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NITRAMINES AND THEIR PREPARATION

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The present invention relates generally to nitramines and more particularly to certain new nitramines having a plurality of nitroxy groups, and to their preparation from readily available raw materials.

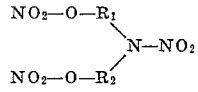
Broadly speaking, the object of the present invention is to provide a new series of nitroxyalkylnitramines suitable for various industrial purposes but of particular interest in connection with the production of military and industrial explosives.

A more particular object is the provision of a new series of nitroxyalkylnitramines of great explosive power and brisance.

Another object is the provision of a number of alternative methods of preparing such nitroxyalkylnitramines from various readily available raw materials.

Other objects and advantages will become apparent as the invention is hereinafter more particularly described.

The novel nitramine explosives with which the present invention is primarily concerned comprise a class of bis-nitroxyalkylnitramines having the general structural formula:



where R_1 and R_2 are divalent aliphatic hydrocarbon radicals, either the same or different. Of this class of compounds, the preferred nitramine consists of bis-nitroxyethylnitramine having the structural formula:

$$(NO_2—O—CH_2—CH_2)_2N—NO_2$$

This compound may also be named dinitroxydiethylnitramine, for which reason it may conveniently be referred to by the trivial designation, "DINA."

As described in detail hereinafter, DINA may be prepared by a variety of different methods as briefly characterized below:

(1) By treating diethanolamine nitrate

$$(NO_2—O—Ch_2Ch_2)_2NH_2.NO_3$$

under conditions effecting the elimination of the elements of water;

(2) by oxidizing bis-nitroxyethylnitrosamine to the corresponding nitramine; and

(3) by treating diethanolamine with nitric acid and a lower fatty acid anhydride, in the presence of a suitable catalyst. The conversion of secondary amines to the corresponding nitramines in the presence of chlorine-containing catalysts is disclosed and claimed in our application Serial Number 570,814 filed of even date herewith.

The product (DINA) obtained by any of the foregoing methods possesses the following important explosive properties:

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(1) Very high explosive power (1.48×TNT in the ballistic mortar);

(2) High brisance and high rate of detonation (ca. 6000 m./sec. at a density of 1.07 and 7300 m./sec. at a density of 1.45);

(3) The ability to gelatinize nitrocellulose;

(4) Relatively low melting point (52° C.), enabling the material to be cast-loaded;

(5) High thermal stability in relation to nitroglycerine.

(6) High heat of combustion (2403 calories per gram);

(7) Good ballistic characteristics: adiabatic flame temperature of 3700° K. (calculated from Ei (2500° K.) =483.2 calories per gram and average heat capacity at constant volume of 0.3653 calorie per gram per degree);

(8) Satisfactory sensitivity to impact, friction, etc.;

In order clearly to disclose the nature of the present invention, a number of specific examples will hereinafter be described in considerable detail. For purposes of convenience, the preparation of DINA will first be discussed in detail and thereafter the properties of DINA will be described. It should be clearly understood, however, that the following examples are given purely for illustrative purposes and are not intended to delineate the scope of the invention in its broad aspects.

I. THE PREPARATION OF DINA

EXAMPLE 1

(Preparation of DINA from dinitroxydiethylamine nitrate)

(a) THE PREPARATION OF DINITROXYDIETHYLAMINE NITRATE

In a 5 l. flask provided with a mercury sealed stirrer was placed 3780 g. (60 moles) of 99–100% nitric acid. The nitric acid was cooled to 10–12° C. and agitated while 420 g. (4.0 moles) of diethanolamine (M. P. 26.5° C.) was added over a 2½ hour period. After the addition was complete the reaction mixture was stirred for one hour at 40° C., moisture being excluded from the flask at all times. The reaction mixture was then poured on 6 kg. of ice and the resulting white crystalline precipitate was filtered immediately at the lowest possible temperature and then washed with 500 cc. of ice water, then with 300 cc. of ethanol and finally with 200 cc. of ether. The dried product melted at 118–119° C. and weighed 846 g., corresponding to a yield of 82% of the theoretical.

