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(54) **ECOLOGICAL FIREWORKS, METHOD OF PREPARATION THEREOF AND METHOD OF REDUCING ENVIRONMENTAL CONTAMINATION WITH HEAVY METAL COMPOUNDS FROM FIREWORKS AND USE OF FIREWORKS AND USE OF MINERAL ADDITIVES IN PYROTECHNIC MATERIALS**

ÖKOLOGISCHE FEUERWERKE, VERFAHREN ZUR HERSTELLUNG DAVON UND VERFAHREN ZUR REDUZIERUNG VON UMWELTVERSCHMUTZUNG MIT SCHWERMETALLVERBINDUNGEN AUS FEUERWERKEN UND VERWENDUNG VON FEUERWERKEN UND VERWENDUNG VON MINERALISCHEN ADDITIVEN IN PYROTECHNISCHEN MATERIALIEN

FEU D'ARTIFICE ÉCOLOGIQUE, SON PROCÉDÉ DE PRÉPARATION ET PROCÉDÉ DE RÉDUCTION DE LA CONTAMINATION DE L'ENVIRONNEMENT PAR DES COMPOSÉS DE MÉTAUX LOURDS ISSUS DE FEUX D'ARTIFICE ET UTILISATION DE FEUX D'ARTIFICE ET UTILISATION D'ADDITIFS MINÉRAUX POUR DES MATÉRIAUX PYROTECHNIQUES

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Description

Technical field

[0001] The invention relates to ecological fireworks, a method of preparation thereof and a method of reducing environmental contamination with heavy metal compounds from fireworks and to use of fireworks and use of mineral additives in pyrotechnic materials to reduce heavy metal environmental emission.

Background art

[0002] Fireworks are known in prior art since approx.2nd century B.C. American patent document [US2130068] teaches that using inorganic salts comprising suitable cations results in colored explosions. Hence, the presence of sodium results in generation of yellow color, calcium results in generation of red color, strontium results in generation of purple color, barium results in generation of green color, potassium results in generation of violet color and copper results in generation of blue or red color. American patent document [US4184901] discloses firework comprising diatomaceous earth, which produces a yellow flame and yellow smoke. Until now, all known fireworks have a disadvantage, such that they contain heavy metal salts which are required for the generation of color effects in the explosion flame. Ashes formed after fireworks are burned also contain significant amounts of these metals, their chemical form being however sometimes altered as a result of explosion and exposition to high temperatures. Accordingly, immediate surroundings of areas where firework shows are organized are inevitably contaminated with heavy metal compounds, particularly with copper, barium and strontium compounds. These compounds are partially water-soluble which is why they may reach water reservoirs, groundwater and surface waters, as well as contaminate drinking water, resulting in dangerous environmental contamination. Contamination with heavy metals is particularly dangerous for the ecosystems of water reservoirs whereupon firework shows take place.

[0003] The object of the invention is to provide improved fireworks, wherein detrimental effects thereof on the environment are reduced by absorption of heavy metal ions in a water-insoluble sorption material. Thus, it was unexpectedly found that the method to limit detrimental effects of fireworks on the environment is to employ additives in the exploding mass that exhibit sorptive properties of binding heavy metal ions in the water-insoluble sorption material, in particular employing additives in the exploding mass showing the ability to permanently bind heavy metal ions, particularly in the form of zeolites. Zeolites are known to have metal ion binding properties, have considerable diversity both in the form of natural materials of mineral origin, as well as in the growing number of synthetic zeolites. Thereupon, metal salts and products thereof after firework explosion become considerably less water-soluble. Insoluble products are not, as a rule, detrimental to the ecosphere.

Disclosure of invention

[0004] The object of the invention are fireworks, containing heavy metal compounds in their composition, characterized by the fact that the composition of the fireworks is supplemented with a water-insoluble or substantially water-insoluble sorption agent binding detrimental metal compounds thereby reducing the solubility of salts of these metals in water. In a preferable embodiment, the heavy metal compounds are salts of copper, barium, strontium. The composition of the fireworks of the invention is supplemented with a water-insoluble or substantially water-insoluble sorption agent, the sorption agent being a mineral additive of a zeolite type, preferably with molecular sieves.

