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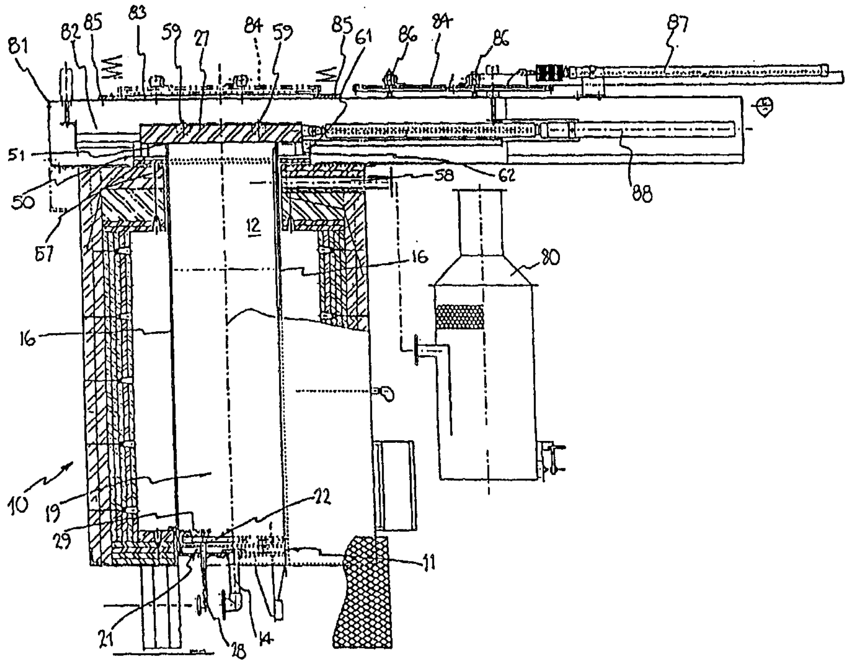

(57) Abstract

A method for treating a substrate in a fluidised bed treatment facility using a halide gas plus a nitrogen and/or carbon containing gas introduced from a source separate to the source of halide gas, such that a surface layer forms on the substrate and includes at least one species chosen from the group comprising carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof. There is also provided an arrangement for introducing gases to a fluidised bed treatment facility.

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SURFACE TREATMENT METHOD AND TREATMENT APPARATUS

The present invention relates to a method of treating the surface of a substrate. More particularly the present invention relates to a method of forming a diffusion surface layer on an article comprising the substrate, the surface layer including at least one species chosen from the group comprising carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof. Even more particularly, the present invention relates to a method of forming the aforementioned diffusion surface layer on an article using a fluidised bed to promote thermochemical diffusion at the surface of the article.

The present invention further relates to improvements in the design of fluidised bed furnaces, particularly for heat treating substrates (preferably metal substrates) under strict controlled atmosphere conditions where unwanted leakage of gases such as oxygen from outside is substantially prevented. These processes may be used to create a hard diffusion surface layer on the substrate but are not necessarily limited to this application. Typically, such diffusion surface layers are created by thermochemical diffusion processes and may be carbides, nitrides, carbonitrides or oxycarbonitrides.

Thermochemical diffusion processes are very well known and work on the basis of diffusing into the surface of a substrate, elements such as carbon and nitrogen. It is known that such surface treatment of substrates such as iron and iron alloys causes improved resistance to abrasion, seizure, oxidation, corrosion, etcetera. Particularly good results are obtained when the substrate forms a surface layer including at least one carbide, nitride or carbonitride of an element of the IVA, VA and VIA groups of elements including principally chromium, vanadium, titanium, niobium, molybdenum and tungsten.

Processes for forming a carbide or nitride layer on the surface of a material to be treated by using a fluidised bed are well known in the art. Examples of relevant processes can be found, for example, in Australian Patent Nos. 594792 (75242/87) and 603839 (81274/87).

Typically, the process of the prior art uses a fluidised bed which is fluidised by means of a fluidising gas such as argon at a specific treatment temperature. The fluidised bed includes a treating agent formed from a mixture of inert refractory materials such as alumina, a powder of a metal or its alloy containing a carbide or nitride forming element and a halide. The halide must be solid at ambient temperature, but sublime or vaporise at the treatment temperature, that is, the halide must not solidify during treatment in order to maintain the fluidisation. The substrate to be treated is embedded in the fluidised bed and a carbide, nitride or carbonitride layer is formed at the surface of the substrate as a result of thermochemical diffusion.

During the process, the carbide or nitride forming element of the treating agent reacts with the halide to form gases. The gases in turn react with carbon and nitrogen respectively at the surface the substrate being treated to form the carbides and nitrides. Alternatively, the nitrides may be formed by introducing a nitrogen gas into the fluidised bed. In conventional processes, ammonia breaks down into atomic nitrogen and hydrogen and provides the nitrogen which diffuses into the surface of the metal, as distinct from the nascent nitrogen gas purchased as liquid nitrogen which is virtually inert.

The processes of the prior art relied upon a halide such as ammonium chloride being introduced to the fluidised bed in the form of a solid. For example, AU-594792 teaches the addition of the solid halide in the form of pellets or powder which are fed into the fluidised bed furnace from an external source. AU-603839 teaches the mixing of halide powder with the refractory material and metal.

Commonly the fluidised bed processes of the prior art use processing temperatures between about 500 and 1200°C, most typically 700 to 1100°C. These relatively high temperatures are required to sublime or vaporise the halide and maintain the halide in a gaseous form during processing. Operating at relatively high temperatures does make it difficult to maintain accurate dimensional and configurational stability of the part or object being treated.

The objective therefore of the present invention is to provide an improved surface treating process and improvements in fluidised bed treatment facilities that will allow improvements in the process of forming thermochemical diffusion surface layers on substrates, particularly metal substrates, and even more particularly ferro based metal substrates.

In particular, it has now been found that significant improvements in the surface treating process can be provided by providing the halide gas and the nitrogen (as ammonia gas for example) or carbon (as carbon dioxide or methane for example) independently, preferably both in the form of gases. In particular, the separate supply of the two gases allows (a) improved control of the activation of the surface of the material to be treated by altering the halide gas flow and (b) improved control of the nitriding potential through control of the nitrogen providing gas and (c) control of the carbon potential by the control of carbon providing gas. It has also been found that improvements in the efficiency of the process, particularly gas consumption, have been provided by the coating of the particles of refractory material with a layer of a metal capable of forming a species chosen from the group which includes carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof.

Accordingly, the present invention now provides a method for treating the surface of a substrate to be treated including:

disposing fluidisable particles in a fluidised bed treatment facility,

introducing a fluidising gas into said fluidised bed treatment facility to fluidise said fluidisable particles,

disposing said substrate to be treated in the fluidised particles,

introducing a halide gas into the fluidised bed treatment facility,

introducing a nitrogen and/or carbon containing gas into the fluidised bed treatment facility, the nitrogen and/or carbon containing gas being introduced from a source separate to the source of halide gas,

heating the fluidised bed treatment facility such that a surface layer is formed on the substrate being treated, the layer including at least one species chosen from the group comprising carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof.

Preferably, the volume of said nitrogen and/or carbon containing gas relative to the volume of the halide gas is adjusted during the treatment process. Conveniently, the process may be carried out with some oxygen present either introduced directly or originating from an oxygen containing gas supplied to the fluidised bed treatment facility.

Although the present invention will be described with particular reference to treatment of ferrous substrates, particularly tool steel or parts made therefrom, it is to be noted that the scope of the present invention is not limited to the described embodiment but rather the scope of the invention is more extensive so as to include other embodiments for achieving the same purpose and to the use of the process for purposes other than that described. Typically, the substrate may also be stainless steels, high nickel content steels such as Inconel, or even non ferrous metals such as aluminium or titanium alloys. The substrate could also be a composite such as carbon fibre in combination with a metal.

The fluidised bed treatment facility may be a furnace and may be heated by any convenient means known in the relevant technology and to any convenient process temperature. Typically, the process temperature may be less than 650°C, but is more typically within a range of from 200 to 650°C or between 400 and 600°C. Operation at these relatively low temperatures has the advantage of avoiding distortion and softening of the substrate to be treated.

Typically, the treatment time is selected within a range of from 2 to 24 hours depending on the composition of the substrate to be treated and the composition and thickness of the surface layer to be formed on the substrate. Generally a relatively short period of treatment time is required at higher processing temperatures while longer periods of time may be required at lower processing temperatures.

