Convention Application for a Patent

We, PRB NOBEL EXPLOSIFS,

of 12, avenue de Broqueville, B-1150 Brussels, Belgium,

hereby apply for the grant of a Patent

for an invention entitled "CONTINUOUS PROCESS FOR THE PRODUCTION OF SYRUPY EXPLOSIVE COMPOSITIONS, AND PRODUCTS OF SUCH PROCESS"

which is described in the accompanying complete specification.

This application is a Convention application and is based on the application numbered 82870005.4 for a patent or similar protection made in Europe on 26th January, 1982.

Our address for service is: CALLINAN AND ASSOCIATES Patent Attorneys, of

48-50 Bridge Road, Richmond, State of Victoria, Australia.

Dated this 12th day of January, 1983.

PRB NOBEL EXPLOSIFS

By its Patent Attorneys:
Deletion in Support of
(a) A Convention Application
(b) An Application
for a Patent on a Patent of Addition

In support of the application/Convention Application made by
(c) PRB NOBEL EXPLOSIFS, hereinafter termed "the said Company"
for a patent on a patent of addition for an invention entitled:
"CONTINUOUS PROCESS FOR THE PRODUCTION OF SYRUPY
EXPLOSIVE COMPOSITIONS, AND PRODUCTS OF SUCH PROCESS"

I/we (a) LUCIEN BRADIER and JACQUES ROEGIERS, Directors of
the said Company,
of (b) 12, avenue de Brogueville, B-1150 Brussels,
Belgium
do solemnly and sincerely declare as follows:

1. (a) LUCIEN BRADIER and JACQUES ROEGIERS,
(b) LUCIEN BRADIER and JACQUES ROEGIERS,
we are authorised by the said Company
the applicant for the patent on a patent of addition to make this declaration on its behalf.

2. (b) The basic application, as defined by Section 141 of the Act was made
in Europe on the 26th day of January 1982
by the said Company.

3. (b) LUCIEN WATERLOT, of Nieuwe Hoevenstraat, 10, B-2400 Mol,
Belgium
is the actual inventor of the invention and the facts
upon which the said Company is entitled to make the application are as follows:

(m) The said Company would, if a patent was to be granted upon an application made by the said
actual inventor, be entitled to have the patent assigned to it.
The present invention relates to improvements made to the continuous manufacture and packaging of syrupy explosive compositions having the property of solidifying rapidly, without sticking, so as to be sufficiently rigid and coherent to allow packaging in a paper case on a cartridge machine of the cutting type.

Claim.

1. A continuous process for the production of syrupy compositions which are adapted to be put in cartridges, wherein an oxidising solution, which is prepared hot, of usual composition and containing inorganic or organic salts dissolved in water, is mixed with a reducing premix consisting of solid fuels based on metal fuels and of a hardener introduced in solid form, prior to the final solidification of the composition, the mixture then being put in cartridges using a cutting machine.
CONTINUOUS PROCESS FOR THE PRODUCTION OF SYRUPY EXPLOSIVE COMPOSITIONS, AND PRODUCTS OF SUCH PROCESS
The present invention relates to improvements made to the continuous manufacture and packaging of syrupy explosive compositions having the property of solidifying rapidly, without sticking, so as to be sufficiently rigid and coherent to allow packaging in a paper case on a cartridge machine of the cutting type.

Syrupy explosives (also called "slurries") appeared on the market a few years ago; in these explosives, the detonation support is provided by the oxidation-reduction reaction which takes place after ignition between a hot prepared oxidising solution of inorganic or organic salts dissolved in water and a reducing premix consisting of solid fuels, mainly different types of aluminium, to the exclusion of any actual traditional explosive substance. Such explosives are described, in particular, in U.S. Patent 3,121,036 and in Belgian Patent 575,043.

In this kind of composition, the sensitivity is mainly due to the presence of aluminium of the "paint" type, while additional sensitivity is provided in accordance with the density of the microbubbles of gas produced by a chemical reaction within the mass; a plastic texture of a more or less rubbery nature is imparted to the explosive by the gelling, by means of a crosslinking agent, of the guar gums present in the formulation.
The said Company would, if a patent was to be granted upon an application made by the said actual inventor, be entitled to have the patent assigned to it.

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The advantage of these compositions lies in an increase in the safety in the course of manufacture and during storage, transportation and use, while the processing methods offer a more extensive diversification than in the case of conventional explosives.

In the form of small diameters (that is to say from 20 to 40 mm), this type of composition is deficient on two counts. On the one hand, as the diameter is reduced, the detonation capacity and the air-gap test values from one cartridge to the next require increasingly active sensitizers in increasingly large proportions; on the other hand, the plastic consistency of the cartridges makes them compressible; in mine holes, this is likely to stop the detonation under the effect of the compression waves which propagate ahead of the detonation front.

