CONTROL OF ELECTRODEPOSITS
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Int. Cl. B01K 5/02; C23b 13/00
U.S. Cl. 204 — 239

ABSTRACT OF THE DISCLOSURE
Parameter of single-component electrophoretic deposit which is function of deposition voltage may be adjusted by adjustment of voltage to compensate for other changes, e.g. depletion of bath. Composition of plural component deposits may be changed by adjustment of deposition voltage. Inventor's discovery that rate of deposit of any given component is not, in general, linearly proportional to applied potential (as prior art taught), and therefore parameter dependent upon ratio of different components in deposit may be controlled by voltage adjustment. Closed-loop servo system of parameter sensor measuring parameter of deposit, controlling voltage to bath in which deposit has been produced.

This invention pertains to the art of depositing materials by the action of an applied electric field, and generally to the coating art. It is a continuation-in-part of my application for United States patent entitled "Control of Composition of Electrodeposits," filed Dec. 19, 1963, Ser. No. 331,766, and now abandoned, which application is assigned to the assignee of the present application.

It is known in the prior art to deposit, upon a surface or within the pores of a porous solid, material suspended in a fluid and having an electric charge, by applying to such material an electric field of such direction as to move the suspended material in the direction of the surface or porous material. This is known generally as electrophoresis and has been applied in a variety of ways which include the precipitation of dusts from gases, spray painting, and the application of coatings to the surface of radio tube parts. In my copending application for United States patent filed Dec. 26, 1961, Ser. No. 161,920, and now abandoned, entitled "Surface Treatment," there is described the strengthening and coloring of anodized surfaces by filling the pores thereof with a densely compacted electrodeposited produced by electrophoresis. However, the prior art generally is concerned with the deposition only of particles of a single kind (as in coating and spray painting) or with the most complete possible deposition of all the material, of whatever kind, in a given suspension (as in dust precipitation). In various applications, particularly in coating, it would be desirable to work with a dispersion of particles of different kinds and to deposit therefrom an electrodeposited in which the proportions of the different kinds of particles are controllable at the will of the operator without the necessity of altering the relative proportions of the different kinds of particles in the dispersion to achieve such control. One of the benefits of such control in a coating operation is that a dispersion of pigments of different colors may be employed to produce coatings whose color is adjustable at will within limits determined by the colors of the different components. More generally, whenever any desired characteristics of an electrodeposited may be controlled by the ratio of different components, such control is useful. Similarly, when only a single kind of particles is being deposited from a suspension, it is useful to control the appearance of the deposit, either to produce deposits of somewhat different appearances from a suspension of given characteristics, or to produce on successively coated work pieces deposits of like appearance despite the depletion of the suspension, or variations in the temperature of the suspension, or other changes which may occur during the course of work.

My invention depends upon the discovery that for different materials dispersed in the same fluid medium, the velocities with which the different materials move in an applied electric field are apparently different non-linear functions of the magnitude of the field. Interpreting this in terms of its application to my invention, I have found that, if deposition in a given electric field from a mixture of two different colloidal materials produces a deposit containing a given proportion of the two materials, an increase in the electric field will increase the rate of deposition of one material more than the rate of decrease of the other material and so change that given proportion. Thus, for example, in electrophoresing a mixture of blue and yellow pigments, I have been able to alter the color of the deposit produced in an anodized aluminum body from blue through green to yellow simply by varying the voltage applied to the electrodeposited material employed either to produce differently colored deposits from the same bath, or alternatively, as a means of maintaining constant color in the deposit despite differential depletion of the bath. In the latter case, if deposition is occurring on a continuously moving strip of stock, it is possible to adjust the applied voltage automatically in response to the signals produced by a spectrometric reflectometer equipped with filters to confine its measurements to a significant portion of the spectrum. If a mixture of black and white were being deposited to produce a particular shade of gray, even such filters would, of course, be unnecessary although possibly convenient in some circumstances.

