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METAL STRIPPERS: THEIR SCIENCE AND TECHNOLOGY.

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SYNOPSIS

Metal strippers in the electroplating industry are often considered to be necessary evils: they add additional processing and cost to correct earlier processing deficiencies yet enable expensive component substrates to be re-coated for prime engineering usage. The stripper solution formulations are generally traditional or proprietary and either way are open to better understanding and effective enhancement. This article explains their usage and formulation and indicates how they may be logically developed for new applications.

INTRODUCTION.

Metal strippers have been in use ever since coatings were applied to substrates and needed to be removed in cases of poor application. The earliest procedures involved simple reversal of the deposition process, partly in order to regenerate the deposition solutions and partly on the simple principle that electrodeposition was a reversible electrochemical process. The concept of such simplicity was soon dispelled and simple solutions were devised to dissolve the coating as effectively as possible without too much concern for solution regeneration but some concern for simplicity and minimal cost.

The drive for stripping has always been related to recovering the substrate for re-coating, a concern especially important for high value components usually due to intricate machining or other manufacturing procedure or to the intrinsic value of the substrate material, typically a valuable alloy. In contrast, low value components, for example steel wire nails or screws, may well be sent for re-melting unless a large batch exists which can be processed as a batch making the batch the unit of cast rather than an individual nail.

The inadequacy of the coating may be due to a number of reasons which can be identified in the normal procedures of quality measurement or inspection.

- Poor surface finish, typically brightness or appearance
- Poor deposit uniformity
- Poor surface coverage or inadequate thickness
- Edge roughness and other high current defects
- Poor adhesion – associated with poor substrate preparation.
- Poor appearance due to staining/tarnishing not solved by rinsing

The component is then subjected to preparation and pre-treatment appropriate to the identified defect. It should be noted that if deposition in a recess was difficult requiring specialist jiggling or agitation, its stripping may be equally challenging.

The stripping process should be as selective as possible, ie. it will dissolve the coating with little or no attack of the substrate. Fortunately, simple acid formulations can cope with many common coating/substrate combinations and these were identified many years ago. To be more selective the solutions exploit complexing agents to promote coating dissolution and inhibitors to reduce or prevent substrate attack. A number of advanced chemical techniques are available but have been little used because of increased cost and the present formulations have in many cases been in use for many years. However, new coating technologies have recently caused some new developments to be invoked and the design of a stripper solution will be considered later in this paper.

It was noted that reversing the deposition process avoids the need for recycling of used stripper solutions. The need to recycle, however, is essential for the precious metal coatings – gold, silver, palladium, rhodium etc. This is often left to specialist contractors or to the metal suppliers as part of the purchasing agreement.

PRINCIPLES

The principle of a stripping solution is to identify a simple and cheap acid or alkali which dissolves the coating and not the substrate. This usually targets sulphuric and nitric acids and precludes hydrochloric and hydrofluoric acids because the latter are oxidative making dissolution faster and simultaneously passivates steel and copper alloys (the commoner substrate metals) and chloride/fluoride ions promote depassivation and consequently promote substrate attack.

If an alkali is needed, typically for the amphoteric metals aluminium, tin and zinc, the choice is primarily between sodium carbonate (weaker alkali) and hydroxide (stronger). The equivalent potassium salts may sometimes be technically superior because of increased solubility but are less-favoured because their cost is often twice that of the sodium version.

Having identified the acid or alkali, a preferred concentration must be chosen. Often the more concentrated solutions work faster but not always because an acid like nitric has a dual role to offer being both an acid and an oxidant and their relative importance changes with concentration. Furthermore, higher concentrations can lead to greater losses due to drag-out and this has cost implications through both loss and neutralisation. A better way of accelerating dissolution rates is to use agitation and to increase temperature by heating but not beyond the point where heat losses and evaporation are unacceptable.

The use of complexants and inhibitors is a specialist field. However, if the complexant used in electrodeposition is available it can probably be used in stripping. Thus cyanides in alkali solution are commonly used. Some cheap inhibitors are available notably silicate and phosphate for alkali solutions but they can have

disadvantages such as leaving a residual film on the surface which may interfere with the recoating steps.

In principle any stripper solution can be calibrated but in practice there are so many variables – age of solution, concentration, agitation and temperature used, work area to solution volume ratio – that an estimate of the stripping time for a given thickness is the best that can be expected. However, it is useful to note the times as an indication of the solution's aging in the context of replenishment or replacement. If an unstable additive is used, eg. hydrogen peroxide, the amount being added for a specific job needs to be calculated and its performance diminishes as the oxidant is depleted. The study by O'Grady for stripping nickel from steel is instructional.

Amongst recent developments are a number of attempts to use more advanced oxidant chemicals and organic oxidant accelerators. Only one or two of these have found regular use either because the advantages are marginal or their cost is considered to be prohibitive. Nitrobenzene, and its nitro-aromatic analogues, is one such chemical. Ecological considerations have further driven developments away from the traditional 'nasty' chemicals which include of course cyanides, nitrates and ammonia which inevitable are amongst the more versatile chemicals for stripping!

