Method and apparatus for measuring weak magnetic fields.

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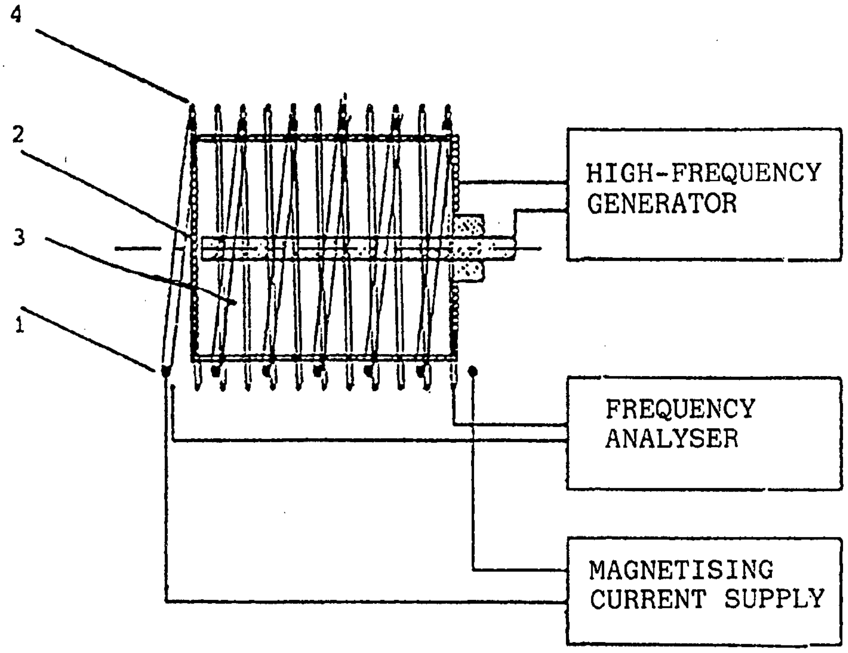

(57) Abstract

When measuring weak magnetic fields, a container containing a medium, such as a solution containing a stable radical, is placed in a polarising magnetic field, which is essentially at right angles to the field to be measured. The polarising field is interrupted rapidly, the interruption being preceded by the impression of a high-frequency electromagnetic signal. The frequency of the signal corresponds to the resonance frequency of the free electron spin. The frequency and amplitude of the precessing nuclei, which are a function of the strength of the measured field, are recorded by a pick-up coil.

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Method and apparatus for measuring weak magnetic fields

The invention refers to the measurement of weak magnetic fields by means of Nuclear Magnetic Resonance (NMR).

Magnetometers, instruments used to measure static magnetic fields, are used in many areas, including physics, geology (including oil and mineral exploration), archaeology and military applications. Due to the nature of the application, these are often portable, battery-powered instruments, in which a combination of low current consumption and high sensitivity is of major importance.

In performing measurements of this type, a known method is to use magnetometers of a type in which a container of liquid with a high hydrogen proton content, such as water or a hydrocarbon, is exposed to a strong magnetic field, or polarising field, which is impressed basically at right angles to the weak magnetic field to be measured. The polarising field is impressed for a short period, such as 2 seconds, and is then interrupted very rapidly, for example within a few hundred microseconds. The container is surrounded by a pick-up coil to record changes in the magnetic moment of the liquid.

The magnetisation of the protons in the liquid will be aligned with the impressed magnetic field under the influence of the latter. However, when the polarising field is interrupted rapidly, the magnetisation of the protons will become aligned slowly with the weak magnetic field as it precesses, but at an instantaneously established precession frequency determined solely by the weak field to be measured. Since the polarising field is absent, the precessing magnetic field will induce a damped electrical oscillation in the pick-up coil at a frequency directly proportional to the strength of the field to be measured. The amplitude of the signal is dependent, among other factors, on the strength of the polarising field, the nuclear magnetic properties of the liquid, and the relationship between the directions of the polarising field and the field to be measured. The amplitude of the signal decreases and the signal is absorbed by the inherent noise of the measuring system after a few seconds according as the magnetisation of the protons is aligned with the weak field to be measured.