Even when only a single pigment is being deposited from the bath, e.g. into the pores of an anodized surface, I have found that the saturation and the reflectivity of the resulting finish may be varied by varying the voltage applied to produce electrophoresis. In general, increase of voltage increases the saturation of the finished surface to match more nearly that of the pigment itself; and it alters the reflectivity of the finished surface to approach more nearly that of the pigment. When a suspension becomes depleted, increase of voltage matches the results obtained at lower voltage with an undepleted suspension. In this instance of a single pigment, it is possible that the increased force which acts upon the suspended particles when the applied voltage is increased drives them more deeply into the pores of the anodized surface, filling the pores more completely, and reducing the dilution, by the anodized surface of the pigment. In the impregnation of porous metals by electrophoresis a comparatively short time of application of the potential (such as one minute) is ordinarily enough not only to impregnate the pores, but also to deposit upon the superficial surface of the piece an excess of pigment, which washes off readily. It thus appears that the effect I have observed is not the result merely of application of a greater total thickness of deposit, but rather of the concentration or density of pigment deposited in the pores.

I recognize that my invention appears to contravene the generally accepted doctrine that the velocities of particles undergoing electrophoresis are strictly proportional to the applied field. (See, for example, The Principles of Electrophoresis, by Andubert & de Mendel, translated by A. J. Pomeranetz, The Macmillan Company, New York, 1960, page 23.) In this respect, my results are surprising and unexpected, since the conventional theory would teach that increasing the applied field would simply pro-
duce a more rapid deposition of the different kinds of particles in suspension, without altering their relative proportions. However, it must be recognized that the quantitative value of the charges upon the particles may be somewhat variable, and that their effective size depends not only upon the physical size of the particle itself, but may be increased by association, with the particle, of molecules of the suspending agent; and it is conceivable that the proportion of associated molecules may be changed by change in the applied field. Thus, while I do not have a complete theory to explain the unexpected results I have observed, it appears that there are known physical effects which can account for them.

I have thus achieved by my invention the following objects:

The control of the color of an electrophoretic deposit from a given suspension of colored particles;

The control of the color of an electrophoretic deposit of reversing different double charge colors;

The production of electrophoretic deposits of different colors from the same suspension;

The automatic maintenance of a constant selected color in an electrophoretic deposit from a suspension which is changing in composition;

The arbitrary control of the composition of an electrophoretic deposit from a suspension of different kinds of material, independently of moderate changes in the composition of the suspension; such deposits may themselves be reactants to be further converted, as in ceramics, metallurgy, and organic synthesis, in all of which fields the production of intimately mixed compacts of controlled composition will greatly facilitate reaction. Many other useful objects will be apparent to those skilled in the art, in the light of the subsequent description and specification.

For the better understanding of my invention, I have provided figures of drawing in which:

FIG. 1 represents schematically an electrophoresis apparatus suitable for the practice of my invention;

FIG. 2 represents schematically a continuous electrophoresis apparatus suitable for the practice of my invention with automatic control of the applied voltage.

Referring to FIG. 1, there is represented a container 12, which may conveniently be of glass for small samples, or of any mechanically suitable non-conductor which is not attacked by the suspending medium, for large work. Two electrical connectors 14 and 16, which may conveniently be conventional busbars, are represented located at the upper end of container 12. Counterelectrode 18, which is perhaps the most striking aspect of my invention. However, practically useful results may also be obtained by

ad hoc symbol would increase, rather than eliminate, confusion. Since the critical parameter which it is necessary to control in the practice of my invention is the electric field which is applied through a substantially non-conductive medium, counterelectrode 18 should ordinarily be so shaped as to produce a substantially uniform field normal to the workpiece 22. This has been achieved, for planar workpiece 22, by making counterelectrode 18 also planar.

