(19)

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11) N° de publication : **LU502423**

(12) **BREVET D'INVENTION** **B1**

(21) N° de dépôt: LU502423

(22) Date de dépôt: 30/06/2022

(51) Int. Cl.:
C08G 18/00, E21F 15/00

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(30) Priorité:
07/04/2022 CN 202210359009.6

(43) Date de mise à disposition du public: 02/01/2023

(47) Date de délivrance: 02/01/2023

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(54) **PHASE-CHANGE HYDROUS SALT POLYMERIC FILLING MATERIAL AND METHODS FOR PREPARING AND USING SAME.**

(57) Provided herein are a phase-change hydrous salt polymeric filling material and methods for preparing and using same. The filling material consists of components A, B and C, wherein component A comprises a polyether polyol, a foaming agent, a fire retardant and a thermally conductive material; component B comprises a polymeric MDI and an adhesive; component C is a phase-change nanofluid, which comprises a polyether polyol, a silicone oil and a composite phase-change nanomaterial, wherein the composite phase-change nanomaterial comprises a porous material, a hydrous salt, a surfactant, a thickening agent, a dispersant and a fire retardant. The method for preparing the filling material comprises: measuring the heat release rate of polyurethane first after components A and B are mixed, and then selecting a corresponding porous material to prepare the composite phase-change nanomaterial; and mixing components A and C according to a formulation ratio to give an A-C mixture component, and mixing the A-C mixture component with component B to give the filling material. With the present invention, temperature self-adaptive adjustment of the polymerization rate of the material can be achieved, the original property of the foaming performance of the material can be ensured, the foaming and curing temperature of polyurethane can be reduced, and the fire problem caused by the high foaming and curing temperature of polyurethane can be solved.

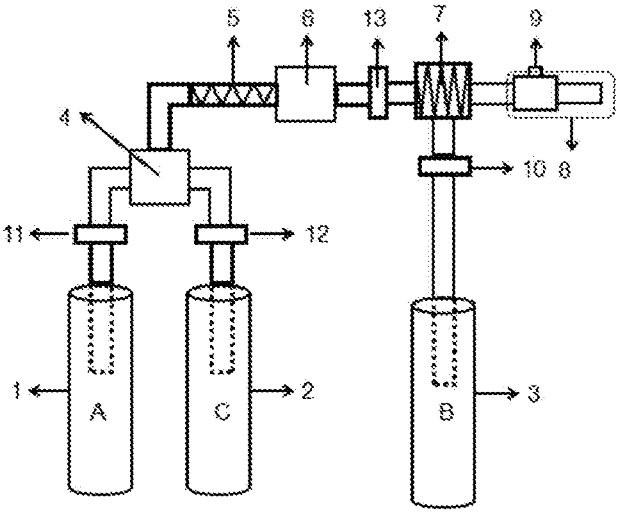

FIG. 1

SPECIFICATION

PHASE-CHANGE HYDROUS SALT POLYMERIC FILLING MATERIAL AND METHODS FOR PREPARING AND USING SAME

TECHNICAL FIELD

The present invention belongs to the technical field of coal mine polymer filling materials, and particularly relates to a phase-change hydrous salt polymeric filling material and methods for preparing and using same.

BACKGROUND

The number of high-risk areas and fissure zones in coal mine shafts increases with the mining depth, leading to frequent fires caused by spontaneous combustion of coal, roof collapses and rib falls, which badly affect the safe production of coal and present risks to the life and health of coal workers. Because polymeric filling materials have the advantages of having large foaming volumes and fast foaming rates and being highly resistant to pressure, they are frequently used for filling protection and for ensuring safety of support and protection in coal mines. However, the existing polymeric filling materials polymerize fast with release of a large amount of heat and thus catches fire easily. For example, on the Panzhihua Huashan Coal Mine + 1030 m horizontal fourth mining area 4238 fully mechanized mining face, when a polyurethane filling material was used for filling a high-risk area on top of an 18-26# support, combustible substances around the material caught fire due to the large amount of heat released by the reaction and the large amount of slurry injected at one time, leading to smoke and fire. A polyurethane foaming filling material was used in Liangbao temple coal mine in Jiaxiang county, Shandong. However, because the total release of heat energy and the peak temperature during the reaction greatly exceeded the maximal values specified by the industry standards for safe production, the core of the filling body was at high temperature for a long time, and the core of the material started to burn by the action of high temperature, combustible gases and oxygen, leading to a fire.

