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ELECTROPHORETIC COATING OF METAL ARTICLES

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This invention relates to the electrophoretic application of coating materials (such as aluminium oxide, or silicon dioxide, or a mixture of said oxides, or an alkaline earth carbonate such as barium carbonate, or strontium carbonate, or a mixture of such carbonates) to heater elements for thermionic valves or other metal articles required to have a coating thereon for enhancing thermionic emissivity or for insulation purposes or the like.

Existing electrophoretic coating methods are not wholly satisfactory, because the coating material particles in suspension in the electrophoretic bath (that is to say, in colloidal solution, or non-colloidal suspension, or partly one and partly the other) tend to coalesce or coagulate in the bath fluid, and then rapidly precipitate, or at best, are sparsely deposited on the article being coated as relatively large particles which do not readily or tenaciously adhere thereto as an unbroken uniform coating.

The main object of the present invention is the provision of an electrophoretic bath fluid which avoids, or practically avoids, this disability. A further object is the provision of such a fluid and a method of employing same, which in a general way enable a highly effective electrophoretic coating to be obtained in a more efficient manner than has been the case heretofore.

The main characteristic of this invention may be stated as consisting in an electrophoretic bath fluid composed of a suspension of a coating material in an organic liquid, and a "dispersive agent" comprising a member of the dual group consisting of tannic acid, and a mixture of an alkylolamine (such as triethanolamine) with nitrocellulose.

In the case where the dispersive agent is a mixture of an alkylolamine and nitrocellulose these two ingredients may be present in almost any proportion of one in relation to the other. However, in the course of experiment, I have found that when the dispersive agent consists entirely, or almost entirely, of triethanolamine the objects of the invention are insufficiently realised; also, nitrocellulose by itself was found to give a deposited coating which by reason of its gelatinous nature lacked mechanical strength and adhesive tenacity. Consequently it is preferred that in the mixture of an alkylolamine with nitrocellulose neither of these ingredients be present in quantity less than about 5% by weight of the mixture.

The preferred organic liquid, which constitutes the bulk of the bath fluid, is acetone or methanol.

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The quantity of coating material included in the bath is such that its weight amounts to from about 3% to about 20% of the weight of the organic liquid, a preferred proportion being about 10%. The dispersive agent is included in such quantity that its weight amounts to from about 0.3% up to as much as 10% of the weight of organic liquid, a preferred proportion being about 1%.

In the coating of articles according hereto, it is found that the electrical resistance of the coatings is somewhat impaired by the presence of carbonaceous residues therein. This forms a basis of comparison of the relative merits of the two kinds of dispersive agent named herein.

In the case of tannic acid the carbon residues may only be removed from a coating with difficulty, but an advantage due to this dispersive agent is that the bath voltage may be very low; for example, from 22 to 50 volts D. C. On the other hand, bath voltage in the case of an alkylolamine-nitrocellulose dispersive agent, may require to be as much as 300 volts D. C., but with thin coatings the carbon content is practically negligible, and with thick coatings (or thin coatings, for that matter) the carbon may be readily removed by burning. A further consideration in regard to the use of tannic acid, is that the deposited coating readily diffuses into any drops of bath liquid which are allowed to remain on the article after removal thereof from the bath, or into the bath liquid itself if the article is allowed to remain therein after the current is turned off. These last-mentioned difficulties may be readily overcome, however, by the precaution of removing the coated article from the bath before the current is switched off, and by giving the article a vigorous shake immediately after it has been removed from the bath.

The following examples illustrate preferred modes of carrying the invention into practical effect:

Example 1

The bath materials consist of the ingredients set forth in the following Table A in (or in about) the proportions there stated:

Table A

Aluminium oxide	grams	10
Silicon dioxide	do	0.3
Nitrocellulose	do	0.7
Triethanolamine	do	1.0
Acetone	mls	100

The particle size of the oxides is preferably of

the order of 40 microns or less. It is essential, or at least desirable, that all traces of moisture be removed from the aluminium oxide. This may be readily effected by heating it at about 1000° C. for about 1 hour; and, if it is not to be used immediately, bottling it as soon as it is cool enough for that operation.

