COMPOSITION AND METHOD FOR BLACK COATING ON METALS
27 Claims, No Drawings

ABSTRACT: This invention relates to the production of a black finish on the surfaces of metals that are electropositive to bismuth, for example, ferrous metals, manganese, and the white metals as aluminum, magnesium, cadmium and zinc. The invention more specifically is that of a method of producing a black finish on the surface of such metal electropositive to bismuth by immersing the metal surface in an acidic solution of a trivalent bismuth salt.
COMPOSITION AND METHOD FOR BLACK COATING ON METALS

Immersing or immersion of the metal surface in the aqueous acid solution of trivalent bismuth includes wetting the surface not only by submerging it in or dipping it into the treating bath of such aqueous acid solution, but also brushing, spraying or rolling such solution over the metal surface or otherwise drenching it with the aqueous acid solution.

As an extension of the method, the resulting black coat then is given a protective coating such as an application of lacquer or plastic (from a solvent solution of either of them) or if the base metal is amenable to phosphate conversion coating, it is subjected to suitable such treatment by acid aqueous phosphate coating bath, in each case to enhance the abrasion resistance of the overall black coating.

Also part of the invention are the aqueous acidic baths containing the trivalent bismuth salts, for application to the metals to be black-finished and also concentrated compositions which on aqueous dilution serve as treating baths to provide the black coating.

The compositions and method of the invention are effective on any of the metals electropositive to bismuth and are especially beneficial on ferrous metal surfaces and others amendable to application of a phosphate coating, i.e., a phosphate reactive for conversion coating.

A further part of the invention is the resulting final product of the overall two-stage method of the invention, namely, the resulting metal article comprising a metal electropositive to bismuth, having on an exposed surface thereof a substantially smooth, black coat or finish which consists essentially of substantially colloid size bismuth particles emmeshed in an adherent lacquer or plastic film or in the lattice structure of an ordinary acid phosphate coating bath-produced phosphate conversion coating. Among such black coated metal articles of the invention are those of manganese, the white metals such as aluminum, magnesium, cadmium and zinc, and particularly the so black coated ferrous metals.

There developed in industry, particularly in the automobile industry, an increasing call for the application of a uniformly appearing black finish or coating on parts, often made separately at different sources, to be assembled into the finished equipment particularly as under the hood parts for automobiles. To meet these requirements, especially of automobile manufacturers, that such parts made for them have a black coating, there have been tried coatings such as black paints or pigmented oils. Attempts also were made to meet this call, by including various additional constituents in certain baths used for otherwise treating metal surfaces.

These prior methods presented undesirable shortcomings not alone in impractical cost and accompanying hazard to workers but also in the risk of fire such as from excessive vaporization of volatile solvents, but also from the fact that the desired uniformly black coating has not been readily obtainable and also that resulting black surfaces could not be provided with the necessary resistance to wear under service.

An important feature of the compositions and method of the invention is the use of an aqueous, safely handled acid vehicle thereby eliminating prior hazards to health and property.

Another feature of the invention is its provision of a simple and rapid process for developing a dependably uniform, dense black finish coating on the surfaces of a variety of extensively used industrially applicable metals.

Still another feature of the invention is the simplicity of application of the treating solutions for providing the black coating finish as well as of control of the treating solution bath and process for providing that finish.

Yet a further feature of the invention is the provision of the desired dense black coatings that manifest not only uniform appearance and thickness but also dependable resistance to abrasion and wear, and at low practical cost.

The method of the invention involves the essential step of subjecting an adequately cleaned panel or other article of the selected metal electropositive to bismuth, to the action of, by immersing the article in, an aqueous acid solution of a trivalent bismuth salt in a concentration to provide in solution at least about 0.1 percent of bismuth (as cation) and for a time sufficient to provide a suitable thickness of the dense black bismuth coating.

The immersion time can be as little as is sufficient for the desired thickness of the black coat to be deposited. That time can vary from even as little as 5 seconds with a fresh treating solution and ordinarily for one to 2 minutes, and can go to about 3 minutes when a control test may show that the concentration of the basis metal in the already used solution, for example, iron, is over 0.5 percent and approaching 1 percent, although for the most part immersion from about a half minute to a minute is often adequate although not to be considered as a limitation, in the indicated practical immersion time a black finished deposit of from about 10 to about 40 milligrams per square foot of basis metal surface is obtained as generally indicated, for example, on steel.

