Producing a thin coloured film on stainless steels – a review. Part 1: electrochemical processes

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ABSTRACT

Stainless steels are often used for decorative purposes, primarily in the architectural industry, but also in homemare and the automotive industry, among others. It is possible to impart colour on articles to enhance aesthetics without impairing the desirable properties of the stainless steel itself. The colour can be non-iridescent and created by the absorbance of light waves of all but a given wavelength, or iridescent and created by a phenomenon known as thin-film interference. Colouring methods have been categorised into three groups, electrochemical, non-electrochemical and laser colouring. Laser colouring can be utilised as either an electrochemical or non-electrochemical process. The colouring technique most widely adopted by industry is a 2-stage electrochemical process, known as the INCO process, which utilises chromic-sulphuric acid baths to produce a thin interference film on the stainless steel surface. Alternatives developed by investigators regularly cite the toxicity of hexavalent chromium as motivation for their work and use the INCO process as a benchmark. Authors claim that alternative techniques match or exceed many of the properties achieved through colouring using hexavalent chromium, however, none are yet widely adopted by industry for the purpose of colouring stainless steel. It is therefore important to consider each technique to understand why this is the case. Part 1 of this review discusses the electrochemical processes utilised to produce coloured films on stainless steel, and Part 2 discusses non-electrochemical and laser processes.

Introduction

Civil engineering and architecture have seen extensive use of stainless steel; one of the earliest and most famous examples being the uppermost section of the Chrysler Building, New York, shown in Figure 1, which remains visually un tarnished after over 80 years. Colouring of stainless steel can further enhance its aesthetics. It has been utilised on structures such as the Millennium Centre, Cardiff, and the Ring of Remembrance, Notre Dame de Lorette, shown in Figures 2 and 3, respectively. There is evidence of colouring processes for iron-based alloys, including steel, as early as 1920. Since then, a variety of processes, using both electrochemical and non-electrochemical techniques have been developed. Part 1 of this review aims to examine the different electrochemical techniques, and Part 2 the non-electrochemical and laser techniques, by which it is possible to apply a thin coloured film to stainless steel.

The history of electrochemical colouring of stainless steel

The first patent for a chemical colouring process on stainless steel was submitted in 1927 by Hatfield and Green, referred to in Kikuti et al. The process involved the immersion of stainless steel parts in a solution of chromic and sulphuric acids. Evans et al. suggested that the limited stainless steel grades available at the time were responsible for Hatfield and Green not realising the potential of their process for producing a range of desirable colours. In 1939, referred to in his 1943 patent, Batcheller was the first to realise the potential to create a colour by using oxidising agents in the colouring bath. The only colour produced, however, was a deep black. Perhaps Batcheller’s most important observation was that the coloured films were soft and easily damaged through light wear and cleaning. He found the reason for this was the films were hydrated and porous but could be hardened by exposing them to elevated temperatures of approximately 400 °C to 650°C, thus driving off the residual water in the film and shrinking the pores.

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An example of a stainless steel façade created using this process is shown in Figure 4, which depicts the Neiman Marcus Department Store, Natick, Massachusetts. A patent by James et al. discusses a process by which designs can be applied to the coloured stainless steel utilising photographic techniques. The stainless steel surface is covered by an acid-resistant photoresist, then exposed to light transmitted through a photographic negative or positive and developed; finally, the surface of the stainless steel is coloured by immersion in a chromic-sulphuric acid bath and the remaining photoresist layer is removed.

In 1972, at International Nickel Company (INCO) Ltd in Birmingham, an electrolytic, chemical hardening process was developed which would greatly improve the wear resistance and minimise the appearance of any staining and finger marks, without the need to bake the stainless steel at high temperatures. The procedure of colouring stainless steel using a chromic-sulphuric acid solution, followed by electrochemical hardening in a separate chromic-sulphuric acid solution became known as the INCO process.

**Colouring processes in chromic-sulphuric electrolyte solutions**

The INCO process was discovered by Evans et al. Their first publication described the colouring process in detail and some of the physical properties of the film were also characterised. A later paper by Evans et al. focussed on the composition and structure of the film, optical properties and the mechanisms of film growth. In 1977, Evans described the film growth in detail by creating a kinetic model to prove that the previously suggested reactions were correct.

