UNCLASSIFIED

DP - 151

Chemistry

AEC Research and Development Report

AN ALL-OVER SPOT TEST

by

V. I. Montenyohl

Pile Materials Division

March 1956

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

253633

UNCLASSIFIED

DP - 151

CHEMISTRY

AN ALL-OVER SPOT TEST

by

Victor I. Montenyohl
Pile Materials Division

Work done by
H. S. Hilborn and R. C. Pugh

March 1956

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed for
The United States Atomic Energy Commission
Contract AT(07-2)-1

Price $0.10 Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

ABSTRACT

The techniques of detecting impurities at the surface of aluminum by electrolytic sampling and colorimetric spot testing have been extended by the development of an indicating coating that can be applied to large and irregular areas by dipping or spraying.

External Distribution according to TID-4500 (10th Ed.)

TABLE OF CONTENTS

AN ALL-OVER SPOT TEST

INTRODUCTION

The chemical spot tests described in DP-88, Spot Tests for Contaminants on Aluminum were limited in application because a preliminary visual inspection had to be made to locate impurities or inclusions. Also, the conventional spot tests could be applied only to surfaces which were sufficiently uniform to provide good contact with wet filter paper. To increase the utility of the tests, a method was desired whereby large and irregular surfaces could be examined.

SUMMARY

An all-over spot test for impurities in aluminum surfaces is made possible by the development of a special coating to supplant the filter paper pad used in conventional spot tests. The use of a coating permits the testing of large areas and irregular contours for contaminants. The coating contains (a) a film former, (b) an electrolyte, (c) an opacifier to mask the color of the underlying metal, and (d) an indicator to form a colored complex with the ions under test. An aqueous slurry that contains these materials is applied to the aluminum surface that is to be tested and is dried at room temperature. The resulting film is adherent. The coated sample is then made the anode in a solution of potassium nitrate, where the color is developed. For example, with potassium ferrocyanide as indicator, iron shows up as a blue stain; copper as a brown stain. The coating is removed after the test by scrubbing with water and a detergent.

The all-over spot test is frequently employed at Savannah River to detect and identify metallic impurities in aluminum surfaces. Although the technique is too slow for use on a production line, it is of great value in identifying causes of pitting corrosion and in tracing impurities to their origins.

DISCUSSION

COMPOSITION OF THE COATING

The composition of the coating is not fixed, but can be varied within reasonable limits to produce the proper viscosity, hiding power, and adherence. The coating is an aqueous slurry that contains a film former, an electrolyte, an indicator, an opacifier, and a wetting agent. The amount of each of these constituents is stated in the following sections as per cent by weight, referred to the weight of the final slurry.

Film Former

The film formers that were found to be satisfactory are listed below in order of preference, on the basis of coverage, adherence, viscosity, and ease of removal. The comparative ratings of these properties are given in the Table on page 8.

(a) Goodrich "Goodrite Carbopol 934," one per cent by weight
(b) Du Pont "Sodium-CMC" (sodium salt of carboxymethylcellulose) Grade 2-WXH, 1.5 per cent by weight
(c) Du Pont "Sodium-CMC" (sodium salt of carboxymethylcellulose) Grade 10-D, four per cent by weight
(d) Dow "Methocel" (methylcellulose), 15 centipoise viscosity, five per cent by weight

Experiments with gelatin as a film former produced recognizable spot tests, but the results were much less satisfactory than those obtained with the four materials listed above.

Electrolyte

In almost all the slurries the electrolyte was five per cent by weight of potassium nitrate. However, other electrolytes can be used, singly or in combinations. In some cases, acetic acid, potassium nitrate, and potassium sulfate were combined; such a combination usually required additional film former in the coating.

Indicator

The indicator is a reagent capable of forming a colored complex or precipitate with the ions sought by the test. Many of the indicators described in DP-88[1] may be included in the coating mixture. Because the impurities most often suspected in aluminum are iron and copper, the indicator used for most of the tests is potassium ferrocyanide, three per cent by weight. Other indicators can be used in the concentrations given in DP-88.

Opacifier

The coating contains about six per cent by weight of pigment-grade titanium dioxide. Other white pigments of high hiding power would be equally satisfactory if they do not interfere with the chemical spot tests.

Wetting Agent

The addition of about 1.5 per cent by weight of a commercial wetting agent such as "Duponol ME" improves the covering power and adherence of the coating.

Accessory Equipment

The accessories consist of a six-volt dry cell, an aluminum electrode, wires and clips to connect the specimen and the aluminum electrode to the dry cell, and a tank to contain the electrolyte solution, which is usually a solution of five per cent potassium nitrate in water.

PROCEDURE FOR THE ALL-OVER SPOT TEST

1. A slurry of the coating mixture is prepared. In tests to detect iron or copper in aluminum, a typical coating slurry has the following composition:

COATING FOR DETECTION OF IRON AND COPPER ON ALUMINUM

650 ml water (at room temperature)
8 g du Pont "Sodium CMC," Grade 2-WXH
21 g potassium ferrocyanide
35 g potassium nitrate
50 g titanium dioxide
12 g "Duponol ME"

The slurry is best prepared by adding the constituents in the order listed, with continuous gentle stirring to insure complete mixing after each addition. The manufacturer's recommendations for mixing the film formers are followed.

