GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 144531 dated 21st June 1978
Application and Provisional Specification No. 918/Cal/1976 dated 6th May 1976.
Acceptance of the complete specification advertised on 29th April 1978.

Index at acceptance— 9D [XXXIII(1)]

International Classification— C 21 c 7/00

"Improvements in or relating to colouring of 2 nickel chrome stainless steel articles".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by BALKUNJE ANANDHA SHENOI, Scientist, RAMASWAMYRA SUBRAMANIAN, Scientist and RAMACHETTY VENKATAGNALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-6, India, and all are Indian Nationals.

PRICE: TWO RUPEES

144331

This invention relates to improvements in or relating to colouring of nickel-chrome stainless steels.

Hitherto it has been proposed to colour these stainless steels by one of the methods mentioned below:

1 Stainless steel when immersed in molten sodium dichromate developed an intensely black possessing considerable strength and elasticity.

2 The stainless steel is sprayed with certain solutions and heated in furnaces at controlled temperatures for a definite time to get different shades of colour.

3 The stainless steel is immersed in aqueous solutions of sulfuric acid containing x oxidising agents such as chromic acid, chromates, permanganates, vanadates.

4 The stainless steel is electrolytically treated in aqueous solutions of sodium carbonate + potassium chloride sodium meta silicate + potassium chloride, potassium chromate + sulfuric acid or mixtures of these at high current densities greater than 500 asf using alternating current of ~~50~~ 50 cycles.

In some later modifications of some of these processes, the coloured film so produced are further protected for improved abrasion resistance by spraying with silicate solutions and baked at temperatures above 300°C for 5 to 15 minutes.

It has also been reported in literature that colouring of stainless steel could be obtained by making the stainless steel articles anodic at a current density of 0.06 asdm in an aqueous solution of 25% by volume concentrated sulfuric acid containing 30 gm per litre of sodium dichromate and maintained at 70-95°C . Various shades of colour ranging from brown, blue, yellow, purple and green have been reported. However, intense black colours could not be obtained from these electrolytes.

It has also been reported that the above range of colours could be obtained by immersion of the stainless steels for varying times in an aqueous solutions of 50% by volume of sulfuric acid and about 12-15 gm per litre of sodium dichromate.

6 As a subsequent improvement of the above process, it has been reported that the oxide film so produced has to be hardened for improved abrasion resistance by cathodic treatment of the coloured stainless steel in a chromic acid electrolyte containing 250 g/l CrO_3 and 2 to 5 g/l H_2SO_4 for 15 minutes at 40°C. The anode used is lead and current density is around 2 - 5 asdm.

These methods are open to the objection that methods 1 and 2 use a molten bath at high temperature and may affect the strength of the steel surface and difficult to control the shades of colour.

Method 3 produces colours of different shades but are not sufficiently abrasion-resistant for day to day application.

Method 4 uses very high current densities involving high investment on equipment. Further, the films are not abrasion-resistant.

Method 5 uses a very low current density which is very critical and use of higher current densities do not produce any colours.

In Method 6 the colour is produced by immersion in chromic-sulphuric acid mixtures at a temperature 70-95°C and hardened in a virtually chromium plating electrolyte at current densities lower than required for the onset of chromium deposition. Considering the poor current distribution of the chromium plating electrolyte, the hardening may cause burning at the corners and edges of the work. Further black colour could not be obtained in this electrolyte.

The object of the present invention is to obviate these disadvantages and also to improve the uniformity of the shades

of colour by immersion process using chromic acid-sulphuric acid electrolyte containing a definite quantity of trivalent chromium in the colouring bath and subsequently hardening in a chromic acid electrolyte in which a definite amount of trivalent chromium ion is produced by reduction with such reducing agents as sulphites, hypophosphite, ascorbic acid, arsenites and tellurites.

It has been found that in the course of investigations that presence of ferric ions in the colouring electrolyte prevented the colour film formation whereas additions of cupric, nickelous and manganous ions hastened the formation of coloured films. Further, the presence of chromium III ions in the electrolyte assisted in the formation of uniform colours from batch to batch. However, the colours so obtained from immersion in the acid electrolyte even though resistant to soft rubbing with cloth could not resist abrasion with washing powders and hard rubbing with dry cloth. The concentration range of the chromic acid could be varied from 200 g/l to 1000 g/l and sulphuric acid could be varied from 30 ml to 350 ml of concentrated sulfuric acid of sp.gr. 1.84 and the range of colours obtained varied from light brown, sky blue, light pink, dark pink, "peacock" greenish-blue, green and golden yellow. The time of treatment increases in the order of shades of colour mentioned and depends on the temperature of treatment - longer the treatment time lower the temperature, and lower the concentration of chromic acid in the colouring bath.

