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(54) Title of the invention : MICROSCOPIC CAVITY TO MACROSCOPIC SURFACE FOR ASYMMETRIC SYNTHESES.

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Filing Date	:NA
(62) Divisional to Application Number	:NA
Filing Date	:NA

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(57) Abstract :

ABSTRACT Chiral compounds, a branch of polar crystals, have wide applications starting from drug molecules in pharmaceutical industry to novel technology. Although synthesis of chiral compounds looks simple, its resolution remained most challenging aspect. Therefore, asymmetric syntheses emerged as most sought field in the realm of organic synthesis which involves direct formation of enantioselective molecule. One of the most common pathway which an asymmetric syntheses employs is the use of chiral ligand around metal center (catalyst) to create microscopic chiral cavity. This microscopic cavity enforces or confines enantioselective pathway for the reaction. Our present invention encloses novel macroscopic or bulk surface for generating enantioselective reaction pathway. This pathway is simple and should be useful for generating asymmetric products, at least axially chiral molecules, by properly adjusting reaction conditions.

No. of Pages : 8 No. of Claims : 9

INTELLECTUAL
PROPERTY **INDIA**
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सत्यमेव जयते

क्रमांक : 022112581
SL No :

भारत सरकार
GOVERNMENT OF INDIA
पेटेंट कार्यालय
THE PATENT OFFICE

पेटेंट प्रमाणपत्र
PATENT CERTIFICATE

(Rule 74 Of The Patents Rules)

पेटेंट सं. / Patent No. : 362870

आवेदन सं. / Application No. : 201721039245

फाइल करने की तारीख / Date of Filing : 03/11/2017

पेटेंटी / Patentee : GHALSASI PRASANNA S.

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित MICROSCOPIC CAVITY TO MACROSCOPIC SURFACE FOR ASYMMETRIC SYNTHESES. नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 3rd day of November 2017 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled MICROSCOPIC CAVITY TO MACROSCOPIC SURFACE FOR ASYMMETRIC SYNTHESES. as disclosed in the above mentioned application for the term of 20 years from the 3rd day of November 2017 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख : 24/03/2021
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **3rd day of November 2019** को और उसके पश्चात प्रत्येक वर्ष मे उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 3rd day of November 2019 and on the same day in every year thereafter.

INTELLECTUAL
PROPERTY **INDIA**
एकस्व/PATENTS|अभिकल्प/DESIGNS|
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उपदर्शन/GEOGRAPHICAL INDICATIONS

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सं. \ No. 201721039245

दिनांक \ Dated the 24/03/2021

सेवा मे, \ To :

Address of Service:- PROF. PRASANNA GHALSASI S. DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA, PRATAPGUNJ, VADODARA-390 002, GUJARAT, INDIA.
Email Id:- prasanna.ghalsasi@gmail.com

विषय :- पेटेंट आवेदन संख्या 201721039245 के संबंध मे अधिनियम की धारा 43 के तहत पेटेंट अनुदान तथा पेटेंट रजिस्टर मे प्रविष्टि की सूचना
Sub :- Intimation of the grant and recordal of patent under section 43 of the Act in respect of patent application no. 201721039245

महोदय/महोदया,
Sir/Madam,

आपको सूचित किया जाता है कि पेटेंट अधिनिय, 1970 की धारा 12 व 13 तथा उस आधार पर बने नियम के तहत उपर्युक्त पेटेंट आवेदन के परीक्षण [व 22/02/2021 को हुई सुनवाई] के उपरांत एतद्द्वारा पेटेंट अनुदान किया जाता है। तथा पेटेंट अनुदान की प्रविष्टि 24/03/2021 को पेटेंट रजिस्टर मे कर दी गयी है।

This is to Inform you that following the examination of above mentioned patent application under section 12 and 13 of The Patents Act, 1970 and Rules made thereunder [and hearing held on 22/02/2021] a patent is hereby granted and recorded in the Register of Patents on the 24/03/2021. The Patent Certificate is enclosed herewith.

पेटेंट संख्या \ Patent No	: 362870
आवेदक का नाम \ Name Of Applicant	: GHALSASI PRASANNA S.
पेटेंट दिनांक \ Date of Patent	: 03/11/2017
पूर्विक्ता तिथि \ Priority Date	: 03/11/2017
परीक्षण हेतु अनुरोध दाखिल करने की तिथि \ Filling date of Request for examination	: 31/10/2018
शीर्षक \ Title	: MICROSCOPIC CAVITY TO MACROSCOPIC SURFACE FOR ASYMMETRIC SYNTHESES.
दावों की संख्या \ Number of claims	: 02

उपर्युक्त पेटेंट के अनुदान का प्रकाशन अधिनियम की धारा 43 के तहत पेटेंट कार्यालय के आधिकारिक जर्नल मे किया जाएगा।
The grant of above mentioned patent will be published in the Official Journal of the patent Office under section 43 of the Act.

पेटेंट अधिनियम 1970 यथा संशोधित पेटेंट (संशोधन) नियम, 2005/ पेटेंट नियम, 2003 यथा संशोधित पेटेंट (संशोधन) नियम, 2016 की धारा 142 की उप-धारा (4) के प्रावधानों के तहत उपरोक्त प्रविष्टि की तिथि से 3 माह के भीतर इस कार्यालय मे नवीकरण शुल्क जमा किया जाना चाहिए।
The payment of renewal fee is required to be made at this office within three(3) months from the aforesaid date of recording according to the proviso in sub-section(4) of Section 142 of The Patents Act,1970, as amended by The Patents (Amendment) Act, 2005 / The Patents Rules, 2003 as amended by The Patents (Amendment) Rules, 2016.

Anjaneyulu Reddi
(नियंत्रक पेटेंट)
Controller of Patents

टिप्पणी / Note :

1. संशोधित नवीकरण शुल्क हेतु कृपया महानियंत्रक पेटेंट, अभिकल्प एवं व्यापार चिह्न की आधिकारिक वैबसाइट www.ipindia.gov.in पर उपलब्ध पेटेंट (संशोधन) नियम 2016 की प्रथम अनुसूची (शुल्क) देखें।
   For revised renewal fees kindly refer to the First Schedule (fees) of The Patents (Amendment) Rules 2016 available on the official website of Controller General of Patents, Designs and Trade Marks www.ipindia.gov.in
2. कार्यालय द्वारा पेटेंट प्रमाणपत्र की कोई भी कागजी प्रति अलग से जारी नहीं की जाएगी।
   No hard copy of Patent Certificate shall be issued separately by the office.

E-101/12960/2018

TITLE OF THE INVENTION

Microscopic cavity to Macroscopic Surface for Asymmetric Syntheses.

ABSTRACT OF THE INVENTION

Chiral compounds, a branch of polar crystals, have wide applications starting from drug molecules in pharmaceutical industry to novel technology. Although synthesis of chiral compounds looks simple, its resolution remained most challenging aspect. Therefore, asymmetric syntheses emerged as most sought field in the realm of organic synthesis which involves direct formation of enantioselective molecule. One of the most common pathway which an asymmetric syntheses employs is the use of chiral ligand around metal center (catalyst) to create 'microscopic chiral cavity'. This microscopic cavity enforces or confines enantioselective pathway for the reaction. Our present invention encloses novel 'macroscopic or bulk surface' for generating enantioselective reaction pathway. This pathway is simple and should be useful for generating asymmetric products, at least axially chiral molecules, by properly adjusting reaction conditions.

FIELD OF INVENTION

Present invention relates to synthesis of an industrially important axially chiral aromatic hydrocarbons containing hydroxyl group, mediated by macroscopic or bulk surface and silver ammine reagent at room temperature with mild conditions, without adding chiral organic reagents or complexes.

This invention opens up ingenious and unusual pathway in the field of chiral synthesis. The use of macroscopic surface as a source of chirality is disclosed here.

Axially chiral Bi-phenol in enantiomeric excess was obtained using polymorph of silica in this method. One can follow similar strategy for asymmetric synthesis of other molecule.

BACKGROUND OF INNOVATION/ DESCRIPTION OF THE PRIOR ART

Chiral compounds are compounds containing different geometric arrangement, in which asymmetric unit such as chiral center or chiral axis are precent.

The chiral molecules in their pure enantiomeric pure forms have different chemical and biological properties, which have wide applications starting drug molecules in the pharmaceuticals industries to novel technology such as nano-moters.

The synthesis methods of enantiomerically pure compounds are well reported in the literature still is challenging, where complexation of one of the enantiomer from racemic mixture or direct chiral synthesis methods are used.

Complexation or co-crystallization method is classical method, used to get optically pure chiral product. In these methods chiral reagents forms complex or supramolecular arrangement with one of the enantiomeric product, these are separated from another enantiomer by precipitation or crystallization method.

The us patent US 9809567 B2 discloses nicortinic acid preparation in racemic form and its resolution by making its salt with (-)-O,O'-di-p-toluoyl-L-tartaric acid.

The US patent US 9988368 B1 has disclosed synthesis method for cis-imidazoline compounds where chiral resolution was obtained by crystallization with chiral acid.

