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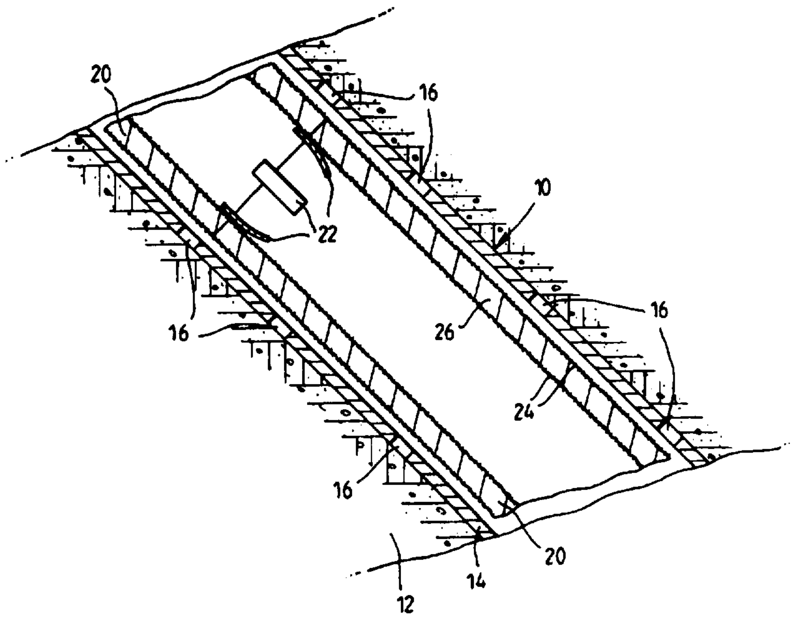

(57) Abstract

Corrosion, scale-formation, or other deleterious processes are inhibited in an oil well by providing within the oil well (10) elements comprising an insoluble porous inorganic material in which is absorbed a well treatment chemical. The material may be in the form of particles or beads, for example porous ceramic spheres impregnated with an inhibitor material. Such particles may be injected as proppant particles into the formation through which the well extends, during a fracturing treatment. Alternatively such particles may be packed as a filter bed (26) in a filter (20) comprising two spaced tubular screens (24) between which the filter bed (26) is located. The inhibitor material gradually dissolves in the well fluids during operation, and may for example inhibit corrosion and/or scale-formation.

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Oil Well Treatment

This invention relates to a method for treating an oil well, for example so as to inhibit scale formation, corrosion and/or other deleterious processes, and to an apparatus for performing this method. Priority is claimed from GB 95 03949.1 only in respect of matter not disclosed in GB 2 284 223 A.

For many oil wells the composition of the fluid or fluids in or adjacent to the well is such that it is beneficial to add to the fluid a material to inhibit deleterious properties which the fluid would otherwise exhibit. For example the fluids may be corrosive to the well casing so a corrosion inhibitor would be added; the fluids might form solid hydrates, or emulsions, for which suitable inhibitors might be added; or the fluids might form scale deposits, so a scale inhibitor would be added. A wide variety of different oil-field treatment chemicals, including such inhibitors, are known and used. Inhibitors may be injected as a liquid, or as described in EP 0 193 369 (Exxon) inhibitor may be provided in a polymer bead from which it leaches out into the well fluid. However such injected inhibitors do suffer some disadvantages; and in the case of sloping or horizontal wells the known techniques of injection are difficult to apply successfully, partly because sand or other sediments tend to collect on the lower side of the bore, and because injected liquids flow into the rock strata preferentially in the regions nearest to the well-head.

According to the present invention there is provided a method for treating an oil well, the method comprising providing within the oil well one or more elements comprising an insoluble porous inorganic material containing a chemical treatment agent.

The elements are preferably particles, but instead each element might be a rod, bar, or ring of porous material containing the chemical treatment agent; a plurality of such elements might be spaced apart within an oil well by a support structure such as a tubular filter screen.

In a preferred method the elements are particles arranged to form a filter bed. For example a filter may comprise two generally coaxial tubular filter screens defining a region between them, the region containing a fluid-permeable bed of the particles. The particles may be bonded together to form a coherent, permeable, tubular element, in which case one or both of the filter screens might be omitted. In another preferred method the elements are particles, and the particles are injected as proppant particles into a formation through which the well extends, in the course of a fracturing treatment with a high pressure fluid.

