METHOD OF PREPARING ROCKET MONO-PROPELLENT COMPOUNDS

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The instant invention relates to novel compounds which are
useful as rocket monopropellant agents and to the
manufacture thereof. More particularly, it relates to
ammonium ozone as a novel composition of matter per se,
and further, to the novel compositions of ammonium
ozone in intimate relationship with ammonia or with
ammonia and other selected materials. Our invention is
also concerned with the various embodiments of the proc-
cess whereby the foregoing novel compositions may be
readily obtained.

It is known that many research workers are making
determined efforts to develop new materials which are
useful as rocket propulsion agents. The problem in-
volved in such developments and at least some of the re-
sults therefrom have been fairly well publicized, subject-
of course, to national security restrictions, and it is evident
from the disclosures that many improvements remain to
be made in the propellant field. Although conventional
materials and techniques have progressed to quite good
operational efficiencies, and in fact some of the accom-
plishments are extraordinary, the need is still felt for
novel compositions of matter which are possessed of the
proper energy requirements and other desirable features
if this particular facet of our technology is to realize a
continuing advance. To the best of our knowledge the
preferred liquid monopropellants now available, under
the most optimal conditions, illustrate a maximum specific
impulse in the order of 235 seconds. The limitations in-
herent in such specific impulse values are well known
to those skilled in this particular art and when such values
are compared with the total energy made available from
compounds presently available, the conclusion is inescap-
able that much better performers are to be sought in the
search for new compositions of matter which are possessed
of the proper energy requirements and other desirable features.
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continuing advance.

At temperatures above --78° C. ozone reacts with
ammonia to yield ammonium nitrate as one end product.
We have found that by carrying out such reactions at
moderately low temperatures (i.e., --100° C. or lower)
such oxidation may be controlled to yield the dark red
compound, NH₄NO₃, instead of the nitrate. The material
so produced is quite stable at such reaction temperatures
and somewhat less stable in the range of from --78 to
--100° C., but rapidly decomposes to form oxygen, water
and ammonium nitrate at temperatures higher than
--78° C.

In its most simple form our process of making both
ammonium ozone and the latter compound in associa-
tion with ammonia consists in the intimate contacting of
ammonia with ozone. Due to the instability of desired
end product at temperatures even slightly above that at
which pure ammonia freezes, various specialized tech-
niques and conditions are required if a suitable and stable
material is to be obtained. Similarly, special procedures
are required if pure NH₄O₃ free of NH₃ is to be isolated,
and accordingly in the following detailed disclosure are
presented the various ramifications of our procedure.

At the onset of the experimentation which gave rise
to our invention, we bubbled dilute gaseous ozone through
liquid ammonia, such liquid being contained in a closed
closed vessel open only to permit the passage of the ozonac-
ous gas. The vessel in turn was surrounded by a refriger-
ator bath maintained at --78° C. The temperature of the
liquid ammonia per se was not determined during the
bubbling process but since it is well established that
ammonia liquefies at --33.3° C. and freezes at --78° C.
(or more exactly --77.8° C.), and since we were utilizing
liquid NH₃ at normal pressures, it is only reasonable to
conclude that we were operating within such temperature
range. Even more specifically, due to the heat transfer
effects between the refrigerant and the liquid ammonia
after a certain contact period it is evident that the NH₃
was only slightly warmer than --78° C. At no time dur-
ing this phase of our work was ammonia permitted to
freeze.

Parenthetically, at this point it should be understood
that by the terms "dilute gaseous ozone" or more simply
"dilute ozone" which are referred to throughout the ex-
amples in the instant specification are meant a gaseous
mixture containing from 1 to 10% ozone, the balance being substantially pure oxygen. It should also be understood that such a pure ozone-oxygen mixture is utilized as an example of only one specific ozone matter which is operative in the process, but that this is not a critical limitation in our invention. As a commercial production ozone produced from air may also be used in our process. This latter material may retain its nearreactive components, primarily nitrogen, without detracting from the end results. The ozone used here was produced by techniques well known in this art and was therefore not a part of our invention. It was generated as required and was substantially at room temperature until its passage into the liquid ammonia. Additionally, for reasons that are more fully elaborated upon below, for most purposes it is preferable that the ozone mixture (i.e., ozone-oxygen or ozone-air) be dry rather than moisture bearing.

