

June 23, 1942.

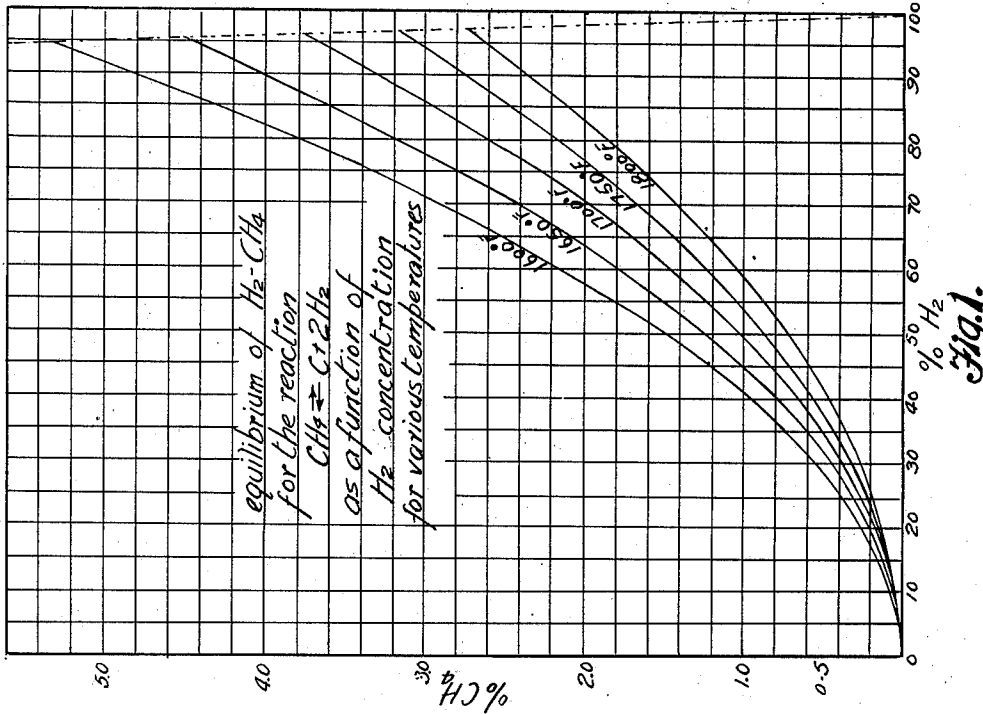
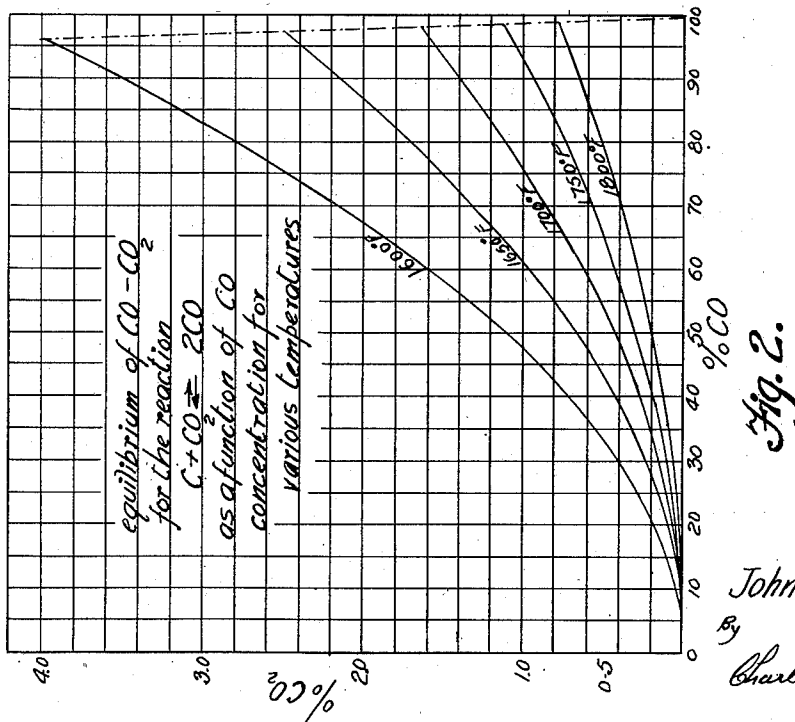
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2,287,651

