

# UNITED STATES PATENT OFFICE.

FEDERICO GIOLITTI, OF ROME, ITALY, ASSIGNOR TO SOCIETÀ ANONIMA ITALIANA GIO.  
ANSALDO ARMSTRONG & C., OF GENOA, ITALY.

MANUFACTURE OF ARMOR-PLATES AND OTHER ARTICLES OF STEEL AND ALLOYS OF  
STEEL.

936,315.

Specification of Letters Patent.

Patented Oct. 12, 1909.

No Drawing.

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*To all whom it may concern:*

Be it known that I, FEDERICO GIOLITTI, a subject of the King of Italy, and residing at No. 35 Via Palestro, Rome, Italy, professor of chemistry, have invented certain new and useful Improvements in the Manufacture of Armor-Plates and other Articles of Steel and Alloys of Steel, of which the following is a specification.

10 This invention relates to the manufacture of armor-plates and other articles of steel or alloys of steel for ships and other uses, and it consists in an improved process of "cementation."

15 All the methods known hitherto for producing in articles of steel or alloys of steel an outer zone which is more highly carburated than the remainder of the article by means of a process of "cementation" 20 at a temperature above 1000 degrees Celsius, have consisted in heating the article either in contact with a powdered or granular substance capable of giving up carbon, or in an atmosphere of gaseous carbids of hydrogen 25 or of vapors of liquid carbids of hydrogen, with or without an admixture of nitrogenous substances (such as the vapors of ammoniacal salts, cyanids etc.) The carburated zones produced by those methods are 30 always characterized by the fact that their outer layers are highly carburated and that the contained carbon diminishes gradually in the deeper layers.

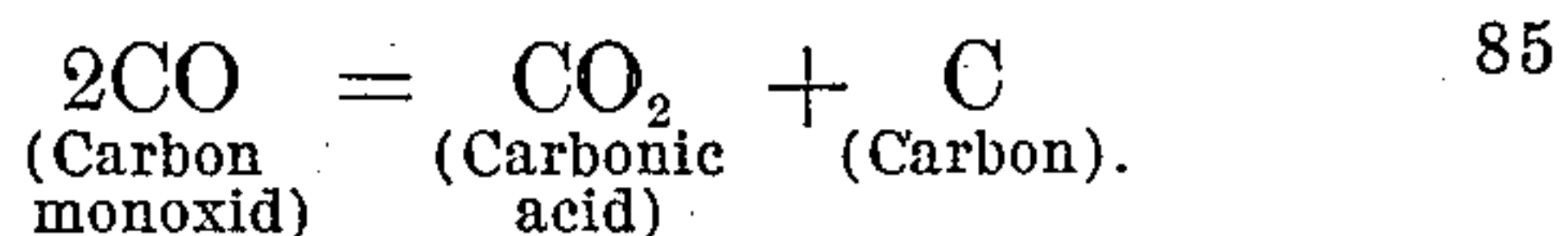
35 It has been hitherto impossible to produce a "cemented" zone in which the superficial or outer layers contain less than from 0.8 to 0.9 per cent. of carbon. In fact these layers contain generally more than 1 per cent. in those cases where the depth of the cementation exceeds 15 to 20 millimeters. It 40 has also been found impossible by known methods to produce cemented layers having a uniform or approximately uniform percentage of carbon throughout a thickness equal 45 to one-half or two-thirds of the total thickness of the carburated zone. This is due to the circumstance that all the known methods produce cemented zones in which the percentage of carbon diminishes continuously 50 toward the inner layers, rapidly at first and then slowly.

Now the present invention has for its object to produce in an article of steel or alloys of steel, a cemented zone of any desired

thickness containing a percentage of carbon 55 which shall not exceed at any point (not even at the surface) a determined amount chosen according to the results to be obtained, between the limits of from 0.2 to 1.3 60 per cent. The improved process also allows of producing a cemented zone in which the percentage of carbon shall be approximately constant throughout a portion of 65 the zone that may be equal to one-half or even two-thirds of the total thickness of the zone.

It is scarcely possible to enumerate all the advantages resulting from the above. A single instance may however be mentioned here, namely that by avoiding a high carburization of the surface layer of the cemented steel article (which high carburization is unavoidable when using the ordinary processes of cementation) it is 70 possible also to eliminate completely the brittleness of the surface layer. This is of particular importance in the manufacture of armor plates, and especially of plates made from chrome steel. But the advantages accruing from the improved process are much 80 greater.

