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Kallianides et al.

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[54] **SLOT APPLICATOR METHOD**

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Related U.S. Application Data

[62] Division of Ser. No. 701,488, Jan. 29, 1968, abandoned.

[52] **U.S. Cl.** ....**29/25.41,** 117/201, 117/49, 117/100 B, 117/102 R, 117/113, 117/213

[51] **Int. Cl.** **B44d 1/18,** C23c 1/10

[58] **Field of Search** ....117/100 B, 201, 113, 117/49, 50, 102 R, 213; 29/25.41

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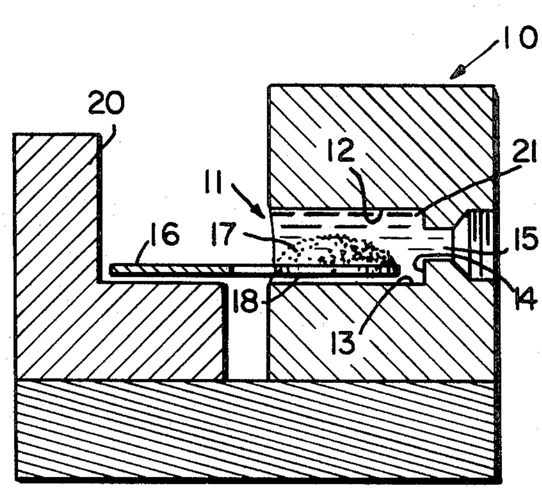
Assistant Examiner—M. F. Esposito
Attorney—Richard H. Childress et al.

[57] **ABSTRACT**

The combination of a reservoir containing a fluid and applicator means for applying the fluid to means carrying a plurality of pellets to be used as capacitors. The applicator means includes upper and lower walls connected by a rear wall so as to form a slot having a determined length and width. A channel is formed in one of the walls so as to couple the slot to the fluid containing reservoir allowing fluid to flow to the slot in a controlled manner. The applicator means applies determined amounts of the fluid to the means carrying said pellets and the pellets passing therethrough.

