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CHEMICAL OXIDATION OF ALUMINIUM FOR PRODUCING BRILLIANT COLOURS

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The cost of anodising and colouring of small aluminium articles meant for lower service life is quite high. In this context chemical oxidation of aluminium and subsequent colouring with organic dyes has a good potential. This process is useful for the bulk treatment of small aluminium articles like rivets, bolts, nuts, screws, nails, washers, chains, jewellery items, etc. Such small articles are very difficult to anodise using conventional methods. Chemical polishing prior to colouring improves the brilliancy of the colour so produced. These are highlighted in this paper.

Key words: Aluminium alloy, chemical oxidation, colouring of aluminium

INTRODUCTION

In recent years, significant progress has been made in the field of metal colouring processes. By suitable chemical or electrochemical means, most of the metals can be coloured to a variety of shades. Aluminium and its alloys have been used for a variety of applications because of its light weight and good corrosion resistance. Its modern applications range from simple to sophisticated forms as well as their utilitarian and high duty applications comprise a wide range. Among the various techniques available for colour finishing of aluminium, anodising plays a major role [1-3]. This is because of the excellent chemical and physical properties of the anodic film so formed, which is subsequently coloured with organic dyes or inorganic pigments or electrolytically coloured [4]. However, anodic oxidation with subsequent colouring calls for a considerable expenditure for the facility and involves power consumption. Added to this, anodising of small parts is extremely difficult since barrel anodising results in higher percentage of rejects.

Substitutes for most of the above finishes can be obtained at much lower cost by chemical colouring processes. Several methods are available for colouring aluminium based on chemical conversion coatings. The drawback of the well known processes such as MBV, Alodine, Alochrome, etc. is that the colour obtained is often iridescent in nature and mostly unattractive. Most of these solutions are operated at higher temperatures ($>80°C$). Further, these finishes cannot be used as such for decorative applications, as they are meant for use as an undercoat providing better adhesion for paints, lacquers and enamels [5-10].

Chemical colouring of aluminium to black and blue colours is well known[11]. A low cost imersion blackening solution for aluminium solar collectors in ammoniacal nickel thiocyanate solution has been recently reported [12]. Solutions based on permanganate, molybdate or antimony chloride are also in use [13]. Chemical colouring of aluminium in sparingly soluble metallic carbonates in alkaline solution has been studied [14].

In this context, chemical colouring of aluminium at ambient temperature offers a wider scope for treating aluminium articles designed for a shorter span of lifetime. The development of a practical solution for colouring aluminium to various shades of yellow and blue have been reported [18]. The solution is based on ferricyanide with additives such as dichromates and ferric chloride. Brilliant colours of yellow and blue only could be obtained in these solutions by employing chemical/electrochemical polishing techniques. Recently chemical oxidation technique has been reported in the literature [15-17].

In this paper the authors have described a chemical oxidation process for aluminium by treating it in an aqueous solution comprising an oxidising agent such as potassium ferricyanide, an accelerating agent like disodium hydrogen phosphate and a buffering agent like sodium carbonate.

EXPERIMENTAL

2S aluminium (min. 99% Al) panels of size 75 x 75 mm were mechanically polished, degreased with trichloroethylene and etched in the following solution:

Sodium bicarbonate	..	100 g/l
Time	..	7 minutes

The etched specimens were washed well with water and desmudged in 100 ml/l nitric acid solution for 2 minutes, then washed well with tap water and then distilled water, and finally immersed in the oxidising solution. The solution contains an oxidising agent, buffering agent and an accelerating agent. The composition of the solution is:

Pottasium ferricyanide	..	75 g/l
Disodium hydrogen phosphate	..	30 g/l
Sodium carbonate	..	20 g/l
pH	..	9-10
Immersion time	..	20-35 minutes
Temperature	..	40-50°C

The panels were thoroughly washed and immersed in the organic colouring solution under the following conditions:

Dye concentration	..	1-5 g/l (for light shades)
Dye concentration	..	10 g/l (for black)
Temperature	..	55-60°C
pH	..	5.5 ± 0.5
Immersion time	..	10-15 min.(depending on the colour required)

The coloured specimens were washed, dried and sealed in colourless lacquer to seal the pores of the oxide film.

All the chemicals used were of LR grade. Distilled or deionised water was used for solution preparation. The temperature was maintained by means of a thermostat. The colour of the panel was judged visually. Adhesion of the coating was examined by tape test.

RESULTS AND DISCUSSION

Influence of oxidising agent

Preliminary experiments with various concentrations of potassium ferricyanide showed that a concentration of 60 to 90 g/l is essential for the formation of strongly absorptive porous oxide film. Higher concentrations (greater than 100 g/l) lead to a dull finish and the coating is muddy with streaks, whereas lower concentrations (less than 50 g/l) lead to haziness of the coating with poor dye absorption. Disodium hydrogen phosphate was also found to be essential for the formation of porous oxide film. A buffer is included when a new bath is made which aids in maintaining constant pH.