If, however, special decorative or other effects are sought, it is possible to produce variation in the color or other characteristics of the deposit on the face of the workpiece by so shaping the counterelectrode as to produce different field intensities over the surface of the workpiece. The effect of electrode shape upon field density is, of course, part of the well-known art of electricity.

In one example of my invention pieces of aluminum alloy of nominal composition 4.5 percent copper, 0.6 percent manganese, 1.5 percent magnesium, remainder aluminum, known by the trade designation of 2024, were treated as follows:

Pieces three inches square and one-sixteenth of an inch thick were anodized for forty-five minutes in a twenty-five percent by weight aqueous solution of sulphuric acid at a current density of 50 amperes per square foot at 20° C., the bath being cooled to maintain the temperature. These were then rinsed in water and allowed to dry.

A suspension was prepared of 1.3305 grams of flavianthrone yellow pigment, sold commercially under the designation "Harmon yellow indofast Y5763" and 1.3292 grams of aqueous dispersion of phthalocyanine blue, supplied under the designation C-520, in 750 cubic centimeters of methyl-ethyl ketone. This suspension was prepared by ultrasonic dispersion, by immersing a flask containing the named materials partly in the liquid bath of a conventional ultrasonic cleaner for 5 minutes. This treatment produced a suspension which was then decanted into a cell basically similar to that represented in FIG. 1. Successive 3 inch square anodized samples, prepared as described previously, were immersed in the cell as workpieces, spaced about 3.5 inches from the counterelectrode. A voltage was then applied to the workpiece and the counterelectrode for one minute; the workpiece was then turned to expose its other side to face the counterelectrode, and the same voltage was applied for another minute. The pores of the workpiece with its electrodeposited were then sealed by a novel process which is the invention of A. Bruin. It is customary to seal porosity in anodized materials by immersing the workpiece in hot, approximately boiling, water for about half an hour. These workpieces were sealed by being held in tongs and immersed in an air muffle furnace, electrically heated to a temperature of 350° C., for one minute. In this operation, the temperature reached by the workpieces was not sufficient to produce any observable change in the color of the surface. After such sealing, the piece was rinsed in water to remove adherent excess pigment.

Successful samples were treated in the manner hereinabove described at applied volatges of 100, 200, 300, 400, and 500 volts. The samples were made yellow; that treated at 500 volts was olive green. The colors of the samples treated at the intermediate voltages ranged monotonically in color from slight greenish yellow at 200 volts, through more green at 300 volts, to green slightly less than olive green at 400 volts. In other words, there was a variation in color corresponding to the variation in voltage, resulting from the varying proportions of yellow and blue pigment deposited at the various voltages. As I have indicated previously, this result is not in accord with the teachings of the theory, and is unexpected.

The actual change in hue which is obtainable by the use of a mixture of pigments and application of various voltages to deposit these pigments is perhaps the most striking aspect of my invention. However, practically useful results may also be obtained by

the use of different voltages for the electrophoretic deposition of a single pigment. For example, samples of the aluminum alloy commercially known as type 2024 were anodized in 25 percent (by weight) aqueous solution of sulphuric acid at a current density of 25 amperes per square foot at 32–33° C. For 1 hour. After rinsing in water and drying at approximately room temperature, these samples were subjected to electrophoretic deposition at various voltages in a suspension in methyl-ethyl ketone of a pigment known as Indofast Brilliant Scarlet presuckle, sold commercially as R–6502.

This suspension was generated by ultrasonic dispersion of about a gram of the pigment in 500 milliliters of the methyl-ethyl ketone. I obtained the following results:

### Appearance of treated surface after rinsing off loose excess pigment:

<table>
<thead>
<tr>
<th>Applied voltage volts</th>
<th>Deep reddish-maroon color</th>
<th>Less deep reddish color</th>
<th>Light red color</th>
<th>Somewhat spotty “roan” color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.100</td>
<td>0.500</td>
<td>0.250</td>
<td>0.100</td>
</tr>
</tbody>
</table>

I have observed that when the single-pigment bath becomes depleted through continued use, an increase in the applied voltage will produce the same color obtained at a lower original voltage with the undepleted bath. If, on the other hand, casual effects such as changes in bath temperature cause the color to become deeper than is desired, reduction in voltage will change the color to the desired value. I have thus found the general practical rule that the intensity of color of the treated surface may be increased by increasing the voltage used in electrophoresis, and inversely.