[0005] In a preferred embodiment, the zeolite is a material containing clinoptilolite, preferably over 85% by weight of clinoptilolite.

[0006] Preferably, the composition of the fireworks is supplemented with a water-insoluble or substantially water-insoluble sorption agent in an amount of 0.1%-30%, 1-30%, 1-20%, 5-20%, 5-15%, 10-30%, 10-20%, 10-15%, preferably about 15% by weight, more preferably with a zeolite in an amount of 0.1 %-30%, 1-30%, 1-20%, 5-20%, 10-30%, 10-20%, 10-15%, 5-15%, preferably about 15% by weight, more preferably with a zeolite in an amount of 5-20% by weight, even more preferably with a zeolite in an amount of up to about 15% by weight.

[0007] The object of the invention is also a method of preparation of fireworks containing heavy metal compounds in their composition characterized by the fact that in the firework preparation process an additive of a water-insoluble sorption agent is used in the form of a zeolite. In a preferred embodiment of the method of the invention, the heavy metal compounds are salts of copper, barium, strontium.

[0008] The object of the invention is also a method of reducing environmental contamination with heavy metal compounds from fireworks, wherein during explosions fireworks of the invention are used.

[0009] In a preferred embodiment of the method of reducing environmental contamination of the invention, firework explosions take place over water reservoirs.

[0010] The object of the invention is also use of the fireworks of the invention to reduce environmental contamination

with heavy metal compounds from fireworks, particularly contamination with copper, barium, strontium compounds. More preferably, such fireworks are used when firework explosions take place over water reservoirs.

[0011] The object of the invention is also use of mineral additives in pyrotechnic materials to reduce heavy metal environmental emission, wherein the mineral additives are inorganic zeolites and the heavy metals are preferably salts of copper, barium, strontium.

[0012] The term "heavy metal compounds" in the present specification is intended to mean compounds including ions of heavy metals, namely elements of density above 4.5 g/cm^3, in particular compounds of copper, barium, strontium.

[0013] The term "sorption agent" or "sorption material" or "sorbent" in the present specification means a material capable of permanently absorbing heavy metal ions, in particular a zeolite. The sorption agent used according to the invention may be of a natural origin as well as synthetic.

[0014] The term "zeolite" in the present specification means an aluminosilicate mineral or group of minerals. There are over 100 various known types of zeolites, wherein natural zeolites are a group of hydrated tecto-aluminosilicates with a specific, very diverse structure including free spaces filled with ions or water molecules having high freedom of movement. In particular, a preferable zeolite for use according to the invention is a material comprising over 85% of clinoptilolite, for example the one commercially available under the name of Nawomix 200 μm).

[0015] The inventors have thus demonstrated that it is possible to reduce detrimental effects of fireworks on the environment by absorption of heavy metal ions in a water-insoluble or substantially water-insoluble sorption material. The material is added to the exploding mass. During explosion of the firework material and after it is extinguished there is a direct contact of the sorbent with heavy metal ions which results in absorption thereof. The soil fallout therefore comprises heavy metal ions absorbed by the water-insoluble material. As a result, a significant decrease in heavy metal ion content in groundwater or in water reservoirs in the areas of firework shows is achieved, whereby detrimental effects of fireworks on the biosphere are significantly reduced.

[0016] The main advantage of the invention is the possibility of reducing the content of barium, a highly harmful component, which is an important accomplishment. The content of copper and strontium were also shown to have considerably decreased solubility after the addition of a sorbent in the form of a zeolite to the fireworks. The invention allows a significant reduction in heavy metals reaching the environment, especially to groundwater and reservoirs of drinking water.

[0017] For better understanding of the invention it has been illustrated by non-limiting embodiments.