Typically, the halide gas will be a halogen salt or acid such as HCl, which may be added to the fluidised bed in combination with an inert gas. The halide gas such as HCl is introduced separately to any other reactive gases which are added to the fluidised bed, such as ammonia or methane. This tends to permit very accurate control of the activation of the surface of the substrate to be treated without the need to alter the flow of other gases into the fluidised bed. Typically, the halide gas is present as 0.1 to 10% v/v in the inert gas or more typically, 1 to 5% v/v in the inert gas.

The fluidisable particles may be typically an inert refractory material, that is inert in the sense that it does not react with the substrate to be treated. In one particularly preferred form of the invention, the fluidisable particles may comprise refractory material particles having a coating of a metal capable of forming a species from the groups of carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof. Alternatively, the fluidisable particles may be a mixture of inert refractory material particles together with particles of a metal capable of forming a species from the group of carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof. In a still further possible alternative, the fluidisable particles may be fully particles of a metal as aforesaid. When a refractory material is utilised, it may include alumina, silica or the like or mixtures thereof. Typically, the particle size of the fluidisable particle material will fall within a range of from 40 to 550 mesh or more typically 60 to 350 mesh as measured by US mesh sizes.

In the coated particle embodiment, the metal capable of forming a species chosen from the group comprising carbides, nitrides, carbonitrides or oxycarbonitrides, may be coated on the particles or refractory material by any convenient method. The particles may be coated with more than one metal of this type or more than one metal of this type could be used in particle form alone or in combination with refractory material particles. Other species may also be present. Typically, the aforementioned metal capable of forming a species chosen from the group which includes carbides, nitrides, carbonitrides or oxycarbonitrides, will comprise 1 to 50 wt% of the refractory material or more typically 5 to 30 wt% of the refractory material. In the coated refractory particle embodiment, the particles may be coated with a layer of the aforementioned metal between 5 and 100 microns thickness, or more typically 5 and 20 microns thickness.

As described above, the metal is capable of forming a species chosen from the group which includes carbides, nitrides, carbonitrides, oxycarbonitrides or mixtures thereof. Typically, the metal forms these species by readily bonding with carbon and/or nitrogen and/or oxygen as appropriate to form a carbide and/or nitride and/or carbonitride and/or oxycarbonitride or mixtures thereof. Without wishing to be bound by theory it is believed that optimal results are achieved when oxycarbonitrides are present in the surface layer. These metals may for example be chosen from the group which includes metals of group IVA, VA, VIA or VIIA, iron or alloys which include these metals. More typically, the metal is chosen from the groups which include titanium, vanadium, niobium and tantalum, tungsten, molybdenum, chromium and manganese. In a particularly preferred embodiment, the metal is chosen from the group which includes vanadium, chromium, molybdenum or titanium or alloys comprising these metals. Suitable alloys include titanium alloys or iron alloys including Fe-V, Fe-Nb, Fe-Ti and Fe-Cr, etcetera.

The substrate to be treated is typically a ferrous metal substrate but it may include aluminium and titanium alloys. Typically, the substrate to be treated is a steel or cast iron or nickel containing carbon, cobalt containing carbon, cemented carbide or a carbonaceous material mainly composed of graphite where it is desired to form a carbide or carbonitride layer. More typically the substrate to be treated is a ferrous substrate such as low carbon steel, nickel steel such as Inconel X or Inconel 600, stainless steel such as AISI designation 300 or 400 series or cast iron. Even more typically the substrate is a ferrous alloy suitable for use as a tool steel or stainless steel.

Typically, where it is intended that the surface layer to be formed includes carbides, the treated substrate will include at least 0.05% carbon.

Typically, the substrate to be treated is in the form of an article such as a tool, part for a machine or other device such as a turbine rotor, or sporting article such as a golf club head.

In a particularly preferred embodiment, the substrate to be treated is pretreated or nitrocarborised to form an outer "white layer", which includes metal nitride or carbonitride. For example, if the substrate to be treated is iron, the white layer will comprise iron nitride, iron carbonitride and iron oxycarbonitride. Typically, the white layer is between 0.1 and 25 microns in thickness, more typically 8 to 10 microns in thickness.

In order to form a surface layer comprising a nitride, it is not always necessary that the treated substrate includes nitrogen (or carbon) - as an alternative various metal materials such as iron, nickel and cobalt, cemented carbide and non-metal materials such as oxides, for example alumina and sintered ceramics may be used. In this case, the fluidising gas may comprise nitrogen as the inert gas, or a nitrogen containing gas such as ammonia or a mixture of a fluidising gas with a nitrogen containing gas, such as ammonia together with argon or nascent nitrogen. Typically, the gas is a nitrogen containing gas which decomposes at elevated temperatures to supply a source of nitrogen for formation of a nitride on the surface of the treated material. The nitride is formed by bonding between the nitrogen and the nitride forming element present in the coating on the refractory particles.

The fluidising gas may be an inert gas, that is, a gas which does not participate in the reaction, such as argon, nitrogen or hydrogen or a mixture of gases or it may be reactive, or comprise a reactive species. Typically, the fluidising gas includes an inert gas, such as argon mixed with a reactive gas such as methane which provides a source of carbon for carbide formation. Alternatively, the fluidising gas may include nitrogen or nitrogen containing gas, such as ammonia. A small amount of hydrogen may be added to the fluidising gas. The gas may be of an ordinary purity, that is, it may include trace amounts of species such as water, oxygen or air, although high purity gases are preferred.

The fluidising gas may be supplied at any desired flow rate in the fluidised bed furnace so long as it is within a range capable of attaining a sufficient and favourable fluidisation. It will be readily apparent to those skilled in the art that too low a flow rate will render the fluidisation insufficient and cause an unfavourable temperature distribution within the fluidised bed. Conversely, if the flow rate is too high the gas consumption is increased and undesirable effects such as slugging or spouting occur.

As mentioned earlier, in either of the cases for forming the carbide layer or the nitride layer, it is possible to use a substrate which is subjected to nitrocarborisation to form a surface white layer which layer includes species chosen from the group including metal nitrides, carbonitrides or oxycarbonitrides, or mixtures thereof.

Nitrocarborisation may be carried out as pre-treatment or during the process of the present invention. Nitrocarborisation is well known in the relevant technology and may be carried out by any means known in the art including nitrocarborisation in a gaseous atmosphere, fluidised bed, salt bath, plasma salt atmosphere or similar.

In a particularly preferred embodiment a substrate undergoes pre-treatment and the process of the present invention in the same fluidised bed. In this particular embodiment the pre-treatment step typically includes the steps of:

introducing a fluidising gas which includes a nitrogenous species into a fluidised bed furnace to fluidise fluidisable particles located therein,

disposing said substrate to be treated in the fluidisable particles,

heating the fluidisable particles such that a surface layer is formed on the substrate to be treated, the layer comprising species chosen from the group comprising carbides, nitrides, carbonitrides, oxycarbonitrides or mixtures thereof.

In a particularly preferred embodiment the substrate is a ferrous material such as iron or steel, pre-treated to comprise a white layer of iron carbonitride, iron nitride and iron oxycarbonitride. The pre-treated substrate is then treated according to the process of the present invention using HCl gas, and a fluidised bed which includes alumina particles coated with chromium. Without wishing to be bound by theory, it is believed that the chromium on the particles reacts with the HCl gas to form chromium chloride. The chromium chloride migrates to the surface of the white layer, where the chromium reacts and begins to diffuse into the white layer, undergoing exchange reactions with the nitrogen and carbon in the iron carbonitride, iron nitride and iron oxycarbonitride present in the white layer. In another particularly preferred embodiment, the white layer is built up during the process of the present invention. In this particular embodiment, the process of the present invention additionally includes the steps of:

heating the fluidisable particles,

introducing fluidising gas to the fluidised bed furnace,

introducing a halide gas or alternatively oxygen,

stopping or reducing the flow of halide gas or oxygen then introducing nitrogen containing gas or carbon-bearing gas to the fluidised bed furnace such that a white layer is built up on the surface of the substrate to be treated wherein the potential of the constituents of the white layer can be varied by varying the flow of halide gas and/or nitrogen-bearing gas and/or carbon-bearing gas.

The present invention further provides an arrangement for introducing gases to a base region of a fluidised bed treatment facility during a treatment process, said arrangement including a first gas distribution means locatable in said base region, and a second gas distribution means locatable in said base region of a fluidised bed treatment facility, each of said first and second gas distribution means having separate gas delivery means whereby separate gas or gas combinations can be supplied to said first and second gas distribution means.

Conveniently, at least one or both of said gas delivery means includes means for adjustably mixing at least two gases. Preferably a halide gas is mixed with a fluidising gas in one of the gas delivery means. In another of the gas delivery means it is possible to carry a nitrogen and/or a carbon containing gas to one of the first or second distribution means. Conveniently one of the gas delivery means is also arranged to carry oxygen or an oxygen containing gas whereby processing of a substrate within the treatment facility will occur in the presence of some oxygen.