The weak forces such as inter molecular hydrogen bonding and π-π interactions plays a role to get co-crystals.

These processes are laborious requires multiple step, apart from that stochiometric amount of chiral reagent and/or metal salts are required for complexation. More than 50% by-product (another enantiomer) formation is one of the main drawback of this method

The metallic complexes having chiral cavity are used as a reagent or catalyst to get selective product called asymmetric synthesis. This is an efficient and atom economic way to minimize the quantity of metal to carry out organic convertions reactions and by-products. These methodologies helped in generating selectivity in the product formation by controlling entry of only pre-oganized reactant molecules or post-organized product, mainly by controlling molecular level non-covalent interactions.

The US patent US 6521769 B1 has disclosed synthesis of chiral phosphenes, transition metal complexes and their use on asymmetric reaction.

In this patent Axially chiral biaryl is synthesized (mainly BINOL) in enantiomeric excess form.

BINOl is 1,1'-bi-2-Naphthol molecule contains chiral axial found in atopisomeric form. BINOL is adaptable template for chiral catalyst and auxiliaries for asymmetric synthesis of chiral ligands, catalysts, complexes, drugs and natural products in industries and pharmaceuticals.

There are reports where the chiral reagent or complexes of copper, iron and vanadium are used to synthesize optically pure product known as chiral synthesis as shown in the references 1, 2 and 3. [1], [2], [3]

These complexes and ligands are synthesized using multiple step process. Recovery and reuse of reagent is still challenging here. Thus there is as requirement of a novel, simple and low coast method which can give desired product.

New fields of surface assisted synthesis are exploring and have received attention towards it as shown in the chemical review 2018.[4], [5], [6]

Thus here use of macroscopic surface instead of microscopic cavity is exploited in the art for asymmetric synthesis. Thus here in the art use of a chiral surface to synthesis axially chiral molecule in enantiomeric excess is disclosed where we have used our previously reported (Indian patent 201621005382 A) reagent silver ammine complex in combination.

The present invention relates to a new method for asymmetric synthesis, where macroscopic surface works as media or catalyst for chiral synthesis of BINOL.

The main advantage is of the surface used here is non organic and cannot degrade easily, thus cannot lose chirality easily and can be reused. Here the surfaces have wide range of scope for other reactions.

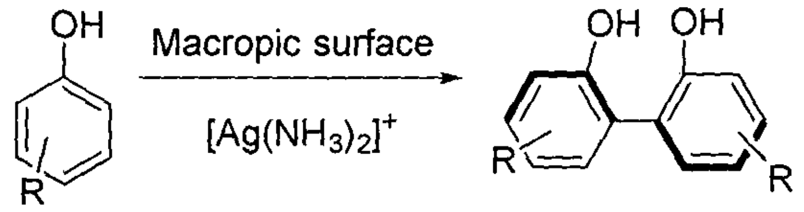
The present invention relates to a use of macroscopic surface for asymmetric synthesis. It relates to an industrially important BINOL synthesis in enantiomeric excess. It relates to a synthesis of axially chiral BINOL in using Silver ammine complex and macroscopic surface. Use of macroscopic surface to stimulate chirality in the product formation is disclosed in the art.

SUMMARY OF INVENTION

The present invention discloses a method to synthesize asymmetric molecules in enantiomeric excess.

Here silver ammine reagent converts phenol into the corresponding carbon-Carbon coupled axially chiral products where the non organic macroscopic surface direct the reaction product in one enantiomeric form.

The silver ammine complex acts as an oxidizing agent and the surface used during the reaction induces chirality in the product.



DETAILED DESCRIPTION OF INNOVATION

The present disclosure provides a method preparing carbon-carbon oxidative coupled chiral biaryl products in enantimeric excess.

Use of surface to synthesize asymmetric molecules is disclosed in the art.

According to early publication silver ammine complex reacts with phenols and forms silver metal and corresponding biphenyl, thus 2-Naphthol is used here as one of the example. The 2-Naphthol converts in to BINOL enantio-selectively, which is axially chiral molecule.

The key component in the reaction is macroscopic surface. Here, the inner surface of vessel provides macroscopic surface in the reaction to get enantiomeric selective product.

These reactions are carried out in dark at room temperature with temperature in a range of 28 °C to 30 °C.

This method provides simplest method for asymmetric synthesis

The chiral synthesis without using external chiral reagents or complexes is reported in the art.

Vessel is made up of polymorph of silica with Dimension of 4.5cm*1cm*1 cm.

The surface used for the reaction is non organic thus reusable, cannot be racemise or deactivated easily and chirality remains intact and does not require further activation.

The metallic silver forms as a side product of the reaction, which is separated by washing.

These reactions are repeated with the same vessel only.

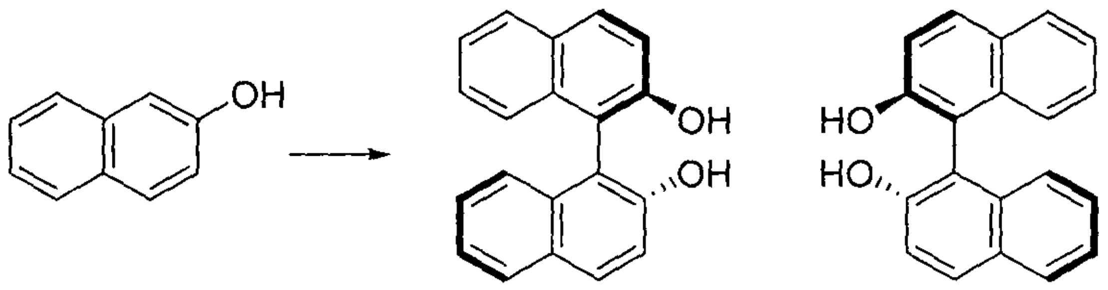
The reproducibility of results can be obtained if the conditions are maintained same.

This invention is not limited to silver ammine complex as a reagent and BINOL as product, other reagents can also be used to get chiral molecules.

BRIEF DISCUSSION OF DRAWING: NO DRAWING

PROCESS

EXAMPLE 1



(R)-BINOL (S)-BINOL

The Silver nitrate (0.043 g, 0.25 mmol) was added and mixed in a liquor ammonia (1.0 mL) solution in a vessel. 2-Naphthol (0.036 g, 0.25 mmol) was dissolved in the absolute ethanol (0.5 mL) in another vessel. The solution of phenol was added to silver nitrate solution using micropipette and mixed. This solution was kept open in to the air in dark at room temperature for 45 to 48 hours.

The metallic silver formation was observed in the vessel. Ethanol washing was given rapidly to separate organics from metallic silver and this solution was passed from anhydrous sodium sulfate. The resultant BINOL (2,2'-dihydroxybinaphthyl) was characterized by using NMR, FTIR analysis and GC-mass analysis. The resultant BINOL mixture shows the enantiomeric excess of S-BINOL 40% to 47% in the crude during repetition.

2,2'-dihydroxybinaphthyl was obtained by column chromatography: Yellowish white solid: 90% isolated column purified yield. Melting point 210-218°C, ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) : δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.25-7.41 (m, 6H), 7.13 (d, *J* =8.3 Hz, 2H), 5.04 (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C) δ δ 152.8(C), 133.5 (C), 131.4 (CH), 129.4

(C), 128.4 (CH), 127.51 (CH), 124.2 (CH), 104.6 (CH),117.8 (CH), 110.9 (C), GCMS m/z: M+: 285.8, IR (KBr): vmax/cm^{-1} 3486, 3403, 3055, 2963, 1798, 1618, 1596

Vessel is made up of polymorph of silica with Dimension of 4.5cm*1cm*1 cm and the same vessel is used during repetition of experiment.

Although the above process is described above skill of experimentalist is required to reproduce the data.

The present invention with the use of polymorph of silica belongs to the scope of the inventor as clamed.

CLAIMS

1. Use of adhesive-cohesive interaction for driving organic transformation or conversions.
2. Use of cohesive interaction and molecular interactions for making adhesion of metal on to chiral any surface.
3. Generating chiral organic compound surface using in a redox reaction, where one product help in surface while other undergoes molecular organic conversion.
4. Generating chiral organic compounds using chiral surface as an inert catalyst.
5. Generating chiral organic compounds using chiral surface.
6. Asymmetric synthesis using chiral surface by in-situ product generation in the reaction.
7. Generating chiral compounds surface without direct use of chiral ligands, chiral salts or chiral catalystcompound..
8. Generating axially chiral compounds with the use of chiral surface which is not directly involved in molecular level interaction, such as absorption or adsorption.
9. Use of chiral surface generated from above mentioned process for generating chiral compounds.

