

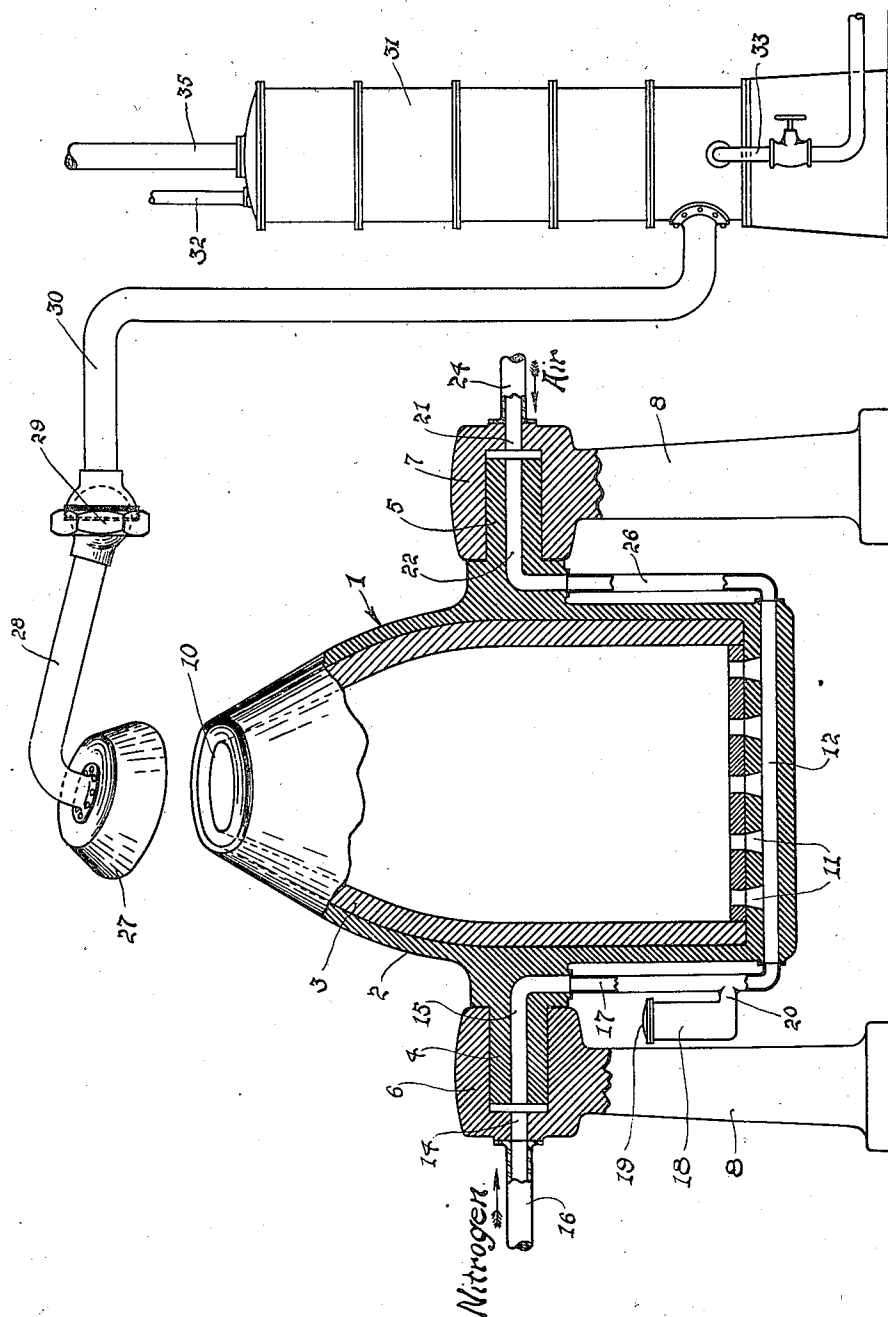
Aug. 19, 1924.

A. NAGELVOORT

1,505,281

PROCESS FOR THE MANUFACTURE OF STEEL AND THE FIXATION OF NITROGEN

Filed May 25, 1921



Inventor
Adriaan Nagelvoort
By *Perley H. Plant*
Attorney.