The bath is prepared by thoroughly mixing the nitrocellulose and triethanolamine together (using a mortar and pestle, for example) to form a homogeneous paste. The oxides are then added to this paste together with sufficient of the acetone to give a doughy consistency to the whole. The resulting doughy mass is then thoroughly kneaded to ensure breaking up of oxide agglomerates. Further acetone is then added in small quantities, and with continued kneading or stirring, until a thin creamy consistency is reached. The remainder of the acetone is then added and the bath fluid thus obtained is given a final stirring, and for preference is stirred from time to time until required for use.

The steps of preparing the bath fluid may be performed manually or mechanically. The essentiality in the mixing, is that all the solid particles be thoroughly wetted. The mixing steps described above achieve this result in a satisfactory manner.

In coating an article, the bath fluid described above may be contained in a beaker or other vessel and the article constitutes the anode. A suitable material for the cathode is nickel. The cathode may be formed as a loop which loosely fits the vessel interior. The bath fluid is preferably stirred continuously, or at least frequently, during the coating operation. The potential difference across the electrodes may be from 100 to 300 volts D. C. We have found that 200 volts, giving a current density of about 250 ma. per square inch of anode area, gives a satisfactory result. At this voltage, the article is immersed in the bath for a period of from 10 to 30 seconds, depending on the coating thickness required. If the article remains in the bath appreciably longer than 30 seconds it is found that gas forms on the anode which tends to dislodge the deposited oxide film. Consequently if the required coating thickness is greater than that which is obtainable within about 30 seconds immersion, it is necessary to effect the coating in two or more stages, and between these stages, to rid the article of gaseous accumulation, and preferably, at the same time effect a stabilization or consolidation of the material already coated. These requirements may be effected by fritting the coating film to the wire (between immersions) by ignition in wet hydrogen at a temperature of about 1600° C. Experiment has shown that the fritting operation gives a sound adherent coating which has a long useful life and is substantially proof against relatively rough usage. Because of this, and irrespective of whether the coating is applied in one or several stages, it is desirable that fritting, as described, be effected as a final step in the coating process.

Where the required thickness of coating is such as to necessitate three or more immersions in the electrophoretic bath, the accumulation of carbonaceous residues in the coating becomes deleterious. This accumulation may be readily removed by preceding or replacing the step of fritting, following the second immersion, by the step of burning the carbonaceous matter in air and at low temperature; that is to say, at a temperature which is not substantially greater than the ignition temperature of carbon.

A cycle of operations which gave a satisfactory result in the coating of thermionic valve heater elements is as follows:

(*a*) Immerse the clean and thoroughly dry heater elements, as anode, in the electrophoretic bath at 200 volts D. C. for about 10 seconds.
(*b*) Dry the element and ignite in wet hydrogen at 1600° C.
(*c*) Re-immerse as in (*a*).
(*d*) Burn off carbonaceous accumulations, at low temperature, in air.
(*e*) Re-immerse as in (*a*).
(*f*) Re-dry and re-ignite as in (*b*).

Example 2

The bath materials consist of the ingredients set forth in the following Table B in (or in about) the proportions there stated:

Table B

Aluminium oxide	grams	10
Silicon dioxide	do	0.3
Tannic acid	do	0.3
Acetone	mls	100

The particle size of the oxides and the dryness of the aluminium oxide are selected or conditioned as set forth in Example 1.

The bath is prepared by thoroughly mixing the oxides and the tannic acid together with some of the acetone, added intermittently and in small quantities, until a creamy consistency is arrived at. The remainder of the acetone is then added and the whole mixed and stirred as set forth under Example 1.

In coating an article, the article is used as anode with a cathode of nickel, and the voltage applied to the electrodes may be about 36 volts D. C. The article is immersed for from 10 to 30 seconds depending on the coating thickness required. Where a thicker coating than that obtainable in 30 seconds is required, the coating may be effected in several stages each of which (or the first and last of which) is (or are) followed by fritting (as, and for the purposes, already described herein).

