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(84) Designated Contracting States: DE FR GB

(71) Applicant: FORD MOTOR COMPANY LIMITED
Eagle Way
Brentwood Essex CM13 3BW(GB)

(84) Designated Contracting States: GB

(71) Applicant: FORD-WERKE AKTIENGESELLSCHAFT
Ottoplatz 2 Postfach 210369
D-5000 Köln 21(DE)

(84) Designated Contracting States: DE

(71) Applicant: FORD FRANCE SOCIETE ANONYME
344 Avenue Napoleon Bonaparte B.P. 307
F-92506 Rueil Malmaison Cedex(FR)

(84) Designated Contracting States: FR

(72) Inventor: Stickles, Charles Arthur
2410 Newport Road
Ann Arbour, Michigan 48103(US)

(72) Inventor: Mack, Claude Melvin
2830 International Drive Apartment 404
Ypsilanti, Michigan 48197(US)

(74) Representative: Drakeford, Robert William et al,
Ford Motor Company Limited 15/448, Research & Engineering Centre Laindon
Basildon Essex SS15 6EE(GB)

(54) **Method of heat treating ferrous workpieces.**

(57) A method of gas heat treating ferrous materials comprises mixing air in a predetermined proportion with a hydrocarbon gas (such as methane or propane) and slowly introducing the mixture to a treating chamber which is held at a temperature of 1500-2000 °F (816-1093°C), so that the gas atmosphere is similar in composition to an independently generated endothermic gas-base atmosphere. The flow through the furnace chamber of the gas atmosphere is controlled to be low so that preferably the ratio of furnace chamber volume (cubic feet) to flow rate (cubic feet/hour) is always at least 0.2 hours. This carburizing process can also be run in a mode in which the atmosphere composition is automatically controlled. In carrying out the process, it is preferred that a constant flow of air be introduced into the furnace chamber and the hydrocarbon flow be regulated to maintain a constant value of furnace atmosphere CO_2 content or oxygen potential.

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DESCRIPTION

This invention relates to method of heat treating ferrous workpieces.

Commercial heat treatment of steel parts for the automotive industry is customarily carried out in furnaces using so-called "endothermic" gas as the furnace atmosphere. In neutral hardening operations, or annealing operations, the furnace atmosphere serves to protect the steel parts from carburization or decarburization. In carburizing operations, propane or other hydrocarbon gas which is the source of the carbon supplied to the steel from the furnace atmosphere.

The endothermic gas is produced in a gas generator, separate from the heat treatment furnace itself. The gas is produced at elevated temperatures, cooled to ambient temperatures, then reheated again in the heat treatment furnace. No provision is made for storing the generated gas, thus, if the generator output cannot be fully utilized at any time, the excess gas is simply flared. This entire mode of operation is inefficient in its use of hydrocarbon gas.

Endothermic gas is usually produced at 1900-2000°F., from methane or propane according to the following approximate reaction:

$$CH_4 + 1/2\ \underbrace{O_2 + 2\ N_2}_{\text{Air}} + \text{Heat} \longrightarrow CO + H_2 + 2\ N_2\ (+CO_2 + H_2 + CH_4)$$

$$C_3H_8 + 3/2\ \underbrace{O_2 + 6\ N_2}_{\text{Air}} + \text{Heat} \longrightarrow 3\ CO + 4H_2 + 6\ N_2\ (+CO_2 + H_2O + CH_4)$$

Thus, the principal constituents of endothermic gas are CO, H_2 and N_2 with minor amounts of CO_2, H_2O and CH_4. The proportions of CO, H_2 and N_2 vary with the C/H ratio of the hydrocarbon used as feed stock. Heat must be supplied to an endothermic gas generator to sustain the reaction of a hydrocarbon with quantities of air substantially less than that needed for complete combustion. To facilitate the reaction, a catalyst is therefore used in the generator by the prior art. The composition of endothermic gas is modulated by varying the ratio of air and hydrocarbon fed to the generator. By this means, it is possible to produce gases which are neutral to (that is, will not carburize or decarburize) steel of a certain carbon content at a particular temperature. Air/Methane ratios of about 2.5 and air/propane ratios of about 7.5 are commonly used when methane or propane is fed to the gas generator. In gas carburizing operations, endothermic gas is enriched with, typically, a 3-12% methane addition at the carburizing furnace (or an equivalent amount of other hydrocarbon gas) so that the overall air/hydrocarbon ratio used to produce carburizing atmospheres may be as low as 1.6 when methane is used, or as low as 6.0 when propane is used.

Control of the air/hydrocarbon ratio for either neutral hardening, annealing or carburizing furnace atmospheres is usually based on an analysis of the amount of CO_2 or H_2O in the furnace atmosphere. If the constituents of the furnace atmosphere are assumed to be in thermodynamic equilibrium, the carburizing tendency of the furnace atmosphere can be related to its CO_2 or H_2O content. Operation of endothermic gas generators and their control is described in detail in the 8th Edition of the Metals Handbook, Volume 2, pp. 67-92 published by the American Society of Metals in 1964.

As indicated, one of the principal disadvantages of the use of endothermic gas for furnace atmospheres has been the requirement that two furnaces must be run, namely the gas generator and the heat treating furnace. As a result, the gas generator often must be run when its output cannot be fully utilized. In addition, endothermic gas generators are inefficient from the standpoint of energy consumption because after reacting air and hydrocarbon in the generator, the reacted gas is cooled to room temperature, piped to the heat treatment furnace, then reheated again when it enters the furnace.

It would be advantageous both from the standpoint of energy consumption and for improved operating efficiency if furnace atmospheres for neutral hardening, annealing and carburizing could be generated within the heat treatment furnace itself. It has been proposed by the prior art, in certain instances, that the endothermic gas be produced directly in the actual furnace used for treatment of metal parts. However, when the process was conducted, undesirable carbon black formed on the surfaces of the work pieces which rendered the surfaces of the work pieces inactive. To solve this problem one approach suggested in U.S. Patents 3,519,257 and 3,620,518, employed a catalyst on the walls of the furnace in which the gas atmosphere was to be generated in situ. Furnace temperatures of 870°C (for carbonitriding) and 900°C (for carburizing) are mentioned. There is no mention of limitations on gas flow rates or means for variables controlling the air/fuel ratio. Such limitations are necessary because (1) the total catalyst surface area available per unit volume of gas will be less in a furnace than in an endothermic generator requiring an adjustment in flow rate and thus gas residency time; the retort of an endothermic gas generator is packed with porous ceramic cubes impregnated with catalyst through which the gas flows which facilitates faster flow rates and reduced residence time; (2) chemical reactions will proceed at a much slower rate at 870-900°C than in an endothermic generator at 1050-1100°C. There is reference in both patents to using a 9:1 air-propane ratio for carbonitriding at 870°C. From thermodynamic calculations (using the method described in the paper by C.A. Stickels in <u>Heat Treatment of Metals</u>, Vol. 1, No.1, 1979) it can be shown that the carbon content of steel in equilibrium with that atmosphere is about 0.13 wt. pct. which is too low for case hardening. If case hardening occurred after that treatment, it was due solely to nitrogen pickup from the ammonia addition, and not due to carbon pickup. In the carburizing example, (Example 2, of U.S. patent 3,620,418), a 9:1 air/propoane mixture is also used with a further enrichment of 50 liters per hour of propane. There is no mention of the flow rate of the 9:1 mixture. Without this information it is impossible to decide whether or not the atmosphere formed in the furnace was similar to an endothermic gas atmosphere. The fact that carburizing occurred is not sufficient, because carburizing will occur at 900°C in an atmosphere of propane alone. It is necessary to show that carburizing occurred in an atmosphere similar in composition to an endothermic gas-base atmosphere. In summary, the evidence available from the patents 3,519,217 and 3,620,518 is insufficient to demonstrate that a furnace atmosphere similar in composition to endothermic gas could be produced by the methods proposed hereinafter and that such atmosphere is controllable to promote uniform and consistent carburizing.

