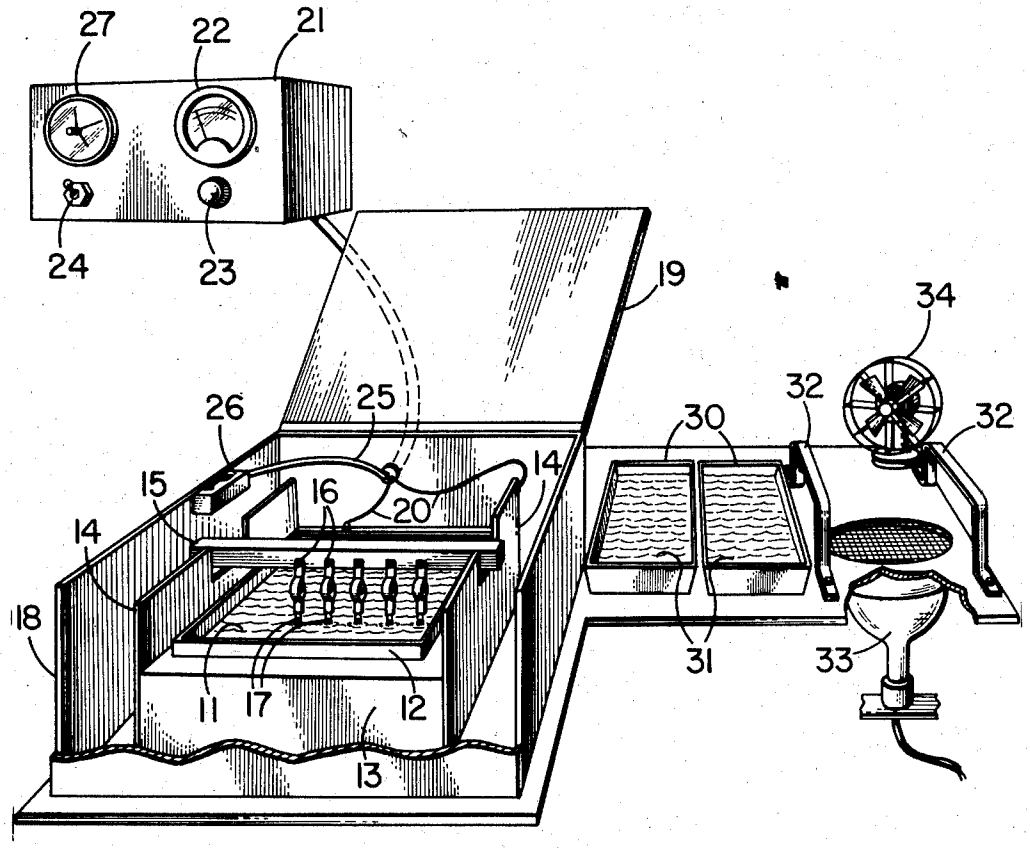
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METHOD OF INSULATING ELECTRON DISCHARGE TUBE ELEMENTS

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METHOD OF INSULATING ELECTRON DISCHARGE TUBE ELEMENTS

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The invention relates to insulating metallic elements of electron discharge tubes and in particular to a particular mixture for cataphoretically coating such elements.

In the art of manufacturing electron discharge devices, an electrically insulating coating often must be affixed to a metallic element. In view of the relatively small size of the elements involved and the high temperatures to which they may be subjected, only refractory materials, as the oxides of aluminum and magnesium, have been found to be satisfactory.

Among the many methods of applying refractory coatings to electron discharge tube elements that have been devised, some of the most commonly used are those based on the phenomenon of cataphoresis. In the prior art processes referred to, particles of an insulating material, as aluminum oxide in a finely divided form, are first suspended colloidally in a substantially non-conducting liquid medium, as a mixture of distilled water and an organic solvent. A small amount of salt to serve as an activator for the cataphoretic process and as a binder, as will be described in more detail hereinafter, is then added to the mixture. When the element to be coated is immersed in such a mixture and an electric force is applied, a thin coating is deposited on the element. This coating consists mainly of the insulating material, but includes a small amount of the activator. It is necessary, therefore, to ensure the conversion of the activator to a non-conducting substance. Such conversion is effected by removing the element from the mixture and heating it in a non-oxiding atmosphere. As a result of this heating, any non-volatile materials trapped in the coating, if the proper activator is used, are converted to non-conducting oxides and a permanent bond between the coating and the element is formed. In connection with this last step, it is sometimes desirable to put a protective coating on the element after it is withdrawn from the cataphoretic mixture by dipping the element in liquid nitrocellulose and drying the film that clings to the element. Such a protective coating makes it easier to handle the element before the heating step, mentioned hereinbefore, is carried out and is completely destroyed during the heating step without leaving any residue or changing the characteristics of the insulating coating in any way.

