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(54) **Coating substrates with high temperature ceramics**

(57) A method of coating a substrate with a high temperature ceramic comprises delivering vaporised methyl acetylene propadiene (MAPP) to a mixing chamber of an oxy-fuel spray gun where it is mixed with oxygen. Subsequently the gas mixture is introduced into a combustion chamber of the spray gas together with a powdered high temperature ceramic entrained in a stream of inert gas. The heated particles of the ceramic are then sprayed on to the surface of the substrate.

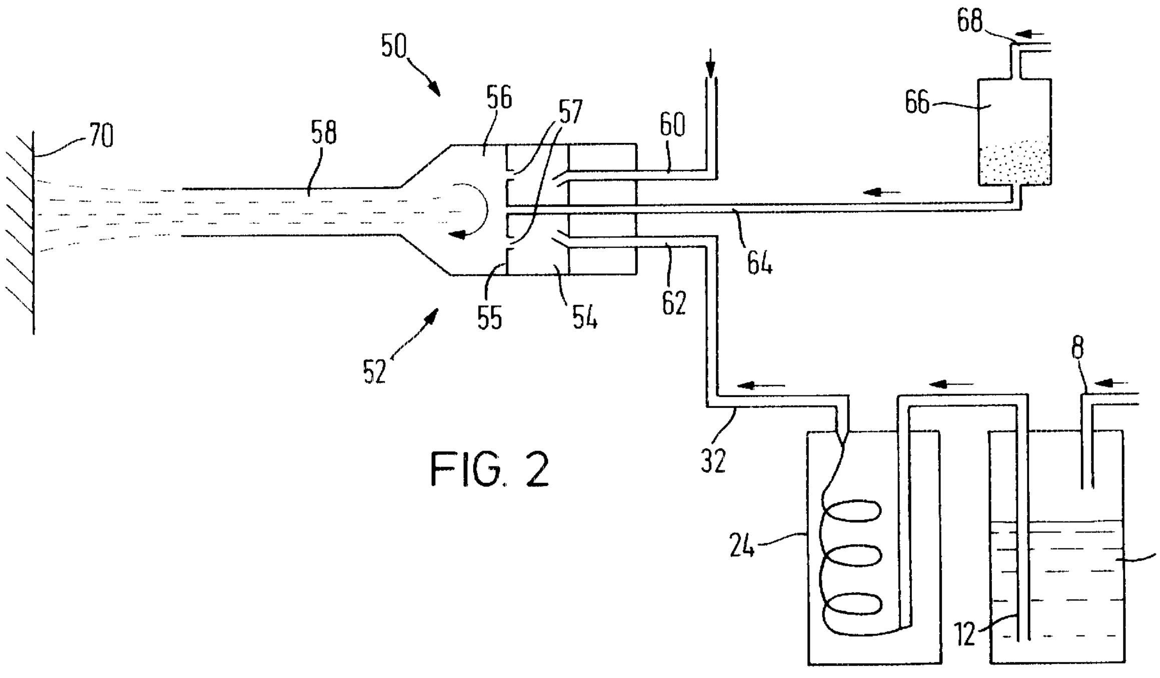

FIG. 2

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Description

The present invention relates to methods of coating a substrate with high temperature ceramics.

Throughout this specification the expression "high temperature ceramics" is intended to encompass oxides, carbides and nitrides of metals such as chromium, aluminium and zirconium having a melting point above 1800°C.

Chromium oxide has been plasma-sprayed on substrates for many years for applications in such industries as the aerospace and automobile industries.

A further need for relatively thick, high hardness and low porosity chromium oxide coatings is in the print roller industry. In this industry, coatings are usually laser engraved thereby producing indents which are designed to hold ink. The harder and thicker the coating, the greater the density of holes that can be achieved. Atmospheric plasma spraying has produced coating densities between 90 - 95% theoretical values, but this allows aggressive gases to penetrate the open porosity and damage both the coating and substrate material. Considerable work has been attempted to reach gas tightness in plasma-sprayed chromium oxide coatings using vacuum plasma spraying, post heat treatments and capsule hot isostatic pressings, but with little success.

Some work has been carried out on the use of acetylene in the high velocity oxyfuel thermal spraying of chromium oxide. However, acetylene is a fuel gas well-known for its tendency to decompose with violence and has to be used at relatively relatively low pressures.