METHOD OF CARBURIZING WITHOUT DETERIORATION OF FURNACE ALLOYS

Filed Sept. 5, 1941

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

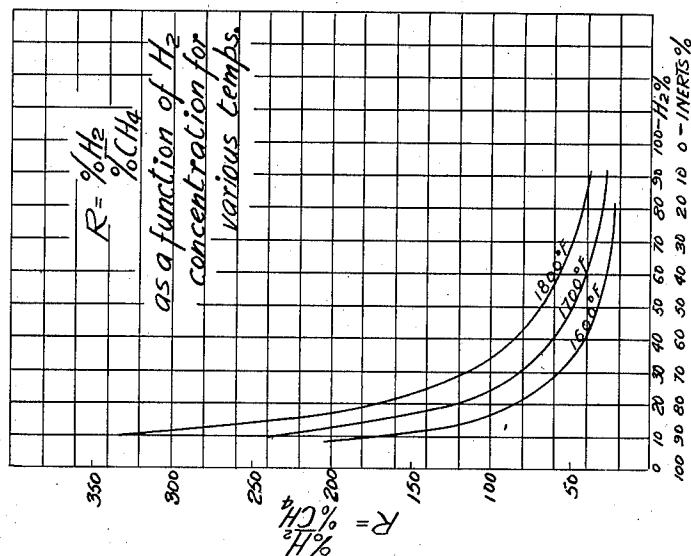


Fig. 3.

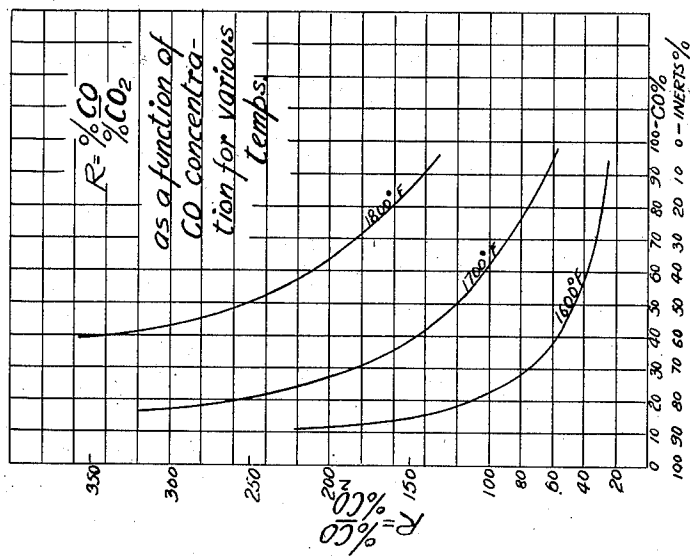


Fig. 4.

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Fig.

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Fig. 5.

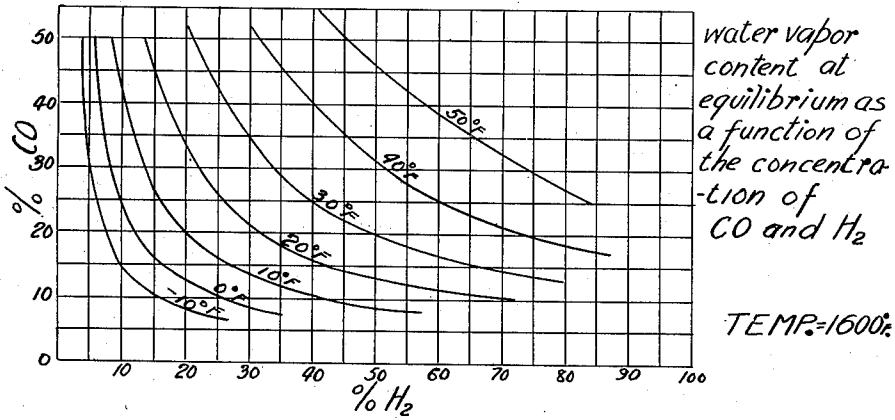


Fig. 6.