UNITED STATES PATENT OFFICE.

ADRIAAN NAGELVOORT, OF PROVIDENCE, RHODE ISLAND, ASSIGNOR TO THE NITROGEN CORPORATION, OF PROVIDENCE, RHODE ISLAND, A CORPORATION OF RHODE ISLAND.

PROCESS FOR THE MANUFACTURE OF STEEL AND THE FIXATION OF NITROGEN.

Application filed May 25, 1921. Serial No. 472,554.

To all whom it may concern:

Be it known that I, ADRIAAN NAGELVOORT, a citizen of the United States, residing at Providence, in the county of Providence and State of Rhode Island, have invented certain new and useful Improvements in Processes for the Manufacture of Steel and the Fixation of Nitrogen, of which the following is a specification.

This invention relates to an improved process for the manufacture of steel and the fixation of nitrogen, and comprises certain novel steps and combinations of steps adapted to facilitate the removal of impurities present in the iron and at the same time effect the formation of cyanogen compounds thus enabling the manufacture of steel to be carried out efficiently from iron which is not readily adapted for use under processes heretofore employed, and at the same time permit the recovery of valuable by-products whereby the cost of the operation may be materially reduced.

One object of my invention is to provide an improved process for the manufacture of steel which may be utilized in effecting the purification of iron containing a high sulfur or phosphorus content, whereby such iron may be used in the manufacture of steel as readily as iron containing little or no sulfur and phosphorus which is now converted into steel by means of the Bessemer process.

Another object of the invention is to provide an improved process whereby the carbon removed from the metal in the manufacture of steel may be combined with nitrogen to form a cyanogen compound and recovered as a valuable by-product, either when treating iron obtained from ores having a high sulfur phosphorus content or when used in treating iron obtained from ores sufficiently free from sulfur or phosphorus to render them capable of use in the production of steel by the Bessemer process.

Other objects of the invention comprise the use of certain steps and combinations of steps in the effectuation of the process as will be more fully disclosed in the detailed description to follow.

In the manufacture of steel by the well-known Bessemer process as heretofore employed, the crude or pig iron is melted and placed in a Bessemer converter in a molten condition, when a current of air is forced through the molten metal to oxidize the silicon and carbon present in the metal, the gaseous combustion products resulting from the oxidation of the impurities mentioned escaping from the converter. In carrying out the Bessemer process as above described, the air is forced into the base of the converter under pressure, through a plurality of openings or tuyères, and passes upwardly through the molten mass into intimate contact with all portions of the metal, the oxygen present in the air reacting with the impurities named to form combustion products which escape from the top of the converter. In effecting the purification of the molten metal as above described, considerable heat is evolved by reason of the strongly exothermic reaction resulting from the oxidation of the silicon and carbon present in the mass. While the molten metal is usually subjected to the air blast for from 10 to 20 minutes in order to effect complete or substantially complete removal of the silicon, and carbon, from 2 to 4 minutes usually suffices to effect the removal of the silicon present in the mass, the remainder of the period of treatment being devoted to the removal of the carbon.

While the above described process has come into extensive use and is well adapted for the treatment of certain grades of iron, for example,—those which contain little or no phosphorus, it is not adapted for use in the treatment of iron containing any appreciable quantity of phosphorus which iron must, at the present time, either be utilized for making cast iron or be converted into steel by the so called basic process which is comparatively expensive.

In United States Patent No. 1,174,944 granted to John E. Bucher March 7, 1916 a method of fixing nitrogen is described wherein a bath of molten metal, such as iron, is saturated with carbon, and nitrogen gas is, together with a metallic vapor such as so-

dium forced into the molten mass to effect the fixation of nitrogen by reason of the affinity of nitrogen for carbon in the presence of an activator, such as the molten iron, and an alkali metal.

In this patent the main object of the invention is the fixation of nitrogen, and means is provided for maintaining the molten metal constantly saturated with carbon by forcing carbon into the metal to maintain a constant supply of free carbon therein in addition to the graphitic and combined carbon normally present in the iron.

