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Rock Island Arsenal Laboratory



TECHNICAL REPORT

HIGH TEMPERATURE, NON-REFLECTIVE EROSION
RESISTANT ALUMINUM FINISH

By

J. Khanishu

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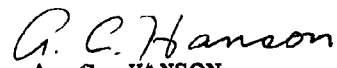
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HIGH TEMPERATURE, NON-REFLECTIVE EROSION
RESISTANT ALUMINUM FINISH

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26 November 1963

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ABSTRACT

A number of soluble inorganic compounds were used in reactions to deposit insoluble colored precipitates (pigments) in the pores of anodized aluminum alloys. Many colors and shades were obtained by using the variables of time of immersion, temperature and concentrations of the coloring solutions. The effects of the alloying constituents were observable in the colors obtained.

There is a notable scarcity of inorganic compounds which can be used to produce a black or olive drab color on anodized aluminum.

Alundum blasting improves variability and depth of colors. By proper control of the hard anodize process, excellent shades of light-fast, nonreflective olive drab colors can be produced.

RECOMMENDATIONS

It is recommended that aluminum parts, which are not to be painted but must have camouflaging, be aluminum blasted and dyed by the inorganic dyeing process. The alternate method of coloration should be the modification of the hardcoating process (Finish 7.5, Table VII, MIL-STD-171B). The method of protecting material against the effects of light using 9-oxa-9,10-dihydrophenanthrene 10-one⁽¹⁾ as proposed by the U.S. Steel Corporation and the invention of Ben H. Kirby,⁽²⁾ assigner to Aluminum Company of America and Koppers Company, Inc., on "Coloring of Oxide-Coated Aluminum," should be investigated. Time did not permit investigations of these processes.

**HIGH TEMPERATURE, NON-REFLECTIVE EROSION
RESISTANT ALUMINUM FINISH**

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HIGH TEMPERATURE, NON-REFLECTIVE EROSION RESISTANT ALUMINUM FINISH

OBJECT

To develop a nonfading, high temperature resistant, olive drab or dark gray coating for aluminum to replace paint on rockets, missiles and launching equipment. To extend the life and reduce the weight of rockets and missiles for improved performances.

INTRODUCTION

The weight factor of rockets, missiles and launching equipment necessitates the use of the lightest metals for greater range and performance. In the selection of these metals the problem of durability is important. The strength of the structural materials not only depends on the composition of the alloy, but also on their corrosion resitability. Corrosion is the scourge of metals in general, but especially of the so-called light metals. A lightweight protective coating is desired.

This work was particularly concerned with the aluminum alloys. Anodizing of aluminum is an excellent method of protection in itself. For camouflage reasons this excellent coating is over-coated with an olive drab paint. This problem was undertaken to develop a camouflage coating for all aluminum parts - a coating which was properly light-fast, corrosion resistant, wear resistant, nonreflective and, above all, lighter in weight.

Considerable work has been done in this country and in Europe on coloring of aluminum, but in general the coloring media have been restricted to various organic dyes. Water soluble dyestuffs do not, as a class, provide a desired light-fast coloring on oxide coated aluminum surface.⁽²⁾ Very little work has been reported in the inorganic dyeing field, because of the limitations on the available inorganic chemicals, which can produce a desired color. Some work was done in an effort to produce an olive drab color simultaneously with the anodizing process.

The process referred to as Finish 7.5, Table VII of MIL-STD-171B produces a dark gray color on aluminum, but the process is uneconomical. Presently, this process is being used at this Arsenal on several components of launching equipment.

The Aluminum Company of America has a patented process⁽³⁾ which produces a black finish on aluminum. ALCOA also has

done work on inorganic chemical dyeing. The Kaiser Aluminum Company also has a light process⁽⁵⁾, which produces colors ranging from a light tan to black. S. Wernick and R. Pinner⁽⁶⁾ stated that various colors can be obtained by consecutively treating aluminum with combinations of two inorganic compounds.