Thus, numerous modifications have been made to these formulations in recent years; amongst these modifications, a particularly valuable one consisted in improving the sensitivity of the priming by the introduction of a crystal modifier into the composition. When the slurry cools, the modifier controls the crystallisation of the salts, preventing the formation of excessively large crystals in favour of microcrystals which assist detonation.

In this way, it was possible to increase the sensitivity, without having to use excessive proportions of aluminium sensitiser, so as to ensure detonation for cartridge diameters of less than 20 mm; an important additional advantage is due to the fact that certain
3. Explosives of this kind can have a solid texture instead of a plastic consistency, thus enabling them to withstand better the effects of the compression waves described above; the efficacy is the greater, the higher the ammonium nitrate content, that is to say the higher the crystallisation point, of the solution used to manufacture the explosive.

The disadvantage generally shown by the explosive slurries improved in this way is the great difficulty associated with packaging: the viscosity of some of the slurries is such that the usual means (machines of the chub-pack type or extrusion guns) are not suitable. Furthermore, a conventional method of filling cartridges with the product cooled in a tank, such as is used for traditional explosives (for example dynamite), from a screw extruder or a cutting machine of the Rollex type, has the dual disadvantage of being a batch process and of completely desensitising the explosive. At this point, moreover, the cooled product is in the form of a solid, but nevertheless powdery and friable mass, the coherence of which is too low for it to be easily put in cartridges.

This is the case, in particular, of the composition described in U.S. Patent 4,033,264, which describes the product obtained as a friable gelled explosive composition.

The object of the present invention is consequently to improve syrupy explosive compositions and to propose a process for their preparation which makes it possible to obtain explosives with a solid final texture permitting a solidification which makes the product rigid, but nevertheless sufficiently coherent to
ing machine of the cutting type.

According to an additional feature of the invention, it is proposed to obtain a product which solidifies rapidly, but without sticking.

The process of the invention makes it possible to obtain cartridges of the type used for dynamite, starting from a syrupy explosive, without the packaging difficulty due to the friability of the product.

Consequently, the invention relates to a continuous process for the production of syrupy compositions which can be put in cartridges, characterised in that an oxidising solution, which is prepared hot, of usual composition and containing inorganic or organic salts dissolved in water, is mixed with a reducing premix consisting of solid fuels based on metal fuels and of a hardener introduced in solid form, prior to the final solidification of the composition, the mixture then being put in cartridges using a cutting machine, preferably a cartridging machine of the Rollex type.

Advantageously, the said mixture is subjected to rapid and immediate cooling on leaving the device for mixing the oxidising solution with the reducing premix.

The above mentioned addition of the hardener makes it possible, on cooling, to obtain the explosive composition in a hardened and bound form, that is to say coherent and not having any property of friability.

Cartridges prepared with this composition and by the above process are characterised, surprisingly, by increased
air-gap test values (about 6 cm) in air in the case of the invention.

Furthermore, because the composition of the invention is no longer compressible, no "channel effect" is observed, as is the case for the composition described in Belgian Patent 698,434, in which setting or hardening of the composition is ensured by means of metal salts.

The hardener required for extrudability is of the carboxymethylcellulose type; its proportion according to the invention, expressed as a percentage by weight relative to the final formulation of the explosive composition, is advantageously between 1 and 3%, preferably between 1.5 and 2.5% and very particularly advantageously of the order of 2%.

Carboxymethylcellulose is a well-known product in the slurried explosives industry; it is frequently cited as a fuel and thickener; this is the case in German Patents 1,813,173, 2,826,569 and 2,643,499, in French Patents 1,550,925 and 1,244,201 or in U.S. Reissue 26,115 and U.S. Patents 3,235,425 and 3,524,777; certain special properties have been found in it and claimed, such as, for example, properties for obtaining a better cross-linking (U.S. Patents 3,344,004 and 3,251,781), or a better water resistance and also longer storage (British Patent 1,238,818), or an improved stability (French Patent 2,006,804); in all these cases, it forms an integral part of the oxidising solution; it is combined with the aqueous phase, either directly or in a premix with glycol (British Patent 2,013,173).
The present invention is based upon another peculiar feature, namely: it has been found that carboxymethylcellulose acts as a hardener, which is essential for extrudability on a cartridging machine of the cutting type, if it is, in accordance with the invention, incorporated into the solid part of the composition (that is to say into the reducing premix); therefore, in contrast to the abovementioned references, there is not simply an action of thickening (which would only have an effect on the higher or lower viscosity of the product), or a crosslinking action (which would make the paste too plastic for the desired purpose), or an action for improved water resistance or on the stability.

