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(Section 42E(1) - Regulation 67B)

The processing under the Patents Act, 1978 of the undermentioned international application designating South Africa is hereby requested on the basis of this form.

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54 Title of invention

ALKALI-METAL-CARBONATE-CONTAINING NITRATE SALT COMPOSITIONS AND USE THEREOF AS HEAT TRANSFER MEDIUM OR HEAT STORAGE MEDIUM

The applicant has claimed priority (if any) as set out in the abovementioned international application

~~This application is for a patent of addition to patent application No.~~
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The abovementioned international application was filed in English or has been published under the Patent Cooperation Treaty in English YES ☐ NO ☒

This application is accompanied by:

	1.	Translation of the international application
	2.	Certified priority document(s)
X	3.	Translation(s) of the priority document(s)
X	4.	A copy of the Form P2 (particulars for the register)
X	5.	A declaration and power of attorney on Form P3
X	6.	Statement on the use of indigenous biological resource, genetic resource traditional knowledge or use on Form P26
X	7.	Form P.8
X	8.	Assignment documents.
X	9.	Verified English translation of the amended sheets

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(54) Title: ALKALI-METAL-CARBONATE-CONTAINING NITRATE SALT COMPOSITIONS AND USE THEREOF AS HEAT TRANSFER MEDIUM OR HEAT STORAGE MEDIUM

(54) Bezeichnung : ALKALIMETALLCARBONAT-HALTIGE NITRATSALZZUSAMMENSETZUNGEN UND DEREN VERWENDUNG ALS WÄRMETRÄGERMEDIUM ODER WÄRMESPEICHERMEDIUM

(57) **Abstract:** The invention relates to a nitrate salt composition, containing as the essential constituents A) an alkali metal nitrate and optionally an alkali metal nitrite in a total amount in the range of 90 to 99.84% by weight, and B) an alkali metal compound selected from the group comprising B1) alkali metal oxide, B2) alkali metal carbonate, B3) alkali metal compound that decomposes in the temperature range of 250°C to 600°C to form alkali metal oxide or alkali metal carbonate, B4) alkali metal hydroxide MetOH, in which Met denotes lithium, sodium, potassium, rubidium, caesium, B5) alkali metal peroxide $\mathrm{Met_2O_2}$, in which Met denotes lithium, sodium, potassium, rubidium, caesium, and B6) alkali metal superoxide $\mathrm{MetO_2}$, in which Met denotes sodium, potassium, rubidium, caesium in a total amount in the range of 0.16 to 10% by weight, the percentages being relative to the nitrate salt composition.

(57) **Zusammenfassung:** Nitratsalzzusammensetzung, enthaltend als wesentliche Bestandteile A) ein Alkalimetallnitrat und gegebenenfalls ein Alkalimetallnitrit in einer Gesamtmenge im Bereich von 90 bis 99,84 Gew.-% und, B) eine Alkalimetallverbindung ausgewählt aus der Gruppe B1) Alkalimetalloxid, B2) Alkalimetallcarbonat, B3) Alkalimetallverbindung, die im Temperaturbereich von 250°C bis 600°C zu Alkalimetalloxid oder Alkalimetallcarbonat zerfällt, B4) Alkalimetallhydroxid MetOH, in welchem Met Lithium, Natrium, Kalium, Rubidium, Cäsium, bedeuten, B5) Alkalimetallperoxid $\mathrm{Met_2O_2}$, in welchem Met Lithium, Natrium, Kalium, Rubidium, Cäsium bedeuten und B6) Alkalimetallsuperoxid $\mathrm{MetO_2}$, in welchem Met Natrium, Kalium, Rubidium, Cäsium bedeuten in einer Gesamt- menge im Bereich von 0,16 bis 10 Gew.-%, jeweils bezogen auf die Nitratsalzzusammensetzung.

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IN THE MATTER OF a South African
Application corresponding to
PCT Application PCT/EP2013/057282

RWS Group Ltd, of Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Buckinghamshire, United Kingdom, hereby solemnly and sincerely declares that, to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and German languages, is a true and correct translation of the PCT Application filed under No. PCT/EP2013/057282.

Date: 28 August 2014

C. E. SITCH
Managing Director – UK Translation Division

For and on behalf of RWS Group Ltd

Nitrate salt compositions comprising alkali metal carbonate and their use as heat transfer medium or heat storage medium

Description

The present invention relates to nitrate salt compositions as defined in the claims, and also to their use as heat transfer medium and/or heat storage medium as likewise defined in the claims.

Heat transfer media or heat storage media based on inorganic solids, in particular salts, are known both in chemical technology and in power station engineering. They are generally used at high temperatures, for example above 100°C, therefore above the boiling point of water at atmospheric pressure.

For example, salt bath reactors are used at temperatures of from about 200 to 500°C in chemical plants for the industrial preparation of various chemicals.

Heat transfer media are media which are heated by a heat source, for example the sun in solar thermal power stations, and transport the heat present therein over a particular distance. They can then transfer this heat to another medium, for example water or a gas, preferably via heat exchangers, with this other medium then being able to drive, for example, a turbine. However, heat transfer media can also transfer the heat present therein to another medium, (for example a salt melt) present in a stock vessel and thus pass on the heat for storage. However, heat transfer media can also themselves be fed into a stock vessel and remain there. They are then themselves both heat transfer media and heat storage media.

Heat stores comprise heat storage media, usually chemical compositions, for example the mixtures according to the invention, which can store a quantity of heat for a particular time. Heat stores for fluid, preferably liquid, heat storage media are usually formed by a fixed vessel which is preferably insulated against heat loss.

A still relatively new field of application for heat transfer media or heat storage media are solar thermal power stations for generating electric energy. In these, focused solar radiation heats a heat transfer medium which passes its heat on via a heat exchanger to water and thus generates steam which drives a turbine which ultimately, as in a conventional electric power station, drives a generator to generate electric energy.

Three types of solar thermal power stations are of particular importance:
the parabolic trough power station, the Fresnel power station and the tower power station.

In the parabolic trough power station, the solar radiation is focused via parabolic mirror grooves into the focal line of the mirrors. There, there is a tube filled with a heat transfer medium. The heat transfer medium is heated by the solar radiation and flows to the heat exchanger where it releases its heat, as described above, in order to generate steam.

