PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
G03H 1/02, C23C 18/16
G03H 1/18

A1

(11) International Publication Number: **WO 91/14975**

(43) International Publication Date: 3 October 1991 (03.10.91)

(21) International Application Number: PCT/US91/01262

(22) International Filing Date: 26 February 1991 (26.02.91)

(30) Priority data:

497,960	22 March 1990 (22.03.90)	US
498,163	22 March 1990 (22.03.90)	US

(71) Applicant: MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).

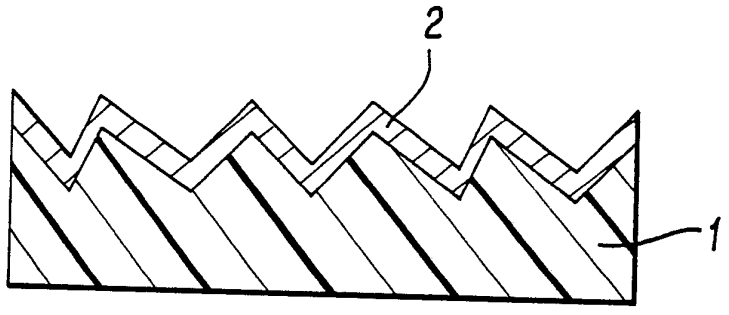
(72) Inventors: MORGAN, Albert, Wayne ; 14243 Cobble Hill Court, Chesterfield, MO 63017 (US). TAYLOR, David, Lawrence ; 114 Sylvester Avenue, St. Louis, MO 63119 (US). TOKAS, Edward, Francis ; 6 North Tealbrook Drive, St. Louis, MO 63141 (US). VAUGHN, George, Douglas ; 1720 Claymont Estates Drive, Ballwin, MO 63011 (US).

(74) Agent: BOLDING, James, Clifton; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), SU.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ELECTROLESSLY DEPOSITED METAL HOLOGRAMS



(57) Abstract

Electrolessly deposited metal holograms comprising a polymeric substrate (1) having a holographic relief-patterned surface and a metal reflective layer (2) electrolessly deposited to conform to and reproduce the holographic relief pattern. Light incident to the metal surface is reflected to provide a holographic reproduction of a holographic image inherent in said relief-patterned polymeric substrate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**ES**	Spain	**MG**	Madagascar
AU	Australia	**FI**	Finland	**ML**	Mali
BB	Barbados	**FR**	France	**MN**	Mongolia
BE	Belgium	**GA**	Gabon	**MR**	Mauritania
BF	Burkina Faso	**GB**	United Kingdom	**MW**	Malawi
BG	Bulgaria	**GN**	Guinea	**NL**	Netherlands
BJ	Benin	**GR**	Greece	**NO**	Norway
BR	Brazil	**HU**	Hungary	**PL**	Poland
CA	Canada	**IT**	Italy	**RO**	Romania
CF	Central African Republic	**JP**	Japan	**SD**	Sudan
CG	Congo	**KP**	Democratic People's Republic of Korea	**SE**	Sweden
CH	Switzerland			**SN**	Senegal
CI	Côte d'Ivoire	**KR**	Republic of Korea	**SU**	Soviet Union
CM	Cameroon	**LI**	Liechtenstein	**TD**	Chad
CS	Czechoslovakia	**LK**	Sri Lanka	**TG**	Togo
DE	Germany	**LU**	Luxembourg	**US**	United States of America
DK	Denmark	**MC**	Monaco		

ELECTROLESSLY DEPOSITED METAL HOLOGRAMS

Disclosed herein are holograms comprising a relief-patterned metal surface electrolessly deposited to conform to a relief-patterned polymeric substrate. Also disclosed are methods for producing electrolessly deposited metal holograms.

BACKGROUND OF THE INVENTION

Holograms and other types of diffraction gratings comprising reflective metal surface on a relief-patterned substrate are commonly used for decorative packaging, artistic images and security devices, e.g. on credit cards, currency and other official documents. Such holograms can be prepared by a variety of methods such as embossing deformable metal foil laminates with a holographic image stamp. Due to the resilience of laminate components, such embossed holograms tend to be of poor quality especially when subjected to elevated temperatures.

An alternative method is disclosed by D'Amato et al. in European Patent Publication 0 338 378 where a holographic polymeric substrate is formed by casting and curing a polymer precursor in contact with a holographic relief-patterned mold to form a polymeric substrate with a holographic relief-patterned surface; a metal reflective surface is then deposited on the relief-patterned surface, e.g. by vapor deposition techniques. The resulting relief-patterned metal surface serves to reflect incident light into a reconstructed image of the hologram. A disadvantage of such metal deposition is the requirement to conduct such metal deposition in a vacuum environment and to mask areas where metal deposition is not desired especially if the hologram is mounted on a document.