Dinitroxydiethylamine nitrate is fairly soluble in acetone, methanol, hot solutions of ethanol, water and nitromethane. It is less soluble in cold ethanol and water and insoluble in benzene, chloroform, ether and petroleum ether. It shows some tendency to be hygroscopic and tends to

hydrolyze when moist. It may be ignited and burns to leave a deposit of carbon. It may be detonated by impact. Repeated crystallizations of the crude salt from methanol, ethanol, acetone and glacial acetic acid raised the melting point to 120.5°.

Analysis: Calc'd for $C_4H_{10}O_9N_4$: Carbon, 18.6; hydrogen, 3.91; nitrogen 21.7. Found: Carbon 18.8; hydrogen, 3.90; nitrogen 21.7.

Dinitroxydiethylamine picrate may be prepared from aqueous solutions of dinitroxydiethylamine nitrate and picric acid. After successive recrystallizations from water, isopropyl alcohol and 1:1 toluene-ethyl acetate, it melted at 136–137°.

(*b*) CONVERSION OF DINITROXYDIETHYLAMINE NITRATE TO DINA

25.8 g. (0.10 moles) of dinitroxydiethylamine nitrate was added to a solution of 0.63 g. (0.01 mole) of 99–100% nitric acid and 0.54 g. (0.004 mole) of zinc chloride in 25.5 g. (0.25 mole) of acetic anhydride. The salt dissolved after the mixture was heated to 55° C. for five minutes. The solution was then poured into 60 cc. of water and the water insoluble portion cooled and stirred until it solidified. This solid was filtered, washed with water until neutral to bromocresol green, and dried to constant weight. The crude DINA melted at 49–51° C., and weighed 22.1 g., corresponding to a yield of 92% of the theoretical. Purification by successive crystallizations from methanol, methanol-ether and benzene-petroleum ether (60–70°) raised the melting point to 51–52° C.

Analysis: Calc'd for $C_4H_8O_8N_4$: Carbon 20.0; hydrogen, 3.36; nitrogen, 23.3. Found: Carbon 20.2; hydrogen, 3.31; nitrogen, 23.0.

EXAMPLE 2

(Preparation of DINA from dinitroxydiethylnitrosamine)

(*a*) PREPARATION OF DINITROXYDIETHYLNITROSAMINE

17.3 g. (0.067 mole) of dinitroxydiethylaminenitrate in 240 cc. of water at 20° C. was mixed with 4.25 g. (0.067 mole) of 70% nitric acid and 9.25 g. (0.134 mole) of sodium nitrite in 20 cc. of water. After mixing, the reaction mixture was cooled to 0° C. and held at this temperature for 30 minutes. The solid product was filtered off, washed with water and dried in a vacuum desiccator. The yield was 14.7 g. or 97.7% of the theoretical.

Dinitroxydiethylnitrosamine is soluble in most organic solvents but quite insoluble in water and petroleum ether. It gives a violet-red coloration in the Liebermann nitrosamine test. It is rapidly decomposed upon heating in boiling water and even pure samples will decompose merely on continued standing. It ignites readily, burning to leave a brown residue. It can be detonated under impact, its sensitivity being about 2.6×TNT. Its explosive power as measured in a ballistic mortar is about 1.50×TNT.

The crude dinitroxydiethylnitrosamine melted at 46° C. It was purified by successive crystallizations from ether and from ether-petroleum ether (28–38°). The purified material melted at 46–47° C.

Analysis: Calc'd for $C_4H_8O_7N_4$: Carbon, 21.4; hydrogen, 3.59; nitrogen 25.0. Found: Carbon, 21.7; hydrogen, 3.60; nitrogen 24.9.