Therefore, it is urgent to solve the problem of the large amount of heat released rapidly in the polymerization foaming process. Aiming at the dangerous characteristic that the existing polyurethanes for coal mine easily catches fire spontaneously at high temperature when used, the fire retardation performance and the spontaneous combustion temperature of polyurethane are improved mainly by developing composite fire retardants at present so as to prevent polyurethane from catching fire spontaneously at high temperature when used. However, this does not reduce the high-temperature property of polyurethane materials used in coal mine shafts, and the polyurethane and the blocking coal body around it are still at risk of catching fire. Although solutions have been developed to the problem of polyurethane reaction heat, the following disadvantages remain:

(1) Adding organic phase-change materials (higher fatty acids, paraffin, etc.) for heat absorption and temperature reduction may pose risk of facilitating combustion and may cause the release of toxic gases, which are not favorable for safe mine construction;

(2) The chemical foaming agent water is still predominant in foaming and releases a large amount of heat energy in the process of chemical foaming. The reaction heat, and thus the temperature of polyurethane, can be reduced by lowering the proportion of water; however, this would change the original foaming performance of polyurethane;

(3) The original performance of the material (the foaming performance of the material) can be affected by the heat-absorbing substance added in the early stage (the reduction of the early-stage reaction heat affects the materials' later-stage gelatinization and curing reaction mechanical properties and the like);

(4) The heat-absorbing substance has low one-time utilization value.

SUMMARY

The present invention is intended to provide a phase-change hydrous salt polymeric filling material and methods for preparing and using same. With the present invention, temperature self-adaptive adjustment of the polymerization rate of the material can be realized, the original property of the foaming performance of the material can be ensured, the foaming and curing temperature of polyurethane can be reduced, and the heat generated by the spontaneous combustion of coal can be absorbed by a composite phase-change nanomaterial, so that the fire problem caused by the high foaming and curing temperature of polyurethane can be solved, and further the spontaneous combustion of coal can be prevent, and the safe production in coal mines can be ensured.

For the above purposes, the present invention provides a phase-change hydrous salt polymeric filling material, which is prepared from the following components in parts by weight: 25–35 parts of component A, 50–60 parts of component B and 20–30 parts of component C, wherein component

A is mainly prepared from the following components in parts by weight: 50–60 parts of a polyether polyol, 3–8 parts of a foaming agent, 8–10 parts of a fire retardant and 1–8 parts of a thermally conductive material; component B is mainly prepared from the following components in parts by weight: 72–80 parts of a polymeric MDI and 3–4 parts of an adhesive; component C is a phase-change nanofluid, which is mainly prepared from the following components in parts by weight: 15–20 parts of a polyether polyol, 6–8 parts of a silicone oil and 10–25 parts of a composite phase-change nanomaterial, wherein the composite phase-change nanomaterial is mainly prepared from the following components in parts by weight: 10–20 parts of a porous material, 60–70 parts of a hydrous salt, 1–4 parts of a surfactant, 2–4 parts of a thickening agent, 2–3 parts of a dispersant and 4–6 parts of a fire retardant.

Further, when the heat release rate of the polymer obtained by mixing component A and component B is detected to be up to or higher than 1.2 °C/s, a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) is selected; when the heat release rate of the polymer obtained by mixing component A and component B is detected to be less than 1.2 °C/s, a thermal conduction parameter-weakened porous material with a thermal conductivity of 0.02–0.2 W/(m·K) is selected.

Preferably, the thermal conduction parameter-enhanced porous material is prepared from the following components in parts by weight: 5–10 parts of expanded graphite, 1–5 parts of graphene, 1–5 parts of carbon fiber and 1–5 parts of expanded vermiculite; and thermal conduction parameter-weakened porous material is prepared from the following components in parts by weight: 5–10 parts of aerogel, 3–10 parts of fly ash cenosphere and 1–5 parts of expanded perlite.

Further, a method for preparing the porous material comprises: grinding the starting materials for preparing the porous material, pouring and immersing the ground starting materials into hot ethanol, adding successively a certain amount of a surfactant, a dispersant and a fire retardant, stirring the mixture for 30–45 min so that the additions are uniformly dispersed, filtering the resulting mixture *in vacuo*, and performing drying *in vacuo* for 12–16 h to give the porous material.

Preferably, the starting materials for preparing the porous material are one or more of expanded graphite, graphene, carbon fiber, expanded vermiculite, expanded perlite, aerogel and fly ash cenosphere; the hydrous salt is one or more of disodium hydrogen phosphate dodecahydrate, sodium sulfate decahydrate, sodium acetate trihydrate, sodium carbonate decahydrate and sodium thiosulfate pentahydrate; the thickening agent is one or more of sodium carboxymethylcellulose, xanthan gum, starch and pectin; the surfactant is one or more of nonylphenol polyoxyethylene ether, fatty alcohol polyoxyethylene ether, sodium dodecyl sulfate and benzyldodecyldimethylammonium bromide; the dispersant is one or more of aqueous sodium silicate, sodium tripolyphosphate, sodium hexametaphosphate and tetrasodium pyrophosphate; and the fire retardant is one or more of melamine pyrophosphate, zinc borate, triphenyl phosphate, zirconium phosphate, ammonium polyphosphate and tricresyl phosphate.

