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METHODS AND COMPOSITIONS FOR STRIPPING NICKEL

Harry K. Tsourmas, North Haven, Conn., assignor to MacDermid, Incorporated, Waterbury, Conn., a corporation of Connecticut

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ABSTRACT OF THE DISCLOSURE

Compositions and aqueous solutions thereof for stripping nickel coatings from substrates, particularly where copper or copper alloys are present in the substrate. The composition comprises generally the combination of an oxidizer consisting of an oxy-halogen compound of the group comprising specifically the chlorites, hypochlorites, bromates and hypobromites; a nickel complexing agent of the group comprising ammonia, the ammonium ion, amines and other known nickel complexers; a divalent sulfur ion-supplying compound, either organic or inorganic, as a nickel activator; and, where necessary to prevent poisoning of the stripping solution by the presence of copper, an organic sulfur ion-supplying compound if the nickel activator is not of such type or present in sufficient amount.

This invention relates to dissolving nickel from a substrate on which it has been plated, and is more particularly directed to compositions for and methods of stripping nickel deposits from ferrous metals where copper or copper alloys may or may not be present. The invention is also useful in stripping nickel from organic, i.e. plastic, or inorganic, i.e. ceramic, substrates.

Fabricated articles incorporating a plating of nickel sometimes fail to pass inspection because of defects in the plate. The reclaiming of the basic fabricated article in many instances is of significant economic importance. Usually the basic article, quite apart from the defective nickel deposit, represents considerable value in terms of labor and materials, and consequently if this can be salvaged in reusable form by removing the defective deposit, worthwhile economies can be effected.

There have been many compositions developed for stripping various plated deposits, including nickel, from their substrates. Some of these incorporate strongly acidic systems which attack the substrate as well as the nickel deposit which it is desired to remove. Others incorporate cyanide compounds which introduce health hazards. Still others involve waste liquor disposal problems. Many of the earlier systems also are rather slow in operation, are critical in respect to control of operating conditions and have rather limited capacity for dissolving nickel before they must be replenished or entirely replaced.

I have discovered improved compositions effective in stripping nickel deposits in aqueous solution which offer certain desirable features and advantages over the prior art. My system is completely alkaline and thus especially adapted to stripping of nickel from ferrous substrates which are rapidly attacked in acid environments employed in many of the stripping systems used heretofore. My system is operative in the presence of copper which very commonly is used as a flash or strike for nickel but which acts as a poison in some of the more effective prior stripping compositions, rendering them useless. My system avoids health hazards inherent in systems employing cyanide compounds used heretofore, being entirely free of cyanides in its make-up. My composition is inherently able to activate the nickel surface to be dissolved and to maintain a high rate of metal dissolution until the rate-

determining component or components are consumed. One of the most important features of my composition is the high rate of nickel dissolution obtained at low, ambient temperatures, which drastically reduces evaporation losses and prolongs the useful life of the stripping system. Another advantage of my system is that it presents no waste liquor disposal problems such as those encountered with cyanides and chromates, since the waste may be discharged as an effluent without treatment other than dilution if local authority permits nickel and copper in the effluent. If this is not permitted, these metals can very readily be precipitated from my system.

The composition is applicable to stripping nickel from the usual ferrous substrates, including those containing a flash deposit of copper as for example in automotive hardware or the like. It is also useful, of course, in stripping from non-metallic basis articles such as plastics and ceramics comonly used in electronic components as well as automotive applications.

The stripping compositions herein disclosed consist essentially of an oxidizer, a complexing agent for the nickel, a sulful-containing activator for the nickel and, where necessary, a deactivating agent for copper to prevent copper poisoning of the stripping solution.

The oxidizers in my system are oxy-halogen compounds selected from the group consisting of the alkali and alkaline earth metal normal chlorites, hypochlorites, bromates and hypobromites. Sodium or potassium chlorites are preferred for reasons of availability and cost.

The nickel complexer may be the ammonium ion from aqueous ammonia or buffered as ammonium carbonate, chloride, fluoride, phosphate, sulfate, nitrate, or acetate salts; amines and substituted amines such as ethylenediamine, the disodium salt of ethylenediamine tetraacetic acid; nitrilotriacetic acid and its salts, and amino acids such as glycine and its salts, e.g. sodium glycinate; the salts of glycolic acid, gluconic acid; and other hydroxy acids such as tataric. The inorganic ammonium salts are especially good from a cost standpoint. The amines on the other hand have the added advantage of lower volatilization losses.

