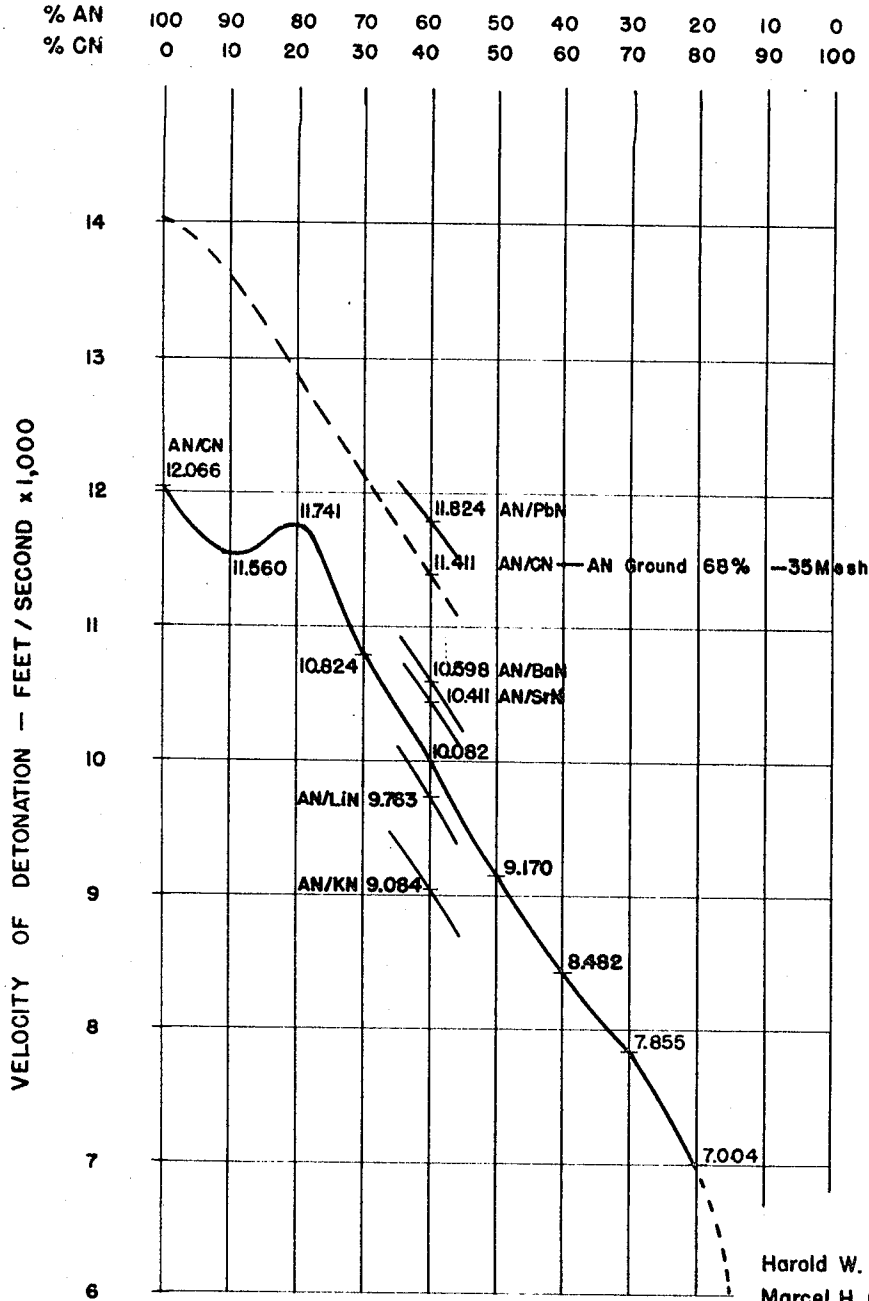


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BLASTING AGENT COMPOSITION CONTAINING A HYDROCARBON FUEL AND COATED AMMONIUM NITRATE

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ABSTRACT OF THE DISCLOSURE

A blasting agent composition employing a commercial prilled ammonium nitrate (AN) having from ½ to 2% of mineral nitrate filler, a metal nitrate and a hydrocarbon fuel; the nitrate being intimately associated with the fuel and in controlled proportions of from +7% to -7% oxygen balance to produce to fully detonatable composition.

Our present invention relates to inexpensive, readily manufactured, stable and powerful blasting agents and more particularly, to detonatable mixtures of commercially available prilled ammonium nitrate and selected metal nitrates with a hydrocarbon, and in some instances including also a gelling agent, or WR flours, or mixtures thereof.