9 Claims, 10 Drawing Figures



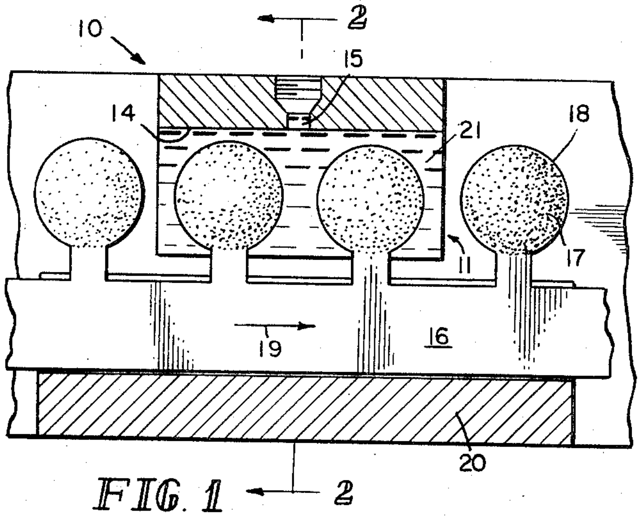


FIG. 1

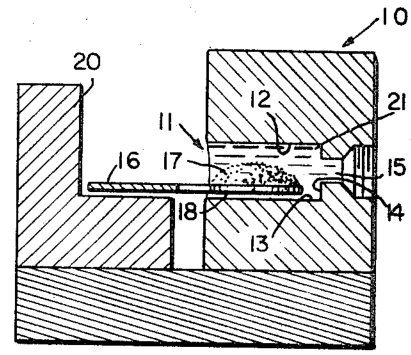


FIG. 2

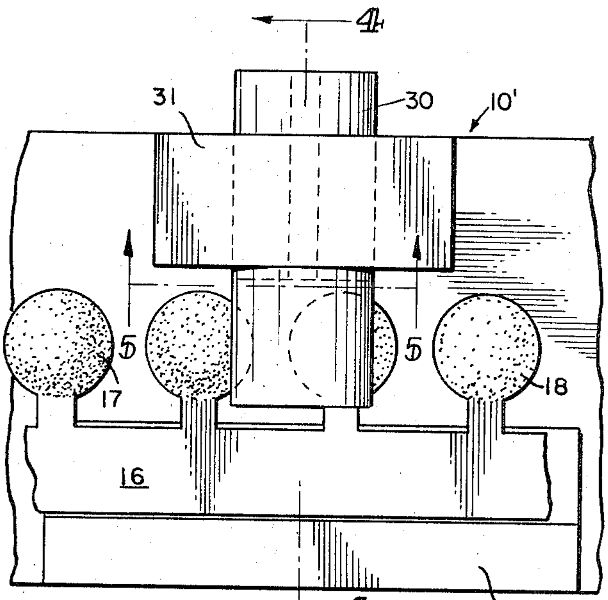


FIG. 3

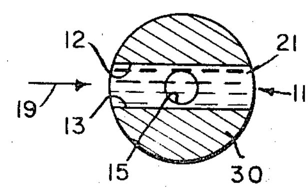


FIG. 5

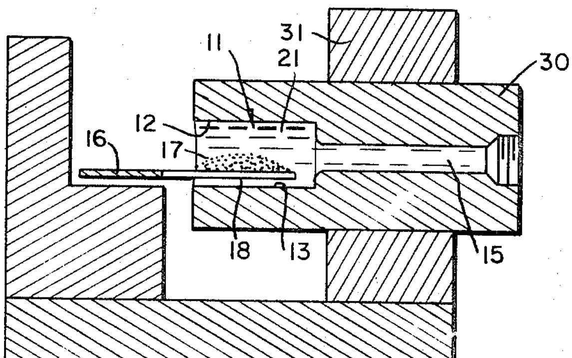


FIG. 4

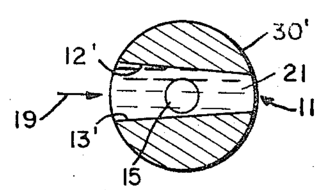


FIG. 6

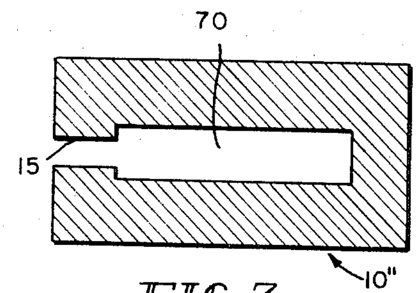


FIG. 7

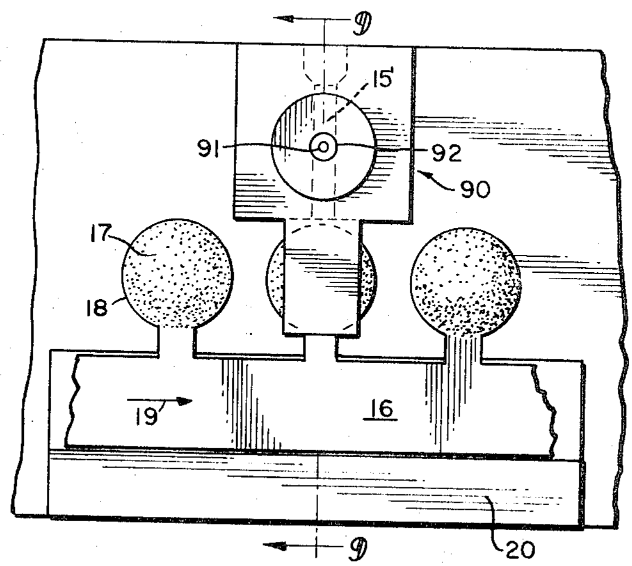


FIG. 8

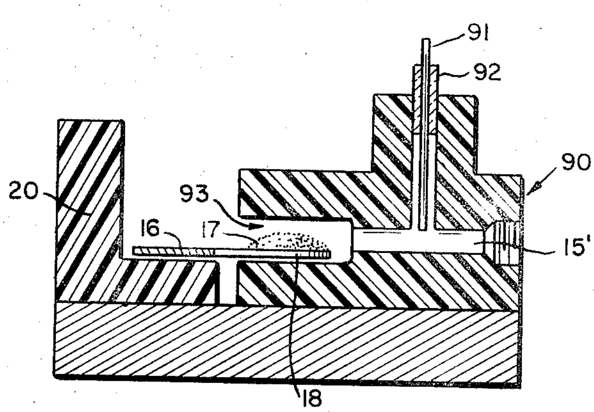


FIG. 9

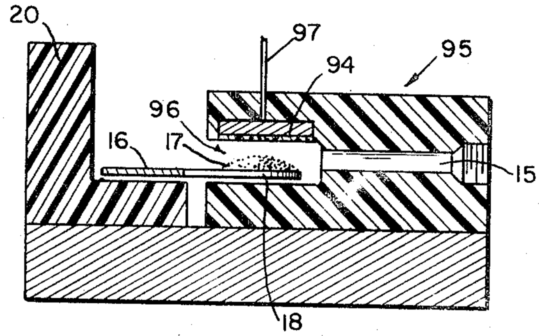


FIG. 10

SLOT APPLICATOR METHOD

This is a division of application Ser. No. 701,488, filed Jan. 29, 1968, now abandoned. U.S. application Ser. No. 93,869, filed Nov. 30, 1970, now U.S. Pat. No. 3,669,062, is a continuation of U.S. application Ser. No. 701,488, filed Jan. 29, 1968.

Solid electrolyte capacitors may be manufactured using any one of several different techniques. For example, a determined amount of a film-forming metal powder selected from the group consisting of tantalum, zirconium, aluminum, niobium, and titanium may be pressed to a desired density and then sintered so as to provide a sintered porous anode slug or pellet. In addition, the anode slug may be prepared using a mixture of metal powder and a binder such as stearic acid or the like. During sintering of the compact, the stearic acid is evaporated without leaving traces of impurities on or in the compact. The binder is used to hold the compressed particles together until the sintering process has been initiated. Sintering cements the individual metal powder particles together so as to form a slug having a myriad of intercommunicating voids. An oxide film formed on the film-forming material using any of the known electro-formation methods. The oxide film has asymmetrical conductive characteristics and serves as the dielectric for the capacitor. In the case of a tantalum slug, the oxide film is tantalum pentoxide. The oxide coated slugs are dipped into a bath of manganese nitrate. The manganese nitrate coated slugs are passed through ovens in which the manganese nitrate is pyrolytically converted to a semiconductive layer of manganese oxide. The manganese dioxide layer is the solid electrolyte of the capacitor. The step of forming the manganese dioxide layer and/or the oxide film layer on the slug may be repeated as many times as is necessary to achieve the desired electrical characteristics. The slugs are dipped into a suitable contact material such as a colloidal dispersion