

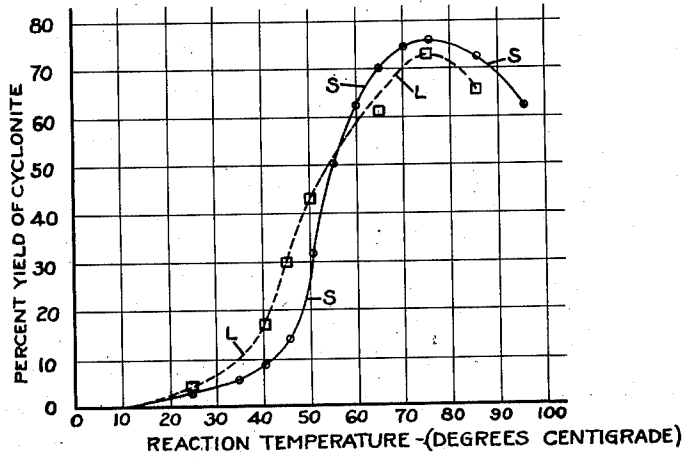
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METHOD FOR PREPARING EXPLOSIVES

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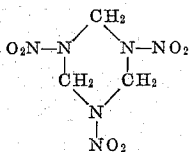
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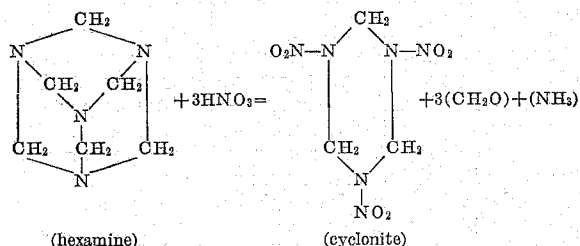
The present invention relates generally to explosives, and more particularly to a new and improved method of preparing a high explosive of great power and brisance.

The explosive material with which the present invention is primarily concerned is a substance which has a molecular formula of $C_3H_5O_6N_6$, and a melting point in the pure state of approximately $205^\circ C$. While its constitution is not known with complete certainty at the present time, in all probability it has the structure:



and therefore, on this assumption, its systematic chemical name is cyclotrimethylenetrinitramine. It has also been variously called "Hexonite," "Hexogen," "T₄," "C₆," and "cyclonite." As a matter of convenience, however, the term "Cyclonite" will hereinafter be used to designate this material.

The explosive in question appears to have been discovered by Henning (D. R. P. 104,280, June 14, 1899), who prepared it by converting hexamethylenetetramine (hereinafter called "hexamine"), to the corresponding dinitrate and then adding the dried dinitrate to cold, very concentrated nitric acid. For a number of years little interest was shown in the new explosive. However, when the development of synthetic methanol opened the door to explosives based on formaldehyde, interest in cyclonite was renewed, and between 1919 and 1921, von Herz (D. R. P. 298,539 and 299,028; G. B. 145,791; Swiss 88,750; U. S. 1,402,693) disclosed a so-called "direct nitration" (nitrolysis) method of preparing cyclonite by treating hexamine directly with cold, concentrated nitric acid, according to the scheme indicated below and referred to herein as Scheme 1 or Equation 1:

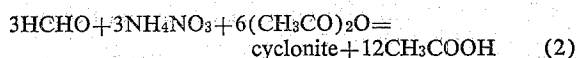


While the reaction by-products are indicated in Equation 1 as "3(CH₂O)" and "(NH₃)" these compounds do not actually appear as such, inasmuch as carbon dioxide, apparently two nitrated formaldehyde products, and oxides of nitrogen are obtained under reaction conditions.