The colouring bath used by Evans et al. had a composition of 250 g L\(^{-1}\) CrO\(_3\) (2.5M) and 490 g L\(^{-1}\) H\(_2\)SO\(_4\) (5M). The temperature of the bath was 70°C and immersion times ranged from approximately 12 to 20 min, depending on the thickness of interference film required to produce the desired colour. The growth of the film can be followed by monitoring the electrochemical potential of the stainless steel in the bath, as discussed by Deguchi. The colour changes with time in the order champagne, blue, bronze, gold, rose gold, red and green and is produced via a phenomenon known as thin-film interference; therefore, it is iridescent in nature. Examples of some of the aforementioned colours are depicted in Figure 5. Examples of structures where stainless steel coloured by the INCO process has been used are depicted in Figures 2 and 3. The process of producing colour by thin-film interference is discussed by...
Pedrotti\textsuperscript{21} and Tipler and Mosca\textsuperscript{22} The hardening bath contained lower levels of sulphuric acid with a bath composition of CrO\textsubscript{3} 250 g L\textsuperscript{-1} (2.5M) and H\textsubscript{2}SO\textsubscript{4} 2.5 g L\textsuperscript{-1} (0.025M). During hardening a cathodic current density of 2.5 A dm\textsuperscript{-2} was applied for a time of 15 min for all samples and at the lower temperature of 40 °C.\textsuperscript{10,18}

Dissolution of the stainless steel into the strongly acidic and oxidising solution occurs via the anodic reaction in Equation (1):\textsuperscript{18}

\[
M \rightarrow M^{n+} + ne^{-} \tag{1}
\]

where \(M\) represents ions of metals from the stainless steel. Only a small amount of the dissolved metal contributes to the formation of the film leading to an overall weight loss of the stainless steel. The cathodic reaction involves the reduction of dichromate anions to trivalent chromium ions. Evans et al.\textsuperscript{18} suggest that it is the highly negative cathodic potential, that drives the reduction of the chromic acid to yield trivalent ions, the production of which is described in Equation (2):

\[
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \tag{2}
\]

For the reaction and growth of the film to be maintained the H\textsuperscript{+} ions in the solution at the cathodic site must be constantly replenished at the rate of their consumption. The cathodic reaction occurs at the film/solution interface, which initially starts at the surface of the stainless steel and moves outwards as the film grows. Evans et al.\textsuperscript{18} postulate that the solution in the interfacial boundary layer must be less acidic than the bulk solution. Once the acidity has fallen accordingly, the consumption and replenishment of H\textsuperscript{+} ions in the boundary layer are balanced. According to Evans et al.\textsuperscript{18}, it is only by this assumption that growth of the oxide would be possible as the bath conditions would not otherwise lend themselves to film formation. Metal ions from both the dissolution of the stainless steel and reduction of the chromic acid contribute to film growth. An idealised model of the film growth can also be seen schematically in Figure 6, which is an adaptation of a figure from Evans et al.\textsuperscript{18}

Evans et al.\textsuperscript{18} and Furneaux et al.\textsuperscript{23} agree that the interference film grows at preferential sites on the stainless steel such as grain boundaries and slip bands, which become anodic upon immersion in the colouring solution; this localised preferential growth leads to the formation of a porous structure. According to Furneaux et al.\textsuperscript{23}, the approximate pore width is 1.3 nm, with the width increasing in size at the metal/film interface. This contradicts the work carried out by Evans et al.\textsuperscript{18} who suggest a pore size of 10–20 nm. Based on the pore size, a pore fraction of 20–30% and a pore density of approximately 10\textsuperscript{11} cm\textsuperscript{-2} are proposed by Evans et al.\textsuperscript{18} However, it was noted that the density varies with the orientation of the substrate, explained by TEM examination of the film structure early in its growth process, Evans et al.\textsuperscript{18} found what they referred to as ‘an almost amorphous structure’. The film structure is further depicted in TEM micrographs taken by Furneaux et al.\textsuperscript{23} which show high levels of porosity in the film following immersion in the chromic-sulphuric acid colouring bath.

The interference film contains a higher percentage of chromium than the substrate steel, up to 21.3 wt-% measured by Evans et al.\textsuperscript{18} compared to the approximately 18 wt-% for the 304 stainless steel substrate.\textsuperscript{24} It was postulated that the increased level of chromium in the oxide film was due to the presence of two sources of chromium, the stainless steel and both the colouring and hardening chromic acid-containing solutions.\textsuperscript{18} Other metallic constituents of the oxide film only have one source, the stainless steel. The interference film owes its wear and corrosion resistance to the high levels of chromium it contains.\textsuperscript{10,18}

Investigations indicated that the film was hydrated, and according to Evans et al.\textsuperscript{18} this was between 5 and 10% by weight and 20–50% by volume. It was suggested that a possible composition for the film could be (CrFe)\textsubscript{2}O\textsubscript{3},(FeNi)O\textsubscript{x}H\textsubscript{2}O.\textsuperscript{18} Furneaux et al.\textsuperscript{23} agreed that a heavily hydrated oxide is produced, however, they did not give a value for a measured or theorised moisture content.