28.10.18

REFERENCES

PATENT CITATIONS

Cited Patent	Filling date	Publication date	Applicant	Title
IP 201621005382 A	16/02/2016	07/07/2017	Prasanna Ghalsasi	C-C OXIDATIVE COUPLING OF PHENOLS AND DERIVATIVES CATALYZED BY SILVER AMMONIA COMPLEX.
US 9809567 B2	08/10/2015	07/11/2017	NJOY , Inc . , Scottsdale , AZ (US)	SYNTHESIS AND RESOLUTION OF NICOTINE
US 9988368 B1	31/08/2017	05/06/2018	Unity Biotechnology , Inc ., Brisbane, CA (US)	CHIRAL SYNTHESIS METHOD FOR PRODUCING CIS - IMIDAZOLINE COMPOUNDS FOR PHARMACEUTICAL USE
US 6521769 B1	19/09/2000	18/02/2003	Xumu Zhang, State College, PA (US)	CHIRAL PHOSPHINES, TRANSITION METAL COMPLEXES THEREOF AND USES THEREOF ASYMMETRIC REACTIONS

NON-PATENT CITATIONS

(1) Narute, S.; Parnes, R.; Toste, F. D.; Pappo, D. Enantioselective Oxidative *Homocoupling and Cross-Coupling of* 2-*Naphthols* Catalyzed by Chiral *Iron* Phosphate Complexes. *J. Am. Chem. Soc.* **2016**, *138* (50), 16553–16560.

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(3) Adao, P.; Barroso, S.; Carvalho, M. F.; Teixeira, C. M.; Kuznetsov, M. L.; Pessoa, J. C. Amino Acid Derived CuII Compounds as Catalysts for Asymmetric Oxidative Coupling of 2-Naphthol. *Dalt. Trans* **2015**, *44* (4), 1612–1626.

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(5) Ma, L.; Cao, Y.; Duan, Y.; Han, L.; Che, S. Silver Films with Hierarchical Chirality.

Angew. Chemie - Int. Ed. **2017**, *56* (30), 8657–8662.

(6) Munakata, M.; Wu, L. P.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N.; Fujita, M. Silver (I) Complex Assemblies with Nonplanar Aromatic Compounds. *Inorg. Chem.* **1999**, *38* (25), 5674–5680.

(12) PATENT APPLICATION PUBLICATION (21) Application No.201621005382 A

(19) INDIA

(22) Date of filing of Application :16/02/2016 (43) Publication Date : 07/07/2017

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(54) Title of the invention : C-C OXIDATIVE COUPLING OF PHENOLS AND ITS DERIVATIVES CATALYZED BY SILVER AMMONIA COMPLEX.

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(51) International classification	:B01J31/18,B01J31/16,C07C211/46
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Filing Date	:NA
(62) Divisional to Application Number	:NA
Filing Date	:NA

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(72)**Name of Inventor :**
1)GHALSASI PRASANNA
2)BHANDERI KHUSHBOO D.

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(57) Abstract :

No. of Pages : 11 No. of Claims : 10

INTELLECTUAL
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सत्यमेव जयते

क्रमांक : 022107994
SL No :

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GOVERNMENT OF INDIA
पेटेंट कार्यालय
THE PATENT OFFICE

पेटेंट प्रमाणपत्र
PATENT CERTIFICATE

(Rule 74 Of The Patents Rules)

पेटेंट सं. / Patent No.	:	333913
आवेदन सं. / Application No.	:	201621005382
फाइल करने की तारीख / Date of Filing	:	16/02/2016
पेटेंटी / Patentee	:	GHALSASI PRASANNA S

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित A METHOD OF CATALYSIS FOR PREPARING A CARBON—CARBON OXIDATIVE COUPLED PRODUCT OF AROMATIC HYDROCARBONS नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 16th day of February 2016 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled A METHOD OF CATALYSIS FOR PREPARING A CARBON—CARBON OXIDATIVE COUPLED PRODUCT OF AROMATIC HYDROCARBONS as disclosed in the above mentioned application for the term of 20 years from the 16th day of February 2016 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख : 04/03/2020
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **16th day of February 2018**को और उसके पश्चात प्रत्येक वर्ष मे उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on **16th day of February 2018** and on the same day in every year thereafter.

INTELLECTUAL
PROPERTY **INDIA**
एकस्व/PATENTS|अभिकल्प/DESIGNS|
व्यापार चिह्न/TRADE MARKS|भौगोलिक
उपदर्शन/GEOGRAPHICAL INDICATIONS

सत्यमेव जयते

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सं. \ No. 201621005382

दिनांक \ Dated the 04/03/2020

सेवा मे, \ To :
Address of Service:- “PANASIAN IP SERVICES, 213, DDA SFS, Pocket-1, Phase -1, Sector – 22, Dwarka, Delhi – 110077, India.
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विषय :- पेटेंट आवेदन संख्या 201621005382 के संबंध मे अधिनियम की धारा 43 के तहत पेटेंट अनुदान तथा पेटेंट रजिस्टर मे प्रविष्टि की सूचना
Sub :- Intimation of the grant and recordal of patent under section 43 of the Act in respect of patent application no. 201621005382

महोदय/महोदया,
Sir/Madam,

आपको सूचित किया जाता है कि पेटेंट अधिनिय, 1970 की धारा 12 व 13 तथा उस आधार पर बने नियम के तहत उपर्युक्त पेटेंट आवेदन के परीक्षण [व -------- को हुई सुनवाई] के उपरांत एतद्द्वारा पेटेंट अनुदान किया जाता है। तथा पेटेंट अनुदान की प्रविष्टि 04/03/2020 को पेटेंट रजिस्टर मे कर दी गयी है।

This is to Inform you that following the examination of above mentioned patent application under section 12 and 13 of The Patents Act, 1970 and Rules made thereunder [and hearing held on -------] a patent is hereby granted and recorded in the Register of Patents on the 04/03/2020. The Patent Certificate is enclosed herewith.

पेटेंट संख्या \ Patent No	: 333913
आवेदक का नाम \ Name Of Applicant	: GHALSASI PRASANNA S
पेटेंट दिनांक \ Date of Patent	: 16/02/2016
पूर्विक्ता तिथि \ Priority Date	: 16/02/2016
परीक्षण हेतु अनुरोध दाखिल करने की तिथि \ Filling date of Request for examination	: 11/09/2017
शीर्षक \ Title	: A METHOD OF CATALYSIS FOR PREPARING A CARBON—CARBON OXIDATIVE COUPLED PRODUCT OF AROMATIC HYDROCARBONS
दावों की संख्या \ Number of claims	: 7

उपर्युक्त पेटेंट के अनुदान का प्रकाशन अधिनियम की धारा 43 के तहत पेटेंट कार्यालय के आधिकारिक जर्नल मे किया जाएगा।
The grant of above mentioned patent will be published in the Official Journal of the patent Office under section 43 of the Act.

पेटेंट अधिनियम 1970 यथा संशोधित पेटेंट (संशोधन) नियम, 2005/ पेटेंट नियम, 2003 यथा संशोधित पेटेंट (संशोधन) नियम, 2016 की धारा 142 की उप-धारा (4) के प्रावधानों के तहत उपरोक्त प्रविष्टि की तिथि से 3 माह के भीतर इस कार्यालय मे नवीकरण शुल्क जमा किया जाना चाहिए।
The payment of renewal fee is required to be made at this office within three(3) months from the aforesaid date of recording according to the proviso in sub-section(4) of Section 142 of The Patents Act,1970, as amended by The Patents (Amendment) Act, 2005 / The Patents Rules, 2003 as amended by The Patents (Amendment) Rules, 2016.

Bhaskar Ghosh
(नियंत्रक पेटेंट)
Controller of Patents

टिप्पणी / Note :

1. संशोधित नवीकरण शुल्क हेतु कृपया महानियंत्रक पेटेंट, अभिकल्प एवं व्यापार चिह्न की आधिकारिक वैबसाइट www.ipindia.gov.in पर उपलब्ध पेटेंट (संशोधन) नियम 2016 की प्रथम अनुसूची (शुल्क) देखें।
For revised renewal fees kindly refer to the First Schedule (fees) of The Patents (Amendment) Rules 2016 available on the official website of Controller General of Patents, Designs and Trade Marks www.ipindia.gov.in
2. कार्यालय द्वारा पेटेंट प्रमाणपत्र की कोई भी कागजी प्रति अलग से जारी नहीं की जाएगी।
No hard copy of Patent Certificate shall be issued separately by the office.

ABSTRACT

A METHOD OF CATALYSIS FOR PREPARING A CARBON—CARBON OXIDATIVE COUPLED PRODUCT OF AROMATIC HYDROCARBONS

Present invention relates to novel process of Carbon-Carbon oxidative coupling of aromatic hydrocarbons containing hydroxyl group and its derivatives mediated by silver (*I*) ammonia complex. In this method silver (*I*) ammonia complex leads to vital benefits normally obtained from both homogeneous and heterogeneous catalysis, although technically it is not employed in catalytic quantity, for complete conversion of main reactant and easy recyclability, respectively. This method apart from high efficiency and easy work-up employs mild condition, and green solvent system. Silver (*I*) ammonia complex is obtained by mixing silver salt, not limited to nitrate, and liquor ammonia. The product, c-c oxidative coupling compound, can be isolated by extracting in ethyl acetate or any organic solvent. Progress of the reaction can be followed by amount of precipitated silver, normally away from the solution. Precipitated metallic silver can be reused by dissolving it in nitric acid.

