

Electrophoresis in the Valve Industry

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The deposition of particles from a suspensoid by the application of an electric field is widely used in the valve industry for coating components. This process, known as electrophoresis, necessitates very careful control of impurities providing ions which form a charged double layer on the particles. Emissive filament, heater and insulator coating methods using electrophoresis are described.

ELECTROPHORESIS is an unfamiliar process to most scientists and technicians, although it is closely analogous to the well known process of electroplating. Electroplating, of course, consists of deposition of a metal on to the negative electrode when D.C. is passed between two electrodes immersed in an electrolyte containing appropriate metal salts in solution. Electrophoresis consists of the deposition of small particles on to one of two electrodes placed in a suspension of the particles in a liquid when a voltage is applied between them. These particles may be sub-microscopically small or may be of the order of a few microns (10^{-3} mm) in diameter. If they are very small, they will stay permanently suspended in the liquid, and the mixture is known as a colloidal suspension, but if greater than about a micron, they will slowly settle to the bottom, and the mixture is called a suspensoid.

The process of electrophoresis is used in a number of ways in the manufacture of radio valves when controllable and quick deposition of particles from suspensoids is required, and it enables operations which are otherwise wasteful and tedious to be done economically and easily. The process thus contributes to the reliability of valves and reduces their cost.

Theory of the Process

THE MOVEMENT OF PARTICLES

A very early experiment by Reuss in 1808 demonstrated the effect of electrophoresis very clearly. Two tubes containing water were inserted into a mass of wet clay and a voltage applied between electrodes dipping into the tubes. It was found that clay particles moved into the tube with the positive electrode, and water out of the clay mass into the tube with the negative electrode. To explain the effect, Helmholtz postulated the existence of a charged double layer on the particles. According to this theory, the particles suspended in the liquid, acquire a layer of negative charges, while the liquid surrounding it becomes correspondingly charged by an equal amount of positive charge. When an electric field is applied across the liquid, the negatively charged particles will tend to move towards the positive electrode and the positively charged liquid toward the negative electrode.

If the state of affairs in the suspension is idealized as in Fig. 1, the velocity v of the particle in an electric field dE/dx is:

$$v = \frac{\epsilon V}{6\pi\eta} \cdot \frac{dE}{dx} (1 + r/\delta)$$

where ϵ is the dielectric constant of the liquid, η the viscosity of the liquid, V the potential difference between the particle surface and the contra-charge layer in the liquid, r the particle radius, and δ the distance between the particle surface and the contra-charge layer. This formula agrees with experiment in showing that the velocity is almost independent of particle size (as r/δ is small) and is proportional to the field. The value of V and δ

depend largely on the concentration and valency of the ions in solution. It may be seen immediately that the efficiency of the process will depend largely on the presence of a small amount of the right kind of ions being present in the liquid. This in turn depends on the presence of a small amount of an appropriate electrolyte in the otherwise insulating liquid.

THE STABILITY OF SUSPENSIONS

Providing particles of a few microns diameter do not coalesce in the suspension, they settle out relatively

