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(71) Applicant: CLARIANT INTERNATIONAL LTD

[CH/CH]; Rothausstr. 61, 4132 Muttenz (CH).

(72) Inventors: FEUSTEL, Michael; Auf der Nonnenwiese 34, 5527 Köngernheim (DE). KRULL, Matthias; Am Rhein-hessenblick 27, 55278 Harxheim (DE). TOLLIDAY, Ian James; 218 Lerderberg Park Road, Merrimu, Victoria, Victoria 3340 (AU). COLLINS, Christopher Robin; 167-177 Faulkners Road, Moount Cottrell, Victoria, Victoria 3024 (AU). FRANJIC, Maja; 6 Poppy Place, Point Cook, Victoria, Victoria 3030 (AU). ROY, Thomas; Feldsieper Str. 50 a, 44809 Bochum (DE).

(74) Agent: MIKULECKY, Klaus; Industriepark Höchst / G 860, 65926 Frankfurt (DE).

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(54) Title: WATER RESISTANCE ADDITIVE FOR PARTICULATE AMMONIUM NITRATE-FUEL OIL (ANFO) EXPLOSIVES

(57) Abstract: The present invention provides for the use of at least one oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups to improve the water resistance of an explosive composition comprising particulate ammonium nitrate and a fuel oil, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain or in the side chains of the oil soluble polymer.

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WATER RESISTANCE ADDITIVE FOR PARTICULATE AMMONIUM NITRATE – FUEL OIL (ANFO) EXPLOSIVES

5 This invention pertains to a fuel-soluble or fuel-dispersible, hydrophobic water-repelling additive which can be added to particulate ammonium nitrate-fuel oil (ANFO) explosive mixtures to impart water resistance.

The current state of the art about ANFO is described in “Ammonium nitrate blasting agents from manufacture to field use”, Proceedings of the 6th. General
10 ISEE, Annual Conference, Tampa, FL, June 28, 2000 by Fred C. Drury, Executive Vice President, ECONIX Incorporated, Wheaton, Illinois.

Ammonium nitrate is often used as an effective and cost-efficient mining explosive, mainly in emulsion-type explosives, in slurry-type explosives or in a mixture with
15 fuel oil.

Emulsion-type explosives are water-in-oil dispersions comprising a continuous phase of fuel and an internal liquid phase of ammonium nitrate and/or other nitrates (oxidizer) in water. Emulsion-type explosives are viscous liquids. Typically
20 they contain 73 to 76 wt.-% of ammonium nitrate and 18 to 20 wt.-% of water, the balance being essentially fuel oil and have a density of 1.30 - 1.35 kg/l. The hydrophobic continuous phase gives the emulsion some inherent water resistance. The intimate contact between the oxidizer in the emulsion droplets and the fuel in the continuous phase results in a higher velocity of detonation than ANFO type
25 explosives. Specialized emulsifiers are required to stabilize emulsion explosives. The disadvantages of emulsion explosives are that they are more difficult to manufacture than ANFO, have a shorter shelf-life than ANFO, are generally more expensive and the emulsions need to be sensitized before they can be used.

30 Slurry explosives, also known as water-gel explosives are suspensions of a solid component in a continuous semi-solid or gel phase. These explosives consist essentially of a water solution of an inorganic oxidizer such as ammonium nitrate or mixtures of ammonium nitrate with sodium or calcium nitrate, the continuous

aqueous phase being thickened, respectively gelled, by Guar gum or other high-molecular weight, water soluble organic polymers. Additional crystalline oxidizer and fuel is suspended in the gel matrix providing a relatively large amount of oxidizer surrounded by a small amount of fuel. Slurry explosives have an acceptable water resistance and give a high velocity of detonation. However, slurry explosives are relatively difficult to manufacture and are generally expensive.

Ammonium Nitrate – Fuel Oil mixtures (ANFO) have been in use since 1955. This type of explosive mixture has the advantage of being the most inexpensive variant. Blasting costs using ANFO are typically from one-half to one-third of the cost compared to emulsion, slurry explosives and even cartridged explosives. ANFO is also relatively easy to manufacture, being a mixture of fuel oil and blasting-grade prilled ammonium nitrate (oxidizer) where the prills typically constitute around 94 % of the mixture. ANFO is comprised of free flowing solid particles which can be readily poured, augered or pneumatically pumped into bore holes. In contrast to emulsion type explosives they do not have to be sensitized before use. The preferred modification of ammonium nitrate applied in explosive applications is low-density ammonium nitrate (LDAN). The high porosity of the LDAN allows for a good oil absorption necessary for optimal blasting energy yield. ANFO explosives, in contrast to emulsion and slurry explosives, are substantially free of water, i.e. they contain less than 2 wt.-%, most often less than 1.0 wt.-% and especially less than 0.5 % of water.

The major disadvantage of ANFO is that it has very poor water resistance. Water is readily absorbed by the ANFO mixture resulting in poor detonation or failure to detonate. Even small amounts of water can radically reduce performance. The primary effect is the water replacing the air between the prills and the air sites in the porous prill which reduces or eliminates sites for adiabatic compression which are essential for propagation of detonation. In more extreme cases where a lot of water is present, the ammonium nitrate will start dissolving resulting in poor detonation or no detonation at all.

In order to use ANFO in wet boreholes, the boreholes either have to be dewatered first or a physical barrier such as a plastic borehole liner or waterproof packaging needs to be used. These methods are labor intensive and add a substantial amount of cost to the blasting.

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Some ANFO products with allegedly improved water resistance (WR-ANFO) are available on the market. The majority of these products utilize a dry water-resistant coating over the ammonium nitrate prills which retards water penetration. These WR-ANFO compositions typically use high percentages of cross-linked guar gums for coating to improve the water resistance of the ANFO prills. In these compositions the guar gum swells to form a barrier upon contact with water and then cross-links. The guar gum component has no inherent water-repelling ability and is extremely hydrophilic. Often large amounts of water are absorbed into the explosive before the protective barrier is established. This often results in desensitization and poor detonation.

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Often polymers are used in the formulation of emulsion and slurry explosives. In the case of slurry explosives, water soluble polymers with high molecular weights are applied in order to increase the viscosity of the aqueous phase. The application of oil soluble polymers to improve the properties of explosives and especially to improve the properties of ANFO is scarce.

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EP-A-256669 teaches improved dry ammonium nitrate blasting agents comprising particulate high density ammonium nitrate in admixture with a liquid carbonaceous fuel, characterized by the presence of a high molecular weight polymer having a high stringiness factor, for example poly(isobutylene). The high molecular weight polymer provides improved fuel retention of the fuel on the particles and thereby improved explosive storage properties. These explosives permit the use of high density ammonium nitrate prills in preparing such improved dry blasting agents. Such higher density particles allow the generation of higher explosion velocities, as compared to porous, low density ammonium nitrate particles of equivalent particle size. The reference teaches that prior art ANFO explosives made with high density prills have not been stable to fuel oil drainage over extended time periods,

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whereas the disclosed explosives can be stored for up to 2 weeks, and even longer, without substantial, detrimental drainage of the fuel oil from the particles. No mention of the water resistance of such ANFO explosives is made.

- 5 US-2541389 is directed to ammonia dynamites which, in addition to normally non-cohesive dynamite ingredients, also include a viscous liquid polybutene product, such as polybutene having Staudinger molecular weights of between 40,000 and about 120,000. The resulting mixture is a cohesive dynamite product.
- 10 JP 2002029877 A discloses water-proof granular explosives comprising ammonium nitrate porous prills and fuel oil, and the ammonium nitrate prills are coated with polymer which is in liquid state by heat-melting or emulsion state and solidifies after covering the prills.
- 15 EP-A-0276934 teaches emulsion explosive compositions comprising a discontinuous phase comprising at least one oxygen-releasing salt; a continuous organic phase; an emulsifying agent; and at least one polymer soluble in the organic phase and wherein the polymer comprises associative functional groups. The associative functional groups are polar groups capable of entering into
- 20 specific association with other associative groups, e.g. a copolymer of tert.-butyl styrene and 4-vinyl pyridine (97:3 by weight). This leads to the formation of highly elastic emulsion explosive compositions which may be loaded into wet boreholes without prior dewatering of the borehole. By mixing such emulsion with solid ANFO the emulsion may coat the ANFO and protect the granules from water to some
- 25 extent. In these highly viscous liquid mixtures, the water resistance is solely due to the presence of the emulsion. However, the blending of emulsion with ANFO requires further specialized equipment. So, EP-A-0276934 does not provide a solution how to improve the water resistance of an ANFO being in the form of free flowing solid particles.
- 30 US-2013140871 relates to ammonium nitrate fuel oil mixtures, and includes compositions comprising (a) ammonium nitrate, (b) a fuel component, (c) a functionalized polymer component, and (d) an oil-soluble anionic surfactant,

wherein the mixture of components (b), (c) and (d) form a gel that will not readily flow. These compositions are reported to provide improve fuel retention and/or water resistance properties, particularly when the compositions use low quality porous prills of ammonium nitrate.

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JP 2001 089285 teaches an ammonium nitrate explosive comprising a surface coating of the powdered or granulated ammonium nitrate with a wax having a melting point of 60 degrees C or more to impart water repellence to the explosive.

- 10 The problem to be solved by the instant invention was to find means to improve the still unsatisfactory water resistance of ANFO and especially the water resistance of low density ammonium nitrate fuel oil mixtures (LDANFO). In particular the reliability of ANFO and especially of LDANFO to detonate even after storage in moist and especially in wet environment as it is often found in blast
- 15 holes was to be improved. The oil soluble high molecular weight polymers disclosed in the state of the art improve the fuel oil retention time on the ammonium nitrate particles. It is reported that this is at least in part due to the autoadhesion property of the polymers ("stringiness" of the polymers) which is more or less exclusively limited to the surface of the ammonium nitrate prills.
- 20 However, as soon as water penetrates this film the ammonium nitrate inside the prills will become wet and/or dissolved. Therefore the polymers of the state of the art do not have a profound effect on water resistance. Furthermore, manufacture of the WR-ANFO should be possible at lower temperatures where handling of the neat fuel oil becomes difficult due to rise of viscosity and/or precipitation of
- 25 paraffins.

