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(54) Title: PROCESS FOR MAKING SOLID HYDROXYLAMINE NITRATE

(57) Abstract: A process for production of hydroxylamine nitrate is disclosed whereby hydroxylamine nitrate can be obtained in solid form at room temperature. According to embodiments disclosed herein, hydroxylamine nitrate in solid form can be produced by reacting a hydroxylamine salt solution with a metal salt dissolved in organic solvent at ambient temperature. The process disclosed herein is simple, safe, cost effective, and can produce solid hydroxylamine nitrate in substantially pure form. Hydroxylamine nitrate produced is free of nitric acid, metal ions, and ammonium nitrate impurities. Precursor metal salt can be regenerated from the by product and the solvent can be recycled, consequently making the process green.



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PROCESS FOR MAKING SOLID HYDROXYLAMINE NITRATE

FIELD OF THE INVENTION

[0001] The present disclosure pertains to technical field of inorganic synthesis. In particular, the present disclosure pertains to synthesis of hydroxylamine energetic oxidiser salts.

BACKGROUND OF THE INVENTION

[0002] The background description includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

[0003] Hydroxylamine nitrate is a salt of hydroxylamine which is used as a reducing agent, in the recovery of spent nuclear fuel, as a reagent for preparing various industrial, speciality and pharmaceutical chemicals, in photographic applications, gas generators, composite propellants etc. Currently hydroxylamine nitrate is explored as monopropellant in space applications (AF-M315E, GPIM NASA) which has a potential to replace hydrazine. Hydroxylamine nitrate required for space applications should be highly concentrated, pure without any impurities like metal ion, nitric acid and ammonium nitrate. Commercially available solution of HAN is very dilute, oftentimes being shipped in inert containers at a maximum concentration of 24%. Various methods for preparing HAN have been proposed over the years. These processes suffers from various drawback from a commercial safety and /or technical perspective.

[0004] Hydroxylamine nitrate was initially made by the reaction of free hydroxylamine base with nitric acid. Free hydroxylamine was prepared by the reduction of NOX compounds in the presence of a noble metal catalyst in an acidic medium. As discussed in US PATENT NO (2827363, 2823101, 3406011, 3649170, 3767758, 3856924). These methods involves the use of NOX compounds which are difficult to

handle and Since the reaction was carried out in an acidic medium, HAN prepared by this method was contaminated with excess nitric acid which is known to sensitize thermal stability of HAN. In addition ammonium nitrate was produced as a side product. All these methods produces HAN which are dilute aqueous solutions and require further distillation to get the concentrated product. The water from aqueous solutions of HAN becomes even more difficult to remove as the HAN concentration increases. This requires ever increasing vacuum and temperature conditions to complete the extraction process. These operating conditions make a processing plant vulnerable to an accident. Therefore the process is difficult, expensive and dangerous.

[0005] Another method (US PATENT – 4066736, 5182092) of preparing hydroxylamine nitrate involves the reaction between aqueous metal nitrate salt mainly sodium, potassium, ammonium, calcium or barium nitrate salts with aqueous hydroxylamine sulphate salt. This method also produces very dilute solutions of HAN which require further time and energy consuming hazardous distillation process. In addition the water soluble impurities like metal ions can interfere with the thermal stability of hydroxylamine nitrate.

[0006] ELECTROLYSIS PROCESS-US PATENT- 4849073 HAN was electrolytically produced from nitric acid. The cathode was made up of mercury and several different anodes were used. 25% HAN was produced initially .Nitric acid concentration in the two electrode chambers is critical for the proper operation of the reactor .At low nitric acid concentration hydroxylamine is reduced to ammonia at cathode .At high nitric acid concentration the HAN produced was oxidised to various NOX compounds .Therefore a balance of nitric acid concentration between the two electrode was required. Final HAN that was produced contained 25% HAN and 2.8 %nitric acid. HAN concentration required for propellant manufacture is 80%. Consequently distillation of 25% HAN without removal of excess nitric acid is very dangerous. Another drawback of this method is the utilization of significant amount of mercury as cathode material which could pose serious problems to environment. Also HAN may contain residual mercury .This process is quite expensive and it is very difficult to obtain consistent concentration of desired product.

[0007] ELECTRODYLYSIS METHOD- European patent No- 0266059B1 Hydroxylamine sulphate is converted to hydroxylamine nitrate by passing an aqueous hydroxylamine sulphate solution through a cation exchange resin bed which adsorbs the hydroxylamine, washing the sulphate ion from the resin bed and eluting the hydroxylamine as HAN. HAN produced by this method is very dilute solution; This method requires an auxiliary cell for electrodialysis. Limitation of area of resin membrane, excess nitric acid issues and hazardous distillation are additional drawbacks of this method.

[0008] Another method (US PATENT- 5213784, 5510097) of preparation involves the direct titration of aqueous hydroxylamine free base with nitric acid. The reaction is highly exothermic, and requires expensive cooling systems. Hydroxylamine free base is very unstable and slowly decomposes to ammonia, which can introduce ammonium nitrate impurities in HAN solutions. This method also produces dilute solutions of HAN which requires further concentration by hazardous distillation step. In addition free hydroxylamine is an expensive starting material.

[0009] In yet another method of HAN preparation (US PATENT NO- 4954328, 6258983B1) wherein the salt of hydroxylamine like sulphate is used as starting material for the synthesis of free hydroxylamine base in an organic medium . The reaction involved is highly exothermic and requires expensive cooling systems. Decomposition of free hydroxylamine by concentrated nitric acid can form ammonia which introduces ammonium nitrate impurity in HAN solutions .Handling of highly concentrated fuming nitric acid is very hazardous . The reaction takes place in an organic medium like methanol which can form methyl nitrate with concentrated nitric acid. Formation of methyl nitrate is very deleterious because of its potential explosive properties.

