Description

The invention relates to the quantitative determination of the concentration of organic additives, additive breakdown products and organic contaminants in plating baths.

The advent of printed circuit boards has made possible the efficient assembly of highly complex electronic instruments such as computers, communication equipment, testing equipment, video equipment, etc. Printed circuit boards are commonly planar, flexible or inflexible sheets of material having thin, conductive lines or paths of metal on their surface onto which electronic components can be mechanically attached in order to electrically interconnect the electronic components into an active circuit. The further advent of high density, double sided or multilayered printed circuit boards that are designed to interconnect very large numbers of very large scale integrated circuits, integrated circuits, transistors, resistors, capacitors and other electronic components, required the development of technology for plating metal through holes in the board to interconnect the sides or layers of metal in the high density board.

During the manufacture of such printed circuit boards and such complex double sided or multilayered plated-through printed circuit boards, close control over the deposition of copper is required so that neither too much nor too little copper is plated on the board or in the plated-through holes and that the copper deposit has a bright shiny uniform appearance with physical properties of high ductility and tensile strength. Methods for plating copper and other metals on printed circuit boards involve the electrodeposition of a metal in which an electrical plating circuit is formed that causes dissolved copper ions in a plating solution, or plating medium, to combine with electrons on a printed circuit board hole or surface and be reduced to base metal. It has been found that the rate of electrodeposition of a metal from solution is important in order to efficiently and repeatedly form a uniform continuous smooth layer of bright shiny metal having a controlled depth or thickness with the good physical properties. Organic additives, used in electroplating baths, effectively control the rate of metal deposition, maintaining control over the physical properties of the plated metal as well as appearance.

Plating baths commonly contain at least one of two different types of additive. Additive systems can contain up to 10 different organic compounds in an electroplating formulation. A first type of additive is commonly called a brightener. This family of chemical constituents are commonly low molecular weight monomeric compounds which must be maintained in a range of concentration in the plating bath of about 0.1 to 1,000 parts of additive per million parts of plating bath in order to obtain acceptable electrode position of the base metal on the printed circuit board. The concentration of brightener fluctuates due to the electrochemical destruction of the additive and the inclusion of the additive in the copper plate. As the brightener concentration drops, the copper electroplate can become coarse-grained or burned and powdery. In the instance that the brightener concentration is too high, the copper plate can again show a burned deposit with brittle or nonuniform results.

Plating baths can also contain one or more of a polymeric additives which are commonly called a leveler or a carrier. Similarly, the polymeric additives can be electrochemically degraded, mechanically degraded, or thermally degraded, resulting in a distribution of a family of polymeric additive by-products which must be quantified to monitor additive quality.

Plating baths can also derive organic contaminants from a number of sources including degradation products of additives, residual contaminants from other processing steps and the organic material from which the circuit board is made.

In the past, the quality of the plating medium has been tested using a Hull cell which is a small electrodeposition cell through which a current is passed and the nature of the copper electroplate is observed as it is plated in the cell. The concentration, purity, quantity of degradation or other quality of the additives and bath constituents can be roughly evaluated by viewing the nature of the electrodeposition. However, the hull cell does not provide a direct measurement of additive concentration. Similarly, Tench, US-A-4,132,605, teaches an electrical voltametric method of monitoring the concentration of additives by measuring the amount of copper plated or removed during a voltametric cycle. In this test the nature and amount of copper plated in the electrical test cell is observed but a direct measurement of the concentration of specified organic additive is not done. I am also aware that Zatco and others have attempted an analysis of organic components of copper plating baths using high pressure liquid chromatography techniques (70th AES Conference, June 1983). Our attempts to perform a reproducible quantitative routine analysis of the organic additives using the Zatco-type methods have not succeeded. We believe that the extremely corrosive, acidic or basic nature of plating baths, that we have attempted to analyze, interfere substantially with the chromatography columns used in the HPLC apparatus.

In liquid chromatography, more particulary high pressure liquid chromatography (HPLC), the sample tc be analzed is placed on the end of a column that commonly contains a silica support which is chemically or physically associated with a stationary phase. A solvent or mobile phase is directed through a chromatographic column and carries the sample over the stationary phase. The differences in affinity between the components of the analyzed material and the stationery phase on the support causes the components in the sample to separate, or be resolved, as the solvent carries the material through the column. The most

common column support material is a silica composition which has the drawback that it can interact with both acidic or basic components of the plating bath, resulting in substantial interference with the separation of free components in the chromatographic column. We have attempted a pre-chromatographic neutralization of the acidic and basic components of the plating bath with a variety of techniques, but have found that the formation and removal of the resulting neutralization products or salts can cause substantial loss of organic material and the neutralization products can cause an unwanted interaction with the silica support during chromatographic analysis.