As I have indicated in my copending application to which reference has already been made herein, electrophoresis is somewhat divided pigments and the possibilities for an anodized surface produces a filling of such compactness that the anodized surface is strengthened and supported by the filling and is strongly resistant to defacement or dislocation by scratching or abrasion. The present samples showed these desirable characteristics.

It will be recognized that the use of my invention is not confined to deposition on anodized surfaces. Electrophoresis upon plain metal electrodes and even upon non-conductive porous substrates interposed between an electrode and a counter-electrode is well known; and the composition of deposits upon such may be controlled by my teachings quite as well as the composition of deposits upon anodized surfaces. Since the electrode and the substrate upon which deposition occurs may be identical or, if different, may be either attached to one another or separated, I employ the term "substrate electrode" to indicate the part or parts which perform the functions of electrode and of substrate for receiving the deposit.

Referring now to FIG. 2, there is represented a supply reel 38 of anodized strip 40. A tank or container 42, of some suitable insulating material, is represented in section to permit viewing of its interior. Supported across the top of tank 42 are busbars 44 and 46 which support counter-electrode 48. This counter-electrode 48 is so shaped as to provide an approximately constant gap between its inner surface and strip 40 as the latter passes from supply reel 38 down into the tank 42, around roller 50, and back up out of the tank around roller 52. The tank 42 is represented as filled with a suspension 54 which is here represented, for convenience and clarity, although it will in fact probably be opaque or translucent. Suspension 54 immerses roller 50 and parts of counter-electrode 48 and strip 40. A schematic representation of a scraper blade assembly 56 is provided to indicate a convenient means of assuring that the surface of roller 50 will not acquire a non-conductively thick material. If roller 50 is of electrically conductive material, there will be a certain tendency for electrophoretic deposition to occur upon it; but the field at its surface will be very much weaker than that at the surface of strip 40, and the deposition will be at a very low rate. Since the surface of roller 50 may be smooth, such a deposit will easily be removed by a scraper such as is represented by assembly 56. If roller 50 is made with a thick surface of electrically non-conductive material, the tendency to deposition will be even more reduced. If roller 50 is of metal, scraper assembly 56 might be used to make electrical contact to the roller 50, which would then afford electrical connection to strip 40; but I have represented instead a roller 58 which is maintained in contact with the edge of strip 40, and which is attached in pillow blocks 60 which may be graphite-lubricated and thus can provide electrical connection to the roller 50 and thence to strip 40. If necessary, a thin sliver may be slit from the edge of strip 40, after anodizing, to expose the base metal. Alternatively, brush connections may be made at supply reel 38 to the end of strip 40. The currents involved in electrophoresis are quite small and the problems of making adequate contact to the workpiece are not nearly so severe as in conventional electroplating.

Bus bar 46 is connected to conductor 62, and pillow block 60 is connected to conductor 64. These conductors 62 and 64 are connected to the output of controllable potential supply 66, the term "potential supply" being used as in connection with FIG. 1, to emphasize the importance of potential as the primary parameter. While it is evident that the connections described will cause electrophoresis to occur in tank 42, detailed description will be deferred pending completion of the description of the apparatus train through which strip 40 passes.