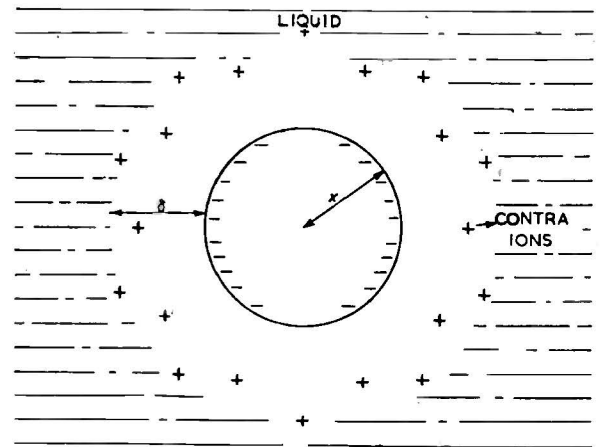


Fig. 1. Particle with charged double layer

slowly, while if they are much smaller than a micron, the Brownian movement will keep them in suspension permanently. Some suspensions, however, settle very quickly because the small particles coagulate. It may be seen from Fig. 1 that as particles with a double layer approach one another, providing the contra ions in the liquid are fairly diffusely distributed, the like charged particles will repel each other before contact. Only those with highest Brownian velocity, will come close enough for surface attraction forces to come into play and cause coagulation. If, however, the contra ion concentration is high close to the particle, they will be able to approach much closer to each other because the presence of the contra ions will neutralize the repulsion of the charges on the particles. There will thus be a much greater chance of coagulation taking place, and this may happen if the concentration of electrolyte becomes too high. The chance of this happening also increases if the particle concentration is high. In addition, it has been shown that as the valency of the contra ion increases, the distance between the contra ion layer and the particle decreases rapidly. Thus very small concentrations of trivalent contra ions such as aluminium, will have a marked effect on rate of electrophoresis and relatively little will cause coagulation, whereas the concentration of monovalent contra ions, such as sodium, will not be so critical. With most suspensions considered here,

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the ions giving the double layer are derived from an electrolyte in the liquid. This electrolyte in turn may be present due to solution of adsorbed impurities on the original solid particles, which dissolve in the liquid and provide a source of ions. This occurs more easily if the liquid is water or contains water as an impurity.

It may thus be seen that conditions for good electrophoretic deposition and good stability of the suspension both depend on provision of the right kind of ions in a suitable concentration. This can only be controlled by extreme care to ensure that the solid particles are free from soluble impurities and that any organic liquids used are water-free, thus any necessary electrolyte can be introduced in the exact quantities required. The actual sign of the charge on the particles and hence whether they deposit on the anode or cathode, depends both on the nature of the particle and the liquid. Basic substances in water tend to become negatively charged, acidic substances positively charged, while neutral substances are usually negatively charged because the negatively charged hydroxyl ion is more easily adsorbed on their surface. When organic liquids are used for the suspending medium the sign of the charge will depend on small quantities of impurities on the particles and also on water or electrolyte already present or added to the liquid.

Processes in Valve Making

EMISSIVE COATINGS: BATTERY FILAMENTS

One important application of electrophoresis in valve making is in the preparation of the thermionic oxide coated cathode. The cathode of a battery valve consists of a very thin nickel or tungsten wire coated before assembly into the valve, with a layer of co-precipitated barium strontium and calcium carbonates. These wires are usually less than 0.001in thick (finer than a human hair), and have to be coated to at least double their thickness with the carbonate layer. This layer can be applied by dragging the wire through a sludge of the carbonate and then baking it on by passing the wire through an oven at about 600° C. This can be a tedious process as many passes are necessary and the high temperature may anneal and weaken nickel wire, or cause oxidation of tungsten wire and thus adversely effect the final performance of the valve.

The carbonates may, however, be applied to the wire by electrophoresis, by passing it through a suitable suspension of the carbonate particles in an organic liquid and applying a voltage between the wire and a surrounding electrode. The coating can thus be applied in a single pass without any high temperature treatment which might spoil the final cathode.

The carbonate particles are usually approximately 1 micron diameter and some agitation of the suspension is necessary to prevent them from settling out. The adhesion of the carbonates to the wire must be sufficient to allow subsequent handling during mounting and some form of binder must be applied to the deposited carbonate layer to provide the necessary adhesion. In one process the carbonates are suspended in a solution of nitro cellulose in various organic solvents and the composition of the suspension is adjusted so that both the nitro cellulose and the carbonates deposit simultaneously on the wire to give a layer with the necessary adhesion.

The co-precipitated carbonates are ball milled into a solution of nitro cellulose in butyl acetate, acetone and methyl alcohol. To provide the necessary free ions to give the charged double layer on the carbonate particles, a small amount of electrolyte is added. This must not harm the final cathode, and strontium nitrate solution in water has been found very suitable, the particles becoming negatively charged.

A diagram of the plant is shown in Fig. 2. The wire is drawn off the spool and passes over a metal pulley and

down through an insulated guide to a pulley of bakelite at the bottom of the coating bath. The wire then comes up to the surface of the bath in the centre of an electrode, thence through a low temperature drying oven to evaporate the organic solvents from the coated layer before it passes over the final pulleys and is spooled. A potential is applied between the wire via the first pulley and the electrode in the bath, the wire being made positive. The thickness of the coating applied can be varied by adjusting the voltage which is usually of the order of 50 volts, and the wire passes through the plant at about 10ft per minute.