The von Herz "direct nitration" method, while superior in certain respects to Henning's two-step process, was characterized by a number of significant disadvantages. In the first place, although only three moles of nitric acid

are theoretically required by Equation 1, in actual practice a very large excess of nitric acid (from 20 to 25 moles per mole of hexamine) is required to obtain yields of 80 to 85%. (See, for example, Hale, Jour. Amer. Chem. Soc., 47, 2754 (1925).) In the second place, the reaction is frequently accompanied by a violent fume-off which renders large scale manufacture hazardous and difficult to control. Thirdly, that portion of the hexamine molecule which is represented in the projection formula as in the middle of the ring (the so-called "central part" of the hexamine) represents one-half (3 moles) of the six moles of formaldehyde required for the preparation of the hexamine. This "half-equivalent" of formaldehyde represented by the "central part" appears to be completely wasted in the direct "nitration" process, through eventual conversion to carbon dioxide and other reaction products. Moreover, the loss of the "half-equivalent" of formaldehyde is attended by a reduction of a large amount of nitric acid to N₂O₄. Accordingly, in large scale manufacture, a very large proportion of the equipment is represented by apparatus for the re-recovery of nitric acid and the oxides of nitrogen, and even though this recovery apparatus may obviate serious nitrogen loss, it will be apparent that the formaldehyde which is oxidized to CO₂ is irretrievably lost. Accordingly, the loss of the "half-equivalent" of formaldehyde per mole of hexamine, and the enormous nitric acid recovery problem, constitute the main defects of the direct "nitration" process.

Despite the many disadvantages of the direct "nitration" processes, for over forty years the foregoing degradative procedures of Henning and of von Herz appear to have been the only known methods available for cyclonite production. Within recent times, however, a synthetic method has been described by Schiessler and Ross in U. S. application Ser. No. 444,254, filed May 23, 1942. This method (which is known as the so-called "McGill Process") involves the treatment of formaldehyde (e. g. in the form of paraformaldehyde) with ammonium nitrate at 60 to 85° C. in the presence of a dehydrating agent (e. g., acetic anhydride) according to the overall Equation 2:



By the foregoing method, cyclonite may be obtained in yields as high as 50 to 55% of the theoretical, based on the material balance indicated by the overall Equation 2.

Now, as indicated in connection with Scheme 1, in the degradative "nitration" process, the three moles of formaldehyde (represented by the "central part") are destroyed per mole of cyclonite produced. On the other hand, in the more recent Schiessler and Ross synthetic method, three moles of formaldehyde are required per mole of cyclonite produced (Scheme 2). It was accordingly of interest to determine whether the formaldehyde lost in the degradative "nitration" process, could be usefully employed in the synthetic process. This proposal neglected important considerations of mechanism, since the wasted "formaldehyde" in the direct "nitration" process appears as certain formaldehyde-nitration products, and ultimately as CO₂, rather than as formaldehyde. Nevertheless, prior investigators carried out the direct "nitration" process in the presence of "ammonia donors" (e. g., ammonium nitrate) in the hope that the wasted formaldehyde might combine with the ammonia donor to reform hexamine and thus be returned to the main reaction. The results, however, gave little encouragement that such a process would effect an appreciable improvement in yield, and indicated that the reaction products of the lost "half-equivalent" of formaldehyde would

not combine with ammonium nitrate in the presence of strong nitric acid to yield cyclonite.

The object of the present invention is to provide a new and improved method of preparing cyclonite from hexamine, whereby two moles of cyclonite are theoretically obtainable from one mole of hexamine, and which actually produces in excess of one mole of cyclonite per mole of hexamine.

A further object is to provide what may loosely be termed a "combination process" wherein both the "degradative" and "synthetic" processes of the prior art may be considered as taking place concurrently.

Another object is to provide a process which is capable of producing higher actual yields of cyclonite per mole of hexamine—assuming optimum conditions and yields in each case—than the aggregate yield obtainable by first carrying out the "direct nitration" process on one mole of hexamine, and then separately carrying out the "McGill process," starting with paraformaldehyde in an amount equivalent to all the formaldehyde "lost" in said direct "nitration" process.

A further object is the provision of a process for preparing cyclonite which obviates the enormous nitric acid requirements of the "direct nitration" process and which requires much less acetic anhydride than the "McGill process."

Still another object is a method of preparing cyclonite which requires less ammonia and formaldehyde equivalents per pound of cyclonite produced, than any previously known method.

