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INORGANIC NITRATE EXPLOSIVE

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The present invention relates to the produc-
tion of new and improved explosive compositions,
wherein ammonium nitrate or other suitable in-
organic nitrate is an important ingredient, and
relates particularly to an improved method of
sensitizing ammonium nitrate for use in such
compositions.

Ammonium nitrate is widely employed as a
constituent of explosives. While it is considered
an explosive salt, it is too insensitive by itself
to be initiated readily or to sustain propagation
consistently.

The methods employed heretofore for the sensi-
tization of ammonium nitrate to produce inor-
ganic nitrate explosives have not been effective
except as excessive amounts of sensitizer were
used, undesirably sensitive materials were em-
ployed, dangerously high temperatures were
necessary for the operations, or other disadvan-
tages were introduced.

The object of the present invention is a new
and improved inorganic nitrate explosive, in par-
ticular, an ammonium nitrate explosive. A fur-
ther object is a process for the production of
an improved explosive in which ammonium ni-
trate or other inorganic nitrate is a chief con-
stituent. An additional object is a process for
producing ammonium nitrate explosives wherein
highly intimate contact between ammonium ni-
trate and sensitizer is obtained without the ne-
cessity of elevated temperatures. Other objects
will be apparent from the detailed description
of my invention hereinafter.

I have found that the foregoing objects are
accomplished by the process which comprises dis-
solving ammonium nitrate or other ammonia-
soluble inorganic nitrate in substantially anhy-
drous liquid ammonia, dispersing in said solution
a sensitizer for said nitrate, expelling the free
ammonia, and thereby forming a product in
which the sensitizing material is dispersed in the
solid nitrate, the latter compound being a con-
tinuous phase.

A large number of inorganic and organic com-
pounds and materials are adapted for use as
sensitizing ingredients according to my invention,
such sensitizers being ordinarily either explosive
compounds themselves or compounds containing
insufficient oxygen for complete combustion,
hence capable of utilizing the excess oxygen
present in the ammonium nitrate. I prefer to
employ as a sensitizer an imperforate material,
since the freedom from pores or cavities that is
implied in this term is a requisite. It is a dis-
persion of the sensitizer in the ammonium ni-
trate which is desired and not saturation of the
sensitizer with an ammonium nitrate solution
prior to solidification. With the use of such im-
perforate sensitizers and the consequent pres-
ence of ammonium nitrate on the outside of the

particles, the explosive possesses the several ad-
vantages of, (1) insensitiveness to shock and fric-
tion, and (2) improved sensitiveness to the deto-
nation impulse, with (3) possibility of wide vari-
ation of bulk strength. As examples of suitable
imperforate sensitizers, I may cite such inorganic
materials as aluminum, magnesium, antimony,
zirconium, ferrosilicon, calcium silicide, sulfur,
and the like; in fact, any inorganic oxygen-ac-
ceptor and sensitizer which is stable under at-
mospheric conditions and in the presence of am-
monium nitrate and ammonia.

Likewise, imperforate organic sensitizers are
highly efficient as sensitizing agents according to
my invention, and, as examples of such com-
pounds, I may cite amines such as diphenylamine,
para-phenylene diamine, aniline hydrochloride,
and the like; acid amides as exemplified by di-
cyan diamide, acetamide, oxamide, etc.; nitro-
compounds such as mononitronaphthalene, di-
nitrotoluene, trinitrotoluene, dinitrophenol, tri-
nitrophenol, tetryl, and the like; alcohols such
as pentaerythritol and polyvinyl alcohols; alde-
hydes as represented by paraldehyde and benz-
aldehyde; various sugars, for example sucrose;
ammonium salts such as ammonium formate
and ammonium thiocyanates; and many others.

While I find it important to use an imperforate
sensitizer, I find it is even more advantageous
to employ a sensitizer which is itself soluble in
liquid ammonia, since extreme intimacy of con-
tact between the ammonium nitrate and sensi-
tizer is thereby readily effected. A large num-
ber of the organic materials named in the fore-
going as imperforate materials are soluble in
liquid ammonia, and it is unnecessary to enu-
merate these desirable sensitizers again. Such
materials as diphenylamine, aniline, dicyandi-
amide, acetamide, trinitrotoluene, sucrose, and
ammonium formate may be cited, however, as
sensitizers soluble in anhydrous liquid ammonia.

