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PIGMENT OF TITANIUM HAVING TITANIUM OXIDE COATING, ELECTROLYTIC METHOD OF MAKING PIGMENT, AND REFLECTOR AND PAINT CONTAINING SAME

Filed March 23, 1961

FIG. 1

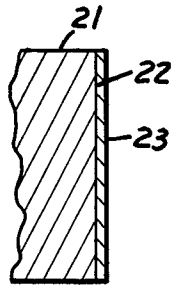


FIG. 2

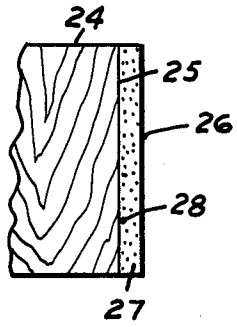


FIG. 3

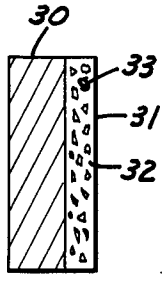
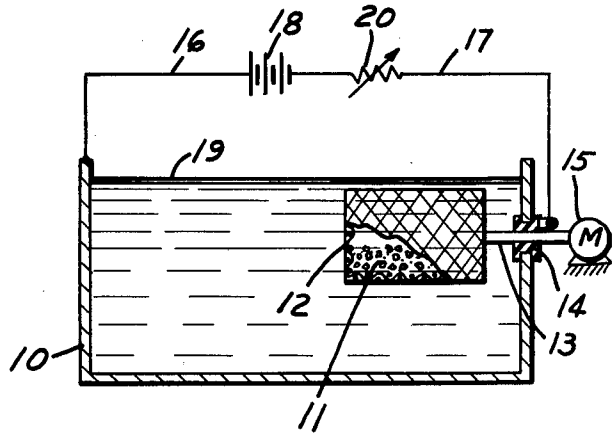


FIG. 4



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PIGMENT OF TITANIUM HAVING TITANIUM OXIDE COATING; ELECTROLYTIC METHOD OF MAKING PIGMENT; AND REFLECTOR AND PAINT CONTAINING SAME

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7 Claims. (Cl. 106—287)

This invention relates to a pigmenting material for selective color reflection.

Many problems relating to selective color reflection in applications such as reflectors for monochromatic light sources, paint pigments, and light-diffusing reflectors, could be expeditiously solved were there available a material which could be provided in any size from powder to extended shiny surfaces, and colored to any suitable depth, and which would be resistant to the effects of the atmosphere, heat and light. Such a material would, of course, be ideal for many purposes and it is the object of this invention to provide the same.

A related object of this invention is to provide a monochromatic light source in the form of a single-surface mirror, which has a reflecting pigmented surface of the order of a few molecules in thickness, thereby providing a reflecting means without the interference and diffraction problems which occur in other types of sources which rely on reflection from thick layers or from passage through colored lenses for the coloration. Furthermore, the pigmented material utilized for the reflecting surface according to this invention is not subject to oxidation or dulling from exposure to most acids, alkalies, or corrosive atmospheres. It is characterized by its stability and its permanence, and provides a reliable, unchanging source of monochromatic light.

Another object of the invention is to provide a pigment, available in a wide range of colors, which can be incorporated in a conventional paint vehicle for coloring the paint any suitable color.

Still another object of the invention is to provide a light-diffusing surface capable of reflecting light from many incident directions to many reflected directions, and which can be incorporated in a transparent matrix to provide a diffusing reflector.

This invention is carried out with the use of a pigmenting material comprising a treated surface of metal comprising titanium. The surface is produced by contacting it with an aqueous electrolyte solution while passing an electric current through the body and electroylte, the body being other than the cathode relative to the current during at least part of the time the current flows therethrough.

The invention will be fully understood from the following detailed description and the accompanying drawings in which:

FIG. 1 is a greatly-magnified fragmentary cross-section of a monochromatic light source according to the invention;

FIG. 2 is a cross-section of a piece of wood coated with a layer of paint according to this invention;

FIG. 3 is a fragmentary cross-section of a diffusing reflector according to the invention; and

FIG. 4 shows means for manufacturing the pigmenting material according to the invention.