The invention also provides an element comprising an insoluble porous inorganic material containing a chemical treatment agent. The invention also provides a tubular filter in which such elements, in the form of particles, define a filter bed; for example the filter may comprise two generally coaxial tubular filter screens defining a region between them, the region containing a fluid-permeable bed of the particles.

In the preferred method the chemical treatment agent is an inhibitor material; the elements act as a reservoir of inhibitor material, which gradually dissolves into the well fluids during operation. Alternatively the chemical treatment agent may be an absorber material. This absorbs material dissolved in the well fluids which would cause, trigger or aggravate the deleterious processes.

For example the absorber might be an ion exchange material, which would absorb calcium, barium and strontium ions, to suppress scale formation. The chemical treatment agent may be adsorbed or precipitated in the porous element.

The particles are insoluble, so they are structurally unchanged as the inhibitor material leaches out; hence the particles continue to form a filter bed, or to act as proppant particles, even after all the chemical treatment agent has leached out. They might be of porous inorganic oxide or ceramic. For example they may be of an aluminium silicate, silicon carbide, alumina, or silica-based material, such as a bauxite or mullite-based material. In particular the particles might be porous beads of silica- or alumina-based material of size in the range 0.3 mm to 5 mm, preferably between 0.5 and 2 mm, for example about 1 mm, which might be made by a sol-gel process. They may have a porosity of in the range 10% to 30%, for example about 20%. The particles might be of non-spherical shapes, for example angular chips of silica gel. Different types of particles may be used, whether in a filter bed or as proppant particles, some of which might not incorporate any inhibitor material, for example sand grains. The particles forming a filter bed might be bonded together, for example by a resin, to form a coherent but permeable layer, and such a layer may also incorporate reinforcing material such as glass fibres. The resulting coherent particulate layer may be strong enough to be used on its own, or with just one of the filter screens.

The invention is applicable in vertical, inclined and horizontal oil wells. Clearly the external diameter of the tubular filter must be less than the bore of the well, so the filters fit in the oil well; and their length might be for example in the range 3 m to 10 m, this being governed by considerations of convenience for handling, and the requirement to pass around any bends in the oil well. Preferably the tubular filters are of diameter just less than the bore of the oil well, so that they act as a lining for the borehole, and adjacent filters abut each other end-to-end; they may be provided with projecting clips or spigots to ensure alignment of adjacent tubular filters along the length of the well.

The invention will now be further described by way of example only, and with reference to the accompanying drawings, in which:

Figure 1 shows a sectional view through part of an oil well incorporating tubular filters; and

Figure 2 shows a sectional view to a larger scale of an alternative tubular filter to that shown in Figure 1.

Where it is desired to enhance the permeability of oil-bearing strata in the vicinity of an oil well, it is known to inject a fluid into the well such that the pressure at the depth of those strata is sufficient to cause cracking or fracturing of the rocks. The fluid injected into the rocks may contain a dissolved polymer which may be cross-linked to form a gel (so it is of high viscosity), and may include particles of solid material such as sand which are carried into the fractures by the injected fluid. The gel subsequently breaks down, and the particles prevent the fractures closing when the pressure is reduced. Such particles may be referred to as proppant particles. One such fracturing fluid, for example, is described in GB 2 172 007 (Nitto Chemical) and contains guar gum or a derivative of it and a stabilizing compound, while a method for controlling the growth of upward vertical fractures during a hydraulic fracturing process is described in GB 2 137 262 (Dow Chemical).

In one example of the present invention some or all of the proppant particles are porous, and are impregnated with material such as scale inhibitor or corrosion inhibitor. They might be for example, porous silica, aluminium silicate, and/or alumina spheres, and might be made by a number of production routes, for example a sol-gel process, electrofusion, pelletisation and chemical and/or thermal modification of proprietary products.

