The 9th William Blum Lecture
Presented at the 55th AES Annual Convention in San Francisco, California,
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Addition Agents, Anions and Inclusions in Bright Nickel Plating

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ABSTRACT

The mode of action of the unsaturated organic addition agents used to produce semi-bright, sulfur-free nickel and sulfur-containing bright nickel is considered from the point of view of their molecular structure and the lattice structure of the nickel surface acting as a hydrogenation catalyst. The possible mechanisms of hydrogenation are outlined. The relationship of various anions, boric acid, carboxylic acid buffers and the pH of the bath to the effectiveness of the addition agents is discussed. The role of molecular inclusions derived from the addition agents is considered for single and multiple-layered plates, as well as the role of inclusions deliberately codeposited as fine non-conducting particles with the nickel to obtain maximum corrosion resistance with minimum thicknesses of nickel in decorative copper-nickel-chromium plating.

The use of organic compounds as addition agents in aqueous electroplating baths is a fascinating field, owing mainly to interesting and important effects produced on the growth and structure and thereby on the character of the deposit by very low concentrations of the additives in the bath. The striking effects on electrocrystallization processes of small concentrations of addition agents point to their adsorption on a high energy surface and deposition on growth sites, thereby producing a poisoning or inhibiting effect on the most active growing sites. It is for these reasons, "the effects seem to be out of proportion to their concentration in the solution."[1]

In this paper, the unsaturated organic addition agents which produce semi-bright and bright nickel plate will be discussed with respect to their molecular structure, and the adsorption, hydrogenolysis and hydrogenation reactions which take place with the freshly depositing nickel acting as catalyst. The effect of the addition agents on the corrosion resistance of the nickel plate with and without the usual thin final chromium plate will be detailed from the standpoint of the nature of the inclusions incorporated in the plate from the additives and from the changed structure of the plate, as well as from purposeful inclusion in the plate of multitudinous very fine dispersed non-conducting particles.

The key to modern bright nickel plating was the discovery of the conjoint use of an organic "carrier" brightener with an auxiliary organic compound (critical in concentration compared to the carrier) that produced brightness and leveling in their conjunctive use. In 1936, the commercial use was started of an aromatic sulfon-compound (p-toluene sulfonamide) together with an unsaturated aldehyde as the brightening system in a Watts nickel bath. By 1940, it was recognized that unsaturation was an essential characteristic for the effectiveness of the aromatic sulfon-compounds (sulfonamides, sulfonimides, sulfonic acids), and also for the effectiveness of the auxiliary cooperative brilliancy-imparting agents (later called leveling agents) in the production of brilliant, ductile, leveling nickel plate from weakly acidic nickel plating baths (see the Appendix).

The carrier nickel brightener which is invariably anionic (through the presence of sulfonic, sulfonamide, sulfonimide or sulfinic groups) and which is practically non-critical in concentration will be considered in relation to its conjoint use with leveling brighteners. The latter are often cationic or if seemingly not at first glance, have a functional group which can be polarized in the cathode film to produce an electron deficient (therefore relatively positive) atom in its structure. These leveling agents if strongly cationic are critical in concentration and cannot be used alone in the bath, but if very weakly cationic in nature are less critical in deleterious effects on ductility and adhesion while still producing optimum leveling effects, and certain ones may be used alone for semi-bright nickel plate. Thus, it has been interesting to study single addition agents of each class, but even more so, the

cooperative effect of two or more additives from each class. This resulted in the finding that an organic addition agent with one type of functional group can cause an increase or a decrease in the codeposition of another organic addition agent with a different functional group. These cooperative effects are not only very important for obtaining maximum brightness and leveling with minimum loss of ductility, adhesion and other important properties, but as will be seen, by full utilization of combinations for their individual good points in multiple-layered plate, have made possible maximum corrosion resistance with minimum thicknesses of nickel plate. The mode of action of the brighteners for acidic nickel baths will be considered not only in terms of the molecular structure of the organic addition agents but also in relationship to the anions, buffers and the pH of the bath. These factors affect the adsorption characteristics of the organic compounds with respect to the metal deposit because they affect the structure of the double layer. For example, the unsaturated carbon-to-carbon linkage may be considered to be, when undisturbed, non-polar. However, the π-electron cloud of the unsaturated bond can become polarized in the strong field of the electric double layer. This polarized bond, or activated linkage, can then be attacked by hydrogen ions, (Fig. 1) as well as have its adsorption characteristics modified by an extremely thin (perhaps monomolecular) nickel hydroxide membrane forming across the cathode surface during the nickel plating. This will be further discussed under leveling agents.
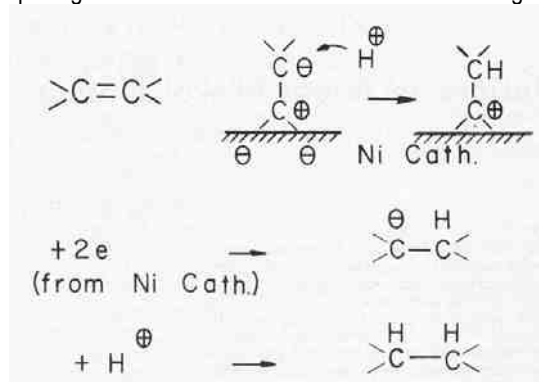

Figure 1 - Possible mechanism of hydrogenation of unsaturated bonds in the cathode double-layer. The normally non-polar

$$\overset{\backslash \quad /}{\underset{/ \quad \backslash}{C = C}}$$

bond is polarized in the strong electric field and is adsorbed. Hydrogenation proceeds by electron transfer from the cathode and hydrogen ion addition as shown. See Burton and Ingold, *J. Chem. Soc.*, p. 2022 (1929), for discussion of the mechanism of hydrogenation of unsaturated compounds with a metal and acid.

Brief review of the past

Probably the first addition agent ever used in plating was, surprisingly, carbon disulfide in alkaline silver cyanide baths in 1847 in England.[2] Another old and very important and versatile addition agent is glue which has had widespread use starting around 1900 in electrorefining, (acid lead and copper baths) and electrowinning (acid zinc and cadmium baths) and is an example of one of the most successful uses of an organic addition agent in electroplating. Its important technical effects led to many early studies[3] on the effect of gelatin (glue) on cathode polarization, cathode efficiencies, increased smoothness and densification of the plate and minimization of nodular growth and treeing (dendritic growth).

Of the early papers on addition agents one of the best and, most perceptive was that of J.A. Henricks,[4] who in 1942 saw the importance in a brightening mechanism of an organic addition agent working in conjunction with an inorganic colloid (hydroxide formed) in the cathode film. He also classified anionic and cationic brighteners and was the first to point out that corrosion inhibitors could function as brighteners through an adsorption mechanism probably similar to that which often occurs during the corrosion inhibition process with the same inhibitor. He also mentioned that the inhibiting effect in plating would be toward restricting or hindering the perpendicular grain growth of the depositing metal. This does not mean, of course, that the best inhibitor for the acid corrosion of iron would necessarily be the best nickel or iron plating brightener, but was suggested as a guide to the selection of materials for initiating studies.