- Surprisingly it has been found that the application of certain groups of oil soluble synthetic polymers with low viscosity, inter alia polymers made from ethylene and other ethylenically unsaturated compounds as well as comb polymers with defined
- 30 side chain lengths, provide water resistance to low density ammonium nitrate-fuel oil mixtures (LDANFO). They preserve the LDANFO's capability to detonate even after storage in damp / wet surrounding. Without being bound to this theory, it is believed that oil soluble polymers with low molecular weights and a certain amount

of polar groups close to the polymer backbone penetrate the ammonium nitrate prills together with the fuel oil and thereby improve the water repellency also inside the prills.

- 5 In a first aspect, the instant invention provides for the use of at least one oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups to improve the water resistance of a particulate explosive composition comprising particulate ammonium nitrate and a fuel oil, said linear polymethylene sequences with in average 10 to 40 consecutive methylene
10 groups may be either in the main chain (meaning the backbone) or in the side chains of the oil soluble polymer.

- In a second aspect, the instant invention relates to a process for improving water resistance of particulate ammonium nitrate fuel oil explosives, the method
15 comprising the step of adding to the explosive composition comprising particulate ammonium nitrate a fuel oil containing an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain (backbone) or in the side chains
20 of the oil soluble polymer.

- In a third aspect, the invention provides a process for manufacturing of water resistant particulate ammonium nitrate fuel oil explosives that can be used according to the first aspect of the invention comprising bringing a particulate
25 ammonium nitrate into contact with a fuel oil, the fuel oil being the solution and/or dispersion of an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain or in the side chains of the oil soluble polymer.

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In a fourth aspect the invention provides a water resistant, particulate, low density ammonium nitrate fuel oil explosive, comprising particulate ammonium nitrate, a fuel oil and an oil soluble polymer comprising linear polymethylene sequences with

an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain or in the side chains of the oil soluble polymer, wherein the ammonium nitrate has a bulk density of between 0.60 to 0.90 g/cm³, the bulk
5 density being determined by weighing an untamped sample of the the ammonium nitrate in a container of known volume.

In the following the preferred embodiments of the invention will be described with respect to the use aspect of the invention. The preferred embodiments are
10 likewise applicable to the other aspects of the invention, in particular to the process for improving water resistance of particulate ammonium nitrate fuel oil explosives, to the process for manufacturing of WR-ANFO especially at low temperatures and to the particulate, low density ammonium nitrate fuel oil explosive.

15 The water resistance as meant herein is measured as the mass portion of ANFO remaining after a given time, as for example after 24, 48 or 72 hours of exposure of solid ANFO to a water saturated substrate. Water resistance is considered to be satisfactory when a defined threshold of ANFO of preferably at least 50 wt.-%, more preferably 75 to 99 wt.-% and especially 90 to 98 wt.-% as for example
20 75 wt.-% or more, 90 wt.-% or more, 50 to 99 wt.-%, 50 to 98 wt.-%, 75 to 98 wt.-% or 90 to 99 wt.-% of the ANFO is recovered after the given time. This value reflects the minimum quantity of ANFO required for a successful detonation. In the water resistance test, ANFO samples are prepared using an oxidizer/fuel
25 ratio of preferably 94:6 by weight. The water resistance additives, if any, are preferably applied as part of the fuel component.

The oil soluble polymers suitable for the use as well as for the processes of the invention are preferably substantially chemically non-reactive with the ammonium
30 nitrate under the temperature conditions in which the ammonium nitrate is contacted with fuel oil / polymer mixture.

The polymers with an average of 10 to 40 consecutive methylene groups suitable for the use as well as for the processes of the invention preferably have a drop melting point below 60°C, more preferred below 55°C, as for example determined according to ASTM D127.

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In a preferred embodiment, the oil soluble and water insoluble polymers are those which are commonly used to improve at least one cold flow property of mineral oils, and especially of mineral fuel oils. Such cold flow properties may be the cloud point, the wax appearance temperature, the pour point and/or the cold filter

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plugging point. In this respect improvement typically means a reduction of the temperature at which the respective phenomenon occurs. Especially preferred oil soluble polymers comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups being either in the main chain

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(backbone) or in the side chains of the oil soluble polymer are

i) copolymers of ethylene with 5 to 18 mol-% of at least one monomer selected from vinyl esters, esters of ethylenically unsaturated monocarboxylic acids and vinyl ethers having a C₁ to C₈ alkyl or alkenyl group,

20

ii) homo- and copolymers of esters, amides and/or imides of ethylenically unsaturated carboxylic acids, said esters, amides and/or imides bearing alkyl residues with an average alkyl chain length of C₁₀-C₄₀, and

iii) graft polymers of homo- and copolymers of esters, amides and/or imides of ethylenically unsaturated carboxylic acids, said esters, amides and/or imides bearing alkyl radicals with an average alkyl chain length of C₁₀-C₄₀ on copolymers of ethylene with 5 to 18 mol-% of at least one monomer selected from vinyl esters, esters of ethylenically unsaturated carboxylic acids and vinyl ethers having a C₁ to C₈ alkyl or alkenyl group.

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In the following, the aforementioned three classes of polymers may be referred to as copolymer i), copolymer ii), and copolymer iii).

If the oil soluble polymers are ethylene copolymers the polymethylene sequences are in the main chain. In case the polymers do not contain ethylene the polymethylene sequences are in the side chains of the polymers. Oil soluble means that the polymers are soluble in aliphatic and / or aromatic solvents like toluene, xylene, aromatic naphtha, heavy aromatic naphtha, kerosene, diesel fuel, decaline or their mixtures to at least 5 wt.-% preferably to at least 10 wt.-% and most preferably to at least 15 wt.-% at 70 °C.

The water resistant ammonium nitrate fuel oil explosive of the invention is a particulate and not in the form of an emulsion. As used herein, "particulate" ammonium nitrate, "particulate" ANFO and "particulate" LDANFO means material in the form of separate, discrete particles, e.g., prills, granules, pellets and fines, as opposed to cast or powdered ammonium nitrate or solutions or dispersions thereof. Preferred particles are small-sized with an average diameter range preferably between 0.5 and 5 mm, more preferably between 1 and 3 mm and especially between 1.3 and 2.5 mm as for example between 0.5 and 3 mm, between 0.5 and 2.5 mm, between 1 and 5 mm, between 1 and 2.5 mm; between 1.3 and 5 mm or between 1.3 and 3 mm. Porous spheres (prills) which have a low bulk density are especially preferred.

The invention is preferably applied for the treatment of ammonium nitrate with a low bulk density of between 0.60 to 0.90 g/cm³, preferably between 0.70 to 0.85 g/cm³ and most preferably between 0.72 and 0.80 g/cm³ as for example between 0.60 and 0.85 g/cm³, between 0.60 and 0.80 g/cm³, between 0.70 and 0.90 g/cm³, between 0.70 and 0.85 g/cm³, between 0.72 and 0.90 g/cm³ or between 0.72 and 0.85 g/cm³. The bulk density is determined by weighing an untamped sample of the prills in a container of known volume. The particle density of the prills is such that, when liquid fuel is properly applied to and mixed with them, the prills absorb the fuel uniformly which enhances blasting activity. The fuel oil is absorbed onto the surface and into the pores of the ammonium nitrate granules.

Preferred ammonium nitrate grades have a purity of at least 90.0 wt.-%, more preferably between 92.0 and 99.9 wt.-%, more preferably between 95.0 and 99.8 wt.-% and especially between 96.0 and 99.7 wt.-% as for example between 90.0 and 99.9 wt.-%, between 90 and 99.8 wt.-%, between 90 and 99.7 wt.-%, between 92.0 and 99.8 wt.-%, between 92.0 and 99.7 wt.-%, between 95 and 99.9 wt.-%, between 95.0 and 99.7 wt.-% or between 95.0 and 99.8 wt.-%.

Optionally, the ammonium nitrate prills are stabilized to improve their physical properties (i.e., to provide greater hardness and resistance to caking, lower moisture sensitivity and/or breakdown in particle size, that is, "dusting") by providing in the ammonium nitrate melt, prior to prilling, any of the conventional ammonium nitrate stabilizers, such as natural phosphates, potassium metaphosphate, mono- and diammonium phosphate, ammonium sulfate, potassium chloride, magnesium salts, calcium salts, sodium silicate, clays, sodium, calcium and potassium nitrates, iron cyanides, metal oxides (e.g., magnesium oxide), etc. Preferably the amount of stabilizer is less than 10 wt.-% and more preferably between 0.1 and 5.0 wt.-% relative to the amount of ammonium nitrate.

Fuel oils suited for the preparation of ANFO are essentially all liquid hydrocarbons with a boiling range between 100 and 450 °C. One preferred kind of hydrocarbons are mineral oil distillates. These may comprise linear, branched or cyclic aliphatic hydrocarbons and mono- di or polycyclic aromatic hydrocarbons and mixtures thereof. The hydrocarbons may be substituted; preferred substituents are C₁-C₂₀ linear or branched alkyl residues and/or functional groups like hydroxyl and nitro groups. Examples for preferred hydrocarbons are toluene, xylene, naphthalene, decane, dodecane, tetradecane, hexadecane, decaline and their mixtures. Especially preferred are mineral oil distillation cuts including diesel, heating oil, jet fuel (particularly "jet A" fuel), kerosene, lube oil, coal oil, kerogen extract (from shale oil) and the like.