It is my purpose to utilize certain of the principles set forth in the above mentioned patent to provide a somewhat different method of operation particularly adapted for use in connection with the production of steel, whereby cyanogen compounds may be formed and recovered as valuable by-products in the manufacture of steel, and the process made available for use not only with iron obtained from ores free or substantially free from sulfur or phosphorous but also with iron containing such a large percentage of sulfur or phosphorous as would ordinarily render the same incapable of use for the manufacture of steel by the Bessemer process.

In one method of carrying out my improved process I may make use of the ordinary Bessemer converter provided with a suitable fire-proof lining, and mounted upon trunnions in the usual manner. At the base of the converter is the usual air chamber communicating with the interior of the converter through a plurality of openings or tuyères. The molten metal may be placed in the converter in the usual manner, and subjected to an air blast for forcing air from the air chamber through the tuyères into the molten metal to remove certain impurities therefrom, such as silicon. Since the reaction between the silicon and the oxygen of the air is strongly exothermic, a considerable degree of heat is evolved during the oxidation of the silicon as above described which serves to raise the temperature of the molten metal, and thus promote the reactions which will be hereinafter described. As the silicon in the crude iron is the first of the various impurities present therein to be removed by the air blast, and since from two to four minutes usually suffices for its removal, I purpose to employ the air blast as above described only for such time as is necessary to remove or substantially remove the silicon, when I cut off the supply of compressed air to the air chamber at the base of the converter, and simultaneously connect the air chamber with a supply of nitrogen maintained under sufficient pressure to force the same through the tuyères and into the molten mass in a similar manner to that in which air is

forced therethrough by the air blast. During the period that the nitrogen blast is in operation, I preferably introduce an alkali metal, such for example, as sodium, into the converter with the nitrogen to assist both in the reaction between the nitrogen and carbon of the molten iron and also to combine with the sulfur, or phosphorus or both present in the iron and form with these elements compounds which may be readily eliminated from the mass.

The alkali metal serves to promote the reaction between the carbon and nitrogen to form cyanogen compounds and also, being strongly basic, reacts with the sulfur and phosphorus present in the iron to form compounds capable of being readily eliminated.

The gaseous products of the reaction resulting from the nitrogen blast may be conducted from the converter through cooling pipes or chambers to scrubbing towers where they are washed with water or purifying solutions to recover the cyanogen compounds formed. In order to facilitate the separation and recovery of the gaseous products formed by the reaction between the nitrogen and the molten material it is advisable to either provide the converter with a hood communicating with the cooling chambers and so formed that it may be opened to permit the escape of the gases formed during the air blast and closed to conduct the gaseous products of the nitrogen blast to said chambers, or the converter may be movably mounted and so positioned that during the air blast the gaseous product formed therein may escape, while allowing the converter to be swung into position beneath a suitable hood just prior to the commencement of the nitrogen blast to conduct the cyanogen compounds formed by reaction with the nitrogen into the cooling chambers. The cyanogen compounds of the reaction which it is desirable to recover comprises cyanogen and alkali metal cyanids, and although these cyanogen bearing gases as they pass from the converter may be mixed with certain other gases, they are capable of being readily separated therefrom in passing through the cooling chambers.

As stated, the silicon content of the iron is removed or substantially removed by the air blast, and the nitrogen supplied to the metal during the nitrogen blast reacts with the carbon present therein at the high temperature of the metal to form cyanogen or a cyanogen compound, the presence of the alkali metal assisting in the promotion of the cyanogen forming reaction. Any suitable means may be employed for supplying the alkali metal to the converter such for example as a reservoir formed in the side of the converter and communicating with the tuyères by passages for permitting the

passage of the metal thereto. The heat of the converter will be sufficient to liquefy the alkali metal and enable it to reach the tuyères while contact with the molten mass will immediately convert it to a vapor.

