March 8, 1938. I. W. D. HACKH ET AL 2,110,220

EXPLOSIVE

Filed Sept. 17, 1934

FIG. 1.

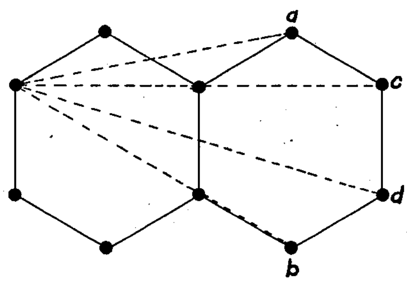


FIG. 2.

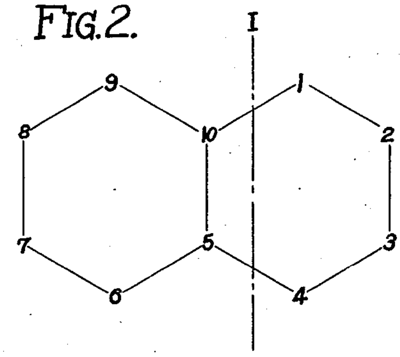


FIG. 3.

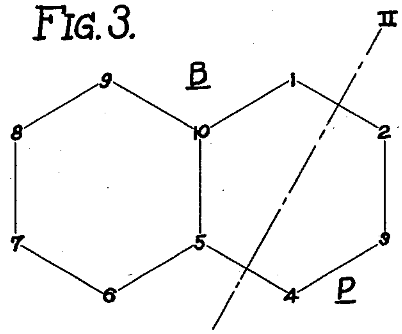


FIG. 4.

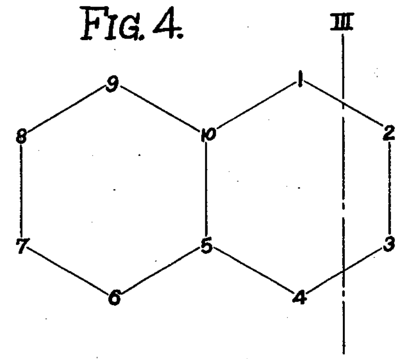
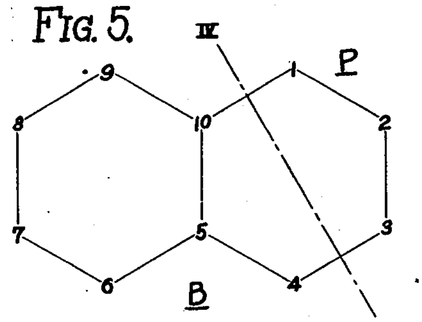


FIG. 5.



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2,110,220

EXPLOSIVE

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Application September 17, 1934, Serial No. 744,362

7 Claims. (Cl. 52—13)

This invention relates to explosives such as the nitro-compound explosives, and has for its objects an improved explosive and method of making the same, which explosive is more economical and safer to make and handle and more effective in use than explosives heretofore. Other objects and advantages will appear in the following description:

In the drawing attached hereto Figs. 1 to 5 are diagrammatic representations of molecular structure to which reference will be made in the specification.

Broadly, our invention relates to the production of a nitro-compound explosive from a basic mixture of nitro-compounds of the single benzene ring such as trinitrobenzene and/or its derivatives such as trinitrotoluene, picric acid, styphnic acid, 1.3.5 trinitro-2-4-dimethyl benzene with the addition of sufficient alkali, ammonium, or alkali earth nitrate to produce complete combustion. Other oxidizers may be used. In basic mixtures of the foregoing type, as is well known in the art, a very small amount of moisture, such as water, is present.

We have found that the foregoing basic explosive mixture is rendered highly explosive by the addition of a promoter or accelerating catalyst of specified molecular structure and a catalytic explosive such as the nitronaphthalenes or their derivatives, namely, α-mononitronaphthalene, β-mononitronaphthalene, (1.2) (1.3) (1.4) (1.6) (1.7) or (1.8)-dinitronaphthalene, which sets off the basic explosive mixture at a rapid rate. It is to be understood that the basic explosive mixture and the promoter and catalytic explosive are intimately mixed in our improved explosive.