From roller 52, strip 40 passes to a sealing-and-washing installation comprising a washer 68 (represented as comprising a housing 70 and a plurality of nozzles 72) and a tunnel furnace 74 (represented as comprising a refractory housing 76 and heating elements 78). After passing first through the furnace 74 for sealing and then through the washer 68 for removal of adherent excess pigment, the strip passes a spectroelectroreflector assembly 80, which is schematically represented as comprising: a light source 82 and a condensing lens 84 which focusses the light from source 82 upon the under side of strip 40; and a converging lens 86 which, through a filter 88, focusses light reflected from the under side of strip 40 upon the sensitive surface of a photosensitive element 90, which may be a photodiode, barrier-layer photocell, vacuum photocell, or other conventional device. Photosensitive element 90 is connected by conductors 92 and 94 to the control amplifier 96, whose output is connected by conductors 98 and 100 to the control terminals of controllable potential supply 66.

From the vicinity of spectroelectroreflector 80 (which vicinity may be designated as a sensing station 102), the strip 40 passes to storage reel 104. Mechanical mounting means, such as bearings, for the various rollers, and drive means such as electric motors have not been represented because these are part of a very old and well-known art, and to represent them would merely divert attention from the more significant features of the drawing.

Furthermore, the usual arrangement of bearings and motors will depend very largely upon the designer's choice, and a particular arbitrary representation of bearings, brackets, and motors would be most unlikely to bear any useful relation to the design chosen in a particular case.

The mode of operation of the apparatus of FIG. 2 will now be described. Anodized strip 40 from the store on supply reel 38 passes roller 55 and descends into tank 42, entering suspension 54 and passing in proximity to counter-electrode 48, moving around roller 50. Controllable potential supply 66, via conductor 62 and bushing 46 on the one side, and conductor 64 and roller 58 on the other side, maintains a potential difference between counter-electrode 48 and substrate electrode strip 40 of proper sign to produce an electrodopos.
in the anodized surface of strip 40. With the counter-electrode geometry represented, this deposition will occur primarily upon the face of strip 40 nearer to counter-electrode 48. It is desired that both sides of strip 40, counter-electrodes 48 may be extended to be in proximity to both sides of the strip; but the particular embodiment shown has been chosen deliberately to demonstrate how it is feasible to economize the consumption of pigment from suspension 54 when deposition occurs on one side only. The speed of travel of strip 40 is so adjusted that the total time spent in the suspension 48 is sufficient for completion of the deposition.

From the tank 42, strip 40, now not only bearing a dense electrophoretic deposit but carrying with it adhering suspension, passes over roller 52 and through tunnel furnace 74, where the pores of strip 40 are sealed, in the way described in connection with FIG. 1. Thence it passes through washer 68 where jets of liquid from nozzles or jets 72 wash off any loosely adherent material.

Strip 40 now passes sensing station 102, where light from source 82 is focussed by lens 84 upon the surface of strip 40 which was nearer to counter-electrode 48 during the strip's passage through tank 42 and is therefore more heavily coated. Light reflected from the strip is focussed by lens 86 upon photosensitive device 90; but filter 88 transmits only a part of the spectrum. Let it first be assumed that suspension 54 contains a mixture of blue and yellow pigments, and that it is desired to deposit a particular shade of green coating. In the example given in connection with the description of FIG. 1, it was indicated that increasing the voltage used for electrophoresis increased the proportion of blue pigment deposited. Let the filter 88 transmit primarily blue light; then the illumination falling upon photosensitive device 90 will increase if the voltage from controllable potential supply 66 is increased, or if the proportion of blue pigment in the deposit is increased for any other reason. This will increase the electrical output applied from device 90 via conductors 92 and 94 to the input of control amplifier 96.

For the situation hypothesized, control amplifier 96 must be so designed that, responsive to such an input signal, it applies via conductors 98 and 100, a signal to controllable potential supply 66 such as to decrease its output potential, which is applied to the electrophoretic process. If filter 88 has been so designed as to transmit primarily yellow light, the phasing or other interconnection of amplifier 96 and potential supply 66 would have to be such that increased illumination on photosensitive device 90 would cause an increase in the output potential of supply 66.