Influence of immersion time

The immersion time has a greater influence on the formation of porous oxide coating and its subsequent dye absorption. A minimum of 15 minutes treatment time is required at 50°C for maximum dye absorption. A prolonged treatment impairs the quality of the coating since the coating becomes hazy or in extreme cases even opaque. The coating produced under correct operating conditions is perfectly clear and transparent. The time required depends on the alloy, the colour desired, amount of protection of corrosion resistance required and the thickness of aluminium. Vacuum deposited aluminium can also be treated in this solution. In general, a longer time is required to obtain darker colours. For producing black colour 30-35 minutes are required.

Dye absorption

The interesting property of the coating is its ability to absorb organic dyes and inorganic pigments. The coloured coating is as brilliant as any dyed anodic coating. In the case of aluminium alloys where anodising has a tendency to dull a bright surface, this process does not mar the surface appearance. Any colour from clear to a deep black is possible. The dye is being used in a stainless steel tank, with good pH and temperature control. Too high pH results in faded colour while too low pH makes for a reddish gold for gold dyes. A few anodising dyes will impart a colour to this treatment, but the colour is far from the same as obtained with anodising. To produce light shades such as gold, concentration of the dye is kept at 1-5 g/l. To produce black colour, a dye concentration of 10 g/l is used.

Influence of aluminium alloys

Aluminium alloys such as 2S, 3S, 26S and 52S are treated by this process to produce different colours by organic colouring. This process consumes very little aluminium in the formation of the coating. Hence the treated surface remains brighter than with anodising. The solution used for processing is alkaline and is less corrosive. Hence assemblies of aluminium with other materials may be treated at once. This process can be applied to large or small aluminium parts.

Solution maintenance

During continued operation, the constituents are consumed due to attack on the metal, decomposition of the ingredients and carry over by the article. The factors which must be controlled include the pH, temperature and concentration. Sludge is formed in operating the solution. Periodical additions of the bath ingredients is necessary for satisfactory operation. The solution can treat about 1 m^2/l of aluminium surface before it is discarded. The concentration may be checked by simple titration and the pH may be maintained automatically.

Smutty surface may be obtained when (i) the article is not properly cleaned (ii) traces of alkali remain on the work (iii) the solution is too hot and concentrated and (iv) treatment time is very long.

Influence of sealing

Finally the sealing treatment is applied to seal the pores, improve corrosion resistance or to impart additional lubricity. Some of the sealants are water emulsions of waxes, various resins, or in some cases lacquer type coating.

Influence of temperature

The solution temperature was varied from 30-90°C. An increase in the solution temperature accelerates both the rate of formation of the coating and the rate of attack on the metal surface. This can result in a change in the appearance of the coating. The temperature of the solution should be maintained between 40-50°C. A lower temperature of the bath (less than 40°C) leads to the formation of thin coatings. The process does not generate heat but temperature must be properly controlled. If temperature varies much, colour variations will occur when the parts are dyed.

Influence of solution agitation

Agitation of the processing solution accelerates the reaction and provides a more uniform film formation. Uniform coatings were produced in this study with air agitation, whereas non-agitated solution gave a poor surface appearance of the coating.

Influence of surface preparation

The appearance of the coating produced depends greatly on the initial surface condition of the metal being treated. The porous oxide film accurately reproduces the surface condition of the base metal. Thus brilliant and attractive shades are produced on polished aluminium (chemically or electrochemically polished), whereas etched and matt finishes produce dull shades.

Influence of top coat

The coatings are very thin (of the order of 2-5 μm) and have less abrasion resistance than anodic coatings. An overcoating of transparent lacquer improves the resistance to wear and abrasion. The coating possesses satisfactory protective properties when it is used in combination with a top lacquer coating.

Economy

Compared with anodic films, chemically oxidised coatings have the advantage of economy and relative simplicity of equipment required for its production. Further, relatively moderate temperatures are used for coating formation. In general, darker colours and applications requiring more corrosion resistance are higher in cost. The greatest part of the chemical cost is in chemicals for the conversion coating itself. They are well suited for producing cheap imitation items like bangles, ear rings, bracelets, chains, buckles, etc. Small parts are coloured by keeping them in plating barrel which is rotated gently as in the case of barrel plating. Using the solutions reported in this study eyelets were coloured to various rainbow shades without any reject. Unlike anodising no heat is generated during processing and racked parts may be placed very close together thus maximising production rates.

CONCLUSION

Aluminium and its alloy can be chemically oxidised and subsequently coloured with organic dyes to various rainbow shades. Optimum composition and operating conditions of the oxidising solution are found to be,

Potassium ferricyanide	..	75 g/l
Disodium hydrogen phosphate	..	30 g/l
Sodium carbonate	..	20 g/l
pH	..	9-10
Immersion time	..	20-35 minutes
Temperature	..	40-50°C

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