PATENT SPECIFICATION

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(54) NUCLEAR MAGNETIC RESONANCE SENSORS

(71) We, INSTITUT KIBERNETIKI AKADEMII NAUK ESTONSKOI SSR., a USSR corporate body of bulvar Lenina, 10, Tallin, USSR., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to nuclearmagnetic resonance NMR radiospectrometry, and more particularly to sensors that generate NMR signals (hereinafter referred to as NMR sensors).

The invention is suitable for use in high-resolution NMR spectrometers used in the investigation of solid bodies. Particular applications of the invention are concerned with the physico/chemical investigation of the structure of organic compounds and polymers.

According to the present invention there is provided a sensor arranged to generate high resolution nuclear magnetic resonance signals in respect of solid test samples, comprising: a radio-frequency NMR coil carried by a support member having a central hole bounded by an internal surface symmetrical about an axis of rotation; means for providing an external polarizing magnetic field; a hollow rotor which in use is positioned completely within said support member of said coil, said rotor having an external surface symmetrical about said axis and being adapted to accommodate a solid test sample arranged coaxially therewithin, said rotor being provided with means for producing rapid rotation thereof, up to 300,000 r.p.m., and said axis of rotation being inclined at an angle with respect to the direction of the induction vector of the external polarizing magnetic field; a substantially uniform gap being defined between said internal surface of said support member and said external surface of said rotor; and means for forming a generally tubular shpaed gas bearing in said gap between said internal surface of said support member and said external surface of said rotor by a compressed gas stream delivered radially into said gap, said rotor being located wholly by said gas bearing.

Preferably, the support member may be cylindrical, with the rotor being a hollow cylinder having a detachable conical lid on at least one of its ends, the external surface of the detachable conical lid being provided with indentations serving as radial turbine blades, and with passages provided in the support member through which, in use, one gas stream is fed into a gap between the rotor and the support member and another gas stream is fed to the radial turbine blades.

Preferably, means are provided whereby, in use, the compressed gas delivered into the gap may be maintained at a temperature required for thermostatic control of the test sample.

The NMR sensor of the invention makes it possible to considerably increase the useful volume of the test sample, since the complete width of the gap of an iron magnet or the central hole of a superconducting magnet, and also the volume of the radio-frequency NMR coil, are utilized more effectively. This results in an increase in both the sensitivity and resolution of the NMR spectrometer in use. The constant width of the gap in the gas bearing ensures stable positioning and rotation of the sensor rotor. The rotor with the test sample is easy to remove and replace. The rotor can be made of inorganic materials such as ceramics, glass or quartz. Such a rotor can be used for measuring high resolution NMR spectra obtained from compacted, powder and suspended solid bodies.

Other features and advantages of the invention will appear from the following description of a preferred embodiment thereof in conjunction with the accompanying drawings in which:

Figure 1 is a longitudinal section of an NMR sensor, according to the invention;

Figure 2 is a diagrammatic top view of the NMR sensor of Figure 1;

Figure 3 is an isometric view of the NMR sensor of Figures 1 and 2 with a radio-frequency NMR coil having two windings.

The NMR sensor shown in the drawings comprises a radio-frequency NMR coil wound on a former 2 made of a non-magnetic material, for example, ceramics, glass or quartz, having a relatively small coefficient of thermal expansion.

The frame 2 has a central through hole 3, which is cylindrical in the described embodiment. A rotor 4, which is a hollow cylinder, is arranged within the hole 3 coaxially therewith. At least one end of the rotor 4 is provided with a detachable lid 5 made for example, of PTFE. Figure 1 illustrates the rotor 4 provided with two lids 5 on its respective ends. The lids 5 are shown as being conical, but cylindrical lids are also possible. A test sample 6, for example, an organic compound having the nuclei of ^{13}C, is introduced into the internal cavity of the rotor 4.

In the illustrated embodiment, a rotation means for the rotor is provided on the external surfaces of the lids 5 in the form of shaped indentations 7 (cut, for example, by milling); these shaped indentations 7 are used as the blades of small radial turbines. Tangential passages 8 are provided in the coil former 2 opposite the indentations 7, to allow a gas stream to pass to the turbine blades.

