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Emulsion explosive composition containing PPAN

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(56) Related Art
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US 5244475 A
CA 2042671 A1
Provatas, A.; "Energetic Polymers and Plasticisers for Explosive Formulations: A Review of Recent Advances"; DSTO Aeronautical and Maritime Research Laboratory, 2000. (https://apps.dtic.mil/sti/tr/pdf/ADA377866.pdf)

ABSTRACT

Disclosed is a PPAN-containing emulsion explosive composition including 40% to 80% by weight of an emulsion explosive composition and 20% to 60% by weight of porous prilled ammonium nitrate (PPAN) as an external oxidizer. The emulsion explosive composition includes (a) 70% to 95% by weight of an oxidizer aqueous solution comprising ammonium nitrate, calcium nitrate, and urea, (b) 0.1% to 10% by weight of an emulsifier, (c) 0.1% to 10% by weight of an oil phase, and (d) 0.1% to 10% by weight of an aliphatic adipate plasticizer serving as a heat-resistant plasticizer.

DESCRIPTION

EMULSION EXPLOSIVE COMPOSITION CONTAINING PPAN

Technical Field

The present disclosure relates to a PPAN-containing emulsion explosive composition.

Background Art

Reactive grounds generally refer to areas containing pyrite, such as sulfide, and contain chemical species capable of reacting with a nitrate. Commercially available nitrate-based explosives may be deteriorated in stability and blasting effect when used in reactive ground or when the temperature of the ground rises. When a nitrate-based explosive is charged into a hole in reactive ground, a nitrate component undergoes reaction with a metal sulfide and an acid to produce heat, which may cause an explosion to occur prematurely. These premature explosions can cause continuous detonation of explosives in adjacent bore holes, resulting in operator injury or death.

When there is volcanic activity in reactive soil, or when the temperature of the reactive soil is high, due to a rise in geothermal temperature by solar radiation, a temperature gradient due to an increase in the depth of the Earth's interior, or a temperature increase due to coal extraction, these reactions may occur more rapidly.

To inhibit reaction with nitrates, metal sulfides, and acids, inhibitors such as phosphates, borates, zinc oxide, urea, or liners can be used. However, there is a problem in that the liner is expensive and difficult to handle. In addition, leaks may occur during loading. Due to these disadvantages, it is more stable and effective to use products containing an inhibitor. Z.-X. Xu et. al. conducted a study on the thermal behavior for the case in which pyrite and an ammonium nitrate-based emulsion meet and react in the report titled "Thermal Stability and Mechanism of Decomposition of Emulsion Explosives in the Presence of Pyrite" (2015). DSC and DTA/TG analysis confirmed that an emulsion gunpowder containing urea as the inhibitor had the best thermal stability.

In general, emulsion explosives use an admixture of porous prilled ammonium nitrate (PPAN) and an emulsion to increase blasting power and sensitivity. In the case of inhibited products including only urea, it is not possible to use an emulsion explosive composition containing porous prilled ammonium nitrate (PPAN) in reactive ground having a temperature as high as 100°C. When the PPAN content in the emulsion composition is 30% or more, the PPAN completely dissolves within 1 to 2 hours at a temperature as high as 100°C, and the emulsion separates into a water layer and an oil layer. Since emulsion is not a completely closed system, when the temperature of the emulsion reaches the high temperature, the emulsion begins to crack, making fine cracks. Therefore, the contents of the emulsion is exposed to high-temperature vapor through the fine cracks, and thus the PPAN is dissolved by the moisture.

Therefore, there is a need for the development of technologies that can solve these problems.

Korean Patent Application Publication No. 2008-0083920 "Water-in-oil Emulsion Explosive" (published as of September 19, 2008) is a related art of the present disclosure.

Each document, reference, patent application or patent cited in this text is expressly incorporated herein in their entirety by reference, which means that it should be read and considered by the reader as part of this text. That the document, reference, patent application or patent cited in this text is not repeated in this text is merely for reasons of conciseness.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Furthermore, throughout the specification, unless the context requires otherwise, the word "include" or variations such as "includes" or "including", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Disclosure

Technical Problem

The present disclosure has been made to solve the aforementioned problems, and

an objective of the present disclosure is to provide an emulsion explosive composition including porous prilled ammonium nitrate (PPAN), the composition having improved high-temperature stability to be stably and safely used even in reactive ground.

Technical Solution

The present disclosure provides a PPAN-containing emulsion explosive composition including

40% to 80% by weight of an emulsion explosive composition and 20% to 60% by weight of porous prilled ammonium nitrate (PPAN) as an external oxidizer.