Accordingly, a substantial need exists for a reproducible, precise, accurate, routine HPLC method which suffers no interference from the highly corrosive acidic or basic nature of the bath, for the analysis of individual and collective organic constituents in electroplating baths that can be rapidly and routinely performed on a day to day basis to determine the types and state of the organic additives in a plating bath. Further such an HPLC method is essential if size exclusion chromatography, total organic carbon analysis and HPLC are to be successfully used to accurately reflect the total state of the plating bath organic constituent. These types of chromatographic techniques lend themselves very well to individual component control in terms of a feedback system for automated addition to allow consistent bath performance.

In U.S. Patent No. 4,341,634, there is disclosed a quantitative analytical method for separating a sample of hydrocarbon compounds contained in a solution into three components, namely, saturates, unsaturates and aromatics present in the sample, by means of high speed liquid chromatography employing two columns connected in series, the first column being one into which a porous silica type packing material is packed and the second column being one into which a silver-containing silica type packing material is packed.

Brief Discussion of the Invention

According to the present invention, there is provided an HPLC apparatus that can determine the concentration of organic additives in an acidic or basic metal plating bath medium, which apparatus comprises:

(a) a chromatographic column, containing a stationary phase and a support phase composition, having an inlet and an outlet;

(b) a detector means for measuring the relative concentration of organic constituents, having an inlet and an outlet wherein the chromatographic column outlet is attached in liquid communication to the detector means inlet;

(c) a second column (referred to herein as a "guard column") having a packing comprising at least a stationary phase composition and an inlet and an outlet wherein the second column outlet is connected in liquid communication with the chromatographic column inlet;

(d) a sample introduction means having an inlet, an outlet and a sample introduction port, wherein the sample introduction means outlet is attached in liquid communication to the second column inlet; and

(e) a source of solvent under pressure attached in liquid communication to the sample introduction means inlet;

characterised in that the second column stationary phase composition consists of silica to which an organic moiety has been chemically bonded whereby the second column stationary phase composition can substantially reduce the affect of the acidic or basic components of the sample on the reproducibility, precision or accuracy of the analysis.

Preferably, between the source of solvent and the sample introduction means, is placed a third column (referred to herein as a "precolumn") having sufficient support phase to saturate the solvent with dissolved support phase.

The present invention further provides a method for the HPLC determination of the concentration of organic additive in an acidic or basic metal plating bath medium, which comprises applying an untreated sample of the plating bath to the sample introduction means of an HPLC apparatus of the invention under conditions of mobile phase flow through the HPLC of about 0.01 to 100 milliliters per minute.

We have found, according to the present invention, that the organic brightener additive constituents of plating baths can be rapidly and routinely analyzed using an HPLC apparatus that comprises a source of solvent under pressure, a precolumn sample introduction means, a guard column containing the analytical column material that can absorb, neutralize, or otherwise render innocuous acidic or basic constituents of the bath sample, a chromatographic column for the separation of the organic constituents of the bath sample, and a detection means which can detect and display some measurement of the concentration of the organic constituents. A precolumn can be placed prior to the sample injection means containing a silica composition that can saturate the mobile phase with dissolved silica and can act to reduce dissolution of silica in the guard column and chromatographic column. Another aspect of the invention resides in a method for the analysis of plating bath which comprises introducing an untreated sample of the plating media into the HPLC apparatus of the invention. A further aspect of the invention resides in the determination of the state of all organic bath constituents including a determination of brightener concentration, molecular weight, distribution of leveler, organic contaminant concentration, etc. with a combined use of size exclusion chromatography, total organic carbon analysis and the novel HPLC method.

Brief Description of the Drawings

FIGURE 1 shows a block flow chart diagram of a preferred embodiment of the invention.

FIGURE 2 shows a computer generated chart, recording the results of an analysis of a copper plating bath.

FIGURE 3 shows a computer generated chart recording the analysis of a commercial brightener additive concentrate composition.

FIGURE 4 shows that the high pressure liquid chromatography technique of the invention produces a linear relationship between additive concentration and the arbitrary integration units produced at the detection means.

