NICKEL PLATING:

SULFUR DEPOSITION IN BRIGHT DEPOSITS

ADVANTAGES AND DISADVANTAGES

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BRIGHT NICKEL PLATING

The development of nickel-plating baths that can produce a fully bright plate directly, without the necessity of buffing, has completely revolutionized the practice of decorative nickel plating (including decorative/protective nickel-chromium systems). The objections to buffing are principally economic. For this reason the advent of “bright nickel” was eagerly accepted by the trade, and “buffed Watts” is now essentially obsolete in decorative nickel plating. Early bright nickel deposits sacrificed a considerable degree of corrosion performance, but later developments in “duplex” nickel plate and microdiscontinuous chromium have rendered modern bright nickel systems equal in performance to buffed Watts.

The earliest brightners were inorganic cations, especially cadmium with cobalt, formaldehyde and formate versions following. Almost all present day formulations rely on organic additions to the Watts bath and are proprietary in nature. The current systems use a combination of organic addition agents for best results.

BRIGHTNERS

Nickel brighteners fall into two classes. Those designated as Class I brighteners include aromatic sulfonic acids, sulfonamides, and sulfinic acids. The aromatic rings attached to these groups are usually benzene or naphthalene rings, but may also be various unsaturated aliphatic groups such as vinyl or allyl. These brightners produce almost bright (hazy or cloudy) plate but cannot “build” brightness as plating proceeds. The concentrations of these additives are not critical; they are used in relatively high amounts, 1 to 10 g/L, without much effect on adhesion and limiting current density. They trend to decrease the tensile stress of the deposit and at higher concentrations can even turn the stress compressive. They introduce sulfur into the deposit, in amounts up to about 0.03 percent at a pH of 3 to 5, when used in warm baths without Class II brighteners.

Class II brighteners are used in combination with those of Class I to produce fully bright, brilliant, and leveling deposits, the luster of which increases with continued plating up to the maximum obtainable (they build brightness). They are usually unsaturated organic compounds, of many types. They introduce carbon or carbon-containing material into the plate. Most Class II brighteners must be used in conjunction with a Class I additive; if used alone, they produce brittleness and tensile stress, as well as inferior adhesion to the substrate.

The most effective Class II brighteners are organic compounds containing such unsaturated groups as aldehyde $H\text{--}\overset{|}{C}\text{==}O$, as in formaldehyde $H\text{--}\overset{H}{\overset{|}{C}}\text{==}O$; the olefinic --C==C-- group, as in coumarin the C≡C linkage, as in butyne diol. These are only a few of the typical groups found in Class II brighteners, almost all of which are the subject of patents and are sold under proprietary names.

These compounds are reduced at the work piece surface along with the nickel metal resulting in their decomposition and the co-deposition of sulfur and carbon into the deposit. It is this co-deposition that is responsible for many of the objectional properties of bright nickel deposits. The literature reports sulfur up to approximately .05% $^{W}/_{W}$ and carbon to 0.1% $^{W}/_{W}$.

CORROSION PROPERTIES

All metals have an “intrinsic” property of corroding relative to one another (battery effect: two dissimilar metals in intimate contact with each other and an electrolyte). This property is best described by the “Electromotive Force Series” where each metals potential to corrode relative to a standard (Hydrogen) is measured and reported as a voltage. For example:

Metal	Voltage
$Zn \leftrightarrow Zn^{+2}$	-.762
$Fe \leftrightarrow Fe^{+2}$	-.441
$Ni \leftrightarrow Ni^{+2}$	-.250
$H_2 \leftrightarrow H^{+}$	0.000
$Au \leftrightarrow Au^{+3}$	+1.50

Metals above another on the list corrode in preference to it. Thus zinc coated iron is a favorable couple since zinc corrodes in preference to the iron thus protecting the structural basis metal iron. Notice that for nickel on iron the situation is reversed where iron will corrode in preference to the nickel. Thus nickel will protect an iron substrate (i.e. there is no iron exposed) only by sealing it. The deposit must be free of voids and cracks. If a discontinuity develops the basis metal, iron, corrodes first generally by deep and severe pitting.

The addition of sulfur and carbon to a nickel deposit shifts the voltage in a more positive direction thus making the potential difference greater. This results in a more severe and rapid corrosion. In addition a deposit which is under tensile stress, is more likely to crack will provide the discontinuity for the corrosion site. It is these two reasons

- smaller potential difference in the electromotive series

- less likely cracking of the deposit

that often leads design engineers to specify a sulfur-free nickel deposit (watts or sulfamate) in a system where nickel is desirable but brightness not a criteria. This is very common in the electronic industry where gold is plated over sulfamate nickel.