For a given temperature, time and concentration of chromic acid additions of cobalt, nickel, manganese and copper ions shorten the time of treatment for a given colour and the colour obtained is more uniform.

The 'hardening' of the film is subsequently carried out in chromic acid-sodium meta silicate electrolyte in which a small fraction of chromium 6 has been reduced by additions of

such reducing agents as selenites, hypophosphites, arsenites, sulphites and tellurites. The stainless steel is made the cathode and another stainless or lead is made the anode and a cathode current density of 1 asdm to 3 asdm is employed for a period of 15 to 20 minutes at temperature 30 to 60°C. After treatment in the hardening electrolyte, the work is rinsed thoroughly and dried. The coloured film so obtained is now resistant to abrasion by washing powders such as vim, talc, kaolin and also vigorous dry cloth rubbing. It has also been found that film was not attacked by sodium chloride solutions or acids like HCl, H_2SO_4 of 0.1 to 2N strength or by chromic acid solution whereas the unhardened film was easily removed by immersion in 2N HCl solution or colour is altered in the chromic acid solution.

It has also been found that the colours could be polished by pure calico cloth mops, without any polishing composition applied to them, on a polishing lathe and thus is abrasion-resistant to hard dry cloth rubbing.

To these ends, the invention broadly consists in colouring the stainless steel panels or articles (such as outdoor and indoor building panels, automobile trims, and stainless steel domestic appliances, picture-frames, household utensils, watch straps, chains and such architectural and decorative applications) by immersion in a chromic acid sulphuric acid electrolyte, in which a fraction of the hexavalent chromium has been reduced to trivalent chromium either electrolytically or by chemical reducing agents such as oxalic acid, arsenites, selenites, ascorbic acid, and also containing copper, nickel, cobalt and/or manganese ions. The concentration of chromic acid can be varied within the limits 200 g/l to 1000 g/l and of sulphuric acid in the limits 30 ml/l to 350 ml/l of concentrated sulfuric acid of specific gravity 1.84 and maintained in such a ratio that CrO_3: H_2SO_4 does not etch the stainless steel surface. The concentration of trivalent chromium can be varied in the limits of 1 to 12 gm/litre by addition of calculated quantities of the above said reducing agents.

The temperature can be varied in the range of 60-90°C but maintained at a desired temperature thermostatically the tolerance being ± 1°C. The time of immersion is from 4 to 30 minutes depending on the concentration of chromic acid, the temperature of treatment, the nature of the surface viz. mechanically polished, etched or electropolished and the colour desired.

Cupric, manganese, nickel and cobalt ions are added as their sulphates the concentration being within 5 grams per litre to produce uniform colours and shorten the treatment time. The coloured stainless steel article is rinsed well in tap water and then electrolytically hardened in chromic acid-sodium metal silicate electrolyte. The concentration of CrO_3 can be varied from 100 to 300 g/l a fraction of which is reduced to trivalent chromium by addition of reducing agents such as selenites, hypophosphites, sulphites, arsenites, or oxalates of alkaline or alkaline earth metals the concentration of which can be varied from 3 to 15 g/l. The sodium meta silicate concentration is varied from 5 to 40 g/l. The coloured article is made the cathode and stainless steel or lead is made the anode. The temperature of the electrolyte could be varied from 30 to 70°C and a cathode current density of 1 asdm to 3 asdm is maintained for a period of 15 to 20 minutes.

When a black colour or maroon type of finish is desired on stainless steel, the work is made cathodic in the following electrolyte with carbon or graphite as anode. The temperature of the electrolyte is maintained between 60 and 90°C and the applied voltage is 1 to 2 volts measured between the electrodes.

The electrolyte consists of:

Molybdate as ammonium or potassium molybdate:	2-5 g/l as MoO_3
Chromate or dichromate of sodium, potassium or ammonium or chromic acid:	5-10 g/l as chromic acid
Arsenite of sodium or potassium:	2-5 g/l as As_2O_3

Sulphite or bisulphite of sodium:	10-20 g/l
Sodium thiosulphate:	20-40 g/l
Chloride of ammonium or potassium or sodium:	35-50 g/l

This colour is resistant to abrasion as such without subsequent hardening treatment.

