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2,860,041

BLASTING EXPLOSIVES

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This invention relates to blasting explosives, of the type designated as dynamites, manufactured with compositions containing wet nitrostarch and a latent sensitizing agent.

The invention provides an explosive composition that is relatively non-sensitive in handling and detonation and non-hazardous during the manufacture and packing of the explosive into cartridges or the like but that acquires full sensitiveness by the time the explosive is to be used.

In the manufacture of nitrostarch, the product subsequent to nitration, purification and washing is in wet condition. It has been the practice to reduce the moisture content by centrifuging. After such centrifuging the damp nitrostarch contains approximately 22% of water. This damp material has been dried by heating before mixing with other ingredients to produce commercial or military explosives. While it would be desirable to utilize the damp nitrostarch and thus avoid the danger and expense due to drying and using the dried material, this has been found to be not practicable; explosives made with damp nitrostarch are so insensitive to detonation as to be unsuitable for use as blasting explosives.

It has been found practicable, on the other hand, to remove some of the moisture from damp nitrostarch by treatment with a solid, water soluble inorganic nitrate such as ammonium nitrate or a concentrated aqueous solution of such a nitrate and again centrifuging. Blasting explosives manufactured from nitrostarch of such reduced moisture content, however, are not physically stable, are prone to exude water during storage, and freeze with consequent decrease in sensitivity when exposed to temperatures below the freezing point of water.

We have now discovered a practical and convenient method by which satisfactorily sensitive explosives are manufactured from damp nitrostarch without recourse to the usual drying operation. The resulting explosive is stable and also satisfactory with respect to freezing. Furthermore, this sensitization of the damp nitrostarch does not take place until after the mixing and packing operations are complete. Manufacture by this method offers, therefore, the safety as well as the economic advantages of using damp material.

Briefly stated, our invention comprises the process of and product resulting from incorporating a latent sensitizing agent with wet nitrated carbohydrate, mixing and packaging the resulting explosive, and then causing the resulting product to stand until the said agent sensitizes the explosive by absorbing water from the originally nitrated carbohydrate. In the commercial embodiment, the invention comprises including ammonium nitrate, either with or without admixed sodium nitrate, in the explosive composition.

The effect of the inclusion of the water absorbing or latent sensitizing agent on the detonating characteristics of the nitrostarch used is illustrated in Table I, the nitrostarch containing 22% water.

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TABLE I

Explosive Consists of—	Minimum Size Blasting Cap Causing Detonation After Storage for—		
	6 hours	24 hours	48 hours
Dry nitrostarch.....	1½	1½	1½
Damp nitrostarch.....	16	16	16
Damp nitrostarch plus 1.5% CMC ¹	12	8	8
Damp nitrostarch plus 3% CMC ¹	3½	3	3
Damp nitrostarch plus 5% CMC ¹	1½	1½	1½
Damp nitrostarch plus 10% CMC ¹	1½	1½	1½

¹ Sodium salt of carboxymethylcellulose.

As to materials used, the nitrated carbohydrate is suitably any nitrostarch of kind and degree of nitration commonly used in nitrostarch blasting dynamites.

The latent sensitizer or water absorbing material is organic and hydrophylic but no hygroscopic, that is, not absorptive of moisture in large proportion from air. It is a material adapted, when particles of it are brought into contact with liquid water, to swell in the surface portions of the particles and form over the particles a viscous layer that retards subsequent absorption and penetration of water. In our compositions, the water to be absorbed is ordinarily a saturated solution of inorganic nitrate. There is thus a delayed action in the final transfer of the water solution of the nitrate from the nitrostarch into the said material. This delay provides working time for completion of the manufacturing and packing operations on the explosive composition before the transfer proceeds to the stage of sensitizing the explosive composition. When the water has been absorbed, the viscous mass of which it is a part is substantially non-penetrating into the nitrostarch. Examples of materials that meet the requirements and illustrate the class of materials to be used as latent sensitizers, are locust bean extract, karaya gum, and CMC, in solid powdered form, as of such fineness to pass to the extent of at least 80% by weight through a 30 mesh screen. These materials have been used heretofore in explosives to absorb moisture with which the explosive, made in dry condition, may later come into contact. Hygroscopic desiccating agents, such as calcium chloride, sulfuric acid, and anhydrous sodium sulfate, are not as satisfactory as latent sensitizers for our purpose. Other materials which have been found to be unsatisfactory include the starches, guar gum, methyl cellulose, and silica gel.

Inorganic nitrate components of conventional blasting explosives are used. Thus we introduce ammonium nitrate and with its ordinarily sodium nitrate.

Other usual materials also are incorporated to advantage. Examples are such inorganic and organic fuels as aluminum powder, pecan meal or like shell meal, and petroleum oil. Zinc oxide as an antacid may be used. All of these minor ingredients are introduced for their usual effects and in conventional proportions.