The emulsion explosive composition includes:

(a) 70% to 95% by weight of an oxidizer aqueous solution containing ammonium nitrate, calcium nitrate, and urea,

(b) 0.1% to 10% by weight of an emulsifier,

(c) 0.1% to 10% by weight of oil, and

(d) 0.1% to 10% by weight of an aliphatic adipate plasticizer as a heat-resistant plasticizer.

In accordance with an aspect of the invention, there is provided A PPAN-containing emulsion composition comprising:

40% to 80% by weight of an emulsion explosive composition and 20% to 60% by weight of porous prilled ammonium nitrate (PPAN) as an external oxidizer,

wherein the emulsion explosive composition comprises (a) 70% to 95% by weight of an oxidizer aqueous solution comprising ammonium nitrate, calcium nitrate, and urea, (b) 0.1% to 10% by weight of an emulsifier, (c) 0.1% to 10% by weight of an oil phase, and (d) 0.1% to 10% by weight of an aliphatic adipate plasticizer serving as a heat-resistant plasticizer for high-temperature stability of the emulsion,

wherein the aliphatic adipate plasticizer comprises one or more plasticizers selected from the group consisting of dioctyl adipate (DOA), di-iso-octyl adipate (DIOA), and di-isodexyl adipate (DIDA).

Advantageous Effects

The PPAN-containing emulsion explosive composition of the present invention has improved high-temperature stability. Therefore, there is an effect that the PPAN-containing emulsion explosive composition can be stably and safely used even in a high-temperature reactive ground.

Description of Drawings

FIG. 1 is a graph showing the results of stability evaluation of an emulsion by storing a PPAN-containing emulsion explosive in an oven heated to 100°C for 8 hours.

FIG. 2 is a graph showing the results of reactivity evaluation of a PPAN-containing emulsion explosive in Experimental Example 3.

Best Mode

Hereinafter, the present disclosure will be described in detail.

An PPAN-containing emulsion composition according to the present disclosure include 40% to 80% by weight of an emulsion explosive composition and 20% to 60% by weight of porous prilled ammonium nitrate (PPAN) as an externally introduced oxidizer.

The emulsion explosive composition includes:

(a) 70% to 95% by weight of an oxidizer aqueous solution containing ammonium nitrate, calcium nitrate, and urea,

(b) 0.1% to 10% by weight of an emulsifier,

(c) 0.1% to 10% by weight of oil, and

(d) 0.1% to 10% by weight of an aliphatic adipate plasticizer as a heat-resistant plasticizer.

In general, emulsion explosives use an admixture of porous prilled ammonium nitrate (PPAN) and an emulsion to increase blasting power and sensitivity. When a simple inhibited emulsion explosive composition is used in reactive ground with a high temperature of 100°C or higher, there is a problem in that the emulsion explosive composition is not allowed to contain porous prilled ammonium nitrate (PPAN). When the PPAN is admixed in the emulsion explosive composition, the PPAN completely dissolves within 1 to 2 hours due to the high temperature, and the emulsion is separated into a water layer and an oil layer. Since the emulsion is not a completely closed system, when the temperature of the emulsion reaches the high temperature, the emulsion begins to crack, making fine cracks. Therefore, the contents of the emulsion is exposed to high-temperature vapor through the fine cracks, and thus the PPAN is dissolved by the moisture.

Therefore, the present disclosure provides a solution to the problem of the conventional PPAN-containing emulsion explosive composition.

The oxidizer aqueous solution may be contained in an amount of 70% to 95% by weight with respect to the total weight of the emulsion explosive composition. When the proportion of the oxidizer aqueous solution is outside the range, the blasting power of the explosive is excessively high, resulting in loss of submicro-vibration characteristics. When the proportion of the oxidizer aqueous solution is excessively low, the explosive may not be exploded.

In one embodiment of the present disclosure, the oxidizer aqueous solution may include 30% to 60% of ammonium nitrate, 30% to 60% of calcium nitrate 30 to 60%, 1% to 20% of water, and 1% to 20% of urea.

In one embodiment of the present disclosure, the emulsifier preferably has a flash point of 100°C or higher, an acid value of 7 to 8, and an amine value of 40 to 60.

The emulsifier is included in an amount of 0.1% to 10% by weight relative to the total weight of the PAN-containing emulsion explosive composition. When the content of the emulsifier falls outside of the above range, an emulsion may not be formed, or the explosive may not be exploded.

