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ELECTROPLATING ZINC

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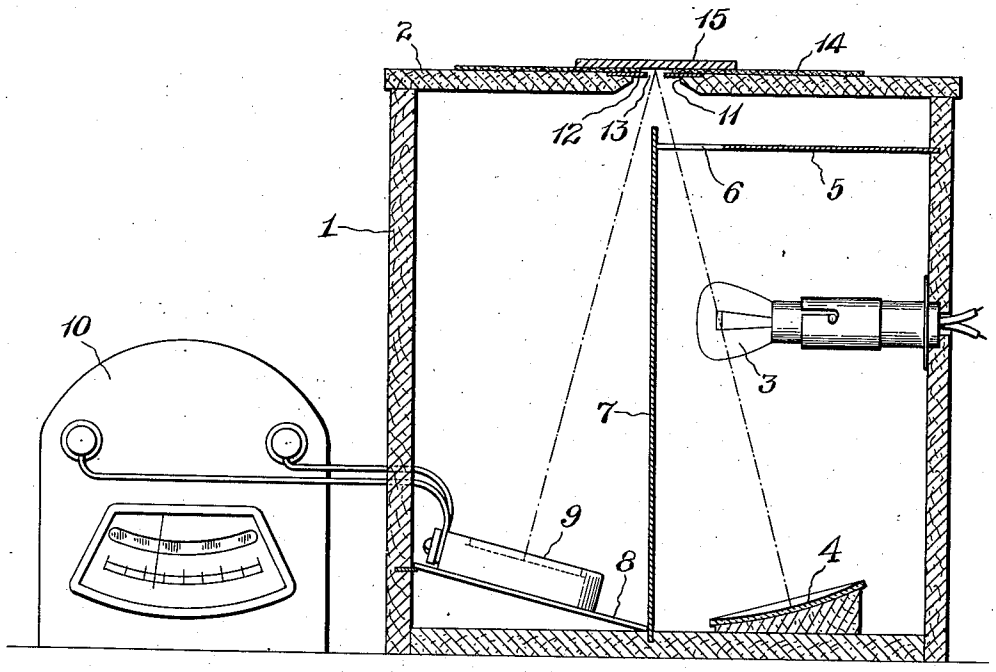

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ELECTROPLATING ZINC

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This invention relates to the electrodeposition of zinc, and is particularly directed to processes and plating solutions wherein a bright, mirror-like zinc deposit is plated from a cyanide-zinc bath which contains both an organic addition agent and a brightening metal. This invention is further directed to the bright zinc deposits obtained, to the processes of obtaining such deposits from cyanide-zinc plating baths, and to processes and solutions employing an oxyheterocyclic compound and a brightening metal.

The electrodeposition of zinc, or electrogalvanizing, has been rather extensively employed because electro deposited zinc coatings, in addition to their low cost, display many characteristics which cause them to be particularly desirable as protective finishes. Zinc, being higher in the electromotive series, will protect iron or steel against rust even after appreciable areas of the base metal are exposed, whereas the corrosion of iron or steel is accelerated by such metals as copper, nickel, and chromium. Despite their numerous advantages over many commonly used coating materials, electrodeposited zinc coatings have not enjoyed the use they deserve because ordinarily they do not possess and do not retain a pleasing appearance, and, consequently, for many purposes they are not acceptable.

Most of the known methods of electrodepositing zinc result in dark colored or dull plates and, even when the deposits at first are fairly satisfactory, they may soon become dark and discolored. The poor appearance of most electrodeposited zinc coatings has limited their use to protective applications, and those working in the art have, for the most part, turned to other protective materials when it was desired to produce a finish of pleasing appearance.

The electrodeposition of zinc has ordinarily been accomplished by the use of either an acid-zinc bath or a cyanide-zinc bath. With neither of these baths has it been possible to obtain satisfactorily smooth and bright deposits, but the acid-zinc bath is more commonly used because it leads to a brighter deposit with a better color than does the cyanide-zinc bath.

While, under favorable conditions, the deposits obtained from acid-zinc baths are relatively white, they are still none too satisfactory because of their relatively coarse crystalline structure.

Numerous attempts have been made to improve the character of zinc deposits obtained from acid baths, and many addition agents, such as glycerine, dextrin, gum tragacanth, licorice, naphthalene compounds, and aluminum compounds have been used in conjunction therewith. While the use of addition agents improved the character of the deposits to some extent, the results were still none too satisfactory.

In addition to the fact that acid-zinc baths do not produce satisfactory deposits, there are numerous other disadvantages attendant upon their use. For one thing, acid-zinc baths have very poor throwing power, and it is exceedingly difficult satisfactorily to plate irregularly shaped objects. Another disadvantage of acid-zinc baths is their low cathode efficiency. As zinc is above hydrogen in the electromotive force series of metals, it is theoretically impossible to deposit zinc from acid solutions, but, of course, the rather great overvoltage of hydrogen does permit zinc deposition. Concurrently with the deposition of zinc, however, there is a very considerable evolution of hydrogen.

While the deposits obtained from cyanide-zinc baths are poor in appearance, they have a relatively fine crystalline structure. A few addition agents, such as alum, gum arabic, and fluorides, have been tried in cyanide-zinc baths, but the results obtained were none too satisfactory. Aside from the poor appearance of deposits obtainable therefrom, cyanide-zinc baths have a number of advantageous characteristics. They have good throwing power, and it is therefore possible to deposit a relatively uniform zinc coating on irregularly shaped and recessed articles. Cyanide-zinc baths, moreover, have a relatively high cathode efficiency which, of course, is very advantageous because the electric current applied to the bath is expended less upon the evolution of hydrogen, and more upon the deposition of zinc.

Despite the advantages of cyanide-zinc baths, they have not been much used by the art because of the poor appearance of zinc deposits obtainable therefrom. Regardless of the disadvantages in operation of acid-zinc baths, they have been favored by those working in the art because of the somewhat better appearing deposits obtainable by their use.

A number of proposals have recently been made for improved methods of electrodepositing zinc. The art has been enabled, using cyanide-zinc baths, to produce relatively smooth and bright zinc plates. Such zinc plates, however, require treatment in a bright-dip, such as dilute nitric acid, before they are entirely satisfactory for some purposes. Those working in the art are frequently desirous of producing as even and bright a finish as possible, and, by using a bright-

dip, a zinc plate may be made brighter and more uniform in appearance. The deposits, after bright-dipping, also display greater resistance to tarnishing and staining.

The use of a bright-dip is illogical and uneconomical. The bright-dip removes some of the zinc, and it is wasteful of time, materials, and labor to apply a zinc coating and then remove part of it. The bright-dip treatment, moreover, involves considerable expense for bright-dipping materials and labor. The zinc should be deposited, therefore, in as bright a condition as possible so that a bright-dip treatment would be used, if at all, only when it is desired to produce extremely bright finishes.

I have found that much brighter deposits than those customarily produced can be made with cyanide-zinc electroplating baths which contain both an oxyheterocyclic addition agent and a metal brightener. The deposits produced according to the better procedures of this invention are brilliant, and reflect images with mirror-like fidelity when deposited on polished surfaces. Bright-dipping such deposits produces no change of any consequence in their appearance, and bright-dipping is unnecessary. The zinc deposits produced on unpolished commercial articles, similarly, are of exceptional brightness and no discernible effect is produced by bright-dipping.

The baths of this invention have great throwing power and extremely wide bright current density ranges and, unlike the baths of the prior art, they produce uniform zinc coatings even on recessed articles. It is therefore unnecessary to use bright-dips for the purpose of making the coatings uniform. Also, by reason of the wide bright current density range displayed by cyanide-zinc baths of this invention, it is possible to plate at much higher current densities than have heretofore been feasible.

Employing the procedures of this invention, there are obtained even, lustrous zinc deposits directly from the plating bath, the deposits requiring no bright-dipping. The deposits are at least equal in appearance to the best bright-dipped zinc deposits now being produced commercially and they are far better than most of the present commercial bright-dipped zinc deposits.

This invention, in its broader aspects, includes some baths which do not produce deposits of the highest brilliance, but which are, nontheless, a distinct improvement over the baths at present in commercial use. It may sometimes be sufficient to produce deposits of moderate brightness, and, in any event, a bright-dip can be employed with results superior to those of the prior art.

As is set forth in my co-pending application Serial Number 14,589, filed April 4, 1935, a number of metals may advantageously be used to produce deposits of great smoothness and brightness. These metals appear to exercise some synergetic action in conjunction with organic addition agents, and this action is particularly noticeable when the metals are used in conjunction with oxyheterocyclic addition agents. Most of the oxyheterocyclic compounds seem to have only a small effect when used in cyanide-zinc baths in the absence of a brightening metal. As will be noted later, however, heterocyclic compounds may sometimes be used alone for the benefit which they do offer.

Oxyheterocyclic compounds, typical of which are furfural derivatives, coumarin, pyronine, and piperonal, are, of course, characterized by the presence of an oxyheterocyclic ring, and it is believed that it is this characteristic which determines the suitability of compounds for my purposes. An oxyheterocyclic ring is, of course, a cyclic ring of carbon and oxygen atoms.

The oxyheterocyclic addition agents employed should be relatively stable in the bath. That is, they should not lose their oxyheterocyclic form upon contact with a cyanide-zinc plating solution. The compounds, moreover, should be at least slightly soluble in a cyanide plating bath. The addition agents suitable for use with brightening metals in accordance with this invention will be discussed in greater detail in the examples given hereinafter.

The brightening metals to be used in conjunction with oxyheterocyclic compounds according to this invention include aluminum, titanium, and metals found in sub-group 1 of groups VI and VII, and in group VIII series 4 of Mendelyeev's periodic arrangement of the elements. Most of these metals themselves exercise a profound effect upon the character of zinc electrodeposits obtained from cyanide-zinc plating baths, and, when used with oxyheterocyclic compounds, they cause the formation of zinc deposits of great brilliance and beauty.

