

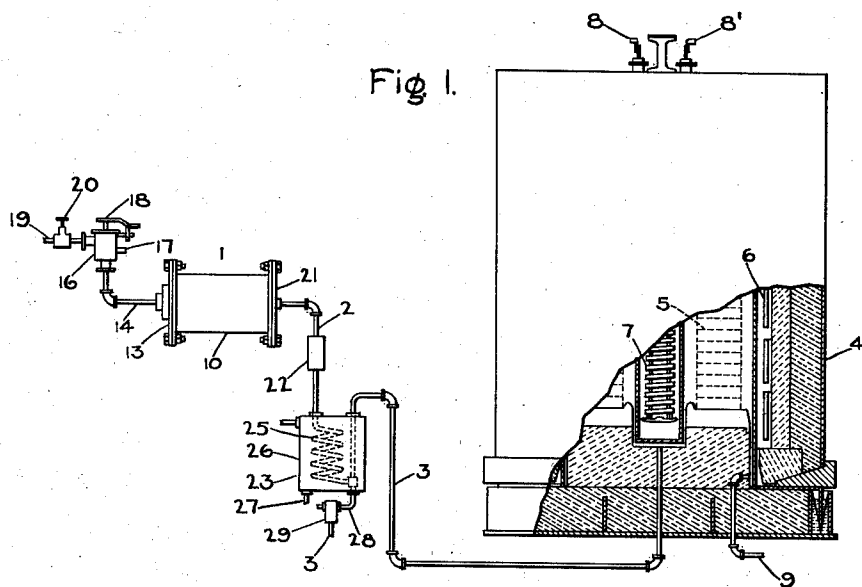
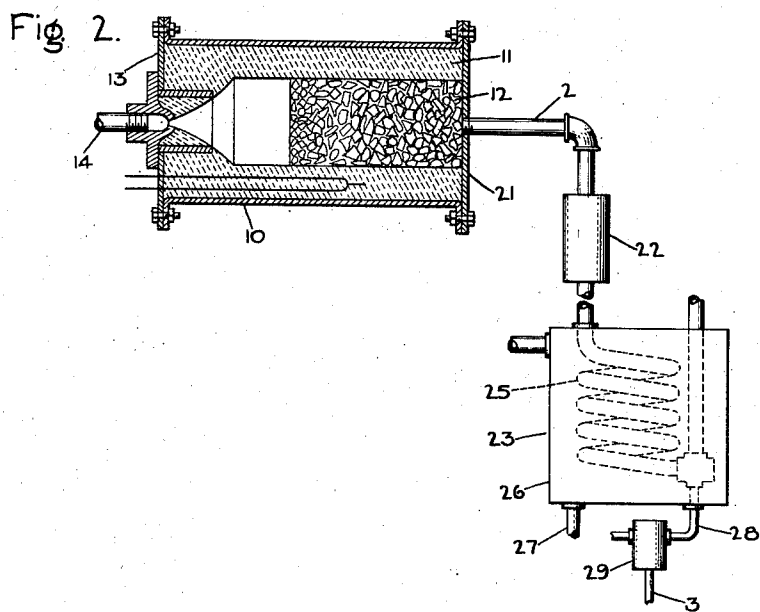
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METALLURGICAL FURNACE ATMOSPHERE

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METALLURGICAL FURNACE ATMOSPHERE

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8 Claims. (Cl. 148—16)

The present invention relates to the protection against etching and dulling of the bright surface of polished steel during heat treatment.

Prior to my invention it was found, when polished steel articles were protected against oxidation during heat treatment by envelopment with gases obtained by the incomplete combustion of hydrocarbon gases, that the steel after having been annealed was badly etched and had a matte surface. This effect was particularly troublesome when the heat treatment period was long, say 25 to 50 hours. Etching could not have been due to oxidation since the enveloping atmosphere would reduce iron oxides at the temperatures involved. While some water vapor was present it was found that the more complete removal of water vapor did not prevent loss of the bright surface. In fact, the drier the gas became, the worse the etch became. Nor was the effect connected with the presence of carburizing gas. Methane even when present in percentages up to ten per cent exerted no influence upon the etching. As it is desirable to maintain the bright or polished surface of steel during anneal, or other heat treatment, the enveloping gas atmosphere conveniently and cheaply obtained by the incomplete combustion of hydrocarbon gas appeared to be unavailable for the protection of such steel articles.

I have discovered that, when the constituents of a gaseous mixture formed by combustion of hydrocarbons are so proportioned as to be in substantial chemical equilibrium with one another at the annealing temperature, that is to say, essentially in chemical equilibrium at the annealing or heat-treating temperature, etching is avoided and the bright surface of the steel remains intact.