Any such bismuth salt soluble in the aqueous acid solution vehicle beneficially of mineral acid such as sulfuric acid, nitric acid, or hydrochloric acid, or mixtures of any of them, can be used. These salts include bismuth sulfite, bismuth trichloride, bismuth trinitrate pentahydrate, and bismuth carbonate (which on solution as in nitric acid or hydrochloric acid used for solution result in bismuth nitrate or hydrochloride).

Bismuth chloride is advantageous in that the chloride ion enhances retention of bismuth in solution over a wide range and also lower level of acid content and also enables obtaining the black coat with a lower concentration of bismuth ion, in addition to improving the smoothness and continuity of the black bismuth coat, and with greater freedom from any tendency toward soft and spongy deposit. However, balance of cost against, and yet without loss of, practicality of operation makes it advantageous to use bismuth trinitrate.

In using bismuth trinitrate, a higher bismuth content is needed in the absence of the chloride anion. However, the benefits otherwise available from the presence of the chloride ion when using bismuth chloride can be provided by including a relatively minor content of that chloride or merely hydrochloric acid. This acid is an efficient, economic and convenient source of the chloride anion. A further economic advantage is provided by dissolving the bismuth trinitrate in aqueous sulfuric acid practically not exceeding about 50 percent H₂SO₄ but at least about 12 percent of it.

The bismuth cation content of the treating bath can vary by weight from a minimum of about 0.1 percent to about 0.58 percent with a beneficial practical operating range from about 0.125 percent to about 0.375 percent, and may be present also up to about two percent by weight. The mineral acid concentration should be sufficient to hold in solution the quantity of the selected trivalent bismuth salt needed to provide the selected operating content of bismuth ion. Calculated as H₂SO₄ equivalent, for general practical operation the acid content can vary from about 12 to about 25 percent.

Addition of a copper salt soluble in the aqueous acid bath, optimally in the ratio to provide copper ion to the extent of from about 8 percent to about 12 percent and optimally about one-tenth that, of the bismuth content, is not only in extending the life of the black treatment or blackening bath but also indicates an apparent improvement in the general nature of the black deposit. Copper nitrate avoids any tendency toward a soft and spongy deposit.

Presence of copper ion in the bath enables working with lower concentration of bismuth in it. Without copper ion in the bath, the bismuth cation concentration may need to be from about 50 to 100 percent greater than that which is effective when the bath contains the cupric cation. Because of the earlier mentioned benefit from presence of the chloride ion in the bath, it is an added benefit to include the copper ion, for example, by adding a proportionate amount of copper chloride.

Applicable blackening baths are illustrated by, but not restricted to, the following wherein the constituents are present in percent by weight:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth nitrate</td>
<td>12.5</td>
</tr>
<tr>
<td>Copper nitrate</td>
<td>0.1</td>
</tr>
<tr>
<td>Acid (H₂SO₄)</td>
<td>25</td>
</tr>
</tbody>
</table>

This composition has been found to provide an excellent black finish coating on any metal, especially those made from or coated with iron or steel.
Example 1

Bismuth Salt Alone In Aqueous Acid

Bismuth Trinitrate Pentahydrate  
Sulfuric Acid (60° B.)  
Water

Example 2

Bismuth Salt In Aqueous Sulfuric And Hydrochloric Acids

Bismuth Trinitrate Pentahydrate  
Sulfuric Acid (60° B.)  
Hydrochloric Acid (20° B.)  
Water

Example 3

Bismuth Salt, Sulfuric And Hydrochloric Acids, And Copper Salt

Bismuth Trinitrate Pentahydrate  
Cupric Chloride Dihydrate  
Sulfuric Acid (60° B.)  
Hydrochloric Acid (20° B.)  
Water

Example 4

Bismuth Salt, Sulfuric Acid, And Cupric Chloride

Bismuth Trinitrate Pentahydrate  
Cupric Chloride Dihydrate  
Sulfuric Acid (60° B.)  
Water

