High Resolution Nuclear Magnetic Resonance Spectroscopy at Elevated Temperatures

J. N. Shoolery and John D. Roberts

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and blown fuses required three to five minutes of the operator's time.

As a result, an automatic centrifuge starter was developed which requires only that the user set the maximum speed or voltage end point, set the centrifugation time-clock, turn it on, and give it no further attention. The starter speeds up the centrifuge with reproducible acceleration rates to a predetermined point as fast as the current limitations of its motor will allow, maintains the motor at the specified speed, and finally shuts off power at a predetermined time.

Figure 1 shows the schematic diagram of the starter which is housed in a $7\times7\frac{3}{4}\times12$-in. cabinet. The starter operates as follows: (1) The timer is set to the desired running time. (2) The speed control variac is turned to zero, and its speed limit actuating arm is set at the desired final speed. (3) The motor current limit is set for the particular centrifuge motor by the rheostat (5 to 10 amp). (4) The circuit-breaker-type switch is turned on which applies power to the speed control and its drive motor. (5) The drive motor increases the voltage to the centrifuge via a friction drive coupled to the variac (one model used friction drive wheels, the other a rubber drive belt over suitable pulleys). The motor drives the variac arm at a rate of 6°/sec until the rated motor current is reached. (6) At this point, the current-limiting relay contacts open. This causes the speed control drive motor to stop, allowing the centrifuge to continue accelerating at constant voltage and build up a counter-emf to reduce the motor current demand. With reduced current, the relay again permits the variac output to increase. (7) Finally, the speed limit switch is actuated by the adjustable arm attached to the speed dial which stops the speed control motor entirely. The limit switch actuating arm is coupled to the speed control shaft with a friction drive so that it can be adjusted by hand but will not slip when actuating the limit switch. (8) At the preset time, power is disconnected from the starter and centrifuge.

It should be noted that the speed control and its drive motor must be so coupled that the speed control may be manipulated

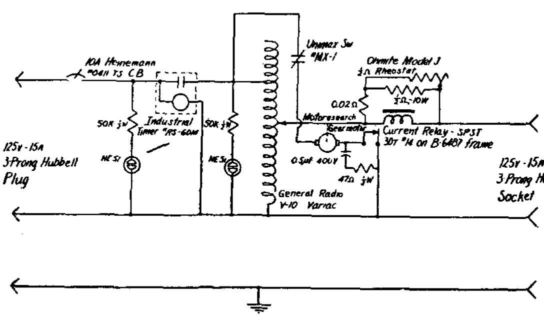

FIG. 1. Schematic diagram of automatic centrifuge starter. NE-51 pilot lamps are mounted in holders having built-in 50K resistors; Variac is connected to deliver 135-v maximum output with 115-v input; Variac drive motor turns in clockwise direction; all resistors around curent relay must be capable of carrying nearly ten amperes; relay is standard long-frame telephone type; resistor and capacitor across relay contacts suppress contact sparking. For safety, design must provide for "automatic" grounding of starter cabinet and centrifuge frame.

by hand, not only to return the control to zero, but to make manual adjustments when so desired. Any friction drive system which will slip at a torque of about 75 ounce-inches would be satisfactory. The drive motor speed is unimportant since the overcurrent cutout relay determines the rate at which the centrifuge accelerates. In the extreme case however, if a very low speed motor is used, the cutout relay would never be activated, and time would be lost in the build-up portion of the speed cycle. The first model has been operating satisfactorily for over a year at temperatures from −12° to 30°C.

* National Institutes of Mental Health and Neurological Diseases and Blindness.

† Now with General Electric Company, Heavy Military Electronic Equipment Department, Syracuse, New York.

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J. N. SHOOLERY, *Varian Associates, Palo Alto, California*
AND
JOHN D. ROBERTS, *California Institute of Technology,* Pasadena, California*

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THE need for liquid samples in high resolution nuclear magnetic resonance (NMR) spectroscopy makes desirable means for heating samples since solubilities generally increase with temperature and many solid substances can be melted without decomposition. Furthermore, reactions often proceed at convenient rates for kinetic studies at elevated temperatures, and the change of reaction rates with temperature permits evaluation of activation energies.

