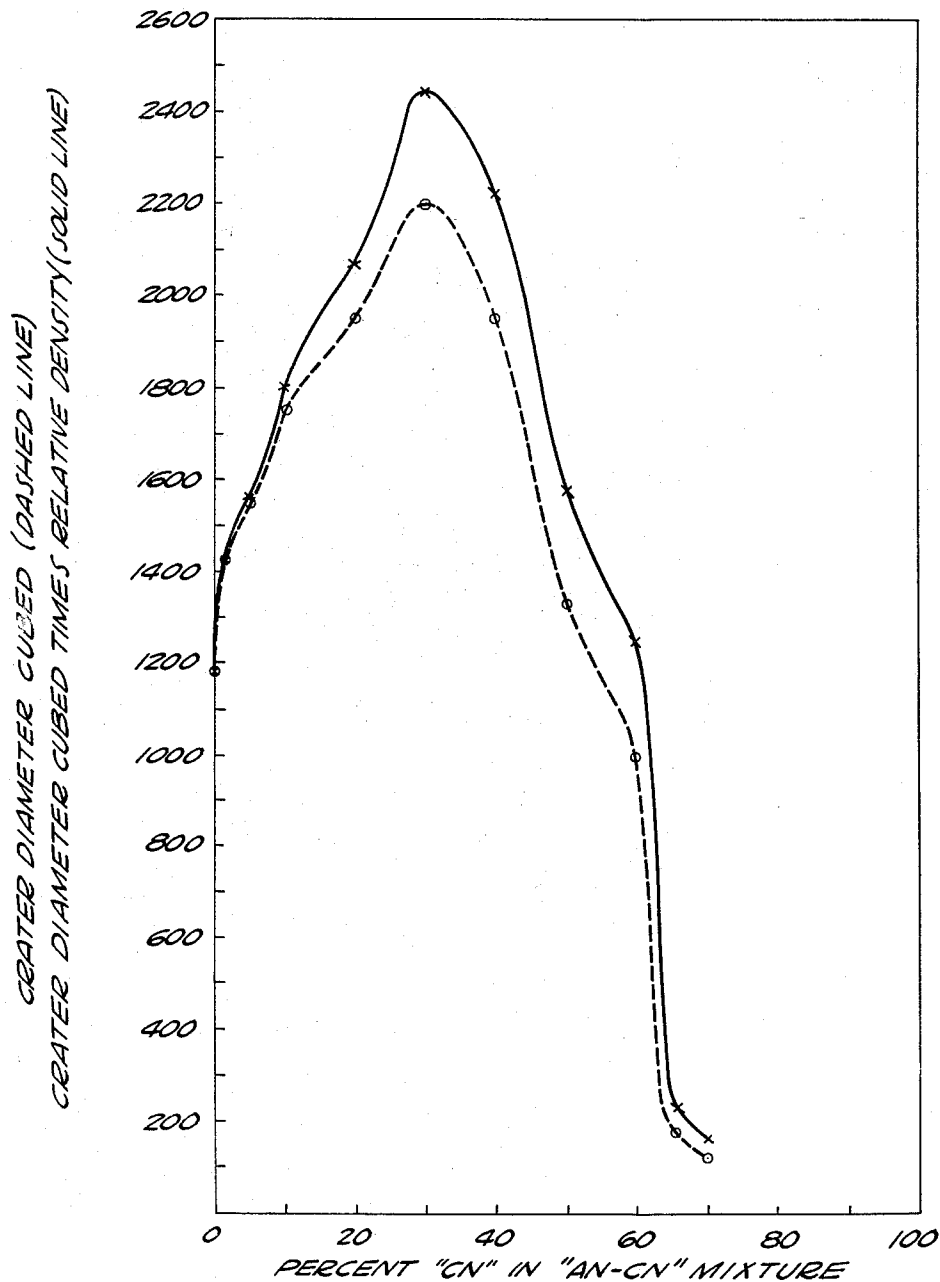


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CONTAINING CALCIUM NITRATE AND OIL  
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EDWIN M. SCOTT, JR.  
INVENTOR.

BY

*Delmar H. Jones*

AGENT

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AMMONIUM NITRATE EXPLOSIVE COMPOSITION

CONTAINING CALCIUM NITRATE AND OIL

Edwin M. Scott, Jr., Los Angeles, Calif.

(Box 323, Tujunga, Calif.)

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This invention relates to explosive compositions and more particularly to detonatable mixtures of ammonium nitrate and calcium nitrate with a hydrocarbon.