The above mentioned results are obtained by utilizing the following reversible reaction:—



This reaction takes place in a different degree and at varying speeds according to the conditions of temperature and pressure and 90 according as there are other substances present that are capable of reacting with one or more of the three substances between which the said reaction takes place. This is in accordance with perfectly defined chemical laws. 95

When carbon monoxid is heated by itself, it becomes decomposed in accordance with the above stated equation (from left to right) until a determined proportion has been 100 reached between the resulting carbonic acid and the carbon monoxid that is not yet decomposed. As soon as this proportion (which varies with the variation of the temperature and pressure of the gases) is 105 reached, the above stated reaction begins to take place at the same speed but in the inverse sense, between the solid carbon and the



carbonic acid, until a state of equilibrium is reached.

Now, on the contrary, when carbon monoxid is heated in the presence of an article of steel or iron, at a temperature (exceeding 900 degrees Celsius) at which the iron (gamma iron) dissolves solid carbon as it is being formed, the inverse reaction which should produce equilibrium (and stop the decomposition of the carbon monoxid) no longer takes place, as in the first mentioned case, between the carbonic acid and free carbon, but between the carbonic acid and the carbon dissolved in the gamma iron, and therefore the speed of this reaction will depend also on the concentration of the carbon dissolved in the iron, that is to say, on the percentage of carbon in the cemented layer. Inversely by suitably regulating the speed of renewal of the carbon monoxid, the temperature and pressure, it will be possible to obtain a determined and constant concentration of the carbon dissolved in the iron, that is to say a determined percentage of the carbon in the cemented layer.

The following example is given for the purpose of illustrating the nature of the invention and in what manner it is to be performed for practical purposes.

It is assumed that it is desired to produce a carburated outer layer in a mild steel having, for instance the following composition:—

|            |                |
|------------|----------------|
| Carbon     | 0.06 per cent. |
| Manganese  | 0.25 per cent. |
| Silicon    | 0.01 per cent. |
| Sulfur     | 0.04 per cent. |
| Phosphorus | 0.03 per cent. |

It is assumed further that it is desired that the layer which is to have a thickness of 22 millimeters shall not contain at any point, not even at the surface, more than 0.4 per cent. of carbon, and that the percentage of its contained carbon shall be approximately uniform throughout the first 15 millimeters of thickness.

As will be perceived the percentage of carbon contained in the cemented layer, chosen for this illustration, is so low that it would be impossible not to exceed it by the ordinary processes of cementation. In order to obtain this special cemented layer, the article to be cemented is heated for about 40 hours at 1100 degrees C., in an atmosphere of carbon monoxid which is being renewed by introducing into the cementation chamber during about every hour a cubic meter of carbon monoxid for each square meter of surface of the article to be cemented. The carbon monoxid which is required for the cementation may be readily obtained by passing a current of carbonic acid over coke heated above 1200 degrees C., in metal tubes or in vessels composed of refractory materials. The carbon

monoxid which has already been caused to give up its carbon to the steel to be cemented, may be regenerated and then used over again, by being passed over coke heated to a temperature exceeding 1200 degrees C., so as to re-convert into carbon monoxid the small quantity of carbonic acid that has been formed during the cementation by the hereinbefore stated reaction.

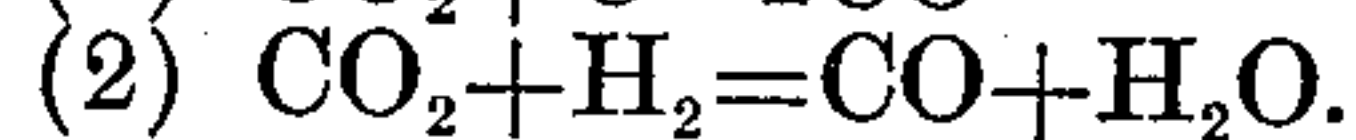
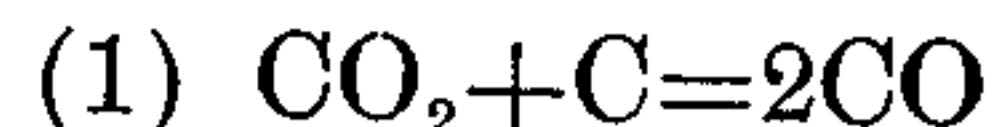
In cases where it is desired to obtain a uniform carburated layer containing a higher percentage of carbon, for instance, from 0.6 to 0.7 per cent., the conditions stated in the preceding example must be varied according to one of the following four methods:—

1. By lowering the temperature (but not below 900 degrees C.). The herein above stated reaction is exothermic and is therefore promoted by lowering the temperature.