To achieve satisfactory frequency determination and, thereby, satisfactory measurement of the magnetic field strength, it is desirable that the amplitude of the voltage induced in the pick-up coils should be high which, all things being equal, requires a strong polarising field to align the spinning moments of a large number of protons with it. However, a strong polarising field is synonymous with an undesirably high power consumption, which increases as the square of the field strength. In practice, the typical polarising field strength is 100 Gauss which, with a terrestrial magnetic field strength of 0.5 Gauss, yields an amplification factor of 100/0.5 = 200 at a power consumption of 40 W.

Another known method is based on the use of a solution of radicals, in which the hydrogen proton nuclear spin of the solution is coupled to the free electron spin of the radicals through the magnetic dipole coupling, and in which the free electron spin of the radicals is also and simultaneously related to a nuclear spin, typically that of a nitrogen atom, within one and the same radical molecule (Fermi coupling).

If a solution of radicals of this type is exposed to a weak magnetic field, such as the earth's magnetic field, the spinning moment of the protons will align itself parallel to the weak magnetic field, while the electron spin will be similarly aligned, but in the opposite direction, so that weak magnetisation is established. The solution, which is surrounded by a pick-up coil, is exposed to high-frequency electromagnetic waves in resonance with the electron spin of the free radicals, producing the phenomenon known as the Overhauser effect. This induces an amplified, continuous oscillation of the pick-up coil at a frequency corresponding to the strength of the weak magnetic field to be measured. The electromagnetic field should preferably be impressed at right angles to the weak magnetic field to be measured.

The electromagnetic radiation influences the free electron spin in such manner that it essentially becomes saturated, which is to say that the magnetic moment of the electron spin in the opposite direction to the weak magnetic field falls almost to zero. Due to the dipole connection between the electron spin and the proton nuclear spin, the proton nuclear spin of the solution is now aligned in the original direction of the electron spin; in other words, in the opposite direction to the weak magnetic field to be measured.

This Overhauser effect may best be illustrated by considering the quantum mechanics processes which occur in a hydrogen proton-bearing solution containing a radical with a free electron spin. Due to the rotation of the charged proton nuclei, the hydrogen protons possess a magnetically positive dipole moment which, because of the quantum mechanics, may assume two energy states, a basic state and an excited state, either with or without an external magnetic field. A greater or lesser proportion of the protons in the equilibrium state may be excited depending on the strength of the magnetic field. At typical magnetic field strengths, the number of protons in the basic state will almost equal the number in the excited state (weak magnetisation) due to the low excitation energy. As in all other quantum mechanics processes, this is a matter of dynamic equilibrium, in which the individual proton constantly changes state due to energy interchange with another proton in the other energy state. This interchange, which takes place predominantly by Brownian movement of the molecules, can be shown to be a relatively slow process, typically of the order of seconds.

If the strength of the external magnetic field is altered, a new equilibrium state will be established slowly as a number of protons change from one energy level to another.

If a radical with a free electron possessing a significant magnetic dipole moment (high excitation energy), but of opposite sign to the hydrogen proton, is added to the solution, the solution will assume a new overall equilibrium state as the dipole moments of the electrons interact with the dipole moments of the protons in such manner that there is a slight excess of electron dipoles in the excited state, reflecting the weak magnetisation in the weak field.

The impression of an intensive, high-frequency electromagnetic field at a frequency corresponding to the excitation energy of the electron dipoles will now cause a shift in the electron dipole distribution between the two energy levels, since there will now be as many electron dipoles in the basic state as in the excited (or 'saturated') state. As a result of the quantum mechanics equilibrium coupling between proton dipoles and electron dipoles, the shift in the electron dipoles, which have a much higher excitation energy than the protons, will cause an even more pronounced shift in the number of protons in the basic and excited states, resulting in over-population of the latter and producing strong magnetisation or amplification. This strong magnetisation, which does not correspond to the strength of the weak, external magnetic field will, during precession and at a frequency proportional to the strength of the weak magnetic field, align itself with the latter, which can result in the generation of an amplified signal (MASER effect) in a pick-up coil surrounding the solution.