of graphite in water or the like and suitably cured in an oven. This is done to deposit a graphite contact layer on the end of the slug remote from the anode riser. Silver "paint" is applied over the graphite layer and cured. Thereafter, the slugs are dipped in solder. The slug is placed in a suitable container or housing generally having an open end and a closed end. The end of the slug coated with solder is suitably attached to the casing. The open end of the container is closed with a suitable end seal.

It was found that solid electrolyte capacitors can be fabricated using a continuous processing method. The process may be initiated by depositing a wet mass of film-forming metallic powder on a substantially continuous foil strip fabricated from the same film-forming metal and sintering the moistened mass of metallic powder in situ to form a porous pellet connected to the foil strip. The use of a moistened mass of film-forming metal powder has several advantages among which are that the powder is moistened so that it flows dropwise from a suitable dispenser means thereby facilitating dispensation of the moistened mass in determined amounts. Another advantage is that the moistened mass has a significantly reduced volume when compared to the volume of the dry powder before moistening thereby providing a green compact having the required density without the necessity of compacting the powder. When the foil strip and the pellet, comprising the anode, are anodized in accordance with generally accepted practices, a dielectric film is formed thereon. A semiconductive layer is formed on the anode using generally accepted procedures. A suitable electrically conductive coating is deposited over the semiconductive layer to form the cathode of the capacitor. The capacitor has leads attached thereto and is suitably encapsulated.

The continuous fabrication process, referred to hereinafter as the "powder on foil" technique, was conceived and developed to eliminate handling problems experienced during the fabrication of small, solid electrolyte capacitors. The "powder on foil" technique of manufacturing small, solid capacitors significantly reduced the handling required of the individual capacitors when compared to the handling required during the fabrication of solid electrolyte capacitors using individual sintered anode slugs. Also, it was found that elimination of the pressing operation and the binder significantly improved the quality of the solid electrolyte capacitor.