Preferably, in component A, the polyether polyol has a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56; the foaming agent is a mixture of water and a physical foaming agent in a weight ratio of 2:5; the physical foaming agent is trichlorofluoromethane and/or HCFC-141b; the thermally conductive material is one or more of carbon fiber, thermally conductive silicone grease and expanded graphite.

Preferably, in component B, the polymeric MDI is polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group is 31–32%; the adhesive is a dry-powder interface agent.

Preferably, component A, component B and component C are all in a fluid state; component A and component B have viscosities of 170–250 cps, and component C has a viscosity of 150–200 cps.

The method for preparing the phase-change hydrous salt polymeric filling material is achieved by using an apparatus for preparing low-exothermicity phase-change hydrous salt polymeric filling materials for use in mining, and comprises the following steps:

a. Preparation of composite phase-change nanomaterial

S1. Stirring the polyether polyol, the foaming agent, the fire retardant and the thermally conductive material according to a formulation ratio to prepare component A; stirring the polymeric MDI and the adhesive according to a formulation ratio to prepare component B;

S2. As measured according to the national standards for polymeric materials for reinforcing coal and rock mass in coal mines, measuring out component A and component B in a volume ratio of 1:1 and mixing them to form a total of 200 mL of a test sample, stirring the test sample in a mixer for 15–30 s and then measuring changes in the reaction heat release temperature before and after the prepared polyurethane is foamed so as to obtain the heat release rate of the polyurethane;

S3. Selecting a starting material for preparing the porous material according to the heat release rate of the polyurethane: selecting a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) when the heat release rate of the polymer is up to or higher than 1.2 °C/s; selecting a thermal conduction parameter-weakened porous material with a thermal conductivity of 0.02–0.2 W/(m·K) when the heat release rate of the polymer is less than 1.2 °C/s;

S4. Stirring the hydrous salt at 55–65 °C so that it is melted at constant temperature into a clear liquid, adding a certain amount of the thickening agent, the dispersant, the fire retardant and the surfactant, stirring the mixture for 30–45 min, adding the porous material selected in S3 to adjust the thermal conductivity of the hydrous salt, after stirring for 1–1.5 h and the mixture was slowly cooled to room temperature in a shaker, immediately putting the mixture in a freezer and storing for 12–16 h, and finally drying the mixture using a lyophilizer for 24–30 h to give the composite phase-change nanomaterial;

b. Preparation of low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

S1. Putting the polyether polyol, the foaming agent, the fire retardant and the thermally conductive material into a material tank A according to a formulation ratio and stirring them to prepare component A; putting the polymeric MDI and the adhesive into a material tank B according to a formulation ratio and stirring them to prepare component B; putting the polyether polyol, the silicone oil and the composite phase-change nanomaterial into a material tank C according to a formulation ratio and stirring them to prepare component C, a phase-change nanofluid;

S2. Mixing component A and component C in a mixing vessel I according to a formulation ratio, then premixing the mixture using a static mixer I for 1–5 min, then fully mixing the mixture in a mixing vessel II by stirring to give an A-C mixture component, and mixing the A-C mixture component with component B using a static mixer II to give the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining;

The apparatus for preparing the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining comprises a material tank A, a material tank B and a material tank C, wherein the material tank A and the material tank C communicate with a mixing vessel I through output pipelines, and the output pipelines of the material tank A and the material tank C are provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I and an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II, respectively;

The mixing vessel I communicate with a mixing vessel II through a static mixer I, and the mixing vessel II communicate with a static mixer II through an output pipeline; the output pipeline of the mixing vessel II is provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV; the static mixer I has a diameter of 140–180 mm and a length of 600–1000 mm;

The material tank B communicate with the static mixer II through an output pipeline, and the output pipeline of the material tank B is provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III; the static mixer II has a diameter of 200–250 mm and a length of 100–200 mm.

The method for using the phase-change hydrous salt polymeric filling material comprises: allowing a spray gun to communicate with the static mixer II so that the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining output from the static mixer II is sprayed from the spray gun, wherein the spray gun is provided with an infrared temperature sensing system, which is in electric signal connection with the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III and the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV; allowing the infrared temperature sensing system to measure the foaming temperature of the polymeric filling material in real time, converting the foaming temperature into electronic signals, feeding the electronic signals back to the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps, allowing the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps to make decisions and process electronic data after the electronic signals are received by the flow pumps and thus to adjust the flow rate of each of the components, wherein component A and component B are both at a flow rate of 4–10 kg/min; when the foaming temperature of the polymeric filling material is lower than 70 °C, the flow rate of component C is adjusted to 0.3–0.5 kg/min; when the foaming temperature of the polymeric filling material is at 70–95 °C, the flow rate of component C is adjusted to 0.5–1 kg/min, and the flow rates of component A and component B are reduced in time to be lower than 4 kg/min; when the foaming temperature of the polymeric filling material is higher than 95 °C, the flow rates of the A-C mixture component and component B are reduced until the foaming stops.