In this respect, it was found, on the contrary, that the rigidity and the cohesion at the time of cartridging were at a maximum when the solution did not contain the guar gums normally used; these gums, by their very nature, in fact always providing the final product with a certain plasticity to the detriment of its rigidity. Guar gums are therefore only to be used in the compositions of the invention when a compromise is sought between plasticity and rigidity; in the normal case in which it is desired to obtain maximum rigidity and maximum cohesion, the guar gum forms an integral part of the solid premix and must be of the self-crosslinking type.

To prevent the explosive compositions obtained from having a sticky consistency, it appears that the addition of a non-stick agent of the talc type makes it possible to facilitate the processing of the compositions of the invention on the cartridging machines.
It was found that the action of the hardener can be enhanced by the presence of a cross-linking agent based on chromium or antimony, which acts on the guar gum when the latter is present.

Accordingly, particularly satisfactory results, easily permitting transposition to cartridging on a machine of the well-known "Rollex" type, can be obtained by this process when the composition undergoes rapid and immediate cooling on leaving the device for mixing the oxidising solution with the reducing premix.

The preparation of the syrupy explosive compositions or "slurries" is well known to those skilled in the art, and the invention extends to compositions of the cited state of the art and incorporated herein by reference, containing a hardener in the solid combustible premix.

The presence, in the solution, of a crystal regulator from the family of the sodium methylnaphthalene-sulphates gives particularly favourable results.

Also, the presence of 5 to 10% of urea in the solution, in addition to the oxidising salts, imparts excellent explosive characteristics to the compositions obtained.

In the case where it is desired to obtain a fibrous rigid texture for the composition, it appeared advantageous to add polyacrylamide to the hardener of the carboxymethylcellulose type.

The invention will be described in greater detail by way of illustration, without implying a limitation, with the aid of the examples which follow.
solution, at 80°C, containing:

- water 16.95 parts by weight
- thiourea 0.11 "
- biopolymer 0.11 "
- crystallisation regulator 2.26 "
- NO$_3$Na 6.78 "
- NO$_3$NH$_4$ 73.79 "

100.00

and on the other hand a premix containing:

- aluminium sensitiser 46.15 parts by weight
- metal fuel 19.23 "
- starch 16.92 "
- self-crosslinking guar gum 2.30 "
- hardener of the carboxymethylcellulose type 15.40 "

100.00

The mixture is prepared, in proportions of 87 parts by weight of solution and 13 parts by weight of premix, by simply passing the ingredients through a slurry mixer, from which the mixture is brought, either under gravity or by pumping, onto the conveyor belt of a "Rollex"-type machine, cooled by water and air, and fed under the knife of the machine, in the form of a mat ready for cutting, at a temperature of about 40 to 45°C, that is to say sufficiently cooled and coherent to be put in cartridges. Each cut portion is moulded individually in a paper case, which, once closed, provides and maintains the shape of
9.

the cartridge thus obtained.

The specific gravity of the explosive, which governs the weight of the cartridges, can, if necessary, be adjusted by introducing 0 to 0.8 part by weight of NO$_2$Na, in a 75/25 solution, into the mixer at the same time as the solution and the premix of Example 1; the explosive, preferably containing 0.4 part by weight of NO$_2$Na, put in a cartridge of 30 mm/200 g, gives, without confinement, an air-gap test value in air of 6 cm and a detonation velocity of 3,800 to 4,100 m/s by priming with a detonator containing 440 mg of hexogen, at a specific gravity of 1.10 - 1.15. If the atomised aluminium is replaced by silicon, the following are obtained, at a specific gravity of 1.10:

- velocity 30 mm - deto 330 mg : - 3,800 m/s
- air-gap test value " deto 440 mg : 3 cm
- power (deto 750 mg) : 360 cc

The power of the explosive of Example 1, determined with a lead block, is 400 cc, that is to say equivalent to that of a dynamite of a very high grade.