The following examples are given to illustrate the invention and not to limit the scope of the invention:

EXAMPLE 1

The stainless steel article, say for example, a rectangular tray is mechanically buffed to a bright finish, degreased, dried and is immersed in the following colouring bath:

Chromic acid:	775 g/l
Sulphuric acid: (Sp.gr. : 22 1.84)	60 ml/l
Trivalent chromium by addition of oxalic acid:	4 g/l
Temperature:	85°C ± 1°C
Time:	5 minutes
Colour obtained:	Golden yellow

Rinsed, washed in tap water dried and hardened in the following electrolyte under the conditions mentioned therein:

Chromic acid:	100 g/l
Sodium meta silicate:	10 g/l
Sodium selenite:	2 g/l
Temperature:	70°C
Stainless steel article:	Cathode
Lead:	Anode
Current density:	1 amp
Time:	15 minutes

144231

EXAMPLE 2

A stainless steel (18:8) tumbler is mechanically buffed to bright finish, degreased and immersed in the following colouring bath:

Chromic acid:	250 g/l
Sulphuric acid: (Sp.gr.: 1.84):	275 ml/l
Trivalent chromium (ascorbic acid used as reducing agent)	10 g/l
Temperature:	70°C ± 1°C
Time:	10 minutes (light brown)
	15 minutes (sky blue)
	18 minutes (pink light)
	21 minutes (dark pink)

The dark pink coloured tumbler is washed in tap water dried and hardened in the following electrolyte:

Chromic acid:	150 g/l
Sodium arsenite:	3 g/l
Sodium meta silicate:	20 g/l
Temperature:	40°C
Lead:	Anode
Stainless steel article:	Cathode
Current density	2 asdm
Time:	15 minutes

The final colour obtained is greenish yellow and is abrasion-resistant.

EXAMPLE 3

Stainless steel panels of 1" x 3" size were mechanically buffed and electropolished in sulphuric acid-phosphoric acid-lactic acid electrolyte at 2 asd at 60°C with lead as cathode and then washed and dried and coloured in the following electrolyte:

Chromic acid:	[illegible] 250 g/l
Sodium hydroxide	40 g/l
Sulphuric acid:	375 ml/l
Trivalent chromium (by a reduction with As_2O_3)	5 g/l
Copper sulphate	7.5 g/l
Temperature:	75°C

Time:	5 minutes	10 minutes	15 minutes	20 minutes	25 minutes
Colour:	No colour	light yellow	Brownish yellow	Sky blue	Greenish blue

One panel was not hardened and rubbed with vim. Vigorously the colour goes away leaving a yellow colour behind. The other panel was hardened in the electrolyte given under Example 2 under the same conditions.

A bluish green colour was obtained which was permanent by vigorous rubbing. Under these conditions a stainless steel soap box was coloured but without electropolishing step at start. A greenish-blue colour was obtained in 25 minutes.

EXAMPLE 4

A stainless steel panel of 2" x 4" was buffed, degreased and anodically etched in CrO_3: H_2SO_4 electrolyte to give a fine-grained surface. Washed, dried and treated in the following electrolyte:

Chromic acid:	100 g/l
Sulphuric acid:	425 ml/l
Trivalent chromium (reduced by addition of ascorbic acid)	10 g/l
Nickel sulphate:	2 g/l
Temperature:	75°C

Time:	upto 22 minutes	25 min.	35 min.	45 min.	55 min.	65 min.
Colour:	No colour	Faint yellow	Sky blue	Blue	Yellow	Dark pink

75 min.

green.

Hardening of the panel in the electrolyte under example 2 under the said conditions resulted in yellowish green colour.

EXAMPLE 5

A stainless steel panel 2" x 4" was mechanically polished to bright finish, cathodically cleaned in hot alkaline cleaner containing:

Sodium carbonate:	35 g/l
Sodium hydroxide:	25 g/l
Temperature:	70°C
Anode	Mild steel
Current density:	15 asdm

rinsed, washed and treated in the following electrolyte:

Sodium dichromate:	10 g/l
Ammonium polybdate as MoO_3	20 g/l
Sodium thiosulphate:	25 g/l
Ammonium chloride:	35 g/l
As_2O_3:	1 g/l
Temperature:	60°C
Voltage across the electmodes:	1.5 V
Cathode:	Stainless
Anode:	Graphite
Time:	15 minutes

A jet black film resistant to abrasion with a calico mop 6" dia. on a polishing latue is obtained.