PROCEDURE

Various procedures in surface preparation were used. The first step always included vapor degreasing. This was followed by immersion of the test pieces in an alkaline etching solution, varying the time of immersion. Smut formation after rinsing necessitated an acid dip. The alkaline etching solution was made-up by dissolving 28 ounces of sodium hydroxide in one gallon of water. Immersion time in this solution was varied in order to change the profile of the aluminum surface. Continuing the etching operation beyond 10 minutes did not appreciably further improve the metal surface for anodizing.

Two acid dipping solutions used in this step to remove smut and surface impurities were of the following compositions:

- By volume: 1. 85% phosphoric acid (85-87%)
 1. 15% nitric acid (69-71%)
 2. 15% nitric acid (69-71%)
 85% water

Other metal pretreatments prior to cleaning included buffing, roughening by emery paper and aluminum blasting.

The anodizing bath contained 12 ounces of sulfuric acid per gallon of water. A 60 gallon tank was used in this process.

The temperature was maintained at $70^{\circ}\text{F} \pm 10^{\circ}\text{F}$, the voltage was held at 15 for most processing and the current density ranges were between 2 and 14 amperes per square foot. The period of anodizing was varied between 10 and 120 minutes. Various solutions of inorganic compounds were used in the coloring process. The inorganic compounds were used at different concentrations, times of immersion and temperatures.

A group of panels of each alloy was anodized according to the Martin Hardcoat process (Finish 7.5, Table VII of MIL-STD-171A). The only deviation from the normal procedure was the time of processing. This was done to investigate.

the possibility of obtaining a color other than gray-black. As the test panels were withdrawn at different intervals, they were rinsed and immersed in the dichromate sealing solution.

To test the feasibility of obtaining a black appearance simultaneous with the anodizing process, the finest carbon blacks were obtained. During the anodizing process the acid solution containing the fine black particles was constantly stirred with the expectation that the fine particles would be trapped in the pores of the anodic coating.

Test panels of 2024, 5086, 6061 and 7075 aluminum alloys were hard coated for controlled intervals, voltage and current density. The results of these tests showed that the best colors for each alloy can be obtained in the period indicated in Table I below:

TABLE I
HARD ANODIC COATINGS

Period No.	Immersion Time Minutes	Voltage	Current Density Amps.	2024	5086	6061	7075
1	30	29	90				
2	40	32	120		X	X	
3	47	39	136				
4	55	58-63	129-120	X			X

Further anodizing of 5086 and 6061 would result in the very dark shades.

Representative test panels were placed in a 5% salt spray (fog) cabinet to determine corrosion resistance. Fade resistance tests were carried out on the colored test panels on the Type FDA-R ATLAS Color Fadometer. Representative panels were checked for coating weights and thickness of the anodize coatings.

Reflectivity tests were made on colored test panels using the Hunter Multipurpose Reflectometer.

RESULTS AND DISCUSSION

The choice of the alloys of aluminum used in these experiments was governed by representatives of the alloys currently used by the Army. The following alloys were chosen: 2024, 5086, 6061 and 7075. 2024 differs from the other alloys, since it contains a considerable amount of copper (3.8 - 4.9%) and nickel (1.7 - 2.3%). 5086 differs mainly in the percentage of magnesium (3.5 - 4.5%). 6061 is constituted by more evenly balanced percentages of alloying elements. 7075 differs by having a medium amount of copper (1.2 - 2.0%) and a very high percentage of zinc (5.1 - 6.1%) in its make-up. The silicon content of these alloys is about equal. The percentage of silicon is low.

Since the organic dyes used in coloring anodized aluminum are not light-fast, this work was directed toward the investigation of other coloring processes. The process of chemically precipitating inorganic pigments in the pores of the oxide layer was investigated. Using such inorganic compounds as lead acetate, ammonium sulphide, potassium dichromate, ferric ammonium oxalate, cobalt acetate, sodium sulphide and potassium sulphide, various colors, including olive drab, were formed.