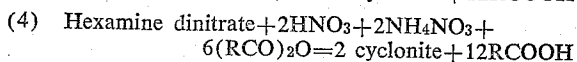
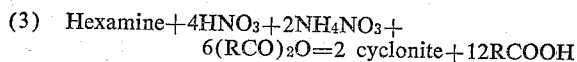
Other objects and advantages will be apparent as the invention is hereinafter more fully described.

As a result of an extended investigation, it has been found that the foregoing objects and advantages may be attained by the process of the present invention, which involves the treatment of a hexamine compound with an ammonia donor and nitric acid under conditions effecting the elimination of the elements of water, the reaction being carried out under certain critical temperature conditions, as hereinafter explained.

The hexamine compound mentioned in the preceding paragraph may consist of hexamine itself, or a hexamine derivative such as a hexamine salt, for example, hexamine acetate, hexamine mononitrate, hexamine dinitrate and the like. The ammonia donor preferably consists of ammonium nitrate, although other ammonium salts such as the acetate and similar equivalent materials may be employed if desired. The elimination of the elements of water is effected in the presence of a volatile fatty acid anhydride, such as a lower fatty acid anhydride, for example, acetic anhydride, propionic anhydride, butyric anhydride and the like, which combines with the eliminated water.

The conditions prevailing when the foregoing reactants are brought together, exert an important influence on the course and extent of the reaction. As a matter of convenience, these conditions may be classified as (1) preferred proportions of reactants and (2) critical ranges of temperature at which the reaction may be carried out.

Considering firstly the preferred proportions of reactants, it has been found that the optimum conditions for the reaction approach those indicated by the theoretical material balance of the overall equations, which (in the case of hexamine and hexamine dinitrate) may be written as follows:



In most cases, an excess of nitric acid, ammonia donor and dehydrating agent over the theoretical amounts required by the overall Equation 3 or 4, are usually desirable. Thus when hexamine itself is employed, excellent yields of cyclonite (over 75% of the theoretical, based

on Equation 3, supra) may be obtained using approximately 2.3 to 3.2 moles of ammonium nitrate, 4.5 to 5 moles of 98% nitric acid and 6.8 to 8.0 moles of acetic anhydride per mole of hexamine. Likewise with hexamine dinitrate, excellent yields (over 80% of the theoretical, based on Equation 4, supra) may be obtained using approximately 2.3 to 3.2 moles of ammonium nitrate, 2.4 to 2.8 moles of 98% nitric acid, and 6.8 to 8 moles of acetic anhydride per mole of hexamine dinitrate.

While the foregoing proportions are preferred, satisfactory yields of cyclonite may be obtained over a wide range of operating conditions, particularly if the reaction temperature and time are varied to suit the particular proportions of reactants selected for carrying out the reaction. Thus for example, Table I gives illustrative ranges for each of the reactants, which may be used to give satisfactory yields of cyclonite when the reaction is carried out at about 60–75° C. For optimum yields, particularly where it is desired to lower the consumption of reactants, the ammonium nitrate and nitric acid are preferably reduced roughly in the same molecular proportions.

TABLE I. MOLAR PROPORTIONS OF REACTANTS

Hexamine	Nitric Acid (98%)	Ammonium Nitrate	Acetic Anhydride
1	4 to 6	2 to 4 (or more)	6 to 8
Hexamine dinitrate	Nitric Acid (98%)	Ammonium Nitrate	Acetic Anhydride
1	2 to 4	2 to 4 (or more)	6 to 8

It will thus be evident that a wide choice in the proportions of reactants is available to the operator in carrying out the process of the present invention. Moreover, nitric acid less concentrated than 98% (e. g., 70%) may be employed, provided additional anhydride is used in an amount equivalent to the water present in the less concentrated nitric acid.

Before leaving the discussion of reactant proportions, it is deserving of emphasis that all four reactants (i. e., hexamine compound, ammonia donor, nitric acid and fatty acid anhydride) appear to be essential to the reaction. If any one of these four is omitted, substantially no cyclonite is obtained. Thus, in one experiment where ammonium nitrate was the only reactant omitted, substantially no cyclonite was produced at 75° C., although it might be expected that at this temperature the "direct nitration" reaction might take place between the hexamine and the nitric acid. Such however, does not appear to be the case, except to a very limited extent (e. g., about 2%). Accordingly, all four reactants are considered necessary to the production of cyclonite by the process of the present invention.

