atmosphere of hydrocarbon gas and carbon dioxide, however, rapidly produce an adherent carbon coating of the necessary thickness without appreciably effecting the stiffness or "spring-back" of the metal.

Good results have been obtained in carbonizing iron strip by feeding the strip at the rate of 30 to 36 inches per minute through a furnace with a heating zone two feet long and about 4 to 5 inches in diameter. The air in the furnace is displaced by my novel mixture of carbon dioxide and hydrocarbon gas, preferably flowing through the furnace at the rate of about 4 cubic feet per hour, the wall of the furnace being maintained at a temperature preferably between 550 and 650° C. The specific gas mixture with which good results have been obtained comprises about one part of acetylene gas to one part of carbon dioxide. By increasing the amount of carbon dioxide the adherence, smoothness, and toughness of the carbon coating is increased, but the rate of deposition of the coating is decreased, it being found feasible to increase the carbon dioxide content up to about twice the acetylene content of the gas. If the CO₂ content is reduced to less than about .75 part for each part of acetylene, the coating becomes fluffy and less adherent which is characteristic of the coating deposited from a pure or undiluted hydrocarbon atmosphere. Strip metal .005 inch in thickness fed through the furnace, above specified, determines to a limited extent the temperature of the wall of the furnace, apparently because, at a speed of 36 inches per minute, the thermal inertia of the strip becomes appreciable. If the iron strip is less than 2 inches wide the furnace temperature for optimum results should be between 550 and 600° C., and where the strip is between 2 and 3 inches wide the furnace temperature should be between 575 and 625° C. While iron strip may be coated, according to my invention, at temperatures as low as 500° C. below this temperature the coating is unsuited for radio tubes because it is gassy, apparently because of hydrocarbon residues in the coating.

If a metal, such as nickel, is used with which carbon does not readily combine to produce carbides, or if the coated metal is preformed so that

die work is not necessary on the metal, the temperatures of carbonizing may be higher. Preformed parts for radio tubes such as iron or nickel anodes, for example, may be batch carbonized in a mixed carbon dioxide and hydrocarbon gas at temperatures as high as 800 or 900° C. for as long as five minutes. The metal carbides or graphitic carbons formed at these temperatures are not objectionable in vacuum tubes.

Roughening of the strip metal, preferably by sandblasting, is desirable to improve adherence of the carbon coating, although sandblasted iron requires slightly longer firing time for a given coating weight. Carbon deposits readily on acid etched metal from my mixture of carbon dioxide and hydrocarbon gas. Adhesion and speed of deposition of the carbon may be increased by dipping the metal just before firing in a dilute solution of alcohol and hydrolized magnesia to produce on the surface of the metal a white transparent film of MgO.

There is very little carbide formed by chemical reaction between the carbon and the iron between 500 and 650° C., as evidenced by tests that show there is no appreciable hardening of the strip during firing. While certain portions of iron strip appear to be slightly case carburized, dies and punches do not wear excessively, indicating but small carbide formation at the surface of the iron. A flame having the appearance of burning carbon monoxide appears in the furnace and indicates that the carbon dioxide decomposes to the monoxide. It is not apparent in what manner the monoxide or dioxide of carbon reacts with the hydrocarbon gas to aid in its decomposition and assist in the deposition of the carbon on the metal, but it is apparent from examination of the coated metal that the carbon dioxide is not entirely inert. Iron or steel has for the first time, according to my invention, been coated with an adherent layer of carbon without hardening of the iron. The coating is smooth and black, and although it has a velvety appearance it is hard and firm and easily distinguished from the more fluffy and more porous coating obtained from the usual hydrocarbons used alone or mixed.

My improved process of coating metals is particularly useful in the factory where speed is important. The metal coated according to my invention is essentially free of gas and the coating is so adherent as to be easily worked in the usual punches and die presses without scrapping and loss of the coating.

I claim:

1. The method of applying an adherent black coating of carbon to sheet metal, comprising heating the metal in a mixed gaseous atmosphere composed essentially of one part of a hydrocarbon gas and between .75 and 2 parts of carbon dioxide, continuing the heating for ½ to 2 minutes to between 500° C. and 900° C., and cooling the metal out of contact with air to below its oxidizing temperature in air.

2. The method of applying an adherent coating of carbon to sheet metal comprising heating the metal to a temperature between 500 and 900° C. in a mixed gaseous atmosphere composed essentially of one part of hydro-carbon gas and between .75 and 2 parts of carbon dioxide, and continuing the heating for a period up to 5 minutes, and cooling the metal out of contact with an oxidizing atmosphere.

3. The method of applying an adherent carbon coating to iron, comprising heating the iron to a temperature between 500 and about 650° C. in a gaseous atmosphere composed essentially of one part of hydrocarbon vapor, and between .75 and 2 parts of carbon dioxide, continuing the heating for one-half to 2 minutes, and cooling the iron out of contact with an oxidizing atmosphere.

4. The method of applying an adherent black coating of carbon to iron, comprising heating the iron to a temperature between about 550 and 650° C. in an atmosphere composed essentially of about equal parts of carbon dioxide and acetylene gas, continuing the heating for one-half to 2 minutes and cooling the iron, out of contact to air, to below the oxidizing temperature of iron in air.

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