The process remains compatible with all the formulations based on the solution of Example 1, in which the proportion of metal fuel in the premix varies from 0 to 8 parts by weight. This will be illustrated in the two examples which follow, giving the characteristics of the two extreme formulations.
Example 2
Composition comprising 89.5% of solution and 10.5% of premix not containing metal fuel (except the Al sensitizer):
- specific gravity : 1.05
- velocity $\varnothing30\text{mm deto}440\text{mg} : 3,890 \text{m/s}$
- air-gap test value " - " : 4 cm
- power (deto 750 mg) : 320 cc

Example 3
Composition comprising 81.5% of solution and 18.5% of premix containing 8 parts of metal fuel (Al) in addition to the Al sensitizer, at a specific gravity of 1.15:
- velocity $\varnothing30\text{mm deto}440\text{mg} : 3,930 \text{m/s}$
- air-gap test value " - " : 6 cm
- power (deto 750 mg) : 430 cc

Example 4
In explosives similar to those of the preceding examples, the effect of the self-crosslinking guar gum added to the premix can be enhanced by 0.5 part by weight of a crosslinking agent based on chromium or antimony.
Example 5

To 86 parts by weight of the solution of Example 1 are added 14 parts by weight of a premix consisting of:

- aluminium sensitiser: 42.85 parts by weight
- metal fuel: 17.85 "
- starch: 15.70 "
- self-crosslinking guar gum: 2.15 "
- carboxymethylcellulose hardener: 14.30 "
- non-stick agent: talc: 7.15 "

100.00

The remaining operations take place as in Examples 1 - 4. The product has excellent non-stick properties and is easily processed on a cartridge machine.

Example 6

In the case where a fibrous rigid texture is desired, the hardener of the carboxymethylcellulose-type can also be combined with polyacrylamide.

In this case, 87 parts by weight of the solution of Example 1 are mixed with 13 parts by weight of the following premix:

- aluminium sensitiser: 42.30 parts by weight
- metal fuel: 15.38 "
- starch: 15.38 "
- self-crosslinking guar gum: 2.30 "
- hardener of the CMC type: 13.10 "
- polyacrylamide: 11.54 "

The characteristics of the products are the same as for Example 1.
Example 7

The solution of Example 1 is replaced by the following solution:

- water : 9.77 to 13.00 parts by weight
- thiourea : 0.11 to 0.15
- biopolymer : 0.11 to 0.15
- crystal regulator : 0.11 to 2.25
- urea : 5.75 to 8.00
- NO₃Na : 17.25 to 7.00
- NO₂NH₄ : 66.90 to 69.45

The rinsing operations are carried out as in the preceding examples, and the results obtained are similar.
The claims defining the invention are as follows:

1. A continuous process for the production of syrupy compositions which are adapted to be put in cartridges, wherein an oxidising solution, which is prepared hot, of usual composition and containing inorganic or organic salts dissolved in water, is mixed with a reducing premix consisting of solid fuels based on metal fuels and of a hardener introduced in solid form, prior to the final solidification of the composition, the mixture then being put in cartridges using a cutting machine.

2. The process according to claim 1, wherein said cutting machine is a cartridging machine of the Rollex type.

3. The process according to claim 1 or claim 2, wherein said mixture is subjected to rapid and immediate cooling on leaving the device for mixing the oxidising solution with the reducing premix.

4. The process according to any one of claims 1 to 3, wherein the hardener used in solid form in the reducing premix is of the carboxymethylcellulose type.

5. The process according to any one of claims 1 to 4, wherein the proportion of hardener, expressed as a percentage by weight relative to the final formulation of the explosives composition, is between 1 and 3%, preferably between 1.5 and 2.5% and very particularly about 2%.

6. The process according to any one of claims 1 to 5, wherein a non-stick agent is incorporated into said mixture.
plastic texture of a more or less rubbery nature is imparted to the explosive by the gelling, by means of a crosslinking agent, of the guar gums present in the formulation.

7. The process according to claim 6, wherein said non-stick agent incorporated is talc.

8. The process according to any one of claims 1 to 7, wherein the action of the hardener is enhanced by the addition of a crosslinking agent based on chromium or antimony.

9. The process according to any one of claims 1 to 8, wherein the metal fuels added are aluminium and/or silicon.

10. The process according to any one of claims 1 to 9, wherein a crystal regulator from the family of the sodium methylnaphthalenesulphonates is added to the oxidising solution.

11. The process according to any one of claims 1 to 10, wherein from 5 to 10% of urea is added to the oxidising solution.

12. The process according to any one of claims 1 to 11, wherein the final specific gravity of the explosive is adjusted by means of from 0 to 0.8% by weight of NO₂Na in a 75/25 solution.

13. Cartridges of syrupy explosive compositions when produced by the process of any one of claims 1 to 12.

14. A continuous process for the production of syrupy compositions, substantially as described herein with reference to any one of the Examples.
15. Cartridges of syrupy explosive compositions, substantially as described herein with reference to any one of the Examples.

DATED this 12th day of January, 1983.

PRB NOBEL EXPLOSIFS
By its Patent Attorneys:
CALLINAN AND ASSOCIATES

[Signature]
END