2. The aluminum to be tested is degreased and dried.

3. The coating slurry is applied by brushing, spraying, or dipping. Coatings applied by dipping are more uniform and adherent than brushed coats, and dipped coatings are preferred when they are applicable.

4. The coating is dried by exposure to air at room temperature for about two hours. In general, a coating that is dried slowly is more adherent than a coating that is rapidly dried. It is not necessary to dry the coating completely; in fact, the coating adheres better if it is not dried completely.

5. The specimen is immersed in an electrolyte bath, usually a five per cent aqueous solution of potassium nitrate.

6. The specimen is connected to the positive pole of a six-volt dry cell. The negative pole is connected to an aluminum electrode immersed in the electrolyte. Electrolysis for 15 to 30 seconds is enough to develop the characteristic colors of iron and copper inclusions. Longer electrolysis causes the colored spots to spread and sometimes causes the coating to slough off the aluminum surface.

7. The specimen is removed from the electrolyte and examined at leisure. In the case of the ferrocyanide test, copper is indicated by red-brown spots, iron by dark blue spots, and uranium by a color very similar to that produced by copper. The inspection for minute traces of iron has to be performed within a few days after electrolysis because most commercial grades of aluminum contain sufficient iron to cause the entire coating to turn a light blue after a period of several days to several weeks.

8. The coatings that contain carboxymethylcellulose and

methylcellulose can be removed from the aluminum by scrubbing vigorously with a detergent in hot water. Cold dilute nitric acid is used to remove the coating of "Carbopol 934."

PRECAUTIONS AND SUGGESTIONS

Preparation and Storage of the Coating Slurry

During preparation of the slurry care should be taken not to beat air into the mixture.

The slurry can be kept for several days if it is covered and protected from the air. Before the slurry is used, any scum should be removed from the surface, and the liquid should be stirred thoroughly. Except when "Carbopol 934" was used, storage of the slurry decreased its ability to adhere to a metal surface.

Indicators and Complex Formation

Most water-soluble indicators[1] can be dissolved in the coating except those which require that several solutions be used successively to form the indicator.

In some cases it is possible to include more than one indicator in the same coating, provided there is no interaction or interference between indicators. For example, potassium ferrocyanide, potassium iodide, and cacotheline can be used together to detect iron, copper, lead, and tin.

Indicators that are not water soluble can not be included in the coating mixture, but these indicators can be used by modifying the procedure. In this case, the specimen is coated with a mixture which does not contain an indicator. After electrolysis, the coated specimen is dipped into a solution of the indicator for several seconds to permit reaction between the ions in the coating and the indicator in solution.

The procedure for the separate application of the indicator permits the testing of one piece of aluminum for inclusions of several metals by the dipping of the piece into several indicators in turn. It also permits the use of indicators which require the successive use of two or more solutions. However, careful handling is required to prevent the ions that are sought from being washed out.

The Electrolyte

Although several electrolytes can be used, it is necessary to exclude electrolytes, such as sodium hydroxide, which attack the film or the aluminum at a significant rate.

Detection of Very Small Holes

One possible application of the all-over spot test is to detect pinholes in the aluminum cladding of uranium fuel elements.

However, the viscosity of the slurry is so high that the film bridges small holes and fails to give an indication of the substrate.

In order to force the slurry into a pinhole, ultrasonic agitation has been employed. A slurry made with "Carbopol 934," the least viscous film former, was agitated with 20-KC ultrasound during the dipping operation. Under these conditions, it was possible to reveal a hole as small as 0.014 inch in diameter and 0.030 inch deep in the aluminum cladding of a uranium fuel element.

However, to test for very small pinholes in aluminum over a core of iron, copper, or uranium, spot tests(1) are generally more satisfactory than the all-over spot test.

V. I. Montenyohl
Pile Materials Division

BIBLIOGRAPHY

1. Hilborn, H. S. and Pugh, R. C. Spot Tests for Contaminants on Aluminum. E. I. du Pont de Nemours and Co., DP-88, November 1954.

TABLE

COMPARISON OF FILM FORMERS

Film Former	Per Cent by Weight	Coverage	Adherence	Apparent Viscosity	Ease of Removal*
"Sodium CMC" - Grade 10-D	4	good	good	thick	fair
"Sodium CMC" - Grade 2-WXH	1-1/2	good	good	moderate	good
"Goodrite Carbopol 934"	1	good	good	thin	poor
"Goodrite Carbopol 934"	0.5	poor	good	very thin	poor
"Goodrite Carbopol 934"	0.75	fair	good	very thin	poor
"Methocel" (15 cps)	5	good	good	thick	fair
"Methocel" (4,000 cps)	2	poor	good	thin**	fair

* The coating was removed by washing in warm water with "Alconox" and a sponge, and the residue was observed. If cold dilute nitric acid were used instead of a detergent solution, the ease of removal of "Carbopol 934" would be changed to "good."

** The mixture was frothy, and the opacifier separated and settled out after standing a short time.

Note: In this comparison, the ability to enter pinholes was not considered.