EXAMPLES

This paper is not intended to give an exhaustive listing of all recommended metal strippers in current use. For a full review more specialist commercial listings are recommended but the following examples will serve to provide tried and tested methods and will illustrate the principles discussed above.

The option always exists to use chemical (CS) or anodic electrochemical (ES) stripping methods. In a few cases one is strongly preferable but in most cases it is a matter of practical convenience, a consideration of which usually leads to chemical dissolution which generally requires less labour-intensive management and control and of course no electrical connection.

Cadmium on steel

CS. Conc. HCl containing 16g/l SbO_3 or SbCl_3 .

CS. 130g/l NH_4NO_3 solution.

Chromium on copper

CS. 10-20% HCl v/v at 20-50°C

Chromium on nickel

CS. 10-20% v/v HCl at 20-50°C

ES. 45-90g/l NaOH at ~6V

ES. 50g/l Na_2CO_3 using 5-10 A.dm²

Chromium on steel

As for Cr on nickel

Copper on steel

CS. 500g/l CrO_3 + 50g/l H_2SO_4 at 20°C

CS. 60g/l nitroaromatic reagent + 15-g/l NaCN + 20g/l NaOH at 60°C

ES. 250g/l CrO_3 at 5 A/dm² at 20°C

Copper on zinc

ES. 120g/l Na₂S at 2V

ES. 220g/l CrO₃ + 2g/l H₂SO₄ at 20°C and 10 A/dm² alternating current

Copper-zinc (brass) on steel

CS. 62.5% v/v NH₄OH + 37.5% v/v 100vol H₂O₂ at 20°C

CS. 37.5% v/v NH₄OH + 75g/l (NH₄)₂S₂O₈ at 20°C

ES 190g/l NaNO₃ at 2 A/dm² at 20°C

Gold on copper

ES. 15g/l KCN + 10g/l Na₂CO₃ + 50g/l K₄Fe(CN)₆ at 60°C and 6V

Gold on nickel

CS. 120g/l NaCN at 20°C. H₂O₂ (100 vol) is added cautiously when stripping is to be commenced; overheating and foaming must be avoided.

ES. 90g/l NaCN + 15g/l NaOH at 20°C and 6V.

Lead on copper

CS. conc HNO₃ + 300g/l NH₄F₂ + 125g/l H₂O₂ at 20-40°C.

ES. 70-100g/l NaOH + 50g/l Rochelle salt at 20-80°C and 2-4V with steel cathodes

Nickel on steel, copper, zinc

CS. Conc. HNO₃

CS. (zinc only) 50% H₂SO₄ at 60-70°C

CS. (steel only) 60g/l nitroaromatic reagent + 150g/l NaCN + 20g/l NaOH at 60-80°C

ES. 60-90% v/v H₂SO₄ + 30 g/l glycerine at 6V or 10-15 A/dm² at 20°C

ES. 550g/l NaNO₃ at 10 A/dm² and 95°C

Electroless nickel (Ni-P)

CS. 60g/l nitroaromatic reagent + 120g/l ethylenediamine + 60g/l NaOH at 75°C

Rhodium on nickel underlayer

ES. 50% v/v H₂SO₄ at 7V at 65°C – dissolves both Rh and Ni

Silver on brass

CS. 95% H₂SO₄ + 5% HNO₃ v/v at 80°C

Silver on steel

ES. 30g/l NaCN at 4-5V

Tin on copper

ES. 120 g/l NaOH anodic at 20°C

Tin on steel

CS. Conc. HCl containing 16g/l SbO₃ or SbCl₃

CS. (removes copper underlayer) 30g/l nitroaromatic reagent + 120g/l NaOH at 80°C

Zinc on steel

CS. Conc. HCl containing 16g/l SbO₃ or SbCl₃

ES. 100 g/l NaOH at 2 A/dm² and 20-40°C

SOLUTION DESIGN.

As has been indicated some general principles for solution design can be defined. Three types of component are required.

1. An acid or alkali solvent usually having oxidative character to promote dissolution of the coating preferentially to the substrate and which may also passivate the substrate.
2. A complexant to promote preferential dissolution and to increase the solubility in solution and promote solution longevity.
3. An inhibitor to minimise attack of the substrate.

Not all components need be present and a well-chosen formulation may be successful with just one, eg. nitric acid. While many reagents are known to be effective, cost can often be an overriding factor eliminating some reagents from consideration.

In many cases an unique chemical characteristic can be exploited. Thus it might be expected that chromium would be difficult to strip but in fact because its corrosion resistance is due to passivity not nobility a solution which attacks the passivity can be remarkably effective. Such a solution is warm dilute hydrochloric acid although over-stripping of chromium on nickel or steel must be avoided otherwise pitting of steel occurs or nickel is also stripped. In this case antimony salts are often employed as inhibitors for steel attack once the coating has been removed. Copper alloys are safe. An alternative for steel is anodic dissolution in dilute caustic solution.