As the dilute ozone was bubbled through the liquid ammonia a red color momentarily appeared at the initial point of each bubble contact but such color rapidly faded and finally the solution became stabilized at a pale yellow. Since it is known that alkali metal oxonates are dark red solids, we felt that the fleeting red color so produced was undoubtedly NH₄NO₂, and that it was rapidly decomposing into ammonium nitrate, and this was later confirmed. In view of this, our problem was in part to determine the procedure and conditions whereby the NH₄NO₂ is stabilized in the formation of NH₄NO₃ technical matter. It is to this result that our invention is in most part directed and in the paragraphs following the procedures are fully discussed.

In order that the above initial procedure may be more specifically envisioned the details thereof are presented. We placed 5 to 10 ml. liquid NH₃ in a glass test tube except for the passage of a glass bubbling tube. Such container was next surrounded by a bath of solid carbon dioxide in trichloroethylene maintained at −78° C. and permitted to cool therein for from 10 to 20 minutes before the dilute gaseous ozone was bubbled through. In various specific instances bubbling took place for from 10 to 25 minutes. Although at the termination of a 25-minute bubbling period the ammonium solution could practically be at the freezing point of pure ammonium two factors primarily stayed freezing. Not only was the ozone atmosphere prior to entering the reaction sphere but furthermore there is a freezing point depressant effect from the solutes produced from the reaction. These factors assume even greater importance when the reactions are performed at lower temperatures.

It should be clearly understood that our process basically consists of the combination of ammonia with ozone at low temperatures. The following exemplary embodiments thereof are included within its scope:

I. To produce a NH₄O₃—NH₃ system:

A. The treatment of liquid ammonia with dilute gaseous oxygen (ozone-oxygen or ozone-air).

B. The treatment of a solution of ammonia in a low freezing point solvent with dilute gaseous ozone.

C. Subjecting an aqueous solution of ammonia to pure ozone.

D. Treating solid ammonia with dilute gaseous oxygen.

E. A methanamine process that is elaborated upon below.

II. Means for producing ammonium nitrate:

A. The treatment of ammonia gas with dilute gaseous ozone.

B. The reaction of an alkali metal oxonate with ammonia chloride.

C. The processes of I above wherein the NH₃ is removed from the system and the NH₄O₃ thus isolated.

Such embodiments of our process will next be considered.
the reaction was to occur at an environmental temperature of approximately \(-100^\circ\) C. In order to suppress the NH$_2$O$_2$-NH$_2$O$_4$ degradation. The medium so selected must meet the requirements of (1) freezing below approximately \(-100^\circ\) C, (2) being capable of dissolving NH$_3$ or at least capable of dispersing it as fine particles, (3) not reacting with ozone at the low operational temperatures involved herein, and (4) not reactive with the ammonium ozonate as it is produced. Many compositions and mixtures fulfill these requirements but we found that a mixture of methyl and ethyl chlorides was the best solvent. Ammonia was dissolved in such latter mixture while the reactor flask was surrounded by a refrigerant bath maintained at \(-100^\circ\) C. Following this, dilute gaseous ozone was bubbled through the solution in the same manner as it was passed through pure NH$_3$ and again red, solid NH$_2$O$_4$ readily precipitated.

In order that this procedure may be fully understood a specific embodiment thereof is presented. To prepare the solvent medium 3 mls. of methyl chloride were mixed with 3 mls. of ethyl chloride in the reaction vessel. Such mixture was then surrounded by a refrigerant bath composed of a mixture of chloroform and trichloroethylene and 3 mls. of liquid NH$_3$ added thereto. Dilute gaseous ozone was bubbled through the solution at a rate of approximately 50 ccs. per minute for 15 minutes to rapidly convert the ammonium ozonate into ozonate.

We also used pure methyl chloride as the solvent. Although it freezes at \(-98^\circ\) C it still satisfies all conditions required of the solvent in this particular practice. In one procedure a 10% ammonia content solution in methyl chloride was utilized and NH$_2$O$_4$ was again readily produced.