As to proportions of major components, the ammonium nitrate is used in large proportion such as 80–250 parts for 100 of the nitrostarch on the dry basis.

This corresponds to 20–60 parts of the nitrate for 100 of the finished explosive composition. Proportions here and elsewhere herein are expressed as parts by weight.

The nitrostarch is used in the proportion of about 8–25 parts on the wet basis and ordinarily 10–15 parts for 100 of the finished explosive composition.

Alkali metal nitrate, such as sodium or potassium nitrate, is used in proportion less than that of the ammo-

nium nitrate and in amount to give approximate oxygen balance in the whole composition. Suitable proportions are 20-140 parts for 100 of the nitrostarch or 5-35 parts for 100 of the finished explosive composition. Inorganic nitrates may be omitted if their economic and other advantages are not desired.

The water content of the mixture used in compounding the explosive composition is about 15-35 parts for 100 of the nitrostarch on the dry basis. Less than 15 parts of water will not give the desired insensitivity during manufacture and packaging of the explosive. More than 35

mixed thoroughly with each other and then added to and distributed throughout the other, previously mixed ingredients. In all cases, the mixing was comparable and thorough.

The final mixtures so obtained were tested, (1) in the loose form and (2) after being loaded in conventional 1¼" x 8" paper dynamite cartridges. The results of such tests are tabulated in Table I. For comparison, test results are given for a similar composition (#8) prepared with dry nitrostarch and no water absorbing agent.

TABLE II

Preparation No.....	1	2	3	4	5	6	7	8
Composition, percent:								
Nitrostarch, dry basis.....	26.7	26.4	26.4	25.6	25.6	25.6	27.0	0
Moisture in nitrostarch.....	20	22	25	25	25	25	25	0
Dry nitrostarch.....	0	0	0	0	0	0	0	27.0
CMC.....	1.0	2.0	2.0	5.0	0	0	0	0
Locust bean gum.....	0	0	0	0	5.0	0	0	0
Karaya gum.....	0	0	0	0	0	5.0	0	0
Ammonium nitrate.....	51.8	51.2	51.2	49.7	49.7	49.7	52.3	52.3
Sodium nitrate.....	16.1	16.0	16.0	15.5	15.5	15.5	16.3	16.3
Aluminum powder.....	2.7	2.7	2.7	2.55	2.55	2.55	2.7	2.7
Pecan meal.....	1.0	1.0	1.0	0.95	0.95	0.95	1.0	1.0
Petroleum oil.....	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc oxide.....	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Test data on above:								
Standard density, grams/ml.....	1.30	1.35	1.40	1.38	1.35	1.36	1.55	1.18
Ballistic pendulum test, grams TNT.....	11.3	11.2	11.0	11.1	11.0	11.2	-----	11.5
Lead block test, mm.....	17.9	17.8	17.7	17.6	17.7	17.5	-----	18.1
Sensitivity to detonation, cap no.—								
1 hr. after mixing.....	16	16	16	16	16	16	16	1½
16 hrs. after mixing.....	1½	2	8	8	8	5	16	1½
40 hrs. after mixing.....	1½	1½	4	1½	2	2	16	1½
Water resistance, detonations in 5 trials after immersion for—								
24 hours.....	5	5	4	5	5	5	-----	5
64 hours.....	2	1	0	2	1	2	-----	5
88 hours.....	0	0	0	0	0	0	-----	5
100° F. Humidor test, sensitivity, cap no. req. after exposure for—								
8 days.....	1½	1½	4	1½	2	2	-----	1½
35 days.....	8	12	16	12	12	12	-----	1½
65 days.....	16	16	16	16	16	16	-----	1½
Freezing test, sensitivity, cap no. req. after exposure at—								
10° F.....	1½	1½	2	1½	1½	1½	-----	1½
0° F.....	1½	10½	2	1½	2	2	-----	1½
-10° F.....	3	3	4	2½	2	3	-----	1½
-20° F.....	5	6	8	4	5	4	-----	1½

parts are unnecessary and add to the requirement of latent sensitizer that must be used to absorb the extra water.

The test data in Table II show that a damp nitrostarch containing more than 22% of moisture requires a higher ratio of water absorbing agent to water, if sensitization to approximately the same extent is desired, than when the nitrostarch contains less water. Calculation shows these ratios to vary from 0.07 gram of absorbing agent per gram of moisture for nitrostarch containing 20% of moisture up to 0.78 gram of absorbing agent per gram of moisture for nitrostarch containing 25% of moisture. The ratio of absorbing agent to moisture may, therefore, be varied from about 7-80 parts of the agent for 100 of water. It is to be noted that if maximum sensitization is not desired, this ratio may be controlled within the foregoing limits so as to yield an explosive having the desired sensitivity.