It has been known for about a century that ammonium nitrate may be detonated when mixed with a small amount of carbonaceous material. In recent years, a relatively new physical form of ammonium nitrate known as prills has become commercially available, and it has been found that this form of ammonium nitrate is particularly well-adapted to explosive uses by the simple admixture of a hydrocarbon such as diesel oil. Since the prills are not solid crystals but aggregations of microcrystals, the liquid hydrocarbon is able to be taken up by the ammonium nitrate prill and to penetrate it, furnishing a particularly intimate admixture of hydrocarbon sensitizer and ammonium nitrate. Mixtures of this sort are detonated with various primer charges, the most common being dynamite, generally in an amount very small compared to the amount of ammonium nitrate which is detonated.

Satisfactory as the known mixtures may be, particularly in comparison to the earlier use of relatively expensive explosives such as dynamite which the ammonium nitrate-oil mixture has displaced to a great extent, nevertheless, the utilization of ammonium nitrate for this purpose is subject to substantial improvement.

An object of the present invention is to provide a composition based on ammonium nitrate which has greater explosive power than the ammonium nitrate compositions of the type described and heretofore known.

Another object of the invention is to provide a novel composition which permits lower cost by the inclusion of calcium nitrate, while at the same time increasing instead of decreasing the explosive effect.

Another object of the invention is to provide an ammonium nitrate type of explosive of substantially greater density than ammonium nitrate while at the same time achieving greater, rather than lesser explosive power.

Other objects of the invention will appear as the description thereof proceeds.

Generally speaking and in accordance with an illustrative embodiment of my invention, I mix together ammonium nitrate prills, free of the clay, diatomaceous earth or other mineral filler coating commonly used thereon, with calcium nitrate prills within a range of relative proportions by weight which I have discovered give extraordinary, unexpected and surprising results, together with a liquid hydrocarbon oil. More particularly, I may use ammonium nitrate prills of the type described and calcium nitrate prills in a mixture in which the calcium nitrate is present within the range of about 1% to about 60% by weight of the total mixture of calcium nitrate and ammonium nitrate. To this mixture of the two nitrates I add a suitable quantity of a hydrocarbon, which most suitably is between 3 and 10 parts

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by weight of hydrocarbon per 100 parts by weight of the nitrate mixture, but optimally about 5.5 parts, and for which I have found liquid hydrocarbon oils such as diesel oil to be best.

As remarked, it has been known for many years that ammonium nitrate is detonatable when sensitized with a carbonaceous material, but this is not true of calcium nitrate, and calcium nitrate has always been considered, and properly so, simply as a sort of lower-performance diluent for ammonium nitrate when used in detonatable mixtures. The usual effects, and indeed those to be expected, from the admixture of calcium nitrate to ammonium nitrate in the commonly used forms of the latter may be seen from the following tabulation:

Table 1

Composition of Mix	Crater Diameters		
	Coated AN Prills	Coated Stengel Flake AN	Coated Grained AN
100 parts AN -----	8"6"	2'0"	6'0"
5.8 parts diesel oil -----			
70 parts AN -----	7"6"	1'6"	4'6"
30 parts CN -----			
5.8 parts diesel oil -----			

In the above table, results are given for three different types of ammonium nitrate, alone and mixed in a 70:30 ratio with prilled calcium nitrate. As set forth hereinbelow, this product is uncoated and substantially anhydrous. The abbreviations "AN," "CN" are used throughout this specification for ammonium nitrate and calcium nitrate respectively.

In the tests the results of which are given in Table I, 18 inch deep holes were bored in a uniform moist clay playa deposit in the Mojave Desert in East Central California, this particular deposit being widely used for explosive tests of this nature. The holes were loaded with 1500 grams of the explosive mixture and half a stick of dynamite. The holes were thoroughly backfilled and tamped, and the dynamite detonated. The crater formed by the blast was measured, and the crater diameters appear in Table I. Experience with this deposit has shown that results are very highly reproducible, because of the uniform nature of the deposit. This is especially true for any given series of runs made at one time.

It will be seen from Table I that in all cases where calcium nitrate was admixed with ammonium nitrate in a 30:70 ratio, markedly poorer results were obtained than with the straight ammonium nitrate, in keeping with the recognized ordinary behavior of calcium nitrate.

