

**Title of Invention**    **"PROCESS FOR PREPARING TRIS CARBOHYDRAZIDE NICKEL PERCHLORATE (NCP)"**

**Abstract**

A process for preparing tris-carbohydrazide nickel perchlorate (NCP), said process characterized by the steps of: (a) adding, drop wise, nickel perchlorate hexahydrate solution containing nickel perchlorate hexahydrate in the range of 0.01 to 0.3 moles to carbohydrazide solution containing 0.01 to 1.05 moles of carbohydrazide, maintained at a temperature in the range of 30 to 50°C over a period of 20 to 60 minutes; (b) maintaining the temperature of mixture of step (a) between 40 to 50°C for a period in the range of 10-30 minutes; (c) cooling the mixture of step (b) to room temperature; (d) stirring the cold mixture of step (c) for a time period in the range of 1 to 2 hours to obtain light blue crystals, and (e) filtering and washing the light blue crystals to obtain tris-carbohydrazide nickel perchlorate.

**FIELD OF THE INVENTION**

The present invention relates to an improved process for the preparation of energetic coordination compound tris carbohydrazide nickel perchlorate (NCP) with desired particle morphology and bulk density. More particularly, the present invention relates to a process for preparing NCP with bulk density in the range of 0.85 to 0.9 g/cm<sup>3</sup>.

**BACKGROUND AND PRIOR ART DESCRIPTION**

Detonators are the key devices needed to initiate an explosive train. The detonators contain a small quantity of a sensitive explosive as a means of its initiation. The inorganic azides {lead azide (LA) and silver azide (SA)} are generally used as an ingredient in detonator composition. Mercury fulminate was the first choice as an initiator. It still finds use as one of the ingredients in some of the cap compositions.

However, disadvantage of using mercury fulminate is that it is highly prone to mechanical stimuli. Another disadvantage of mercury fulminate is that it has poor stability during storage. Yet another disadvantage of mercury fulminate is that it gets "dead pressed" and becomes insensitive to ignition by flash when compressed under a pressure of 200 MPa.

**Full Text**

Service lead azide (SLA) replaced mercury fulminate as it does not get dead pressed. The disadvantage of using SLA as initiatory compound is that it is highly sensitive towards impact and friction and is highly prone to hazards during manufacturing and handling. Another disadvantage of SLA is its instability in presence of moisture and carbon dioxide resulting in the formation of hazardous hydrazoic acid on exposure to them. Yet another disadvantage of SLA is its poor compatibility with other metals like copper used for detonator casing resulting in the formation of the azides (copper azide).

Recently, a basic lead azide (BLA) has replaced SLA in most of the detonators in India. Although, BLA containing lead oxide in combination with SLA overcomes some of the problems associated with SLA alone, inherent drawbacks of SLA persist though to a lesser extent. Yet another disadvantage of BLA is its relative insensitivity to flame. Lead styphnate (LS) is another initiatory compound, which is widely used to render BLA flash sensitive. The disadvantage of using LS is that it is having less initiating power than other initiatory explosives and cannot be used as a main initiator. Another disadvantage of using LS is its high sensitivity to electrostatic charge. Yet another disadvantage of LS is that it accelerates the decomposition of LA into hydrazoic acid and thereby facilitates the formation of hazardous products.

The standard tubular detonators normally contains ASA composition (Azide, Styphnate,

Aluminium) which contains mixture of service lead azide (65%), lead styphnate (32.5%) and aluminium powder (2.5%), which is pressed above the initially pressed base charge of high explosive tetryl/penta erithritoltetranitrate. The disadvantage of using ASA composition is similar to above described drawbacks of lead azide and lead styphnate. Efforts are on to replace these commonly used initiatory explosives by introducing lead (Pb) free chemical compounds having lower sensitivity and greater stability. 5-cyanotetrazolatepentaamine cobalt (III) perchlorate (CP) is one such type of lead free initiator. It has been reported as possible replacements for primary explosives such as LA and LS. The disadvantage of CP is that one of the starting materials used for its preparation is cyanogens, which is one of the banned chemical due to severe environmental protection agency (EPA) restrictions.

Efforts are on to replace CP by another energetic co-ordination compound Bis(5-nitrotetrazolato)tetraamine cobalt perchlorate (BNCP), which is found to have greater explosive output than CP and undergoes deflagration to detonation to transition (DDT) with less confinement. This material is of interest for low voltage, hot wire detonator applications like semiconductor bridge detonators.