Description of embodiments

EXAMPLE 1

[0018] Fireworks were prepared in the following way: a sorbent was mixed with a ready-made pyrotechnic material, the obtained pyrotechnic material was placed in shot tubes, a sample was shot producing a pyrotechnic effect in the sky.

[0019] The composition of the pyrotechnic article used in the study: ready-made pyrotechnic products were used (SM19-02D, SM19-03D, SM19-06D, SL19-02D, SL19-05D, SL19-07D) manufactured by Fireworks Europe Innovation sp. z o.o, the full chemical composition and detailed descriptions being available in the CE 1008-F2-69247833 certificate issued by TUV RHEINLAND INTERCERT KFT.

Studying the effect of the addition of a sorbent on effectiveness of a firework show

[0020] For the study, ready-made pyrotechnic products were used, listed and prepared as described above.

[0021] Firstly, a study of the effect of the addition of a sorbent (zeolite) on the effectiveness of a firework show was done. The study provided an answer as to the concentration range of the sorbent additive that does not lead to observed deterioration of visual effects of the fireworks. To this end, a series of test firework explosions was performed in conditions corresponding to those of firework shows, the fireworks comprising 10%, 20% and 30% by weight of the Navomix 200 sorbent respectively. It was shown that the addition not exceeding 20% by weight does not adversely affect the visual effects of fireworks. Accordingly, further studies were performed using additives not exceeding 15% by weight of zeolite as a sorbent.

[0022] The study used ready-made fireworks (batteries of shot tubes), manufacturer: Fireworks Europe Innovation Sp. z o.o.

EXAMPLE 2

Determination of the reduction in water solubility of heavy metal salts from fireworks after they are absorbed in a sorption material.

[0023] In the next example, the total pro-ecological effect was studied. In this study, it was determined to what extent the solubility of heavy metal salts in water can be decreased after they are absorbed in a sorption material.

[0024] In this study, zeolite, commercially available under the name of Nawomix 200 μm (clinoptilolite content over 85% by weight) was used as the sorption material. This material is completely environmentally safe and moreover it is used in agriculture and horticulture as a valuable additive to fertilizer mixtures and to absorb heavy metals. A major advantage of the material is also its resistance to high temperatures. A number of studies was performed to determine the extent of decrease in water solubility of heavy metal compounds after the addition of zeolite was introduced to fireworks. The methodology of the study was as follows:

[0025] The following shot tubes were used for the study: SM19-02D (effect: comet), SM19-03D (effect: crackling with red and green glitter), SM19-06D (effect: comet with crackling), that were mixed with the Nawomix 200 μm sorption factor as described in Example 1.

[0026] Firework explosions were conducted in an enclosed space (steel barrel with a volume of 100 liters), and then the ashes formed during explosion were carefully collected and passed for analysis. Samples with a mass of 200 mg were mixed with 10 ml of distilled water and allowed to rest for 24 hours with shaking (occasionally), afterwards the content of heavy metal ions was measured spectrometrically after the solutions were filtered.

[0027] The UV/Vis spectrometer from Perkin Elmer of the Lambda 650 type was used. The samples were diluted if a decrease in ion concentration to the appropriate level for an analysis with this method was required.

[0028] The results were as follows, for example the addition of 10% of zeolite to a firework (multi shot SM19-06D, 25mm caliber, manufacturer: Fireworks Europe Innovation, CE certificate number: 1008-F2-69247833) SM19-06D caused a twofold reduction of barium and strontium content in water extracts. Similar beneficial changes were observed repeatedly in other samples. The applied procedure is not however free from random and/or measurement errors, mainly due to heterogeneity of individual firework composition. Therefore, systematic comparisons were made using the above mentioned fireworks, having Cu or Sr or Ba as the color-giving dominant, prepared as described in Example 1 and explosions were performed as described above. The tests were repeated multiple times to avoid accidental conclusions. Ash samples in an amount of 200 mg were placed in measurement flasks with a volume of 10 ml and filled with distilled water. The solutions were occasionally shaken. After two days the solutions were filtered off and subjected to spectrometric measurements. The tests were performed in room temperature. The results, being a key experiment showing the applicability of the invention, are summarized in table below.