We find that the promoters or accelerating catalysts are very active and extremely efficient when they contain an essential atomic distance very closely approaching some one of the essential atomic distances in the naphthalene complex which is used as the catalytic explosive. These essential atomic distances are indicated by the dotted lines in Fig. 1 of the drawing and are according to modern X-ray investigations and calculated from the recently published results by Linus Pauling and M. L. Huggins (Zeitschrift fur Kristallographic, vol. 87, page 205, 1934, published by Akademische Verlagsgesellschaft M. B. H., Leipzig) and from the findings of E. H. Westling published in Chemical News (London) July 17, 1931.

Referring to Fig. 1, the essential atomic distances in the naphthalene complex are:

Distance	Angstrom units
a	3.83
b	4.19
c	4.84
d	5.13

We have found that such molecules as come near to the above distances in their essential atomic distance between the end atoms of their respective molecules, exclusive of hydrogen atoms, are very efficient promoters in a powder mixture containing nitro-derivatives of naphthalene. Taking the carbon kernel as .09 angstrom units in thickness, we find from extensive experiments that all molecules having a molecular length falling between 3.73–3.93; 4.09–4.29; 4.74–4.94; and 5.03–5.23 angstrom units are extremely effective promoters in breaking the naphthalene ring by collision.

For example, we have found that propionic acid or its alpha derivatives such as lactic acid, alanine, iso-butyric acid, a-chloropropionic acid, etc., or propanol or its alpha derivatives such as 1.1-dimethyl propanol, iso-butyl alcohol, etc., or its beta derivatives such as 2-methyl propanol, 2.2 dimethyl propanol, etc., or allyl alcohol and others, all have a distance within .09 angstrom units of being 3.83 angstrom units between their end atoms, and when any of these ingredients are added to a suitable explosive mixture containing nitronaphthalenes it produces a very good brisance and great shattering power.

Similarly we have found that 1.2-dichloroethane, ethylene chlorhydrine, and trans-dichloroethylene and others have atomic distances close to 4.19 angstrom units and act as good promoters in setting off a mixture containing nitronaphthalenes.

Butanol and its alpha derivatives such as 1-methyl butanol, 1.1-dimethyl butanol or beta derivatives such as 2-methyl butanol, 2.2 dimethyl butanol, or its gamma derivatives such as 3-methyl butanol, 3.3 dimethyl butanol, or its alpha and gamma derivatives such as 1.1.3.3-tetramethyl butanol or its alpha-beta-gamma derivatives such as 1.2.3-trimethyl butanol, or butyric acid or its alpha derivatives such as 1-hydroxy butyric acid, 1-methyl butyric acid, 1-amino butyric acid, or its beta derivatives such as 2-hydroxy butyric acid, 2-methyl butyric acid or butyric aldehyde or its alpha derivatives such as 1-methyl butyric aldehyde, or its beta derivatives such as 2-methyl butyric aldehyde propane-1.3-diol, glycerol, methoxyethanol, ethyl acetate, methyl propionate, act as good promoters in setting off an explosive mixture containing nitronaphthalenes since they have atomic distances close to 4.84 angstrom units. The molecular length of butyric aldehyde is closest to 4.84 angstrom units, hence is the most effective of the compounds named.

Similarly, benzyl alcohol or its derivatives such as o-hydroxy benzyl alcohol, m-hydroxy benzyl alcohol, v-dihydroxy benzyl alcohol, o-methyl benzyl alcohol, m-methyl benzyl alcohol or benzaldehyde or its derivatives such as o-hydroxy benzaldehyde, m-hydroxy benzaldehyde, v-dimethyl benzaldehyde, or benzoic acid such as salicylic acid, m-hydroxy benzoic acid, o-methyl benzoic acid, m-methyl benzoic acid, or p-hydroxytoluene, hydrochinone, quinone, nitrobenzene, benzylamine, and anisol or the derivatives of any of those above following and including p-hydroxytoluene come close to 5.13 in their molecular lengths, hence are good promoters in an explosive mixture containing nitronaphthalenes. Of the foregoing, benzoic acid has a slower brisance than benzaldehyde, their respective molecular lengths being 5.18 and 5.11 angstrom units, which are within the limits of the atomic distances which act catalytically on the naphthalene complex.