FORM 2
THE PATENTS ACT, 1970
(39 of 1970)
&
THE PATENTS RULES, 2003

COMPLETE SPECIFICATION
(See Section 10 and Rule 13)

"A METHOD OF CATALYSIS FOR PREPARING A CARBON-CARBON OXIDATIVE COUPLED PRODUCT OF AROMATIC HYDROCARBONS"

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The following specification particularly describes the invention and the manner in which it is to be performed:

B101/2483/2017

C-C OXIDATIVE COUPLING OF PHENOLS AND ITS DERIVATIVES MEDIATED BY SILVER AMMONIA COMPLEX.

FIELD OF INVENTION

Present invention relates to an industrially important Carbon-Carbon bond formation reaction between aromatic hydrocarbons containing hydroxyl group in a solvent or mixture of solvents, mediated by an ammonia complex of silver (Ag-ammonia complex), obtained by treating silver salts such as silver nitrate, silver halide, silver carbonate, silver chromate, silver sulfate in neutral to basic condition with ammonia, at room temperature to high temperature depending on solvent system employed.

Combination of Homogeneous and heterogeneous *catalyzer*: Ag-ammonia complex drives reaction in forward direction, similar to homogeneous phase, and is effectively isolated and recycled, similar to heterogeneous phase.

Environmentally conscious pathway: Mild reaction conditions, versatility, environmentally green solvents, trouble-free work up, and clean recycling process.

The silver ammonia complex can be reused similar to catalyst.

BACK GROUND OF INVENTION/ DESCRIPTION OF THE PRIOR ART

It is well known in the art that two aromatics can be oxidized in presence of oxidizing agent to yield self condensed product, such as *biaryl* compounds. The process employed is known as a carbon-carbon oxidative coupling or C-C coupling. The process is well exploited in literature for family of phenols to yield *biphenols* and *binaphthols*.

There are wide range of resources, including various metals, salts and complexes there of having previously been disclosed as useful and promising oxidative coupling agents or catalysts of phenols and naphthols.

Most of the reports are based on phenols and 2-naphthol derivatives with at least one vacant position (that means there is a presence of C-H bond) at *ortho* or *para* sites.

To the best of our knowledge, most of the reports present phenols and 2-naphthol derivatives with at least one vacant position (that means there is a presence of C-H bond) at *ortho* or *para* position suitable for C-C oxidative coupling.

In the previously reported patent US4008266, use of toxic mercury metal in the form of mercuric *oxyanion* is disclosed for C-C coupling. The method describes harsh conditions for the reactions such as high temperature (up to 200°C). This method also results in low yield due to side reactions such as cross coupling and polymerization.

In the previously reported patent US4096190, use of *monovalent* copper, divalent copper, nickel or manganese or trivalent chromium or iron is reported for the C-C coupling reactions of phenol. In this method comparatively lower temperature (~80°C) is used for the reaction. The time required to complete the reaction is found to be more compare to the present invention.

In the previously reported patent WO2004018401, use of cuprous chloride complex with *tetraalkylalkylenediamine* is reported for the C-C coupling reactions of phenol. Here also the reactions are carried out at as high temperature (upto160°C). In this method, quinone forms directly due to over oxidation of phenol, making yield of desired products less than ~30%.

In the previously reported patent US4965384, use of copper halide complexes with *tetramethylethylenediamine* is reported for the C-C coupling reactions of phenol. In this method high temperature (>100°C) is employed. The yield of desired products is less than ~30%.

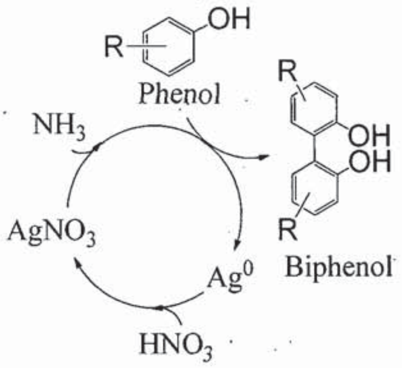
Most of the literature cite 'metal' and/or 'metal ion' as a catalyst or reagent during these reactions. When 'metal' and/or 'metal ion' acts homogeneously, better yields were observed at the cost of their recyclability. On the other hand, recyclability of 'metal' and/or 'metal ion' is worked out under heterogeneous medium, but with harsh reaction condition and poor yield.

Four areas of concerned for robust C-C oxidative coupling are (a) under mild conditions, (b) maximum isolable yield, (c) easy isolation of catalyst, (d) recycling of catalyst.

There is aways demand for 'quality' check of reagent/catalyst during and after reaction. Introduction of significant protocols or procedures or steps for 'checking' quantitatively, and reliably the amount of deactivation-reactivation/regeneration of catalyst is always remained challenge.

The present invention relates to a new method for C-C coupling using silver ammonia complex which is efficient and reusable reagent. It relates to a novel use of silver ammonia complex, for the oxidative coupling of substituted phenols under mild conditions, which can be readily recycled and reused, similar to catalyst. Thus in short, present invention relates to a new method for oxidative coupling of substituted phenols under mild conditions. It relates to application of novel silver ammonia complex as an efficient and reusable reagent, similar to catalyst.

SUMMARY OF INVENTION



The present disclosure provides a novel mild, easy and efficient process of Carbon-Carbon oxidative coupling of phenols and its derivatives mediated by silver ammonia complex.

Here, silver ammonia complex acts as a 'smart *catalyzer*', key word in invention, because of its detectable as well as inter-convertible character. Smart *catalyzer* changes 'phase of catalyzer' during the progress of the reaction from homogeneous to heterogeneous, initially homogeneous for driving reaction effectively in forward direction and later on heterogeneous for clean and complete recovery.

DETAILED DESCRIPTION OF INVENTION

The present disclosure provides a method of preparing Carbon-Carbon oxidative coupled product of aromatic hydrocarbons containing a hydroxyl group and its derivatives mediated by silver (*I*) ammonia complex.

According to an embodiment of the invention, the silver (*I*) ammonia complex is homogeneous during the reaction.

According to yet another embodiment of the invention, the silver (*I*) ammonia complex becomes heterogeneous after completion of the reaction.

According to yet another embodiment of the invention, the aromatic hydrocarbon especially phenols and/or its derivatives that containing at least one position vacant from ortho or para to the hydroxyl group (vacant position means there is a presence of C-H bond).

According to yet another embodiment of the invention, the aromatic hydrocarbon is selected from 2-naphthol, 2,4-di-tert-butylphenol, 2,6-di-tert-butylphenol and 2,4-di-methylphenol.

The reaction is carried out under neutral to basic conditions.

The ammonia silver complex is obtained by adding liquor ammonia to silver nitrate solid or in a suitable solvent or mixture of solvents such as water, methanol, ethanol, *acetonitrile*, toluene, acetone and the like. Addition of small amount of KOH or NaOH before addition of ammonia is some time beneficial.

The C-C oxidative coupling reaction of phenols with at least one vacant *ortho or para* position using ammonia complex of silver (*I*) salt in aqua media is disclosed in the art.

The C-C oxidative coupling reaction without use of any additional free radical initiator and reactant is reported in the art.

The use of reusable and recyclable reagent is disclosed in the art.

The easy method to recover efficient reagent system is also disclosed in the art.

The key component in the reaction is silver ammonia complex, *catalyzer*, is the reagent system of the intervention.

In the reagent, the ammonia plays important role not only to smoothening reaction pathway but also to boosting the strength of silver ion.

The reaction is carried out in a range of room temperature to higher temperature, depending on solvent system used for the present invention.

The products are obtained by evaporation of solvent followed by purification by column chromatography.

The reagent is homogeneous during the reaction and becomes heterogeneous after the reaction. The reagent converts to the shiny particle or foil of metallic silver on the wall or in the solution, which makes process of separation and recovery easy in the present art. This unique property of reagent facilitates monitoring progress of the reaction.

The silver formed is isolated from organic compounds by washing it initially with methanol and then organic solvents such as ethyl acetate, acetone etc. All the solvents used for washing are separated and added to extracted organic product. The pure silver was collected after the washing. The silver nitrate was recovered by treating silver with concentrated nitric acid. The recovered Silver salt was reused for further cycle.

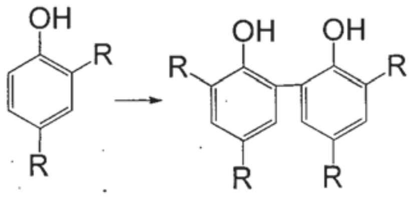
The recovery of reagent is quantitatively detected using standard methods such as *conductometric* and/or *potentiometric* titrations.

BRIEF DISCUSSION OF DRAWING: NO DRAWINGS

Examples:

The disclosure is further illustrated by the following examples which in no way should be construed as being further limiting. One skilled in the art will readily appreciate that the specific methods and results described are merely illustrative.