This process contemplates preferably the use in a Bessemer converter, or modified form of Bessemer converter, of pure nitrogen made by liquefaction of air, the oxygen content of which may be advantageously used in a blast furnace to enrich the air blast: If the oxygen is employed in a blast furnace an increased yield of pig iron will result by reason of the elevated temperature at the tuyères.

The nitrogen readily unites both with the graphitic carbon and the combined carbon present in the iron to form cyanogen compounds at the temperature to which the molten mass is raised by reason of the oxidation of the silicon.

As an alternative method of carrying out the invention I may use producer gas, or any gaseous mixture the main constituents of which are nitrogen and hydrogen, as a substitute for the pure nitrogen gas mentioned above as preferably used in the nitrogen blast, in which case the gaseous products are cooled and passed through scrubbing towers to recover the cyanogen and cyanogen compounds in the same manner as has been previously described. However, when producer gas is substituted for pure nitrogen the alkali metal previously mentioned should not be used since alkali metal cyanids break down in the presence of CO and CO₂ at high temperatures to form carbonates thus preventing the recovery of the nitrogen in the form of cyanogen compounds. If, however, a gaseous mixture containing nitrogen and hydrogen is used in which CO and CO₂ are not present the alkali metal may be used in conjunction therewith for assisting in the cyanogen forming reaction.

The hydrogen gas present in the producer gas or the gas mixture described will act as a basic element in place of the alkali metal to form gaseous compounds such as sulfuretted hydrogen and phosphoretted hydrogen with the sulfur and phosphorus content of the iron, while the cyanogen resulting from the reaction between the nitrogen and carbon will pass off as cyanogen or hydrocyanic acid. While it is preferable to maintain as low a percentage of carbon monoxid and carbon dioxid as possible in the gases used for the nitrogen blast, the presence of a small percentage of gaseous hydrocarbons therein exerts no deleterious effect, but their presence on the contrary tends to increase the yield of cyanogen compounds since they serve to increase the quantity of carbon capable of uniting with nitrogen.

As an example of one form of apparatus which may be employed in carrying out my

improved process, reference is made to the accompanying drawings, wherein is shown a diagrammatic arrangement of apparatus, partially in section, including a Bessemer converter and means for conveying gaseous products from the converter to a suitable scrubbing tower for further treatment.

Referring to the drawings 1 designates a Bessemer converter of the conventional type, having a metal shell 2, a suitable heat resistant lining 3, and provided with trunnions 4 and 5 projecting outwardly from the metal shell 2 for mounting in bearings 6 and 7 respectively, the bearings being each supported by a suitable base frame 8.

The converter is provided with the usual mouth 10, and tuyères 11 formed in the base of the converter to place the interior thereof in communication with a passage 12 formed in the base thereof. The bearing 6 is provided with a bore 14 communicating with the interior thereof and with a passage 15 formed in the trunnion 4, while a pipe 16 is secured to the bearing 6 in any desired manner and communicates with the bore 14 and the passage 15 formed in the trunnion 4.

A pipe 17 connects the passage 15 in the trunnion 4 with the passage 12 in the base of the converter, and a receptacle 18 may be supported from the converter body or the pipe 17. The receptacle 18, which serves as a container for the alkali metal may be provided with a removable cover 19, and has an outlet 20, communicating with the pipe 17. When found necessary or desirable any suitable means may be employed for forcing the alkali metal in the receptacle 18 into the connecting pipe 17. The bearing 7 is provided with a bore 21, communicating with the interior thereof and with a passage 22 formed in the trunnion 5, while a pipe 24 is secured to the bearing 7 in any suitable or desired manner and communicates with the bore 21 and the passage 22, all of which parts are similar to those previously mentioned in connection with the bearing 6 and trunnion 4. A pipe 26 connects the passage 22 with the passage 12 in the base of the converter. Suitable stuffing boxes may be provided in the bearings 6 and 7, as is obvious to one skilled in the art, and any suitable or desired means for making the connections between the pipes 16, 17, 24 and 26 and the bearings, trunnions and converter, may be employed as conditions may require.