Experience has shown that the particular salt used to activate the liquid medium must be chosen with care and must possess certain characteristics. First of all, it must be soluble in the liquid medium being used in order that some degree of dissociation occur to permit cataphoresis. In addition, the salt must be so constituted that it leaves an electrically non-conducting, non-electron-emissive residue in the insulating coating, or be capable of conversion to such a residue. As a result, various metallic nitrate salts, for example, the salts of mercury, aluminum or magnesium, have been the only satisfactory activators. While such salts are of great practical value, difficulty is encountered when they are used, especially in large scale production. After the coating process has been carried on for some time, the rate at which coating is accomplished decreases. This decrease is due to the fact that the concentration of the activator in the mixture drops off as quantities of the activator are trapped in the coating. In order to maintain the desired rate of coating, it is necessary to replenish the activator. Unfortunately, it is difficult, if not impossible, to add the correct amount of activator to the mixture to maintain the concentration at any predetermined level without stopping the process. Moreover, even if great care is taken, the concentration of the activator is likely to vary, making the process very difficult to control except under laboratory conditions.

It has also been found necessary to process the coated elements further in order to obtain a completely refractory coating. Small amounts of the salt used to activate the cataphoretic mixture are trapped in the coating. Such salts have a much lower resistivity than the insulating material and, therefore, affect the coating adversely. The entrapped salt must be converted to a form having at least as high insulating properties as the refractory material in the coating. Conversion may be accomplished by thermal decomposition of the salt, when aluminum nitrate is used, for example, it may be converted to aluminum oxide by heating it above the temperature at which it decomposes (150° C.). Since such heating is necessary, it has been common practice to heat the coated element to a temperature far higher than that required to decompose any entrapped salt to sinter the coating to the element. It is preferable that this heating be eliminated or considerable time and energy is consumed which increases the cost of manufacture.

Those versed in the art have recognized the fact that the use of salts have the foregoing deficiencies, but have not overcome them. It has been felt that any activator that may be considered to be chemically active, that is, either a base or an acid, would probably have such an adverse effect on the metallic element being coated that such activators would not be practical.

An object of the invention is to provide a process for the cataphoretic coating of metallic elements that may be closely controlled over a long period of time;

Another object of the invention is to provide a cataphoretic process in which the activator cannot at any time leave a conducting residue on the element being coated;

Still another object of the invention is to provide an easily proportioned mixture for use in a cataphoretic process.

According to the invention, an insulating coating of excellent properties is obtained with a mixture that comprises an organic liquid medium, an organic binder, refractory particles and a nitric acid activator employed in a cataphoretic process. The organic liquid medium may be any non-electrically conducting substance although it is highly desirable that it be a solvent for the particular organic binder used. The mixture may be prepared by dissolving the proper amounts of the binder and the activator in the liquid medium and then introducing to that solution a sufficient amount of the refractory particles to form a thick colloidal suspension. The metallic element or elements to be coated are immersed in the mixture and an electric potential is impressed between the metallic elements and an electrode, which may be the container itself, in such a manner that electric current flows through the mixture. At least a portion of the refractory particles are then deposited on the immersed surfaces of the metallic elements along with portions of the binder and the acid activator. The organic binder assists in bonding the refractory particles to the metallic element yet is easily driven off when removal is desired. The nitric acid activator is also easily removed. Furthermore, the rate at which coating is effected may be maintained within very close limits in the present process by maintaining a constant current. Small amounts of the

nitric acid activator may be added to accomplish this whenever the current tends to decrease. Since the acid is much more readily dissociated than any salt, it is evident that the time lag between the time at which nitric acid activator is added and the time at which it takes effect is very much smaller than would be the case if a salt were used. As a matter of fact, replenishment of the nitric acid activator may be accomplished at any time without stopping the process. After the coating has been deposited, it is necessary only to remove any excess clinging to the elements and to dry them so that they may be handled. The small amount of binder and activator entrapped in the coating may be advantageously removed after the element is assembled in the tube in which it is to be used during processing thereof, since there is no necessity of converting any part of the coating.