In quantum mechanics terms, the maximum magnetisation amplification factor (Mf) which can be achieved in this manner is

$$Mf = 1/2*(Ee/Ep)*SAT-1$$

where Ee is the excitation energy of the electron spin, Ep is the excitation energy of the proton spin and SAT is the degree of saturation of the electron dipoles. This shows clearly that the amplification may be increased provided that the excitation energy of the electron dipoles can be increased. In the case of a free electron which is not coupled with a nucleus i.e. where a Fermi coupling is not present, the ratio Ee/Ep is 658, giving a maximum magnetic amplification factor of 329.

If a Fermi coupling is present between the electron spin and nuclear spin within the same molecule, the excitation energy of the electron dipole in a low external magnetic field will be considerably higher than in the uncoupled state (known as the 'hyperfine coupling constant') since, in practice, the Fermi coupling acts as a local, polarising magnetic field of, for example, 15 Gauss opposing the electron spin. This high (in relation to the weak external magnetic field) hyperfine coupling constant will produce an extremely high amplification factor in accordance with the above formula. Typical amplification factors of 1500, at a power consumption of about 2 W, have been achieved in practice.

Although higher amplification factors are achievable in theory, the value is limited, in weak fields, by short electron relaxation times caused by the high hyperfine coupling constant. These short relaxation times increase the width of the electron resonance lines, increasing the power consumed in generating the high-frequency field. In addition, these wider lines increase the resonance overlap, which can be shown to produce a reduced Overhauser effect.

However, since there is a need for even more accurate measurement of weak magnetic fields than can be achieved with the methods afforded by existing technology, the purpose of the present invention is to provide a method, and an apparatus for performing the said method, which will permit such measurements to be carried out without increasing the power consumption. This aim is achieved by means of a method in accordance with the invention, which is characterised by the provisions of the characterising section of patent claim 1, and using an apparatus for performing the said method, which is characterised by the arrangement specified in the characterising section of patent claim 5.

The invention affords significantly improved results by using a particular combination of the two methods described earlier, in that when measuring the weak magnetic field, a container with a special medium, such as a liquid containing a stable radical, is placed in a polarising magnetic field arranged essentially at right angles to the weak magnetic field to be measured. It is further assumed that the polarising field can be interrupted quickly so that the proton spin is aligned with the weak magnetic field. Prior to this interruption, the medium in the container is exposed, in the presence of the polarising field, to a high-frequency electromagnetic signal corresponding to the resonance frequency of the free electrons.

Further improved results can be achieved using two measuring arrangements, each with an individual container, the strong homogeneous magnetic fields being aligned in opposite directions to eliminate magnetic interference and, finally, by using two or three measuring arrangements at right angles to each other.

The invention is described in detail below with reference to the appended drawings, of which

Fig. 1 is a schematic representation of an apparatus in accordance with the invention and

Fig. 2 is a schematic representation of another embodiment of the invention.

If a container of a medium containing constituents with a free electron spin and constituents with a nuclear magnetic spin, the nuclear magnetic spin being coupled to the free electron spin by a purely magnetic dipole coupling, is exposed to a strong polarising magnetic field, the relative distribution of the quantum mechanics energy levels of the electron spin moments and the nuclear spin moments will adapt itself to both the direction and strength of the polarising magnetic field, in such manner that the magnetisation will correspond to the strength of the impressed field. In this manner, as described above, an amplification factor of 200 will be achieved when measuring terrestrial magnetic fields, on interrupting a polarising field of 100 Gauss.

If the container is exposed, in the presence of the polarising magnetic field, to high-frequency electromagnetic radiation of a frequency corresponding to the resonance frequency of the electron spin and impressed at right angles to the polarising field, the electron spin will become essentially saturated. Due to the dipolar coupling between the electron spin and the nuclear spin, the electron spin distribution in the solution will now be altered (Overhauser effect) in such manner that the nuclear magnetisation will be aligned in opposition to the polarising field and at right angles to the weak, external magnetic field to be measured. Since the electron dipoles are now influenced by the strong polarising field, the excitation energies of the dipoles will be increased in direct proportion to the strength of the polarising field, causing a large number of nuclear dipoles to shift between the energy levels and resulting in strong magnetisation of the solution.