In a particularly preferred embodiment, the first gas distribution means includes a wall means separating a lower gas receiving zone from an upper zone of the fluidised bed treatment facility containing particle material to be fluidised, one of said gas delivery means leading into said lower gas receiving zone, and said wall means including at least one porous section permitting gas flow therethrough while preventing said particle material from entering said lower gas receiving zone. Preferably a plurality of said porous sections are provided in a spaced array comprising at least one said porous section centrally located and a plurality of said porous sections distributed around said one or more centrally located porous sections. Conveniently the second gas distribution means includes a pipe or conduit means located in the base region above said walls means, the other of said gas delivery means leading directly into said pipe or conduit means, and a plurality of gas discharge apertures formed in said pipe or conduit means adapted to allow gas to enter the base region from said pipe or conduit means. The pipe or conduit means may be in the form of at least two concentric rings with a diametral pipe section joining each of the rings. It is particularly preferred that a particle material or a coarse grit size is supported on the wall means and surrounds said second gas distribution means, said particle material of a coarse grit size being sufficiently large to be not fluidised during normal treatment processing.

In a further preferred embodiment the first and second gas distribution means each include a separate pipe or conduit means, each said pipe or conduit means having a plurality of gas discharge apertures formed in said pipe or conduit means adapted to allow gas to enter the base region therefrom. Conveniently, a particle material or a coarse grit size is supported to surround said first and second gas distribution means, said particle material of a coarse grit size being sufficiently large to be not fluidised during normal treatment processing.

Fluidised bed treatment facilities, while being generally cleaner and safer to use than salt bath facilities, still have certain practical difficulties, particularly when it is desired to maintain an object to be treated in a desired atmosphere, either during treatment or perhaps when being transported between treatments. These problems become more significant particularly when the treatment concerned uses particularly dangerous gases that need to be retained within the facility. The particular difficulty with fluidised bed facilities is that almost inevitably fine particulate material is thrown upwardly and out of the retort making primary seals for retaining the material and any dangerous gases quite ineffective and often of limited life. It is desired therefore to provide an effective seal arrangement which will ensure dangerous gases do not escape while at the same time permitting loading and unloading of objects to be treated to and from the retort and also permitting transport of the treated object while maintaining desired atmospheres there around.

Accordingly, the present invention provides a fluidised bed treatment facility including a retort for retaining particulate material to be fluidised, means for selectably supplying gas flow to the particulate material within the retort to fluidise same, means to selectably heat the particulate material within the retort, an upwardly facing first access opening enabling, when open, an object or objects to be treated to be introduced into the particulate material within the retort, a first closure member adapted in a first closure position to close said first access opening, said first closure member including peripheral seal means to prevent or minimise the escape of particulate material or gases from said retort, said closure member being movable to a second position providing access to said access opening, a chamber arranged above said retort having a second access opening generally above and in line with said first access opening, a second closure member adapted in a first closure position to close said second access opening, said second closure member including peripheral seal means to prevent the escape of gases from said chamber when the second closure member is in said first closure position. Preferably the peripheral seal means of the first closure member includes at least one downwardly depending skirt member receivable within a trough containing particulate material, said particulate material being fluidisable at least when said first closure member is moved to said first closure position. Preferably the fluidised bed treatment facility also includes a gas distribution arrangement as described above located in a base region of the retort.

Preferred embodiments of the present invention will hereinafter be described with reference to the accompanying drawings, in which:

Figure 1 is a longitudinal cross-sectional view through a preferred form of fluidised bed treatment facility in accordance with the present invention;

Figure 2 is a section view along line 6 of Figure 1;

Figure 3 is a top plan view of the facility shown in Figure 1;

Figure 4 is a detail plan view of a gas distribution system for introducing gases into the retort of the facility shown in Figure 1;

Figure 5 is a representative cross-sectional view of the arrangement shown in Figure 4;

Figure 6 is a partial cross-sectional view of a seal configuration for use in the facility illustrated in Figure 1;

Figure 7 is a detail of part of the seal arrangement shown in Figure 6;

Figure 8 is a longitudinal cross-sectional view through another preferred form of fluidised bed treatment facility;

Figure 9 is a horizontal section view along line 6' of Figure 8;

Figure 10 is a vertical section view along line A-A of Figure 9 when the seal configuration is in the fully closed position; and

Figure 11 is a vertical section view along line A-A of Figure 9 when the seal configuration is in the fully open position.

Referring now to the drawings, Figure 1 shows a fluidised bed treatment facility 10 having a retort 12 with a surrounding wall 16 for containing particle material to be fluidised during a treatment process. The retort 12 and the particulate material contained therein is heated by any conventional means well known to persons skilled in this art and will not be further described herein. Unless otherwise described, other features of the facility may also be constructed in conventionally known ways.

Within the base region 11 of the retort, a gas distribution arrangement 13 is provided in accordance with one preferred aspect of this invention allowing both fluidising gas flow to be introduced as well as other active treatment gases. This gas distribution arrangement 13 is illustrated schematically but in more detail in Figures 4 and 5. The arrangement 13 includes a first gas delivery pipe or conduit 14 centrally located leading directly into a lower chamber 15 within the base region 11 of the retort. A baffle plate 17 distributes the gas flow across the chamber 15 rather than permitting streaming in line with the pipe 14. Arranged immediately above the lower chamber 15 is a wall 18 that both supports the particulate material 19 within the retort 12 and allows gas flow therethrough. To allow a relatively evenly dispersed gas flow through the wall 18, a plurality of porous inserts 20 are provided which in the embodiment illustrated are circular (in plan view) and five in number. One such insert 20 is centrally located with four inserts 20 located around the central insert. The number of such inserts are not critical but it is highly desirable to achieve a relatively evenly dispersed gas flow upwardly through the wall 18. The lower chamber 15 and the wall 18 form a first gas distribution means 21. The inserts 20 may be made from porous metal but if the gases used are too corrosive, then the inserts might be formed by porous ceramic materials. Arranged immediately above the wall 18 is a second gas distribution means 22 formed by pipes or conduits 23 with a plurality of gas discharge apertures 24 formed therein. In the illustrated embodiment, the pipes 23 are formed by two concentric rings 25, 26 joined by a diametrical pipe section 30. A second gas delivery pipe 28 is arranged to deliver gas to the second gas distribution means 22 without contact or mixing with the gas or gases delivered by pipe 14. The main purpose of the two distributor means is to separate gases which can react, such as ammonia and HCl which can form a compound such as ammonium chloride which would block the flow of gas through the distributor. The second distribution means 22 is conveniently located within a layer of coarse grit particles 29 that are not fluidised during normal fluidisation of the smaller and lighter particles above this layer 29. Alternatively, the second distributor may be placed in the active fluidised bed of smaller particles, just above the coarse grit particles. The exact location of the distributor and the hole configuration in the distributor can be adapted to depend on the type of process treatment being performed in the fluidised bed.

In one use of the gas distribution arrangement as described above, bed fluidising gas such as argon or nitrogen is supplied via the first gas delivery pipe 14 and, when it is required, ammonia and possibly other gases are substantially uniformly mixed with the fluidising gas before it reaches the lower chamber 15. A control system (not illustrated) for controlling the flow rate of the fluidising gas and the ammonia, and for controlling independently the flow rate of the ammonia relative to the fluidising gas flow rate is provided. The second gas delivery pipe 28 may be arranged to deliver gas, a halide gas (such as HCl) or a combination of gases conveniently with some oxygen present or with a gas capable of providing oxygen within the retort 12. Again the gases (if more than one) are substantially uniformly mixed before they reach the second gas distribution means and their flow rates are individually capable of regulation relative to each other and relative to the gas flow delivered via pipe 14.

