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⑪ Publication number: **0 040 023**
A1

⑫ # EUROPEAN PATENT APPLICATION

㉑ Application number: **81301882.7**

㉒ Date of filing: **28.04.81**

(51) Int. Cl.³: **C 23 C 11/10**
C 23 C 11/12, C 23 C 11/14
C 23 C 11/18

㉚ Priority: **02.05.80 GB 8014712**

㊸ Date of publication of application:
18.11.81 Bulletin 81/46

(84) Designated Contracting States:
AT BE CH DE FR IT LI LU NL SE

(71) Applicant: **AIR PRODUCTS AND CHEMICALS, INC.**
P.O. Box 538
Allentown, Pennsylvania 18105(US)

(72) Inventor: **Paterson, Alan**
4 Hayfields Grove
Audlem Crewe(GB)

(74) Representative: **Lucas, Brian Ronald**
c/o Air Products Limited Coombe House St. George's Square
New Malden Surrey, KT3 4HH(GB)

(54) **Gas carburizing.**

(57) Carrier gases formed by the reaction of rich mixtures of hydrocarbon and air and heretofore considered unsuitable for gas carburizing can be used for gas carburizing if introduced into the heat treamtment chamber (4) at or below a specified flow rate. This flow rate is inversely proportional to the amount of CO_2 and H_2O present in the carrier gas and can be increased by, for example, removing H_2O from the gas. The invention has particular commercial value since it enables exothermic gas generators (8) to be used for providing carrier gas for gas carburizing with excellent control of the carbon potential by monitoring the reacted furnace atmosphere and making hydrocarbon additions in the usual way. Three forms of apparatus are also described which may be used for producing suitable carrier gases in the heat treatment chamber (4) itself.

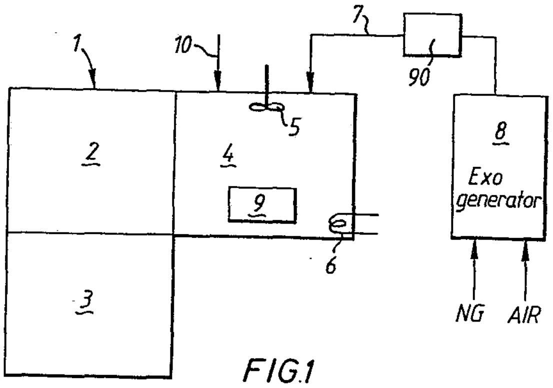

FIG.1

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This invention relates to a method of gas carburizing.

Traditionally gas carburizing has been carried out using endothermic gas as a carrier gas together with hydrocarbon additions. Various suggestions have been made as to alternative carrier gases which might be used but many of these have been very difficult to control without the use of very sensitive control equipment due to the high proportion of nitrogen in the final reacted atmosphere.

Heretofore, atmospheres based on exothermic gas have been regarded as "not suitable for -- hardening of carbon or alloy steels" (Metals Handbook page 71 column 1) although stripped and dried exothermic gas has been described as offering "a moderate range of control" (Metals Handbook page 94 column 2).

We have now discovered that an extensive spectrum of gases formed by the reaction of a rich mixture of hydrocarbon selected from the group consisting of natural gas, methane, butane, propane, and mixtures thereof together with air or oxygen enriched air are suitable as carrier gases for gas carburizing provided that they are metered to the heat treatment chamber at a rate determined by the equation:

$$R \ngtr \frac{90V^{\frac{2}{3}}}{D}$$

Where

V is the free (i.e. unloaded) internal volume of the heat treatment chamber in cubic feet;

R is the flowrate of carrier gas into the heat treatment chamber in standard cubic feet per hour; and

D is the percentage of CO_2 and H_2O (by volume) entering the heat treatment chamber in the carrier gas (i.e. excluding any hydrocarbon additions) (e.g. for 6% CO_2 and 1% H_2O $D=7$)

From this equation it is clear that exothermic gas can be used for gas carburizing if the flow rate through the heat treatment chamber is reduced sufficiently. However, because of the dangers of explosion associated with the ingress of air into the heat treatment chamber there is a practical lower limit for R which varies from furnace to furnace.