Approximately one century after Nobel discovered an explosive composition, commonly known as dynamite, and further developed his original discovery by replacing a substantial part of its nitroglycerine with ammonium nitrate, subsequent inventors found that a less expensive composition could be produced by making intimate mixtures of ammonium nitrate and sodium nitrate with a hydrocarbon. The ammonium nitrate is commercially available in a prilled form as disclosed in United States Patent No. 3,061,488 but to serve as a blasting agent component, this patentee thought it necessary to employ substantially uncoated prills (less than ½%, by weight, of a mineral coating). His test indicated to him that quantities of coating greater than ½% decreased the strength to weight ratio to such a degree as to make its use commercially impractical.

A few years later it was developed that other metal nitrates, alkali metal and alkaline earth metal nitrates, and mixtures thereof, could be used to produce stable and powerful explosive compositions. However, in this subsequent development, it was thought to be necessary for the metal nitrate to be substantially anhydrous, that is to say, less than 2% moisture and preferably less than 0.5% moisture. It was also considered that a mineral coating on the metal nitrate component rendered the composition less sensitive and resulted in a very inferior explosive performance. (United States Patent No. 3,178,325 q.v.).

The patentee (3,178,325) considered it desirable, in some instances, to employ fuels which are highly toxic when using metal nitrates and conceived that his choice of sensitizing agent was crucial to achieve results which approach those of the former AN-SN-fuel compositions.

Prilled ammonium nitrate with ½% or less of a mineral coating is not a readily available commercial product and thus the cost is relatively greater than the available prilled ammonium nitrate generally used.

We have found that it is not necessary to use: "Uncoated" prills of ammonium nitrate and/or other metal nitrates; anhydrous metal nitrates and the more expensive and more combustible mononitroaromatic hydrocarbons but, rather, commercial grades of prilled ammonium ni-

trate having a mineral filler coating of up to 2%, hydrated or anhydrous metal nitrates and the cheapest hydrocarbon, i.e., diesel fuel oil (DFO) in various combinations produce commercially acceptable blasting agents when considering original cost, transporting, storage and blasting results.

Commercial prills of ammonium nitrate as employed herein, and their manufacture are described in an article "Ammonium Nitrate" in Industrial and Engineering Chemistry, vol. 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 round porous aggregations of microcrystals, which are termed "prills," about ¾" to 1" of an inch in diameter. The basic process widely used is described in United States Patent No. 2,402,192. Instead of using gravity to move the droplet 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 manner described with an anticaking agent, which most commonly consists of about 2% by weight of a mineral filler powder such as diatomaceous earth, attapulgite clay, talc, ground limestone and the like. Accordingly, throughout this specification and the claims which follow, the term "prills" is to be understood as the prills of ammonium nitrate as having from ½% to about 2% of the said mineral filler coating.

Other forms of ammonium nitrate, as for example, flake, crystalline, grained or ground, have been found to function acceptably. The ground nitrate functions at optimum when they are ground to 60% thru 35 mesh approximately. Obviously, the VOD and brisance may vary by changing the size of the ground particles, since the intimacy of the fuel and the AN, and the rate of reaction is affected thereby.

Our present invention utilizes compositions of certain metal nitrates and ammonium nitrate (AN) in one of its least expensive forms.

In our blasting agent formulations we employ selected metal nitrates, either hydrated or anhydrous, together with the readily available commercial forms of AN (having up to 2% of a mineral filter coating) and fuel oil (FO) and still obtain very desirable results because we carefully control the intimacy of the FO-nitrate mixture and maintain the oxygen balance within limits established by experimentation and theory.

While the fuel or hydrocarbon used in our compositions may be any of the mononitroaromatic hydrocarbons, of the highly combustible and thus dangerous-to-handle types, our formulations are admirably adapted for utilizing diesel fuel oil (DFO) and perhaps some coke or other intimately mixed hard hydrocarbon, when desired, to produce an inexpensive mixture, safe to handle and suitable for pouring or blowing into drill holes and such like.

We have found that when the coated AN prills, metal nitrates (anhydrous or hydrated as aforesaid) and hydrocarbons are mixed with fuel oil (FO) in an oxygen balanced ratio not to exceed plus or minus 7% with the AN metal nitrate ratio within 15% to 95% AN and 5% metal nitrate and the compound then compacted to a density equal to that effected by at least a three foot column of said compound pressing upon the charge, the explosive reaction is complete and predictable.

The AN component may consist of any of the commercially available prills of the "porous" variety, having an amount of inert parting agent not to exceed 2%. However, any of the other varieties of AN, that is, agri-

cultural prills, grained, crystalline and flake, will also function in these compositions, though at lesser efficiencies for the most part.