Apparently the etching of the surface formerly experienced was due to gas reactions which occurred most energetically at the surface of the steel by contact catalysis. The two reactions which were mainly involved are (1) the so-called water gas reaction $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ and (2) the producer gas reaction $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$. While both of these reactions appear to be responsible for etching it is the first-mentioned which must be guarded against especially if loss of brightness of the work should be avoided. There is a larger margin of tolerance in the second reaction, but it must also be prevented, or retarded, to prevent etching.

In carrying out my invention the ratio of air to hydrocarbon gases and other conditions of combustion are controlled and the water vapor

content of the gaseous products of combustion is regulated to keep the carbon monoxide, water vapor, carbon dioxide and hydrogen content of the gaseous combustion products used as enveloping atmosphere within such range of relative proportions that substantially no reaction occurs between such gases at the temperature of the metallurgical operation in connection with which etching is otherwise encountered.

In the accompanying drawing Fig. 1 is a somewhat diagrammatic view of an apparatus suitable for carrying out my invention shown in connection with an annealing furnace; and Fig. 2 is a side elevation partly in section of a part of the apparatus shown on a larger scale.

Referring to Fig. 1 of the drawing, a gaseous mixture suitable for enveloping steel, or other work subject to etching, is derived by the burning of hydrocarbon fuel in the presence of air in a combustion apparatus 1 which is connected by suitable conduits 2 and 3 to a heat-treating furnace 4 (which is here represented on a reduced scale). The wall of the heat-treating furnace is indicated as being partly broken away in order to show the work 5 within the furnace. Any suitable source of heat such as electric resistors 6 and 7 may be employed to heat the heat-treating furnace up to the required temperature. Electric terminals for the heater are shown at 8, 8'. In the case of an annealing furnace the temperature may be within a range of 400 to 1000° C., depending on the character of the steel and other conditions. The excess gas may escape through an outlet conduit 9.

The combustion apparatus for furnishing the enveloping gas as shown in Fig. 2 is provided with an external casing 10 which is provided with a suitable refractory lining 11, the space within the refractory lining being filled with a mass 12 of fragments of refractory material which become heated during the burning of the hydrocarbon within the combustion apparatus and thereby facilitate the combustion reaction. The fragments may consist of fire brick, alumina, magnesia, or the like. Secured to the head 13 of the furnace is an inlet nozzle 14 whereby a gaseous or vaporized hydrocarbon fuel is supplied to the combustion chamber. The fuel which is burned may consist of a hydrocarbon mixture commonly known as city gas, or of natural gas, or of vaporized butane, or of other hydrocarbon commercially obtainable in liquid form. Various means may be employed for mixing the gaseous fuel and air and for supplying it at the proper pressure to the combustion nozzle of the furnace.

For example, such means may consist of a suitable pump (not shown) to which is connected a mixing device 16 (Fig. 1) having suitable air inlet 17 to which is connected an adjusting handle

18. Any well-known form of mixing device may be used, as for example devices such as sold by The Selas Company or the Kemp Company of Philadelphia, Pennsylvania. The hydrocarbon fuel is supplied to the mixing device by the pipe 19 in which is shown a valve 20. By adjusting the setting of the mixing device 16 the proportion of hydrocarbon fuel and air may be varied at will thereby varying the relative proportion of the products of combustion, except that of water vapor. A suitable combustion apparatus is described in a co-pending application of O. S. Haskell, Serial No. 720,149, filed April 11, 1934.

The gaseous mixture is led from the combustion apparatus by a conduit 2 secured to the head 21 to a chemical purifier 22 and then through a drier 23 into the conduit 3 which conducts the gaseous mixture into the furnace 4. The chemical purifier 22 is provided with suitable chemical reagents, as, for example, copper, or iron turnings, and is heated to a sufficiently high temperature to remove residual oxygen if any remains and any unsaturated hydrocarbons, such as ethylene, which may be present.

The drier 23, whereby water vapor produced by the combustion reaction is removed, may consist of a cooling coil 25 (see Fig. 2) which, as shown, is surrounded by a cooling fluid in a container 26 supplied by an inlet tube 27 and removed by an outlet tube 28 which is provided with a dump valve 29 whereby the water is removed without allowing gas to escape. As a cooling fluid ordinary tap water may be used which, when in contact with the gas conduit, condenses a portion only of the water vapor content of the gas passing through the drier.

As has already been stated above, the gaseous oxides of carbon, water vapor, and uncombined hydrogen should be in chemical equilibrium at the heat treating temperature. It may be said with greater exactness that the ratio

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

when the work is the annealing of low carbon-steel, should fall within the range of .06 to 1. Otherwise stated, the product resulting when the partial pressure of carbon monoxide expressed in atmospheres is multiplied by the partial pressure of water vapor divided by the product resulting when the partial pressure of carbon dioxide is multiplied by the partial pressure of hydrogen should fall approximately in this range. These values apply, for example, for an annealing or other heat-treating temperature within a range of about 400° to 700° C., for instance at an annealing temperature of about 650° C. which is that commonly used for low carbon steel.

