

The invention relates to a process for manufacturing compressible wax-bound explosive substance granulates according to the concept of patent claim 1.

Solid crystalline explosive substances, also called detonators, such as trimethylene trinitramine (Hexogen, RDX), tetramethylene tetranitramine (Octogen, HMX), pentaerythritol tetranitrate (Nitropenta, PETN) in a pure form, or if appropriate with additions of metal powders such as aluminium, tungsten etc. for special applications, are conventionally phlegmatized by a coating of wax onto the particle surface in concentrations between 2 and 20%. The wax has the property of a plastic binder which reduces frictional forces. It thus permits laboratory treatment by a compression method and also reduces the sensitivity of compressed charges to being bombarded. The phlegmatizing effect increases with the wax concentration; however, it also reduces the detonation speed and thus the output of the explosive substance. An even application of the wax layer and a therein embedded metal powder on the surface of the explosive substance crystals is essential for optimization relative to output and sensitivity. Furthermore, the use of possibly pure wax, i.e. non-exudating wax, with a melting point above 71°C is desirable, as ammunition requires an upper temperature application limit of at least 71°C. Exudation is understood to mean exuding of impurities at increased temperature.

A great number of processes for manufacturing wax-bound explosive substances is known. For example, in a most basic process, explosive substance crystals and the wax are heated in an aqueous slurry under intensive stir-

ring to above the wax melting point. During cooling, the wax is precipitated on the explosive substance crystals. This process produces dropshaped irregular and incomplete covering of the detonating material crystals. Therefore, the quality of thus produced detonating material relative to susceptibility to cracking and phlegmatization is not satisfactory. Improvements relative to an even encasement of the explosive substance crystals with a wax layer, carried out in an aqueous phase, are achieved with the aid of aqueous wax dispersions, wherein the wax particles are present in particle sizes between 1 and 20 μm , depending on the chosen process. The precipitation of wax particles in a dispersed form on the explosive substance is carried out by breaking the dispersions by way of precipitating means. As a rule, the aqueous wax dispersions are produced separately and added to the stirred detonator substance slurry. The wax dispersions are produced by intensively stirring the wax together with salts of fatty acids with or without additional tensides in water at temperatures above the wax melting point. An autoclave is to be used if temperatures above 100°C are required. Preferred are natural or synthetic wax with a melting point in the region between 50 and 100°C, for example polyethylene-, polypropylene-, montan-, Fischer-Tropsch-, bees-, amide-waxes etc. Dispersing tenside are alkali-, ammonium-, morpholine-, triethanolamine- and diethanolamine salts of fatty acids, such as for example myristin-, palmitin-, stearin-, oil-acids etc. The precipitation is carried out with water-soluble organic acids or mineral acids such as acetic acid, sulfuric acid, hydrochloric acid, phosphoric acid etc. or with aqueous solutions of multivalent metal salts, for example barium chloride.

In processes of this type, dispersions produced with the aid of the salts of fatty acids do not offer even distribution during precipitation of the wax on the explosive crystals. Furthermore, precipitation by means of acids from water-soluble salts of the fatty acids forms water-insoluble free fatty acids. These are precipitated together with the wax. They reduce its melting point and can exudate under increased temperature (exudation). Furthermore, during precipitation with water-soluble multivalent metal salts, the water-insoluble metal salts of the fatty acids are formed which are precipitated together with the wax. They are undesirable if present in a relatively high concentration.

If a mixed explosive substance is produced which, apart from a pure explosive substance, also contains very fine aluminium powder, then a rapidly occurring reaction between the metal and the water takes place whilst forming hydrogen after precipitation of the dispersion by the addition of acids or multivalent metal salts. The increasing reaction speed can become uncontrollable and, in the event of large applications, cause a risk of danger. Furthermore, the developing hydrogen interferes with the precipitation of the wax-aluminium mixture on the explosive substance crystals. To reduce this undesirable and dangerous effect to a tolerable level, relatively coarse grain aluminium powders with a grain size of at least 50 μm have to be applied, which causes insufficient adherence to the explosive material surface and increased tendency of de-mixing. Finally, wax encased explosive substance crystals are susceptible to electrostatic charging, which become apparent during discharge, sieve or apportioning operations by unpleasant adhesion or splashing.

It is an object of the invention to improve known processes for manufacturing compressible wax-bound explosive substance granulates in such a manner that both optimally effective phlegmatization is ensured and uncontrollable forming of hydrogen is prevented when using aluminium powder.

This object is achieved by the operations contained in the characterizing part of the claims.