In the early development of addition agents for bright nickel,[5] the work of Schlotter in Germany, of Pine and Lind at Harshaw, of Weisberg and Hinrichsen was very important in the commercial growth of bright nickel plating during the years 1934-40. The

work of Clifton and of Waite and Martin[6] on suitable surfactants for anti-pitting agents in nickel plating was also of great importance. The use of bright nickel plate in 1940 before the second world war broke out was very widespread, but during the war bright nickel plating practically vanished. After the end of the war in 1945, there was a very rapid expansion of bright nickel plating, and the addition agents that made it possible began to receive attention from many workers. As is now very well known,[7] the work of Edwards on the mode of action of addition agents in nickel plating has been outstanding as has been the work of Gardam, Watson, DuRose, Kardos, Fischer, Raub, Beacom, Trivich, Rogers, Ibl, Epelboin, Kruglikov and their co- workers. Kardos[7] and also Ibl[7] have recently definitively reviewed the great mass of work in this field. The fate of an adsorbed addition agent depends on the pH of the nickel bath as well as on other entities, buffers for example. At bath pH values of about 1.5, Rogers and Taylor[7] have shown that the leveling type of addition agent is reduced to a species different from that formed at pH values of about 4.5. The percentage of inclusion in the nickel deposit derived from the addition agent also depends on the pH of the bath, as does the leveling.

It was known before 1941 that sulfide sulfur[8] was present in the nickel deposits from baths using aromatic sulfon-compounds, and it was also known that carbonaceous material was present in the plate from non-sulfur containing brighteners.[9] With the discovery that unsaturation was a very significant characteristic of the structure of the compounds which produced brightness or leveling, it was logical to assume that the freshly depositing nickel was probably functioning as a hydrogenation catalyst similar to Raney nickel. Thus, the possibility existed of reduction of oxygen-containing groups such as the aldehyde group as well as hydrogenation and hydrogenolysis reactions.

With the realization that the depositing nickel was functioning as a hydrogenation catalyst,[10] the question occurs concerning "active catalytic sites" on the cathode surface. In the study of formed or prepared nickel catalysts, the old idea of "active sites" was always mentioned, and these sites are now better understood to be lattice distortions and imperfections, such as edge dislocations, screw dislocations, point defects such as vacancies, the presence of interstitial atoms, etc. There is also the fact that one face of a nickel crystal may be much more catalytically active than another due to its different lattice spacing. The latter is also controlled by electronic factors such as the partially filled d-bands, that is, by the vacant atomic d-orbitals present in nickel. Films of nickel which preferentially exposed (110) type planes were found by Beeck, Smith and Wheeler[11] to be five times as active in vapor-phase hydrogenation of ethylene as non-oriented films which were considered to be composed of approximately equal amounts of (100), (110) and (111) type planes. The (110) planes in crystallites of nickel contain the 3.51 Å spacing which presumably would result in a lower heat of adsorption for the ethylene (the C = C bond distance is 1.34 Å) than on the 2.48 Å spacing. Thus, the 3.51 Å lattice spacing would have higher catalytic activity for hydrogenation of aliphatic carbon-to-carbon unsaturated bonds. Whether the hydrogenation of double or triple bonds during nickel plating proceeds by attack by atomic hydrogen at the cathode surface (Fig. 2), or by hydrogen ion attack of the unsaturated bonds polarized in the strong field of the electric double layer, or both, is not determined.
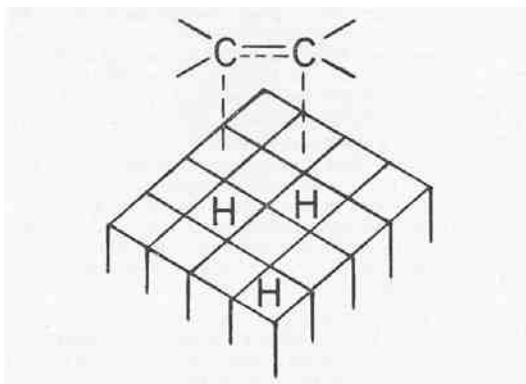

Figure 2 - Possible mechanism of hydrogenation of an adsorbed unsaturated linkage by atomic hydrogen dissolved in the nickel cathode or by nickel hydride. The dashed lines indicate π-electron bonding. However, since electrons and protons are involved in the cathodic reduction, the question of whether the addition of the electrons from the nickel cathode is directly to the adsorbed polarized highly electron-conducting unsaturated molecule (Fig. 1), or first to the hydrogen ion forming atomic hydrogen or hydride ion (if two electrons are added) for the reduction step, is not easily answered.

At the low pH value of the nickel bath of 1.5, Rogers and Taylor[12] found that the unsaturated compounds, propargyl alcohol, butyne diol and coumarin, yielded different hydrogenation products from those formed at a pH value of 4.5. Hydrogenation went farther at the low pH value. For example, with propargyl alcohol at a bath pH of 1.5, the reduction went very close to 100% propane, whereas at pH 3.0 about 20% is reduced to propane and the balance may be mostly propyl alcohol. Perhaps the aliphatic unsaturated carbon-to-carbon bonds are hydrogenated mainly on the 3.51 Å lattice spacing at pH values of 4.0 to 5.0. At these bath pH values there seems to be good evidence for an extremely thin nickel hydroxide membrane cyclically forming across the cathode, modifying the adsorption characteristics. In contrast, at bath pH values of around 1.5 where the leveling practically disappears, the cathode surface doesn't have this thin nickel hydroxide membrane across it or across the growth sites, or where the hydrogen ion is being discharged. Under these conditions the unsaturated compounds could adsorb on the 2.48 Å lattice spacing where they would be held much more strongly, and electrons from the cathode could then rapidly pass into the activated conducting chain, and reduction of the carbonyl group of adsorbed coumarin, and alcohol groups of propargyl alcohol and of butyne diol could take place. That is, the absence of a thin nickel hydroxide membrane at the lower pH values would favor a "cleaner" or more active cathodic nickel surface. Adsorption would then predominate on the 2.48 Å lattice spacing, and with the presence of higher concentrations of hydrogen ions at the low pH values, reduction proceeds extremely rapidly to other groups and to farther steps.

The knowledge derived by physicists of lattice array and imperfections has helped the understanding of catalytic activity and of catalyst promoters, and has greatly aided in understanding crystal growth and thereby electrocrystallization,[13] even if it has not very often led to the production of better solid catalysts. It has helped to better understand trace catalyst poisons, and in electrocrystallization it has provided clues to why very low concentrations of addition agents can very markedly influence plate appearance, by adsorbing or codepositing on growth sites. In recent years, great progress has been made in the field of homogenous catalysis dealing with transition metal ions coordinated with unsaturated compounds. For example, olefins may be catalytically hydrogenated by transfer of hydrogen from a hydrido-transition metal complex.[14] Actually, at the nickel cathode there may not be too great a difference between a heterogeneous catalytic action and a homogenous one in that the surface of the nickel cathode may be hydrated, hydroxylated or solvated at least partially like an ion. While this limited comparison may have little value, nevertheless the data obtained from commercial hydrogenation studies with nickel catalysts are helpful for nickel plating, because in some cases parallel interpretations can often be made for the hydrogenation of the unsaturated organic addition agents in nickel plating. Radioactive tracer and gas chromatography work have greatly helped to trace the fate of some of the organic addition agents, and especially important is the very well-known work[15] of Rogers and Taylor, Edwards and Levett in England and Trivich, Beacom, Riley and Doty in the U.S.A.

The organic sulfon- and sulfin-compounds
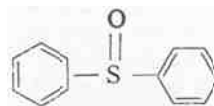
The "carriers" are always anionic. For example, (di) phenyl sulfoxide which is weakly cationic in the nickel bath (in the sense that it is weakly basic and can add on a strong acid) is not a carrier. At saturation concentrations (about 0.5 g/L) in the warm Watts bath it causes brittle semi-bright, poorly-adherent nickel plate containing 0.2% sulfur. Phenyl sulfone is only very slightly soluble in the Watts bath (about 0.3 g/L) and only about 0.006% sulfur is found in the nickel plate which remains dull, ductile and of good adhesion. If instead of one of the phenyl groups of phenyl sulfoxide, an -OH group is present, then we have an excellent anionic carrier brightener, benzene sulfinic acid.