According to the present invention, there is provided a method of heat treating ferrous based workpieces in a furnace chamber by heating said workpieces therein to the temperature range of 1500-2000°F (800-1100°C) while in the presence of an endothermic type gas, characterised in that the gas is passed through the said chamber at a low flow rate.

In the preferred method of the invention ferrous based workpieces are subjected to a heated furnace chamber maintained at heat treating temperature (1500-2000°F) while introducing a supply of air and hydrocarbon gas into the furnace chamber at a predetermined ratio which, when heated by the furnace chamber, chemically reacts to form an endothermic type gas, the endothermic type gas being controlled to flow through the furnace chamber at a low flow rate which preferrably maintains the average residency time of the endothermic type gas in said furnace at least 0.2 hours (12 minutes).

When the process is employed for carburization of the workpiece, it is preferred that the air/hydrocarbon ratio be 1.6-2.4 when methane is selected and 6.0-7.2 when propane is selected. With such air/hydrocarbon ratios, soot-free carburization can be accomplished using the in situ generated atmosphere at lower temperatures without the necessity for special catalysts.

Because of the required slower flow rate of the endothermic type gas through the furnace chamber, the process becomes more sensitive to air contamination by leakage into the furnace chamber or by being carried into the furnace chamber on or in the workpiece. The carburizing or decarburizing potential of the endothermic atmosphere will be detrimentally affected if the air/hydrocarbon gas supply is not variably adjusted. It is preferred therefore to introduce the air component for the air/hydrocarbon gas mixture at a constant flow rate and to automatically vary the hydrocarbon gas supply to maintain a constant value of CO_2 and/or oxygen potential. The oxygen potential, if used as a reference, is preferably measured by a zirconia oxygen sensor device.

Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings, in which:-

Figures 1-4 are graphical illustrations of various gas furnace atmosphere characteristics when the furnace temperature is maintained at 927°C. and the gas flow rate therethrough is 15 liters per minute (after allowing for the volume expansion which occurs when air and propane react). Figure 1 depicts average weight gain in the carburized article after 2.5 hours as a function of air-propane ratio, Figure 2 depicts the CO_2 gas constituent as a function of air-propane ratio, Figure 3 depicts CH_4 content as a function of air-propane ratio and Figure 4 depicts the carbon content as a function of distance inwardly from the outer surface of the test samples;

Figures 5-8 depict similar gas atmosphere data as that in Figures 1-4 but for the conditions where the furnace temperature is maintained at 843°C., the reacted gas flow rate is 10 liters per minute, and the carburizing time is 6 hours.

Figures 9 and 10 are graphical illustrations of carburization process control at 927°C and 843°C, respectively, using an automatic control system based on the output of a zirconia oxygen sensor.

Figure 11 is a schematic graphical illustration of the composition of the furnace atmosphere gas plotted against time depicting the rate of change of furnace atmosphere composition when the inlet gas composition changes from C_0 to C_1.

Figure 12 is a schematic graphical illustration similar to Figure 11 with gas composition in a dimensionless form.

Figure 13 is a graphical illustration of the time rate of change of furnace atmosphere composition at 925°C with an inlet gas flow rate of 15 liters per minute for a batch-type sealed-quench carburizing furnace.

Figure 14 is a graphical illustration like that in Figure 11 for the same furnace, but at 843°C and an inlet gas flow rate of 10 liters per minute.

Figure 15 is a graphical illustration depicting the estimated minimum mean residence time for furnace gases at various temperatures to achieve adequate reaction of the furnace gases.

Figure 16 is a schematic diagram of a gas blending system used to introduce gas elements in fixed proportions to the furnace; the nitrogen gas supply being used for purging of the furnace chamber and workpiece.

Figure 17 is a schematic diagram of a furnace atmosphere control system employing a constant flow of air and a variable flow of hydrocarbon gas. The flow of hydrocarbon gas is automatically adjusted to maintain a constant voltage output on a zirconia oxygen sensor.

For heat treating ferrous workpieces according to this invention, the method comprises supplying air and hydrocarbon gas to a furnace chamber at a predetermined ratio where the heat of the furnace chamber (maintained at a heat treating temperature of 1500-2000°F) causes the gases to react and produce in situ an endothermic type gas atmosphere. The endothermic type gas atmosphere is caused to flow through the furnace chamber at a low flow rate and the generation of the atmosphere can preferably be variably controlled to overcome the sensitivity of the method to impurities at such low flow rate.

In particular, the air and hydrocarbon gas reacts rapidly to produce CO, H_2, CO_2, H_2O, CH_4 and N_2. The proportions of these molecular constituents, however, are not the proportions expected at thermodynamic equilibrium. The minor constituents of the initially reacted gas, CO_2, H_2O and CH_4, are invariably present in much greater quantity than is expected at equilibrium. If the reacted gas is allowed to remain in the furnace, the CO_2 and H_2O are slowly reduced by the methane by reactions such as

$$CO_2 + CH_4 = 2\ CO + 2\ H_2$$

$$H_2O + CH_4 = CO + 3\ H_2$$

The result is that the longer the reacted gases remain in the furnace, the lower is the amount of CO_2, H_2O and CH_4.

Carbon is transferred from the furnace atmosphere to ferrous workpiece or vice-versa, by reactions such as

$$(1)\ CO + H_2 = C\ (\text{in Fe}) + H_2O$$

$$(2)\ 2\ CO = C\ (\text{in Fe}) = CO_2$$

$$(3)\ CH_4 = C\ (\text{in Fe}) + 2\ H_2$$

The first two of the above reactions are known to be much faster than the third reaction. The result of this behaviour is that the carburizing/decarburizing tendency of the furnace atmosphere is strongly affected by the H_2O and CO_2 contents of the atmosphere, and only weakly affected by the methane content. If the CO_2, H_2O and CH_4 contents of the atmosphere are all much higher than the equilibrium amounts, the atmosphere will be more decarburizing than it would be if the gaseous constituentswere in equilibrium. The carburizing effect of the high methane content does not offset the decarburizing effect of the high CO_2 and H_2O contents.

As a result, it has been found that when air and methane, (or propane) in fixed proportions are introduced into a furnace, the furnace atmosphere is more carburizing the lower the flow rate of gas into the furnace. The resident time of the gases in the furnace increases as the inlet flow rate decreases, so the CO_2, H_2O and CH_4 contents of the furnace atmosphere are lower the lower the flow rate. When the flow rates are sufficiently low, the furnace atmosphere becomes very similar in composition to an endothermic gas-base atmosphere. In addition, because the carburizing/decarburizing tendency of the gas is dominated by reactions (1) and (2) above, the CO_2 and H_2O contents of the furnace gas serve as indices of its potential for carburizing just as with endothermic gas-base atmosphere.

For the purposes of this invention, an endothermic type gas is defined to mean one where the air and hydrocarbon gas are reacted to produce CO, H_2, CO_2, H_2O, CH_4 and N_2. In the gas used in the invention the proportions of CO, H_2, CO_2 and H_2O are substantially the same at thermodynamic equilibrium as for an independently generated endothermic gas, but the proportion of methane is typically 2-3 times higher.

This invention has provided a way of obtaining soot-free carburizing without the necessity for catalyst or pre-heating of the oxygen supply, and yet save energy up to 75% over comparable energy units used by the state of the art carburizing techniques. This is based on the appreciation that if air/hydrocarbon blends similar to those used in endothermic gas-base atmospheres are permitted a long residence time in the heat treatment furnace at temperature by using very low inlet gas flow rates, a satisfactory carburizing atmosphere can be produced.

Low flow rate or slow flow of air/hydrocarbon gas herein shall mean a gas movement which is sufficiently long to permit the immediate reaction products of air and hydrocarbon gas at heat treating temperature to additionally react to lower the CO_2 and H_2O content of the gas to substantially thermodynamic equilibrium amounts. "Low flow rate" can also be defined as that rate of gas movement which allows the mean residency time for all molecules of the gas reaction products to be in the heat treating chamber for at least 0.2 hours (12 minutes). The preselected air/hydrocarbon gas ratio will control the character of the equilibrium atmosphere as to being carburizing, neutral or decarburizing for purposes of hardening, annealing or carburizing.