An of the commercially available alkaline earth metal nitrates, alkali metal nitrates or metal nitrates may be used, whether crystalline, granular, powered or prilled. They again, may or may not contain an inert coating not to exceed 2% and may be either in the hydrated or anhydrous form.

The carbonaceous fuel may be either a liquid or solid hydrocarbon or a combination of both. Gelling agents, guar flours, and nonexplosive nitrated hydrocarbons are also potential fuels and may be used to impart specific desirable properties to the basic compositions.

All of the test work was carried out with porous AN commercial prills reported by the manufacturer to contain 0.75% of an organic parting agent, and from 0.50% to 1.00% of inert parting agent. A commercial grade of hydrated calcium nitrate, CN prill was used as the main alkaline earth nitrate, and contained 14% of water by weight. The fuel consisted of #2 DFO and/or a fine granular petroleum coke, and in some instances an aluminum stearate (AS) fuel gelling agent.

Raw materials for the mixes were selected from one manufacturer's lot to insure uniformity. After quality testing, they were set aside in sufficient quantity to complete the series of mixes anticipated without further change of materials.

The overall oxygen balance ratio of the blasting agent compositions is very important to the successful practice of the present invention. The following table sets forth the oxygen values of the components involved herein:

TABLE.—OXYGEN VALUES

	(OV)
Ammonium nitrate (AN) -----	+ .200
Lead nitrate (PbN) -----	+ .242
Strontium nitrate (SrN) -----	+ .378
Calcium nitrate (CN) -----	+ .419
Barium nitrate (BaN) -----	+ .306
Lithium nitrate (LiN) -----	+ .580
Potassium nitrate (KN) -----	+ .396
Diesel fuel oil (DFO) -----	- 3.46
Petroleum coke -----	- 2.67
Aluminum stearate -----	- 2.78

The oxygen balance is calculated by employing the following formula:

The difference between: Percentage of nitrate times its oxygen value, and percentage of fuel oil times its oxygen value.

For example, in an AN/FO blasting agent having 94.0% AN, 5.4% DFO and 0.6% inert mineral coating utilizing the foregoing formula;

$$94 \times +0.200 = +18.80$$

$$5.4 \times -3.46 = -18.68$$

$$\text{Overall oxygen bal.} = +0.12$$

By these simple calculations the percentage of AN and metal nitrate ratios times their respective oxygen values sum minus the negative oxygen value of the fuel percentage will result in the overall oxygen balance of a specific composition. It should be understood that while compositions outside of approximately +7% and -7% oxygen balance will detonate, it has been observed that the detonation is not as efficient and therefore less desirable from the commercial standpoint. The most efficient detonations are within plus or minus 1% of theoretical oxygen balance.

In mixing the formulations the dry ingredients were first thoroughly blended together before adding the #2 DFO. The oiled mixes were aged for 72 hours during which period of time they were remixed to insure uniformity of distribution. Loading of the test bombs followed a uniform jolting procedure, which has been ex-

perimentally equated to equal the density attained in a twenty foot drill hole under actual loading conditions.

The velocity tests were carried out with 12" lengths of 3" diameter, schedule 40 steel pipe, each length having a 4" x 4" x 1/4" steel plate spot welded to the bottom end. These bombs were shot in the upright position with the primer charge taped to the top end. This primer charge was a 3" diameter by 4" 750-gram charge of 75% high velocity gelatin dynamite. The Dautriche method of determining velocity was used throughout the testing. Velocity leads were inserted in 1/4" holes on 6" centers, at 3" and 9" respectively from the top end of the steel bomb. In addition to velocity of detonation (VOD), density of the composition was determined by weighing each of the bombs to the nearest gram. Cutting, scouring and denting effects were carefully observed on the remnants of the bottom plates after detonation. These observations gave a relative measure of the brisance of each composition tested. The blasting agent compositions which are the subject of this patent have certain definite advantages over conventional blasting agent mixes of prilled AN and fuel oil (FO).

These are:

- A precise control of density over a wide range, from 0.88 to greater than 1.35 (grams/cc.)
- A selection of velocity of detonation over a considerable range, from 7000'/sec. to over 13,500'/sec.
- A choice of explosive strengths over a wide range.
- Economy—the CN formulations while giving all of the above advantages, are also less expensive than AN/FO. In the other metals nitrate compositions, the very high densities possible can partially offset the modest increase in cost over AN/FO.
- Control of sensitivity to detonation in varying degrees; all compositions however being less sensitive than conventional prilled AN/FO mixes.