[0010] Accordingly, there exists a need in the art for a simpler, safer and cost effective method for producing hydroxylamine nitrate salt. There is also a need in the art for a method that enables preparation of solid hydroxylamine nitrate salt that is essentially free of undesirable contaminants.

[0011] The present invention satisfies the existing needs, as well as others, and generally overcomes the deficiencies found in the prior art.

[0012] All publications herein are incorporated by reference to the same extent as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference. Where a definition or use of a term in an incorporated reference is inconsistent or contrary to the definition of that term provided herein, the definition of that term provided herein applies and the definition of that term in the reference does not apply.

[0013] In some embodiments, the numbers expressing quantities of ingredients, properties such as concentration, reaction conditions, and so forth, used to describe and claim certain embodiments of the invention are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable. The numerical values presented in some embodiments of the invention may contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0014] As used in the description herein and throughout the claims that follow, the meaning of “a,” “an,” and “the” includes plural reference unless the context clearly dictates otherwise. Also, as used in the description herein, the meaning of “in” includes “in” and “on” unless the context clearly dictates otherwise.

[0015] The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g. “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed.

[0016] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member can be referred to and claimed individually or in any combination with other members of the group or other elements found herein. One or more members of a group can be included in, or deleted from, a group for reasons of convenience and/or patentability.

OBJECTS OF THE INVENTION

[0017] It is an object of the present disclosure to provide a simpler and safer process for producing hydroxylamine nitrate salt.

[0018] It is a further object of the present disclosure to provide a process for producing solid hydroxylamine nitrate without the use of high temperature distillation or evaporation steps.

[0019] It is another object of the present disclosure to provide a process that produces hydroxylamine nitrate salt that is essentially free of undesirable contaminants.

[0020] It is another object of the present disclosure to provide a process by which hydroxylamine nitrate salt can be obtained in substantially pure form without the use of extraction or recrystallization procedures.

[0021] It is another object of the present disclosure to provide a process that enables preparation of solid hydroxylamine nitrate salt at ambient temperature.

[0022] It is another object of the present disclosure to provide a process for producing hydroxylamine nitrate salt at reduced capital, energy, and operating costs.

SUMMARY OF THE INVENTION

[0023] The present disclosure relates to process for production of hydroxylamine nitrate whereby hydroxylamine nitrate can be obtained in solid form at room temperature. The process disclosed herein can produce solid hydroxylamine nitrate that is essentially free of undesirable contaminants such as, but not limited to metal ions, nitric acid and ammonium nitrate. Further, the disclosed process can facilitate isolation of hydroxylamine nitrate in solid form without the use of high temperature distillation or evaporation steps.

[0024] In an aspect, the present disclosure provides a process for preparation of solid hydroxylamine nitrate, the process can include the step of reacting a hydroxylamine salt solution with a metal salt dissolved in organic solvent.

[0025] In an embodiment, the hydroxylamine salt that can be utilized in the process disclosed herein can be selected from the group consisting of hydrochlorides, sulphates, phosphates, nitrates, borates, nitrites, hydrogen phosphates, and sulphites.

[0026] In an embodiment, the metal salt used in the process disclosed herein can be selected from the group consisting of zinc chloride, zinc nitrate, lead nitrate, lead chloride, lead sulphate, thallium nitrate, thallium chloride, thallium sulphate, silver chloride, silver nitrate, silver sulphate, mercury nitrate, mercury chloride, mercury nitrate, antimony nitrate, antimony fluoride, nickel nitrate, nickel chloride, nickel sulphate, cadmium nitrate, cadmium chloride, cadmium sulphate, chromium nitrate, manganese nitrate, manganese sulphate and manganese chloride.

[0027] In an embodiment, the solvent used in the process disclosed herein can be selected from the group consisting of ethanol, methanol, dichloromethane, diethyl ether, ethyl acetate, hexane, heptane, isopropanol, butanol, n-butanol, isobutanol, ethyl acetate, methyl tertiary butyl ether, and mixtures thereof.

[0028] In an embodiment, the hydroxylamine salt and the metal salt can be reacted at a temperature ranging from 20°C to 35° C to form hydroxylamine nitrate in solid form.

[0029] In an embodiment, hydroxylamine nitrate can be recovered or isolated from the reaction mixture by distillation, filtration or counter current extraction.

[0030] In an embodiment, solid hydroxylamine nitrate obtained according to the methods of the present disclosure have a purity of at least 99.99% measured by ion chromatography.

[0031] In an embodiment, solid hydroxylamine nitrate obtained according to the methods of the present disclosure can be free from one or more impurities selected from the group consisting of metal ions, ammonium nitrate and nitric acid.

[0032] In an embodiment, metal salt precursor can be regenerated from the by-product

[0033] In an embodiment solvent can be recycled for subsequent batches

[0034] Various objects, features, aspects and advantages of the inventive subject matter will become more apparent from the following detailed description of preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] The accompanying drawings are included to provide a further understanding of the present disclosure, and are incorporated in and constitute a part of this specification. The drawings illustrate exemplary embodiments of the present disclosure and, together with the description, serve to explain the principles of the present disclosure.

[0036] FIG. 1 shows FTIR spectrum of hydroxylamine nitrate (HAN) produced in accordance with embodiments of the present disclosure.

[0037] FIG. 2 shows Raman spectrum of hydroxylamine nitrate (HAN) produced in accordance with embodiments of the present disclosure.

[0038] FIG. 3 shows the DSC curve of hydroxylamine nitrate (HAN) produced in accordance with embodiments of the present disclosure.

[0039] FIG. 4a shows the DTA trace of 90% hydroxylamine nitrate (HAN) prepared by neutralisation method, and 90% HAN prepared by double decomposition reaction in an organic solvent in accordance with embodiments of the present disclosure.

[0040] FIG. 4b shows the TGA curves of 90% HAN prepared by neutralisation method, and 90% HAN prepared by double decomposition reaction in an organic solvent in accordance with embodiments of the present disclosure.