The preparation of a surface for this invention will be described in detail in connection with the applications shown in FIGS. 2 and 3, which involve a tumbling operation. Process equipment for this purpose is shown in FIG. 4. This includes a tank **10** made of a conductive metal, such as stainless steel, which contains a quantity

of an aqueous electrolyte solution. The presently preferred solution is made up by adding five parts by volume of sulphuric acid solution whose specific gravity is 1.84 at 60° F. and which assays between 95% and 98% H_2SO_4 to 995 parts by volume of distilled water. The material to be coated, such as powder or chips **11**, is made of a metal comprising titanium. This comprehends titanium or titanium alloys. This material is charged into a tumbling cage **12**. This tumbling cage is made of a perforated conductive metal, such as stainless steel, and is rotatably supported in the tank beneath the surface of the electrolyte by a shaft **13** journaled to a bearing **14** in the side of the tank. The bearing is insulated from the tank. Shaft **13** is connected to a motor **15**, and is made of conductive metal, conductively connected to the tumbling cage so that a current passed through leads **16**, **17**, originating at a battery **18** or other voltage source, renders the tank and the tumbling cage the opposite terminals of an electric circuit completed by the electrolyte **19**. In order to assure that the material is thoroughly treated, the cage is turned to tumble it as the electrolytic action progresses. The material in direct contact with the cage will, during the time of direct contact, be one of the electrodes. So will other bits of material which are in electrical connection with them at the same time. Therefore, at one time or another during the tumbling operation, all of the powder and all of the chips will become an electrode.

Lead **17** incorporates a rheostat **20** for adjusting the voltage between the electrodes. The negative terminal of the battery is connected to the tank, and the positive terminal is connected through the rheostat to the shaft. Thus, when a battery is used, the tank is the cathode, and the tumbling cage is the anode.

A non-conductive tank could have been used instead of a conductive tank, in which event lead **16** would have been connected to an electrode (not shown) dipped in the electrolyte, instead of to the tank.

When a large smooth surface is to be treated, such as the surface shown in FIG. 1, the surface is either connected directly to the tumbling cage, or connected directly to lead **17**, and placed in the electrolyte solution. It is not tumbled. The tumbling practice is illustrated to show how powders and chips may be treated according to the invention to give them a uniform surface treatment.

The color which is developed on the surface with the above technique is primarily determined by the voltage that is applied thereto. A short exposure, even for a few seconds, will serve to color the surface. Applying the voltage for a longer time, even for as long a period as a half hour or more, does not appear to change the basic color, although the surface becomes somewhat cloudy as the time of treatment is extended. The cloudiness probably is due to the depth of the layer produced. The color, even in thin layers, is very stable over a wide temperature range. It is stable in color and chemically resistant to strong acids, caustics, corrosive atmospheres, and light.

Tests have been made to determine the relationship between the color developed and the voltage applied. The technique used for making such tests has been to embed a number of test specimens of 6AL–4V titanium alloy in a non-conductive matrix and to polish the exposed surfaces. Thereafter, the matrix containing the specimens is submerged in the aqueous electrolyte solution (the sulphuric acid solution above-described) in a tank such as shown in FIG. 1. Then a hand-held probe is applied individually to said specimens, the voltage being varied from specimen to specimen. The probe is connected to the positive terminal of a battery so that the samples are made the anode. In one run of twenty (20) samples, the D.C. voltage was changed in five-volt steps from sample to sample, and the colored surfaces which

were obtained are listed in the table below. The color definitions used in describing these colors were obtained from "A Dictionary of Color" by Maerz & Paul, published 1930 by McGraw Hill Book Company, Inc., New York, New York. The names of the colors are given wherever they were provided in this dictionary, together with the plate, page and block number of the respective colors.