The present invention is based on the following principle: the present invention adopts the phase-change hydrous salt composite material, which can reduce the heat release temperature of the foaming and curing of polyurethane while the original foaming ratio and mechanical properties of polyurethane are retained. Firstly, according to the heat release rate of polyurethane, the thermal conductivity of the hydrous salt is adjusted using the porous material, so that the phase change time of the hydrous salt is delayed or shortened in the foaming process of polyurethane and that the early foaming of polyurethane is not affected; in the curing and heat storage stage after foaming is completed, the hydrous salt composite material with low phase-change temperature and high latent heat is utilized to perform phase change heat absorption, during which the hydrous salt phase-change composite material absorbs heat more quickly and uniformly and the temperature of polyurethane is reduced more significantly because the thermal conductivity of polyurethane is adjusted by the addition of a material with high thermal conductivity. The peak reaction temperature of the polyurethane modified herein is 70–88 °C, which meets the requirement of ≤ 95 °C in China.

Compared with the prior art, the present invention has the following advantages:

(1) With the composite hydrous salt phase-change material of the present invention, the heat absorption can be delayed or accelerated, temperature self-adaptive adjustment of the polymerization rate can be realized, and the foaming performance of polyurethane can be ensured;

(2) By adding the thermally conductive material, the mechanical properties of polyurethane is enhanced, the thermal conductivity of polyurethane is improved, and the heat dissipation capacity of polyurethane is improved, so that the heat absorption range of polyurethane is compatible with that of the hydrous salt phase-change material;

(3) In preparing the phase-change nanofluid, bubble merging and bubble collapse of polyurethane resulting from the uneven heat absorption of the composite hydrous salt phase-change material are avoided;

(4) The composite phase-change nanomaterial of the present invention can be recycled after the temperature reduction of polyurethane is completed, and can be used for absorbing heat generated by low-temperature oxidation of coal and reducing the occurrence of fires caused by spontaneous combustion of coal;

(5) In the present invention, the flow rates are controlled in time by infrared temperature detection, so that the risk of polyurethane-related fires is reduced;

(6) In the present invention, the addition of the fire retardant and the porous material greatly improves the oxygen index and the fire retardation performance of the material; when the composite

nanomaterial is added, the fire retardation effect of the fire retardant absorptive porous material leads to an increase in the oxygen index to some extent;

(7) The adding process of the present invention is simple and is suitable for all markets of polyurethane for use in mining; the material added costs little, is environment-friendly and pollution-free, and has the advantages of suppressing smoke production and being halogen-free fire retardant.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a schematic view of an apparatus for preparing and using the present invention;

where: 1. a material tank A; 2. a material tank B; 3. a material tank C; 4. a mixing vessel I; 5. a static mixer I; 6. a mixing vessel II; 7. a static mixer II; 8. a spray gun; 9. an infrared temperature sensing system; 10. an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III; 11. an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I; 12 an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II; 13. an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV;

FIG. 2 shows changes in the measured reaction temperature of a reference group (common polyurethane sample) and the filling material prepared in Example 1 (modified polyurethane) over time.

DETAILED DESCRIPTION

The present invention will be further illustrated in detail with reference to the accompanying drawings and specific examples.

Example 1

A method for preparing a phase-change hydrous salt polymeric filling material, achieved by using an apparatus for preparing low-exothermicity phase-change hydrous salt polymeric filling materials for use in mining, comprises the following steps:

a. Preparation of composite phase-change nanomaterial

S1. 50 parts of a polyether polyol, 8 parts of a foaming agent, 8 parts of melamine pyrophosphate and 4 parts of carbon fiber were stirred according to a formulation ratio to prepare component A, wherein the polyether polyol had a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56, and the foaming agent was a mixture of water and HCFC-141b in a weight ratio of 2:5; 80 parts of a polymeric MDI and 3 parts of an adhesive were stirred according to a formulation ratio to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%; the adhesive was a dry-powder interface agent; component A and component B had viscosities of 170–250 cps;