A guard column which can be used in the apparatus and method of the invention commonly comprises a flexible or inflexible tube made of plastic, ceramic, metal, glass or other material having dimensions of about 1 to 100 centimeters in length, and about 0.1 to 15 millimeters in inside diameter. The guard column commonly contains the same packing material as the analytical column (discussed below) which can absorb, interact with, neutralize or otherwise render innocuous the highly corrosive acidic or basic constituents of the plating bath. The packing material is retained within the column using commonly available retention means. At the inlet and the outlet of the guard column is installed commonly available means for attaching the guard column in liquid communication with other apparatus components. The guard column when used in conjunction with the precolumn (discussed below) which can saturate the mobile phase with silica, introduces reproducibility and stability into the chromatographic system for plating bath analysis.

The nature of the packing material in the guard column is important in order to result in substantial removal of the acidic or basic components of the plating bath while maintaining sufficient solvent flow and reducing pressure drop across the analytical column. The support material should be of sufficiently small particle size to present sufficient surface area for complete interaction between the acidic and basic components and the packing material. However, the particle size of the silica should be large enough to prevent the tendency of relatively small particles to plug and reduce the permeability of the chromatographic column increasing the pressure drop across the precolumn. Accordingly, the packing material should have a particle size of 2 to 100 µm, preferably 5 to 20 microns, and most preferably, for reasons of low cost, high component resolution, and low pressure drop, 3 to 10 µm.

Attached to the guard column inlet in liquid communication is the outlet of a sample introduction means. The sample introduction means commonly is an apparatus which permits the introduction of highly accurate but very small volume of a liquid sample into the high pressure liquid chromatography apparatus. A broad variety of known sample introduction means can be used. Most commonly, sample injection means are used into which a hypodermic needle can be introduced to deposit the to-be-analyzed sample into the solvent stream. The sample introduction can be made using a solvent diverting valve which can allow introduction by flowing the solvent through a sample loop of the injection valve. Commonly the sample size can range from about 1 to 1,000 microliters (µL). The outlet end of the sample introduction means is attached to the inlet of the guard column in liquid communication. The sample is inserted into the mobile phase at the sample introduction means which carries the sample first into the guard column and then into the chromatographic column.

The solvent or mobile phase is generated by a source of solvent under pressure. The solvent can be a single phase aqueous solvent or organic solvent. Alternatively, the solvent can comprise a mixture of organic and aqueous phases in constant proportion or can have the aqueous and organic components in continual varying concentration. Using the single phase solvent, the source of solvent commonly comprises a container of solvent in liquid communication with a pump that can generate pressures from about 1-10,000 pounds per square inch (psi, 1 psi = 6.9×10^3Pas) and can deliver the solvent under pressure and a controlled flow rate from 0.01 to 5.0 ml/min to the inlet of the sample introduction means. In the instance a mixed solvent having a fixed solvent ratio or a mixed solvent of continually varying component concentrations is needed, the source of solvent comprises two containers of differing solvents, a gradient device in liquid communication with the two containers which mixes the solvents in proportions as programmed by the operator. The solvents then are transferred from the gradient device to the pump where pressure is increased for application to the sample introduction means. Preferred pressures for the HPLC apparatus can range from about 100-5,000 psig and most preferably, for ease of use resolution, pressures can range from about 200-3,500 psig.

Attached to the guard column outlet in liquid communication is a chromographic column having an inlet and an outlet. The chromographic column can be a tube made of plastic, ceramic, metal, glass or other material having dimensions of about 1 to 100 centimeters in length and about 0.1 to 15 millimeters in inside diameter. The chromographic column commonly contains a packing which comprises an inert support material which is physically coated or chemically bonded to a stationary phase and can contain other material. The support material is of a particle size which is sufficiently small to present sufficient surface area for efficient resolution of additive components but is of large enough size that the column is permeable to the flow of solvent and does not plug. Relatively small particle size support material can plug the column and reduce the permeability of the chromographic column. Accordingly, the support material has a particle size of 2 to 100 µm, preferably 2 to 20 µm, and most preferably for reasons of low cost and high component resolution 3 to 10 µm.

The stationary phase which interacts with the

analyzed material in the presence of the mobile phase to resolve the materials is commonly an organic material which is physically coated or chemically bonded to the stationary phase. The stationary phases are commonly silica to which specific moieties have been chemically bonded (phenyl, octadecyl, octyl, dimethyl, amino, nitrile, diol are typical moieties). Preferred stationary phases for use in the high pressure liquid chromatography apparatus of this invention comprise C_{6-24} aliphatic hydrocarbons chemically bonded to the support. These stationary phases are available as reacted supports or as a prepacked commercial analytical columns.