Because the flow rates are low compared to conventional furnace operations, there is a substantial savings of hydrocarbon gas. The prior art has intentionally avoided this area of development; this may in part be explained by the fact that the art has generally accepted that a low flow rate of a methane or propane mixture would allow air infiltration into the vestibule of the furnace creating potentially explosive gas mixtures in the vestibule and destabilizing the atmosphere for carburization purposes. This concern has been shown to be unwarranted. Furthermore, it was the general notion of those skilled in the art of carburizing with endothermic gas-base atmospheres that to improve the rate of carburizing, it was necessary to increase the flow of gases into the furnace. It has also been discovered that when air/hydrocarbon blends are used to produce the furnace atmospheres, increasing the flow rate will not help in the carburising process. Instead, there must be an allowance of time for secondary chemical reactions to take place which in turn will improve the carburizing character of the atmosphere. The rate of carburizing can then be controlled by regulating the air/hydrocarbon ratio, while maintaining the flow of reacted gas essentially constant.

The following Examples illustrate the invention:-

EXAMPLE I

A first series of heat treat experiments were run to determine if carburization by an in situ generated endothermic gas atmosphere at low flow rates can in fact take place, and if so, can be controlled by regulating the proportions of air and hydrocarbon gas entering the furnace.

Carburizing experiments were run in a batch-type sealed quench carburizing furnace manufactured by the Lindberg Division of Sola Basic Industries. Test specimens were made of small stampings of AISI 1010 sheet steel; each specimen weighed about 65 grams and each had a surface area of about 63 square centimeters. About 20 specimens were run for each trial. Propane and air were introduced into the furnace chamber at a predetermined ratio and flow rate. The inlet gases were directed toward the inlet side of a recirculating fan within the furnace chamber. The fan is employed to insure a uniform flow from inlet to furnace outlet. The flow rates were computed as follows:

F: Total flow of gas mixture at ambient temperature and pressure after complete reaction to form CO, H_2 and N_2.
A/P: Ratio of air flow to propane flow.
A: Flow rate of air measured at ambient temperature and pressure.

To produce a given flow F at a particular air-propane ratio (A/P), the necessary air and propane flows are:

$$P = \frac{F}{1+1.624\ (A/P)} \qquad A = \frac{F\ (A/P)}{1+1.624\ (A/P)}$$

From preliminary experiments it was found that satisfactory carburizing could be achieved at 927°C. (1700°F) using a flow rate F of 15 liters per minute. Keeping F constant, a series of experiments were run for 2.5 hours at 927°C. at various air-propane ratios to determine the effect of atmosphere composition on the amount of carburizing. Figure 1 shows the average weight gain (due to carbon pick-up) of five specimens taken from each of these trials as a function of air-propane ratio to obtain a desired carburization. Figures 2 and 3 show, respectively, the CO_2 and CH_4 contents of the furnace gas (measured by infrared gas analysis near the end of each trial) as a function of air-propane ratio. The solid lines are computed assuming thermodynamic equilibrium under two different conditions:

(I) when methane is stable in the furnace atmosphere,

(II) when the furnace atmosphere is in equilibrium with graphite.

The significance of Figures 2 and 3 is that while thermodynamic equilibrium is not achieved, it is approached reasonably closely so that the process is controllable using CO_2 analysis if that is desired. At high flow rates with the same gas blends, weight gains would be low, and the CO_2 and CH_4 contents much higher, far from the equilibrium values. Furthermore, at high flow rates carburizing is not uniform. Parts near the gas inlet in the furnace chamber will carburize less than parts located at some distance from the gas inlet. Figure 4 shows the gradient of carbon content measured by electron microprobe analysis for samples from several of these trials. Figure 4 demonstrates that the inventive process can obtain the same carbon increases as would the prior art at about the same air-propane ratios, except that it is accomplished without prior reaction of the air and propane in a gas generator.

In a similar manner, another series of trials were run at 843°C. (1550°F.) for six hours at a flow rate F of 10 liters per minute. Figures 5, 6 and 7 show the average weight gain, atmospheric CO_2 and CH_4 contents as a function of air-propane ratio. Figure 8 similarly shows the carbon gradient found on samples taken from several of the trials. Figure 5-8 demonstrate a similar degree of control and relatively close approximation to theoretical calculations.

These results show that over the range of temperatures most frequently used for gas carburizing, the amount of carburizing which takes place can be controlled by regulating the proportions of air and propane entering the furnace. If endothermic gas is produced from propane using air-propane ratio of 7.5 at the gas generator according to prior art techniques, and if the endothermic gas is then enriched with 1.5% propane as it enters a carburizing furnace, the overall air-propane ratio used to form the furnace atmosphere is 6.25. At the same air-propane ratio (6.25), the present invention yields product results which are essentially identical to those obtained with conventional endothermic gas-base atmospheres.

EXAMPLE II

When utilizing low flow rates for the introduction of an air/hydrocarbon gas mixture, the carburizing process becomes more sensitive to air contamination (air that leaks into the furnace chamber or air that is carried into the furnace chamber by the workpiece). If a fixed, predetermined air/hydrocarbon ratio were to be relied upon, the atmosphere would not compensate for such air contamination and heat treating quality, particularly carburization quality, would decrease. Because of the CO_2 content, oxygen potential of the furnace gas varies systematically with air/propane ratio in Example I, automatic control of the furnace atmosphere composition based on CO_2 or oxygen potential analysis is possible. In this example, it will be shown that automatic atmosphere composition control is possible using a zirconia oxygen sensor to measure the oxygen potential of the atmosphere.

The automatic control system is designed so that the total reacted gas flow does not change appreciably as the inlet air/hydrocarbon ratio changes. Ideally, this can be done by regulating the flows of both air and hydrocarbon gas. However, if just the hydrocarbon flow is altered, with the air flow held constant, the variation in reacted gas flow (and residence time of the gases within the furnace) is small enough so that it does not appreciably affect process control. Table 1 shows that the computed flow of reacted gas varies only 20% for air/propane ratios from 3 to 9 and a constant air flow.

Table 1

Computed Flows of Reacted Gas With a Constant Air Flow and Variable Propane Flow

A/P	Air Flow, lpm	Propane Flow, lpm	Reacted Gas Flow, lpm
3	8.5	2.83	17.70
4	8.5	2.13	15.93
5	8.5	1.70	15.50
6	8.5	1.42	15.22
7	8.5	1.21	15.02
8	8.5	1.06	14.87
9	8.5	0.94	14.75

Using an automatic control system to regulate the flow of propane gas, test samples were run at 927°C and 843°C as in the previous example. Figure 9 shows that the weight gain due to carburization after 2.5 hours at 927°C increases systematically as the set oxygen sensor voltage is increased. The surface carbon content of samples, determined by microprobe analysis, also increases systematically as the oxygen sensor voltage increases. The air flow rate employed was chosen to give approximately the same residence time for gases within the furnace as in the previous example, Figures 1 - 4.

Figure 10 shows similar results for samples carburized for 6 hours at 843°C. Again, the air flow rate was chosen to give approximately the same residence time for gases within the furnace as in the previous example, Figures 5 - 8.

One of the main advantages of automatic process control, as illustrated in this example, is that the inadvertant entry of air into the furnace chamber is automatically offset by adjustments to the air-hydrocarbon raito of the inlet gases. In Example I, samples were held in the furnace vestibule for several hours while the furnace and vestibule were purged in order to minimize the entry of air into the furnace chamber when the samples were charged into the furnace. A long purging time was necessary because the flow rates employed were low. In Example II, on the other hand, no special effort was made to avoid entry of air into the furnace chamber. Samples were held in the furnace vestibule for about 15 minutes before charging into the furnace; this holding time in the vestibule is typical of commercial practice with endothermic gas-base atmospheres.