(*b*) OXIDATION OF DINITROXYDIETHYLNITROSAMINE TO DINA

100 g. (0.0042 mole) dinitroxydiethylnitrosamine was dissolved in 10.0 g. (0.16 mole) of 99–100% nitric acid cooled to 2–3° C. To this solution was gradually added 2.74 g. (0.0125 mole) of ammonium persulfate along with a trace of silver nitrate. The mixture was maintained at 0° C. for 15 minutes and then at 25° C. for one hour. The reaction mixture was poured on 20 g. of ice producing a precipitate which was filtered, washed with water and dried; the product weighed 0.59 g. and melted at 47–49° C. The crude material was dissolved in 7.0 cc. of 70% nitric acid and precipitated by dilution with 2 volumes of water. The recovered material melted at 50.5–51° C. and weighed 0.24 g., corresponding to a yield of 22% of the theoretical. A mixed melting point with DINA showed no depression. The DINA prepared by oxidation gave a green coloration with the Liebermann nitrosamine test rather than a violet-red color produced with the nitrosamine. A slightly improved yield (32%) was obtained by replacing the silver nitrate with 0.01 mole of zinc chloride per mole of nitrosamine and then decomposing the nitrosamine remaining in the crude product by heating the latter in boiling water.

EXAMPLE 3

(One-step preparation of DINA from diethanolamine)

A 2-gal. stainless steel jacketed kettle fitted with a thermometer and pedal stirrer rotating at 150 R. P. M. was equipped with 2 graduated dropping funnels. One of the funnels was filled with 823 g. (7.84 mole) of diethanolamine, the other with 1646 g. (25.6 moles) of 98% nitric acid (nitrous acid content 0.11%). 2754 g. (27 moles) of acetic anhydride was placed in the kettle and cooled to 5° C. by running tap water through the jacket of the kettle. 62 g. of nitric acid was run into the kettle followed by 23 g. (0.16 mole) of diethanolamine hydrochloride. With the reaction mixture maintained at 15–18° C., the remainder of the nitric acid and diethanolamine was added at proportional rates during 45 minutes. When the addition was complete the temperature of the reaction mixture was raised to 40° C. for 10 minutes after which the reaction mixture was permitted to flow into 6480 cc. of water cooled at 5° C., the water being agitated during the addition of the reaction mixture which took about 10 minutes. The product was filtered at 22° C. and washed with 25–30 l. of water until neutral to bromocresol green. An aliquot of the damp crude product was dried in a vacuum pistol above refluxing ether. The computed crude yield was 1737 g. or 90.5% of the theoretical. The filtrate remaining after separation of the precipitate was cooled to 0° C. whereupon 25 g. of DINA was precipitated, raising the total yield to 1762 g. or 91.8%. The crude product melted at 49.5–51.5°. Similar yields were obtained when 95% nitric acid was used provided enough additional acetic anhydride was added to compensate for the water present in the 95% nitric acid.

EXAMPLE 4

(Preparation of DINA from diethanolamine using nitric and hydrochlorid acids)

105 g. (1.0 mole) of diethanolamine was added dropwise to 954 g. (15 moles of 99% nitric acid maintained at 20° C. The resulting solution was cooled to 0–5° C., and hydrochloric acid gas passed into the solution until the increase in weight was

36.5 g. (1.0 mole of hydrochloric acid). The reaction mixture was then heated to 55° C. for 20 minutes and poured onto 1900 g. of ice. The crude DINA was filtered off; it melted at 49–51° C. and weighed 100.8 g., corresponding to a yield of 42% of the theoretical.

Small yields of DINA were obtained when the hydrochloric acid was replaced by phosphorus pentachloride, phosphorus trichloride phosgene and chlorine while no yield was obtained with sulfuryl chloride or thionyl chloride.