The outlet of the chromographic column is commonly connected in liquid communication with a detector means. The detector means commonly comprises a cell which can measure the ultra-violet absorbance, refractive index, thermal or electrical conductivity, electrochemical activity, or other indication of the resolved component in the mobile phase as it flows through the cell. Such characteristics are electronically monitored and are read out onto a recording chart, stored by electronic or computer components, or otherwise recorded. A combination of the above detectors or monitors can be used to determine the presence and relative concentration of each resolved additive component as it flows through the cell.

The preferred HPLC apparatus of the invention contains a precolumn means inserted in fluid communication between the pump and the sample introduction means. The purpose of the precolumn means is to condition the solvent with dissolved silica to prevent dissolution of silica support in the guard and chromatographic columns. The silica material in the guard and the chromatographic columns has a small but finite solubility in a variety of the solvent systems and used as the mobile phase in the HPLC apparatus and method. The stability of the chromatographic column is of primary importance since minor changes in the column can result in major inaccuracy. The precolumn contains silica which comes in contact with the mobile phase as it passes through the precolumn and dissolves into the mobile phase at a known or measurable rate. Since the rate of dissolution of silica into the solvent stream is known, the precolumn can be changed at predetermined intervals to ensure that the solvent stream is continually conditioned for accurate chromatography. The precolumn can commonly comprise a flexible or inflexible tube, containing a silica composition, made of plastic, ceramic, metal, glass or other material having dimensions of about 1 to 100 centimeters in length and about 0.1 to 10 millimeters in inside diameter. The precolumn can contain a silica material identical with the analytical column packing or can contain a silica composition essentially free of the stationary phase material. The precolumn packing material is retained within the column using commonly available retention means. At the inlet and outlet of the precolumn is installed commonly available means for attaching the precolumn in liquid communication with the sample introduction means and the pump.

Similarly with the packing material in the guard column and the chromatographic column the stationary phase packing material is selected to maintain sufficient solvent flow and to reduce pressure drop across the column. The stationary phase packing should be of sufficiently small particle size to present sufficient surface area for dissolution of silica material, however the particle size of the stationary phase should be large enough to prevent the tendency of the relatively small particles of stationary phase to plug and reduce the permeability of the chromatographic column thus increasing pressure drop across the guard column. Accordingly the packing material should have a particle size of 2 to 20 mm, and most preferably for reasons of low cost, high component resolution and low pressure drop, of about 3 to 10 µm.

The mobile phase after detection commonly flows into a waste collection system.

Aqueous solvents useful in the HPLC apparatus and method commonly comprise well known buffers adjusted to closely control the pH for maximum resolution of components. The aqueous phase can also contain an ion paring agent which will shift the ionic equilibria between the analyte and the column support to aid in enhanced resolution. Many organic solvents such as acetonitrile, methanol, ethanol, and tetrahydrofuran are organic solvents and have utility in the invention. Preferred organic solvents include acetonitrile and tetrahvdrofuran, etc. A mobile phase used in the HPLC apparatus and method can be a mixed aqueous organic solvent wherein the solvent contains about 1 part of aqueous solvent per each 0.01 to 100 parts of organic solvent.

The high pressure liquid chromatography apparatus can be programmed so that a continually varying proportion between organic and aqueous phases can be applied to the sample introduction means. The above high pressure liquid chromotrography apparatus is primarily adapted to the quantitative determination of relatively low molecular weight brightener organic compounds having a molecular weight of less than about 2,000. Higher molecular weight polymeric constituents are most commonly analyzed after separation from the plating media using size exclusion chromatography (SEC) which provides an accurate measurement of polymer size and size distribution.

Further information can be derived from the analysis of plating media by measuring the total organic carbon content of the media. A typical total organic carbon analysis is detailed in method 4.15.I, "Methods for chemical analysis of water and wastes", EPA-600/479-020, EMSL, Cincinnati, (1979). A combination of the high pressure liquid chromatography analysis, the size exclusion chromatography analysis, and the total organic carbon analysis of plating baths provide a

highly accurate control scheme enabling plating operators to monitor plating bath additions and to optimize the plating quality of the metal deposit Using these monitoring systems, the concentration of brightener can be made, molecular weight distribution of the polymeric constituents can be made, and a determination of the contamination of the plating bath by other organic constituents can be made by subtracting a known brightener concentration and the polymer concentration from the total organic determination value. Using these data, it no longer is guesswork to determine when a plating bath requires treatment to add or remove organic constituents or to replace or replenish additives with fresh material for consistent plating bath performance.

A Hewlet Packard 1084B liquid chromotograph was equipped with a chromatographic column (40) mm in inside diameter and 250 millimeters in length. The chromatographic column contained packing comprising a silica support having approximately 1 gram of a C_{18} alcohol chemically ...ided to the silica hydroxyl groups (in an ...tadecyl silyl bonded phase).