The benzene and naphthalene sulfonic acids (mono-, di- and tri-sulfonic acids) in Watts baths or in low all-chloride baths, 100 g/L $NiCl_2 \cdot 6H_2O$, produce grain refinement, with inclusion in the plate of a nickel sulfide. The naphthalene sulfonic acids are more effective than the benzene derivatives and produce more luster than the benzene sulfonic acids. They produce fine-grained, cloudy, almost bright nickel on highly lustrous surfaces such as buffed brass. The presence of chloro and especially bromo groups on the aryl rings increases the effectiveness of the compounds, especially for benzene sulfonic acid, which normally would require 15 g/L for maximum effectiveness. Benzene and toluene sulfonamide are more effective with lower concentrations, (1.0 g/L) than the corresponding sulfonic acids. Naphthalene sulfonamides have low bath solubility, and also the tendency of naphthalene derivatives to give less ductile plate than the benzene sulfon-derivatives is more manifest with the sulfonamides. These aryl sulfon-compounds are not sufficiently effective in high chloride baths (over 150 g/L $NiCl_2 \cdot 6H_2O$) to produce brightness. The concentrations of all these sulfon-compounds are not critical, saturation values can be used, that is, after a certain degree of grain-refinement and brightness is obtained, further large increases in concentration produce only very
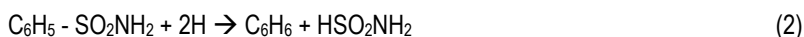
small effects. This brightening process is not very significantly pH-dependent in the range of about 2.0 to 6.0. There is some temperature dependence when the baths are hotter than about 80°C, which varies with the type of un-saturated sulfon-compounds.[16] The beta-unsaturated sulfonic acids, 2-propene-l-sulfonic acid and 2-propyne-l-sulfonic acid, do not lose as much of their brightening action at the higher temperatures compared to the aryl sulfonic compounds. The effect of pH of the bath on the sulfide sulfur content of the nickel plate with the alpha and beta unsaturated aliphatic sulfonic acids present in the bath is in the opposite direction compared to the simple aryl sulfon-compounds. With the latter, decreasing the pH from 5.5 to 2.0 causes an increase in sulfur content of about 0.03 to about 0.04% at bath temperatures of about 60°C, whereas with the alpha and beta unsaturated sulfonic acids, the same decrease in pH causes a decrease in sulfur content. The decrease may be from about 0.06 to about 0.01% sulfur and depends on the structure of the various alpha and beta unsaturated sulfonic acids. The variation of the sulfur content of the plate with concentration of sulfon-compound in the bath follows closely the form of an adsorption isotherm. Carbonaceous material in low percentage is also usually found in the plate, but it is also usually found in nickel plate from the plain Watts bath. The latter needs to be checked with the Watts bath in the complete absence of CO_2. The best evidence indicates that if carbon is present from these benzene and naphthalene sulfon-compounds, it is present in very small amounts. However, in the case of the beta unsaturated aliphatic sulfonic acids as the only brightening additive, both sulfide sulfur and carbonaceous material are found in the plate.[17]

After electrodeposition of nickel has proceeded for several hours with the aryl sulfon-compounds present in the bath, the odor of free benzene and naphthalene can easily be detected from the baths containing the corresponding sulfon-compounds.[18] The evidence for the hydrogenolysis of the aryl sulfon-compounds at the nickel cathode is clear. That is, benzene (or naphthalene) and sulfurous acid (or its nickel salt) are probably first formed by hydrogenolysis at the nickel cathode and the sulfite ion or nickel sulfite is there reduced to sulfide. In the case of benzene sulfonamide, hydrogenolysis would yield, beside benzene, transitory amidosulfinic acid. Benzene sulfinic acid would yield transitory sulfoxylic or its nickel salt. These steps would be followed by reduction of these unstable acids or more probably their nickel salts to nickel sulfide. The hydrogenolysis reactions in their simplest forms would be as follows, with the benzene sulfinic acid the easiest to reduce and the benzene sulfonic acid the most difficult:

Hydrogenolysis at the nickel cathode

$$C_6H_5 - SO_2OH + 2H \rightarrow C_6H_6 + HSO_2OH \qquad\qquad (1)$$

$$C_6H_5 - SO_2NH_2 + 2H \rightarrow C_6H_6 + HSO_2NH_2 \qquad\qquad (2)$$

$$C_6H_5 - SOOH + 2H \rightarrow C_6H_6 + HSOOH \qquad\qquad (3)$$

The hydrogenolysis does not affect the unsaturation of the benzene ring. The $C-S^+$ bond is activated by the oxygen atom and the π-electrons of the aromatic unsaturated linkage in alpha position to the sulfur of the sulfon- and sulfin-group. This alpha unsaturation is, however, part of three conjugated double bonds of the cyclic aromatic system. This involves six delocalized electrons (6 π-electrons) which make all bonds of the ring of the same length, thus stabilizing the ring by resonance; and this is apparently why the sulfur content of the plate from the aryl sulfon-compounds increases with lower pH values of the bath. At the lower pH, more hydrogen is available at the cathode, but for hydrogenolysis only. If the pH of the bath is lowered to about 0.5 (cathode efficiency about 70%), the brightening by the aryl sulfon-compounds is confined mainly to the lower current density areas. Bisulfite added to the Watts bath does not produce appreciable brightness even though by regulation of the concentration, exactly the same amount of sulfide can be included in the nickel plate as with an aryl sulfon-compound. This shows that mere sulfide inclusion is not the cause of the bright plate with the aryl sulfon-compounds. In fact, if about 1 g/L of sodium bisulfite, or sodium thiosulfate is added to the nickel bath about 0.65% sulfur is incorporated in the plate. With this high sulfide inclusion, unlike with high carbonaceous inclusion, there is no tendency for the plate to exfoliate. This may be due to the possibility that the nickel sulfide may, in part at least, be an alloy and have metallic conductivity. With the presence in the bath of 0.5 to 1.0 g/L of sodium bisulfite or thiosulfate, the brightening effects produced by the aryl sulfon-compounds as well as by other brighteners are almost completely eliminated.

Tests with sodium thiosulfate, in a concentration of about 0.03 g/L alone in a 200-L warm Watts bath, pH 2.5, often show a patch of brightness on a large smooth basis metal cathode that is similar to that produced by the aryl sulfon-compounds over the entire cathode. These patches of ductile bright plate may persist even in 25 to at least 75-μm thick nickel deposits, but these patches

of bright plate are in general fleeting and difficult to obtain in small scale plating tests. The above concentration of thiosulfate puts about 0.03 to 0.04% sulfur in the plate, similar to the percentage of sulfur included from the aryl sulfon-compounds. There is no evidence that the aryl ring of the sulfon-compound is hydrogenated at the cathode, nor are there any mercaptan-like odors on dissolving the nickel plate in hydrochloric acid containing a trace of platinic chloride.