In addition it is desirable to be able to control the carbon potential of the atmosphere (formed by adding hydrocarbon additions to the the carrier gas) accurately and we have found that this can be readily achieved by using the same procedures as used in endothermic gas practice, i.e. by monitoring the concentration of water or carbon dioxide or oxygen in the reacted furnace atmosphere and controlling the hydrocarbon additions in response to such concentrations.

Our discovery is of some significance since endothermic gas generators can now be replaced by more economic exothermic generators or by apparatus described hereinafter which can produce an atmosphere which is somewhat richer in hydrogen and carbon monoxide than that produced by exothermic generators.

In many installations we have found that the maximum value of R is too low for safe furnace operation if rich exothermic gas is to be used as a carrier gas for gas carburizing and in order to deal with this problem we remove at least part of the water vapour from the gas thereby increasing the maximum value of R.

If carrier gas flowrates greater than R are employed hydrocarbon additions reduce the concentration of carbon dioxide and water in the furnace atmosphere and nominally raise the carbon potential of the atmosphere. However, the ability of such atmospheres to provide carbon to the work is strictly limited and, in many cases, shallow and irregular cases are the best that can be obtained even after prolonged exposure to such atmospheres.

In all our work so far we have found that practical considerations have made it very difficult to work at flow rates less than 0.4R max. This is because it is important to adequately pressurize the heat treatment chamber to inhibit the ingress of ambient air. Thus the lower limit of R appears to be determined by practical considerations.

According to the present invention we therefore provide a method of gas carburizing using a carrier gas enriched with a hydrocarbon addition in a heat treatment chamber at or above 690°C, wherein said carrier gas is formed by the partial or complete reaction of a rich mixture of a hydrocarbon selected from the group consisting of natural gas, methane, butane, propane and mixtures thereof together with air or oxygen-enriched air, characterized in that the volumetric ratio of said hydrocarbon to <u>oxygen</u> used to produce said carrier gas (discounting any hydrocarbon which does not react) is:

1. when the hydrocarbon is methane or natural gas, between 0.8:1; and 1.5:1
2. when the hydrocarbon is butane, between 3.6:1 and 5:1; and
3. when the hydrocarbon is propane between 1.8:1 and 3:1.

and said carrier gas is introduced into said heat treatment chamber at a rate determined by the equation

$$R \ngtr \frac{90V^{\frac{2}{3}}}{D}$$

Where

V is the free internal volume of the heat treatment chamber in cubic feet;

R is the flowrate of carrier gas into the heat treatment chamber in standard cubic feet per hour; and

D is the percentage of CO_2 and H_2O (by volume) entering the heat treatment chamber in the carrier gas (i.e. excluding any hydrocarbon addition)

The present invention is applicable to both batch and semi-continuous carburizing furnaces.

Preferably D is between 2.5 and 10 and more preferably between 3 and 7.

If an exothermic gas generator is used the exothermic gas is preferably dried before being introduced into the heat treatment chamber as carrier gas.

In one embodiment of the invention, said carrier gas is prepared by indirectly heating said air or oxygen-enriched air in said heat treatment chamber, mixing said heated air or oxygen enriched air with said hydrocarbon, reacting said mixture in a chamber within said heat treatment chamber and using the hot gas to preheat said air or oxygen-enriched air.

In another embodiment of the invention the carrier gas is prepared by premixing air or oxygen enriched air with said hydrocarbon, preheating said mixture, reacting said mixture in a chamber within but separate and distinct from said heat treatment chamber, and using the hot gas to preheat said mixture.

Advantageously the gas emerging from said chamber (in either embodiment) is at least partially dried before being introduced into said heat treatment chamber.

Advantageously said drying is carried out by withdrawing said gas from said chamber to a location outside the heat treatment chamber, cooling said gas to condense at least part of the water vapour therein, separating said condensed water from said gas and introducing the gas into the heat treatment chamber.

Advantageously the hydrocarbon is natural gas or methane and said ratio of hydrocarbon to oxygen is between 1.0:1 and 1.35:1.

When the hydrocarbon is propane the ratio of hydrocarbon to oxygen is preferably between 2:1 and 2.6:1.