In addition to the soluble sensitizers, it will
be understood that imperforate material insol-
uble in liquid ammonia are desirable for use and
may be readily dispersed in solutions of ammo-
nium nitrate or other inorganic explosive salt
therein. The inorganic materials enumerated
under the imperforate sensitizers are such ex-
amples and many insoluble organic sensitizers
are likewise desirable. As such insoluble, advan-
tageous materials, I may cite mononitronaph-
thalene, pentaerythritol tetranitrate, and par-
affin. A highly efficient sensitization is also ef-
fected by employing a sensitizer insoluble in
liquid ammonia, together with a dispersing agent,
the latter being miscible with said ammonia. As
an example of this type, I may cite the use of
dinitrotoluene dispersed by means of the soluble
trinitrotoluene, sulfur dispersed by means of
saponin, and many other insoluble sensitizers

which may be brought into intimate contact with ammonium nitrate by dispersing in a soluble material prior to, or during, their introduction with the solution of ammonium nitrate in anhydrous liquid ammonia.

In carrying out the process of my invention, the materials enumerated are introduced into the system in any desired sequence, but the following procedure is suitable. The determined amount of sensitizer or mixture of sensitizers in finely divided form is introduced into a solution of ammonium nitrate in substantially anhydrous liquid ammonia. The solution is preferably nearly saturated with respect to ammonium nitrate. The free ammonia of the solvent is then expelled by evaporation, with employment of reduced pressure, if desired. The mass is preferably agitated vigorously during the escape of the free ammonia. The solid material resulting from this process may be described as a dispersion product in which extremely minute regions of the sensitizer are disseminated within crystals of ammonium nitrate, the latter being the continuous phase.

It will be understood that the sensitizer may be one soluble itself in the liquid ammonia, or it may be insoluble therein, or again may be one of increased solubility or miscibility when first mixed with a dispersion agent. In the latter case, the substantially insoluble sensitizer is preferably thoroughly mixed with the dispersion agent before addition to the liquid ammonia solution, desirably with agitation.

The following examples are illustrative of my invention and give details sufficient to enable anyone skilled in the art to practice said invention.

Example 1

817 grams of ammonium nitrate was placed in a one-liter container provided with two glass conduits, one for the introduction of liquid ammonia, and the other for the venting of gaseous ammonia. Sufficient anhydrous liquid ammonia was introduced into this container to dissolve the ammonium nitrate and form an approximately saturated solution of ammonium nitrate in liquid ammonia at 20° C. The saturated solution was introduced into a jacketed mixing vessel provided with means of agitation. 183 grams of finely divided aluminum was added to the solution, with stirring. The vessel was closed to the atmosphere and the free ammonia expelled by heating and evacuating the gas, while agitating. The solution boiled freely until the temperature reached approximately 28° C., when solidification occurred. Upon subsequent heating of the system and further removal of the ammonia therefrom, the temperature first fell to around -10° C. and then rose to approximately 30° C. At this point, the product was removed from the system, and consisted of ammonium nitrate in continuous phase, containing minute regions of aluminum disseminated within said continuous phase.

Example 2

160 grams of finely divided sulfur was incorporated in 840 grams ammonium nitrate by the process described in Example 1. The product comprised minute regions of sulfur disseminated within crystals of ammonium nitrate.

Example 3

100 grams of finely divided sucrose was dissolved in 900 grams of ammonium nitrate, in solution in liquid ammonia. The process was

then carried out as described in Example 1. The product consisted of ammonium nitrate as a continuous phase, containing minute regions of sucrose disseminated therein.

Example 4

100 grams of polyvinyl alcohol was incorporated in 900 grams of ammonium nitrate by the process of Example 1. The product comprised a very intimate mixture of ammonium nitrate and polyvinyl alcohol, the ammonium nitrate being present as the continuous phase.