If benzene sulfonamide is dissolved in water containing Raney nickel catalyst and also boric acid, the Raney nickel catalyst does not show the formation of nickel sulfide. It does show the formation of nickel sulfide when sodium bisulfite or sodium benzene sulfinate is added instead of benzene sulfonamide. Another interesting point is that the plain aryl sulfonic acids and sulfonamides do not produce bright plate in the high chloride acidic nickel baths. By introducing more strongly unsaturated groups on the aryl ring than just the aromatic unsaturation of the benzene and naphthalene rings, then brightness is also obtained in the high chloride baths. For example, o-benzaldehyde sulfonic acid, o-benzoyl sulfimide, p-vinyl benzene sulfonic, also p-cyanobenzene sulfonamide give brightness, but with the latter, the plate is very brittle. 2-propene-l-sulfonic acid, 2-propyne-l-sulfonic acid (0.3 g/L), 2-butyne-l, 4-disulfonic acid or 2-cyanoethane-l-sulfonic acid also give bright plate on polished surfaces in high chloride baths as well as in Watts baths. Pyridine-3-sulfonic acid (6.0 g/L) also gives bright plate. Thiophene 2-sulfonamide or 2-sulfonic acid at 0.3 to 1.0 g/L gives bright but very brittle plate from both Watts and high chloride baths, and the plate has a very high sulfur content, 0.4%. Benzene and toluene sulfinic acids, added as salts, also produce brightness in the high chloride as well as in the Watts baths in concentrations of about 0.1 to 1.0 g/ l. Also, they are unusual in that they produce bright ductile plate in straight acidic cobalt baths, though not in iron baths. When these sulfinates are used in straight acidic cobalt baths of the sulfate-chloride type similar to the nickel baths, then the brightening systems of the nickel baths can be used to give brilliant ductile leveling cobalt plate. Without the benzene or toluene sulfinates present, the acidic cobalt plating bath is more sensitive to the concentration of certain of the nickel brilliancy-imparting agents, and darkish plate is obtained. However, this is completely overcome with the sulfinate.[19] Nevertheless, rather high concentrations of cobaltous and ferrous ions may be present with the usual nickel brightening agent systems without impairment of ductility and brilliancy (actually there is an improvement of these properties) as long as at least about 60% nickel is in the plate.

With the beta unsaturated sulfon-compounds, carbonaceous material as well as sulfur is found in the plate, and a faint mercaptan-like odor is noticed on dissolving the nickel plate in platinized hydrochloric acid. When the pH is dropped to about 0.5, the nickel plate is completely dull and there is practically no sulfur in the plate. This is just the opposite of the aryl sulfon-compounds. It appears that, instead of hydrogenolysis, hydrogenation of the aliphatic unsaturated bond occurs predominantly at these low pH values. Pure saturated sulfonic acids do not have any appreciable effect on the properties of the nickel plate. For example, cyclohexane, ethane, propane and butane sulfonic acids do not put sulfur in the plate or otherwise noticeably alter the dull plate. The beta unsaturated sulfonic acids are in part hydrogenated to the saturated sulfonic acid and in part hydrogenolyzed at pH values of 3.0 to 6.0. If the unsaturated bonds in aliphatic sulfonic acids are present in gamma or more distant positions from the sulfonic group, no appreciable sulfur is found in the plate, and the type of brightness is not similar to the type produced by the beta unsaturated aliphatic sulfonic acids.[20] When the unsaturated bond is in gamma or delta position, and especially when an ether linkage is present between the unsaturated bond and the sulfonic group, then while the entire molecule can be classified as anionic, nevertheless the unsaturated aliphatic group can be polarized to a dipole in the electric double layer, while the rest of the chain with its sulfonic group is outside the electric double layer most of the time. The latter is about 3 Å thick[21] whereas the molecule may be about 8 Å or more in length. Aryl thiols (negative valent sulfur) show little tendency for cathodic C-S bond cleavage, also they do not produce appreciable brightness.

Omega sulfomethyl naphthalene (5.0 g/L) has slight brightening effects in the Watts bath, which is better than the corresponding omega benzyl sulfonic acid, showing again the weakness of the aromatic unsaturation due to resonance, and also showing that the 1, 2 positions on the naphthalene ring have slightly more double bond character. Of the plain aryl sulfonic acids, those of phenyl, biphenyl or terphenyl, are not as effective as those of naphthalene.

The role of the chloride ion in the cathode film has not been sufficiently studied. It does give a somewhat different nickel hydroxide precipitation curve with varying nickel chloride concentration compared to nickel sulfate. It probably is important in the hydration coordination of the nickel ion, forming such ions as $[Ni(H_2O)_5Cl]^{+l}$. The plain high nickel chloride baths (above about 150 g/L $NiCl_2 \cdot 6H_2O$) give much more brittle plate than the Watts bath, and this indicates some modification of the nickel hydroxide film formed at the cathode. Thus, the unsaturated compounds would compete with other adsorbed entities on the nickel cathode besides nickel hydroxide. However, a 100 g/L $NiCl_2 \cdot 6H_2O$ + 40 to 50 g/L H_3BO_3 bath gives a plate as ductile as from a Watts bath. Bromide ions in high concentrations give nickel plating results similar to sulfate rather than to chloride ions,

especially with respect to plate ductility. The fluoride ion, however, tends to eliminate the leveling caused by the unsaturated addition agents. This is probably due to the formation of a nickel fluoride film in the cathode layer which replaces or greatly modifies the thin nickel hydroxide film that normally forms. The nickel fluoride film apparently seriously hinders the adsorption of the unsaturated addition agents. There doesn't seem to be any strong evidence of any addition complexes forming in aqueous acidic solutions between unsaturated compounds and the nickel ion. What is more likely is that, in the cathode film where higher pH conditions prevail, periodic formation of an incipient thin nickel hydroxide film takes place which affects electron transfers and the adsorption and hydrogenation of the unsaturated organic addition agents.

Leveling agents

In low chloride Watts baths of pH about 3.8 to 5.5, beta-unsaturated esters of simple structure such as methyl acrylate, dimethyl fumarate, trimethyl aconitate, benzo alpha pyrone (coumarin) which contain the unsaturated grouping

$$- \overset{|}{C} = \overset{|}{C} - COO - \overset{|}{\underset{|}{C}} -$$
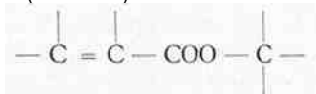
(Fig. 3) produce cloudy lustrous nickel plate with excellent leveling and ductility. With increasing concentration of beta-unsaturated ester or lactone, the luster and leveling increase at a remarkable rate without appreciable decrease of ductility or adhesion. With further increase of concentration (of the coumarin past 0.3 g/L and the esters beyond about 1.0 g/L) there is no further improvement of leveling. In fact there is a very noticeable decrease in leveling except in the high current density areas. Also, there is little change in ductility. All of these compounds have a limited solubility of about 2.0 g/L in the warm concentrated baths. They are the only unsaturated compounds which produce ductile, sulfur-free, high leveling plate when used alone in the Watts bath. These compounds decrease the grain size but not greatly, and the columnar structure of the Watts nickel is practically undisturbed even though carbonaceous material is found in the plate (0.06% carbon). It is interesting to compare methyl acrylate with allyl formate. The latter does not have beta conjugation of the double bond with the ester carbonyl group, and does not give comparable brightness. The low current density plate is brittle and darkish, and poorly adherent.
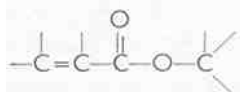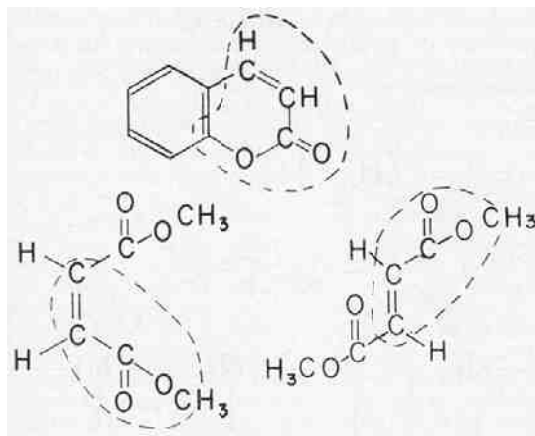

Figure 3 - The [structure] conjugated linkage present in coumarin, dimethyl maleate and dimethyl fumarate is responsible for producing high leveling, ductile, semi-bright, sulfur-free nickel plate from the Watts bath. The esters are not stable to acid hydrolysis; coumarin, however, is.