Located at the upper end of the retort 12 is a first cover member 27 adapted in a closed position as illustrated in Figure 1 to overlie but not engage an upper edge 51 of the retort wall 16. The cover member 27 has peripheral sealing flanges 62, 63 receivable in a surrounding seal arrangement 50. The seal arrangement 50 includes a trough formed partially by the retort wall 16 and is annularly disposed about the retort, however, it should be appreciated that the retort 16 need not be circular in cross-section. The trough 50 includes a pair of fluidising gas distribution pipes 52, 53 extending around its base wall 54, each of which have downwardly angled apertures 55 to allow gas to be dispersed into the trough. A gas flow introduction pipe 56 is provided to introduce gas into the pipes 52, 53. At various spaced localities around the trough 50, a number of low height walls 57 are provided to provide a limit stop for the seal region of the cover member 27 so as to prevent any damage occurring to the pipes 52, 53. The trough 50 is conveniently filled with a particulate material, preferably a refractory material. The refractory material is preferably the same material as contained within the retort 16 such that if material is thrown out of the retort 16 into the trough 50, it will have little or no effect on the sealing ability of the seal arrangement. The passage 58 leading from the retort may be provided so as to lead particle material from the retort into a grit collection box 80 with return of the separated particle material to the retort by a separate passage. This arrangement tends to limit the amount of particles thrown out of the retort but does not necessarily prevent this occurring altogether. The cover member 27 includes a number of axled rollers 59 running on rails 60 so as to enable movement of the cover member sideways relative to the retort 16. The rails 60 are movable upwardly and downwardly by a sufficient distance to allow the cover member and its associated sealing regions to clear the retort 16 when moving sideways. As shown in Figures 6 and 7, the cover member 27 includes a circumferential sealing region 61 which includes at least a main depending skirt 62 and preferably also a secondary depending skirt 63. In the closed position illustrated in Figure 6, the main skirt 62 rests on the low height stop walls 57 when the cover member 27 rests or approaches resting on the top edge of the retort 16. The ability to depend the skirts 62, 63 into the particulate material in the trough 50 is achieved by fluidising the particulate material as the cover approaches the closed position.

This sealing arrangement provides an effective means of sealing the environment within the retort 12 and enables reliability of being able to make this seal effective.

In addition to the foregoing primary sealing arrangement, a substantially closed housing 81 forming a chamber 82 is located above the closure member 27. In the closed access housing 81, a second access opening 83 is provided which again is closable by a second closure member 84. In Figure 1 the closure member 84 in full outline is shown opening the access opening 83 whereas the dashed outline shows the closure member 84 when in a closing position. The closure member 84 may include an "O"-ring seal or similar acting between the member 84 and a seal plate 85 when in the closed position. The closure member 84 further includes a pair of air activated lift pads 86 to, when desired, lift the member 84 a short distance while supporting same on an air cushion. In this state the member 84 is easily shifted transversely by an actuator 87 to either close or open the access opening 83. The chamber 82 may be kept at a small vacuum pressure to both ensure the closure member 84 seals the opening 83 and further that any gases that might escape from the retort are not discharged to the general atmosphere. These gases may be communicated from the chamber 82 to the grit collection box 80 where gases otherwise exiting the retort 12 are also collected and passed to treatment stations (not illustrated) either to permit reuse or to safely dispose of same. When it is desired to transport articles treated or part treated between separate fluidised bed treatment facilities under controlled atmosphere conditions, a closable hood (not shown) can be provided that will include bellow type seals (or the like) 89 that can seal with seal plate 85, the hood then being able to receive the object or objects being treated and transport same under sealed controlled conditions to another locality.

Another embodiment of the fluidised bed treatment facility of the present invention is depicted in Figure 8. The sealing arrangement of this embodiment differs from the fluidised bed treatment facility of Figure 1, but in all other respects the facilities are the same.

The sealing arrangement comprises a double fluidised bed seal. The cover member 27' has peripheral sealing flanges 62', 63' receivable in a surrounding fluidised seal arrangement 50'. A second closure member 84' rests on a fluidised seal arrangement 95 when in the closed position. The two fluidised seal arrangements are located one above the other. An inert gas such as nitrogen or argon may be constantly fed into the chamber 82' between the upper surface of the second closure member 84' and the lower surface of the cover member 27'. In this configuration an "O"-ring seal is not required.

Figure 10 depicts the cover member 27' and the second closure member 84' in the fully closed position.

Figure 11 depicts the cover member 27' and the second closure member 84' in the fully open position, such that a gap 101 can be seen as the second closure member has been moved upwards and clear of the fluidised seal arrangement.

The invention will now be further described with reference to the following non-limiting examples:

EXAMPLES

EXAMPLE 1

PRE-TREATMENT

A tool steel die was immersed in the fluidised bed of a fluidised bed reactor as depicted in Figure 1.

The fluidised bed comprised particles of alumina which have been melt coated with chromium. A fluidising gas comprising a mix of nitrogen, methane and ammonia was introduced to fluidise the bed. The temperature of the fluidised bed and tool steel substrate was maintained at 580°C for 4 hours. The flow of reactive gases was varied to control the various potential, and therefore the thickness and chemical composition of the resultant "white layer". The resulting "white layer" comprising iron carbonitride, iron oxycarbonitride and iron nitride was about 10 microns thick.

TREATMENT ACCORDING TO THE PROCESS OF THE PRESENT INVENTION

The tool steel die was left in the fluidised bed, the temperature of the fluidised bed being maintained at 580°C. A continuous flow of a mixture of 1% HCl in N_2 was then commenced together with ammonia and carbon dioxide to protect the integrity of the white layer produced in the pre-treatment stage and the flow continued through the fluidised bed for a period of 4 hours. The rate of reaction of the chromium with the carbon and nitrogen in the nitrocarborised layer was controlled by controlling the percentage volume of HCl and ammonia with the inert gases remaining proportionally as carrier gases.

EXAMPLE 2

A steel tool die was immersed in the fluidised bed of a fluidised bed reactor comprising particles of alumina which have been melt coated with chromium. A fluidising flow of nitrogen was introduced to the fluidised bed reactor and the temperature raised to 580°C. HCl gas was introduced to activate the surface of the tool steel and the flow continued for 5 minutes. The flow of HCl was then ceased prior to commencement of a flow of ammonia gas and carbon dioxide mixture.

During this process the white layer was built up by diffusion. The potential of the various constituents was then varied by varying the flow of HCl, ammonia and carbon dioxide.

EXAMPLE 3

A gear made from AISI 4140 steel, hardened and tempered, was machined to final size and then immersed in the fluidised bed of a fluidised bed reactor comprising particles of alumina at 550°C. The gear was heated under nitrogen gas to the bed temperature.

When the gear had reached 550°C, ammonia and carbon dioxide were proportionally added to the nitrogen and a nitrocarborised white layer was built up on the surface of the gear (at the same time as some nitrogen was also diffusing into the gear increasing the hardness under the surface) until the white layer was 15 microns thick. The building up of the white layer in this manner took approximately 3 hours.

EXAMPLE 4

A golf club head made from 17-4 PH stainless steel was heat treated and finished to final size. The golf club head was immersed in the fluidised bed of a fluidised bed reactor. The fluidised bed comprised alumina particles at 560°C and nitrogen, heated to the temperature of the fluidised bed.

When the temperature of the golf club head reached 560°C, ammonia and HCl gas were added to the flow of nitrogen. The potentials of the chromium and nitrogen (ie, their ability to diffuse into the surface) were controlled by varying the ratio of the ammonia to HCl. The cycle time for the treatment was 4 hours after which the golf club head was removed from the fluidised bed reactor and cooled under a flow of nitrogen.

The chromium diffused to a depth of 20 microns into the alloy surface. In this case the white layer was not visible to the eye or at low magnification but the surface hardness had increased from 400 VHN to 1250 VHN using a 50 g load.

The process described has been advanced by explanation and many modifications may be made without departing from the spirit and scope of the invention which includes every novel feature and novel combination of features as herein disclosed.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the invention.

CLAIMS:

1. A method for treating the surface of a substrate to be treated including:

disposing fluidisable particles in a fluidised bed treatment facility,

introducing a fluidising gas into said fluidised bed treatment facility to fluidise said fluidisable particles,

disposing said substrate to be treated in the fluidised particles,

introducing a halide gas into the fluidised bed treatment facility,

introducing a nitrogen and/or carbon containing gas into the fluidised bed treatment facility, the nitrogen and/or carbon containing gas being introduced from a source separate to the source of halide gas,

heating the fluidised bed treatment facility such that a surface layer is formed on the substrate being treated, the layer including at least one species chosen from the group comprising carbides, nitrides, carbonitrides, oxycarbonitrides and mixtures thereof.

2. A method according to claim 1 wherein relative volumes of said nitrogen and/or carbon containing gas and said halide gas are adjusted during the treatment process.

3. A method according to claim 1 or 2 wherein the substrate to be treated is chosen from the group which includes ferrous metals, ferrous alloys, aluminium alloys and titanium alloys.

4. A method according to any one of claims 1 to 3 wherein the halide gas is a halogen salt or halogen acid.

5. A method according to any one of claims 1 to 4 wherein the fluidisable particles are chosen from the group comprising refractory particles, refractory particles coated with a metal and mixtures thereof.