If the first assumption, that suspension 54 contains a mixture of pigments, is replaced by an alternative second assumption, that suspension 54 contains only a single pigment, it may be shown that the apparatus will still function as follows: Let the pigment be, for example, Indofast brilliant scarlet pigment, which (as has been shown) produces a darker colored deposit the higher the voltage used to deposit it. If filter 88 is omitted entirely, the light falling upon photosensitive device 90 will decrease if the voltage from controllable potential supply 66 is increased, since there will result a darker deposit which will reflect less light. If, for any other reason, the density of the deposit of pigment should increase the light falling upon photosensitive device 90 will similarly decrease. This will increase the electrical output applied from device 90 via conductors 92 and 94 to the input of control amplifier 96.

For the situation now assumed, control amplifier 96 must be so designed that, responsive to such an input signal, it applies via conductors 98 and 100, a signal to controllable potential supply such as to decrease its output potential, which is applied to the electrophoretic process. As has hereinbefore been described, such a decrease in the potential applied will reduce the density of the deposit produced. If, on the other hand, the deposit becomes light (as by depletion of the suspension) the reverse of the preceding will occur; more light will be reflected to device 90, and the applied potential will be increased, producing a more dense deposit.

It is evident that the mode of operation described, in which a detected change produces an alteration in conditions such as to eliminate the detected change, is a closed-loop servo system which can be made to produce stability with only minor oscillations around the stable point. Thus casual variations in the color of the deposit from random causes, such as depletion of the suspension of its total pigment content, or of more of one component than another, may be minimized. The operation of such systems has been the subject of much published analysis, and only elementary points concerning them will be discussed here. One such point is the fact that there is a time lag between a variation in color produced in tank 42 and the detection of this variation at sensing station 102, the time lag being the time of transit of the variant portion of strip from the tank to the sensing station.

The response of the system comprising amplifier 96 and potential supply 66 must be comparable slow, in order to eliminate instability (known in the servo art as "hunting") with oscillations in the color of the deposit. Since most of the foreseeable random factors tending to produce variations are slow-acting, this will not be objectionable. It is possible to reduce the lag time by locating sensing station 102 closer to the tank in the chain of equipment. If the color of the strip prior to sealing by passage through tunnel furnace 74 is adequately related to its final color, the sensing station may be located before furnace 74; or, if the color before washing is thus adequately related, the sensing station 102 may be located to inspect the strip before its entry into washer 68.

To alter the color of the deposit produced, filter 88 may be replaced by one having a different spectral characteristic; or the initial voltage setting of controllable potential supply 66 and/or the gain of control amplifier 96 may be varied.

While the process has been described specifically with respect to the determination of deposit color, it is evident that it may be applied to control any parameter of a multi-component deposit which is a function of the ratio of components and can be sensed by a sensor whose indications are capable of being used to adjust the output voltage of controllable potential supply so as to alter the ratio of dielectric or magnetic and non-magnetic materials may be controlled by replacing spectroreflectometer 80 by a device to measure permeability. Similarly, materials of different dielectric losses may be controlled in proportion by the use of a sensor capable of measuring dielectric losses in the deposit. It is, of course, possible to employ measurement of any convenient parameter which is different for the two components, but adequately constant in each, to control the proportion of the components in the deposit, even though what it is primarily desired to control is not the value of the measured parameter, but rather some other characteristic which is a function of the proportion of components in the deposit.

Similarly, there have not been represented in FIG. 2 certain auxiliaries which may be useful in particular instances. For instance, it may be convenient to provide a circulator in tank 42 to prevent extreme local depletion of suspension 54 in the vicinity of the electrodes; or it may be useful to provide automatic means for monitoring the concentration of suspension 54 and for adding more pigments in an auxiliary tank connected with tank 42 and provided with a suitable suspending device such as an ultrasonic oscillator. These are matters of known art, and not necessary to be shown to disclose mass-producing.