The percentage of water vapor can be readily varied by varying the rate of flow or temperature of the cooling fluid in the drier 23. With the proportion of air and hydrocarbon gas in the combustion apparatus so regulated that the content of carbon monoxide (CO) in the gas is about 8.0%, the content of carbon dioxide (CO₂) is about 5.7%, and the proportion of uncombined hydrogen (H₂) is about 13.4%, which is a favorable condition for the operation of the combustion apparatus, then the moisture content of the gas should be at the precipitation value, or at a saturation temperature of approximately 23° C.

(73° F.). With a properly designed condenser this saturation temperature is easily attained by the use of tap water, the temperature of which ordinarily is within the range of 60 to 70° F., the water being carried through the condenser at a sufficiently high speed and the condenser surface being sufficiently extensive to assure cooling the gaseous products of combustion nearly to the temperature of the cooling water. If desired, ice, or an artificial refrigerating means, may be employed to reduce the temperature of the cooling fluid if necessary to reduce the water vapor concentration to the desired value.

As a second condition for the establishment of chemical equilibrium in the gaseous products of combustion, it is required that the ratio of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

should be less than one-half, or, in other words, the square of the partial pressure of carbon monoxide divided by the partial pressure of carbon dioxide should be less than one-half. This ratio may be maintained by varying the amount of air supplied to the combustion apparatus, the amount of air being insufficient for complete combustion. In all cases when air is used to support combustion nitrogen will be present as a diluent in the products of combustion. When employing "city gas" for combustion purposes I may use two to three parts of air to one part of city gas. With these mixtures the ratio of (CO)² to (CO₂) is naturally less than 0.5 and the moisture content can be readily adjusted so that the ratio (CO) (H₂O) to (CO₂) (H₂) lies in the range 1.0 to 0.06.

Some hydrocarbon gases, such as methane, for example, exerted no deleterious influence other than that of a diluent when present up to about ten per cent. Unsaturated hydrocarbon gas, such as ethylene, must be removed if present. Also uncombined oxygen should be removed, if present. However, if the combustion of the hydrocarbon gas is properly carried out little if any of such gases will be present in the combustion products.

By observing these conditions, it is possible to anneal low carbon steel without the appearance of oxidation in the presence of substantial percentages of water vapor in the products of combustion obtained from hydrocarbon gases. The described gaseous atmosphere is applicable for use in preventing the dulling of shiny surfaced metal articles such as bright surfaced steel while heated, for example, up to about 700° C. and while cooling from the maximum temperature to room temperature. The following table shows typical gaseous mixtures suitable for use as enveloping atmospheres for carrying out the bright anneal of low carbon steel at a temperature of about 650° C.

Number	Nitrogen	Carbon monoxide	Carbon dioxide	Hydrogen	Water vapor
1.....	70	8.0	5.7	13.4	2.6
2.....	77	6.8	7.0	8.5	0.6
3.....	63	10.0	4.8	19.6	2.6

As the concentrations given above are expressed in per cent by volume they should be changed to partial pressure in atmospheres for all purposes of calculation.

Wherever I use the term "partial pressure" herein, it is intended to be understood that the term means partial pressure in atmospheres, this

being the meaning commonly accepted and understood by those skilled in the art and is so recognized and used in the chemical literature.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. An enveloping gas for protecting during heat treatment metal articles having a shiny surface, said gas containing substantial quantities of carbon monoxide, carbon dioxide, hydrogen and water vapor, and the relative proportions of said carbon monoxide, carbon dioxide, hydrogen and water vapor being such that the product of partial pressures in atmospheres of carbon monoxide and water vapor divided by the product of partial pressures in atmospheres of carbon dioxide and hydrogen is within a range of 0.06 to 1 and the ratio of the square of partial pressure in atmospheres of carbon monoxide divided by the partial pressure in atmospheres of carbon dioxide is less than five-tenths.

2. An enveloping gas for protecting during heat treatment metal articles having a shiny surface, said gas being obtained by the combustion of hydrocarbon-containing material in a deficiency of air and consisting mainly of nitrogen, carbon monoxide, carbon dioxide, hydrogen, and water vapor, the relative proportions of the carbon monoxide, carbon dioxide, water vapor, and hydrogen being such that the product of partial pressures in atmospheres of carbon monoxide and water vapor divided by the product of partial pressures in atmospheres of carbon dioxide and hydrogen is within a range of 0.06 to 1 and the ratio of the square of partial pressure in atmospheres of carbon monoxide divided by the partial pressure in atmospheres of carbon dioxide is less than five-tenths.