Resulting color:	Volts
Unnamed whitish color, Plate 11, page 45, Block A1	5
Amber white, Plate 11, page 45, Block C1	10
Tennis, Plate 12, page 47, Block L 6	15
Unnamed reddish-violet color, Plate 44, page 111, Block I1	20
Egypt, Plate 34, page 91, Block H11	25
Unnamed light blue color, Plate 35, page 93 Block G10	30
Lucky Stone, Plate 34, page 91, Block G6	35
Light blue 6T, Plate 34, page 91, Block F2	40
Unnamed pale blue color, Pate 34, page 91, Block C1	45
New Silver +, Plate 11, page 45, Block B1	50
Unnamed pale yellow color, Plate 11, page 45, Block G1	55
Palmleaf, Plate 14, page 51, Block L1	60
Sulphine Y, Plate 12, page 47, Block L4	65
Oak buff, Plate 13, page 49, Block D7	70
Claret cup, Plate 6, page 35, Block B4	75
Raspberry, Plate 6, page 35, Block I5	80
Clochette, Plate 43, page 109, Block D9	85
Larkspur, Plate 35, page 93, Block K5	90
Tuileries, Plate 35, page 93, Block J7	95
Sulphate Green, Plate 26, page 75, Block J8	100

Speaking generally, a somewhat golden color is obtained at 15 volts, a magenta color at 20 volts, a dark blue at 25 volts, with the shades of blue paling to silverish as the voltage increases to about 45 volts. The colors vary progressively from silverish darkening through yellow to orange as the voltage increases from 50 to 65 volts, then orange darkening to vermillion from 70 to 85 volts, and light blue shading into green from 85 to 100 volts. The most pronounced colors are the gold at about 15 volts, the dark blue at about 25 volts, vermillion at about 80 volts, and emerald green at about 100 volts. The colors given in this paragraph are common names. For exact color reference should be had to the above definitive descriptions derived from the Dictionary of Color.

In carrying out the anodizing operation, it has been found that the color will spread evenly over the surface in all cases. Usually about ten seconds of application of the current is adequate to develop the color over a disc about one quarter inch diameter. It is preferable to carry out the invention with the use of direct current, and making the surface to be treated the anode.

It is preferable to carry out the invention with the use of direct current, and making the surface to be treated the anode. This is for the reason that it is theorized that nascent oxygen is developed at the anode, and that this oxygen combines with the titanium to form an extremely thin integral coating of various complex titanium oxides of varying colors. The oxide formed is theorized to be a function of voltage applied, and it appears that selection and careful control of the voltage applied results in the selection of a coating of a particular oxide or a mixture of oxides to produce a characteristic and distinctive color for each voltage, and which color corresponds to said voltage. Thus, a color for a coating can be selected from a wide range of colors simply by selecting the voltage to be applied. It is to be understood that the above is the present theory of why the various colors are formed. It has not been possible to make a suitable chemical or physical analysis of this coating, so that the above is merely a theory. However, the facts as to the preparation of coatings of various colors are as stated.

It is also possible to carry out this process using alternating current as a direct substitute for the batteries illustrated because the metal being coated will be the anode at least half of the time, and will never be always the cathode. However, because hydrogen may be liberated at the cathode, this treatment should not be carried out with direct current when the metal is the cathode, and alternating current is less desirable than direct current, because the metal is the cathode at least some of the time. Hydrogen is developed at the cathode which tends to enter the titanium and embrittle it, thereby spoiling its physical properties for many applications. Therefore, the preferred embodiment of the invention utilizes direct current with the metal to be treated the anode, even though coatings produced by alternating current are as useful as those produced by direct current for many uses. The same circuit connections are used for alternating current as for direct current. The disadvantage in having the metal be the cathode resides in the fact that hydrogen is developed.

Now with respect to the applications for the materials produced as above, reference is initially made to FIG. 1, in which a metal base **21** is provided with a polished surface **22**. This polished surface is exposed to electrolyte and current as aforesaid, with the voltage adjusted to produce the desired coloration. This produces a colored layer **23** on the polished surface whose thickness is greatly magnified in FIG. 1 for purposes of illustration. A use for this device is as a reflecting mirror for a monochromatic light source. The coating is very bright and is an efficient reflector. Ordinarily, this surface will be left in the solution and exposed to current for no more than about ten seconds because the object is to produce a layer of the order of only a few molecules thick. This enables a reflecting surface to be prepared which, because of its thinness, avoids interference and diffraction problems which occur in reflecting mirrors which have reflecting surfaces of appreciable thickness, or in second-surface reflection in general. Furthermore, the color of the reflecting surface is permanent.

