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CHEMICAL PROCESS

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This invention relates to the coloring of metal surfaces of massive bodies, and more particularly to the conversion of certain metal surfaces to the metal porphyrizine. Still more particularly it relates to the treatment of metals at elevated temperatures with fluid (i. e., liquid or vaporous) reagents comprising a porphyrizinogenic substance, e. g., phthalonitrile.

Metal phthalocyanine pigments have heretofore been prepared by the reaction of porphyrizinogenic substances with many powdered metals. These pigments, in the preparation of which all or nearly all the metal is consumed, have been used in the usual manner in coating compositions; i. e., they are dispersed in suitable vehicles and are affixed to metal and other surfaces by the adhesive or binding action of such vehicle, the film which is produced resulting directly and only from the film-forming ability of the vehicle. Metals so coated lose their metallic appearance, the surface taking on the visual aspect of an ordinary pigmented film; the resistance of the coating to heat and chemicals is relatively low, and can be no higher than the resistance of the vehicle or binder; the film is of considerable thickness and often lacks the desired adhesion, especially when the metal is flexed or bent; and the coating is relatively costly to prepare and apply.

This invention has as an object the conversion of metal surfaces to a porphyrizine, e. g., a phthalocyanine, of the metal. Another object is the coloring of a metal surface in a uniform decorative manner. A further object is the providing of an economical method for producing uniform, adherent, and chemically inert colored surfaces which are resistant to high temperatures, deformation, and abrasion. Another object is the phthalocyanization of a metal surface. Other objects will be apparent from the reading of the following description of the invention.

These objects are accomplished by the following invention which comprises immersing a body having a metallic surface, which surface is in massive form as opposed to powdered form and which metallic surface contains as an essential component a structurally useful base metal melting above 300° C. and forming a nitrate in which the metal is divalent in a fluid (i. e., liquid or gaseous) medium containing a porphyrizinogenic substance, such as phthalonitrile, at a temperature below the melting point of the metallic surface and within the range of from 200° C. to 550° C. The majority of the metals which are suitable may also be classified as common non-noble

metals of Groups 1-B, 2-B, 4-B, and 8 of the Mendelyeev's Periodic Table, which metals have a melting point above 300° C. Under the conditions just given, the surface of the metal is converted to the metal porphyrizine. The depth of conversion varies with the exact conditions but is usually quite small. The metal porphyrizine remains, as it were, a part of the metal and cannot be removed without being destroyed. Depending on conditions, it may be colored greenish blue, blue or reddish blue, in shades ranging from pale blue to blue-black. This metal porphyrizine surface is highly resistant to heat and chemicals, is continuous and uniform, and is not affected by the flexing or bending of the metal since it appears to exist in and about the interstices of the metal, i. e., is actually a part of the metal in the sense of being united by some force, possibly intermolecular, which is far greater than the forces joining a metal and a paint film containing a porphyrizine of that metal.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof, since many modifications may be made without departing from the spirit and scope of this invention.

Example 1

A 2" x 4" panel of 20-gauge iron (auto body steel) was dipped in a 20% solution of phthalonitrile in acetone, drained, dried, and placed in a closed, gas-heated furnace of one quart capacity. An additional three grams of phthalonitrile was added, and the furnace sealed and heated to 350° C. over a period of one hour; it was then cooled in a stream of water and opened. The iron panel was found to be colored a deep, uniform blue. The color adhered strongly to the metal, and was not removed by brisk rubbing with a cloth or by ordinary buffing. The panel could be bent double without causing the colored surface to crack or flake off, and the color was not removed from the bent portions of the panel when these were rubbed with a cloth. The colored surface had no deleterious effect on the properties of subsequently applied oils, waxes, or other clear coating compositions.

Example 2

A panel of auto body steel as in Example 1 was suspended in the refluxing vapor of phthalonitrile at 310° C. and atmospheric pressure, a large test tube fitted with an air-cooled condenser arm being used for this purpose. In twenty minutes

the surface was converted in a uniform manner to the blue metal phthalocyanine, the appearance of the panel being similar to that of Example 1.

