

1

2,937,940

SELECTIVE STRIPPING OF ELECTROPLATED METALS

Mark Weisberg, Providence, R.I., and Florence P. Butler, Amherst, Mass., assignors, by mesne assignments, to Eltex Chemical Corporation, Providence, R.I., a corporation of Rhode Island

No Drawing. Filed July 1, 1957, Ser. No. 668,858

15 Claims. (Cl. 75—97)

This invention relates to dissolving metals by chemical action and particularly it is concerned with selective solution of metals commonly encountered in electroplating operations.

In any electroplating plant a serious economic problem is centered around the recovery of those plated articles which have imperfections, discolorations, poor adhesion or other non-optimum characteristics of the plated film which make them unusable. The recovery of the base article by separating the plated metal from it is of prime importance in the electroplating field because of the value of the article being plated. Conventional methods of removing such faulty plates have included three classes of operation—namely, (1) chemical oxidation of the plated metal with acids to form a soluble salt; (2) oxidation of the plated metal by electrolysis with subsequent formation of a soluble salt or an insoluble precipitate or a redeposited metal film; (3) oxidation of the plated metal with a strong oxidizing agent with solution of the insoluble metallic compound.

A very common base coat in any electroplating operation is copper. Frequently it is applied in minute flashes, sometimes only a few millionths of an inch in thickness. Hydrochloric, nitric, sulfuric and chromic acid, or mixtures of these acids, are commonly used to remove copper from the base metals. Nickel and cobalt, being somewhat less reactive than copper, require a more drastic acid treatment and for this purpose strong nitric acid or concentrated sulfuric acid or mixtures thereof may be used.

Electrolytic oxidation is accomplished by reversing current flow in the conventional electroplating bath. However, most electrolytic reductions are carried out using strong acids as the electrolytes, since the reaction products are usually soluble in those solutions. Common practice involves the use of additives in an effort to reduce the action of the acid on the base metal and thereby avoid pitting. Chromic acid is a popular electrolyte for the electrolytic oxidation of copper, and sulfuric and hydrochloric or mixtures of strong acids are used in electrolytes for the oxidation of nickel or cobalt.

Oxidation of copper metal to copper oxide which in turn is dissolved by suitable complexing agents, is quite easily accomplished using ammonium persulfate and ammonium hydroxide or hydrogen peroxide and ammonium hydroxide. Polysulfides may also be used in the case of copper in which case copper sulfide is formed and sodium or potassium cyanide is used to dissolve the sulfide and to complex the copper. These oxidizing agents, while suitable for copper, are not strong enough for nickel and more efficient systems must be used.

United States Patent 2,649,361, issued August 18, 1953, describes a system composed of nitro-substituted aromatic compounds, alkali cyanides and caustic. Such systems are described as producing oxidation potentials of more than minus 0.9 volt, when measured between a sheet nickel electrode and a saturated potassium chloride calomel electrode, the implication in the patent being that such high potentials are required to oxidize nickel.

The potential of the oxidizing medium in itself is not

2

indicative of whether or not the systems will function as an oxidizing agent or solvent for the metal in question.

The variety of prior art methods being practiced emphasizes the economic importance of the problem and, to some extent, the deficiencies of specific methods proposed. That is, none of the compositions in use in the art is sufficiently selective and safe for use in the removal of plated films from commonly used base metals. The strong acids are corrosive to practically every metal and the etched surface must be refinished after removal of the electrodeposited plate. Electrolytic oxidation of the plated metal is also quite non-selective, because the voltages used cannot be made completely selective and because the electrolyte is inherently corrosive. The prime function of the current is to speed the reaction and the metal involved almost invariably forms a soluble salt which is dissolved in the electrolyte.

Chemical oxidation by strong oxidizing agents in the presence of caustic or cyanide has serious drawbacks, because of the alkalinity and instability of the solution. The base metals such as aluminum, zinc, lead, tin or other commonly used alloys are badly corroded by caustic or cyanide. Fundamental in any of the existing operations also is the risk involved in using the very highly toxic cyanide in the nickel and copper plating shop, where most plating is done from acid solutions.