Attached to the inlet of the chronographic column in fluid communication was the outlet of a guard column containing 0.1 gram of the same packing of the analytical column. The inlet of the guard column was attached in fluid communication with the outlet of a sample injection system having an injection volume of 10 microliters. Attached to the inlet of the sample injection valve is the outlet of a precolumn containing a silica packing. Attached to the inlet of the precolumn was a source of solvent under pressure. A mixed aqueous mobile phase was used which comprised in the aqueous phase a 0.01 molar KH_2P0_4 buffer of pH 2.3 and an organic phase comprising acetonitrile. A solvent means was programmed to permit solvent flow at the rate of 1.0 milliliters per minute and to mix the organic and agueous phase at a ratio of about 10 parts of organic phase per 100 parts of total solvent flow. A solvent column and precolumn were maintained at 50°C. The ...romatograph used an ultraviolet light detector adjusted to a wavelength of 205 µm.

FIGURE 1 shows a block diagram of a preferred embodiment of the high pressure liquid chromatography of this invention. The source of solvent, or mobile phase, 11 comprises two containers, one having an organic solvent and the other an aqueous solvent. The gradient device 12 mixes the aqueous and organic solvents at constant or varying ratios and delivers the mixture to a pump 13 which provides high pressure for the chromographic analysis. The mobile phase passes through a precolumn 14 which saturates the mobile phase with silica. The sample is injected into the high pressure liquid mobile phase at the sample introduction means 15 and carried to the guard column 16. The guard column packing absorbs substantially all the highly acidic or basic components in the sample and the balance of the sample passes from the guard column into the chromatographic column 17. The interaction between the organic constituents of the sample and the stationary phase in the presence in the mobile phase resolves the sample into detectable segments which are detected in the detector 18.

FIGURE 2 shows an analysis of a plating bath having two major peaks. The first peak 21 comprises very small amounts of inorganics such as $CuSO_4$, H_2SO_4, Cl^-, which remain after treatment in the guard column and the second peak 22 is the organic brightener component.

FIGURE 3 shows a high pressure liquid chromatographic analysis of a commercial brightener additive. The analysis shows that it has three major components 30, 31 and 32.

FIGURE 4 shows that the high pressure liquid chromatography analysis of the brightener in the plating bath has a linear relationship between the concentration of additive and integration units.

I have shown that using the high pressure liquid chromatography method and apparatus of this invention in combination with a total organic carbon analysis and a size exclusion chromatography or gel permeation chromatography analysis, the nature of the bath additives can be monitored. The concentration of the brighteners or levelers can be measured, the molecular weight distribution of the polymer can be monitored for the creation of low molecular weight species from the high molecular polymer, and the total organic concentration of the bath can be measured using the total organic carbon analysis to yield a measure of plating bath contaminants. With such monitoring the concentration of the additives can be augmented or the organic constituents of the bath can be removed by peroxide treatment before any adverse effects result on the printed circuit board.

The specification and Drawings are illustrative of the invention. However, since the invention can have many embodiments, the invention resides solely in the claims hereinafter appended.

Claims

1. An HPLC apparatus that can determine the concentration of organic additives in an acidic or basic metal plating bath medium, which apparatus comprises:

(a) a chromatographic column (17), containing a stationary phase and a support phase composition, having an inlet and an outlet;

(b) a detector means (18) for measuring the relative concentration of organic constituents, having an inlet and an outlet wherein the chromatographic column outlet is attached in liquid communication to the detector means inlet;

(c) a second column (16) having a packing comprising at least a stationary phase composition and an inlet and an outlet wherein the second column outlet is connected in liquid communication with the chromatographic column inlet;

(d) a sample introduction means (15) having an inlet, an outlet and a sample introduction port, wherein the sample introduction means outlet is

highly accurate control scheme enabling plating operators to monitor plating bath additions and to optimize the plating quality of the metal deposit Using these monitoring systems, the concentration of brightener can be made, molecular weight distribution of the polymeric constituents can be made, and a determination of the contamination of the plating bath by other organic constituents can be made by subtracting a known brightener concentration and the polymer concentration from the total organic determination value. Using these data, it no longer is guesswork to determine when a plating bath requires treatment to add or remove organic constituents or to replace or replenish additives with fresh material for consistent plating bath performance.

A Hewlet Packard 1084B liquid chromotograph was equipped with a chromatographic column (40) mm in inside diameter and 250 millimeters in length. The chromatographic column contained packing comprising a silica support having approximately 1 gram of a C_{18} alcohol chemically bonded to the silica hydroxyl groups (in an octadecyl silyl bonded phase).