Referring now to the critical temperature for the preparation of cyclonite, there is, in general, an unusually narrow minimum temperature range for each specific set of reaction conditions (e. g., proportions of reactants, time of reaction and details of procedure). If the proportions of reactants or the time of treatment or the details of procedure, are changed, this narrow minimum temperature for cyclonite production may shift somewhat. Generally speaking, however, the minimum temperature range for appreciable cyclonite yields will be found to lie somewhere above approximately 35° C. to 40° C.

The foregoing general principles may best be illustrated by reference to the single figure of the appended drawing which is a graphical representation of the effect of time and temperature changes on cyclonite yield when the reaction is carried out in all cases with the same proportions of reactants and the same general procedure. Curve S (solid line) shows the effect of temperature on yields of cyclonite when the reaction time is relatively short (12½ minutes). Curve L (broken line) shows the tem-

perature effect when the reaction time is relatively long (45 minutes). In each case the reactants were used in the following proportions: hexamine, 33.6 g.; nitric acid (98%), 75 g.; ammonium nitrate, 55 g.; and acetic anhydride, 180 cc. Except for the variations indicated, the procedure in all cases was substantially otherwise identical with that described hereinafter in connection with Example IV.

By inspection of the two curves shown in the drawing it will be evident that the effect of temperature on the yield is unusually pronounced in both instances. Moreover, in the case of the relatively short reaction time (curve S) the minimum temperature appears to lie above 40° C., whereas for the relatively long reaction time, the minimum lies above about 35° C.

It should be noted that the temperature-yield relationship shown in the drawing applies, strictly speaking, only to the particular proportions of reactants (mentioned above) which were maintained in obtaining the data for the graph. If the proportions of reactants, or the time of treatment, or both are modified, the curve may be somewhat displaced to the left or right on the horizontal axis, and the shape of the curve may also be altered. Thus an increase in the reaction time tends to raise the yields at the lower reaction temperature. However, the graph gives a general picture of the pronounced effect of temperature on the yield for any specific reaction condition. Moreover, it appears generally to be true that the minimum critical temperature for cyclonite production lies somewhere above about 35° to 40° C.

If the reaction is carried out below this minimum temperature range (for example, at 30-35° C.) the principal reaction product is usually a substance melting at about 154° C. which appears to have at least one acyl group in the molecule. At temperatures somewhat above the minimum range given above, cyclonite will be obtained in varying yields depending on the time of reaction and proportions of reactants used. The cyclonite so obtained may contain the above low-melting impurity to a varying but usually small degree, depending on the precise conditions obtained during the reaction. This impurity, however, is readily removed by digesting the unneutralized reaction mixture with water at 90-100° C. for 1½ to 12 hours, which converts the low melting compound to water soluble and volatile products without, however, detrimentally affecting the cyclonite. If the preparative reaction is carried out at temperatures 15 to 30° above 35 to 40° C. the amount of low-melting impurity is considerably decreased, while the yield of cyclonite improves. Thus the optimum temperature range for cyclonite production appears to be between 50 to 90° C., and for commercial operations 60 to 75° C. will usually be found to be most satisfactory.

In regard to a possible "ceiling" reaction temperature for cyclonite preparation, as the temperature increases, the yield and quality of the crude cyclonite may fall off somewhat at temperatures above about 80-85° C. Cyclonite has, however, been obtained above this temperature (e. g., 95° C.). The actual maximum temperature at which cyclonite is to be produced should be determined with reference to safety considerations, and from this point of view one hesitates to run the reaction above 100° C.