Example 3

- 5 A 4" x 1/2" panel of 20-gauge auto body steel was immersed at atmospheric pressure in boiling phthalonitrile (310° C.). In five minutes a thin, adherent, uniform, somewhat greenish-blue color
10 was developed on the metal surface. The properties of this colored surface were similar to those described under Example 1.

Example 4

- 15 A 2" x 4" panel of 20-gauge copper sheet was treated as in Example 1, with the exception that the furnace was heated to 250° C. in the course of one hour. The panel was colored an adherent reddish-blue which stood up satisfactorily under
20 the tests described in Example 1.

Example 5

- A 4" x 1/2" strip of 20-gauge sheet copper was immersed in boiling solution of 20 parts of
25 phthalonitrile and one part of ammonium chloride (as catalyst) dissolved in 100 parts of dibutyl phthalate. After treatment at 310° C. for half an hour, the panel took on an adherent blue color which withstood the tests for abra-
30 sion and bending resistance as indicated under Example 1.

Example 6

- An air-cooled reflux condenser, consisting of a
35 glass tube of 14 mm. diameter and 18" long, was sealed into the side of a 500 cc. Erlenmeyer flask. A 2" x 1/2" strip of 20-gauge copper was placed in the bottom of the flask to act as a catalyst, and was then covered with four grams of
40 phthalonitrile. A number of 4" x 1/2" strips of 20-gauge sheet steel, which had been "Parkerized" but not treated with chromic acid, were stacked in the flask. The flask was stoppered with an alundum crucible cemented in place by
45 means of asbestos and fire clay, and was placed in an iron container. The latter was heated on a bath of molten lead at 330° to 350° C. for half an hour, after which it was removed from the metal bath and allowed to cool. The iron panels
50 were colored blue-black, were not affected by rubbing with a cloth or bending, and showed greater resistance to abrasion with steel wool than did a sample of ordinary "blued" steel. The catalytic action of the copper in this ex-
55 ample is apparently due to formation of copper phthalocyanine.

Example 7

- A panel of steel was treated as in Example 1,
60 with the exception that a catalyst consisting of approximately 0.3 gram of copper phthalocyanine was added to the reaction chamber. The steel panel was colored a reddish blue with a somewhat bronzed sheen. The bronze effect
65 was removed by brisk polishing with a cloth while the metal was still hot. The resulting reddish blue sheet had properties similar to those described under Example 1.

Example 8

- 70 A panel of steel was treated as in Example 1, except that the temperature was carried to 310° C. in 45 minutes. The panel was colored a pale, greenish blue and was similar in other
75 respects to that described under Example 1.

Example 9

A panel of steel which was treated as in Example 1, except that the temperature was carried to 555° C. in 65 minutes. A surface which
8 was gray-blue in color, but otherwise similar to that of Example 1, was obtained.

Example 10

A copper panel was treated as in Example 1,
10 except that the temperature was held at 200° C. for half an hour. An adherent, reddish-blue colored surface was obtained.

Example 11

15 Fifteen 2" x 4" panels of 20-gauge sheet iron were stacked in a pall of one-half gallon capacity, a thin layer of powdered phthalonitrile being placed between panels 1 and 2, 2 and 3,
20 3 and 4, and so on up to panel 11. In order that they would be exposed only to phthalonitrile vapor, no phthalonitrile was placed between the top panels 12 to 15. The pall was then closed and heated for one-half hour at 200° to 300° C.,
23 after which it was cooled and opened. The surfaces of all the panels had been converted to iron phthalocyanine, as evidenced by a blue coloration, thus showing that metal surfaces can be treated with both liquid and vapor porphyrzino-
30 genic substances.