Molybdenum is by far the most satisfactory of the brightening metals for use with oxyheterocyclic compounds, the deposits obtainable by the use of such a combination being markedly superior to those obtainable with most other combinations disclosed herein.

The brightening metals, molybdenum, chromium, tungsten, and uranium found in group VI sub-group 1, may be added to a cyanide-zinc bath in the form of a molybdate, chromate, tungstate, or uranate of sodium or potassium, or other such compounds which are soluble in the bath. The metals of group VII sub-group 1, manganese and rhenium, similarly, should be added in the form of soluble compounds. Aluminum may be added as aluminum sulfate, and titanium may be added as titanyl sulfate.

The metals of group VIII series 4 of the periodic system have little effect upon the character of a zinc electrodeposit when used alone but, in common with the other brightening metals, they exercise a synergetic action with oxyheterocyclic compounds. The metals of group VIII series 4 are also advantageously employed by reason of their effect upon the metals of sub-group 1 of groups VI and VII. These metals may be added to the bath in the form of such alkali or cyanide-soluble compounds as potassium ferrocyanide, cobalt sulfate, nickel sulfate, cobalt oxide, and nickel oxide.

The combination of an oxyheterocyclic compound and a brightening metal is employed in a cyanide-zinc bath, numerous examples of which will be given hereinafter. While the cyanide-zinc baths shown herein are typical, it will be understood that the principles of my invention are applicable to any cyanide-zinc plating bath. To obtain the best results it is desirable that the cyanide-zinc plating bath be as pure as possible, and it is particularly important that lead compounds be absent.

Zinc deposits are ordinarily examined visually and described loosely as "rough," "treed," "smooth," or "bright." These inexact designations are differently used by different observers, and it is virtually impossible to compare zinc deposits obtained at different times or made by different individuals.

So that electrodeposited zinc coatings could be more accurately described, an instrument was designed to measure the amount of light reflected by the coatings. This "reflectometer," shown in the drawing, is similar to instruments heretofore used for the study of enameled surfaces, paint films, and the like.

In the drawing, 1 designates a box having a cover 2 and divided by a central partition 7. In one side of the box there is provided a light source 3, a fifty candlepower automobile headlight bulb. To furnish current to the bulb, a storage battery is used, the current being regulated by the use of a rheostat so that about three volts are supplied to the lamp.

Below the bulb there is provided a concave mirror 4 which serves to intensify the light to some extent. This concave mirror is about three inches below the bulb.

Above the light bulb there is a black partition 5 provided with a one-half inch slit. The bulb is about three and one-half inches from the specimen being tested.

Light from the bulb 3 passes thru the slit 6 and is reflected by the specimen to the selenium photoelectric cell 9. The photoelectric cell is on a slight incline, being supported by the member 8. The cell is about five and one-half inches from the specimen.

The photoelectric cell is connected to a micro-ammeter 10 which shows directly the number of microamperes generated by the cell in response to the light reflected by the specimen.

The top 2 of the box 1 has a slit 11 therein thru which light can pass. A metal plate 12 is set over the hole, the plate having a one-quarter by three-quarter inch rectangular slit. On top of the box and covering the metal plate there is positioned a chamois skin 14 upon which specimen plates may be placed without danger of scratching. The chamois is provided with an opening registering with the slit 13.

Before starting to use the reflectometer, it was calibrated with a standard reflecting surface. A silver mirror was made by plating a polished copper sheet with silver and then buffing. The mirror was placed face down on the chamois over the slit. The current supplied to the bulb 3 was then adjusted until the micro-ammeter read 49.

In view of the fact that a silver mirror quickly loses its maximum brilliance, and in view of the difficulty of preparing new silver mirrors, a less changeable secondary standard was established. A silvered glass mirror was placed face down over the slit 13 and its position so marked that the same surface could be found when desired. The glass mirror gave a reading of 45 microamperes.

Each time that the reflectometer was used, it was recalibrated with the glass mirror. This is necessary because with the same applied current the bulb gives varying amounts of light depending upon its temperature and upon other variables. At frequent intervals a new polished silver mirror was prepared in accordance with the best practice and used to recheck the glass mirror so that when the silver mirror read 49 microamperes, a portion of the glass mirror reading 45 microamperes would be used as standard.

When no specimen is placed on top of the reflectometer, a reading of less than one microampere is obtained. This reading represents the error by reason of light leaking to the photoelectric cell.

In the following examples, unless otherwise stated, specimens were plated on polished copper sheets at current densities from five to one hundred and fifty amperes per square foot. Specimens plated at current densities of about seven, twenty-five, forty, and eighty amperes per square foot were placed on the reflectometer for brightness determinations.

So that the results would be comparable, the deposits were made on copper plates polished so that on the reflectometer, readings of 30 to 35 would be obtained over the whole surface. When plates differing as much as 5 microamperes were zinc plated under the same conditions and from the same bath, the zinc deposits differed by only about one microampere or less.

While most commercial zinc plating is not done on polished surfaces, the deposits obtained on polished copper sheets are nonetheless significant. A bath which produces a dull deposit on a polished surface will produce a dull and poor deposit on a matte surface, while a bath which produces a bright deposit on a polished surface will produce a correspondingly better deposit on a matte surface. The deposits obtained on polished sheets are therefore valuable in indicating which of a number of baths would lead to the brightest deposits when applied to ordinary commercial work.

In the following examples, unless otherwise stated, a cyanide-zinc bath of the following composition was used:

	Grams per liter
Zinc cyanide ($Zn(CN)_2$)	60
Sodium hydroxide (NaOH)	78
Sodium cyanide (NaCN)	42

At the time the bath was made up, two and five-tenths grams per liter of zinc dust was added together with the bath constituents. The zinc dust effected a removal of deleterious impurities from the bath.

In the following examples the effect of a bright-dip was observed by subjecting the deposits to the action of a one-fourth per cent solution of nitric acid for about fifteen seconds.

Example 1

The oxyheterocyclic compound piperonal is a colorless crystalline material sparingly soluble in water and in cyanide-zinc plating baths. The compound is also known as heliotropin and as 3,4-methylenedioxybenzaldehyde, and it is characterized by an intense heliotrope-like odor.

A cyanide-zinc plating bath was made up according to the above standard method, and there was added thereto:

	Grams per liter
Molybdenum trioxide (MoO_3)	8.0
Piperonal	3.5

Zinc was deposited on a number of polished copper sheets, and its brightness determined on the reflectometer according to the above discussed methods. The results at the current densities indicated were as follows:

Current density (amps. per sq. ft.)	7	25	40	80
Not bright-dipped	33	38	38	30
Bright-dipped	37	38	40	36

The deposits were extremely brilliant and they

reflected images with mirror-like fidelity when visually observed. While the reflectometer shows a considerable difference between bright-dipped and unbright-dipped plates, it is noted that when zinc plated sheets were bright-dipped for about one-half of their area, very little difference could be observed visually. In some instances it was possible to discern a line where the bright-dipped and unbright-dipped portions met, but on several deposits no such line could be distinguished.

A plate, part of which had been bright-dipped, was subjected to a corrosive atmosphere which ordinarily tarnishes unbright-dipped platings in a few hours, and after six days the upbright-dipped portion appeared as bright as the portion which had been bright-dipped.

A large number of commercial steel articles of various kinds were plated in various types of installations. All of the zinc deposits were of excellent character and uniformity, and bright-dipping the articles did not visually appear in any way to improve the appearance or tarnish-resistance of the deposits.

The cyanide-zinc plating bath of this example displayed excellent throwing power and a wide bright current density range which extended as high as tests were made, one hundred and fifty amperes per square foot.

Piperonal may be used in widely varying concentrations tho it is preferably used at about the limit of its solubility in the bath. Much smaller amounts may be employed with good results. At one gram per liter, for instance, the results were not substantially different from those obtained with the bath given above.

The piperonal does not deteriorate in the bath as do certain oxyheterocyclic addition agents mentioned hereinafter. It is interesting to note that the presence of piperonal in a bath such as the one of this example seems to increase slightly the content of molybdenum in the deposit.

For purposes of comparison, an electroplating bath of the prior art was examined according to the methods given herein. The bath selected is a very excellent one described in the second edition of Blum and Hogaboom's "Principles of Electroplating" on page 331, formula No. 1. This bath was made up as follows:

	Grams per liter
Zinc cyanide ($Zn(CN)_2$)	60
Sodium cyanide (NaCN)	23
Sodium hydroxide (NaOH)	53

A number of specimen plates were made according to the above described procedure and the brilliance determined on the reflectometer with the following results:

Current density (amps. per sq. ft.)	7	25	40	80
Not bright-dipped	12	15	4	9
Bright-dipped	29	29	18	27

It will be observed that without a bright-dipping treatment the plate obtained was exceedingly dull. The use of a bright-dip effected a very great improvement in the deposit, tho even after bright-dipping the deposit was not as bright as those obtained according to this example even without a bright-dipping treatment.

The cyanide-zinc plating bath used as standard in this application was made up without the use of addition agents, and a number of deposits made therewith. The following brightness readings were obtained:

Current density (amps. per sq. ft.)	7	25	40	80
Not bright-dipped	15	15	4	7
Bright-dipped	30	30	19	17

A cyanide-zinc plating bath was made up using 3.5 grams per liter of piperonal but omitting molybdenum. Zinc electro-deposits obtained from this bath gave the following brilliance readings:

Current density (amps. per sq. ft.)	7	25	40	80
Not bright-dipped	25	11	8	10
Bright-dipped	36	29	27	26

It will be observed that piperonal alone effects some improvement in the deposits, tho the deposits, before bright-dipping particularly, are still rather dull.

