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(71) **Applicant: SARASWATI PIGMENTS PVT. LIMITED** [IN/IN]; Plot No. L/121 6/3, Phase IV - G.I.D.C., Naroda, Ahmedabad 382 330, Gujarat (IN).

(72) **Inventors: INGALE, Muralidhar;** A/5, Revati Tower, Satellite, Ahmedabad 380 015, Gujarat (IN). **PATEL, Kamlesh;** of Saraswati Pigments Pvt. Ltd., (Regd. Office), Plot No. L/1216/3, Phase IV - G.I.D.C., Naroda, Ahmedabad 382 330 Gujarat (IN). **PATEL, Harshad;** of Saraswati Pigments Pvt. Ltd., (Regd. Office), Plot No. L/12 16/3, Phase IV - G.I.D.C., Naroda, Ahmedabad 382 330 Gujarat (IN). **PATEL, Ajay;** of Saraswati Pigments Pvt. Ltd., (Regd. Office), Plot No. L/12 16/3, Phase IV - G.I.D.C., Naroda, Ahmedabad 382 330 Gujarat (IN).

(74) **Agents: PRATAP, Prabhakar Mani** et al; VUTTS & ASSOCIATES LLP, Advocates, No. 704, The Castle, Plot 36-A, Sector 56, Gurgaon 122 009, Haryana (IN).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available):* AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

[Continued on next page]

(54) **Title:** A COST EFFECTIVE, PROCESS OF CONVERTING WASTE AMMONIA AND CARBON DIOXIDE INTO PHTHALOCYANINE COMPOUNDS VIA INTERMEDIATES

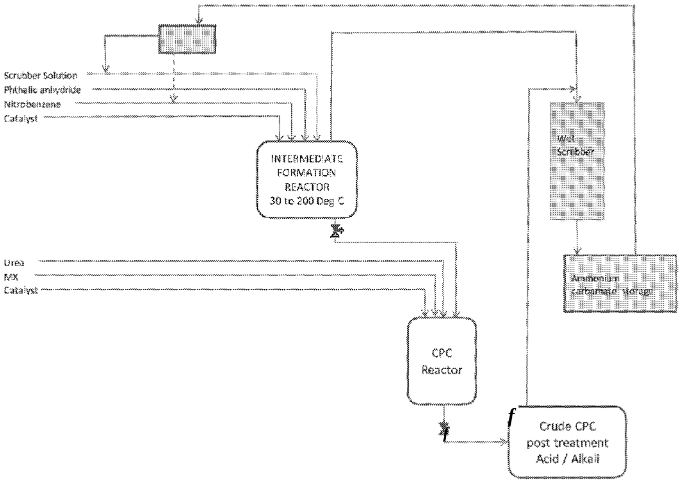

Figure 2 : Flow Diagram for Copper phthalocyanine preperation using scrubber solution and minimum urea compounds.

FIG. 2

(57) **Abstract: A** cost effective, environment friendly and industrially viable process for the preparation of phthalocyamne compounds more particularly copper phthalocyamne, other metal phthalocyanines and metal free phthalocyamne, the process comprising the steps of: scrubbing the waste ammonia and carbondioxide gaseous streams generated during /byphthalic anhydride - urea processin aqueous solution; saturating the aqueous solution to produce ammonia in the range of about 10-35 %; treating the saturated solution with phthalic anhydride and one or more suitable solvents to convert into phthalocyanine intermediates in the presence of one or more suitable catalyst; converting in-situ the phthalocyanine intermediatesto copper phthalocyanine or other metal / metal free phthalocyanine with the help of minimal amount of urea compound and metal salt.

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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(Hi))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

Description

A COST EFFECTIVE, PROCESS OF CONVERTING WASTE AMMONIA AND CARBON DIOXIDE INTO PHTHALOCYANINE COMPOUNDS VIA INTERMEDIATES

[1] CROSS-REFERENCE TO THE RELATED APPLICATION

[2] This application claims priority from Indian Patent Application No. 2755/MUM/2012 dated September 24, 2012, the entire disclosure of which is incorporated herein by reference.