Determination of Appropriate Flow Rate

In the previous examples, suitable flow rates at two different temperatures were found by trial and error. Under the selected condition of temperature and flow rate there is sufficient time for the CO_2 and H_2O in the atmosphere to be reduced by reaction with CH_4 so that carburizing can take place. If the gas residency time is know, then for any other furnace (regardless of size or design) flow rates can be adjusted to produce the same gas residency time. If the gas residency time is the same in the two different furnaces operating at the same temperature with furnace atmospheres formed from air and a hydrocarbon gas in the same proportions, similar rates of carburizing (or similar effective carbon potentials) are effected.

All gas molecules entering a furnace chamber do not remain in the chamber for the same length of time. At any fixed inlet gas flow rate there is a distribution of residence time for the molecules. The mean residence time for all the gas molecules can be readily defined and measured.

Mean residence times were measured by the following experiment. The furnace at the temperature of interest is purged with nitrogen at the flow rate of interest, F. A gas sample is drawn from the furnace chamber and is continually monitored by infrared analysis for CO_2 content. After a number of hours of purging, a low stable value for CO_2 content of the furnace is obtained. This value is defined as C_0. At this point, the inlet gas composition is switched to C_1% CO_2 in nitrogen and the time rate of change of the furnace gas composition is recorded. Schematically, the furnace gas composition C changes in response to a change in inlet gas composition in the manner shown in Figure 11, where C is the composition of the gas phase in the furnace at any time t and C_0 at the moment the inlet gas composition phase is changed.

If the composition is expressed in dimensionless form $\dfrac{C_1 - C}{C_1 - C_0}$ the experimental data can be replotted as shown in Figure 10. Then, the mean residence time t_m, is given by the area under the curve in Figure 12, that is

$$t_m = \int_0^{\infty} \left(\frac{C_1 - C}{C_1 - C_0} \right) dt$$

Regardless of how complex the shape of the curve experimentally, the mean residence time can always be found by a method of graphical or numerical integration. The calculation of mean residence time will be simpler if a mathematical model for the furnace is used. For example, if the furnace chamber has a volume V and the flow rate of gas into and out of the furnace occurs at a rate f, then if perfect mixing occurs in the furnace chamber, it can be shown that

$$\frac{C_1 - C}{C_1 - C_0} = \exp\left(-\frac{f}{v}t\right)$$

and the mean residence time is

$$t_m = \frac{v}{f}$$

The gas flow behaviour of real furnaces will be more complex than the simple model.

Mean gas residence times were measured in the manner described for the Lindberg carburizing furnace used to obtain the results described in the previous example. For inlet gas flows of 15 liters per minute and a furnace temperature of 927°C. the data shown in Figure 13 was obtained. At a flow rate of 10 liters per minute and a furnace temperature of 843°C., the response shown in Figure 14 was measured. From these data, minimum mean residence times of 26 and 48 minutes, respectively, were computed. Therefore, it is anticipated that results similar to those depicted in the series of examples could be obtained on any other furnace provided that gas flow rates were adjusted to yield mean residence times at least as long as 26 minutes at 927°C, and 48 minutes at 843°C. The steep line in each graph at short times represents the influence of the volume of the main furnace chamber, and the shallow line for longer times represents the influence of the volume of the vestibule chamber. It is very difficult to theoretically calculate ahead of time the mean residence time. The volumes of such chambers can be directly measured but the rate of recirculation of gases between the furnace chamber and the vestibule cannot be predicted. Therefore, an experimental measurement of mean residence time is needed to determine appropriate flow rates. Alternatively, appropriate flow rates can be found by progressively lowering the flow rates and simultaneously monitoring furnace gas composition until the furnace gas is close to the equilibrium composition.

Figure 15 gives typical means residence times needed to produce satisfactory furnace atmospheres for neutral hardening, annealing or carburizing by this invention for temperatures from

800 to 1000°C.

An illustrative method for carburizing ferrous based workpieces is an follows.

(a) Mix air and a hydrocarbon gas to create an endothermic type gas when reacted at heat treating temperature levels, the air and hydrocarbon gas being mixed in a predetermined ratio which varies with the specific hydrocarbon gas employed. For example, propane gas which would require a ratio of 6.0 - 7.2, and methane gas which would require a ratio of 1.6 - 2.4 for carburizing; a suitable gas blending apparatus is shown in Figure 16. Air and propane are supplied separately through passages 10 and 11, respectively, at ambient temperature; each are regulated as to pressure indicated. The nitrogen supply is used for purging the furnace chamber and is not used for generation of the endothermic type atmosphere. The amount of air and propane admitted to the furnace is regulated by motorized valves 12 and 13, respectively, which are controlled to operate to maintain a constant air/propane ratio. The ratio is preset in controller 14 and variances in the flow ratio as sensed by flow meter s 15 and 16 causes the individual controllers 17 or 18 to maintain the preset ratio in controller 14. Alternatively, the atmosphere composition may be controlled automatically by monitoring the furnace atmosphere CO_2 content by infrared gas analysis or by measuring the oxygen potential of the atmosphere by means of a zirconia oxygen sensor. The hydrocarbon gas addition is automatically regulated to maintain predetermined levels of CO_2 content or oxygen potential. A suitable system for automatic atmosphere control is shown schematically in Figure 17. The valve controller 20 and 21 adjust the opening of the respective motorized valve 22 and 23 to match the voltage output of the respective flowmeter 24 and 25 to the control voltage. For the air supply, the control voltage is set by adjusting a potentiometer on the valve controller 21. For the propane supply, the control voltage is derived from the proportional controller 26. The output of the proportional controller depends on the difference between the signal received from the zirconia oxygen sensor 27 and a reference voltage obtained by setting a potentiometer. The necessary voltage-to-voltage and voltage-to-current converters are not shown.

(b) Feeding said mixture to said furnace at a slow flow rate. For a furnace without a vestibule, or for a large furnace with small vestibules, the necessary flow may be estimated by requiring that the flow ratio (furnace chamber volume in cubic feet divided by the flow rate in cubic feet per hour measured at the furnace temperature) be greater than about 0.2 hours. For a furnace with a large vestibule, such as was used in these trials, the allowable flow rates are higher, but must be determined either by trial or by a direct measurement of residence time of the gases. For a large commercial furnace of 400 cubic feet volume operated at 1700°F, a slow flow rate would be about 400 standard cubic feet/hour for a flow ratio of 0.25 hours.

(c) Reacting said gas mixture in the furnace to generate a desired endothermic gas-like atmosphere, said reacted gases having a mean residence time in said furnace in proportion to the temperature of said atmosphere, which mean residence time typically may vary between 69 minutes at 800°C and 17 minutes at 1000°C. The flow rate is controlled to achieve a specific mean residence time.

It should be pointed out that the process of this invention is not limited to the preferred modes described, but can include certain modifications without deviating from the invention. For example; carbonitriding may be carried out by the process described provided a predetermined amount of ammonia (up to 5%, preferably 3-4%) is added to the prescribed atmosphere. Moreover, carburizing may be carried out with special hydrocarbon additions other than the described propane or methane, such as butane.

CLAIMS

1. A method of heat treating ferrous based workpieces in a furnace chamber by heating said workpieces therein to the temperature range of 1500 -2000°F (800 - 1100°C) while in the presence of an endothermic type gas, characterised in that the gas is passed through the said chamber at a low flow rate.

2. A method according to Claim 1 in which said endothermic type gas comprises CO, H_2, CO_2, H_2O and CH_4 formed by the reaction of air and hydrocarbon gas and additional products formed by the reduction of CO_2 and H_2O by CH_4.

3. A method according to Claim 1 or Claim 2 in which the flow rate produces an average residency time of said gas reaction products in said chamber of at least 0.2 hours.

4. A method according to any one of Claims 1 to 3 wherein the endothermic type gas is formed by the reaction of air and propane or methane.

5. A method according to Claim 4 wherein endothermic gas is formed from a gas mixture having an air/propane ratio of 1.6 - 2.4 or an air/methane ratio of 6.0 - 8.0.

6. A method according to Claim 5 wherein the said gas is formed from a mixture having an air/methane ratio of 6.0-7.2.

7. A method according to any one of Claims 1 to 6 in which the proportion of hydrocarbon gas used in the generation of the endothermic type gas is controlled in response to variations in the amount of oxygen in said chamber atmosphere.