A cyanide-zinc plating bath was made up with eight grams per liter of molybdenum trioxide but omitting the piperonal. The following brilliance readings were obtained on deposits produced in this bath:

Current density (amps. per sq. ft.)	7	25	40	80
Not bright-dipped	15	22	30	30
Bright-dipped	28	30	33	30

From the above it will be apparent that the use of a combination of piperonal and molybdenum results in zinc deposits of much greater brightness and uniformity than would be expected. I believe that there is a synergetic action between the organic addition agent and the metal brightener, each being influenced by the other, and both cooperating to produce deposits of unexpected character.

Example 2

A cyanide-zinc plating bath was made up using piperonal with another brightening metal. To the standard cyanide-zinc bath above given, there was added:

	Grams per liter
Chromium sulfate ($Cr_2(SO_4)_3 \cdot 15H_2O$)	4.0
Piperonal	3.5

A number of zinc deposits were produced using this bath, and the following reflectometer readings obtained:

Current density	7	25	40	80
Not bright-dipped	34	34	32	30
Bright-dipped	38	34	31	30

The deposits obtained had a very excellent and brilliant appearance, and to the eye they appeared even brighter than the deposits obtained in Example 1.

Unfortunately, the chromium slowly precipitates from the solution, and for this reason is not as desirable a metal brightener as molybdenum. The metal content of the bath can, of course, be maintained by adding chromium sulfate to replace the chromium which leaves the solution.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	19	19	24	23
Bright-dipped	24	24	25	20

Example 3

A cyanide-zinc bath employing two metal brighteners in addition to an oxyheterocyclic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45.
Sodium hydroxide (NaOH)	38.
Sodium cyanide (NaCN)	100.
Molybdenum trioxide (MoO_3)	3.
Manganese-cyanide	2.5
Piperonal	3.5

The bath was made up with very pure zinc oxide, sodium hydroxide, and sodium cyanide, and electrolytic zinc anodes were employed to avoid the introduction of deleterious impurities into the bath.

The manganese was added to the bath in the form of a manganese-cyanide complex which was prepared by precipitating it from a water solution of manganese sulfate by the addition of a water solution of sodium cyanide. The amount of manganese-cyanide used is equivalent to about twenty-five hundredths of a gram per liter of manganese. The molybdenum trioxide used corresponds to about two grams per liter of molybdenum.

Excellent results were obtained using this bath. The zinc deposits were very bright, particularly after bright-dipping. The reflectometer readings taken on specimens made at the indicated current densities were as follows:

Current density	7	25	40	80
Not bright-dipped	35	36	36	32
Bright-dipped	40	41	39	33

Example 4

A cyanide-zinc plating bath employing a combination of metals of Group VI sub-group 1, Group VII sub-group 1, and Group VII series 4 was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Manganese-cyanide	10
Potassium ferrocyanide ($K_4Fe(CN)_6.3H_2O$)	5
Molybdenum trioxide (MoO_3)	4
Piperonal	3

Zinc deposits made from the bath of this example were of about the same appearance regardless of current density. Irregularly shaped objects, accordingly, were given a coating of very uniform appearance by the use of this bath. The reflectometer readings were as follows:

Current density	7	25	40	80
Not bright-dipped	33	35	35	35
Bright-dipped	38	38	38	38

Example 5

A cyanide-zinc bath employing a metal of Group VIII series 4 as well as an oxyheterocyclic compound was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4.7H_2O$)	8.
Piperonal	3.5

At current densities up to about forty amperes per square foot very good results were obtained using this bath. The reflectometer readings at the current densities indicated were:

Current density	7	25	40	80
Not bright-dipped	34	32	7	12
Bright-dipped	39	37	15	24

The cobalt sulfate used corresponds to about one and twenty eight hundredths of a gram per liter of cobalt. Very similar results were obtained using sixty four hundredths of a gram per liter of cobalt, or about four grams per liter of cobalt sulfate.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflector readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	10	23	23	7
Bright-dipped	24	33	34	23

Example 6

A cyanide-zinc bath employing a metallic brightening agent from Group VII sub-group 1 in conjunction with an oxyheterocyclic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45.
Sodium hydroxide (NaOH)	38.
Sodium cyanide (NaCN)	100.
Manganese sulfate ($MnSO_4.4H_2O$)	1.
Piperonal	3.5

The manganese sulfate corresponds to about twenty-five hundredths of a gram per liter of manganese. Both the piperonal and the manganese sulfate were used in about the maximum amount soluble in the bath. More manganese sulfate was added to the bath in various tests without appreciably different results being obtained. Excellent results were obtained using the bath of this example, and the following reflectometer readings were noted:

Current density	7	25	40	80
Not bright-dipped	29	30	10	2
Bright-dipped	40	34	18	6

It is noted that the deposits were somewhat cloudy before bright-dipping, therefore causing the reflectometer readings to be rather unexpectedly low. After bright-dipping, however, the deposits were quite brilliant and of very good character.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	16	13	3	2
Bright-dipped	31	27	5	2

Example 7

A cyanide-zinc bath using another metal of Group VIII series 4 in conjunction with piperonal was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4.7H_2O$)	0.5
Piperonal	3.5

Using this bath, some deposits of pleasing appearance where obtained. The deposits were somewhat white in color and probably for this reason the reflectometer readings were not as high as one would expect from visual examination. The reflectometer readings were as follows:

Current density	7	25	40	80
Not bright-dipped	30	29	30	12
Bright-dipped	31	28	27	12

Bright-dipping the plates was not very successful because the bright-dip treatment caused the deposit to become dark and streaked.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	31	10	24	23
Bright-dipped	29	16	22	24

Example 8

A cyanide-zinc bath was made up with:

	Grams per liter
Potassium ferrocyanide ($K_4Fe(CN)_6 3H_2O$)	12.
Piperonal	3.5

Zinc deposits obtained using this bath had a brownish film. Reflectometer readings were obtained as follows:

Current density	7	25	40	80
Not bright-dipped	23	14	14	14
Bright-dipped	37	35	35	35

It will be observed that bright-dipping the plates removed the film and led to the production of very satisfactory deposits.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	13	12	9	9
Bright-dipped	23	27	26	27

Example 9

A cyanide-zinc plating bath was made up with:

	Grams per liter
Titanyl sulfate ($TiOSO_4$)	0.5
Piperonal	3.5

Employing this bath, specimens were obtained with the following reflectometer readings:

Current density	7	25	40	80
Not bright-dipped	27	24	13	7
Bright-dipped	34	32	28	30

These deposits were dull by reason of a film thereon which bright-dipping removed.

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	16	14	11	13
Bright-dipped	33	29	25	27

Example 10

A cyanide-zinc plating bath was made up with:

	Grams per liter
Potassium perrhenate ($KReO_4$)	0.1
Piperonal	3.5

Deposits produced at the indicated current densities gave the following reflectometer readings:

Current density	7	25	40	80
Not bright-dipped	22	21	27	24
Bright-dipped	32	29	35	36

To observe the effect of the metal brightener apart from the organic addition, a bath was made up as above but omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	24	24	22	5
Bright-dipped	30	23	27	14

Example 11

A cyanide-zinc plating bath was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45.
Sodium hydroxide (NaOH)	38.
Sodium cyanide (NaCN)	100.
Tungsten trioxide (WO_3)	8.
Piperonal	3.5

The tungsten trioxide used corresponds to about six and four-tenths grams per liter of tungsten. Specimen plates were made up at the below indicated current densities with the following results:

Current density	7	25	40	80
Not bright-dipped	32	33	13	4
Bright-dipped	38	36	17	8

To observe the effect of the mtal brightener apart from the organic addition, a bath was made up as above omitting the piperonal. The reflectometer readings on plates made with this bath were:

Current density	7	25	40	80
Not bright-dipped	12	23	8	1
Bright-dipped	31	28	9	1

Example 12

Another oxyheterocyclic compound which may advantageously be employed is piperonylic acid. This compound, also known as methylene protocatechuic acid, may be regarded as a derivative of piperonal. Like piperonal, piperonylic acid is characterized by the presence of the methylenedioxyphenyl group. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdic acid	8
Piperonylic acid	4

The piperonylic acid went into solution rather readily. A number of polished copper sheets were zinc plated using this bath, and the following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	17	36	36	29
Bright-dipped	33	40	37	30

A cyanide-zinc plating bath was also made up as above using piperonylic acid but omitting the molybdic acid. When not using the metal brightener, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	18	17	16	11
Bright-dipped	30	33	30	21

Example 13

A cyanide-zinc plating bath was made up with:

	Grams per liter
Aluminum sulfate ($Al_2(SO_4)_3$)	12
Piperonylic acid	5

The deposits obtained using this bath were of very good character tho the reflectometer readings were somewhat low before bright-dipping.

The deposits obtained at the indicated current densities gave the following results.

Current density	7	25	40	80
Not bright-dipped	24	21	23	23
Bright-dipped	41	35	34	32

A cyanide-zinc plating bath was made up as above but omitting the organic addition agent piperonylic acid. With aluminum thus used as a metal brightener, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	6	6	3	2
Bright-dipped	14	16	11	7

Example 14

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr_2(SO_4)_3 \cdot 15H_2O$)	4
Piperonylic acid	4

Employing this bath, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	36	33	26	24
Bright-dipped	36	32	28	26

Example 15

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Piperonylic acid	4

Zinc deposits obtained from this bath gave the following results:

Current density	7	25	40	80
Not bright-dipped	22	33	29	14
Bright-dipped	34	37	37	21

Example 16

Another oxyheterocyclic compound closely allied to piperonal is piperine. This compound is characterized by the presence of the methylenedioxyphenyl group. Piperine is only slightly soluble in water, and in the following examples it was added to the cyanide-zinc baths in alcohol solution. A bath employing this oxyheterocyclic compound together with my preferred metal brightener was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Piperine	1

It is observed that even less than the one gram per liter of the piperine seemed to be dissolved in the solution. After one plate was made using this bath, a white flocculent precipitate appeared. Zinc deposits made on polished copper sheets and using the bath of this example gave the following reflectometer readings at the indicated current densities.