As has been pointed out, any porphyrzino-
35 genic substance may be used in treating the metal surface. These substances are those which react to form tetra-aza-porphyrins, such as phthalocyanines or substituted-phthalocyanines. For the purposes of the present application, the metal-free phthalocyanines, so-called, although
40 themselves porphyrzines, are not considered to be embraced by the term "porphyrzino-genic substance". The most suitable and the preferred porphyrzino-genic substances are the aromatic o-dinitriles. The aromatic nucleus may be of the benzene series, or it may contain a plurality of aromatic rings, condensed or not,
45 such as the naphthalene, anthracene, phenanthrene, or diphenyl nucleus. Any of these nuclei may contain other substituents, such as halogen, nitro, alkyl, alkoxy, aryl, acyl, and aryloxy. The phthalonitriles, however, and phthalonitrile itself in particular, are most gen-
50 erally available and give best results. Examples of specific aromatic o-dinitriles that are suitable include the following: phthalonitrile, 4-chlorophthalonitrile, 3-nitrophthalonitrile, 4-methoxyphthalonitrile, 4-ethoxyphthalonitrile, 4-methylphthalonitrile, 4-phenylphthalonitrile, 4-benzoylphthalonitrile, 4-chloro-3',4'-dicyanobenzophenone, and 1,2-dicyanonaphthalene. Also in-
55 cluded by the term "porphyrzino-genic substance" are compounds which, under the temperature of treatment and through the intermediate formation or not of an o-dinitrile, convert the metal surface to the metal porphyrzine, e. g., the metal phthalocyanine. Examples of suitable compounds in this category are the
60 o-arylcyanamides, the o-aryldiamides, and related compounds, such as phthalic acid diamide, o-cyanobenzamide, ammonium phthalate, ammonium phthalamate, and the ammonium salt of o-cyanobenzoic acid. Compounds such as the
70 latter three, although theoretically containing enough nitrogen to form the phthalocyanine molecule, in use actually require the presence of ammonia or an ammonia-supplying agent such as primary amines, amides, cyanamides, urea,
75

etc. Compounds such as phthalic acid diamide should be employed in the presence of a dehydrating catalyst and added ammonia. It is also possible to employ such mixtures of compounds as alkali metal cyanides and o-halogen aromatic mononitriles, such as, for example

potassium cyanide and o-chlorobenzonitrile or sodium cyanide and 3-chloro-4-cyanodiphenyl. The porphyrizinogenic substance, e. g., phthalonitrile or other aromatic o-dinitrile, may be employed as a vapor, as a liquid, or as a solution in solvents, such as dibutyl phthalate and diphenyl, which boil above about 200° C. at 760 mm. and which, under the conditions of the process, are solvents for the o-dinitrile and chemically inert to o-dinitrile and porphyrazine formed.

The porphyrizinogenic substance may be used to color surfaces of copper, magnesium, cobalt, zinc, cadmium, lead, nickel, and iron, as well as alloys of those metals such as brass, "Monel" metal, certain steels, German silver, and the like. Of course, only those alloys melting above 200° C. are suitable inasmuch as the temperature of treatment must be at least this high. Metals on which a significant color apparently does not develop include aluminum, antimony, chromium, silver, tin, tungsten, and "black" (i. e., heavily oxidized) iron. There is no simple classification for the suitable metals, but the majority may be designated as common non-noble metals of Groups 1-B, 2-B, 4-B, and 8 of the Mendelyev's Periodic Table, which metals have a melting point above 300° C. By the word "common", it is intended to exclude the rare earths which are of no practical importance, and on which no information is available. By "non-noble" it is intended to exclude unsuitable metals such as silver and other noble metals, such as gold and the Group 8 metals of higher atomic number than nickel, on which data are at present lacking. The melting point limitation excludes metals such as mercury and tin. The suitable metal may also be grouped as structurally useful base metals melting above 300° C., and their alloys melting above 200° C., which metals form nitrates in which the metal is divalent. As already indicated, the metal should be in the massive form. Powdered metals are entirely consumed and unsuitable. The massive metal may be in an irregular shape, but it is customarily in some regular form or manufacture, such as bars, rods, sheets, plates, cups, and the like. It may be a plating on some other metal. The metal or metal surface treated may be subjected to various preliminary treatments such as pickling, sanding, or etching. Pickling is necessary if the metal surface has been treated with chromic acid, and for this purpose 10% sulfuric acid and a temperature of 25° to 100° C. are suitable. The metals, and iron especially, may also be treated with hot solutions of acid phosphates (e. g., ferric, sodium, and zinc acid phosphates) prior to reaction with the porphyrizinogenic body. Examples of well known commercial treatments of this type are "Bonderizing" and "Parkerizing".