Tris carbohydrazide nickel perchlorate (NCP) is another energetic co-ordination compound. It is thermally stable even at temperature above 300°C, has free flow morphology with bulk density of 0.85-0.90 g/cm<sup>3</sup>. To the best of the Inventors knowledge none of the publications reports the actual process for the preparation of NCP and its use in detonators. Although, Beijing Institute of technology, China and Mendeleev University of Technology, Russia have reported the preparation of similar energetic co-ordination compounds for energetic ballistic modifier applications, none of these institutes mention the potential use of NCP as an initiator compound.

Initiator compounds for the detonators have been placed by the United States Military manual under category number 27. The ideal qualities which the initiator compounds should have are also given in the category.

#### OBJECTS OF THE PRESENT INVENTION

The main object of the present invention is to provide a process for preparation of energetic coordination compound Tris carbohydrazide nickel perchlorate (NCP) for use as an initiator compound.

Another object of the present invention is to provide a process for the preparation of NCP having bulk density in the range of 0.85 to 0.90 g/cm<sup>3</sup> and with free flow morphology.

Yet another object of the present invention is to utilize NCP thus prepared alone and in combination with tetryl (CE) for detonator applications.

#### BRIEF DESCRIPTION OF THE PRESENT INVENTION

The present invention provides a process for the preparation of Tris carbohydrazide nickel perchlorate (NCP) of desired particle size of 90-200 microns having bulk density of 0.85-0.90 g/cm<sup>3</sup> with free flow morphology. The process of the present invention involves the reaction of nickel perchlorate hexahydrate with carbohydrazide at elevated temperature. The reaction mixture is cooled to room temperature for 1 to 2 hours under constant stirring to obtain NCP crystals having particle size in the range of 90 to 200 microns. The Tris carbohydrazide nickel perchlorate thus obtained is filtered, washed (with propanol) and dried at 60 to 80°C. The NCP having particle size in the range of 90-200 micron was pressed in detonator No. 27 at 7-8 MPa pressure with dwell time of 45-60 seconds and

detonated with the aid of safety fuse on a witness plate (3-4 mm lead plate). The incorporation of NCP into detonators containing tetryl, resulted in punched neat holes having 7 to 8 mm diameter.

More particularly, the present invention provides an improved process for preparing carbonylhydrazide nickel perchlorate (NCP), said process comprising the steps of:

- a. adding a solution containing nickel perchlorate hexahydrate solution to carbonylhydrazide solution maintained at a temperature in the range of 30 to 55°C over a period of 15 to 90 minutes;
- b. maintaining the temperature of the mixture of step (a) between 40 to 50°C for a period in the range of 10-30 minutes;
- c. cooling the mixture of step (b) to room temperature;
- d. stirring the cold mixture of step (c) for a time period in the range of 1 to 2 hours to obtain light blue crystals, and
- e. filtering the blue crystals and washing the same to obtain tris-carbonylhydrazide nickel perchlorate.

In another embodiment of the present invention wherein in step (a), the carbonylhydrazide solution and the nickel perchlorate hexahydrate solution are aqueous solutions.

In yet another embodiment of the present invention, the solution containing nickel perchlorate hexahydrate is added in a drop-wise manner to the carbonylhydrazide solution.

In still another embodiment of the present invention, the temperature of the carbonylhydrazide solution is marginally decreased by about 1-4°C after adding the nickel perchlorate hexahydrate solution.

In one more embodiment of the present invention wherein in step (e), the blue crystals thus obtained are washed with water and subsequently with methyl alcohol or ethyl alcohol or propyl alcohol isopropyl alcohol.

In one another embodiment of the present invention, wherein the molarities of the nickel perchlorate hexahydrate solution is in the range of 0.01 to 0.3 moles and preferably between 0.01 to 0.2 moles.

In yet another embodiment of the present invention, wherein the molarities of the carbonylhydrazide solution is in the range of 0.01 to 1.05 moles and preferably 0.01 to 0.70 moles.