The hardening process closes the pores in the film, however, in doing so it increases the overall film thickness.\textsuperscript{10,18,23,25} Wang et al.\textsuperscript{25} argue that the hardening stage of the INCO process produces a separate outer layer of oxide formed from oxides and hydroxides of chromium resulting from the formation of Cr\textsuperscript{3+} on the surface of the interference film. It is known that hydrogen evolution takes place during the cathodic hardening and causes the reduction of Cr\textsuperscript{5+} to Cr\textsuperscript{3+}. Wang et al.\textsuperscript{25} provide Equation 2, originally given by Evans et al.\textsuperscript{18}, for the cathodic reaction in the colouring bath, as the reduction reaction also taking place in the hardening bath.

The interference film created during the INCO process is primarily chromium (III) oxide, the same type of oxide which

\[
Cr_2O_3 + 3H_2 \rightarrow 2Cr + 3H_2O \tag{2}
\]
naturally forms on stainless steel giving its excellent corrosion resistance, thus allowing the coloured product to be utilised in a wide range of environments. Evans et al.\textsuperscript{10} conducted atmospheric corrosion testing of uncoloured, coloured and hardened stainless steel samples and found that in marine and industrial environments samples performed equally to 'satisfactory standards.' During a 24 hr copper accelerated acetic acid salt spray (CASS) test it was found that coloured and hardened stainless steel showed less corrosion and staining than both uncoloured and coloured samples. Wang et al.\textsuperscript{25} measured the pitting potential in HCl of samples produced in the same way as those of Evans et al.\textsuperscript{10} and both coloured and coloured and hardened samples had a higher pitting resistance than uncoloured stainless steel.

The colouring process does not interfere with other desirable characteristics of stainless steel such as strength and the ability to possess good mechanical properties at both high and low temperatures.\textsuperscript{10} Evans et al.\textsuperscript{10} found a substantial increase in wear and scratch resistance of the interference film as a result of the hardening process. It was found that the wear resistance of the interference film increased from 2 to 4 cycles with a 500 g weighted pencil eraser to penetrate the oxide to 200 cycles post hardening. Scratch resistance to a hardened steel needle also improved from needing only a 5 g load to penetrate the unhardened oxide film to 50–120 g post hardening.

Detrimental aspects of the INCO process include the inability to repair the film if it becomes damaged, as is the case with other interference films grown via electrochemical processes. The hardening process reduces the risk; however, scratches and other damage can still occur, during cleaning for example.\textsuperscript{10} It is not possible to simply re-immers the damaged article into the colouring solution as the thickness of the entire film would increase, thus altering the colour. It is possible to leave a cosmetically damaged article in the field as the naturally occurring chromium oxide layer will self-heal (if oxygen is present) and protect the product against staining and corrosion, however, the aesthetics would be impaired as colour would be lost from the damaged area.\textsuperscript{2}

The toxicity of hexavalent chromium is the primary concern regarding the process. Waste containing hexavalent chromium has to be subjected to a multi-stage treatment before it is safe to dispose of.\textsuperscript{26} Furthermore, it has been listed as a Category 2 carcinogen on the list of Substances...
of Very High Concern (SVHC) according to the European Union (EU) Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations, which has seen its use significantly restricted.27

In 1950 Naylor introduced the concept of applying an anodic current to stainless steel as an alternative to a simple immersion process to produce a coloured finish.28 However, other than an aqueous-alkaline based, alternating current process by Evans and James in 1967,29 few publications have been produced detailing electrolytic processes until the mid-1990s. In 1994 Ogura et al.30 described a process utilising an anodic square wave potential pulse, between 0.53 and 1.23 V vs. a saturated calomel electrode (SCE), with promising results. A series of processes described by various investigators followed over the next 14 years.9,25,31–40 Some of these9,33,36 cite the inspiration for their pulsing conditions as those described by Ogura et al.30,34 in their 1994 and 1996 publications, the latter of which investigated the use of an alternating current applied with a triangular waveform.