EXAMPLE 1



R= tertiary butyl

METHOD OF REACTION:

The silver nitrate (0.034 g, 0.2 mmol) was added in a liquor ammonia (0.2 mL) solution in a glass container (centrifuge tube). 2,4-di-tert-butylphenol (0.041 g, 0.2 mmol) was dissolved in the absolute ethanol (0.2 mL). The solution of phenol was added to silver nitrate solution. The mixture was stirred for 1hour at room temperature. The reaction progress was monitored using thin layer chromatography.

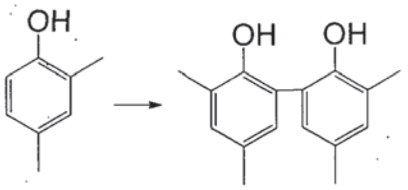
SEPARATION OF PRODUCT:

The reaction mixture was subjected to centrifugation for separating precipitated silver metal. The remaining crude was washed with organic solvent such as methanol and ethyl acetate. All these solvent was dried over Na_2SO_4 and evaporated. The residue was purified by using column chromatography on silica gel (hexane/ ethyl acetate = 20:1) to yield the desired product as a solid.

PRODUCT:

3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl was obtained by column chromatography:, 95% isolated column purified yield: 80% isolated column purified yield (average yield of six cycles). Melting point 188-190 °C, ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) δ1.34 (s, 18H), 1.47 (S, 18H), 5.24 (broad, 2H, OH), 7.12 (d, $J = 2.4$ Hz, 2H), 7.41 (d, $J = 2.4$ Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C) δ 29.6, 31.5, 34.5, 35.2, 122.3, 124.8, 125.3, 136.2, 142.9, 149.8., GCMS m/z: M+1 410.2

EXAMPLE 2



METHOD OF REACTION:

The Silver nitrate (0.034 g, 0.2 mmol) was added in a liquor ammonia (0.2 mL) solution in a glass container (centrifuge tube). 2,4-di-methylphenol (0.024 g, 0.025 mL, 0.2 mmol) was dissolved in the absolute ethanol (0.2 mL). The solution of phenol was added to silver nitrate solution. The mixture was stirred for 30 minutes at room temperature. The reaction progress was monitored using thin layer chromatography.

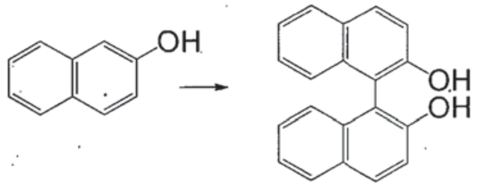
SEPARATION OF PRODUCT:

The reaction mixture was subjected to centrifugation for separating precipitated silver metal. The remaining crude was washed with organic solvent such as methanol and ethyl acetate. All these solvent was dried over Na_2SO_4 and evaporated. The residue was purified by using column chromatography on silica gel (hexane/ ethyl acetate = 10:1) to yield the desired product as a white solid.

PRODUCT:

3,3’,5,5’tetra-methyl-2,2’-biphenol was obtained by column chromatography: white solid:, 70% isolated column purified yield: Melting point 134°C, ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) δ 2.29(s, 12H), 5.09 (broad, 2H, OH), 6.88 (s, 2H), 7.02 (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C) δ 16.21, 20.46, 122.1, 125.2, 128.5, 130.0, 132.0, 149.1.

EXAMPLE 3



METHOD OF REACTION:

(A) ROOM TEMPERATURE REACTION:

The Silver nitrate (0.034 g, 0.2 mmol) was added in a liquor ammonia (0.2 mL) solution in a glass container (centrifuge tube). 2-Naphthol (0.029 g, 0.2 mmol) was dissolved in the absolute ethanol (0.5 mL). The solution of phenol was added to silver nitrate solution. The mixture was stirred for 46 hours at room temperature. The reaction progress was monitored using thin layer chromatography.

SEPARATION OF PRODUCT:

The reaction mixture was subjected to centrifugation for separating precipitated silver metal. The remaining crude was washed with organic solvent such as methanol and ethyl acetate. All these solvent was dried over Na_2SO_4 and evaporated. The residue was purified by using column chromatography on silica gel (hexane/ ethyl acetate = 20:1) to yield the desired product as a solid.

PRODUCT:

2,2'-dihydroxybinaphthyl was obtained by column chromatography: Yellowish white solid:, 90% isolated column purified yield. 71% isolated column purified yield (average yield of six cycles), Melting point 212 °C.

(B) REACTION BY HEATING:

The Silver nitrate (0.034 g, 0.2 mmol) was added in a liquor ammonia (0.2 mL) solution in a glass container (centrifuge tube). 2-Naphthol (0.029 g, 0.2 mmol) was dissolved in the absolute ethanol (0.2 mL). The solution of phenol was added to silver nitrate solution. The mixture was stirred at 65°C for 30 minutes. The reaction progress was monitored using thin layer chromatography.

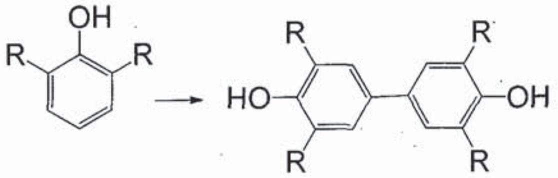
SEPARATION OF PRODUCT:

The reaction mixture was subjected to centrifugation for separating precipitated silver metal. The remaining crude was washed with organic solvent such as methanol and ethyl acetate. All these solvent was dried over Na_2SO_4 and evaporated. The residue was purified by using column chromatography on silica gel (hexane/ ethyl acetate = 20:1) to yield the desired product as a solid.

PRODUCT:

2,2'-dihydroxybinaphthyl was obtained by column chromatography: Yellowish white solid:, 70% isolated column purified yield. 60% isolated column purified yield (average yield of six cycles), Melting point 210°C, ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) : δ 5.04 (s, 2H), 7.17 (d, J =8.0 Hz, 2H), 7.31-7.42 (m, 6H), 7.92 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 9.0 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C) δ 110.9, 117.8, 124.0, 124.2, 127.5, 128.4, 129.4, 131.4, 133.4, 152.8., GCMS m/z: M+1: 285.8

EXAMPLE 4



R= tertiary butyl

METHOD OF REACTION:

The Silver nitrate (0.034 g, 0.2 mmol) was added in a liquor ammonia (0.2 mL) solution in a glass container (centrifuge tube). 2,6-di-tert-butylphenol (0.041 g, 0.2 mmol) was dissolved in the absolute ethanol (0.2 mL). The solution of phenol was added to silver nitrate solution. The mixture was stirred room temperature for 30 minutes. The reaction progress was monitored using thin layer chromatography.

SEPARATION OF PRODUCT:

The reaction mixture was subjected to centrifugation for separating precipitated silver metal. The remaining crude was washed with organic solvent such as methanol and ethyl acetate. All these solvent was dried over Na_2SO_4 and evaporated. The residue was purified by using column chromatography on silica gel (hexane/ ethyl acetate = 10:1) to yield the desired product as a solid.

PRODUCT:

3,3',5,5'-tetra-*tert*-butyl-4,4'-biphenol was obtained by column chromatography : solid, 90% isolated column purified yield: 70% isolated column purified yield (average yield of six cycles). Melting point 182°C, ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) δ 1.32 (s, 18H), 7.77 (s, 2H), 8.29 (broad, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C) δ 29.6, 36.0 ,124.0, 126.0, 136.0, 136.1, 150.5 , 186.5. GCMS m/z: M+ 410.2

NOTE:

The reaction was also carried out with other solvents or mixture of solvents such as water, methanol, alcohols, *acetonitrile* instead of absolute ethanol. Time required for completion of reaction depends on solvent and temperature used for the reaction.

The centrifugation method was used mainly to separate solid phase i.e. silver metal from solvents.

The product can be extracted with organic solvents not limited to ethyl acetate, diethyl ether, *dichloro methane*, chloroform.

All of these reactions were successfully recycled, minimum six times, in multiple, more than four sets. The % yield shown is an average yield of these four reactions.

METHOD OF SEPARATION, RECYCLE AND REUSE OF REAGENT:

Catalyzer, a key reagent, Ag-ammonia complex, gets converted to metallic silver in the form of foil, layer or particle. Therefore reaction medium is subjected to centrifugation for its complete and easy recovery. The remaining reaction mixture was washed with organic solvent such as Methanol, acetone, Chloroform before drying.

The amount of reagent was quantitatively detected using two methods by 1) direct weighing of silver metal and 2*) conductometric/potentiometric* titration.

97 % reagent was recovered after 5th cycle of use.

Precipitated silver (0.2 mmol) was reused by treating it with HNO_3 (0.2 ml, 98% solution).

The liquor ammonia (0.5 mL) was added into the recycled silver nitrate (0.2 mmol) and used directly for the reaction.

The reagent was highly efficient and reusable after reuse of 5th cycle.

The time required for heating to complete the reactions was found to be more for recycled reagent.

The average isolated column purified yield of recycled reagent is: 1st cycle 99.96%, 2nd cycle 99%, 3rd cycle 98%, 4th cycle 98%, 5th cycle 97%, and 6th cycle 95%.