I have found that the application of my invention is not confined to a single or two-component mixture to be deposited, but will also function satisfactorily with a three-component mixture. There is no reason why any number.
of pigments should not be employed as required; but since there is only the one parameter, applied voltage, to be readily varied, an increase in the number of pigments will not necessarily increase the number of degrees of control obtainable, although it may be employed conveniently to adjust the range of colors obtained within a convenient range of voltages.

For convenience of the reader, I have provided a table of the results of a number of demonstrations of my invention; the effects of variation in anodizing current density, change of the electrophoresis suspending medium, and of variation of the applied potential are illustrated. All anodizing was conducted in 25 percent sulphuric acid solution (by weight) and at room temperature (20 to 22° C.), the bath being maintained at room temperature. Anodizing time was 45 minutes. The yellow and blue pigments were those previously described hereinabove. A red pigment supplied under the designation "Harmon Indofast Scarlet R (6502)" was also used. Ultrasonic vibration was employed to disperse the pigments in the medium indicated in each case.

**TABLE I**

<table>
<thead>
<tr>
<th>Bath</th>
<th>Red pigment 1.5602 grams, yellow pigment 1.5044 grams, 600 ml. methyl-ethyl ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>100 min 3 Tm, Canary yellow.</td>
</tr>
<tr>
<td>38</td>
<td>50 min 1 Tm, Chocolate.</td>
</tr>
<tr>
<td>38</td>
<td>70 min 1 Tm, Medium brown.</td>
</tr>
</tbody>
</table>

2. (Bath: Red pigment 1.00 gram, blue pigment 1.00 gram, 1 liter methyl-ethyl ketone)

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Time, minutes</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>200</td>
<td>Deep magenta.</td>
</tr>
<tr>
<td>38</td>
<td>500</td>
<td>Light magenta.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Very dark purple.</td>
</tr>
<tr>
<td>38</td>
<td>250</td>
<td>Light blue.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Light red.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Reddish brown.</td>
</tr>
</tbody>
</table>

3. (Bath: Red pigment 1.827 grams, yellow pigment 1.2415 grams, blue pigment 1.0814 grams, 600 ml. methyl-ethyl ketone)

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Time, minutes</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>250</td>
<td>Very light yellow.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Deep yellow.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Brownish yellow.</td>
</tr>
</tbody>
</table>

4. (Bath: Red pigment 1.159 grams, yellow pigment 1.047 grams, 400 ml. trichlorehylene)

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Time, minutes</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>500</td>
<td>Deep yellow.</td>
</tr>
<tr>
<td>38</td>
<td>1000</td>
<td>Brownish yellow.</td>
</tr>
</tbody>
</table>

It is observable that the colors produced are controllable over a very wide range simply by variation in the anodizing current and the applied voltage, as is illustrated quite strikingly by the results with Bath 2. Bath 3 shows the results obtainable with a three-component mixture of pigments, and Bath 4 illustrates the fact that the effect is not particularly to the peculiar suspending medium.

The effect of variation in the current density employed in the anodizing process is not particularly a deterrent in the application of the process, as it is conventional in anodizing to control the anodizing current at a fixed value to produce the desired physical characteristics in the anodized surface, and minor variations in the anodizing current may be compensated by varying the voltage used in electrophoresis. It is hypothesized that the change in porosity produced by major changes in the anodizing current causes changes in the color observed in the electrophoretic deposit through altering the electric field existing at the outer part of the anodized surface where pigment deposition occurs, or by altering the size of the pores, with consequent alterations in the size of the aggregates of pigment formed therein. Control of the exact colors produced by mixtures of pigments has, for many years, been recognized in the paint and lacquer art as largely empirical, and the necessity for preliminary testing of the effect of particular mixtures has not prevented the production of standardized colors. Similarly, in the application of my invention, the necessity for maintaining a degree of constancy in the preparation of materials to be colored or otherwise coated does not vitiate its practical usefulness.