S2. As measured according to the national standards for polymeric materials for reinforcing coal and rock mass in coal mines, component A and component B were measured out and mixed in a volume ratio of 1:1 to form a total of 200 mL of a test sample, and the test sample was stirred in a mixer for 15–30 s and then poured into a vessel with a diameter of 50 mm; a thermocouple wire was placed in the center of the vessel, 40 mm from the bottom of the vessel; changes in the reaction heat release temperature before and after the prepared polyurethane was foamed were measured, and thus a heat release rate of 1.5–2 °C/s was obtained for the polyurethane;

S3. When the heat release rate of the polymer was up to or higher than 1.2 °C/s, a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) was selected; the method for preparing the porous material is as follows: 11 parts of a starting material for preparing the porous material were ground, wherein the starting material was prepared from 5 parts of expanded graphite, 2 parts of graphene, 2 parts of carbon fiber and 2 parts of expanded vermiculite; the ground starting material was poured and immersed into hot ethanol, and 2 parts of the surfactant nonylphenol polyoxyethylene ether, 2 parts of the dispersant aqueous sodium silicate and 4 parts of the fire retardant melamine pyrophosphate were successively added; the mixture was stirred for 30–45 min to uniformly disperse the additions, filtered *in vacuo* and dried *in vacuo* for 12–16 h to give the thermal conduction parameter-enhanced porous material;

S4. 60 parts of disodium hydrogen phosphate dodecahydrate were stirred at 60 °C so that they were melt at constant temperature into a clear liquid, and 4 parts of sodium carboxymethylcellulose, 2 parts of sodium tripolyphosphate, 1 part of sodium dodecyl sulfate and 4 parts of zinc borate were added; after the mixture was stirred for 30 min, 10 parts of the thermal conduction parameter-enhanced porous material obtained in S3 were added to adjust the thermal conductivity of the hydrous salt; after being stirred for 1–1.5 h, the mixture was slowly cooled to room temperature in a shaker, immediately put in a freezer and stored for 12 h, and finally dried using a lyophilizer for 24 h to give a thermal conduction-enhanced composite phase-change nanomaterial with a thermal conductivity of 0.6–0.8 W/(m·K);

b. Preparation of low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

S1. 50 parts of a polyether polyol, 8 parts of a foaming agent, 8 parts of melamine pyrophosphate and 4 parts of carbon fiber were put into a material tank A 1 according to a formulation ratio and stirred to prepare component A, wherein the polyether polyol had a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56, and the foaming agent was a mixture of water and HCFC-141b in a weight ratio of 2:5; 80 parts of a polymeric MDI and 3 parts of an adhesive were put into a material tank B 3 according to a formulation ratio and stirred to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%; the adhesive was a dry-powder interface agent; component A and component B had viscosities of 170–250 cps; 20 parts of the polyether polyol, 8 parts of a silicone oil and 10 parts of the composite phase-change nanomaterial were put into a material tank C 2 according to a formulation ratio and stirred to prepare component C, a phase-change nanofluid with a viscosity of 150 cps;

S2. 25 parts of component A and 30 parts of component C were mixed in a mixing vessel I 4 according to a formulation ratio, then premixed for 1–5 min using a static mixer I 5, and then fully mixed in a mixing vessel II 6 by stirring to give an A-C mixture component, and the A-C mixture component was mixed with 60 parts of component B using a static mixer II 7 to give a low-exothermicity phase-change hydrous salt polymeric filling material for use in mining.

As shown in FIG. 1, the apparatus for preparing the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining comprised a material tank A 1, a material tank B 3 and a material tank C 2, wherein the material tank A 1 and the material tank C 2 communicated with a mixing vessel I 4 through output pipelines, and the output pipelines of the material tank A 1 and the material tank C 2 were provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I 11 and an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II 12, respectively;

The mixing vessel I 4 communicated with a mixing vessel II 6 through a static mixer I 5, and the mixing vessel II 6 communicated with a static mixer II 7 through an output pipeline; the output pipeline of the mixing vessel II 6 was provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV 13; the static mixer I 5 had a diameter of 140–180 mm and a length of 600–1000 mm;

The material tank B 3 communicated with the static mixer II 7 through an output pipeline, and the output pipeline of the material tank B 3 was provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III 10; the static mixer II 7 had a diameter of 200–250 mm and a length of 100–200 mm.

As shown in FIG. 1, a method for using the phase-change hydrous salt polymeric filling material comprises the following steps: a spray gun 8 was allowed to communicate with the static mixer II 7 so that the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining output from the static mixer II 7 is sprayed from the spray gun 8, wherein the spray gun 8 was provided with an infrared temperature sensing system 9, which was in electric signal connection with the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I 11, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II 12, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III 10 and the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV 13; the infrared temperature sensing system 9 was allowed to measure the foaming temperature of the polymeric filling material in real time, the foaming temperature was converted into electronic signals and fed back to the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps, and the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps was allowed to make decisions and process electronic data after the electronic signals are received by the flow pumps and thus to adjust the flow rate of each of the components, wherein component A and component B were both at a flow rate of 4–10 kg/min; when the foaming temperature of the polymeric filling material was lower than 70 °C, the flow rate of component C was adjusted to 0.3–0.5 kg/min; when the foaming temperature of the polymeric filling material was at 70–95 °C, the flow rate of component C was adjusted to 0.5–1 kg/min, and the flow rates of component A and component B were reduced in time to be lower than 4 kg/min; when the foaming temperature of the polymeric filling material was higher than 95 °C, the flow rate of the mixture component of component A and component C and the flow rate of component B were reduced until the foaming stopped.