Example 5

35 grams of hexamethylene tetramine was dispersed in 965 grams of ammonium nitrate, in solution in anhydrous liquid ammonia. The explosive was then prepared in accordance with the process described in Example 1. The product consisted of finely divided particles of hexamethylene tetramine disseminated throughout a continuous phase of ammonium nitrate.

Example 6

918 grams of ammonium nitrate was introduced into a jacketed graining kettle equipped with agitation means. 82 grams of alpha nitronaphthalene in molten form was then added and the mixer closed. 250 grams of anhydrous liquid ammonia was then run into the graining kettle and agitation of the mixture was maintained until all the ammonia nitrate was in solution. The free ammonia was then removed by heating the kettle to 30-35° C., with final evacuation under reduced pressure. The agitation was continued throughout the drying, yielding a dry, loose product comprising minute regions of mononitronaphthalene disseminated within crystals of ammonium nitrate.

Example 7

30 grams of crude trinitrotoluene was dissolved in 70 grams of dinitrotoluene at a temperature between 50° and 60° C. This solution was added, while hot, to a solution of 900 grams of ammonium nitrate in anhydrous liquid ammonia. The dinitrotoluene by itself is difficultly soluble in the ammonia solution, but dispersion took place readily in the presence of the trinitrotoluene. The process was then continued according to the method described in Example 1. The product consisted of a continuous phase of ammonium nitrate containing minute regions of trinitrotoluene and dinitrotoluene disseminated intimately therethrough.

The following table shows the detonating characteristics of sensitized ammonium nitrate compositions prepared according to the process of my invention. These compositions were all sensitive to propagation by means of a standard No. 6 commercial blasting cap.

Sensitizer	Percent sensitizer	Percent ammonium nitrate	Velocity meters/second
Aluminum	18.3	81.7	2980
Sulfur	16.0	84.0	2000
Dicyandiamide	10.0	90.0	2860
Diphenylamine	6.7	93.3	2600
Polyvinyl alcohol	8.8	91.2	2260
Sucrose	10.0	90.0	2300
Hexamethylenetetramine	8.9	91.1	3000
Dinitrotoluene	7.5	92.5	1927
Trinitrotoluene	20.0	80.0	3500
Mononitronaphthalene	8.2	91.8	1606
Tetryl	29.7	70.3	4530
p-Phenylenediamine	7.8	92.2	3010

It will be appreciated that the velocity values

given in the table are merely illustrative and do not show the relative or limiting values of the compositions, since no attempt was made to maintain uniform densities.

The ammonium nitrate sensitized according to my invention may be employed as an explosive, either alone as tabulated, or mixed with other material. Desirable blends may be produced from the sensitized material with other explosive material, for example by the use of my sensitized product with ordinary untreated ammonium nitrate or with ammonium nitrate recrystallized from liquid ammonia. The blends may be rendered cap-sensitive or not for a given density, as desired, by regulating the amount of sensitizer used or the amount of sensitized ammonium nitrate in the blend. Very high strength values are obtained with the material of my invention. Oxygen balance will be adjusted to the desired value by control of the relative amounts of sensitizer and ammonium nitrate.

I find the type of explosive illustrated in Example 7 to be a preferred and very advantageous form of my invention, where dinitrotoluene, dispersed by means of trinitrotoluene, is itself dispersed in the ammonium nitrate in solution in anhydrous liquid ammonia. The following table shows the properties of explosives so prepared, with varying methods of blending. It will be noted that sodium nitrate as well as ammonium nitrate may be incorporated in the compositions by solution in liquid ammonia. While the tabulated compositions show sodium nitrate only in explosives containing ammonium nitrate also, it will be understood that sodium nitrate, or other inorganic nitrate soluble in liquid ammonia, may be present as the sole oxidizing ingredient.