Current density	7	25	40	80
Not bright-dipped	17	22	27	24
Bright-dipped	32	32	30	26

A bath similar to that of this example was made up using piperine but omitting molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	17	7	7	6
Bright-dipped	32	21	21	18

Example 17

A cyanide-zinc bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Piperine	1

Using this bath, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	30	27	28	28
Bright-dipped	37	32	31	28

Example 18

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel ammonium sulfate ($NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$)	1
Piperine	1

Plates made using this bath were quite satisfactory without bright-dipping and, as is usual with deposits made employing nickel, bright-dipping was not advantageous. The reflectometer readings at the current densities indicated were as follows:

Current density	7	25	40	80
Not bright-dipped	35	36	34	23
Bright-dipped	35	33	28	15

Example 19

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Piperine	1

Employing this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	17	27	25	17
Bright-dipped	28	35	31	23

Example 20

Safrole, the oxyheterocyclic compound from which piperonal is commercially derived, is also characterized by the presence of a methylenedioxyphenyl group. Safrole is quite insoluble in water, and even adding it to the bath in alcohol solution does not greatly increase the amount of safrole which can be dissolved. Despite the almost negligible solubility of this compound, baths employing it show a very considerable improvement. Employing this oxyheterocyclic compound and applicant's preferred metal brightener, a cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Safrole	1

Deposits of good appearance were obtained using this bath. The reflectometer readings were as follows at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	13	25	28	27
Bright-dipped	27	34	35	34

A bath was also made up using safrole but omitting the molybdenum. With this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	12	10	9	8
Bright-dipped	30	29	28	28

Example 21

A cyanide-zinc bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Safrole	1

Employing this bath, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	21	23	23	22
Bright-dipped	28	29	29	32

Example 22

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Safrole	1

The following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	15	23	27	20
Bright-dipped	26	31	31	31

Example 23

Another oxyheterocyclic compound characterized by the presence of the methylenedioxyphenyl group is piperonyl alcohol. This compound was employed together with a metal brightener in a cyanide-zinc plating bath made up including:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Piperonyl alcohol	5

Good results were obtained using this bath and at a current density of about forty amperes per square foot reflectometer readings of thirty one were obtained on unbright-dipped plates, and of thirty five on bright-dipped plates.

A bath was also made up employing piperonyl alcohol but omitting the molybdenum. This bath was improved slightly by the use of the piperonyl alcohol, the following reflectometer readings being obtained:

Current density	7	25	40	80
Not bright-dipped	13	14	10	11
Bright-dipped	27	30	30	30

Example 24

Another oxyheterocyclic compound related to piperonal and characterized by the presence of the methylenedioxyphenyl group is piperonal acetophenone. This compound was employed in conjunction with a metal brightener in a bath made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Piperonal acetophenone	1

The piperonal acetophenone was quite insoluble, tho the small amount which dissolved effected considerable improvement. Employing this bath the following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	29	34	28
Bright-dipped	33	36	35	31

A similar cyanide-zinc bath was made up employing piperonal acetophenone but omitting molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	15	23	25	21
Bright-dipped	28	30	33	33

Example 25

As a further example of suitable oxyheterocyclic compounds, the use of coumarin will be described. Coumarin is an oxyheterocyclic compound also known as 1,2-benzopyrone, or as o-hydroxy-cinnamic lactone. Employing coumarin, a cyanide-zinc bath was made up as follows:

	Grams per liter
Zinc cyanide ($Zn(CN)_2$)	60.
Sodium hydroxide (NaOH)	80.
Sodium cyanide (NaCN)	40.
Molybdenum trioxide (MoO_3)	8.4
Coumarin	3.

At the time of mixing the bath, 2.4 grams per liter of zinc dust was used to remove deleterious impurities. The bath had a faint pleasant odor.

Using this bath to plate a number of polished copper sheets and a number of stamped steel articles, excellent results were obtained. The zinc deposits on the polished copper sheets were brilliant and lustrous, and reproduced reflected images with mirror-like fidelity. Reflectometer readings were obtained on specimen plates made at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	30	32	35	26
Bright-dipped	32	35	34	35

When the bath of this example was used to plate work of commercial character, zinc deposits of excellent appearance were obtained. Bright-dipping the plated articles effected no discernible change in the appearance of the deposits.

Using the bath of this example, deeply recessed articles were coated with a zinc deposit of uniform appearance. Brilliant deposits were obtained from current densities of from about three to about one hundred and fifty amperes per square foot. The bath was operated for several days and, unlike some of the baths hereinafter described, it appeared to be quite stable.

The coumarin may be used in varying amounts in the bath, of course, the amounts used in this example being about optimum. This concentration is about the upper limit of the solubility of coumarin in the bath used. Smaller amounts of coumarin may advantageously be employed and results which were not greatly different were obtained when one gram per liter of coumarin was used in a bath of the same composition. Even smaller amounts of coumarin exercise a beneficial effect, tho in general it is preferable to use about one gram per liter or more.

A bath was made up as above using coumarin but omitting the molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	14	14	11	11
Bright-dipped	30	30	24	23

Example 26

A cyanide-zinc bath employing two metal brighteners in addition to the oxyheterocylic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45.
Sodium hydroxide (NaOH)	38.
Sodium cyanide (NaCN)	100.
Molybdenum trioxide (MoO_3)	3.
Manganese-cyanide	2.5
Coumarin	3.

The bath was made up with very pure zinc oxide, sodium hydroxide, and sodium cyanide, and elec-

trolytic zinc anodes were employed to avoid the introduction of deleterious impurities into the bath. The manganese was added to the bath in the form of a manganese-cyanide complex which was precipitated from a water solution of manganese sulfate by adding thereto a water solution of sodium cyanide. The amount of manganese-cyanide used is equivalent to about twenty-five hundredths of a gram per liter of manganese. The molybdenum trioxide used corresponds to about two grams per liter of molybdenum.

Using this bath on polished copper sheets and on metal stampings, brilliant, lustrous deposits comparable to those obtained above were produced. At a current density of about twenty-five amperes per square foot, an unbright-dipped deposit gave a reflectometer reading of thirty-three, and a bright-dipped deposit gave a reading of thirty-seven.

Example 27

A cyanide-zinc bath containing a metallic brightening agent from group VII sub-group 1 as well as an oxyheterocylic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	80
Manganese sulfate ($MnSO_4.4H_2O$)	1
Coumarin	3

A number of deposits were made using this bath and it was found that the bath has a more restricted bright range than does the bath of the preceding example. At a current density of about twenty-five amperes per square foot, an unbright-dipped plate had a reflectometer reading of twenty-one and a bright-dipped plate a reading of thirty-four. Manganese sulfate was also used to the amount of fifteen grams per liter in a bath such as that of this example without greatly different results being obtained.

Example 28

A cyanide-zinc plating bath similar to those of the above examples but containing a metal brightener of group VI sub-group 1 was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Tungsten trioxide (WO_3)	5
Coumarin	3

The tungsten trioxide corresponds to about four grams per liter of tungsten. Polished plates and commercial articles were given a zinc electrodeposit using this bath with excellent results. On a polished copper plate at a current density of twenty-five amperes per square foot, an unbright-dipped deposit gave a reflectometer reading of seventeen, and a bright-dipped deposit a reading of thirty-two.

Example 29

A cyanide-zinc bath using a metal brightener from group VIII series 4 together with an oxyheterocyclic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	110
Cobalt sulfate ($CoSO_4.7H_2O$)	12
Coumarin	3

The cobalt sulfate used corresponds to about two and fifty-two hundredths of a gram of cobalt per liter. This bath had a rather restricted bright range, the deposit being brightest at current densities from about thirty to about sixty amperes per square foot. At about forty amperes per square foot, an unbright-dipped plate gave a reflectometer reading of about twenty-five, and a bright-dipped plate gave a reading of thirty-four. A cyanide-zinc plating bath was made up as above but using three grams per liter of cobalt sulfate. Very similar results were obtained using this bath, tho they were not quite as good as the results obtained with the bath above given.

Example 30

A cyanide-zinc bath employing brightening metals of group VI sub-group, group VII sub-group 1, and group VIII series 4, as well as an oxyheterocyclic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hyroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Manganese-cyanide	10
Potassium ferrocyanide ($K_4Fe(CN)_6.3H_2O$)	5
Molybdenum trioxide (MoO_3)	4
Coumarin	3

The molybdenum trioxide used corresponds to about two and seven tenths grams per liter of molybdenum, the potassium ferrocyanide corresponds to about sixty-six hundredths of a gram per liter of iron, and the manganese-cyanide, a complex prepared as in Example 26, corresponds to about one gram per liter of manganese. It is observed that the iron compound exercises a solubilizing effect on the manganese compound. At a current density of about seven amperes per square foot an unbright-dipped deposit gave a reflectometer reading of thirty-two, and a bright-dipped deposit at the same current density gave a reading of thirty-seven.

Example 31

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3.15H_2O$)	4
Coumarin	3

It is noted that the chromium sulfate did not entirely dissolve in the bath. Using this bath for zinc plating a number of polished copper sheets, the following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	24	22	20	16
Bright-dipped	32	27	23	23

Example 32

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4.7H_2O$)	0.5
Coumarin	3.