An object of this invention is to provide such reflective metal holograms which can be prepared by metal deposition techniques that do not require vacuum environments or masking. One method for depositing metal onto polymeric substrates is electroless deposition. However, electroless deposition of metal has some disadvantages which do not commend it to such hologram preparation. For instance, many techniques for electroless deposition of metal onto plastics require etching to achieve a effective level of adhesion; such etching, e.g. with strong acids or solvents, can destroy the holographic relief pattern of the polymeric substrate surface. Moreover, electroless deposition techniques often utilize catalytic materials of a size on the order of magnitude of the holographic relief pattern; deposition of dispersed particulate catalytic materials can distort the reproduction of the holographic relief pattern in the metal coating.

SUMMARY OF THE INVENTION

Despite the disadvantages inherent in many electroless deposition techniques, this invention provides a hologram comprising a relief-patterned metal surface electrolessly-deposited to conform to a relief-patterned polymeric substrate, whereby light incident to the surface of said metal opposite to said polymeric substrate is reflected to provide a holographic reproduction of a holographic image inherent in said relief-patterned polymeric substrate. Such metal surface is provided in a thin, conforming layer that reproduces the holographic relief-patterned surface of the polymeric substrate by electroless deposition techniques.

This invention also provides methods of preparing electrolessly deposited metal holograms, e.g. preparing a polymeric substrate having a holographic relief-patterned surface and electrolessly

depositing a conforming holographic metal reflective layer on said relief-patterned surface. In a preferred embodiment a polymeric substrate having a holographic relief-patterned surface is prepared by casting and curing polymeric precursor in a holographic relief-patterned mold. The conforming holographic metal reflective surface is prepared by electrolessly depositing metal onto the holographic relief-patterned surface in a method comprising:

(a) coating a holographic relief-patterned polymeric substrate surface with a film-forming solution of a polymer and a Group 8 metal;

(b) drying said film-forming solution to form a polymeric film essentially conforming to and reproducing said holographic relief pattern;

(c) heating said polymeric film to provide a catalytic surface thereon;

(d) applying to said catalytic surface an electroless depositing metal solution for sufficient time to electrolessly deposit thereon a metal surface which essentially conforms to and reproduces said holographic relief pattern. The electrolessly deposited metal layer allows light incident to the holographic reproduced metal surface, which is opposite to the holographic relief-patterned polymeric substrate, to be reflected to provide a holographic reproduction of an holographic image inherent in said relief patterned polymeric substrate.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic representation of an electrolessly deposited metal hologram according to this invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Referring to Figure 1 there is illustrated a polymeric substrate 1 which can be prepared by molding a molten thermoplastic, e.g. a high glass temperature thermoplastic such as a polyimide or polyetherketone,

in a mold having a holographic relief pattern on its surface. Preferably, such polymeric substrate can be prepared by casting and curing thermoset polymer precursor, e.g. crosslinkable material such as an acrylate, urethane or epoxy polymer precursor, in a mold having a holographic relief pattern. Methods for preparing such substrates are known in the art and are disclosed by D'Amato et al. in European Patent Publication 0 338 378, the specification of which is incorporated herein by reference.

Conforming to the holographic relief pattern of the polymeric substrate is an electrolessly deposited metal layer 2 which provides reflective surfaces from which incident light can be reflected into a reconstructed image of the hologram inherent in the holographic relief pattern. As indicated above many electroless deposition techniques are inherently incompatible for use in preparing holographic metal surfaces. It has been discovered that electroless deposition techniques such as those disclosed by Morgan et al. in U.S. Patent 4,910,072 and by Vaughn in U.S. Application Serial No. 07/454,565, the specifications of both of which are incorporated herein by reference, are surprisingly advantageous and efficacious in the preparation of holographic metal surfaces. The improved electroless deposition methods of this invention comprise: (a) coating a holographic relief-patterned polymeric substrate 1 with a film-forming solution, preferably substantially aqueous, comprising a polymer, e.g. polyvinyl alcohol, and a Group 8 metal, e.g. a palladium salt; (b) drying said film-forming solution to form a polymeric film essentially conforming to and reproducing said holographic relief pattern; (c) heating said polymeric film by exposure to a temperature of at least about 200° C to provide a catalytic surface thereon; (d) applying to said catalytic surface an electroless

depositing metal solution for a contact time of less than 20 seconds to electrolessly deposit thereon a metal surface 2 which essentially conforms to and reproduces said holographic relief pattern. The drying and heating can be simultaneously effected.