of between 50 and 100 m/sec. were observed for each per cent of material passing through said 50-mesh screen. In other words, controlled reductions or increases in velocity in a velocity range never reached heretofore in ammonium nitrate explosives, were obtained by controlling the degree of coarseness of the sensitized ammonium nitrate material so that a predetermined amount of fines passing through a 50-mesh screen was present. The velocity can be controlled as well as by selecting sensitized ammonium nitrate of such a degree of coarseness that it will be held on screens somewhat finer than said 50-mesh screen, the fineness of the screen and resulting fineness of material passed therethrough to be determined in accordance with the particular velocity sought. #5 and #6 are compositions containing sodium nitrate, both (#5) mixed dry with dry explosive of my invention and (#6) with the sodium nitrate dissolved likewise in liquid ammonia. In the foregoing tabulation, the sensitiveness is expressed as the maximum air space, in inches, across which one cartridge will consistently detonate a second cartridge with undiminished velocity of detonation. The latter property is expressed in meters per second. Explosives of this type preferably will contain ammonium nitrate in an amount in excess of 85% and preferably between 88 and 98%, desirably with 4 to 8% dinitrotoluene, and 2 to 6% trinitrotoluene.

The foregoing tabulations and examples are to be construed as illustrative and not limiting. Ammonium nitrate may be employed in amounts much less than 85% and, indeed, may be added in any convenient proportion. It may be added entirely by means of the ammonia process, or

Ingredients	1	2	3	4	5	6
Ammonium nitrate.....	90.0.....	90.0.....	92.0.....	95.0.....	81.0.....	81.0.....
Dinitrotoluene.....	7.0.....	7.0.....	5.6.....	3.5.....	6.3.....	6.3.....
Trinitrotoluene.....	3.0.....	3.0.....	2.4.....	1.5.....	2.7.....	2.7.....
Sodium nitrate.....					10.0.....	10.0.....
Method of incorporation.	Simple mixture.	Ammonia process.	1 part coarse, dry ammonium nitrate blended with 4 parts dry #2 composition.	11 parts coarse AN added to a saturated solution in liquid ammonia of a composition approximating #2. (9 parts) ammonia then expelled.	1 part dry sodium nitrate blended with 9 parts of dry #2 composition.	1 part sodium nitrate incorporated with 9 parts #2 by the ammonia process.
Density:						
Ctgs./50 lbs.....	135.....	144.....	137.....	135.....	136.....	148.....
Sensitiveness to propagation.	Failed.....	7".....	5".....	1-1.5".....	5".....	8-9".....
Velocity, m/sec.....	None.....	3550.....	3400.....	1230.....	3020.....	3480.....

The foregoing tabulation is illustrative of my process and the properties of the compositions prepared thereby. The advantages of the ammonia process are shown strikingly by comparison of #2 and #1. The composition which failed to shoot when incorporated by simple dry mixture showed excellent explosive properties when blended by the liquid ammonia process. Whereas the use of the ammonia process of incorporation gave a less dense powder than the simple mixture of #1, the addition of coarse ammonium nitrate, that is, material of such particle size that the greater part will pass a 35-mesh screen but will be held on a 60-mesh, brought again the dense product shown in #1. #4 illustrates a very low velocity explosive of reasonably satisfactory sensitiveness, which would be very advantageous for certain types of blasting. Approximately minimum velocity was obtained with material wherein substantially none of the sensitized ammonium nitrate passed through a 50-mesh screen. Increases in velocity to the extent

in part by blending additional amounts of the salt with any of the products of the ammonia process.

Likewise, the amount of sodium nitrate need not be limited to 10%, as shown in the tabulation, but may be employed either alone or with ammonium nitrate or other ammonia soluble inorganic nitrate in widely varying amounts. For instance, the sodium nitrate or other inorganic nitrate may be present as 60% of the entire composition, for example.

Numerous advantages are gained by operation according to my invention, since it provides a safer, more rapid, and more efficient method of sensitizing ammonium nitrate to produce ammonium nitrate explosives than the methods employed heretofore. In the first place, my ammonia process allows the production of a dry, desirably sensitive material without the employment of other than relatively low temperatures. Hence, no hazard is possible from this source. In my ammonia process, the solvent ac-

tion of ammonia on ammonium nitrate is very rapid, even at low temperatures, and relatively high concentrations of ammonium nitrate are obtainable at pressures below one atmosphere. Furthermore, high temperature is unnecessary for driving off the free ammonia after a homogeneous product has been formed. It is a remarkable characteristic of solutions of ammonium nitrate in liquid ammonia that, at approximately 28° C., a solution of around 20% ammonia and 80% ammonium nitrate becomes solid, and remains so at all higher temperatures, though still containing an appreciable amount of ammonia. The remainder of the ammonia can be removed and recovered completely, either by evacuation or application of heat, or by a combination of both methods. A relatively low temperature such as 50° C. is sufficient, for example, at one atmosphere pressure. Using such temperatures, no danger is involved of thermal decomposition of the sensitized material.