A practical embodiment of the invention, given by way of example only, is described with reference to the drawing, the sole figure of which shows complete apparatus for carrying out the process according to the invention.

As illustrated, a mixture **11** is placed in an electrically conductive container **12**. The mixture **11** may be formed by first making up a non-conducting organic solution consisting, for example, of normal butanol, 40%, by weight; nitrocellulose 2%, by weight, and normal butyl acetate 58%, by weight. It should be noted that the proportions of the various materials may be changed without affecting the invention, the limiting factor in practice being that the amount of nitrocellulose in the mixture not be so great as to make the mixture too viscous to be considered a liquid. Sufficient finely divided aluminum oxide, say 60% by weight, of the solution may be added to the solution and mixed therewith until a milky, rather thick colloidal suspension results. An activator, in the present example, nitric acid, in the amount of approximately 15 grams per liter of the colloidal suspension, is added to electrolyze the solution, activating the cataphoretic process. The container **12** is surrounded with an electrically insulating jacket **13** having upwardly projecting extensions **14** as shown. These projections **14** are preferably notched to receive a work support **15**. A number of resilient connectors **16** are attached to the work support **15** and the metallic members **17** to be coated are supported therein so that each is immersed in the mixture **11** out of contact with the container **12**. The container **12** may be advantageously placed in a protective box **18** having a hinged cover **19** to protect the mixture **11** from contamination and to provide an interlocking system, as will be described, for the safety of the operator of the process. Alternatively, an insulated container may be used and a suitable electrode arranged therein. Electric connections are made to the electrode or to the metallic container **12** and to the work support **15** and suitable leads **20** from each are brought out through an opening in the box **18** to a power source **21**. While this power source may take any of a larger number of known forms, it is preferred that the potential output be variable, as by a potentiometer **23**, and the current metered, as shown, by an ammeter **22**. The interlocking system previously mentioned may be connected in series with an on-off switch **24** by a separate pair of leads **25** running from the power source **21** to a switch **26** mounted in box **18**. Switch **26** is so arranged that it is closed only when the hinged cover **19** is closed. By connecting the switch **26** in series with the circuit in the power source **21** controlled by the on-off switch **24**, it is evident that power cannot be taken from the power source **21** unless both switches are closed. A timing device **27** may also be advantageously incorporated in power source **21** so that the output current is automatically shut off a predetermined length of time after the process is initiated. The exact length of time current is applied, of course, depends on the thickness of the desired coating and the rating of the power source **21**. It is an easy matter to determine the length of time power should be applied.

In this connection, it has been found that the voltage of the power supply should be held at about 150 volts and the current at about 4 milliamperes for each element (when the element is such as a heater wire of the type commonly used in miniature tubes) for about 10 seconds. Any slight drop in the current flowing during the 10 second period is normal, being caused by the buildup of the insulating material on the element which increases the resistance through which the current must flow.

After the desired thickness of coating has been empirically attained, the hinged cover **19** is lifted and the work support **15** with its depending elements **17** is removed and preferably passed through two rinsing trays **30** containing an appropriate rinsing liquid **31**, say denatured alcohol. Two trays are preferred in order to ensure better rinsing and removal of any of the excess of mixture **11** that may be clinging to the elements. After rinsing, it is preferred that the work support **15**, again with its depending elements **17**, be transferred to a drying station. This latter station may be very simple, as shown, consisting only of a pair of supports **32** upon which the work support **15** is placed. A heat lamp **33** is positioned so as to accelerate the drying of elements **17**. In addition, a drying fan **34** may also be used. While the drying station is preferred, it may be eliminated without detriment. Its sole purpose is to permit earlier safe handling of the coated elements **17**. As previously pointed out, there is no need, in the present process, to ensure the conversion of any conducting material, especially metals, entrapped in the coating to a non-conducting oxide since there are none present. The nitrocellulose is driven off by induction heating in evacuation of the tube leaving a substantially pure non-conducting oxide layer on the tube parts.