8. A method according to Claim 7 in which the amount of oxygen is sensed by the use of a zirconia oxygen sensing device.

9. A method according to any one of Claims 1 to 6 wherein the proportion of hydrocarbon gas used in the generation of the endothermic type gas is controlled in response to variations in the gas in the said chamber.

10. A method according to any one of Claims 1 to 9 wherein the ferrous based workpiece is exposed to said endothermic type gas in said chamber for a period of time sufficient to obtain a carbon gradient in the workpiece proceeding from the outer region thereof.

11. A method according to any one of Claims 1 to 10 wherein the workpieces are heated to a temperature of at least 820°C.

12. A method according to any one of Claims 1 to 11 wherein the endothermic type gas is fed into the chamber at a rate sufficient to provide a mean residence time in said furnace in proportion to the temperature of said atmosphere which varies between 69 minutes at 800°C and 17 minutes at 1000°C.

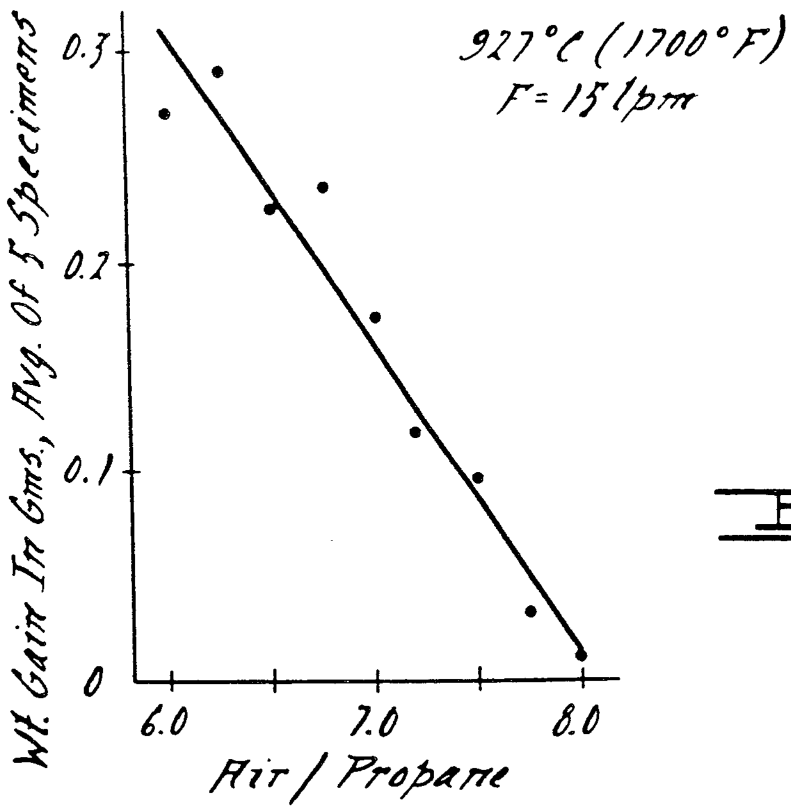

927°C (1700°F)
F=15 lpm
Wt. Gain In Gms., Avg. Of 5 Specimens
0.3
0.2
0.1
0
6.0
7.0
8.0
Air / Propane

FIG. 1.

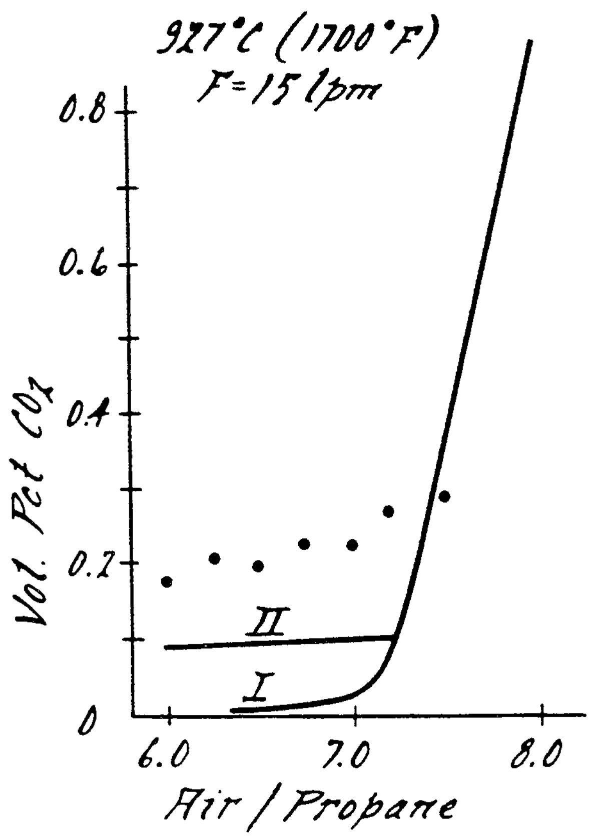
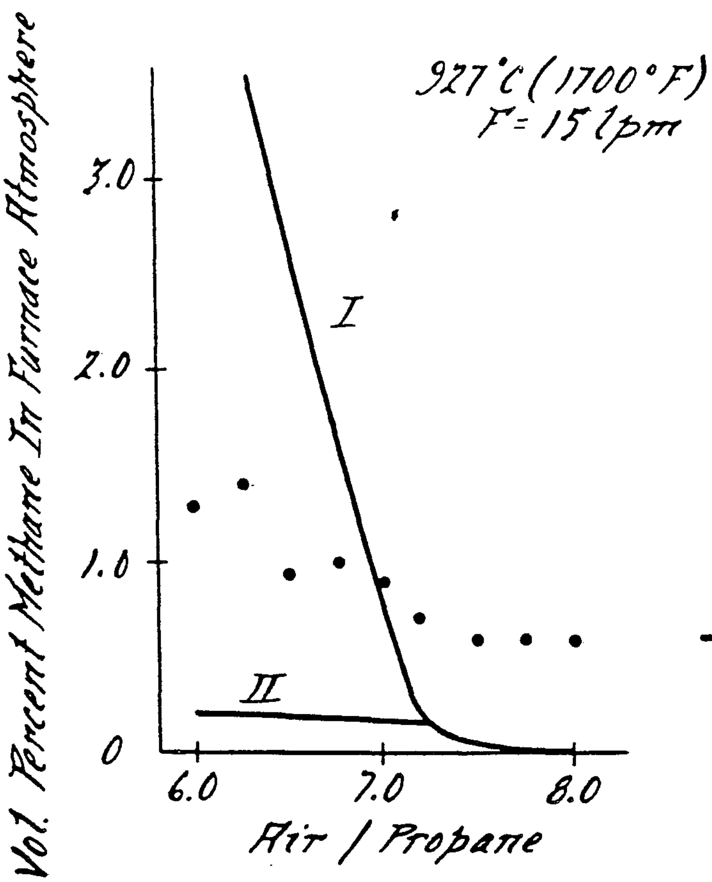
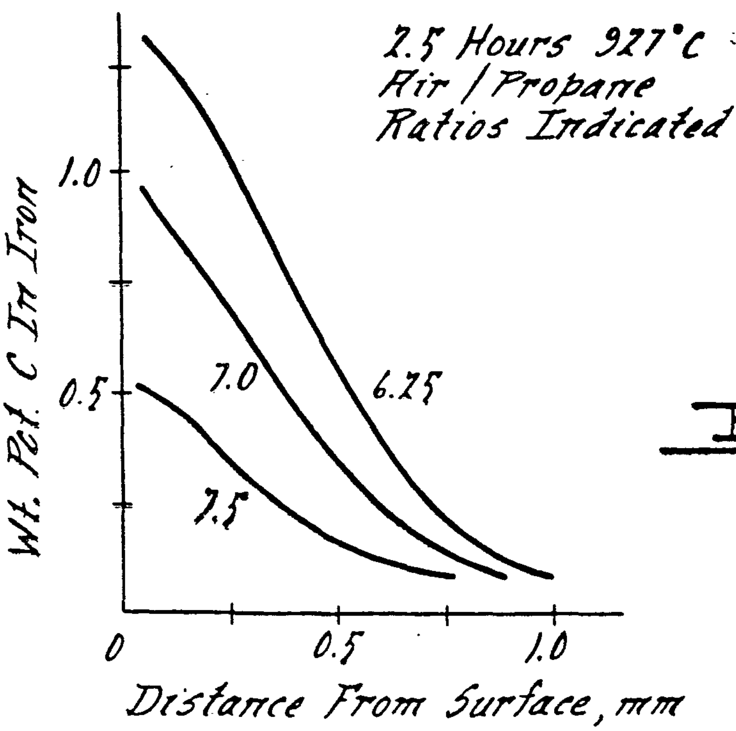

927°C (1700°F)
F=15 lpm
Vol. Pct CO2
0.8
0.6
0.4
0.2
0
II
I
6.0
7.0
8.0
Air / Propane

FIG. 2.