Example 5

(Purification of DINA)

1750 g. of crude DINA was added while still damp to 3800 cc. of boiling water. Steam was blown through the molten DINA for 15 minutes. The supernatant water was then decanted and the molten DINA run from a pre-warmed separatory funnel into 1100 cc. of 95–98% acetone. The acetone solution of DINA was filtered through paper and then diluted in 3800 cc. of water containing 10 cc. of 28% ammonium hydroxide solution, dilution being carried out by running the acetone in solution as a slow stream into the water which was violently stirred with a "Lightnin'" mixer (1725 R. P. M.). As the initial portion of the acetone solution was added to water, previously purified DINA was introduced in order to induce crystallization. During dilution the temperature of the water was maintained at 5–8° C. by cooling with tap water. The process of dilution required about one hour. The precipitated DINA was filtered from the acetone-water liquor using mild suction. The product was repeatedly washed with cold water until further washing failed to remove color. The purified DINA was dried in a forced draft drier operating at room temperature, 48 hours in this drier reducing the moisture content to 0.13–0.07% by weight. The usual weight of purified material was 1650 g., corresponding to a recovery of 85% of the theoretical. The purified DINA melted at 50.5–52° C. and gave an Abel heat test at 100° C. of 12–16 minutes.

An alternative method of crystallization which produces distinct crystals of DINA having a bulk density reliably higher than that produced by the process described above may be carried out where adequate stirring facilities and temperature regulation are available. This slight modification of the procedure described above depends on the formation of a finely divided DINA fast dispersed by violent agitation in water-acetone at 25° C. and is accomplished by mixing water with the DINA-acetone solution as quickly as possible, the heat of mixing being removed by means of a cooling jacket. The order of the addition of solution and diluent is not important.

In carrying out this alternative purification procedure, crude DINA was melted in a jacketed aluminum vessel and poured into acetone (0.104 Imp. gal./lb. DINA). The solution at 77° F. was filtered into 10 gal. cylindrical aluminum kettle 12" in diameter by 22" high and equipped either with a "Lightnin'" propeller type stirrer (1750 R. P. M.) or with one fitted with four flat blades $1\frac{7}{16}$" wide staggered at right angles along the shaft and sweeping a total diameter of 6½". There were no baffles in the kettle. The agitation was started at 1750 R. P. M. and water at 77° (twice the volume of the acetone employed in preparing the DINA-acetone solution) was added as rapidly as possible. The temperature rise was 3–9° F. depending on whether the kettle was one-fourth or completely filled. The heat of dilution was dissipated by cooling water in the jacket in order to hold the temperature rise to below 10° F.; if the temperature rise exceeds 10° F., the rate of crystallization is inordinately slow. Crystallization was complete in about 7 minutes as evidenced by clearing of the liquor which was then cooled to 60° F. to complete crystallization and prevent caking of the product on the nutsch. The mixture was filtered and the crystals on the nutsch were washed until acid-free and then dried in a forced air drier at 104° F.

DINA sometimes contains an impurity capable of forming a deep red water soluble derivative with ammonia. This impurity may or may not result in a product of inferior quality with respect to vacuum stability. In any event, however, if the purification procedure described immediately above is modified by adding an equal volume (0.25 volume per cent) of concentrated aqua ammonia to the acetone and if desired also to the water, the purification improves the vacuum stability of the DINA and the resulting solutions vary in color from deep red to brown. Since the addition of ammonia does not adversely affect the crystallization procedure in other respects, its inclusion in all crystallization purification of DINA is to be recommended.

Example 6

(Recovery of acetone from the purification of DINA)

The purification of DINA on the scale described in Example 5 requires 1900 cc. (1.50 kg.) of 95–98% acetone which is diluted with 3800 cc. of water to produce 5.31 kg. of 27–28% acetone solution. The recovery of acetone from the resulting solution presents few difficulties and may be accomplished by distillation of the filtered solution either with or without the addition of a small amount of lime to the acetone solution before distillation. If distillation is carried out on an acetone solution that has not been treated with lime, a very small amount (about 0.23 g./l. of dilute acetone solution) of DINA may remain in the still. If the dilute acetone solution is treated with a small amount of lime (for example 1% by weight of lime) no DINA will be found in the residual water.