The present invention also provides an apparatus for producing a carrier gas for use in a method in accordance with the present invention, which apparatus comprises means mountable in said heat treatment chamber for heating air or oxygen enriched air, a chamber, and means for mixing said heated air or oxygen enriched air with a hydrocarbon selected from the group consisting of natural gas, methane, butane, propane and mixtures thereof in said chamber wherein said mixture can react and means for using the hot gas produced by said reaction to heat said air and/or oxygen enriched air.

The present invention further provides an apparatus for producing a carrier gas for use in a method in accordance with the present invention, which apparatus comprises an inner tube mountable in said heat treatment chamber for conveying a mixture of air or oxygen enriched air and hydrocarbon into the confines of said heat treatment chamber, a chamber downstream of said inner tube in which said mixture can combust, and an outer tube for directing the hot gas produced by said combustion along the outside of said inner tube to, in use, heat said mixture as it flows through said inner tube.

Preferably the apparatus includes means to dry the reacted mixture.

Advantageously, the means comprises means to cool said gas to condense water therefrom, and means to separate the remaining gas from said water.

For a better understanding of the invention and to show how the same may be carried into effect reference will now be made, by way of example, to the accompanying drawings, in which:

Figure 1 shows a sealed quench furnace carburizing on dried exothermic gas with hydrocarbon addition;

Figure 2 shows the same furnace being used to carburize on a mixture of carrier gas supplied by one embodiment of an apparatus in accordance with the present invention enriched with hydrocarbon addition;

Figure 3 shows a modification of the apparatus shown in Figure 2; and

Figure 4 shows another embodiment of apparatus in accordance with the present invention.

Referring to Figure 1, there is shown a sealed quench furnace which is generally identified by reference numeral 1. The furnace 1 comprises a vestibule 2, a quench tank 3 and a heat treatment chamber 4 which is provided with a fan 5 and radient tubes 6 which maintain the heat treatment chamber 4 at approximately 925°C during carburizing.

A carrier gas comprising (by volume)

H_2	11%
CO	8%
CO_2	6.5%
H_2O	0.6%
N_2	73.9%

was supplied to to the heat treatment chamber 4 through pipe 7. The carrier gas was synthesised by the reaction of 1 volume of natural gas and 6½ volumes air in an exothermic gas generator 8 and was subsequently dried to a dew point of 0°C using a refrigerator 90. Hydrocarbon addition was added from a pipe 10.

As the heat treatment chamber 4 had an internal volume $V = 4.1\ \mathrm{ft}^3$, then:

$$R \ngtr \frac{90.\ (4.1)^{\frac{2}{3}}}{(6.5+0.6)} = 32.5\ \mathrm{scfh}$$

The following results were obtained:

Furnace: Ipsen RT25
Carrier Gas: 8% CO, 11% H_2, 6.5% CO_2, 0.6% H_2O, bal. N_2.

Carrier Flow (scfh)		Addition (Nat Gas) (scfh)	Carb-urizing Time (hr)	Furnace Analysis			Effective Case (to 550 Hv)	Surface Hardness (Hv)
				CO%	Dew.Pt.	O_2 Probe (Volts)		
24		6 to 4.5 (O_2 control)	5½	16	-11°C	1.149	.042-.045"	840-860
20	boost	8 to 5 (")	2¼	15	-13°C	1.165		
	diffuse	0 to 3 (")	¾	16	-12°C	1.138	.030"	840

Referring now to Figure 2 instead of using exothermic gas generator 8, the carrier gas was formed by using an apparatus which is generally identified by reference numeral 11. The apparatus 11 comprises an outer annular passageway 12 and an inner annular passageway 13 which are separated by a wall 14. In use air is preheated by the hot gases in the heat treatment chamber as it flows from pipe 15 through outer annular passageway 11 and is then further heated as it flows along inner annular passageway 13 until it reaches holes 16 arranged circumjacent the outlet of a pipe 17 carrying hydrocarbon. The preheated air or oxygen enriched air reacts with the hydrocarbon in chamber 18 to produce the carrier gas. Using this technique, it is possible to use a richer mixture of hydrocarbon to air than in an exothermic generator because of the preheating and this in turn leads to the formation of less H_2O and CO_2.