Ammonium nitrate prills, as mentioned, are a relatively recent development. Their manufacture is described in an article entitled "Ammonium Nitrate" in Industrial and Engineering Chemistry, volume 45, pages 496-504, March 1953. Essentially, the process consists in spraying hot concentrated ammonium nitrate solution from the top of a tower and allowing the droplets to descend against a countercurrent stream of air at a lower temperature, forming solid particles which are essentially aggrega-

tions of microcrystals, which are termed prills, about  $\frac{1}{16}$  to  $\frac{3}{32}$  of an inch in diameter. The basic process widely used is described in United States Patent 2,402,192. Instead of using gravity to move the droplets of ammonium nitrate solution through a tower, prilling may also be accomplished in a rotating drum, as described in Chemical and Engineering News, June 22, 1959, pages 38-39. Ammonium nitrate is subject to caking, particularly in storage, so that it is common practice to coat the prills formed in the fashion described with an anti-caking agent, which most commonly consists of 2% to 3½% by weight of a mineral filler powder such as diatomaceous earth, attapulgite clay, talc, ground limestone, and the like. As appears from Table I above, however, coated prills are not improved in explosive character by the admixture of calcium nitrate, but rather just the opposite. Indeed, this statement applies to the other available forms of ammonium nitrate as well, as also appears from Table I. It is an essential feature of the present invention that ammonium nitrate must be used not only in its prill form but also in the form of prills which are free of the common mineral filler coating. Accordingly, throughout this specification and the claims which follow, the term "uncoated prilled ammonium nitrate" is to be understood as the prills of this substance as produced in a prilling tower or drum or by like means, and free of the usual 2 or 3 or 4% of mineral filler. I have carried out experiments with slightly coated prills, and find that the ammonium nitrate prills may have up to and including ½% by weight, but no more, of a mineral filler coating, and still be operative in my invention. Any increase in coating over this amount greatly decreases the efficiency. Minute quantities of organic additives which are occasionally used to improve the physical properties of the prills, such as  $\frac{1}{20}$  to 1% of an organic surface active agent or a wax, do not interfere with the practice of the invention. Materials of this sort are more or less soluble in the diesel or other hydrocarbon oil which is used in the practice of my invention, and combust along with the oil.

By way of further explanation of Table I and exemplary of other forms of ammonium nitrate which do not work in my invention are the so-called Stengel flake, made in accordance with Stengel Patent No. 2,568,901, which as the name implies is in flake form and thus wholly unlike a prill; and grained ammonium nitrate which is made by open-pan evaporation and results in granules which are considerably smaller than prills but do not have the microcrystalline structure of the prills. The manufacture of ammonium nitrate by graining is described in the Industrial and Engineering Chemistry article already cited, and Stengel flake in IEC 46, 622-632 (1954).

The prilled calcium nitrate which I use is substantially anhydrous, the moisture content being considerably less than 1% by weight. So far as I have been able to determine, and certainly to the best of my knowledge, it is not practicable to make a calcium nitrate prill with any appreciable water content. Prilled calcium nitrate as used in my invention is, furthermore, free of any non-combustible coating, just as has been described in connection with prilled ammonium nitrate hereinabove. Prilled calcium nitrate is an article of commerce and most, if not all, of the material available in the United States is imported from Scandinavia, most importantly from Norway. The commercial article is quite pure, is snow-white in appearance, and free of clay or like coating and also free of water. Thus, this material differs sharply from commercial flake calcium nitrate, for example, which contains a quite substantial amount of water, in fact between 25% and 30%. This latter form will not work at all, nor will the laboratory-grade of calcium nitrate

monohydrate, which contains 8% or 9% water. As already stated, in order to practice my invention it is necessary to use prilled calcium nitrate. Where this term is used hereinafter and in the claims which follow it is to be understood that the material is substantially anhydrous, viz., it has less than 1% moisture, and, like the prilled ammonium nitrate already described, it has not more than ½% of non-combustible coating, and, indeed, in the presently available commercial article, none.

The hydrocarbon used in the practice of my invention may be any commonly available hydrocarbon, such as petroleum, petroleum fractions, waxes, asphalts, coal tar hydrocarbons, pinewood hydrocarbons, and the like. The best I have found to be liquid or readily liquefiable hydrocarbon oils, and particularly petroleum hydrocarbon oil of the types included within the range of kerosene through light lubricating oil. In general, hydrocarbons of higher gravity than kerosene are too volatile for convenience in use, although they may still be used, while lubricating oils heavier than about SAE 10 are not only more expensive but take too long to become absorbed to equilibrium by the prills. The best hydrocarbon oil which I know of is No. 2 diesel oil which is known as Class 2 Diesel Fuel Oil in the United States Military Specifications.

A striking feature of compositions made in accordance with my invention is that the mixture of ammonium nitrate and calcium nitrate is no longer subject to the caking of the straight ammonium nitrate. This is especially surprising in view of the deliquescent property of calcium nitrate generally.