Several variables are considered when pulsing current or potential, first, the shape of waveform. Waveforms for this process are typically square wave in shape,9,25,30–32,36–38,40–43 however, triangular waveforms9,32,44 have also been utilised, examples of both are shown in Figure 7. The potential or current can be pulsed simply ‘on’ and ‘off’ or can be pulse-reversed so the polarisation of the sample is inversed from being anodic to cathodic and vice versa. The magnitude and frequency of the pulses are essential for achieving the desired outcome of film formation. Pulse magnitude and frequency do not necessarily have to be symmetrical, the ‘off’ or reverse constituent of the pulse can have a completely different magnitude and application time to the ‘on’ constituent. The higher and lower or positive and negative potentials are often referred to as Ehigh and Elow, or E+, and E−, respectively and upper and lower or positive and negative current as Ihigh and Ilow or I+, and I−, respectively. Figure 7(a) demonstrates a square wave potential which has a shorter pulse time (t) and lower magnitude cathodic potential (E−) relative to the anodic potential, whereas Figure 7(b) depicts a triangular wave positively pulsed current with symmetrical pulse times and magnitude.

Most authors investigating the electrolytic colouring of stainless steel using chromic acid-based solutions conducted investigations utilising the same bath chemistry as the colouring stage of the INCO process.9,25,30–32,36,45,46 Cheng et al.39 were an exception to this, making use of the INCO chemistry as a starting point, but including optional additives such as ammonium molybdate tetrahydrate, zinc sulphate and magnesium sulphate to increase wear resistance, stabilise colouring potential and accelerate colouration, respectively. They were also one of few studies making use of an anodic direct current or potential.39,46

Some motivation behind the use of pulsed currents and potentials has been cited as being either to improve colour consistency and reproducibility or to reduce operating temperature, both relative to the INCO process.25 Consistency and reproducibility were further improved as utilising an electrolytic process removes the need for a subsequent hardening stage, during which the oxide would continue to thicken and must be compensated for during the colouring stage.32,35 Corredor et al.36 state that it is preferred industrially to operate at room temperature, with several investigators operating at this condition. However, Wang et al.25,32 state that the best colour chromaticity is achieved at elevated temperatures. They were not the only authors to utilise elevated temperatures.31,35,37,39 Many investigations focussed on characterisation of mechanical properties, notably wear resistance, and corrosion resistance.9,25,35,36,38,45 Authors investigating the corrosion performance of the pulsed colours compared results to those from the INCO process and as received 304 stainless steel. Findings showed corrosion performance typically exceeded both in the short term, with some identifying that over longer tests, corrosion performance was almost equivalent to, or exceeded the INCO process and as received samples.9,25,36 Furthermore, colours achieved included some of those produced using the INCO process, as well as some intermediary colours; these are given in Table 1 for Kikuti et al.37, Wang et al.25 and Conrado et al.36. Although chromaticity coordinates were given for the colours achieved by investigators, images of coloured samples were not.

Investigations on the application of currents and potentials for processes utilising chromic acid became more infrequent following increased scrutiny of the use of hexavalent chromium in the REACh regulations, which initially came into force in 2007.27 Corredor et al.36 did, however, release a publication in 2014 which described the application of a triangular wave current to stainless steel in a chromic-sulphuric acid solution, the growth of the oxide film remained a 2-stage process. Unlike previous authors, the process included a photochemical stage whereby the stainless steel sample was left at open circuit potential and a fluorescent mercury lamp used as the visible light source. To avoid interference from other light sources the electrochemical cell and light source were contained in an aluminium chamber throughout. Corredor et al.46 postulated that the light accelerates oxide growth by increasing Cr3+ ions produced by the reduction of Cr6+. Despite the claims of authors throughout the 1990s and early 2000s, no evidence was found to suggest an electrolytic

Table 1. Colours achieved by investigators using pulsed or alternating waveforms and claiming improved wear resistance and corrosion performance relative to the INCO process.

| Author(s) | Waveform | Potentials/Currents |
|-----------|-----------|---------------------|
| Kikuti et al.37 | Alternating | Triangular |
| Wang et al.25 | Alternating | Triangular |
| Conrado et al.36 | Alternating | Triangular |

Figure 7. (a) non-symmetric waveform for a pulse-reversed potential, (b) symmetrical triangular waveform for an anodic pulsed current.
process was adopted by the stainless steel colouring industry in place of the INCO process.

**Electrolytic colouring processes in sulphuric acid solutions**

In 1989, Yuan et al.\(^{40}\) realised the potential of electrolytic colouring of stainless steel using a sulphuric acid solution as the electrolyte, citing concerns over chromic acid waste created by the INCO process as the motivation behind their research. Several authors,\(^{33,41–44,47–51}\) including Yuan et al.\(^{40,52,53}\) continued to investigate sulphuric acid-based colouring processes during the 1990s and into the early 2000s, all of which involved the application of a pulsed or alternating current or potential.