With the beta-unsaturated esters, the nickel plate loses its luster and leveling (except at the very highest current density areas) when the pH of the Watts bath is even a little below about 2.5. If the temperature of the bath is above about 70 or 80°C, the luster and leveling are also greatly decreased and the plate is about as dull as plain Watts nickel. If extremely vigorous agitation is used in the vicinity of the cathode, then at temperatures of 70 to 80°C and pH values around 2.5, the plate will be bright with only a trace of blue haze, but leveling will not occur. Dimethyl acetylene dicarboxylate acts similarly to dimethyl fumarate or maleate though it doesn't level as well at its optimum concentration, which is lower than for the maleate or fumarate. It also

hydrolyzes faster in the bath, and the free acetylene dicarboxylic acid is very harmful to the plate, much more so than fumaric or maleic acids (see the Appendix). Coumarin, with its beta-unsaturated lactone ring stabilized to acid hydrolysis through nucleation with the benzene ring and in resonance with it, has a fault that its main hydrogenation product, melilotic acid, as it accumulates in the bath, causes darkish brittle plate, especially in the lower current density areas. However, the melilotic acid can be readily removed from the bath by activated carbon, which is not true for the simple aliphatic carboxylic acids. Coumarin is weakly cationic in the nickel bath. It is very soluble in concentrated sulfuric acid.

When a benzene sulfon-compound is used in conjunction with the above beta-unsaturated esters or lactones, fully-bright, ductile, high leveling nickel plate is obtained. However, a higher concentration of the beta-unsaturated ester or lactone must be used with the sulfon-compound to obtain the same leveling as when the unsaturated ester or lactone is used alone. This is different than with most other unsaturated compounds when lower concentrations can be used conjointly with the aryl sulfon-compounds to obtain brilliance.[22] In nickel fluoborate baths, the leveling is greatly decreased whether the unsaturated esters are used alone or with the sulfon-compound. In the high chloride bath, used alone they cannot overcome the inherent brittleness of the nickel deposit from this bath when the pH is 3.0 to 6.0. With the addition of a sulfon-compound which produces bright, ductile plate in high chloride baths, then fully-bright, ductile, leveling plate is obtained, but the plate now contains sulfur. The exact nature of the carbonaceous inclusion in the plate from the unsaturated esters or lactone is not very well known. Whether during adsorption on the most active sites during the plating at bath pH values of about 3.8 to 6.0 some free radical formation occurs with rapid dimerization or polymerization[*] to a larger molecule, or whether the molecule is incorporated without change on these active sites, is not established. At lower pH values 1.5 to 2.5, the unsaturated esters and lactones are hydrogenated more rapidly, that is, more is consumed, and more breakdown products are left in the bath and yet much less luster and leveling are produced and less carbonaceous material is found in the plate. Rogers and Taylor, in a very important work already mentioned, have investigated these phenomena with coumarin, butyne diol and propargyl alcohol, and found that the reduction went much further than just hydrogenation of the C = C bond when the low pH values were used. The presence of buffers like acetates, citrates, etc., greatly decreases leveling in the nickel baths, even at pH values of 4.5 to 5.5, which are normally optimum for leveling, and this effect may be similar to lowering the pH of the cathode film. These buffers unlike boric acid probably prevent formation of the thin nickel hydroxide membrane which influences the adsorption and reduction behavior of the unsaturated compounds.
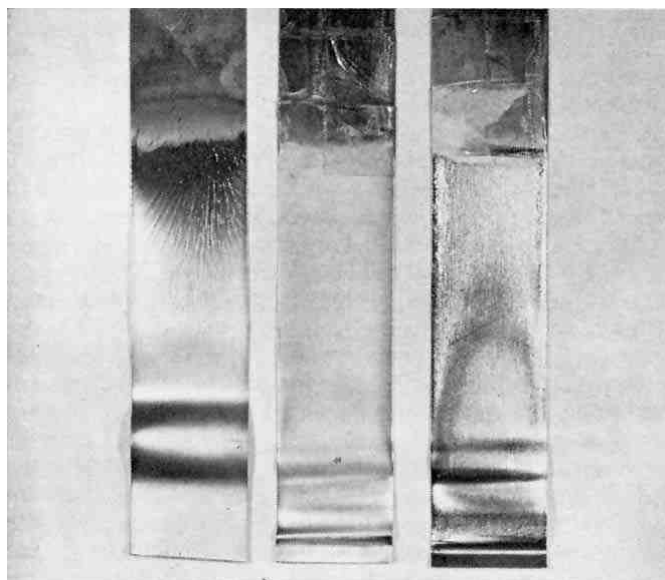

Figure 4 - Irregular surface channeling (striations) caused by absence of boric acid in the Watts bath when a leveling agent such as coumarin (left panel) or butyne diol (right panel) is present in the bath at pH values of 3.8 to 5.5. The center panel is obtained with coumarin when boric acid is present in the usual formulation of the Watts bath.

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[*] See G.W. Poling, *J. Electrochem Soc.*, **114**, 1209 (1967).

Thus, it appears that either traces of basic nickel salts formed as colloids or formed as a membrane across the cathode are necessary to help modify the nickel crystal growth, that is, modify the growth sites and modify and regulate thereby the adsorption characteristics. This is also doubtless involved in the following phenomenon. If boric acid is omitted from a Watts bath containing coumarin, butyne diol or other leveling agents used alone in the bath, then dense irregular surface striations appear in the plate (Fig. 4), similar to the effect of a slight excess of thiourea in acid copper sulfate plating baths. Even about 5.0 g/L of boric acid prevents the surface striations in the nickel plate due to the leveling agents, but the main and unique quality of boric acid (recommended for acidic nickel plating by Edward Weston[23] in 1878) is that it is the only "buffer" that will prevent the striations from the unsaturated esters, lactones and alcohols at the pH values of 3.8 to about 6.0[**] and still allow high leveling. Boric acid could only be a buffer in the cathode film where it may effectively add on to oxygen atoms of nickel hydroxide. Carboxylic acid buffers such as acetate, citrate, fumarate, etc., also eliminate striation formation at pH values of 3.8 to about 6.0, but they do not allow very much leveling to take place. The anionic carrier sulfon- and sulfin-compounds also eliminate striation formation in the plate from baths void of boric acid but containing the levelers. An interesting point in this connection is the comparison of saturated carboxylic acids such as acetic and succinic acids which are not brighteners and indeed greatly retard leveling, with unsaturated carboxylic acids such as maleic, fumaric and acetylene dicarboxylic acids. The latter, like the saturated acids, acetic, succinic, etc., prevent striations but unlike the saturated carboxylic acids, they cause brittle, darkish plate, with no leveling, whereas the saturated acids actually increase the ductility somewhat. The above mentioned unsaturated acids used together with the best aryl sulfon-compounds in acidic nickel baths, with or without boric acid present, produce easily stained, fine, grained brittle plate with or without boric acid. In this respect, acetylene dicarboxylic acid is exceptionally harmful, giving darkish and extremely brittle plate. Raub[24] from different data has also pointed out that acetylene dicarboxylic acid is not a nickel brightener. Thus, the carboxylic acids produce no surface striations when boric acid is omitted from the nickel baths. However, when the carboxylic acid group is in alpha position to an unsaturated carbon to carbon linkage (Fig. 5) they produce unfavorable results on ductility, leveling and brightness. It would therefore appear that not only is the very thin nickel hydroxide film formation in the cathode film hindered or prevented, whether as a membrane or as colloidal particles, but there is perhaps a harmful anionic bridging effect occurring because of too strong adsorption on the cathode. The following conjugated structure would be an excellent electron conductor.
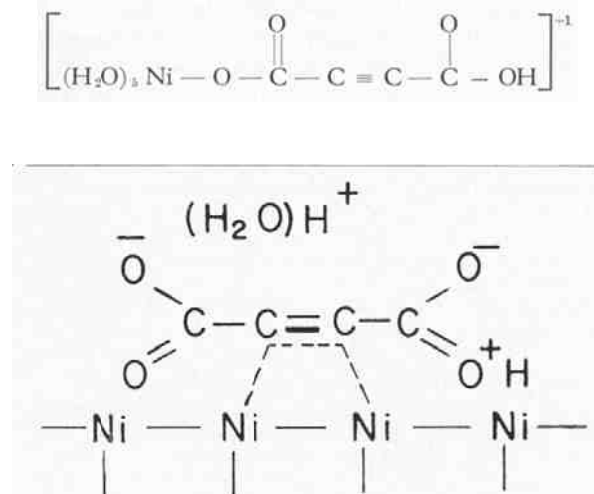

