

ELECTROLYTIC COLOURING OF IRON

Part I

M.I. BHATTI, MUHAMMAD YAR and ALLAH BAKHSH CHAUDHRY

PCSIR Laboratories, Lahore 16

(Received August 18, 1972; revised March 8, 1973)

Abstract. An attempt has been made to develop a suitable method for electrolytic colouring of iron from different electrolytic media, using different cathode materials and various addition agents to the NaOH-NaNO₃ baths. The effect of addition agents, viz. sodium nitrite, potassium permanganate, and ammonium molybdate on the electrolytic colouring has been studied. The surface texture before and after the colouring was observed under the magnifying lens ($\times 10$). The limits of the optimum operating variables studied for different compositions are given and their results shown.

The chemical reactivity of certain metals very frequently makes it necessary to protect them against environmental corrosive attacks by applying upon their surfaces some form of insulating barrier. This barrier may be in the form of an organic coating such as paint, enamel or lacquer or it may be metallic in character and be applied by electrodeposition, hot dipping or metal spraying. Still another method of providing a protective barrier for a reactive metal is to convert a portion of the surface into corrosion-resistant, nonreactive coatings which are produced by these treatments, are formed by chemical or electrochemical modification of the metallic surface, and as such are an integral part of the parent metal.¹ The electrolytic processes make use of an externally applied potential to promote the formation of oxides coatings² or films on the metallic surfaces. Work has been carried out on the colouring of iron by an electrolytic method using different recipes at suitable temperature, current density and duration of electrolytic operation. Different shades of colours have been obtained from easily available electrolytes with small amounts of addition agents to produce the desired effect.

Experimental

Preparation and Finishing of the Work-Piece. The work-piece was cleaned as if preparing the metal surface for electroplating.³ It was rinsed well to remove any particle before immersing in the electrolytic-bath. After the operation the work-piece was lacquered with a good quality lacquer and dried.

Method. The experiments were carried out in a 600-ml beaker containing the electrolyte. It was placed on a sand-bath heated by an electric heater and the temperature was controlled within $\pm 2^\circ\text{C}$. The stainless-steel cathode and the specimen as anode were hung in the vertical position from busbars and with a sliding arrangement to adjust the distance between the electrodes. A stirrer was fitted in the beaker and a thermometer dipped in the solution to note the temperature. A variable rheostat, a voltmeter and a 20-amp ammeter was connected to tap-out the desired amperages and voltages. The anode connection was so constructed that the specimen could be

removed easily from the cell for washing or any other subsequent treatment. The position of the specimen with respect to the anode was kept fixed during the operation to avoid unnecessary variation in current density and internal cell resistance. The cathode selected was such that it could not react with the electrolyte. In each electrolyte the specimen was electro-coloured and the state of the surface and the colouring effect observed through a magnifying lens ($\times 10$). The results of the studies are summarised in Tables 1 and 2.

Results and Discussion

The electrolytic colouring effect due to the combination of the electrolytes with and without the addition agents has been studied and conditions approaching optimum were achieved in each case. A comparative study of the addition agents used such as sodium nitrite, potassium permanganate,⁴ and ammonium molybdate⁵ was carried out at different current densities, temperatures and periods of electrolytic colouring. It was found that a NaOH-NaNO₃ mixture was capable of producing encouraging results. The colouring effect produced due to the variation in the concentration of the electrolyte NaOH-NaNO₃ current density,⁶ temperature and duration of electro-colouring is given in Table 1. From amongst the various cathodic materials tried, e.g. iron, copper, brass and stainless-steel, only stainless-steel gave good results in the highly alkaline oxidising baths used. It is observed from Table 1 that the judicious combination of NaOH-NaNO₃ alone is found to be 200 g NaOH and 50 g NaNO₃ in 400 ml electrolyte.