[0041] FIG. 5 shows the schematic of a batch reactor, in accordance with embodiments of the present disclosure.

[0042] FIG. 6a shows the dP (extent of reaction) and dP/dT (rate of reaction) values for the 90% hydroxylamine nitrate at 100 degree centigrade in a batch reactor (simulation of

space thruster), prepared from neutralisation of 50% hydroxylamine with 70% nitric acid at low temperature.

[0043] FIG. 6b shows the dP (extent of reaction) and dP/dT (rate of reaction) values for the 90% hydroxylamine nitrate at 100 degree centigrade in a batch reactor (simulation of space thruster), prepared by double decomposition reaction in an organic solvent in accordance with embodiments of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0044] The following is a detailed description of embodiments of the disclosure depicted in the accompanying drawings. The embodiments are in such detail as to clearly communicate the disclosure. However, the amount of detail offered is not intended to limit the anticipated variations of embodiments; on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present disclosure as defined by the appended claims.

[0045] Unless the context requires otherwise, throughout the specification which follow, the word “comprise” and variations thereof, such as, “comprises” and “comprising” are to be construed in an open, inclusive sense that is as “including, but not limited to.”

[0046] Reference throughout this specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

[0047] As used in the description herein and throughout the claims that follow, the meaning of “a,” “an,” and “the” includes plural reference unless the context clearly dictates otherwise. Also, as used in the description herein, the meaning of “in” includes “in” and “on” unless the context clearly dictates otherwise.

[0048] In some embodiments, the numbers expressing quantities of ingredients, properties such as concentration, reaction conditions, and so forth, used to describe and

claim certain embodiments of the invention are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable.

[0049] The recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g. “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0050] The headings and abstract of the invention provided herein are for convenience only and do not interpret the scope or meaning of the embodiments.

[0051] All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g. “such as”) provided with respect to certain embodiments herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[0052] Various terms are used herein. To the extent a term used in a claim is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in printed publications and issued patents at the time of filing.

[0053] The present disclosure relates to process for production of hydroxylamine nitrate whereby hydroxylamine nitrate can be obtained in solid form at room temperature. The process disclosed herein can produce solid hydroxylamine nitrate that is essentially free of undesirable contaminants such as, but not limited to, metal ions, nitric acid and ammonium nitrate. Further, the disclosed process can facilitate isolation of hydroxylamine nitrate in solid form without the use of high temperature distillation or evaporation steps.

[0054] In an aspect, the present disclosure provides a process for preparation of solid hydroxylamine nitrate, the process can include the step of reacting a hydroxylamine salt with a metal salt dissolved in an organic solvent.

[0055] In an embodiment, the hydroxylamine salt that can be utilized in the process disclosed herein can be selected from the group consisting of hydrochlorides, sulphates, phosphates, nitrates, borates, nitrites, phosphates, hydrogen phosphates, and sulphites.

[0056] In an embodiment, the metal salt used in the process disclosed herein can be selected from the group consisting of zinc chloride, zinc nitrate, lead nitrate, lead chloride, lead sulphate, thallium nitrate, thallium chloride, thallium sulphate, silver chloride, silver nitrate, silver sulphate, mercury nitrate, mercury chloride, mercury nitrate, antimony nitrate, antimony fluoride, nickel nitrate, nickel chloride, nickel sulphate, cadmium nitrate, cadmium chloride, cadmium sulphate, chromium nitrate, manganese nitrate, manganese sulphate and manganese chloride.

[0057] In an embodiment, solid hydroxylamine nitrate can be produced by reacting a hydroxylamine salt with a metal salt dissolved in an organic solvent. Suitable organic solvent can be selected from the group consisting of ethanol, methanol, dichloromethane, diethyl ether, ethyl acetate, hexane, heptane, isopropanol, butanol, n-butanol, isobutanol, methyl acetate, methyl tertiary butyl ether and mixtures thereof.

[0058] In some embodiments, the hydroxylamine salt and the metal salt can be reacted in solvent or a mixture containing different organic solvents and at least one water soluble organic solvent.

[0059] In an exemplary embodiment, the hydroxylamine salt and the metal salt can be reacted in a solvent mixture that contains ether and an alcohol solvent.

[0060] In an embodiment, the hydroxylamine salt and the metal salt can be reacted at a temperature ranging from 22°C to 35° C, preferably from 20°C to 30°C to form

hydroxylamine nitrate in solid form. Thus, the process can be safe and it does not lead to exothermic or explosive reactions.

[0061] In an illustrative embodiment, the process for producing solid hydroxylamine nitrate can include the steps of: (a) dissolving a hydroxylamine salt in an organic solvent to form a first solution; (b) dissolving a metal salt in an organic solvent to form a second solution; (c) mixing the first solution and second solution to form a reaction mixture; (d) maintaining the reaction mixture for a period of time sufficient to form hydroxylamine nitrate; and (e) recovering the hydroxylamine nitrate from the reaction mixture in solid form.

[0062] In an embodiment, maintaining the reaction mixture in step (d) can include maintaining the reaction mixture under stirring at room temperature. The reaction between the hydroxylamine salt and the metal salt can be instantaneous at room temperature and proceed to completion within a few minutes.

[0063] In an embodiment, recovery of hydroxylamine nitrate from the reaction mixture in solid form in step (e) can be accomplished by distillation, filtration or counter current extraction.

[0064] In an exemplary embodiment, recovery of hydroxylamine nitrate from the reaction mixture in solid form in step (e) can be accomplished by any filtration method known in the art.

[0065] In an alternative embodiment, recovery of hydroxylamine salt from the reaction mixture can be accomplished by distillation of the reaction mixture at a temperature ranging from 20°C to 35°C.

[0066] In an embodiment, insoluble by-product salts formed during the synthesis of hydroxylamine nitrate can be removed from the reaction mixture by an appropriate means. For example, insoluble by-product salt formed during the synthesis of hydroxylamine nitrate can be removed by filtration, and the resulting filtrate can be distilled at room temperature to obtain solid hydroxylamine nitrate.