According to a preferred embodiment of the present invention, the process for preparing NCP is carried out in the following manner:

- (a) drop wise addition of nickel perchlorate hexahydrate (0.01 to 0.3 mol) solution to carbonylhydrazide (0.01 to 1.05 mol) solution over a period of 15 to 20 minutes;
- (b) warming of the reaction mixture on water bath at 40 to 60°C for 10 to 30 minutes;
- (c) cooling the reaction mixture at room temperature for 1-2 hours with constant mechanical stirring;
- (d) filtration of NCP obtained in step (c);
- (e) washing of NCP obtained in step (d) using R-OH, where R = methyl/ ethyl/ n-propyl/ isopropyl;
- (f) drying of NCP of step (e) at 60-80°C for 2 to 3 hours to obtain constant weight;
- (g) characterization by metal content analysis, infrared (IR) spectra analysis, differential thermal analysis (DTA) and electron spectroscopy for chemical analysis (ESCA).

(h) Determination of impact and friction sensitivity.

The invention is hereafter described in the following paragraph by way of examples. The examples are given for the sole purpose of illustration and the present invention should not be construed to be limited by the examples.

#### FILLING AND EVALUATION OF NCP IN TUBULAR DETONATORS:

Details of filling of tubular detonator and its evaluation are given below: a) Filling of the compound obtained in the present invention i.e. NCP followed by its pressing in to tubular detonator No. 27 at 7-8 MPa with dwell time in the range of 45 to 60 seconds;

b) Insertion of safety fuse (20 cm length) in the filled tubular detonator tube touching NCP filling;

c) Soft crimping of the filled tubular detonator of step (b);

d) Placement of filled tubular detonators vertically over 3-4 mm lead plate (witness plate);

e) Firing of tubular detonators by igniting safety fuse using safety match;

f) Measuring of the diameter of the punched hole on the lead plate and comparison with the firing results of standard filled tubular detonator No. 27.

#### FILLING OF TETRYL (CE) AND NCP IN TO TUBULAR DETONATOR AND EVALUATION

Description of filling of CE and NCP in tubular detonators and their evaluation are given below:

(a) Filling of tubular detonators with 500 - 600 mg of tetryl (CE) and pressing at 7-8 MPa for dwell time of 45 -60 seconds;

(b) Filling of 350-450 mg of NCP above CE and pressing at 7-8 MPa for dwell time of 45-60 seconds;

(c) Insertion of safety fuse (20 cm length) in the filled tubular detonator tube touching NCP filling;

(d) Soft crimping of the filled tubular detonator of step (c);

(e) Placement of filled tubular detonators vertically over 3-4 mm lead plate (witness plate);

(f) Firing of tubular detonators by igniting safety fuse using safety match resulting in the initiation of detonation of NCP which in turn initiates tetryl detonation;

(g) Measuring of the diameter of the neat punched hole on the witness plate.

#### WORKING EXAMPLE 1:

A solution containing carbonylhydrazide (3.66 gms) (0.07 mol) in 30-35 cm<sup>3</sup> of water was charged into three necked round bottom flask placed in water bath. The solution was kept under stirring and heated to the temperature in the range of 40-50°C. 7.32 gms of (0.02 mol) of Nickel perchlorate hexahydrate was dissolved in 25-30 cm<sup>3</sup> of water and the solution was added to carbonylhydrazide solution over a period of 20 minutes to one hour at temperature in the range of 30-50°C. The addition of the reactant resulted in marginally exothermic reaction leading to an increase in temperature by about 1-4°C. the reaction was allowed to remain at 40-50°C for about 10-30 minutes. Subsequently, the flask was removed from the steam bath and the contents were cooled to 25-30°C, while stirring during the course of about 1 to 2 hours. Light blue crystals were formed, which were filtered through buchner funnel. After sucking out the liquor, the crystals were washed with distilled water (4X 50 cm<sup>3</sup>) followed by methyl / ethyl / propyl alcohol (50 cm<sup>3</sup>). The material was allowed to dry in air for about 2-3 hours at 60 to 80°C. The yield obtained was 8.9 gms (85 to 90%). The compound was characterized by metal content, IR, DTA and ESC A techniques (refer to table 1). The synthesized compound was also

further subjected for impact and friction sensitivity tests. Table 1: Characterization of NCP (Table Removed)