Oily liquids derived from plant and animal origins as well as their synthetic equivalents such as alcohols (e.g. having an alkyl residue with 6 to 18 carbons, or

more), glycols, amines, esters and/or ketones may also be used instead of fuel oil. Supplementary fuels of the fatty acid type which are suitable for use in the carbonaceous fuel component include octanoic acid, decanoic acid, lauric acid, palmitic acid, stearic acid, oleic acid, behenic acid and their mixtures.

- 5 Supplementary fuels of the higher alcohol type which are suitable for use in the carbonaceous fuel component include hexyl alcohol, octyl alcohol, nonyl alcohol, lauryl alcohol, cetyl alcohol, stearyl alcohol and their mixtures.

Further preferred fuels oils are derived from renewable resources (biofuels).

- 10 Preferred biofuels are esters from fatty acids with 8 to 30 carbon atoms with lower alcohols containing 1 to 6, preferably 1 to 4 and especially 1 to 3 carbon atoms. Preferably the alcohol contains 1 to 6 and especially 1 to 3 hydroxyl groups, e.g. methanol, ethanol, ethylene glycol, propylene glycol and glycerine. Especially preferred are esters of fatty esters and methanol as for example rape methyl ester, 15 cocoa nut methyl ester or soy methyl ester and partial as well as full esters of glycerine with fatty acids.

- Similarly suited are synthetic fuels oils which are accessible for example by Fischer-Tropsch synthesis or by hydrodeoxygenation and optionally isomerization 20 of biofuels.

- Fuels oils derived from renewable resources, supplementary fuel oils and synthetic fuel oils may be used sole or in a mixture of two or more selected from mineral oils, synthetic and renewable fuels.

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- Preferred fuel oils have a pour point above -25 °C, however, the invention is also applicable to fuel oils having a pour point above -10 °C, above 0 °C and even above +10 °C as for example to fuel oils having a pour point between -25 and +30 °C, between -20 and +30 °C, between -20 and +20 °C or between -25 and 30 +20 °C. The pour point can be determined according to DIN ISO 3016.

Preferably the amount of fuel oil added to the ammonium nitrate is between 1 and 20 wt.-%, more preferably between 2 and 15 wt.-% and especially between 4 and

10 wt.-% as for example between 1 and 15 wt.-%, between 1 and 10 wt.-%, between 2 and 20 wt.-%, between 2 and 10 wt.-%, between 4 and 20 wt.-% or between 4 and 15 wt.-% of the ammonium nitrate.

- 5 In a preferred embodiment the oil soluble and water insoluble polymers containing linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups are provided to the ammonium nitrate fuel oil explosive by dissolving and /or dispersing the polymer in the fuel oil and applying the fuel oil containing the polymer to the solid ammonium nitrate. Preferably the concentration
- 10 of the polymer in the fuel oil is between 0.1 and 15 wt.-%, more preferably between 1 and 12 wt.-% and especially between 3 and 10 wt.-% as for example between 0.1 and 12 wt.-%, between 0.1 and 10 wt.-%, between 1 and 15 wt.-%, between 1 and 10 wt.-%, between 3 and 20 wt.-% or between 3 and 15 wt.-%.
- 15 According to the state of the art the manufacture of WR-ANFO from ammonium nitrate and fuel oil requires temperatures above the pour point and especially also above the cloud point of the fuel oil. Operating temperatures below the pour point of the fuel oil cause severe handling issues with pumping of the fuel oil, inability to achieve uniform mixing and incomplete penetration of the fuel oil into the porous
- 20 ammonium nitrate prills. However, the manufacture of ANFO according to the invention may successfully proceed at temperatures below the pour point of the neat fuel oil, e.g. at temperatures frequently 3 °C, often 5 °C and sometimes 10 °C below the pour point and / or 5 °C, often 10 °C and sometimes 15 °C below the cloud point of the neat fuel oil. Neat fuel refers to the fuel oil component without
- 25 the incorporation of the oil soluble polymer according to the invention.

- In a preferred embodiment the ratio of ammonium nitrate to fuel oil containing the polymer is in the range between 99:1 and 80:20, especially between 98:2 and 90:10 and especially preferred between 93:7 and 95:5 as for example between
- 30 99:1 and 90:10, between 99:1 and 95:5, between 98:2 and 80:20, between 98:2 and 95:5, between 93:7 and 80:20 or between 93:7 and 90:10. In a further preferred embodiment 0.05 to 5.0 wt.-% and especially 0.1 to 2.0 wt.-% as for

example 0.05 to 2.0 wt.-% or 0.1 to 5.0 wt.-% of the oil soluble polymer per weight unit of ammonium nitrate is applied.

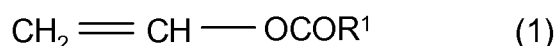
Preferably the water resistant ammonium nitrate fuel oil explosive of the invention
 5 contains between 80 and 99 wt.-%, especially between 90 and 98 wt.-% and especially preferred between 93 and 95 wt.-% as for example between 80 and 98 wt.-%, between 80 and 95 wt.-%, between 90 and 99 wt.-%, between 90 and 95 wt.-%, between 93 and 99 wt.-% or between 93 and 98 wt.-% of ammonium nitrate. Typically it contains less than 2 wt.-%, most often less than 1.0 wt.-% and
 10 especially less than 0.5 % of water.

In one preferred embodiment, the oil soluble and water insoluble polymer containing linear polymethylene sequences with an average 10 to 40 consecutive methylene groups is a copolymer of ethylene and 5 to 18 mol-%, preferably 6 to
 15 16 mol-% and especially 8 to 15 mol-% of at least one vinyl ester, acrylic ester, methacrylic ester, and/or alkyl vinyl ether having a C₁ to C₈ alkyl or alkenyl group (referred to as copolymer (i)).

In preferred ethylene copolymers the comonomers are statistically distributed.
 20 They contain the linear polymethylene sequences in the polymer backbone (main chain polymers). The calculation of the average length of the polymethylene sequence (PS(i)) is based on the molar comonomer fraction of the copolymer with the comonomer contributing one additional methylene group to the polymethylene sequence. The alkyl chains of the comonomer, if present, are not considered in
 25 this calculation.

$$PS(i) = \left(\frac{\text{molar content of ethylene}}{\text{molar content of comonomer}} \right) * 2 + 1$$

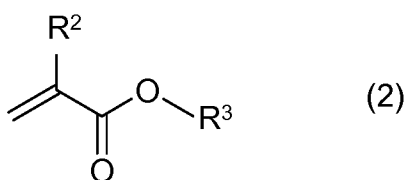
As comonomers for ethylene copolymers preferred vinyl esters are those of the
 30 formula (1)



in which R¹ is C₁- to C₈-alkyl, preferably C₂- to C₇-alkyl, especially C₄- to C₆-alkyl as for example C₁- to C₇-alkyl, C₁- to C₆-alkyl or C₁- to C₄-alkyl. The alkyl radicals may be linear or - in case they have 3 or more carbon atoms - branched. In a preferred embodiment, the alkyl radicals are linear alkyl radicals having 1 to 8 carbon atoms. In a further preferred embodiment, R¹ is a branched alkyl radical having 3 to 8 carbon atoms and preferably having 3 to 7 carbon atoms. Suitable vinyl esters include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl 2-ethylhexanoate. An especially preferred vinyl ester is vinyl acetate. In a further embodiment, the alkyl groups mentioned may be substituted by one or more hydroxyl groups.

In a further embodiment, these ethylene copolymers contain vinyl acetate and at least one further vinyl ester of the formula 1 in which R¹ is C₂- to C₈-alkyl, preferably C₄- to C₇ alkyl. Preferred further vinyl esters are the above-described vinyl esters of this chain length range.

As comonomers for ethylene copolymers preferred acrylic and methacrylic acid esters are those of formula (2)



in which R² is hydrogen or methyl and R³ is C₁- to C₈-alkyl, preferably C₂- to C₇-alkyl, especially C₄- to C₆-alkyl as for example C₁- to C₇-alkyl, C₁- to C₆-alkyl, C₁- to C₄-alkyl, C₂- to C₈-alkyl, or C₄- to C₈-alkyl. The alkyl radicals may be linear, branched or cyclic. In a preferred embodiment, they are linear. In a further preferred embodiment, they possess a branch in the 2 position to the ester moiety.

Suitable acrylic esters include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n- and isobutyl (meth)acrylate, and hexyl

(meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and mixtures of these comonomers, the formulation "(meth)acrylate" including the corresponding esters of acrylic acid and methacrylic acid. Said esters of acrylic acid are especially preferred.

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As comonomers for ethylene copolymers preferred alkyl vinyl ethers are preferably compounds of the formula (3)



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in which R^4 is C_1 - to C_8 -alkyl, preferably C_2 - to C_7 -alkyl, especially C_4 - to C_6 -alkyl as for example C_1 - to C_7 -alkyl, C_1 - to C_6 -alkyl or C_1 - to C_4 -alkyl. The alkyl radicals may be linear, branched or cyclic. Examples include methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether.

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The alkyl radicals R^1 , R^3 and R^4 may bear minor amounts of functional groups, for example amino, amido, nitro, cyano, hydroxyl, keto, carbonyl, carboxyl, ester and sulfo groups and/or halogen atoms, provided that they do not significantly impair the hydrocarbon character of the radicals mentioned. In a preferred embodiment, the alkyl radicals R^1 , R^3 and R^4 , however, do not bear any basic groups and especially no nitrogen-containing functional groups.

20

Particularly preferred terpolymers contain, apart from ethylene, preferably 3.5 to 17 mol-% and especially 5 to 15 mol-% of vinyl acetate, and 0.1 to 10 mol-% and especially 0.2 to 5 mol-% of at least one long-chain vinyl ester, (meth)acrylic ester and/or alkene, where the total comonomer content is between 5 and 18 mol-%, preferably between 6 and 16 mol-% and especially between 8 and 15 mol-%.