In addition to the low-melting, readily removable by-product mentioned above, the cyclonite produced by the process of the present invention may also contain a high-melting compound (M. P. about 279-280° C.) in varying amounts (up to 10%, for example), depending on the proportions and conditions employed. This compound, however, appears to be an explosive substance quite similar to cyclonite in explosive power and brisance, and is believed to be a homologue of cyclonite (i. e., cyclotetramethylenetetranitramine) for which reason it may conveniently be designated by the trivial term, "homocyclonite." Regardless of its structure, the presence of

homocyclonite in the cyclonite produced by the process of the present invention is not objectionable from the point of view of ballistic power and brisance of the product and therefore homocyclonite is not to be regarded as an undesirable "impurity" in the cyclonite produced by the present process. For this reason, conditions which favor the formation of relatively high proportions of homocyclonite (e. g., up to 10%) as a "by-product" in cyclonite production are not objectionable in respect to the explosive power of the product. These homocyclonite-favoring conditions appear to include high anhydride and low nitric acid proportions.

Where preferred, additional materials may be employed, for example, as reaction media or as solvents for one or more of the reactants. Thus, the mother liquor from a previous run may be used as a reaction media, or the hexamine may be dissolved in a suitable inert solvent, for example, a substantially anhydrous lower fatty acid such as glacial acetic acid. Moreover, by the use of a hexamine solution in conjunction with a suitable combination of the other reactants; a procedure may be employed wherein all the reactants are charged to the reaction vessel in liquid form. Thus the hexamine may be dissolved in acetic acid and the ammonium nitrate in the nitric acid, with acetic anhydride as the third liquid, to provide an "all-liquid-feed" modification within the ambit of the present invention. The details of this "all-liquid-feed" modification are more particularly described and claimed in the copending application of George F. Wright, Douglas C. Downing and Henry H. Richmond, Serial No. 495,082, filed July 16, 1943, issued as Patent No. 2,434,879, January 20, 1948.

In order more clearly to disclose the nature of the present invention, several illustrative embodiments will hereinafter be described in considerable detail. It should clearly be understood, however, that this is done solely by way of example, and is not to be construed as in any manner limiting the spirit or scope of the appended claims.

Example I

(SOLID AND LIQUID FEEDS, USING HEXAMINE DINITRATE)

A five necked, 1-liter flask was used (one neck for an efficient mechanical stirrer, one for a thermometer, two for burettes, and a large flanged one for the addition of solid). The flask was placed in a water bath not much larger in diameter than itself. This bath was equipped with a thermometer and could be heated by steam and cooled by running water.

Three operators are desirable to regulate the addition and control the temperature for the reaction. Sixty-five grams of hexamine dinitrate was divided into 26 substantially equal portions (each portion was weighed into a test tube for convenience in handling); 145 cc. of acetic anhydride was placed in a burette calibrated in 26 substantially equal portions; and 26 cc. of 98% nitric acid was placed in another burette calibrated in 28 substantially equal portions.

At the beginning of the run, 50 g. of dry ammonium nitrate (60-120 mesh) and 30 cc. of glacial acetic acid were placed in the flask. The temperature was raised to 75° C. and 30 cc. of acetic anhydride was added (this is 30 cc. in addition to the 145 cc. in the burette). The resulting mixture was quite fluid and easily stirred. Efficient agitation is essential for optimum yields.

A quarter portion of hexamine dinitrate was added to the mixture in the flask. This serves to inhibit the violent reaction between the acetic anhydride and the nitric acid. Two portions of nitric acid were then slowly added. The third portion of nitric acid was then added simultaneously with the addition of the first portion of acetic anhydride and the remaining three-quarters of a portion of hexamine dinitrate.

The remaining 25 portions of the three reagents were then added equivalently and simultaneously (i. e., quar-

ter-portion for quarter-portion) over a period of about twelve minutes. The temperature within the flask was maintained at 74–76° C. throughout the addition. The first operator added the nitric acid and watched carefully the inside and outside temperatures, regulating the steam and cooling water. The second operator added the acetic anhydride to correspond to the addition of the nitric acid and, watching the nitric acid burette, called off the addition in quarter-portions (i. e., one-quarter, one-half, three-quarters, all added). The third operator added the solid (hexamine dinitrate) to correspond to the addition of the nitric acid; he added a quarter of the contents of a test tube at a time. The addition of the liquids was continuous, and that of the solids, effectively so (i. e., in 100 quarter-portions).