An important advantage of my ammonia method of sensitization lies in the fact that a much more intimate dispersion of the sensitizer particles is achieved than has heretofore been possible, with the result that a much superior product is obtained. The properties of liquid ammonia that make possible its ready removal, when desired, assure the maintenance of the intimate contact of sensitizer and ammonium nitrate.

It is further characteristic of compositions according to my invention that the tendency to set or become hard on storage is greatly reduced over that of ammonium nitrate compositions where crystallization has been from water.

When incorporated with ammonium nitrate by the ammonia process, sensitizers soluble or dispersible in liquid ammonia give products sensitive to initiation by a standard commercial blasting cap, with a much lower percentage of sensitizer than is necessary to produce that result with products of other methods. In addition, a number of materials which fail to produce cap-sensitive compositions when incorporated in ammonium nitrate by the methods of the art, give cap-sensitive products when incorporated by the ammonia process.

A further desirable feature of the ammonia process of sensitization lies in the fact that sensitiveness of ammonium nitrate to intentional initiation is enhanced, without rendering the material increasingly sensitive to shock, friction, or flame. It is known that sensitized ammonium nitrate compositions produced by other methods seem to partake of the qualities of the sensitizer employed, so far as shock, friction, and flame are concerned. My compositions, however, are approximately as insensitive in this respect as pure ammonium nitrate. While compositions of sensitized ammonium nitrate prepared by my process are less sensitive to shock, friction, and accidental means of initiation, they are, as a matter of fact, more readily initiated by blasting caps or other controlled detonating influence than compositions prepared by other methods.

The fact that the compositions according to my invention are insensitive to shock and friction not only makes them attractive from a safety standpoint during manufacture, packaging, and charging operations, but also removes the hazards which normally accompany the occurrence of misfires in the borehole. When a misfire occurs, the drill may be inserted in the hole and the powder drilled out along with the tamping, without danger of explosion. The cap should, of

course, first be removed from the hole, after a misfire.

Explosive compositions having an extremely high velocity may be readily produced by my process. Unexpectedly, however, this velocity does not fall off rapidly with increase in density as is the case with other ammonium nitrate explosives. This permits pelleting of the powders to a high bulk strength even in small diameters, without extreme loss in sensitiveness.

Throughout this specification, the emphasis has been placed on ammonium nitrate compositions prepared by the ammonia process. It should be understood, however, that my invention is likewise applicable to explosives containing sodium nitrate, potassium nitrate, calcium nitrate, or other inorganic nitrate soluble in anhydrous liquid ammonia, and blended with a sensitizing material by use of said solvent.

For some purposes it has been found useful to replace a portion or all of the ammonium nitrate with one or more of the other ammonia soluble inorganic nitrates. For example, the strength of a given ammonium nitrate composition, as prepared by the ammonia process, may be lowered or controlled by the addition or substitution of a portion of sodium nitrate or other ammonia soluble inorganic nitrate. These other nitrates may be added either by introduction into the ammonia process or by blending amounts of said nitrates with material already sensitized in the ammonia process. In this manner a wide range of explosive strengths may be achieved with the use of much smaller amounts of ammonia nitrate itself.

In the present specification and the subsequent claims, I have designated the type of desirable sensitizer as imperforate. It will be understood that this term describes a normally solid material which is substantially and characteristically free from pores, cavities, and internal crevices, when in solid form.

As many apparently different embodiments of this invention may be made without departing from the spirit and scope thereof, I intend to be limited only by the following patent claims.