25

Particularly preferred termonomers are vinyl 2-ethylhexanoate, vinyl neononanoate and vinyl neodecanoate. Further particularly preferred copolymers contain, in addition to ethylene and 3.5 to 17.5 mol-% and especially 5 to 16 mol-% of vinyl esters, also 0.1 to 10 mol-% and especially 0.2 to 5.0 mol-% of one or more olefins such as propene, butene, isobutene, hexene, 4-methylpentene, octene, diisobutylene, norbornene and/or styrene, the total

30

comonomer content being between 5 and 18 mol-%, preferably between 6 and 16 mol-% and especially between 8 and 15 mol-%.

The number average molecular weight of the ethylene copolymers (i) is preferably
5 between 500 and 100,000 g/mol and especially between 1,000 and 50,000 g/mol
as for example between 500 and 50,000 g/mol or between 1,000 and
100,000 g/mol as determined by Gel Permeation Chromatography using
poly(styrene) standards. Often the molecular weight of ethylene copolymers (i) is
determined in terms of the melt viscosity of the solvent free polymer at elevated
10 temperatures, e. g. at 140 °C (V_{140}). The melt viscosity V_{140} of preferred ethylene
copolymers (i) is between 20 and 2,000 mPas and especially between 50 and
1,000 mPas, for example between 20 and 1,000 mPas or between 50 and
2,000 mPas. The degrees of branching of polymers (i) determined by means of ¹H
NMR spectroscopy are preferably between 1 and 9 CH₃/100 CH₂ groups,
15 especially between 2 and 6 CH₃/100 CH₂ groups, which do not originate from the
comonomers.

In a preferred embodiment mixtures of two or more of the abovementioned
ethylene copolymers are used. The polymers on which the mixtures are based
20 more preferably differ in at least one characteristic. For example, they may contain
different comonomers, different comonomer contents, different molecular weights
and/or different degrees of branching.

The copolymers (i) are prepared by known processes (on this subject, see, for
25 example, Ullmanns Encyclopädie der Technischen Chemie, 5th edition, vol. A 21,
pages 305 to 413). Suitable methods are polymerization in solution, in suspension
and in the gas phase, and high-pressure bulk polymerization. Preference is given
to employing high-pressure bulk polymerization, which is performed at pressures
of 50 to 400 MPa, preferably 100 to 300 MPa, and temperatures of 50 to 350 °C,
30 preferably 100 to 300 °C. The reaction of the comonomers is initiated by free-
radical-forming initiators (free-radical chain initiator). This substance class
includes, for example, oxygen, hydroperoxides, peroxides and azo compounds,
such as cumene hydroperoxide, t-butyl hydroperoxide, dilauroyl peroxide,

dibenzoyl peroxide, bis(2-ethyl hexyl)peroxodicarbonate, t-butyl permaleate, t-butyl perbenzoate, dicumyl peroxide, t-butyl cumyl peroxide, di(t-butyl peroxide, 2,2'-azobis(2-methylpropanonitrile), 2,2'-azobis (2-methylbutyronitrile). The initiators are used individually or as a mixture of two or more substances in
5 amounts of 0.01 to 20 % by weight, preferably 0.05 to 10 % by weight, based on the comonomer mixture.

The desired molecular weight of the copolymers (i), for a given composition of the comonomer mixture, is adjusted by varying the reaction parameters, e.g. of
10 pressure and temperature, and if appropriate by adding moderators. Useful moderators have been found to be hydrogen, saturated or unsaturated hydrocarbons, for example propane and propene, aldehydes, for example propionaldehyde, n-butyraldehyde and isobutyraldehyde, ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, or
15 alcohols, for example butanol. Depending on the desired viscosity, the moderators are employed in amounts up to 20 % by weight, preferably 0.05 to 10 % by weight, based on the comonomer mixture.

In another preferred embodiment, the oil soluble and water insoluble polymer
20 containing linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups is a homo- or copolymer of esters, amides and/or imides of ethylenically unsaturated carboxylic acids (referred to as homo- or copolymer (ii)). Preferred homo- and copolymers (ii) contain linear polymethylene sequences with an average of 11 to 32 and especially 12 to 24 consecutive
25 methylene groups as for example with 10 to 32, 10 to 24, 11 to 40, 11 to 24, 12 to 40 or 12 to 32 consecutive methylene groups. In this group of polymers the linear polymethylene sequences are originating from the alkyl groups of the comonomers and are located in the polymer side chains. In case of side chain polymers the terminating methyl groups of alkyl residues are included in the counting of
30 methylene groups.

For homo- and copolymers (ii) the average length of the polymethylene sequences (PS(ii)) is calculated from the molar average carbon chain length in the alkyl radicals of the monomers according to the formula:

$$PS(ii) = m_1 \cdot \sum_i w_{1i} \cdot n_{1i} + m_2 \cdot \sum_j w_{2j} \cdot n_{2j} + \dots + m_g \cdot \sum_p w_{gp} \cdot n_{gp}$$

where

$m_1, m_2, \dots, m_g$ are the molar fractions of the comonomers in the polymer and the sum of the molar fractions m_1 to $m_g = 1$,

$w_{1i}, w_{2j}, \dots, w_{gp}$ are the proportions by weight of the individual chain lengths $i, j, \dots, p$ of the alkyl radicals of the different comonomers 1 to g , and

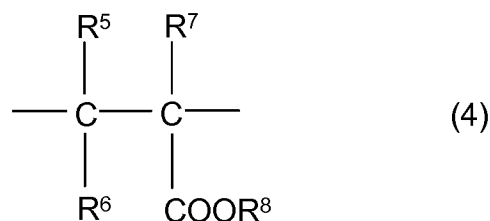
$n_{1i}, n_{2j}, \dots, n_{gp}$ are the chain lengths of the alkyl radicals $i, j, \dots, p$ of the comonomers 1 to g .

15

Preferred homo- and copolymers (ii) contain at least 50 mol-%, preferably 65 to 99 mol-% and especially 80 to 95 mol-% as for example at least 65 mol-%, at least 80 mol-%, 50 to 99 mol-%, 50 to 95 mol-%, 80 to 99 mol-% or 65 to 95 mol-% structural units derived from monomers carrying 1 (or up to two in case of

20 dicarboxylic acid derivatives) alkyl residue(s) with 10 to 40, preferably 11 to 32 and especially 12 to 24 consecutive methylene groups as for example alkyl residues with 10 to 32, 10 to 24, 11 to 40, 11 to 24, 12 to 40 or 12 to 32 consecutive methylene groups. As stated above, for the counting of methylene groups in the alkyl residues the terminal methyl groups are included. In a preferred embodiment
25 homo- and copolymers (ii) do not contain structural units derived from further monomers. Should structural units derived from further comonomers be present, they are disregarded when calculating the parameter PS(ii).

Suitable homo- or copolymers of esters of ethylenically unsaturated carboxylic
30 acids (ii), said esters bearing C₁₀-C₄₀-, preferably C₁₁-C₃₂ and especially C₁₂ to C₂₄ alkyl radicals, are especially those which contain repeat structural elements of the formula (4)



wherein

- 5 R^5 and R^6 are each independently hydrogen, phenyl or a group of the formula $COOR^8$,
 R^7 is hydrogen, methyl or a group of the formula $-CH_2COOR^8$ and
 R^8 is a C_{10} - to C_{40} -alkyl or -alkenyl radical, preferably a C_{11} - to C_{32} -alkyl or -alkenyl radical and especially a C_{12} to C_{24} -alkyl or alkenyl radical,
 10 with the proviso that these repeat structural units contain at least one and at most two carboxylic ester units in one structural element.

- Particularly suitable homo- and copolymers are those in which R^5 and R^6 are each hydrogen and R^7 is hydrogen or methyl or in which one of R^5 and R^6 is hydrogen
 15 and the other a group of the formula $COOR^8$ and R^7 is hydrogen or in which R^5 and R^6 are hydrogen and R^7 is a group of the formula $-CH_2COOR^8$. These structural units derive from esters of monocarboxylic acids, for example acrylic acid, methacrylic acid, cinnamic acid, or from mono- or diesters of dicarboxylic acids, for example maleic acid, fumaric acid and itaconic acid. Particular
 20 preference is given to the esters of acrylic and methacrylic acid.

- Preferred alcohols for the esterification of the ethylenically unsaturated mono- and dicarboxylic acids as basis for the repeat structural elements of formula (4) are those alcohols having 10 to 32 consecutive methylene groups, more preferably
 25 those having 12 to 26 consecutive methylene groups and especially those having 18 to 24 consecutive methylene groups, terminal methyl groups being included in this counting. They may be of natural or synthetic origin. The alkyl radicals are preferably linear or at least very substantially linear. Suitable fatty alcohols include
 30 1-decanol, 1-dodecanol, 1-tridecanol, isotridecanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, eicosanol, docosanol, tetracosanol, hexacosanol

and their mixtures. Naturally occurring fatty alcohol mixtures, for example coconut fatty alcohol, tallow fatty alcohol, hydrogenated tallow fatty alcohol and behenyl alcohol are equally suited.