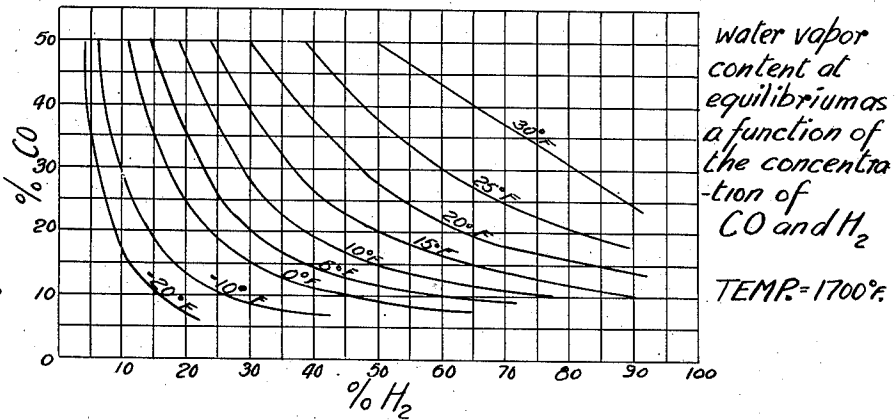
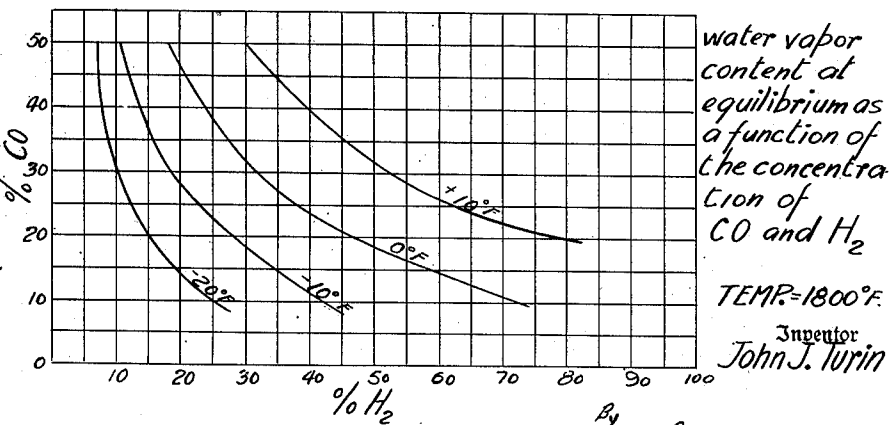


Fig. 7.



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UNITED STATES PATENT OFFICE

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METHOD OF CARBURIZING WITHOUT DETERIORATION OF FURNACE ALLOYS

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Gaseous carburizing processes involving the use of a hydrocarbon in gaseous state have always been very seriously handicapped by the comparatively rapid deterioration of the heat resisting alloy parts required inside the furnace chamber wherein the carburizing operation is conducted. This deterioration, often referred to as the "carbon corrosion" of heat resisting alloys, takes place only in carburizing atmospheres at carburizing temperatures. These same alloys may be held for practically indefinite periods of time at carburizing temperatures in non-carburizing atmospheres without deterioration. Examination of such deteriorated specimens has shown an apparent super carburization of the alloy, and it has therefore been assumed that the deterioration has been caused by prolonged carburization and therefore a necessary evil in gas carburizing operations. Although attempts have been made to provide a solution to this costly and annoying problem of alloy deterioration as by changing the composition of said alloys in order to reduce the carburization and otherwise render said alloys less susceptible to carburization, no satisfactory solution has heretofore been proposed. I have discovered that the fault is not necessarily with the alloys; that the deterioration of the said alloys takes place not as a result of prolonged carburization in the sense of cementation, but as a result of carbon deposition, and that by using a novel atmosphere for carburizing whose constituents are properly balanced against one another, carburizing of the steel articles may be accomplished in a gaseous atmosphere without deteriorating the heat resisting alloys within the furnace chamber.