Attached to the inlet of the chronographic column in fluid communication was the outlet of a guard column containing 0.1 gram of the same packing of the analytical column. The inlet of the guard column was attached in fluid communication with the outlet of a sample injection system having an injection volume of 10 microliters. Attached to the inlet of the sample injection valve is the outlet of a precolumn containing a silica packing. Attached to the inlet of the precolumn was a source of solvent under pressure. A mixed aqueous mobile phase was used which comprised in the aqueous phase a 0.01 molar KH_2P0_4 buffer of pH 2.3 and an organic phase comprising acetonitrile. A solvent means was programmed to permit solvent flow at the rate of 1.0 milliliters per minute and to mix the organic and agueous phase at a ratio of about 10 parts of organic phase per 100 parts of total solvent flow. A solvent column and precolumn were maintained at 50°C. The chromatograph used an ultraviolet light detector adjusted to a wavelength of 205 µm.

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FIGURE 2 shows an analysis of a plating bath having two major peaks. The first peak 21 comprises very small amounts of inorganics such as $CuSO_4$, H_2SO_4, Cl^-, which remain after treatment in the guard column and the second peak 22 is the organic brightener component.

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FIGURE 4 shows that the high pressure liquid chromatography analysis of the brightener in the plating bath has a linear relationship between the concentration of additive and integration units.

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(a) a chromatographic column (17), containing a stationary phase and a support phase composition, having an inlet and an outlet;

(b) a detector means (18) for measuring the relative concentration of organic constituents, having an inlet and an outlet wherein the chromatographic column outlet is attached in liquid communication to the detector means inlet;

(c) a second column (16) having a packing comprising at least a stationary phase composition and an inlet and an outlet wherein the second column outlet is connected in liquid communication with the chromatographic column inlet;

(d) a sample introduction means (15) having an inlet, an outlet and a sample introduction port, wherein the sample introduction means outlet is

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attached in liquid communication to the second column inlet; and

(e) a source (11) of solvent under pressure attached in liquid communication to the sample introduction means inlet;

characterised in that the second column stationary phase composition consists of silica to which an organic moiety has been bonded whereby the second column stationary phase composition can substantially reduce the affect of the acidic or basic components of the sample on the reproducibility, precision or accuracy of the analysis.

2. An HPLC apparatus as claimed in claim 1, wherein, between the source of solvent and the sample introduction means, is placed a third column (14) having sufficient support phase to saturate the solvent with dissolved support phase.

3. An HPLC apparatus as claimed in claim 1 or 2, wherein the second column packing has a particle size of about 2 to 20 micrometers.

4. An HPLC apparatus as claimed in any of claims 1 to 3, wherein the third column packing has a particle size of about 2 to 20 micrometers.

5. An HPLC apparatus as claimed in any of claims 1 to 4, wherein the chromatographic column packing has a stationary phase comprising a silica and a support comprising a C_{6-24} aliphatic hydrocarbon chemically bonded to the silica, and wherein the packing has a particle size of 2 to 20 micrometers.

6. An HPLC apparatus as claimed in any of claims 1 to 5, wherein the source of solvent under pressure comprises as least one or more solvent containers, a gradient device that can provide a mixture of solvent under constant or varying ratio, and a pump which can provide a solvent flow of 0.01 milliliters per minute to 10 milliliters per minute at a pressure of about 6.9×10^3 to 6.9×10^7 N/m^2 (about 1 to 10,000 psi).

7. An HPLC apparatus as claimed in any of claims 1 to 6, wherein the sample introduction means has a sample size of about 1 to 200 microliters.

8. An HPLC apparatus as claimed in any of claims 1 to 7, wherein the detector means is able to detect the relative absorption of ultraviolet light by the organic additive.

9. A method for the HPLC determination of the concentration of organic additive in an acidic or basic metal plating bath medium, which comprises applying an untreated sample of the plating bath to the sample introduction means of an HPLC apparatus as claimed in any of claims 1 to 8 under conditions of mobile phase flow through the HPLC of about 0.01 to 100 milliliters per minute.

10. A method according to claim 9, wherein the plating bath medium is analyzed for polymer size distribution and total organic carbon.