While I have illustrated the practice of my invention by examples of the use of commercially available organic pigments, upon anodized surfaces, any material suitable for electrophoretic deposition may be used with any suitable substrate electrode. Organic pigments offer some advantages of stability, particularly at elevated temperatures, and may be preferable for particular applications. Those which are produced by precipitation from solution may conventionally be so produced under conditions which render the precipitated pigment finely divided. For example, it is well known that some sulphides, such as zinc and cadmium sulphides, tend ordinarily to be precipitated in substantially colloidal condition. While such precipitation is usually regarded as undesirable in the production of pigments for paints and lacquers, it may be beneficial in the production of pigments for electrophoresis.

In those applications of my invention in which electrophoresis is employed to produce intimate and compact mixtures of reactants of controlled proportions (as, for example, a latex deposit containing a controlled proportion of originally colloidal sulphur for subsequent vulcanization), the nature of the reactants to be deposited will necessarily determine the manner of their production and how they are produced in colloidal state. The colloidal art is so extremely voluminous that it is obviously impossible to summarize its teachings here. It may be observed, however, that the field of ceramics is replete with teachings for the production of suspensions of raw materials, known in that art as "slips"; the ceramic field is believed worthy of this special mention because it, like the organic plastics art, is particularly adapted to benefit by the teachings which my invention affords of the control of the composition of electrophoretically deposited compacts of reactants of particular shapes (as by deposition upon shaped mandrels or in molds).

What is claimed is:

1. In apparatus for controlled electrophoresis of colloidally dispersed material comprising:
   (a) a container adapted to contain a dispersion of colloidally dispersed material;
   (b) counterelectrode means in said container;
   (c) means to support a substrate electrode in said container;
   (d) adjustable potential supply means connected to said counterelectrode means and adapted to be connected to said substrate electrode to apply a potential therebetween;
   (e) sensing means adapted to sense a parameter characteristic of the light reflectivity of an electrophoretically produced deposit of the said material which parameter is a function of the potential used to produce the said deposit;
   the improvement comprising:
   (f) connecting means connecting the said sensing means to the said adjustable potential supply means to adjust the said potential responsive to the value of the said parameter sensed by the said sensing means.

2. In apparatus for controlled electrophoresis of colloidally dispersed material comprising:
   (a) a container adapted to contain a dispersion of colloidally dispersed material;
   (b) counterelectrode means in said container;
   (c) means to support a substrate electrode in said container;
   (d) adjustable potential supply means connected to said counterelectrode means and adapted to be connected to said substrate electrode to apply a potential therebetween;
   (e) sensing means adapted to sense a parameter characteristic of the color of an electrophoretically produced deposit of the said material which parameter is a function of the potential used to produce the said deposit;
   the improvement comprising:
   (f) connecting means connecting the said sensing means...
3,502,563

3. In apparatus for controlled electrophoresis of a plurality of colloidally dispersed materials comprising:
(a) a container adapted to contain a dispersion of a plurality of colloidally dispersed materials;
(b) counterelectrode means in said detector;
(c) means to support a substrate electrode in said container;
(d) adjustable potential supply means connected to said counterelectrode means and adapted to be connected to said substrate electrode to apply a potential therebetween;
(e) sensing means adapted to sense a parameter characteristic of the color of an electrophoretically deposited mixture of the said materials which parameter is a function of the relative proportion in the said mixture of the materials comprised in the said plurality;
(f) connecting means connecting the said sensing means to the said adjustable potential supply means to adjust the said potential responsively to the value of the said parameter sensed by the said sensing means.

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HOWARD S. WILLIAMS, Primary Examiner

U.S. Cl. X.R.

204—300
CERTIFICATE OF CORRECTION


Inventor(s) Francis J. Schmidt

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column II, line 8, change "detector" to -- container --

SIGNED AND SEALED

JUL 28 1970

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents