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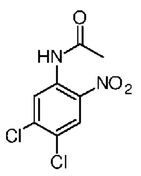
(54) **Title:** A PROCESS FOR THE PREPARATION OF 2-NITRO-4,5-DICHLOROACETANILIDE



2-Nitro-4,5-dichloio acetanilide **(I)**

(57) **Abstract:** 2-Nitro-4,5-dichloroacetanilide is an important intermediate in the dyestuff industry. In the present disclosure 2-nitro-4,5-dichloroacetanilide is prepared from 3,4-dichloroacetanilide using a nitrating agent in the presence of resultant sulfuric acid having strength of 104% w/w, in a simple, efficient and environmentally friendly process. (I) 2-Nitro-4,5-dichloroacetanilide is obtained in high yield with purity in the range of 90.0% to 98 %.

A PROCESS FOR THE PREPARATION OF 2-NITRO-4,5-DICHLOROACETANILIDE

FIELD

The present disclosure relates to a process for the preparation of 2-nitro-4,5-dichloroacetanilide.

BACKGROUND

2-Nitro-4,5-dichloroacetanilide is an important intermediate in the dyestuff industry for preparing pigments and an intermediate for preparing triclabendazole.

Typically, the preparation of 2-nitro-4,5-dichloroacetanilide involves nitrating 4,5-dichloroacetanilide with a nitrating mixture comprising nitric acid and sulfuric acid. This method involves formation of significant amount of corresponding ortho isomer 2-nitro-3,4-dichloroacetanilide as an impurity, which is difficult to separate from the product 2-nitro-4,5-dichloroacetanilide. This drawback can be eliminated by using a process that nitrates 3,4-dichloroacetanilide at 2 position with high regioselectivity, thereby providing 2-nitro-4,5-dichloroacetanilide of high purity.

There is, therefore, felt a need to provide a simple, and efficient process for preparing 2-nitro-4,5-dichloroacetanilide with high purity, and in high yield.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows.

An object of the present disclosure is to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

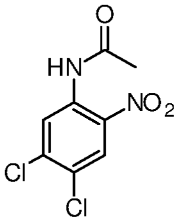
Another object of the present disclosure is to provide a simple and efficient process for the preparation of 2-nitro-4,5-dichloroacetanilide.

Still another object of the present disclosure is to provide a process for the preparation of 2-nitro-4,5-dichloroacetanilide in high yield, and with high purity.

Other objects and advantages of the present disclosure will be more apparent from the following description, which is not intended to limit the scope of the present disclosure.

SUMMARY

The present disclosure relates to a process for the preparation of 2-nitro-4,5-dichloroacetanilide **(I)** from 3,4-dichloroacetanilide.



2-Nitro-4,5-dichloroacetanilide **(I)**

In accordance with the present disclosure, the process for preparing 2-nitro-4,5-dichloroacetanilide from 3,4-dichloroacetanilide comprises the step of mixing 3,4-dichloroacetanilide with sulfuric acid at a temperature in the range of 0 °C to 35 °C, and stirring for a time period in the range of 0.5 to 1 hour, followed by adding oleum at a temperature in the range of 0 °C to 15 °C to obtain a mixture containing 3,4-dichloroacetanilide and resultant sulfuric acid. The strength of the resultant sulfuric acid is in the range of 100% w/w to 107% w/w, and the molar ratio of 3,4-dichloroacetanilide to the resultant sulfuric acid is in the range of 1:2 to 1:15. 3,4-Dichloroacetanilide is nitrated by slowly adding at least one nitrating agent to the mixture while stirring at a temperature in the range of 0 °C to 25 °C over a time period in the range of 0.5 to 10 hours, followed by further stirring the resultant mixture for a period in the range of 0.5 hours to 5 hours to obtain a product mixture comprising 2-nitro-4,5-dichloroacetanilide. The product mixture is cooled, and the cooled product mixture is poured over a mixture of ice and water to obtain a dispersion. The dispersion is filtered to obtain a residue, the residue is washed, and the washed residue is dried to obtain 2-nitro-4,5-dichloroacetanilide **(I).**

In accordance with the embodiments of the present disclosure, the concentration of sulfuric acid is in the range of 98% w/w to 99% w/w.