Carburizing atmospheres now commonly employed tend to deposit carbon to a greater or lesser degree upon the articles being carburized because the atmospheres commonly employed are very unstable at the operating temperature and their hydrocarbon constituents have a great tendency to break down their molecular forms completely into carbon and hydrogen with resulting deposition of carbon on all parts inside the enclosure in which the carburizing operation is carried out. It has been the conclusion of many investigators that this breakdown of the hydrocarbon is necessary in order to produce "nascent" carbon to penetrate the steel at a rapid rate. For this reason ethane, propane, butane, and like hydrocarbons have been generally classed as "active" carburizing agents; whereas, in the group of neutral gases such as nitrogen and hydrogen there has been included carbon-monoxide and

methane. Hydrogen has been classed as neutral because it has a relatively meager decarburizing effect and carbon monoxide has been included because it has a relatively meager carburizing effect. Methane has often been included in the neutral gas group because it is relatively stable at the higher temperatures as compared to the other hydrocarbons and it has generally been conceded that it takes a large amount of methane to produce results equivalent to those produced by a comparatively small amount of the higher hydrocarbons in neutral gas mixtures.

It is well known that water vapor, carbon dioxide, and oxygen have strong decarburizing tendencies and are generally classed as decarburizing agents. The effect of these impurities has been commonly overcome in methods heretofore used by utilizing an excess of active carburizing agents. However, the complement of this practice is that the atmosphere has a more or less pronounced carbon deposition tendency which results in the rapid deterioration of the heat resisting alloys by means of the following phenomena. Since carburizing is usually carried out at high temperatures in the neighborhood of 1700° F. the temperature of the heat resisting alloys composing the furnace, regardless of its type, is subject to a continuous variation in temperature, say at least $\pm 5^\circ$ F. even though the heating is controlled very carefully by accurate temperature control instruments. These heat resisting alloys therefore vary in dimensions according to their coefficients of expansion as a function of their temperature and consequently are continuously "breathing." Since heat resisting alloys and particularly those which are formed by casting (which is the general rule) exhibit microscopic cracks, the gases penetrate these cracks when the metal is expanded and deposit carbon. When the temperature subsequently drops slightly the metal tries to contract back to its original shape, but because of the carbon present in the cracks it cannot do this, and must therefore crack the metal further. The net result, therefore, when using a gas that is potentially carbon depositing, is that after operating for a period of months, the heat resisting alloy is permeated by a whole network of such cracks in which carbon has deposited, so that there is a network of pure carbon throughout the structure of the alloy which subsequently causes the alloy to warp so badly and lose so much of its strength that it becomes useless and must be replaced. An examination of the microstructure of such a deteriorated alloy specimen therefore presents the

appearance of apparent prolonged carburization and could be easily mistaken for such. It is apparent that all carburizing processes utilizing atmospheres which are unstable or potentially carbon depositing must ultimately result in the deterioration of the heat resisting alloys used.

It should be understood that the constituents of an unstable atmosphere are not in equilibrium with one another, and that the more unstable the atmosphere the further removed are the constituents from their equilibrium concentrations. In the case where an atmosphere is unstable because the hydrocarbon content has been increased to increase the carburizing power, the constituents try to approach equilibrium concentrations, at the temperature in question by breaking down part of the excess hydrocarbon into carbon and hydrogen. Although such breakdown reactions tend to occur everywhere throughout the heated volume, they occur most rapidly in the neighborhood of catalytic surfaces, which function to promote the velocity of the reaction and hasten the approach to equilibrium. In carburizing furnaces the work and the heat resisting nickel-chrome alloys provide excellent catalytic surfaces which have the tendency to promote the deposition of carbon upon themselves. Consequently, when a virgin metal surface is exposed by a crack opening up on expansion, the interior of such a crack is an ideal place for the penetrating gases to break down with the deposition of carbon in their attempt to reach equilibrium.

I have discovered that carburizing can be accomplished without alloy deterioration by using an atmosphere which is relatively stable at the temperatures necessary for carburizing if the impurities and decarburizing agents are held within certain close limits and balanced properly against the carburizing agents carbon monoxide and methane.