[0067] In an embodiment, the first solution, the second solution and/or the reaction mixture can be optionally subjected to activated carbon treatment to further reduced impurities.

[0068] According to embodiments, solid hydroxylamine nitrate obtained according to the methods of the present disclosure can have a purity of at least 99.99% as measured by ion chromatography.

[0069] In an embodiment, solid hydroxylamine nitrate obtained according to the methods of the present disclosure can be free from one or more impurities selected from the group consisting of metal ions, ammonium salts and nitric acid.

[0070] In an embodiment, by-product metal salt can be converted into precursor metal salt by appropriate methods known in the art, consequently making the process green.

[0071] In an embodiment, solvent can be recycled for subsequent batches.

[0072] While the foregoing description discloses various embodiments of the disclosure, other and further embodiments of the invention may be devised without departing from the basic scope of the disclosure. The invention is not limited to the described embodiments, versions or examples, which are included to enable a person having ordinary skill in the art to make and use the invention when combined with information and knowledge available to the person having ordinary skill in the art.

EXAMPLES

[0073] The present disclosure is further explained in the form of following examples. However, it is to be understood that the foregoing examples are merely illustrative and are not to be taken as limitations upon the scope of the invention. Various changes and modifications to the disclosed embodiments will be apparent to those skilled in the art. Such changes and modifications may be made without departing from the scope of the invention.

Example 1: Preparation of hydroxylamine nitrate (HAN):

[0074] 25 g of zinc nitrate was dissolved in 100 ml 7:3 ethanol/methanol mixture in a round bottom flask equipped with nitrogen, thermometer and dropping funnel. The reaction mass was stirred for 1 hour to ensure complete dissolution of zinc nitrate. 18.3486 g of hydroxylamine hydrochloride was dissolved in 100 ml methanol, and the resulting solution was added to the solution of zinc nitrate through a dropping funnel. The reaction between zinc nitrate and hydroxylamine hydrochloride was instantaneous at room temperature and the reaction completed within few minutes. Hydroxylamine nitrate precipitate formed was

separated by centrifugation followed by filtration. The filtrate was distilled at room temperature to recover the solvent for next reaction batch. Zinc chloride obtained was converted back to starting material and the solvent was recycled for the next batch. Consequently making the process green.

Example 2: Preparation of hydroxylamine nitrate (HAN):

[0075] 25 g of silver nitrate was dissolved in 500 ml ether in a round bottom flask equipped with nitrogen, thermometer and dropping funnel. The reaction mass was stirred for 3 hour to ensure complete dissolution of silver nitrate. 12.078 g of hydroxylamine sulphate was dissolved in 100 ml ether, and the resulting solution was added to the solution of silver nitrate through a dropping funnel. The reaction between silver nitrate and hydroxylamine sulphate was instantaneous at room temperature and the reaction completed within few minutes. HAN precipitate formed was separated by centrifugation followed by filtration. The filtrate was distilled at room temperature to recover the solvent. The etherate distillate was used for next reaction batch. Silver sulphate obtained can be converted back to silver nitrate. Consequently starting material i.e. silver nitrate and the solvent can be recovered making it a green process.

Example 3: Preparation of hydroxylamine nitrate (HAN):

[0076] 25 g of lead nitrate was dissolved in 500 ml ether in a round bottom flask equipped with nitrogen, thermometer and dropping funnel. The reaction mass was stirred for 2 hour to ensure complete dissolution of lead nitrate. 10.4906 g of hydroxylamine hydrochloride was dissolved in 100 ml ether, and the resulting solution was added to the solution of lead nitrate through a dropping funnel. The reaction between lead nitrate and hydroxylamine hydrochloride was instantaneous at room temperature and the reaction completed within few minutes. Lead chloride (by-product) precipitate formed was separated by centrifugation followed by filtration. Then the filtrate was distilled at room temperature to isolate solid HAN. The etherate distillate was used for next reaction batch. Lead chloride can be converted back to lead nitrate and the ether solvent can be recycled for the next batch making the process green.

Example 4: Preparation of hydroxylamine nitrate (HAN):

[0077] 25 g of chromium nitrate was dissolved in 100 ml ethanol in a round bottom flask equipped with nitrogen, thermometer and dropping funnel. The reaction mass was stirred for 1 hour to ensure complete dissolution of chromium nitrate. 15.38 g of hydroxylamine sulphate was dissolved in 100 ml of 3:7 methanol/water solution, and the resulting solution was added to the solution of chromium nitrate through a dropping funnel. The reaction between chromium nitrate and hydroxylamine sulphate was instantaneous at room temperature and the reaction completed within few minutes. HAN precipitate formed was separated by centrifugation followed by filtration. The filtrate was distilled at room temperature to recover the solvent for next reaction batch.

Characterization and performance evaluation of hydroxylamine nitrate:

[0078] Hydroxylamine nitrate compounds as produced above were characterized by IR and Raman spectra which are shown in Figs. 1 and 2 respectively. The spectral bands observed in FTIR and RAMAN were in agreement with the reported literature values. The peaks- 1300, 1400, 727, 830, 1050 cm^{-1} corresponded to nitrate ion concentration and the bands-1179, 1512, 2720, 2955, 3150, 1007 cm^{-1} corresponded to hydroxylammonium ion concentration. Peaks corresponding to water content of the HAN samples were 3000-3750, 1655 cm^{-1} . The band corresponding to frequencies 1300 cm^{-1} and 1179 cm^{-1} were concentration dependant whereas the bands corresponding to frequencies 1050 cm^{-1} and 1007 cm^{-1} were found independent of HAN concentration. In Raman spectra nitrate ion band at 1048 cm^{-1} was prominent when compared to FTIR peak, also the hydroxylammonium cation band at 1007 cm^{-1} weak in FTIR was detected in Raman.