In the use of inorganic compounds as the dyeing media, the effects of different alloys were discernible. However, metal pretreatments and anodizing conditions were more decisive as contributing factors in the effects obtained. The sealing step variables - time of immersion, temperature of solution, pH and the solute in use had to be taken into consideration.

Since the alkaline etch followed by acid dissolution of the surface impurities of the alloying elements, did not seem to be effective in producing a very dull surface on the different alloys, it was reasoned that blasting might produce a good surface for dyeing. On the blasted surfaces the rough profile remained after anodizing and the increase in surface presented an increase in pores. This promoted good dyeing on all alloys. The depth of color was controllable. This method of surface preparation assures a successful treatment.

Alkaline solution (room temperature) etching of aluminum is a necessary step in surface preparation. Beyond a certain immersion time, such as 15 minutes, there was only insignificantly effective changes in the surface profile. After the alkaline immersion and thorough rinsing, a nitric acid dip removes any smut that remains on the surface.

The following three acid solutions were used with equal success:

- | | | |
|---|------------|--------------------------------|
| 1 | By volume: | 85% phosphoric acid |
| | " | 15% nitric acid |
| | | Room temperature 2 - 5 minutes |
| 2 | " | 15% nitric acid |
| | " | 85% water |
| | | Room temperature 2 - 5 minutes |
| 3 | " | 10% hydrofluoric acid |
| | " | 10% nitric acid |
| | " | 80% water |
| | | Room temperature 2 - 5 minutes |

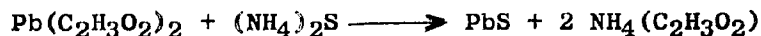
The hydrofluoric acid in solution No. 3 dissolved any silicon remaining on the surface.

Anodizing for short periods such as 10 to 15 minutes proved unsuccessful in the production of quality dyeing. Longer periods such as 30 to 60 minutes were necessary to ready the surface for the dyeing step.

There are many theories regarding the enlargement of the pores in the aluminum oxide film. Keller, et al.⁽⁷⁾ suggest "that at the beginning when a pore has started, increased current flows through this point and causes a local rise in temperature. This rise in temperature causes more rapid chemical dissolution of the oxide in the pores, which explains the mechanism of the depth increasing process." It follows then, that in order to obtain a surface condition which is conducive to good dyeing and corrosion resistance, longer periods of anodizing are essential.

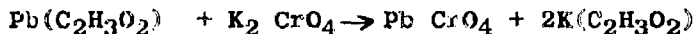
During the experiments of precipitating inorganic pigments, a great number of colors and shades were obtained. Since this work is mainly concerned with dark grays, blacks, and olive drabs, only those tests pertinent to these colors will be discussed.

A very dark brown, nearly black, color was developed by immersing an anodized aluminum panel in a solution of lead acetate (20 oz/gal) for 5 minutes at 125°F, rinsing and immersing in a solution of ammonium sulphide (30 ml/liter) for 10 minutes. This resulted in a nearly black color. The reaction is as follows:



Experience from various tests proved that the use of ammonium sulphide was the best compound for supplying the sulfide ions. An excellent black color can be obtained by this reaction.

It was reasoned that since yellow and black are the colors with which an olive drab color is produced, that it might be possible to cause a reaction between a yellow producing compound and the black dyed aluminum to produce an olive drab. Potassium dichromate was used to supply the yellow pigment in this procedure. Different dilutions of the dichromate (1 gm per 100 ml to 24 gms per 100 ml) were employed. By controlling the depth of black coloring and the immersion time in the dichromate solution, various shades of olive drab or a greenish hue of olive drab could be produced. Also, by using the less concentrated solutions of dichromate and raising the temperature to 180°C to 210°F, simultaneous coloration and sealing could be effected. The dichromate reacts with the uncombined lead acetate in the pores to form the yellow lead chromate pigment. This reaction can be assumed to be:



Therefore, the coloring elements are the insoluble compounds lead sulphide and lead dichromate. The above reactions can be produced in reverse with equal success. In other words, after the yellow color is effected, black can be imposed to produce an olive drab color. The above procedures produced an excellent coating on the 2024 alloy. Color control on the 5086 and 6061 alloys were less successful.