In the Fresnel power station, the solar radiation is focused by means of generally flat mirrors onto a focal line. There, there is a tube through which a heat transfer medium flows. In contrast to the parabolic trough power station, the mirror and the tube do not jointly follow the position of the sun, but instead the setting of the mirrors is adjusted relative to the fixed tube. The setting of the mirrors follows the position of the sun so that the fixed tube is always in the focal line of the mirrors. In Fresnel power stations, too, molten salt can be used as heat transfer medium. Salt Fresnel power stations are at present largely still being developed. The generation of steam in the salt Fresnel power station is carried out analogously to the parabolic trough power station.

In the case of the solar thermal tower power station, a tower is ringed by mirrors which focus the solar radiation onto a central receiver in the upper part of the tower. In the receiver, a heat transfer medium is heated to produce steam in order to generate electric energy via heat transfer media in a manner analogous to the parabolic trough power station or Fresnel power station.

At present, an organic heat transfer medium composed of diphenyl ether and biphenyl, also referred to as "thermal oil" is used in the parabolic trough power station. However, this heat transfer medium can be used only up to 400°C since it decomposes during prolonged operation above this range.

However, it is desirable to increase the temperature of the heat transfer medium on arrival in the heat exchanger of the steam generator (the steam entry temperature) to above 400°C since the efficiency of the steam turbine is then increased (at a steam entry temperature of 400°C, the Carnot efficiency is about 42%; at 500°C, for example, it increases to above about 50%).

If a mixture of about 60% by weight of sodium nitrate ($NaNO_3$) and about 40% by weight of potassium nitrate (KNO_3) is used as heat transfer medium instead of the organic heat transfer medium, as has already been implemented in solar thermal tower power stations, this can be heated to a maximum of about 565°C in the long term. Above this temperature, the nitrate mixture mentioned also decomposes over time, generally with release of nitrous oxides, usually nitrogen monoxide and/or nitrogen dioxide.

It would in principle be quite possible technically to heat the heat transfer media in solar thermal power stations to temperatures of about 650°C, for example at the focal point of a tower power station, and thus achieve higher efficiencies of the steam turbine, similar to the case of fossil fuel-fired power stations.

It is therefore desirable to increase the thermal stability of heat transfer media in long-term operation to above about 565°C.

It is very desirable to match the generation of electric energy in a solar thermal power station, regardless of which type, to the demand on the grid. This is made possible, for example, by heat being stored during times of high incident solar radiation and being able to be utilized to generate electric energy when required after sundown or during phases of bad weather.

The storage of heat can be effected directly by storage of the heated heat transfer medium in generally well insulated stock tanks or indirectly by transfer of the heat from the heated heat transfer medium to another medium (heat store), for example in a sodium nitrate-potassium nitrate salt melt.

An indirect method has been realized in the 50 MW Andasol I power station in Spain, where about 28 500 metric tons of a melt of sodium nitrate and potassium nitrate (60:40 in % by weight) are used as heat storage in a well insulated tank. During periods of incident solar radiation, the melt is pumped from a relatively cool tank (about 290°C) via a thermal oil-salt heat exchanger to a hotter tank and in the process heated to about 390°C. Here, heat energy is withdrawn from the thermal oil (here functioning as heat transfer medium) via a heat exchanger and introduced into the salt melt (thermal oil-salt heat exchanger). During times of low incident solar radiation and at night, the power station can be operated under full load for about 7.5 hours when the heat store is fully charged.

However, it would be advantageous to use the heat transfer medium as heat storage medium as well, since the corresponding thermal oil-salt heat exchangers could be saved in this way.

In addition, possible contact of the thermal oil, which has reducing properties, with the strongly oxidizing nitrate melt could be avoided in this way. Owing to the significantly higher price of the thermal oil compared to the sodium nitrate-potassium nitrate melt, thermal oil has hitherto not been considered as heat store.

It is an object of the invention to provide a readily available, improved nitrate salt composition as heat transfer medium and/or heat storage medium which can be used in long-term operation at elevated temperature, preferably above 565°C, with the release of nitrous oxides, usually nitrogen monoxide and/or nitrogen dioxide, being reduced or suppressed.

A nitrate mixture composed of about 60% by weight of sodium nitrate ($NaNO_3$) and about 40% by weight of potassium nitrate (KNO_3) is, for example, offered for sale under the name Hitec® Solar Salt by Coastal Chemical Co., L.L.C. This product is offered for use as heat transfer medium or heat storage medium. It can, in addition to further components, comprise small amounts of up to a maximum of 0.15% by weight of sodium carbonate (Na_2CO_3) (product information sheet Hitec® Solar Salt).

For reasons of simplicity, the nitrate salt compositions defined in the description and in the claims, especially their preferred and particularly preferred embodiments, will hereinafter also be referred to as "nitrate salt composition of the invention".

The nitrate salt composition of the invention comprises an alkali metal nitrate and optionally an alkali metal nitrite as significant constituents A).

The alkali metal nitrate here is a nitrate, preferably a virtually water-free nitrate, particularly preferably a nitrate free of water of crystallization, of the metals lithium, sodium, potassium, rubidium or cesium, generally described as $MetNO_3$, where Met represents the above-described alkali metals; the term alkali metal nitrate encompasses both a single nitrate and mixtures of the nitrates of these metals, for example potassium nitrate plus sodium nitrate.

The alkali metal nitrite here is a nitrite, preferably a virtually water-free nitrite, particularly preferably a nitrite which is free of water of crystallization, of the alkali metals lithium, sodium, potassium, rubidium and cesium, generally described as $MetNO_2$, where Met represents the above-described alkali metals. The alkali metal nitrite can be present as single compound or else as a mixture of various alkali metal nitrites, for example sodium nitrite plus potassium nitrite.

The constituent A) is present in a total amount in the range from 90 to 99.84% by weight, preferably in the range from 95 to 99.84% by weight, particularly preferably in the range from 95 to 99.8% by weight, very particularly preferably in the range from 98 to 99.8% by weight, in each case based on the nitrate salt composition of the invention.

The constituent A) can comprise an alkali metal nitrite, as described above, in an amount in the range from 0 to 50% by weight, preferably in the range from 1 to 10% by weight, particularly preferably in the range from 2 to 5% by weight, in each case based on the constituent A).

A well-suited alkali metal nitrate component $MetNO_3$ of the constituent A) is composed, for example, of

A1) potassium nitrate in an amount in the range from 20 to 55% by weight,
A2) sodium nitrate in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrate component $MetNO_3$ of the constituent A).