It is necessary to provide some form of stirring to prevent the particles of the suspension settling to the bottom and this may be accomplished by having inclined fins on the outside of the open mesh cylindrical electrode in the suspension and rotating the bath on its vertical axis at about 100 rev/min. This type of suspension has an appreciable electrolytic conductivity and a current of some milliamperes passes during the coating process.

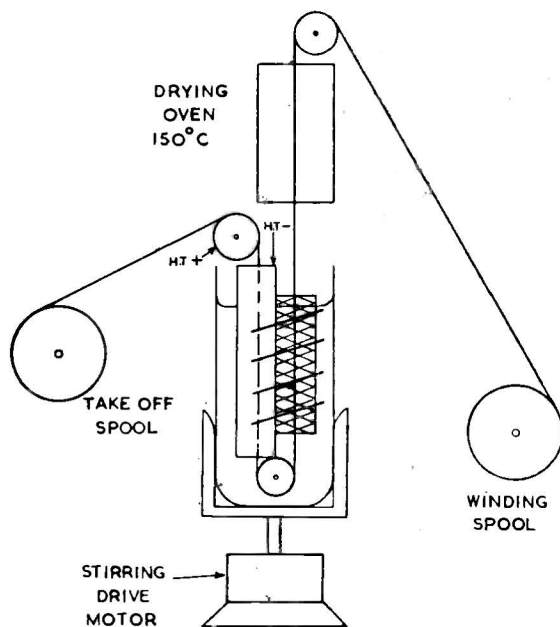


Fig. 2. Plant for coating wire

The alternative process applies the carbonates from a suspension in one of the alcohols in the range from methyl to amyl alcohol. In this case, the particles take up a positive charge, and the wire must, therefore, be made the cathode in the coating bath. As the wire passes through the suspension, it becomes coated with the carbonates, but without binder. Before contacting any pulleys or guides, the alcohol must be evaporated from the coating by passing the coated wire through an oven, and a binder such as nitrocellulose solution or molten paraffin wax applied to the wire, by passing it through the binder carried in the deep groove in a pulley, or some other suitable applicator. The plant can be laid out in a similar manner to that previously described or it can be arranged horizontally and the suspension stirred by circulation. The voltage across the coating bath is of the order of 50 volts, and a coating speed of a few feet per minute is usually employed.

Suspensions for this process are very poor electrical conductors and the current through the bath is less than a milliampere. These suspensions have a considerable tendency to coagulate and will not coat satisfactorily if the ion concentration rises above a very low value and

it is, therefore, essential to use very pure water-free alcohol. The carbonates must also be well washed and precipitated in such a manner as to avoid excessive adsorbed impurities. One other difficulty sometimes encountered is that although the particles migrate to the wire, surface tension forces strip the coating off as it leaves the surface. This is caused by the particles carrying excess liquid with them, and usually is associated with a slight tendency to particle coagulation in the suspension.

RECTIFIER STRIPS

A directly heated rectifier cathode consists of a length of nickel ribbon about 1mm wide, coated initially with co-precipitated barium, strontium, and calcium carbonates. This coating can be carried out by dragging the strip through a sludge previously described for wire coating, but it has been found that the cathoretic coating process has some advantages. Due to surface tension forces, the sludge method gives a coating with the cross section shown in Fig. 3(a). By using cathoretic coating, a strip with cross section as in Fig. 3(b) can be obtained, and such a strip gives a better thermionic emission which is very desirable.

The suspension used is similar to that containing nitrocellulose, as described previously. For strip coating, a plasticizer is usually advisable, as pure nitrocellulose

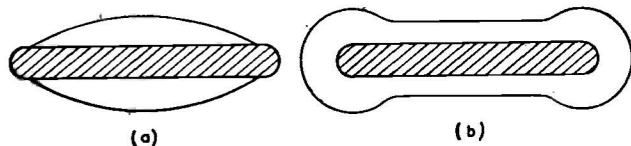


Fig. 3. Cross-section of filament strips
(a) drag coated. (b) cathoretically coated

binder is rather brittle. The usual plasticizers such as dibutyl phthalate or camphor are found quite suitable. The plant is similar in layout to that used for wire coating, but it has been found that more satisfactory quick drying can be obtained by warming the strip by radio frequency eddy currents, and thus drying the coating from the inside. The strip passes through a coil 9in long and 1in diameter carrying the radio frequency current. On this plant, the strip can also be given a channel section before coating, by passing through suitable rollers, and it thus has greater inherent rigidity in the final valves.