Another way in which such particles may be provided in an oil well is in the form of a filter bed, as shown in Figure 1 to which reference is now made. Figure 1 shows part of an inclined oil well 10 extending through an oil-bearing stratum 12. The oil well 10 is lined with steel pipe 14 through which are perforations 16. Within the pipe 14 are tubular filters 20 each of diameter 5 mm less than the bore of the pipe 14, arranged end to end, abutting each other (only parts of two filters 20 are shown). The lower end of each filter 20 is provided with a plurality of curved projecting fingers 22 which ensure adjacent filters 20 are aligned. Each filter 20 comprises two wire mesh cylinders 24, coaxial with each other so as to define an annular gap 26 between them of radial width 10 mm, and the gap 26 is filled with a bed of porous silica spheres each of diameter 1 mm. Some of the spheres are impregnated with scale inhibitor and the rest with corrosion inhibitor.

Such porous silica spheres, whether for use as proppant particles or in a filter bed, might be made by the method described in GB 1 567 003, that is by dispersing solid primary particles of silica (produced by a vapour phase condensation method) in a liquid to form a sol, forming droplets of the sol, drying the droplets to form porous gel spheres, and heating the gel to form the porous ceramic spheres. For example silica powder produced by flame hydrolysis and consisting of primary particles of diameter 27 nm were added to water to give a concentration of 100 g/litre, rapidly stirred, and then 100 ml of 0.125 M ammonium hydroxide added to a litre of mixture. This gave a sol in which there were aggregates of the primary particles, the aggregates being of diameter about 0.74 µm. If it is dried to form a gel the porosity may be 80%.

As described in GB 1 567 003, similar sols can be made from alumina powder produced by flame hydrolysis, or from flame hydrolysed titania. When dried, the resulting gels are porous. Furthermore the porosity remains high when the gel is heated to form a ceramic, as long as the temperature is not raised too high - in the case of the alumina gel it must not exceed about 1100°C. Such high porosity particles provide a large surface area onto which inhibitors can be adsorbed.

An alternative method for making the porous spheres is that described in GB 2 170 189 B, in which an organic compound of the appropriate element (e.g. silicon) in dispersed form is hydrolysed, in the presence of a protective colloid. The protective colloid might for example be a polyvinyl alcohol, or a water-soluble cellulose ether. For example a mixture of 40 ml ethyl silicate and 20 ml n-hexanol was added as a thin stream to a stirred aqueous ammoniacal solution of polyvinyl alcohol (50 ml of 5 percent by weight polyvinyl alcohol and 200 ml of 0.880 ammonia) and stirred for half an hour. Small droplets of organic material are dispersed in the aqueous solution, and gel due to hydrolysis. The mixture was then poured into 1 litre of distilled water and left to settle overnight. The supernatant liquid was decanted, the residue re-slurried in 500 ml of distilled water, and steam passed into it for an hour. The suspension was then filtered. The product was microspheroidal silica gel particles smaller than 90 µm.

It will be understood that a variety of different materials can be used for the particles, and that in a single tubular filter 20 there might be a variety of different particles. The particles might be of non-spherical shapes, for example they might comprise angular chips of silica gel; or they might comprise hollow fibres, for example glass fibres, with an inhibitor material precipitated or otherwise impregnated into their bores. Furthermore some of the particles might be of non-porous material.

<u>Example</u>

A method of making porous particles of various shapes, such as round-ended cylinders, spherical beads, and irregular beads, suitable for use as proppant particles or in the tubular filter 20 is as follows:

(i) Ball clay (500g of dry clay) is dispersed in 12 litres of water, then 4500g of flame-hydrolysed silica powder is suspended in the dispersion, and water added to give a total volume of 15 litres. The suspension is spray-dried by disc atomisation to produce a gel powder with particles about 5 µm to 25 µm in diameter.

(ii) A mixture is made of 630 g of the gel powder of stage (i), with 70 g of dry ball clay, 630 g of water, and 300 g of starch (PH101 Avicel); this mixture has the requisite rheology for extrusion, and the added clay gives stronger beads. The mixture is extruded through a profile screen, and the extruded lengths are spheronised (in a NICA Spheroniser S 320) to give particles with the desired shape characteristics. These shaped beads are dried in a fluidised bed dryer, and subsequently fired, typically to 1000°C, to produce porous silica-based ceramic beads, of about 20% porosity, typically about 1 mm in width.