Table 1. Cu, Ba and Sr content determined spectrophotometrically (with atomic spectrometry ASA) (in ppb - part per bilion) after the procedure described above (percentage errors of the analytical measurements shown in brackets). Depletion coefficients shown in the last column were calculated as a ratio of the content of the particular major element (shown in bold) in a *sample without the addition of* zeolite to the content in a *sample with the addition of zeolite.*

Sample identification - percentage of zeolite additive in brackets	**Cu** [ppb]	**Sr** [ppb]	**Ba** [ppb]	Depletion coefficient for the major element
Cu (0%)	**1109(0.4)**	0.16 (7)	0.59 (12)	-
Cu (5%)	**563 (2)**	0.64 (3)	0.79 (11)	2
Cu (15%)	**621 (2)**	1.02 (3)	0.22 (5)	1.8
Sr (0%)	0.26 (6)	**444 (2)**	0.495 (7)	-
Sr (5%)	0.59 (4)	**131 (2)**	0.42 (3)	3.4
Sr (15%)	0.96 (7)	**161 (2)**	0.82 (3)	2.8
Ba (0%)	0.2 (9)	0.81 (2)	**1468 (3)**	-
Ba (5%)	0.51 (11)	1.87 (3)	**158.3 (2)**	9.3
Ba (15%)	0.97 (6)	2.29 (3)	**109 (2)**	13.5

EXAMPLE 3 *Determination of the effectiveness of other zeolites*

[0029] In the manner described above studies were also performed using zeolites ZSM-5 (Xian Lvneng Purification Technology) and CBV100 (Zeolyst International, USA) and fireworks SM19-02 (effect comet) [1], SM19-06 (effect comet) [2] and SM19-06 (effect crackling) [3], manufactured by Fireworks Europe Innovation sp. z o.o. The tests demonstrated over twofold reduction in the concentration of Cu^{2+} and Sr^{2+} salts in [1], Cu^{2+}, Sr^{2+} and Ba^{2+} in [2] when using ZSM-5 and a 1.5-fold reduction in Sr^{2+} and Ba^{2+} in [3] when using CBV100.

[0030] The inventors have thus demonstrated that it is possible to reduce detrimental effects of fireworks on the environment by absorption of heavy metal ions in a water-insoluble sorption material. The material is added to the exploding mass. During explosion of the firework material and after it is extinguished there is direct contact of the sorbent with heavy metal ions which results in absorption thereof. The soil fallout therefore comprises heavy metal ions absorbed by the water-insoluble material. As a result, a significant decrease in heavy metal ion content in groundwater or in water reservoirs in the areas of firework shows is achieved, whereby detrimental effects of fireworks on the biosphere are significantly reduced.

[0031] The main advantage of the invention is considered to be the possibility of reducing the content of barium, the most harmful among the studied components, which is an important accomplishment. The content of copper and strontium were also shown to have considerably decreased solubility after the addition of zeolite to the fireworks. The invention allows a significant reduction in heavy metals, particularly heavy metals and salts thereof, reaching the environment, especially to groundwater and reservoirs of drinking water.

Claims

1. Fireworks, containing heavy metal compounds in their composition, **characterized in that** the composition of the fireworks is supplemented with a water-insoluble or substantially water-insoluble sorption agent binding detrimental metal, in particular heavy metal compounds thereby reducing the solubility of salts of these metals in water, wherein the water-insoluble or substantially water-insoluble sorption agent is a mineral additive of a zeolite type, preferably with molecular sieves.

2. Fireworks according to claim 1, **characterized in that** the heavy metal compounds are salts of copper, barium, strontium.

3. Fireworks according to claims 1-2, **characterized in that** the zeolite is a material containing clinoptilolite, preferably over 85% by weight of clinoptilolite.

4. Fireworks according to claims 1-3, **characterized in that** the composition of the fireworks is supplemented with a zeolite in an amount of 5-20% by weight, preferably to about 15% by weight.