Advantages achieved by the invention are to be seen essentially in that an axudate-free wax on its own or, if appropriate, with a metal powder is evenly deposited on the explosive substance crystals. Furthermore, the hydrogen forming reaction between the aluminium powder and the water is suppressed. Furthermore, unmixing of the explosive granulate is prevented and its suitability for laboratory treatment is improved.

The invention will now be described, based on further explanations and examples.

Optimally effective phlegmatization of an explosive substance with a specified binder concentration requires even precipitation of the wax on the explosive substance crystals. Even precipitation is understood to mean a complete covering of the crystal surface, with an even layer thickness and free of blank spaces. This object is achieved according to the invention by precipitation of a wax soap micro-dispersion using particle sizes of $< 0.1 \mu\text{m}$. It is optically clear, but shows the Tyndall effect and is therefore no genuine solution in the physical meaning. Dispersion of light on the smallest dispersed particles is described as the Tyndall effect.

The wax soap micro-dispersion is preferably produced by pouring a hot wax soap solution into an intensively stirred hot aqueous slurry of the explosive substance

crystals, in which respect preferably a wax soap solution is used of at least 40 % by weight 1-propanol, a non-ionogenic tenside and an acid wax the carboxyl groups of which are partially or fully converted with an amine. Conversion of the carboxyl groups of the acid wax is carried out by adding the amine, whilst stirring, to the propanolic wax solution slightly below its boiling point. Well suited amines for this purpose are morpholine, triethanolamine and others.

If in addition to the pure explosive substance crystals a metal powder in the form of an aluminium powder with a mean grain size of less than 10 μm is added for slurring the explosive substance crystals in the aqueous micro-dispersion of the wax soap, then the wax is quantitatively precipitated with a quantity, which is equivalent with the applied amine, of a strong mineral acid, for example sulfuric acid. Thereafter, the pH-value of the water phase is set by addition of a buffer solution, for example to a value of 3.8 ± 1.0 , preferably 3.8 ± 0.2 . The wax released from the amine derivative then forms initially a very fine gel which, on heating the slurry, encases the metal particles, and which deposits itself on the explosive substance crystals as an even wax metal powder layer of increasing density. The precipitation is achieved just below the wax melting point. Above the wax melting point, the encased explosive substance crystals combine into units which increase in size with rising temperature. The grain size can then be controlled by way of temperature. Graphite powder is added and cooled when a desired grain size has been arrived at.

Buffering can be dispensed with if work is to be carried out without the addition of a metal powder. The precipitation process of the wax gel particles on the explosive substance crystals remains unchanged.

A non-ionic water-soluble tenside is used for even precipitation of the wax on its own or together with a metal powder on the explosive substance crystals. Furthermore, the tenside makes it easier to establish a micro-dispersion. It is, therefore, preferably added to the wax solution.

The water phase can be composed of either de-ionised water or water for general use. If the latter is used, slight cloudiness will occur after addition of a wax soap solution due to the formation of a difficult to dissolve Ca- and Mg salts of the acid wax. This effect is non-interfering.

The establishment of a wax soap micro-dispersion depends on the degree of saponification of the acid wax, the applied amine, the portion of 1-Propanol in the wax soap solution, the temperature of the water phase and the wax soap solution. A complete micro-dispersion is preferably established when the temperature of the wax soap solution is at least 85°C, the temperature of the water phase is at least 65°C, and the saponification degree of the wax with amine corresponds at least with a quantity of 30 mg KOH/g.

The wax soap micro-dispersion offers the additional advantage that no salts of fatty acids are used as dispersion aids, which after precipitation with acid form the free, low melting and wax impurifying fatty acids. Hydrophil amine groups required to achieve the micro-dispersion are reversibly included in the wax molecule. During acidification, the free wax is produced, and so are the fully water soluble amine salts of the acid which has been used for precipitation. A precipitation of a wax layer is then achieved, which is free of impurities and therefore non-exudatory.

Furthermore, a phlegmatized mixed explosive substance of explosive substance crystals which are encased in wax and metal powder are required to be sufficiently mechanically stable, i.e. there must be no demixing between the metal powder and the explosive substance crystals by mechanical stress, such as transport vibrations. Demixed explosive substances of the described type produce unconscious pressed articles of differing composition. An inclination towards demixing is increased mainly by the use of coarse metal powders, which are embedded in the relatively thin wax layer and adhere insufficiently to the explosive substance crystals. This is remedied by a preferred use of fine metal powders with a grain size of less than 10 μm . These have to be fully encased by the wax layer in order that these fine metal powders can be applied to the explosive substance crystals in an even manner and with adhesion. This is made possible by means of the inventive wax soap micro-dispersion, the particle size of which, and therefrom originating gel particles after breaking of the dispersion, are smaller than the metal particles to be encased.