Dated this 29th day of April, 1975

Council of Scientific & Industrial Research

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

"IMPROVEMENTS IN OR RELATING TO COLOURING OF NICKEL CHROME STAINLESS STEEL ARGICLES".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:-

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist, RAMACHANDRA SUBRAMANIAN, Scientist and RAMASUBBU VENKATACHALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-623006, India, and all are Indian Nationals.

The invention relates to improvements in or relating to colouring of nickel-chrome stainless steel articles.

Hitherto it has been proposed to colour the stainless steels by one of the methods mentioned below:

1. Stainless steel when immersed in molten sodium dichromate developed an intensely black possessing considerable strength and elasticity.
2. The stainless steel is sprayed with certain solutions and heated in furnace at controlled temperatures for a definite time to get different shades of colour.
3. The stainless steel is immersed in aqueous solutions of sulfuric acid containing oxidising agents such as chromic acid, chromates, permanganates, vanadates.
4. The stainless steel is electrolytically treated in aqueous solutions of sodium carbonate-potassium chloride sodium meta silicate + potassium chloride, potassium chromate + sulfuric acid or mixtures of these at high current densities greater than 500 amf using alternating current of 50 cycles.

5. In some later modifications of some of these processes, the coloured film so produced are further protected for improved abrasion resistance by spraying with silicate solutions and baked at temperatures above 300°c for 5 to 15 minutes.

It has also been reported in literature that colouring of stainless steel could be obtained by making the stainless steel articles anodic at a current density of 0.06 asdm in an aqueous solution of 2% by volume concentrated sulfuric acid containing 30 gm per litre of sodium dichromate and maintained at 70-95°c. Various shades of colour ranging from brown, blue,yellow,purple and green have been reported. However, intense black colours could not be obtained from these electrolytes.

It has also been reported that the above range of colours could be obtained by immersion of the stainless steels for varying times in an aqueous solutions of 50% by volume of sulfuric acid and about 12-15 gm per litre of sodium dichromate.

6. As a subsequent improvement of the above process, it has been reported that the oxide film so produced has to be hardened for improved abrasion resistance by cathodic treatment of the coloured stainless steel in a chromic acid electrolyte containing 250g/1 CrO_3 and 2 to 5g/1 H_2SO_4 for 15 minutes at 40°c. The anode used is lead and current density is around 2-5 asdm.

These methods are open to the objection that methods 1 and 2 use a molten bath at high temperatures and may effect the strength of the steel surface and difficult to control the shades of colour.

Method 3 produces colours of different shades but are not sufficiently abrasion resistant for day to day application.

Method 4 uses very high current densities involving high investment on equipment. Further, the films are not abrasion resistant.

Method 5 uses a very low current density which is very critical and use a higher current densities do not produce any colours.

In method 6, the colour is produced by immersion in chromic-sulphuric acid mixtures at a temperature 70-95°c and hardened ins virtually chromium plating electrlyte at current densities lower than required for the onset of chromium deposition. Considering the poor current distribution of the chromium plating electrolyte, the hardening may cause burning at the corners and edges of the work.

The main object of the present invention is to obviate these disadvantages and to improve the uniformity of the shades of colour and also to shorten the time of colouring by immersion process using chro acid sulphuric acid electrolyte containing a definite quantity of trivalent chromium in the colouring bath and subsequently hardening in a chromic acid electrolyte in which a definite amount of trivalent chromium ion is produced by reduction with such reducing agents as selenites and arsenites.

The main finding underlying the invention is that colours ranging from light brown, sky blue, violet, rose, light pink, dark pink, peacock, greenish blue, green to golden yellow may be produced by immersion process in a chromic acid sulphuric acid electrolyte containing suitable reducing agents to produce certain amount of trivalent chromium and suitable metallic salts to shorten the duration of colouring at a given temperature in the colouring bath and subsequently hardening in a chromic acid bath containing addition agents to make the coloured coating resistant to abrasion.

