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3,377,561

POSITIVE TEMPERATURE COEFFICIENT TITANATE THERMISTOR

Filed July 13, 1965

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FIG. 1

TIME-TEMPERATURE CURVE - TUNNEL KILN
MAXIMUM & MINIMUM FIRING SCHEDULES

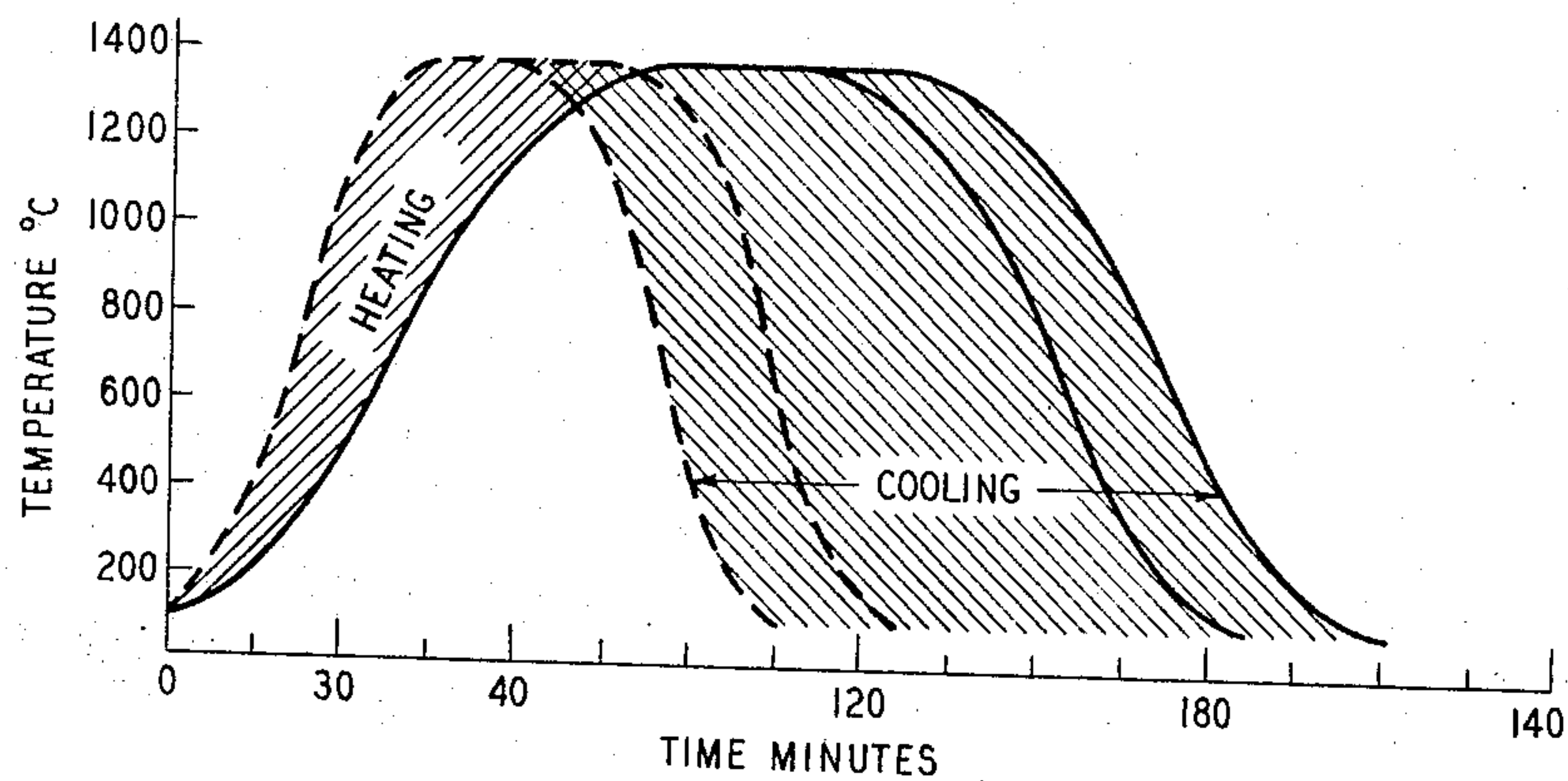
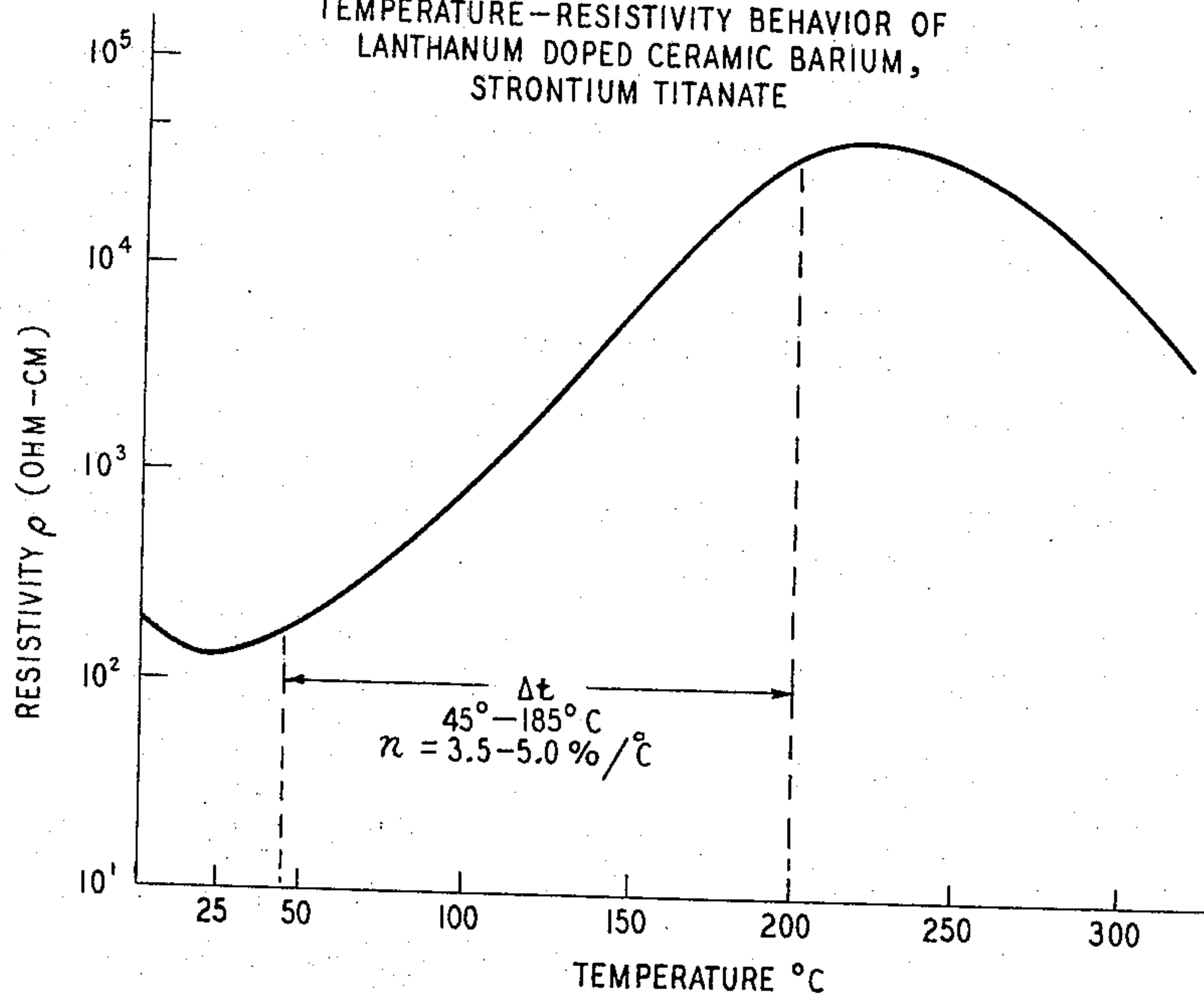