If both the polarising magnetic field and the high-frequency electromagnetic field are interrupted suddenly and simultaneously, the nuclei will precess into the weak magnetic field at a frequency proportional to the strength of that field and with an amplitude proportional to its projection on the normal to the polarising field. Both the frequency and amplitude of nuclear precession can be recorded with the aid of a pick-up coil surrounding the container.

A particularly advantageous configuration can be achieved using a low-viscosity solution with a high hydrogen proton concentration, containing a radical with a free electron spin which is not coupled to a nucleus in the molecule itself (i.e. no Fermi coupling), or a radical with a nuclear magnetic spin, in which the said nuclear magnetic spin is coupled to the free electron spin through a pure magnetic dipole coupling and in which the line width at the high-frequency electron transition is narrow, since this ensures extremely efficient utilisation of the high-frequency electromagnetic radiation. A hyperfine coupling between the electron and a nucleus in the radical causes the resonance frequency of the electron spin to be split into several levels, and the high-frequency electromagnetic field thus contains several resonance frequencies.

If the medium used is a hydrogen proton-based nuclear magnetic type containing a high concentration of radicals with a free electron without a Fermi coupling, it is theoretically possible to achieve an overall amplification factor of 329*100/0.5, or 65,800, when using the invention to measure the earth's magnetic field with a 200 Gauss polarising field. In practice, an Overhaus-based amplification factor of 200, resulting in an overall amplification factor of approx. 40,000 at a power consumption of about 1 W, may be expected when using a solution volume of a few millilitres and a radical concentration of a few millimoles.

Fig. 1 shows an apparatus in accordance with the invention, which is provided with a device 1, such as a coil, for transmitting a suitably strong and homogeneous magnetic field, which device is capable of interrupting the impressed field within a fraction of a millisecond. The strong magnetic field shall be aligned essentially at right angles to the weak magnetic field to be measured. The apparatus is, furthermore, provided with an arrangement for mounting a container 2 containing a special medium 3 in the strong, polarising magnetic field. A high-frequency electromagnetic field from a variable frequency generator is impressed at right angles to the polarising magnetic field and, finally, the container 2 is surrounded by a pick-up coil 4 connected to recording equipment. The direction of the field in the coil is essentially parallel to that of the polarising magnetic field.

Fig. 2 shows another embodiment of the invention featuring two containers 2, with respectively opposed polarising magnetic fields and pick-up coils 4, which arrangement affords the particular advantage that any induced electromagnetic interference from the surroundings is equalised by 'common mode rejection'.

Patent claims

1. Method for measuring weak magnetic fields by means of nuclear magnetic resonance, characterised in that a medium with a nuclear spin, containing a constituent with a free electronic spin moment, is placed in an homogeneous, polarising magnetic field which can be interrupted rapidly, and in that prior to interruption of the magnetic field, the medium is exposed to high-frequency electromagnetic oscillations of a frequency corresponding to the resonance frequency of the free electron spin, and in that signals from a pick-up coil surrounding the medium are received and recorded.

2. Method in accordance with patent claim 1, characterised in that the medium is a hydrogen proton-bearing solution containing a stable radical with a free electronic spin moment.

3. Method in accordance with patent claims 1 and 2, characterised in that the hydrogen proton-bearing solution is a low-viscosity solution containing a stable radical with a free electron spin, which is not coupled to any other nucleus in the molecule, or in which the Fermi coupling giving rise to the hyperfine coupling is extremely small or non-existent.

4. Method in accordance with patent claims 1-3, characterised in that it employs a low-viscosity hydrogen proton-bearing solution containing a stable radical with a free electron spin with a spin quantum number of 1/2, which is not coupled to any other nucleus in the molecule, or in which the Fermi coupling giving rise to the hyperfine coupling is extremely small or non-existent, which radical has a narrow line width at the high-frequency electron transition of less than 1 Gauss, and in that the homogeneous, polarising magnetic field is greater than 1 Gauss.