Heater Coating

WIRE COATING

The mains valve cathode consists of a nickel tube of rectangular, oval or circular cross section coated on the outside with the normal barium strontium calcium oxide. To maintain it at 750°C the nickel tube contains a heater which must be electrically insulated from the cathode. The insulation resistance must be at least 10MΩ at running temperature. Such heaters are made from tungsten or molybdenum tungsten alloy wire coated with a layer of pure aluminium oxide. The heater can be made from a straight wire bent into a multi-limb form, or maybe a double helix or a small coil bent into a V. The multi-limb type of heater is usually made by pre-coating the wire with alumina and then winding it round a sharp edged former similar to a double-edged razor blade. To make this heater successfully, the coating must have a good adhesion and should not break off at the bends, but only crack locally, and there is then little danger of the tips of the bends short-circuiting with each other. This pre-coating can be accomplished very successfully by electrophoresis. The process is similar to that for coating emitting filaments from a suspension using binder.

Pure alumina with a crystal size of the order of 1 to 5 microns, is ball milled into a nitrocellulose solution in acetone and methyl alcohol. Various additions have been used to provide the free ions necessary to form the double layer, and make electrophoresis possible. The most effective is a small controlled amount of ordinary salt solution. The chlorine ions are adsorbed on to the alumina particles which become negatively charged, and are deposited on the wire given a positive potential in the bath. The wire is passed through the apparatus shown in Fig. 2 at a speed of about 15 feet per minute, and a layer 0.06mm thick is applied. The variation in the speed of coating with the addition of salt solution to the suspension is shown in Fig. 4. These are experimental curves taken with a current of 50mA flowing through the bath. It may be seen that the optimum ion concentration is obtained when the quantity of sodium chloride is 0.2 per cent of the alumina content. To ensure sufficient water to ionize it properly, the salt must be added as a solution at a concentration of not more than 3 per cent. If this concentration is exceeded, there is

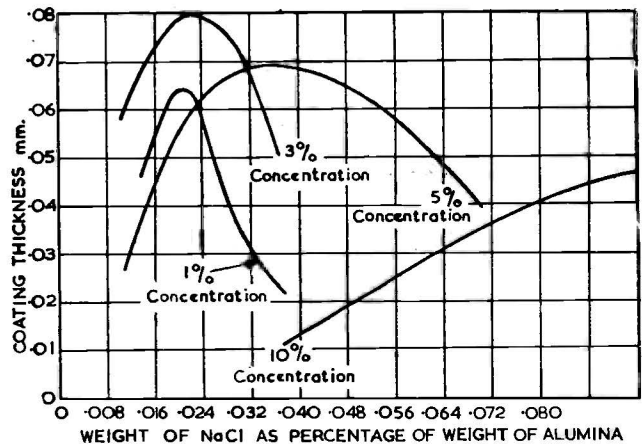


Fig. 4. Effect of salt on coating of alumina

not enough water to ionize the salt sufficiently, and more salt is necessary.

When excess water is added, the conductivity of the bath increases, and the applied voltage to give 50mA drops. As the rate of deposition is proportional to the field, the coating thickness drops correspondingly. The current must be limited to about 50mA as the excess gas produced by electrolysis disrupts the coating.

It has been found essential that the alumina is well washed so as to be free from soluble impurities, particularly those with divalent or trivalent ions which would decrease the speed of coating. Also, if excess electrolysis takes place, the gases produced may spoil the texture of the final coating.

When the wire has been coated, the heaters are made by winding on a former, and are inserted in alumina tubes. They are then heated at about 1600°C for a few minutes in hydrogen in a molybdenum wound tube furnace to remove the nitrocellulose binder and sinter the alumina into a hard coating. The tips of such heaters are shown in Fig. 5 compared with those obtained with the alternative drag coating process.

TIP COATING

In certain high voltage low current heaters, a large number of limbs of thin wire are necessary, and relative movement of the limbs and short-circuiting between tips may take place. This can be avoided by dipping the end of the heater into a bath containing a suitable cathoretic suspension and applying coating locally on the tips. A suspension of finely divided bentonite clay in water can be used for this purpose.