(iii) The porous beads are placed in a pressure vessel, and the vessel evacuated to about 1 mbar (100 Pa) absolute to remove air from the pores. The vessel is then filled under vacuum with a solution of a diethylene-triamine penta(methylenephosphonic acid)-based scale inhibitor (15% by volume of inhibitor, in distilled water containing 2000 ppm Ca^{++} in the form of chloride, at pH 5), and the pressure raised to 200 atm (20 MPa). The vessel is heated to 93°C to promote inhibitor adsorption and precipitation within the porous beads, while being kept at constant pressure, and left in this state for 24 hours. The vessel is then depressurised, drained, and cooled, and the beads removed.

(iv) Water is then removed from within the porous beads by a freeze drying process which produces a dry and easily handled material. This drying procedure allows the impregnation process (iii) to be repeated, to retain still more inhibitor within the pores of the beads.

(v) The dry, impregnated beads may then be coated with a permanent, porous film and/or a non-permanent, non porous coating to control the release of the impregnated chemical treatment agent during bead placement and use.

It will be appreciated that the porous particles may be of different sizes and shapes to those described above, and may be of a wide range of different inorganic materials. It will also be appreciated that the porous particles may be produced by processes other than those described above. Furthermore some or all of the porous particles may contain oil field chemicals different from the inhibitor material discussed above. For example some or all of the particles might comprise hydrogen sulphide scavenging materials, hydrate inhibitors, corrosion inhibitors, wax, asphaltene and other organic deposition inhibitors, biocides, demulsifiers, other types of scale inhibitor and any other oil field treatment chemical.

The mesh cylinders 24 of a filter 20 might be made of a variety of different materials, such as steel; clearly they must be fluid permeable, but instead of wire mesh they might comprise perforated metal plate or a wire-wound structure. They might also be of a non-metallic material. The apertures or perforations through the cylinders 24 must be small enough to prevent the particles from falling out of the annular gap 26, but are desirably not so small as to impede fluid flow significantly.

Referring now to Figure 2 there is shown a sectional view of an alternative tubular filter 30, only a part of one side of the filter 30 being shown, the longitudinal axis of the filter 30 being indicated by the chain dotted line 31. The filter 30 includes a steel tube 32 whose bore is of diameter 45 mm, and whose walls are provided with many perforations 34. The outer surface of the tube 32 is enveloped by a tube 36 of woven fine wire mesh (for example the wires might be of diameter 0.1 mm and be 0.3 mm apart). An annular space 38 of radial width 10 mm is defined between the mesh tube 36 and an outer tube 40, and this space 38 is filled with a bed of porous silica spheres 42 of diameters between 1.5 and 2 mm. The outer tube 40 comprises twenty longitudinal steel strips 44 equally spaced around the circumference of the tube 40, and a helically-wound steel wire 46 each turn of which is welded to each strip 44. The wire 46 is of truncated wedge-shape in cross-section, and at the outer surface of the tube 40 the wire 46 is 2 mm wide and adjacent turns are separated by a gap of width 0.3 mm.

The filter 30 is of overall length 9 m; about 50 mm from each end the mesh tube 36 and the outer tube 40 terminate, and the outer tube 40 is welded to the tube 32. The projecting end portions of the tube 32 do not have any perforations 34, and define threaded joints (not shown) so one filter 30 can be securely joined to another. Hence several filters 30 can be joined end to end to make up a desired length, for example to extend through an oil-bearing stratum.

It should be appreciated that the filters 20 and 30 may differ from those described, while remaining within the scope of the invention. In particular the particles may be of a different size and shape, and the radial width of the annular gap 26 or of the annular space 38 may be different, preferably being between 5 mm and 25 mm. The particles in the gap 26 or in the space 38 may be free-flowing, or may be bound together with a binder such as a resin, as long as the resultant bonded structure remains readily fluid-permeable. Such a coherent, bonded structure may also incorporate glass fibres by way of reinforcement, and may be strong enough to be used without the outer tube 40. Such porous particles containing inhibitors may additionally be packed into the space outside the filter 20 or 30, between the filter 20, 30 and the inner surface of the liner pipe 14. The invention may also be practised using a conventional filter, by packing porous particles containing inhibitor into the space around the filter, between the filter and the inner surface of the liner pipe 14. And a filter 20 or 30 may be installed after provision of proppant particles as described earlier.