After the addition was complete, the mixture was stirred for 15 minutes at the same temperature. The water bath was then removed and the mixture was allowed to cool to 60° C. (about 10 min. were required). It was then filtered through a warm, coarse Jena funnel. The first-crop product was washed with 30 cc. of cold glacial acetic acid, and then with two 50 cc. portions of hot water. The air-dried product was granular and of good appearance; M. P. 201–203° C. (corr.) with previous softening; yield, 81.1 g. or 75% of the theoretical, based on Equation 4, supra, representing an actual yield of about 1.5 moles of first-crop, high grade cyclonite per mole of hexamine dinitrate. A second crop of less pure cyclonite may be obtained by drowning the filtrate in an equal volume of water, then digesting the mixture for one hour or more at about 95° C. and cooling. In this manner, from 8 to 10 grams of less pure cyclonite, melting at about 190–200° C., may be recovered from the filtrate.

The reaction may be run more slowly, the reagents being added over a one or two hour period. The temperature of the reaction mixture may be maintained at 65° C. if desired, essentially the same results being obtained with these modifications. The longer the time of addition, the lower the reaction temperature, within limits. If it is desired to reduce the number of liquid feeds, the nitric acid may be mixed with the acetic anhydride. In this case however, the nitric-acid-acetic anhydride mixture should be prepared and used at low temperatures (e. g., 5–15° C.) as soon as prepared.

Example II

(SOLID AND LIQUID FEEDS, USING HEXAMINE INSTEAD OF THE DINITRATE)

The apparatus was the same as that described above. 33.6 g. of hexamine, 43 cc. of 98% nitric acid and 160 cc. of acetic anhydride were used. Addition of the reagents required about 15 minutes. The temperature was maintained at 73–77° C. during the reaction. Before the other reagents were added, 50 g. ammonium nitrate was placed in the flask together with 30 cc. of the cool, clear mother liquor from a previous run. The procedure was similar to that used in Example I. After portion number 5 of the other reactants was added, 25 g. of additional ammonium nitrate was added to the reaction mixture. In a typical run, a yield of 73% of the theoretical (based on Equation 3, supra) was obtained; M. P. (corr.) 197–202° C. This represents an actual yield of approximately 1.46 moles of first-crop cyclonite per mole of hexamine employed. A second-crop may be obtained from the filtrate by the procedure described in Example I. As in Example I, the second-crop cyclonite is less pure than the first-crop and may contain a relatively high proportion (e. g., 10 to 20%) of homocyclonite.

Example III

(ALL-LIQUID FEED TO SUSPENSION OF AMMONIUM NITRATE IN Ac_2O , USING HEXAMINE INSTEAD OF THE DINITRATE)

In a 1-liter five-necked flask equipped with a mechanical stirrer, a thermometer and three burettes, are placed

65 g. of ammonium nitrate (granular or finely divided) dried at 50° C. for 18 hours, and 60 cc. of 95% acetic anhydride. The mixture is stirred and heated in a water bath 75° C. (internal temperature). To the hot mixture are added separately and concurrently, from the three burettes (Note 1, infra), 130 cc. of 95% acetic anhydride, 43 cc. (64.5 g.) of 98% nitric acid, and a solution of 33.6 g. of hexamine in 53 cc. of glacial acetic acid (Note 2, infra), during a period of about fifteen minutes.

The temperature is held at 74–76° C. during additions. The reaction mixture is heated at 74–76° C. with stirring for five to fifteen minutes after the reactants have been introduced.

Without cooling, the mixture is diluted to a concentration of about 30% acetic acid by the addition of 675 cc. of warm water (60° C.) and then heated on the steam bath (90–100° C.) with stirring for one to twenty-four hours. This digestion step destroys the low-melting impurities, as more particularly described and claimed in my copending application, Serial No. 495,079, filed of even date herewith, now Patent No. 2,680,651.

The mixture is cooled to 20° C., with constant stirring, and filtered immediately by suction. The white, glistening, sandy single-crop crystals are washed with four 50 cc. portions of warm water (60° C.) and oven dried at 50° C. The yield is 76–79 g., or 71–74% of the theoretical based on Equation 3, supra, representing about 1.4 moles of cyclonite per mole of hexamine; M. P. 196–197° C. (corr.) with previous softening at 191° C. The main filtrate (but not the washings) is reserved for recovery operations.