The contact time for applying said electroless deposition solution should be sufficient to electrolessly deposit a metal layer 2 in sufficient thickness, e.g. at least about 5 nanometers thick, to provide a mirror like surface and sufficiently thin, e.g. not more than about 300 nanometers thick so as to not obscure the underlying holographic image. A balance of good reproduction of the holographic image and durability of a mirror like finish is achieved when the metal layer is between about 10 and 100 nanometers thick. Most preferred metal layers are about 20 to 60 nanometers thick. Preferred contacts times are less than 10 seconds, more preferably less than 5 seconds. The contact time can be effectively reduced by adjusting the electroless deposition environment, e.g. by elevating temperatures of the substrate and the electroless deposition solution for instance up to about 80 - 90° C.

Useful metals for the electrolessly deposited layer include nickel, cobalt, copper, palladium, silver, platinum and gold which can be applied as a single metal layer or a laminate of metal layers. The metal layer can be optionally overcoated with a protective wear layer, e.g of a clear acrylate or urethane topcoat which does not interfere with the transmission of light to and from the metal layer.

An advantage of the electrolessly deposited holograms of this invention is the application of methods of preparation thereof to continuous processing of web material containing such holograms including web material comprising holograms of extended length as on artistic or decorative sheets

and web material comprising holograms on selected areas of the web as on security documents. Such continuous processes are disclosed in European Patent Publication 0 338 378 referred to hereinabove. The electroless deposition methods can be effected by applying the film forming solution and electrolessly depositing metal solutions from solution saturated surfaces in register with a moving web so as to contact the holographic relief surface of the polymeric substrate and catalyzed relief surface, respectively.

The following examples serve to illustrate certain embodiments and aspects of this invention but are not intended to imply any limitation of the scope of the invention.

EXAMPLE

This example illustrates the electroless deposition of a nickel onto a relief-patterned polymeric substrate.

A catalytic metal solution was prepared from 0.1 g palladium (II) acetate, 2.0 ml water and 10 ml acetone. A water soluble polymer solution was prepared from 0.12 g polyvinylalcohol (125,000 M.W., 88 mole % hydrolyzed) and 0.013 g Triton X-100 polyoxyethylene surfactant (Rohm & Haas) and about 6 ml water. The catalytic metal solution, followed by 50 ml of rinse water and 0.25 ml triethylamine, was mixed with the water soluble polymer solution to provide a substantially aqueous film forming solution. A polymeric substrate having a hologram generating relief-patterned surface was coated by wiping the surface with a sponge saturated with the film forming solution. The film forming solution was dried by holding the dry side of the polymeric substrate in a 220° C air stream for about 10 seconds to provide a catalytic surface on the hologram generating relief-patterned surface. The polymeric substrate was placed

on a 95° C surface while the catalytic surface was covered for about 5 seconds with a solution of electroless depositing nickel solution (obtained from MacDermid, Inc. identified as XD7054EN) comprising 6 g/l nickel and 30 g/l sodium hypophosphite monohydrate adjusted to pH 5.5 with ammonium hydroxide solution and maintained at about 80° C. After the 5 second exposure, the nickel solution was rinsed off with water providing a reflective holographic nickel surface.

While specific embodiments have been described herein, it should be apparent to those skilled in the art that various modifications thereof can be made without departing from the true spirit and scope of the invention. Accordingly, it is intended that the following claims cover all such modifications within the full inventive concept.

What is claimed is:

1. A hologram comprising a relief-patterned metal surface electrolessly-deposited to conform to a relief-patterned polymeric substrate, whereby light incident to the surface of said metal opposite to said polymeric substrate is reflected to provide a holographic reproduction of a holographic image inherent in said relief patterned polymeric substrate.

2. A hologram according to claim 1 wherein said relief-patterned polymeric substrate comprises a crosslinked polymer.

3. A hologram according to claim 2 wherein said electrolessly deposited metal comprises nickel, cobalt, copper, palladium, silver, platinum or gold.

4. A hologram according to claim 1 wherein said electrolessly deposited metal layer is 5 to 300 nanometers thick.

5. In a hologram comprising a reflective metal surface in contact with a relief-patterned polymeric substrate, the improvement wherein said reflective metal surface is electrolessly deposited onto said relief-patterned polymeric substrate to provide holographic image producing surfaces on both the relief-patterned polymeric substrate side and opposite side of said metal surface, wherein light incident to both of said metal surfaces is reflected to provide a holographic reproduction of a holographic image inherent in said relief patterned polymeric substrate.

6. A method of preparing electrolessly deposited metal holograms comprising:

(a) forming a polymeric substrate having a holographic relief-patterned surface;

(b) electrolessly depositing thereon a metal layer conforming to and reproducing said holographic relief pattern.

7. A method according to claim 6 wherein said substrate is formed by casting and curing crosslinkable polymer precursor against a holographic relief-patterned mold.