FIG. 2

TEMPERATURE-RESISTIVITY BEHAVIOR OF
LANTHANUM DOPED CERAMIC BARIUM,
STRONTIUM TITANATE



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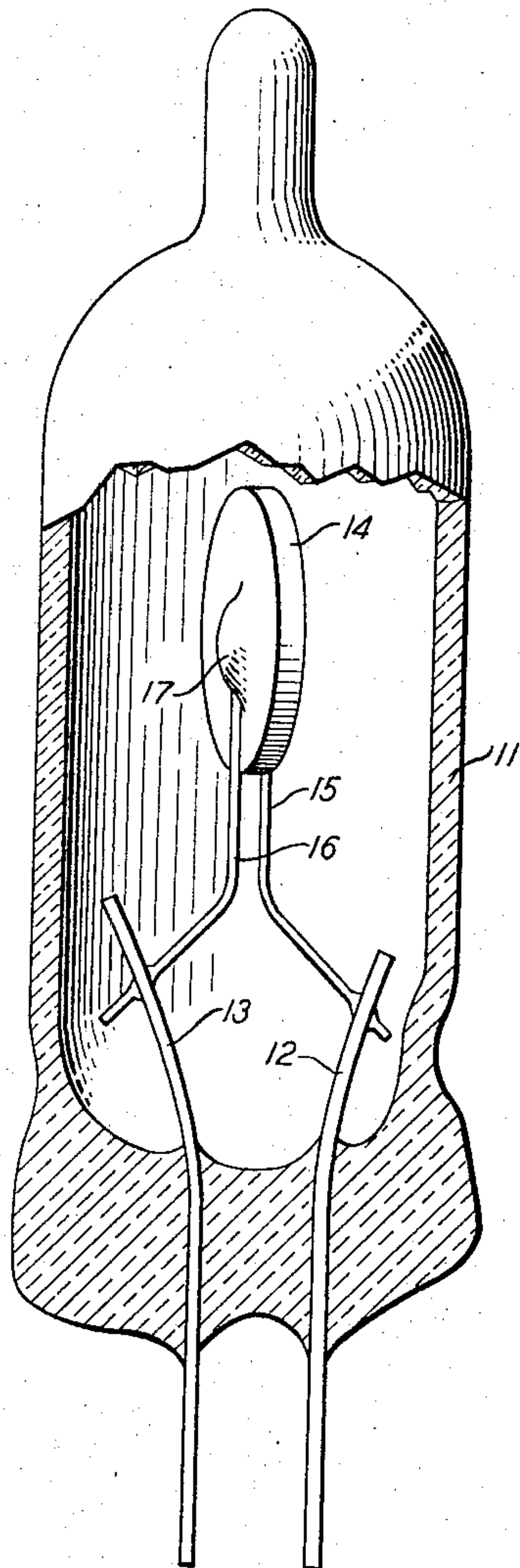
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FIG. 3



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POSITIVE TEMPERATURE COEFFICIENT TITANATE THERMISTOR

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Continuation-in-part of application Ser. No. 404,098, Oct. 15, 1964. This application July 13, 1965, Ser. No. 471,572

4 Claims. (Cl. 338—22)

ABSTRACT OF THE DISCLOSURE

A positive temperature coefficient thermistor of the lanthanum-barium-strontium titanate system fired in accordance with a critical schedule, ground to a specific geometry and encapsulated in air at atmospheric pressure having a partial pressure of oxygen within the range of 3 to 3½ pounds per square inch evidences a current resistance characteristic restricted to the boundaries defined by telephone loop circuitry.

This application is a continuation-in-part of copending application, Ser. No. 404,098, filed Oct. 15, 1964, now abandoned.

This invention relates to a current limiting type thermistor with rapid time response comprising a ceramic body evidencing a positive temperature coefficient of electrical resistance within a specified range and to a process for the fabrication of such devices.

Ceramic semiconductor materials are generally known as possessing negative temperature coefficients of resistance, that is, the electrical resistance decreases as the temperature increases. In recent years, several materials evidencing positive temperature coefficients of resistance have been disclosed.

For series loop equalization in telephone transmission networks, it is necessary to have available a thermistor evidencing a marked positive temperature coefficient of electrical resistance. More specifically, a thermistor is required which manifests a predesigned current-resistance characteristic dictated by the transmission requirements of the telephone.