More particularly I have discovered that an atmosphere containing only small amounts of methane can be made to carburize steel rapidly without exhibiting any carbon depositing tendency if the amount of methane used in the atmosphere is counterbalanced by the proper amount of hydrogen almost in equilibrium with the methane present at the temperature of operation, providing the decarburizing agent carbon dioxide is counterbalanced by at least that amount of carbon monoxide necessary to be in chemical equilibrium with the carbon dioxide at the temperature of operation, and providing that free oxygen and water vapor are sufficiently excluded from the atmosphere. I have found that an atmosphere balanced in such a manner will carburize steel articles very energetically at carburizing temperatures without depositing carbon either upon the articles being carburized or upon the heat resisting alloys making up the furnace structure.

The higher and unsaturated hydrocarbons, such as, ethane, propane, butane and butylene are so unstable at the high temperatures of operation required for carburizing that I have found it impossible to counterbalance them with sufficient hydrogen to prevent them from breaking down into carbon, methane and hydrogen. It is therefore impossible to keep carbon from depositing when utilizing an atmosphere containing these higher and unsaturated hydrocarbons because the actual carburizing agent in the final analysis turns out to be methane and before methane is obtained carbon will have deposited.

As previously explained the decarburizing

agents oxygen, water vapor and carbon dioxide are very active and must be taken into account in balancing the constituents of an atmosphere to be used for carburizing without carbon deposition because even if relatively small amounts of these agents are present in the atmosphere in improperly balanced proportions, it would be necessary to increase the hydrocarbon content of the atmosphere to the point where a virtual carbon sheath is deposited on the surface of the articles.

In practice I have found that oxygen must be entirely excluded; that the amount of carbon monoxide must be at least equal to that amount necessary to be in chemical equilibrium with the amount of carbon dioxide present, and that the methane content should be maintained between one and ten times that amount of methane required to be in chemical equilibrium with the hydrogen present at the temperature of operation, all depending upon the exact water vapor content, and that the water vapor content for most practical types of atmosphere must not be in excess of 0.3% water vapor by volume or not more than a dewpoint of 20° F. It is not to be inferred that the above mentioned limitations merely specify the ratio of the methane to hydrogen and the ratio of carbon dioxide to carbon monoxide allowable for a given temperature of operation. Indeed these ratios I have found to be not only widely varying functions of the temperature but also widely varying functions of the concentrations of the hydrogen and carbon monoxide as well.

In Fig. 1 of the accompanying drawings I have shown the amount of methane in chemical equilibrium with hydrogen for various concentrations of hydrogen and for various carburizing temperatures in accordance with the reaction $\text{CH}_4 = \text{C} + 2\text{H}_2$. If there is more hydrogen present than that necessary to balance the amount of methane present in the mixture, the atmosphere will be decarburizing; whereas, if there is less hydrogen present than that necessary to balance the methane the mixture will be carburizing. However, if there is too much methane present compared to that necessary to balance the hydrogen the mixture will be carbon depositing.

In Fig. 2 I have shown similar data for the amount of carbon dioxide in chemical equilibrium with various concentrations of carbon monoxide at various carburizing temperatures according to the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$. Here, too, if more CO_2 is present than is necessary to be in equilibrium with the CO present the mixture will be decarburizing, and will be carburizing if less CO_2 than that amount is present.

In Fig. 3 I have shown the equilibrium ratio of hydrogen to methane for equilibrium as a function of the hydrogen content for three carburizing temperatures. The ratio of the percentage of hydrogen to that of methane present at 1700° F. is shown to vary from 26 to 220 for mixtures ranging from only hydrogen and methane to almost 90% nitrogen or other gases practically inert to methane and hydrogen, such as CO, He, etc.

Similarly in Fig. 4, I have shown similar data for carbon dioxide and carbon monoxide. Here for a mixture containing only these two gases to one containing approximately 84% inerts such as nitrogen, helium, hydrogen, etc., at 1700° F. the ratio of the percentage of carbon monoxide to carbon dioxide varies from approximately 60 to 320 over this range.