In some instances better yields may be obtained with the above procedure if slight variations are made; for example, by adding some acetic acid and a small amount of the nitric acid to the acetic anhydride in the flask at the start of the reaction. Another alternative is to maintain the above described reaction mixture at 54–58° C., rather than at 75° C., with no other changes. The yields obtained with either of these modifications run as high as 82% of the theoretical, based on Equation 3, supra.

Note 1.—In order to secure a uniform introduction of the reactants in equivalent amounts, the three burettes were marked with calibrations corresponding to 25 cc. portions of each reactant.

Note 2.—This solution has a volume of about 75 cc. Since the solution is quite viscous and does not drain readily in the burette, it is convenient to prepare a small excess of the solution and determine the amount actually introduced by difference in weight.

Example IV

(“ALL-LIQUID-FEEDS,” USING HEXAMINE INSTEAD OF THE DINITRATE)

A yield of 70–90% cyclonite may be obtained by a modification of the procedure described in Example III, which permits the use of “all-liquid-feeds.” In this modification, the first liquid feed consists of the ammonium nitrate dissolved in the nitric acid with the formation of a clear, water-white solution (after the evolution of oxides of nitrogen). The second liquid feed consists of the hexamine dissolved in glacial acetic acid. The acetic anhydride constitutes the last liquid feed.

Thus, a solution of 55 g. ammonium nitrate in 50 cc. 75 g.) of 98% nitric acid was prepared and placed in one burette. In another burette was placed 150 cc. of acetic anhydride while in a third burette was placed a solution of 33.6 g. of hexamine dissolved in 55 g. of acetic acid, 6 cc. of the ammonium nitrate-nitric acid solution in the one burette was added to 30 cc. of acetic acid and 30 cc. acetic anhydride (this amount is in addition to the 150 cc.) in the reaction flask. Thereafter the remaining three liquids in the three burettes were all added concurrently and equivalently. The reaction conditions and procedure were otherwise similar to those described in Example III.

Certain aspects of the "all-liquid-feed" modifications of the present invention are more particularly described and claimed in the aforesaid application of George F. Wright, Douglas C. Downing and Henry H. Richmond, Serial No. 495,082, filed July 16, 1943, issued as Patent No. 2,434,879, January 20, 1948.

PURIFICATION

The cyclonite produced in accordance with the present invention may be purified, if desired, either by recrystallization from any convenient cyclonite-solvent, (for example, 70% nitric acid, 50% acetic acid, dioxane, monobutyl ether of ethylene glycol, nitromethane, acetone, and the like); or by digestion with dilute nitric acid in an amount insufficient completely to dissolve the crude material. A particularly advantageous method of effecting the first-mentioned method of purification (i. e., recrystallization) is more particularly described and claimed in the copending application of Johnson, Blomquist and McCrone, Serial No. 495,081, both of which are filed on even date herewith.

The second-mentioned method of purification (i. e., digestion with dilute nitric acid) is illustrated in the following example.

Example V

(PURIFICATION)

The first-crop material of Example I (melting point 201–203° C. corr.) was stirred with 55% nitric acid at 70° C. for one-half hour, 25 cc. of nitric acid being used for every 5 g. of crude cyclonite. During the digestion, some gas was evolved as the nitric acid attacked and destroyed oxidizable impurities. The digested mixture was then cooled and the solid filtered. A 96% recovery of high grade cyclonite, melting at 205–206° C., with no softening below 200° C., was obtained. The second-crop material from Example I and II (which usually contains considerably more homocyclonite than first-crop material) may also be purified by digestion in a similar manner but with a somewhat longer period of digestion. Likewise the single-crop product obtained in Examples III and IV (which is intermediate in purity between the first and second-crop materials of Examples I and II) may be purified by the same general procedure. If the digestion is carried out for several hours (e. g., 6–7 hours) the crystals increase in particle size.