A well-suited alkali metal nitrite component $MetNO_2$ of the constituent A) is composed, for example, of

A1) potassium nitrite in an amount in the range from 20 to 55% by weight,
A2) sodium nitrite in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrite component $MetNO_2$ of the constituent A).

In a further embodiment of the nitrate salt composition, the constituent A) comprises only one type of alkali metal nitrate, for example potassium nitrate or sodium nitrate.

The nitrate salt composition of the invention further comprises, as significant constituent B), an alkali metal compound selected from the group B1) alkali metal oxide Met_2O, in which Met is lithium, sodium, potassium, rubidium, cesium, preferably sodium and/or potassium, B2) alkali metal carbonate, B3) alkali metal compound which decomposes into alkali metal oxide or alkali metal carbonate in the temperature range from 250°C to 600°C, B4) alkali metal hydroxide MetOH, in which Met is lithium, sodium, potassium, rubidium, cesium, preferably sodium and/or potassium, B5) alkali metal peroxide Met_2O_2, in which Met is lithium, sodium, potassium, rubidium, cesium, preferably sodium and/or potassium, and B6) alkali metal superoxide $MetO_2$, in which Met is sodium, potassium, rubidium, cesium, preferably sodium and/or potassium, in a total amount in the range from 0.16 to 10% by weight, preferably in the range from 0.16 to 5% by weight, particularly preferably in the range from 0.2 to 5% by weight, very particularly preferably in the range from 0.2 to 2% by weight, in each case based on the nitrate salt composition.

Preference is given to alkali metal compounds B3) which decompose into alkali metal oxide, preferably sodium oxide, or into alkali metal carbonate, preferably sodium carbonate, at the typical high operating temperatures of nitrate salt melts in a solar thermal power station, i.e. at from 250° to 600°C, preferably from 300°C to 500°C, under the corresponding oxidizing conditions. Examples of such alkali metal compounds are alkali metal salts such as lithium, sodium, potassium, rubidium or cesium salts of carboxylic acids such as formic acid, acetic acid, oxalic acid, for example sodium formate, sodium acetate, potassium oxalate.

The nitrate salt composition of the invention comprises as preferred significant constituent B) an alkali metal carbonate in a total amount in the range from 0.16 to 10% by weight, preferably in the range from 0.16 to 5% by weight, particularly preferably in the range from 0.2 to 5% by weight, very particularly preferably in the range from 0.2 to 2% by weight, in each case based on the nitrate salt composition.

The alkali metal carbonate is a carbonate, preferably a virtually water-free carbonate, of the alkali metals lithium, sodium, potassium, rubidium and cesium, generally described as Met_2CO_3, where Met represents the above-described alkali metals. The alkali metal carbonate can be present as single compound or else as a mixture of various alkali metal carbonates, for example sodium carbonate plus potassium carbonate.

In a well-suited embodiment of the nitrate salt composition, the constituent B) is formed virtually exclusively by alkali metal carbonate Met_2CO_3, preferably by sodium carbonate Na_2CO_3 either alone or together with further alkali metal carbonates selected from the group consisting of lithium carbonate Li_2CO_3, potassium carbonate K_2CO_3, rubidium carbonate Rb_2CO_3, cesium carbonate Cs_2CO_3, preferably lithium carbonate Li_2CO_3 and/or potassium carbonate K_2CO_3.

The amount of constituent B), preferably alkali metal carbonate, in particular sodium carbonate, present in the nitrate salt composition of the invention should, according to the present state of knowledge, be not less than 0.16% by weight, preferably 0.2% by weight, since otherwise the stabilizing effect of the constituent B), preferably the alkali metal carbonate, is lost.

The amount of constituent B), preferably alkali metal carbonate, in particular sodium carbonate, present in the nitrate salt composition of the invention should not exceed 10% by weight, preferably 5% by weight, particularly preferably 2% by weight.

At higher contents of constituent B), preferably alkali metal carbonate, there is a risk that particles of the constituent B), preferably alkali metal carbonate particles, which are, for example, too large and/or are not dissolved in the melt of the nitrate salt composition of the invention can give rise to malfunctions in the piping, pump and apparatus system of the solar thermal power station or the chemical plant.

The upper limit to the content of constituent B), preferably the alkali metal carbonate content, of the nitrate salt composition of the invention can be influenced by various parameters, for example the temperature of a corresponding melt of the nitrate salt composition of the invention or the precise composition thereof.

Apart from the abovementioned significant components, the nitrate salt composition of the invention can additionally comprise traces of impurities, for example sodium chloride, sodium sulfate, calcium oxide, magnesium oxide, silicon dioxide, aluminum oxide, iron oxide or water. The sum of these impurities is generally not more than 1% by weight, based on the nitrate salt composition of the invention.

The sum of all constituents of the nitrate salt composition of the invention is 100% by weight.

The nitrate salt composition of the invention goes over into the molten and usually pumpable form at a temperature above from about 150 to 300°C, depending, inter alia, on the nitrite content and the ratio of the cations forming the constituent A) and/or B).

The nitrate salt composition of the invention, preferably in molten form, for example as pumpable liquid, is used as heat transfer medium and/or heat storage medium, preferably in power stations for generating heat and/or electricity, in chemical process engineering, for example in salt bath reactors, and in metal hardening plants.

Examples of power stations for generating heat and/or electric energy are solar thermal power stations such as parabolic trough power stations, Fresnel power stations, tower power stations.

In a well-suited embodiment, the nitrate salt compositions of the invention are used, preferably in the molten state, for example as pumpable liquid, both as heat transfer medium and as heat storage medium in the solar thermal power stations, for example the parabolic trough power stations, the tower power stations or the Fresnel power stations.

In a further well-suited embodiment, the nitrate salt compositions of the invention are used, preferably in the molten state, for example as pumpable liquid, either as heat transfer medium or as heat storage medium in the solar thermal power stations, for example the parabolic trough power stations, the tower power stations, the Fresnel power stations.

For example, the nitrate salt compositions of the invention are used, preferably in the molten state, for example as pumpable liquid, in tower power stations as heat transfer medium and/or as heat storage medium, particularly preferably as heat transfer medium.

When the nitrate salt compositions of the invention are used, preferably in the molten state, for example as pumpable liquid, as heat transfer medium in the solar thermal power stations, for example the parabolic trough power stations, the tower power stations, the Fresnel power stations, the heat transfer media are conveyed through tubes heated by the heat of the sun. They usually convey the heat arising there to a heat store or to the heat exchanger of the steam heater of a power station.