According to the present invention , there is provided a process for colouring nickel chrome stainless steel articles comprises polishing, degreasing and colouring in chromic acid and sulphuric acid mixture by immersion of the article in amixture of chromic acid and sulphuric acid containing a maximum trivalent chromium ions ($Cr3^{+}$) of 10 g/1 and other ions with 5 g/1 such as Ni^{2+}, Cu^{2+}, Mn^{2+} as their sulphates and hardening the same by cathodic treatment. Nickel chrome stainless steel with greater than 7% chromium may be coloured by the invented process.

The composition of the immersion bath may be in the limits of 100-775 g/1 of CrO_3 and 60-425 ml/1 of sulphuric acid of specific gravity 1.84

The temperature is maintained at any temperature between 70°c and 90°c. The tolerance limit is ±1°c.

The time of immersion may be in the range 5 mins. to 85 mins.

The Cr^{3+} ions may be produced by the reduction of Cr^{6+} with reducing agents such as oxalic acid, arsenous oxide, ascorbic acid and sodium thiosulphate.

The colour so obtained on the work may be hardened by treating the work as cathode in a bath containing 100-150 g/1 chromic acid, sodium arsenite 3 g/1 or sodium selenite 10 g/1 and sodium meta silicate 10-20 g/1 at a low current density of 1 to 2A/dm^2 at 40°c for about 10-25 min.

Thus stainless steel panels ar articles (such as outdoor and indoor building panels, automobile trimsand stainless steel domestic appliances, picture frames, household utensils, watchstraps, chains and such architectural and decorative applications) are coloured by immersion in achromic acid sulphuric acid electrolyte, in which a fraction of the hexavalent chromium has been reduced to trivalent chromium by chemical reducing agents such as oxalic acid, arsenites, selenites, ascorbic acid, and also containing copper, nickel, cobalt and/or manganese ions, The concentrations of chromic acid can be varied within the limits 100 g/1 to 775 g/1 and of sulphuric acid in the limits 60 ml/1 to 425 ml/1 of concentrated sulfuric acid of specific gravity 1.84 and maintained in such a ratio that CrO_3 H_2SO_4 does not etch the stainless steel surface. The concentration of trivalent chromium can be varied in the limits of 2 to 10 gm /litre by addition of calculated quantities of the above said reducing agents. The temperature can be preferably be varied in the range of 60-90°c but maintained at a desired temperature thermostatically the tolerance being ± 1°c. The time of immersion is in that case from 3 to 85 minutes depending on the concentration of chromic acid, the temperature of treatment , the nature of the surface, viz mechanically polished , etched or electropolished and the colour desired.

Cupric, manganese, nickel and cobalt ions are added as their sulphates the concentration being within 5 grams per litre to produce uniform colours and shorten the treatment time. The coloured stainless steel articles is rinsed well in tap water and then electrolytically hardened in chromic acid sodium meta silicate electrolyte . The concentration of CrO_3 can be varied from 100 to 300 g/1 a fraction of which is reduced to trivalent chromium by arsenites, of alkaline metals, the concentration of which can be varied from 3 to 10 g/1. The sodium meta silicate concentration is varied from 10 to 20 g/1. The coloured article is made the cathode and stainless steel or lead is made the anode. The temprature of the electrolyte could be varied from 30 to 70°c and a cathode current density of 1 asdm to 2 asdm is maintained for a period of 15 to 20 minutes.

The following examples are given to illustrate the invention and not to limit the scope of the invention.

Example 1

Stainless steel (18:8) sheets of size 6" x 3" were mechanically polished to a bright finish, degreased with trichloroethylene and were cathodically cleaned in hot alkaline cleanser containing.

Sodium carbonate	35 g/1
Sodium hydroxide	25 g/1
Temperature	70°c
Anode	Mild steel
Current density	15 A/dm^2
Time	1-2 minutes

The plates were washed and finally immersed in the following colouring bath.

a)

Chromic acid	775 g/1
Sulphuric acid (spgr 1.84)	60 ml/1
Temperature	70 ± 1°c

Time	Colour
10 minutes	light grey
15 minutes	Yellowish grey
20 minutes	Medium yellow
25 minutes	Golden yellow

b) An addition of 4 g/1 of oxalic acid was then made and pieces of the same stainless steel was immersed in this to give the following results.