Example 5

Bismuth Chloride, Copper Nitrate, Sulfuric Acid

Bismuth Trichloride  
Cupric Nitrate Tribromide  
Sulfuric Acid (60° B.)  
Water

In any of the foregoing bath compositions, the respective sulfuric acid content can be replaced but only in a minor part by a correspondingly equivalent amount of any of the other applicable acids, benefitting some other mineral acid such as hydrochloric and/or nitric acid, to provide a resulting acid concentration within the range from about 12 to about 25 percent H₂SO₄ equivalent. In any of the foregoing complete examples and just described possible modifications of them, the desired chloride ion content can be provided in the form of hydrochloric acid, alkali metal chloride such as sodium chloride, or as ammonium chloride, bismuth trichloride or cupric chloride. The range of chloride ion is not critical for it can be used to retain the bismuth salt in solution.

The copper ion can be provided within the range of about 8 to about 12, percent and optimally about 10, percent of the bismuth ion content, in the form of cupric chloride or nitrate as in examples 3–4 and 5 respectively or other water-soluble compatible cupric salt such as cupric sulfate, or mixtures of any of them.

All of the thus described modifications of any of the foregoing examples and described modifications of any of them are to be considered as if actually separately respectively set forth in full by the foregoing descriptions of them, to avoid unduly extending this specification. In any of the resulting respective examples, a comparatively small amount such as about 0.05 weight percent of a compatible anionic wetting agent can be included to enhance the customary rinsing operation after the desired extent of bismuth black coat has been applied.

In any of the examples 1–5, 0.05 weight percent numerically of the water content can be replaced by 0.05 weight percent of an anionic wetting agent.

The method of the invention is illustrated by, but not restricted to, the use of each of the above baths separately, by immersing in it the various articles made of a metal electropositive to bismuth such as steel parts, for example, for use under the hood in automobiles, black coat bismuth coating to deposit on them. The parts then are removed with the resulting satisfactory uniform dense black coating over their exposed surface. Small parts, such as screws and nuts, are treated in the same way with the same solutions, conveniently in a slowly rotating barrel much like that used in barrel plating, or in a basket.

No reference to operating temperature is made in the description of the blackening treatment with any of the baths of the foregoing examples and any of the described modifications of them. That is so because the blackening process does not require any special temperature operating condition but rather is carried out at any ambient shop conditions even when the temperature is below 50° F. At temperatures below that obviously the reaction rate can be expected to be slower and even so at temperatures down in the upper thirties.

Thus, a temperature from 50° F. up to about 100° F. is satisfactory. Also, the treatment can be conducted at temperatures above 100° F. and even above 120° F., but the resulting increased rate of reaction at such elevated temperatures usually is not needed when the blackening operation may require only a minute or from a half minute to about 1½ minutes at the lower ambient temperatures.

The black coated articles from the blackening treatment are adequately rinsed to remove adhering blackening bath solution, thereby providing the product of that essential part of the invention.

As an extension of the invention, the abrasion resistance of the foregoing initially black-coated product is enhanced by a further step of giving the black coat a protective coating. As already indicated, that can be done by applying by suitable readily available known means a transparent lacquer coating or transparent plastic coating by suitably applying a film of lacquer or plastic from a suitable solution of either in readily volatile solvent, and removing solvent as under air drying.

Alternatively, any of the effective phosphate conversion coatings can be applied to the black-coated metal surface by customary immersion of the black-coated articles in any of the effective acid phosphate-ion-containing conversion coating baths. Suitable such phosphate coating conversion baths are illustrated by, but not restricted to, those described and exemplified in U.S. Pat. Nos. 2,502,441 and 2,820,731, and also referred to in the copending U.S. Pat. No. 3,400,021 column 7, including the methods of application therein described. Nothing special is necessary as to the composition of the phosphate coating baths.

The resulting applied phosphate conversion coating is integrally associated with the black-coated surface of the treated articles with the result that in the final dried product the abrasion resistance of the black-coat is enhanced by its being enmeshed within the lattice structure of the phosphate conversion coating, thereby leaving the thus finished articles with an overall uniform jet black finish capable of withstand ing the rigid conditions to which they will be exposed in their ultimate application and use. Any of the effective chrome conversion coatings are used in the same way particularly with the bismuth coating on a white metal such as aluminum, magnesium, and zinc, for example, from the chrome coatings of U.S. Pat. Nos. 2,438,877, 2,796,370; and 2,796,371.