A hood 27 is secured to a pipe section 28, which is in turn connected by a hinge joint 29 to a pipe 30, and adapted to be swung downwardly over the mouth 10 of the converter or swung upwardly therefrom in order to receive the gaseous products given off from the converter or permit the escape of such products as desired.

The pipe 30 enters the base of a scrubbing

tower 31 to convey selected gaseous products from the converter to the scrubbing tower where they may be contacted with certain reagents admitted to the tower through the pipe 32, the products resulting from contact of the gaseous products with the reacting agents being removable through the pipe 33 or by other suitable means. The pipe 35 is provided for conveying the gaseous products remaining after treatment in the scrubbing tower to a second tower for further treatment or to any desired point for further utilization.

In carrying out my improved process by means of the apparatus shown, when the converter has received its required charge of molten metal, air is forced in through the pipe 24 and the air blast is maintained for a sufficient time to remove or substantially remove the silicon content of the metal and raise the temperature thereof to the required degree. During this portion of the operation the hood 27 is raised to permit the escape of the gaseous products given off from the converter. When this portion of the operation has been completed the supply of air through the pipe 24 is shut off and nitrogen gas, or its equivalent as stated, is admitted through the pipe 16 and forced through the molten metal in the converter. Immediately upon the commencement of the nitrogen blast, or as soon thereafter as the gaseous reaction products resulting from the union of the nitrogen with the carbon content of the metal are given off in the required degree, the hood 27 is lowered over the mouth of the converter and the gaseous products conveyed through the pipe 30 to be admitted suitably cooled to the base of the tower 31. When nitrogen alone is admitted through the pipe 16, the requisite quantity of alkali metal contained in the receptacle 18 is permitted to pass through the outlet 20 into the pipe 17 and be carried along by the nitrogen blast into the molten metal.

When the above described process is carried out either by using pure nitrogen gas in the presence of an alkali metal or by the use of nitrogen gas in the presence of hydrogen, the nitrogen unites with the combined and graphitic carbon of the iron to form cyanogen compounds which pass off as gases and are recovered as by-products either as cyanogen compounds or as derivatives thereof. The alkali metal or hydrogen act as basic elements uniting with the sulfur or phosphorus or both in the iron to form compounds which are eliminated from the molten mass during the treatment. The term basic element as used throughout the specification and claims, is employed as embracing either hydrogen gas or an alkali metal, either of which acts as a base in uniting with the sulfur or phosphorus to form a sulfid or phosphid.

The gases obtained by treating the molten mass with nitrogen gas, producer gas, or a gas mixture as described, after being cooled to below 800° C. in the cooling chambers, may be treated with steam to form ammonia or ammonia compounds, or converted into nitric acid by well known methods.

After the removal from the molten iron of the impurities mentioned, any desired grade of steel may be obtained by the addition of suitable proportions of metallic alloys as is the usual practice in the manufacture of steel by the Bessemer process.

Throughout the specification and claims the term iron is employed to designate generally the crude iron commonly known as "pig iron" in the condition of partial purification in which it exists after being removed from the blast furnace, and before being subjected to further treatment by the Bessemer, open hearth or other method of treatment employed for converting the same into steel. While pig iron containing a certain percentage of sulfur may be used in the Bessemer process, this process will permit the use of iron containing a higher sulfur content than can be ordinarily used in the Bessemer process. Iron such as is ordinarily treated by the open hearth process may be used in carrying out the process herein described.

In order to prevent circumlocution in the specification and claims the term cyanogen compounds has been generally employed in designating the carbon-nitrogen products resulting from the reaction between nitrogen and carbon in the molten mass. It is to be understood, however, that this term has been used to designate generally not only cyanogen compounds of alkali metals and other basic elements, but also cyanogen gas which under certain circumstances may be included in the products of the said reaction. Although I have described in considerable detail certain precise steps and sequence of steps which I have found it desirable to employ as well as certain particular substances and compounds which I have found to be efficient in use, in order to make clear to those skilled in the art one method of practicing the invention, it is to be understood that I do not desire or intend to be limited to the precise materials designated as preferred nor the exact steps or sequence of steps indicated as preferred except as the same may be included within the terms of the following claims when broadly construed in the light of my invention.