Figure 5 - Possible mechanism of adsorption of an anion of acetylene dicarboxylic acid following the scheme shown in Fig. 2. The above representation shows the dissociated part (the left side) and the undissociated part (the right side) of the dicarboxylic acid. The C = C bond length is 1.20 Å. The nickel lattice spacing is larger. The dashed lines indicate π-bonding.

In the case of the brightener systems employing aniline dyes, such as fuchsine or phenosafranine with aryl sulfon-compounds, the brightening process involves "irreversible" adsorption of the large dye cation without any hydrogenation of the dye, unless perhaps when azo linkages are present. The entire dye molecule is found in the nickel deposit. The simplest aryl sulfonic acid,

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[**]If the pH is dropped to about 1.5, the surface striations disappear and so does the leveling. The striations appear to be caused by a non-uniform nickel hydroxide film resulting in a non-uniform adsorbed organic film.

benzene sulfonic acid (15.0 g/L) does not produce brightness when used in conjunction with the aniline dyes, but does produce fully-bright plate when used in conjunction with the pyridine or quinoline or iso-quinoline compounds.[25] The latter cationic heterocyclics level better than the dyes. Aniline itself is not a brightener even with the best aryl sulfon-compounds, whereas p-aminodiphenyl or alpha naphthyl amine are brighteners though not quite as good as some of the larger aniline dyes. Pyridine and the quinolines appear to be hydrogenated to a certain extent to piperidine and 1, 2, 3, 4 tetrahydoquinolines respectively (These materials would plate out.), at the nickel cathode.[26]

Improved adhesion, ductility, brightness and leveling of the nickel plate can be obtained especially by quaternization of the tertiary nitrogen of pyridines and qufuolines.[27] The C = N bond in pyridine, quinoline or isoquinoline is very effective not only by virtue of its π-bond but also its σ-bond. It is much more effective in the aromatic ring than when the C = N group is present in an aliphatic compound. In the aromatic structure there is more total unsaturation in a large molecule. The nitrogen of the pyridine structure takes up a hydrogen ion in acidic solution and the molecule becomes cationic and is attracted by the cathode. If the pyridine is quaternized the pyridine structure is cationic, that is, the cation part of a salt. The C = N group is, of course, not found in rings.

The C = C group is also not generally found in rings, even though a very unstable benzyne ring has been synthesized. Acetylene was reported to cause high brightness in nickel plate by Lambris[28] in 1909 in connection with electro-analytical studies of nickel. Lambris compared ethane, ethylene and acetylene for introduction of carbonaceous matter into nickel electrodeposits. It is interesting to note that the triple bond in nitrogen $N \equiv N$, does not have unsaturation. When it is reacted with hydrogen, that is, hydrogenated, it forms ammonia and not hydrazine ($H_2N - NH_2$). This is due to its weak σ-bond. In the case of diazines such as quinazoline, the brightening effect is much less than with quinoline or iso-quinoline. The reason for this was not clear until lately. The recent finding of A. Albert[29] that quinazoline dissolved in dilute acid has ultra-violet spectra and ionization constants which are incompatible with the orthodox formulation of this molecule clears this problem; that is, the quinazoline formula is only for the anhydrous species (a), but the cation formed in dilute acidic solution is stable only in the hydrated form (b).
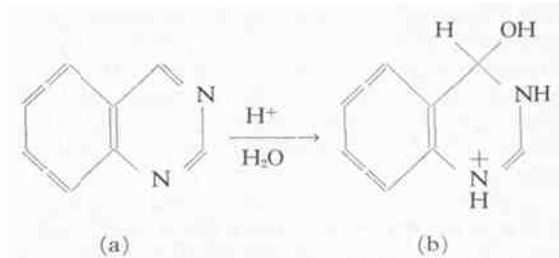
Thus, the resonance is lost in the hetero-ring, also an -NH group is now attached to the carbon carrying the unsaturated linkage, which is in general harmful because the hydrogen becomes acidic (see the Appendix). Amines such as piperidene or I, 2, 3, 4 tetrahydroisoquinoline do not give leveling when used conjointly with the aryl sulfon-compounds. The brightness with saturated amines is a little better than with just the aryl sulfon-compounds present alone, but there is practically no leveling.

The nitrogen cationic brighteners cause an appreciable increase in sulfide inclusion derived from the sulfon-compounds, for example, 0.03 to 0.08% sulfur. This is believed to result from increased polarization[30] and partially from the slightly increased hydrogen evolution caused by the cationic compounds, but perhaps mainly from a change in the number of adsorption sites, that is by a change in structure of the nickel plate as brilliantly shown by Edwards and Levett.[31] The unsaturated esters, lactones and similar unsaturated compounds, and especially aldehydes which are strong hydrogen acceptors, do not cause a significantly appreciable increase in nickel sulfide inclusion. In fact, in some cases they may cause a slight decrease in sulfide content depending on the type of sulfon-compound that is used. The brightening and leveling, which occurs when the sulfon-carrier brighteners are used conjointly with the leveling agents in the nickel plating baths, probably involves the cyclic formation of a nickel sulfide film across the cathode either separately from the nickel hydroxide film or simultaneously to form a mixed film. This would give the rhythmic banding shown by etching cross-sectioned bright nickel plate. Depending on whether weakly-cationic strong hydrogen acceptors (short chain aldehydes, beta unsaturated esters or lactones), or the strongly cationic brilliancy-imparting agents such as pyridine compounds are present, there are variations in the nickel sulfide and nickel hydroxide film

formation. With the strong hydrogen acceptors, less nickel sulfide is incorporated in the plate, unlike with the strong cationic brilliance-imparting agents.

The important fact of obtaining increased sulfide content of the nickel plate by the conjoint use or the aryl sulfon-compounds with the nitrogen compounds, and of making possible decreased sulfide content by using the short chain aldehydes makes possible the use of unusual multiple-layered nickel deposits for maximum corrosion protection of the basis metal, as will now be shown.

Efforts toward maximum corrosion protection

After it was found that sulfur-containing bright nickel with the usual thin chromium plate was not giving satisfactory corrosion protection to steel or zinc die castings in outdoor exposure in damp, cold industrial atmospheres compared to dull sulfur-free nickel with the same thin final chromium plate, it was thought that the answer might be a sulfur-free bright nickel. Outdoor exposure tests were made with the bright side of a Watts sulfur-free thick nickel foil obtained by plating ductile dull nickel on top of a passivated bright nickel surface. This thick Watts nickel foil with one side brilliant and one side dull was chromium plated with 0.25 μm of the usual final chromium plate on both the bright side and the normal dull side. The foil was then cut into two pieces and each side was exposed in an industrial atmosphere for three years.[32] The chromium plated dull side showed a dense distribution of fine pits. The bright side showed much less dense pitting, but very large deep pits just as with sulfur-containing bright nickel. Buffing the dull Watts nickel surface and chromium plating gave similar results to no buffing, that is, dense, very fine pitting with very little penetration downward. These experiments pointed to the importance of the degree of porosity of the chromium plate, at least for static exposure in a damp industrial atmosphere.