Water vapor, carbon dioxide and oxygen are not only capable of decarburizing steel at carburizing temperatures but when present in sufficient amounts may even cause oxidation of the steel surfaces. If these decarburizing agents are present in a carburizing atmosphere only in smaller amounts than are necessary to be in equilibrium with the remaining gases making up the atmosphere, they will not react with the steel surfaces to cause decarburization or oxidation. However, if these gases are present in larger amounts than are necessary to be in equilibrium with the remaining gases present they will seek to establish equilibrium with the remaining gases by reacting with them and with the steel surfaces exposed and cause decarburization or even oxidation.

Although oxygen cannot exist in equilibrium with gases such as hydrogen, carbon monoxide or methane at carburizing temperatures, water vapor and carbon dioxide can exist, and the amounts of these two gases in existence at equilibrium are dependent upon one another when both hydrogen and carbon monoxide are contained in the atmosphere. In such atmospheres the amounts of water vapor and carbon dioxide required to be in equilibrium at a given temperature are determined by the concentrations of hydrogen and carbon monoxide in accordance with the equilibrium condition of the water gas reaction $H_2 + CO_2 = H_2O + CO$ and the breakdown reaction of carbon monoxide $2CO = CO_2 + C$. The equilibrium concentration for the latter reaction have already been shown in Fig. 2, from which it obviously follows that even if pure carbon monoxide were allowed to enter a heated chamber that carbon dioxide would be formed until the proper equilibrium had been attained. The equilibrium constant for the water gas reaction as written above may be expressed as

$$K = \frac{(H_2O) \times (CO)}{(H_2) \times (CO_2)}$$

where the concentrations of the constituents are expressed in terms of partial pressures in atmosphere, and K represents a number which varies only as a function of temperature. This may be rewritten to express explicitly the concentration of water vapor

$$H_2O = K \times \frac{(H_2)}{(CO)} \times CO_2$$

from which it becomes apparent that at any given temperature the concentration of water vapor at equilibrium is a definite function of the concentration of carbon dioxide present at equilibrium. Actually the value of K above varies roughly from 1 to 2 over the range of carburizing temperatures so that in atmospheres where the concentrations of hydrogen and carbon monoxide are approximately the same, the concentration of water vapor at equilibrium is approximately the same as the concentration of carbon dioxide.

If an atmosphere contains less water vapor and carbon dioxide than is required to be in equilibrium with the remaining constituents, the proper amounts of water vapor and carbon dioxide will be formed by the reactions mentioned above without reaction with the steel surfaces. However, if an atmosphere contains more water vapor and carbon dioxide than is required to be in equilibrium with the remaining constituents the water vapor and the carbon dioxide will not only react with the other constituents of the at-

mosphere in the attempt to attain their equilibrium concentrations but will react with the steel surfaces as well, causing decarburization or acting as a bar to prevent carburization. When free deposited carbon is present, equilibrium may be reached by reaction with the carbon; however, if carburizing is to be accomplished without carbon deposition it is, therefore, obvious that the constituents water vapor and carbon dioxide must be present in equilibrium or less than equilibrium concentrations.

In Figs. 5, 6 and 7 I have shown for three carburizing temperatures the equilibrium concentration of water vapor, expressed as the dew-point, for carburizing atmospheres having various amounts of hydrogen and carbon monoxide, the bulk of the remaining gases making up the atmosphere being inert gases such as nitrogen, helium etc., but of course also containing CO_2 , and CH_4 in the proper amounts.

From the curves shown it may be seen that for an atmosphere of given analysis in CO and H_2 the amounts of water vapor, carbon dioxide and methane decrease with increasing temperature. For example, an atmosphere which contains 35% H_2 , 20% CO, and the bulk of the remainder being nitrogen, the amounts of CH_4 , H_2O and CO_2 present at equilibrium are shown in the following table:

	Per cent H_2	Per cent CO	Per cent CH_4	Per cent CO_2	H ₂ O		Approx. Per cent N ₂
					Dew-point	Per cent	
					°F.		
1600° F.	35	20	.72	.18	21	+.36	44
1700° F.	35	20	.50	.08	+7	.18	44
1800° F.	35	20	.34	.03	-7	.086	44

It may be understood therefore, according to the principle expressed that an atmosphere which had been brought into equilibrium at 1600° F. would be decarburizing at 1700° F. because it contains almost twice as much water vapor and CO_2 as would be required to be in equilibrium at 1700° F. However, the methane content is slightly higher than is required to be in equilibrium at 1700° F. and from that standpoint the mixture might be considered carburizing. This, however, is not the case since the water vapor and carbon dioxide constitute a bar to carburizing.