It should, of course, be understood that other suitable ammonia solvents or dispersants such as Freon 13 may also be used in the instant process.

Following the precipitation of the NH$_2$O$_4$ it may be readily separated in part from NH$_3$, CH$_2$Cl and C$_2$H$_4$Cl by a vacuum process. The organic chlorides are removable practically in toto but here again it is not possible to free all of the NH$_2$O$_4$ from ammonia and likewise we reasoned that some of the moleculearly bound NH$_2$O$_4$ gave rise to the difficulties encountered in such isolation procedure. It should be appreciated, of course, that this molecularly bound ammonia concept is merely that and the instant invention is not primarily based upon such theory. However, it will be further readily realized that in accordance with our process regardless of the theory of combination an extremely satisfactory factory monopropellant composition is produced from this invention.

C. Subjecting an aqueous solution of ammonia to pure ozone.—We carried several experiments in the attempt to combine liquid ammonia and concentrated ozone. Such experiments were performed at the temperature range of from \(-183^\circ\) to \(-77^\circ\) C. When a 100% ozone gas was contacted with solid NH$_3$ at \(-183^\circ\) C, there was apparently no reaction. However as the materials were warmed slightly an explosion occurred. At higher temperatures (but still below \(-77^\circ\) C) whenever liquid NH$_3$ was permitted to contact concentrated ozone an explosion followed.

In view of the foregoing explosion problem and in the attempt to moderate the reaction, we diluted the NH$_3$ with water. Exemplifying the use of such aqueous solution is the treatment of a 28% aqueous ammonia solution with 30% ozone. More specifically, 2.8 grms of liquid NH$_3$ were dissolved in 7.2 grm of water and such solution subjected to concentrated ozone bubbling at the rate of approximately 50 ccs. per minute for a period of 10 to 20 minutes. The reactor was submerged in a refrigerant bath during the reaction period. There was no reaction at \(-183^\circ\) C, but when the ammonia-water solution was warmed to sufficiently utilize a portion of the ammonia the red color indicative of NH$_2$O$_4$ appeared.

Subsequent warming of such solution to above \(-77^\circ\) C resulted, as we had expected from our prior work, in a color loss with the attendant conversion of the ozonate to the nitrate.

At this point it should be mentioned that although NH$_2$O$_4$ formation can occur in either the presence or absence of water, if the material is to be used as a rocket propellant the water content should be kept to a minimum. Water adds merely weight but no actual propellant properties to the system and an excess of water will substantially dampen the propellant properties of ammonium ozonate. For this reason if the aqueous ammonium-concentrated ozone reaction is used it is necessary to remove the water from the system. Similarly, this is the reason for using substantially dry ozone or dry ozone-bearing air in the non-aqueous embodiments of our processes. It should be further mentioned that the reaction of ozone upon ammonia produces a very slight amount of water but in such amounts there is no practical reduction in propellant capabilities.

In addition to the process utilizing aqueous ammonia with a 100% ozone stream it is also possible to carry out such embodiment using lesser percentages of ozone. For example, we used a 25% concentration of ozone in Freon 13. Small quantities of liquid NH$_3$ at \(-77^\circ\) C were added to such ozone-Freon solution. A vigorous reaction occurred to yield the white solid, ammonium nitrate, but there were no explosions. In view of the presence of NH$_2$O$_4$ it was reasoned that the reaction proceeded too rapidly through the ozonate stage.

In order to moderate the foregoing reaction an ammonium-methylcyclohexane mixture was added to the ozone-Freon 13 solution rather than merely ammonia per se. A deep red color indicative of ammonium ozonate appeared in the ammonia layer. It should be cautioned however that in some cases even this reaction can result in explosion.

Although Freon 13 is a well known commercial product, for the sake of clarity in the instant specification, it has the chemical composition: chlorofluorocarbons.