[0079] The DSC curve of hydroxylamine nitrate (HAN) is shown in Fig. 3. The heat of fusion of the material was in agreement with the reported literature *value*.

[0080] **Monopropellant Decomposition Studies:** The monopropellant decomposition was followed using thermal analyzer and constant volume batch reactor. Thermal analysis studies were carried out using Perkin Elmer STA 6000 thermal analyzer. 10 mg of sample was heated at a rate of 10°C/min in flowing nitrogen atmosphere. DTA-TGA analysis gave

information on onset temperature of decomposition, % weight loss, rate of decomposition and energy released during decomposition, and the data is shown in Figs. 4a and 4b.

[0081] The onset of decomposition of 90% HAN prepared by neutralization method was 149°C and the onset of decomposition of 90% HAN prepared by the method of the present disclosure was 147°C which was almost similar for two different HAN prepared by different methods (FIG. 4a). Also the slope of weight loss curve was more or less similar for HAN prepared by neutralization method and HAN prepared by present method (FIG. 4b).

[0082] **Batch reactor analysis:** In a constant volume batch reactor, 200 micro liters of HAN solution was injected through a syringe infusion pump into a chamber preheated to fixed temperature. The pressure and the temperature rise inside the chamber were recorded against time. A schematic of the batch reactor is shown in Fig. 5.

[0083] Batch reactor analysis provided information on rate of decomposition by following the rate of pressure rise when HAN is injected into a preheated chamber. This isothermal decomposition simulates a realistic condition and isolates the thermal history of the sample unlike in a conventional thermal analysis technique.

[0084] Solid HAN was diluted to 90%. In a constant volume batch reactor, 200 micro litre of HAN solution was injected through a syringe infusion pump to the reactor chamber which was preheated to 100 degree centigrade. The pressure and the temperature on decomposition was recorded as a function of time. Batch reactor studies provided information on extent of decomposition (ΔP) and rate of decomposition ($\Delta P/\Delta T$) which shows the performance of the monopropellant.

[0085] Fig. 6a represents the ΔP and $\Delta P/\Delta T$ values of 90% HAN at 100°C prepared by neutralisation method (titration of 50% free hydroxylamine base with 70 % nitric acid at sub ambient temperature), and Fig. 6b represents the ΔP and $\Delta P/\Delta T$ values of 90% HAN at 100°C prepared by the methods of the present disclosure (double decomposition between a stable salt of hydroxylamine and organic solution of a metal nitrate salt at room temperature). It is evident from the data that the performance of 90% HAN prepared by the present method is far more better (higher ΔP and higher $\Delta P/\Delta T$ values) than 90% HAN prepared by neutralisation method at the same temperature in a batch reactor.

ADVANTAGES OF THE INVENTION

[0086] The present disclosure provides a more economical and less hazardous way of producing solid hydroxylamine nitrate.

[0087] The present disclosure provides a process for producing solid hydroxylamine nitrate without the use of high temperature distillation or evaporation steps.

[0088] The present disclosure provides a process by which hydroxylamine nitrate salt can be produced in solid form at room temperature.

[0089] The present disclosure provides a process for producing solid hydroxylamine nitrate at room temperature without involving expensive heating and cooling systems.

[0090] The present disclosure provides a process that produces solid hydroxylamine nitrate that is essentially free of undesirable contaminants such as metal ions, nitric acid and ammonium nitrate.

[0091] The present disclosure provides a process that produces solid hydroxylamine nitrate in which metal salt precursor can be regenerated from the by-product making the process green.

[0092] The present disclosure provides a process that produces solid hydroxylamine nitrate in which solvent can be recycled for the preparation of next batch.

[0093] The present disclosure provides a process by which solid hydroxylamine nitrate salt can be obtained in substantially pure form without the use of extraction or recrystallization procedures.

[0094] The present disclosure provides a process for producing solid hydroxylamine nitrate which overcomes the disadvantages commonly associated with the known processes.

CLAIMS

We claim

1. A process for producing solid hydroxylamine nitrate comprising, reacting a hydroxylamine salt with a metal salt dissolved in an organic solvent.
2. The process according to claim 1, wherein the hydroxylamine salt is selected from the group consisting of hydrochlorides, sulphates, phosphates, nitrates, borates, nitrites, phosphates, hydrogen phosphates and sulphites.
3. The process according to claim 1, wherein the metal salt is selected from the group consisting of zinc chloride, zinc nitrate, lead nitrate, lead chloride, lead sulphate, thallium nitrate, thallium chloride, thallium sulphate, silver chloride, silver nitrate, silver sulphate, mercury nitrate, mercury chloride, mercury nitrate, antimony nitrate, antimony fluoride, nickel nitrate, nickel chloride, nickel sulphate, cadmium nitrate, cadmium chloride, cadmium sulphate, chromium nitrate, manganese nitrate, manganese sulphate and manganese chloride.
4. The process according to claim 1, wherein the organic solvent is selected from the group consisting of ethanol, methanol, dichloromethane, diethyl ether, ethyl acetate, hexane, heptane, isopropanol, n-butanol, isobutanol, ethyl acetate, methyl tertiary butyl ether, and mixtures thereof.
5. The process according to claim 1, comprising the steps of:
 - (a) dissolving the hydroxylamine salt in the organic solvent to form a first solution;
 - (b) dissolving the metal salt in the organic solvent to form a second solution;
 - (c) mixing the first solution and second solution to form a reaction mixture;
 - (d) maintaining the reaction mixture for a period of time sufficient to form hydroxylamine nitrate; and
 - (e) recovering the hydroxylamine nitrate from the reaction mixture in solid form.
 - (f) regenerating the precursor metal salt from the by-product.