Other pressurised gas fuels have been used in high velocity oxyfuel thermal spraying processes including a stabilised mixture of methylacetylene and propadiene (MAPP). MAPP is a mixture of methylacetylene and propadiene together with diluents or stabilisers such as propane and propylene. Other diluents can be present for example, methane, butane or ethane but in small percentage amounts. MAPP is used extensively particularly in the United States as a safer and more economic substitute for acetylene. However, difficulties have been experienced since it is customary to store liquid MAPP in a pressurised cylinder and eject the liquid MAPP as a gas under vapour pressure to employ the same in high pressure, high flow rate oxyfuel thermal spraying applications. It has been found that high vapour withdrawal rates effectively results in a fractional distillation of the MAPP gas components resulting in composition changes as the cylinder content decreases. This has been found to cause fluctuations in flame temperature and a need to adjust the flow rate of oxygen to avoid excess carbon build-up or excess oxygen.

Maintaining a constant pressure and flow rate presents further problems. This is because as the level of the liquid fuel in the pressurised cylinder decreases, the temperature likewise decreases due to the latent heat of vaporization. A reduction in temperature within the pressurised cylinder results in a reduction of pressure which adversely affects both the pressure and flow rate of the vaporized fuel stream.

It is an aim of the present invention to provide an improved method of coating a substrate with a high temperature ceramic using a high velocity oxyfuel thermal spraying technique in which the fuel gas is MAPP gas.

According to the present invention, a method of coating a substrate with a high temperature ceramic comprises the steps of:

a) injecting an inert gas under pressure into a container containing liquid methyl acetylene propadiene (MAPP) sufficient to generate a stream of liquid;

b) removing said stream of liquid MAPP from the container;

c) vaporising said stream of liquid MAPP;

d) delivering the vaporised MAPP to a mixing chamber of a high velocity oxygen fuel spray gun where it is mixed with oxygen under pressure;

e) introducing said mixture into a combustion chamber of the high velocity oxygen fuel spray gun together with a powdered high temperature ceramic entrained in a stream of an inert gas; and

f) spraying the heated particles of the high temperature ceramic on to the surface of a substrate.

An embodiment of the invention will now be described, by way of example, reference being made to the Figures of the accompanying diagrammatic drawings in which:

Figure 1 is a diagrammatic sketch of an apparatus for producing MAPP gas having a substantially constant pressure, flow rate and gas composition;

Figure 2 is a diagrammatic sketch of an apparatus for coating a substrate with a high temperature ceramic and incorporating the apparatus illustrated in Figure 1; and

Figure 3 is a diagrammatic sketch of a high velocity oxyfuel gun forming part of the apparatus of Figure 2.

Referring first to Figure 1 which illustrates an apparatus 2 for generating a vaporised stream of MAPP gas having a substantially constant pressure, flow rate and composition. The apparatus 2 includes a storage container 4 for liquid MAPP having an inlet 6 for receiving an inert gas, for example, nitrogen via a conduit 8 extending from a pressurised nitrogen gas cylinder 10. The storage container 4 contains a tube 12 which extends almost to the floor 14 of the container and which provides a pathway for the flow of liquid MAPP when pressure is applied by the incoming nitrogen. The storage container 4 includes an outlet 16 through which pressurised liquid MAPP can pass into a conduit 18 via a flexible delivery tube 20. The flow of MAPP liquid through the conduit 18 is controlled by a valve 22.

The conduit 18 is connected to a vaporiser 24 operating at a temperature sufficient to vaporise the liquid MAPP. One such example of a suitable vaporiser is a hot water/glycol vaporiser maintained at a temperature sufficient to vaporise each component of the liquid MAPP, typically between 30 and 100°C by means of a thermastatically controlled immersion heater 26.

The flow of liquid MAPP from the conduit 18 into the vaporiser 24 is controlled by a temperature sensitive shut off valve 28 which includes a thermal probe 30 which detects the temperature of the water bath within the vaporiser. The valve 28 is operated to prevent the flow of the liquid MAPP into the vaporiser 24 until the water bath has attained a minimum desired temperature sufficient for vaporisation of the liquid MAPP. The valve 28 therefore prevents flooding of the vaporiser 24 with the liquid MAPP before it has reached operating temperature and thus avoids any liquid fuel carry over into the vaporising portion of the apparatus 2.