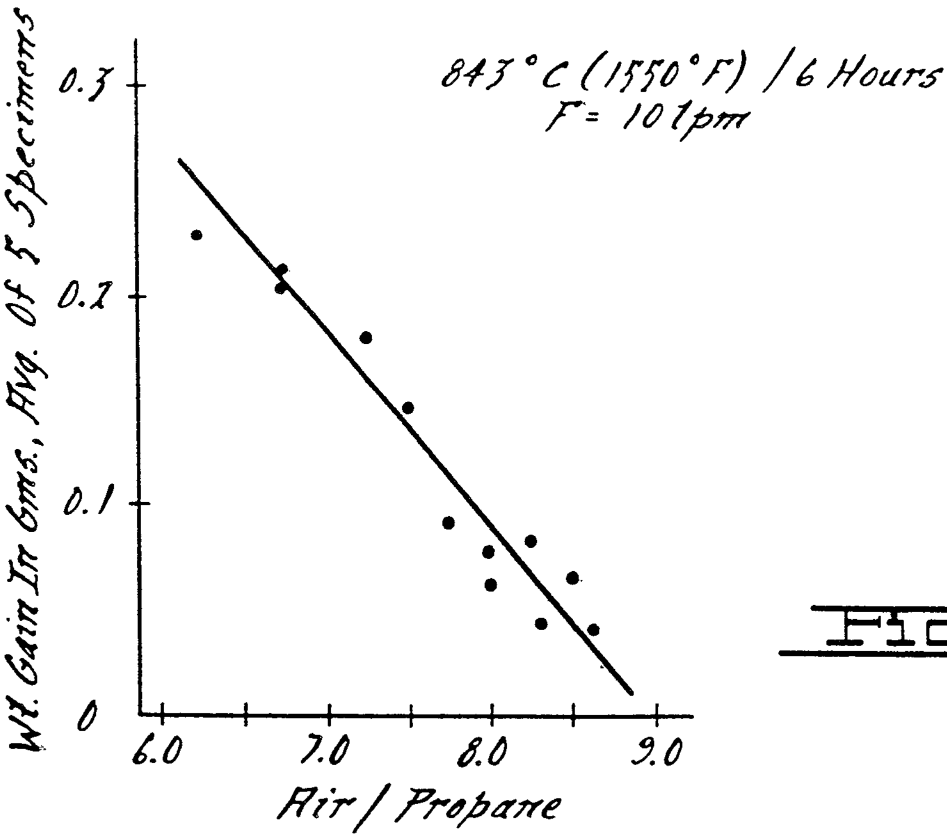
927°C (1700°F)
F=15 lpm
I
II
Vol. Percent Methane In Furnace Atmosphere
3.0
2.0
1.0
0
6.0
7.0
8.0
Air / Propane

FIG.3.



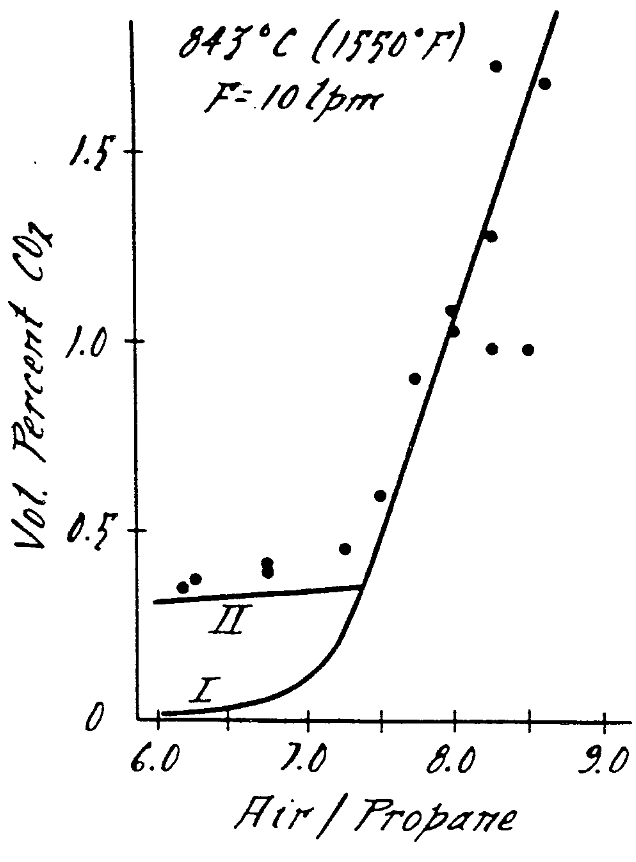
2.5 Hours 927°C
Air / Propane
Ratios Indicated
Wt. Pct. C In Iron
1.0
0.5
7.0
6.25
7.5
0
0.5
1.0
Distance From Surface, mm

FIG.4.



843°C (1550°F) / 6 Hours
F = 10 lpm
Wt. Gain In Gms., Avg. Of 5 Specimens
0.3
0.2
0.1
0
6.0
7.0
8.0
9.0
Air / Propane

FIG. 5.



843°C (1550°F)
F = 10 lpm
Vol. Percent CO2
1.5
1.0
0.5
0
II
I
6.0
7.0
8.0
9.0
Air / Propane

FIG. 6.

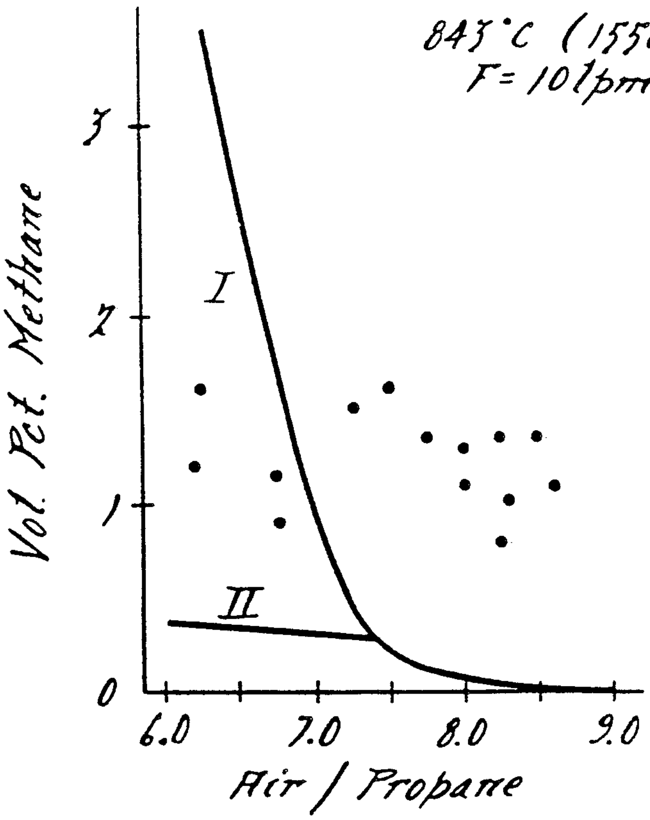
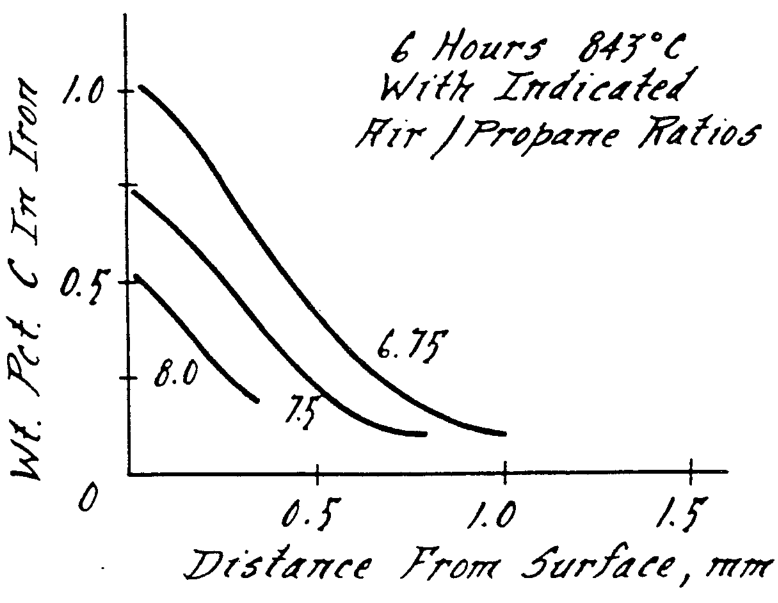