Employing the bath of this example the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	19	20	32	31
Bright-dipped	19	25	30	28

It will be noted that, as is usual with baths containing nickel as a brightener, the action of a bright-dip was quite erratic. At a current den-

sity of seven amperes per square foot the bright-dip had no appreciable effect on the reflectometer reading. At twenty five amperes per square foot there was an improvement. At forty amperes per square foot the bright-dip injured the plate, and at eighty amperes per square foot the bright-dip was even more injurious.

Example 33

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furfural	6

It is observed that the molybdenum trioxide used corresponds to about five and four-tenths grams per liter of molybdenum. Using this bath immediately after it was made up, a number of polished copper plates were given a coating of zinc at current densities from about three to about one hundred and fifty amperes per square foot. Over this wide range of current densities the zinc deposits were brilliant and lustrous, reflecting images with mirror-like fidelity when observed visually. Deposits made on copper sheets were bright-dipped over a portion of their area, and when these partially dipped plates were visually observed it was barely possible to discern a line of demarcation between the bright-dipped and the unbright-dipped portions. The following reflectometer readings were obtained with deposits made at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	20	34	33	33
Bright-dipped	28	36	36	35

The bath of this example was also used shortly after it was prepared to plate a number of steel stampings. The deposits obtained directly from the bath were excellent in appearance and, apparently, were in every respect equal to deposits obtained after bright-dipping.

While the use of furfural in conjunction with molybdenum leads to exceptionally good results when the bath is fresh, after a short time the bath deteriorates becoming less and less satisfactory. Not only does the effectiveness of the furfural seem to diminish, but some action appears to occur which results in a poisoning of the solution. The addition of more furfural does not revivify the bath. Furfural, then, can only be used to produce very brilliant deposits for a relatively short time.

If, after a bath such as that shown in this example becomes poor, it is desired to improve its characteristics, this may be done by allowing the bath to pass slowly thru a column of zinc turnings, after which an amount of furfural equivalent to that originally used may be added. By repeated revivification and addition of furfural, the bath may be made to operate continuously, but this is a relatively troublesome and expensive procedure and would not ordinarily be resorted to unless some particular circumstances offer justification.

It is to be observed that while furfural is used at about an optimum concentration in this example, the amount employed may be widely varied. It is generally desirable to use from about two grams per liter to about five grams per liter of furfural in baths of the type of this example.

A bath was made up using furfural as above, but omitting the molybdenum. With this bath the following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	22	25	31	31
Bright-dipped	34	32	33	30

Example 34

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4.7H_2O$)	0.5
Furfural	6.

Good deposits were obtained using this bath, but a bright-dip should not be used on this type of deposit because of the fact that nickel was used as the metal brightener. The following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	32	32	31	29
Bright-dipped	20	24	23	17

Example 35

Another oxyheterocyclic compound which may be used with metallic brighteners according to my invention is furfuran. This oxyheterocyclic compound may be considered a furfural derivative which contains the characteristic oxyheterocyclic ring of four carbon atoms and one oxygen atom.

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furfuran	5

Excellent zinc deposits were obtained using this bath. The following reflectometer readings were taken at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	28	29	26
Bright-dipped	25	32	35	30

This bath was operated for several days and, unlike the results obtained with the bath of Example 33, there was no apparent deterioration. Furfuran, however, is quite volatile, and the loss by evaporation should be replaced if the bath is to be operated continuously.

A similar bath was made up employing furfuran but omitting molybdenum. The following reflectometer readings were obtained on deposits made at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	11	16	21	23
Bright-dipped	23	28	34	33

Example 36

A cyanide-zinc bath containing a metallic brightening agent from group VII sub-group 1 as well as an oxyheterocyclic compound was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	80
Manganese sulfate ($MnSO_4 \cdot 4H_2O$)	15
Furfuran	7

The manganese sulfate employed corresponds to about three and seven-tenths grams per liter of manganese. Zinc deposits were made on polished copper sheets, and at a current density of about seven amperes per square foot an unbright-dipped deposit gave a reflectometer

reading of twenty four, and a bright-dipped deposit gave a reading of thirty three.

Example 37

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Furfuran	5

Employing this bath, deposits with the following characteristics were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	9	24	24	16
Bright-dipped	22	35	33	32

Example 38

A cyanide-zinc plating bath was made up with:

	Grams per liter
Potassium perrhenate ($KReO_4$)	0.1
Furfuran	5.

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	23	30	23	17
Bright-dipped	26	34	37	27

Example 39

Another oxyheterocyclic compound which may be used as an addition agent according to my invention is pyronine. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Pyronine	5

This bath was employed to zinc plate a number of polished copper sheets and a number of commercial steel articles. The zinc deposit on the polished copper sheets was brilliant and lustrous, and reflected images with a mirror-like fidelity when visually observed. Zinc deposits made at the indicated current densities gave the following reflectometer readings:

Current density	7	25	40	80
Not bright-dipped	16	29	27	25
Bright-dipped	30	35	32	32

The pyronine caused the bath to become deep red in color, and during electrolysis of the bath there was some foaming presumably caused by the pyronine. Pyronine was also used in a bath of similar composition at a concentration of two grams per liter with excellent results.

A bath similar to that above described was made employing five grams per liter of pyronine but omitting the molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	13	12	12	13
Bright-dipped	26	29	29	27

Example 40

A cyanide-zinc plating bath similar to that of the preceding example but containing as a metal brightener a compound of group VI sub-group 1 was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	100
Tungsten trioxide (WO_3)	5
Pyronine	2

The tungsten trioxide corresponds to about four grams per liter of tungsten. The deposits obtained employing this bath were not quite as good as those of the preceding example, largely, I believe, by reason of the smaller efficacy of tungsten as a brightener. At a current density of about seven amperes per square foot, an unbright-dipped deposit gave a reflectometer reading of about sixteen, and a bright-dipped deposit made at the same current density gave a reading of about thirty one.

Example 41

A cyanide-zinc bath using a metal of group VI sub-group 1 and a metal of group VIII series 4 as well as an oxyheterocyclic compound, was made up as follows:

	Grams per liter
Zinc oxide (ZnO)	45
Sodium hydroxide (NaOH)	38
Sodium cyanide (NaCN)	110
Molybdenum trioxide (MoO_3)	2
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	1
Pyronine	2

The molybdenum trioxide corresponds to about one and three-tenths grams per liter of molybdenum and the cobalt sulfate corresponds to about twenty-one hundredths of a gram per liter of cobalt. Zinc deposits made employing this bath were of good character. Deposits made at a current density of about twenty-five amperes per square foot gave a reflectometer reading without bright-dipping of about twenty-four, and bright-dipped, a reading of thirty-three.

Example 42

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Pyronine	5

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	11	21	21	10
Bright-dipped	26	33	30	26

Example 43

Another furfural derivative characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom, furfuryl alcohol, was used in conjunction with a metal of group VI sub-group 1 in a cyanide-zinc plating bath made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furfuryl alcohol	5

The bath was deep red in color. A number of polished copper sheets and a number of commercial steel articles were plated employing this bath. Deposits made on polished copper sheets gave the following results at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	15	28	27	2
Bright-dipped	25	33	32	2

The bath of this example was studied over a considerable period of time and, unlike baths containing furfural, the bath of this example appeared to be quite stable.

A bath similar to that of this example was made up employing furfuryl alcohol but omitting the molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	16	3	1	1
Bright-dipped	31	9	3	2

Example 44

A cyanide-zinc plating bath was made up with:

	Grams per liter
Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$)	12
Furfuryl alcohol	5

A number of zinc deposits made at the below-indicated current densities gave the following results:

Current density	7	25	40	80
Not bright-dipped	14	15	20	21
Bright-dipped	25	26	28	30

It is to be observed that deposits employing iron as a metal brightener tend to have a superficial colored film. While the plates sometimes appear quite bright when visually observed, the reflectometer readings of the unbright-dipped plates are much lower than would be expected.

Example 45

A cyanide-zinc plating bath was made up with:

	Grams per liter
Titanyl sulfate ($TiOSO_4$)	0.5
Furfuryl alcohol	5.0

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	11	13	17	20
Bright-dipped	23	26	31	32

Example 46

A cyanide-zinc bath employing still another oxyheterocyclic compound which is a furfural derivative characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom, tetrahydrofurfuryl alcohol, was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Tetrahydrofurfuryl alcohol	8

At a current density of about twenty-five amperes per square foot, quite bright deposits were obtained. At this current density, unbright-dipped deposits gave a reflectometer reading of about thirty, and bright-dipped deposits thirty-eight.

A cyanide-zinc bath was made up using eight grams per liter of tetrahydrofurfuryl alcohol but omitting molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	13	19	11	8
Bright-dipped	28	29	34	26

Example 47

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Tetrahydrofurfuryl alcohol	7

Employing this bath, very good deposits were obtained when compared with other deposits resulting from the use of chromium as a brightener. Deposits made on polished copper plates gave the following results at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	24	23	24	25
Bright-dipped	30	28	27	27

Example 48

A cyanide-zinc plating bath was made up as follows:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Tetrahydrofurfuryl alcohol	7

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	11	20	29	30
Bright-dipped	21	31	35	36

Example 49

Furoin is another example of an oxyheterocyclic compound which may be considered as a furfural derivative and which is characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furoin	5

A number of zinc deposits were made employing the bath of this example and, at the indicated current densities, the following results were obtained on polished copper sheets:

Current density	7	25	40	80
Not bright-dipped	17	27	28	26
Bright-dipped	26	33	32	32

The furoin colored the bath a deep red. It is also to be noted that after the bath was several days old it did not give as good results. Apparently furoin deteriorates in the bath, tho not nearly so quickly as does furfural.