Such use of anodic currents can be scientifically advantageous but technologically inconvenient. Thus it is possible to enhance dissolution and eliminate the use of an oxidant additive as well as control the anodic potential to minimise substrate attack. However, careful control may be needed. By contrast, chemical stripping may be slower but can often be left without constant attention. Speed is not of the essence and low currents are often safer to minimise substrate attack once the coating is partially removed.

Process enhancement must be carefully carried out as chemical accelerators can produce undesirable side reactions notably attack of the substrate. If the commencement of attack is slow activators may be helpful particularly for passive surfaces. Otherwise the following are usually safe:

- Heating to increase temperature to 60-70°C above which evaporation may be a risk.
- Agitation to increase mass transport. If oxidants are involved air or oxygen agitation may be considered.
- Use of anodic currents.
- Optimization of pH especially if solutions become seriously depleted.

Selection of an oxidant can be based purely on the oxidising capability which in a broad sense is related to cost – the strongest oxidants are the most expensive. Such a rule of thumb must be tempered by the identity of the anions and the metallic element involved.

The two obvious oxidants are nitric acid and hydrogen peroxide. The former is both acid and oxidant and can also passivate steel and copper alloy substrates but gives rise to serious fuming. The latter is relatively unstable and spontaneously decomposes both in solution and in store; however, it can be used to activate a solution by just adding enough to complete a component strip after which the solution can be allowed

to lat dormant until a further use is required. So regular supply and solution additions are required. A fuller list is given in Table 1.

TABLE 1. OXIDANTS SUITABLE FOR STRIPPING SOLUTIONS.

INORGANICS	ORGANICS
Ferric chloride	Nitrobenzene, nitro benzoic acid
Ceric sulphate	Nitrochloro benzene
Hydrogen peroxide	Nitroaniline
Nitric acid	Nitrophenol
Chromate or dichromate	Nitrophthalic acid
Chlorate or perchlorate	
Hypochlorate	
Bromates or iodates	
Permanganate	

The common complexants are those widely used in electroplating solutions because they are largely required to carry out a similar function ie. promote solubilisation of the metal concerned. It is well-known that cyanide is probably the most versatile complexant in this context and must be used in an alkali solution to maintain toxic safety. This however is adequate to enable its use for several metals including Cd, Zn, Cu, Ni Au, Ag etc.

TABLE 2. COMMON METAL COMPLEXANT RADICALS.

Cyanide, hydroxyl, ammonia/ammines
 Pyrophosphate
 Sulfite, thiosulfate
 Carboxylic acids: oxalic, citrate, tartaric, gluconate, heptonate, glycollic

Inhibitors are both metal and pH sensitive. Consequently to list general-purpose inhibitors is difficult if not misleading. However, some of the common radicals which find use for more than one metal include silicate and metasilicate, phosphate and phosphonate, chromate, borate, sulphide.etc. Organic reagents include amines for steel substrates and mercapto- benzo-thiazole for copper substrates. Obviously, environmental and toxic considerations cause several to be avoided including arsenic and antimony salts for steel and now chromates for several substrate metals.

EFFLUENT DISPOSAL

By their very nature stripper solutions are corrosive and toxic and are not suitable for recycling into primary processing solutions as if a dragout or rinse.. Furthermore, the use of complexants ensures that precipitation of metals from solution is inhibited. A multi-stage treatment is usually followed during which attempts are made to mix the acid and alkaline streams of the factory to attain neutrality. The stages may include:

- Neutralisation of the acids and alkalis
- Destruction of cyanide with hypochlorite or similar treatment
- Decomposition of amines by oxidation
- Reduction of hexavalent chromates by reduction with bisulfites or similar
- Precipitation of each metal at optimal pH, from 8-11 using lime and caustic alkali.

Specialist disposal companies may be employed if recovery of metal is desirable for which it is always vital to know the chemical make-up of the solution.

FUTURE CHALLENGES.

The practice of metal stripping has been remarkably static for many years because while improved formulations using, for example, organic oxidants have become available cost has precluded their widespread use because stripping is perceived as a 'necessary evil' in coating businesses. But with the increasing use of high technology coatings in the ceramic and refractory metal area, produced in general of course by non-electrochemical processing, the use of chemical metal strippers still exists because PVD processes cannot provide *own technology* reversal. Thus the challenge is to coatings based on carbides, nitrides, borides, silicides etc.

Two examples have recently been documented in the literature. Sen et al have described the stripping of CrN from coated high speed tool steels prior to re-sharpening etc. Anodic stripping in 100g/l NaOH at 6V anodic current was effective and likened to removing Cr coatings. They also considered the stripping of CrN from titanium, when the attack on Ti by alkali has to be considered and found to be unacceptable, and analogous behaviour for TiN coatings on high speed steel. In this last case chemical stripping in 80g/l NaOH containing 20g/l H₂O₂ was effective. It is thus apparent that the oxidative effect of an anodic current/voltage can be replaced by a chemical oxidant; if hydrogen peroxide is found to be too unstable an alternative such as KMnO₄ might be feasible.

FURTHER READING.

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