- 5 Preferred homo- and copolymers of amides and/or imides of ethylenically unsaturated carboxylic acids (ii) can be obtained by reaction of (co)polymers of ethylenically unsaturated carboxylic acids and/or their anhydrides and/or their esters with lower alcohols with 1 to 4 carbon atoms with amines having one or, in case of amides one or two, alkyl residues with 10 to 40, preferably 11 to 23 and especially 12 to 24 consecutive methylene groups, terminal methyl groups being included in this counting. The alkyl radicals are preferably linear or at least very substantially linear. Suitable amines include 1-decyl amine, 1-dodecyl amine, 1-tridecyl amine, isotridecyl amine, 1-tetradecyl amine, 1-hexadecyl amine, 1-octadecyl amine, eicosyl amine, docosyl amine, tetracosyl amine, hexacosyl amine and their mixtures. Naturally occurring fatty amine mixtures, for example coconut fatty amine, tallow fatty amine, hydrogenated tallow fatty amine and behenyl amine are equally suited. Similarly, suitable homo- and copolymers of amides and/or imides of ethylenically unsaturated carboxylic acids (ii) can be obtained by homo- or copolymerization of amides and/or imides of ethylenically unsaturated carboxylic acids amidated resp. imidated with above mentioned amines having one or, in case of amides one or two, alkyl residues with 10 to 40, preferably 11 to 23 and especially 12 to 24 consecutive methylene groups, terminal methyl groups being included in this counting.
- 25 The polymers (ii) may, in addition to the C₁₀-C₃₀-alkyl esters, amines and/or imides of the unsaturated carboxylic acids, comprise further comonomers such as vinyl esters of the formula (1), short-chain (meth)acrylic esters of the formula (2) in which R² is hydrogen or methyl and R³ is C₁- to C₉-alkyl or >C₄₀-alkyl, alkyl vinyl ethers of the formula (3) and/or alkenes.

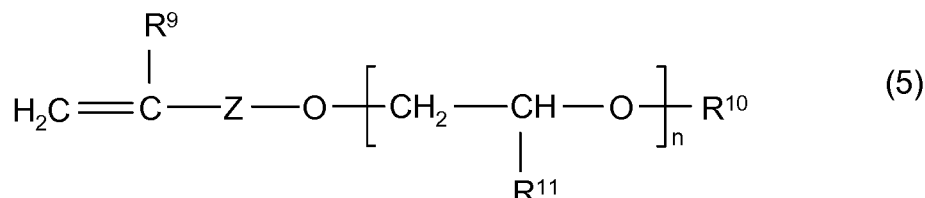
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Preferred vinyl esters for use as further comonomer in polymers (ii) correspond to the definition given for formula (1). Particular preference is given to vinyl acetate.

Preferred alkenes for use as further comonomer in polymers (ii) are α -olefins, i.e. linear olefins with a terminal double bond, preferably with chain lengths of 12 to 42 and more particularly 13 to 34 and especially 14 to 26, as for example 18 to 24, carbon atoms. Examples of suitable α -olefins are 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-henicosene, 1-docosene, 1-tetracosene. Likewise suitable are commercially available chain cuts, for example C_{13-18} - α -olefins, C_{12-16} - α -olefins, C_{14-16} - α -olefins, C_{14-18} - α -olefins, C_{16-18} - α -olefins, C_{16-20} - α -olefins, C_{22-28} - α -olefins, C_{30+} - α -olefins. In a particularly preferred embodiment α -olefins are included in the calculation of the average length of the polymethylene sequence according to formula PS(ii) with the average length of the polymethylene sequences of the ester, amide/imide units and the side chains stemming from the α -olefins being between 10 and 40, preferably between 11 and 32 and especially between 12 and 24. For α -olefins the length of the alkyl residue attached to the double bond is considered for the calculation of PS(ii). Ethylene is not a suitable Comonomer here.

Further monomers suitable as comonomers in polymer (ii) are ethylenically unsaturated compounds bearing functional groups and/or heteroatoms, for example allyl polyglycols, benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, dimethylaminoethyl acrylate, perfluoroalkyl acrylate and the corresponding esters and amides of methacrylic acid, vinylpyridine, vinylpyrrolidone, p-acetoxystyrene and vinyl methoxyacetate. Their proportion in the polymer (ii) is preferably less than 20 mol-%, especially between 1 and 15 mol-%, for example between 2 and 10 mol-%. In a preferred embodiment polymer (ii) does not contain ionic functional groups which are capable of protolytic reactions and/or groups capable of forming H bonds.

Allyl polyglycols suitable as comonomers in polymer (ii) may, in a preferred embodiment of the invention, comprise 1 to 50 ethoxy or propoxy units and correspond to the formula (5):



wherein

R⁹ is hydrogen or methyl,

5 Z is C₁-C₃-alkylene,

R¹⁰ is hydrogen, C₁-C₃₀-alkyl, cycloalkyl, aryl or -C(=O)-R¹²,

R¹¹ is hydrogen or C₁-C₂₀-alkyl,

R¹² is C₁-C₃₀-alkyl, C₃-C₃₀-alkenyl, cycloalkyl or aryl and

n is from 1 to 50, preferably 1 to 30.

10

Particular preference is given to comonomers of the formula 5 in which R⁹ and R¹¹ are each hydrogen and R¹⁰ is hydrogen or a C₁-C₄-alkyl group.

Preferred copolymers (ii) contain at least 10 mol-%, more particularly 20 to

15 95 mol-%, especially 30 to 80 mol-%, specifically 40 to 60 mol-% as for example 10 to 95 mol-%, 10 to 80 mol-%, 10 to 60 mol-%, 10 to 40 mol-%, 20 to 80 mol-%, 20 to 60 mol-%, 20 to 40 mol-%, 30 to 95 mol-%, 30 to 60 mol-%, 40 to 95 mol-% or 40 to 80 mol-% of structural units derived from esters of ethylenically unsaturated carboxylic acids, said esters bearing alkyl residues with 10 to 40, preferably with 11 to 32 and especially with 12 to 24 consecutive methylene groups, as for example with 10 to C₃₂, with C₁₀ to C₂₄, with 11 to 40, with 11 to 24, with 12 to 40 or with 12 to 32 consecutive methylene groups, including terminal methyl groups.

25 In a specific embodiment, the polymers (ii) consist solely of structural units derived from esters of ethylenically unsaturated carboxylic acids, said esters bearing C₁₀- to C₄₀-alkyl radicals, preferably C₁₁- to C₃₂-alkyl radicals and especially C₁₂- to C₂₄-alkyl radicals as for example C₁₀- to C₃₂-alkyl radicals, C₁₀ to C₂₄-alkyl radicals, C₁₁- to C₄₀-alkyl radicals, C₁₁- to C₂₄-alkyl radicals, C₁₂- to C₄₀-alkyl radicals or C₁₂- to C₃₂-alkyl radicals.

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Preferred homo- or copolymers of esters of ethylenically unsaturated carboxylic acids (ii), said esters bearing C₁₀-C₄₀- alkyl radicals, preferably C₁₁ to C₃₂-alkyl radicals and especially C₁₂ to C₂₄-alkyl radicals, are, for example, poly(alkyl acrylates), poly(alkyl methacrylates), copolymers of alkyl(meth)acrylates with vinylpyridine, copolymers of alkyl(meth)acrylates with allyl polyglycols, esterified copolymers of alkyl(meth)acrylates with maleic anhydride, copolymers of esterified ethylenically unsaturated dicarboxylic acids, for example dialkyl maleates or fumarates, with α -olefins, copolymers of esterified ethylenically unsaturated dicarboxylic acids, for example dialkyl maleates or fumarates, with unsaturated vinyl esters, for example vinyl acetate, or else copolymers of esterified ethylenically unsaturated dicarboxylic acids, for example dialkyl maleates or fumarates, with styrene. In a preferred embodiment, the inventive copolymers (ii) do not contain any comonomers carrying basic groups and more particularly no nitrogen-containing comonomers.

The molecular weights or molar mass distributions of preferred homo-and copolymers (ii) are characterized by a K value (measured according to Fikentscher in 5 % solution in toluene) of 10 to 100, preferably 15 to 80. The number average molecular weights M_n may be within a range from 4,000 to 200,000, preferably from 6,000 to 100,000 and especially from 25,000 to 80,000, and are determined, for example, by means of gel permeation chromatography GPC against poly(styrene) standards.

The homo- and copolymers (ii) are prepared typically by (co)polymerizing esters, amides and/or imides of ethylenically unsaturated carboxylic acids, especially alkyl acrylates and/or alkyl methacrylates, optionally with further comonomers, by customary free-radical polymerization methods.

A suitable preparation method for preparing the homo- and copolymers (ii) consists in dissolving the monomers in an organic solvent and polymerizing them in the presence of a free-radical chain initiator at temperatures in the range from 30 to 150 °C. Suitable solvents are preferably aromatic hydrocarbons, for example

toluene, xylene, trimethylbenzene, dimethylnaphthalene or mixtures of these aromatic hydrocarbons. Commercial mixtures of aromatic hydrocarbons, for example Solvent Naphtha, Shellsol® and Solvesso® grades, also find use. Suitable solvents are likewise aliphatic hydrocarbons.

5

Alkoxylated aliphatic alcohols or esters thereof, for example butylglycol, also find use as solvents, but preferably as a mixture with aromatic hydrocarbons. In specific cases, a solvent-free polymerization to prepare the cold flow improvers is also possible.

10

The free-radical initiators used are typically customary initiators such as azobisisobutyronitrile, esters of peroxy-carboxylic acids, for example t-butyl perpivalate and t-butyl per-2-ethylhexanoate, or dibenzoyl peroxide.

15 A further means of preparing the homo- and copolymers (ii) consists in the polymer-analogous esterification or transesterification respectively amidation or aminolysis of already polymerized ethylenically unsaturated carboxylic acids, the esters thereof with short-chain alcohols e.g. with C₁- to C₄-alcohols, or the reactive equivalents thereof, for example acid anhydrides with fatty alcohols and/ or fatty
20 amines having 10 to 40, preferably C₁₁ to C₃₂-alkyl radicals and especially C₁₂ to C₂₄-alkyl radicals. For example, the transesterification of poly(meth)acrylic acid with fatty alcohols or the esterification of polymers of maleic anhydride and α -olefins with fatty alcohols leads to polymers (ii) suitable in accordance with the invention.

25

In another preferred embodiment, the oil soluble and water insoluble polymer containing linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups is a graft polymer wherein a graft layer which comprises ethylenically unsaturated esters is grafted onto a graft base that is an
30 ethylene copolymer (referred to as polymer (iii)).