6. A method according to claim 5 wherein the fluidisable particles are mixed with particles of metal.

7. A method according to claim 5 or 6 wherein the metal is capable of forming a species chosen from the group which includes carbides, nitrides, carbonitrides or oxycarbonitrides.

8. A method according to claim 7 wherein the metal is chosen from the group which includes metals of group IVA, VA, VIA or VIIA, iron or alloys which include these metals.

9. A method according to any of the preceding claims wherein the processing temperature is less than 650°C , ammonia is used as the nitrogen containing gas and the halide gas is HCl which is present at a level of between 0.1 and 10% v/v in nitrogen as an inert carrier gas.

10. A method according to any one of the preceding claims wherein the substrate has been pre-treated by a method which includes the steps of:

introducing a fluidised gas comprising a nitrogenous species into a fluidised bed furnace to fluidise fluidisable particles located therein,

disposing said substrate to be treated in the fluidised particles,

heating the fluidised bed treatment facility such that a surface layer is formed on the substrate to be treated, the layer comprising species chosen from the group including carbides, nitrides, carbonitrides, oxycarbonitrides or mixtures thereof.

11. A method according to claim 10 wherein the pre-treatment and treatment are carried out as a single process.

12. An arrangement for introducing gases to a base region of a fluidised bed treatment facility during a treatment process, said arrangement including a first gas distribution means locatable in said base region, and a second gas distribution means locatable in said base region of a fluidised bed treatment

facility, each of said first and second gas distribution means having separate gas delivery means whereby separate gas or gas combinations can be supplied to said first and second gas distribution means.

13. An arrangement according to claim 12 wherein at least one said gas delivery means includes means for adjustably mixing at least two gases.

14. An arrangement according to claim 12 or claim 13 wherein each said gas delivery means includes means for adjustably mixing at least two gases.

15. An arrangement according to claim 13 or claim 14 wherein a halide gas is mixed with a fluidising gas in one of said gas delivery means.

16. An arrangement according to claim 13 or claim 14 wherein one of said gas delivery means is arranged to carry a nitrogen and/or a carbon containing gas to one of said first or second gas distribution means.

17. An arrangement according to claim 16 wherein said one gas delivery means is arranged to carry both a nitrogen and a carbon containing gas.

18. An arrangement according to any one of claims 15 to 17 wherein said one gas delivery means is also adapted to carry oxygen or an oxygen containing gas.

19. An arrangement according to any one of claims 12 to 18 wherein the first gas distribution means includes a wall means separating a lower gas receiving zone from an upper zone of the fluidised bed treatment facility containing particle material to be fluidised, one of said gas delivery means leading into said lower gas receiving zone, and said wall means including at least one porous section permitting gas flow therethrough while preventing said particle material from entering said lower gas receiving zone.

20. An arrangement according to claim 19 wherein a plurality of said porous sections are provided in a spaced array comprising at least one said porous section centrally located and a plurality of said porous sections distributed around said one or more centrally located porous sections.

21. An arrangement according to claim 19 or claim 20 wherein the second gas distribution means includes a pipe or conduit means located in the base region above said wall means, the other of said gas delivery means leading directly into said pipe or conduit means, and a plurality of gas discharge apertures formed in said pipe or conduit means adapted to allow gas to enter the base region from said pipe or conduit means.

22. An arrangement according to claim 21 wherein said pipe or conduit means is formed in at least two concentric rings with a diametral pipe section joining each of said rings.

23. An arrangement according to any one of claim 19 to 22 wherein a particle material of a coarse grit size is supported on said wall means and surrounds said second gas distribution means, said particle material of a coarse grit size being sufficiently large to be not fluidised during normal treatment processing.

24. An arrangement according to any one of claims 12 to 18 wherein said first and second gas distribution means each include a separate pipe or conduit means, each said pipe or conduit means having a plurality of gas discharge apertures formed in said pipe or conduit means adapted to allow gas to enter the base region therefrom.

25. An arrangement according to claim 24 wherein a particle material of a coarse grit size is supported to surround said first and second gas distribution means, said particle material of a coarse grit size being sufficiently large to be not fluidised during normal treatment processing.

26. A fluidised bed treatment facility including a retort for retaining particulate material to be fluidised, means for selectably supplying gas flow to the particulate material within the retort to fluidise same, means to selectably heat the particulate material within the retort, an upwardly facing first access opening enabling, when open, an object or objects to be treated to be introduced into the particulate material within the retort, a first closure member adapted in a first closure position to close said first access opening, said first closure member including peripheral seal means to prevent or minimise the escape of particulate material or gases from said retort, said closure member being movable to a second position providing access to said access opening, a chamber arranged above said retort having a second access opening generally above and in line with said first access opening, a second closure member adapted in a first closure position to close said second access opening, said second closure member including peripheral seal means to prevent the escape of gases from said chamber when the second closure member is in said first closure position.

27. A fluidised bed treatment facility according to claim 26 wherein one or both of the peripheral seal means is a fluidised seal.

28. A fluidised bed treatment facility according to claim 26 wherein the peripheral seal means of the first closure member includes at least one downwardly depending skirt member receivable within a trough containing particulate material, said particulate material being fluidisable at least when said first closure member is moved to said first closure position.

29. A fluidised bed treatment facility according to claim 26 or claim 28 further including an arrangement according to any one of claims 12 to 26.

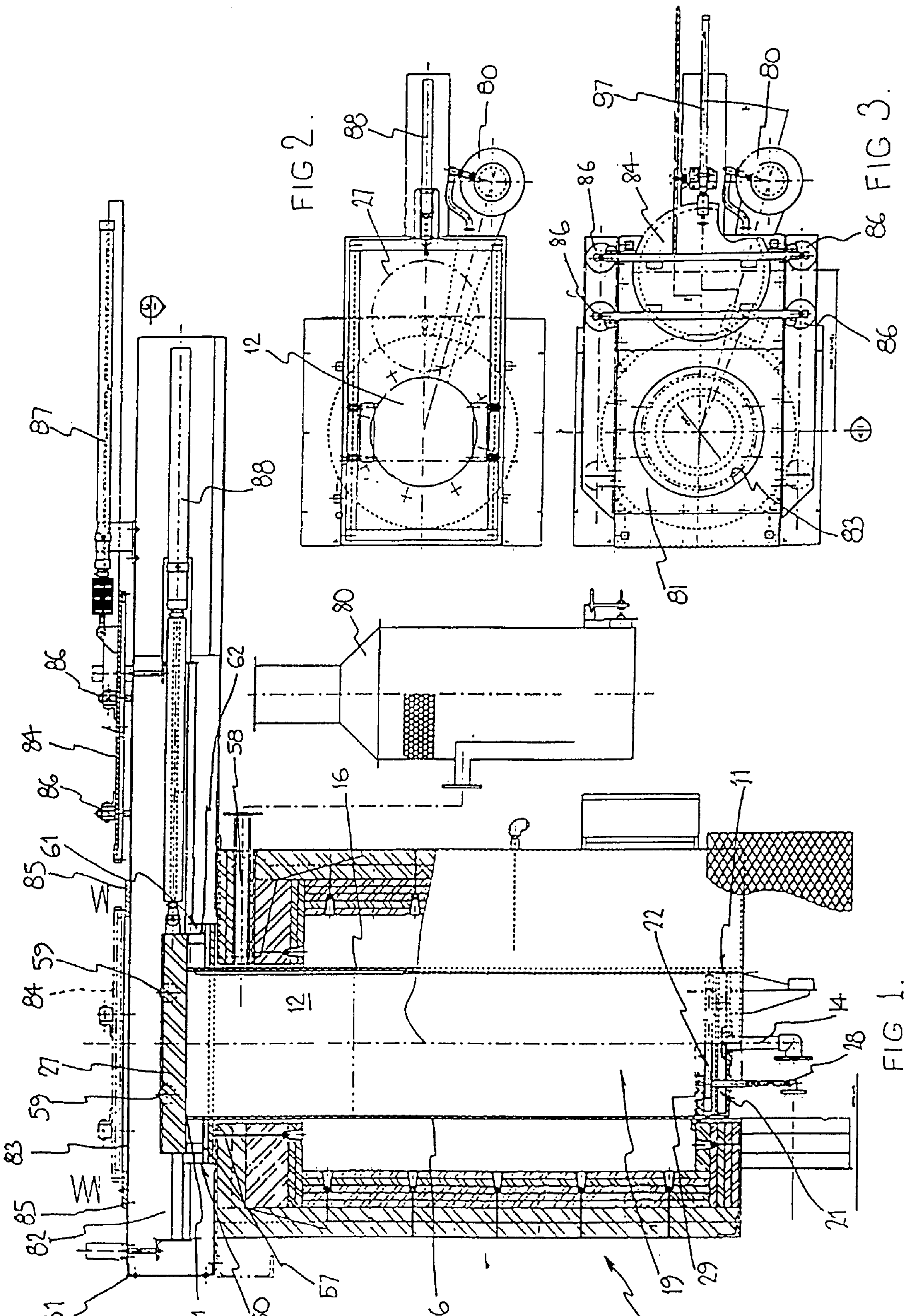
FIG 1.
FIG 2.
FIG 3.