In accordance with the embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide to sulfuric acid is in the range of 1:1 to 1:12.

In accordance with the embodiments of the present disclosure, the concentration of oleum is in the range of 20% w/w to 35% w/w.

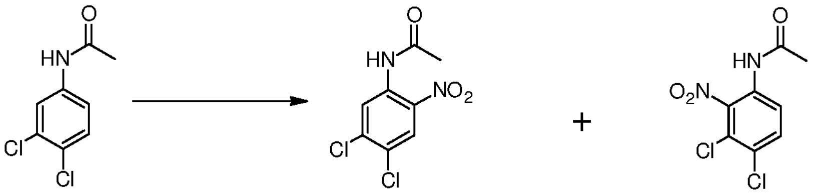
In accordance with the embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide to oleum is in the range of 1:0.5 to 1:12

In accordance with the embodiments of the present disclosure, the nitrating agent is nitric acid.

In accordance with the embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide to the nitrating agent is in the range of 1:1 to 1:1.2.

DETAILED DESCRIPTION

2-Nitro-4,5-dichloroacetanilide **(I)** is an important intermediate in the dyestuff industry and for the preparation of triclabendazole, a veterinary drug. Conventionally, 2-nitro-4,5-dichloroacetanilide **(I)** is prepared by nitration of 3,4-dichloroacetanilide **(II)** with a nitrating mixture comprising nitric acid and sulfuric acid. However, nitration of 3,4-dichloroacetanilide **(II)** with the nitrating mixture leads to the formation of two regioisomers 2-nitro-4,5-dichloroacetanilide **(I),** and 2-nitro-3,4-dichloroacetanilide **(III).**



3,4-dichloroacetanilide
(II)

2-nitro-4,5-dichloroacetanilide
(I)

2-nitro-3,4-dichloro acetanilide
(III)

The present disclosure envisages a simple, and efficient process for the preparation of 2-nitro-4,5-dichloroacetanilide **(I)** in high yield, and with high purity.

The present disclosure provides a process for the preparation of 2-nitro-4,5-dichloroacetanilide **(I)** from 3,4-dichloroacetanilide **(II).** The process involves the following steps:

3,4-Dichloroacetanilide is mixed with sulfuric acid at a temperature in the range of 0 °C to 35 °C, and stirring for a time period in the range of 0.5 to 1 hour, followed by adding oleum at a temperature in the range of 0 °C to 15 °C to obtain a mixture containing 3,4-dichloroacetanilide and resultant sulfuric acid. The strength of the resultant sulfuric acid is in the range of 100% w/w to 107% w/w, and the molar ratio of 3,4-dichloroacetanilide to the resultant sulfuric acid is in the range of 1:2 to 1:15.

The process of the present disclosure leads to the formation of 2-nitro-4,5-dichloroacetanilide **(I)** with high regioselectivity. The high regioselectivity for the formation of **I** is achieved by nitrating 3,4-dichloroacetanilide with a nitrating mixture containing nitric acid, and the resultant sulfuric acid having strength in the range of 100% to 107%, and by using the molar ratio of 3,4-dichloroacetanilide to the resultant sulfuric acid in the range of 1:2 to 1:15.

3,4-Dichloroacetanilide is nitrated by slowly adding at least one nitrating agent to the mixture while stirring at a temperature in the range of 0 °C to 25 °C over a time period in the range of 0.5 to 10 hours, followed by further stirring the resultant mixture for a period in the range of 0.5 to 5 hours to obtain a product mixture comprising 2-nitro-4,5-dichloroacetanilide.

The product mixture is cooled, and the cooled product mixture is poured over a mixture of ice and water to obtain a dispersion.

The dispersion is filtered to obtain a residue, the residue is washed, and the washed residue is dried to obtain 2-nitro-4,5-dichloroacetanilide **(I).**

In accordance with the embodiments of the present disclosure, the concentration of sulfuric acid is in the range of 98% w/w to 99% w/w.

In accordance with exemplary embodiment of the present disclosure, the concentration of sulfuric acid is 99% w/w.

In accordance with the embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to sulfuric acid is in the range of 1:1 to 1:12.