A graft polymer (iii) based on an ethylene copolymer as graft base is considered to be an ethylene copolymer for the purpose of calculation of the average length of

the linear polymethylene group sequence. Therefore the limits for the calculation of PS(i) have to be fulfilled, based on the comonomer content of the ethylene copolymer.

- 5 In a preferred embodiment it proved to be advantageous that the limits for the calculation of both PS(i) for the graft base and PS(ii) for the graft layer are fulfilled.

Preferred graft copolymers (iii) are, for example, those which

- 10 a) as graft base, comprise an ethylene copolymer which, in addition to ethylene, contains 5 to 18 mol-% preferably 6 to 16 mol-% and especially 8 to 15 mol-% of at least one vinyl ester, acrylic ester, methacrylic ester, alkyl vinyl ether and/or alkene, onto which
- 15 b) as graft layer, a homo- or copolymer of an ester of an α,β -unsaturated carboxylic acid with a C₁₀- to C₄₀-alcohol has been grafted.

The vinyl ester, acrylic ester, methacrylic ester, alkyl vinyl ether and/or alkene that are the comonomers of graft base a) are those as described for copolymer (i) of
20 this invention. Except for the molecular weight, the graft base a) will satisfy all limitations as described for copolymer (i) of this invention. Preferably the ethylene copolymers used as graft base have for (iii) have higher molecular weights than those used for (i). Such molecular weights are often determined via the melt flow index MFI(190/2,16) according to DIN ISO EN 1133-1 at 190 °C and an applied
25 load of 2.16 kg. Preferred ethylene copolymers as graft base for (iii) have MFI(190/2,16) values between 1 and 1,200 g/10 min and especially between 10 and 900 g/min as for example between 1 and 900 g/10 min or between 10 and 1,200 g/10 min. The degrees of branching determined by means of ¹H NMR spectroscopy are preferably between 1 and 9 CH₃/100 CH₂ groups, especially
30 between 2 and 6 CH₃/100 CH₂ groups, which do not originate from the comonomers.

The (co)polymers b) grafted onto the ethylene copolymers a) contain preferably 40 to 100 % by weight and especially 50 to 90 % by weight of one or more structural units derived from alkyl acrylates and/or alkyl methacrylates. Preferably at least 10 mol-%, more particularly 20 to 100 mol-%, especially 30 to 90 mol-%, for example 40 to 70 mol-%, as for example 20 to 90 mol-%, 20 to 70 mol-%, 30 to 100 mol-%, 30 to 70 mol-%, 40 to 100 mol-% or 40 to 90 mol-% of the grafted structural units bear alkyl radicals having at least 10 and more preferably at least 11 and especially at least 12 carbon atoms.

- 10 Particularly preferred monomers for grafting are alkyl (meth)acrylates having C₁₀-C₄₀-alkyl radicals, preferably C₁₁-C₃₂-alkyl radicals and especially C₁₂-C₂₄-alkyl radicals as for example C₁₀- to C₃₂-alkyl radicals, C₁₀ to C₂₄-alkyl radicals, C₁₁- to C₄₀-alkyl radicals, C₁₁- to C₂₄-alkyl radicals, C₁₂- to C₄₀-alkyl radicals or C₁₂- to C₃₂-alkyl radicals (including the terminal methyl group of the alkyl residue).

15

The grafted polymers b) optionally contain 0 to 60% by weight, preferably 10 to 50 % by weight, for example 10 to 60 % by weight or 0 to 50 % by weight of one or more further structural units which derive from further ethylenically unsaturated compounds. Suitable further ethylenically unsaturated compounds are, for example, vinyl esters of carboxylic acids having 1 to 20 carbon atoms, α -olefins having 6 to 40 carbon atoms, vinylaromatics, dicarboxylic acids and anhydrides and esters thereof with C₁₀-C₃₀-fatty alcohols, acrylic acid, methacrylic acid and especially ethylenically unsaturated compounds bearing further functional groups and/or heteroatoms, for example benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, p-acetoxystyrene, vinyl methoxyacetate, dimethylaminoethyl acrylate, perfluoroalkyl acrylate, the isomers of vinylpyridine and derivatives thereof, N-vinylpyrrolidone and (meth)acrylamide and derivatives thereof, such as N-alkyl (meth)acrylamides with C₁-C₂₀-alkyl radicals. Also suitable as further ethylenically unsaturated compounds are allyl polyglycols of the formula (5).

30

The graft polymers (iii) preferably contain ethylene copolymer a) and homo- or copolymer of an ester of an α,β -unsaturated carboxylic acid with a C₁₀- to

C₄₀-alcohol b) in a weight ratio of 1:10 to 10:1, preferably of 1:8 to 5:1, more preferred of 1:5 to 1:1, as for example in a weight ratio of 1:10 to 5:1, 1:10 to 1:1, 1:8 to 10:1, 1:8 to 1:1, 1:5 to 10:1 or 1:5 to 5:1.

- 5 The number average molecular weights M_n of preferred graft polymers (iii) may be within a range from 4,000 to 200,000 g/mol, preferably from 6,000 to 100,000 g/mol and especially from 10,000 to 80,000 g/mol as for example from 4,000 to 100,000 g/mol, from 4,000 to 8,000 g/mol, from 6,000 to 200,000 g/mol, from 6,000 to 80,000 g/mol, from 10,000 to 200,000 g/mol or from 10,000 to 100,000 g/mol, and are determined, for example, by means of gel permeation chromatography GPC against poly(styrene) standards.
- 10

Graft polymers (iii) are prepared by known methods. For example, the graft polymers (iii) are obtainable by mixing ethylene copolymer a) and comonomer or comonomer mixture b), optionally in the presence of an organic solvent, and adding a free-radical chain initiator.

15

The manufacture of water resistant ammonium nitrate fuel oil explosives (WR-ANFO) according to the third aspect of the invention comprises bringing a particulate ammonium nitrate into contact with a fuel oil, the fuel oil being the solution and/or dispersion of an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups. In a preferred embodiment the WR-ANFO is formed by charging dry, free-flowing ammonium nitrate prills to a mixing appliance, for example a planetary mixer, ribbon blender or cement mixer to which then the liquid mixture containing the fuel oil and the oil soluble polymer are added. The addition of the liquid mixture may happen at once or, preferably, over a longer time span of e.g. 2 minutes, preferably between 5 minutes and 5 hours and especially between 10 minutes and 2 hours as for example between 5 minutes and 2 hours or between 10 minutes and 5 hours. By mixing dry, free-flowing WR-ANFO prills are formed.

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The oil soluble polymers (i), (ii) and (iii) can be applied to the fuel oil as such, i.e. solvent free. However, due to their viscosity a concentrate of the polymers in

hydrocarbons has proven to facilitate their handling. Accordingly, concentrates containing 20 to 90 wt.-%, preferably 30 to 80 wt.-% and especially 40 to 75 wt.-% as for example 20 to 80 wt.-%, 20 to 75 wt.-%, 30 to 90 wt.-%, 30 to 75 wt.-%, 40 to 80 wt.-% or 40 to 90 wt.-% of the polymer in a suitable solvent are preferably
5 used for the manufacture of the WR-ANFO. Hydrocarbons with a boiling range between 100 and 450 °C have been successfully applied as solvent for such concentrates.

10 In a further preferred embodiment the oil soluble polymers (i), (ii) and (iii) are applied to the fuel oil as a dispersion in water or in mixtures of water with polar organic solvents like monoethylene glycol, diethylene glycol, glycerine and the like.

In a preferred embodiment the WR-ANFO according to the invention is substantially free of water, i.e. it contains less than 2 wt.-%, most often less than
15 1.0 wt.-% and especially less than 0.5 % water.

By incorporation of the above described oil soluble polymers into the fuel oil used for the manufacture of LDANFO the resistance of LDANFO towards water is increased. This ensures unchanged blasting efficiency of the LDANFO even in
20 moist environments and improves the reliability of the blasting process. Furthermore, the protection against water damage improves the completeness of detonation. An ideal detonation of ANFO will generate carbon dioxide, nitrogen gas and water vapour. Degradation of ANFO caused by water can result in the generation of post blast fume which consists of oxides of nitrogen (NO_x) which are
25 toxic and environmental pollutants. By protecting the ANFO from water degradation, the above described polymers will reduce the generation of NO_x gases.

Additionally the process for manufacture of the WR-ANFO according to the
30 invention allows the use of heavier and cheaper fuel oil grades with inferior cold flow properties respectively the manufacture of WR-ANFO with a given fuel oil at lower temperatures which improves safety and energy consumption of the manufacturing process.

In this specification, percentages are weight percentages unless otherwise noted.

5

EXAMPLES

10

Water resistance tests

In these examples, the water resistance is determined as the mass portion remaining after a sample of ANFO has been exposed to a water saturated substrate for 24, 48 respectively 72 hours. In the water resistance test, ANFO samples are prepared using the LDAN/Fuel ratio given in Table 4 (weight-%). The oil soluble polymers, if present, are part of the fuel component.

For testing water absorbent sponges are placed in trays of water so that the bottom half of the sponges are immersed keeping the entire surface of each sponge damp. A paper towel is laid over the sponges to give a uniform surface. The paper towel is kept saturated with water by the sponges below. 10.0 g samples of ANFO are weighed into cylindrical molds sitting on temporary plastic sleeves. The molds are then placed on the saturated paper towel and the temporary bottom sleeve is removed exposing the ANFO to the damp surface. After 24, 48 respectively 72 hours storage at ambient temperature the remaining amount of ANFO is reweighed and the loss of ANFO calculated as the weight loss.