In one embodiment of the present disclosure, the emulsifier may use one or more emulsifiers selected from the group consisting of sorbitan mono oleate (SMO) and amine salt of polyisobutylenesuccinicanhydride but is not limited thereto.

Preferably, the emulsifier may contain an amine salt of polyisobutylenesuccinicanhydride having a flash point of 100°C or higher, an acid value of 7 to 8, and an amine value of 40 to 60. The emulsifier may be composed only of an amine salt of polyisobutylenesuccinicanhydride.

The oil is included in an amount of 0.1% to 10% by weight relative to the total weight of the emulsion explosive composition. The oil may include fuel oil and oil.

Preferably, the fuel oil may be a carbonaceous fuel oil liquified at a temperature in a range of 50°C to 80°C. For example, one or more oils selected from the group consisting of wax, mineral oil, and light oil may be used.

As the oil, one or more oils selected from mineral oils, lubricating oils, and the like may be used.

An aliphatic adipate plasticizer, which is one of the heat-resistant plasticizers, may be included in an amount of

0.1% to 10% by weight relative to the total weight of the emulsion explosive composition. When the aliphatic adipate plasticizer is included in an amount less than the above described range, the stability of the PPAN-containing emulsion explosive composition may be insufficient in a high-temperature reactive ground. When the content of the aliphatic adipate plasticizer exceeds 10% by weight, it is not desirable because the blasting power is reduced.

The aliphatic adipate plasticizer may be one or more plasticizers selected from the group consisting of dioctyl adipate (DOA), di-iso-octyl adipate (DIOA), and di-isodexyl adipate (DIDA).

Herein below, the present disclosure will be described in more detail with reference to examples described below. The examples are intended to describe the present disclosure in more detail but the scope of the present disclosure is not limited by the examples. A number of changes may be made to the following examples without departing from the scope of the present disclosure.

Example 1: Preparation Of PPAN-containing Emulsion Explosive

An oxidizer aqueous solution was prepared by mixing 10% by weight of urea with 40% by weight of ammonium nitrate, 40% by weight of calcium nitrate, and 10% by weight of water.

Next, 90% by weight of the prepared oxidizer aqueous solution was placed in a mixer and heated to and maintained at 70°C. In another container, 3% by weight of mineral oil, 6% by weight of dioctyl adipate (DOA) as a heat-resistant plasticizer, and 1% by weigh of an emulsifier were heated to a temperature of 50°C or higher and mixed uniformly. The prepared mixtures were mixed in a mixer. When the nitrate completely dissolved, the admixture was agitated at high speed for 2 minutes for uniform blending. Thus, a composition of an emulsion explosive was obtained.

Next, a PPAN-containing emulsion explosive composition was prepared by mixing 70% by weight of an emulsion explosive composition and 30% by weight of porous prilled ammonium nitrate (PPAN).

Example 2: Preparation Of PPAN-containing Emulsion Explosive

A PPAN-containing emulsion explosive composition was prepared in the same manner as in Example 1, except that 50% by weight of the emulsion explosive composition was mixed with 50% by weight of porous prilled ammonium nitrate (PPAN).

Comparative Example 1: Preparation Of PPAN-containing Emulsion Explosive

A PPAN-containing emulsion explosive composition (30% by weight of PPAN) was prepared in the same manner as in Example 1 except that the content of mineral oil was increased to 9% by weight and a heat-resistant plasticizer was not used.

Comparative Example 2: Preparation Of PPAN-containing Emulsion Explosive

A PPAN-containing emulsion explosive composition (50% by weight of PPAN) was prepared in the same manner as in Example 2 except that the content of mineral oil was increased to 9% by weight and a heat-resistant plasticizer was not used.

Comparative Example 3: Preparation of Emulsion Explosive Composition (PPAN not Included)

An oxidizer aqueous solution was prepared by mixing 10% by weight of urea with 40% by weight of ammonium nitrate, 40% by weight of calcium nitrate, and 10% by weight of water.

Next, 90% by weight of the prepared oxidizer aqueous solution was placed in a mixer and heated to and maintained at 70°C. In another container, 3% by weight of mineral oil, 6% by weight of dioctyl adipate (DOA) as a heat-resistant plasticizer, and 1% by weigh to of an emulsifier were heated to a temperature of 50°C or higher and mixed uniformly. The prepared mixtures were mixed in a mixer. When the nitrate completely dissolved, the admixture was agitated at high speed for 2 minutes for uniform blending. Thus, a composition of an emulsion explosive was obtained.