#### WORKING EXAMPLE 2:

A solution containing carbohydrazide (1.83 gms) (0.01 mol) in 20-30 cm<sup>3</sup> of water was charged into three necked round bottom flask placed in water bath. The solution was kept under stirring and heated to the temperature in the range of 35-45°C. 7.32 gms of (0.07 mol) of Nickel perchlorate hexahydrate was dissolved in 30-40 cm<sup>3</sup> of water and the solution was added to carbohydrazide solution over a period of 20 minutes to one hour at temperature in the range of 30-60°C. The addition of the reactant resulted in marginally exothermic reaction leading to an increase in temperature by about 2-4°C. The reaction mixture was allowed to remain at 50-60°C for about 10-30 minutes. Subsequently, the flask was removed from the steam bath and the contents were cooled to 20-30°C, while stirring during the course of about 1 to 7 hours. Light blue crystals were formed, which were filtered through buchner funnel. After sucking out the liquor, the crystals were washed with distilled water (7X 50 cm<sup>3</sup>) followed by methyl / ethyl / 'propyl alcohol (2X 50 cm<sup>3</sup>). The material was allowed to dry in air for about 1-7 hours at 60 to 80°C. The yield obtained was 4.5 gms (85 to 90%). The compound was characterized by instrumental technique.

#### FILLING AND EVALUATION OF THE TUBULAR DETONATORS:

Tubular detonators were filled in the following manner:

300-400 mg NCP was placed in the standard tube of tubular detonator No. 27, pressed gently at 7-8 MPa with dwell time of 45-60 sec. Safety fuse of 20 cm length was inserted into tubular detonator touching the NCP layer and crimped softly. Humidity (RH In another set of experiments, tetryl (500 to 600 mg) was filled in the tubular detonators and pressed at 7-8 MPa pressure with dwell time of 45 -60 seconds. NCP (300-400 mg) was pressed above to the pressed tetryl at 7-8 MPa under identical conditions. Safety fuse of 20 cm length was inserted into the filled tubular detonator tube touching the filled NCP layer and crimped softly. The filled tubular detonator tube was vertically placed on the lead plate of 3-4 mm thickness and then safety fuse was ignited using safety match. The diameter of the neat punched hole formed was measured.

In another set of experiment, standard tubular detonator No. 27 was tested similarly. The standard tubular detonator normally contains mixture of service lead azide (SLA) (65%), lead styphnate (32.5%) and aluminium powder (2.5%), which is pressed above the initially pressed base charge of high explosive tetryl/penta erithritoltetranitrate. The tubular detonator was initiated and the diameter of the neatly punched hole was measured (5-6 mm). It is to be understood that the process of the present invention is susceptible to modifications, changes and adaptations by those skilled in the art. Such modifications, changes and adaptations are intended to be within the scope of the further set forth under the following claims.

#### We Claim:

1. A process for preparing tris-carbohydrazide nickel perchlorate (NCP), said process characterized by the steps of:

(a) adding, drop wise, nickel perchlorate hexahydrate solution containing nickel perchlorate

hexahydrate in the range of 0.01 to 0.3 moles to carbonylhydrazide solution containing 0.01 to 1.05 moles of carbonylhydrazide, maintained at a temperature in the range of 30 to 50°C over a period of 20 to 60 minutes;

(b) maintaining the temperature of mixture of step (a) between 40 to 50°C for a period in the range of 10-30 minutes;

(c) cooling the mixture of step (b) to room temperature;

(d) stirring the cold mixture of step (c) for a time period in the range of 1 to 2 hours to obtain light blue crystals, and

(e) filtering and washing the light blue crystals to obtain tris-carbonylhydrazide nickel perchlorate.

2. The process as claimed in claim 1, wherein in step (a), the carbonylhydrazide solution and the nickel perchlorate hexahydrate solution are aqueous solutions.

3. The process as claimed in claim 1, wherein the temperature of the carbonylhydrazide solution is increased by 1-4°C after adding the nickel perchlorate hexahydrate solution.

4. The process as claimed in claim 1, wherein in step (e), the blue crystals thus obtained are washed with water and subsequently with methyl alcohol or ethyl alcohol or propyl alcohol or isopropyl alcohol.

5. The process as claimed in claim 1, wherein the nickel perchlorate hexahydrate solution contains nickel perchlorate hexahydrate preferably in the range of 0.01 to 0.2 moles.

6. The process as claimed in claim 1, wherein the carbonylhydrazide solution contains carbonylhydrazide preferably in the range of 0.01 to 0.70 moles.