Patentansprüche

1. HPLC-Vorrichtung, welche die Konzentration der organischen Additive in einem sauren oder basischen Metallplattierungsbadmedium bestimmen kann und welche aufweist:

(a) eine Chromatographiekolonne (17), die eine stationäre Phase und eine Trägerphasenverbindung enthält, und welche einen Einlaß und einen Auslaß hat,

(b) eine Detektoreinrichtung (18) zum Messen der relativen Konzentration der organischen Bestandteile, welche einen Einlaß und einen Auslaß hat, wobei der Auslaß der Chromatographiekolonne in Flüssigkeitsverbindung mit dem Einlaß der Detektoreinrichtung ist,

(c) eine zweite Kolonne (16), die ein Füllmaterial hat, das wenigstens eine Verbindung mit einer stationären Phase aufweist, welche einen Einlaß und einen Auslaß hat, wobei der Auslaß der zweiten Kolonne in Flüssigkeitsverbindung mit dem Einlaß der Chromatographiekolonne steht,

(d) eine Probeneinführungseinrichtung (15), die einen Einlaß, einen Auslaß und eine Probeneinführungsöffnung hat, wobei der Auslaß der Probeneinführungseinrichtung in Flüssigkeitsverbindung mit dem Einlaß der zweiten Kolonne steht, und

(e) eine Quelle (11) für unter Druck stehendes Lösungsmittel, die in Flüssigkeitsverbindung mit dem Einlaß der Probeneinführungseinrichtung steht,

dadurch gekennzeichnet, daß die Zusammensetzung der stationären Phase der zweiten Kolonne aus Siliciumdioxid besteht, an dem ein organischer Teil chemisch gebunden ist, wobei die stationärphasige Zusammensetzung der zweiten Kolonne im wesentlichen die Auswirkungen der sauren oder basischen Bestandteile der Probe auf die Reproduzierbarkeit, die Präzision oder die Genauigkeit der Analyse reduzieren kann.

2. HPLC-Vorrichtung nach Anspruch 1, bei der zwischen der Lösungsmittelquelle und der Probeneinführungseinrichtung eine dritte Kolonne (14) vorgesehen ist, die eine ausreichende Trägerphase hat, um das Lösungsmittel mit der gelösten Trägerphase zu sättigen.

3. HPLC-Vorrichtung nach Anspruch 1 oder 2, bei der das Füllmaterial der zweiten Kolonne eine Teilchengröße von etwa 2 bis 20 µm hat.

4. HPLC-Vorrichtung nach einem der Ansprüche 1 bis 3, bei der das Füllmaterial der dritten Kolonne eine Teilchengröße von etwa 2 bis 20µm hat.

5. HPLC-Vorrichtung nach einem der Ansprüche 1 bis 4, bei der das Füllmaterial der Chromatographiekolonne eine stationäre Phase hat, die ein Siliciumdioxid und einen Träger aufweist, der einen C_{6-24}-aliphatischen Kohlenwasserstoff aufweist, der an Siliciumdioxid chemisch gebunden ist, und bei der das Füllmaterial eine Teilchengröße von 2 bis 20µm hat.

6. HPLC-Vorrichtung nach einem der Ansprüche 1 bis 5, bei der die Quelle für unter Druck stehendes Lösungsmittel wenigstens ein oder mehrere Lösungsmittelbehälter, eine Zumeßeinrichtung, die ein Gemisch aus Lösungsmittel mit konstantem oder sich änderndem Verhältnis zubereiten

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kann, und eine Pumpe aufweist, die einen Lösungsmittelstrom von 0,01 ml/min bis 10 ml/min bei einem Druck von etwa $6,9 \times 10^3$ bis $6,9 \times 10^7$ N/m² (etwa 1 bis 10 000 psi) liefern kann.

8 HPLC-Vorrichtung nach einem der Ansprüche 1 bis 6, bei der die Probeneinführungseinrichtung eine Probengröße von etwa 1 bis 200 ml hat.

8 HPLC-Vorrichtung nach einem der Ansprüche 1 bis 7 bei der die Detektoreinrichtungen die relative Absorption des Ultraviolettlichts durch das organische Additiv detektieren kann.

9. Verfahren zur HPLC-Bestimmung der Konzentration eines organischen Additivs in einem sauren oder basischen Metallplattierungsbadmedium, bei dem eine unbehandelte Probe des Plattierungsbades an der Probeneinführungseinrichtung der HPLC-Vorrichtung nach einem der Ansprüche 1 bis 8 unter den Bedingungen eines mobilen Phasenstromes durch die HPLC von etwa 0,01 bis 100 ml/min zur Anwendung gebracht wird.

10. Verfahren nach Anspruch 9, bei dem das Plattierungsbadmedium auf die Polymergrößenverteilung und den organischen Gesamtkohlenstoff analysiert wird.