Samples used in high resolution work are necessarily small due to limitations in field homogeneity; therefore, it is preferable to heat only the sample rather than the entire crossed-coil head of the NMR spectrometer.[1] This was accomplished by replacing the plug-in receiver coil with the vacuum-jacketed coil shown in Fig. 1.

This device was constructed as follows. First, a double-walled Pyrex vessel was fabricated and pierced in two places; at the bottom to bring out the receiver coil leads, and near the top to permit introduction of a controlled-temperature air stream. The jacket was evacuated, sealed off, and a coaxial fitting attached with epoxy resin.

Some complications arise from the need to rotate the sample rapidly.[2] A Teflon cup serves as a lower bearing for the 5-mm Pyrex sample tube. The upper bearing is the turbine rotor. Several holes in the inner glass tube between the cup and the receiver coil allow the heated air to pass into the annular space between the sample and receiver coil support and thence out of the apparatus.

A ground glass joint was included because of the need to rotate the receiver coil to obtain minimum coupling to the surrounding transmitter coils. The side arm prevents rotating the entire insert; consequently, the coil could be balanced by rotating the tapered joint and then immobilized with epoxy resin. A model which obviates the need for this joint is being constructed.

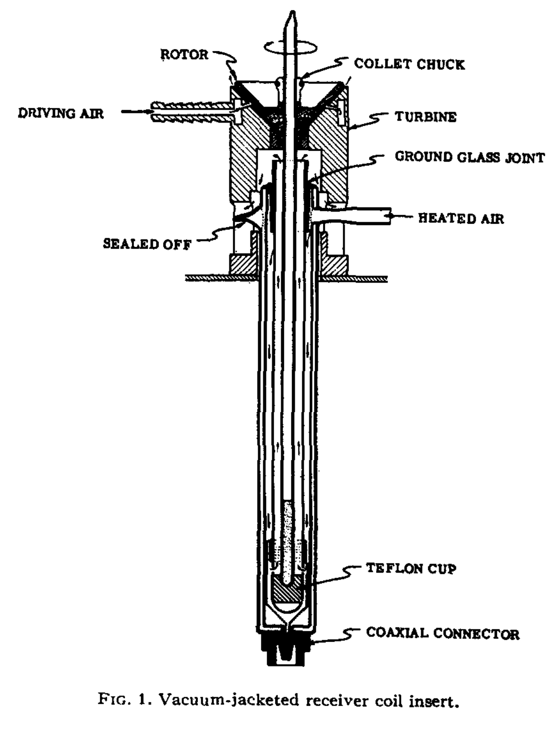

FIG. 1. Vacuum-jacketed receiver coil insert.

Air is heated in a closed brass oven surrounding a 600-w Nichrome heating element connected to a Variac. Air flow is controlled by a needle valve. It is advisable to filter the heated air to prevent ferromagnetic contamination of the insert. In order to allow a rigid connection to be maintained while searching for optimum field homogeneity, the heater and NMR head were balanced on opposite ends of an aluminum bar mounted on a movable holder.

This insert can be heated to 170°C in a few minutes and maintained at temperatures in this vicinity. Epoxy resins are available which permit operation at 300°C. A thermocouple inserted in the side arm indicated temperatures 10°C higher than the effluent gas. Thermocouple wire is available which will go into the annular space near the receiver coil (but far enough away to avoid electrical coupling) and permit continuous and accurate temperature measurement.

For the first trial of the apparatus the thermal isomerization of 5-ethylaminotetrazole was studied.[3] Subsequent experiments include barrier measurements for internal rotation in dimethyl formamide, observation of narrow resonances in high polymers at temperatures in excess of 100°C, and temperature effects on the resonances of hydrogen attached to nitrogen.[4]

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Unsupported Area High Pressure Seal*

D. M. Warschauer, *Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

AND

William Paul, *Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts*

(Received October 5, 1956)

One of the more commonly used seals for high pressure is the unsupported area seal developed by P. W. Bridgman.[1] The principle of operation is well known, and is explained in Bridgman's book, so that it does not require description here.