6. The process according to claim 5, wherein maintaining the reaction mixture in step (d) comprises maintaining the reaction mixture at a temperature ranging from 20°C to 30° C.
7. The process according to claim 5, wherein recovery of the hydroxylamine nitrate from the reaction mixture in solid form in step (e) is accomplished by distillation, filtration or counter current extraction.
8. The process according to claim 5, wherein recovery of the hydroxylamine salt from the reaction mixture in solid form in step (e) is accomplished by filtration.
9. The process according to claim 5, wherein recovery of the hydroxylamine salt from the reaction mixture in solid form in step (e) is accomplished by distillation of the reaction mixture at a temperature ranging from 20°C to 30°C.
10. The process according to claim 5, further comprising the step of separating insoluble by-product salt by filtration from the reaction mixture after step (d).
11. The process according to claim 5, further comprising the step of regenerating the precursor metal salt from the by-product after step (e).
12. The process according to claim 5, further comprising the step of recycling the solvent for the subsequent batches.
13. The process according to claim 1, wherein the solid hydroxylamine nitrate obtained has a purity of at least 99.99% as measured by ion chromatography.
14. The process according to claim 1, wherein the solid hydroxylamine nitrate obtained is free from one or more impurities selected from the group consisting of metal ions, ammonium salts and nitric acid.