The invention will be further illustrated by detailed description in connection with the following specific examples of the practice of it. In these examples, the water absorbing material was of size to pass 100 mesh and the nitrostarch contained 13.0% nitrogen.

Example 1

Mixtures having the compositions shown by Table II were prepared in the usual manner by passing through a sieve or by mixing in a bowl. In some cases all the ingredients other than the damp nitrostarch were well mixed and the damp nitrostarch was then added to and distributed throughout this mixture. In other cases the damp nitrostarch and water absorbing material were

These results illustrate the use of various latent sensitizers and the effect of varying proportions of one of them on the properties of the explosive composition. In this example, the aluminum powder is an inorganic fuel and also a sensitizer. Pecan meal and petroleum oil are examples of organic fuels. The zinc oxide is an anticid stabilizing agent.

The ballistic pendulum test determines the number of grams of the explosive composition equivalent to 10 grams of TNT in the explosion. The lead block test shows the relative extents of compression of small lead cylinders by the various explosives.

In making the compositions for these tests of Table II, the materials were thoroughly mixed. Water, when used, was associated in advance with the nitrostarch.

It will be seen that the retention in the explosive composition of the water added with the nitrostarch does not materially affect the explosive power of the composition when the moisture absorbing agent is incorporated, but increases the bulk density of the packed explosive. The water, however, desensitizes the explosive composition as a whole during the manufacturing and packing operations. The small percentage of sodium carboxymethylcellulose, locust bean gum or karaya gum makes this desensitization effect of limited duration. As a result, the sensitivity of the explosive returns within 16 hours so that the explosive is suitable for practical use.

After absorption of the moisture by the sensitizing agent, the explosive is not unduly desensitized by subsequent exposure to low temperatures.

With the limited proportions of sensitizing agent used

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in conjunction with damp nitrostarch or nitrocellulose, these agents on the other hand do not have the water resistance effect they are known to exhibit in conjunction with dry nitrostarch or nitrocellulose.

Example 2

Nitrostarch that has been made and centrifuged to a water content of approximately 22% is mixed with 8 parts of sodium carboxymethylcellulose for 100 parts dry weight of the nitrostarch.

The resulting material after standing for 16 hours was sensitive to detonation although not an economical commercial explosive.

Example 3

The procedure and composition of Example 2 were used with the incorporation of 200 parts of ammonium nitrate for 100 of the nitrostarch.

The product of this example is reasonably satisfactory as a blasting explosive but does not show the desired oxygen balance between oxygen consuming and oxygen supplying components.

It is to be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. In making an explosive composition of reduced hazard during manufacture and of substantially full sensitiveness to detonation at the time of use, the process which comprises mixing nitrostarch in water wet condition, the water content being 15-35 parts by weight for 100 of the nitrostarch on the dry basis, with a solid, finely divided, non-hygroscopic water absorbent selected from the group consisting of locust bean gum extract, gum karaya, and an alkali metal salt of carboxymethylcellulose, the absorbent being in the proportion of about 7-80 parts by weight for 100 of water in the explosive, serving as a water absorbing latent sensitizer of the composition and, in absorbing water, forming first a viscous swollen

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surface layer over the particles of the absorbent and this viscous layer delaying subsequent absorption so that water is not absorbed from the nitrostarch in amount to sensitize the explosive until the manufacturing operation is completed.

2. The process of claim 1 which includes incorporating into the explosive, in wet condition, ammonium nitrate in the proportion of 80-250 parts by weight for 100 of the nitrostarch on the dry basis.

3. An explosive composition of lower sensitiveness when first compounded than after aging, the composition consisting of nitrostarch in wet condition, the proportion of water being 15-35 parts by weight for 100 of the nitrostarch on the dry basis, and a hydrophilic non-hygroscopic organic material selected from the group consisting of locust bean gum extract, gum karaya, and an alkali metal salt of carboxymethylcellulose, the proportion of the said hydrophilic organic material being about 7-80 parts by weight for 100 of water in the explosive composition.

4. An explosive composition as described in claim 3, the water being absorbed substantially completely in the said water absorbent in the form of a viscous mass that is substantially non-penetrating into the nitrostarch and the said composition being the product of the process of claim 1.

5. The composition of claim 3 which includes ammonium nitrate in the proportion of 80-250 parts by weight for 100 of the nitrostarch on the dry basis.

6. The composition of claim 5 which includes sodium nitrate in the proportion of 20-140 parts by weight for 100 of the nitrostarch on the dry basis, the sodium nitrate giving approximate oxygen balance in the composition.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,860,041

November 11, 1958

George L. Griffith, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 20, for "no hydroscopic" read -- not hygroscopic --;
line 52, for "its" read -- it --; column 3, line 46, for "waster" read
-- water --.

Signed and sealed this 3rd day of February 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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