PATENT CITATIONS

Cited Patent	Filling date	Publication date	Applicant	Title
US4008266	2 Jan 1974	15 Feb 1977	Monsanto Company	Coupling of aromatic compounds in the presence of molecular oxygen, a mercuric oxyanion compound, and a group VIII metal or group VIII metal oxyanion compound
US4965384	5 May 1989	23 Oct 1990	Amoco Corporation	Production of copper amine salt complexes for catalysts

				for the oxidative coupling of alkylphenols
US4096190	20 Jan 1976	26 Jan 1978	ICI Americas Inc., Wilmington, Del.	oxidative coupling of alkylphenols catalyzed by metal ammonia complexes
WO2004018401	26 Aug 2002	4 Mar 2004	Wiley Organics Inc	Preparation of biphenols by oxidative coupling of alkylphenols using a recyclable copper catalyst

NON-PATENT CITATIONS

References: No references

We Claim

1) A method of preparing a Carbon-Carbon oxidative coupled product of aromatic hydrocarbons containing a hydroxyl group and its derivatives mediated by silver ammonia complex.
2) The method, as claimed in claim 1, where in the silver (*I*) ammonia complex is homogeneous during the reaction.
3) The method, as claimed in claim 1, where in the silver (*I*) ammonia complex becomes heterogeneous, due to reduction, after completion of the reaction.
4) The method, as claimed in claim 1, where in the reaction is carried out under neutral to basic conditions.
5) The method, according to claim 1, the aromatic hydrocarbon are phenols that contain at least one position vacant from ortho or para to the hydroxyl group.
6) The method, according to claim 5, the vacant position is carbon hydrogen single bond (-CH).
7) The method, according to claim 6, where in the phenols are selected from 2-naphthol, 2,4-di-tert-butylphenol , 2,6-di-tert-butylphenol and 2,4-di-methylphenol.
8) The method, as claimed in claim 1, where in the reagent system comprises silver (*I*) ammonia complex.
9) The method, as claimed in claim 8, where in the silver (*I*) ammonia complex is prepared by addition of liquor ammonia solution to silver nitrate solid or aqueous solution.
10) The method, as claimed in claim 8, where in the silver (*I*) ammonia complex is prepared by addition of liquor ammonia solution to silver nitrate solid or aqueous solution followed by small amount sodium hydroxide solution.

(12) PATENT APPLICATION PUBLICATION
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(22) Date of filing of Application :03/09/2021

(21) Application No.202121039964 A
(43) Publication Date : 01/10/2021

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(54) Title of the invention : TECHNIQUES FOR SILVER COATING ON PAPER/FABRIC

(51) International classification	:G02B0005080000, B02C0023060000, H01B0001220000, A01N0059160000, D21H0025060000
(86) International Application No Filing Date	:NA :NA
(87) International Publication No	: NA
(61) Patent of Addition to Application Number Filing Date	:NA :NA
(62) Divisional to Application Number Filing Date	:NA :NA

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Name of Applicant : NA
Address of Applicant : NA
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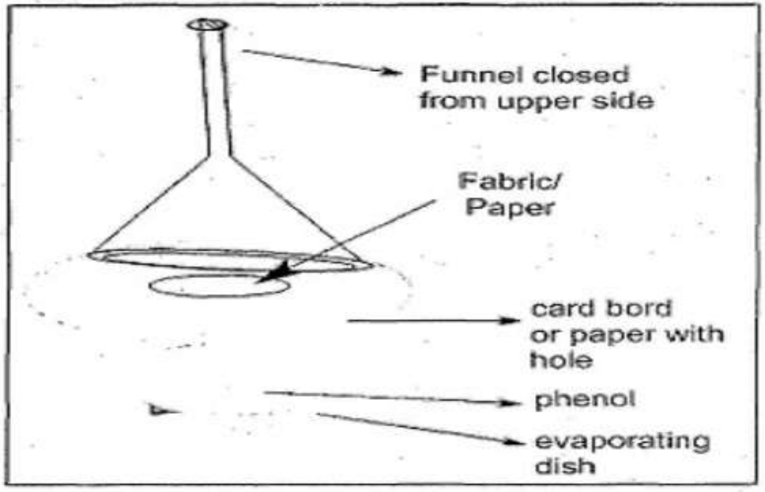
(57) Abstract :

ABSTRACT The present invention provides two novel techniques for deposition/coating/staining of silver on fabric or on paper. This techniques provides staining on selected area of substrate, which shows high conductivity and low-resistivity. To coat silver over-substrates with admirable adhesion between substrate and silver, mild conditions, easy and efficient methods are disclosed. Here in the 1st technique, the freshly sublimated, pure phenols reacts in-situ with silver ammine complex spread over fabric or paper, which gives silver staining and coating on the selected area where both reagent unites at molecular level. Here in the 2nd technique, the silver ammine complex made to react with reducing agents (phenol derivatives or aldehyde derivatives) using capillary action to form silver over paper. These methods provides economically arid environmentally benign selective area staining of silver over fabric or paper which are faster procedure, without using harsh conditions and technological advancement.

FIGURE 1



No. of Pages : 12 No. of Claims : 8

FORM 2

THE PATENTS ACT, 1970

(39 of 1970)

The Patents Rules, 2003

COMPLETE SPECIFICATION

(See section 10 and rule 13)

1. TITLE OF THE INVENTION

TECHNIQUES FOR SILVER COATING ON PAPER/FABRIC

2. APPLICANT

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3. PREAMBLE TO THE DESCRIPTION

COMPLETE SPECIFICATION

The following specification particularly describes the invention and the manner in which it is to be performed.

TECHNIQUES FOR SILVER COATING ON PAPER/FABRIC

FIELD OF INVENTION

The present invention relates to methods or techniques for the deposition/coating/staining of silver on paper or on fabric. These techniques open scope for the preparation of conductive metallic silver coating, which can be useful for various industrial applications. The present invention further fascinates silver metallic staining over selected area on a paper. These techniques are advantageous in terms of requirement of mild conditions, readily available chemicals, faster and trouble-free work up.

BACK GROUND OF INVENTION/ DESCRIPTION OF THE PRIOR ART

The silver stained substrates can be obtained using various methods and have applications, not limited in, electrically-conducting flexible fabrics/e-textile technologies, paper-printing technology, reflective films, wearable electronics, solar energy, electromagnetic interference shielding, and cellulose coated sensor. Therefore, the silver staining on paper/fabric remained an challenging area not only scientists but also to industries.

The reported techniques such as metallic spray deposition/ metal-vapor phase deposition as disclosed in US8062701B2, have huge drawbacks due to the requirement of advanced techniques and high-temperature conditions.

On the other hand, JP2002129259A discloses a method of forming a film by performing vacuum deposition using silver on the surface of flexible substrates. However, in the case of vacuum deposition, a high vacuum chamber is required, and there are restrictions on the shape and size of the substrate, and the coating thickness is not uniform. However, there is a problem due to high equipment costs.

In the US8012676B2, the pattern or coating of silver is explored by exposing silver salts light-sensitive material on substrate. The major drawback of these type of ink is prepared by using photosensitive silver salts, which are difficult to handle/store. Apart from that most of these inks are made up of many organics, requires multiple step synthesis, mainly separate step is required to prepare the silver particles/colloid.

Apart from that in the US20170354372A1 and CN102365127B, CN101909786B, The silver nanoparticle containing fluid is applied to wet coating material, dried and washed. And the extra fluid is removed by heating, flash-heating, distillation, evaporation, suction, vacuum, or any combination thereof. This method needs silver salts, stabilizer, impurity stabilizer, polymeric dispersant, organic solvents etc. In these process silver particles should be prepared separately, and purified also which becomes lengthy and multiple step process. This technique do not requires separate step for attachment of silver with substrate.

On the other hand, present invention shows novel techniques for the coating/staining of silver over fabric or paper. The present invention is advantageous in terms of reaction condition, single step approach. The invention can be used and adoptable for bulk as well as microscale industrial process. The variety of reagents can be used for this techniques not limited to examples shown below. The method is much cheaper and faster compare to other techniques. The method also gives an advantageous staining or coating over selective area, and thus unwanted staining can be ignored, without using protection step.

SUMMARY OF INVENTION

The present disclosure provides two novel techniques for deposition of silver over selectable area of fabric/paper, which requires mild conditions, easy and efficient methods.

Here in the 1st technique, the freshly sublimated pure phenols reacts in-situ with silver ammine complex spread over fabric or paper, which gives silver staining and coating on the selected area where both reagent unites at molecular level.

Here in the 2nd technique, the silver ammine complex made to react with reducing agents (phenol derivatives or aldehyde derivatives) using capillary action to form silver over paper.

Both these methods provides economically and environmentally benign silver staining with minimal wastage of reagents.

DETAILED DESCRIPTION OF INVENTION

The present disclosure provides two techniques for obtaining industrially important metallic silver film on paper/fabric (substrate) as a material.

According to yet embodiment of the invention, the silver (*I*) ammine complex is used as a oxidizing agent and aldehyde/phenol derivatives as reducing agents.

In the 1st technique, the pair of silver ammine complex and phenols is disclosed for the reaction.

Herein the silver(*I*) ammine complex is prepared by dissolving silver nitrate in to the liquor ammonia and sprinkled over fabric/ paper.