Previously, "powder on foil" capacitors were fabricated by dispensing a predetermined amount of a moistened mass including a film-forming metallic powder in the form of a droplet or droplets on a selected area on a film-forming metal foil. The metal foil may be provided with depressions or indentations for locating and retaining the slurry at a predetermined area on the foil. The moistened mass of film-forming metallic powder and the metal foil must be the same film-forming metal. The foil carrying the moistened mass is processed in a substantially continuous fashion until the individual capacitors are separated from one another as the last step of the process. It is seen that the outlined procedure reduces the amount of handling required during fabrication of capacitors, substantially eliminates contamination which may occur during handling and minimizes the possibility of structural damage occurring during fabrication by eliminating the steps of pressing and adding binders to the powder prior to sintering. After the pellet is formed on the foil strip, the cathode formation is accomplished by using the generally accepted method steps for fabricating solid electrolyte capacitors. Generally, the foil strip and the associated pellets are dipped in an appropriate solution such as manganous nitrate, a dispersion of graphite in water, silver paint and the like during processing.

It was found that the depth of immersion of the pellet in the appropriate solution should be accurately controlled in order to limit undesirable build-up of excess material on the pellet. Generally, dipping of the pellet in the appropriate solution was accomplished by rotating the foil strip and the attached pellets about 90° and immersing the foil strip and pellets by dipping in containers or vats. The depth of immersion is determined by the position of the foil strip and the level of the solution. It was found that both of these factors were difficult to control within the accuracy required to achieve a quality capacitor.

In addition, it was found that when the foil strip and the pellets were dipped into the appropriate solution, the solution had to be discarded after a determined amount of use or passage of time due to the nature of the dipping process and the nature of the properties of the reagents in the solutions. For example, the manganous nitrate solution is diluted as water soaked anodes are immersed therein and on standing for a length of time, the solution may become contaminated. In order to prevent contamination of the pellet with impurities or the like, the solution should be discarded after a determined amount of use and replaced by a "fresh" solution. In the case of the colloidal dispersion of graphite in an aqueous solution, deterioration thereof during standing results in the loss of a large portion of ammonia from the aqueous solution. Dilution of the colloidal dispersion of graphite in an aqueous solution may occur due to water carried by the pellets from previous process stations mixing with the aqueous solution. Silver "paint" is particularly sensitive to standing for periods of time in contact with air. It was found that the silver "paint" dries quickly and tends to form a skin on the surface thereof which makes dipping of the pellets therein more difficult and leads to a considerable waste of the relatively expensive silver "paint".

The present invention has eliminated the above-mentioned problems by using slot applicator means which permits immersion of the foil strip and the attached pellet or pellets in the appropriate solution while being displaced with their major axis in the horizontal plane. It was also found that the depth of immersion of the foil strip and the attached pellets can be easily reproduced and conveniently controlled within close tolerances. A major advantage of the slot applicator means over the standard technique of dipping capacitor anodes in solution containing vats is that waste by contamination and the like of the solution is minimized since the major portion of the solution is retained in an enclosed reservoir removed from the applicator means. The solution to be supplied to the applicator means is retained under substantially clean and uncontaminated conditions. In addition, since the solution is drawn from a reservoir where the environment is closely controlled, variations of the electrical properties of the pellet due to changes in the composition of the solutions in which the pellet is immersed are substantially eliminated. The variations in the solutions due to large surface area contact with ambient air when retained in dipping vats having large openings to allow for dipping the anodes therein is substantially eliminated due to the relatively small surface area contact of the solution with ambient air when dispensed using the slot applicator means of the present invention. Cleaning or washing of the pellet to remove loose particles or solution excess therefrom is most effective when the washing fluid and foil strip retaining the pellet are displaced in opposite directions. In addition, the amount of washing fluid necessary to obtain a desired cleaning result is less if the fluid flows in a direction opposite to the displacement of the pellet. The slot applicator means permits the flow of the fluid in a direction opposite to the movement of the foil strip and pellet.

With slight modifications, the slot applicator or slotted means may be used as an in-line monitoring device. The monitoring device permits the measurement of the electrical parameters of the capacitor. The slotted means contains a suitable electrode which is the cathode of a measuring cell. Electrical characteristics of the pellet such as capacitance, equivalent series resistance and leakage current can be determined for individual pellets at any one of several selected points in the process without interrupting the movement of the foil strip during fabrication of the capacitors. It is seen that substantially continuous in-line monitoring of the electrical properties of a capacitor is a reality. The contact slot has to remain in contact with an individual pellet until the measurement of capacitance, DF, or DCL has been completed. With a continuously moving strip this can be realized by either reducing the length of the slot so that there is a sufficient time interval without electrolyte bridging between adjacent pellets, or by moving the measuring slot synchronously with the tape for a distance equivalent to the time needed to complete the measurement.