The surprising results achieved in the practice of my invention may be most readily appreciated by reference to the drawing, in which two curves are shown which show the explosive effectiveness of mixtures made in accordance with my invention as a function of the percent calcium nitrate in the mixture of the two nitrates. The figures which are plotted in the drawing appear below as Table II.

Table II

Percent CN in AN-CN Mixture	Relative Bulk Density	Crater Diameter (in feet) Cubed <sup>1</sup>	Crater Diameter (in feet) Cubed times Relative Density <sup>2</sup>
0-----	1.00	1,185	1,185
1-----	1.00	1,425	1,425
5-----	1.01	1,550	1,565
10-----	1.03	1,750	1,800
20-----	1.06	1,950	2,070
30-----	1.11	2,200	2,440
40-----	1.14	1,950	2,225
50-----	1.19	1,330	1,580
60-----	1.26	1,000	1,260
65-----	1.29	180	230
70-----	1.31	125	165

<sup>1</sup> Plotted in drawing as dashed line.

<sup>2</sup> Plotted in drawing as solid line.

In the tests which were made which are shown in Table II, uncoated ammonium nitrate prills were mixed in various proportions with prilled calcium nitrate. The percentage of calcium nitrate in the mixture of the two nitrates appears in column 1. The second column shows the relative bulk density of the mixture of the nitrates and diesel oil, which was held constant at 5.5 parts by weight of diesel oil per 100 parts of nitrate mixture. The third column of Table II shows the cube of the crater diameter in feet, while the fourth column shows this figure multiplied by the relative bulk density which appears in column 2.

In commercial blasting operations, such as for example the open-pit mining of coal, iron ore, and the like, an

appreciable part of the cost of the blasting operation is the drilling of the holes to receive the charge. If one explosive has a lesser bulk density than another, then it will be necessary to drill a larger hole when using the first than when using the second, and in consequence the overall blasting costs will be greater for the first than for the second, even if explosive effectiveness on a weight basis and cost per unit weight were the same for both explosives. Frequently hard, dense rock formations are encountered that require greater shattering action than the bulkier explosives can develop. It has been well established both by theory and practice that of two explosives having equal strength to weight ratio, the one having the greater density will develop the greater shattering effect or "brisance." This is because the shock wave in the denser explosive will have a greater velocity providing both have the same strength, to weight ratio. Heretofore efforts to increase density of ammonium nitrate type explosives have always resulted in decreasing the strength to weight ratio so that any advantage in cramming more mass into the drill hole has been virtually nullified by the decreased strength to weight ratio. This is particularly true with additives such as calcium nitrate when mixed with conventionally coated prills. In consequence, I have plotted in the drawing both the cube of the crater diameter for an equal weight of charge in each case, which gives an accurate measure of explosive effectiveness; and I have also plotted as a solid line in the drawing these same figures multiplied by the relative bulk density, which comes closer to being a practical measure of over-all explosive effectiveness for the reasons stated, when taking into account the cost of drilling holes.

Turning now to Table II and the drawing, it will be seen that even small additions of calcium nitrate, including the lowest tested concentration of 1% calcium nitrate in the mixture, increase the efficiency of the ammonium nitrate when sensitized with diesel oil. This is most surprising, and is completely in contrast to results obtained with other forms of ammonium nitrate, as already shown in Table I. The super-additive effect holds over a wide range, and reaches a peak at about 30% CN. For percentages of calcium nitrate greater than about 60%, the explosive efficiencies drop off to a very low value. Charges greater than 70% calcium nitrate did not give any crater at all and therefore are not plotted in the drawing.

Another rather surprising effect is that the liquid hydrocarbon used may be varied over a considerable range with no lessening of effectiveness. I have found that in general about 5.5 parts of hydrocarbon oil per 100 parts of the nitrate mixture works very well for all percentages of calcium nitrate within the inventive range, and this is best concentration that I know of. This again is a somewhat surprising result, because the stoichiometrically equivalent amount of hydrocarbon oil increases greatly as the percentage of calcium nitrate increases, because of the great difference in oxygen balance of the two nitrates. The amount of diesel oil which I have found to be generally optimum, however, is not necessarily the stoichiometric quantity, but, as mentioned, simply about 5.5%.