In accordance with the preferred embodiment of the present disclosure, 3,4-dichloroacetanilide **(II)** is mixed with sulfuric acid at a temperature in the range of 10 °C to 15 °C.

In accordance with one embodiment of the present disclosure, 3,4-dichloroacetanilide **(II)** is mixed with sulfuric acid at 13 °C.

In accordance with the preferred embodiment of the present disclosure, the concentration of oleum is in the range of 29% w/w to 33% w/w.

In accordance with one embodiment of the present disclosure, the concentration of oleum is 31.1%.

In accordance with the embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to oleum is in the range of 1:0.5 to 1:12.

In accordance with the preferred embodiment of the present disclosure, the oleum is added at a temperature in the range of 5 °C to 10 °C.

In accordance with one embodiment of the present disclosure, the oleum is added at 8 °C.

In the process of the present disclosure, the regioselectivity of nitration depends upon the molar ratio of resultant sulfuric acid and 3,4-dichloroacetanilide **(II).** It is observed that higher molar ratio of the resultant sulfuric acid to 3,4-dichloroacetanilide **(II)** provides 2-nitro-4,5-dichloroacetanilide **(I)** with higher purity.

In accordance with the preferred embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to the resultant sulfuric acid is in the range of 1:8 to 1:12.

In accordance with one embodiment of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to the resultant sulfuric acid is 1:10.

The regioselectivity of nitration depends upon the strength of resultant sulfuric acid in the process of the present disclosure. It is observed that the resultant sulfuric acid of higher strength provides **I** with higher purity. Furthermore, it is observed that when the nitration is carried out using sulfuric acid having strength less than 100%, the regioselectivity of nitration is low. Therefore, in the process of the present disclosure nitration is carried out using resultant sulfuric acid having strength in the range of 100% to 107%.

In accordance with the preferred embodiments of the present disclosure, the strength of the resultant sulfuric acid is in the range of 102% w/w to 106% w/w.

In accordance with one embodiment of the present disclosure, the strength of the resultant sulfuric acid is 104% w/w.

In accordance with the embodiments of the present disclosure, the nitrating agent is nitric acid.

In accordance with one embodiment of the present disclosure, concentration of the nitric acid is 98% w/w.

In accordance with the preferred embodiments of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to the nitrating agent is in the range of 1:1 to 1:1.2.

In accordance with one embodiment of the present disclosure, the molar ratio of 3,4-dichloroacetanilide **(II)** to the nitrating agent is 1:1.07.

In accordance with the preferred embodiment of the present disclosure, the nitrating agent is added to the mixture at a temperature in the range of 0 °C to 5 °C.

In accordance with one embodiment of the present disclosure, the nitrating agent is added to the mixture at 3 °C.

In accordance with the preferred embodiment of the present disclosure, the nitrating agent is added to the mixture over a time period in the range of 2 to 6 hours.

In accordance with one embodiment of the present disclosure, the nitrating agent is added to the mixture over a time period of 5 hours.

In the step of nitrating 3,4-dichloroacetanilide **(II),** the progress of nitration is monitored by the consumption of 3,4-dichloroacetanilide **(II).** If 3,4-dichloroacetanilide **(II)** in the reaction mixture is not completely consumed over a time period in the range of 2 to 6 hours, an additional amount of nitric acid (98%) can be added to the reaction mixture.

The product mixture comprising 2-nitro-4,5-dichloroacetanilide **(I)** is cooled, and the cooled product mixture is poured over a mixture of ice and water to obtain a dispersion. It is observed that 2-nitro-4,5-dichloroacetanilide **(I)** obtained by the process of the present disclosure has purity in the range of 90.0% to 98 %. The amount of the corresponding isomer 2-nitro-3,4-dichloroacetanilide **(III)** formed is in the range of 1.46% to 7.3%.

Further, 2-nitro-4,5-dichloroacetanilide **(I)** is obtained with a yield greater than 95% in the process of the present disclosure.

2-Nitro-4,5-dichloroacetanilide **(I)** obtained by the process of the present disclosure can be further purified using methanol.

Thus, 2-nitro-4,5-dichloroacetanilide **(I)** is obtained in high yield and with high purity by the process of the present disclosure. The yield of 2-nitro-4,5-dichloroacetanilide **(I)** is greater than 95% by the process of the present disclosure. Therefore, the process of the present disclosure is efficient.