Comparative Example 4: Preparation of Emulsion Explosive Composition (PPAN not Included)

An oxidizer aqueous solution was prepared by mixing 40% by weight of ammonium nitrate, 40% by weight of calcium nitrate, and 20% by weight of water.

Next, 90% by weight of the prepared oxidizer aqueous solution was placed in a mixer and heated to and maintained at 70°C. In another container, 3% by weight of mineral oil, 6% by weight of dioctyl adipate (DOA) as a heat-resistant plasticizer, and 1% by weigh to of an emulsifier were heated to a temperature of 50°C or higher and mixed uniformly. The prepared mixtures were mixed in a mixer. When the nitrate completely dissolved, the admixture was agitated at high speed for 2 minutes for uniform blending. Thus, a composition of an emulsion explosive was obtained.

Experimental Example 1: Stability Evaluation of PPAN-containing Emulsion Explosive

The PPAN-containing emulsion explosives of Examples 1 and 2 and Comparative Examples 1 and 2 were stored in an oven at 100°C for 8 hours to evaluate the emulsion stability. The stability evaluation results are shown in FIG. 1.

As illustrated in FIG. 1, in the case of the PPAN-containing emulsion explosives of Comparative Examples 1 and 2 in which a heat-resistant plasticizer was not used, after 8 hours of storage, the emulsion was separated into a water layer and a fuel layer, and the PPAN completely dissolved. On the other hand, in the case of the PPAN-containing emulsion explosives of Examples 1 and 2 in which a heat-resistant plasticizer was used, the particle size of the PPAN was slightly reduced, but no emulsion separation was observed.

These results indicate that the PPAN-containing emulsion explosive compositions of the present disclosure have very good stability in high-temperature environments.

Experimental Example 2: Evaluation of Performance after Long-term Storage of PPAN-containing Emulsion Explosive

The PPAN-containing emulsion explosive prepared as in Example 1 was stored in an oven at 100°C for 32 hours, and the explosion speed was evaluated. The results are shown in Table 1 below.

[Table 1]

Classification	Example 1 (70/30), 100℃ (m/s)			Specific gravity (g/cc)
	Shot1	Shot2	Average	
Immediately after preparation	4100	3580	3840	1.10

8 hours	-	3945	3945	
16 hours	3938	3829	3884	
24 hours	3887	3685	3786	
32 hours	4186	3850	4018	

The results of Table 1 indicate that the PPAN-containing emulsion explosive according to the present disclosure maintains its initial performance even after 32 hours of storage at 100°C. These results indicate that the PPAN-containing emulsion explosive composition of the present disclosure does not change in performance even after a long period of storage in high-temperature environments.

Experimental Example 3: Evaluation of Performance after Long-term Storage of PPAN-containing Emulsion Explosive

The reactivity evaluation of Examples 1 and 2 was performed according to a reactivity testing method prescribed in Edition 4 of Australian Explosives Industry Safety Group (AEISG) Code of Practice for Elevated Ground Temperature and Reactive Ground.

The compositions of the emulsion explosives of Example 1, Example 2, Comparative Example 3, and Comparative Example 4 were tested, and the test results were compared. The composition of Example 1 contains 30% by weight of PPAN, the composition of Example 2 contains 50% by weight of PPAN, the composition of Comparative Example 3 does not contain PPAN, and the composition of Comparative Example 4 does not contain PPAN and urea. While being in compliance with the reactivity testing method, the evaluation was performed using pyrite (FeS_2, 100%, 300 mesh, manufactured by Aldrich Company) instead of actual lock due to an inability to supply of rock samples. The results are shown in FIG. 2.

As shown in FIG. 2, the composition of the emulsion explosive of the present disclosure did not react with pyrite regardless of PPAN content, and no gas development was observed on the naked eye.

In addition, in the case of the composition of the emulsion explosive of Comparative Example 4 in which urea serving as an inhibitor is not included, the temperature rose rapidly as shown in the graph. However, in the case of Examples 1, 2, and 3 in which urea is included, it was confirmed that a temperature unchanging period is maintained for more than 32 hours. This means that the PPAN-containing emulsion explosive compositions of Examples 1 and 2 of the present disclosure can be safely used without generation of NOx in reactive grounds.