In this particular embodiment the following results were obtained on two different furnaces:

Furnace: Ipsen RT25. Free internal vol. 4.1ft^3.
Propane/Air feedstock for carrier gas at 10½:1 producing 20%H_2, 17%CO, 6%H_2O, 2½%CO_2, bal. N_2
Rmax = 27 scfh

Carrier Gas Flow from burner (scfh)		Addition propane (scfh)	Carburizing Time (h)	Furnace Analysis CO %	Furnace Analysis O_2 Probe volts	Effective Case Depth (to 550 Hv)	Surface Hardness (Hv)
20		1	2	23	1.132	.022"	890
20	boost	(2 (O_2 control)	2½	23	1.155)	.033"	890
	diffuse	(0-1.5 (O_2 control)	¾	23	1.127)		

Furnace: British Furances Allcase. Free internal vol 60ft^3.
Nat Gas/Air feedstock at 5¼:1 producing 15.5%H_2, 10%CO, 4%CO_2, 12%H_2O, bal. N_2.
Rmax = 86 scfh.

Carrier Gas flow from burner (scfh)	Nitrogen flow to furnace (scfh)	Additions Nat. Gas (scfh)	Carburizing time (h)	Effective Case Depth (to 550 Hv)	Surface Hardness (Hv)
60	40	50	4½	.030"	63HR_C

It will be noted that in the second example, because the combustion of natural gas with air forms a higher percentage of water than when propane is burnt the value of RMAX is too low to enable adequate pressurization of the furnace. Therefore in this case nitrogen was also added as a bulking agent.

Referring now to Figure 3, instead of introducing gas from chamber 18 directly into the heat treatment chamber 4 it is led from the chamber 18 through pipe 19 where it passes some of its heat to the gas in the heat treatment chamber. The gas is then cooled in coil 20 in which water vapour condenses. The water is then separated from the gas in phase separator 21 and the drier gas is returned to the heat treatment chamber 22. (The coil 20 could of course be replaced with a dessicant or molecular sieve although care should be taken to ensure that sufficient CO_2 remains to facilitate control). This embodiment was used to increase the value of RMAX in the British Furnace referred to above. In particular the dried carrier gas had an analysis of 17% H_2, 11% CO, 4½% CO_2 and 2.3% H_2O (Dew Point 20°C) thereby raising RMAX to 203 scfh. The nitrogen addition then became redundant and using a flow rate of 150 scfh almost identical metallurgical results were obtained.

Referring now to Figure 4, apparatus 11 can be replaced with an apparatus which is generally identified by reference numeral 40. The apparatus 40 comprises an inner tube 41 which conveys premixed air or oxygen enriched air and hydrocarbon to a chamber 42 where they combust. The hot gas produced is directed along the outside of the inner tube 41 by an outer tube 43 and leaves via a pipe 44 from which it can either be fed directly into the heat treatment chamber or dried and fed to the heat treatment chamber as desired.

Various modifications can be made to the process described, for example the hydrocarbon additive could be made to the carrier gas in pipe 7 instead of through pipe 10.

CLAIMS

1. A method of gas carburizing using a carrier gas enriched with a hydrocarbon addition in a heat treatment chamber at or above 690°C, wherein said carrier gas is formed by the partial or complete reaction of a rich mixture of a hydrocarbon selected from the group consisting of natural gas, methane, butane, propane and mixtures thereof together with air or oxygen-enriched air, characterized in that the volumetric ratio of said hydrocarbon to <u>oxygen</u> used to produce said carrier gas (discounting any hydrocarbon which does not react) is:

    1. when the hydrocarbon is methane or natural gas, between 0.8:1; and 1.5:1
    2. when the hydrocarbon is butane, between 3.6:1 and 5:1; and
    3. when the hydrocarbon is propane between 1.8:1 and 3:1.

and said carrier gas is introduced into said heat treatment chamber at a rate determined by the equation

$$R \ngtr \frac{90V^{\frac{2}{3}}}{D}$$

Where

V is the free internal volume of the heat treatment chamber in cubic feet;

R is the flowrate of carrier gas into the heat treatment chamber in standard cubic feet per hour; and

D is the percentage of $CO_2 + H_2O$ (by volume) entering the heat treatment chamber in the carrier gas (i.e. excluding hydrocarbon additions.