Influence of Concentration of Electrolyte on Electrolytic Colouring. Appreciable results are obtained when concentration of NaOH and NaNO₃ does not fall below 37.5 and 12.5% respectively (Table 1). The Table shows that with 25% NaOH and 2.5-10% NaNO₃ the shades vary from steel grey to black at a C.D. of 18.0 amp/dm² and within a temperature range of 100-112°C. At lower temperatures the colouring layers observed were not strong and tenacious enough to retain the shade; the specimen could be rubbed off, cleaning the surface partially. At a

TABLE 1. EFFECT OF CONCENTRATION OF CAUSTIC SODA AND SODIUM NITRATE AT DIFFERENT CURRENT DENSITIES, FOR DIFFERENT INTERVALS OF TIME AND AT DIFFERENT TEMPERATURES, ON THE ELECTROLYTIC COLOURING OF IRON (total volume of electrolyte, 400 ml; cathode, stainless-steel; inter-electrode distance, 3-4 cm).

No.	Concn of NaOH(%)	Concn of NaNO ₃ (%)	C.D./dm ²	Volt	Time (min)	Temp (°C)	Colour	Remarks
1	25	2.5	18	2.5	5	100	Steel grey	Light, uniform
2	25	2.5	18	2.5	5	105	Dark grey	Uniform better than No. 1
3	25	2.5	18	2.5	5	112	Medium black	Uniform
4	25	10.0	18	2.5	5	112	Black	Darker than No. 3
5	37.5	12.5	20	2.0	5	112	Blue black	Medium shade
6	37.5	12.5	20	2.0	8	115	Bluish black	Peeling off the surface at the periphery
7	50.0	12.5	15.5	2.5	15	90	Black	Medium shade
8	50.0	12.5	15.5	2.5	10	110	Black	Medium shade, better than No. 7
9	50.0	12.5	18.0	2.0	5	112	Black	Better than No. 8
10	50.0	12.5	18.0	2.0	8	114	Black	Better than No. 9
11	50.0	12.5	20.0	2.0	5	112	Black	Deep shade better than No. 10
12	62.5	12.5	18.0	2.0	8	112	Black	Peeling off the colour layer

TABLE 2. EFFECT OF ADDITION AGENTS ON THE ELECTROLYTIC COLOURING OF IRON (NaOH taken 50%; NaNO₃, 12.5%; volume of electrolyte, 400 ml; cathode, stainless-steel; inter-electrode distance, 3-4 cm).

No.	Addition agents	C.D./dm ²	Volts	Time (min)	Temp (°C)	Colour	Remarks
1	NaNO ₂ (5%)	14.4	2.5	5	115	Bluish black	Light shade
2	"	18.0	2	5	112	Black	Light shade better than No. 1
3	"	22.2	2	5	112	Black	Light, dull with brown patches
4	KMnO ₄ (1.25%)	13.3	2	5	108	Steel grey	Metallic shade
5	"	15.5	2	5	110	Black	Uniform lustrous better than No. 11 (Table 1)
6	(NH ₄) ₆ Mo ₇ O ₂₄ (1.25%)	16.6	2.5	5	112	Black grey	Light uniform better than No. 2 (Table 1)
7	"	20.0	2.5	5	112	Black grey	Uniform better than No. 7
8	"	26.6	2.5	3	112	Black	Dark shade, better than No. 5

concentration of 37.5% NaOH and 12.5% NaNO₃ the spectrum of colour shades varies from light blue black to bluish black at a C.D. of 20 amp/dm² at temperature of 112-115°C for 5-8 min. The shades produced were fairly strong and desirable but after 8 min peeling off the layer at the periphery started. However, a good colouring effect is obtained with 50% NaOH; 12.5% NaNO₃ at a C.D. of 20 amp/dm² at 112°C for 5-8 min. With an increase in concentration of NaOH from 50 to 62.5% with 12.5% NaNO₃, the colouring effect shifted from black to non-adherent blackish layers at the same C.D., temperature and duration of the process. In order to ensure better results it was found advisable to have a concentration in the range of 45-55% NaOH. Beyond this limit the effect is not enhanced; even a change in the C.D. did not help in producing any appreciable

shade. Therefore, for further experimentation, workable concentrations of 50 and 12.5% for NaOH and NaNO₃ were selected. In some experiments galvanized mild steel pieces were tried. The zinc layer was first dissolved by hot caustic alkali solution making the surface exposed for further action.