5. Apparatus for performance of the method in accordance with patent claims 1-4, characterised in that it comprises a device (1) for

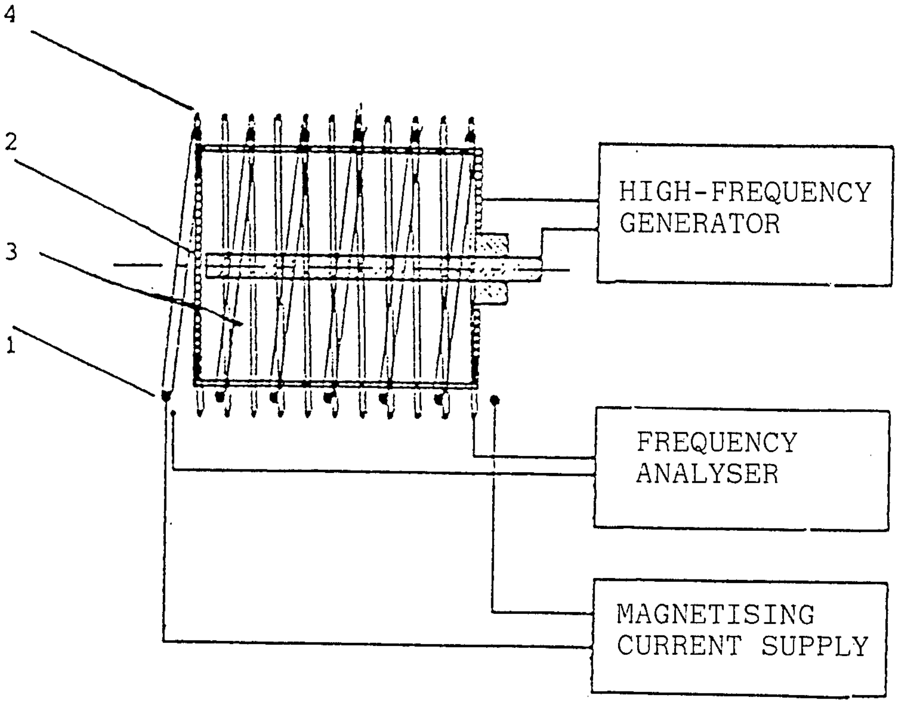
producing a strong, homogeneous magnetic field, which is arranged to permit rapid interruption of the field, a device for mounting a test container (2) in the strong, homogeneous magnetic field, an oscillator to produce a high-frequency alternating field, and which is connected to a resonator, from which high-frequency electromagnetic waves are transmitted in a direction essentially at right angles to the strong, homogeneous magnetic field, and a pick-up coil (4) surrounding the container and connected to apparatus for recording signals from the coil, and in that the direction of the field in the pick-up coil is essentially parallel to the strong magnetic field.

6. Apparatus in accordance with patent claim 5, characterised in that the device (1) for transmitting a strong, homogeneous magnetic field, and which is arranged to permit rapid interruption of the field, consists of a single coil or a combination of several coils.

7. Apparatus in accordance with patent claims 5 and 6, characterised in that the pick-up coil (4) is contained within the aforesaid coil or combination of several coils, or forms part thereof.

8. Apparatus in accordance with patent claims 5-7 employing two sets of test containers arranged in line, characterised in that the strong, homogeneous field in aligned in opposite directions in each container (2) and that the pick-up coils (4) surrounding each container (2) are wound in opposite directions.

9. Apparatus in accordance with patent claims 5-8, characterised in that two or three measuring arrangements at right angles to each other are used.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2
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1
HIGH-FREQUENCY GENERATOR
FREQUENCY ANALYSER
MAGNETISING CURRENT SUPPLY