The temperature of the treatment with the porphyrizinogenic substance depends to some extent upon the metal which is being coated. For example, copper reacts slowly at 200° C., while with iron it is preferred to operate at temperatures above 300° C. The lower limit, therefore, may be set at 200° C., and the extreme upper limit at 500° to 550° C., at which tempera-

ture the phthalocyanine or other porphyrazine begins to sublime off the surface. The preferred range is 250° to 400° C., though in some instances (particularly with metal surfaces having a previous acid phosphate treatment) temperatures up to 550° C. are desirable e. g., to reduce the iridescence of the coating.

The time of treatment depends upon the metal, the condition of the surface, and the presence or absence of catalysts, and may range from a few seconds (if the metal is preheated and catalysts are present) to an hour or more. Suitable catalysts are copper and copper compounds, such as copper oleate and copper phthalocyanine, and ammonium salts, such as ammonium chloride. The amount of the catalyst may range from a trace up to 10%, based on the aromatic o-dinitrile. The preheating, when resorted to, may be carried out in air or in a reducing or inert atmosphere, and is customarily but not necessarily below 200° C. The conditions of preheating will naturally vary somewhat with the metal, iron, for example, preferably being heated in the presence of hydrogen if the temperature is 300° C. or above.

Measurements have been made to determine the extent to which the present treatment penetrates into the metal surface. It has been found that the depth varies, according to conditions of treatment, from one-millionth of an inch to one-thousandth of an inch. At the maximum depth of one-thousandth of an inch, the metal porphyrazine begins to have a tendency to loosen and flake off when the metal is flexed or bent. For practical purposes the depth of the surface conversion should range from one-millionth of an inch to one ten-thousandth of an inch, and preferably from three-millionths of an inch to fifty-millionths of an inch.

The color of the treated surface will vary with the metal. Iron surfaces may, by varying conditions, be given a variety of colors, but most of the other metals can apparently be colored only a reddish-blue. Iron will be colored greenish-blue by relatively short treatments, blue by somewhat longer treatments, and reddish-blue by very long treatments. Shade, i. e., whether light or dark, can be varied by subjecting the iron to various treatments before or after it is colored; for example, a prior treatment with an acid phosphate results in a deep blue-black shade, and the shade may also be darkened by application of oil and wax.

A coating of oil, wax, or clear lacquer may be applied, if desired, to the finished surface. Such treatments aid in inhibiting corrosion and, as just indicated, in deepening the shade. Also, oil or wax applied to the still-warm treated metal will serve to reduce the bronze sheen or iridescence that is often evident. For many purposes, of course, this iridescence may however be desirable or not objectionable.

This invention is not only useful for the purpose of producing a decorative coloring on a metallic article but also for the purpose of preparing the article for use in subsequent treatment where the physical or chemical properties of the tetra-aza-porphyrin surface assist in the application of said subsequent treatments. Thus, for example, the massive body, such as copper wire or auto body steel, can be treated for the purpose of producing a bonding surface or anchor layer thereon, such surface being subsequently lacquered, enameled, or banded with any type of coating composition; e. g., those based on oils,

resins, cellulose derivatives, and the like, and optionally containing the usual ingredients of coatings, such as pigments, driers, solvents, and the like. Also metal type may be treated according to the process of the present invention for the purpose of causing the printer's ink to adhere more evenly to the surface thereof. The surface of metal bearings can be treated for the purpose of increasing the absorptive power of said surface for lubricating oils. Wires to be subsequently insulated with rubber, iron to be subsequently made into tank cars which are to be rubber lined, metal surfaces to which organic plastics are to be joined directly or by adhesives, metals to which boiler cements or other cements are to be applied, lead-in wires for blasting caps, metals to be used in photo-engraving, all can first be treated in accordance with the present invention for the purpose of increasing the bonding effect of said surface. A copper photoelectric surface can be treated for the purpose of sensitizing same.

The present process also includes within its scope the conversion of random or predetermined portions of metal surfaces to the tetra-aza-porphyn; thus stencils or designs of any type may be placed on metals by treating a predetermined area of the metal and then optionally applying to the treated portion of the surface an ink, paint or other material to produce, bring out, or accentuate the design, or even by using directly in the process a mixture of the coating material and the porphyrizinogenic substance.