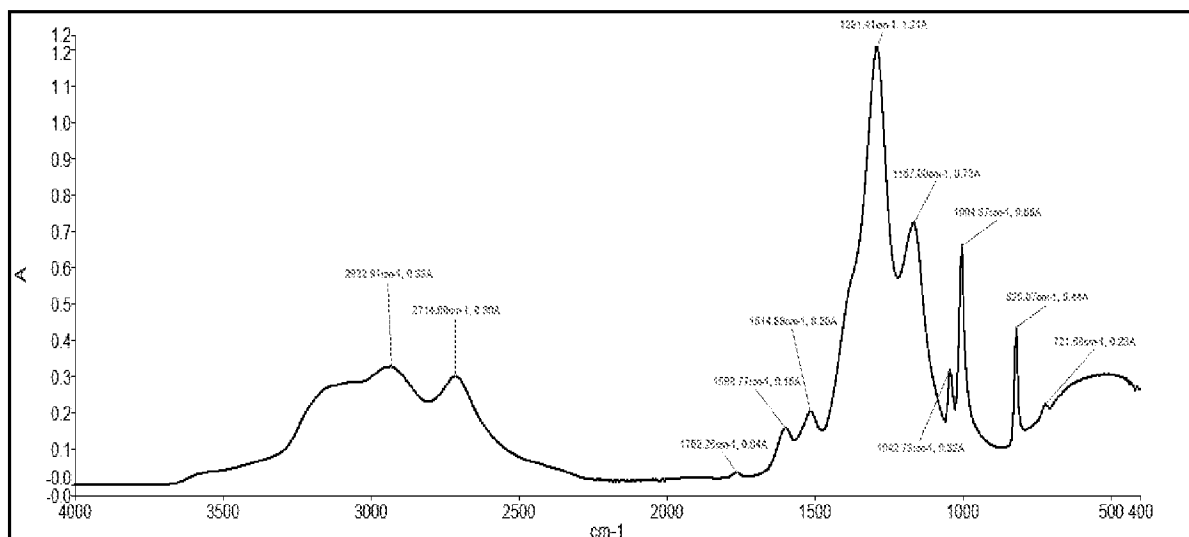


Fig 1: FTIR Spectrum of solid HAN

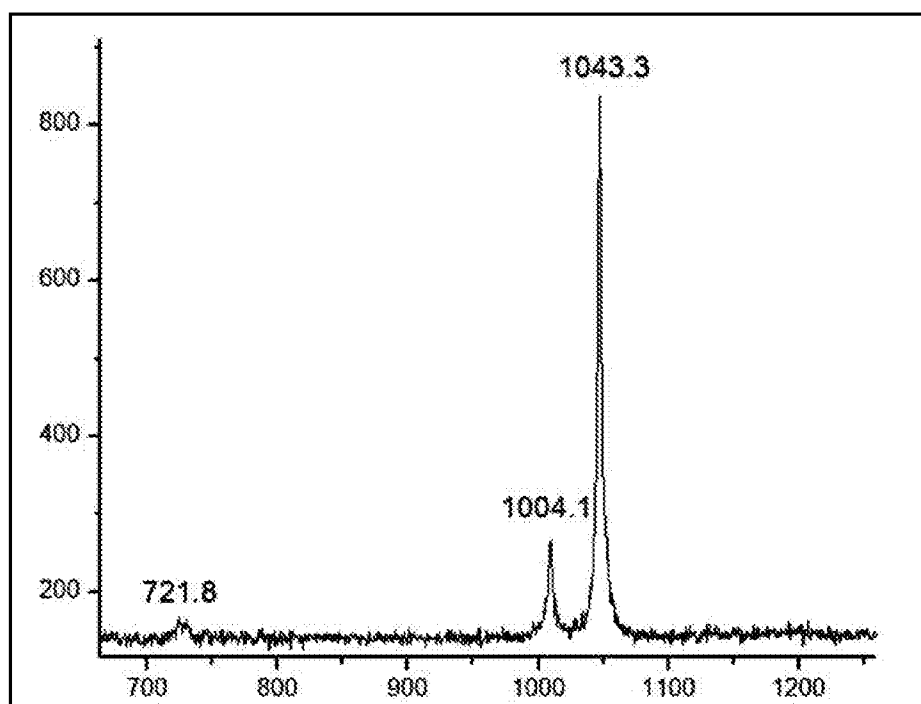


Fig 2: Raman Spectrum of solid HAN

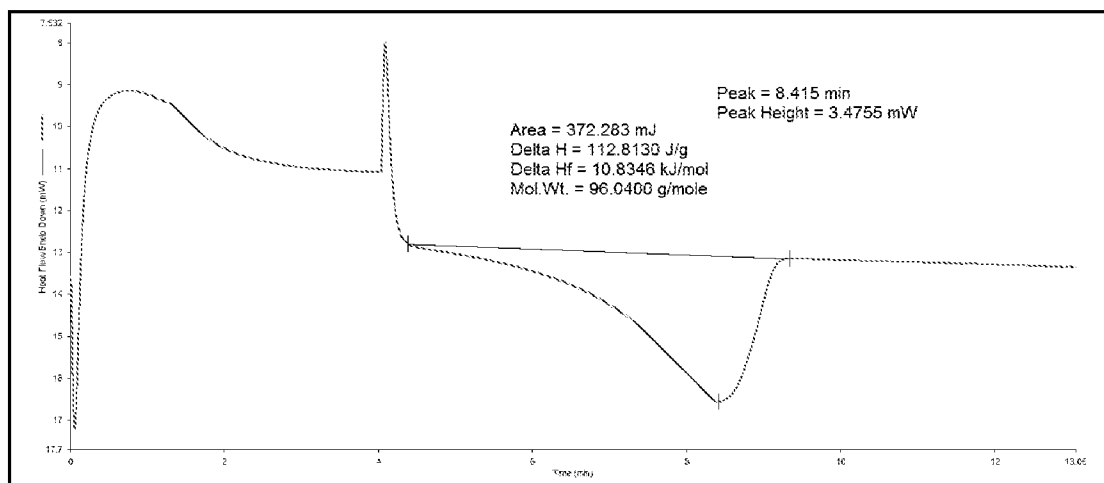


Fig 3: Heat of fusion obtained from DSC curve

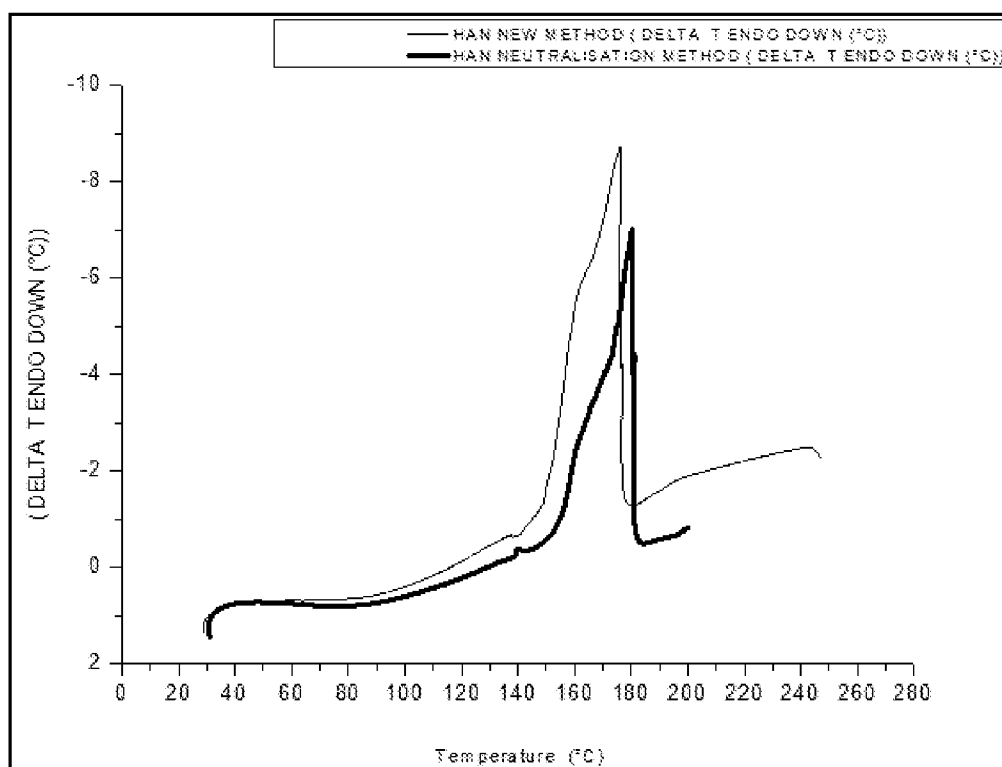


Fig 4a: DTA curve of 90% HAN prepared by embodied novel method and neutralisation method

