

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C06B 47/08, C01B 21/16	A1	(11) International Publication Number: WO 94/10104 (43) International Publication Date: 11 May 1994 (11.05.94)
(21) International Application Number: PCT/NL93/00230 (22) International Filing Date: 3 November 1993 (03.11.93) (30) Priority data: 9201916 3 November 1992 (03.11.92) NL (71) Applicant (for all designated States except US): AERO-SPACE PROPULSION PRODUCTS B.V. [NL/NL]; Lange Kleiweg 137, NL-2288 GJ Rijswijk ZH (NL). (72) Inventors; and (75) Inventors/Applicants (for US only) : ZEE, Fransiscus, Wilhelmus, Marie [NL/NL]; Kievitsheuvel 12, NL-2411 LL Bodegraven (NL). MUL, Johannes, Maria [NL/NL]; Cruquiusstraat 31, NL-2012 GC Haarlem (NL). HOR-DIJK, Arie, Cornelis [NL/NL]; Gruttostraat 8, NL-3145 CB Maasluis (NL).		(74) Agents: SMULDERS, Th., A., H., J. et al.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL). (81) Designated States: CA, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD OF PREPARING HYDRAZINE NITROFORM (57) Abstract The invention relates to a method of preparing hydrazine nitroform (HNF) by dissolving nitroform of a purity of more than 98.5 wt% in a solvent and reacting it with hydrazine in the presence of a small amount of proton-transferring medium.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

Title: Method of preparing hydrazine nitroform.

This invention relates to a method of preparing hydrazine nitroform and more particularly to a method of preparing hydrazine nitroform in a pure and stable form which renders the hydrazine nitroform suitable in particular as a solid
5 propellant.

High-energy solid oxygen oxidizers that are suitable for use as propellant have long been searched for. Suitable compounds should possess a high density, be thermally stable and exhibit high impact resistance, both alone and in mixtures
10 with other compounds.

In the 1960s it was already found that hydrazine nitroform (HNF), alternatively referred to as hydrazine nitroformate or hydrazine nitroformiate, is a very strong oxidizer which renders this compound useful as fuel. The
15 compound has a high energetic value, so that it is particularly suitable as a solid propellant.

It has been found that this compound, contrary to the suggestion of the structural formula $\text{NH}_2\text{NH}_2\cdot\text{HC}(\text{NO}_2)_3$, is thermally stable. Indeed, most nitroform compounds decompose
20 rapidly at room temperature or even below room temperature.

The compound is relatively impact resistant and, even when mixed with aluminum, no reduction of the impact resistance arises. This is of importance because hydrazine nitroform, as described in U.S. Patent No. 3,307,985, is often
25 mixed with aluminum, among others, to improve the properties regarding its performance as a solid propellant. Aluminum, but also magnesium, beryllium or other metals, is then employed as powdery fuel compound.

Methods of preparing hydrazine nitroform have long been
30 known. U.S. Patent No. 3,297,747 describes a method of preparing hydrazine nitroform through dissolving nitroform in alcohol and slowly, dropwise adding hydrazine thereto. The hydrazine nitroform formed then precipitates as a salt. This salt can be isolated by means of filtration and optionally be
35 further purified by recrystallization from a solution in a

short chain alcohol, such as isopropyl alcohol. The yield of hydrazine nitroform achieved by means of this method is 50%.

Such a method is also described in U.S. Patent 3,378,594, where equimolar amounts of hydrazine (hydrated or non-
5 hydrated) are mixed with nitroform at 0°C to 50°C and atmospheric pressure. Water can be present as solvent and is then present in large amounts. Preferably, however, the method is effected in the presence of an organic solvent such as methanol.

10 In the Encyclopedia of Explosives and Related Items, S.M. Kaye, vol 8, page M78-M80 (1978) a method for preparing HNF is described, in which hydrazine is mixed with nitroform in water. The end product can also be prepared by adding anhydrous hydrazine to nitroform in isopropyl alcohol.

15 However, as appears from numerous publications from the 1960s and 1970s, the hydrazine nitroform produced in this way did not exhibit the desired stability. As described in U.S. Patent 3,418,183, the hydrazine nitroform tends to form bubbles, or, as it is called, the hydrazine nitroform
20 'gasses'. This tendency to 'gas' is attributed to impurities of the hydrazine nitroform produced. It appears from U.S. Patent 3,378,595 that the stability of the hydrazine nitroform depends on the ratio of the hydrazine to the nitroform and on the purity of nitroform and solvent.