Performance tests were carried out on the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining obtained in this example according to regulations of "Safety Administration of Reactive Polymeric Materials for Coal Mine Shafts (for Trial Implementation)" Department of Technology and Equipment of State Administration of Coal Mine Safety [2020] No. 18 and Notice of "Detailed Rules for Fire Prevention and Extinguishing in Coal Mines" Mine Safety [2021] No. 156. The results are shown in Table 1.

Table 1. Performance test results of the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

No.	Item		Performance	National index	Performance of commercially available product
1	Peak reaction temperature/°C		88	≤95°C	120-150°C
2	Pressure resistance/MPa		43	≥40MPa	32
3	Oxygen index/%		30	≥28	26
4	Expansion ratio/times		3.5	≥1.0	3.5
5	Fire retardation performance	Vertical combustion	V-0	V-0	V-1
		Combustion persistence test	Not persistent	Not persistent	Not persistent

Example 2

A method for preparing a phase-change hydrous salt polymeric filling material, achieved by using an apparatus for preparing low-exothermicity phase-change hydrous salt polymeric filling materials for use in mining, comprises the following steps:

a. Preparation of composite phase-change nanomaterial

S1. 60 parts of a polyether polyol, 5 parts of a foaming agent, 10 parts of triphenyl phosphate and 1 parts of thermally conductive silicone grease were stirred according to a formulation ratio to prepare component A, wherein the foaming agent was a mixture of water and trichlorofluoromethane in a weight ratio of 2:5; 80 parts of a polymeric MDI and 4 parts of an adhesive were stirred according to a formulation ratio to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%;

S2. As measured according to the national standards for polymeric materials for reinforcing coal and rock mass in coal mines, component A and component B were measured out and mixed in a volume ratio of 1:1 to form a total of 200 mL of a test sample, and the test sample was stirred in a mixer for 15–30 s and then poured into a vessel with a diameter of 50 mm; a thermocouple wire was placed in the center of the vessel, 40 mm from the bottom of the vessel; changes in the reaction heat release temperature before and after the prepared polyurethane was foamed were measured, and thus a heat release rate of 0.5–1 °C/s was obtained for the polyurethane;

S3. When the heat release rate of the polymer was up to or lower than 1.2 °C/s, a thermal conduction parameter-weakened porous material with a thermal conductivity of 0.02-0.2 W/(m·K) was selected; the method for preparing the porous material is as follows: 16 parts of a starting material for preparing the porous material were ground, wherein the starting material was prepared from 8 parts of aerogel, 3 parts of fly ash cenosphere and 5 parts of expanded perlite; the ground starting material was poured and immersed into hot ethanol, and a certain amount of 3 parts of the surfactant fatty alcohol polyoxyethylene ether, 2 parts of the dispersant sodium tripolyphosphate and 4 parts of the fire retardant triphenyl phosphate were successively added; the mixture was stirred for 30–45 min to uniformly disperse the additions, filtered *in vacuo* and dried *in vacuo* for 12–16 h to give the thermal conduction parameter-weakened porous material;

S4. A mixture of 40 parts of disodium hydrogen phosphate dodecahydrate and 30 parts of sodium sulfate decahydrate was stirred at 60 °C so that they were melt at constant temperature into a clear liquid, and 3 parts of xanthan gum, 3 parts of aqueous sodium silicate, 2 parts of fatty alcohol polyoxyethylene ether, 4 parts of zirconium phosphate and 2 parts of ammonium polyphosphate were added; after the mixture was stirred for 30 min, 13 parts of the thermal conduction parameter-weakened porous material obtained in S3 were added to adjust the thermal conductivity of the hydrous salt; after being stirred for 1–1.5 h, the mixture was slowly cooled to room temperature in a shaker, immediately put in a freezer and stored for 12 h, and finally dried using a lyophilizer for 24 h to give a thermal conduction-weakened composite phase-change nanomaterial with a thermal conductivity of 0.20-0.30 W/(m·K);

b. Preparation of low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

S1. 60 parts of a polyether polyol, 5 parts of a foaming agent, 10 parts of triphenyl phosphate and 1 parts of thermally conductive silicone grease were put into a material tank A 1 according to a formulation ratio and stirred to prepare component A, wherein the foaming agent was a mixture of water and trichlorofluoromethane in a weight ratio of 2:5; 80 parts of a polymeric MDI and 4 parts of an adhesive were put into a material tank B 3 according to a formulation ratio and stirred to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%; 15 parts of the polyether polyol, 7 parts of a silicone oil and 15 parts of the composite phase-change nanomaterial were put into a material tank C 2 according to the proportion and stirred to prepare component C, a phase-change nanofluid with a viscosity of 200 cps;