A gap 9 is formed between the external cylindrical surface (the surface of revolution) of the rotor 4 and the cylindrical surface of the hole 3 (the internal surface of the frame 2). Compressed gas is delivered into the gap 9 through passages 10 to create the gas pillow of a gas bearing provided by the above-mentioned cylindrical surfaces. Means are preferably provided to permit the compressed gas to be maintained at a temperature required for thermostatic control of the test sample 6, for example, within a range from −150 to +200°C.

A housing 11 made of non-magnetic material accommodates the coil former 2 with the coil 1 and rotor 4. The housing 11 has vents 12, 13 which connect, together with the passages 8, 10, the internal cavity of the coil former 2 with a compressed gas source (not shown in the drawings). Also, the housing 11 has at its ends vents 14 through which the internal cavity of the coil former 2 is connected with an outer space.

A conduit 17 (Figure 2) is provided through which gas may be fed to vent 12 and thus into the gas bearing gap 9. A further conduit 18 is provided through which gas may be fed to vents 13 and thus to the turbine passages 8.

Figure 2 shows the NMR sensor attached to a screening mounting 15 which is disposed in the gap 16 of an electromagnet, illustrated diagrammatically by its poles N and S, which provides a steady magnetic field. The sensor is fixed in the screening mounting 15 so that the axis of revolution of the rotor 4 is directed at an angle φ, close to 54°44′, to the induction vector H_0 of the steady magnetic field. Arrows V and H_0 are used to indicate, respectively, the direction of the axis of revolution of the rotor 4 and that of the induction vector H_0 (see the top of Figure 2).

Though Figure 2 illustrates the NMR sensor in the gap of a conventional electromagnet, it is possible to use that sensor in conjunction with a superconducting magnet. It is necessary in this case that the shape of the screening mounting 15 be in correspondence with the central hole of the superconducting magnet.

In the described embodiment, the radio-frequency NMR coil comprises two windings having their turns at right angles to each other. Figure 3 shows the NMR sensor of the invention with two such windings 1′ and 1″, the winding 1′ being used as an excitation field winding and the winding 1″ being used as a sensing winding.

The NMR sensor according to the invention operates as follows.

The sensor, with a test sample disposed in its rotor, and attached to the screening mounting 15 (Figure 2), is set in the gap 16 of the electromagnet N-S.

Compressed gas from a gas source (not shown in the drawings), after it has been subject to thermostatic control when necessary, is passed through the conduit 17 into the gap 9 of the gas bearing to create a gas pillow. Another stream of compressed gas passes through the conduit 18 to strike the turbine blades (indentations 7) of the rotor and this causes the rotor 4 to rotate rapidly and steadily. The rotational speed of the rotor 4 is controlled by changing the pressure of the gas delivered to the turbine blades through the conduit 18. A variable frequency generator (not shown in the drawings) produces a radio-frequency voltage, continuous-wave or pulsed, which is applied to the radio-frequency NMR coil 1. This results in a variable magnetic field that acts on the test sample. When the generator frequency is brought into coincidence with the Larmor precession freqeuncy of the nuclei under investigation, the radio-frequency NMR coil 1 generates an NMR signal that is transferred to a receiving equipment (not shown in the drawings) through the coaxial cable 19.

The embodiment of Figure 3 provides for good isolation of the NMR signal induced in the winding 1″ from the radio-frequency voltage applied to the winding 1′.

To replace the test sample, proceed as follows: withdraw the screening support 15 with the sensor from the gap 16; withdraw the rotor 4 from the central hole 3 of the frame 2; take off one of the lids 5; and replace the test sample with a new one.

Test results show that the sensor rotor

rotates steadily at a rotational speed of up to 5 kHz — i.e. up to 300,000 r.p.m. (at temperatures ranging from −150 to +200°C) and in this case its axis of revolution may adopt any desirable inclination to the induction vector to the external magnetic field. This allows for the use of the proposed NMR sensor in conjunction with NMR spectrometers that employ very diverse magnets, including the superconducting magnets. The rotor can rotate steadily for long periods so that its rotational speed is changed by not more than 1% per hour. This feature tends to broaden the capabilities of the NMR method of investigation of solid bodies, since NMR signals can be accumulated for long periods and radio-frequency pulses can be modulated in synchronism with the speed of rotation of the rotor.

As compared to a known NMR sensor with a gas bearing, the NMR sensor of the invention provides at least a 3-fold increase in sensitivity, with the result that the measurement time may be decreased ten-fold approximately.