According to an embodiment of the invention, the phenols containing benzene ring at least substituted with one hydroxyl functional group can be used for the reaction.

According to an embodiment of the invention, the phenol derivatives are selected from 2-naphthol, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butylphenol.

The phenol derivative was added in an evaporating dish. It was covered with a card board having big hole in the center. The paper/fabric (substrate) was kept over cardboard. The assembly was covered with a glass funnel. The end of glass funnel was covered with cotton plug, as shown in figure 1.

The evaporating dish was heated externally gradually to sublimate phenol derivatives. After almost complete sublimation (around 5 minutes), the assembly was cooled down, and the substrate was brought out.

The silver coated substrate was washed with dichloromethane to remove organic counterpart (phenol and C-C coupled bi-phenol product), and kept in dark at room temperature to dry.

According to an embodiment of the invention, the silver (*I*) ammonia complex reacts to phenol derivatives and forms silver (0) during the reaction. The sublimation of phenol gives purified phenol, which sublimates in hall assembly but this reaction happens only over the part where the sublimated phenol derivatives mix with silver ammine complex, thus the reaction gives silver staining or coating over selected part on a substrate.

In the 2nd technique the silver(*I*) ammine complex was added to a vial/vessel. This silver ammine complex was prepared by adding sodium hydroxide solution in to silver nitrate and dissolving it in to the liquor ammonia.

According to an embodiment of the invention, the reducing agents was added to another vial/vessel. The reducing agent are from aromatic compounds containing at least one aldehyde or hydroxyl functional group or aliphatic compounds with at least one aldehyde functional group.

The reducing agent are chosen/selected from glucose, formaldehyde, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butylphenol.

The two vials/vessels containing silver(*I*) complex and reducing agents were connected with a paper by dipping end of papers in it. The assembly was kept at room temperature for silver film formation, as shown in figure 2.

The silver coated paper was removed from assembly and washed with water and dichloromethane to remove organic counterpart. The silver coated paper was kept in dark at room temperature to dry.

According to an embodiment of the invention, the silver (*I*) ammonia complex reacts to phenol derivatives/aldehyde derivatives and forms silver (0) during the reaction. The reaction happens only over the selected part of paper, where the reducing agents mixes to the silver ammine complex, which results in silver staining or coating over it.

The silver coated paper was analyzed using optical microscopy and shiny silver metallic staining was observed clearly. The resistivity and conductivity of silver stained paper were noted using digital multimeter, and high conductivity and law resistance was observed. No effect was observed on paper/fabric by washing it with water and ethanol many time vigorously.

The organic solvents other than dichloromethane can be used for removal of organics from paper or fabric.

The thickness of silver film can be varied by changing concentration of complex.

On adding silver ammine complex in required area of paper/fabric, the silver staining can be obtained over it.

This invention reveals the feasibility of the reaction over a particular area on a substrate, molecular level boundary condition for mixing of the reagents.

DRAWING:

FIGURE 1

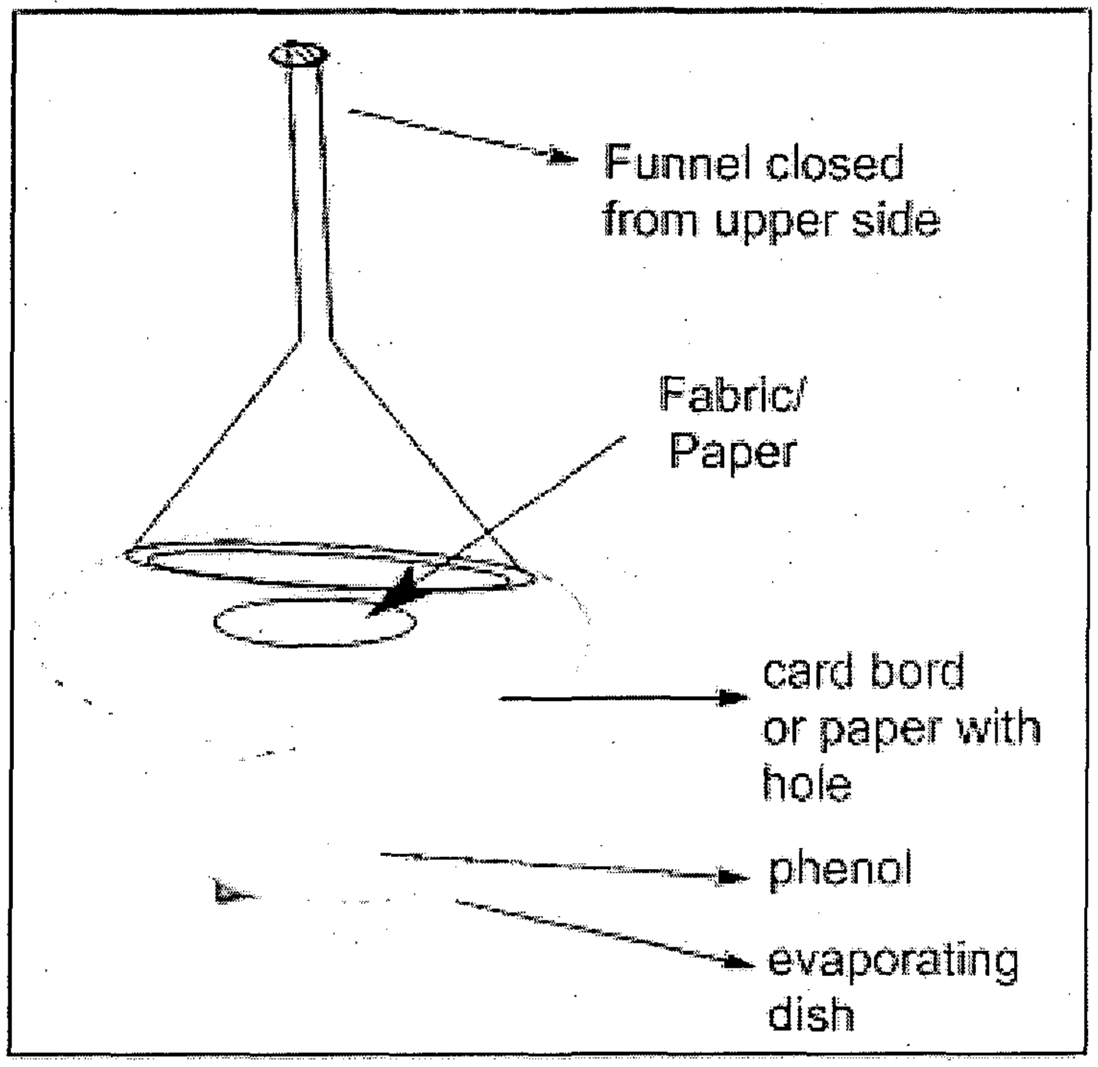
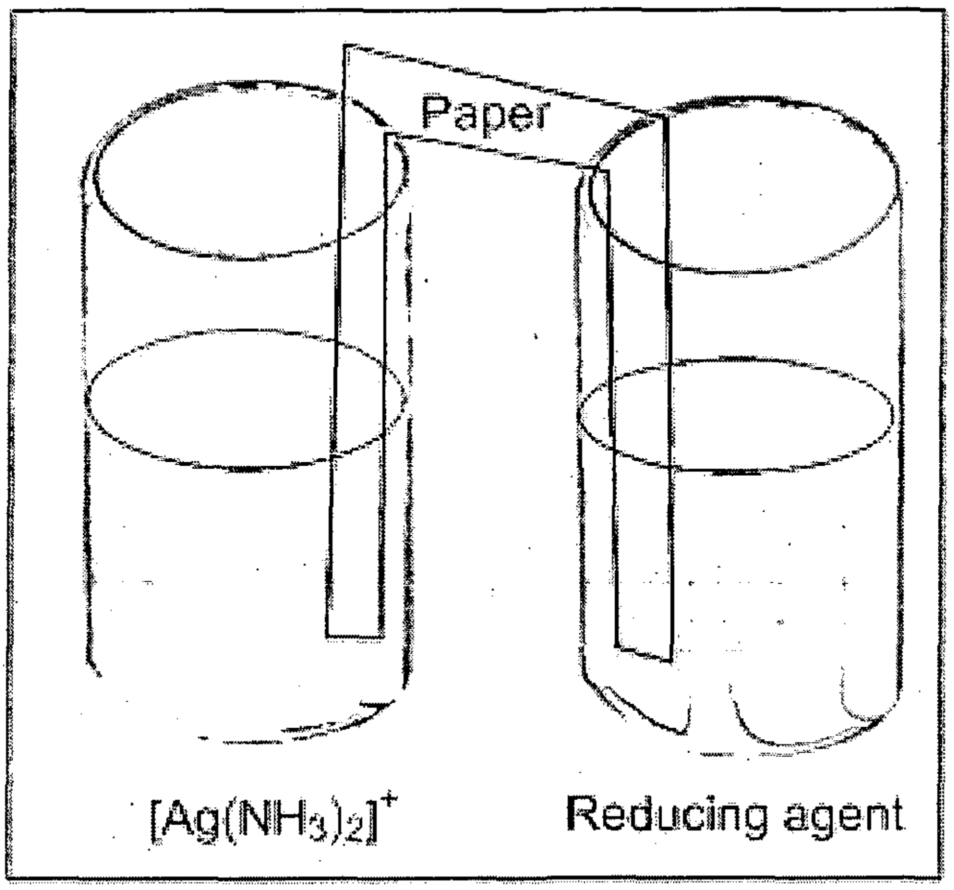


FIGURE 2



BRIEF DISCUSSION OF DRAWING:

Figure 1: Technique 1

Figure 2: Technique 2

EXAMPLES:

The disclosure is further illustrated by the following examples, which in no way should be construed as being further limiting. One skilled in the art will readily appreciate that the specific techniques and results described are merely illustrative. The example 1 to 3 presents 1st technique (Figure 1) and example 4 to 7 presents 2nd technique (Figure 2). The "room temperature" indicates 25-30 °C temperature in the following examples.