COILED HEATER COATING

It is possible to coat preformed coiled heaters by electrophoresis. Coating the reverse helix type is not very satisfactory, as the suspension tends to be retained by the coil on withdrawal from the bath, causing uneven coating and turns which are locked together, and the relatively wasteful method of spraying is therefore usually adopted. The close wound coil formed into a V can, however, be coated very satisfactorily by electrophoresis. The coils are usually of tungsten, wound on a molybdenum mandrel which can be left in position for the coating process. The heaters are held in a clip with the vertex of the V downwards and dipped into the coating bath to the required depth, the voltage applied for a few seconds and the coated heaters then withdrawn. This process can be mechanized on a multi-head machine or done on a semi-mechanized single head machine as described in the next section. The coated heater is sintered in hydrogen at

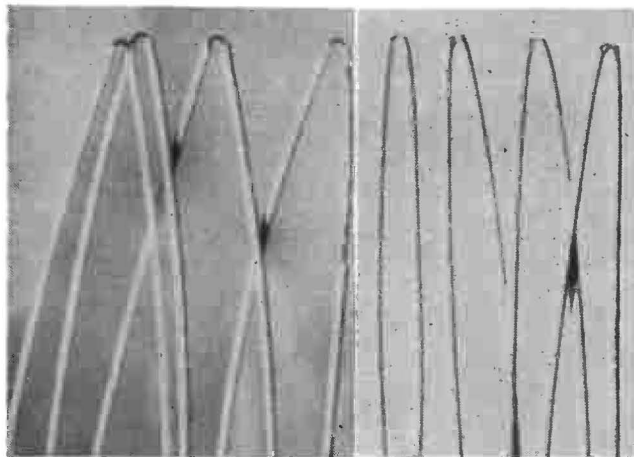


Fig. 5. Heater tips ($\times 10$)
(left) drag coated (right) cataphoretically coated

1 600°C and the molybdenum mandrel dissolved in acid subsequently.

Suspensoids containing nitrocellulose binder can be used, although their relatively high viscosity gives a tendency for liquid to be retained in the tip of the V, and the lower viscosity suspensoid of alumina in alcohol is better from this point of view.

INSULATED SUPPORT COATING

In battery valves, the filament is often located at points along its length by being pulled against a support from the control grid or other electrode. This increases the natural frequency of vibration of the filament and reduces microphony very considerably. It is essential that these supports are covered with an insulated layer and electrophoresis is the best way of accomplishing this. The supports are usually of 0.1mm diameter molybdenum wire with one end bent to the desired shape and coated with the insulator, and the other end attached to the grid side rod. To coat the supports a large number are fixed to a thick wire to form a comb. The tips of the comb are then immersed in the coating bath and the voltage applied for a few seconds and the wires with coated tips then withdrawn. They are subsequently sintered in hydrogen to give a strong insulating layer.

An alumina heater coating suspension can be used but a coating with lower sintering temperature is suitable, as the temperature of operation in the valve is quite low and such mixtures give adequate insulation. Such a suspensoid consists of alumina and clay suspended in a dilute aqueous solution of sodium silicate and only a few volts need be applied to the bath for coating at a suitable rate.

Coating is performed on a single head machine shown in Fig. 6. The "comb" is fixed in a clip and a cam operated dipper raises the coating from the main container till the comb dips in the surface to the right depth. The voltage is then applied for the appropriate time and the dipper then lowered. The coating is stirred continuously in the main container by rotation at about 60 rev/min and inclined vanes are attached to the outside of the dipper, to assist the mixing.

Other Uses of Electrophoresis

Electrophoresis can be used in other ways in valve making. Zirconium metal powder is applied to the anodes



Fig. 6. Comb-type coating plant

of transmitting valves to act as a getter, and this is sometimes applied by electrophoresis in preference to painting. Grids which have to dissipate a lot of heat can be coated with a carbon layer by electrophoresis to increase their thermal radiation and thus reduce the temperature.

Conclusion

It is hoped that this outline will have demonstrated how a relatively obscure branch of physical chemistry has become of use to the valve engineer to enable him to make valves more reliably and efficiently. The process will no doubt continue to be used in these and other ways in the industry.

Acknowledgments

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