25 One possibility of preventing hydrazine nitroform from 'gassing' could be to purify the hydrazine nitroform. However, this option is laborious and hence expensive.

Accordingly, to sufficiently ensure stability, it proved necessary to always add stabilizers. A great deal of research
30 was focused on finding a stabilizer which, in small amounts, is capable of stabilizing the hydrazine nitroform to a sufficient degree.

Publications which can be mentioned in this connection include the above-mentioned U.S. Patent 3,418,183, where
35 anhydrides of dicarboxylic acids are proposed, U.S. Patent 3,658,608, where nitroguanidine is proposed, and U.S. Patent

3,384,674, disclosing the addition of non-volatile aldehyde compounds such as benzaldehyde for increasing the stability of hydrazine nitroform.

U.S. Patent 3,384,675 discloses the stabilization of
5 nitroform salts with salts of (in)organic acids. However, a drawback of such addition is that if, for instance, mercurous oxalate is used, this compound only regulates the high impact sensitivity.

From the large number of publications about possibly
10 suitable stabilizers, it appears that finding a stabilizer that is useful in all respects presents major problems.

A drawback of the use of stabilizers in general, incidentally, is that they reduce a part of the weight of the fuel to useless mass because they do not contribute to the
15 supply of energy.

Accordingly, it has long been attempted to find a method which makes it possible to prepare hydrazine nitroform of such purity that the use of stabilizers could be reduced or even rendered superfluous.

20 An initiative to that effect was the marketing of 'High Purity Grade' hydrazine (HPG hydrazine). This is hydrazine with a purity of at least 99.0% and a maximum water content of 1.0 wt.%. The hydrazine hitherto used was Standard Grade hydrazine with a purity of 98% and a maximum water content of
25 1.5%.

The expectation was that if a purer starting product was used, the end product would also possess a higher purity.

However, after tests with this HPG hydrazine, in which hydrazine nitroform was prepared in conventional manner with
30 nitroform in an anhydrous reaction medium, it appeared that the hydrazine nitroform obtained was only as pure as, or even less pure than, the product prepared with Standard Grade hydrazine.

Thus, the use of HPG hydrazine did not initially seem to
35 lead to the desired increased purity of the product.

Surprisingly, it has now been found that it is possible to obtain hydrazine nitroform with a very high purity and yield, starting from HPG hydrazine.

It has in fact been found that a small amount of proton-transferring medium dispersed in the reaction medium catalyzes the salt formation, whereby at the same time a purer end product is formed.

Both water and lower (C_1 - C_6) alcohols are suitable as proton-transferring media.

Of the lower alcohols, methanol and isopropanol are preferred, but other C_1 - C_6 alcohols can be used as well.

This new method enables the production of hydrazine nitroform of so high a purity that it is no longer necessary to use any stabilizer at all, since the lack of stability was found to be caused by the presence of impurities.

The yield of hydrazine nitroform prepared by this new method is greater than the yield obtained by the known methods and the process as a whole accordingly leads to a major saving in cost.

In the preparation according to the present invention, nitroform (NF, melting point 22.0°C) is mixed with an organic solvent.

For reasons of safety, the nitroform is mostly supplied as aqueous solution, for instance in a 32% aqueous solution.

In that case, the nitroform can be used by extracting it from the aqueous solution by means of dichloroethane.

The nitroform can also be utilized by salting it out from the solution by means of, for instance, NaCl, KCl, NaNO_3 or other salts suitable therefor. NaCl is preferred here.

In salting out, a two-phase system is formed, comprising a water layer and a nitroform layer. The nitroform layer is separated from the salt-containing water layer and also the residual water is removed from the nitroform layer to ensure that salts and other impurities present in the water will be present in the end product to the least possible extent.

In particular the presence of chlorine ions in the residual water is undesirable, since their presence leads to the end product exhibiting increased chlorine emission upon combustion, which is undesirable on account of the additional environmental pollution involved. Further, the presence of chlorine ions can give rise to a reduction of the stability.

An amount not exceeding 0.05 wt.% chlorine relative to the amount of HNF can still be regarded as acceptable.