EXAMPLE 1

2-Naphthol (0.100 g, 0.694 mmol) was added to an evaporating dish. This dish was covered with cardboard having hole in the center. The silver ammine complex was prepared by dissolving silver nitrate (0.0600 g, 0.35 mmol) into 0.5 ml liquor ammonia. This freshly prepared silver ammine complex was sprinkled on a paper/fabric (as a substrate), kept over cardboard, and covered with a glass funnel. The evaporating dish was heated gradually in an oil bath to sublimate 2-Naphthol (~161 °C). After almost complete sublimation (around 5 minutes), the assembly was kept aside for cooling, and the substrate was brought out.

The substrate was washed with dichloromethane to extract organic counterpart (2-naphthol and BINOL). Now the substrate, mainly containing silver, was kept in dark and dried at room temperature.

EXAMPLE 2

2,4-di-*tert*-butylphenol (0.100 g, 0.485 mmol) was added to an evaporating dish. This dish was covered with cardboard having hole in the center. The silver ammine complex was prepared by dissolving silver nitrate (0.0600 g, 0.35 mmol) into 0.5 ml liquor ammonia. This freshly prepared silver ammine complex was sprinkled on a filter paper/cotton (as a substrate), kept over cardboard, and covered with a glass funnel. The evaporating dish was heated gradually in an oil bath to sublimate 2,4-di-*tert*-butylphenol (at 115 °C). After almost complete sublimation (around 5 minutes), the assembly was kept aside for cooling, and the substrate was brought out.

The substrate was washed with dichloromethane to extract organic counterpart. Now the substrate, mainly containing silver, was kept in dark and dried at room temperature.

EXAMPLE 3

2,6-di-*tert*-butylphenol (0.100 g, 0.485 mmol) was added to an evaporating dish. This dish was covered with cardboard having hole in the center. The silver ammine complex was prepared by dissolving silver nitrate (0.0600 g, 0.35 mmol) into 0.5 ml liquor ammonia. This freshly prepared silver ammine complex was sprinkled on a filter paper/cotton (as a substrate), kept over cardboard, and covered with a glass funnel. The evaporating dish was heated gradually in an oil bath to sublimate 2,6-di-*tert*-butylphenol. After almost complete sublimation (around 5 minutes at around 118 °C), the assembly was kept aside for cooling, and the substrate was brought out.

The substrate was washed with dichloromethane to extract organic counterpart. Now the substrate, mainly containing silver, was kept in dark and dried at room temperature.

EXAMPLE 4

0.5 ml of liquor ammonia and 1.0 ml 0.01 N silver nitrate solution in water was mixed in a glass vial of capacity 2 ml. 1.5 ml of 2,4-di-*tert*-butylphenol solution (0.01 N in absolute ethanol) was taken in another similar glass vial. These two vials were kept 0.5 cm away from each other, and connected by a single paper strip. The reaction was kept at room temperature for 1 hour. The silver stained paper was bring out and washed with water and dichloromethane. The silver stained paper was kept in dark and dried at room temperature.

EXAMPLE 5

0.5 ml of liquor ammonia and 1.0 ml 0.01 N silver nitrate solution in water was mixed in a glass vial of capacity 2 ml. 1.5 ml of 2,6-di-*tert*-buty- phenol solution (0.01 N in absolute ethanol) was taken in another similar glass vial. These two vials were kept 0.5 cm away from each other, and connected by a single paper strip. The reaction was kept at room temperature for 1 hour. The silver stained paper was bring out and washed with water and dichloromethane. The silver stained paper was kept in dark, and dried at room temperature.

EXAMPLE 6

0.5 ml of liquor ammonia and 1.0 ml 0.01 N silver nitrate solution in water was mixed in a glass vial of capacity 2 ml. 1.5 ml of formaldehyde solution (0.01 N in water) was taken in another similar glass vial. These two vials were kept 0.5 cm away from each other and connected by one paper. The reaction was kept at room temperature for 1 hour. The silver stained paper was bring out and washed with water. The silver stained paper was kept in dark and dried at room temperature.

EXAMPLE 7

0.5 ml of liquor ammonia, 0.5 ml 0.01 N sodium hydroxide and 0.5 ml 0.02 N silver nitrate solution in water were mixed in a glass vial of capacity 2 ml. 1.5 ml of glucose solution (0.01 N in water) was taken in another similar glass vial. These two vials were kept 0.5 cm away from each other, and connected by a single paper strip. The reaction was kept at room temperature for 4 hour. The silver stained paper was bring out and washed with water. The silver stained paper was kept in dark and dried at room temperature.

Date 31/08/2021
Signature: -
Name: Ghalsasi Prasanna S.

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Name BHANDERI KHUSHBOO D.

PATENT CITATIONS

Cited Patent	Filling date	Publication date	Applicant	Title
IN333913	16/02/2016	07/07/2017	Ghalsasi Prasanna S	A Method of catalysis for preparing a Carbon-Carbon oxidative coupled product of aromatic hydrocarbons
US8062701B2	11/01/2010	06/05/2010	3M Innovative Properties Co	Method of transferring nanoparticles using a microporous article having metallic nanoparticle coating
US20170354372A1	03/08/2017	14/12/2017	NANOWEAR Inc	Smart materials, dry textile sensors, and electronics integration in clothing, bed sheets, and pillow cases for neurological, cardiac and/or pulmonary monitoring
CN102365127B	17/03/2010	29/02/2012	BASF SE	Preparation of shaped metal particles and application thereof
CN101909786B	25/12/2008	08/12/2010	Dowa electronics materials Co Ltd	Silver micropowder, silver ink, silver coating, and methods for production of these materials
JP2002129259A	31/10/2000	09/05/2002	Furuya Kinzoku	Highly heat-resistant reflection film and laminated body, reflection plate for liquid crystal display element and glass as building material using the film

NON-PATENT CITATIONS

References: No references

Date 31/08/2021

Name: Ghalsasi Prasanna S. Bhanderi Khushboo D.

We Claim

1. The metallic silver coating on paper/fabric compounds by two techniques: 1st by evaporating/sublimating phenol derivative kept in evaporating dish, covered with a card board having big hole in the center, keeping silver(*I*) ammine complex containing paper/fabric (substrate) over it, and covering it with closed glass funnel. 2nd by connecting the silver(*I*) ammine complex containing vial to the reducing agents containing vial/vessel with paper/fabric at room temperature.

2. In the claim 1, the silver staining or coating accurse on the selected part of fabric, where the reducing agents mixes at the molecular level with the silver(*I*) ammine complex.

3. According to claim 1, the silver(*I*) ammine complex is prepared freshly by dissolving silver salt of nitrate/chloride in ammonia.

4. According to claim 1, the phenols used for the reaction contains benzene ring substituted with at least one hydroxyl functional group.

5. According to claim 4, the phenol derivatives are selected from 2-naphthol, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butylphenol.

6. According to claim 1 in the 1st method, the phenols are heated till evaporation or sublimation.

7. According to claim 1 in the 2nd method, the reducing agent are selected from aromatic compounds containing at least one aldehyde or hydroxyl functional group or aliphatic compounds with at least one aldehyde functional group.

8. According to claim 7, the reducing agent are chosen/selected from glucose, formaldehyde, 2,4-di-*tert*-butylphenol, and 2,6-di-*tert*-butylphenol.

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ABSTRACT

The present invention provides two novel techniques for deposition/coating/staining of silver on fabric or on paper. This techniques provides staining on selected area of substrate, which shows high conductivity and low-resistivity. To coat silver over substrates with admirable adhesion between substrate and silver, mild conditions, easy and efficient methods are disclosed.

Here in the 1st technique, the freshly sublimated pure phenols reacts in-situ with silver ammine complex spread over fabric or paper, which gives silver staining and coating on the selected area where both reagent unites at molecular level.

Here in the 2nd technique, the silver ammine complex made to react with reducing agents (phenol derivatives or aldehyde derivatives) using capillary action to form silver over paper.

These methods provides economically and environmentally benign selective area staining of silver over fabric or paper which are faster procedure, without using harsh conditions and technological advancement.

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