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Laroche

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[54] PROCESS AND APPARATUS FOR DETERMINING THE POROSITY OF A DIELECTRIC LAYER COATING A METALLIC SURFACE

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[58] Field of Search 324/54, 65; 204/1 T, 181

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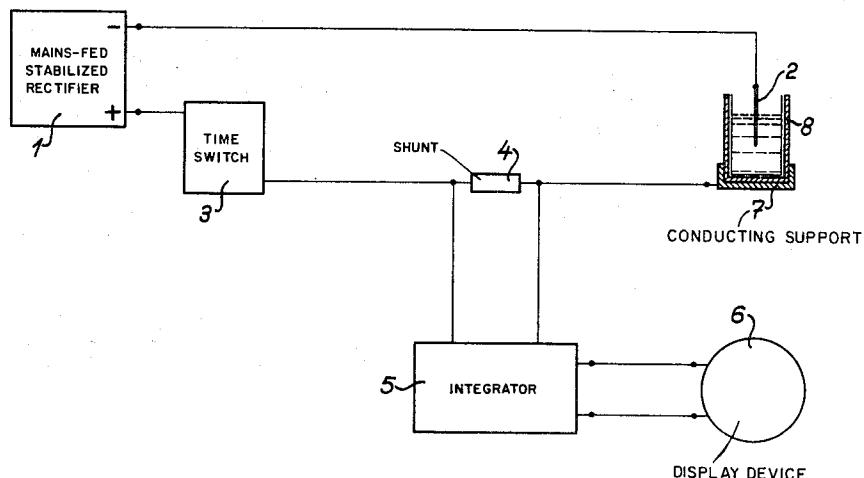
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[57]

ABSTRACT

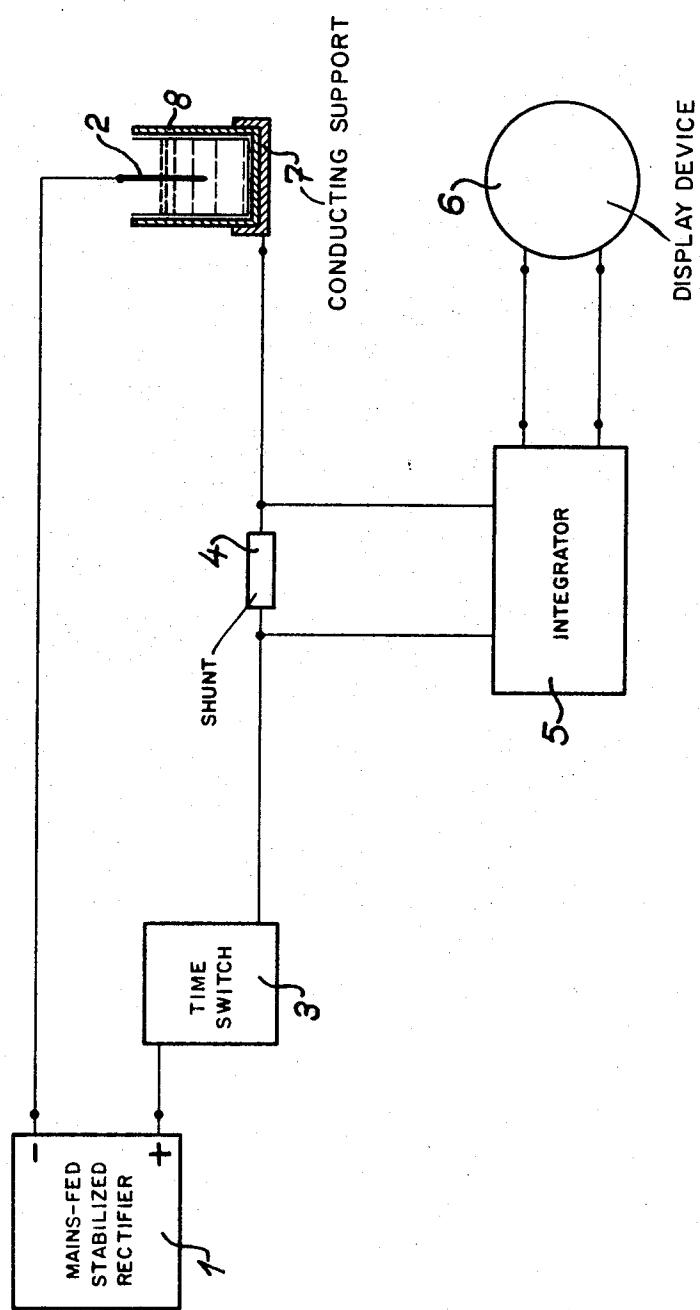
A process for determining the porosity of a layer of dielectric material coating a metallic surface comprises electrophoretically depositing an insulating component of an electrophoretic varnish on parts of the metallic surface in the pores. The quantity of the current consumed is measured and displayed in units of surface area.