A bath was made up employing five grams per liter of furoin as above but omitting molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	16	16	1	1
Bright-dipped	32	32	3	1

Example 50

A cyanide-zinc plating bath was made up with:

	Grams per liter
Manganese sulfate ($MnSO_4 \cdot 4H_2O$)	1
Furoin	5

This bath displayed a quite bright range at relatively low current densities. Zinc deposits obtained using this bath gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	19	31	21	2
Bright-dipped	27	35	30	2

Example 51

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Furoin	5

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	13	19	18	22
Bright-dipped	26	27	25	25

Example 52

A cyanide-zinc plating bath was made up with:

	Grams per liter
Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$)	12
Furoin	5

Deposits made from the bath of this example were much influenced by bright-dipping as is customary with deposits obtained from baths containing iron as a brightener. The following results were obtained with deposits made at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	15	24	24
Bright-dipped	32	27	33	30

Example 53

A cyanide-zinc plating bath was made up with:

	Grams per liter
Titanyl sulfate ($TiOSO_4$)	1
Furoin	5

The following results were obtained using this bath:

Current density	7	25	40	80
Not bright-dipped	13	16	26	22
Bright-dipped	30	27	35	29

Example 54

Hydrofurfuramide is still another oxyheterocyclic compound which may be considered as a furfural derivative, and it is characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom. Employing this compound, a bath was made up with:

	Grams per liter
Molybednum trioxide (MoO_3)	8
Hydrofurfuramide	5

Using this bath to make specimen zinc deposits on polished copper sheets, the following results were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	25	27	21
Bright-dipped	27	36	34	29

The bath was colored a dark red by the hydrofurfuramide.

Similar baths were also made up employing various other amounts of hydrofurfuramide and at one gram per liter, for instance, deposits only slightly less brilliant were obtained.

A cyanide-zinc plating bath was also made up with five grams per liter of hydrofurfuramide omitting the molybdenum. With this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	16	8	1	1
Bright-dipped	32	19	4	2

Example 55

Furoic acid is another furfural derivative characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom. Employing this compound, a cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furoic acid	8

Deposits produced employing this bath were considerably poorer than the deposits obtained by the bath of the preceding example. The furoic acid, however, effected a considerable improvement in the character of the deposit. The baths of this example were studied for a considerable period of time and were found to be stable.

Example 56

A cyanide-zinc plating bath employing the oxyheterocyclic compound paraldol was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Paraldol	5

The paraldol was not as pure as that used in some of the subsequent examples and considerable difficulty was encountered in dissolving it. The paraldol was added in alcohol solution. Specimen plates made using this bath gave the following results:

Current density	7	25	40	80
Not bright-dipped	14	24	30	28
Bright-dipped	21	29	38	33

A bath similar to that given above was made up employing five grams per liter of paraldol but omitting molybdenum. Zinc deposits made on polished copper sheets at the indicated current densities gave the following results:

Current density	7	25	40	80
Not bright-dipped	6	17	24	23
Bright-dipped	16	30	37	36

Example 57

A cyanide-zinc bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	0.5
Paraldol	5.

The paraldol used in this example was much purer than that of Example 56, and it dissolved readily without the use of alcohol. Employing this bath, specimen zinc plates were made up and the following reflectometer readings obtained:

Current density	7	25	40	80
Not bright-dipped	33	32	21	42
Bright-dipped	34	30	21	36

As is usual with deposits made from baths containing nickel as an addition agent, the deposits obtained were not greatly benefited by the use of a bright-dip.

Example 58

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Paraldol	5

The paraldol used was the purer paraldol referred to in Example 57. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	23	21	28	29
Bright-dipped	30	30	33	33

Example 59

Ethyl furoate is an oxyheterocyclic compound which may be regarded as a derivative of furfural. Like furfural, it contains an oxyheterocyclic ring of four carbon atoms and one oxygen atom. Employing this compound a bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Ethyl furoate	3

The bath was colored red by the organic compound. Using the bath to plate a number of

zinc specimens, the following results were obtained at the indicated current densities:

Current density	40	80
Not bright-dipped	22	32
Bright-dipped	35	37

A cyanide-zinc plating bath was also made up with three grams per liter of ethyl furoate but omitting the metal brightener. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	10	13	9	9
Bright-dipped	23	31	28	28

Example 60

Methyl furoate is an oxyheterocyclic compound very similar to the one of the preceding example. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Methyl furoate	5

The inclusion of methyl furoate in the bath caused it to become dark brown in color, and it is probable that the methyl furoate reacted with some constituent in the bath to form a detrimental product. However, when the bath was freshly made up, fairly good deposits were obtained as below indicated:

Current density	7	25
Not bright-dipped	30	25
Bright-dipped	35	32

A similar bath was made up but omitting the molybdenum, the following results being obtained:

Current density	7	25	40	80
Not bright-dipped	13	12	10	9
Bright-dipped	31	29	25	23

Example 61

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4.7H_2O$)	0.5
Methyl furoate	5.

The methyl furoate was not entirely soluble in the bath, and some of the organic material remained undissolved. Surprisingly excellent results were obtained with the combination of this example. Specimen plates were made at the below indicated current densities:

Current density	7	25	40	80
Not bright-dipped	37	37	37	26
Bright-dipped	28	30	33	8

Example 62

A cyanide-zinc plating bath was made up with:

	Grams per liter
Aluminum sulfate ($Al_2(SO)_4)_3$)	12
Methyl furoate	5

This bath gave unexpectedly good results tho the methyl furoate did not behave as well as in the preceding example. Specimen deposits gave the following reflectometer reading at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	9	20	21	20
Bright-dipped	22	30	32	30

Example 63

Another oxyheterocyclic compound which may be considered a derivative of furfural is furfurylamine. This compound, like furfural, is characterized by the presence of an oxyheterocyclic ring made up with four carbon atoms and one oxygen atom. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furfurylamine	5

The furfurylamine seemed to react with some constituent of the bath, tho so far as could be determined this action was not detrimental. The bath, however, did not give as good results as might be expected. The following results were obtained:

Current density	25	40
Not bright-dipped	21	27
Bright-dipped	34	35

A cyanide-zinc bath was also made up as above with five grams per liter of furfurylamine but omitting the metal brightener. Specimens plated in this bath gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	10	11	10	8
Bright-dipped	23	25	28	27

Example 64

Furfuramide is another oxyheterocyclic compound characterized by the presence of an oxyheterocyclic group of four carbon atoms and one oxygen atom. This compound may also be considered a derivative of furfural. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Furfuramide	3

A number of specimen plates were made using this bath, and the following results obtained:

Current density	7	25	40	80
Not bright-dipped	19	28	29	24
Bright-dipped	29	34	35	29

The bath gave good deposits when it was first made, but upon standing it apparently deteriorated. The deterioration was not as rapid nor as complete as was the case with furfural, however.

A similar bath was made up employing furfuramide but omitting molybdenum. With this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	16	18	5	2
Bright-dipped	30	31	17	12

Example 65

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Furfuramide	3

It is observed that baths containing furfuramide are red in color. Zinc deposits were made on a number of polished copper sheets and the following reflectometer readings obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	20	18	23	26
Bright-dipped	33	29	29	25

Example 66

A cyanide-zinc plating bath was made up with:

	Grams per liter
Titanyl sulfate ($TiOSO_4$)	0.5
Furfuramide	3

Deposits of uniform appearance were obtained, but they were not unusually bright. At a current density of about forty amperes per square foot an unbright-dipped plate gave a reflectometer reading of twenty one, and a bright-dipped plate gave a reading of twenty seven.

Example 67

Tetrahydrofurfurylamine is another furfural derivative characterized by the presence of an oxyheterocyclic ring of four carbon atoms and one oxygen atom. A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Tetrahydrofurfurylamine	5

A precipitate formed upon standing, and it appears that the organic addition agent of this example is not entirely stable. Zinc deposits were made using this bath with the following results:

Current density	7	25	40	80
Not bright-dipped	14	18	24	18
Bright-dipped	26	29	33	33

A similar cyanide-zinc plating bath was made up with five grams per liter of tetrahydrofurfurylamine but omitting the molybdenum. A number of zinc deposits were made employing this bath and the following reflectometer readings were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	14	16	13
Bright-dipped	29	28	28	29

Example 68

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Dihydroxymethylxanthene	5

The oxyheterocyclic compound caused the bath to become red in color, and foaming was caused during electrolysis. Using this bath, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	13	17	27	31
Bright-dipped	24	28	35	35

A similar cyanide-zinc plating bath was made up employing the same amount of dihydroxymethylxanthene but omitting the molybdenum. A number of zinc deposits were made employing this bath with the following results:

Current density	7	25	40	80
Not bright-dipped	13	14	20	20
Bright-dipped	19	25	30	36

Example 69

A cyanide-zinc plating bath was made up with:

	Grams per liter
Chromium sulfate ($Cr(SO_4)_3 \cdot 15H_2O$)	4
Dihydroxymethylxanthene	5

A number of specimens were electrodeposited on polished copper sheets, and reflectometer readings obtained at the indicated current densities as follows:

Current density	7	25	40	80
Not bright-dipped	24	23	22	25
Bright-dipped	32	30	27	28

Example 70

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Dihydroxymethylxanthene	5

Zinc deposits made employing this bath gave the following results:

Current density	7	25	40	80
Not bright-dipped	12	27	18	22
Bright-dipped	31	35	26	29

Example 71

A cyanide-zinc plating bath was made up with:

	Grams per liter
Aluminum sulfate ($Al_2(SO_4)_3$)	12
Dihydroxymethylxanthene	5

Zinc specimens plated employing this bath gave the following results:

Current density	7	25	40	80
Not bright-dipped	15	17	19	21
Bright-dipped	30	27	31	35

Example 72

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Fluorescin	5

The bath of this example exhibited the fluorescence which would be expected, and there was a certain amount of foaming during electrolysis. Zinc deposits produced from this bath gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	25	27	23
Bright-dipped	28	34	36	31

A similar cyanide-zinc plating bath was made up employing five grams per liter of fluorescin but omitting the metal brightener. The following results were obtained:

Current density	7	25	40	80
Not bright-diped	18	9	10	7
Bright-dipped	30	28	26	18

Example 73

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel ammonium sulfate ($NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$)	1
Fluorescin	5

Zinc deposits produced using this bath gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	35	31	28	20
Bright-dipped	32	30	23	17

As is customary with baths employing nickel as an organic brightener, the deposits are of better character before bright-dipping than they are after bright-dipping.