In their first publication Yuan et al.\(^{40}\) performed preliminary investigations using ferritic stainless steel samples and found that it was possible to obtain a coloured interference film in sulphuric acid (H\(_2\)SO\(_4\)) by applying a pulsed potential.

Preliminary testing included varying process parameters such as solution concentration, temperature and square wave potential pulse magnitude and duration.\(^{52,53}\) It was found that a coloured film formed on the surface of 430 stainless steel samples in 0.5–10 mol L\(^{-1}\) sulphuric acid (H\(_2\)SO\(_4\)) from 298 K to 353 K. Results showed that film formation was accelerated with increased solution concentration and temperature. Colours including blue, gold, red, purple, green and black were achieved at potential pulse values of \(E_{\text{H}} = 0.9\) V and \(E_{\text{L}} = 0\) V (vs. SCE) for \(t_{\text{H}} = t_{\text{L}} = 0.1\) s. All colours, except black (50 min), were achieved within 18 min of treatment, excess colouring resulted in the dissolution of the film.\(^{40,53}\)

No film was formed at pulse times greater than 0.5 s and the film did not adhere to the substrate for anodic pulse potentials greater than 1 V (vs. SCE).\(^{50}\) Yuan et al.\(^{53}\) postulated that this occurs as the anodic phase of the pulse is long enough or of high enough magnitude to subject any film that has formed, during the cathodic pulse, to complete dissolution.

Film thickness was measured using Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) from cross-sections. It was found that after 30 and 60 min of colouring the film thickness was approximately 0.5 and 1 μm, respectively, when coloured in a 5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution at 353 K with \(E_{\text{H}} = 0.9\) V, \(E_{\text{L}} = 0\) V (vs. SCE) and \(t_{\text{H}} = t_{\text{L}} = 0.1\) s.\(^{53}\) Further measurements revealed a linear relationship between film thickness and colouring time with films up to 4 μm in thickness being measured.\(^{52,53}\) AES further revealed that the interference film formed using sulphuric acid contained mostly chromium, iron and oxygen. As the stainless steel substrate was the only source of chromium, it was suggested that Cr\(_2\)O\(_7\)^{2–} ions were formed by oxidation during \(E_{\text{H}}\) at the metal-film interface and then reduced during \(E_{\text{L}}\) at the film-solution Interface.\(^{53}\)

Yuan et al.\(^{52}\) later found that the coloured interference films could be formed using the same process on austenitic 304 stainless steel as well as ferritic 430 stainless steel. SEM analysis revealed a porous structure and cracked surface morphology. The diameter of the pores on the surface of the ferritic sample was found to be approximately 0.2–0.3 μm.\(^{52}\) X-ray diffraction showed that, although larger in scale, the sulphuric acid produced film consisted of a spinel oxide containing an amorphous network of pores.\(^{52}\)

Ferritic stainless steel samples were subjected to corrosion testing in 0.1 mol L\(^{-1}\) sodium chloride (NaCl) solution. The measured pitting potential was found to be higher than that of the untreated stainless steel and that resistance to pitting increased with electrolysis time, thus the interference film offers greater corrosion protection than the native oxide.\(^{52}\)

Fujimoto et al.\(^{41,47–50}\) followed on from the work of Yuan et al.\(^{40,52,53}\) and considered the optimum \(E_{\text{H}}\) and \(E_{\text{L}}\) values for 304 stainless steel also in a 5 mol L\(^{-1}\) H\(_2\)SO\(_4\) however, at the lower temperature of 323 K. Perhaps the most significant development by Fujimoto et al. was the identification of two possible growth mechanisms, which are referred to throughout their work as either the ‘cathodic’ or ‘anodic process’, schematics of the two possible growth mechanisms are shown in Figure 8.\(^{50}\) What they referred to as the ‘cathodic’ process is the same as that described by Yuan et al.\(^{52}\) where \(E_{\text{H}}\) is in the transpassive region for chromium and \(E_{\text{L}}\) in the passive region. The anodic growth mechanism occurred when \(E_{\text{L}}\) was in the active region for chromium and above the corrosion potential for iron. This was described as the preferable potential for \(E_{\text{L}}\) by Fujimoto et al.\(^{41}\) as film formation was most rapid at this potential, \(E_{\text{H}}\) was in the passive region allowing for the process to be easily controlled. The chosen potentials of \(E_{\text{H}}\) and \(E_{\text{L}}\) mean that the anodic process involved no cathodic reaction. Fujimoto et al.\(^{46}\) suggested that an alternative growth mechanism occurs, whereby at \(E_{\text{L}},\) Cr contained within the substrate stainless steel undergoes active dissolution to supply ionic species of chromium, mainly Cr(II) and Cr(III), to the solution adjacent to the substrate. At \(E_{\text{H}},\) the cations then form a hydroxide or oxide of Cr(III) through re-oxidation and/or dehydration.