5. A method of preparation of fireworks containing heavy metal compounds in their composition, **characterized in that** in the firework preparation process an additive of a water-insoluble sorption agent is used, wherein the water-insoluble sorption agent is a mineral additive of a zeolite type.

6. The method according to claim 5, **characterized in that** the heavy metal compounds are salts of copper, barium, strontium.

7. A method of reducing water-solubility of heavy metal compounds therefore reducing detrimental effects of environmental contamination with heavy metal compounds from fireworks, **characterized in that** during explosions fireworks as defined in claims 1-4 are used.

8. The method of reducing environmental contamination with heavy metal compounds from fireworks according to claim 7, **characterized in that** firework explosions take place over water reservoirs.

9. Use of the fireworks as defined in claims 1-4 to reduce water-solubility of heavy metal compounds therefore reducing detrimental effects of environmental contamination with heavy metal compounds from fireworks, particularly contamination with copper, barium, strontium compounds.

10. The use of fireworks according to claim 9, **characterized in that** firework explosions take place over water reservoirs.

11. Use of mineral additives in fireworks to reduce water-solubility of heavy metal compounds therefore reducing detrimental effects of heavy metal environmental emission, **characterized in that** the mineral additives are inorganic zeolites, and the heavy metals are preferably salts of copper, barium, strontium.

Patentansprüche

1. Feuerwerke, aufweisen Schwermetallkomponenten in deren Zusammensetzung, **gekennzeichnet dadurch, dass** die Zusammensetzung der Feuerwerke mit einem wasserunlöslichen oder im Wesentlichen wasserunlöslichen Sorptionsmittel, das schädliche Metalle bindet, insbesondere Schwermetallkomponenten, und dabei die Wasserlöslichkeit von Salzen dieser Metalle vermindert, wobei das wasserunlösliche oder im Wesentlichen wasserunlösliche Sorptionsmittel ein mineralisches Additiv von zeolithischer Art, vorzugsweise mit molekularen Sieben ist.

2. Feuerwerke nach Anspruch 1, **gekennzeichnet dadurch, dass** die Schwermetallkomponenten Salze von Kupfer, Barium, Strontium sind.

3. Feuerwerke nach den Ansprüchen 1-2, **gekennzeichnet dadurch, dass** das Zeolith ein Material ist, das Klinoptilolith, und vorzugsweise über 85 Gew.-% Klinoptilolith enthält.

4. Feuerwerke nach den Ansprüchen 1-3, **gekennzeichnet dadurch, dass** die Zusammensetzung der Feuerwerke mit 5-20 Gew.-% und vorzugsweise zu ungefähr 15 Gew.-% eines Zeoliths ergänzt wird

5. Verfahren zur Vorbereitung von in deren Zusammensetzung Schwermetallkomponenten aufweisenden Feuerwerken, **gekennzeichnet dadurch, dass** im Vorbereitungsverfahren der Feuerwerke ein Additiv eines wasserunlöslichen Sorptionsmittels eingesetzt wird, wobei das wasserunlösliche Sorptionsmittel ein mineralisches Additiv von zeolithischer Art ist.

6. Verfahren nach Anspruch 5, **gekennzeichnet dadurch, dass** die Schwermetallkomponenten Salze von Kupfer, Barium, Strontium sind.

7. Verfahren zur Verringerung der Wasserlöslichkeit von Schwermetallkomponenten, das die Schädlichkeitswirkungen der Kontamination mit Schwermetallkomponenten durch Feuerwerke verringert, **gekennzeichnet dadurch, dass** während der Explosionen Feuerwerke nach den Ansprüchen 1-4 eingesetzt werden.

8. Verfahren zur Verringerung der Umweltkontamination mit Schwermetallkomponenten aus Feuerwerken nach Anspruch 7, **gekennzeichnet dadurch, dass** die Feuerwerksexplosionen über Gewässern stattfinden.