4 Claims, 1 Drawing Figure



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**PROCESS AND APPARATUS FOR DETERMINING
THE POROSITY OF A DIELECTRIC LAYER
COATING A METALLIC SURFACE**

This invention relates to the determination of the porosity of dielectric layers on a metallic surface.

The permeability of a protective layer determines its effectiveness against corrosion of metallic objects. It has already been proposed (U.S. Pat. No. 2,572,597, German Patent No. 664 598) to measure the permeability or "porosity" of dielectric layers by the passage of a continuous or alternating current between the metallic substratum and an electrolyte on the surface of the protective layer. The results of these measurements, expressed in milliamperes or in ohms, indicate only very approximately the overall quality of the protective layer. These measurements are, moreover, liable to errors of interpretation depending on insufficiently defined factors, such as: the applied voltage; the polarity of the d.c. voltage; the potential difference in the measurement apparatus; the potential difference in the electrolyte; the nature of the current; the nature and concentration of the electrolyte; the temperature of the electrolyte; the effects of electro-chemical polarization; the shape and the distribution of the pores; and the time elapsed between connecting up and taking a reading.

In certain cases, the localization of defects enables the analysis of the causes of the defect by marking by means of a chemical or electro-chemical reaction. For example U.K. Patent No. 1,081,858 proposes electrodeposition of copper or other metal, using the metallic surface as one electrode, so that a detectable deposit is formed at the pores in the surface. German Patent No. 664 598 discloses changing a colored indicator by the electro-chemical reaction of one of the compounds of an electrolyte during the passage current.

Other examples are the formation of protuberances of aluminum hydroxide by reaction of the non-protected metal with the ambient humidity, after amalgamation by means of a solution of mercury chloride, and the electrodeposition of an organic colorant, in solution or aqueous colloid, onto non-protected parts of the metal.

All of these localization methods suffer from defects and each contain several sources of error for the measurement of porosity.

It is an aim of the invention to provide an improved non-destructive test of the permeability of protective layers, in particular for the control of products before delivery. A further aim is to enable, if required, determination of the distribution of the pores.

According to the main aspect of the invention, a process for determining the porosity of a layer of dielectric material coating a metallic surface, comprises the steps of:

- i. covering the layer with an electrolyte containing an electrophoretic varnish;
- ii. applying an e.m.f. between a first electrode in the electrolyte with the metallic surface as second electrode to cause electrodeposition of a non-conducting component of the varnish on parts of the metallic surface in the pores; and
- iii. measuring the quantity of current consumed.

The principle upon which the process according to the invention is based is that the electrodeposition of

the electrophoretic varnish can only take place on the non-protected metallic parts of a dielectric layer.

It can also be arranged that the amount of current required to deposit the varnish is proportional to the accessible area of the metallic surface. The validity of this relationship depends upon the following conditions:

10 a fixed, stable value of the electro-chemical equivalence of the varnish;

a fixed depositing time; and

the chemical resistivity of newly deposited varnish must be adapted to the deposition electromotive force.

15 During electrophoretic deposition, the quantity of material deposited at the electrodes is directly proportional to the quantity of current used, if the conditions of deposit are defined and constant.

20 In the case of a porous dielectric layer on a metallic surface, the quantity of an electrophoretic deposit on the non-protected surface (i.e. the pores) will be, for a given thickness of deposit, directly proportional to the latter thickness. Hence, the non-protected surface area, i.e. the surface area of the pores, is therefore proportional to the quantity of electricity used during the 25 electrophoresis.

25 At constant voltage, the current delivered during the electrophoretic deposit of a non-conductive component varies exponentially in time. Nevertheless, when the quantity of current becomes small, a balance 30 is obtained between the applied e.m.f. and the chemical resistance of the deposited material: the thickness thus has a practically constant value.

On the other hand, for a constant voltage, for a given short duration of deposition and a given surface to be covered, the quantity of electrophoretic deposit will be slightly different according to the arrangement and properties of the surface to cover. If an extreme case is taken as an example, the renewal of the electrophoretic solution into depositable particles will be more difficult 40 near a uniform surface than near a multitude of points over the electrode. This distortion decreases very rapidly as the electrodepositing time increases. In view of the above, the invention proposes a process which is 45 carried out such that the measurement of the quantity of electrophoretic current continues until the current is very small; with semi-colloidal solutions of the acid polar resin type, this time varies between 5 and 30 seconds.

50 The readings taken of the current consumed can be calibrated by electrodepositing varnish onto a metallic surface of known surface area in conditions identical to testing a coated metallic surface. To detect a porosity beyond a certain norm, an electrophoretic varnish of a 55 different color to that of the dielectric layer can be used, which enables localization of the defects in the protective layer, after rinsing with water, by color contrast. Specimens can also be cooked in an oven, which fixes indication of the defects, in order to conserve them, for proof or study.

The single FIGURE of the accompanying drawings shows schematically and by way of an example, an embodiment of a device for carrying out the process according to the invention.