The heat store generally comprises two large vessels, normally a cold vessel and a hot vessel. The nitrate salt composition of the invention, preferably the molten state, for example as pumpable liquid, is usually taken from the cold vessel of the solar plant and heated in the solar field of a parabolic trough plant or a tower receiver. The hot molten salt mixture which has been heated in this way is usually conveyed into the hot vessel and stored there until there is demand for the production of electric energy.

The hot nitrate salt compositions of the invention are then usually taken off in the molten state, for example as pumpable liquid, from the hot tank and pumped to the steam generator of a steam power station. The steam produced there and pressurized to above 100 bar generally drives a turbine and a generator which supplies electric energy to the electricity grid.

At the steam generator, the nitrate salt compositions of the invention are generally cooled to about 290°C in the molten state, for example as pumpable liquid, and usually conveyed back into the cold tank. When transferring heat from the tubes heated by heat from the sun to the store or to the steam generator, the nitrate salt composition of the invention in molten form acts as heat transfer medium. Introduced into the heat storage vessel, the same nitrate salt composition of the invention acts as heat storage medium in order to make demand-oriented production, for example, of electric energy possible.

However, the nitrate salt composition of the invention is, preferably in molten form, also used as heat transfer medium and/or heat storage medium, preferably heat transfer medium, in chemical process engineering, for example for heating reaction apparatuses of chemical production plants where, in general, a very large heat flow has to be transferred at very high temperatures within narrow fluctuation limits. Examples are salt bath reactors. Examples of the abovementioned production plants are acrylic acid plants or plants for producing melamine.

Examples

Example 1

500 g of solar salt (300 g of $NaNO_3$, 200 g of KNO_3) were admixed with 5 g of sodium carbonate (corresponding to 0.11% by mass of carbon) and heated to 300°C in a stainless steel vessel. 6 g of NO mixed with 5 l of water- and carbon dioxide-free air were subsequently introduced into the melt over a period of one hour. Analysis of the melt after the end of the experiment gave a total carbon content of 0.031% by mass. In this experiment, 2 g of NO equivalents were able to be bound by conversion of the carbonate.
The nitrate/nitrite ratio (in % by weight) had not changed significantly, as was confirmed by wet chemical analysis of the corresponding ions.

Example 2

500 g of HITEC® (35 g of $NaNO_3$, 265 g of KNO_3, 200 g of $NaNO_2$) were admixed with 5 g of sodium carbonate (corresponding to 0.11% by mass of carbon) and heated to 300°C in a stainless steel vessel. 15.2 g of NO mixed with 10 l of water- and carbon dioxide-free air were subsequently introduced into the melt over a period of two hours. The originally insoluble sodium carbonate was completely dissolved after the experiment. Analysis of the melt indicated a total carbon content of 0.02% by mass. In this experiment, 2.3 g of NO equivalents were able to be bound by conversion of the carbonate.
The nitrate/nitrite ratio (in % by weight) had not changed significantly, as was confirmed by wet chemical analysis of the corresponding ions.

Example 3

500 g of solar salt (300 g of $NaNO_3$, 200 g of KNO_3) were admixed with 5 g of Na_2O/Na_2O_2 (80:20) and heated to 400°C in a stainless steel vessel. 10.4 g of NO mixed with 5 l of water- and carbon dioxide-free air were subsequently introduced into the melt over a period of one hour. After hydrolysis, the hydroxide content of the salt melt was below the detection limit (< 0.1 g/100 g). In this experiment, 4.6 g of NO equivalents were thus able to be bound by conversion of the oxide.
The nitrate/nitrite ratio (in % by weight) had not changed significantly, as was confirmed by wet chemical analysis of the corresponding ions.

Example 4

500 g of solar salt (300 g of $NaNO_3$, 200 g of KNO_3) were admixed with 5 g of NaOH and heated to 300°C in a stainless steel vessel. 12.8 g of NO_2, greatly diluted with 50 l of water- and carbon dioxide-free air, were subsequently introduced into the melt. After hydrolysis, the hydroxide content of the salt melt was 0.1 g/100 g. In this experiment, 4.4 g of NO_2 equivalents were thus able to be bound by conversion of the hydroxide.
The nitrate/nitrite ratio (in % by weight) had not changed significantly, as was confirmed by wet chemical analysis of the corresponding ions.

Example 5

500 g of HITEC® (35 g of $NaNO_3$, 265 g of KNO_3, 200 g of $NaNO_2$) were admixed with 8 g of NaOH and heated to 200°C in a stainless steel vessel. 15.3 g of NO mixed with 10 l of water- and carbon dioxide-free air were subsequently introduced into the melt. After hydrolysis, the hydroxide content of the melt was below the detection limit (< 0.1 g/100 g). In this experiment, 6 g of NO equivalents were able to be bound by conversion of the hydroxide.
The nitrate/nitrite ratio (in % by weight) had not changed significantly, as was confirmed by wet chemical analysis of the corresponding ions.

Examples 1 to 5 show that the alkali metal compounds B) according to the invention bind nitrogen oxides at high temperatures without the nitrate/nitrite ratio changing.

Example 6

Comparative experiment without alkali metal compounds B) according to the invention
100 g of HITEC® (7 g of $NaNO_3$, 53 g of KNO_3, 40 g of $NaNO_2$) were heated to 595°C in a stainless steel tube and maintained at this temperature (± 5 K) for 2.5 hours. 10 l/h of argon were passed over the melt in order to convey the gases formed into two wash bottles. The two wash bottles were filled with 135.6 and 151.2 g, respectively, of hydrogen peroxide solution (3%). Analysis of the total nitrogen content indicated 22 and 5 mg/kg, respectively, in the solutions, corresponding to a total amount of 7.7 mg of nitrogen or 16.6 mg of NO, which were given off from the salt melts.

Experiment according to the invention
In the same experimental set-up, 100 g of HITEC® (7 g of $NaNO_3$, 53 g of KNO_3, 40 g of $NaNO_2$) together with 1 g of Na_2CO_3 were heated to 600°C and maintained at this temperature (± 5 K) for 2.5 hours in a second experiment. 10 l/h of argon were likewise passed over the melt in order to convey the gases formed into two wash bottles. The two wash bottles were filled with 148.2 and 149.4 g of hydrogen peroxide solution (3%). Analysis of the total nitrogen content indicated 9 and 7 mg/kg, respectively, in the solutions, corresponding to a total amount of

4.8 mg of nitrogen or 10.2 mg of NO, which were given off from the salt melts.
It was thus able to be shown that 1% of sodium carbonate as additive in HITEC® reduces the liberation of nitrogen oxides by about 40% by weight.