Influence of Current Density and Time on the Colouring Effect. During the initial stages of anodic attack before the colouring conditions were established, a C.D. considerably higher than the optimum value was found to be desirable in order to minimize the time taken to establish the colouring conditions. Below the optimum value of the C.D. the anodic film necessary for the controlled oxidation and colouring of the metal does not give the desired colour and the different shades thus produced do not fix to the surface and are rubbed off easily. With higher C.D.,

the surface acquires a grained appearance, resulting in pitting and peeling off the surface. This effect is more pronounced at the edges and tends to cover the whole area as the C.D. goes up. It is safe to conclude that a C.D. of 20 amp/dm² is effective but higher values up to 25 amp/dm² do not change the nature of the colouring effect. At low temperatures the colour pattern was not well-defined and the specimen was mixed-shaded. It was observed that an increase in C.D. above the optimum value always caused a decrease in shine, smoothness and the peeling-off effect was there. The voltage was kept low, the average voltage for different electrolytic compositions with different C.Ds. ranging from 2-4 volts.

Influence of the Addition Agents on the Colouring. Table 2 shows the effect of addition agents such as NaNO₂, KMnO₄ and (NH₄)₆ Mo₇O₂₄ on the nature of colour, when incorporated in the parent electrolyte, viz. NaOH 50% and NaNO₃ 12.5%. The results in the table show that NaNO₂ did not produce better colour shades than that given by the parent composition under similar conditions. Whereas a black shade is obtained with a C.D. of 18.0 amp/dm² at 112°C for 5 min, addition of NaNO₂ only made the colour lighter in shade (comparison: Table 1, expts 3 and Table 2, expt. 2). The table also shows the results when 1.25% KMnO₄ was added in the parent electrolyte. It is noted that at C.Ds. of 13.3-15.5 amp/dm² at 108-110°C for 5 min the colours produced are steel grey, and then black. At a C.D. of 15.5 amp/dm² the colour produced (expt. 5) is better than that obtained from the parent electrolyte. KMnO₄ has added to the colouring effect.

The table further shows the influence of ammonium molybdate as the addition agent. In this case a C.D. of 20 amp/dm² at 112°C for 5 min produces blackish grey colour of appreciable dark shade but the optimum result is obtained at a C.D. of 26.6 amp/dm² at a

temperature 112°C for 3 min. The black colour formed after 3 min was dark and uniform metallic shade superior to all black shades produced with or without using any addition agent. It is better than the colours shown (expts. 4 and 5). The only difference is that this is produced at a higher current density, i.e., 26.6 amp as compared with 20 amp/dm² (Table 1, expt. 11) and 15.5 amp/dm² (Table 2, expt. 5).

Conclusion

Conditions for the electrolytic colouring of iron from NaOH-NaNO₃ baths have been studied. Effects of different concentrations of NaOH and NaNO₃ have been observed by reference to the formation and nature of the colouring layers. A range of concentration of 50% NaOH and 12.5% NaNO₃ with current density of 18-20 amp/dm² has been found satisfactory.

A number of experiments were carried out using the addition agents, viz. NaNO₂, KMnO₄ and (NH₄)₆ Mo₇O₂₄ (1.25%) gave the tenacious film of appealing black colour.

References

1. R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology* (Interscience, New York, 1952), vol. IX, p. 20.
2. H.N. Gilbert, U.S. Patent 2, 377,876 (June 12, 1945).
3. M. Rodgers, Thomas, *Handbook of Electroplating* (Macmillan, New York, 1959), p. 103.
4. T. Fijumura, Japan Patent 4863 (November 21, 1952).
5. A. Pacz, German Patent 510,380 (October 30, 1927).
6. L.S. Palatnik, U.S.S.R. Patent 123,005 (October 10, 1959).