This characteristic indicates that as the current in an operating telephone circuit increases up to approximately 40 milliamperes, the resistance of the circuit is maintained constant. Thereafter, there is a sudden break in which the resistance increases with a minimal change in current while the circuit resistance increases from approximately 25 to 600 ohms. For effective operation, the current-resistance function must remain within the boundaries defined by the telephone circuit parameters. Control of the amplitude of the resistance swing in the current-resistance behavior is effected by shunting the thermistor with a resistance ranging from 400 to 1000 ohms as dictated by the required transmission performance. The shunt also serves the purpose of desirably minimizing the current back-up in the rising portion of the current-resistance characteristic, so assuring that the current will not fall below a specified threshold value during the resistance rise. In order to obtain this current-resistance function, the thermistor composition utilized is required to evidence a relatively constant predetermined resistivity in the vicinity of room temperature and then a sudden increase in resistance within a selected temperature range. A further requirement for stable performance of such a device is that the ceramic thermistor body be freely suspended in a suitable encapsulant containing a nonreducing atmosphere, preferably air, with a partial pressure of oxygen, within the range of 3 to 3.5 pounds

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per square inch. Unfortunately, the prior art thermistors have not been completely satisfactory for such purposes.

In accordance with the present invention, there is described a technique for the fabrication of a novel thermistor structure including a titanate ceramic body evidencing the characteristics required for use in telephone loop circuitry. It has been determined that ceramic materials comprising 1 mol of titanium dioxide and 1 mol including (a) barium oxide within the range of 0.600 to 0.850 mol, (b) strontium oxide within the range of 0.150 to 0.400 mol and (c) lanthanum oxide within the range of 0.001 to 0.005 mol, when intimately and homogeneously combined and fired in a critical schedule result in a body evidencing a substantially constant resistivity of about 100 ohm-cm. from 5° C. to 45° C., an over-all range of resistivity ranging from 100 to 90,000 ohm-cm. over a temperature range of from 25–240° C. and a temperature coefficient of resistivity, n , equal to 3.5 to 5.0 percent per degree Centigrade over a temperature range of 45–185° C. where n is defined by the equation:

$$n = \frac{1}{0.4343 \Delta t} \log_{10} \frac{R}{R_0}$$

wherein:

Δt = change in temperature

R_0 = low temperature resistivity

R = high temperature resistivity.

It has further been determined that the compositions described herein may be effectively utilized in telephone loop circuitry in a structure which includes a wafer of the described composition hermetically sealed and freely suspended in an encapsulant at atmospheric pressure.

The invention will be more readily understood by reference to the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a graphical representation on coordinates of time in minutes against temperature in degrees Centigrade showing the firing schedule required for the practice of the present invention;

FIG. 2 is a graphical representation on coordinates of resistivity in ohm-cm. against temperature in degrees Centigrade showing the temperature resistivity characteristic of an exemplary composition; and

FIG. 3 is a front elevational view, partly in section, of a thermistor structure of the invention.

A general outline of the procedure employed in preparing the compositions described herein together with satisfactory ranges of operating parameters will now be given.

The thermistor compositions of the present invention comprise stoichiometric proportions of titanium dioxide and a mixture of the oxides of barium, strontium and lanthanum. More specifically, it has been found advantageous to employ 1 mol of titanium dioxide and 1 mol including (a) barium oxide within the range of 0.600 to 0.850 mol, (b) strontium oxide within the range of 0.150 to 0.400 mol and (c) lanthanum oxide within the range of 0.001 to 0.005 mol. Variations from the noted ranges have been found to adversely affect the electrical characteristics of the resultant composition from the standpoint of its use as a thermistor in telephone loop circuitry.

In preparing the compositions of interest, titanium dioxide, for example, anatase, is combined with barium oxide and strontium oxide or compounds which may be converted to such oxides during the processing, as, for example, carbonates. The lanthanum may be added in the oxide form or, preferably, in the oxalate form. The compounds chosen are preferably of high purity.