Example 7

Comparative experiment without alkali metal compounds B) according to the invention

100 g of solar salt (60 g of $NaNO_3$, 40 g of KNO_3) were heated to 600°C over a period of 2 hours in a stainless steel tube and maintained at this temperature (± 5 K) for 1 hour. 5 l/h of water- and carbon dioxide-free air were passed over the melt in order to introduce the off-gases formed into a scrubbing tower. After the end of the experiment, the apparatus was flushed with argon for half an hour. The scrubbing tower was filled with 57 g of scrubbing solution composed of 0.1 mol/l of $KMnO_4$ together with 0.2 mol/l of NaOH in water. Analysis of the total nitrogen content indicated 51 mg/kg in the solution, corresponding to a total amount of 2.9 mg of nitrogen or 6.2 mg of NO, which were given off from the salt melts.

Experiment according to the invention
In the same experimental set-up, 100 g of solar salt together with 1 g of Na_2CO_3 (corresponding to 0.11% by mass of carbon) were heated to 600°C over a period of 2 hours in a stainless steel tube and maintained at this temperature (± 5 K) for 1 hour in a second experiment. 5 l/h of water- and carbon dioxide-free air were passed over the melt in order to introduce the off-gases formed into a scrubbing tower. After the end of the experiment, the apparatus was flushed with argon for half an hour. The scrubbing tower was filled with 56 g of scrubbing solution composed of 0.1 mol/l of $KMnO_4$ together with 0.2 mol/l of NaOH in water. Analysis of the total nitrogen content indicated 34 mg/kg in the solution, corresponding to a total amount of 1.9 mg of nitrogen or 4.1 mg of NO, which were given off from the salt melts.
It was thus able to be shown that 1% of sodium carbonate as additive in solar salt reduces the liberation of nitrogen oxides by about 30%.

Examples 6 and 7 show that the alkali metal compounds B) according to the invention greatly reduce the liberation of nitrogen oxides at very high temperatures.

Claims

1. A nitrate salt composition comprising as significant constituents

A) an alkali metal nitrate and optionally an alkali metal nitrite in a total amount in the range from 90 to 99.84% by weight and

B) an alkali metal compound selected from the group B1) alkali metal oxide, B2) alkali metal carbonate, B3) alkali metal compound which decomposes into alkali metal oxide or alkali metal carbonate in the temperature range from 250°C to 600°C, B4) alkali metal hydroxide MetOH, in which Met is lithium, sodium, potassium, rubidium, cesium, B5) alkali metal peroxide Met_2O_2, in which Met is lithium, sodium, potassium, rubidium, cesium, and B6) alkali metal superoxide $MetO_2$, in which Met is sodium, potassium, rubidium, cesium, in a total amount in the range from 0.16 to 10% by weight, in each case based on the nitrate salt composition.

2. The nitrate salt composition according to claim 1, wherein the constituent B) is an alkali metal carbonate.

3. The nitrate salt composition according to claim 1 or 2, wherein the constituent B) is comprised in an amount in the range from 0.2 to 5% by weight.

4. The nitrate salt composition according to any of claims 1 to 3, wherein the constituent A) comprises an alkali metal nitrite in a total amount in the range from 0 to 50% by weight, based on the constituent A).

5. The nitrate salt composition according to any of claims 1 to 4, wherein the alkali metal nitrate component of the constituent A) is composed of
A1) potassium nitrate in an amount in the range from 20 to 55% by weight,
A2) sodium nitrate in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrate component of the constituent A).

6. The nitrate salt composition according to any of claims 1 to 5, wherein the alkali metal carbonate is selected from the group consisting of sodium carbonate Na_2CO_3 and potassium carbonate K_2CO_3.

7. The nitrate salt composition according to any of claims 1 to 6, wherein the alkali metal carbonate is sodium carbonate Na_2CO_3.

8. The nitrate salt composition according to any of claims 1 to 7 in molten form.

9. The use of a nitrate salt composition as defined in any of claims 1 to 8 as heat transfer medium and/or heat storage medium.

10. The use according to claim 9, wherein the nitrate salt composition is present in molten form.

11. The use according to claims 9 to 10 in power stations for generating heat and/or electricity, in chemical process engineering and in metal hardening plants.

12. The use according to claim 11 in solar thermal power stations.

13. The use according to claim 12 as heat transfer medium in solar thermal power stations.

14. The use according to claim 13 as heat storage medium in solar thermal power stations.

15. The use according to claim 11 as heat transfer medium for heating reaction apparatuses of chemical production plants.

IN THE MATTER OF a South African
Application corresponding to
PCT Application PCT/EP2013/057282

RWS Group Ltd, of Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Buckinghamshire, United Kingdom, hereby solemnly and sincerely declares that, to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and German languages, is a true and correct translation of the amended sheets of the PCT Application filed under No. PCT/EP2013/057282.

Date: 28 August 2014

C. E. SITCH
Managing Director – UK Translation Division

For and on behalf of RWS Group Ltd

Claims

1. A nitrate salt composition comprising as significant constituents

   A) an alkali metal nitrate and an alkali metal nitrite in a total amount in the range from 98 to 99.84% by weight and
   B) an alkali metal compound selected from the group B1) alkali metal oxide, B2) alkali metal carbonate, B3) alkali metal compound which decomposes into alkali metal oxide or alkali metal carbonate in the temperature range from 250°C to 600°C, B5) alkali metal peroxide Met_2O_2, in which Met is lithium, sodium, potassium, rubidium, cesium, and B6) alkali metal superoxide $MetO_2$, in which Met is sodium, potassium, rubidium, cesium, in a total amount in the range from 0.16 to 2% by weight, in each case based on the nitrate salt composition.

2. The nitrate salt composition according to claim 1, wherein the constituent B) is an alkali metal carbonate.

3. The nitrate salt composition according to claim 1 or 2, wherein the constituent B) is comprised in an amount in the range from 0.2 to 2% by weight.

4. The nitrate salt composition according to any of claims 1 to 3, wherein the constituent A) comprises an alkali metal nitrite in a total amount up to 50% by weight, based on the constituent A).