[3] FIELD OF THE INVENTION

[4] The present invention relates to a metal and metal freephthalocyanines especially copper phthalocyanine blue manufacturingprocess but not limited to other phthalocyanines than copper phthalocyanine blue (CuPC). More particularly, the present invention relates to acost effective, environment friendly and industrially viable processfor utilizing and converting waste ammonia and carbon dioxide gaseous streams which is also referred as ammonium carbamate solution into usable pthalocyanine intermediates and in-situ conversion thereof into phthalocyanine compounds for example CuPc to reduce raw material consumptions especially urea compounds or their salts to produce phthalocyanine compounds at reduced cost and with very less environmental liability for treatment of phthalocyanine process waste streams.

[5] The present invention makes the process of manufacturing phthalocyanines more eco-friendly and economical which is the need of today in order to manufacture these compounds at lower cost and with minimal waste generation. Moreover, the present invention drastically reduces the load of ammonical nitrogen in waste stream generated in the phthalocyanine manufacturing plants.

[6] BACKGROUND OF THE INVENTION

[7] For the production of for example copper phthalocyanines, conventionally, there is industrially most widely employed a method in which a phthalic anhydride and/or its derivative, a copper compound and urea are heated in an inert solvent in the presence of a catalyst, and this method is known as a urea method or Wyler method.

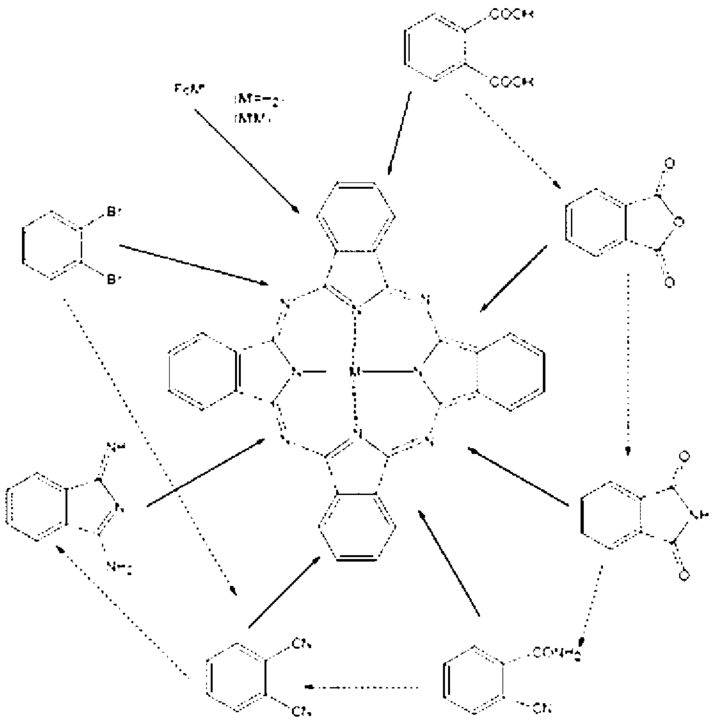
[8] The above urea method is widely used industrially at present.In the process, phthalic

anhydride is reacted with urea compounds and a metal (I) salt in the presence of a catalyst, in general ammonium molybdate or MoO_3, if appropriate in an inert solvent such as, for example, Hysolve, trichlorobenzene or nitrobenzene or nitroalkyl benzene, sulfolane, dichlorobenzene at temperatures between 150° and 250°C, the solvent, if present, is removed, for example by filtration or distillation under vacuum, and the crude CuPc is extracted by boiling with dilute mineral acid. This gives yields of only between 70 and 90% of theory, relative to phthalic anhydride or Cu salt especially in the case of copper phthalocyanine, though an excess of urea is employed, in most cases 2 to 4 moles per mole of phthalic anhydride. Generally, the reaction time of phthalic anhydride/urea process is about 12 to 16 hours. In the course of the reaction, however, the urea compounds decompose throughout the course of reaction partly reacting and partly going out of the reactor into the atmosphere. In the commercial process these waste gaseous streams are absorbed in water and disposed or treated to produce ammonia solution or its salt such as ammonium sulphate, ammonium phosphate, ammonium carbonate and other salts.