Using TEM to investigate the film structure Fujimoto et al.\(^{50}\) like Yuan et al.\(^{52}\) found it consisted of an amorphous, spinel oxide containing a network of pores. For the anodic process on 304 stainless steel, Fujimoto et al.\(^{49,50}\) measured the grain size of a preliminary sample to be 5–20 nm, however, future samples were measured to have a grain size of 20–30 nm. When considering the thickness of the film Fujimoto et al.\(^{41}\) agreed with Yuan et al.\(^{52}\) that the growth is linear and therefore easy to control and achieve the desired thickness. The authors also achieved similar growth rates for their respective cathodic processes. Fujimoto et al.\(^{49}\) found that the growth rate of the anodic process was considerably slower. Although sharing largely the same structure, the cathodic and anodic film structures were found to differ slightly. This was noted by Fujimoto et al.\(^{49,50}\) while investigating the electrochemical properties of the films. It appeared that the anodic film had an electric capacitance proportional to film thickness, whereas the cathodic film had an electric capacitance independent of thickness and approximately equal to that of the stainless steel substrate. Thus, unlike the cathodic film, the anodic film must have an interconnected pathway of electrically conducting grains. Fujimoto et al.\(^{50}\) proposed that the spinel oxide grains produced in the cathodic process must have a thicker, insulating layer of disordered chromium hydroxide that separates the grains, whereas in the anodic film the layer surrounds the oxide, rather than forming between individual grains. As a result of the thicker hydroxide layer, the pores of the cathodic film are narrower and the structure more compact.

In 2005, both Zhang et al.\(^{52}\) and Vasconcelos et al.\(^{44}\) cited avoiding the use of chromic acid as the motivation for the development of their electrolytic sulphuric acid-based processes. Although both opted for the use of an H\(_2\)SO\(_4\) based...
solution, different concentrations were utilised, Zhang et al.\textsuperscript{42} opting for 2.5 mol L$^{-1}$ compared to 5 mol L$^{-1}$ for Vasconcelos et al.\textsuperscript{44} Variations in processes continue, with Zhang et al.\textsuperscript{42} utilising a square wave pulsed potential, whereas Vasconcelos et al.\textsuperscript{44} chose a triangular pulsed current, citing the optimised parameters of Ogura et al.,\textsuperscript{34} who utilised the same pulsed current in a chromic-sulphuric acid solution. It was noted when comparing the waveforms of Zhang et al.\textsuperscript{42} and Vasconcelos et al.\textsuperscript{44} that the optimum t$_{hi}$ + t$_i$ was considerably lower at 0.2 s, for the square wave alternating voltage, than 2.5 s for the triangular pulsed current. Both Zhang et al.\textsuperscript{42} and Vasconcelos et al.\textsuperscript{44} set E$_{hi}$ and E$_i$, respectively to allow for transpassive dissolution. Both processes yielded different maximum film thicknesses, Vasconcelos et al.\textsuperscript{44} cite a maximum film thickness of 270 nm, whereas Zhang et al.\textsuperscript{42} produced a film approximately twice the thickness, however, still lower than the film grown by the cathodic process of Fujimoto et al.\textsuperscript{49} Zhang et al.\textsuperscript{42} stated that their films were compact with small pores which contradicts the findings of both Yuan et al.\textsuperscript{52} and Fujimoto et al.\textsuperscript{50} who describe a lower density structure with larger pores. Both Zhang et al.\textsuperscript{42} and Vasconcelos et al.\textsuperscript{44} achieved colours comparable to Yuan et al.\textsuperscript{40,52,53} and Fujimoto et al.\textsuperscript{47,48,50} all of whom achieved colour via thin-film interference. Proving their colours were produced by this phenomenon, Zhang et al. noted that the refractive index, R, of the film was governed by its thickness and that varying it produced different colours. Based on this theory, Zhang et al. produced Table 2, which shows the thickness, R values, colour and forecast colour of the interference films.