Example 7

(Recovery of acetic acid from the preparation of DINA)

The preparation of DINA according to the method described in Example 3 produces about 1.96 parts of acetic acid per part of DINA, this acetic acid being obtained as a 30–33% solution containing nitric acid and organic impurities. Assuming that the DINA has been filtered from this solution at 22° C., the solution contains about 3.2 g. of DINA per liter. If the acetone solution is cooled to 0° C. before filtration, the DINA content may be reduced to about 0.8 g./l.

From the standpoint of safety it is desirable to destroy the residual DINA before the 30% aqueous acetic acid solution is concentrated. It is also desirable to remove the other impurities such as nitric acid, nitrous acid, formic acid and unidentified organic reducing substances. If the aqueous acetic acid is merely distilled without prior treatment, a distillate consisting of acetic acid contaminated with nitric acid is obtained and if the distillation is carried too far a violent explosion occurs.

The residual DINA in the dilute acetic acid may be destroyed either by refluxing the dilute acetic acid or by digesting it with 2% concentrated sulfuric acid or with 2½% sodium chloride or with sulfuric acid and either iron filings or manganese dioxide. However, the distillate obtained in all these cases contains nitric acid.

A much more satisfactory method of recovering the acetic acid is to heat the dilute acetic acid to 200° C. in a stainless steel pressure vessel for about 30 minutes, prior to distillation. The pressure digestion completely destroys the DINA and subsequent distillation of the pressure digested solution gives at least a 95% recovery of acetic acid free from significant amounts of nitric, nitrous and formic acids. Corrosion of the pressure vessel may be reduced by adding about 3 cc. of ethanol per 50 cc. of dilute acid prior to pressure digestion. Since an ester of acetic acid is customarily used as an entrainer in the concentration of dilute acetic acid, addition of an alcohol to the liquor does not introduce an undesirable contaminant. The recovery procedure is conveniently carried out by passing the liquor, heated at 200° C., through a stainless steel tube column under pressure, releasing the liquor through a degassing heat exchanger and then distilling the liquor using the heat dissipated in the heat exchanger to effect distillation.

II. THE PROPERTIES OF DINA

(a) Chemical Properties

DINA is very soluble in acetone; quite soluble in nitric acid, glacial acetic acid, methanol, ethanol, benzene and ether; and insoluble in water, carbon tetrachloride and petroleum ether.

DINA gives a red coloration with the Franchimont reagents (Rec. trav. chim. 16, 227, 1897), and a green color with the Liebermann test. It may be reduced with sodium amalgam to give a small yield of hydrazine which was identified as salicyl aldazine.

The stability of DINA in water depends upon the temperature. Thus 5 g. of DINA were shaken with 10 cc. of water for six weeks at 25° C.; a 99.2% recovery of DINA was obtained, the water remaining neutral to indicators. A 39% loss occurred when DINA was heated in boiling water for six hours. DINA was completely destroyed after heating for one hour and 10 minutes in an equal weight of boiling 5% aqueous sodium hydroxide.

DINA is rapidly decomposed in concentrated sulfuric acid even at 0° C. On the other hand when DINA was maintained in solution in glacial acetic acid or 99% nitric acid for three hours at 25° almost no loss of DINA occurred.

Pure DINA shows no gassing when heated to 100° C. About 165° C. slow evolution of gas begins and above about 180–185° C. the formation of nitrogen oxides is vigorous. No ignition was obtained when a small quantity of DINA was heated to 240° C. at the rate of 5° per minute; the sample, however, decomposed between about 180° and 200° C. Ignition was obtained when DINA was dropped into a test tube maintained in a bath heated to 200° C. but no ignition was obtained at lower temperatures.

3 g. of DINA were introduced into a test tube ⅝" in diameter, gently shaken down and subjected to flash from a piece of C. I. L. "Cloverleaf" fuse resting vertically on the surface. Ignition was not obtained nor did ignition take place under similar circumstances when the lower end of the fuse was split.