5 minutes	Light grey
8 minutes	Yellowish grey
10 minutes	Light yellow
15 minutes	Golden yellow

c) When 7.5 g/1 of copper sulphate was added to the above solution, pieces of the same stainless steel were coloured in the times shown below

3 minutes	Light grey
5 minutes	Yellowish grey
7.5 minutes	Light yellow
10 minutes	Golden yellow

The coloured plates were then hardened in the following electrolyte under the conditions mentioned therein.

Chromic acid	100 g/1
Sodium meta silicate	10 g/1
Sodium selenite	2 g/1
Temperature	70°c
Stainless steel article	Cathode
Lead	anode
Current density	1 A/dm^2
Time	15 minutes

One panel in each set of experiments were rubbed vigorously with vim before hardening treatment. The colour went away leaving the bare metal. The other hardened plates were rubbed vigorously with vim and the colour did not go away.

Example 2

Stainless steel (18:8) plates were pretreated as in Ex.1 before colouring and immersed in the following colouring bath.

a)	Chromic acid	250 g/1
	Sulphuric acid (sp gr 1.84)	210 ml/1
	Temperature	80 ± 1°c

The plates were coloured according to the times given below

Time	Colour
15 minutes	light brown
25 minutes	dark brown
40 minutes	blue
50 minutes	violet
60 minutes	medium yellow
70 minutes	rosy yellow

b) An addition of 10 g/1 of ascrobic acid to an identical solution was then made and pieces of the same stainless steel were immersed in this to give the following results.

Time	Colour
10 minutes	light brown
15 minutes	dark brown
25 minutes	blue
30 minutes	violet
35 minutes	yellow
40 minutes	rose

When 2 g/1 of nickel sulphate was added to the above solution pieces of the same stainless steel were coloured in times pieces of the same stain -less steel were coloured in the times shown below.

5 minutes	light brown
7,5 minutes	dark brown
10 minutes	blue
15 minutes	violet
17.5 minutes	yellow
20 minutes	rose

One panel in each of the above experiments were rubbed vigorously with vim. The colour went away leaving the bare metal. The other plates were hardened in the followin electrolyte:

Chromic acid	150 g/1
Sodium arsenite	3 g/1
Sodium metasilicate	20 g/1
Temperature	40°c
Current density	2 A/dm^2
Cathode	stainless steel article
Anode	lead
Time	15 minutes

The hardened plates were then vigorously rubbed with vim and the colour did not go away. The hardened plates were also polished with a calico mop of 15 cm dia. on a polishing lathe. The colour was abrasion resistant.

Example 3

Stainless steel panels of 7.5 cm x 2.5 cm size were mechanically polished and buffed, electropolished in sulphuric acid-phospheric acid-lactic acid electrolyte at 25 A/dm^2 at 60°c with lead as cathode and then washed and coloured in the following electrolyte:

Chromic acid	250 g/1
Sulphuric acid (sp gr 1.84)	375 ml/1
Sodium hydroxide	40 g/1
Temperature	75± 1°c

The plates get coloured according to the time indicated below.

Time	Colour
20 minutes	light yellow
25 minutes	brownish yellow
30 minutes	sky blue
35 minutes	greenish blue
40 minutes	green

An addition of 5 g/1 of arsenous oxide to an identical solution was then made and pieces of the same stainless steel were immersed in this to give the following results.

Time	Colour
15 minutes	light yellow
20 minutes	brownish yellow
25 minutes	sky blue
30 minutes	greenish blue
35 minutes	green

When 4 g/1 of cobalt sulphate was added to the above solution, pieces of the same stainless steel were coloured in the times shown below

Time	Colour
7.5 minutes	light yellow
10 minutes	brownish yellow
15 minutes	sky blue
17 minutes	greenish blue
20 minutes	green

One panel in each of the above experiments were rubbed vigorously with Vim. The colour went away leaving the bare metal. The other panels were hardened in the electrolyte given under Ex. 1. The colour did not go away upon rubbing vigorously with vim. The hardened plates were also polished with a calico mop of 15 cm dia. on a polishing lathe. The colour was abrasion resistant.

Example 4

Stainlesssteel panels of size 10 cm x 15 cm were mechanically polished and buffed, degreased and anodically etched in chromic acid and sulphuric acid mixture to give a fine grained surface and immersed in the following solution.