The correct proportions of the titanium dioxide, barium and strontium oxides or carbonates and lanthanum oxide or oxalate are added to a mill jar and wet mixed in distilled water containing a wetting and dispersing agent for

approximately 24 hours utilizing a suitable grinding media, so resulting in a homogeneous mixture. In order to obtain the optimum electrical properties in a reproducible manner, the size and type of mill as well as the size of the grinding media should be chosen to provide the lowest milling time, the most efficient mixing and grinding, and the least contamination.

The resultant intimate admixture is filtered and dried as, for example, at 120° C. and then calcined in a refractory crucible at a temperature of approximately 1100° C. for several hours in air. The calcined product comprises an intimate mixture of the oxides of barium, strontium, titanium and lanthanum. After cooling, the calcined product is returned to the mill jar and remilled as described above, filtered and dried.

Following, the resultant fine powder may be admixed with a volatile organic binder and then pressed in a suitable die at pressures within the range of 1500 to 2000 pounds per square inch.

The pressed bodies are then in readiness for the critical firing step which is responsible for developing the desired electrical properties in the compositions. This step is conducted in a tunnel kiln having the entry end closed during firing in order to maintain an atmosphere of static air. It is absolutely essential that the temperature profile of the kiln be maintained within the limits delineated in FIG. 1 wherein there is shown the required heating and cooling cycles for the preparation of compositions manifesting the temperature-resistivity characteristic shown in FIG. 2.

With reference now more particularly to FIG. 1, it is noted that the firing schedule requires heating the compositions of interest from the ambient temperature to a minimum of approximately 1380° C. over a time period ranging from 45–85 minutes at a rate within the range of 0.25–0.45 inch per minute. A range of from 1380° C. to 1400° C. is dictated by usual apparatus limitations. After attaining the peak temperature, the compositions are permitted to soak (at that temperature) for a time period within the range of 20–35 minutes and are then cooled to room temperature over a time period ranging from 45–70 minutes. For one type of apparatus the limits may be determined by the rate of travel through a kiln. It is to be noted that the temperature profile and the dynamics of firing are inter-related parameters and failure to follow the course delineated, particularly in the hot zone (1380°–1400° C.) and while cooling results in an undesirable composition. Operation in the described manner results in a temperature-resistivity characteristic as shown in FIG. 2. Reference to FIG. 2 reveals that the positive temperature coefficient of resistivity ranges from 3.5 to 5.0 percent degree centigrade over a temperature range of 45° C.–185° C.

As indicated, thermistors comprising the described compositions and positive temperature coefficient of resistance range are of particular interest for use in telephone loop equalization circuitry. However, it has been found that certain critical parameters are required to assure the presence of the desired current-resistance characteristics for such applications. Thus, it has been found essential in such applications to employ titanate wafers having a diameter within the range of 0.278 inch to 0.282 inch and a thickness ranging from 0.018 inch to 0.020 inch. Diameters and thicknesses greater than the noted maxima result in objectionably high time delays as evidenced by a shift in the break-point in the current resistance characteristic to higher currents whereas diameters and thicknesses less than the noted minima result in break-points lower than that required for satisfactory equalization in the operation of the thermistor.

Wafers of the desired dimensions are then plated with ohmic electrical contacts comprising either electroless nickel-electroless gold or electroless nickel-electroless palladium by conventional means.

Thereafter, leads comprised of silver plated nickel, hav-

ing a diameter ranging from 0.008 inch to 0.009 inch and a length ranging from $15\frac{1}{32}$ inch to $17\frac{1}{32}$ inch, are attached to the plated thermistor wafer by means of a fired silver-glass paste.

Finally, the resultant assembly is inserted into a glass ampoule and hermetically sealed, freely suspended, in air maintained at atmospheric pressure, the silver plated nickel wafer leads being spot welded to lead-in wires of the ampoule.

Unfortunately, the use of conventional means of protection such as dip coatings and molded plastics, which are in intimate contact with the thermistor wafer, were found to produce unsatisfactory time delays due to the fact that thermal losses to the contacting material prevent rapid self-heating of the wafer by the available telephone circuit currents. Further, such encapsulants were found to subject the piezoelectric titanates to varying pressures which resulted in unpredictable changes and instability in electrical properties.