Fig. 1

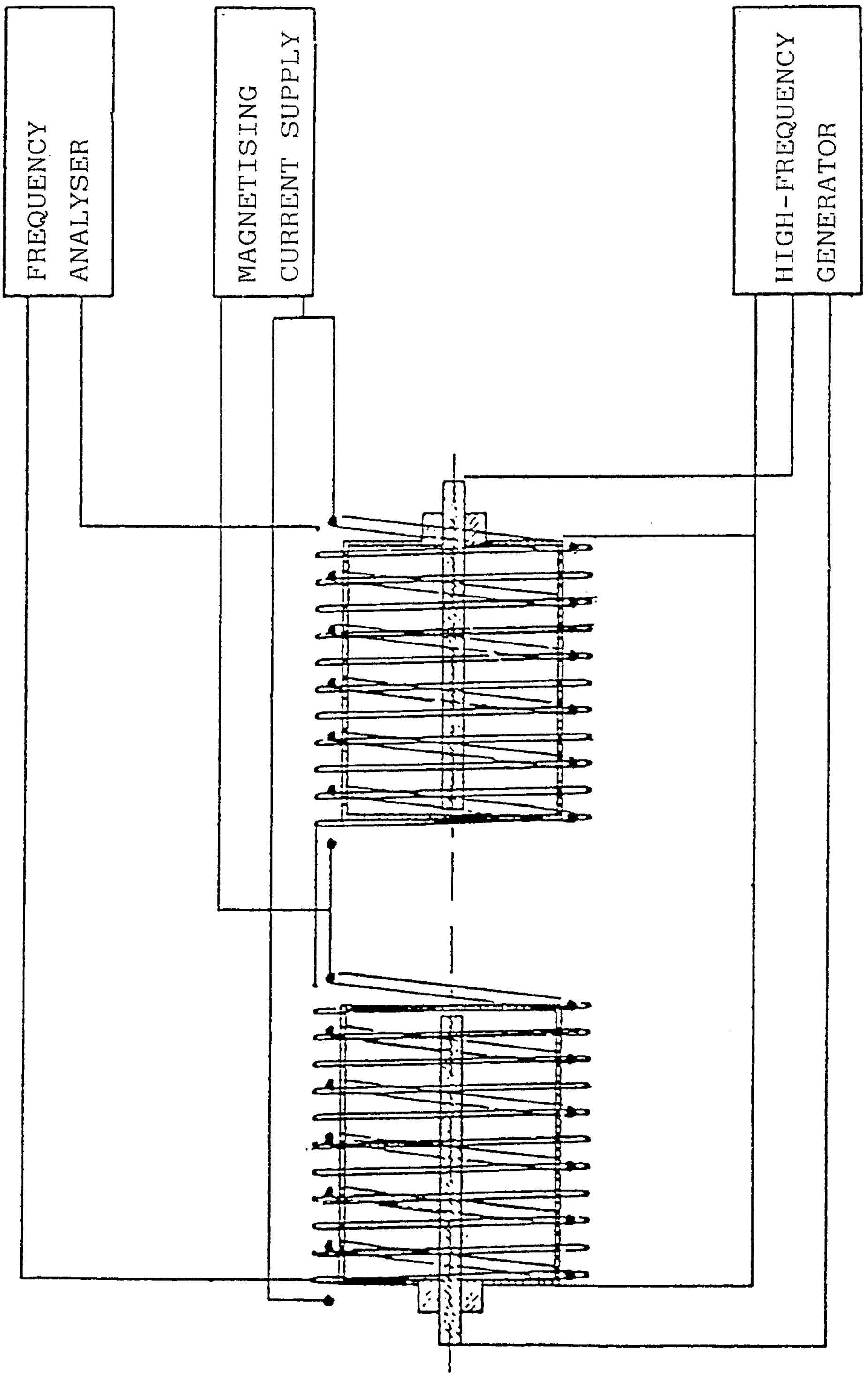
FREQUENCY ANALYSER
MAGNETISING CURRENT SUPPLY
HIGH-FREQUENCY GENERATOR

Fig 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 94/00480

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01R 33/62 // G01R 33/24
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)

IPC6: G01R

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

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A1, 9204640 (NATIONAL RESEARCH DEVELOPMENT CORPORATION), 19 March 1992 (19.03.92), whole document --	1-9
X	EP, A2, 0409292 (HAFSLUND NYCOMED INNOVATION AB), 23 January 1991 (23.01.91), whole document --	1-9
A	US, A, 4891593 (JOHN LURIE ET AL), 2 January 1990 (02.01.90), abstract --	1-9
A	US, A, 4682106 (DIMITRIOS VATIS ET AL), 21 July 1987 (21.07.87), abstract --	1-9

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5189370 (HEINRICH KOLEM ET AL), 23 February 1993 (23.02.93), abstract -- ---------	1-9

INTERNATIONAL SEARCH REPORT
Information on patent family members

25/02/95

International application No.
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