Meanwhile, the use of a high leveling, ductile, sulfur-free, semi-bright nickel became very prominent[33] in the plating of automobile bumpers. This plate was easily buffed bright and then chromium plated. Later in order to eliminate the buffing step, sulfur-containing bright nickel was applied on top of the semi-bright nickel in a thickness less than that of the semi-bright.[34] While it wasn't apparent from static roof tests, the corrosion resistance performance on cars of this double layered nickel coating was superior to even the good performance of the chromium plated sulfur-free buffed semi-bright nickel. This superior performance was manifested in cities that used salt to de-ice streets during the winter. Further improvements were obtained by using a thin layer of nickel with a relatively high content of sulfur, sandwiched between the semi-bright and bright nickel.[35] This three-layered nickel plate used a 50-50 ratio of semi-bright to bright nickel instead of the 70-30 preferred ratio for the double nickel. Finally, the porosity of the chromium plate received increased attention,[36] and the first important result was the development of microcracked chromium plate.[37] Next was the development of microporous chromium plate by plating the usual chromium plate on top of a thin bright nickel plate containing densely codeposited, extremely fine nonconducting particles.[38] In this indirect way, the final chromium plate of 0.25 to about 0.75 μm thick is made microporous. With highly porous chromium plate, the corrosion protection results with just bright nickel on top of a copper coating showed very important improvement (Fig. 6). Using highly-porous chromium on top of double nickel (50-50 ratio of sulfur-free nickel to bright sulfur-containing nickel), further improvements were obtained (Fig. 7), and still further improvements were obtained when using the highly-porous chromium on top of the triple nickel plate already described. With the highly-porous final chromium plate, it has been found that copper is markedly beneficial as an underneath coat to nickel, and it is now possible to obtain remarkable results in the CASS, Corrodkote and the EC accelerated tests with much thinner total nickel plate than thought possible only a few years ago.

Finally, by utilizing each of the properties of the unsaturated additives for nickel plating it is possible to almost hide the surface corrosion pits, after 100 hr CASS tests or five Corrodkote cycles, as shown in Fig. 8. The semi-bright, sulfur-free nickel is followed by sulfur-containing bright nickel, which is followed by a thin nickel containing cathodic hydrogen acceptors (aldehydes and unsaturated non-sulfur containing compounds) to cause the final nickel which is bright to have an appreciably lower sulfur content derived from the organic sulfon-compounds than the bright nickel plate underneath it. The latter has unsaturated compounds which promote increased sulfur content from the aryl sulfon-compounds. The final thin bright nickel plate with the lower sulfur content also has preferably codeposited with it, multitudinous fine nonconducting particles (which were dispersed in the plating bath) to cause chromium plate to be micro-porous.
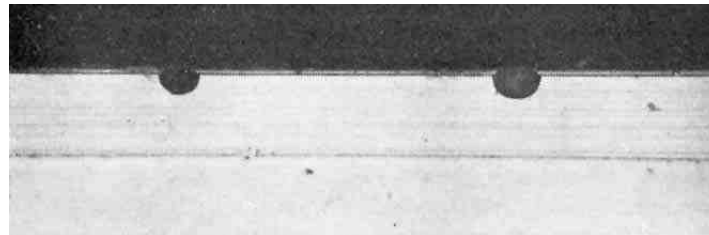
Figure 6 - Very small hemispherical corrosion pits (original magnification 500X) developing in the bright nickel plate underneath microporous chromium, after five cycles of Corrodkote. The nickel is 25 μm thick. Corrodkote results are excellent without the copper layer, but in outdoor exposure, copper was found to be highly beneficial under the nickel when highly-porous chromium was used on the bright nickel. The best results are obtained with multiple-layered nickel plate as shown in Figs. 7 and 8.
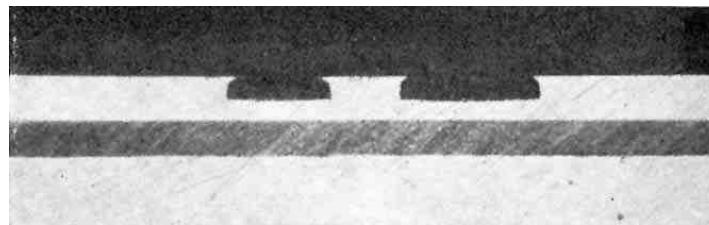

Figure 7 - Flat bottom surface corrosion pits (original magnification 500X) in the bright nickel layer and stopping at the semi-bright, sulfur-free nickel and proceeding laterally after 100 hr CASS test. Copper is underneath the double nickel layer and microporous chromium is on top of the bright nickel. The total nickel thickness is 15 μm, the copper 10 μm and the chromium 0.25 μm.
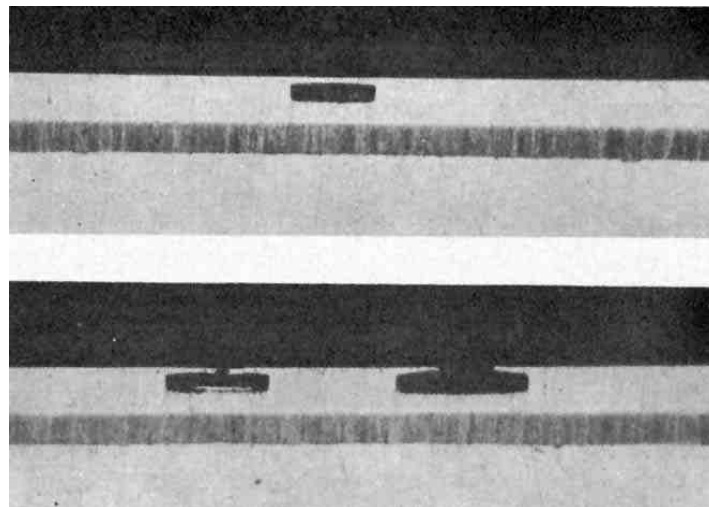

Figure 8 - After 100 hr CASS corrosion testing with a three-layered nickel plate (original magnification 500X) consisting of semi-bright, sulfur-free nickel, followed by an equal thickness of bright nickel followed by a thin layer of bright nickel which has multitudinous, codeposited, very fine, non-conducting particles in its surface, thereby inducing microporosity in the final chromium plate. The total nickel thickness is 15 μm, the copper 10 μm and the chromium 0.25 μm. The section showing the hidden corrosion pit but no surface corrosion pit was not polished to the center as in the other section. These surface corrosion pits require at least 100X to be seen directly.

The road leading to developments in the decorative nickel-chromium plating field was long and arduous for both the platers and suppliers but the path was made much less rough by the fundamental work done in universities, and institutions such as the U. S. Bureau of Standards [now NIST]. In the fifth William Blum lecture,[39] Dr. Wesley said, "Any record of the long struggle to

develop a science out of the old art of electroplating must be replete with references to the part played by William Blum." It could not have been better said.