With reference now to FIG. 3, there is shown a front elevational view, partly in section, of a thermistor of the invention. Shown in the figure is an hermetically sealed ampoule 11 having a pair of electrical leads 12 and 13 protruding therefrom, ampoule 11 having disposed therein a wafer 14 comprising a lanthanum-barium-strontium titanate prepared as described above. Wafer 14 is shown freely suspended (in air at atmospheric pressure) by means of silver plated nickel leads 15 and 16 which are attached by solder to leads 12 and 13, respectively, and to wafer 14 by means of silver paste applied to the silver-plated nickel lead and ohmic electrical contact 17.

An example of the practice of the present invention is set forth below. This example is intended to be illustrative in nature only and not restrictive in character.

EXAMPLE

This example describes the preparation of a thermistor having the formula $\text{La}_{0.004}\text{Ba}_{0.800}\text{Sr}_{0.196}\text{TiO}_3$. 552.6 grams of BaCO_3 , 101.3 grams of SrCO_3 , 282.5 grams of TiO_2 and 4.928 grams of $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ were introduced into a one-gallon porcelain mill jar (18% Al_2O_3 –77% SiO_2) together with 1500 milliliters of distilled water containing 1 gram of "Tamol SN," a wetting and dispersing agent. The charge was milled for 24 hours at 50 r.p.m. using 55–60 mullite balls, 1.25–1.5 inches in diameter, as the grinding media.

After milling, the charge was filtered using a Buchner funnel and the mill jar thoroughly rinsed with distilled water which was then used to wash the product. Finally, the entire filter cake was washed with approximately 2 liters of acetone and vacuum dried.

Following the overnight air drying step, the filtered material was placed in a fire clay sagger which was then placed in an air atmosphere furnace at room temperature. Over a period of 3 hours the furnace temperature was raised to 1100° C. at which it was maintained for 3 hours. The resultant calcined material was cooled to room temperature, placed in a mill jar and remilled as above for 6 hours, then filtered and dried in the described manner.

Then, the ceramic powder was mixed with $\frac{1}{2}$ of 1% by weight of rubber, which was in the form of a 2% rubber solution in toluene, in a beaker with a sufficient excess of toluene to result in a fluid consistency. Next, the volatile toluene was removed by heating the mixture at 90° C. The powder with the rubber binder was then pressed into a 2 gram disc in a $1\frac{1}{8}$ inch Carver Test Cylinder and then placed on stabilized ZrO_2 plates.

Firing was conducted in a sillimanite tube tunnel kiln, 3 inches I.D. x 48 inches long having one end closed during firing to maintain an atmosphere of still air. The pressed disc was drawn through the kiln on the zirconia plate at a rate within the range of 0.320 to 0.375 inch per minute. The furnace evidenced the profile shown in FIG. 1. The disc was heated to a temperature of 1380° C. over a time period of approximately 50 minutes, main-

tained that temperature for approximately 35 minutes and cooled to below 200° C. over a period of approximately 70 minutes.

The resultant fired disc was ground on a surface grinder equipped with a diamond wheel to a thickness of 0.020 inch.

Next, employing an automatic plating apparatus, ohmic electrical contacts were applied essentially in the manner described in U.S. Patent 2,071,522. Following plating, the disc was rinsed in acetone, air-dried and heat treated by placing it on a stabilized ZrO₂ plate and heating at 400° C. for 15 minutes in air.

The disc so prepared was next cemented to a 2 inch square glass plate at a temperature of 140° C. with glycol phthalate cement and allowed to cool. Next, a circular glass cover, 0.006 inch thick was cemented to the upper surface of the disc and wafers 0.280 inch in diameter diced from the disc by ultrasonic cutting.

Following, silver plated nickel leads, 0.009 inch in diameter and 0.5 inch in length were attached to a plated thermistor wafer by means of fired silver glass paste prepared by mixing 15 grams of a low temperature solder glass with 5 grams of silver powder. The dry powders were milled in a small glass bottle with alumina balls for approximately 8 hours. Next, a vehicle for the paste was prepared by adding 40 milliliters of powdered isobutyl methacrylate polymer to 160 grams of dibutyl phthalate. The paste itself was then prepared by mixing 10 grams of the silver glass mixture with 5 grams of vehicle with repeated stirring and folding of the paste on a glass plate using spatulas with flexible stainless steel blades.