D. Treating solid ammonium with dilute gaseous ozone.—In this procedure the ammonia is permitted to freeze at the bottom of the reaction vessel and dilute gaseous ozone is permitted to flow across the frozen surface. Because of the vapor pressure, however slight, a portion of the ammonia is entrained in the ozone and intimate contact results in the reaction to form ammonium ozonate in combination with only a small amount of ammonia. In addition to the gas-gas reaction, the solid ammonia per se reacts with the gaseous ozone. The ammonium ozonate-ammonia is deposited upon the side walls of the reaction vessel and in many instances has a substantially lower ammonia content than the end product resulting from liquid ammonia procedures.

In order to increase the reaction rate it is feasible to enlarge the surface area of the ammonia solid. This may be readily accomplished by depositing the ammonia on a porous, glass wool matrix, or on other non-reactive matrices. For another procedure, particulate, frozen NH$_3$ may be dispersed in Freon 13, for example, prior to reaction with the dilute ozone.

E. The process using methylamine.—In this embodiment the ammonium ozonate is first produced. Following this, methylamine (CH$_3$NH$_2$) is distilled into the ammonium ozonate bearing solution. The temperature of the solution is then raised to about \(-95^\circ\) C, from which results a liquid ammonia solution bearing ammonium ozonate and methylamine. Such solution is quite useful since methyl amine freezes at a considerably lower temperature than ammonia, i.e. \(-92^\circ\) C, and has excellent propulsion features. The various concentrations of the three main constituents may be varied practically at will.

\(-183^\circ\) A. The treatment of ammonia gas with dilute gaseous ozone.—The problems and difficulties involved in the vacuum removal of ammonia in the NH$_2$O$_2$-NH$_2$O$_4$ sys-
tem are readily realized by those skilled in the operation of similar techniques, and in order to circumvent such problem we developed the instant procedure of forming NH₄O₃ free of NH₃ directly upon reaction. Ammonia is first permitted to freeze at the bottom of the reactor vessel. A stream of pure gaseous nitrogen is then passed over the frozen ammonia surface in much the same manner as the ozone indicated above. The frozen ammonia presents adequate vapor pressure whereby very small quantities of NH₃ are entrained in the nitrogen stream. Into such stream is then directed the flow of dilute gaseous ozone which reacts with the entrained NH₃ to result in the deposition of solid NH₄O₃ on the walls of the reactor vessel. Since the amount of ammonia carried from the solid is in part determined by the temperature of operation (e.g., approximately −196 °C), it is removed at such a slow rate that it fully reacts with the ozone and thus there is no problem of NH₃ combination in such process.

The characteristics and properties of ammonium ozonate will next be considered. For such purposes the alkali ozonate-ammonium chloride reaction, discussed below, is used. We first decomposed the NH₄O₃ in the presence of ammonia. It is possible that the presence of the NH₃ may alter the mode of NH₄O₃ decomposition but this is not probable or in any event not a serious defect. The non-condensable gas found among the decomposition products was found to be oxygen. The vapor pressure of such gas at liquid nitrogen temperatures was found to be 155 mm. of mercury. Since the reported vapor pressure of O₂ at this temperature is 157 mm. Hg this is well within the range of experimental error to prove the presence of diatomic oxygen.

Following the removal of the oxygen the volatile products of the NH₄O₃—NH₃ material were checked by infrared analysis. To insure proper sampling three fractions were collected—a top, a middle and a low of the NH₄O₃—NH₃ mass. The only bands found were those that could be attributed to NH₃. By such method water may not be detected in the presence of ammonia but we were able to note its presence by the reaction with sodium whereby hydrogen is liberated. X-ray diffraction analysis indicated the presence of ammonium nitrate, and a qualitative test for the nitrate ion was positive. Since ammonium ion is the only cation present and equivalent amounts of nitrogen were found for the NH₃ and the nitrate, the compound must be in the form of ammonium nitrate, NH₄NO₃. We were thus able to establish qualitatively that oxygen, water and NH₄NO₃ are the decompositions of ammonium ozonate, i.e.

\[ \text{NH}_4\text{O}_3 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{NH}_4\text{NO}_3 \]

while quantitatively:

\[ 2\text{NH}_4\text{O}_3 \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} + \text{NH}_4\text{NO}_3 \]