S2. 30 parts of component A and 20 parts of component C were mixed in a mixing vessel I 4 according to a formulation ratio, then premixed for 1–5 min using a static mixer I 5, and then fully mixed in a mixing vessel II 6 by stirring to give an A-C mixture component, and the A-C mixture component was mixed with 50 parts of component B using a static mixer II 7 to give a low-exothermicity phase-change hydrous salt polymeric filling material for use in mining.

The apparatus for preparing the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining was the same as in Example 1.

The method for using the phase-change hydrous salt polymeric filling material was the same as in Example 1.

Performance tests were carried out on the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining obtained in this example according to regulations of "Safety Administration of Reactive Polymeric Materials for Coal Mine Shafts (for Trial Implementation)" Department of Technology and Equipment of State Administration of Coal Mine Safety [2020] No. 18 and Notice of "Detailed Rules for Fire Prevention and Extinguishing in Coal Mines" Mine Safety [2021] No. 156. The results are shown in Table 2.

Table 2. Performance test results of the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

No.	Item		Performance	National index	Performance of commercially available product
1	Peak reaction temperature/°C		79	≤95°C	120-150°C
2	Pressure resistance/MPa		41	≥40MPa	32
3	Oxygen index/%		31	≥28	26
4	Expansion ratio/times		3.5	≥1.0	3.5
5	Fire retardation performance	Vertical combustion	V-0	V-0	V-1
		Combustion persistence test	Not persistent	Not persistent	Not persistent

Example 3

A method for preparing a phase-change hydrous salt polymeric filling material, achieved by using an apparatus for preparing low-exothermicity phase-change hydrous salt polymeric filling materials for use in mining, comprises the following steps:

a. Preparation of composite phase-change nanomaterial

S1. 60 parts of a polyether polyol, 3 parts of a foaming agent, 10 parts of ammonium polyphosphate and 8 parts of expanded graphite were stirred according to a formulation ratio to prepare component A, wherein the polyether polyol had a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56, and the foaming agent was a mixture of water and HCFC-141b in a weight ratio of 2:5; 72 parts of a polymeric MDI and 3 parts of an adhesive were stirred according to a formulation ratio to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%; the adhesive was a dry-powder interface agent; component A and component B had viscosities of 170–250 cps;

S2. As measured according to the national standards for polymeric materials for reinforcing coal and rock mass in coal mines, component A and component B were measured out and mixed in a volume ratio of 1:1 to form a total of 200 mL of a test sample, and the test sample was stirred in a mixer for 15–30 s and then poured into a vessel with a diameter of 50 mm; a thermocouple wire was placed in the center of the vessel, 40 mm from the bottom of the vessel; changes in the reaction heat release temperature before and after the prepared polyurethane was foamed were measured, and thus a heat release rate of 1.3–1.8 °C/s was obtained for the polyurethane;

S3. When the heat release rate of the polymer was up to or higher than 1.2 °C/s, a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) was selected; the method for preparing the porous material is as follows: 13 parts of a starting material for preparing the porous material were ground, wherein the starting material was prepared from 7 parts of expanded graphite, 1 part of graphene, 2 parts of carbon fiber and 3 parts of expanded vermiculite; the ground starting material was poured and immersed into hot ethanol, and a certain amount of 2 parts of the surfactant sodium dodecyl sulfate, 3 parts of the dispersant sodium hexametaphosphate and 4 parts of the fire retardant triphenyl phosphate were successively added; the mixture was stirred for 30–45 min to uniformly disperse the additions, filtered *in vacuo* and dried *in vacuo* for 12–16 h to give the thermal conduction parameter-enhanced porous material;