Table 1: Characterization of the low density ammonium nitrate (LDAN) used:

30

Ammonium nitrate content	99.5 wt.-%
Water content	0.15 wt.-%

pH (5 %) solution	5.0
Oil retention	> 10 wt.-%
Bulk Density	0.75 g/cm ³

5 Table 2: Characterization of fuel oils used for the preparation of ANFO samples

	FO (I)	FO (II)
Type	Diesel	Heavy Fuel Oil
Cloud Point (EN 23015)	-15 °C	+23 °C
Pour Point (DIN ISO 3016)	-19 °C	+18 °C
Viscosity	4 cSt at 40 °C	650 mm ² /s at 50 °C
Density (15 °C)	0.845	0.860
Water content	0,006 wt.-%	0,008 wt.-%

Table 3: Characterization of the polymers

Polymer	Characterization	(PS)*
P1	Copolymer of stearyl acrylate and 5 % allyl polyglycol, 50 % active in xylene. The K-value determined according to Fikentscher in 5 % solution on toluene was 31.	18,0
P2	Ethylene-vinyl acetate copolymer (11 mol-% vinyl acetate, an MFI(190/2,16) of 7 g/10 minutes) grafted with behenyl acrylate comprising as main components 6 mol-% C ₁₈ -, 18 mol-% C ₂₀ -, 74 mol-% C ₂₂ - and 1 mol-% C ₂₄ -acrylate in a weight ratio of 4:1 as a 25 % active mixture in Solvesso 200,	(i) = 17,2 (ii) = 21,2

P3	Ethylene-vinyl acetate copolymer (11 mol-% vinyl acetate, an MFI(190/2,16) of 7 g/10 minutes) grafted with behenyl acrylate comprising as main components 4 mol-% C ₁₈ -, 51 mol-% C ₂₀ -, 26 mol-% C ₂₂ -, 14 mol-% C ₂₄ - and 4 mol-% C ₂₆ -acrylate in a weight ratio of 4:1, 35 % active in Solvesso® 100	(i) = 17,2 (ii) = 21,0
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P4	Copolymer of maleic anhydride and C ₂₀ -C ₂₄ α -olefin (comprising 2 mol-% C ₁₈ , 44 mol-% C ₂₀ , 34 mol-% C ₂₂ , 17 mol-% C ₂₄ , 1 mol-% C ₂₆) which had been esterified with behenyl alcohol comprising as main components 6 mol-% C ₁₈ -, 18 mol-% C ₂₀ -, 74 mol-% C ₂₂ - and 1 mol-% C ₂₄ -alcohol, as a 20 wt.-% active in Shellsol® AB.	21,1
P5	Ethylene-vinyl acetate copolymer (8 mol-% vinyl acetate, an MFI(190/2,16) of 500 g/10 minutes) grafted with a mixture of alkyl acrylates comprising as main components 35 mol-% C ₁₈ -, 33 mol-% C ₂₀ -, 18 mol-% C ₂₂ -, 10 mol-% C ₂₄ - and 2 mol-% C ₂₆ -acrylate in a weight ratio of 3:1, 35 % active in Solvesso® 100.	(i) = 24,0 (ii) = 19,8
P6	Ethylene-vinyl acetate copolymer (11 mol-% vinyl acetate, V ₁₄₀ of 250 mPas, 50 % active in kerosene	17,2
P7 (comp.)	Copolymer of ethylene and propylene with an ethylene content of 68 % and a Mw of 6000 g/mol as determined by GPC using poly(styrene) standards.	n.a.
P8	Ethylene-vinyl acetate copolymer (8 mol-% vinyl acetate, V ₁₄₀ of 600 mPas, 50 % active in kerosene	24,0
P9	Ethylene-vinyl acetate copolymer (6 mol-% vinyl acetate, V ₁₄₀ of 500 mPas, 50 % active in kerosene	32,3
P10 (comp.)	Ethylene-vinyl acetate copolymer (20 mol-% vinyl acetate, V ₁₄₀ of 3500 mPas, 40 % active in kerosene	9,0
P11 (comp.)	Ethylene-vinyl acetate copolymer (4 mol-% vinyl acetate, MFI(190/2,16) of 135 g/10 min; 20 % active in decaline	49,0
P12 (comp.)	Poly(methylacrylate) with a Mn 12,000 g/mol determined by GPC using polystyrene standards, 30 % active in acetone	1
P13 (comp.)	Poly(isobutylene) with a Mn of 600,000 g/mol as determined by GPC using polystyrene standards (corresponding to a Mv of approx. 1,200,000)	n.a.

(*) PS = average length of linear polymethylene sequence; n.a. = not applicable

All polymers used were essentially water free, i.e. they contained less than 100 ppm (wt/wt) of water.

Preparation of ANFO

Samples of ANFO, each about 2 kilograms, were prepared from low density ammonium nitrate (AN) miniprills characterized in table 1 and the fuel

5 characterized in table 2 containing the polymers characterized in table 3 in the amounts given in table 4. The polymers were dissolved in the fuel oil in the concentrations given in table 4. The ANFO samples were formed by charging the dry, free-flowing ammonium nitrate miniprills to a planetary mixer to which was then added the liquid mixture containing the fuel oil containing the oil soluble
10 polymer in order to form dry, free-flowing ANFO miniprills having the compositions set forth in Table 4 below.

The improvement of water resistance was rated according to the scale
Excellent > Very Good > Good > Fair > Poor

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Table 4: Water resistance (WR) of ANFO

Example	Polymer	FO type	wt.-% of polymer in FO	Ratio LDAN : FO	wt.-% ANFO remaining after			WR rating
					24 hours	48 hours	72 hours	
1	blank	FO (I)	0	94:6	5	2	1	Very poor
2	blank	FO (II)	0	94:6	6	3	1	Very poor
3	P1	FO (I)	10	94:6	90	86	82	Very good
4	P2	FO (I)	10	94:6	88	72	60	Good
5	P3	FO (I)	10	94:6	96	91	86	Very good
6	P4	FO (I)	10	94:6	86	70	58	Good
7	P5	FO (I)	10	94:6	89	75	64	Good
8	P6	FO (I)	5	94:6	95	81	56	Good
9	P6	FO (I)	10	94:6	97	93	90	Excellent
10	P6	FO (II)	10	94:6	97	94	92	Excellent
11	P6	FO (I)	10	92:8	98	96	93	Excellent
13	P6	FO (I)	10	96:4	95	92	89	Excellent

14	P8	FO (I)	10	94:6	95	91	85	Very good
15	P8	FO (II)	3	92:8	96	92	76	Excellent
16	P9	FO (I)	10	94:6	93	88	81	Very good
17	P9	FO (II)	15	96:4	98	95	93	Excellent
18 (comp.)	P7	FO (I)	10	94:6	62	38	30	Fair
19 (comp.)	P10	FO(I)	10	94:6	65	42	36	Fair
20 (comp.)	P 11	FO (I)	10	94:6	28	19	11	Poor
21 (comp.)	P 12	FO (I)	10	94:6	38	29	21	Poor
22 (comp.)	P 13	FO (I)	10	94:6	36	27	16	Poor

Detonation tests

In further examples, the water resistance is determined by the success of detonation as measured by Velocity of Detonation (VOD) after ANFO has been exposed to a water saturated sand for 24 hours. For the detonation test, ANFO samples are prepared using a LDAN/Fuel ratio of 94:6 (by weight-%) using fuel oil (I) as described above in the water resistance section. The oil soluble polymers, if present, are part of the fuel component.

- For testing, a 90 mm diameter cylinder with a height of 500 mm was formed from fly-wire mesh having a mesh size of approximately 1mm. A 20 mm wide strip of PVC with 8 VOD cables mounted in holes drilled at 30 mm intervals was attached vertically to the side of the fly-wire. The fly-wire mesh cylinder was placed in the centre of a 30 litre plastic bucket. A length of 90 mm PVC pipe was placed inside the mesh to provide temporary support while the mesh was surrounded by 35 kg of washed Sydney sand which was saturated with 5 litres of water. A standard mass of 2.5 kg of ANFO was then poured inside the centre pipe after which the PVC pipe was removed thereby exposing the ANFO to the wet sand via the mesh. The ANFO was left exposed to the wet sand for 24 hours. After 24 hours 150 g of a Pentolite 50/50 cast booster was placed in the ANFO with the top of the initiator level with the top of the column of ANFO. The ANFO was then detonated and the VOD measured. A velocity of detonation (VOD) of at least 2400 metres per second indicates a successful detonation. The tests were made in duplicate.

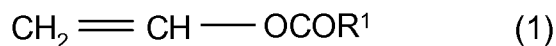
Table 5: Results of detonation tests

Example	Polymer	wt.-% of polymer in FO	Ratio LDAN : FO	VOD [m/s]
23 (comp.)	none	0	94:6	failed to detonate
24 (comp.)	none	0	94:6	failed to detonate
25	P1	8	94:6	3150

26	P1	8	94:6	3100
27	P4	12	94:6	2750
28	P4	12	94:6	2850
29	P6	10	94:6	3200
30	P6	10	94:6	3350

Patent claims

1. Use of at least one oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, to improve the water resistance of a particulate explosive composition comprising particulate ammonium nitrate and a fuel oil, and wherein said linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups may be present either in the main chain or in the side chains of the oil soluble polymer.
2. Use according to claim 1, wherein the oil soluble polymers comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups are copolymers (i) of ethylene with 5 to 18 mol-% of at least one monomer selected from vinyl esters, esters of ethylenically unsaturated monocarboxylic acids and vinyl ethers.
3. Use according to claim 1 and/or 2, wherein the monomer selected from vinyl esters, esters of ethylenically unsaturated monocarboxylic acids and vinyl ethers has a C₁ to C₈ alkyl or alkenyl group.
4. Use according to claim 2 and/or 3, wherein the vinyl esters correspond to formula (1)



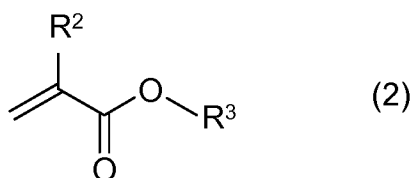
in which R¹ is C₁- to C₈-alkyl.