The method according to the invention is preferably carried out in a solvent that, on the one hand, is a dissolvent medium for the nitroform and, on the other, is a nonsolvent for the hydrazine nitroform to be formed. In addition, it functions as 'heat sink' for the reaction (to absorb a part of the reaction heat). Suitable solvents include, among others, organic solvents as dichloroethane (DCE) and dichloromethane (DCM). Dichloroethane is preferred. The ratio of nitroform to solvent is preferably between 3:1 and 1:9, preferably between 1:2 and 1:3 and is for instance 1:2.5. Preferably, sufficient solvent will be present to dissipate the heat produced in the reaction.

To the mixture of nitroform and solvent a small amount of water or C₁-C₆ alcohol is then added, 'small amount' meaning more than 0.5 vol.%, preferably 0.5 - 20 vol.%, more preferably 1 - 10 vol.% and most preferably 2.5 - 7 vol.%, calculated on the amount of solvent.

The mixture is then cooled and hydrazine is added dropwise, with the temperature of the reaction system remaining preferably under 5°C. Generally, this temperature will be between -5°C and +5°C. After the hydrazine has been added, preferably stirring is continued for a period of time at a temperature of approximately 0°C (i.e. between -10°C and +5°C). This period of time is generally between 5 and 240 min.

The amounts of nitroform and hydrazine used are generally between 0.9 and 1.1 on a molar basis, but the amounts are preferably equimolar. The requisite amount of hydrazine is determined on the basis of the amount of nitroform initially

present. If desired, a separate determination can take place, for instance by means of a titrimetric determination of the amount of nitroform.

After stirring, the crude HNF is removed from the reactor, the supernatant liquid is decanted and the wet product is dried.

Optionally, the crude product thus obtained can be purified by means of recrystallization, for instance as described in U.S. Patent 3,297,747, utilizing isopropyl alcohol. This recrystallization can generally be carried out from a solution in a short chain alcohol.

Recrystallization can also be carried out by preparing a solution of the coarse HNF which is subsequently poured out in a nonsolvent. Suitable media for this purpose are methanol as solvent and methylene chloride as nonsolvent.

The present invention will be further explained in and by the following examples.

In these examples, for reasons of safety, a stock solution of nitroform is employed, but the nitroform can naturally be used in undiluted form as well.

Preparation of hydrazine nitroform

Example 1

25

1000 ml of a stock solution of a 32% (w/w) nitroform (NF) in water is introduced into a glass 2-liter vat, provided with a glass stirrer, without any metal parts being present in order to prevent catalytic decomposition of hydrazine or compounds thereof. Then at room temperature 216 g NaCl is added with stirring, whereby the nitroform is displaced from the water layer by the NaCl. A two-phase system forms, with the liquid nitroform separating from the NaCl-saturated water layer.

35 After separation with the aid of a separating funnel, 500 ml dichloroethane (DCE) is added to the nitroform layer

and this mixture is again introduced into a clean separating funnel. Again a small amount of water separates, which is also removed.

The NF/DCE mixture is introduced into a reactor, 30 ml
5 water is added to the reaction mixture (6 vol.% relative to the amount of solvent) and the mixture is cooled to 0°C. With continuous stirring, an equimolar amount of HPG hydrazine is added to the solution in dropwise manner. The rate of addition is set such that the temperature in the reaction vat remains
10 between 0 and 5°C. After all of the hydrazine has been added, stirring is continued for another 60 minutes to ensure that the reaction has proceeded to completion.

Then the coarse HNF is taken from the reactor, the DCE is removed by means of decanting and the coarse material is dried
15 for 48 hours in a vacuum dry oven at 30°C under vacuum.

The yield of the coarse product is approx. 100%, based on hydrazine.

The coarse HNF, after being dried, appears to have a melting point of 115°C.

20 The coarse product is purified by means of recrystallization, a solution being made in methanol, which solution is subsequently poured out in methylene chloride. The end product then precipitates.

The end product has a melting point of 120°C.
25

Comparative example 1

Hydrazine nitroform is prepared by the method described in Example 1, starting from High Purity Grade hydrazine.
30 However, no water is added during the preparation.

The product obtained, after being dried, has a melting range of 58-70°C.

Comparative example 2

Hydrazine nitroform is prepared by the method described in Example 1, starting, however, from Standard Grade hydrazine without addition of water. A product is obtained which, after drying, has a melting range of 60-80°C.