5. The nitrate salt composition according to any of claims 1 to 4, wherein the alkali metal nitrate component of the constituent A) is composed of
   A1) potassium nitrate in an amount in the range from 20 to 55% by weight,
   A2) sodium nitrate in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrate component of the constituent A).

6. The nitrate salt composition according to any of claims 1 to 5, wherein the alkali metal carbonate is selected from the group consisting of sodium carbonate Na_2CO_3 and potassium carbonate K_2CO_3.

7. The nitrate salt composition according to any of claims 1 to 6, wherein the alkali metal carbonate is sodium carbonate Na_2CO_3.

8. The nitrate salt composition according to any of claims 1 to 7 in molten form.

9. The use of a nitrate salt composition as defined in any of claims 1 to 8 as heat transfer medium and/or heat storage medium.

10. The use according to claim 9, wherein the nitrate salt composition is present in molten form.

11. The use according to claims 9 to 10 in power stations for generating heat and/or electricity, in chemical process engineering and in metal hardening plants.

12. The use according to claim 11 in solar thermal power stations.

13. The use according to claim 12 as heat transfer medium in solar thermal power stations.

14. The use according to claim 13 as heat storage medium in solar thermal power stations.

15. The use according to claim 11 as heat transfer medium for heating reaction apparatuses of chemical production plants.

IN THE MATTER OF a South African
Application corresponding to
PCT Application PCT/EP2013/057282

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Date: 28 August 2014

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Claims

1. A nitrate salt composition comprising as significant constituents

   A) an alkali metal nitrate and an alkali metal nitrite in a total amount in the range from 98 to 99.84% by weight and
   B) an alkali metal compound selected from the group B1) alkali metal oxide, B2) alkali metal carbonate, B3) alkali metal compound which decomposes into alkali metal oxide or alkali metal carbonate in the temperature range from 250°C to 600°C, B5) alkali metal peroxide Met_2O_2, in which Met is lithium, sodium, potassium, rubidium, cesium, and B6) alkali metal superoxide $MetO_2$, in which Met is sodium, potassium, rubidium, cesium, in a total amount in the range from 0.16 to 2% by weight, in each case based on the nitrate salt composition.

2. The nitrate salt composition according to claim 1, wherein the constituent B) is an alkali metal carbonate.

3. The nitrate salt composition according to claim 1 or 2, wherein the constituent B) is comprised in an amount in the range from 0.2 to 2% by weight.

4. The nitrate salt composition according to any of claims 1 to 3, wherein the constituent A) comprises an alkali metal nitrite in a total amount up to 50% by weight, based on the constituent A).

5. The nitrate salt composition according to any of claims 1 to 4, wherein the alkali metal nitrate component of the constituent A) is composed of
   A1) potassium nitrate in an amount in the range from 20 to 55% by weight,
   A2) sodium nitrate in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrate component of the constituent A).

6. The nitrate salt composition according to any of claims 1 to 5, wherein the alkali metal carbonate is selected from the group consisting of sodium carbonate Na_2CO_3 and potassium carbonate K_2CO_3.

7. The nitrate salt composition according to any of claims 1 to 6, wherein the alkali metal carbonate is sodium carbonate Na_2CO_3.

8. The nitrate salt composition according to any of claims 1 to 7 in molten form.

9. The use of a nitrate salt composition as defined in any of claims 1 to 8 as heat transfer medium and/or heat storage medium.

10. The use according to claim 9, wherein the nitrate salt composition is present in molten form.

11. The use according to claims 9 to 10 in power stations for generating heat and/or electricity, in chemical process engineering and in metal hardening plants.

12. The use according to claim 11 in solar thermal power stations.

13. The use according to claim 12 as heat transfer medium in solar thermal power stations.

14. The use according to claim 13 as heat storage medium in solar thermal power stations.

15. The use according to claim 11 as heat transfer medium for heating reaction apparatuses of chemical production plants.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057282

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/12
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)
C09K F24J

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.
X	US 4 421 662 A (FIORUCCI LOUIS C [US] ET AL) 20 December 1983 (1983-12-20) Ansprüche, Beispiele -----	1-15
X	US 2011/162829 A1 (XIANG XIAODONG [US]) 7 July 2011 (2011-07-07) paragraphs [0002], [0100]; table 3 -----	1-4,6-15
X	US 4 559 993 A (PICARD GERARD [FR] ET AL) 24 December 1985 (1985-12-24) Ansprüche column 1, lines 9-12,54-60 column 6, lines 30-55 column 7, lines 55-63 -----	1,3,4, 8-15
A	US 3 719 225 A (MEKJEAN M ET AL) 6 March 1973 (1973-03-06) Ansprüche, Beispiele ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 11 July 2013	Date of mailing of the international search report 18/07/2013
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 Schoenhentz, Jérôme

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057282

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 043 381 A1 (MODINE MFG CO [US]) 11 October 2000 (2000-10-11) the whole document -----	1-15
A	US 2012/056125 A1 (RAADE JUSTIN [US] ET AL) 8 March 2012 (2012-03-08) the whole document -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/057282

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 4421662	A	20-12-1983	NONE			
US 2011162829	A1	07-07-2011	NONE			
US 4559993	A	24-12-1985	ES	8404794	A1	16-08-1984
			FR	2533578	A1	30-03-1984
			GR	78975	A1	02-10-1984
			IT	1164440	B	08-04-1987
			US	4559993	A	24-12-1985
			YU	191683	A	31-12-1988
US 3719225	A	06-03-1973	NONE			
EP 1043381	A1	11-10-2000	AT	243242	T	15-07-2003
			CN	1270201	A	18-10-2000
			DE	60003358	D1	24-07-2003
			DE	60003358	T2	04-12-2003
			EP	1043381	A1	11-10-2000
			JP	2000328049	A	28-11-2000
			KR	20010049249	A	15-06-2001
			US	6784356	B1	31-08-2004
US 2012056125	A1	08-03-2012	NONE			

TRANSLATION

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PF 73237 SE	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/EP2013/057282	International filing date *(day/month/year)* 08.04.2013	Priority date *(day/month/year)* 10.04.2012
International Patent Classification (IPC) or national classification and IPC C09K5/12		
Applicant BASF SE		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

3. This report is also accompanied by ANNEXES, comprising:

a. ☒ *(sent to the applicant and to the International Bureau)* a total of 3 sheets, as follows:

☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).

☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4*bis*, 70.2(e), 70.16 and 91.2).

☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b))

b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s))

______________________, containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*bis* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
Name and mailing address of the IPEA/EP Facsimile No.	Authorized officer Telephone No.

Form PCT/IPEA/409 (cover sheet) (July 2014)

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2013/057282

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:

☒ the international application in the language in which it was filed

☐ a translation of the international application into ______________________, which is the language of a translation furnished for the purposes of:

☐ international search (Rules 12.3(a) and 23.1(b))

☐ publication of the international application (Rule 12.4(a))

☐ international preliminary examination (Rule 55.2(a) and/or 55.3(a))

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

☐ the international application as originally filed/furnished

☒ the description:

pages 1-11 as originally filed/furnished.

pages* ______________ received by this Authority on ______________

pages* ______________ received by this Authority on ______________

☒ the claims:

nos. ______________ as originally filed/furnished.

nos.* ______________ as amended (together with any statement) under Article 19

nos.* 1-15 received by this Authority on 01.07.2014

☐ the drawings:

pages ______________ as originally filed/furnished.

pages* ______________ received by this Authority on ______________

pages* ______________ received by this Authority on ______________

☐ a sequence listing – see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages ______________

☐ the claims, Nos. ______________

☐ the drawings, sheets/figs ______________

☐ the sequence listing *(specify)*: ______________

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rule 70.2(c) and *(c-bis)*):

☐ the description, pages ______________

☐ the claims, Nos. ______________

☐ the drawings, sheets/figs ______________

☐ the sequence listing *(specify)*: ______________

5. ☐ This report has been established:

☐ taking into account **the rectification of an obvious mistake authorized** by or notified to this Authority under Rule 91 (Rules 66.1(d-*bis*) and 70.2(e)).

☐ without taking into account **the rectification of an obvious mistake authorized** by or notified to this Authority under Rule 91 (Rules 66.1*bis* and 70.2(e)).

6. With regard to top-up searches (Rules 66.1ter and 70.2(f)):

☒ A top-up search was carried out by this Authority on 12.06.2014

☒ Additional relevant documents have been discovered during the top-up search.

☐ No top-up search was carried out by this Authority because it would serve no useful purpose.

7. ☐ Supplementary international search report(s) from Authority(ies) ______________ has/have been received and taken into account in establishing this report (Rule 45*bis*.8(b) and (c)).

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

Box No. V **Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-15	YES
	Claims		NO
Inventive step (IS)	Claims	1-15	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-15	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Reference is made to the following documents:

D1	US 4 421 662 A (FIORUCCI LOUIS C [US] ET AL) 20 December 1983 (1983-12-20)
D2	US 2011/162829 A1 (XIANG XIAODONG [US]) 7 July 2011 (2011-07-07)
D3	US 4 559 993 A (PICARD GERARD [FR] ET AL) 24 December 1985 (1985-12-24)
D4	US 3 719 225 A (MEKJEAN M ET AL) 6 March 1973 (1973-03-06)
D5	EP 1 043 381 A1 (MODINE MFG CO [US]) 11 October 2000 (2000-10-11)
D6	US 2012/056125 A1 (RAADE JUSTIN [US] ET AL) 8 March 2012 (2012-03-08)

1. **Novelty and Inventive Step**

The present application satisfies the requirements of PCT Article 33(1) because the subject matter of claims 1-15 involves an inventive step within the meaning of PCT Article 33(3).

1.1. Document **D3**, which is considered the prior art closest to the subject matter of claim 1, discloses (claims 1-7) a process for stabilizing molten alkali metal nitrates or nitrites by the addition of alkali metal hydroxides.

The subject matter of claim 1 differs in that the nitrate salt composition as component B) uses an alkali metal compound which is different from the alkali metal hydroxide used in document **D3**.

Therefore, the subject matter of claim 1 is novel (PCT Article 33(2)).

The technical effect can be seen as that of providing a nitrate/nitrite salt composition which reduces the release of nitric oxides at high temperatures without thereby changing the nitrate/nitrite ratio in the melt at the same time.

Neither document **D3** nor documents **D1, D2 and D4 to D6** disclose a nitrate/nitrite salt composition in combination with an alkali metal compound, as described in component B).

Document **D2** merely discloses the use of sodium nitrate in connection with sodium carbonate without any indication of adding a nitrite salt.

Document **D1** discloses exactly the opposite and addresses the problem, for example, of removing carbonate from a mixture of molten sodium nitrate and potassium nitrate.

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The essence of document D3 is a process for stabilizing molten alkali metal nitrates or nitrites, but by the addition of alkali metal hydroxides.

Proceeding from D3 as the closest prior art, it is not obvious to replace the hydroxide used there with the components B) of the current claim 1, especially since D3 does not indicate the range of amounts for the components B) and since D1 teaches the removal of carbonate and hydroxide.

Therefore, the subject matter of claim 1 involves an inventive step and fulfills the criterion set forth in PCT Article 33(1) and (3).

1.2. Claim 9 relates to the use of the nitrate salt composition according to claim 1 as a heat transfer medium and thus likewise satisfies the PCT requirements with respect to novelty and inventive step.

1.3. Claims 2-8 and 9-15 are dependent upon claims 1 and 9 and thus likewise satisfy the PCT requirements with respect to novelty and inventive step.

It is very desirable to match the generation of electric energy in a solar thermal power station, regardless of which type, to the demand on the grid. This is made possible, for example, by heat being stored during times of high incident solar radiation and being able to be utilized to generate electric energy when required after sundown or during phases of bad weather.

The storage of heat can be effected directly by storage of the heated heat transfer medium in generally well insulated stock tanks or indirectly by transfer of the heat from the heated heat transfer medium to another medium (heat store), for example in a sodium nitrate-potassium nitrate salt melt.

An indirect method has been realized in the 50 MW Andasol I power station in Spain, where about 28 500 metric tons of a melt of sodium nitrate and potassium nitrate (60:40 in % by weight) are used as heat storage in a well insulated tank. During periods of incident solar radiation, the melt is pumped from a relatively cool tank (about 290°C) via a thermal oil-salt heat exchanger to a hotter tank and in the process heated to about 390°C. Here, heat energy is withdrawn from the thermal oil (here functioning as heat transfer medium) via a heat exchanger and introduced into the salt melt (thermal oil-salt heat exchanger). During times of low incident solar radiation and at night, the power station can be operated under full load for about 7.5 hours when the heat store is fully charged.