843°C (1550°F)
F= 10 lpm
Vol. Pct. Methane
3
2
1
0
I
II
6.0
7.0
8.0
9.0
Air / Propane

FIG. 7.

FIG. 8.


6 Hours 843°C
With Indicated
Air / Propane Ratios
Wt. Pct. C In Iron
1.0
0.5
0
8.0
7.5
6.75
0.5
1.0
1.5
Distance From Surface, mm

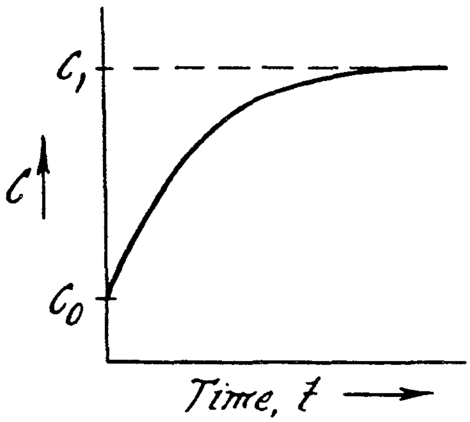


FIG. 9.

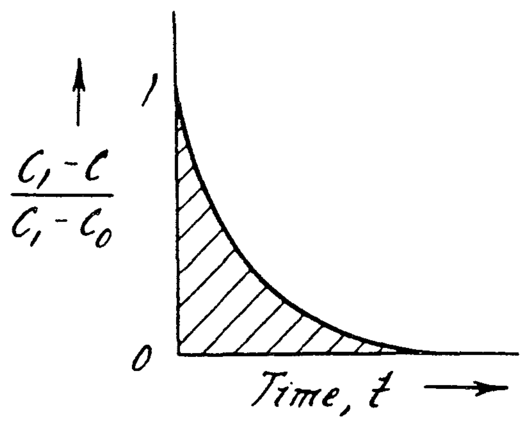


FIG. 10.

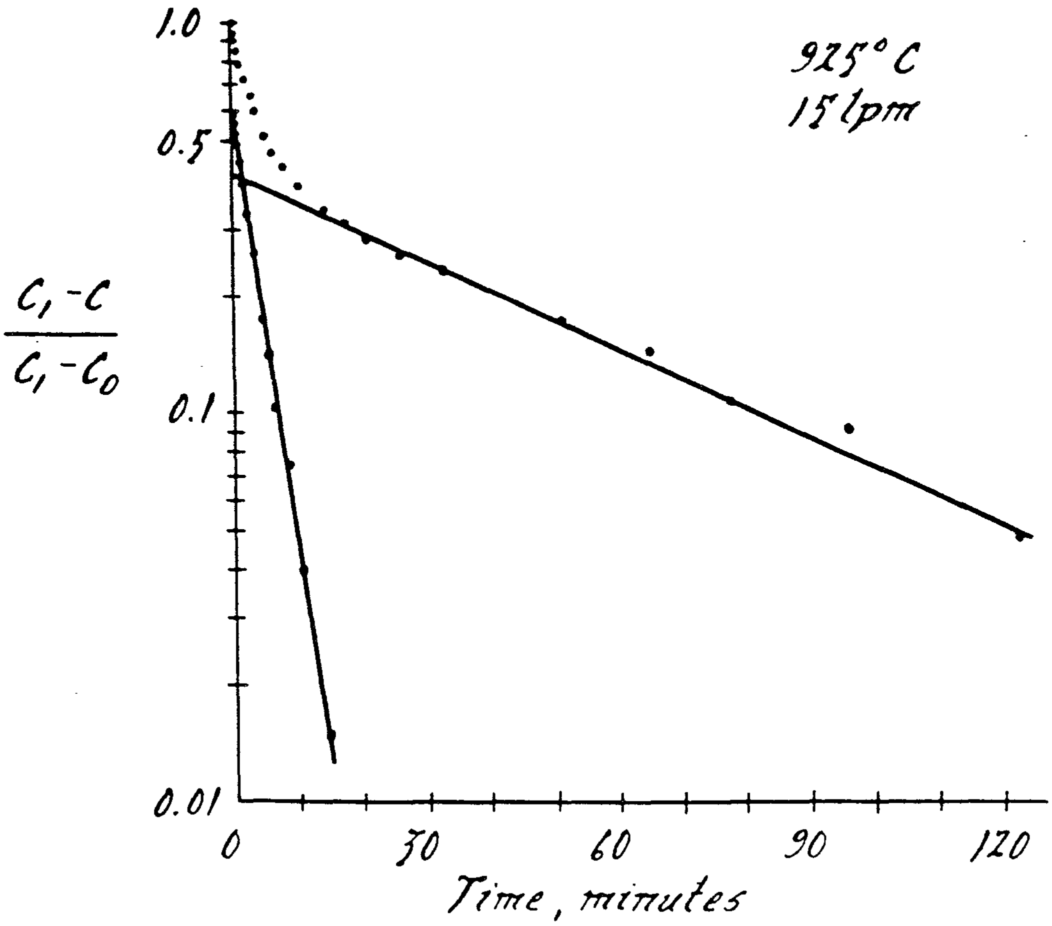
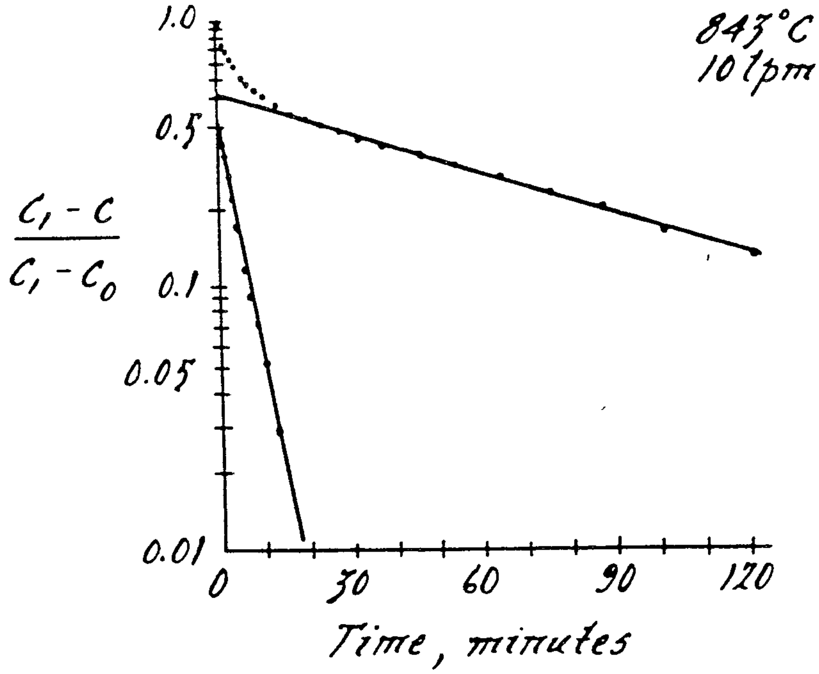
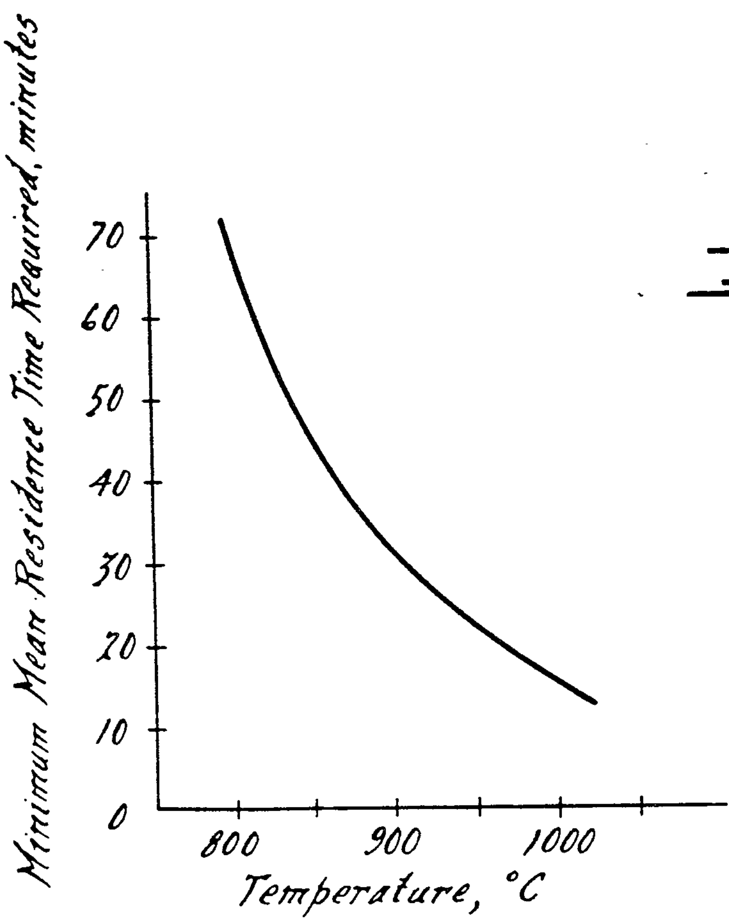