In the embodiments described above with reference to the drawings the tubular filters are located within the part of the oil well 10 in which the liner is perforated. Alternatively, tubular filters may be connected to the lower end of the production tubing; for example three 9 m long tubular filters of structure similar to those of Figure 2 and of external diameter the same as the production tubing (for example 125 mm) might be joined end to end and used to form the lower end of the production tubing string.

Claims

1. A method for treating an oil well the method comprising providing within the oil well one or more elements comprising an insoluble porous inorganic material containing a chemical treatment agent.

2. A method as claimed in Claim 1 wherein at least one element is a rod, bar, or ring of porous material containing the chemical treatment agent.

3. A method as claimed in Claim 1 wherein the elements are particles arranged to form a tubular filter bed.

4. A method as claimed in Claim 3 wherein a filter comprises two generally coaxial tubular filter screens defining a region between them, the region containing the filter bed of the particles.

5. A method as claimed in any one of the preceding Claims wherein a tubular filter screen is installed within the oil well, the method comprising injecting particles into a gap outside the filter screen at least some of the injected particles being said elements.

6. A method as claimed in any one of the preceding Claims wherein at least some of the elements are particles, and wherein a formation through which the well extends is subjected to a fracturing treatment with high pressure fluid and proppant particles, at least some of the proppant particles being the said elements.

7. A method as claimed in any one of Claims 3 to 6 wherein the particles are porous beads of silica-, aluminium silicate-, or alumina-based material of size in the range 0.3 mm to 5 mm, preferably between 0.5 and 2 mm.

8. A tubular filter for use in the method as claimed in Claim 4, comprising two generally coaxial tubular filter screens defining a region between them, the region containing a fluid-permeable bed of particles comprising an insoluble porous inorganic material containing a chemical treatment agent.

9. Oil well treatment elements comprising an insoluble porous inorganic material containing a chemical treatment agent, suitable for use in a method as claimed in any one of Claims 1 to 7.

10. Elements as claimed in Claim 9 wherein the chemical treatment agent is selected from scale inhibitor and corrosion inhibitor.

11. A method of making elements for use in a method as claimed in any one of Claims 1 to 7 wherein porous inorganic elements are enclosed in a vessel, the vessel is evacuated, and the vessel is then injected with the chemical treatment agent; the elements are then removed from the vessel and are freeze-dried.