CLAIMS

1. A PPAN-containing emulsion composition comprising:

40% to 80% by weight of an emulsion explosive composition and 20% to 60% by weight of porous prilled ammonium nitrate (PPAN) as an external oxidizer,

wherein the emulsion explosive composition comprises (a) 70% to 95% by weight of an oxidizer aqueous solution comprising ammonium nitrate, calcium nitrate, and urea, (b) 0.1% to 10% by weight of an emulsifier, (c) 0.1% to 10% by weight of an oil phase, and (d) 0.1% to 10% by weight of an aliphatic adipate plasticizer serving as a heat-resistant plasticizer for high-temperature stability of the emulsion,

wherein the aliphatic adipate plasticizer comprises one or more plasticizers selected from the group consisting of dioctyl adipate (DOA), di-iso-octyl adipate (DIOA), and di-isodexyl adipate (DIDA).

2. The composition of claim 1, wherein the oxidizer aqueous solution comprises 30% to 60% of ammonium nitrate, 30% to 60% of calcium nitrate 30 to 60%, 1% to 20% of water, and 1% to 20% of urea.

3. The composition of claim 1, wherein the emulsifier comprises an amine salt of polyisobutylenesuccinicanhydride

(PIBSA) having a flash point of 100°C or higher, an acid value of 7 to 8, and an amine value of 40 to 60.

FIG. 1
(PRIOR ART)