[9] Disposal of such byproduct poses a great problem. Also, these treatment / preparation involve the cost and hence decrease the profit margins. As a result, not only the cost, but also the extra consumption of urea compounds is not avoidable in todays manufacturing scenario in order to get purity and yield of the product.

[10] There are no processes which overcomes the above defects/problems reducing the manufacturing cost. It has been and is therefore strongly desired to develop a process for producing a highly pure (copper) phthalocyanines at high yields in the most cost effective way by converting the waste ammonia and CO_2 streams in to useful intermediates like phthalimide, 1, 3-diiminoisoindoline etc. and their in situ conversion into high purity phthalocyanines in good yield by reacting them with just sufficient urea compounds in the presence of metal salt and high boiling solvent. The present inventor has made diligent studies to overcome the above problems and to accomplish the above requirements, and have found the following invention. Various intermediates which eventually leads to phthalocyanine compounds in the presence of urea compounds and metals salts are shown below in Fig. 1.

[11]



[12] **Fig. 1**

[13] [Various intermediates which finally leads to the formation of Phthalocyanines]

[14] SUMMARY OF THE INVENTION

[15] According to the present invention, a process has now been found which is able to solve and reduce, in a simple manner all the waste ammonia and carbon dioxide streams and related treatment problems which have been described, by scrubbing the waste ammonia and carbon dioxide streams in aqueous solution during reaction and saturated to give ammonia strength in the range of about 10-35 %. This solution is then treated with phthalic anhydride and one or more solvents to produce phthalocyanine process intermediates such as phthalimide, 1,2-phthalodinitrile, l,3-diiminoisoindoline,l,2-dihydro-3H-indazol-3-one with small amount of ortho phthalodinitrileetc. at 110 to 250° C in the presence of one or more suitable catalysts.These intermediates are then in-situ converted to copper phthalocyanine or other metal free and metal phthalocyanines such as Iron phthalocyanine, Magnesium phthalocyanine, Cobalt phthalocyanine, Aluminium phthalocyanine, and other metal phthalocyanines such as Si, Cr, Mn, Ti, Ni, Zn, Ru, Li, etc. with the help of threshold amount of urea compound which are just sufficient and metal salt. The process utilizes almost complete ammonical Nitrogen and small unreacted ammonical nitrogen is again captured and recycled to get phthalocyanine intermediates similarly as described above.

[16] Suitable solvents of the instant invention are high boiling solvents such as nitro benzene, Nitro toluenes, chlorinated toluenes such as dichlorotoulene, chlorinated

benzenes, linear alkyl benzenes, sulfolane, 1,2-dichlorobenzene, N,N-dimethylformamide and derivatives thereof.

[17] Suitable catalysts of the instant invention arephthalimide, 1,3-diminoisoindoline orl,2-dihydro-3H-indazol-3-one and inorganic compounds such as dilute nitric acid or its alkali metals salts.

[18] Yet another aspect of the present invention relates to thecopper phthalocyanine produced by the above processes.

[19] The process flow diagram for synthesis of copper phthalocyanine (CuPc) according to the present invention is illustrated in Fig. 2 below:

[20]