Wax- or plastic-bound mixed detonator substances often display unpleasant spraying of the fine particles during pouring or apportioning, and adhesion to the binding wall can also occur. These unpleasant effects are due to electrostatic charging. This interfering event can be disposed of by subsequent addition of graphite powder to the dry detonator substances. Graphite which has been added in its dry state has the disadvantage of low adhesion to the surface of the detonator granulates and uneven distribution. In order to apply an even graphite layer, the graphite is preferably added as early as in the aqueous phase after precipitation of the wax at maximum temperature of the

detonator substance slurry. This procedure simplifies the process and offers improved adhesion and distribution, as the graphite particles can adhere well to the wax layer which is still soft due to increased temperature.

If aluminium powder is to be used in the manufacture of wax-bound metal-containing explosive substance in the aqueous phase, the above problems mentioned in the introduction occur due to the high reactivity of this metal to water. According to the invention, the use of fine aluminium powder with a grain size of less than 10 μm is required if the object of reduced demixability and good homogeneity of the detonator substance is to be achieved. It is, therefore, a further object of the invention to make the fine aluminium powder accessible to the process by suitable methods of suppressing the forming of hydrogen. This is achieved according to the invention by stabilization of the pH-value of the aqueous phase after precipitation of the micro-dispersion to a value of 3.8 ± 1.0 by means of a buffer system, preferably with a formate buffer, to a value of 3.8 ± 0.2 .

In the following Chart I is illustrated the influence of the pH-value of aqueous solutions to fine grain aluminium powder. The test series clearly shows the high reactivity of lime containing water for general use and distilled water in the pH-range of 6-7. At 80°, aluminium reacts strongly whilst foaming. Diluted sulfuric acids have a reactive minimum at pH 4 with a drastically reduced speed. This allows the deduction that a stabilisation of the proton concentration by buffering in the minimum range must result in a sufficient reduction of the reactive speed. The aqueous wax soap dispersion in the critical pH-range of 7, consisting of an acid wax, which has been partially sapon-

nified with morpholine, with a pH-value of approximately 7, presents an extraordinarily stabilizing effect relative to the foamed aluminium. This surprising effect is apparently caused by the forming of difficult to dissolve aluminium salts of the wax which form on the surface of the aluminium particles, then offering protection from further attack by protons or hydroxyl ions. An indication of this mechanism is the clouding of remaining solution after prolonged storage, caused by the hard to dissolve aluminium salt of the wax.

In the following Chart II is shown the effect of buffer systems in the favourable pH-range of 3-5. The data confirm the hypothesis based on the previous tests (Chart I).

The aqueous phase set to pH 3.8 by means of the formate buffer system shows the expected reactivity minimum relative to the aluminium, characterised by an extraordinarily high reaction inertia at a temperature of 80°C.

Increased reactivity can be observed again in the pH-range below and above 4, set with citrate buffer (pH 3.1) and acetate buffer (pH 4.8). However, both buffer systems are still effective enough for use with the intended application.

Further tests have revealed that the three usable buffer systems are effective in the range between 0.02 to 0.2 mol/l. With lesser concentrations, the effectiveness worsens due to reducing capacity, i.e. the pH-value increases too rapidly as a result of unavoidable weak reaction under consumption of protons. With higher concentrations, the deteriorated effectiveness is probably caused by a changed activity coeffi-

cient. In this respect, the formate buffer system shows its greatest effectiveness in the pH-range of 4.

Concentrations given for the buffer solutions are to be seen as a sum of the acid and anion base concentration in mol/l at an unchanged molar acid-anion base ratio of 1:1. A preferably determined optimum pH-value 3.8, which was established with the formate buffer system with molar acid-anion base ratio of 1:1, can naturally also be obtained by way of different buffer systems by changing the acid-anion base ratio according to the following general relation:

$$C_{H+} = K_s \times \frac{C_s}{C_b} \quad \text{or}$$

$$pH = - \left(\log C_{Ks} + \log \frac{C_b}{C_s} \right)$$

K_s	[mol/l]	Dissociation constant of the acid
C_s	[mol/l]	Concentration of the acid
C_b	[mol/l]	Concentration of the corresponding anionic base.

The use of other buffer systems for the desired pH-value cause a loss of buffer capacity.