It is also apparent, according to the principle expressed, that an atmosphere which had been brought into equilibrium at 1800° F. would have less H_2O and CO_2 than would be required for equilibrium at 1700° F., therefore, such an atmosphere might be called carburizing when used at 1700° F. However, it would only be feebly carburizing insofar as there would also be less methane than is required to be in equilibrium with the hydrogen and therefore the carburizing power of the atmosphere would be limited to carburizing by means of CO alone, and as later discussed could therefore not be an energetic carburizer.

Although I have found that from one to ten times the methane required for chemical equilibrium with the hydrogen present at the temperature of operation, depending upon the exact water vapor concentration, can be utilized in the atmosphere for energetic carburizing without carbon deposition, this amount of methane is still very small, in fact is practically minute compared to methods heretofore used.

For example, if it were proposed to carburize

steel at 1700° F. using practically pure anhydrous nitrogen and methane, it is obvious from the principles expressed that even 0.5% methane would be decidedly carbon depositing. If, however, hydrogen were included so that there was approximately 17% hydrogen by volume, then between 0.1% and 1% methane could be utilized for carburizing without carbon deposition.

If pure anhydrous carbon monoxide were used for carburizing at 1700° F. the CO₂ content should be maintained at appreciably below 1.6% for a relatively feeble light case carburizing atmosphere. However, if it were necessary to accelerate the action by an addition of methane, hydrogen should be added so that the resulting mixture contained approximately 22% hydrogen in order to utilize between 0.2 to 2% methane. Furthermore, the dewpoint should then be maintained less than 20° F. and the CO₂ content less than 1% in order to carburize heavily and actively without carbon deposition.

A gaseous mixture comprising about 33% CO and the remainder nitrogen is sometimes utilized for light case carburizing. However, to utilize such a mixture according to the principle expressed, it would be necessary to add hydrogen so that the mixture contained 20% hydrogen in order to use between .2 and 2% methane. If the atmosphere then contained 33% CO and 20% H₂, the CO₂ content should be less than 0.64% and the dewpoint less than 20° F. when carburizing at 1600° F.

An easily controllable atmosphere which might be used for carburizing contains approximately 35% H₂, 20% CO and the remainder nitrogen. According to the curves shown, in order to utilize between 0.5 and 5% methane for very active carburizing the dewpoint should be maintained below 20° F. when carburizing at 1600° F., and below +8° F. when carburizing at 1700° F. with the CO₂ content less than 0.1% by volume.

The carburizing of steel, as I now understand it, occurs by having a gaseous carbon containing molecule, which is relatively stable at the temperature of operation, diffuse into, or penetrate the outer layers of the lattice structure of the steel article. Although the surface of the steel article presents a continuous structure to the naked eye, it presents a porous conglomerate of moving molecules to the entering gaseous molecule. After penetrating the outer layers of the crystal lattice of the steel article, the carbon containing gaseous molecule then has a definite probability of diffusing back out of the lattice without reacting, and another definite probability of reacting with the iron molecules making up the lattice and thus undergoing a transformation during which it is stripped of its carbon atom. This carbon atom is maintained in the lattice structure while the residual gaseous molecules must diffuse back out of the metal lattice alone and subsequently away from the metal surface.

Since the diffusion of gases into metals is dependent inversely upon the square of the molecular weight of the gas, it is apparent that methane, with a molecular weight of only 16, should diffuse into the metal lattice much more easily than carbon monoxide with the molecular weight of 28. Furthermore, after the reaction in the lattice has taken place, the carbon atom of the methane molecule is left in the crystal lattice and it is relatively easy for the very light hydrogen atoms thus liberated to diffuse back out of the lattice and subsequently away from the

metal surface. Carbon monoxide, however, has more difficulty diffusing into the lattice structure originally, and even after penetration of the lattice it must react with another carbon monoxide molecule in the immediate vicinity as well as with the iron lattice molecules to form carbon dioxide before it can give up a carbon molecule to the lattice. Since the carbon dioxide molecule thus formed is even heavier than the original entering carbon monoxide it consequently experiences much more difficulty in diffusing back out of the crystal lattice and subsequently away from the surface. From the foregoing discussion it is therefore obvious that methane gas is a more active carburizing gas than carbon monoxide.