While the baths and method of the invention have been illustrated by detailed written descriptions as applied to ferrous
metal articles, each of the blackening bismuth treatments available from each of the foregoing illustrative examples and described modifications of them can be considered as repeated in full as separately applied to production of the corresponding uniform black bismuth coat on each of the other metals electropositive to bismuth and specifically also to manganese, individual white metals such as aluminum magnesium, cadmium and zinc, and also to any other ferrous metal articles. The bismuth tends to avoid attack on the basis metal by the acid in the aqueous bath.

Similarly, the resulting bismuth black-coat on any articles of any such other metal electropositive to bismuth also can be given any earlier above described protective coating such as a lacquer or plastic coating. Likewise, any of such black bismuth-coated other metal electropositive to bismuth and which is amendable to a phosphate conversion coating, alternatively can be treated with any of the earlier mentioned compatible suitable acid phosphate-ion-containing conversion coating baths to be given a suitable phosphate conversion protective-coating.

Thereby there is produced the corresponding uniform, smooth jet black bismuth finish in the form of the colloid size bismuth particles black-coat enmeshed within the selected protective coating, for example, enmeshed within the lattice structure of a phosphate conversion coating.

Any of these metal articles bearing such resulting combined phosphate conversion coating black bismuth finish can be suitably rinsed by submersion in a cold, continuous overflowing rinse, for which ordinarily about a minute is adequate. Then, rather than merely drying the articles, it is beneficial to give them a separate supplementary rust preventative finish such as commonly is applied after the ordinary phosphate conversion coating, for example, treatment with known conversion inhibiting aqueous chromate or chromic acid solution, or a so-called water-soluble oil application, or both.

The expression “water-soluble oil”, well understood in the art, is generic to the various complex metal salts of mineral acid, and especially phosphoric acid, esters, which salts are soluble or readily dispensible in water as well as in organic solvents, and are exemplified by those described in U.S. Pat. Nos. 2,080,299; 2,820,723; and 2,861,907.

To reduce at least in part the shipping cost, any of the foregoing illustrative blackening baths or the described variations of them can be prepared simply by adequately diluting with the required amount of suitable water a corresponding one of various concentrates which are illustrated by, but not restricted to, the following, wherein content of each respective ingredient is in percent by weight.

Example 6

Bismuth Salt, Sulfuric Acid, Water

Bismuth nitrate pentahydrate 0.90
Sulfuric acid (66° B.) 32.50, and Water 66.60.

Example 7

Bismuth Salt, Sulfuric Acid, Hydrochloric Acids, Water

Bismuth nitrate pentahydrate 0.90
Sulfuric acid (66° B.) 32.00
Hydrochloric acid (20° B.) 2.00, and Water 65.10.

Example 8

Bismuth Salt, Copper Salt, Mineral Acids, Water

Bismuth nitrate pentahydrate 0.80
Cupric chloride dihydrate 0.10
Sulfuric acid (66° B.) 32.00
Hydrochloric acid (20° B.) 2.00, and Water 65.10.

Any of the concentrates of examples 6 to 8 or any of the hereinafter described modifications of them can be diluted at the point of use with from about 50% to about 14 times their respective volume of water.

Example 9

All Ingredients Higher Than In Example 8

Bismuth nitrate pentahydrate 1.5
Cupric chloride dihydrate 0.3
Sulfuric acid (66° B.) 47.1
Hydrochloric acid (20° B.) 4.0, and Water 47.1.

One part of this concentrate can be diluted (for use as a treating solution) with 3 times its volume of water.

Example 10

Varying Proportions Of Bismuth Salt, Copper Salt, And Sulfuric Acid

(a) Bismuth trichloride 2.0
Cupric nitrate trihydrate 0.4
Sulfuric acid (66° B.) 47.0, and Water 50.6.

This concentrate can be diluted by its own weight of water.

(b) Bismuth trichloride 2.20
Cupric nitrate trihydrate 0.43
Sulfuric acid (66° B.) 52.00, and Water 45.37.