2. A method according to Claim 1, characterized in that D is between 2.5 and 10.

3. A method according to Claim 2, characterized in that D is between 3 and 7.

4. A method according to Claim 1, 2 or 3, characterized in that said carrier gas is formed by reacting said air or oxygen enriched air and hydrocarbon in an exothermic generator and drying the gas leaving said exothermic generator.

5. A method according to Claim 1, 2 or 3, characterized in that said carrier gas is prepared by indirectly heating said air or oxygen-enriched air in said heat treatment chamber, mixing said heated air or oxygen enriched air with said hydrocarbon, reacting said mixture in a chamber within said heat treatment chamber and using the hot gas to preheat said air or oxygen-enriched air.

6. A method according to Claim 1, 2 or 3, characterized in that said carrier gas is prepared by premixing air or oxygen enriched air with said hydrocarbon, preheating said mixture, reacting said mixture in a chamber within but separate and distinct from said heat treatment chamber and using the hot gas to preheat said mixture.

7. A method according to Claim 5 or 6, characterized in that the gas emerging from said chamber is at least partially dried before being introduced into said heat treatment chamber.

8. A method according to Claim 7, characterized in that said said drying is carried out by withdrawing said gas from said chamber to a location outside the heat treatment chamber, cooling said gas to condense at least part of the water vapour therein, separating said condensed water from said gas and introducing the gas into the heat treatment chamber.

9. A method according to any preceding Claim, characterized in that said hydrocarbon is natural gas or methane and said ratio of carrier gas to oxygen is between 1.0:1 and 1.35:1.

10. A method according to any one of Claims 1 to 8, characterized in that said hydrocarbon is propane and the ratio of said hydrocarbon to oxygen is between 2:1 and 2.6:1.

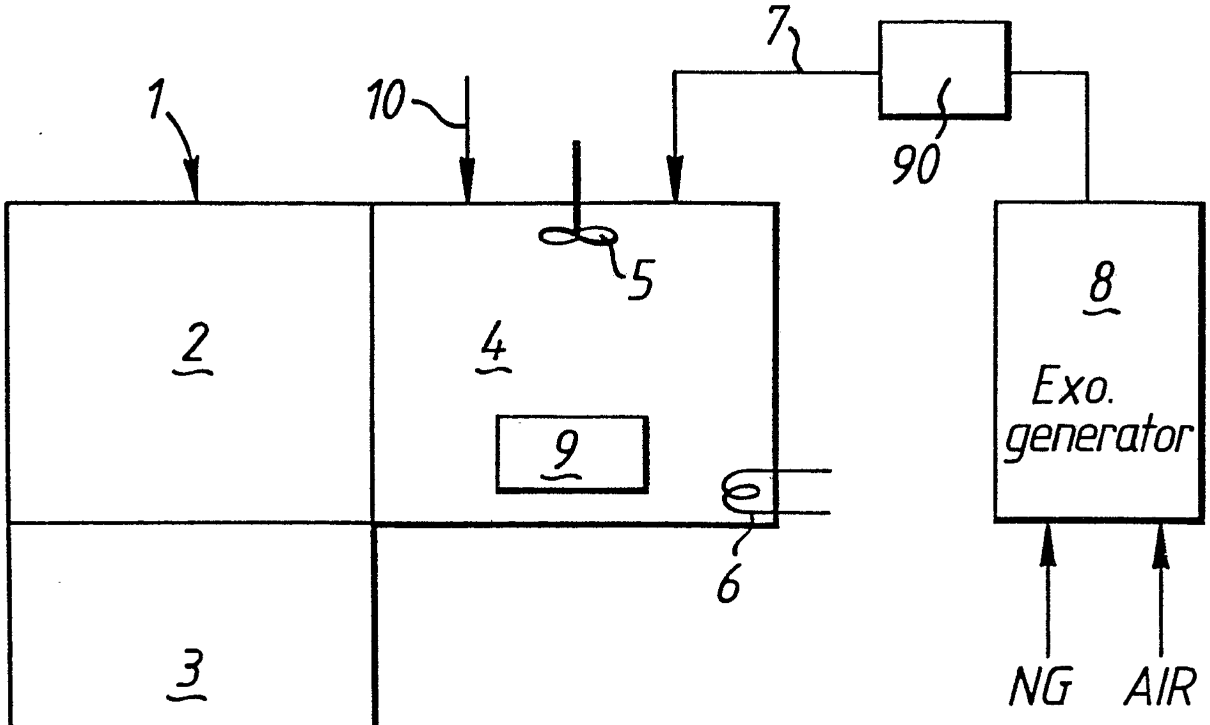
11. An apparatus for producing a carrier gas for use in a method according to Claim 1, characterized in that said apparatus comprises means mountable in said heat treatment chamber for heating air or oxygen enriched air, a chamber, and means for mixing said heated air or oxygen enriched air with a hydrocarbon selected from the group consisting of natural gas, methane, butane, propane and mixtures thereof in said chamber wherein said mixture can react and means for using the hot gas produced by said reaction to heat said air and/or oxygen enriched air.