A train of DINA was laid in an iron trough of semi-circular section ½" in diameter. The trough was heated at one point until ignition of DINA took place at the point immediately above the flame; the material did not burn beyond the point of ignition.

(b) Physical Properties

Pure DINA melts at 51–52° C. It may be cast to a density of 1.67. Its heat of fusion is 23.5±0.2 cals./g. and its specific heat is 0.38±0.02 cal./g.

A determination of hygroscopicity at room temperature showed no gain at 90% relative humidity and a 0.002% gain at 100% relative humidity.

DINA crystallizes from acetone in the form of flattened prisms. DINA exhibits polymorphism and four different polymorphs may exist.

(c) Physiological Effects of Dina

DINA appears to have no significant toxic properties. When fed to a dog it caused some formation of methaemoglobin but there was no evidence of haemoglobin destruction. It was applied to rabbits in a salve without effect.

(d) Explosive Properties

DINA was not detonated when struck on stone or wood with a rawhide mallet. Detonation was obtained however when DINA on steel or stone was struck with a steel hammer. The impact sensitivity of DINA appears to be about 3.2×TNT. No detonations could be obtained on a sliding shot friction impact machine at a maximum fall with a 12 lb. shot.

Rifle tests showed DINA to be sensitive. A block 2"×2"×4" (density, 1.60) was faced with ⅛" mild steel and backed by ⅜" mild steel. It detonated completely when struck squarely by a .303 rifle bullet. A second block which was backed by 1" mild steel but without facing was shattered by a rifle bullet with no indication of explosion.

The sensitivity of DINA to influence was determined by placing a sample of well-cast DINA (density 1.6) at a measured distance from 4" lengths of 1" diameter 60 polar dynamite. The DINA fired when the distance was 0, ½" and 1" and failed at 1". In a similar test with granular DINA, the sample fired at 1", 2" and 3" and no failures were obtained.

The explosive power of DINA as measured in the ballistic mortar is approximately 1.48×TNT for well-cast DINA and 1.45 for granular DINA.

20 g. cast blocks of DINA were fired with a No. 8 E. B. cap upon 4"×4"×¼" mild steel plates. Clean holes similar to that produced by high density cyclonite were blown through plates laid on clean Ottawa sand.

The rates of detonation of DINA at different densities lies slightly below those of cyclonite.

(e) Use of Dina in Demolition

Four 2"×2"×4" blocks of DINA (density 1.60) were exploded on top of a 2' cube of concrete. Three of the DINA blocks were laid side by side and the fourth block placed on top, the upper block being fired by a No. 8 detonator. The concrete was completely reduced to rubble 2"–3" in diameter together with much dust and fines.

In another experiment a MK–111 shaped charge was filled by pouring into it a mixture of water and molten DINA, the excess water being run off to leave a container full of DINA which solidified overnight. The shaped charge was fired on 10" of mild steel, No. 8 cap and a 1 oz. CE

primer being used to obtain detonation. The steel plate was completely pierced and the scab on the steel was driven 20'' into the earth and rock.

(f) USE OF DINA IN PROPELLANT COMPOSITIONS

DINA offers several properties which will recommend it as a component for high power propellants. Its calorific value is about 1260–1350 cals.

Nitrocellulose colloids containing DINA have greater force than comparable propellant containing nitroglycerine. Moreover, the tensile strength of propellant containing, for example, 40% DINA is 1225 lbs./sq. in. as compared with a comparable propellant containing 40% nitroglycerine with tensile strength of 800 lb./sq. in. The stiffness of the former is 29 "Smith-Tabor" units as compared with 15 units for the latter. Because of such mechanically advantageous properties the composition of propellant containing DINA can be varied conveniently over wider limits than can those containing nitroglycerine and, especially than those containing diethyleneglycol dinitrate. Moreover compositions containing DINA are safer to manufacture than those containing nitroglycerine and are more stable in storage. Examples of such propellant compositions are:

(1) 49% nitrocellulose (13.1% N), 48% DINA and 3% carbamite (ethyl centralite).