If desired, the filtrate from the digestion procedure may be used to digest further quantities of crude product. In some instances it may also be desirable to dissolve the crude cyclonite in 70% nitric acid and then to dilute the solution to 55% nitric acid strength (thereby partly precipitating the material), before carrying out the digestion. Regardless of the details employed, however, the digestion procedure may be used to effect a substantial improvement in the size and quality of the cyclonite crystals (where the starting material is inferior in this respect), and also to destroy many of the oxidizable impurities which may be present in the material prior to treatment. If it is desired to lower the acidity of the digested material, the product may be ground and digested with a large volume of boiling water, or the acid-digested product may be purified by recrystallization, for example, in accordance with the procedure set forth in the above-identified copending applications.

Another method of purification which may be used, if desired, is to digest the crude cyclonite with hot water containing either a small amount (e. g., 25%) of acetone, or a small amount (e. g., 1%) of a buffering agent such as sodium tetraborate or sodium perborate. Thus the crude cyclonite may be poached at 75° C. for 3 to 6 hours with water containing 1% perborate. The thus purified material generally exhibits an increased frothing point and melting point, and is neutral to methyl red.

It will be apparent to those skilled in the art that the

present invention has been described in great detail in the foregoing specification and also that many variations may readily be made without departing from the spirit and scope of the invention. I therefore intend to be limited only in accordance with the following patent claims.

I claim:

1. A process of producing an explosive, which comprises reacting a hexamine compound selected from the group consisting of hexamine itself and hexamine salts, with an ammonia-yielding ammonium salt, concentrated nitric acid and a lower fatty acid anhydride, the reaction being carried out at a temperature above about 35° to 45° C.
2. A process of preparing cyclonite which comprises reacting a hexamine compound selected from the group consisting of hexamine itself and hexamine dinitrate, with ammonium nitrate and concentrated nitric acid in the presence of a fatty acid anhydride, said reactants being used approximately in the proportions of two to four moles of ammonium nitrate, four to six moles of concentrated nitric acid and six to eight equivalents of anhydride per mole of hexamine compound in the case of hexamine itself, and approximately in the proportions of two to four moles of ammonium nitrate, two to four moles of concentrated nitric acid and six to eight equivalents of anhydride per mole of hexamine compound in the case of hexamine dinitrate.
3. The process of claim 2 wherein said anhydride comprises acetic anhydride.
4. The process of claim 2 wherein said reaction is carried out at a temperature above about 35°–45° C. and below about 100° C.
5. A process of preparing cyclonite which comprises treating hexamine with ammonium nitrate and concentrated nitric acid in the presence of acetic anhydride, approximately in the proportion of 2.3 to 3.2 moles of ammonium nitrate, 4.5 to 5 moles of concentrated nitric acid and 6.8 to 8 moles of acetic anhydride per mole of hexamine, said reaction being carried out at a temperature sufficient to effect the formation of more than one mole of cyclonite per mole of hexamine.
6. The process of claim 5 wherein said reaction is carried out at a temperature above about 35 to 45° C. and below about 100° C.
7. The process of claim 5 wherein said reaction is carried out at 60–75° C.
8. The process of preparing cyclonite which comprises reacting hexamine dinitrate with ammonium nitrate and concentrated nitric acid in the presence of a lower fatty acid anhydride, approximately in the proportions of 2.3 to 3.2 moles of ammonium nitrate, 2.4 to 2.8 moles of concentrated nitric acid and 6.8 to 8 moles of anhydride per mole of hexamine dinitrate, said reaction being carried out at a temperature sufficient to effect the formation of more than one mole of cyclonite per mole of hexamine dinitrate.
9. The process of claim 8 wherein said reaction is carried out at a temperature above about 45° C. and below about 100° C.
10. The process of claim 8 wherein said reaction is carried out at 60–75° C.
11. A process of preparing cyclonite which comprises reacting hexamine with ammonium nitrate and concentrated nitric acid in the presence of acetic anhydride, approximately in the proportions of 2.3 to 3.2 moles of ammonium nitrate, 4.5 to 5 moles of concentrated nitric acid, and 6.8 to 8 moles of acetic anhydride per mole of hexamine, the reaction being carried out at 60° to 75° C.

References Cited in the file of this patent

Bachmann et al.: *Journal Amer. Chem. Soc.*, vol. 71 (1949), pp. 1842–1845.