12. An apparatus for producing a carrier gas for use in a method according to Claim 1, characterized in that it comprises an inner tube mountable in said heat treatment chamber for conveying a mixture of air or oxygen enriched air and hydrocarbon into the confines of said heat treatment chamber, a chamber downstream of said inner tube in which said mixture can combust, and an outer tube for directing the hot gas produced by said combustion along the outside of said inner tube to, in use, heat said mixture as it flows through said inner tube.

13. An apparatus as claimed in Claim 11 or 12, characterized in that it includes means to dry the reacted mixture.

14. An apparatus as claimed in Claim 13, wherein said means comprises means to cool said gas to condense water therefrom, and means to separate the remaining gas from said water.

For the Applicants
Brian Lucas
Brian Lucas
CHARTERED PATENT AGENT
EUROPEAN PATENT ATTORNEY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Exo.
generator
NG
AIR

FIG.1

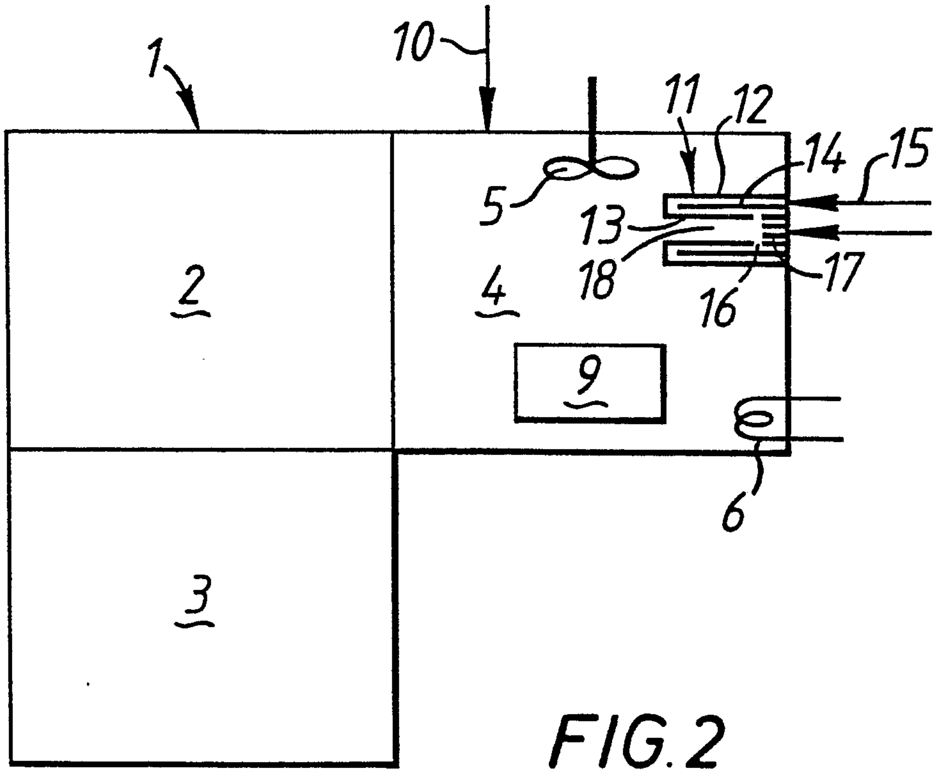
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FIG.2

