

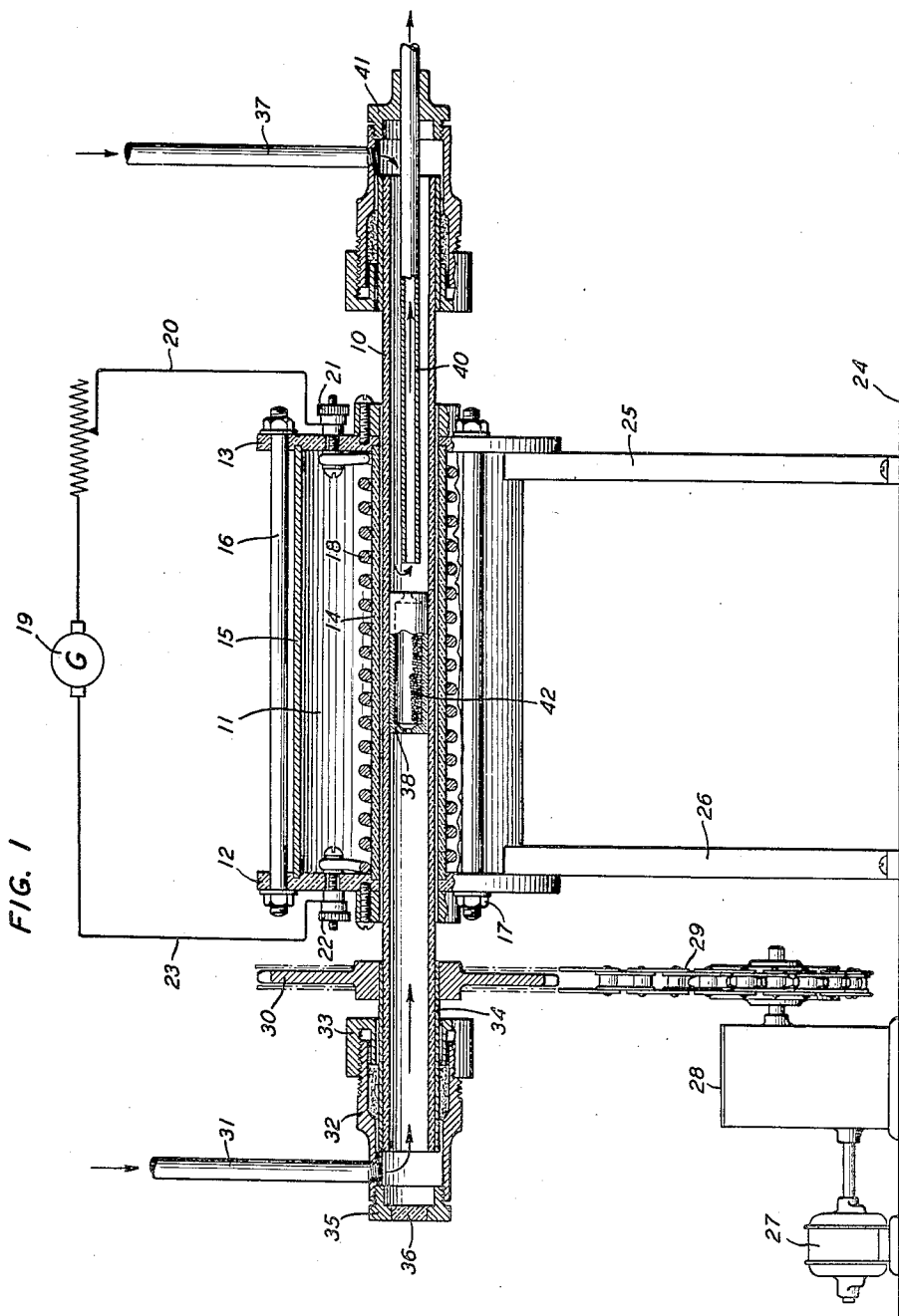
Sept. 18, 1934.

F. S. GOUCHER ET AL
RESISTANCE VARYING MATERIAL

1,973,703

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2 Sheets-Sheet 1



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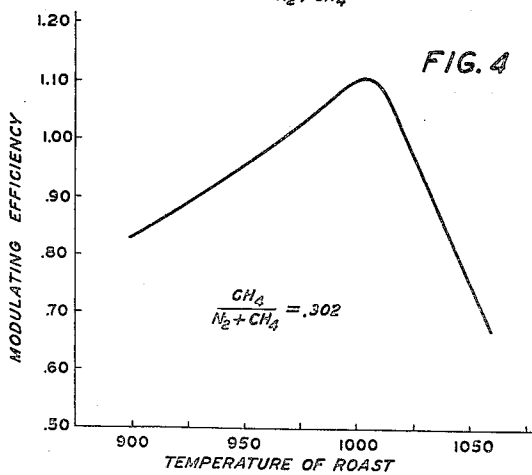
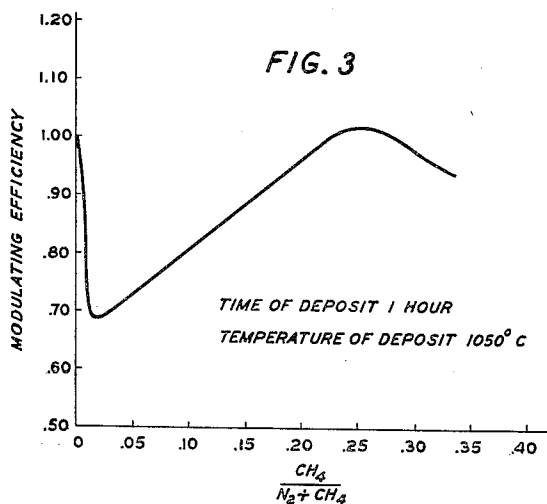
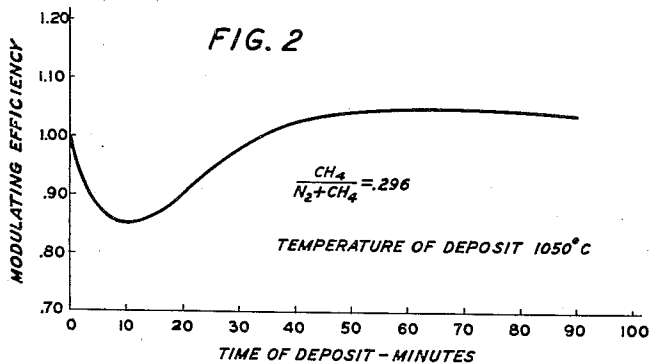
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RESISTANCE VARYING MATERIAL

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5 Claims. (Cl. 179—190)

This invention relates to resistance varying material and its process of manufacture and more particularly to granules for use in connection with microphonic instruments such as telephone transmitters.

The resistance varying material heretofore used in telephone transmitters has been generally made from finely divided anthracite coal. While, in general, such material is satisfactory, yet to obtain uniform results the greatest care must be exercised in selecting the coal in order to make certain that it is of high and uniform quality. The coal so chosen is crushed until the resulting particles reach a certain size, 60–80 mesh, for example, after which they are washed to free them from dust and finally they are heat treated until they have attained the desired microphonic characteristics. In addition to the high cost of producing microphonic material in this manner it is difficult to obtain particles of uniform transmission characteristics due to the fact that any slight variation in the quality of the coal brings about a corresponding change in its microphonic characteristics.

An object of the present invention is to provide granular material of improved microphonic characteristics which is capable of use in telephone transmitters and the like. A further object is to provide methods and apparatus by means of which such material may be readily and economically manufactured with a high degree of uniformity in its microphonic performance.

The microphonic material of this invention preferably comprises particles of a desired size upon which is deposited a thin layer of substantially pure carbon. While any suitable method may be employed in securing this layer of carbon it is preferably accomplished by subjecting heated particles to a stream of a hydrocarbon gas so that the gas in contacting with the heated particles is decomposed, the resulting carbon being deposited on the particles in a uniform coating of a thickness depending primarily upon the duration of the treatment, the concentration of the hydrocarbon gas and the temperature. Thus, a small vessel or boat containing the granules to be coated may be placed in a rotating tube which is heated to a temperature sufficient to decompose the hydrocarbon gas passing there-through. Other features of this invention will be described hereinafter.

For a better understanding of this invention reference is made to the following detailed description taken in connection with the drawings, in which:

Fig. 1 is a cross-sectional view of one type of furnace which may be employed in producing the desired carbon deposit; and

Figs. 2, 3 and 4 illustrate respectively how the microphonicity or modulating efficiency of the material may vary with variation in time of deposit, concentration of the carbon yielding gas and temperature of the furnace.

The furnace of Fig. 1 comprises a tube 10 of suitable refractory material such as sillmanite which passes through the center of a heat chamber 11. This heat chamber comprises circular side walls 12 and 13, an inner cylindrical tube 14 and an outer cylindrical tube 15, the whole being clamped together by means of suitable bolts such as bolts 16 and 17. The inner diameter of tube 14 is only slightly greater than the outer diameter of tube 10. A heating element 18 is helically wrapped around the inner cylindrical tube 14, electrical connections being made from a suitable source of power such as generator 19 to one end of the coil by means of conductor 20 and terminal 21 while the other end of the coil is connected to the generator through a similar terminal 22 and conductor 23. The heat chamber just described is supported from table 24 by means of stanchions 25 and 26. The tube 10 is adapted to be rotated by power supplied by motor 27 through a suitable gearing arrangement in gear box 28, chain 29 and the sprocket 30 which is attached to tube 10.

The particles to be coated with carbon are placed in a tubular member or boat 38 of refractory material such as graphite which is closed except for a central opening at each end for loading purposes as well as to afford a passage for gas therethrough. The loaded boat is placed in the center of the heat chamber and is designed to fit snugly within the tube 10, so that the boat 38 will rotate with the tube and so that practically all the gas passing through tube 10 will of necessity pass through boat 38 by means of the central opening at each end as described above.

Tube 31 is connected to a suitable source of gas supply comprising in part at least a carbon yielding gas which will split off carbon on pyrolysis, such as methane for example. This gas mixture under suitable pressure passes through tube 10 through the boat 38 after which it is withdrawn from the chamber by an inner tube 40, one end of which lies closely adjacent boat 38 and the other end of which projects beyond tube 10 to the outer atmosphere. Another tube 37 is connected to a suitable source of inert

gas such as nitrogen and the nitrogen from tube 37 passes between tubes 10 and 40 towards the boat 38 where it reverses its direction and passes out through tube 40 along with the gas mixture from the supply source connected to tube 31. The purpose of this supply of inert gas will be described later.

Tubes 10 and 31 are connected by a suitable stuffing box arrangement comprising a wrapping 34 of asbestos wool or other compressible material about the tube 10 and offset tubular member 32 fits over this material at one end of the tube 10 and is in threaded engagement with a collar 33, the space between the offset portion of member 32 and collar 33 being packed with an additional quantity of the asbestos wool to insure a substantially air-tight joint. In order to permit viewing the inside of tube 10 a member 35 carrying a small pane of glass 36 is screwed into the end portion of the offset tubular member 32. A similar stuffing box arrangement is employed for connecting tubes 37 and 10 except that tube 40 projects through the stopper member 41.

In operation, the boat 38 is filled with particles to be coated in an amount insufficient to cause any substantial amount to escape during the rotation of the boat within the furnace. The source of current is connected to the heating coil to bring the furnace up to the desired temperature, the tube 10 during this heating being filled with a non-oxidizing gas such as hydrogen. The loaded boat is then placed in the center of the heat chamber, as shown in the drawing, and the motor 27 started to rotate tube 10 at a predetermined speed. As an alternative, the loaded boat may be placed in the furnace before the furnace has reached the desired high temperature providing the interior of tube 10 is filled with a non-oxidizing atmosphere until the desired high temperature is reached. A gas such as methane diluted with a neutral gas such as nitrogen is then supplied under pressure through tube 31 to tube 10 and through boat 38 to outlet tube 40; and at the same time an inert gas such as nitrogen enters tube 10 from tube 37 and also passes out through tube 40. The carbon yielding gas when it contacts with the surface of the particles 42 is decomposed and the resulting carbon is deposited as a uniform coating on these particles. The other decomposition products as well as the gas not decomposed are swept out through tube 40 into the open air after joining the flow of nitrogen at the entrance to tube 40 adjacent the boat. The sweeping action of the stream of nitrogen from tube 37 aids materially in preventing any of the undesired decomposition products from depositing on the inner walls of tube 10. After a carbon coating of the desired thickness has been obtained the methane supply and the nitrogen supply are disconnected, the tube 10 is filled with a non-oxidizing gas, such as hydrogen, and the boat 38 removed towards the end of tube 10 away from the hottest portion of the furnace. The boat and its contents are kept in tube 10 and in the atmosphere of hydrogen until the boat has cooled down to approximately room temperature. The boat may then be removed from tube 10, the boat refilled with other material and the process repeated. It will be apparent from the above that considerable care must be taken to protect the carbon coating from oxidation or contamination while the particles are being cooled down to room temperature. If the boat should be taken immediately from the hot furnace to the outer air, the microphonicity

of the carbon coating on the particles would be seriously impaired.

The thickness of the coating of carbon on the particles is preferably not greater than 10^{-4} cm. and in particular a thickness of about 10^{-5} cm. has been found satisfactory. Increasing the thickness increases the cost of manufacture and also increases the danger of contamination of the product.

The behavior of the coated particles thus produced as a microphonic material or their modulating efficiency depends upon several factors such as the time of deposit, the gas concentration and the roasting temperature. The effect of these factors will now be explained by means of curves for the case where the material to be coated consists of particles of anthracite carbon, the carbon yielding gas employed being methane.

In the curves of Figs. 2, 3 and 4 the values plotted along the vertical axis represent the relative desirability of the material for microphonic purposes and are values of the so-called modulating efficiency of the material, according to an arbitrary scale, where the modulating efficiency of the material is defined as

$$\frac{R_{\max} - R_{\min}}{R_{\max} + R_{\min}}$$

where $R_{\max}$ and $R_{\min}$ are the maximum and minimum values of the resistance of a definite volume of material when the material is subjected to a cycle of a definite amplitude and frequency in a standard test set, one form of which will be described later.

The curve of Fig. 2 discloses the effect of time of deposit on modulating efficiency, other conditions remaining constant. The ordinates represent values of modulating efficiency as defined above, while the time of deposit in minutes is plotted along the horizontal axis. The actual ordinate values disclosed are not of primary interest since their value will depend upon the type of test set employed in their measurement. In securing the data from this curve the temperature of deposit was 1050° C. and the carbon yielding gas consisted of methane mixed with nitrogen in such proportions that the gas mixture entering tube 10 from tube 31 comprised 29.6% methane. It will be noted that the highest modulating efficiency is obtained with the coated particles only after a certain time of deposit and that the optimum time of deposit under the cited conditions was in the neighborhood of an hour, bearing in mind that an increase in the time beyond an hour would merely increase the cost of manufacture without producing any substantial increase in the modulating efficiency. The point where the curve of this figure touches the vertical axis, indicating zero time of deposit, represents the value of modulating efficiency of high quality anthracite carbon particles after careful selection and heat treatment, but without any carbon deposit thereon, such as the material widely used in telephone transmitters in the United States at the present time. This point where the curve of Fig. 2 touches the vertical axis is arbitrarily taken as unity as shown by the ordinates of the figure; in other words, the modulating efficiency of high quality anthracite carbon particles uncoated has been designated as unity for reference purposes.

Fig. 3 shows the effect of gas concentration on the modulating efficiency of the coated material when various mixtures of methane and nitrogen are employed, the values of modulating efficiency being plotted along the vertical axis and the per-

centage of methane in the gas mixture being plotted along the horizontal axis. The curve of Fig. 3 is taken for a time deposit of one hour and a deposit temperature of 1050° C. As the concentration of methane in the deposition gas increases from zero, the modulating efficiency rapidly falls to a minimum value, gradually rises to a maximum value and then again falls off to low values of modulating efficiency with further increase in the percentage of methane. A high percentage of methane is objectionable at high temperatures because of the contamination of the hard deposited carbon by the formation of soot and other pyrolysis products such as tars. The point where the curve reaches the vertical axis represents the same value of modulating efficiency as explained in connection with Fig. 2.

However, the preferred gas concentration depends upon the roasting temperature and lowering the roasting temperature increases the percentage of carbon yielding gas which may safely be employed. For example, with a roasting temperature of about 950° C. methane with little or no diluting gas may be safely employed.

Accelerating the velocity of deposit by increase of the roasting temperature appears to give roughly the same characteristic as speeding it by increase of methane concentration. In Fig. 4 the curve is obtained by plotting temperature of roast along the horizontal axis and the corresponding values of modulating efficiency along the vertical axis. For this curve the time of deposit was taken as one hour with 30.2% methane in the methane-nitrogen mixture. The modulating efficiency of the material rises with increase in the temperature of deposit until the formation of soot or other pyrolysis products gives a dirty carbon with a consequent decrease in the efficiency.

Summarizing the above data, it appears that the best microphonic carbons are associated with a high velocity of deposit provided the product is not contaminated with soot, tar or other undesired pyrolysis products. For the type of furnace employed above, and using anthracite carbon particles and methane, it will appear that quite satisfactory results will be obtained with a roasting temperature of about 1050° C., a methane concentration of about 30% and a time of deposit varying from about 30 minutes to 90 minutes.

Particles of other refractory material may be employed as the base material such as silicon carbide, crystalline quartz, or other siliceous material. If desired, the base particles may be taken from a material having a definite line of cleavage so as to be capable of being crushed into particles of substantially uniform shape. It appears, however, that the character of the surface of the carbon coating, such as its roughness, has a more important bearing on the microphonic efficiency of the material than the shape of the particles. That is, roughness, probably sub-microscopic, appears to be definitely correlated with microphonic efficiency.

While methane is a suitable carbon yielding gas, other gases from which carbon will split off on pyrolysis may be employed such as carbon monoxide, petroleum ether, benzene and illuminating gas. The diluting gas employed may be any non-reactive gas such as hydrogen or an inert gas such as argon or helium.

In order to obtain the best and reproducible results with the type of furnace described above the roasting temperature should be kept constant within quite narrow limits. The coating should take place only in the central portion of the heated

zone, preferably in the region where the temperature gradient is not large. Other suitable methods may be employed in depositing the surface layer of carbon on the particles such as by passing the granules through a rotating tube through which a stream of a hydrocarbon gas is passed.

The carbon coating produced in accordance with the present invention is distinguished by great hardness, high elasticity, small crystallite size, great compactness, non-friability, great stability toward heat and chemical reaction, small absorptive capacity, a relatively low electrical resistance with a high negative temperature coefficient and high purity with no ash content. The uniformity in the quality of the carbon produced by this invention is an important factor along with the fact that the carbon deposit is free from cracks and zones of low density. Also, the aging characteristics of carbon deposited in accordance with this invention are quite satisfactory with respect to resistance change with time and other microphonic properties. Since it is believed that the total microphonic action takes place in a thin surface layer of the granule, it may be readily understood that great care should be exercised in securing the proper carbon coating on the granular material in order to secure the desired microphonic properties. It also follows that the microphonic properties of the base material are relatively unimportant and hence the base material employed does not require as high degree of care in its selection and treatment as is necessary for the uncoated anthracite carbon heretofore widely employed in telephone transmitters.

In comparing the desirability or efficiency of various materials as to microphonicity, it is, of course, necessary to make the comparisons under similar conditions. The important criterion which is called "modulating efficiency" is the ratio of the change in resistance of material to the average resistance of the material when subjected to a force cycle of a definite amplitude and frequency. The method employed in obtaining the data on modulating efficiency presented herein was to employ a transmitter button of the barrier type such as that disclosed in the C. R. Moore U. S. Patent 1,565,581, issued December 15, 1925, the mica diaphragm of which was arranged to be driven by a balanced armature receiver unit such as that of the H. C. Egerton U. S. Patent 1,365,898, issued January 18, 1921. The transmitter button employed held 0.355 cc. of the microphonic material and was so constructed that it could be refilled without disturbing the vibrating system. After filling the button with the material to be tested, the button was connected to a source of constant direct current of a known value corresponding to that normally present in standard telephone subscribers' equipment. The receiver unit was driven by an oscillator of constant amplitude and with a frequency of 500 cycles per second. The maximum and minimum values of the voltage drop across the button were measured during the force cycle while the button was being driven by the receiver unit. The maximum and minimum values of the resistance of the carbon button could then be readily computed from the measured values of the button current and the maximum and minimum voltage across the button and as previously stated, the modulating efficiency is equal to

$$\frac{R_{max} - R_{min}}{R_{max} + R_{min}} \times \frac{2}{1}$$

The values so obtained for various carbon coatings on anthracite carbon in accordance with this invention have been plotted in the curves of Figs. 2, 3 and 4 and as previously stated the point where the curves of Figs. 2 and 3 touch the vertical axis has been taken as the point corresponding to the value of modulating efficiency of high quality uncoated anthracite carbon measured under the same conditions as the coated material as described above, such as the granular material now employed in standard telephone transmitters throughout the United States.

While certain embodiments of this invention have been described above for illustrative purposes, it is to be understood that the invention is not limited thereto but comprehends such a range of equivalents as is embraced by the language of the appended claims.

What is claimed is:

1. Resistance varying material of high modulating efficiency for microphonic purposes comprising refractory material in the form of comminuted particles upon the entire surface of which has been deposited a uniform and thin coating of substantially pure carbon.

2. A process for manufacturing particles of refractory material to render them of high modulating efficiency for microphonic purposes which comprises heating said particles to a high temperature and subjecting said particles to a gas stream comprising a carbon yielding gas and a

neutral gas, said temperature being sufficiently high to cause the decomposition of said carbon yielding gas.

3. A process for obtaining granular material of high modulating efficiency from particles coated with a thin layer of carbon obtained by the decomposition of a carbon yielding gas, which comprises heating said particles to a temperature which will give optimum modulating efficiency for the particular carbon yielding gas employed and subsequently subjecting said particles to a stream of said gas mixed with a neutral gas.

4. A process for obtaining granular material of high modulating efficiency from particles coated with a thin layer of carbon obtained by the decomposition of a carbon yielding gas, which comprises heating said particles to a high temperature, subjecting said particles to a stream of said carbon yielding gas mixed with a neutral gas, in which the neutral gas preponderates, and carrying away the other decomposition products by a stream of a neutral gas.

5. A process for coating particles with a thin layer of carbon which comprises heating said particles to a temperature in the neighborhood of 1000° C. and subjecting said particles to a stream of methane gas mixed with a neutral gas, in which the neutral gas preponderates.

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