The vaporiser 24 transforms the liquid MAPP into a super heated high pressure, high flow rate vaporised fuel stream having a temperature of typically up to about 50°C. The vaporised MAPP stream exits the vaporiser 24 through a conduit 32 controlled by a valve 34. The conduit 32 may be heated and/or insulated to prevent condensation of the vaporised MAPP stream. For example, the conduit 32 may be wrapped in a heating tape for this purpose.

In use, nitrogen from the gas cylinder 10 is fed to the storage container 4 via the conduit 8. A pressure regulator 36 is provided to ensure that the nitrogen is fed into the storage container 4 at a suitable pressure, typically from about 115 to 190 psig, preferably from about 140 - 175 psig.

A safety valve 38 is provided in the conduit 8 to allow the release of the nitrogen through a vent 40 when the storage container 4 has been substantially relieved of the liquid MAPP.

The nitrogen enters the head space 42 of the container 4 thereby exerting a downward force against the surface 44 of the liquid MAPP. The MAPP is therefore forced upwardly through the tube 12 and out of the outlet 16 and thus eventually into the vaporiser 24.

Referring now to Figure 2, there is illustrated an apparatus 50 for coating a substrate with a high temperature ceramic such as chromium oxide. The apparatus 50 includes a high velocity oxyfuel gun 52 (see also Figure 3) having a gas mixing chamber 54, a combustion chamber 56 and a nozzle 58 extending outwardly from the combustion chamber 56. The chambers 54, 56 are divided by a partition 55 provided with holes 57.

As shown, communicating with the gas mixing chamber 54 is a first conduit 60 connected to a source of oxygen under pressure and a second conduit 62 connected to the conduit 32 extending from the vaporiser 24.

Extending through the mixing chamber 54 and communicating directly with the combustion chamber 56 is a third conduit 64. Conduit 64 extends from a chromium oxide powder reservoir 66. A pipe 68 extends from a source of argon under pressure into the upper (as shown) end of the reservoir 66.

The gun 52 is provided with channels 70 for a coolant, for example water.

In use, MAPP vapour is supplied to the gas mixing chamber 54 from the vaporiser 24 via conduits 32, 62 at a substantially constant pressure, flow rate and gas composition. Simultaneously, a stream of oxygen is supplied via the conduit 60 into the gas mixing chamber 54. The oxygen and the MAPP vapour are mixed in the mixing chamber and exit the mixing chamber to enter the combustion chamber 56 of the gun 52 via the holes 57 where they are ignited. Simultaneously, argon under pressure passes through the pipe 68 into the reservoir 66 where it entrains chromium oxide powder and thereafter passes through the conduit 64 directly into the combustion chamber 56. Exhaust flames and heated powdered chromium oxide particles leave the combustion chamber through the nozzle 58 and are deposited on the substrate 70.

<u>Example</u>

Chromium oxide coated test samples were produced using a Miller Thermal HV2000 High Velocity Oxyfuel Gun, having a 22 millimetre combustion chamber designed for high melting point powders. Sulzer Metco's Amdry 6417 high purity chromium oxide, powder size range between 5 and 22 μm was used to spray all test samples at a powder feed rate of 25 grams per minute using high purity argon carrier gas at 11.5 litres per minute. The MAPP vapour was introduced into the combustion chamber at a pressure of 85 psi and a flowrate of 70 l/min and the oxygen was introduced into the combustion chamber at a pressure of 150 psi and a flow rate of 233 l/min. Surface treatment of all test samples with 40 grit alumina gave a minimum sample surface roughness ($r\alpha$) of 7 - 10 μm. All test pieces were coated to a thickness between 200 - 260 μm, keeping coating temperatures below 150°C. Thicknesses greater than 380 μm were achievable using many of the conditions

It has been found that the deposition on a substrate of a high temperature ceramic such as chromium oxide or zirconium oxide using high velocity oxyfuel thermal spraying where the fuel gas is MAPP delivered at a substantially constant pressure, flow rate and composition results in a coating of high quality having very little porosity and high hardness.

Claims

1. A method of coating a substrate with a high temperature ceramic comprising the steps of

   a) injecting an inert gas under pressure into a container containing liquid methyl acetylene propadiene (MAPP) sufficient to generate a stream of liquid;

   b) removing said stream of liquid MAPP from the container;

   c) vaporising said stream of liquid MAPP;

   d) delivering the vaporised MAPP to a mixing chamber of a high velocity oxygen fuel spray gun where it is mixed with oxygen under pressure;

   e) introducing said mixture into a combustion chamber of the high velocity oxygen fuel spray gun together with a powdered high temperature ceramic entrained in a stream of an inert gas; and

   f) spraying the heated particles of the high temperature ceramic on to the surface of a substrate.