A cycle of operations which gave a satisfactory result in the coating of thermionic valve heater elements is as follows:

(*a*) Immerse the clean and thoroughly dry heater element, as anode, in the electrophoretic bath at 36 volts D. C. for 10 seconds.
(*b*) Withdraw the element from the bath, without switching off the current prior to withdrawal, and give the withdrawn element a vigorous shake immediately it is clear of the bath.
(*c*) Dry the element and ignite in wet hydrogen at 1600° C.
(*d*) Twice repeat steps (*a*), (*b*) and (*c*) (in that order).

It will be appreciated that although in both examples set forth herein the article to be coated is used as anode, the article may constitute the cathode, depending on the migration direction of the coating material suspensoids due to the electrical properties thereof and the nature of the organic liquid employed. In short, the dispersive agent is effective independently of the migration direction.

It is to be noted that, although the dispersive agent preferably consists wholly of tannic acid or wholly of a mixture of an alkylolamine (such as triethanolamine) with nitrocellulose as described herein, these two agents constitute a "two-member" or dual group in which the members have in common the properties which give the desired result herein set forth. Hence, these two agents may be used concurrently as a mixture in any proportion of one in relation to the other. Such an admixture however (within the present range of our experiments) displays no great advantage over the use of a single one of the two dispersive agents, inasmuch as, while inclusion of tannic acid with the alkylolamine-nitrocellulose mixture enables operating voltages to be somewhat lowered, it also introduces the difficulty (referred to herein) of removing carbon from a deposited coating; and for this reason the alkylolamine-nitrocellulose mixture (by itself) is the preferred dispersive agent when it is essential that the coatings be free of carbon, and tannic acid (by itself) is preferred when freedom from carbon is not absolutely essential.

It is to be noted further, in regard to the alkylolamine-nitrocellulose member of the dual group, that alkylolamines other than triethanolamine (such as monoethanolamine or diethanolamine, for example) may be employed. In our experiments, however, best and satisfactory results have been obtained with triethanolamine and consequently that compound is presently preferred as against other alkylolamines.

What is claimed is:

1. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes in a bath having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	3 to 20
A dispersive agent	0.3 to 1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent.

2. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes for a period of 10 to 30 seconds in a bath having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	3 to 20
A dispersive agent	0.3 to 1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent.

3. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes for a period of 10 to 30 seconds in a bath having substantially

the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	3 to 20
A dispersive agent	0.3 to 1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent, the potential applied to the electrodes being 100 to 300 volts direct current.

4. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes in a bath having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	10
A dispersive agent	1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent.

5. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes for a period of 10 to 30 seconds in a bath having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	10
A dispersive agent	1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent.

6. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes for a period of 10 to 30 seconds in a bath having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	10
A dispersive agent	1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the said dispersive agent, the potential applied to the electrodes being 100 to 300 volts direct current.

7. A process as defined in claim 1 wherein the alkylolamine is triethanolamine.

8. A process as defined in claim 4 wherein the alkylolamine is triethanolamine.

9. In a process for coating a metal article with an inorganic refractory substance by electrophoresis; the step that comprises making the article the anode of two electrodes in a bath

having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Aluminum oxide	10
Silicon dioxide	0.3
Nitrocellulose	0.7
Triethanolamine	1.0

10. A bath for use in process for coating a metal article with an inorganic refractory substance by electrophoresis using the article to be coated as the anode of two electrodes, having substantially the following composition expressed in proportions based on weight:

	Parts
An organic liquid of the class consisting of acetone and methanol	100
Inorganic refractory substance	3 to 20
A dispersive agent	0.3 to 1

said dispersive agent being a mixture consisting of an alkylolamine and nitrocellulose each constituting at least 5% by weight of the dispersive agent.

11. A bath for use in process for coating a metal article with an inorganic refractory substance by electrophoresis using the article to be coated as the anode of two electrodes, having substantially the following composition expressed in proportions based on weight:

	Parts
Acetone	100
Aluminum oxide	10
Silicon dioxide	0.3
Nitrocellulose	0.7
Triethanolamine	1.0

said aluminum oxide and silicon dioxide having a particle size of 40 microns or less.

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