It is, accordingly, a fundamental object of this invention to provide a stripping solution for use in the reclamation of plated objects, which has improved selectivity for removal of plated metals while leaving the base metals relatively unaffected.

Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

In accordance with this invention, the improved selective stripping system is characterized by its combination of nitro organic compounds and amines per se or in water or non-aqueous solvents. More specifically the stripping medium is composed of a binary system of active components, which may be in a solvent, the first component being an aromatic nitro organic compound containing one, two or three nitro groups, or mixture, or a nitro-aliphatic compound or mixture, wherein the aliphatic radical contains from one to about six carbon atoms, the second component being an amine, such as simple alkyl amines, diamines, etc., and mixtures thereof. Solvents such as methyl, propyl, isopropyl and butyl alcohols may be used. Since many of the mixes are naturally liquids no solvent is really necessary in some cases. It is used, however, to dilute the system and increase its fluidity. To increase the water solubility of the nitro organic component in water it may carry other substituents such as hydroxyl groups, carboxylic groups or sulfonic acid groups.

Suitable nitro compounds are: o-, m-, p-nitrochlorobenzenes and mixtures thereof; o-, m-, p-nitrobenzoic acids and mixtures thereof; and nitrobenzene sulfonic acids and mixtures thereof; o-, m-, p-nitroanilines and mixtures thereof; o-, m-, p-nitrophenols and mixtures thereof. Other aromatic nitro compounds suitable for use in accordance with this invention may be found listed in United States Patent 2,698,781 and United States Patent 2,649,361.

The nitroparaffins are preferably those of relatively low molecular weight, which have some solubility in water and which are relatively non-volatile. Thus, the nitropropanes, nitrobutanes, nitropentanes, mono, di and tri substituted, are useful.

Suitable amines representative of the several classes of useful ones, are methyl amine, monoethanol amine, ethylene diamine, aminoethylethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentamine, diethanolamine, triethanolamine, ethanolisopropanol

amine, dimethyl amine, diethylamine, and mixtures thereof. Substituted amines are useful provided they retain basicity. Since the stripping is usually conducted at elevated temperatures to accelerate the operation, the higher boiling and substituted amines are preferred.

The stripping system may have a pH ranging from weakly acid values to strongly alkaline values, but in no case, however, is a strong base used, such as caustic, to produce a high pH in the medium. That is, the alkalinity of the medium is produced solely from the natural alkalinity of any excess amine which might be present. In utilizing the material in accordance with the invention, the article may be dipped directly at ambient temperature of 20°–30° C. into a bath containing ingredients in the recommended proportions, with or without a solvent diluent, and agitated gently until the plated surface has been removed and base metal is uniformly exposed. The process may be speeded by raising the temperature of the bath to the boiling point. If higher temperatures are desired, equipment could be pressurized.

The system has greater selectivity than conventional solutions, and we have found that pH control may be of substantial help in the stripping operation and in improving the effectiveness of the removal of plated metal. Since the system contains an amine which is present to assist in dissolving and to complex the metal ions formed and since most amines are effective complexing agents as such through a wide pH range, we have found we can conduct stripping operations under conditions which cannot be handled by other systems.

For example, we have found that at pH below 8, the system has no real affinity for the solution of copper, but it will dissolve nickel quite rapidly. At pH above 8 both nickel and copper are dissolved by the system, but copper is more slowly dissolved than nickel. This particular phenomenon is of great importance in stripping die castings since it is quite common to apply a flash coating of copper on a die cast article being plated and then to apply nickel over the copper. This selectivity is useful in removing nickel from a plated die cast article down to the copper flash, because salvaging the residual film speeds up the refinishing operation. However, in the absence of a copper film the nickel will be removed with no corrosion of the die casting. (Zinc and zinc alloys are common die casting metals, as are aluminum and magnesium alloys.)

We have found that while most simple primary and secondary amines are effective as complexing agents in the system, the degree of effectiveness does not seem to be related to the stability constant of the metal complex which is being formed with the amine.

We have found a specific system composed of nitroisophthalic acid and ethylenediamine is efficient. A system composed of nitroisophthalic acid and diethylene triamine is somewhat less efficient; and the efficiency appears to decrease with increasing molecular weight of the polyamine. This decreased efficiency of the system is observable even though the amines are used in the system on equivalent molar basis. However, the same systems may be made with mixed isomers of nitro acids, i.e., nitroisophthalic or nitrobenzoic or nitrobenzene sulfonate. In fact many of the nitro isomeric compounds which function poorly with cyanide are very effective with amines in systems made in accordance with this invention.

In preparing the stripping bath using the nitro acids identified, we have found the advantage of polyamines resides not only in high stability and low volatility but also in the fact that they have a buffer capacity and will perform as complexing agents over a wide range pH. To a limited extent the strong mineral acids may be used to adjust or lower the pH of the system. The sulfate ion is generally not desirable, because it has a tendency to produce insoluble deposits on the base metal being stripped. Thus, HCl or HNO₃ or organic acids such as

acetic, chloroacetic, lactic, citric, and the like, are satisfactory.

Through use of the stripping system to remove plated metals from the base the aromatic acid components gradually become spent and the amine gradually becomes more and more nearly saturated with metal ions being held in complex form. It is feasible, however, to make additions of both the aromatic nitro compound and the amine to a partially spent bath so as to maintain a useful concentration of the free amine and the nitro compound oxidizing agent.

The invention is illustrated by the following specific examples:

Example I

A stripping bath of the following proportions of ingredients was prepared:

	Mols
Aromatic nitro compound	1
Ethylenediamine	4

The molar ratio of the two constituents may be varied widely, the optimum ratio being that which will exhaust the oxidizing agent which brings the metal being stripped into solution and the amine which complexes it at approximately the same time, because that ratio produces maximum economy.

We have found that one mol of nitro compound oxidizes about 1.7 mols of nickel. To complex nickel, 3 mols of ethylene diamine are needed per mol of nickel. An optimum useful composition, therefore, is about 5 mols of the amine per mol of oxidizing agent.

The concentration of nitro compound-amine may vary widely. Effective removal of nickel is obtained with as little as 1 percent nitro compound in the presence of 99 percent amine; or with as much as 99 percent nitro compound in the presence of 1 percent amine. The dilution of either active stripping composition may be of the level of as little as 1 percent of the nitro compound-amine mixture in 99 percent of water or other solvent. The effectiveness of the extreme dilutions is low, but they are operative.

Thus, in accordance with this basic operating principle, the following composition was tested:

	Parts by weight
Nitro benzoic acid (mixed isomers)	6.85
Ethylenediamine	13.13
Water	200

will remove 3.90 parts of nickel from steel or other base metal without affecting the base metal.

If the base metal is brass, there will be some solution of metal from it which will cause a minor etching of the surface to give it a satiny appearance.

This attack of the brass can be avoided by lowering pH to about 7.8 by adding acid, e.g., sulfuric or hydrochloric. At this pH nickel is dissolved with no effect on the brass surface.

The stripping with the solution above identified was carried out at about 80°–85° C. and this may be considered a preferred convenient or optimum range for general operation, but operation at higher temperature will give increased stripping rates.

In place of the nitrobenzoic in the formulation given in Example I, the following nitro compounds may be used in the stated amounts:

- | | |
|---|-----------------------|
| (a) Mixed isomers of nitrobenzoic acid (commercial grade) | 7.9 parts by weight. |
| (b) Mixed isomers of nitrophthalic and isophthalic acids (commercial grade) | 8.65 parts by weight. |
| (c) Nitrobenzene sulfonate acid, crude mixture (sulfated, nitrated benzene) | 10 parts by weight. |
| (d) o-, m-, p-Nitro-phenols; o-, m-, p-nitro anilines | 0.041 mol parts. |

5

Systems made up in accordance with Example I and Example I(a), (b), (c), and (d) when compared with each other give essentially the same rates of stripping. Stripping rates will, however, vary quite widely depending upon the amine used.

The use of salts in place of the acids in equivalent amounts is permissible but the efficiency of the bath is lowered.

Generally any of the nitro organic compounds useful in cyanide stripping baths are useful in systems made in accordance with this invention with the advantage that pure single isomers need not be used. Thus, mixed o-, m-, p-isomers of the compounds given in United States Patents 2,649,361 and 2,698,781 may be used.

Example II

Using composition formulated in accordance with Example I, experiments with stripping nickel plate from a steel base were made and it was found consistently that there was no detectable weight loss of the steel base in the operations. With other base metals such as brass, or die casting alloy, we found no weight loss of base metal or only negligible weight loss and there was no pitting or etching of the base surface at near neutral pH. Since brass and die casting alloy are industrially important metals, this is a valuable property of the system. Thus, a system made up as follows:

Parts

Nitrobenzoic acid (commercial mixed isomers o, m, p, about 70 percent metal acid)-----	6.8
Ethylene diamine (100 percent basis)-----	11.24

The pH of this system as prepared is about 10.5. It may be altered by varying the proportion of acid or amine. Thus, adjusted to pH 6-8 it is most useful in stripping nickel from brass and die casting alloys, because it leaves the base metal unetched and without pits. Ethylenediamine is preferred as the amine but it may be replaced with a corresponding molar amount of any of the amines or polyamines defined.

The nitroparaffin compounds are somewhat less effective as stripping agents than the aromatics. The following illustrates a typical stripping composition based on a nitroparaffin compound.

Example III

Parts by weight

Dinitropropane -----	2.72
Ethylene diamine -----	11.24
Water -----	200

The solution made up in this concentration stripped nickel from base metal (steel, brass, die cast) at a rate about 70 percent as fast as a solution based on the same amount of water, diamine and 6.85 parts of nitrobenzoic acid.

Observation of the solution indicated that not all of the nitropropane was in solution. As the stripping action progressed more of the nitro compound went into solution, thereby to maintain a working concentration. Solvents may be used to put all components of the stripping composition in a single phase, but they do not improve efficiency.

In the formulation of stripping solution using the nitroaliphatic compounds, when molar ratios corresponding to those used for the nitroaromatics are employed, efficiencies, as measured by speed of stripping, are attained corresponding to about 70 percent of those reached with nitroaromatics. Useful nitroaliphatic compounds are nitromethane, nitroethane, nitropropane, hydroxynitropropane, trishydroxymethylnitromethane, nitrourea.

Based on a variety of observations involved in stripping metal from several bases using compositions made in accordance with the invention in which the nature of the amine was varied or with other sequestering agents in the bath, we have determined that the value of the stability constant of the metal complex formed by the

6

stripped metal and the amine compound in solution seems not to be a determining factor in identifying whether a given complexing agent is workable. For example, ethylenediamine tetraacetic acid salts are capable of forming very strong complexes with nickel, but are not operative in the presence of the aromatic nitro compound to strip metals from the base. Similarly tertiary amines such as triethanol amine do not function with a commercially attractive stripping rate nor do the high molecular weight amines such as five or six membered ethylenediamine polymers.

Hot plated nickel has a coarse highly strained grain structure and is the most commonly used nicked plate, because of the brilliance of the nickel deposit. This type of plate dissolves most rapidly in the nitro compound-amine system of this invention. Cold nickel plating baths produce a finer grained nickel film with less strain and consequently the rate of solution of this plate is slightly slower than in the case of bright, hot nickel deposit. This sensitivity to strain appears to be unique with the combinations which characterize this invention.

We have found that metals such as nickel, copper and cobalt can, if desired, be easily reclaimed from the stripping bath. In some cases this can be done by merely adding sulfide ions, which, in the case of ethylenediamine complexes, results in the precipitation of the sulfide of the nickel complex of ethylenediamine. With other amines the precipitate may be either an amine complex sulfide or the metal sulfide. Such recovery practices are not practical when cyanide-based stripping baths are used. If desired the amine nitro acid stripping bath may be acidified with concurrent release of metal ions which may then be plated from the solution, by conventional electroplating procedures, onto a sheet electrode. This nickel sheet can then be used in the conventional nickel bath thus effecting essentially 100 percent recovery of the metal stripped.

In general the stripping solution is used to reclaim a plated article, usually Ni, Co, Cd plate, because the value of the article substantially exceeds the cost of stripping. Hence, the solution will usually be in about the concentrations described in the examples. Extreme dilutions, of the order of 0.01 to 1 percent of active components are useful when the mass of the article is small. For example, if it is necessary to strip nickel from an extremely fine gauge copper wire, the solution described in Example I, at neutral pH, and concentration of about 0.01 percent is useful. It removes the nickel rapidly enough to be economically useful, yet the conditions are such that the copper base, itself very small, is not affected.