8. A method according to claim 7 wherein said electrolessly depositing comprises (a) coating said holographic relief-patterned surface with a film-forming solution of a polymer and a Group 8 metal; (b) drying said film-forming solution to form a polymeric film essentially conforming to and reproducing said holographic relief pattern; (c) heating said polymeric film to provide a catalytic surface thereon; (d) applying to said catalytic surface an electrolessly depositing metal solution to electrolessly deposit thereon a metal which essentially conforms to and reproduces said holographic relief pattern; wherein light incident to the surface of said metal, which is opposite to the holographic relief-patterned polymeric substrate, is reflected to provide a holographic reproduction of a holographic image inherent in said relief patterned polymeric substrate.

9. A method according to claim 8 wherein said heating is effected by exposure of said polymeric film to a temperature of at least about 200° C to provide a catalytic surface thereon.

10. A method according to claim 8 wherein said electrolessly depositing metal solution is applied to said catalytic surface for a contact time of less than 20 seconds to electrolessly deposit thereon a metal which essentially conforms to and reproduces said holographic relief pattern.

11. A method according to claim 9 wherein said drying and heating are simultaneously effected by exposure to a temperature of at least about 200° C.

12. A method according to claim 8 wherein said relief-patterned polymeric substrate comprises a crosslinked polymer.

13. A method according to claim 8 wherein said electrolessly deposited metal comprises nickel, cobalt, copper, palladium, silver, platinum or gold.

14. A method according to claim 8 wherein said applying of an electroless deposition solution is effected for sufficient time to provide an electrolessly deposited metal layer of 5 to 300 nanometers thick.

15. A method according to claim 8 wherein said film forming solution is substantially aqueous.

16. A method according to claim 8 wherein a plurality of said holograms is prepared on a moving web.

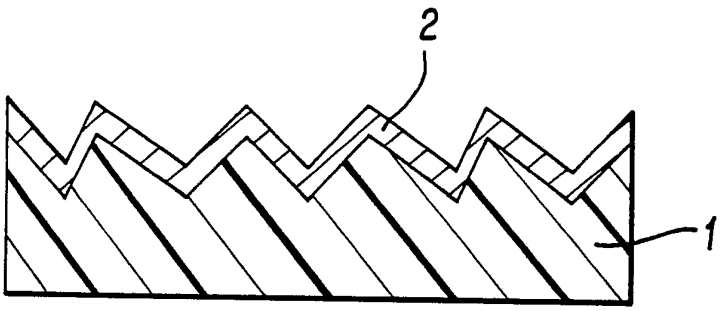


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/01262

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: G 03 H 1/02, C 23 C 18/16, G 03 H 1/18

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	G 03 H

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	EP, A, 0201323 (DAI NIPPON) 12 November 1986 see abstract; page 8, lines 7-16; page 16, line 18 - page 17, line 26; page 18, lines 33-35; page 19, lines 3-12; page 5, lines 14-21 ---	1-9,11-16
Y	EP, A, 0149861 (PHILIPS) 31 July 1985 see page 7, lines 9-38 ---	1-9,11-16
Y	EP, A, 0271466 (MONSANTO) 15 June 1988 see claims 1,12; page 7, line 43 & US, A, 4910072 cited in the application ---	3,8,9,11,13,15
Y	EP, A, 0328298 (MARKEM SYSTEMS) 16 August 1989 see column 1, lines 31-49 ---	7,16

./.

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
5th July 1991	27. 08. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	miss T. MORTENSEN

International Application No PCT/US 91/01262

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	Patent Abstracts of Japan, volume 5, no. 36, (P-51)(708), 7 March 1981, & JP, A, 55157705 (NIPPON DENKI) 8 December 1980 ---	6
A	US, A, 3585113 (MORRIS) 15 June 1971 see abstract ---	1
A	Patent Abstracts of Japan, volume 4, no. 82, (P-15)(564), 13 June 1980, & JP, A, 55045121 (TORAY) 29 March 1980	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9101262 SA 45394

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 21/08/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0201323	12-11-86	JP-A- 61254975	12-11-86
		JP-A- 61272772	03-12-86
		JP-A- 62131284	13-06-87
		US-A- 4856857	15-08-89
EP-A- 0149861	31-07-85	NL-A- 8304084	17-06-85
		AU-B- 584068	18-05-89
		AU-A- 3590184	06-06-85
		CA-A- 1229265	17-11-87
		JP-A- 60131974	13-07-85
EP-A- 0271466	15-06-88	US-A- 4900618	13-02-90
		AU-B- 598055	14-06-90
		AU-A- 8087387	12-05-88
		JP-A- 63159410	02-07-88
		US-A- 4910072	20-03-90
EP-A- 0328298	16-08-89	GB-A- 2215863	27-09-89
US-A- 3585113	15-06-71	None	