As mentioned, the amount of hydrocarbon oil which will be found to give good results in the practice of my invention for various mixtures of prilled ammonium nitrate and prilled calcium nitrate within the scope of my invention have been found to lie within the range for which the lower limit is three parts and the upper limit is ten parts of hydrocarbon oil per 100 parts of the mixed nitrates. Some test results for varying percentages of hydrocarbon oil appear in Table III below. These results are supplementary to those already given in Table II above, all of the ingredients being the same, and merely the amount of hydrocarbon oil being varied as shown in the table.

TABLE III

Percent CN in AN-CN Mixture	Percent Fuel Oil per 100 Parts Mixture	Crater Diam- eter in Feet and Inches
10	5.5	12'1"
10	6.24	12'0"
20	5.5	12'6"
20	6.98	12'6"
30	5.5	13'0"
30	7.72	13'0"
40	5.5	12'6"
40	8.46	12'6"
50	4.5	10'7"
50	5.0	11'6"
50	5.5	11'0"
50	6.0	11'0"

The results of proceeding in accordance with the invention have been tested repeatedly by numerous experiments. Nevertheless, I am unable to offer any theory of action which would explain the surprising results obtained by the use of calcium nitrate with uncoated prilled ammonium nitrate. Possibly the mineral filler coating so commonly employed on prills has some dampening effect, but that this is far from the entire explanation is made clear by the fact that a 50-50 mixture of uncoated ammonium nitrate prills and potassium nitrate instead of calcium nitrate, together with 5.8 parts of diesel oil per 100 parts of nitrate mixture, fails, to detonate at all. The explanation of the unusual results obtained with the inventive compositions must await intensive and fundamental research.

I have found that the inventive mixtures described and claimed herein may be advantageously used in combination with the inventive mixtures described and claimed in my co-pending application, Serial No. 840,453, filed September 16, 1959, now Patent No. 3,061,488. That co-pending application discloses mixtures of prilled ammonium nitrate and sodium nitrate ("SN") with a hydrocarbon oil. As an example of the good results obtainable by combining the inventive mixtures discussed herein and the inventive mixtures disclosed in my aforesaid co-pending application, the following test results are given, in which mixtures made up in accordance with both of my applications were prepared, and then combined and tested in the manner already set forth, for example, as shown in the table hereinabove (1500 grams charges, as throughout). The prilled calcium nitrate in all these tests was of  $\frac{1}{32}$  to  $\frac{1}{16}$  inch pellet diameter, this being the commercial size, and thus was of slightly finer mesh than the prilled ammonium nitrate.

Table IV

Composition	Crater Diameter
3 parts of: 60 AN, 40 SN, 5.5 fuel oil	12'8"
1 part of: 60 AN, 40 CN, 5.5 fuel oil	
1 part of: 60 AN, 40 SN, 5.5 fuel oil	
1 part of: 60 AN, 40 CN, 5.5 fuel oil	12'8"
1 part of: 60 AN, 40 SN, 5.5 fuel oil	
3 parts of: 60 AN, 40 CN, 5.5 fuel oil	12'8"
100 AN, 5.5 fuel oil (control)	10'9"

While the invention has been described with the aid of numerous specific examples, it will be evident from the disclosure that numerous variations of detail are permissible within the broad scope of the invention, keeping in mind, however, the experimental findings which I have set forth in the specification.

Having described the invention, I claim:

1. A detonatable composition consisting essentially of uncoated prilled ammonium nitrate and uncoated prilled calcium nitrate in a weight ratio within the range of 40% ammonium nitrate-60% calcium nitrate and 99% am-

monium nitrate-1% calcium nitrate, together with a liquid hydrocarbon in a weight ratio of between 3 and 10 parts for each 100 parts of the mixture of the said nitrates.

2. A detonatable composition consisting essentially of prilled ammonium nitrate, prilled calcium nitrate, and non-combustible coating not in excess of about ½% of the weight of said prilled nitrate, said nitrates being present in a weight ratio within the range of 40% of ammonium nitrate-60% calcium nitrate and 99% ammonium nitrate-1% calcium nitrate, together with a liquid hydrocarbon in a weight ratio of between 3 and 10 parts for each 100 parts of the mixture of the said nitrates.

3. The composition of claim 1 in which the liquid hydrocarbon is a petroleum hydrocarbon.

4. The composition of claim 2 in which the liquid hydrocarbon is a petroleum hydrocarbon.

5. The composition of claim 1 in which the liquid

hydrocarbon is a petroleum hydrocarbon oil within the range of kerosene through light lubricating oil.

6. The composition of claim 2 in which the liquid hydrocarbon is a petroleum hydrocarbon oil within the range of kerosene through light lubricating oil.

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CARL D. QUARFORTH, *Primary Examiner.*

OSCAR R. VERTIZ, *Examiner.*