Unlike Vasconcelos et al.\textsuperscript{44} Zhang et al.\textsuperscript{42} subjected their samples to mechanical and corrosion testing to investigate the durability of the interference film. Applying wear testing via a rotating rubber wheel, they found that it took over three times as many abrasions to penetrate through their film compared to a film produced using a chromic-sulphuric acid colouring process. Mechanical testing also included formability testing, through which it was found that the film did not detach from the substrate surface when bent through 90°, however, the colour did change to a lighter shade. Neutral salt spray corrosion testing showed that chromic-sulphuric acid coloured and alternating voltage (AV) sulphuric acid coloured samples did not display any corrosion product, whereas pitting was evident on as-received stainless steel and samples coloured in sulphuric acid using a direct current (DC). Pitting tests yielded slightly different results with AV and DC sulphuric acid colouring demonstrating higher pitting resistance in iron chloride (FeCl$_3$) solution than as-received and chromic-sulphuric acid coloured samples.

Although the results of the authors discussed appeared promising, subsequent new publications on the use of sulphuric acid colouring stainless steel appear to be rare.

**Electrochemical molybdate-based processes**

There is limited literature on molybdate based solutions being used to produce colour on stainless steels. Wanklyn\textsuperscript{54} discusses observations of a blue colour on 316 stainless steel while investigating the role of molybdenum in crevice corrosion. It was noted that during cathodic polarisation of 316 stainless steel in sodium chloride (NaCl) solution containing molybdenum VI (Mo(VI)), a series of coloured films formed which eventually resulted in a black deposit. No mention was made of which other colours appeared. Wanklyn\textsuperscript{54} postulated that it was likely the films consisted of molybdenum dioxide (MoO$_3$), which could possibly be hydrated. It was also suggested that films produced in the correct conditions resulted in interference colours.

![Figure 8](image-url)  
**Figure 8.** Schematics of (a) anodic film formation and (b) cathodic film formation, described by Fujimoto et al.,\textsuperscript{50} which occur during square wave potential pulse polarisation of Type 304 stainless steel in sulphuric acid solution. Schematics based on a figure by Fujimoto et al.\textsuperscript{50}
Processes utilising molybdates in the colouration of stainless steel have most frequently appeared in the form of patents, the earliest being filed by Pacz55,56 in 1929 and then again in 1932. The next patents to be filed using molybdates to colour stainless steel were not published until the twenty-first century where several were filed in China over the course of approximately 10 years.57–60 All cited the toxicity of hexavalent chromium and poor mechanical properties of previous electrochemical processes, some specifically citing the INCO process, as justification for their work. However, there was little evidence of the superior properties claimed, unlike Evans et al.10,18 and other authors describing hexavalent chromium-based processes. Furthermore, none of the authors provided details on interference film formation mechanisms, morphology, composition or performance.

Pacz55 claims in the first patent that a protective, dense, adherent coating can be applied to iron, steel, tin, aluminium, lead, magnesium and their alloys by simple immersion in a solution of molybdenum compounds. It is further claimed that the process is inexpensive, rapid, simple and safe. The molybdenum compounds suggested for the process are those of the alkali metals, sodium, potassium, lithium and ammonium. Various modifying or controlling salts for addition to the molybdate solution are suggested depending upon the substrate to be coated and the desired results. Pacz55 indicates that a full range of colours includes blue, yellow, red, green, brown and black, however, this range was mentioned in relation to a lead substrate; there was no explicit suggestion that this range applied to other films on metallic substrates.

For ferrous articles, Pacz55 suggests that immersion in a copper-containing solution prior to immersion in the molybdate bath results in a substantially improved deposit. Further as a post-treatment for ferrous articles a process is described which involves boiling the article in a 5% chromate solution for 15–60 min. Colouring current density is given as 0.02–0.6 A dm⁻², bath temperature as 15–60 °C and colouring time as 10 s to 60 min.

In 2013, Zhuhai et al.58 claimed that their process produces stable and high-quality colour and is simple, non-toxic and beneficial to environmental protection. However, as with the hexavalent chromium used in the INCO and other electrochemical processes, boric acid, a substance used by Zhuhai et al.58 was added to the candidate list in 2010 for SVHC as part of the EU REACH regulations.27

As with the processes of Luo et al.57 Yu59 and Li60 the process described by Zhuhai et al.58 is electrolytic in nature, with a current density range given as 0.1–5 A dm⁻² with colouring times of 1–30 min. The quoted current density range is mostly higher than that quoted by Luo et al.57 however, the time range is within that given by Luo et al.57 and also comparable to other processes which are not molybdate based.10,40 Like Yu59 the article to be coloured in the process described by Zhuhai et al.58 is designated as the anode in the electrochemical cell and a lead plate as the cathode and counter electrode. As well as molybdate and boric acid, antimony nitrate is added to the solution to increase the rate of film formation and lanthanum nitrate to improve film anti-fouling and corrosion resistance properties.