(2) 57% nitrocellulose (12.6% N), 35% DINA and 8% carbamite.

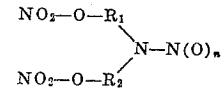
In connection with this particular application of DINA reference is made to the copending application of John F. Kincaid, Ser. No. 570,808, filed of even date herewith, which describes and claims a flashless, high velocity propellant composition containing nitrocellulose plasticized with DINA together with nitroguanidine as a coolant.

Certain nitroxyalkylamine nitrates such as that obtained by treatment of various ethanolamines with nitric acid have been disclosed in the prior art. Thus Herz (German Patent 630,079) describes the pentanitrate of the quaternary base prepared from triethanolamine and ethylene oxide. Likewise, "Dynamit act Gesellshaft" (French Patent No. 639,632; German Patent No. 500,407 and 513,635; and British Patent 357,581) described the nitration of monoethanolamine. The first of these "DAG" patents also mentions a "trinitrat" of diethanolamine as having a melting point of 120 C. which identifies it as bis(nitroxyethyl)amine nitrate, Moreover, Aubry in Men. poudres, 25, 189–193 (1932–33) in discussing the preparation of "Monoethanolamine dinitrate" states that the nitrates of di- and tri-ethanolamines are unstable, thus indicating that he has prepared bis(nitroxyethyl) amine nitrate which is of course merely a "starting material" for the preparation of DINA according to one method of the present invention. It is therefore apparent that the compounds of the present invention are new products having decidedly different properties from those of the unstable amine nitrates of the prior art.

It will be apparent to those skilled in the art that many variations may be made from the above detailed description of the preferred embodiment of the present invention. Thus, for example, as an obvious variation of the preparative method described in Example 1, the diethanolamine may be mixed with nitric acid in the proper proportions necessary to form the nitrate, the resulting mixture cooled and then used as a liquid feed to a vessel containing acetic anhydride and the chloride catalyst, this modification obviating the isolation of the amine salt as a solid material. Other lower fatty acid anhydrides, such as those of propionic and butyric acids may be used although acetic anhydride is preferred under existing market conditions. Many other variations and modifications will be readily apparent to those skilled in the art. It is to be clearly understood that all such modifications and variations are embraced within the scope of the appended claims.

We claim:

1. As a new composition of matter, a member of the group consisting of the nitramines and nitroso-amines having the structural formula



wherein R_1 and R_2 are alkylene radicals and n is a whole number less than 3.

2. A method of preparing bis-nitroxyethylnitramine which comprises treating diethanolamine with nitric acid to form a nitrate and treating the product with nitric acid and a lower fatty acid anhydride in the presence of a chloride catalyst.

3. A method of preparing bis-nitroxyethylnitramine which comprises treating diethanolamine with nitric acid and a lower fatty acid anhydride in the presence of a small proportion of a chloride salt as a catalyst.

4. A method of preparing bis-nitroxyethylnitramine which comprises treating diethanolamine with nitric acid and acetic anhydride in the presence of a small proporton of diethanolamine hydrochloride, said reactants being employed in the proportions of at least 3 moles of nitric acid and at least 4 moles of acetic anhydride per mole of diethanolamine.

5. A method as defined in claim 2 wherein the product is purified by treating the same with boiling water, passing steam through the molten nitramine, separating the molten nitramine from the supernatant water, dissolving the nitramine in a water-miscible solvent and then diluting the solution with water whereby to precipitate purified bis-nitroxyethylnitramine.

6. A method as defined in claim 2 wherein the catalyst is zinc chloride.

7. A new composition of matter as defined in claim 1 in which the alkylene radicals are CH_2—CH_2 and n is 2.

8. A new composition of matter as defined in claim 1 in which the alkylene radicals are CH_2—CH_2 and n is 1.

GEORGE F. WRIGHT.
WALTER JOHN CHUTE.

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The following references are of record in the file of this patent:

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