Therefore, it is an object of the present invention to provide method which overcomes the above-mentioned problems.

Another object of the present invention is to provide a method for applying an appropriate solution to a plurality of pellets passing therethrough with substantially no waste and/or contamination of the solution.

Yet another object of the present invention is to provide a method for applying a controlled amount of an appropriate solution to a continuous succession of pellets carried on a continuous foil strip passing therethrough.

A further object of the present invention is to provide a method for applying an appropriate solution to a plurality of pellets carried by a foil strip, said means being an integral part of a continuous process for fabricating an infinite strip of anodes for solid electrolytic capacitors.

Yet another object of the present invention is to provide method which accurately applies a predetermined amount of an appropriate solution to pellets carried by a film-forming metal strip, said pellet, metal strip and solution operating so as to form a portion of an electrolytic capacitor.

Another object of the present invention is to provide a method having apparatus comprising an applicator means including slotted head means wherein the head means includes a slot which is capable of accommodating pellet thicknesses of about 0.1 inches.

Yet another object of the present invention is to provide a method having apparatus comprising a slotted applicator means having a slotted head in which the slot retains an appropriate fluid due to the geometry of the slot and the surface tension of the fluid.

Still another object of the present invention is to provide a method having apparatus comprising a slotted applicator means wherein fluid is gravity fed to the slot from a reservoir means located above the applicator means and coupled to the applicator means by a suitable conduit means.

Yet another object of the present invention is to provide a method for in-line monitoring of the electrical characteristics of capacitors as the capacitors pass through the slot of the slotted means.

A further object of the present invention is to provide method for applying a determined amount of an appropriate solution to a pellet as the pellet passes through the slotted applicator and further including means for removing excess amounts of the solution from the pellet as the pellet leaves the slotted applicator means.

Yet still another object of the present invention is to provide method for applying a determined amount of an appropriate solution to a pellet as the pellet passes through the slotted applicator without wasting and/or contaminating the solution that is efficient, effective and accurate in application of the solution to the pellet.

The present invention, in another of its aspects, relates to the novel features of the instrumentalities of the invention described herein for teaching the principal object of the invention and to the novel principles employed in the instrumentalities whether or not these features and principles may be used in the said object and/or in the said field.

With the aforementioned objects enumerated, other objects will be apparent to those persons possessing ordinary skill in the art. Other objects will appear in the following description, appended claims and appended drawing. The invention resides in the novel construction, combination, arrangement, and cooperation of elements as hereinafter described and more particularly as defined in the appended claims. The appended drawings illustrate an embodiment of the present invention constructed to function in the most advantageous modes devised for the practical application of the basic principles involved in the hereinafter described invention.

In the drawings:

FIG. 1 is an enlarged top view of the slotted applicator means illustrating cut-out cups formed in a substantially continuous foil strip means carrying a pellet consisting essentially of film-forming metal powder passing through a slot of the applicator means.

FIG. 2 is an enlarged cross sectional view of the slotted applicator means and the foil strip means carrying pellets taken across the lines 2—2 of FIG. 1.

FIG. 3 is an enlarged top view of applicator means adjustable with respect to the foil strip means and the pellets allowing accurate adjustment of the depth of immersion of the pellets in the solution retained in the slot of the applicator.

FIG. 4 is an enlarged cross sectional view of the slotted applicator means and the foil strip means carrying pellets taken across the lines 4—4 of FIG. 3.

FIG. 5 is an enlarged partial side view of the slot of the slotted applicator means taken across lines 5—5 of FIG. 3 illustrating the spaced, parallel relationship of the top and bottom walls of the applicator means.

FIG. 6 is an enlarged partial side view of the slot of the slotted applicator means illustrating the top and bottom walls at an angle with respect to one another so as to facilitate removal of excess solution from the pellet as the pellet exits the applicator means.

FIG. 7 is an enlarged partial cross sectional view of an apertured applicator means for washing the foil strip and attached pellets.

FIG. 8 is an enlarged partial cross sectional view of a slotted means including an electrode for measuring selected electrical characteristics of the foil strip and attached pellets passing therethrough.

FIG. 9 is an enlarged side view of the slotted means taken across the lines 9—9 of FIG. 8.

FIG. 10 is an enlarged partial cross sectional view of slotted means including an electrode for measuring selected electrical characteristics of the foil strip and attached pellets passing therethrough.