9. Gebrauch von Feuerwerken nach den Ansprüchen 1-4 zur Verringerung der Wasserlöslichkeit von Schwermetallkomponenten das die Schädlichkeitswirkungen der Umweltkontamination mit Schwermetallverbindungen aus Feuerwerken verringert werden, und insbesondere der Kontamination mit Kupfer-, Barium-, Strontiumverbindungen.

10. Gebrauch von Feuerwerken nach Anspruch 9, **gekennzeichnet dadurch, dass** die Feuerwerksexplosionen über Gewässern stattfinden.

11. Gebrauch von mineralischen Additiven zur Verringerung der Wasserlöslichkeit von Schwermetallkomponenten, das die Schädlichkeitswirkungen der Emission von Schwermetallen in die Umwelt verringert werden, **gekennzeichnet dadurch, dass** die mineralischen Additive anorganische Zeolithe sind, und die Schwermetalle vorzugsweise Salze von Kupfer, Barium, Strontium sind.

Revendications

1. Feux d'artifice, contenant des composés de métaux lourds dans leur composition, **caractérisés en ce que** la composition des feux d'artifice est complétée par un agent de sorption insoluble dans l'eau ou substantiellement insoluble dans l'eau, liant un métal nuisible, en particulier des composés de métaux lourds, réduisant ainsi la solubilité des sels de ces métaux dans l'eau, où l'agent de sorption insoluble dans l'eau ou substantiellement insoluble dans l'eau est un additif minéral de type zéolite, de préférence avec des tamis moléculaires.

2. Feux d'artifice selon la revendication 1, **caractérisés en ce que** les composés de métaux lourds sont des sels de cuivre, de baryum, de strontium.

3. Feux d'artifice selon les revendications 1 à 2, **caractérisés en ce que** la zéolite est un matériau contenant de la clinoptilolite, de préférence plus de 85% en poids de clinoptilolite.

4. Feux d'artifice selon les revendications 1 à 3, **caractérisés en ce que** la composition des feux d'artifice est complétée par une zéolite en une quantité de 5 à 20% en poids, de préférence à environ 15% en poids.

5. Une méthode de préparation des feux d'artifice contenant des composés de métaux lourds dans leur composition, **caractérisée en ce que** dans le processus de préparation des feux d'artifice un additif d'un agent de sorption insoluble dans l'eau est utilisé, où l'agent de sorption insoluble dans l'eau est un additif minéral de type zéolite.

6. La méthode selon la revendication 5, **caractérisée en ce que** les composés de métaux lourds sont des sels de cuivre, de baryum, de strontium.

7. Une méthode de réduction de la solubilité des composés de métaux lourds dans l'eau, réduisant ainsi les effets néfastes de la contamination de l'environnement avec des composés de métaux lourds provenant des feux d'artifice, **caractérisée en ce que** pendant les explosions les feux d'artifice tels que définis dans les revendications 1 à 4 sont utilisés.

8. La méthode de réduction de la contamination de l'environnement avec des composés de métaux lourds provenant des feux d'artifice, **caractérisée en ce que** des explosions des feux d'artifice ont lieu sur des réservoirs d'eau.

9. Utilisation des feux d'artifice tels que définis dans les revendications 1 à 4 pour réduire la solubilité des composés de métaux lourds dans l'eau, réduisant ainsi les effets néfastes de la contamination de l'environnement avec des composés de métaux lourds provenant des feux d'artifice, en particulier la contamination avec des composés de cuivre, baryum, strontium.

10. L'utilisation des feux d'artifice selon la revendication 9, **caractérisée en ce que** des explosions des feux d'artifice ont lieu sur des réservoirs d'eau.

11. Utilisation d'additifs minéraux dans des feux d'artifice pour réduire la solubilité des composés de métaux lourds dans l'eau, réduisant ainsi les effets néfastes de l'émission des métaux lourds dans l'environnement, **caractérisée en ce que** les additifs minéraux sont des zéolites inorganiques, et les métaux lourds sont de préférence des sels de cuivre, de baryum, de strontium.

REFERENCES CITED IN THE DESCRIPTION

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