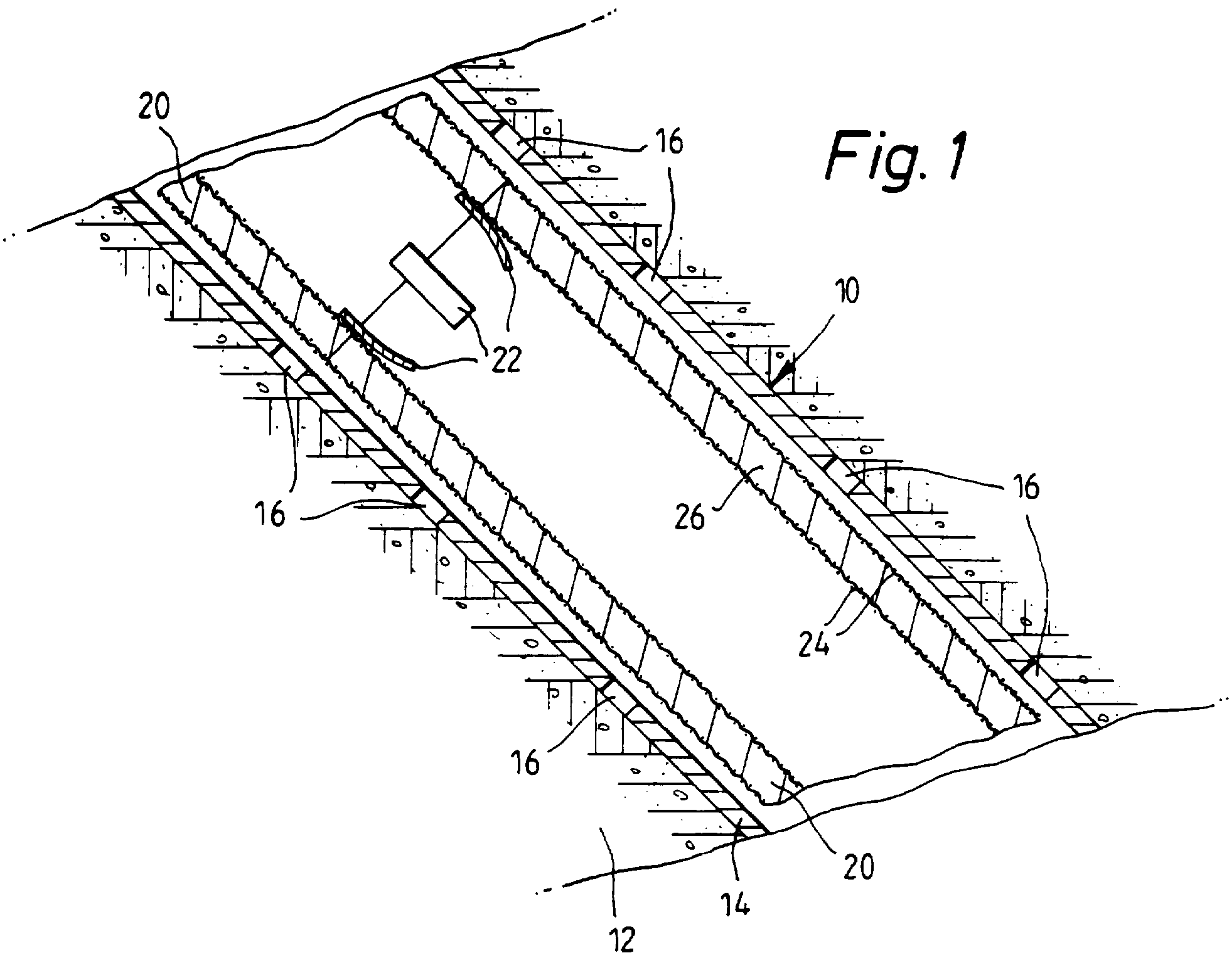
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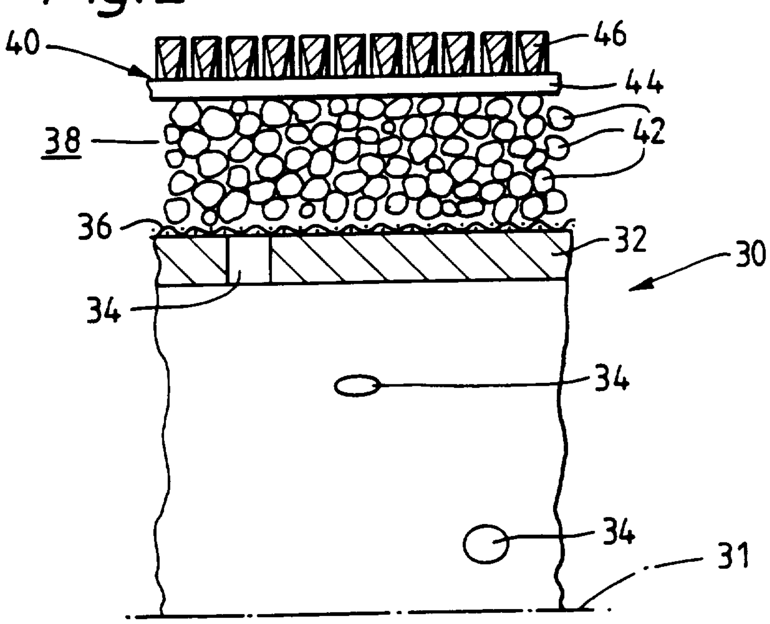
Fig. 1

Fig. 2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INTERNATIONAL SEARCH REPORT

Inter nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B37/06 E21B41/02

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Week 9419 Derwent Publications Ltd., London, GB; AN 94-158056 & SU,A,1 799 893 (IVASHEV V I) , 7 March 1993	1,9,10
Y	see abstract ---	2-6,8
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
3 November 1995	14 -11- 1995

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INTERNATIONAL SEARCH REPORT

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