As nickel activators, I use sulfur-containing compounds belonging to the groups comprising metallic sulfides, non-metallic sulfides, thioacids and their salts, aliphatic nitrogen sulfur compounds and aromatic nitrogen sulfur compounds. In fact almost any organic or inorganic sulfur compound having at least limited solubility in aqueous solution is effective.

Finally, where a deactivator for copper is needed, I prefer to use diethyldithiocarbamic acid sodium salt, substituted dithiocarbamates, thioanilids, and organic sulfur-containing carbamides.

In each of the foregoing categories, mixtures of the agents mentioned, rather than just a single agent, may be employed provided of course the mixture does not itself interact to destroy the effectiveness of the agents.

Solutions containing the foregoing combination of components are operative over a pH range of about 8.0 to 13.0 and, where necessary, an amine is added to effect the desired degree of alkalinity within these limits. Generally a pH of 8.5 to 10.5 is preferred.

The stripping solution is not critical as to concentration of oxidizer, nickel complexer, activator for the nickel or deactivator for the copper. Practically useful solutions are obtained when the oxidizer concentration is as little as 0.1 mol per liter up to near saturation. The complexer concentration is dependent upon the amount of nickel to be dissolved. The system is operative where the complexer is present at a mol ratio of at least 1:1 but for practical operation, more useful stripping speeds are obtained with a mol ratio preferably of 3:1 or greater. The amount of

the complexer needed may be determined from the amount of the oxidizer required to oxidize the elemental nickel deposit to be dissolved by converting it to the nickelous state. The activator is found to be effective in molar concentrations from trace amounts as little as 0.00023 to 0.23 mol per liter. The preferred concentration is about 0.0023. The copper deactivator is likewise found to be effective over a range of concentrations from about 0.008 to 0.2 mol per liter, preferably within the limits of solubility, or about 0.01 to 0.015 mol per liter. In some cases a single sulfur-containing compound may serve both as activator for nickel and as deactivator for copper, in which case the molar concentration should equal the sum of the concentrations of the separate components.

The temperature of the solution used in stripping nickel is not critical, and the system exhibits outstanding improvement over earlier systems at ambient room temperatures, making commercial operation practical under conditions which minimize evaporation losses and effect related advantages of economy and installation simplification.

In this system, in the process of activating the nickel surface by the sulfur-containing compounds, a film forms on the dissolving nickel or on the substrate. This film is essential for dissolution of the nickel but should be removed from the substrate before performing further plating or finishing operations. Such film or smut removal may be accomplished in any of several well known ways, or it can be effected in a solution of the same oxidizer and complexer, but without a nickel activator, used in the stripping bath itself.

Examples of typical solutions within the purview of the invention, and the stripping rates obtained by them, are as follows:

Example 1

The following solutions are useful in stripping nickel from a substrate where no copper is present:

	Mol/l.	Mol/l.	Mol/l.
Ammonia, aqua	4.50	3.37	2.25
Ammonium carbonate	2.25	3.37	4.50
Sodium chlorite	0.375	0.375	0.375
Ammonium thiocyanate	0.0023	0.0023	0.0023
	Mil/Min. (At 25° C.)	Mil/Min. (At 25° C.)	Mil/Min. (At 25° C.)
Nickel stripping speed	0.062	0.058	0.062

Substitution of any of the anions named hereinabove for carbonate in the ammonium complexer is effective, and produces no significant change in stripping rate at the same mol concentrations. Likewise substitution may be made of other cations, such as potassium, lithium or calcium for example, in the oxidizer, again without change in molar concentration, and will be operative.

Example 2

Where copper is present as a strike under the nickel, the following system is effective:

	Mol/l.
Ammonia, aqua	450.
Ammonium carbonate	2.25
Sodium chlorite	0.375
Ammonium thiocyanate	0.0023
Sodium diethyldithiocarbamate	0.008 to 0.016
Nickel stripping speeds, (mil/min. at 25° C.)	0.060.

Example 3

Compositions identical with those of Examples 1 and 2 except for the substitution of different complexers provide effective stripping also. For example, in place of the ammonia-ammonium carbonate, equal molar concentrations of ethylene-diamine may be employed. Providing also that the pH of the solution is maintained at the aforesaid level of 8.0 to 13.0, where necessary by the addition of aqueous ammonia or ethylene-diamine, other complexers such as disodium ethylenediamine tetraacetic acid, nitrilotriacetic acid, glycine or glycolic, gluconic and tartaric acids and their salts may likewise be used. The molar concentrations of these complexers, either singly or in combination, must of course be sufficient to provide the desired mol ratio of at least 1:1 and preferably higher in respect to the amount of nickel to be dissolved. One of the major advantages of the foregoing group of complexers is a lower volatility than the straight aqueous ammonia-ammonium salt compositions. Stripping rates are generally satisfactory although generally lower than in Example 1. The system is operative at a temperature as low as 15° C. but a preferred practical lower limit is around 25° C. for the system of Examples 1 and 2. Other systems, as noted hereinafter may require somewhat higher temperatures on the order of 50° to 75° C. to provide practical stripping speeds. Examples using other complexing agents than the ammonia-ammonium carbonate are given in Table 1.

TABLE 1

	Mol/l.	Mol/l.
Ethylenediamine	1.8	
Sodium glycinate		1.5
Sodium chlorite	0.375	0.375
Ammonium thiocyanate	0.0023	0.0023
pH	8.4	9.8–10
	Mil/Min.	Mil/Min.
Nickel stripping speed (at 70–75° C.)	0.002	0.03

Example 4

In place of sodium chlorite in Examples 1 and 2, other oxidizers may also be used. Thus, other chlorite salts such as potassium, lithium or calcium are fully operative when substituted in equal molar concentrations. Still other oxidizers of the oxy-halogen group which are effective are the corresponding bromate salts and the hypobromites. The iodates and fluorates do not appear to be operable in this system. Again, typical nickel stripping rates for systems employing some of these other oxidizers are as follows:

TABLE 2

	Mol/l.	Mol/l.
Ammonia, aqua	4.0	9.0
Ammonium carbonate	2.25	4.45
Sodium hypochlorite	0.375	
Sodium hypobromite		0.75
Sodium thiocyanate	0.0023	0.0023
pH	9–10	9–10
	Mil/Min. (At 49–54° C.)	Mil/Min. (At 25–27° C.)
Nickel stripping	0.002	0.0005

Example 5

Nickel activators other than ammonium thiocyanate as given in Examples 1 and 2 includes such divalent sulfur ion-supplying compounds as sodium, potassium, ammonium, calcium, barium, magnesium, aluminum and hydrogen sulfides, and carbon disulfide. Organic nitrogen-sulfur compounds, both aliphatic and aromatic, are operative. For example, thioanilids and thiocarbamides, such as dimethyl- or diethyl-thiourea and the corresponding dithiocarbamic acids, and their salts, thioacetic acid and thioamide (e.g. thioacetamide) derivatives, are typical of useful aliphatic compounds. Correspondingly, aromatic nitrogen-sulfur compounds such as thiocarbanilide (diphenylthiourea) and phenyldithiocarbamic acid and its salts are operative. Again at the same molar concentra-

tions, the nickel stripping rates remain good with such activators.

TABLE 3

	Mol/l.
Ammonia, aqua	4.0
Ammonium carbonate	2.25
Sodium chlorite	0.375
Thiourea	0.023
Nickel stripping speed (mil/min. at 25° C.),	0.0137.

Example 6

The organic activators mentioned in the preceding example may serve a dual function in the stripping system, in that not only are they effective for activating the nickel but they also serve as deactivators for copper where this is encountered, preventing poisoning of the system by the copper. For instance, in Example 2 above, ammonium thiocyanate may be omitted if the molar concentration of sodium diethyldithiocarbamate is at a level of about 0.01 or better.

Example 7

For practical purposes, a minimum molar concentration of the complexer in solution should be about 3:1 relative to the nickel. With this in mind it is sometimes advantageous to prepare a composition in the form of a concentrate for reducing transportation costs. In such a case, a solution having a make-up composition of complexer, oxidizer and activator mol ratio of around 3.0:0.3:0.003 is quite suitable. Where a combined activator-deactivator is used, the ratio should be 3.0:0.3:0.01. Preferably, a higher concentration of complexer in the bath is desirable but this can be conveniently added in the form of aqueous ammonia, ethylenediamine, etc. at the time of making up the actual solution to be used in the stripping process. The minimum pH of 8.0 must also be observed, of course.

Example 8

It is also possible to use ethylenediamine tetraacetic (EDTA) both as a nickel complexing agent and as a copper deactivator, but in such instance a sulfur-type nickel activator must also be present. While the EDTA might itself serve as the only nickel complexer in solution, this increases the expense and therefore it is more practical to use it in combination with ammonia or one of the ammonium salts such as the nitrate or sulfate. The molar concentrations of EDTA, either alone or in combination with an ammonium ion supplying component, should in this case equal the total of the molar concentrations recommended above for the complexer plus the copper deactivator. Since the latter requires only trace amounts to be effective, maintaining the molar concentration of the complexing agent (EDTA alone or in combination with others named) above the minimums recommended for the complexing agent alone will be sufficient.

As discussed above, one of the principal advantages of the systems herein disclosed is that they are operable in terms of practical commercial use where copper ions get into the stripping solution. This can and does occur, for example in the commonly encountered situation where there is, in addition to the nickel plate, a flash coating of copper on the substrate. This flash coating is on the order of 0.03 mil thick in a typical case, and is stripped along with the nickel in my solution. But the copper thus brought into solution does not poison the stripping bath so long as its concentration remains below a weight ratio of about 1:60 relative to nickel. The amount of copper in the usual flash coating is well below that needed to reach such a concentration. Thus my solution has the advantage of far higher stripping rates than cyanide and other alkaline solutions, and also avoids the health hazards of the cyanide systems.

What is claimed is:

1. A nickel stripping composition for use in aqueous solution, which consists essentially of:

(a) an oxidizer selected from the group consisting of the sodium, potassium, calcium and lithium salts of hypochlorite, normal chlorite, bromate and hypobromite;

(b) a nickel-complexing agent selected from the group consisting of ammonia and ammonium carbonate, chloride, fluoride, phosphate, sulfate, nitrate and acetate; ethylenediamine, ethlenediamine tetraäcetic acid; nitrilotriacetic acid; glycine, glycolic, gluconic and tartaric acids and salts thereof; and

(c) a divalent sulfur ion-supplying compound as a nickel-activating agent, said compound being selected from the group consisting of sodium, potassium, calcium, barium, magnesium, aluminum, ammonium, hydrogen sulfides and carbon disulfide; thiocyanates, thioacetates, thioamides, thioanilids, thiocarbamides and the salts thereof;

said oxidizer being present in amount to provide in solution from about 0.1 mol per liter to near saturation; said complexing agent being present in a mol ratio of at least 1:1 relative to the nickel to be dissolved; and said activating agent being present in small but effective amount up to about 0.23 mol per liter.

2. A composition for selectively stripping nickel deposits from substrates on which they are plated, which composition is operative in the presence of copper ions in the stripping solution and which consists essentially, in combination with the composition defined in claim **1**, of a copper-deactivating agent selected from the group consisting of methyl, ethyl and phenyl substituted thioanilide and dithiocarbamide and the sodium, potassium and ammonium salts thereof, said copper-deactivating agent being present in small but effective amount up to about 0.23 mol per liter.

3. A composition for selectively stripping nickel deposits from substrates on which they are plated, which composition is operative in the presence of copper ions in the stripping soluiton and consists essentially of:

(a) an oxidizer selected from the group consisting of the sodium, potassium, calcium and lithium salts of hypochlorite, normal chlorite, bromate and hypobromite;

(b) a nickel complexing agent selected from the group consisting of ammonia and ammonium carbonate, chloride, fluoride, phosphate, sulfate, nitrate and acetate; ethylenediamine; ethylenediamine tetraäcetic acid; nitrilotriacetic acid; glycine, glycolic, gluconic and tartaric acids; and

(c) a nickel-activating, copper-deactivating divalent sulfur ion-supplying compound selected from the group consisting of thiocarbanilide, dimethyldithiocarbamic, diethyldithiocarbamic and phenyldithiocarbamic acids and salts thereof;

said oxidizer being sufficient to provide in solution at least 0.1 mol per liter to near saturation, said complexing agent being present in a mol ratio of at least 1:1 relative to nickel to be dissolved; and said nickel-activating, copper-deactivating agent being present in small but effective amount up to about 0.23 mol per liter.

4. A nickel stripping composition for use in aqueous solution which consists essentially of ammonium carbonate, sodium chlorite and ammonium thiocyanate in mol ratios of approximately 3.0:0.3:0.003.

5. A nickel stripping composition for use in aqueous solution which consists essentially of approximately 3 mols of ammonium carbonate, 0.3 mol sodium chlorite, and 0.01 mol sodium diethyldithiocarbamate.

6. A composition for use in aqueous solution in dissolving nickel deposits from substrates on which they are plated, which consists essentially, in addition to water, of an oxidizer selected from the group consisting of the sodium, potassium, calcium and lithium salts of chlorite,

hypochlorite, bromate and hypobromite; a nickel complexing agent selected from the group consisting of ethylenediamine, disodium ethylenediamine tetraäcetic acid, nitrilotriacetic acid, glycine, glycolic, gluconic and tartaric acids; and a sulfur-containing nickel activating agent capable of providing divalent sulfur ions in solution; said oxidizer being present in amount to provide in solution from about 0.1 mol to near saturation, said complexing agent being present in a mol ratio of at least 1:1 relative to the nickel to be dissolved, and said nickel activating agent being present in small but effective amount up to about 0.23 mol per liter.

7. A composition for use in aqueous solution for dissolving nickel deposits from substrates on which they are plated, which consists essentially, in addition to water, of an oxidizer selected from the group consisting of the sodium, potassium, calcium and lithium salts of hypochlorite, normal chlorite, bromate and hypobromite; a nickel complexing agent selected from the group consisting of ethylenediamine, disodium ethylenediamine tetraäcetic acid, nitrilotriacetic acid, glycine, glycolic, gluconic and tartaric acids; and a sulfur-containing nickel activating agent capable of providing divalent sulfur ions in solution; said oxidizer being present in amount to provide in solution from about 0.1 mol per liter to near saturation, said complexing agent being present in a mol ratio of at least 1:1 relative to the nickel to be dissolved, and said activating agent being present in small but effective amount up to about 0.23 mol per liter.

8. A composition as defined in claim 7, wherein the sulfur-containing nickel activating agent is selected from the group consisting of sulfide, thiocyanate, thioacetate, thioamide, thioanilid and thiocarbamide.

9. The method of dissolving metallic nickel deposits from articles having deposits thereof on their surfaces, which comprises subjecting the surface of the article to an aqueous solution consisting essentially, in addition to water, of:

(a) an oxidizing agent in amount of from about 0.1 mol per liter to near saturation, selected from the group consisting of the sodium potassium, calcium, and lithium salts of hypochlorite, normal chlorite, bromate and hypobromite;

(b) a nickel-complexing agent, in amount providing a mol ratio of at least 1:1 relative to the nickel to be dissolved, selected from the group consisting of ammonia and ammonium carbonate, chloride, fluoride, phosphate, sulfate, nitrate and acetate; ethylenediamine; ethylenediamine tetraäcetic acid, nitrilotriacetic acid; glycine, glycolic, gluconic and tartaric acids and salts thereof; and

(c) a divalent sulfur ion-supplying compounds as a nickel activating agent, in small but effective amount up to about 0.23 mol per liter, selected from the group consisting of sodium, potassium, calcium, barium, magnesium, aluminum, ammonium, hydrogen sulfides and carbon disulfide; thiocyanates, thioacetates, thioamides, thioanilids, thiocarbamides and the salts thereof;

while maintaining said solution at temperatures ranging from approximately 15° to 75° C.

10. The method defined in claim 9 wherein copper ions may also be present in solution, which comprises subjecting the surface of the article to an aqueous solution as defined in claim 9 but also containing a small but effective amount up to about 0.23 mol per liter of a copper deactivating agent selected from the group consisting of the methyl, ethyl and phenyl substituted thioanilids and dithiocarbamides and the sodium, potassium and ammonium salts thereof.

11. The method defined in claim 9 wherein copper ions may also be present in solution, which comprises subjecting the surface of the article to an aqueous solution as defined in claim 9, wherein said nickel activator is present in amount of at least about 0.01 mol per liter and is selected from the group consisting of thiocarbanilide, dimethyldithiocarbamic, diethyldithiocarbamic and phenyldithiocarbamic acids and the sodium, potassium and ammonium salts thereof.

12. The method of dissolving metallic nickel deposits from articles having deposits thereof on their surfaces, which comprises subjecting the surface to an aqueous solution consisting essentially in addition to water of an oxidizer selected from the group consisting of the sodium potassium, calcium and lithium salts of chlorite, hypochlorite, bromate and hypobromite; a nickel complexing agent selected from the group consisting of ethylenediamine, disodium ethylenediamine tetraäcetic acid, nitrilotriacetic acid, glycine, glycolic, gluconic and tartaric acid; and a sulfur-containing nickel activating agent capable of providing divalent sulfur ions in solution; said oxidizer being present in amount to provide in solution from about 0.1 mol to near saturation, said complexing agent being present in a mol ratio of at least 1:1 relative to the nickel to be dissolved, and said nickel activating agent being present in small but effective amount up to about 0.23 mol per liter; while maintaining said solution at temperatures ranging from approximately 15° to 75° C.

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LEON D. ROSDOL, *Primary Examiner.*

M. WEINBLATT, *Assistant Examiner.*