It is observed that higher molar ratio of the resultant sulfuric acid to 3,4-dichloroacetanilide **(II)** provided 2-nitro-4,5-dichloroacetanilide **(I)** with higher purity.

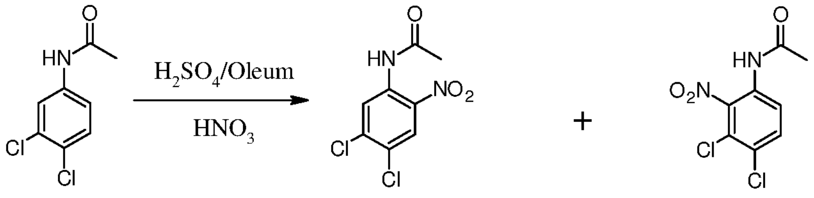
The process of the present disclosure is simple and is carried out without the use of organic fluid medium. Therefore, the process of the present disclosure is economical and environmentally friendly.

The disclosure will now be described with reference to the accompanying experiments which do not limit the scope and ambit of the disclosure. The description provided is purely by way of example and illustration.

The laboratory scale experiments provided herein can be scaled up to industrial or commercial scale.

EXPERIMENT

Experiment 1: Preparation of 2-nitro-4,5-dichloroacetanilide **(I)** from 3,4-dichloroacetanilide **(II).**



3,4-dichloroacetanilide **(II)**

2-nitro-4,5-dichloroacetani]ide **(I)**

2-nitro-3,4-dichloro acetanilide **(III)**

3,4-Dichloroacetanilide (II) (150 g, 0.74 moles) was slowly added to a reactor containing sulfuric acid (270 g, 99%, 2.7 moles) at 13 °C, followed by stirring for 0.5 hours and then cooling to 8 °C. To this, oleum (422 g, 31.1%, 4.61 moles) was added slowly, to obtain a mixture. The mixture comprised resultant sulfuric acid having strength of 104%. The molar ratio of 3,4-dichloroacetanilide (II) and the resultant sulfuric acid in the mixture was 1:10. The mixture was further cooled to 3 °C, and nitric acid (51 g, 98%, 0.79 moles) was slowly added to the mixture over 5 hours. The resultant mixture was further stirred and the progress of the reaction was monitored by thin layer chromatography (TLC). 3,4-Dichloroacetanilide was completely consumed within 1 hour and a product mixture was obtained. The product mixture was carefully poured over 1650 g ice in 200 ml water while maintaining the temperature below 15 °C, followed by stirring for 15 min to obtain a dispersion. The dispersion was filtered to obtain a residue comprising 2-nitro-4,5-dichloroacetanilide (I). The residue was washed with water till it was free of residual acid, and the washed residue was dried to obtain 2-nitro-4,5-dichloroacetanilide (I) (174 g, yield = 95.23%, HPLC purity = 97.83%).

HPLC analysis of the product showed the presence of 1.46% III.

Experiments 2, and **3**

Experiments 2, and 3 were carried out using similar experimental procedure as described in **Experiment 1.**

Experiment 2: 3,4-Dichloroacetanilide (II) (150 g, 0.735 moles), sulfuric acid (654.5 g, 99% w/w, 6.61 moles), oleum (65.5 g, 31.1% w/w, 0.715 moles) and nitric acid (51 g, 98% w/w, 0.79 moles) were used. The mixture comprised resultant sulfuric acid having strength of 100%. The molar ratio of 3,4-dichloroacetanilide (II) to the resultant sulfuric acid in the mixture was 1:10. The reaction conditions, product yield and product purity are summarized in **Table 1.**

174 g of 2-nitro-4,5-dichloroacetanilide (I) was obtained (yield = 95.23% and HPLC purity of 93.77%). HPLC analysis of the product showed the presence of 5.56% III.

On comparing the results of **Experiments 1,** and **2,** it is evident that the resultant sulfuric acid of higher strength provides I with higher purity.