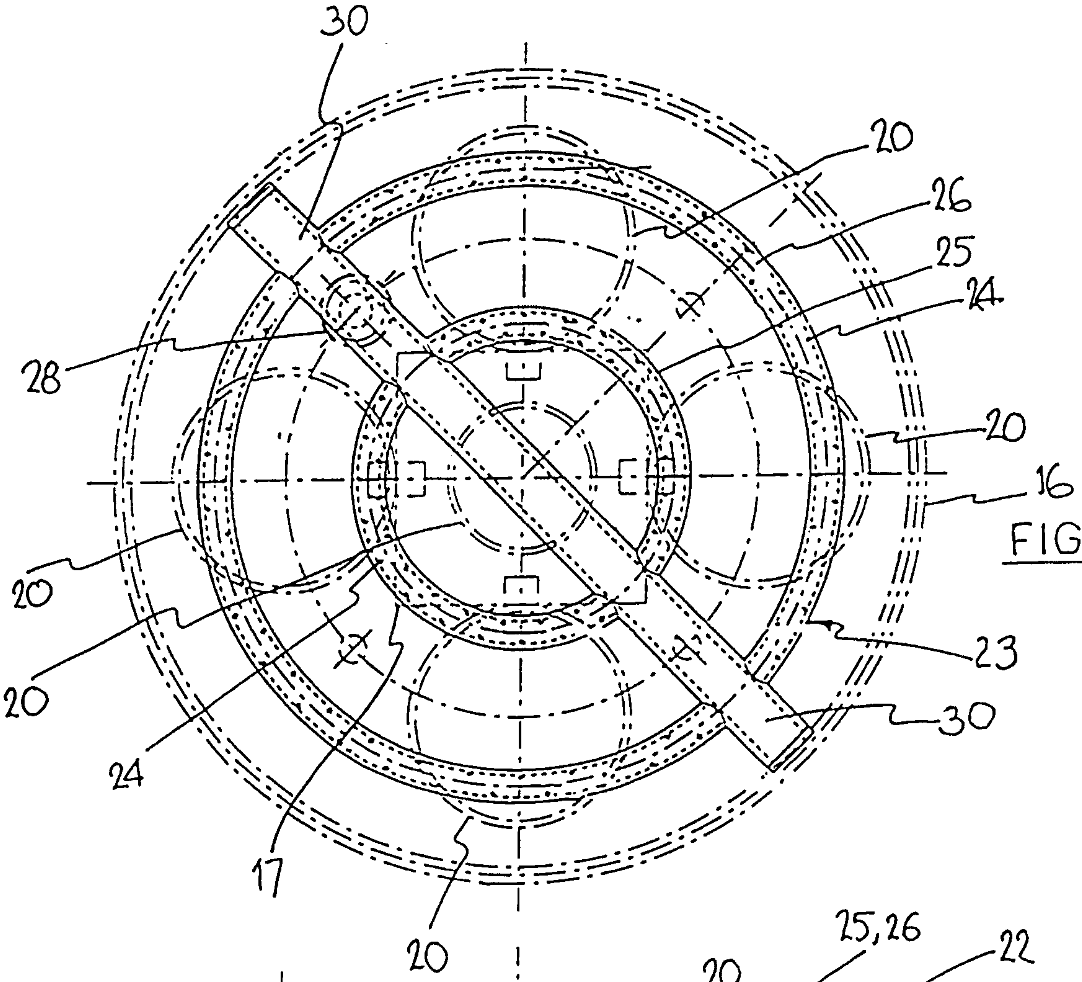
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FIG 4.

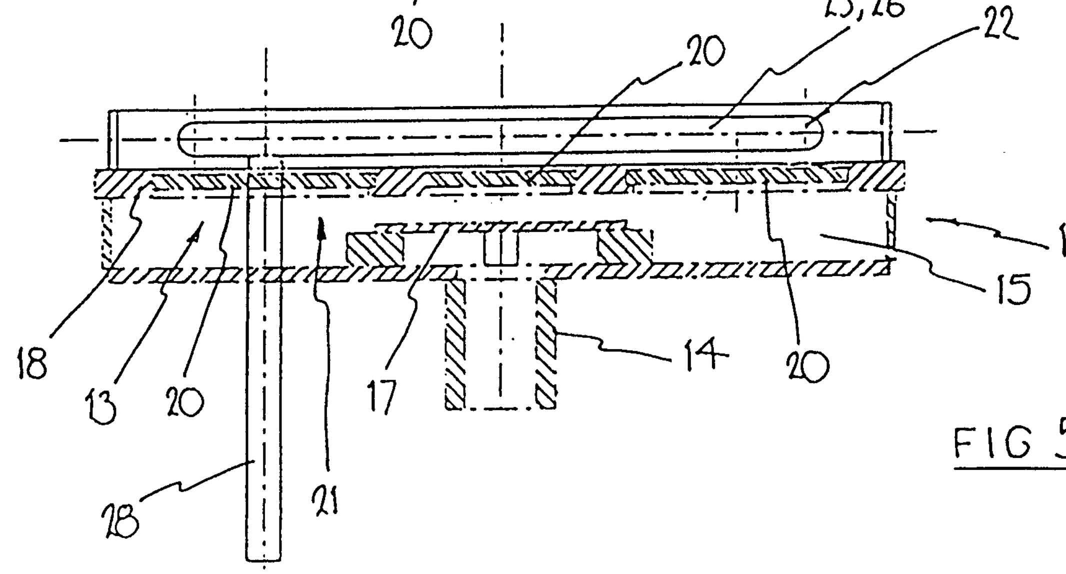
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FIG 5.

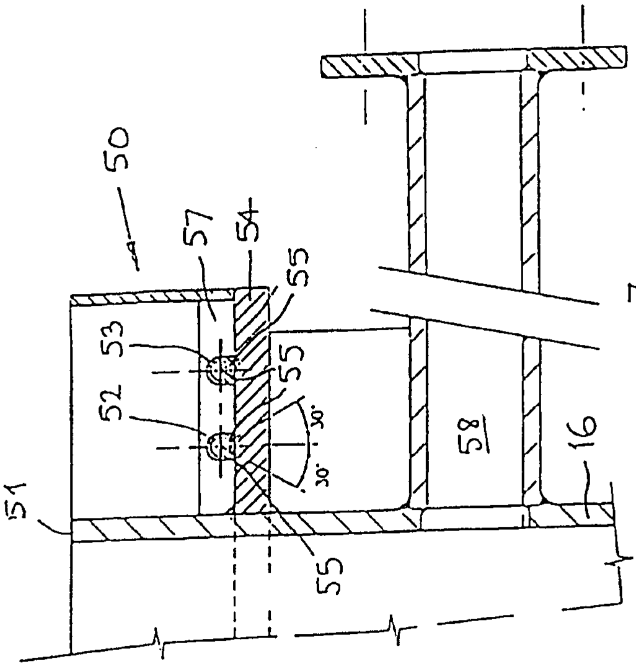
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FIG 7

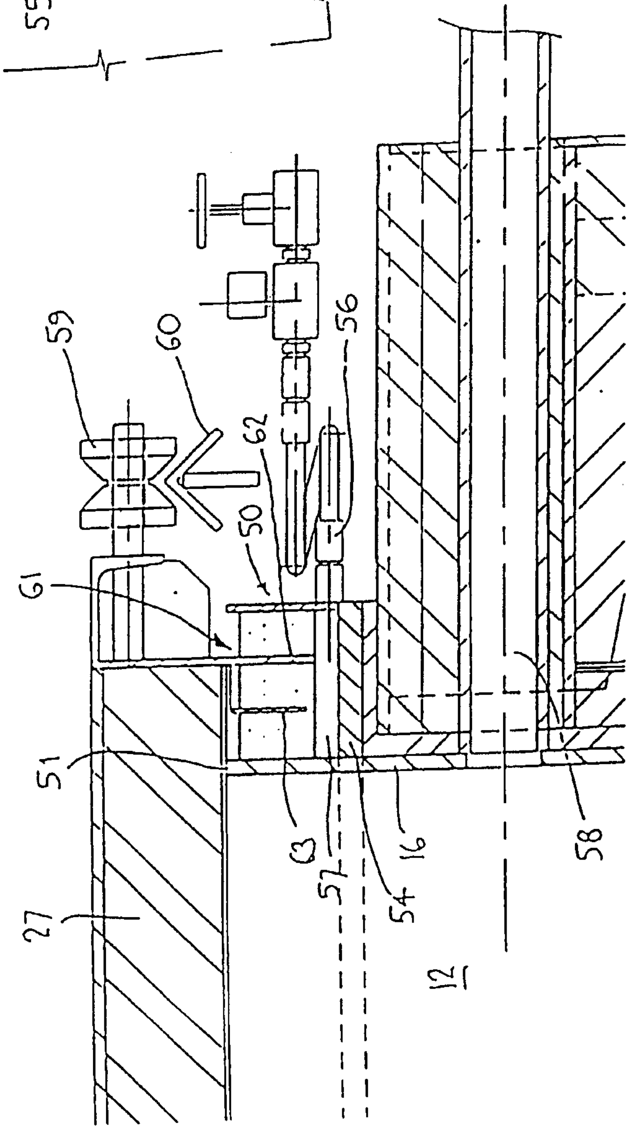
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FIG 6

Fig 9.