The following Table I gives the detailed test results of the complete family of (AN/CN) compositions. The columns headed "Percent AN/CN," "Density in grams/cc.," and "Velocity in ft./sec." are self-explanatory. In the fourth column, titled "Brisance," the attempt to apply the old concept of ingredient strength used in the explosives industry for many years to calculate the weight strength of nitroglycerine (NG) sensitized explosives, proved inadequate to accurately describe the results of these blasting agent tests. It was observed in these compositions that the explosive detonation sheared a circular disc out of the center of the base plate on all tests from 100% AN/0% CN through and including 50% AN/50% CN, indicating a very brisant detonation. Calculation of ingredient strength indicates a loss of strength in the same compositions from 66.21% to 31.93% based on TNT as 100%, but both the velocity and cutting effects belie these calculations. Calculation of brisance (cutting or shattering effect) by the standard formula, $\text{brisance} = 3.5 \times (\text{VOD}) / 2500$ gives a much more believable result and corresponds closely to the observed strength.

Costs in the fifth column titled "Ingredient cost/100#" are based on (car load) quantity prices (in 80# bags), delivered in the area of Spokane, Wash.

TABLE I

Ratio of nitrates component, percent AN/CN	Density, Gm./cc.	Velocity, ft./sec.	Relative brisance	Ingredient, cost/100#
100/00-----	0.895	12,006	16.89	\$3.80
90/10-----	0.884	11,560	16.18	3.69
80/20-----	0.921	11,741	16.44	3.59
70/30-----	0.945	10,824	15.15	3.48
60/40-----	0.981	10,082	14.11	3.37
50/50-----	1.000	9,170	12.84	3.26
40/60-----	1.034	8,482	11.87	3.16
30/70-----	1.064	7,855	11.00	3.06
20/80-----	1.120	7,004	9.81	2.96
10/90-----	1.180	(1)	(1)	(2.86)
00/100-----	1.238	(1)	(1)	(2.77)

¹ Incomplete detonation.

FORMULAE FOR TABLE I

Comp.	AN	CN	No. 2 DFO	Alum. stearate Nuodex	Petro- leum coke	Oxygen bal.
AN 100.....	94.59		5.41			-0.01
AN 30 CN 10.....	84.56	9.35	5.50	0.59		-0.03
AN 80 CN 20.....	74.59	18.64	5.60	0.58	0.61	-0.03
AN 70 CN 30.....	64.78	27.77	5.68	0.57	1.10	±0.00
AN 60 CN 40.....	55.13	36.75	5.75	0.58	1.79	-0.03
AN 50 CN 50.....	45.61	45.61	5.81	0.58	2.39	-0.02
AN 40 CN 60.....	36.22	54.34	5.86	0.59	2.99	-0.03
AN 30 CN 70.....	26.98	62.95	5.90	0.59	3.58	+0.02
AN 20 CN 80.....	17.86	71.45	5.94	0.59	4.17	+0.05
AN 10 CN 90.....	8.87	79.77	5.98	0.60	4.77	+0.05
CN 100.....		88.03	6.02	0.60	5.36	-0.05

In calculating the costs for Table I, the Nuodex was eliminated as it is relatively high cost and not really necessary. The percent of aluminum stearate could be added to the percent of petroleum coke which costs the same as DFO, or \$0.02 per pound Nuodex brand aluminum stearate has about the same oxygen value as the coke so no formula change would be involved. This is used as a cost calculation in Table I.

By referring to Table I, it can be seen that these completely detonatable compositions employing a percentage of CN give a range in density from 0.88 to 1.12 gm./cc. and a range in velocities from 11,741'/sec. to 7,004'/sec. Further increases in velocity and sensitivity along with changes in density can be achieved by grinding the AN and/or CN. For example, a 60/40 AN/CN composition having the AN component ground to 68% thru 35 mesh gave a velocity of 11,411'/sec. and a density of 1.06, as compared to 10,082'/sec. and 0.98 density for the unground mix. Grinding of the AN component serves to increase sensitivity also, but the sensitivity of the AN/CN/FO compositions is always less than the sensitivity of ground AN/FO. Grinding of the CN component for the same composition results in an increase in density from 0.98 to 1.01, but no significant change in velocity or sensitivity.

Applicability of the foregoing data trends to other metal nitrates was determined and confirmed by testing of the 60/40 AN/metal nitrate compositions of the alkaline earth metal nitrates of barium (BaN) and strontium (SrN), the alkali metal nitrates of lithium (LiN) and potassium (KN) and the metal nitrate of lead (PbN). These again were oxygen balanced formulations (within about +7 and -7%). Results and formulae are given in Tables II and II-A, respectively, with the comparable AN/CN composition included for reference, and for comparative purposes as graphically shown in the accompanying line drawing.