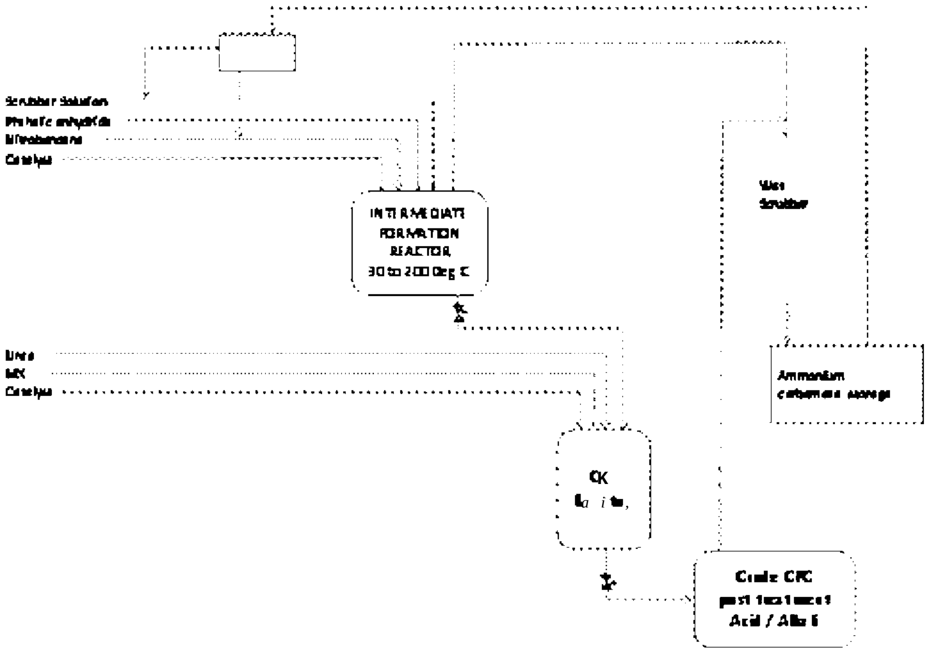


Figure 2 : Flow Diagram for Copper phthalocyanine preparation using scrubber solution and minimum urea compounds.

[21] Therefore, one object and advantage of the present invention is to provide a process which converts waste ammonia and carbon dioxide streams into usable intermediates in the copper phthalocyanine (CuPc) and other metal / metal free phthalocyanine manufacturingprocess to produce highly pure phthalocyanines at high yields in the cost effective and environmentally friendly way. The process is not limited to the other metal and metal free phthalocyanines mentioned above.

[22] Another object and advantage of the present invention is to provide a process forin-situ conversion ofthe intermediates formedin the copper phthalocyanine (CuPc) manufacturingprocess to produce a highly pure copper phthalocyanine at high yields.

[23] Another object and advantage of the present invention is to provide a process which completely eliminates the ammonia and carbon dioxide waste stream disposal problem and converts the waste into valuable intermediates for the production ofhighly pure copper phthalocyanine at high yields.

[24] Another object and advantage of the present invention is to provide a process which utilizes minimal quantity urea compound which eventually helps in saving on waste generation as well as treatment cost and raw materials consumption costs.

[25] Another object and advantage of the present invention is to provide a process for the production of copper phthalocyanine by a urea process, which enables the production of a highly pure copper phthalocyanine and/or derivative thereof suitable for commercial use with high economic performance.

[26] Yet another object and advantage of the present invention is to provide an economic and environmentally benign process with the desired consistency on the commercial scale.

[27] DETAILED DESCRIPTION OF THE INVENTION

[28] The present inventor has made diligent studies to achieve the above objects, and as a result, have found thatthe intermediates obtained in accordance with the process of the invention can, in-situ be added to the starting components, so that to have practically 92-95% yield, relative to Cu salt and phthalic anhydride/urea process, results.

[29] Furthermore, it is not necessary to constantly add excess quantity of urea compound in the process since the ammonical value is always recovered along with carbon dioxide and recycled in the process in an active form. Because of the simple and economical manner of recovery and recycling of the reaction by-products it is furthermore not necessary to maximize the yield of the synthesis step, which *inter alia* has the consequence that it is possible to dispense with some of the large excess of urea as a result of which the flue gas problems, but above all the biological oxygen demand of the effluent, can be greatly restricted without substantially impairing the economics of the process.