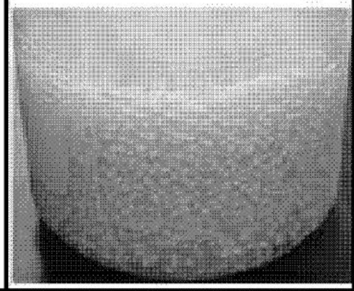
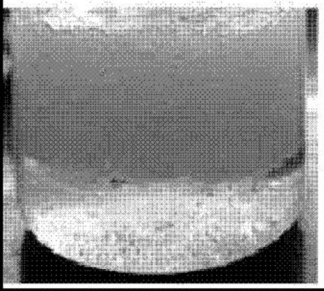
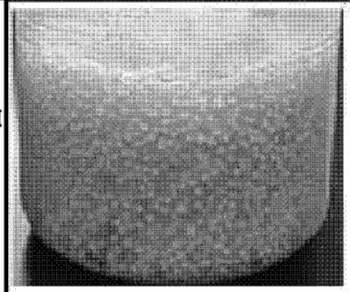
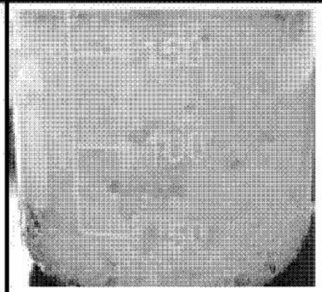
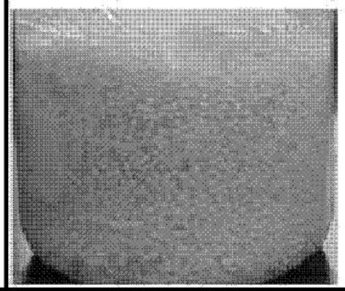
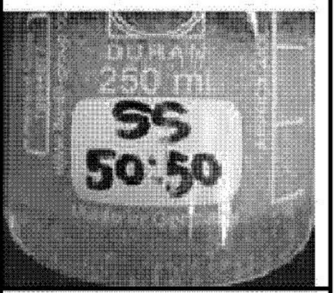
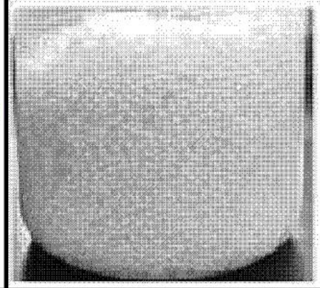
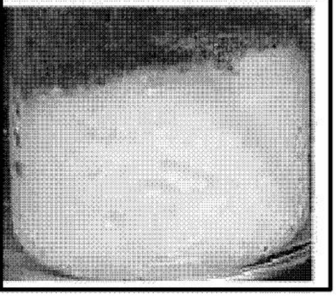
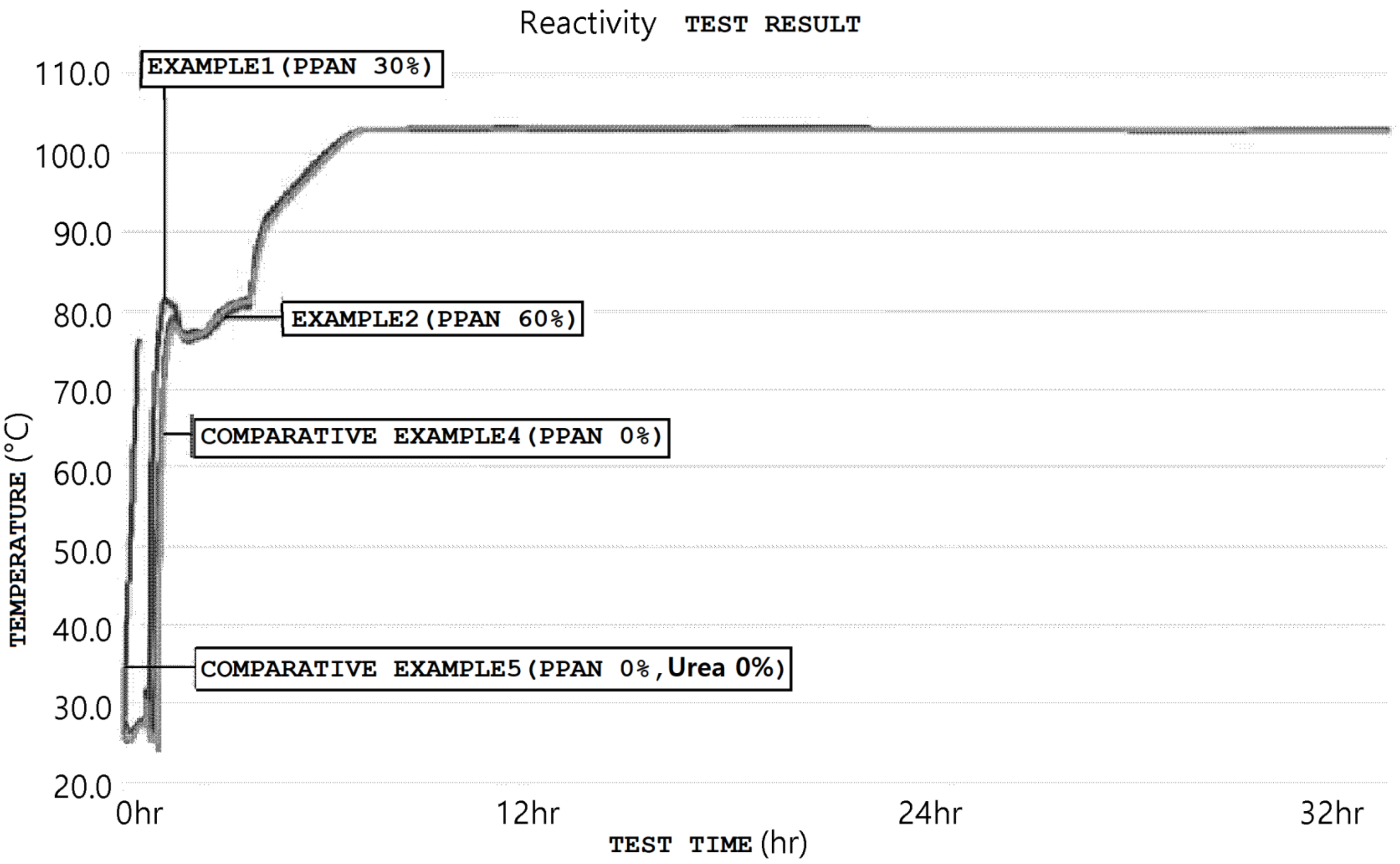
PPAN CONTENT	CLASSIFICATION	IMMEDIATELY AFTER PREPARATION	100°C, 8 HOURS AFTER PREPARATION
30%	COMPARATIVE EXAMPLE1 (COMPOSITION WITHOUT HEAT-RESISTANT PLASTICIZER)		
	EXAMPLE1 (COMPOSITION WITH HEAT-RESISTANT PLASTICIZER)		
50%	COMPARATIVE EXAMPLE2 (COMPOSITION WITHOUT HEAT-RESISTANT PLASTICIZER)		
	EXAMPLE2 (COMPOSITION WITH HEAT-RESISTANT PLASTICIZER)		

FIG. 2


Reactivity TEST RESULT
EXAMPLE1 (PPAN 30%)
EXAMPLE2 (PPAN 60%)
COMPARATIVE EXAMPLE4 (PPAN 0%)
COMPARATIVE EXAMPLE5 (PPAN 0%, Urea 0%)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
TEMPERATURE (°C)
0hr
12hr
24hr
32hr
TEST TIME (hr)