Generally speaking, the means and methods of the present invention relate to an applicator means in combination with a reservoir containing fluid. The applicator means includes a slot through which a foil strip and pellets pass in substantially continuous fashion. The slot of the applicator means applies determined amounts of the fluid from the reservoir to the foil strip and pellets passing therethrough.

Referring now to the figures of the drawing and more particularly to FIG. 1, the slotted applicator means is generally indicated by the reference number 10. The applicator means has a substantially C-shaped cross section and is fabricated from any suitable material such as stainless steel, teflon, plexiglas or the like. The applicator means includes a slot 11, upper wall 12, lower wall 13 in substantially spaced parallel relationship with the upper wall 12, end wall 14 which couples upper wall 12 to lower wall 13 and a channel 15 formed in end wall 14. The channel connects the slot 11 with a reservoir (not shown) containing an appropriate solution through a conduit means (not shown). The solution is illustrated in FIG. 1 as 21.

A substantially continuous foil strip 16 fabricated from a suitable film-forming metal selected from the group consisting of tantalum, zirconium, aluminum, niobium and tantalum has attached thereto a pellet 17 which generally has a hemiellipsoidal shape. The foil strip includes a plurality of substantially equally spaced cut-out cups 18. Each of the cups includes a depression or indentation (not shown) for predeterminately locating the pellet on the foil strip. The foil strip is displaced in the direction of arrow 19 by any suitable means such as a conveyor means or the like (not shown). The foil strip may have a thickness of about 0.002 inch and the cups may have a diameter of about 0.2 inch. The cup may or may not have an indentation of about 0.02 inch. The pellets of film-forming metal typically have a thickness of about 0.02 to 0.1 inch. Typical dimensions of the pellet are a width of about 0.2 inch and thickness of about 0.05 inch which provides a capacitor having a capacitance value of about 50 microfarad-volt. It is to be understood that the thickness of the droplet is proportional to the capacitance of the device, therefore the limits given as to the thickness of the droplets aremmerely illustrative of how thin the anodes are and are not intended to be limiting with regard to the inventive aspects of the present invention. The anodes may be made thicker or thinner if desired.

As the foil strip advances in the direction of arrow 19, a cut-out cup 18 and its attached pellet are introduced to the slot 11 of the applicator means 10 as shown in FIGS. 1 and 2. An appropriate solution 21 such as manganous nitrate, a colloidal dispersion of graphite in water, silver paint or the like is applied to the cup and the pellet by the applicator means. The retention of the solution in the slot 11 is due to the surface tension of the fluid and the geometry of the slot. The width and height of the cut-out cup and the attached pellet are compatible with the slot 11 of the applicator means. The length of the slot of the applicator means is proportional to the elapsed time required for optimum soaking of the individual units. The application time depends, therefore, on the length of the applicator means and the foil strip speed.

The appropriate solution is fed into the slot 11 through one or more channels in the applicator. FIG. 1 shows a single channel 15 through which the fluid from the reservoir flows to the slot of the applicator means. The channel or channels are formed in the rear wall of the slotted applicator means equally spaced from one another and the extremities of applicator means in order to provide substantially uniform feeding of the solution to all areas of the slot of the applicator means. For relatively short applicator means, as shown in FIGS. 1 and 3, which are on the order of a few inches in length, one channel is thought to be adequate. In applicator means having extended lengths, one channel for every 3–5 inches of length is thought to be desirable.

The applicator means should be provided with a suitable guide means **20** for maintaining the foil strip properly positioned with respect to the slot **11**. In order to prevent bridging of the gap between slot and guide means **20**, it may be necessary to place guides at the ends of the slot only.

The appropriate solution is gravity fed to the slot **11** from a reservoir (not shown) positioned above the slot and connected to it through a suitable conduit (not shown) such as capillary tubing. The flow rate of the solution may be adjusted by altering the height of the reservoir above the slot **11** or by changing the length or diameter of the capillary tubing. It is thought that accurate and reproducible feed rates can be obtained through the use of suitable metering pumps (not shown).