[30] Moreover, the advantages of the process of waste ammonia and carbon dioxide streams treatment according to the present invention are particularly important when using solvent-free synthesis processes or using processes which use small amounts of water-soluble or acid-soluble solvents, since in that case the entire reaction by-products pass into the effluent from the extractive boiling with acid. In order fully to be able to utilize the advantages of the process according to the invention even when using water-insoluble solvents, it is necessary first to distil off the solvent and then to extract the product by boiling with acid.

[31] In the present invention, the conversion ofwaste ammonia and carbon dioxide streamsinto useful intermediates has outstanding importance in that the intermediates produced are the part of copper phthalocyanine (CuPc) manufacturingprocess itself. It has also great advantage over the consumption of urea compounds as the process utilizes lesser urea compound and, therefore, results into good economics.

[32] The process, thus, provides for a complete recycling of ammonia compounds which

were earlier going in to waste increasing waste treatment costs during reaction of phthalic anhydride/urea process in the copper phthalocyanine manufacturing process. Since, the process utilizes lesser urea compound it controls the economics by saving costs on waste treatment as well as on raw material consumptions.

[33] The use of minimum urea compounds is advantageous with respect to manufacturing cost and environmental as well as logistics concerns. The overall economics of the commercial process of making phthalocyanines particularly copper phthalocyanine results into 8 to 10% reduction in cost as compared to the current standard process followed in the Industry.

[34] **EXAMPLES**

[35] In order to more clearly describe the nature of the present invention, specific example(s) will hereinafter be described.

[36] **EXAMPLE 1**

[37] 1000 kg Parts of phthalic anhydride and 1400 parts of urea, 175 parts of cuprous chloride, 2.5 parts of ammonium molybdate, were heated in 3500 kg nitrobenzene. The off waste stream (ammonia and Carbon dioxide) both coming from main reaction and post treatments were eventually scrubbed in water scrubber to produce 25 w % ammonium carbamate liquid. The product obtained after solvent removal gave 925 parts of a crude copper phthalocyanine (purity 97.6 %, yield 94.0 %).

[38] In another reactor the above ammonium carbamate solution obtained from scrubber was reactedat 35 to 90° with phthalic anhydride (1000 parts) which was added while continuously removing water. After that, 1000 parts nitro benzene and 950 parts Urea was added. To this mixture further added 175 parts CuCl and 2.5 parts Ammonium molybdate. The whole mixture was heated at 185 to 220° to get almost quantitative yield of copper phthalocyanine (CuPc)crude which is equivalent to the normal crude produced.

[39] **EXAMPLE 2**

[40] The ammonium carbamate solution is generated as described in Example 1 only Cobalt Chloride was used instead of copper (I) chloride and this solutions is recycled and reused to produce cobalt phthalocyanine as described in this invention.

[41] The ammonium carbamate solution obtained from scrubber was reactedat 35 to 90° with phthalic anhydride (1000 parts) which was added while continuously removing water. After complete removal of water, 1000 parts nitro benzene and 950 parts Urea was added. To this mixture further added 165 parts $CoCl_26H_20$ and 2.5 parts Ammonium molybdate. The whole mixture was heated at 185 to 220° to get almost quantitative yield of cobalt phthalocyanine (CuPc)crude which is equivalent to the normal crude produced.

[42] From the foregoing description, it will be apparent to one of ordinary skill in the art

that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

[43] Accordingly, it is not intended that the scope of the foregoing description be limited to the description set forth above, but rather that such description be construed as encompassing all of the features of patentable novelty that reside in the present invention, including all the features and embodiments that would be treated as equivalents thereof by those skilled in the relevant art. Thus, it is intended that the scope of the present invention herein disclosed should not be limited by the particular disclosed embodiments described above but should be determined only by a fair reading of complete specification and claims to follow.

Claims

[Claim 1] A cost effective, environment friendly and industrially viable process for the preparation of phthalocyanine compounds more particularly copper phthalocyanine, other metal phthalocyanines and metal free phthalocyanine, the process comprising the steps of:

scrubbing the waste ammonia and carbondioxide gaseous streams generated during /byphthalic anhydride - urea processin aqueous solution;

saturating the aqueous solution to produce ammonia in the range of about 10-35 %;

treating the saturated solution with phthalic anhydride and one or more suitable solvents to convert into phthalocyanine intermediates in the presence of one or more suitable catalyst;

convertingin- situ the phthalocyanine intermediatesto copper phthalocyanine or other metal / metal free phthalocyanine with the help of minimal amount of urea compound and metal salt.