Used in conjunction with high-resolution NMR SPECTROMETERS, THE PROPOSED NMR sensor is suitable for investigation of molecular structure and microdynamic properties of solid bodies such as polymers, plastics and other organic compounds. This can be done in laboratories and under industrial conditions as well (for example, production control of polymeric materials in chemical industry).

WHAT WE CLAIM IS:–

1. A sensor arranged to generate high resolution nuclear magnetic resonance signals in respect of solid test samples, comprising: an radio-frequency NMR coil carried by a support member having a central hole bounded by an internal surface symmetrical about an axis of rotation; means for providing an external polarizing magnetic field; a hollow rotor which in use is positioned completely within said support member of said coil, said rotor having an external surface symmetrical about said axis and being adapted to accommodate a solid test sample arranged coaxially therewithin, said rotor being provided with means for producing rapid rotation thereof, up to 300,000 r.p.m. and said axis of rotation being inclined at an angle with respect to the direction of the induction vector of the external polarizing magnetic field; a substantially uniform gap being defined between said internal surface of said support member and said external surface of said rotor; and means for forming a generally tubular shaped gas bearing in said gap between said internal surface of said support member and said external surface of said rotor by a compressed gas stream delivered radially into said gap, said rotor being located wholly by said gas bearing.

2. A sensor in accordance with claim 1, wherein: said internal surface of said coil support member is cylindrical; said rotor is a hollow cylinder of symmetrical form having conical lids at its ends; one at least of said lids being detachable; said means for producing said rotation comprises shaped indentations formed on the external surfaces of said lids and serving as radial turbine blades for cooperation with a first gas stream fed thereto; said conical lids serving to stabilize the position of said rotor along said axis of rotation in both directions; said support member having a first set of passages, through which said first gas stream is arranged to be fed to said turbine blades, and a second set of passages, through which another gas stream, distinct from said first gas stream for said gas turbine, is arranged to be fed radially into said gap between said rotor and said coil support member.

3. A sensor in accordance with claims 1 or 2, wherein said angle of said axis of rotation to the direction of the induction vector of the polarizing magnetic field is close to 54°44′.

4. A sensor in accordance with claims 1, 2 or 3, wherein means are provided for said compressed gas stream delivered into said gas bearing to be maintained at a temperature required for thermostatic control of said test sample in said rotor.

5. A sensor in accordance with claim 4, wherein said temperature maintaining means is arranged for said compressed gas to be temperature controlled within a range from −150° to +200°C.

6. A sensor in accordance with claim 2 or any one of claims 3, 4 or 5 appended to claim 2, wherein the rotational speed of said rotor is arranged to be controlled and stabilized by varying the pressure of said first gas stream, fed to said radial turbine blades.

7. A sensor in accordance with any preceding claim, arranged for the rotation of said rotor to be maintained at up to 300,000 r.p.m. with said axis of rotation tilted at said inclined angle with respect to the induction vector of the external polarizing magnetic field.

8. A nuclear magnetic resonance sensor substantially as hereinbefore described with reference to the accompanying drawings.

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1594042 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

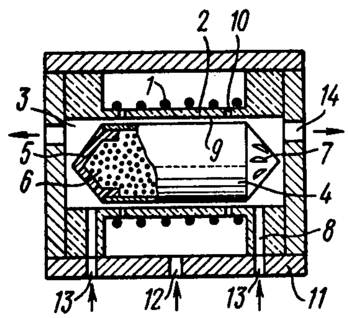

FIG.1

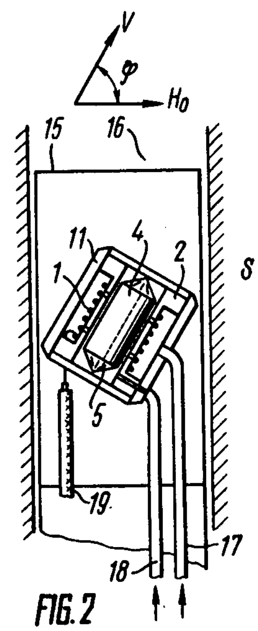

FIG.2

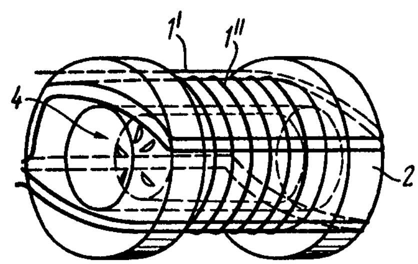

FIG.3