FIGS. **3** and **4** illustrate an adjustable applicator means **10'** in which a slotted head **30** carried by guide means **31** of the applicator means may be adjusted with respect to the foil strip thereby allowing accurate adjustment of the depth of immersion of the cut-out cup and the attached pellet in the appropriate solution. The slot illustrated in FIG. **3** is of such length so as to accommodate the entire area of a single capacitor. The so-called "short" applicator means are more suitable for the application of viscous solutions such as silver paint to the strip and pellet than the "long" applicator means although the "short" applicator means may be used to apply other solutions thereto. The upper and lower walls of the applicator means may be in substantially spaced parallel relationship as shown in FIG. **5** or the walls may be tapered as shown in FIG. **6** at **12'** and **13'** in such a way that the excess solution, if any, applied to the pellet is removed as the capacitor foil strip and attached pellet exit the slot.

It is thought that slurries such as silver paint and the colloidal dispersion of graphite should be agitated while confined within the reservoir in order to keep the particles appropriately dispersed in the liquid.

Slot applicator means may be used for washing and rinsing of the foil strip and the attached pellet. However, the length of the slot required may make it more desirable to move the foil strip and attached pellet through aperture **70** which is substantially completely enclosed as illustrated in FIG. **7**. Channel **15** is used to feed water into aperture of the applicator means. Another embodiment which increases the washing efficiency of the applicator means is realized by displacing the foil strip and pellet through a series of "short" slots.

FIGS. **8** and **9** show a slotted means **90** fabricated from any suitable material such as Teflon or the like including a sensing slot **93** and an electrode **91** fabricated from platinum wire for measuring selected ones of the electrical properties of capacitors passing through the slot and in close proximity to the electrode. The electrode is coupled to any suitable measuring device (not shown). The slot of the means **90** is of such length that no bridging of the electrolyte occurs between adjacent capacitor units. The electrode **91** includes an insulative spacer **92** which spaces the electrode from the side wall of T-shaped channel **15**. Channel **15'** is used to provide a suitable electrolyte solution to the slot **93**. The electrolyte is used during the testing of the capacitors.

FIG. **10** shows another embodiment of the slotted means at **95**. The slotted means includes a sensing slot **96**. An electrode **97** is retained by the applicator means in such a way that it contacts the electrolyte in the slot fed thereto by supply channel **15**. The electrode **92** includes a relatively large sensing area and is fabricated from a platinized platinum material. The slotted means **95** is used for measuring the capacitance of the pellets and foil passing therethrough. The electrode is positioned in the slot itself and is separated from the capacitor unit by a suitable porous separator **94**. When the slotted means is used to make electrical measurements, the foil strip is the anode, the electrode in the slotted means the cathode.

While this invention is illustrated and described in embodiments, it will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of this invention and as set forth in the appended claims.

Having thus described our invention, we claim:

1. A method of applying a fluid to strip means carrying a pellet for use as a capacitor anode, comprising the steps of,

depositing a moistened mass of film-forming metallic powder on strip means of film-forming metal,

forming the moistened mass to provide a porous pellet joined to the metal strip means,

passing the portion of the metal strip means carrying the pellet joined thereto through slot means formed in slot applicator means, the slot means of determined length and width, and

contacting the portion of the metal strip means and the pellet passing through the slot with liquid retained in the slot due to the surface tension of the liquid and the geometry of the slot.

2. The method of claim **1**, wherein said slot has an upper wall, lower wall and an end wall retaining said upper wall and said lower wall in spaced relationship.

3. The method of claim **1**, wherein the porous pellet joined to the metal strip means is formed by sintering the metallic powder in situ to form a porous pellet joined to the metal strip.

4. The method of claim **1**, wherein the liquid contacting the pellet and the strip is selected from the group including manganous nitrate, a colloidal dispersion of graphite in water or silver paint.

5. The method of claim **4**, wherein the film-forming metallic powder and the strip means of film-forming metal are selected from the group including tantalum, zirconium, aluminum, niobium and titanium.

6. The method of claim **5**, wherein the film-forming metallic powder and the strip means of film-forming metal are tantalum.

7. The method of claim **1**, including the further steps of, subsequent to contacting the metal strip means and pellet with the liquid, providing a second slot means, passing the liquid contacted metal strip means and pellet through the slot of the second slot means and monitoring the electrical characteristics of the metal strip means and pellet in the slot.

8. The method of claim **1** including the further step of, subsequent to contacting the metal strip means and pellet with the liquid, removing unjoined metallic powder and excess liquid by moving fluid in a direction different from the direction of movement of the metal strip means and pellet.

9. A method of making a capacitor using the anode of claim **1**, comprising contacting the metal strip means and the pellet with dielectric means, contacting the dielectric means with electrolyte means, and contacting the electrolyte means with cathode means.

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