Chromic acid	100 g/1
Sulphuric acid	425 ml/1
Temperature	75 ± 1°c

The plates got coloured according to the time indicated below,

Time	Colour
35 minutes	faint yellow
45 minutes	sky blue
55 minutes	dark blue
65 minutes	yellow
75 minutes	dark pink
85 minutes	green

An addition of 10 g/1 of sodium selenite to an identical solution was then made and pieces of the same stainless steeel were immersed in this gives the following results:-

Time	Colour
30 minutes	faint yellow
40 minutes	sky blue
50minutes	dark blue
60 minutes	yellow
70 minutes	dark pink
80 minutes	green

A fubther addition of 5 g/1 manganese sulphate was added to the above solution,pieces of the same stainless steel were coloured in times shown below

Time	Colour
20 minutes	faint yellow
30 minutes	sky blue
40 minutes	dark blue
50 minutes	yellow
60 minutes	dark pink
70 minutes	green

One panel in each of the above experiments were rubbed vigorously with vim. The colour went away leaving the metal. The other panels were hardened in the electrolyte given under Ex. 2. The colour did not go away upon vigourosly rubbing with vim

The following are among the main advantages of the invention:

1) This process is simple to operate and requires only conventional equipment used in metal finishing.

2) Coloured and hardened stainless steel may be subjected to considerable deformation eg. drawing ,bending etc. without damaging the coloured film or reducing its colour intensity. Similarly ,uncoloured steel which has been subjected to forming operations can be coloured after forming.

3) Coloured designs and patterns can be printed onto stainless steel surface by means of photographic techniques using photoresist which are resistant to the colouring and hardening solutions. With these techniques it is possible to produce attractive combination of coloured design and patterns..

This invention broadly consists in colouring the stainless steel panels or articles by immersion in a chromic acid sulphuric acid electrolyte in which a fraction of the hexavalent chromium has been reduced to trivalent chromium by chemical reducing agents such as oxalic acid, arsenites, selenite ascorbic acid and also containing copper, nickel, cobalt and/or mangagese ions. The concentration of chromic acid can be varied within the limits 100 g g/l to 775 g/1 and of sulphuric acid(density 1.84) in the limits 60 ml /1 to 425 ml/1 and maintained in such a ratio that CrO_3:H_2SO_4 does not etch the stainless steel surface. The concentration of trivalent chromium can be varied in the limits of 2 to 10 g/1 by addition of calculated quantities of the above said reducing agents. The temperature can be varied in the range of 60-90 c but maintained at a desired temperature thermostatically the tolerance being $\pm$ 1°c . The time of immersion is from 53 to 85 min. depending on the concentration of chromic acid, the temperature of treatment, the nature of the surface, viz mechanically polished , etched or electropolished and the colour desired.

We claim

1. A process for colouring of Nickel chrome stainless steel articles comprises polishing degreasing and colouring in chromic acid and sulphuric acid mixture by immersion of the article at a temperature between 70 c and 90 c with tolerance limit being ± 1 c wherein the colouring mixture contains trivalent chromium ions (Cr^{3+}) of 10 g/1 and other ions 5 g/1 such as Ni^{2+} Cu^{2+} Co^{2+} Mn^{2+} present as their sulphates and hardening the same by cathodic treatment.

2. A process as claimed in claim 1 wherein stainless steel article with greater than 7% chromium content is coloured.

3. A process as claimed in claim 1 or 2 wherein the composition of immersion bath is in the limits of 100-775 g/1 of CrO_3 and 60-425 ml/1 of sulphuric acid of specific gravity 1.84 mins

4. A process as claimed in any of the preceding claims wherein the time of immersion is in the range 5 mins to 85 mins.

5. A process as claimed in any of the preceding claims wherein Cr^{3+} ions are produced by the reduction of Cr^{6+} with reducing agents such as oxalic acid, arsenous oxide, ascrobic acid and sodium thisulphate.

6. A process as claimed in any of the preceding claims wherein the colour on the article is hardened by treatment the article as cathode in a bath containing 100-150 g/1 chromic acid, sodium arsenite 3 g/1 or sodium selenite 10 g/1 and sodium meta silicate 10-20 g/1 at a low current density of 1 to $2A/dm^2$ at 40 c to a period of 15 minutes preferably between 10 and 25 minutes.

Dated this 18th day of June, 1976

sd/-

I.M.S.Mamak
Scientist E (Patents)
Council of Scientific &
Industrial Research