I claim:

1. An ammonium nitrate explosive which comprises a solid dispersion of an inorganic nitrate soluble in anhydrous liquid ammonia and a comminuted imperforate sensitizer, said dispersion resulting from crystallization from substantially anhydrous liquid ammonia.

2. An ammonium nitrate explosive comprising ammonium nitrate as a continuous phase, in which minute regions of an imperforate sensitizer are disseminated, said sensitized ammonium nitrate possessing non-setting properties as the result of crystallization from substantially anhydrous liquid ammonia.

3. An ammonium nitrate explosive comprising a solid dispersion of ammonium nitrate and a comminuted imperforate sensitizer, said dispersion resulting from crystallization from solution in substantially anhydrous liquid ammonia.

4. An ammonium nitrate explosive comprising a solid solution of ammonium nitrate and an ammonia-soluble sensitizer, said solution resulting from crystallization from solution in substantially anhydrous liquid ammonia.

5. An ammonium nitrate explosive which comprises 88 to 98% ammonium nitrate, 4 to 8% dinitrotoluene, and 2 to 6% trinitrotoluene, said dinitrotoluene and trinitrotoluene being intimately disseminated within the crystals of am-

monium nitrate as the result of dispersion by means of crystallization from substantially anhydrous liquid ammonia.

6. The process of producing an inorganic nitrate explosive, which process comprises dissolving said inorganic nitrate in anhydrous liquid ammonia, dispersing in said solution a comminuted imperforate sensitizer for said inorganic nitrate, and vaporizing the free ammonia to produce a solid dispersion product wherein the inorganic nitrate is a continuous phase.

7. The process of preparing an inorganic nitrate explosive, which comprises dissolving said inorganic nitrate in substantially anhydrous liquid ammonia, dispersing in said solution a comminuted imperforate sensitizer for said inorganic nitrate, and expelling the free ammonia therefrom.

8. The process of preparing an ammonium nitrate explosive which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, dispersing in said solution a comminuted imperforate sensitizer, and expelling the free ammonia therefrom.

9. The process of preparing an ammonium nitrate explosive which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, dispersing in said solution a comminuted imperforate inorganic sensitizer, and expelling the free ammonia therefrom.

10. The process of claim 9, in which the inorganic sensitizer is aluminum.

11. The process of claim 9, in which the inorganic sensitizer is sulphur.

12. The process of claim 9, in which the inorganic sensitizer is ferrosilicon.

13. The process of preparing an ammonium nitrate explosive which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, dissolving a soluble sensitizer therein, and expelling the free ammonia therefrom.

14. The process of preparing an ammonium nitrate explosive which comprises dissolving ammonium nitrate in substantially anhydrous

liquid ammonia, dissolving in said solution an organic sensitizer soluble in liquid ammonia, and expelling the free ammonia therefrom.

15. The process of claim 14, in which the soluble organic sensitizer is sucrose.

16. The process of claim 14, in which the soluble organic sensitizer is trinitrotoluene.

17. The process of claim 14, in which the soluble organic sensitizer is dicyandiamide.

18. The process of preparing an ammonium nitrate explosive which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, dispersing in said solution a comminuted imperforate organic sensitizer, and expelling the free ammonia therefrom.

19. The process of claim 18, in which the insoluble organic sensitizer is pentaerythritol tetranitrate.

20. The process of claim 18, in which the insoluble organic sensitizer is paraffin.

21. The process of claim 18, in which the insoluble organic sensitizer is mononitronaphthalene.

22. The process of preparing an ammonium nitrate explosive, which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, disseminating an imperforate sensitizer in said solution with the aid of a dispersing agent, and expelling the free ammonia therefrom.

23. The process of preparing an ammonium nitrate explosive, which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, disseminating therein an imperforate aromatic nitrocompound substantially insoluble in liquid ammonia by dispersion of said insoluble nitrocompound with an aromatic nitrocompound soluble in liquid ammonia, and expelling the free ammonia therefrom.

24. The process of preparing an ammonium nitrate explosive, which comprises dissolving ammonium nitrate in substantially anhydrous liquid ammonia, disseminating dinitrotoluene therein by dispersion by means of trinitrotoluene, and expelling the free ammonia therefrom.

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