Example 74

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Morpholine	5

Employing this bath, zinc deposits were made up and the following results obtained:

Current density	7	25	40	80
Not bright-dipped	10	19	27	29
Bright-dipped	24	31	34	31

A similar cyanide-zinc bath was made up using morpholine but omitting the molybdenum. With this bath the following reflectometer readings were obtained with zinc deposits made at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	10	11	15	13
Bright-dipped	26	28	30	28

Example 75

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Morpholine ethanol	5

Employing this bath, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	10	22	28	27
Bright-dipped	28	32	35	34

A similar cyanide-zinc plating bath was made up using morpholine ethanol but omitting the molybdenum with the following results:

Current density	7	25	40	80
Not bright-dipped	11	7	8	6
Bright-dipped	26	30	31	32

Example 76

A cyanide-zinc plating bath was made up using:

	Grams per liter
Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$)	12
Morpholine ethanol	5

As is usual with baths containing iron as a brightener, there is a slight film on the deposit which seems to prevent the reflectometer readings being as high as would be expected from a visual observation. Zinc specimens plated in the bath of this example gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	13	18	20	17
Bright-dipped	27	32	33	31

Example 77

A cyanide-zinc plating bath was made up with:

	Grams per liter
Aluminum sulfate ($Al_2(SO_4)_3$)	12
Morpholine ethanol	5

Using this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	15	20	22	20
Bright-dipped	26	31	34	33

Example 78

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Phenylmorpholine hydrochloride	0.5

It is observed that larger amounts of the phenylmorpholine hydrochloride were not soluble in the bath. Employing this bath, cyanide-zinc deposits were made and the following reflectometer readings obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	16	19	28	31
Bright-dipped	34	31	34	35

A similar cyanide-zinc plating bath was made up employing the organic addition agent but omitting the metal brightener. Zinc deposits obtained from this bath gave the following reflectometer readings at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	17	10	4	4
Bright-dipped	34	30	25	15

Example 79

A cyanide-zinc plating bath was made up with:

	Grams per liter
Cobalt sulfate ($CoSO_4 \cdot 7H_2O$)	8
Phenylmorpholine hydrochloride	0.5

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	19	29	28	26
Bright-dipped	29	33	37	35

Example 80

An oxyheterocyclic compound similar to that of the preceding example was used in a cyanide-zinc plating bath made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Butylmorpholine hydrochloride	5

Deposits made from this bath were examined using the reflectometer, and the following results were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	12	17	27	30
Bright-dipped	24	27	34	36

A similar cyanide-zinc plating bath was made up employing the organic addition agent but omitting the molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	11	7	2	2
Bright-dipped	31	26	21	13

Example 81

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Diphenylene oxide	0.5

The diphenylene oxide was very difficultly soluble, and it is probable that somewhat less than the one-half gram per liter used dissolved in the bath. Employing the bath of this example, zinc deposits were made and examined under the reflectometer with the following results:

Current density	7	25	40	80
Not bright-dipped	17	27	29	28
Bright-dipped	26	32	34	35

A similar cyanide-zinc plating bath was made up employing diphenylene oxide but omitting the molybdenum with the following results:

Current density	7	25	40	80
Not bright-dipped	15	13	9	9
Bright-dipped	30	28	26	27

Example 82

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Cyclohexene oxide	3

While three grams per liter of cyclohexene oxide were added, probably not more than one gram per liter was actually dissolved. The remainder formed an oily film on the surface of the bath. During electrolysis the film became dark brown in color. The following results were obtained when the bath was used to plate specimen zinc deposits on polished copper sheets:

Current density	7	25	40	80
Not bright-dipped	9	21	28	24
Bright-dipped	25	32	35	30

A similar bath was made up omitting molybdenum and the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	10	9	11	12
Bright-dipped	26	22	26	28

Example 83

A cyanide-zinc plating bath was made up including:

	Grams per liter
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	0.5
Cyclohexene oxide	3.

The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	21	28	20	24
Bright-dipped	30	29	20	30

Example 84

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Glycol formal	5

Zinc deposits made employing this bath gave the following readings using the reflectometer at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	10	23	31	30
Bright-dipped	25	33	35	34

A similar cyanide-zinc plating bath was made up using glycol formal but omitting molybdenum, and the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	12	7	7	13
Bright-dipped	32	27	27	25

Example 85

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	0.5
Glycol formal	5.

It seems doubtful that the glycol formal would remain in the bath as such, it being probable that the compound polymerizes. At a current density of about seven amperes per square foot an unbright-dipped zinc deposit gave a reflectometer reading of thirty, and a bright-dipped deposit a reading of twenty three.

Example 86

Coumalic acid, an oxyheterocyclic compound also known as 2-keto-1,2-pyran-5-carboxylic acid was included in a cyanide-zinc plating bath made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Coumalic acid	3

It is observed that coumalic acid is probably not stable in the bath as it hydrolyzes very readily. Zinc deposits made using this bath gave the following results at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	12	25	30	27
Bright-dipped	30	33	36	34

A similar cyanide-zinc plating bath was made up using three grams per liter of coumalic acid but omitting molybdenum. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	10	8	8	8
Bright-dipped	24	29	33	28

Example 87

Kojic acid, an oxyheterocyclic compound, also known as 3-hydroxy-gamma-pyrone, was included in a cyanide-zinc plating bath made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8.
Kojic acid	3.3

At a current density of about twenty-five amperes per square foot an unbright-dipped zinc deposit obtained using this bath gave a reflectometer reading of twenty-five, and a bright-dipped deposit gave a reading of thirty-five. Kojic acid alone was used as an addition to a cyanide-zinc plating bath with the following results:

Current density	7	25	40	80
Not bright-dipped	17	26	22	30
Bright-dipped	21	29	29	29

Example 88

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Phthalide	5

When the bath was freshly made up, deposits made at a current density of about forty amperes per square foot gave, before bright-dipping, a reflectometer reading of twenty-three, and, after bright-dipping, a reading of thirty-five. It appears that phthalide is not stable in the bath because upon standing a dark precipitate formed.

Example 89

A cyanide-zinc plating bath was made up with:

	Grams per liter
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	0.5
Phthalide	5.

A number of copper plates were zinc coated at the below indicated current densities with the following results:

Current density	7	25	40	80
Not bright-dipped	31	28	24	9
Bright-dipped	31	28	24	10

A cyanide-zinc plating bath was made up using five grams per liter of phthalide but omitting the nickel. With this bath the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	12	8	11	10
Bright-dipped	31	28	29	28

Example 90

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Thioxane	5

The organic compound was quite insoluble, and it floated upon the bath in small droplets. A slight precipitate formed after the bath was allowed to stand. Employing this bath, the following results were obtained at the indicated current densities:

Current density	7	25	40	80
Not bright-dipped	11	18	23	27
Bright-dipped	28	30	33	33

A similar bath was made up using thioxane but omitting the metal brightener. Zinc deposits made at the indicated current densities gave the following results:

Current density	7	25	40	80
Not bright-dipped	16	9	10	10
Bright-dipped	27	25	25	22

Example 91

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Formvar	1

This oxyheterocyclic addition compound was quite insoluble in the bath, but it appears that some slight amount at least was dissolved. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	12	25	29	29
Bright-dipped	26	32	34	34

A bath was also made up using formvar but omitting the metal brightener with the following results:

Current density	7	25	40	80
Not bright-dipped	12	10	13	13
Bright-dipped	22	25	29	29

Example 92

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Phthalidylphenylsulfide	5

With this combination of an oxyheterocyclic compound and metal brightener, the following results were obtained:

Current density	7	25	40	80
Not bright-dipped	15	21	27	27
Bright-dipped	33	29	35	35

A bath was also made up as above but omitting the molybdenum with the following results:

Current density	7	25	40	80
Not bright-dipped	8	8	5	5
Bright-dipped	27	27	23	22

Example 93

A cyanide-zinc plating bath was made up with:

	Grams per liter
Molybdenum trioxide (MoO_3)	8
Rotenone	1

The organic compound was almost entirely insoluble in the bath, somewhat less than one gram per liter being actually dissolved. During electrolysis of the bath, the addition agent caused some foaming, particularly at higher current densities. A number of zinc deposits were made using this bath, and the specimen plates examined using the reflectometer. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	11	17	27	14
Bright-dipped	32	26	33	32

A cyanide-zinc plating bath similar to the one above, using on gram per liter of rotenone but omitting the molybdenum, was made up. The following results were obtained:

Current density	7	25	40	80
Not bright-dipped	6	10	18	18
Bright-dipped	21	22	31	33

While, in the foregoing examples, the brightening metals are employed in about the optimum amounts for the particular baths shown, the quantities used may be greatly varied. Generally, the metals must be used in substantial amount to have a satisfactorily cooperative effect.

It will readily be understood that the optimum amount of the various metals will depend upon the particular bath used, upon the organic addition agent used, and upon whether or not the metals are used in combination with other brightening metals. The best proportion of bath constituents may readily be determined for each particular instance by a few trials.