[Claim 2] The process as claimed in claim 1, wherein thephthalocyanine intermediates are phthalimide, 1,3-diminoisoindoline orl,2-dihydro-3H-indazol-3-one with small amount of ortho phthalodinitrile,

[Claim 3] The process as claimed in claim 1, wherein the step of treating the saturated solution of waste gaseous stream with phthalic anhydride is conducted at a temperature of 110° to 250° C.

[Claim 4] The process as claimed in claim 1, wherein the suitable solvents are high boiling solvents comprising nitro benzene, Nitro toluenes, chlorinated toluenes such as dichlorotoulene, chlorinated benzenes, linear alkyl benzenes, Dimethylformamide, sulfolane etc. and derivatives thereof.

[Claim 5] The process as claimed in claim 1, further comprising the step of recycling the saturated aqueous ammonium carbamate solution comprising ammonical nitrogen in an active form.

[Claim 6] The process as claimed in claim 1, wherein the suitable catalystsare selected from phthalimide, 1,3-diminoisoindoline orl,2-dihydro-3H-indazol-3-one and inorganic compounds such as dilute nitric acid or its alkali metals salts.

[Claim 7] The process as claimed in any of the preceding claims, wherein the process utilizes almost complete ammonical Nitrogen and small unreacted ammonical nitrogen is again captured and recycled to get phthalocyanine intermediates.