TABLE II

60/40 AN/metal nitrate	Density, gm./cc.	Velocity, ft./sec.	Relative brisance	Ingredient cost/100#
AN/BaN/FO.....	1.24	10,598	14.84	8.28
AN/SrN/FO.....	1.26	10,411	14.58	6.38
AN/LiN/FO.....	1.14	9,763	13.67	5.81
AN/KN/FO.....	1.12	9,084	12.72	15.49
AN/PbN/FO.....	1.28	11,824	16.55	3.37
AN/CN/FO.....	0.98	10,082	14.11	

TABLE II-A

Nitrates Com- ponent ratio 60/40	AN	Metal nitrate MN	No. 2 DFO	Alum. stearate Nuodex	Petro- leum coke	Oxygen bal.
AN/BaN.....	55.93	37.28	5.38	0.58	0.83	-0.01
AN/SrN.....	55.38	36.91	5.37	0.58	1.76	-0.02
AN/LiN.....	53.98	35.92	5.34	0.57	4.27	+0.01
AN/KN.....	55.24	36.83	5.37	0.58	1.98	-0.011
AN/PbN.....	56.43	37.62	5.39	0.56		+0.01
AN/CN.....	55.13	36.75	5.75	0.58	1.79	-0.03

The same basis was used for calculating costs-conversion of Nuodex brand aluminum stearate to petroleum coke. Cost of lithium nitrate was not included because it is \$1.25 per pound and this puts it out of commercial practicability.

Referring to Table II in general, the fact that all of these compositions detonated at relatively high velocities in the 60/40 ratio establishes that each metal nitrate reacts in a different but characteristic manner with the ammonium nitrate and fuels, and further, that each has a characteristic density, velocity and strength curve of its own shown on the accompanying drawing in these compositions, analogous to the AN/CN curves.

While the compositions of Table II are more expensive to manufacture than AN/FO, they offer the possibility of very high densities (equaling the density of some slurry explosives) to offset the additional cost, and several give higher velocities than the comparable AN/CN/FO mix. Keeping this in mind, that grinding of the AN component of the Table II mixes will increase velocities and densities to even higher levels, the density of this new family of blasting agents can range from 0.88 gm./cc. to over 1.35 gm./cc., and velocities from 7000'/sec. to over 13,500'/sec.

As these compositions are blasting agents, they are not cap sensitive. Being less sensitive than AN/FO, particularly in the low AN-higher density compositions, they require some degree of confinement for the most efficient detonation. As with all blasting agents, high strength, high velocity gelatin primers or cast primers are recommended.

To one skilled in the art it will be immediately apparent from the data in this disclosure that by minor changes in the basic formulations, such as addition of sensitizers, WR flours, metalizing, and other such variations, improvements can be made. All such variations not specifically embodied in this disclosure or claims, are nevertheless included in this invention by intent.

Having thus described our invention, we desire to secure by Letters Patent of the United States the following:

1. A blasting agent composition of the hydrocarbon fuel and nitrates class consisting essentially of:

between about 3.5% and 14.7% of the total composition being said fuel; and

between about 15% and 95% of the nitrate portion being ammonium nitrate including from more than ½% to about 2% of mineral filler coating; and the balance of the nitrate portion being metal nitrate selected from a group consisting of calcium nitrate, barium nitrate, strontium nitrate, lithium nitrate, potassium nitrate, lead nitrate and mixtures thereof, in anhydrous or hydrated form;

said fuel oil being intimately associated with the said nitrates and in proportions resulting in an oxygen balance therebetween of from about +7% to about -7%.

2. The blasting agent according to claim 1 wherein said hydrocarbon fuel is diesel fuel oil.

3. The blasting agent according to claim 1 wherein said nitrates selected from a range of commercial prills from 0% to 60% thru 35 mesh, approximately.

4. The blasting agent according to claim 2 wherein said nitrates selected from a range of commercial prills from 0% to 60% thru 35 mesh, approximately.

5. The blasting agent according to claim 1 wherein the ammonium nitrate is selected from agricultural prill, flake, crystalline, grained, or ground.

6. The blasting agent according to claim 1 wherein the metal nitrate is calcium nitrate.

7. The blasting agent according to claim 1 wherein the metal nitrate is barium nitrate.

8. The blasting agent according to claim 7 wherein the metal nitrate is strontium nitrate.

9. The blasting agent according to claim 1 wherein the metal nitrate is lithium nitrate.

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10. The blasting agent according to claim 1 wherein the metal nitrate is potassium nitrate.
 11. The blasting agent according to claim 1 wherein the metal nitrate is lead nitrate.

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