Experiment 3: 3,4-Dichloroacetanilide (II) (150 g, 0.735 moles), sulfuric acid (156.0 g, 99% w/w, 1.576 moles), oleum (260.5 g, 31.1% w/w, 2.844 moles), and nitric acid (51 g, 98% w/w, 0.79 moles) were used. The mixture comprised resultant sulfuric acid having strength of 104%. The molar ratio of 3,4-Dichloroacetanilide (II) to the resultant sulfuric acid in the mixture was 1:6. The reaction conditions, and product yield and purity are summarized in **Table 1**.

177 g of 2-nitro-4,5-dichloroacetanilide (I) was obtained (yield = 92% and HPLC purity of 92%). HPLC analysis of product showed the presence of 6% of III.

On comparing the results of **Experiments 1,** and **3,** it is evident that higher molar ratio of the resultant sulfuric acid to 3,4-dichloroacetanilide (II) provides higher purity of 2-nitro-4,5-dichloroacetanilide (I).

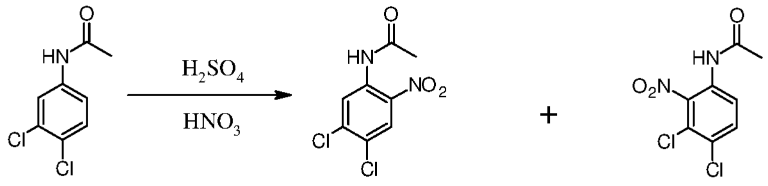
Table 1: Reaction conditions and yield of I

Expt. No.	Molar Ratio				Resultant Sulfuric Acid (Sulfuric acid + Oleum)		2-Nitro-4,5-dichloroacetanilide (**I**)		Amount of (**III**) %
	II	Sulfuric acid (99%)	Oleum (31.1%)	Nitric Acid (98%)	Strength (%)	Molar ratio	Yield % (**I**)	Purity %	
1	1	3.67	6.27	1.07	104	10	95.23	97.8	1.46
2	1	8.99	0.97	1.07	100	10	95.23	93.77	5.56
3	1	2.14	3.87	1.07	104	6.0	96.73	92	6

From **Table 1,** it is evident that 2-nitro-4,5-dichloroacetanilide (I) is obtained in yield greater than 95% in all the experiments.

Control Experiment

Nitration of 3,4-dichloroacetanilide **(II)** using 99% sulfuric acid and without use of oleum.



3,4-dichloroacetanilide (ID   2-nitro-4,5-dichloroacetanilide (I)   2-nitro-3,4-dichloroacetanilide (HI)

3,4-Dichloroacetanilide **(II)** (150 g, 0.74 moles) was slowly added to a reactor containing sulfuric acid (436 g, 99%, 4.4 moles) at 13 °C, under stirring, to obtain a mixture. The mixture was stirred for 0.5 hours and then cooled to 3 °C. Nitric acid (51 g, 98%, 0.79 moles) was slowly added to the mixture, over 5 hours and the resultant mixture was further stirred. Progress of the reaction was monitored by thin layer chromatography (TLC). 3,4-Dichloroacetanilide was completely consumed within 1 hour and a product mixture was obtained. The product mixture was carefully poured over 1650 g ice in 200 ml water while maintaining the temperature below 15 °C and further stirred for 15 min to obtain a dispersion. The dispersion was filtered to obtain a residue comprising 2-nitro-4,5-dichloroacetanilide **(I).** The residue was washed with water till it was free of residual acid, and the washed residue was dried to obtain 2-nitro-4,5-dichloroacetanilide **(I)** (177 g, 0.7 moles, yield = 96.73%, purity = 87.87% HPLC).

The mixture comprised resultant sulfuric acid having strength of 99% w/w. The molar ratio of 3,4-Dichloroacetanilide **(II)** to the resultant sulfuric acid in the mixture was 1:6.

HPLC of the product showed the presence of 10.33% of **III.**

Thus, the control experiment showed that the purity of **I** was low when the nitration was carried out using 99% sulfuric acid.

TECHNICAL ADVANCES AND ECONOMICAL SIGNIFICANCE

The process of the present disclosure described herein above has several technical advantages including, but not limited to, the realization of;

- a process for the preparation of 2-nitro-4,5-dichloroacetanilide with high yield and high purity, and

- a simple, and efficient process for the preparation of 2-nitro-4,5-dichloroacetanilide.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

The numerical values mentioned for the various physical parameters, dimensions or quantities are only approximations and it is envisaged that the values higher/lower than the numerical values assigned to the parameters, dimensions or quantities fall within the scope of the disclosure, unless there is a statement in the specification specific to the contrary.