We have tried many other substances, each approaching in its molecule one of the four essential atomic distances 3.83; 4.19; 4.84; or 5.13 angstrom units, and we find that the catalytic action will best occur if the effective distance occurs only at one place or direction in the molecule of the promoter. Thus phthalic acid or phthalic aldehyde have the distance 5.18 or 5.11 in two directions, at an angle between the directions such that the average distance becomes quite different to 5.18 or 5.11, the effective distance of benzoic acid and therefore phthalic acid or phthalic aldehyde is less efficient as a promoter than benzoic acid or benzaldehyde, for the tendency of the molecules to collide sideways prevents either of the useful distance 5.18 in phthalic acid or either of the useful distance 5.11 in phthalic aldehyde, to be effective.

The reason for nitronaphthalene molecules to decompose rapidly in the presence of a promoter is the tendency of the naphthalene ring to break between the carbon atoms 1 and 2, and the carbon atoms 4 and 5 as shown diagrammatically in Figure 3 of the attached drawing (Figs. 2 to 5 inclusive showing the four possible ring fractures).

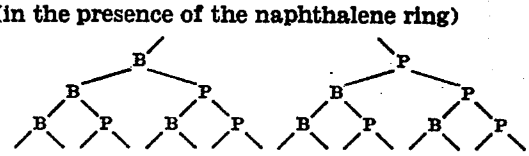
Of the four possibilities shown in Figs. 2 to 5, inclusive, III and V are identical and form a benzyl radical B as well as a propyl radical P according to the equation:

$$C_{10}H_7NO_2 \rightarrow C_6H_4C'' + C_3H_3'' + NO_2'$$

where C_6H_4C'' is the skeleton of benzaldehyde, B, and C_3H_3'' an easily oxidized propionic residue P, while NO_2' is an active oxidizing group. Thus in the presence of either B or P the naphthalene ring is broken into B and P, these decomposition products reacting again with the naphthalene ring to produce B and P. As long as molecules containing the naphthalene ring are present, this process will go on as a geometrically progressive chain reaction of the type:

B or P

(in the presence of the naphthalene ring)



and so on (as long as the naphthalene ring system is present).

Some of the residues B will temporarily supply a new molecule of benzaldehyde, thus acting as additional promoter, while some of them, having been newly formed, will be in active vibration and oscillation and act as a disturbing and exciting agency in the presence of trinitrobenzene compounds, such as trinitrotoluene, picric acid or trinitrobenzene.

Therefore, a promoter containing the useful atomic distance of about 3.83, 4.19, 4.84, or 5.13 angstrom units will first decompose the nitronaphthalene, then the residual compounds of nitronaphthalene will partly act as catalysts to the nitrobenzene compounds in the explosive mixture, and will partly act as promoters in breaking down more naphthalene rings and partly oxidize themselves and aid in the explosion, thus behaving as a catalytic explosive by taking an integral part in the catalysis of the reaction as well as in the combustion.

While both benzaldehyde residues and propionic residues are formed from the naphthalene ring, and while also phthalic residues and ethyl radicals may be formed in the splitting of the ring, and while all these may act as catalysts during the explosion, we find that for the initial splitting of the naphthalene ring any compound of the specified molecular length can act as a promoter. In general, the relative amounts, by weight, of the promoter we add to the nitronaphthalene may be from 0.2 to 4%.

The general formula (by weight) for our explosive mixture is thus:

0.005 to 2% promoter of approximate molecular length such as specified.
5 to 10% catalytic explosive, such as nitronaphthalene derivatives.
15 to 55% explosive, such as trinitrobenzene and its derivatives.
40 to 80% oxidizer, such as the alkali nitrates which include ammonium nitrate.