(c) Bismuth trichloride 2.5
Cupric nitrate trihydrate 0.5
Sulfuric acid (66° B.) 56.5, and Water 40.5.

One part by volume of each of concentrate (b) and (c) can be diluted with twice its volume of water.

In any of the foregoing concentrate examples 6 through 10, the respective sulfuric acid content can be replaced but only in a minor part by a correspondingly equivalent amount of any of the other applicable acids, beneficially some other mineral acid such as hydrochloric and/or nitric acid, to provide a resulting acid concentration within the range from 25 to about 53 percent, calculated as H₂SO₄.

In any of the foregoing complete concentrate examples and just described possible modifications of them, the desired chloride ion content can be provided in the form of hydrochloric acid, alkali metal chloride such as sodium chloride, or as ammonium chloride, bismuth trichloride or cupric chloride. The range of chloride ion is not critical for it can be used to retain the bismuth salt in solution.

The copper ion can be provided within the range of about 8 percent to about 12 percent, and optimally about 10 percent, of the bismuth ion content, in the form of cupric chloride or nitrate or other water-soluble compatible cupric salt such as cupric sulfate, or mixtures of any of them.

All of the thus described modifications of any of the foregoing concentrates and described modifications of any of them are to be considered as if actually separately respectively set forth in full by the foregoing descriptions of them, to avoid unduly extending this specification. In any of the resulting respective concentrates, a comparatively small amount such as from about 0.05 to about 0.15 weight percent of a compati-
bile anionic wetting agent can be included to enhance the customary rinsing operation after the desired extent of bismuth black coat has been applied by the treating bath.

The black bismuth deposits of the invention indicate enhancement of the lubricating activity manifested by the heavy metal phosphate conversion coatings, such as the zinc phosphate coating, in the metal-working and drawing operations.

While the invention has been explained more extensively by detailed description of certain specific illustrative embodiments of it, it is understood that various modifications and substitutions can be made in any of the thus described embodiments within the scope of the appended claims which are intended also to include equivalents of any such embodiments.

What is claimed is:

1. An article having a surface composed of a basis metal electropositive to bismuth, which surface is covered with a continuous relatively uniform finish of substantially colloidal size black bismuth metal particles emmeshed in a protective coating member of the class consisting of a transparent plastic coating, a phosphate conversion coating, and a chromate conversion coating, fixedly applied to said metal surface and fixedly holding said bismuth particles to said surface; said bismuth particles providing to said surface through said protective coating an overall substantially uniform, continuous black color.

2. An article as claimed in claim 1, wherein said basis metal surface is a metal member of the class consisting of a ferrous metal, manganese, aluminum, magnesium, cadmium, and zinc.

3. An article as claimed in claim 2, wherein said basis metal surface is one amenable to taking on a phosphate conversion coating when subjected to the action of an acid aqueous phosphate ion-containing conversion coating solution, and said protective coating is a said phosphate conversion coating produced on and thus integral with said metal surface after said surface initially was covered alone with said relatively uniform finish of black bismuth particles.

4. An article as claimed in claim 3, wherein said article is a ferrous metal article and said so covered surface is of ferrous metal, and said phosphate conversion coating is integral with said ferrous ion-containing surface by having been produced thereon.

5. An aqueous coating bath effective to deposit a dense black bismuth coat on an article of a metal electropositive to bismuth, upon immersing said article metal in clean state in said bath for a time sufficient for said bismuth coat to be deposited on it from said bath which comprises an ionizable trivalent bismuth salt dissolved, to an extent sufficient to provide at least about 0.1 percent content of bismuth cation by weight, in water containing dissolved therein inorganic mineral acid in an amount of at least about 12 percent calculated as HSO₄, equivalent and sufficient to dissolve the quantity of said bismuth salt provided in that aqueous acid medium.

6. A coating bath as claimed in claim 5, wherein said mineral acid consists essentially of sulfuric acid and hydrochloric acid.

7. A coating bath as claimed in claim 6, wherein the sulfuric acid is the major part of said mineral acids which jointly provide by weight in said bath the equivalent of at least about 12 percent calculated as H₂SO₄.