The metals of group VI sub-group 1 may be used in widely varying amounts, the upper limit on the quantity being largely determined by economic considerations. In view of the high cost of the metals of this group, it would not at the present time be commercially feasible to employ them in large quantities. More specifically, the metals of group VI sub-group 1 should be used in amounts not substantially less than about one hundredth of a gram per liter, and no more than about forty grams per liter can economically be used.

Molybdenum is the best metal of this group and it is, in fact, by far the best of the brightening metals. I generally prefer to use from about twenty-five hundredths of a gram to twenty-five grams per liter of molybdenum. More specifically, it is preferred to use from about one to twelve grams per liter of molybdenum. It will be understood that while reference is made to the amount of metal used, the metal is present in the bath in the form of a soluble compound.

The metals of group VII sub-group 1 should also be employed in substantial amounts. It is generally desirable to use no less than about five-thousandths of a gram per liter and not substantially more than about fifteen grams per liter. Manganese is preferably used in amounts between about one and five grams per liter, while, more specifically, about one to three grams per liter should be used.

The metals of group VIII series 4, similarly, should be used in substantial amounts as soluble compounds such as potassium ferrocyanide, cobalt sulfate, cobalt chloride, cobalt oxide, nickel sulfate, nickel chloride, and nickel oxide. Generally a soluble compound equivalent to no less than about five-hundredths of a gram per liter of one of these metals should be used.

When titanium is employed as a brightening metal, an amount equivalent to about one-half

gram per liter of titanyl sulfate should be used, tho, of course, larger or smaller amounts may be employed if desired.

While the amount of aluminum used as a brightening metal may be greatly varied, it is generally desirable to employ an amount of aluminum equivalent to about five to twelve grams per liter of aluminum sulfate.

While an attempt has been made above to outline, roughly, some of the considerations involved in selecting the quantities of metal brighteners, it will be understood that in a particular instance the requirements may most readily be determined by a few simple trials.

Each of the brightening metals has characteristics peculiar to itself, and the selection of a metal brightener for a particular bath may be influenced by the characteristics desired. While, generally speaking, I may employ any metal brightener in conjunction with organic addition agents, it is preferred to use a metal from the group consisting of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, rhenium, aluminum, and tungsten.

Molybdenum is by far the best of the brightening metals as has been pointed out above, tho occasionally some other brightening metal will give comparable results in a particular combination.

Chromium is very satisfactory as a brightening metal, but it has the fault of hydrolyzing in the bath and precipitating out. This characteristic of chromium brighteners makes their use too expensive for most purposes.

Cobalt and nickel both have the fault of accelerating anode corrosion tho nickel is a much worse offender than cobalt. When cobalt is used as a metal brightener the deposits appear a little white, and the reflectometer readings are lower than one would expect from visual observation. In many combinations nickel produces quite satisfactory deposits but the deposits should not be bright-dipped. Deposits produced from baths containing nickel as a brightener darken when bright-dipped tho they still appear bright to the eye.

When manganese or tungsten are used as brightening metals, the deposits have a brownish film. Despite the fact that many deposits of pleasing and brilliant appearance are obtained using these metals, the deposits almost uniformly give much lower reflectometer readings than would be expected from visual observation. The brownish film is removed when the deposits are bright-dipped.

Iron, like manganese and tungsten, causes the formation of a slight film on the deposit. This film also lowers the reflectometer readings without making the plates appear correspondingly dull to the eye. The film, however, is removed by bright-dipping.

Titanium occasionally causes the formation of a slight gray film which greatly lowers the reflectometer readings. The gray film is not ordinarily removed by bright-dipping the deposit.

When aluminum is used as a metal brightener the deposits ordinarily have a whitish appearance, and while the deposits are very pleasing and bright when visually observed, the reflectometer readings are astonishingly low. Bright-dipping does not entirely change the whitish appearance of the deposit.

Rhenium is quite excellent as a brightening metal, but it is so rare at the present time that its commercial application would be impractical. Should the metal become less expensive, it could be used very satisfactorily as a brightener.

While my invention is particularly directed to the cooperative use of organic addition agents and metal brighteners, it will be understood that oxyheterocyclic compounds are somewhat efficacious apart from metal brighteners and that it may sometimes be found desirable to use them alone.

While, as has been noted above, I may employ any oxyheterocyclic compound, it will be understood that the compound should retain its oxyheterocyclic structure in cyanide-zinc plating baths and, of course, the compound should be to some extent soluble in the bath. If an oxyheterocyclic compound is not readily soluble, it may be more satisfactorily dissolved by adding it in a solvent such as alcohol or acetone.

While I may employ any oxyheterocyclic compound with or without a metal brightener, it is preferred to employ an oxyheterocyclic compound from the group consisting of piperonal, piperonyl alcohol, piperonylic acid, piperine, safrole, piperonal acetophenone, coumarin, furfural, furfuran, pyronine, tetrahydrofurfuryl alcohol, hydrofurfuramide, paraldol, ethyl furoate, methyl furoate, furfural amine, tetrahydrofurfuralamine, dihydroxymethylxanthene, fluorescein, morpholine ethanol, phenyl morpholine hydrochloride, butyl morpholine hydrochloride, diphenylene oxide, cyclohexene oxide, glycol formal, coumalic acid, and furfuramide.

The oxyheterocyclic compounds are preferably employed in about the amounts given in the above examples. It will be understood that the quantity used in the examples was determined in each instance by trying the organic addition agent at widely varying concentrations until about an optimum was found. If it is desired to employ a particular oxyheterocyclic compound in a still different specific instance, the amount to be used may readily be determined by a few simple tests.

The brightness figures given in the above examples refer, of course, to the number of microamperes read on the micro-ammeter **10** of the reflectometer. The figures are therefore specific to the apparatus used for the determinations. In view of the fact that the current developed by the photoelectric cell is directly proportional to the light it receives, and in view of the method of standardizing the instrument, the data can be given an absolute significance by referring to a silver mirror. For example, a plate with a reflectometer reading of 38 microamperes is $^{38}/_{40}$ as bright as a polished silver mirror.

While I have shown a number of specific processes and cyanide-zinc baths in the foregoing, it will be understood that I do not intend to be limited thereto. Those skilled in the art may readily make numerous modifications of the discussed processes and baths without departing from the spirit of this invention.

This application is a continuation in part of my co-pending application Ser. No. 14,589, filed April 4, 1935 now Patent No. 2,080,520, and of my co-pending application Ser. No. 70,400, filed March 23, 1936 now abandoned.

I claim:

1. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of an oxyheterocycle compound.

2. In a process for the electrodeposition of zinc

from a cyanide-zinc plating bath of the type containing a brightening metal, the step comprising depositing zinc from the bath in the presence of an oxyheterocyclic compound.

3. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of an oxyheterocyclic compound and a soluble compound of a metal of the group consisting of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, rhenium, aluminum, and tungsten.

4. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of an oxyheterocyclic compound selected from the group consisting of coumarin, furfural, furfuran, pyronine, tetrahydrofurfuryl alcohol, hydrofurfuramide, paraldol, ethyl furoate, methyl furoate, furfuralamine, tetrahydrofurfurlamine, dihydroxymethylxanthene, fluorescein, morpholine ethanol, phenyl morpholine hydrochloride, butyl morpholine hydrochloride, diphenylene oxide, cyclohexene oxide, glycol formal, coumalic acid, and furfuramide.

5. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of an oxyheterocyclic compound selected from the group consisting of coumarin, furfural, furfuran, pyronine, tetrahydrofurfuryl alcohol, hydrofurfuramide, paraldol, ethyl furoate, methyl furoate, furfural amine, tetrahydrofurfurylamine, dihydroxymethylxanthene, fluorescein, morpholine ethanol, phenyl morpholine hydrochloride, butyl morpholine hydrochloride, diphenylene oxide, cyclohexene oxide, glycol formal, coumalic acid, and furfuramide, and a soluble compound of a metal of the group consisting of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, rhenium, aluminum, and tungsten.

6. A cyanide-zinc plating composition containing an oxyheterocyclic compound.

7. A cyanide-zinc plating composition including a brightening metal and characterized by containing an oxyheterocyclic compound.

8. A cyanide-zinc plating composition containing an oxyheterocyclic compound and a soluble compound of a metal of the group consisting of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, rhenium, aluminum, and tungsten.

9. A cyanide-zinc plating composition containing an oxyheterocyclic compound selected from the group consisting of coumarin, furfural, furfuran, pyronine, tetrahydrofurfuryl alcohol, hydrofurfuramide, paraldol, ethyl furoate, methyl furoate, furfural amine, tetrahydrofulfurylamine, dihydroxymethylxanthene, fluorescein, morpholine ethanol, phenyl morpholine hydrochloride, butyl morpholine hydrochloride, diphenylene oxide, cyclohexene oxide, glycol formal, coumalic acid, and furfuramide, and a soluble compound of a metal of the group consisting of molybdenum, chromium, cobalt, manganese, nickel, iron, titanium, rhenium, aluminum, and tungsten.

10. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of coumarin.

11. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of furfural.

12. In a process for the electrodeposition of zinc, the step comprising depositing zinc from a cyanide-zinc bath in the presence of paraldol.

13. A cyanide-zinc plating composition containing coumarin.

14. A cyanide-zinc plating composition containing furfural.

15. A cyanide-zinc plating composition containing paraldol.

16. A cyanide-zinc plating composition containing an oxyheterocyclic compound selected from the group consisting of coumarin, furfural, furfuran, pyronine, tetrahydrofurfuryl alcohol, hydrofurfuramide, paraldol, ethyl furoate, methyl furoate, furfuralamine, tetrahydrofurfurylamine, dihydroxymethylxanthene, fluorescein, morpholine ethanol, phenyl morpholine hydrochloride, butyl morpholine hydrochloride, diphenylene oxide, cyclohexene oxide, glycol formal, coumalic acid, and furfuramide.

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