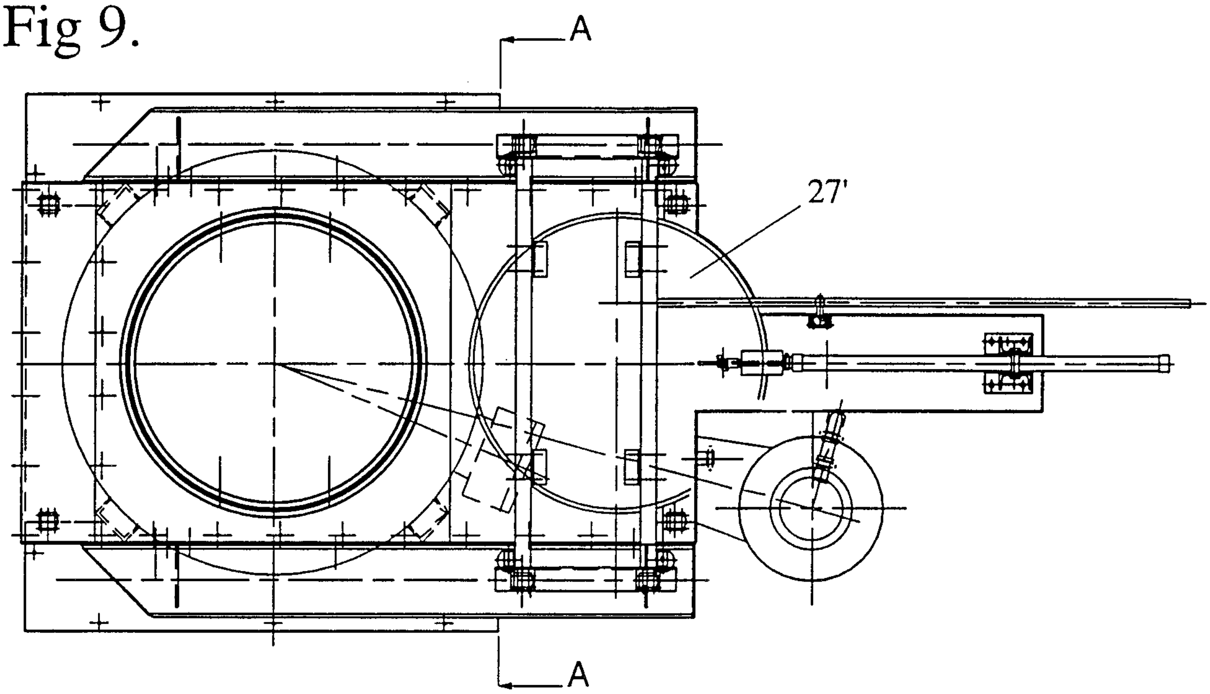


Fig 8.

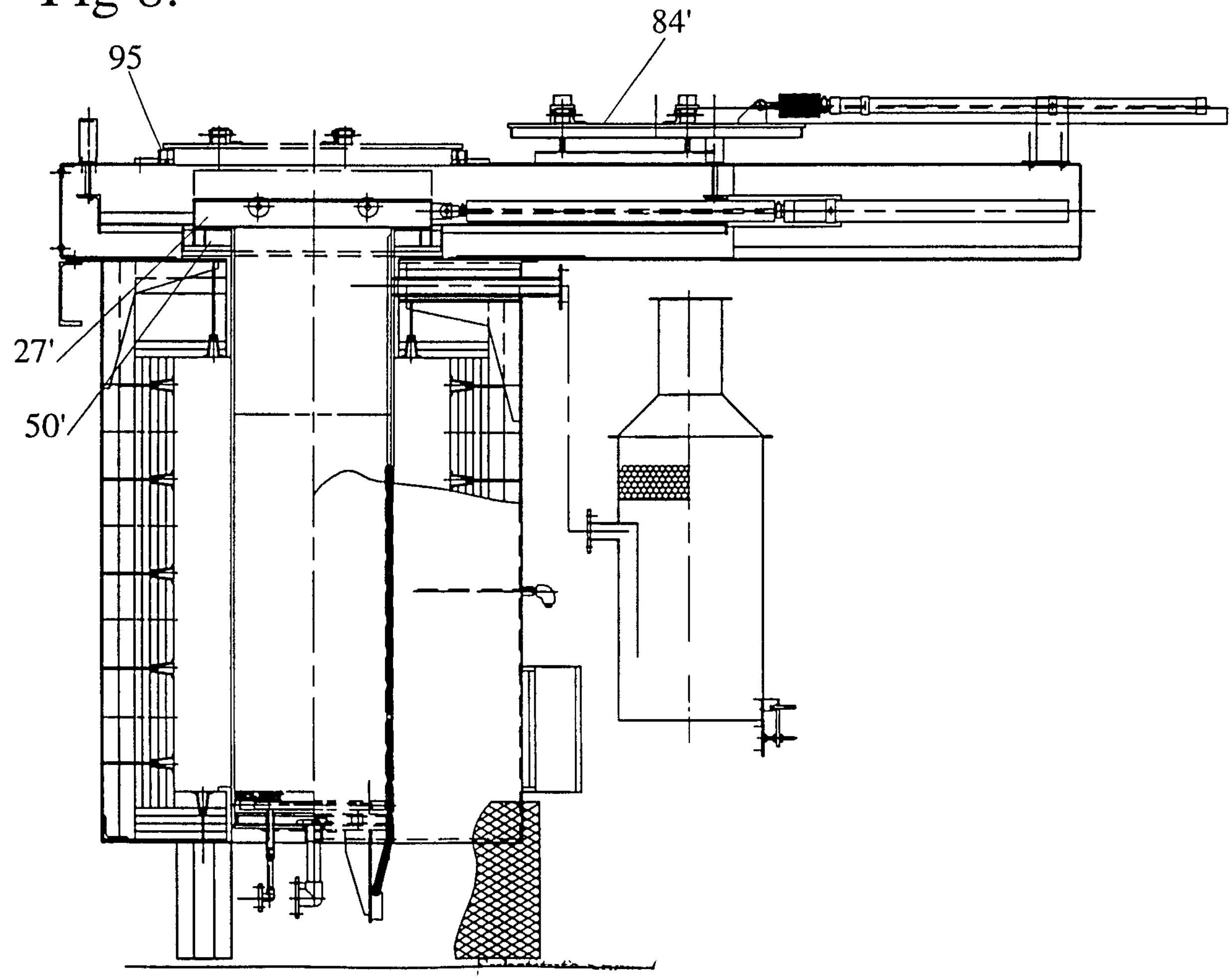


Fig 10.