8. A coating bath as claimed in claim 7, wherein said bismuth salt is one of the class consisting of its sulfate, the trinitrate, and the trichloride, and is present to the extent to provide a maximum of about 2.0 percent of bismuth cation by weight; the hydrochloric acid is present to the extent of from about 0.5 to about 5.0 percent by weight calculated as 20° B. acid; and said mineral acids provided jointly by weight a maximum of about 25 percent calculated as H₂SO₄.

9. A coating bath as claimed in claim 5, wherein an ionizable copper salt soluble in said bath is present in an amount sufficient to provide the cupric cation to the extent of from about 8 to about 12 percent of the bismuth content of the bath.

10. A coating bath as claimed in claim 9, wherein said copper salt is selected from cupric chloride, cupric nitrate, and cupric sulfate, and is present in an amount to provide said cupric cation to the extent of about 10 percent of said bismuth.

11. A coating bath as claimed in claim 5, wherein sulfuric acid is at least the major part of said mineral acid, and dissolved in the bath is a chloride-ion-providing substance selected from hydrochloric acid, an alkali metal chloride, ammonium chloride, bismuth chloride, and copper chloride.

12. A coating bath as claimed in claim 10, which comprises: from about 17.5 to about 34.6 parts of H₂SO₄, from about 0.4 to about 0.5 parts of HCl, from about 0.06 to about 0.075 parts of CuCl₂, from about 0.224 to about 0.284 parts of bismuth, and from about 120 to about 190 parts of water.

13. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 5 and for a time sufficient for said black bismuth coating to be produced on said surface.

14. The method as claimed in claim 13, which comprises thereafter immersing said black bismuth coating-bearing surface in a phosphate conversion coating bath for a time sufficient to produce on said black bismuth coating-bearing surface a phosphate conversion coating emmeshing said black bismuth coating.

15. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 7 and for a time sufficient for said black bismuth coating to be produced on said surface.

16. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 8 and for a time sufficient for said black bismuth coating to be produced on said surface.

17. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 9 and for a time sufficient for said black bismuth coating to be produced on said surface.

18. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 10 and for a time sufficient for said black bismuth coating to be produced on said surface.

19. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 11 and for a time sufficient for said black bismuth coating to be produced on said surface.

20. A method of producing a relatively uniform black bismuth coating over the surface of an article of a metal which is electropositive to bismuth, which method comprises immersing said metal surface in an aqueous acid coating bath as claimed in claim 12 and for a time sufficient for said black bismuth coating to be produced on said surface.

21. The method as claimed in claim 20, which method comprises thereafter immersing said black bismuth coating-bearing surface in a phosphate conversion coating bath for a time sufficient to produce on said black bismuth coating-bearing surface a phosphate conversion coating emmeshing said black bismuth coating.

22. An aqueous concentrate which upon suitable dilution with water provides an aqueous acid coating bath effective to deposit a dense black bismuth deposit on a metal electroposi-
tive to bismuth by immersing therein said metal for a sufficient time thereafter, which concentrate comprises an ionizable trivalent bismuth salt dissolved to an extent sufficient to provide from about 0.6 to about 2 percent content of bismuth cation by weight, in water containing dissolved therein mineral acid in the range of from about 25 to about 53 percent by weight calculated as H₂SO₄ and with sulfuric acid being the major part of said acid content; and hydrochloric acid from none to about 10 percent, calculated as 20° B. acid, by weight of said concentrate.

23. The aqueous concentrate as claimed in claim 22, wherein the mineral acid consists substantially entirely of sulfuric acid.

24. The aqueous concentrate as claimed in claim 22, which includes also a chloride-ion-providing substance selected from the class consisting of hydrochloric acid, an alkali metal chloride, ammonium chloride, bismuth trichloride, and cupric chloride, to the extent to provide at most about 3.2 percent chloride ion by weight, and the bismuth cation content is at most said 2 percent.

25. The concentrate as claimed in claim 22, wherein said concentrate contains a water-soluble cupric salt in an amount to provide the cupric cation to the extent of from about 8 to about 12 percent of the bismuth.

26. The concentrate as claimed in claim 25, wherein hydrochloric acid is present within its said range.

27. A coating bath as claimed in claim 5, wherein said ionizable bismuth salt is present therein to the extent to provide therein up to a maximum of about 2.0 percent of bismuth cation.