The quantitative results and procedures involved therein may be of interest. For such purposes we used the potassium ozonate-ammonium chloride reaction at −30 °C:

\[ \text{KCl} + \text{NH}_4\text{Cl} \rightarrow 2\text{NH}_4\text{Cl} \text{ liquid NH}_3 \]

Known quantities of KO₂ and NH₄Cl may be combined and the weight of the KCl precipitate readily determined. At −30 °C, the resultant NH₄O₃ rapidly decomposes and the amount of O₂ thus liberated may readily be determined. The driving force for this reaction is the formation of potassium chloride which, as indicated, is insoluble in liquid ammonia. The NH₄O₃ is quite unstable and only momentarily appears before its subsequent conversion to ammonium nitrate; however despite the instability we found that such procedure provided a very valuable analytical tool in characterizing ammonium ozonate.

For this process 0.5 gram NH₄Cl was dissolved in 10 ml liquid ammonia. A second solution was next prepared of 5 ml. of liquid NH₄Cl containing 5% KO₂ and the latter such solution added to the ammonium chloride in ammonia. Prior to solution mixing the potassium-ozonate solution is maintained at approximately −196 °C. As the reaction mixture is permitted to warm through to −30 °C KCl is precipitated and the red color of the solution disappears as the result of NH₄O₃ decomposition.

We first determined the purity of the KO₂ available for such reaction by the following decomposition:

\[ \text{KO}_2 \rightarrow \text{K}_2\text{O}_2 + \text{O}_2 \]

By weighing the sample of potassium ozonate and then measuring the volume of oxygen liberated we found that our KO₂ sample was 92% pure. We then reacted the KO₂ with NH₄Cl in the following molar amounts:

\[ \text{K}_2\text{O}_2 + \text{NH}_4\text{Cl} \rightarrow \text{KCl} + \text{NH}_4\text{O}_3 \]

(2.92 mols) (15)

and:

\[ \text{NH}_4\text{O}_3 \rightarrow \text{KCl} + \text{NH}_4\text{O}_3 \]

(2.92) (2.92)

From such procedures the empirical formula of ammonium ozonate is calculated as NH₄₂O₃O₂. From electron paramagnetic resonance studies we deduced the true formula to be NH₄O₃.

Our work on ammonium ozonate electron paramagnetic resonance studies was performed with the use of a Varian electron paramagnetic resonance spectrometer which consists of a 12-inch diameter electromagnet, a highly regulated magnetic power supply and a microwave generator and detector. In operation a tube containing the sample was placed in a specially designed Dewar which in turn is placed in a microwave cavity located between the magnetic pole faces. The Dewar used at both room and liquid nitrogen temperatures so as not to change the physical characteristics of the cavity. The sample is exposed to microwave radiation of a fixed frequency of 9300 megacycles per second. The magnetic field is slowly varied linearly and data corresponding to energy absorbed by the sample versus the magnetic field is displayed on the graphic recorder. Because of the detection scheme the recorder traces are proportional to the derivative of the absorption line. Although it is convenient to observe the absorption most of the required information is found in the derivative curve and so an integration is not performed.

It was found that ammonium ozonate at liquid nitrogen temperatures showed a strong absorption having a line width of 29 oersteds and a g. value of 2.0110. From this it is concluded that ammonium ozonate has an unpaired electron and a magnetic dipole movement of 1.73 Bohr magnetons. The possibility of two unpaired electrons is excluded since only a single resonance absorption was observed with no fine structure, and thus we concluded that the structure of ammonium ozonate is NH₄O₃. Such unpaired electron is of the utmost importance in providing the free radical reactions in the monopropellant.

The instant compositions, whether ammonium ozonate per se, ammonium ozonate with ammonia, or with methylamine, are burned, or exploded in the usual manner to utilize their rocket propulsion abilities.

It will be understood that modifications and variations may be effected without departing from the spirit or scope of the instant invention.

We claim as our invention:

The method of making an ammonium ozonate-ammonia mixture which comprises reacting dilute gaseous
ozone with frozen ammonia, and maintaining said mixture at a temperature below -78°C.

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