2. By increasing the pressure of the carbon monoxid.

3. By increasing the amount of carbon monoxid which is caused to pass during a given time, around the steel articles to be cemented.

4. By mixing with the carbon monoxid varying quantities (to be determined by experiment in each particular case) of gaseous carbids of hydrogen, or vapors of liquid carbids of hydrogen for the purpose of regenerating (more or less completely and rapidly according to their quantity and quality) the carbon monoxid which has been converted into carbonic acid during the cementation process, the carbids of hydrogen acting as reducers by means of their carbon and their hydrogen, and converting the carbonic acid back into carbon monoxid in accordance with the two equations:—



By employing one of these methods, or two or three of them in combination, or all four of them, the articles of steel or alloys of steel can have formed in them carburated layers of any desired thickness containing any desired percentage of carbon between a minimum of 0.2 per cent. and a maximum of 1.3 per cent. The article thus treated may be subjected to one of the ordinary processes of cementation in order to produce an external layer of a high degree of carburization, or to one of the ordinary refining processes for the purpose of producing an external decarburized layer, or to a refining and to a cementing process in succession. The article may also be subjected to ordinary thermic treatments such as hardening, tempering, annealing, or to mechanical treatment by means of a press, rolling mill, hammer etc., adapted to impart to it the desired shape and properties.

Having thus described my invention what



I claim as new and desire to secure by Letters Patent is:—

1. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform throughout a depth not less than one half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter in depth of the desired thickness of the carburized zone, and introducing into said chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount of carbon absorbed by the articles during the period immediately following the last addition of carbon monoxid, as set forth.

2. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform through a depth not less than one-half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter in depth of the desired thickness of the carburized zone, raising the temperature to produce a lower percentage of carbon within said percentages, lowering the temperature to produce a higher percentage of carbon within said percentages, and introducing into said chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount of carbon absorbed by the article during the period immediately following the last addition of carbon monoxid, as set forth.

3. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform throughout a depth not less than one half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter in depth of the de-

sired thickness of the carburized zone, varying the pressure of the carbon monoxid within the limits of 1 and 30 atmospheres pressure, whereby the percentage of carbon in the carburized zone is varied in direct proportion, and introducing into said chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount of carbon absorbed by the article during the period immediately following the last addition of carbon monoxid, as set forth.

4. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform throughout a depth not less than one half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter in depth of the desired thickness of the carburized zone, increasing the pressure of the carbon monoxid within the limits of 1 and 30 atmospheres pressure by one additional atmosphere to produce approximately one millimeter per hour increase in the speed of the cementation process, and introducing into said chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount absorbed by the article during the period immediately following the last addition of carbon monoxid, as set forth.

5. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform throughout a depth not less than one half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid in the presence of a solid mixture of granular carbonaceous substances at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter in depth of the desired thickness of the carburized zone, and introducing into said chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount absorbed by the article during the period immediately following the last addition of carbon monoxid, as set forth.

6. The improved process of manufacture applicable to armor plates and other articles of steel or alloys of steel for ships and other uses, for the purpose of providing such



articles with a carburized zone of any desired thickness containing any desired percentage of carbon between 0.2 per cent. and 1.3 per cent. which is uniform throughout a  
5 depth not less than one half the thickness of the carburized zone, said improved process consisting in subjecting the article in a closed chamber to the action of carbon monoxid mixed with from 3 to 5 per cent. of vol-  
10 atile vapors of hydrocarbons such as benzin, petroleum and the like, at a temperature exceeding 900 degrees centigrade, for a period of not less than 1 hour for each millimeter

in depth of the desired thickness of the carburized zone, and introducing into said 15 chamber at intervals so much fresh carbon monoxid as is necessary to compensate for the amount of carbon absorbed by the article during the period immediately following the last addition of carbon monoxid, as set forth. 20

In testimony whereof, I affix my signature in presence of two witnesses.

FEDERICO GIOLITTI.

Witnesses:

G. B. ZANOREDO,  
G. BIZSARRI.