In 2014, Yu59 described his patented molybdate based process. The colouring bath, which predominantly contains molybdate, further contains sodium nitrate as an oxidising agent, sodium malonate as a pH stabiliser and sulphuric acid to activate the metal surface. The process is electrolytic in nature, utilising the stainless steel workpiece as the anode and a lead plate as the cathode and counter electrode. The range of applicable DC current densities is given as 0.1–20 A dm⁻² and the colouring voltage range as 1.5–2.5 V. Although the current density range does overlap that of Luo et al.57 the upper limit is considerably higher. Unfortunately, a range of achievable colours was not given. Attempts were made by Alliott51 to recreate the process described by Yu59 however, it was found that instead of the stainless steel anode being coloured, the lead cathode was coloured. Alliott51 found that reversing the polarity, making the

| Sample no. | Thickness (nm) | Refractive index | R (nm) | Film colour | Predicted colour |
|------------|----------------|------------------|-------|-------------|------------------|
| 1          | 101.7          | 1.94             | 394   | Light brown | Yellow–brown     |
| 2          | 123.1          | 2.53             | 622   | Grey-blue   | Blue             |
| 3          | 224.3          | 2.10             | 942   | Golden      | Yellow           |
| 4          | 322.8          | 2.27             | 1470  | Rose coloured | Light red       |
| 5          | 408.8          | 2.26             | 1766  | Blue–green  | Green            |
| 6          | 475.3          | 2.10             | 1996  | Green       | –                |
| 7          | 532.1          | 2.06             | 2192  | Red–purple  | Purple           |

Table 2. Relationship between optical properties and colour of films, produced by Zhang et al.42
stainless steel the cathode, resulted in a molybdenum oxide film being deposited and subsequently colours being produced on the desired electrode.

Finally, in 2016, a patent by Li et al. was published describing an electrolytic process based on a colouring bath primarily consisting of sodium hydroxide and sodium molybdate. In the process described the film-forming substances are sodium molybdate, cerium nitrate and sodium tungstate, suggesting that a film consisting of several oxides is the likely outcome. Antimony nitrate is also added to the solution to increase its activity. Li further suggests the inclusion of a non-ionic surfactant to enhance the ability of the solution to deposit an oxide on the surface of the stainless steel, something not previously suggested by other authors. Like previous molybdate based processes, the process described by Li includes surface cleaning and activation stages prior to colouring. Furthermore, a post colouring, film hardening process, is also described, with the same aim as that described by Pacz, however, avoiding the use of hexavalent chromium, instead Li opts to use a hot sodium silicate solution.

Conclusions

Various electrochemical colouring processes for stainless steels have been developed since the 1920s, however, none were industrially established until the discovery of the INCO process in 1972. This process combined simple immersion colouring in a chromic-sulphuric acid bath with a subsequent cathodic hardening process.

The INCO process results in a hydrated, porous, spinel oxide of predominantly chromium and iron. However, as with other electrochemical processes, it is not possible to repair the colour of a damaged interference film and the use of hexavalent chromium is coming under increased scrutiny due to its toxicity. Several authors developed single stage electrolytic processes, utilising a variety of square and triangular current waveforms. Although authors claimed to produce results, including colour consistency, uniformity and corrosion resistance, which were equal to or better than the established INCO process, none appear to have been widely adopted by industry.

Sulphuric acid-based processes were developed during the 1990s and early 2000s. The processes were electrolytic in nature and produced films of a similar porous structure and spinel oxide to those produced in chromic-sulphuric acid solutions. Colours were also produced in equivalent pitting corrosion resistance studies. Limited information exists in the literature regarding colouring stainless steel using a molybdate based process; that which does exist is predominantly in the form of processes patented in the twenty-first century. However, little information is provided with regards to interference film formation mechanisms, film morphology and precise performance of films in testing, although many desirable properties are claimed.

Considering the pertinent literature discussed in Part 1 of this review, non-hexavalent chromium techniques have yielded promising results. However, despite investigators reporting the performance of various non-hexavalent techniques to be equal to or exceed that of the INCO process testing, none have been widely adopted by industry. Part 2 reviews the non-electrochemical and laser processes for producing coloured films on stainless steel.

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