There is considerable variation in the method of application of this seal in different laboratories and in commercial equipment. Nevertheless, this seal depends eventually on the development of pressure in some sort of packing (rubber, leather, Teflon, copper, lead, steel) in excess of that in the fluid whose leaking is to be prevented. This excess pressure must not be too low; otherwise, sealing is unlikely. Nor must it be too high; otherwise, pinch-off[1] is liable to occur. Bridgman[1] found that sealing plug stems would pinch off when the pressure on them was approximately the maximum tensile strength of the stem material. However, when the packing is made thinner, then the heavily stressed part of the stem receives considerable support and the stem is less likely to pinch off. This cannot be carried too far, since some bearing area is required for sealing against the plug surface. Although the amount of packing pressure and the packing dimensions must be designed for the experimental situation being handled, it is of some interest to report the values of these parameters in a specific case.

Our own motive for looking at this experimental problem was a desire, in building an optical high pressure bomb, and optical plugs with apertures down their centers, to minimize the ratio of packing hole diameter to optical aperture. For a given aperture and a small experimental volume, the smaller the diameter of the packing hole in the bomb, the smaller the pressure vessel can be made. However, the excess pressure in the packing increases as the hole diameter is decreased if the stem diameter is held constant (see Fig. 1). At the suggestion of Professor Bridgman, we undertook some experiments to determine to what extent one could increase this excess packing pressure without causing rapid deterioration of the packing or pinch-off of the plug stem.

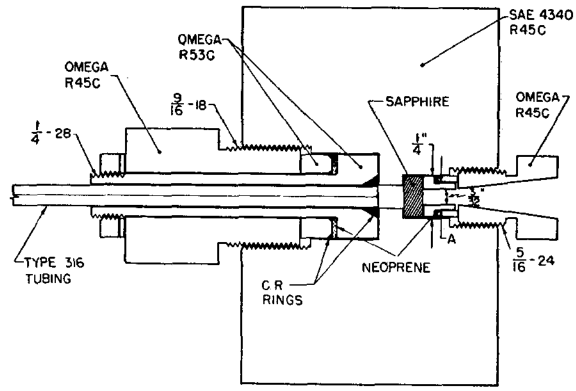

Fig. 1. Test bomb. Dimension A was $\frac{5}{32}$, $\frac{3}{16}$, and $\frac{7}{32}$ in. diam successively with the inside diameter of the push piece adjusted accordingly.

Figure 1 shows the test arrangement used. Steels and hardnesses are indicated in this figure. The pressure was introduced via stainless steel tubing as previously reported.[2]

Neoprene rubber was used as the packing material on both tubing and optical plugs. The thickness of Neoprene used was in each case only $\frac{1}{64}$ in., so as to reduce the force on the stem causing pinch-off. This small thickness was successful, although the care taken in ensuring good surfaces and fits quite probably contributed to this. We have sometimes used Teflon as packing material with considerable success; similar work has been reported from another laboratory.[3] We found more difficulty with Teflon than with Neoprene in producing an *initial* pressure seal; it is often advantageous to use Teflon and Neoprene in combination to take advantage of the sealing properties at low pressures of the Neoprene and the lubricating qualities of the Teflon.

Starting from a dimension A of $\frac{5}{32}$ in., corresponding to a packing pressure to fluid pressure ratio, x, of 1.25 the usual order of value in this Laboratory, we tested the assembly to just over 10 000 kg/cm^2. For dimensions of A up to $\frac{7}{32}$ in., corresponding to $x=4.0$, the assembly held pressures to 10 000 kg/cm^2 without any evidence of leaking. The packing on disassembly showed no ill effects. The tests were not taken above 10 000 kg/cm^2 because it was not convenient to do so on the test apparatus at that time; the seals may well hold to higher pressures, as they do for x values of about 1.2 in our normal work. Moreover, we stopped at $x=4$ because the conical washers were then $1/128 \times 1/128$ in. triangular shape, and could not easily be reduced. There seems no reason to suppose that the same excess pressure could not be applied to larger plugs with similar success.

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