Chart 1

The influence of temperature and pH-value
on the forming of hydrogen
of an aqueous aluminium-powder slurry

Method: Adding 1 g Al powder to 40 cm³ solution (85°C)
and observing the forming of hydrogen under good illumination by way of a magnifying glass during cooling.

Rating of the gas formation:

0	none, i.e. under given conditions not or hardly recognizable
weak	recognizable
strong	easily recognizable
excessive	foaming

The tests show that there is a reaction minimum at pH4. Above the minimum, the reactivity increases again. The stabilizing effect of the wax soap micro-dispersion (MD) at pH 7 is apparently based on the formation of a difficult to dissolve aluminium wax soap on the surface of the aluminium particles which substantially protects the metal from further attack.

Solution	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄	H ₂ O dist.	H ₂ O	MD
Normality [mol/l]	10 ⁻²	10 ⁻³	10 ⁻⁴			
pH	2	3	4	5	6-7	7
Temp. °C						
80	strong	weak	0	excessive	strong	0
60	strong	0	0	strong	strong	0
40	weak	0	0	strong	strong	0
20	0	0	0	weak	weak	0

Materials Used: - aluminium powder, spherical, mean grain size < 10 µm

- the pH-values < 5 were set by dilution of 0.1 n sulfuric acid
- H₂O dist: distilled water, containing CO₂
- H₂O : water for general use, containing lime
- MD : wax micro-dispersion with the following composition:

H ₂ O dist.	560 g
* Höchst wax S	4.20 g
Morpholine	0.72 g
1-Propanol	4.20 g
** Arkopal N-300	0.85 g

* Product name of Messrs. Höchst, Federal Republic of Germany, for an acid wax with a mean acid number of 145 mg KOH/g

** Product name of Messrs Höchst, Federal Republic of Germany, for a tenside of the class nonylphenol polyglycol ether. 76% of the carboxyl groups of the wax are converted by way of the shown quantity of morpholine.

Chart 2

The effect of different buffer systems
in the pH-range between 3 and 5
on the forming of hydrogen
of an aqueous aluminium powder slurry.

Method: 1 g Al powder is heated to 80°C whilst being stirred in 40 cm³ buffer solution and cooled to room temperature. After having repeated this operation three times, the samples were left unstirred at room temperature, and the pH-value, the forming of hydrogen and the state of the sedimented Al powder was checked at different periods in time.

This test series clearly shows that the greatest stability is achieved at pH 3.8, set by means of the formate buffer. After 14 days, the slurry shows an unchanged pH-value of 3.8, and there are no indications of a noticeable forming of hydrogen and therewith associated change in the aluminium powder.

a) Buffer Solution	Citrate	Formate	Acetate
b) Concentration [mcl/l]	0.040		
pH-value [rounded off]	3.1 [3]	3.8 [4]	4.8 [5]
Condition after:			
1 day H ₂ forming Condition A1 pH	weak no change [3]	no no change [4]	no no change [5]
7 days H ₂ forming Condition A1 pH	weak hard, caking [4-5]	no no change [4]	weak hard, caking [6]
14 days H ₂ forming Condition A1 pH	weak hard, caking [6]	no no change [4]	strong hard, caking [6]

a) For the production of buffer solutions, the following acids with corresponding anionic base at a molar ratio of 1:1 were used:

Citrate: Citric acid monohydrate, sodium dihydrogen citrate

Formate: Formic acid 98/100%, sodium formate

Acetate: acetic acid 100%, potassium acetate

b: For the given concentration, the total molar figure represents acid and base per litre of solution.

The following examples serve to further explain the invention:

Example 1

360 g *Höchst* wax S, 360 g 1-Propanol and 9.0 g Arkopal N-300 were, whilst being stirred, heated to slight boiling (94°C). After complete dissolution of the solids and lowering the temperature by approximately 2°C, 39.6 g morpholine were poured into the clear wax solution. The solution of unchanged clarity with partially saponified wax serves the production of the wax soap micro-dispersion.

Under the described conditions, 50% of the carboxylic group used in the acidic wax are saponified.

Applied raw materials:

Höchst wax S acid wax of Messrs. Höchst, Federal Republic of Germany, with an acid value of 145 mg/KOHg and a dropping point of between 81 and 87°C

Arkopal N 300 tenside of the class of nonylphenol polyglycolether of Messrs. Höchst, Federal Republic of Germany

1-Propanol quality purum, boiling point approximately 96-98°C

Morpholine quality purum, purity > 98%, boiling point 124 - 128°C.