2. A method as claimed in Claim 1, in which the high temperature ceramic is chromium oxide which is applied to the substrate up to a thickness of 380 µm.

3. A method as claimed in Claim 1, in which the high temperature ceramic is zirconium oxide.

4. A method as claimed in Claims 1, 2 or 3 in which the injected inert gas is nitrogen.

5. A method as claimed in any one of Claims 1 to 4 in which the high temperature ceramic is entrained in a stream of argon.

6. A method as claimed in any one of Claims 1 to 5 in which the vaporised MAPP is supplied to the mixing chamber at a substantially constant pressure, flow rate and composition.

7. A method of coating a substrate with a high temperature ceramic substantially as hereinbefore described with reference to Figures 1, 2 and 3 of the accompanying drawings.

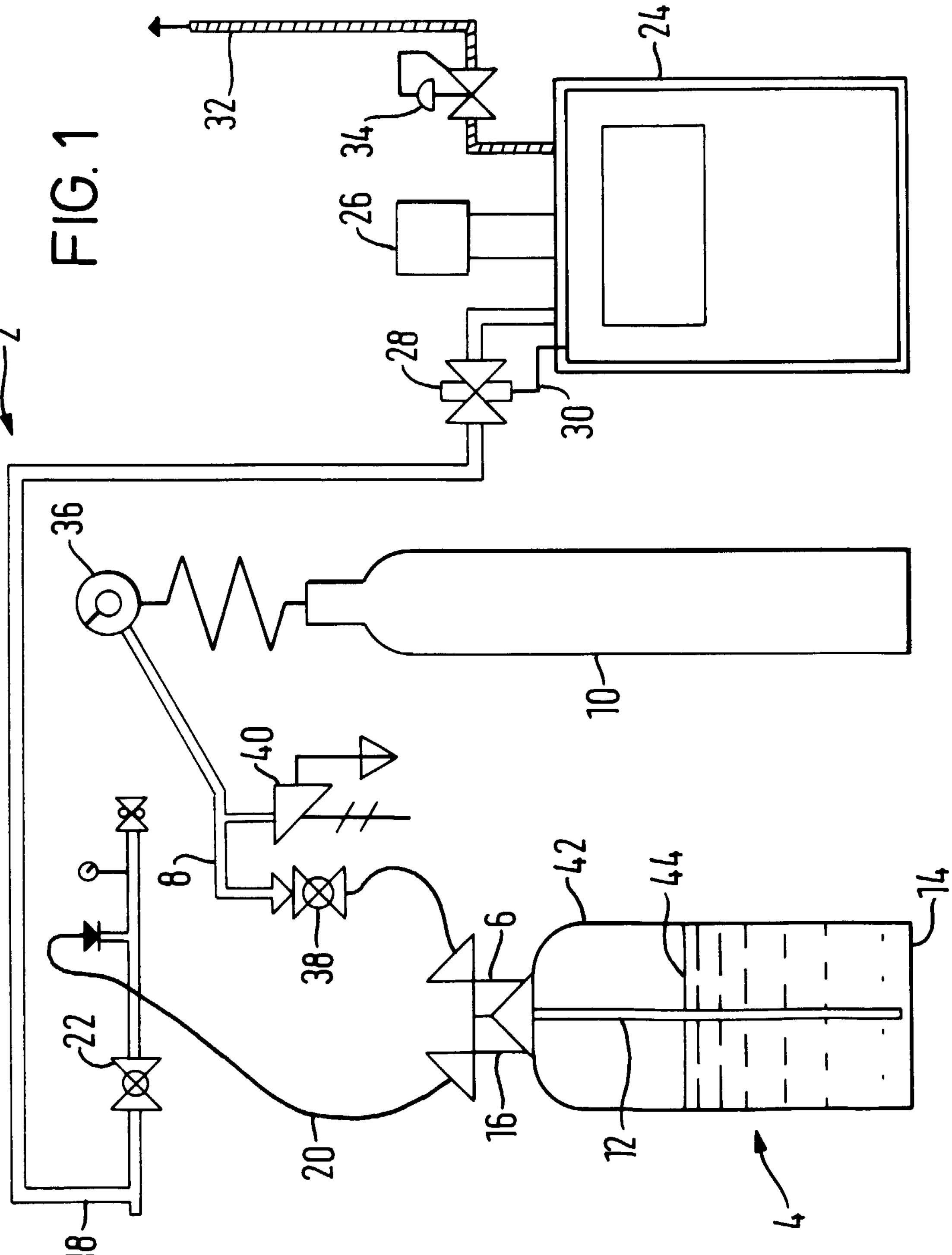

FIG. 1

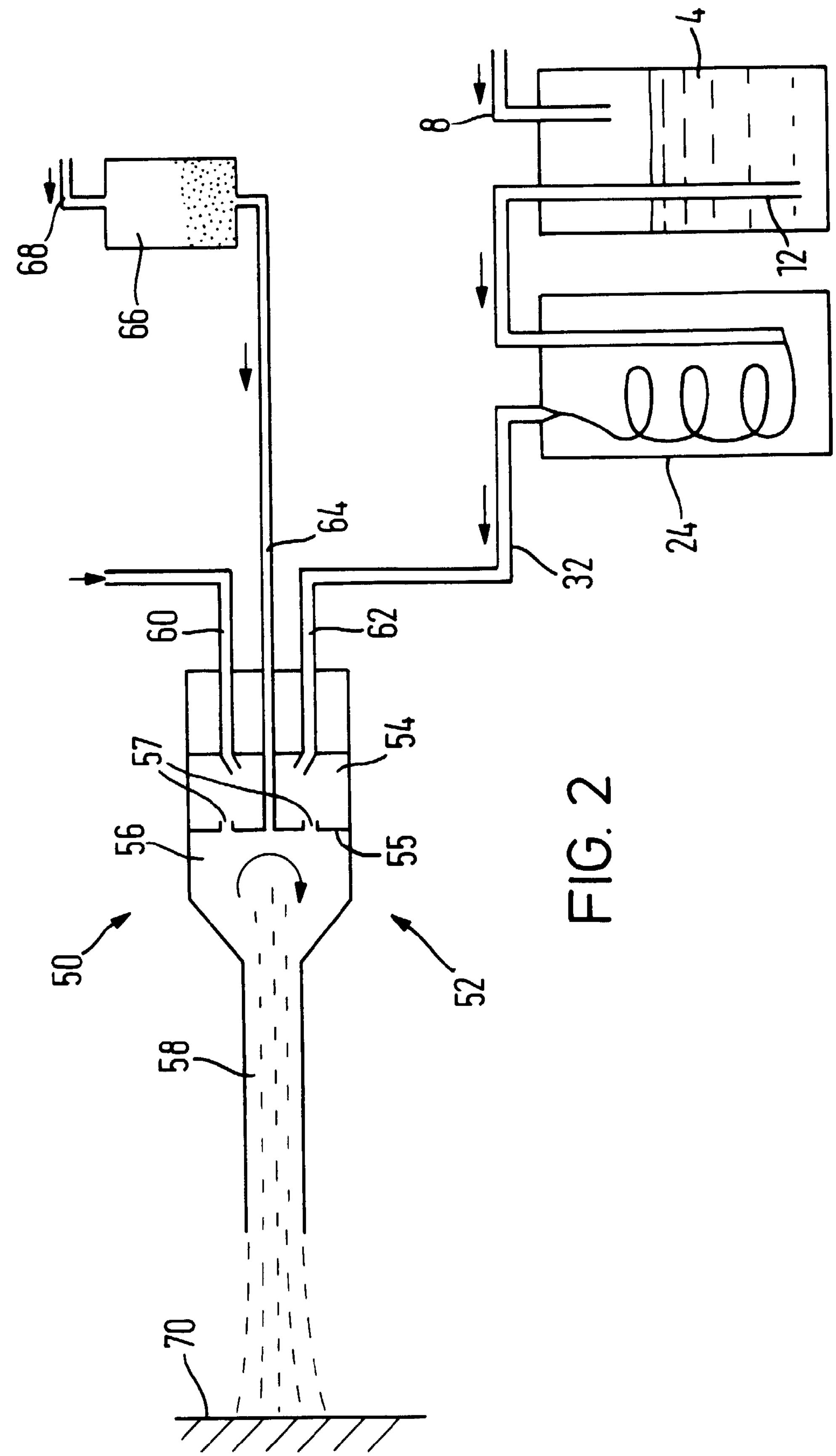

FIG. 2

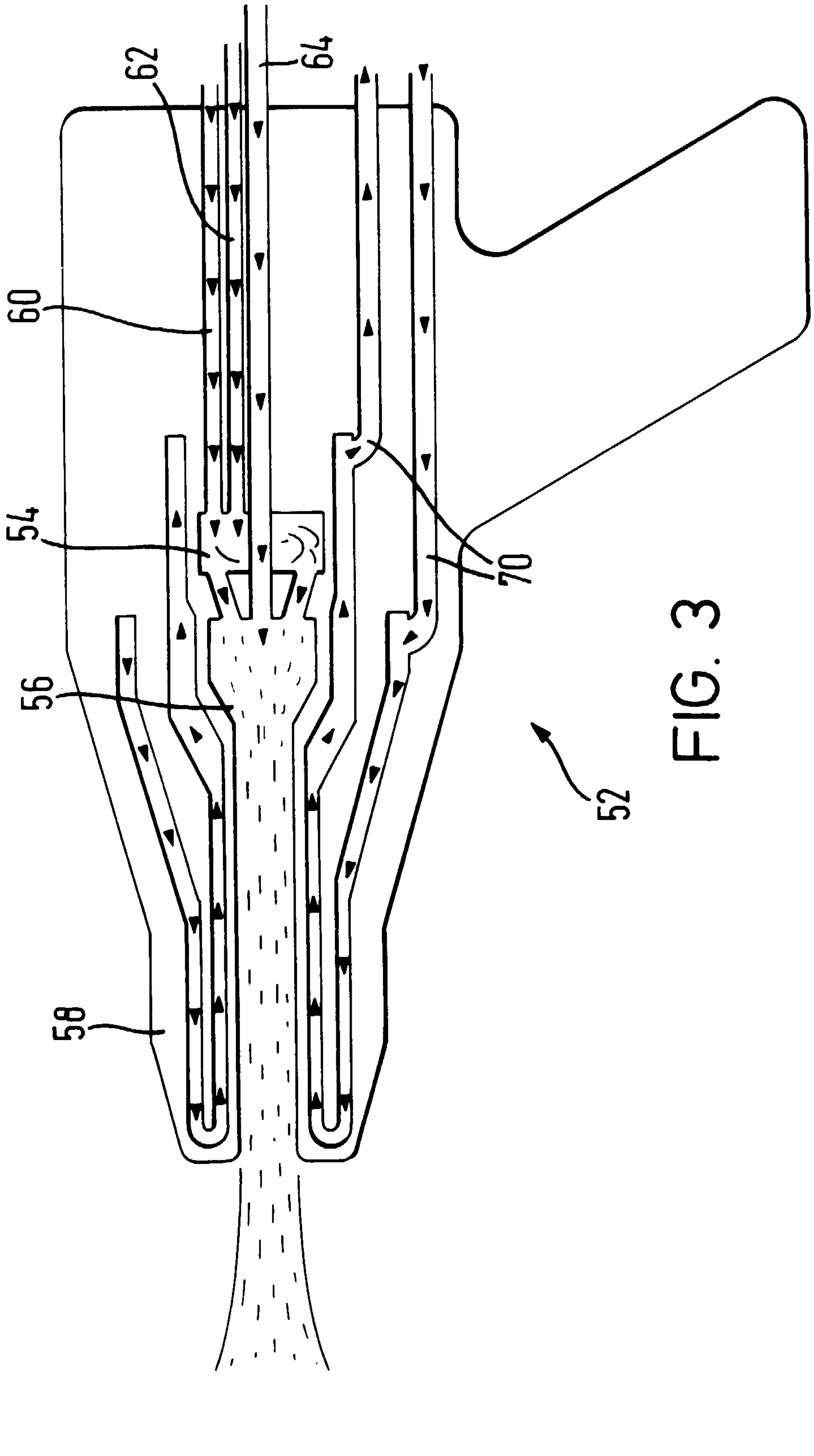

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 5993

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 621 079 A (THE PERKIN-ELMER CORPORATION) * column 6, line 38 - column 7, line 11 *	1	C23C4/12
A	EP 0 612 567 A (UTP SCHWEISSMATERIAL) * column 1, line 22 - line 31 * * column 11, line 17 - line 26; claims 1,19 *	1	
A	DE 38 43 436 A (LINDE)		
A	GB 1 115 738 A (METALLISATION)		
A	US 4 006 838 A (RICHARD S. BAUMANN)		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C23C
B05B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 November 1997	Elsen, D

CATEGORY OF CITED DOCUMENTS

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