While considerable emphasis has been placed herein on the components and component parts of the preferred embodiments, it will be appreciated that many embodiments can be made and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other changes in the preferred embodiment as well as other embodiments of the disclosure will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

CLAIMS:

1. A process for preparing 2-nitro-4,5-dichloroacetanilide from 3,4-dichloroacetanilide, the process comprising:
    (a) mixing 3,4-dichloroacetanilide with sulfuric acid at a temperature in the range of 0 °C to 35 °C and stirring for a time period in the range of 0.5 to 1 hour, followed by adding oleum at a temperature in the range of 0 °C to 15 °C to obtain a mixture containing 3,4-dichloroacetanilide and resultant sulfuric acid; wherein the strength of the resultant sulfuric acid is in the range of 100% w/w to 107% w/w, and the molar ratio of 3,4-dichloroacetanilide to the resultant sulfuric acid is in the range of 1:2 to 1:15;
    (b) nitrating 3,4-dichloroacetanilide by slowly adding at least one nitrating agent to the mixture while stirring at a temperature in the range of 0 °C to 25 °C over a time period in the range of 0.5 to 10 hours, followed by further stirring the resultant mixture for a period in the range of 0.5 to 5 hours to obtain a product mixture comprising 2-nitro-4,5-dichloroacetanilide;
    (c) cooling the product mixture, and pouring the cooled product mixture over a mixture of ice and water to obtain a dispersion; and
    (d) filtering the dispersion to obtain a residue, washing the residue, and drying the washed residue to obtain 2-nitro-4,5-dichloroacetanilide (I).

2. The process as claimed in claim 1, wherein the concentration of sulfuric acid is in the range of 98% w/w to 99% w/w.

3. The process as claimed in claim 1, wherein the molar ratio of 3,4-dichloroacetanilide to sulfuric acid is in the range of 1:1 to 1:12.

4. The process as claimed in claim 1, wherein the concentration of oleum is in the range of 20% w/w to 35% w/w.

5. The process as claimed in claim 1, wherein the molar ratio of 3,4-dichloroacetanilide to oleum is in the range of 1:0.5 to 1:12.

6. The process as claimed in claim 1, wherein the nitrating agent is nitric acid.

7. The process as claimed in claim 1, wherein the molar ratio of 3,4-dichloroacetanilide to the nitrating agent is in the range of 1:1 to 1:1.2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/050274

A. CLASSIFICATION OF SUBJECT MATTER
C07C205/06, C07C205/07, C07C205/12 Version=2017.01

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)

C07C 205/06, C07C 205/07, C07C 205/12

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)

Patseer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US4745219 (A) MONSANTO CO [US] Publication Date : 17th May 1988 (17.05.1988) SEE : EXAMPLES I & II, CLAIMS 1-5.	1-7
Y	CN 102070466 (A) JUNKAI TIANJIN CHEMICAL CO LTD Publication Date : 25th May 2011 (25.05.2011) SEE : EXAMPLE 4 & 5	1-7
Y	US4302599 (A) SCHERING CORP Publication Date : 24th Nov 1981 (24.11.1981) SEE : Examples 1-10	1-7
Y	CN102531923 (A) NANTONG DONGCHANG CHEMICAL IND CO LTD Publication Date : 04th July 2012 (04.07.2012) SEE : Abstract, Examples 1& 2	1-7
Y	RU2205821 (CI) PIGMENT AOOT Publication Date : 10th June 2003 (10-06-2003) SEE : Abstract, Examples 1-8	1-7

☐ 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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 26-07-2017	Date of mailing of the international search report 26-07-2017
Name and mailing address of the ISA/ Indian Patent Office Plot No. 32, Sector 14, Dwarka, New Delhi-110075 Facsimile No.	Authorized officer Srinivasu Chintala Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2017/050274

Citation	Pub.Date	Family	Pub.Date
US 4745219 A	17-05-1988	BE 901066 A1	17-11-1983
		ZA 8408969 B	11-11-1983