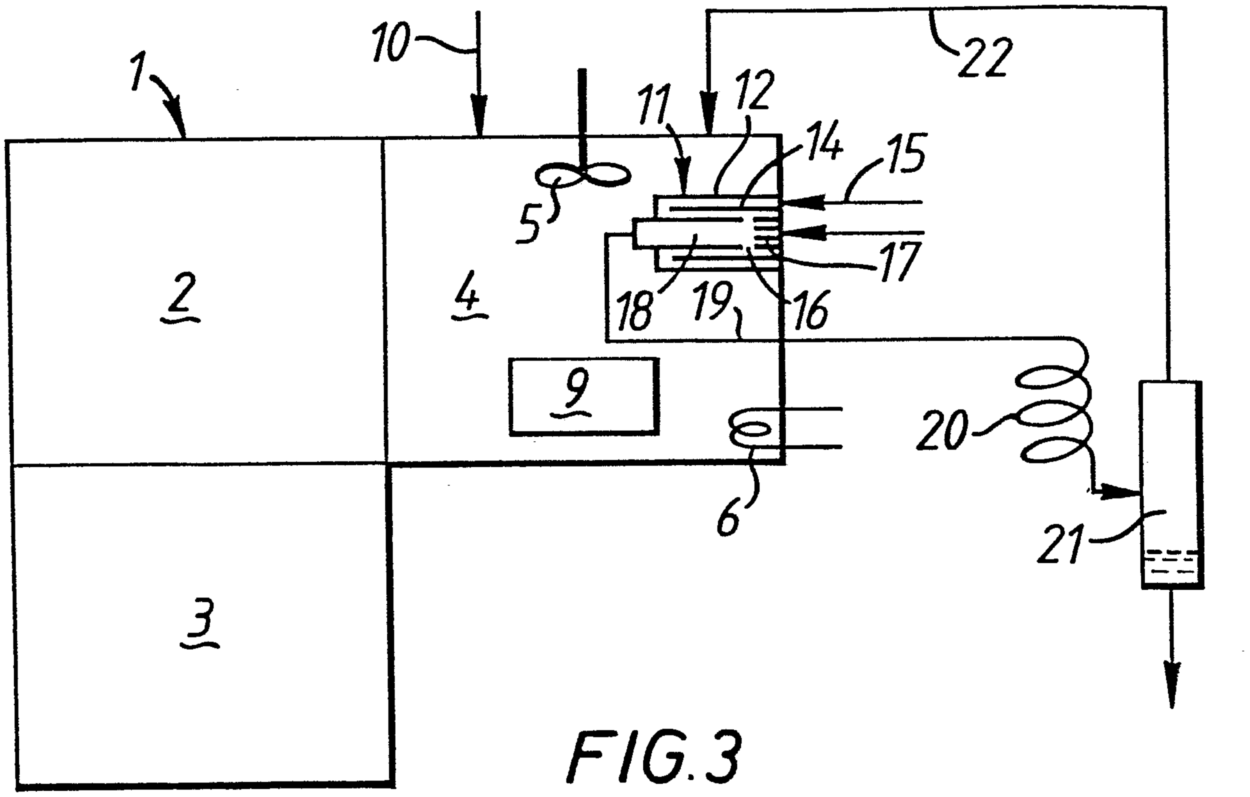

FIG. 3

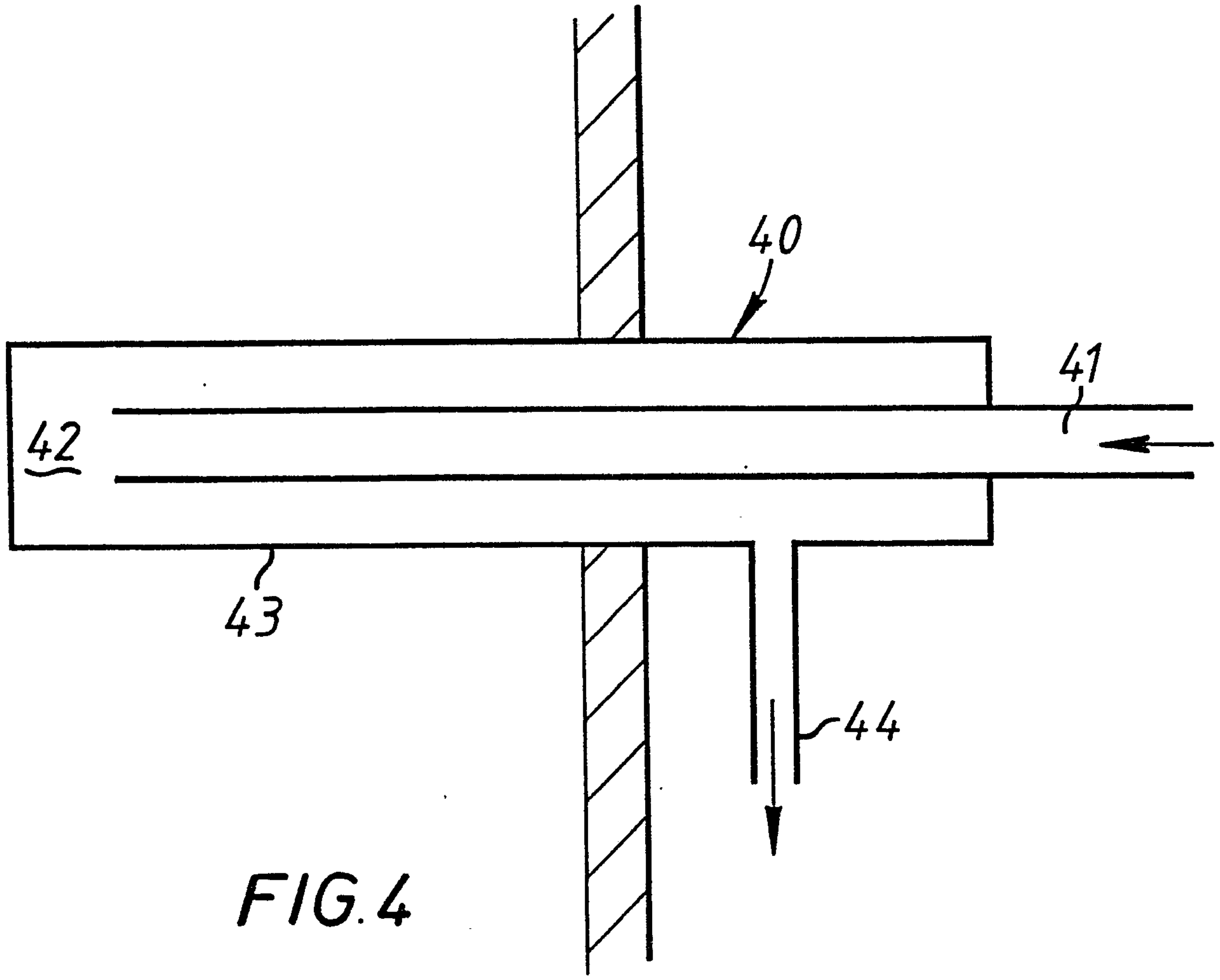

FIG. 4

European Patent
Office

EUROPEAN SEARCH REPORT

0040023

Application number
EP 81301882.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 145 232 (JACK SOLOMON) + Totality + --	
A	US - A - 4 035 203 (MATHURIN L' HERMITE et al.) + Totality + --	
A	US - A - 4 006 042 (WOLFGANG KIEFERLE) + Totality + --	
A	GB - A - 1 544 214 (GENERAL ATOMIC COMPANY) + Totality + --	
A	GB - A - 1 382 075 (C.I. HAYES INC.) + Totality + --	
A	US - E - 29 881 (HERBERT W. WESTEREN et al.) + Totality + ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 23 C 11/10
C 23 C 11/12
C 23 C 11/14
C 23 C 11/18

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 23 C

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
VIENNA	22-07-1981	SCHÜTZ

EPO Form 1503.1 06.78