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AUTOMATED
ANALYSIS OF
HYPOPHOSPHITE
IN ELECTROLESS
NICKEL SOLUTIONS

BDX-613-499

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Final Report

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ABSTRACT

The problems of controlling hypophosphite in electroless nickel baths are discussed. An automated indirect colorimetric analysis of hypophosphite is described. Application of the process to control the composition of electroless nickel deposits is discussed.

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SUMMARY

A contract was placed by Bendix Kansas City with Battelle-Northwest to develop an automated instrumental method for determining hypophosphite in electroless nickel plating solutions. Three methods were considered: nuclear magnetic resonance (NMR), electrochemical oxidation, and chemical oxidation. NMR was believed to be too expensive and was not studied. Electrochemical oxidation was studied but no satisfactory method was found. However, a successful chemical oxidation method was developed.

The method uses oxidation of the hypophosphite with iron(III) in 0.5 M HCl. The iron(II) produced is complexed with orthophenanthroline and the complex is measured colorimetrically. The analysis procedure was automated with an elapsed time of 27 minutes between sampling and readout.

DISCUSSION

SCOPE AND PURPOSE

This project was initiated when some nickel-phosphorus deposits were prepared* with varying thicknesses and phosphorus contents in order to determine the effects of these variables on the strengths of braze joints between electroless nickel plated parts. Control of the phosphorus content was found to be a problem. The hypophosphite contents of electroless nickel plating baths is an important variable in determining the phosphorus content of the alloy deposited from these baths and also in determining the rate of deposition. Known methods for determining the hypophosphite content of electroless nickel plating baths are manual and require several hours. The objective of this project was to find a method of analysis that is rapid and suited to automation. A contract was placed by Bendix Kansas City with Battelle-Northwest in June, 1969, to develop an automated instrumental method for determining the hypophosphite content.** The work performed at Battelle is summarized in this report. The details of the activity are given in two reports issued earlier by Battelle. These reports are on file at Bendix.

PRIOR WORK

There has been no prior work at Bendix on this project.

ACTIVITY

Three approaches were considered: nuclear magnetic resonance(NMR), electrochemical oxidation, and chemical oxidation with differential kinetics. The NMR approach is believed to be feasible and to have the most potential for continuous instantaneous analysis, but no studies were made because of the high cost of instrumentation. Electrochemical studies were conducted, but a satisfactory method was not found. A differential kinetic method of oxidation was developed using an indirect colorimetric procedure for the determination of the hypophosphite.

*PDO 6984359

**PDO 6984649

Differential kinetics is the process of creating differences in reaction rates of chemically similar compounds, in this case, hypophosphite and phosphite. Phosphite is a by-product of the electroless nickel process and is therefore present in all but freshly prepared plating solutions. The oxidation rates of hypophosphite and phosphite are significantly different, phosphite being practically non-reactive, at pH values around 0.3 to 1.0. The analysis is performed by oxidizing hypophosphite with iron(III) in 0.5 M hydrochloric acid solution at 90°C. The iron(II) produced during the oxidation reaction is complexed with orthophenanthroline at pH 4.8 and the complex is measured colorimetrically. There is no significant interference by the other solution constituents.

To demonstrate its potential for automatic process control the analysis was automated using commercially available equipment (Technicon Instrument Corp., Tarrytown, New York). The heart of the automated process is a proportioning pump, which operates by moving steel rollers over flexible tubes containing the sample and reagents. Movement of the rollers along the tubes squeezes the liquids along at volume rates determined by the inside diameters of the tubes. The sample and reagents are mixed at appropriately placed junctions in the tubing system. The tubing system carries the solution through a thermostatically controlled oil bath, for oxidation of the hypophosphite, and a colorimeter, for measurement of the iron(II)-orthophenanthroline complex. The colorimeter measurement is traced on a strip chart recorder. The elapsed time between sampling and readout is 27 minutes.

ACCOMPLISHMENTS

An automated method for the determination of hypophosphite in electroless nickel plating solutions was developed. Although analysis time is 27 minutes, the method can be used to provide automatic control of the hypophosphite content.

FUTURE WORK

Analytical techniques for hypophosphite, nickel, and pH can be applied to a controlled plating process by directing the signals from the analytical instrumentation to valves and pumps controlling the addition of solutions of nickel, hypophosphite, and acid to the plating bath. Additional effort would be required to set up a working process.

Close control of the nickel-phosphorus composition may require instantaneous readout of the hypophosphite concentration. NMR may be the best way to reach this goal. Consequently, the investigation of continuous analysis of hypophosphite by NMR may be justifiable in the future.

REFERENCES

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