However, it would be advantageous to use the heat transfer medium as heat storage medium as well, since the corresponding thermal oil-salt heat exchangers could be saved in this way.

In addition, possible contact of the thermal oil, which has reducing properties, with the strongly oxidizing nitrate melt could be avoided in this way. Owing to the significantly higher price of the thermal oil compared to the sodium nitrate-potassium nitrate melt, thermal oil has hitherto not been considered as heat store.

A need of the invention exists to provide a readily available, improved nitrate salt composition as heat transfer medium and/or heat storage medium which can be used in long-term operation at elevated temperature, preferably above 565°C, with the release of nitrous oxides, usually nitrogen monoxide and/or nitrogen dioxide, being reduced or suppressed.

A nitrate mixture composed of about 60% by weight of sodium nitrate ($NaNO_3$) and about 40% by weight of potassium nitrate (KNO_3) is, for example, offered for sale under the name Hitec® Solar Salt by Coastal Chemical Co., L.L.C. This product is offered for use as heat transfer medium or heat storage medium. It can, in addition to further components, comprise small amounts of up to a maximum of 0.15% by weight of sodium carbonate (Na_2CO_3) (product information sheet Hitec® Solar Salt).

4.8 mg of nitrogen or 10.2 mg of NO, which were given off from the salt melts.
It was thus able to be shown that 1% of sodium carbonate as additive in HITEC® reduces the liberation of nitrogen oxides by about 40% by weight.

Example 7

Comparative experiment without alkali metal compounds B) according to the invention

100 g of solar salt (60 g of $NaNO_3$, 40 g of KNO_3) were heated to 600°C over a period of 2 hours in a stainless steel tube and maintained at this temperature (± 5 K) for 1 hour. 5 l/h of water- and carbon dioxide-free air were passed over the melt in order to introduce the off-gases formed into a scrubbing tower. After the end of the experiment, the apparatus was flushed with argon for half an hour. The scrubbing tower was filled with 57 g of scrubbing solution composed of 0.1 mol/l of $KMnO_4$ together with 0.2 mol/l of NaOH in water. Analysis of the total nitrogen content indicated 51 mg/kg in the solution, corresponding to a total amount of 2.9 mg of nitrogen or 6.2 mg of NO, which were given off from the salt melts.

Experiment according to the invention
In the same experimental set-up, 100 g of solar salt together with 1 g of Na_2CO_3 (corresponding to 0.11% by mass of carbon) were heated to 600°C over a period of 2 hours in a stainless steel tube and maintained at this temperature (± 5 K) for 1 hour in a second experiment. 5 l/h of water- and carbon dioxide-free air were passed over the melt in order to introduce the off-gases formed into a scrubbing tower. After the end of the experiment, the apparatus was flushed with argon for half an hour. The scrubbing tower was filled with 56 g of scrubbing solution composed of 0.1 mol/l of $KMnO_4$ together with 0.2 mol/l of NaOH in water. Analysis of the total nitrogen content indicated 34 mg/kg in the solution, corresponding to a total amount of 1.9 mg of nitrogen or 4.1 mg of NO, which were given off from the salt melts.
It was thus able to be shown that 1% of sodium carbonate as additive in solar salt reduces the liberation of nitrogen oxides by about 30%.

Examples 6 and 7 show that the alkali metal compounds B) according to the invention greatly reduce the liberation of nitrogen oxides at very high temperatures.

"Comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof.

Claims

1. A nitrate salt composition comprising as significant constituents

   A) an alkali metal nitrate and an alkali metal nitrite in a total amount in the range from 98 to 99.84% by weight and

   B) an alkali metal compound selected from the group B1) alkali metal oxide, B2) alkali metal carbonate, B3) alkali metal compound which decomposes into alkali metal oxide or alkali metal carbonate in the temperature range from 250°C to 600°C, B5) alkali metal peroxide Met_2O_2, in which Met is lithium, sodium, potassium, rubidium, cesium, and B6) alkali metal superoxide $MetO_2$, in which Met is sodium, potassium, rubidium, cesium, in a total amount in the range from 0.16 to 2% by weight, in each case based on the nitrate salt composition.

2. The nitrate salt composition according to claim 1, wherein the constituent B) is an alkali metal carbonate.

3. The nitrate salt composition according to claim 1 or 2, wherein the constituent B) is comprised in an amount in the range from 0.2 to 2% by weight.

4. The nitrate salt composition according to any one of claims 1 to 3, wherein the constituent A) comprises an alkali metal nitrite in a total amount up to 50% by weight, based on the constituent A).

5. The nitrate salt composition according to any one of claims 1 to 4, wherein the alkali metal nitrate component of the constituent A) is composed of
   A1) potassium nitrate in an amount in the range from 20 to 55% by weight,
   A2) sodium nitrate in an amount in the range from 45 to 80% by weight, in each case based on the alkali metal nitrate component of the constituent A).

6. The nitrate salt composition according to any one of claims 1 to 5, wherein the alkali metal carbonate is selected from the group consisting of sodium carbonate Na_2CO_3 and potassium carbonate K_2CO_3.

7. The nitrate salt composition according to any one of claims 1 to 6, wherein the alkali metal carbonate is sodium carbonate Na_2CO_3.

8. The nitrate salt composition according to any one of claims 1 to 7 in molten form.

9. The use of a nitrate salt composition as defined in any one of claims 1 to 8 as heat transfer medium and/or heat storage medium.

10. The use according to claim 9, wherein the nitrate salt composition is present in molten form.

11. The use according to claim 9 or 10 in power stations for generating heat and/or electricity, in chemical process engineering and in metal hardening plants.

12. The use according to claim 11 in solar thermal power stations.

13. The use according to claim 12 as heat transfer medium in solar thermal power stations.

14. The use according to claim 13 as heat storage medium in solar thermal power stations.

15. The use according to claim 11 as heat transfer medium for heating reaction apparatuses of chemical production plants.

16. The nitrate salt composition as claimed in any one of claims 1 to 8, substantially as hereinbefore described or exemplified.

17. The nitrate salt composition including any new and inventive integer or combination of integers, substantially as herein described.

18. The use of a nitrate salt composition as claimed in any one of claims 9 to 15, substantially as hereinbefore described or exemplified.

19. The use of a nitrate salt composition including any new and inventive integer or combination of integers, substantially as herein described.