5. Use according to claim 2 or 3, wherein the vinyl ester is selected from the group consisting of vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate and vinyl 2-ethylhexanoate.
6. Use according to one or more of claims 2 to 5, wherein the vinyl ethers correspond to formula (3)



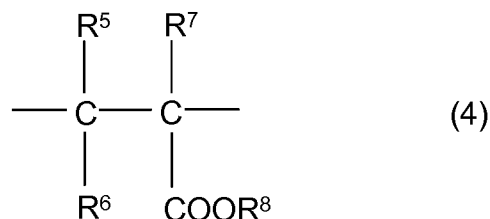
in which R^4 is C_1 - to C_8 -alkyl.

- 5 7. Use according to one or more of claims 2 to 6, wherein the esters of ethylenically unsaturated monocarboxylic acids correspond to formula (2)



- 10 in which R^2 is hydrogen or methyl and R^3 is C_1 - to C_8 -alkyl.

8. Use according to one or more of claims 2 to 7, wherein the esters of ethylenically unsaturated monocarboxylic acids are selected from the group consisting of methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n- and isobutyl (meth)acrylate, and hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and mixtures of these comonomers, the formulation "(meth)acrylate" including the respective esters of acrylic acid and methacrylic acid.
- 15 9. Use according to claim 1, wherein the oil soluble polymers comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups are homo- and copolymers (ii) of esters, amides and/or imides of ethylenically unsaturated carboxylic acids, said esters, amides and/or imides bearing alkyl residues with an average alkyl chain length of C_{10} - C_{40} .
- 20 10. Use according to claim 9, wherein the homo- and copolymers (ii) are esters of ethylenically unsaturated carboxylic acids and comprise repeat structural units of formula (4)
- 25



wherein

R^5 and R^6 are each independently hydrogen, phenyl or a group of the formula $COOR^8$,

R^7 is hydrogen, methyl or a group of the formula $-CH_2COOR^8$ and

R^8 is a C_{10} - to C_{40} -alkyl radical,

with the proviso that at at most one of R^5 and R^6 and R^7 include a carboxylic ester group $COOR^8$.

11. Use according to claim 10, wherein the ethylenically unsaturated carboxylic acid esters are esters of ethylenically unsaturated carboxylic acids selected from the group consisting of acrylic acid, methacrylic acid, cinnamic acid, maleic acid, fumaric acid and itaconic acid.

12. Use according to one or more of claims 9 to 11, wherein R^8 has 10 to 40, preferably 11 to 32 consecutive methylene groups.

13. Use according to one or more of claims 9 to 12, wherein the the ethylenically unsaturated carboxylic acid esters are esters of alcohols, selected from the group consisting of 1-decanol, 1-dodecanol, 1-tridecanol, isotridecanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, eicosanol, docosanol, tetracosanol, hexacosanol and their mixtures.

14. Use according to claim 9, wherein the homo- and copolymers (ii) are homo- and copolymers of amides and/or imides of ethylenically unsaturated carboxylic acids and are obtained by reaction of homo- and copolymers of ethylenically unsaturated carboxylic acids, their anhydrides, and/or their esters with lower

alcohols with 1 to 4 carbon atoms, with amines having one or, in case of amides one or two, alkyl residues with 10 to 40 consecutive methylene groups.

15. Use according to claim 14, wherein the amines are selected from the group consisting of 1-decyl amine, 1-dodecyl amine, 1-tridecyl amine, isotridecyl amine, 1-tetradecyl amine, 1-hexadecyl amine, 1-octadecyl amine, eicosyl amine, docosyl amine, tetracosyl amine, hexacosyl amine and their mixtures.
16. Use according to one or more of claims 9 to 15, wherein the copolymers (ii) contain 10 to 95 mol % of structural units derived from esters of ethylenically unsaturated carboxylic acids.
17. Use according to one or more of claims 9 to 13, wherein the homopolymers (ii) consist solely of structural units derived from esters of ethylenically unsaturated carboxylic acids, said esters bearing C₁₀-C₄₀-alkyl radicals.
18. Use according to one or more of claims 10 to 13, 16 and 17, wherein R⁵ and R⁶ are each hydrogen and R⁷ is hydrogen or methyl.
19. Use according to one or more of claims 10 to 13, 16 and 17, wherein one of R⁵ and R⁶ is hydrogen and the other a group of the formula COOR⁸ and R⁷ is hydrogen, or wherein R⁵ and R⁶ are hydrogen and R⁷ is a group of the formula -CH₂COOR⁸.
20. Use according to claim 1, wherein the oil soluble polymers comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups are graft polymers (iii) of homo- and copolymers b) of esters, amides and/or imides of ethylenically unsaturated carboxylic acids, said esters, amides and/or imides bearing alkyl radicals with an average alkyl chain length of C₁₀-C₄₀ on copolymers a) of ethylene with 5 to 18 mol-% of at least one monomer selected from vinyl esters, esters of ethylenically unsaturated carboxylic acids and vinyl ethers having a C₁ to C₈ alkyl or alkenyl group.

21. Use according to claim 20, wherein the graft polymers (iii) contain ethylene copolymer a) and a homo- or copolymer of an ester of an α,β -unsaturated carboxylic acid with a C₁₀- to C₄₀-alcohol b) in a weight ratio of 1:10 to 10:1.

5 22. Use according to one or more of claims 2 to 8, wherein the number average molecular weight of the ethylene copolymers (i) is between 500 and 100 000 g/mol as determined by Gel Permeation Chromatography using poly(styrene) standards.

10 23. Use according to one or more of claims 9 to 19, wherein the number average molecular weights M_w of the homo- or copolymer (ii) is within a range from 4000 to 200 000 g/mol and is determined by means of gel permeation chromatography GPC against poly(styrene) standards.

15 24. Use according to one or more of claims 1 to 23 wherein the explosive composition comprises low density ammonium nitrate.

20 25. Use according to one or more of claims 1 to 24 wherein the explosive composition comprises particulate ammonium nitrate particles with an average diameter range between 0.5 and 5 mm.

26. Use according to one or more of claims 1 to 25 wherein the ammonium nitrate has a purity of at least 90 wt.-%.

25 27. Use according to one or more of claims 1 to 26 wherein the fuel oil is selected from the group consisting of mineral oil distillates, biofuels, synthetic fuel oils and oily liquids derived from plant and animal origin and their synthetic equivalents.

30 28. Use according to one or more of claims 1 to 27 wherein the fuel oil has a pour point above -20 °C.

29 Use according to one or more of claims 1 to 28 wherein the fuel oil has a pour point below +30 °C.

30. Use according to one or more of claims 1 to 29 wherein 0.05 to 5.0 wt.-% of oil soluble polymer per weight unit of ammonium nitrate is applied.

5 31. Use according to one or more of claims 1 to 30 wherein at least 50 wt.-% of solid ANFO is recovered after 24 hours of exposure of solid ANFO to a water saturated substrate, a water saturated substrate being defined as a system wherein a water absorbent sponge is placed in a tray of water so that the bottom
10 a paper towel is laid over the sponge to give a uniform surface and the paper towel is kept saturated with water by the sponge below.

32. Use according to one or more of claims 1 - 31, wherein the particulate explosive composition comprises less than 2 wt.-% of water.

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33. Use according to one or more claims 1 - 32, wherein the particulate explosive composition is in the form of free flowing solid particles.

34. Use according to one or more claims 1 - 33, wherein the oil soluble polymer
20 comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups is applied to the ammonium nitrate in form of a solution and/or dispersion of said polymer in the fuel oil.

35. Process for improving water resistance of particulate ammonium nitrate fuel
25 oil explosives, the method comprising the step of adding to the explosive composition comprising particulate ammonium nitrate a fuel oil containing an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain
30 or in the side chains of the oil soluble polymer.

36. Process for manufacturing of particulate water resistant ammonium nitrate fuel oil explosives comprising bringing a particulate ammonium nitrate into contact

with a fuel oil, the fuel oil being the solution and/or dispersion of an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain
5 or in the side chains of the oil soluble polymer.

37. Process according to claim 36 wherein the fuel oil contains 0.1 to 15.0 wt.-% of the oil soluble polymer.

10 38. Process according to one or more of claims 36 and/or 37, wherein the process is performed at a temperature below the pour point of the fuel oil without the oil soluble polymer.

39. A water resistant, particulate, low density ammonium nitrate fuel oil
15 explosive, comprising particulate ammonium nitrate, a fuel oil and an oil soluble polymer comprising linear polymethylene sequences with an average of 10 to 40 consecutive methylene groups, said linear polymethylene sequences with in average 10 to 40 consecutive methylene groups may be either in the main chain or in the side chains of the oil soluble polymer, wherein the ammonium nitrate has
20 a bulk density of between 0.60 to 0.90 g/cm³, the bulk density being determined by weighing an untamped sample of the the ammonium nitrate in a container of known volume.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/055769

A. CLASSIFICATION OF SUBJECT MATTER
INV. C06B23/00 C06B31/28
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001 089285 A (ASAHI KASEI CORP) 3 April 2001 (2001-04-03) cited in the application paragraphs [0003], [0026]; example 4 -----	1-39
A	EP 0 256 669 A2 (EXXON CHEMICAL PATENTS INC [US]) 24 February 1988 (1988-02-24) cited in the application page 3, line 53 - page 4, line 19; examples 17, 19; tables I, VIII -----	1-39
A	US 2013/140871 A1 (FEDOROV ANDREI B [GB] ET AL) 6 June 2013 (2013-06-06) cited in the application paragraphs [0006] - [0009], [0034] - [0043], [0062]; example 3 ----- -/-	1-39



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

24 May 2017

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02/06/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Kappen, Sascha

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/055769

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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