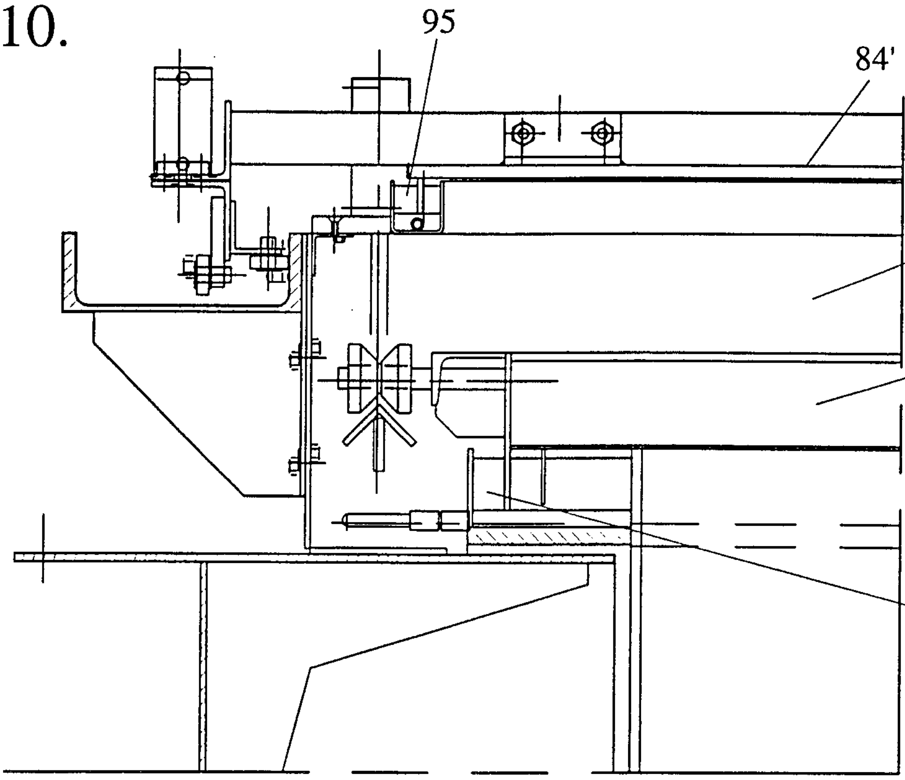
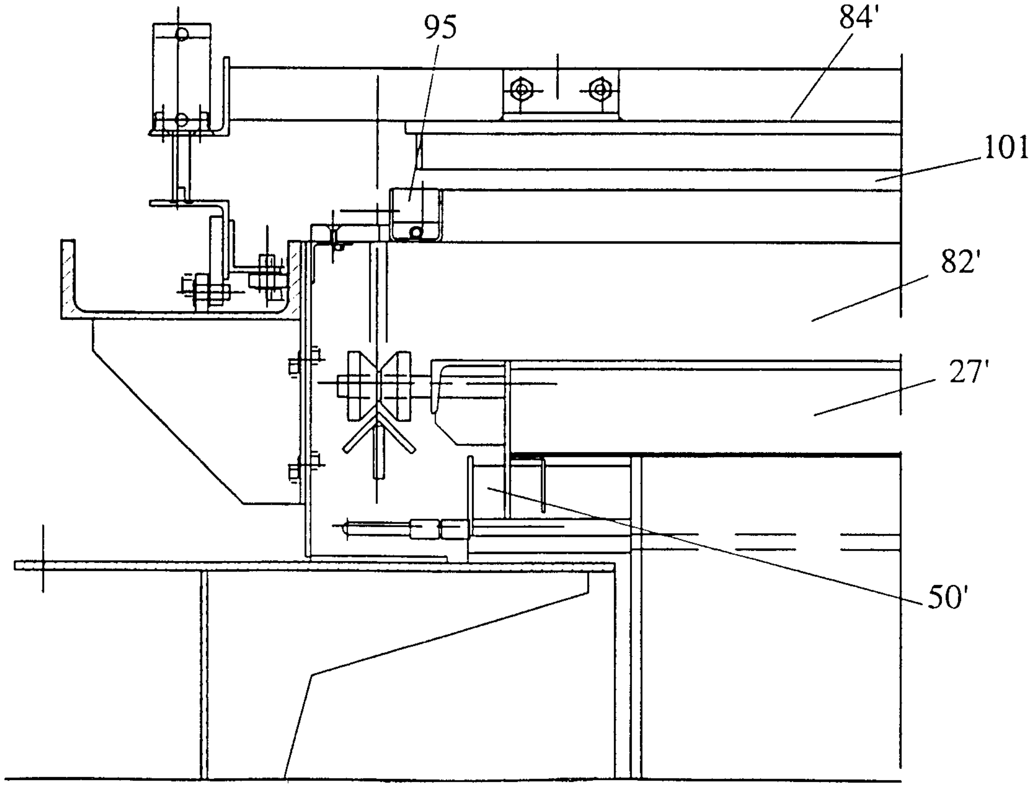


Fig 11.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 00/00069

A.	**CLASSIFICATION OF SUBJECT MATTER**
Int Cl[7]:	C23C 8/06, 8/08, 8/20, 8/22, 8/24, 8/26, 8/28, 8/30, 8/32, 16/442, B01J 8/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C 8/06, 8/08, 8/12, 8/14, 8/16, 8/18, 8/20, 8/22, 8/24, 8/26, 8/28, 8/30, 8/32, 11/00, 11/1+ ,16/44, 16/442, 16/54, B01J 8/46, 15/00, C21D 1/53, F27B 15/08, 15/02, 15/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI: IPC (C23C 8/--, 16/--, F27B 15/--) AND FLUIDI+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 471276 A1 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) 19 February 1992.	1-13, 15-19
X	EP 252480 A2 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) 13 January 1988.	1-5, 10-13, 15-19
X	EP 303191 A2 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) 15 February 1989.	1-5, 10-13, 15-19, 23

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 April 2000	17 APR 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **R.P. ALLEN** Telephone No.: (02) 6283 2134

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5855678 A (SANJURJO et al.) 5 January 1999	1-9
X	US 5227195 A (SANJURJO et al.) 13 July 1993	1-9
X	US 4623400 A (PROCEDYNE CORP) 18 November 1986	1-5, 12-13, 15-19
X	WO 92/08819 A (DAIDOUSANSO CO. LTD) 29 May 1992 See abstract and figure 1	1-4
X	US 4730811 A (HATTORI et al.) 15 March 1988	26-27
X	WO 98/14291 A1 (PROCEDYNE CORP) 9 April 1998	26
X	US 3925024 A (HOLLINGSWORTH et al.) 9 December 1975	12, 19-21, 23
X	US 4387120 A (BARNERT) 7 June 1983	12, 19-22
X	US 4080927 A (BROWN) 28 March 1978	12, 19-21
X	EP 325657 A1 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) 2 August 1989	12-13, 24
X	Derwent Abstract Accession No.89-369457/50, Class Q77, SU 1486730 A (CHELY CAR IND AUTOM) 15 June 1989	12-13, 24
Y	Derwent Abstract Accession No.98-189645/17, Class M24, JP 10046232 A, (PARKER NETSUSHORI KOGYO KK) 17 February 1998	27-28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 00/00069

Box 1 Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos :

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos :

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims 1-11 directed to a method for treating the surface of a substrate in a fluidised bed.
2. Claims 12-25 directed to an arrangement for separately feeding gas to a generalised fluidised bed.
3. Claims 26-29 directed to a generalised fluidised bed.

As reasoned on the extra sheet::

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: II

The international application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. In coming to this conclusion the International Searching Authority has found that there are different inventions as follows:

1. Claims 1-11 directed to a method for treating the surface of a substrate in a fluidised bed with halide gas and nitrogen and/or carbon containing gasIt is considered that introducing a halide into a fluidised bed treatment facility comprises a first "special technical feature".

2. Claims 12-25 directed to an arrangement for separately introducing gas to a generalised fluidised bed. It is considered that each gas distribution means having separate gas delivery means comprises a second "special technical feature".

3. Claims 26-29 directed to a generalised fluidised bed. It is considered that the closure member being movable to a second position providing access comprises a second "special technical feature".

Since the abovementioned groups of claims do not share any of the technical features identified, a "technical relationship" between the inventions, as defined in PCT rule 13.2 does not exist. Accordingly the international application does not relate to one invention or to a single inventive concept.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 00/00069

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
EP	471276	CA	2048872	US	5443662	JP	5005172
EP	252480	AU	75242/87	CA	1300440	CN	87104781
		IN	169705	JP	63014856	US	4844949
EP	303191	AU	20987/88	CA	1336150	CN	1031570
		IN	171675	JP	1047844	US	4892759
EP	325657	JP	63096482	US	5354039	WO	8802839
US	5855678	EP	979316	WO	9849366		
US	5227195	EP	417253	WO	9011858	US	5149514
US	4623400	CA	1272077	DE	3605744	FR	2577944
		GB	2171420	JP	61243178		
WO	9208819	EP	511409	JP	4187754		
US	4730811	JP	61285632				
WO	9814291	EP	954398				
US	4387120	DE	3007711	FR	2477274	GB	2070962
		JP	56133582				
US	4080927	DE	2744611	FR	2366870	GB	1581283
		JP	53045676	US	4098224	US	4116160
		US	4221182				

END OF ANNEX