Revendications

1. Appareil de chromatographie en phase liquide sous haute pression (HPLC) pouvant déterminer la concentration d'additifs organiques dans un bain acide ou basique d'un agent de placage de métal, cet appareil comprenant:

(a) une colonne chromatographique (17) contenant une phase stationnaire et une composition de phase de support, comportant un orifice d'entrée et un orifice de sortie;

(b) un dispositif détecteur (18) pour mesurer la concentration relative des constituants organiques, ayant un orifice d'entrée et un orifice de sortie, dans lequel l'orifice de sortie de la colonne chromatographique est relié en communication de liquide à l'orifice d'entrée du dispositif détecteur;

(c) une seconde colonne (16) comportant une garniture constituée d'au moins une composition de phase stationnaire et un orifice d'entrée et un orifice de sortie, dans laquelle l'orifice de sortie de la seconde colonne est relié en communication de liquide à l'orifice d'entrée de la colonne chromatographique;

(d) un dispositif (15) d'introduction d'échantillons ayant un orifice d'entrée et un orifice de sortie et un orifice d'introduction d'échantillons, dans lequel l'orifice de sortie du dispositif d'introduction d'échantillons est relié en communication de liquide avec l'orifice d'entrée de la seconde colonne; et

(e) une source (11) de solvant sous pression reliée en communication de fluide à l'orifice d'entrée du dispositif d'introduction d'échantillons;

caractérisé en ce que la composition de la phase stationnaire de la seconde colonne consiste en silice à laquelle a été lié chimiquement un groupement organique, grâce à quoi la composition de la phase stationnaire de la seconde colonne peut réduire notablement l'effet des composants acides ou badiques de l'échantillon sur la reproductibilité, la précision ou la netteté de l'analyse.

2. Appareil de chromatographie en phase liquide sous haute pression suivant la revendication 1 dans lequel une troisième colonne (14) est disposée entre la source de solvant et le dispositif d'introduction d'échantillons, ce dispositif (14) ayant une phase de support suffisante pour saturer le solvant avec de la phase de support dissoute.

3. Appareil de chromatographie en phase liquide sous haute pression suivant la revendication 1 ou 2, dans lequel la garniture de la seconde colonne présente une dimension de particules d'environ 2 à 20 micromètres.

4. Appareil de chromatographie en phase liquide sous haute pression suivant l'une quelconque des revendications 1 à 3, dans lequel la garniture de la troisième colonne présente une dimension de particules d'environ 2 à 20 micromètres.

5. Appareil de chromatographie en phase liquide sous haute pression suivant l'une quelconque des revendications 1 à 4, dans lequel la garniture de la colonne de chromatographie comprend une phase stationnaire constituée par de la silice et un support comprenant un hydrocarbure aliphatique C_{8-24} lié chimiquement à la silice, et dans lequel la garniture a une dimension de particules de 2 à 20 micromètres.

6. Appareil de chromatographie en phase liquide sous haute pression suivant l'une quelconque des revendications 1 à 5, dans lequel la source de solvant sous pression comprend au moins un ou plusieurs conteneurs de solvant, un dispositif à gradient qui peut fournir un mélange de solvant sous des rapports constants ou variables, et une pompe qui peut fournir un débit de solvant de 0,01 millilitres par minute à 10 millilitres par minute sous une pression d'environ $6,9 \times 10^3$ à $6,9 \times 10^6$ N/m² (1 à 10.000 psi).

7. Appareil de chromatographie en phase liquide sous haute pression suivant l'une quelconque des revendications 1 à 6, dans lequel le dispositif d'introduction d'échantillons délivre des échantillons d'une dimension d'environ 1 à 200 microlitres.

8. Appareil de chromatographie en phase liquide sous haute pression suivant l'une quelconque des revendications 1 à 7, dans lequel le dispositif détecteur est apte à détecter l'absorption relative de lumière ultra-violette par l'additif organique.

9. Procédé pour déterminer par chromatographie en phase liquide sous haute pression la concentration d'additif organique dans un bain acide ou basique de placage de métal, qui comprend l'application d'un échantillon non traité du bain de placage au dispositif d'introduction d'échantillons d'un appareil de chromatographie en phase liquide sous haute pression tel que

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défini suivant l'une quelconque des revendications 1 à 8, dans des conditions d'écoulement de la phase mobile à travers l'appareil de chromatographie en phase liquide sous haute pression d'environ 0,01 à 100 millilitres Par minute.

10. Procédé suivant la revendications 9, dans lequel le bain de placage est analysé pour la répartition en taille des polymères et par le carbone organique total.

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