Almost countless metallic articles of manufacture may be treated according to the present process (or the treatment may be carried out prior to or at some stage during the manufacture of such articles). The enhanced utility of such products may depend upon the coloration or other advantageous properties developed. Among such articles of manufacture are wire screens; e. g., those of iron, copper, or galvanized iron; iron and copper cooking utensils, such as waffle irons, pancake griddles, and kettles; electrical apparatus such as coils, "wafers" for photoelectric cells, and condensers; the metallic parts of firearms, such as barrels, receivers, magazines, bolts, sights, triggers, trigger guards and butt plates; the metallic components of ammunition, such as projectiles, cases, primers, battery cups and anvils; and miscellaneous articles such as cutlery, razor blades, stove pipes, cameras, hot water and steam radiators, stoves, refrigerators, radios, ash trays, drawing instruments, carpet tacks, screw drivers, and the like.

Generally speaking, the invention is useful for producing colors on any article having a metallic surface of or essentially comprising any of the metals previously named, or their alloys. The invention is particularly well suited to cases where (a) painting or lacquering is not feasible because the object so coated is to be subjected to high temperatures and/or to the action of chemicals that attack coating composition vehicles, where (b) resistance to corrosion is not a primary consideration and where (c) speed and economy of treatment are paramount.

The colored surfaces which are formed by the process of this invention are superior to paint and lacquer coatings in that they are in general more resistant to heat and chemicals, and are less expensive to prepare and apply. The fact that surface colorings of the type described herein cannot be produced on certain metals, such as antimony and tin, which in the powdered (as opposed to massive) form readily yield phthalocyanines, is evidence that the present process is not one of forming a "pigment" in situ. A further and obvious distinction from the art on phthalocyanine pigments, of course, is that in the present process the entire metal is not consumed, only the surface being affected.

In its application to steel, the present process is superior to the ordinary "blue" finishing in that it is more economical and in that the product has a more uniform color and in some instances greater abrasion resistance.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A process of treating a massive body having a metallic surface containing as an essential component a structurally useful base metal melting above 300° C. and forming a nitrate in which the metal is divalent, which comprises contacting said metallic surface with a porphyrizinogenic substance in fluid form at a temperature between 200° and 550° C.

2. A process of coloring a massive body having a metallic surface containing as an essential component a common non-noble metal of Groups 1-B, 2-B, 4-B, and 8 of the Mendelyev's Periodic Table, which metal has a melting point above 300° C., by forming on said massive body a relatively thin, tenaciously-adherent, abrasive-resistant, colored surface, which comprises contacting said metallic surface with a porphyrizinogenic substance in fluid form at a temperature between 200° C. and 550° C.

3. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature between 250° and 400° C.

4. The process in accordance with claim 1 characterized in that the reaction is carried out in the presence of a catalyst.

5. The process in accordance with claim 1 characterized in that the porphyrizinogenic substance is an aromatic ortho-dinitrile.

6. The process in accordance with claim 1 characterized in that the porphyrizinogenic substance is phthalonitrile.

7. The process in accordance with claim 1 characterized in that the metal surface contains iron.

8. The process in accordance with claim 1 characterized in that the metallic surface contains iron which has been subjected to a preliminary treatment with an acid phosphate, and in that the temperature is from 300° to 550° C.

9. A composition of matter comprising a massive body having as its essential component at its surface a structurally useful base metal melting above 300° C. and forming a nitrate in which the metal is bivalent, the surface of said metal being at least partially converted to a tera-aza-porphyn.

10. A composition of matter comprising a massive body having a relatively thin colored surface tenaciously adherent to a metal under-surface, said metal under-surface comprising as an essential component a common non-noble metal of Groups 1-B, 2-B, 4-B, and 8 of the Mendelyev's Periodic Table, which metal has a melting point above 300° C., said colored surface comprising a tera-aza-porphyn of said metal.

11. The product in accordance with claim 9 characterized in that the surface of said massive

sive body, prior to being converted to a tetra-azaporphyn, was smooth and bright.

12. The product in accordance with claim 9 characterized in that the metal under-surface, prior to the formation of said composition of matter, extended to the surface of said massive body and was smooth and bright.

13. The product in accordance with claim 9 characterized in that the base metal is iron.

14. The product in accordance with claim 9 characterized in that the base metal is iron and the surface of said metal is at least partially converted to a phthalocyanine of iron.

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