Although little reference has been made to the rate of carburizing, it is not to be inferred that by utilizing such low methane contents as I have set forth for the purpose of eliminating the deposition of carbon, there will result a lesser rate of carburizing compared to processes heretofore utilized making use of much higher methane and other hydrocarbon contents. In fact the rates of carburizing utilizing the present process are even enhanced and may be utilized to yield any desired concentration in case carbon.

The actual rate of carburizing a steel article depends directly upon the rate of diffusion of carbon into steel, and is a function only of the temperature and of the concentration of carbon in the outermost layers. Consequently the rate of penetration of the carbon into the steel depends only upon the temperature if a high carbon concentration is maintained in the region of the outer surface layers of the article. Often the "carburizing potential" or "carburizing power" of an atmosphere is discussed in connection with processes of gaseous carburizing. This terminology obviously can only have reference to the rate of carburizing of the most external surface layers. Furthermore the rate of carburizing of the external layers is strictly a function of the number of "potentially carburizing" molecules striking a surface of unit area per unit of time. It is obvious that if the article being carburized is encased in a sheath of deposited carbon, then the number of potentially carburizing molecules striking the surface per unit time will be reduced by the presence of this carbon sheath since they must penetrate and pass through the sheath before they can contact the surface. For this reason when the deposition of carbon is prevented the number of potentially carburizing molecules contacting the surface per unit time is increased because of the absence of this filter or carbon sheath, and there is therefore an accompanying increase in the carburizing power of the atmosphere if it is maintained carburizing and yet not carbon depositing.

Although little reference has been made to the effect of surface velocities of the carburizing atmosphere in the neighborhood of the articles being carburized, obviously this factor is of importance. In order to obtain the maximum carburizing rate, the carbon concentration of the outer surface layers must be maintained in equilibrium with the rate of diffusion of carbon from these outer surface layers into the steel. Since the number of potentially carburizing molecules striking a unit area of the surface per unit time determines the carbon concentration of the outermost surface layers, it follows that the surface velocity of the atmosphere passing over the articles must be sufficient to allow this factor

to be constant. That is, the gases must be moved at such a velocity, that the reaction products of carburizing, namely, hydrogen, and CO_2 , do not build up their concentrations in the neighborhood of the metal surface to the point where they alter the average number of potentially carburizing molecules striking the surface per unit time. In practice, this means that a stagnant atmosphere should not be used for carburizing, for the condition described above will most certainly be reached in a short time. I have found that if sufficient velocity is maintained through the carburizing regions so that the constituents of the gas exiting from these regions are still at least about in equilibrium according to the values predicted by the curves shown, that most rapid carburizing will result without deposition of carbon, and furthermore there will be a uniformity of case from article to article throughout the load of articles being carburized.

What I claim is:

1. The method of carburizing steel articles which comprises enveloping the articles at carburizing temperature in an atmosphere whose dewpoint is not in excess of 20°F. and which

contains hydrogen and carbon monoxide and which contains less carbon dioxide than that necessary to be in equilibrium with the carbon monoxide at the said temperature and which contains from one to ten times the amount of methane required to be in equilibrium with the hydrogen at the said temperature, the remainder of the atmosphere consisting of nitrogen and constituting at least forty per cent by volume of said atmosphere.

2. The method of carburizing steel articles within a furnace in a manner to avoid carbon corrosion of heat resisting alloy within the furnace which method comprises enveloping the articles at carburizing temperature in an atmosphere whose dewpoint is not in excess of 20°F. and which contains hydrogen and carbon monoxide and which contains less carbon dioxide than that necessary to be in equilibrium with the carbon monoxide at the said temperature and which contains from one to ten times the amount of methane required to be in equilibrium with the hydrogen at the said temperature, the remainder of the atmosphere consisting of nitrogen.

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