Example 2

1,710 g Hexogen are heated in 9 l de-ionized water whilst being intensively stirred. At a temperature of 70°C, the entire wax soap solution (Example 1) is at a temperature of 90°C poured into the detonator slurry. After cooling to 65°C, 900 g aluminium powder are added. After 5 minutes, the wax soap micro-dispersion is broken up by the addition of 231 g sulfuric acid [approximately 10%], and subsequently the pH-value is stabilized at a value of 3.8 by addition of 50 cm³ of 4-molar formate buffer solution. After heating to 77°C, follows a rapid addition of 30.0 g graphite powder and immediate cooling to a temperature of 50°C. The explosive substance granulate is filtered in a conventional manner, washed clear of acid by way of water for general use and dried at 50°C under vacuum until a constant weight is achieved.

The quantity of sulfuric acid is equivalent to the quantity of morpholine contained in the wax solution (Example 1). The precise requirements are calculated by way of titrimetrically determined specific acidic quantity by the following method:

- | | |
|------------------------|---|
| A [cm ³ /g] | specific acid use for morpholine |
| D [g/cm ³] | density of sulfuric acid of approximately 10% |
| M [g] | amount of applied morpholine |

$$\text{Acid quantity [g]} = A \times D \times M.$$

For Example 2, the following data apply:

A = 5.50 cm³/g

D = 1.061 cm³/g

M = 39.6 g.

Raw materials used:

Hexogen	product of a mean grain size of 400 μ m
Aluminium powder	spherical product with a mean grain size of 7 μ m and a precious metal content of >95%
Formate buffer solution	aqueous solution with a concentration of 2 mol/l of formic acid and sodium formate respectively
(4 molar)	product of a mean grain
Graphite powder	size of less than 40 μ m.

The product produced according to Example 2 is of the following composition:

Hexogen	57.0 % by weight
aluminium powder	30.0 % by weight
wax	12.0 % by weight
graphite	1.0 % by weight



Patent Claims

- 1: Process for manufacturing compressible wax-bound explosive substance granulate by way of slurring pure explosive substance crystals whilst stirring in an aqueous wax soap dispersion, breaking of the dispersion and precipitating the formed wax gel particles on the surface of the explosive substance crystals, **characterised in that** a wax soap micro-dispersion with particle sizes $< 0.1 \mu\text{m}$ is used as an aqueous wax soap dispersion.
- 2: Process according to claim 1, **characterised in that** metal powder with a mean grain size of less than $10 \mu\text{m}$ is used in addition to the explosive substance crystals.
- 3: Process according to claim 1 or 2, **characterised in that** the wax soap micro-dispersion is a wax soap solution poured at a minimum temperature of 85°C into an intensively stirred aqueous phase with a minimum temperature of 65°C .
- 4: Process according to claim 3, **characterised in that** a wax soap solution is used of at least 40% by weight 1-Propanol, an acidic wax with an acid ratio of at least 30 mg KOH/g and a dropping point of at least 77°C , an amine and a non-ionic tenside.
- 5: Process according to claim 4, **characterised in that** the used quantity of the amine corresponds at least with a quantity of carboxyl groups of



the applied acid wax equivalent to an acid ratio of 30 mg KOH/g.

- 6: Process according to claim 4, characterised in that in the wax soap solution is used a tenside of the class of nonylphenol polyglycolether of the general formula $C_9H_{19}(C_6H_4)-O-(CH_2CH_2O)_xH$ with at least 23 (x) ethylene oxide groups in a polyglycolether chain.
- 7: Process according to claim 4, characterised in that the tenside quantity in the wax soap solution is such that its concentration in the aqueous phase after addition of the wax soap solution is maximum 0.30 % by weight.
- 8: Process according to one of claims 3 to 7, characterised in that the wax soap micro-dispersion is broken at a maximum temperature of 70°C by the addition of sulfuric acid at a quantity equivalent to that of the amine.
- 9: Process according to claim 8, characterised in that the metal powder is an aluminium powder and that immediately after breaking the wax soap micro-dispersion a formate powder is added for setting the pH-value of the aqueous phase.
- 10: Process according to claim 9, characterised in that the pH-value is set to 3.8 ± 1.0 , preferably to 3.8 ± 0.2 .
- 11: Process according to claim 9 or 10, characterised in that the temperature of the broken wax soap micro-dispersion is increased after addition of the buffer until the wax is precipitated together with the metal powder on the explosive substance crystals.



- 12: Process according to claim 11, characterised in that graphite powder is added on reaching the maximum temperature, and subsequently cooled.