The results of the examples are summarized in the table below.

Table

Starting material + treatment	melting point/ melting range (°C) *
High purity grade hydrazine + 6 % added water **	115
High purity grade hydrazine + 6 % added water + recrystallization	120
High purity grade hydrazine, without added water ***	58 - 70
Standard Grade hydrazine, without added water ****	60 - 80

* the pure salt decomposes at 123°C.

** relative to the amount of solvent.

*** HPG hydrazine contains up to 1% water.

**** Standard Grade hydrazine contains up to 1.5% water.

From this table it clearly appears that the best results are obtained if High Purity Grade hydrazine is employed in the presence of a small amount of water.

If the known techniques are employed, such as for
5 instance in Comparative example 2, then the hydrazine nitroform obtained is considerably less pure than the hydrazine prepared by the method according to the present invention.

CLAIMS

1. A method of preparing hydrazine nitroform (HNF) by dissolving nitroform of a purity of more than 98.5 wt.% in a solvent and reacting it with hydrazine in the presence of a small amount of proton-transferring medium.
- 5 2. A method according to claim 1, wherein the proton-transferring medium is water or a lower (C₁-C₆) alcohol.
3. A method according to claim 2, wherein the lower (C₁-C₆) alcohol is methanol or isopropanol.
4. A method according to any one of claims 1-3, wherein
10 the solvent is an organic solvent, preferably dichloroethane or dichloromethane, and most preferably dichloroethane.
5. A method according to any one of claims 1-4, wherein the amount of proton-transferring medium is greater than 0.5 vol.%, is preferably between 0.5 en 20 vol.%, more
15 preferably between 1 and 10 vol.% and most preferably between 2.5 and 7 vol.%, based on the amount of solvent.
6. A method according to any one of claims 1-5, wherein the nitroform to solvent ratio is between 3:1 and 1:9 and preferably between 1:2 and 1:3.
- 20 7. A method according to any one of claims 1-6, wherein the hydrazine used is High Purity Grade hydrazine.
8. A method according to any one of claims 1-7, wherein the hydrazine to nitroform ratio is approximately stoichiometric.
- 25 9. A method according to any one of claims 1-8, wherein the mixture of nitroform and solvent, prior to the addition of the pure hydrazine, is cooled to a temperature below approximately 5°C, preferably to approximately 0°C.
10. A method according to any one of claims 1-9, wherein
30 as source for the nitroform an aqueous solution of nitroform is used.
11. A method according to claim 10, wherein the nitroform is extracted from the aqueous solution by means of dichloroethane.

12. A method according to claim 10, wherein the
nitroform is salted out from the aqueous solution by means of
a salt, whereby the liquid nitroform separates from the salt-
saturated water layer, which layers are separated from each
5 other.
13. A method according to claim 12, wherein the salting-
out step is carried out with NaCl.
14. A method according to any one of claims 1-13,
wherein the hydrazine nitroform obtained is purified by means
10 of recrystallization.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 93/00230

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C06B47/08 C01B21/16

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)

IPC 5 C06B C01B C07C

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 378 594 (J.R. LOVETT) 16 April 1968 cited in the application see column 1, line 40 - column 2, line 44 see column 3, line 42 - line 57 ---	1
A	US,A,3 297 747 (J.R. THORTON) 10 January 1967 cited in the application see column 1, line 49 - line 64 see example 1 ---	1
A	US,A,3 378 595 (J.A. BROWN ET AL.) 16 April 1968 cited in the application see column 1, line 32 - line 40 ---	1
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 document but published on or after the international filing date
- *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)
- *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

14 March 1994

Date of mailing of the international search report

22.03.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schut, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 93/00230

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 418 183 (H.E. RICE) 24 December 1968 cited in the application see column 1, line 59 - line 67 ---	1
A	US,A,3 384 674 (J.A. BROWN ET AL.) 21 May 1968 cited in the application see column 1, line 44 - column 2, line 5 ---	1
A	GB,A,896 450 (W.R. GRACE & CO.) 16 May 1962 see claims 10-21; example 3 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 93/00230

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3378594		NONE	
US-A-3297747		NONE	
US-A-3378595		NONE	
US-A-3418183		NONE	
US-A-3384674		NONE	
GB-A-896450		NONE	