In making our explosive we first mix the organic substances by melting the nitronaphthalene, incorporating the promoter and adding the explosive, such as trinitrobenzene or its derivatives. Into this mixture, while still in the molten state, we incorporate the finely powdered nitrate so that the granules of the latter are coated with the organic explosive mixture. The mixture can now be exploded by an ordinary detonating cap or otherwise.

A typical formula for our explosive mixture is as follows:

	Per cent
Alpha or beta-nitronaphthalene	7.5
1.5-dinitronaphthalene	0.4
Normal butanol	0.1
Trinitro benzene	33
Sodium nitrate	59

The above proportions are by weight, and the resultant mixture will decompose completely and produces only a white smoke and no nitrous gases.

Another good explosive mixture is:

	Per cent
Alpha-nitronaphthalene	7.15
1.8-dinitronaphthalene	.45
Propionic acid	.08
1.3.5-trinitrotoluene	31.4
Sodium nitrate	60.92

This mixture explodes with a high brisance and leaves on explosion a white smoke and no nitrous gases.

A still further formula is:

	Per cent
Beta-nitronaphthalene	7.5
1.5-dinitronaphthalene	0.5
Benzaldehyde	0.08
Picric acid	33.12
Sodium nitrate	58.8

This mixture also explodes with a high brisance and leaves a white smoke and no objectionable gases.

We do not wish to limit ourselves to these three formulas. They merely indicate the use of trinitrobenzene, trinitrotoluene and picric acid. We find that the promoters can be interchanged. Thus butanol can be used in all three mixtures. Likewise a mixture of promoters can be used. As set out above, the promoter acts as an accelerating catalyst upon the nitronaphthalene, which in turn is the catalytic explosive which sets off the explosive proper consisting of trinitrobenzene or its derivatives.

In the claims the term "molecular length" is the distance between the opposite end atoms in the molecules whether of the aromatic or aliphatic group, exclusive of the hydrogen atoms. This is the average or equilibrium distance.

We claim:—

1. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, an organic promoter in an amount not greater than 2% by weight of the entire mixture, said promoter being one of the compounds of a group in which the atomic distance between the opposite end atoms most remote from each other in each molecule therein exclusive of hydrogen is within .09 angstrom units of being equal to one of the four characteristic atomic distances of the naphthalene ring complex, namely 3.83; 4.19; 4.84; 5.13 angstrom units.

2. A nitro-compound explosive mixture comprising a member of the group consisting of mononitro-naphthalene, dinitro-naphthalene, trinitro-naphthalene, tetranitro-naphthalene, an oxidizer, and an organic promoter in an amount not greater than 2% by weight of the entire mixture, said promoter being one of the compounds of a group in which the atomic distance between the opposite end atoms most remote from each other in each molecule therein exclusive of hydrogen is within .09 angstrom units of being equal to one of the four characteristic atomic distances of the naphthalene ring complex, namely 3.83; 4.19; 4.84; 5.13 angstrom units.

3. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, and an organic promoter in an amount not greater than 2% by weight of the entire mixture, said promoter being one in which the atomic distance between the opposite end atoms most remote from each other in each molecule therein exclusive of hydrogen is within .09 angstrom units of being equal to one of the four characteristic atomic distances of the naphthalene ring complex, said promoter comprising a member of the group consisting of propanol, butanol, propionic acid, lactic acid, butyric acid, alanine, butyric aldehyde, benzaldehyde, benzoic acid and salicylic acid.

4. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, and a promoter, said promoter being benzaldehyde in an amount not greater than 2% by weight of the entire mixture.

5. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, and a promoter, said promoter being butanol in an amount not greater than 2% by weight of the entire mixture.

6. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, and a promoter, said promoter being propionic acid in an amount not greater than 2% by weight of the entire mixture.

7. A nitro-compound explosive mixture including a nitro-derivative of naphthalene, an oxidizer, and an organic promoter, said promoter being one of the compounds of a group in which the atomic distance between the opposite end atoms in each molecule therein measured in the direction of the greatest length of the molecule, exclusive of hydrogen, is within .09 angstrom units of being equal to one of the four characteristic atomic distances of the naphthalene ring complex, namely 3.83; 4.19; 4.84; 5.13 angstrom units.

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