FIG. 1

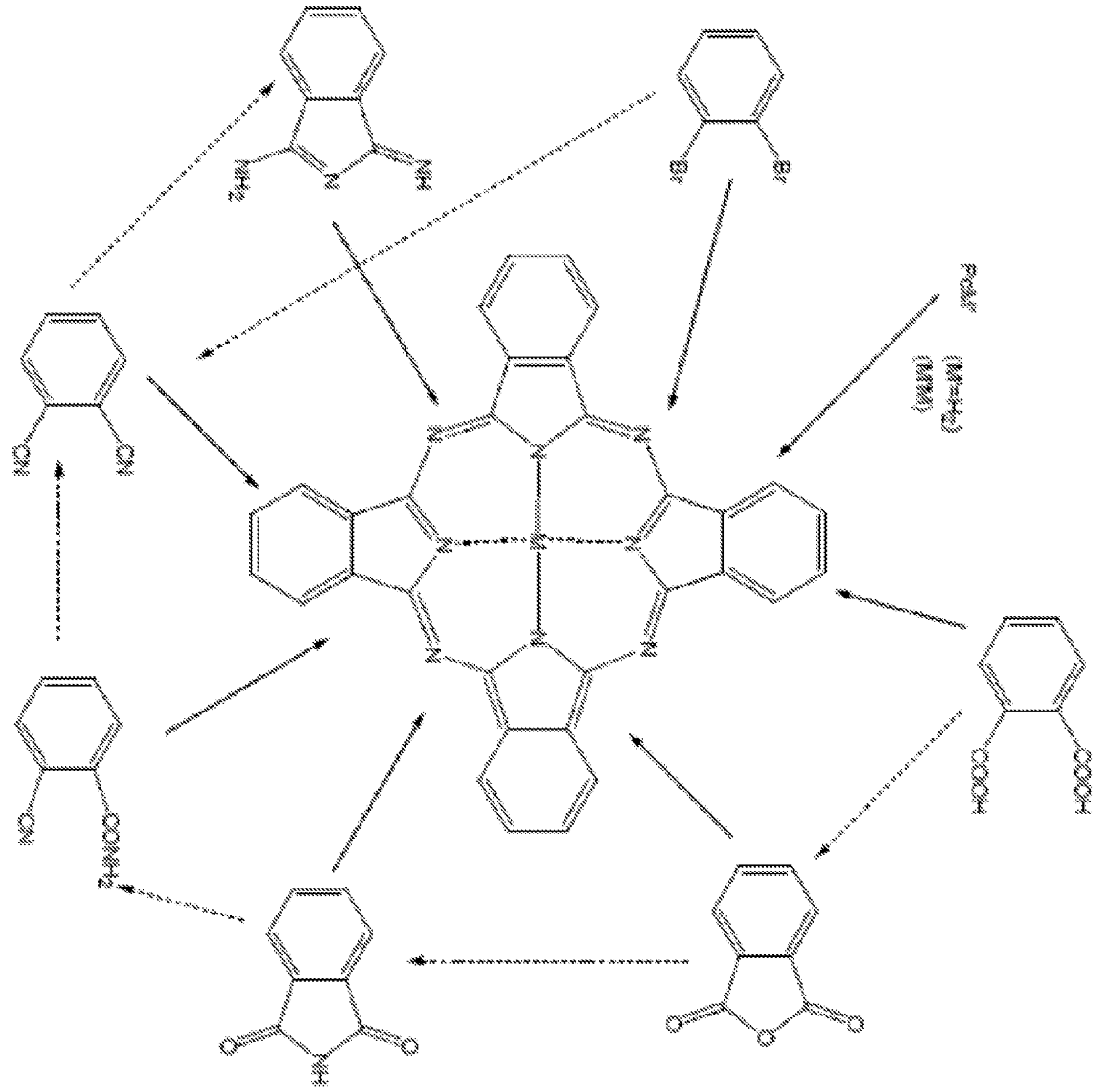


FIG. 2

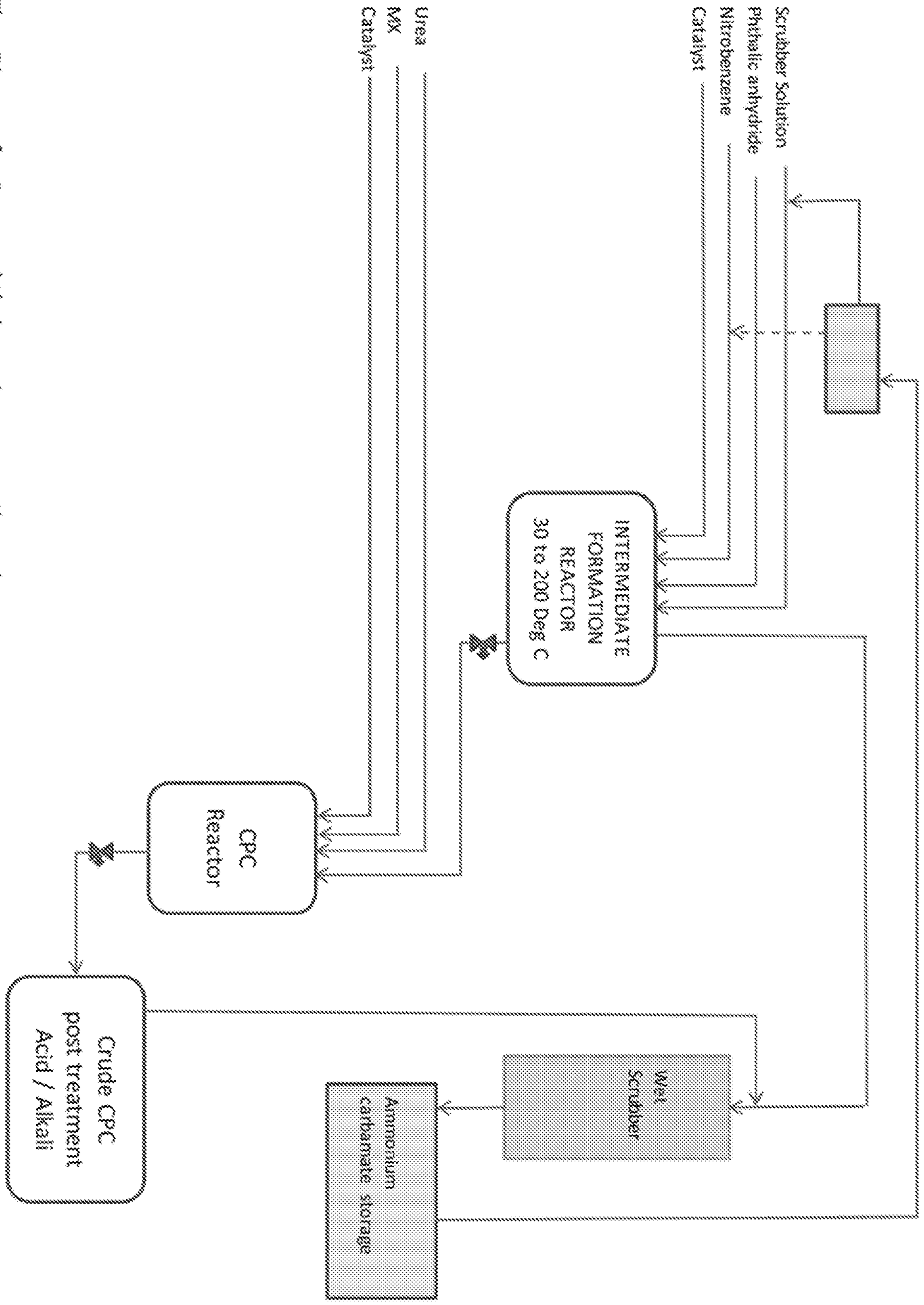


Figure 2 : Flow Diagram for Copper phthalocyanine preperation using scrubber solution and minimum urea compounds.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2013/058758

A. CLASSIFICATION OF SUBJECT MATTER

C09B 47/06 (2006.01) C09B 67/50 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

(1) Database : CAPLUS with keywords; phthalocyanine, phthalic anhydride, ammonia, carbon dioxide, scrubbing, wastes and like terms (2) Databases: WPI, EPODOC with class marks; C09B47/04/LOW, C07D487/22, C09B67/50 and above keywords. (3) Databases: NPL, XMISC with above kyewords (4) Database: TXTE with above keywords and (5) USPTO, ESPACENET and GOOGLE Advanced Patent Search with above keywords.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 30 January 2014	Date of mailing of the international search report 30 January 2014

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au
Facsimile No.: +61 2 6283 7999

Authorised officer

Kosala Gunatillaka
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262223652

INTERNATIONAL SEARCH REPORT