Having described my invention, what I claim is:

1. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to remove certain impurities therefrom, and then reacting up-

on said iron with nitrogen to effect a union between the nitrogen and the carbon present in the iron.

2. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to oxidize certain impurities therein with evolution of heat, and then reacting upon said iron at the elevated temperature produced by the first reaction with nitrogen to combine the nitrogen with the carbon present in the iron.

3. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to remove certain impurities therefrom, and then reacting upon said iron with nitrogen in the presence of a basic element to remove carbon therefrom in the form of a cyanogen compound.

4. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to oxidize certain impurities therein with evolution of heat, and then reacting upon said iron at the elevated temperature produced by the first reaction with nitrogen in the presence of a basic element to effect the formation of a compound containing carbon and nitrogen.

5. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to remove certain impurities therefrom, and then reacting upon said iron with nitrogen in the presence of an alkali metal.

6. The process for forming steel from molten iron which comprises, subjecting the molten iron to an air blast to oxidize certain impurities in the iron with evolution of heat, and reacting upon said iron at the elevated temperature produced by the first reaction with nitrogen in the presence of an alkali metal.

7. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation, and reacting upon the said iron with nitrogen to remove carbon therefrom by combining the carbon present in the iron with nitrogen.

8. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation, and reacting upon the said iron with an alkali metal in the presence of nitrogen to effect a combination between the alkali metal and the sulphur or phosphorus content of the iron and remove the sulphur or phosphorus from the iron.

9. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation, and reacting upon the said iron with nitrogen in the presence of a basic element to form a cyanogen compound and effect the removal of the carbon from the metal.

10. The process for forming steel from

molten iron which comprises, removing the silicon content from said iron by oxidation, and reacting upon the said iron with nitrogen in the presence of an alkali metal to remove carbon and other impurities therefrom.

11. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation with evolution of heat, and reacting upon said iron at the elevated temperature produced by the oxidation of the silicon content thereof with nitrogen to remove carbon therefrom.

12. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation with evolution of heat, and reacting upon said iron at the elevated temperature produced by the oxidation of the silicon content thereof with an alkali metal in the presence of nitrogen to effect a combination between the alkali metal and the sulphur or phosphorus content of the iron and remove the sulphur or phosphorus from the iron.

13. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation with evolution of heat, and reacting upon said iron at the elevated temperature produced by the oxidation of the silicon content thereof with nitrogen in the presence of a basic element to effect a union of the nitrogen with carbon contained in the metal.

14. The process for forming steel from molten iron which comprises, removing the silicon content from said iron by oxidation with evolution of heat, and reacting upon said iron at the elevated temperature produced by the oxidation of the silicon content thereof with nitrogen in the presence of an alkali metal to remove carbon therefrom.

15. The process for forming steel and recovering cyanogen compounds from molten iron which comprises, subjecting the molten iron to an air blast to remove certain impurities therefrom, effecting a reaction between the carbon remaining in the molten iron, nitrogen and a basic element to form a cyanogen compound, and recovering the cyanogen compound.

16. The process for forming steel and recovering cyanogen compounds from molten iron which comprises, subjecting the molten iron to an air blast to remove certain impurities therefrom, effecting a reaction between the carbon remaining in the molten iron, nitrogen and an alkali metal to form a cyanogen compound, and recovering the cyanogen compound.

17. The process for forming steel and recovering cyanogen compounds from molten iron which comprises, removing the silicon

content from said iron by oxidation, effect-
ing a reaction between the remaining car-
bon content of the iron, nitrogen and a basic
element to form a cyanogen compound, and
5 recovering the cyanogen compound.

18. The process for forming steel and re-
covering cyanogen compounds from molten
iron which comprises, removing the silicon

content from said iron by oxidation, effect-
ing a reaction between the remaining car- 10
bon content of the iron, nitrogen and an
alkali metal to form a cyanogen compound,
and recovering the cyanogen compound.

In testimony whereof I have affixed my
signature.

ADRIAAN NAGELVOORT.