Conclusion

If one principle could be emphasized from this presentation, it might be a doctrine of diametrically opposed alternatives. For example:

1. The sulfide-containing bright nickel corroded so rapidly under the usual final chromium plate that its use for severe outdoor industrial or marine exposure was not very satisfactory. However, by utilizing an underlayer sulfur-free, bright nickel, this bad point was turned into a good point because of its sacrificial corrosion compared to the underneath sulfur-free nickel. Thereby, the corrosion pit is diverted laterally instead of rapidly penetrating to the basis metal. Normally, one wouldn't think of using nickel as a sacrificial coating.
2. Logically, it would first appear that crack-free, pore-free, that is, flaw-free, chromium on top of bright nickel would give the best corrosion protection results. However, the best decorative bright chromium plate to apply over nickel for good corrosion protection turned out to be just the opposite, that is, a highly porous one.
3. After all the admonitions to keep the nickel baths crystal clear and filtered continuously to obtain a nickel plate with optimum corrosion protection, it turned out that dispersing in the nickel bath of as much as 50 g/L of extremely fine, bath-insoluble, nonconducting particles which codeposit with the nickel made possible highly improved corrosion resistance by indirectly making the top decorative chromium plate micro-porous.

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Appendix

The following are the first two pages of a U. S. patent application filed by the author on November 20, 1940 as Serial No. 366,385.

In these two pages there is discussed the cooperative effect of the aryl sulfon-compounds with bath-soluble unsaturated organic compounds to produce brilliant nickel plate. Also, the harmful effect of certain groupings attached to a carbon atom carrying the unsaturated bond. Later data[40] by other investigators fully substantiate the findings given in these two pages submitted in 1940.

"This invention relates to the electrodeposition of nickel from an aqueous acid bath.

One object of this invention is to decrease the grain size and increase the luster of the nickel deposit.

A second and major object is the electrodeposition of brilliant highly lustrous ductile nickel plate.

I have found that these objects can be accomplished by the use of organic compounds carrying certain functional groups.

The first object can be accomplished by the addition to the Watts type of nickel bath or its modifications, of certain organic compounds which contain unsaturated linkages, such as the aldehydic (and ketonic carbonyl), the olefinic type of unsaturated bond, double or triple, and the unsaturated carbon to nitrogen bond, double or triple, *i.e.*,

$$-C=O, \quad -C=C-, \quad -C=N-, \quad -C\equiv C-, \quad -C\equiv N \qquad (1)$$
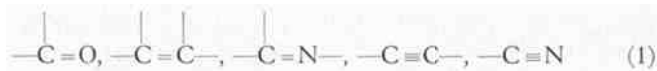
Compounds in the bath containing such groups cause the nickel plate to be very fine grained (even though cloudy and milky in appearance) and show marked increasing luster with continued plating.

However, not all unsaturated linkages produce the desired effects, for example, unsaturated bonds not connected to carbon, for example, N = O, N = N. Also the unsaturated bonds carbon to carbon, carbon to oxygen, or carbon to nitrogen, where an -OH, or -NH$_2$ or -NH- group is also attached to the carbon atom carrying the unsaturated bond, for example:

$$-C-OH, \quad -C-NH_2, \quad -C-OH, \quad -C-NH, \quad -C-NH, \quad -C-OH \qquad (2)$$
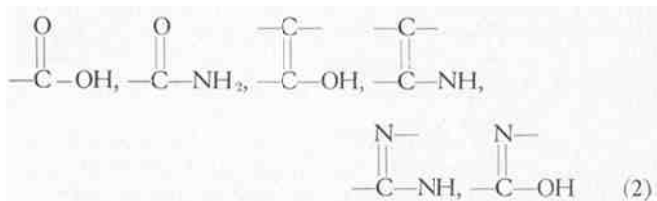
It was further found that the second object, the production of brilliant highly lustrous ductile nickel plate, could be accomplished by the use in conjunction with the active unsaturated groups (1), another, different functional group, namely, the ethylene sulfon group, $-C=C-SO_2-$ as exemplified by aryl sulfonamides, sulfonimides or aryl sulfonic acids. Compounds with either group alone in the bath gave no obvious indication of the remarkably different and enhanced result which occurs when both groups are present.

While the simpler aryl sulfonamides and some of the aryl sulfonic acids produce bright and mirror-like deposits on buffed metals such as buffed brass, they fail to accomplish the same result on steel polished, for example, with 200 Emery or on top of mat [sic] (but unburnt) copper plate of 0.0003 to 0.0005 in. [7.6 to 12.7 µm] thickness, and yield in these cases plate of dull and grey appearance.

The compounds carrying the active unsaturated groups (olefinic, aldehydic, etc.) while giving a different type of plate than that produced by the aryl sulfons, nevertheless give at best a cloudy plate on either buffed or mat [sic] metal. Their rate of improvement of luster of the basis metal is, however, faster than that produced by aryl sulfonamides or aryl sulfonic acids."

About the author

Born in West New York, New Jersey, in 1907, **Henry Brown** grew up in Kansas City, Missouri, attending elementary and high school there. He received an A.B. degree in chemistry at the University of Kansas where Professor H.P. Cady was one of his teachers. He obtained a teaching assistantship at the University of Michigan and studied under the late Professor F.E. Bartell and also under Professor L.O. Case, receiving a Ph.D. degree in 1933 in physical chemistry. In 1934 he went to work for The Udylite Corporation in Detroit under the late Gustaf Soderberg, when only two chemists were employed in the laboratory. His first assignment was to improve an acid cadmium plating bath and develop a high-speed alkaline cadmium cyanide bath. The latter cyanide bath was later used by the British Atomic Energy Commission.

As written by Paul Lewis, in the New York Times at the time of his passing:

"...there had been other earlier and less obvious beneficiaries of his skill at making dull metals shiny. In the austere war years, he showed the United States Treasury how to make steel pennies gleam and invented a high-speed process for brass plating shell cases so they did not stick in artillery guns. ... in 1943 he joined the Manhattan Project as a research chemist developing porous nickel screens for separating atomic particles."

As time passed, his principal work became the development of organic addition agents especially for bright nickel plating baths. To this field he contributed the sulfonamide and sulfonamide "carrier" brightener system; the elucidation of unsaturation as one of the essential characteristics of the best organic addition agents for bright nickel plating, which devolved into the system of using an unsaturated organic sulfon-compound together with auxiliary unsaturated compounds which is the basis for all modern bright nickel baths. He was the earliest to show that the premature outdoor corrosion failure of decorative nickel-chromium plate was not due to any inherent porosity in the relatively thick nickel plate, but was due instead to the inherent porosity of the thin final chromium plate and the galvanically induced porosity developed in the underlying nickel plate, and that a high density of pores or craze-cracks in the final chromium plate would give much better corrosion protection than a low density.

In 1951 he suggested the development of the perfluoro alkane sulfonic acid surfactants for the purpose of suppressing acidic spray. These unique surface-active agents which took three years to develop were found to be perfectly stable in the presence of strong oxidizing agents including the Pb-PbO anode used in chromium plating and the acid lead storage battery. Other work involved the development of an indirect and novel method to obtain decorative micro-porous chromium plate by plating over bright nickel containing multitudinous co-deposited very fine non-conducting particles.

Dr. Brown retired from Udylite in 1972, but continued to make many contributions to science for the rest of his life, including cancer research. He died on March 15, 2001 at his home in Palo Alto, California at the age of 93.

To this writer's knowledge, Dr. Brown may be the only individual from our industry to be recognized, on the occasion of his passing, in a popular national newsweekly. In the April 16, 2001 issue of Time, in the Milestones section, was the following obituary:

DIED. HENRY BROWN, 93, chemist who discovered that sulfurous organic compounds could make chrome more brilliant; in Palo Alto, Calif. His innovation produced shinier faucets, sparklier bumpers and brighter pennies.

Dr. Brown's time was the era of bright decorative nickel-chromium plating for automotive bright work, the leading segment of our industry at the time. The entire multilayer copper-nickel-chromium system was a critical technological achievement in those days. Through his career, Dr. Brown's intimate knowledge of the functions of organic additives in plating chemistries was the key to the development of brightener systems. His was a unique and critical contribution. This paper is a definitive summary of that important work.