FIG. 11.



843°C
10 lpm
$\frac{C_1 - C}{C_1 - C_0}$
1.0
0.5
0.1
0.05
0.01
0
30
60
90
120
Time, minutes

FIG. 12.



Minimum Mean Residence Time Required, minutes
70
60
50
40
30
20
10
0
800
900
1000
Temperature, °C

FIG. 13.

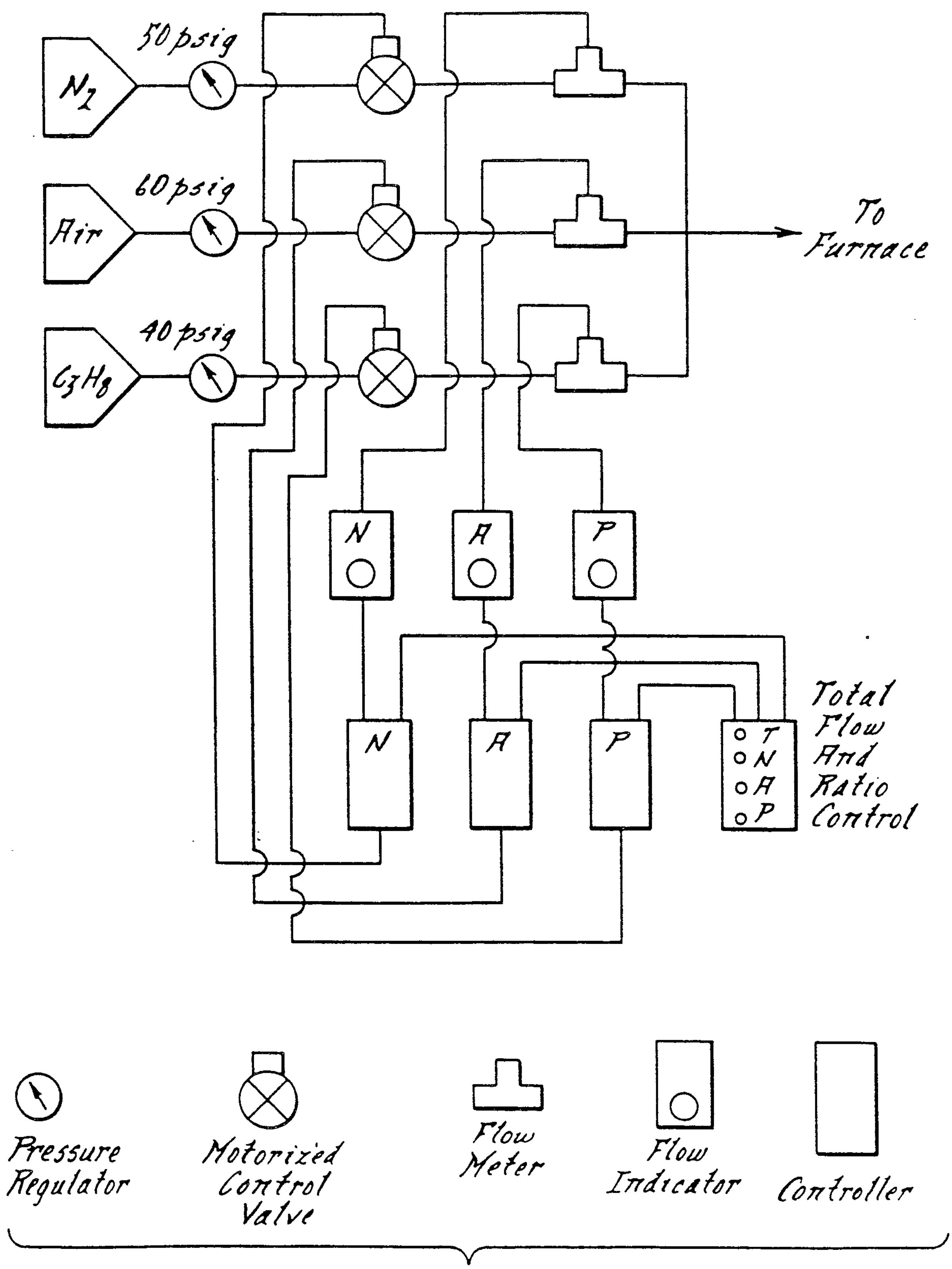

50 psig
60 psig
40 psig
N_2
Air
C_3H_8
To Furnace
N
A
P
N
A
P
T
N
A
P
Total Flow And Ratio Control
Pressure Regulator
Motorized Control Valve
Flow Meter
Flow Indicator
Controller

FIG. 14.

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 80 30 2236.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	US - A - 4 049 473 (R.L DAVIS II et al.) * columns 4 and 5 * --	1
A	US - A - 3 413 161 (W. GOEHRING) --	
A	US - A - 4 049 472 (E.J. ARNDT) --	
A,P	GB - A - 2 016 698 (IPSEN INDUSTRIES) --	
A	DE - B - 1 918 923 (INDUGAS) --	
A	METAL PROGRESS, Vol. 113, No. 4, April 1978 K.D. GLADDEN et al. "Furnace Atmosphere Control by the Oxigen Potential Method" pages 40 to 44 --	
D,A	US - A - 3 519 257 (K.-H. WINTER et al.) --	
D,A	US - A - 3 620 518 (K.-H. WINTER et al.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 21 D 1/76
C 23 C 11/12
C 23 C 11/18

TECHNICAL FIELDS SEARCHED (Int.Cl.3)

C 21 D 1/76
C 23 C 11/12
C 23 C 11/18

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	18-11-1980	SUTOR

EPO Form 1503.1 06.78