60 A mains-fed stabilized rectifier 1 delivers a stabilized voltage at a value selected between 20 and 100V, for example 75V stabilized at ± 1 percent.

The negative pole of the rectifier is connected to an electrode 2.

The positive pole of the rectifier is connected to a time switch 3, for example an electronically delayed triggering device closing the circuit for a selected interval, for example, 10 seconds following actuation by a pushbutton, not shown. A shunt 4 and an integrator 5 are connected in parallel between the time switch 3 and a conducting support 7.

This integrator is composed of a conventional RC system with amplifier and enables measurement of the quantity of current Q delivered between times O and t , Q being given by the formula

$$Q = \int_0^t Idt,$$

where I is the value of the current.

This integrator 5 comprises a display device 6, where the results of measurements are indicated by a hand moving in front of a scale graduated directly in surface area units (mm^2), or by a digital computer.

The integrator 5 has several selectable sensitivities so that the units shown on the graduated scale of display device 6 can be multiplied by a factor of 10, 100, or 1,000. The operating button of time switch 3 also operates the time zero setting of the device 6. Calibration of the display device 6 will be explained later on.

The illustrated measurement device is used to check the surface state of a metallic container such as a box, or a flexible or rigid can or tube, the inner surface of which has a coating of dielectric material to protect against corrosion. The dielectric layer can, for example, be a varnish, paint, a layer of synthetic material applied by atomization, an enamel, or a layer of anodic oxide.

The conducting support 7, connected to shunt 4 and device 6, carries the metallic container 8 to be tested. The container 8 is filled up to a fixed level, for example 40 1 cm below the top edge, with an electrolyte in which the electrode 2 is immersed. The electrolyte is an electrophoretic varnish based on acrylic esters with a concentration comprised between 5 and 15 percent in water. It is strongly colored or pigmented in order to contrast with the layer to be checked.

The deposit time is selected by means of the time switch, and the sensitivity of the integrator is also selected as a function of the type of container being tested. The time switch is then actuated by a pressure on the operating button, the display device 6 is consequently automatically set to zero, and the electric circuit is closed for the selected time, for example 10 seconds.

During this time, varnish is deposited by electrophoretic action on the parts of the metallic surface adjacent to pores.

When the selected time has elapsed, the circuit is automatically cut off by the time switch and the result of the measurement can be read on the display device 6 until the next measurement takes place.

A similar procedure is used to calibrate the display device 6. The metallic container 8 is replaced by a test container with no porosity. An enamelled wire with a 1 mm^2 cross-sectional area is connected to the external

conducting surface of the container so that it acts as electrode instead of the metallic surface. The end surface of the free end of the wire is polished so that the varnish can be deposited thereon by electrophoresis when the free end is immersed in the electrolyte.

5 A test is carried out by actuating the time switch 3, and at the end of the test, the display device 6 should indicate a free surface of 1 mm^2 . If the reading is not exact, the composition of the varnish is corrected by modification of its pH and its amine content.

According to a varied embodiment, not shown, the device for carrying out the process can be adapted to measurements on a planar metallic surface covered by a dielectric. The modified device comprises a suction 15 valve applying hermetically against the surface over a certain surface area thereof. The shunt 4 is connected to the metallic part of the surface, the electrode 2 is immersed in an electrophoretic solution in the suction valve, and measurements are carried out in the same way as has been described.

After carrying out a test as indicated above on, for example, a metal sheet, the tested surface is washed with water and the distribution of the pores are visible in the form of colored traces or points. If it is desired to conserve the sheet, it is then baked for approximately 5 minutes at 220°C .

What is claimed is:

1. A process for determining the porosity of a layer of dielectric material coating a metallic surface, comprising the steps of:

- i. covering the layer with an electrolyte containing an electrophoretic varnish;
- ii. applying direct current e.m.f. between a first electrode in the electrolyte with the metallic surface as a second electrode for a selected period of time to cause electrodeposition of a nonconducting component of the varnish on unprotected parts of the metallic surface in the pores; and
- iii. measuring the integrated quantity of current consumed in such electrodeposition by integrating the current during said selected period of time.

2. A process according to claim 1, in which the said component of varnish is of a color contrasting with the color of the dielectric material.

3. Apparatus for determining the porosity of a layer of dielectric material coating a surface of a metallic body, comprising a circuit including a stabilized source of direct current e.m.f. having opposite terminals, means for contacting said coated surface with an electrolyte containing an electrophoretic varnish, an electrode in contact with said electrolyte, and means for connecting said metallic body with one terminal of said source and said electrode with the other terminal of said source to cause current to flow through said electrolyte to electrodeposit said electrophoretic varnish in pores of said dielectric coating, said connecting means including a time switch permitting said current to flow during a preset selected period, and current integrator means for measuring the integrated quantity of current consumed by such electrodeposition during said selected period.

4. An apparatus according to claim 3, comprising means for displaying a measurement of the current integrator means in units of surface area.

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