FIG. 2 shows a piece of wood **24** with a surface **25** coated with a layer **26** of paint. The paint comprises a vehicle **27** and pigment **28**. The term "pigment" is sometimes used for convenience herein, even though the particle sizes used are somewhat larger than conventional pigment sizes. The powder which is anodized to carry a colored surface is actually a body for supplying colors to paint, the "pigmentation" being carried by its outer surface. The pigment is the powder obtained by the process shown in FIG. 4, the powder granules being of the order of five microns in diameter. This powder can easily be obtained from a ball mill and then treated in the aforesaid fashion. The powder produced is essentially a body comprising titanium with a colored permanent self-contained and adherent layer thereon. This layer is not affected by acids, alkalies, light or temperature, and the pigment thereby becomes a very suitable long-lasting means of coloration for the paint. This pigment is suitable for use in any paint formulation, the same as other types of pigments.

In FIG. 3, there is shown a body **30**, which may be wood, metal or plastic, to which there is applied a layer **31** consisting of a transparent matrix **32**, which might be clear plastic, perhaps of a vinyl or polyethylene material, which suspends a large number of small chips **33** of metal comprising titanium. These chips are of the type frequently produced in the machining of titanium, which are treated in the tumbling operation shown in FIG. 4 to give them a color. This develops a reflecting surface similar to the surface shown in FIG. 1, but, because the surfaces on these chips are randomly oriented and often are curved, broken or irregular, light incident from many directions will be scattered in many directions so that the reflector of FIG. 3 is of the type commonly known as a "safety" reflector which diffusely reflects light from nearly any source

back to nearly any other direction within its "field of vision."

It will be seen from the above that the invention provides a technique of coloring the surface of bodies comprising titanium to produce selective color reflection and that such color reflection is utilizable in such means as monochromatic reflectors, paints, and diffusing, safety reflectors. The basic pigmentation produced is easily secured in a variety of colors which colors are attainable merely by selecting the voltage applied during the anodizing operation.

At the present time, it is believed that any aqueous electrolyte solution will perform to good advantage in preparing the surface. However, for convenience in the operation, it has been found that sulphuric acid or hydrochloric acid solutions are to be preferred.

This invention is not to be limited by the embodiments shown in the drawings and described in the description which are given by way of example and not of limitation, but only in accordance with the scope of the appended claims.

We claim:

1. The method of preparing a coloring agent for supplying color to paint comprising reducing metal selected from the group consisting of titanium and titanium alloys to a particulate, loose and uncompacted powder of a particle size of the order of about 5 microns, and coloring the surface of said powder by forming on the surface thereof an integral layer of a selected color, the metallic constituent of said layer being derived from the body of powder which it coats, by immersing it in an aqueous electrolyte solution and agitating said loose powder in the solution while simultaneously passing through said powder and electrolyte an electric current between an anode and a cathode at a selected voltage within the range of from about 5 to 100 volts, substantially each of the powder partices being brought into direct electric connection with said anode at least part of the time while agitating.

2. The method according to claim 1 in which the voltage of said current is adjusted to produce the selected color.

3. The method according to claim 2 in which said current is direct current.

4. A coloring agent for supplying color to paint comprising loose powder particles of a metal selected from the group consisting of titanium and titanium alloys of a particle size of the order of about 5 microns, said particles possessing a thin uniform coating of titanium oxide of a selected, chemically resistant color, the titanium oxide being formed as a coating on the body of metal, the titanium therein being derived from said body.

5. A colored reflector comprising a base, a transparent matrix, and a multiplicity of loose powder particles dispersed therein and composed of a metal selected from the group consisting of titanium and titanium alloys, said titanium particles possessing a thin uniform surface coating of titanium oxide of a selected characteristic, chemically resistant color, the titanium oxide being formed as a coating on the body of metal, the titanium therein being derived from said body.

6. A colored reflector according to claim 5 in which said particles are distributed randomly in said matrix, and thereby serve to diffusely reflect light incident thereto.

7. A paint comprising a paint vehicle and, dispersed in said vehicle as a coloring agent therefor, a loose and uncompacted powder of metal selected from the group consisting of titanium and titanium alloys of a particle size of the order of about 5 microns, the particles of said powder possessing a thin uniform titanium oxide coating of a selected characteristic, chemically resistant color, the titanium oxide being formed as a coating on the body of metal, the titanium therein being derived from said body.

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