The wafer was then placed on a flat piece of nichrome wire gauze of proper size to fit the furnace employed in the subsequent firing step. Then, one end of the lead wire is dipped into the paste so as to pick up a small quantity of paste approximately equal, in volume, to a sphere 1 mm. in diameter. Next, the lead wire was placed in the center of the wafer, the other end being supported so as to keep the wire parallel to the upper surface of the wafer and prevent the attachment from loosening prior to firing.

Following, the gauze containing the wafer with one lead attached, is placed upon a hot plate maintained at approximately 250° C. and heated for 50 minutes, so eliminating volatile solvents and imparting enough strength to the attachment to permit handling. The wafer was then turned over and a silver plated nickel lead attached to the other side in like manner.

The paste was then fired in an air atmosphere conveyor furnace at 500° C. The furnace employed was 4 feet in length with an effective heat zone of 12 inches.

Next, the wafer was inserted in a glass ampoule having a pair of lead-in wires 0.016 inch in thickness and comprised of a copper clad nickel-iron alloy (42 percent Ni-balance Fe). The silver plated nickel wafer leads were spot welded to the lead-in wires and the assembly sealed under atmospheric conditions into the ampoule by conventional techniques.

The thermistor prepared in the described manner evidenced a positive temperature coefficient, n , of 3.5–5.0 percent per degree centigrade over a temperature range of 45° C. to 185° C.

While the invention has been described in detail in the foregoing description, the aforesaid is by way of illustration only and is not restrictive in character. The

several modifications which will readily suggest themselves to persons skilled in the art are all considered within the broad scope of this invention, reference being had to the appended claims.

What is claimed is:

1. A thermistor including an hermetically sealed ampoule having a pair of lead-in wires, the said ampoule having disposed therein a wafer having a diameter within the range of 0.278 to 0.282 inch and a thickness within the range of 0.018 to 0.020 inch, the said wafer being freely suspended in air at atmospheric pressure having a partial pressure of oxygen within the range of 3 to 3.5 pounds per square inch, said wafer consisting essentially of a composition having the general formula $\text{La}_x\text{Ba}_y\text{Sr}_z\text{TiO}_3$ wherein x is within the range of 0.001 to 0.005, y is within the range of 0.600 to 0.850 and z is within the range of 0.150 to 0.400, the said wafer being connected to said lead-in wires by means of silver plated nickel leads, the said leads being attached to each of the major surfaces of said wafer by silver paste, the said thermistor evidencing a resistivity ranging from 100 to 90,000 ohm-cm. over a temperature range of from approximately 25–240° C. and a positive temperature coefficient of resistivity, n , within the range of 3.5 to 5.0 percent per degree centigrade over a temperature range of 45–185° C.

2. A thermistor in accordance with claim 1 wherein said silver plated nickel leads have a diameter within the range of 0.008 inch to 0.009 inch and a length varying from $1\frac{1}{32}$ inch to $1\frac{7}{32}$ inch.

3. A process for the preparation of a thermistor having the general formula $\text{La}_x\text{Ba}_y\text{Sr}_z\text{TiO}_3$ wherein x is within the range of 0.001 to 0.005, y is within the range of 0.600 to 0.850 and z is within the range of 0.150 to 0.400, a resistivity ranging from 100 to 90,000 ohm-cm. over a temperature range of from 25–240° C. which comprises the steps of reacting the constituent components of said thermistor in stoichiometric proportions and firing the resultant composition in accordance with the schedule of FIGURE 1 grinding the resultant composition to a diameter within the range of 0.278 to 0.282 inch, and a thickness within the range of 0.018 to 0.020 inch, freely suspending the ground composition in air maintained at atmospheric pressure in an encapsulant having a partial pressure of oxygen within the range of 3 to 3.5 pounds per square inch and hermetically sealing said encapsulant.

4. A method in accordance with claim 3 wherein firing is conducted at a rate within the range of 0.25 to 0.45 inch per minute wherein a temperature of approximately 1380° C. was attained over a time period within the range of 45–80 minutes.

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