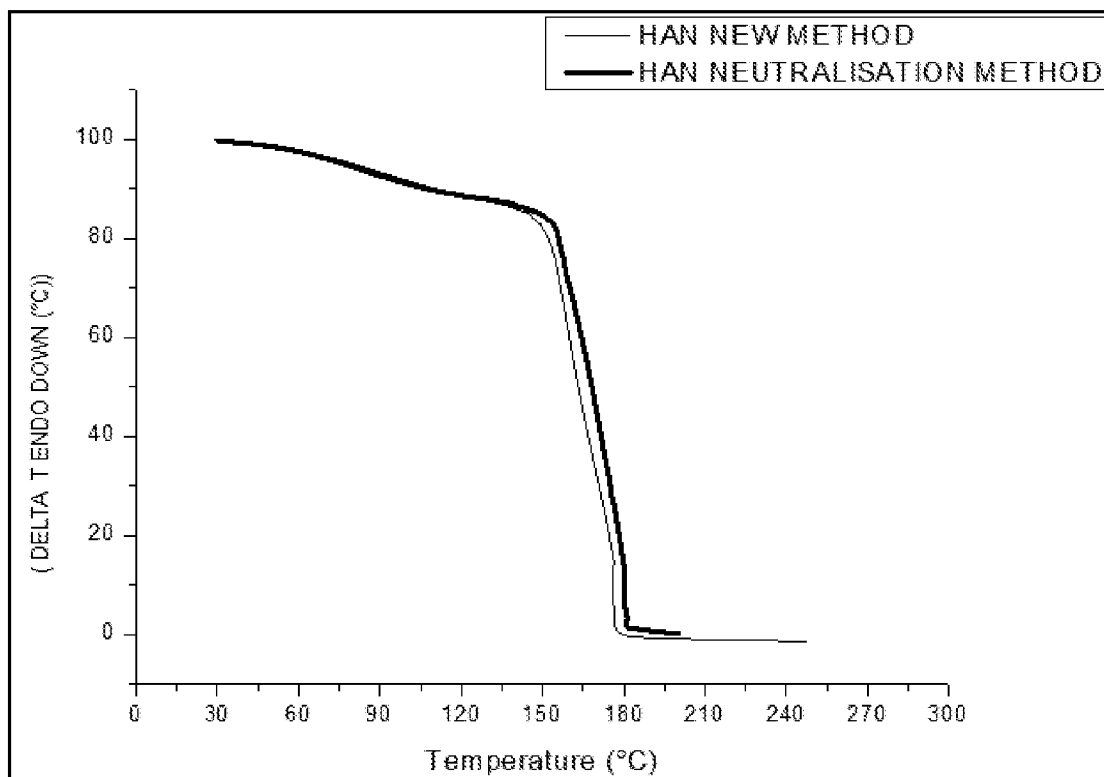


Fig 4b: TGA curve of 90% HAN prepared by novel method and neutralisation method

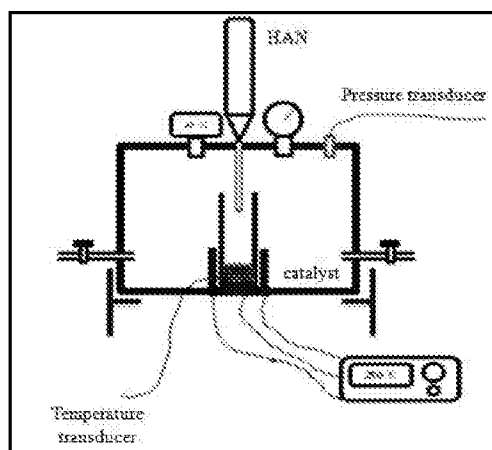


Fig.5: Schematic of a batch reactor

| P1 | P2 | T1 | T2 | ΔP | ΔT | $\Delta P/\Delta T$ (BARS/SEC) | $\Delta P/\Delta T$ (MILLIBARS/SEC) |
|---------|---------|---------|---------|------------|------------|--------------------------------|-------------------------------------|
| 0.18207 | 0.52432 | 158.398 | 164.817 | 0.342253 | 6.419397 | 0.053315444 | 53.3154438 |
| 0.16882 | 0.5214 | 245.575 | 251.977 | 0.352582 | 6.401632 | 0.055076893 | 55.07689289 |
| 0.18655 | 0.54498 | 347.411 | 353.269 | 0.358436 | 5.858073 | 0.061186674 | 61.1866735 |
| 0.18069 | 0.47009 | 539.638 | 544.535 | 0.289399 | 4.896955 | 0.059097745 | 59.09774544 |
| 0.17914 | 0.50246 | 632.785 | 638.763 | 0.323315 | 5.978101 | 0.054083228 | 54.0832281 |
| 0.1924 | 0.49351 | 727.85 | 732.579 | 0.301107 | 4.728955 | 0.063673053 | 63.6730525 |
| 0.16003 | 0.54206 | 808.649 | 814.636 | 0.382022 | 5.987656 | 0.063801594 | 63.80159448 |
| 0.19085 | 0.49506 | 903.496 | 909.057 | 0.304206 | 5.560691 | 0.05470651 | 54.7065104 |
| 0.1776 | 0.51709 | 986.63 | 992.474 | 0.339498 | 5.844039 | 0.058093041 | 58.09304147 |
| 0.17329 | 0.50384 | 1060.08 | 1065.88 | 0.330546 | 5.803433 | 0.056956977 | 56.95697702 |
| | | | | 0.332336 | | | 57.99911596 |

Fig.6a: Batch reactor data (Performance evaluation) of thermal decomposition of 90% HAN prepared by neutralization method

| P1 | P2 | T1 | T2 | ΔP | ΔT | $\Delta P/\Delta T$ (BARS/SEC) | $\Delta P/\Delta T$ (MILLIBARS/SEC) |
|-------------|-------------|------------|------------|-------------|------------|--------------------------------|-------------------------------------|
| 0.152627 | 0.553637 | 472.507245 | 476.704274 | 0.40101 | 4.197029 | 0.095546159 | 95.54615896 |
| 0.154041 | 0.577153 | 647.163459 | 651.620843 | 0.423112 | 4.457384 | 0.094923839 | 94.92383874 |
| 0.130525 | 0.563892 | 733.263455 | 738.021639 | 0.433367 | 4.758184 | 0.091078235 | 91.07823489 |
| 0.126573801 | 0.545554971 | 289.087674 | 293.461434 | 0.41898117 | 4.37376 | 0.095794275 | 95.79427541 |
| 0.126909665 | 0.395377178 | 377.845633 | 380.373449 | 0.268467513 | 2.527816 | 0.106205322 | 106.2053223 |
| | | | | 0.419163 | | | 93.84941086 |

Fig.6b: Batch reactor data (Performance evaluation) of thermal decomposition of 90% HAN prepared by embodied novel method

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2016/054509

A. CLASSIFICATION OF SUBJECT MATTER
C01B21/14 Version=2016.01

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)

C01B

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 | US4066736 A, 03 Jan 1978, THE UNITED STATES OF AMERICA AS REPRESENTED BY THE SECRETARY OF THE NAVY. FAMILY-NONE See abstract, examples 1-5 and claims 1-12 ----- | 1-14 |
| Y | US5182092 A, 26 Jan 1993, THE UNITED STATES OF AMERICA AS REPRESENTED BY THE SECRETARY OF THE NAVY. FAMILY-NONE See abstract and claims 1-7 ----- | 1-14 |
| Y | US6258983 B1, 10 July 2001, THE UNITED STATES OF AMERICA AS REPRESENTED BY THE SECRETARY OF THE NAVY. FAMILY-NONE See abstract, example 1-6 and claims 1-10 | 1-14 |



Further documents are listed in the continuation of Box C.



See patent family annex.

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24-10-2016

Date of mailing of the international search report

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