Rinsing thoroughly after each step is imperative, since the coloring must be in the pore only. Any deposition outside the pores would present a loose powder-like layer with poor adhesion.

Using the above metal salt solutions on alundum-blasted aluminum surfaces, color control was completely successful. The control of the shade and reflectivity of the olive drab was very flexible.

Hard anodize coated panels of each alloy and inorganically dyed panels of each alloy, blasted and unblasted, were placed in an oven at 500°F for 40 minutes. There was no thermal breakdown. The temperature was raised to 750°F for 40 minutes and slight fading occurred on all panels. The greatest effects showed on the hard coated set and blasted panels. The temperature was raised further to 1000°F and held for 40 minutes. No further effects were observable.

The possibility of using a very fine (channel) anionic carbon black and producing a black anodized surface was investigated. The carbon black beads were broken down by the use of an osterizer. Using the carbon black suspension a sulfuric acid anodizing (17%) solution was made up. During the anodizing process constant stirring was in effect. The results were negative. Since the pores cannot absorb solid pigments according to H. Bengston(8), solutions which can produce pigments in the pores must be used.

In the salt spray test (5%) early (within 4 hours) corrosion developed on the unblasted inorganically dyed panels of each alloy. The alundum blasted (5086 and 6061) panels began to show corrosion by 312 hours. 2024 (blasted) failed at 4 hours. The hard anodize coated panels were still corrosion free at 1694 hours (121 days).

Results of the 400 hour Fadometer test was insignificant since no loss of color was indicated on alloys which were inorganically dyed or hard coated. This result completely overshadows the Fadometer test on organic dyed anodized coatings. The organically dyed coatings had faded considerably in the Fadometer by the 200th hour of exposure. At the end of the 400th hour the colors had faded to the point of unacceptability. Referring to Federal Color Standard No. 595, note such a difference as that between colors 34087 and 34128 of Table VI.

CONCLUSIONS

When considering the results of such tests as colorability, corrosion resistance, heat resistance and reflectivity, alloy 5086 performed the best.

2024 alloy was most amenable to coloration.

Alundum blasting improves corrosion and heat resistance.

The hard anodize coated panels were very corrosion resistant but did lose some color when exposed to extremely high temperatures.

Alundum blasting is an important factor in producing a nonreflective and adherent colored coating on aluminum alloys.

LITERATURE REFERENCES

1. British Patent Specification No. 851.649, dated 19 October 1960.
2. U.S. Pat. 3,058,855, dated 16 October 1962, lines 41-45, Ben H. Kirby, Jr & Willian C. Cochran.
3. ALCOA "Drianodic 800" ALCOA Process Development Labs.
4. "Techniques for Coloring Anodized Aluminum," by R. V. VandenBerg. ALCOA Process Development Labs. Products Finishing Feb. 1960.
5. "Kalcolor," by Kaiser Aluminum Company
6. "Finishing of Aluminum," by S. Wernick and R. Pinner. Robt. Draper Ltd., Middlesex, England 1956. pp. 348-349.
7. "Anodic Oxide Films," L. Young, Academic Press London & New York, pp. 204 - 205. 16.11, lines 1-4. pp 205, lines 21-23. F. Keller, M.S. Hunter, D.L. Robinson (1953) Journal Electrochemical Society 100,411.
8. "Colored Anodic Coatings on Aluminum," H. Bengston Plating, July 1956 p 919 para 6, lines 2-5.

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