3. An enveloping gaseous atmosphere for protecting ferrous articles having a shiny surface during an annealing treatment thereof, said gaseous atmosphere being obtained by the combustion of hydrocarbon-containing gas in a deficiency of air and consisting mainly of nitrogen, carbon monoxide, carbon dioxide, hydrogen and water vapor, the relative proportions of the carbon monoxide, carbon dioxide, hydrogen and water vapor being such that the product of partial pressure in atmospheres of carbon monoxide and water vapor divided by the product of partial pressures in atmospheres of carbon dioxide and hydrogen is within a range of 0.06 to 1 and the ratio of the square of partial pressure in atmospheres of carbon monoxide divided by the partial pressure in atmospheres of carbon dioxide is less than five-tenths.

4. A method for preventing the dulling of a metal article having a bright surface during a heat treatment thereof which comprises enveloping said article, while heated, by a gaseous atmosphere obtained by the combustion of hydrocarbon-containing material in a deficiency of air and consisting mainly of nitrogen, carbon monoxide, carbon dioxide, hydrogen and water vapor, the relative proportions of the carbon monoxide, carbon dioxide, water vapor and hydrogen being such that the product of the partial pressures in atmospheres of carbon monoxide and water vapor divided by the product of the partial pressures in atmospheres of carbon dioxide and hydrogen is within a range of 0.06 to 1.0 and the ratio of the square of the partial pressure in atmospheres of carbon monoxide divided by the partial pressure in atmospheres of carbon dioxide is less than five-tenths.

5. The process of preventing the dulling of

steel articles having a bright surface, during heat treatment thereof, at temperatures within a range of about 400° to 700° C., which consists in enveloping said articles by an atmosphere obtained by the combustion of hydrocarbon containing gas in a deficiency of air and containing substantial quantities of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂) and water vapor (H₂O), and so regulating the relative partial pressures in atmospheres of said gaseous ingredients that the ratio of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

is less than one-half and the ratio of

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

is kept within the limits of 0.06 to 1.0 by controlling the water vapor content of the gaseous mixture.

6. The method which comprises heat treating a bright surfaced ferrous article at a temperature within a range of about 400° to 700° C. in a gaseous atmosphere obtained by the combustion of hydrocarbon-containing material in a deficiency of air and containing substantial quantities of carbon monoxide, carbon dioxide, hydrogen and water vapor in such relative proportions that at the heat-treating temperature the ratio of partial pressures in atmospheres of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

is less than one-half and the ratio of partial pressures in atmospheres of

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

is within a range of 0.06 to 1.0, said ration of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

being maintained by controlling the conditions of combustion including the ratio of air to hydrocarbon-containing material and said ratio of

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

being maintained by removing water vapor from the gaseous products of combustion in an amount sufficient to produce said ratio between said gaseous components; and cooling the heat-treated ferrous article in said gaseous atmosphere.

7. The process of annealing a shiny surfaced ferrous article at a temperature within a range of about 400° to 700° C. followed by cooling, which process comprises surrounding said article during heating and cooling with an enveloping gaseous atmosphere obtained by first burning a hydrocarbon-containing gas with an insufficiency of air to produce a gaseous mixture consisting mainly of nitrogen, carbon monoxide, carbon dioxide, hydrogen and an excess of water vapor and then cooling said gaseous mixture to a temperature of approximately 23° C. to condense out part of the water vapor, said enveloping gaseous atmosphere containing carbon monoxide, carbon dioxide, hydrogen and water vapor in such relative proportions that at the annealing temperature the ratio of partial pressures in atmospheres of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

is less than one-half and the ratio of partial pressures in atmospheres of

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

5 is within a range of 0.06 to 1.0.

8. The process of preventing the dulling of polished low carbon steel during annealing thereof at a temperature of about 650° C. which consists in
10 enveloping said steel by an atmosphere obtained by the combustion of hydrocarbon containing gas in a deficiency of air and containing substantial quantities of carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂) and water vapor
15 (H₂O), and so regulating the relative partial

pressures in atmospheres of said gaseous ingredients that the ratio of

$$\frac{(\text{CO})^2}{\text{CO}_2}$$

is less than one-half and the ratio of

$$\frac{(\text{CO}) \times (\text{H}_2\text{O})}{(\text{CO}_2) \times (\text{H}_2)}$$

is kept within the limits of 0.06 to 1.0 by cooling
10 the gaseous products of combustion to a temperature sufficient to condense out part of the water vapor and thereby controlling the water vapor content of the gaseous mixture.

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