After the coating process has been in operation for some time, it will be observed that the current flowing, as indicated by ammeter **22** will decrease. This decrease has been found to be a direct indication of a decrease in the rate at which the coating is being deposited on the element. It is evident that, unless the period during which coating is carried out is lengthened, a thinner coating than desired will be deposited. In order to prevent such an occurrence, a small amount of the nitric acid activator may be added to the mixture **11** to bring the current indicated by ammeter **22** back to its original value. Since the acid is completely and almost instantly miscible, its effect on the rate of coating is immediately evident. In connection with replenishing the activator, it may be desirable, although not essential, that the mixture **11** be agitated as by a stirrer (not shown). However, good results have been obtained without agitating the mixture.

The foregoing process is especially well adapted to the fabrication of insulated parts for electron discharge tubes. For example, a convenient number of formed heater elements may be attached to the work support **15** in place of the metallic elements **17** and coated in the manner described hereinbefore. Since it is highly desirable that the ends of the heater elements be free from any coating to facilitate connecting such elements to other components as by welding, the ends are clipped in the resilient connectors **16** and are kept out of the mixture **11**. After the heater elements are rinsed and dried, they may safely be handled and assembled in a tube envelope. The nitrocellulose binder is then removed during the processing of the tube, preferably during the step of evacuating the envelope. It is necessary to heat the entire tube to a red heat anyway during the evacuation step in order to liberate any gases occluded in the elements so it is just as easy to defer the removal of the nitrocellulose in the coating until that time.

The invention claimed is:

1. The method of affixing an insulating coating to the surface of a metallic element comprising the steps of

forming a solution of normal butanol, 40% by weight, nitrocellulose, 2% by weight, and normal butyl acetate, 58% by weight, suspending finely divided aluminum oxide in said solution to form a colloidal suspension, the quantity of said aluminum oxide being equal, by weight, to 60% of the weight of said solution, adding nitric acid in the amount of 15 grams per liter of said colloidal suspension, immersing said metallic element in said colloidal suspension and applying a potential to said metallic element through said colloidal suspension to cause a portion of said aluminum oxide to be deposited on the surface of said metallic element by cataphoresis.

2. A method for cataphoretically coating the surface of a metallic element comprising the steps of preparing a liquid colloidal suspension consisting essentially of an electrically non-conducting organic liquid medium, an organic binder, and finely divided refractory oxide particles, adding to said colloidal suspension nitric acid as an activator in an amount approximately equal to fifteen grams per liter of said colloidal suspension to activate the cataphoretic process, immersing said metallic element in said colloidal suspension, and passing a current through said colloidal suspension to deposit a coating of oxide particles on said surface of said metallic element by cataphoresis.

3. A method for cataphoretically coating the surface of a metallic element comprising the steps of preparing a liquid colloidal suspension consisting essentially of an electrically non-conducting organic liquid medium, an organic binder, and finely divided refractory oxide particles, adding to said colloidal suspension nitric acid as an activator in an amount approximately equal to fifteen grams per liter of said colloidal suspension to activate the cataphoretic process, immersing said metallic element in said colloidal suspension, passing a current through

said colloidal suspension to deposit a coating of oxide particles on said surface of said metallic element by cataphoresis, and periodically adding nitric acid to said colloidal suspension in an amount sufficient to maintain said current constant.

4. A method for cataphoretically coating the surface of a metallic element comprising the steps of preparing a liquid colloidal suspension consisting essentially of an electrically non-conducting organic liquid medium, an organic binder, and finely divided refractory oxide particles, adding to said colloidal suspension nitric acid as an activator in an amount approximately equal to fifteen grams per liter of said colloidal suspension to activate the cataphoretic process, immersing said metallic element in said colloidal suspension, passing a current through said colloidal suspension to deposit a coating of oxide particles on said surface of said metallic element by cataphoresis, cleaning the coated metallic element, and heating said metallic element to sinter said coating of oxide particles and to drive off residues of said organic binder in said coating of oxide particles.

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