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

International application No.
PCT/IB2013/058758

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3519641 A (NITZSCHMANN et al.) 07 July 1970 Whole document	1 - 7
A	GB 1180018 A (BADISCHE ANILIN & SODA-FABRIK AKTIENGESELLSCHAFT) 04 February 1970 Whole document	1 - 7
A	US 5910585 A (ENDO et al.) 08 June 1999 Abstract, claims 1 - 6 and example 1	1 - 7
A	JP S5322524 A (NIPPON PETROCHEMICALS CO. LTD) 02 March 1978 Abstract Retieved from WPI	1 - 7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2013/058758

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
US 3519641 A	07 Jul 1970	None	
GB 1180018 A	04 Feb 1970	CH 484244 A	15 Jan 1970
		DE 1569650 A1	06 May 1970
		DE 1569650 B2	28 Feb 1974
		FR 1525678 A	17 May 1968
		GB 1180018 A	04 Feb 1970
		NL 6707440 A	04 Dec 1967
US 5910585 A	08 Jun 1999	EP 0878514 A2	18 Nov 1998
		EP 0878514 B1	21 Nov 2001
		JP H10310717 A	24 Nov 1998
		JP 3368797 B2	20 Jan 2003
		TW 450986 B	21 Aug 2001
		US 5910585 A	08 Jun 1999
JP S5322524 A	02 Mar 1978	JP S5911620 B2	16 Mar 1984

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.