Though the invention has been described in terms of a limited number of examples, it is to be understood that variants thereof may be practiced without departing from its spirit or scope.

What is claimed is:

1. A composition for selectively dissolving nickel, cobalt, and alloys thereof deposited on a basis metal, which composition consists essentially of an ingredient selected from each of the following groups, (a) and (b); (a) nitro-substituted aromatic compounds containing at least one NO₂ attached to a benzene ring which also carries a radical having a water-solubilizing effect on the nitro-substituted aromatic compound and water soluble nitro-substituted aliphatic compounds and those which have a water solubilizing group attached thereto, and (b) primary and secondary amines, and tertiary amines having comparable alkalinity to said primary and secondary amines, the said composition being in the liquid phase, containing at least 0.01 percent by weight of the combination of nitro-containing compound and amine, in a ratio of at least 1 part nitro-containing compound to 50 parts of the amine-containing compound and not exceeding 9 parts of nitro compound to 1 part amine.

2. A composition in accordance with claim 1 consisting essentially of a nitro aromatic compound and an

7

amine, in a molar ratio of about 1 mol of nitro radical to about 4 mols of amine.

3. A composition in accordance with claim 1 consisting essentially of a nitro aliphatic compound and an amine in a molar ratio of about 1 mol of nitro radical to about 4 mols of amine.

4. A composition in accordance with claim 2 consisting essentially of, in liquid phase, nitroisophthalic acid and ethylenediamine.

5. A composition in accordance with claim 2 consisting essentially of, in liquid phase, nitrobenzoic acid and ethylenediamine.

6. A composition in accordance with claim 2 consisting essentially of, in liquid phase, about 7 parts of nitrobenzoic acid, and about 9 to about 12 parts of ethylenediamine.

7. A composition in accordance with claim 2 consisting essentially of, in liquid phase, nitrobenzene sulfonic acid and ethylenediamine.

8. A composition in accordance with claim 2 consisting essentially of, in liquid phase, nitrochlorobenzene sulfonic acid and ethylenediamine.

9. A method of stripping electroplated nickel, cobalt and alloys thereof from basis metal comprising providing a liquid bath consisting essentially of a composition formulated with an ingredient from each of the following groups, (a) and (b); (a) nitro-substituted aromatic compounds containing at least one NO_2 attached to a benzene ring which also carries a radical having a water-solubilizing effect on the nitro-substituted aromatic compound and water soluble nitro-substituted aliphatic compounds and those which have a water solubilizing group attached thereto, and (b) primary and secondary amines, and tertiary amines having comparable alkalinity to said primary and secondary amines, the said composition being

8

in the liquid phase, containing at least 0.01 percent by weight of the combination of nitro-containing compound and amine, in a ratio of at least 1 part nitro-containing compound to 50 parts of the amine-containing compound and not exceeding 9 parts of nitro compound to 1 part amine, immersing said electroplated article in said bath, maintaining said bath at a temperature in the range from about ambient to boiling, maintaining said article in said bath until said electroplated metal has been dissolved, and recovering from the bath said article substantially unaffected by said bath.

10. The method in accordance with claim 9 in which the bath consists essentially of nitro benzene sulfonic acid and ethylene diamine in a molar ratio of about 1:4.

11. The method in accordance with claim 10 in which the article is a nickel plated die casting.

12. The method in accordance with claim 10 in which the article is nickel plated on a copper alloy base.

13. The method in accordance with claim 9 in which the bath contains about 4 to 5 mols of amine per mol of nitro radical in the nitro compound.

14. The method in accordance with claim 13 in which the bath contains ethylenediamine and nitro benzene sulfonate.

15. The method in accordance with claim 13 in which the bath contains ethylenediamine and nitrobenzoic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,033,444	Nisizawa	Mar. 10, 1936
2,132,511	Hentrich	Oct. 11, 1938
2,649,361	Springer	Aug. 18, 1953
2,698,781	Meyer	Jan. 4, 1955