S4. A mixture of 30 parts of sodium acetate trihydrate and 30 parts of sodium thiosulfate pentahydrate was stirred at 60 °C so that they were melt at constant temperature into a clear liquid, and 2 parts of xanthan gum, 3 parts of sodium tripolyphosphate, 2 parts of nonylphenol polyoxyethylene ether, 2 parts of benzyldodecyldimethylammonium bromide and 5 parts of zirconium phosphate were added; after the mixture was stirred for 30 min, 15 parts of the thermal conduction parameter-enhanced porous material obtained in S3 were added to adjust the thermal conductivity of the hydrous salt; after being stirred for 1–1.5 h, the mixture was slowly cooled to room temperature in a shaker, immediately put in a freezer and stored for 12 h, and finally dried using a lyophilizer for 24 h to give a thermal conduction-enhanced composite phase-change nanomaterial with a thermal conductivity of 0.8 W/(m·K);

b. Preparation of low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

S1. 60 parts of a polyether polyol, 3 parts of a foaming agent, 10 parts of ammonium polyphosphate and 8 parts of expanded graphite were put into a material tank A 1 according to a formulation ratio and stirred to prepare component A, wherein the polyether polyol had a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56, and the foaming agent was a mixture of water and HCFC-141b in a weight ratio of 2:5; 72 parts of a polymeric MDI and 3 parts of an adhesive were put into a material tank B 3 according to a formulation ratio and stirred to prepare component B, wherein the polymeric MDI was polyaryl polymethylene isocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group was 31–32%; the adhesive was a dry-powder interface agent; component A and component B had viscosities of 170–250 cps; 20 parts of the polyether polyol, 6 parts of a silicone oil and 25 parts of the composite phase-change nanomaterial were put into a material tank C 2 according to a formulation ratio and stirred to prepare component C, a phase-change nanofluid with a viscosity of 180 cps;

S2. 35 parts of component A and 30 parts of component C were mixed in a mixing vessel I 4 according to a formulation ratio, then premixed for 1–5 min using a static mixer I 5, and then fully mixed in a mixing vessel II 6 by stirring to give an A-C mixture component, and the A-C mixture component was mixed with 55 parts of component B using a static mixer II 7 to give a low-exothermicity phase-change hydrous salt polymeric filling material for use in mining.

The apparatus for preparing the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining was the same as in Example 1.

The method for using the phase-change hydrous salt polymeric filling material was the same as in Example 1.

Performance tests were carried out on the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining obtained in this example according to regulations of "Safety Administration of Reactive Polymeric Materials for Coal Mine Shafts (for Trial Implementation)"

Department of Technology and Equipment of State Administration of Coal Mine Safety [2020] No. 18 and Notice of "Detailed Rules for Fire Prevention and Extinguishing in Coal Mines" Mine Safety [2021] No. 156. The results are shown in Table 3.

Table 3. Performance test results of the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

No.	Item		Performance	National index	Performance of commercially available product
1	Peak reaction temperature/°C		70	≤95°C	120-150°C
2	Pressure resistance/MPa		41	≥40MPa	32
3	Oxygen index/%		31	≥28	26
4	Expansion ratio/times		3.5	≥1.0	3.5
5	Fire retardation performance	Vertical combustion	V-0	V-0	V-1
		Combustion persistence test	Not persistent	Not persistent	Not persistent

Preparation of the reference group (common polyurethane): 70 parts of a polyether polyol, 8 parts of HCFC-141b and 8 parts of melamine pyrophosphate were put into a vessel according to a formulation ratio and stirred to prepare component A; 80 parts of a polymeric MDI and 3 parts of an adhesive were put into a vessel according to a formulation ratio and stirred to prepare component B; component A and component B were mixed in a volume ratio of 1:1 to prepare the common polyurethane. The reaction temperature of the common polyurethane was measured over time, and the results are shown in FIG. 2.

From the above Table 1–3 and FIG. 2, it can be seen that the peak reaction temperature of the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining was reduced significantly from 120–150 °C (the peak reaction temperature of the common commercially available polyurethane) to about 80 °C, indicating that the peak reaction temperature decreases as a composite phase-change nanomaterial is added. The common polyurethane has a high peak reaction temperature and releases heat fast. The improved polyurethane has improved fire retardation performance. The thermal conductivity of the hydrous salt is adjusted by adding a composite phase-change nanomaterial, so that the original foaming ratio of polyurethane is ensured while the peak reaction temperature is reduced.

The heat release of the polyurethane of Example 2 in foaming is slow. By adding different proportions of a composite phase-change nanomaterial, the thermal conductivity of the material is reduced, temperature self-adaptive slow adjustment of the polymerization rate is achieved, the original foaming performance of polyurethane is ensured, the expansion ratio fundamentally remains unchanged (about 3.5-fold), and the temperature reduction of polyurethane is achieved. The heat release of the polyurethanes of Example 1 and Example 3 in foaming are fast. By adding a porous material with high thermal conductivity, the thermal conductivity of the material is increased, temperature self-adaptive fast adjustment of the polymerization rate is achieved, the original foaming performance of polyurethane is ensured, the expansion ratio fundamentally remains unchanged (about 3.5-fold), and the temperature reduction of polyurethane is achieved. Therefore, by adjusting the thermal conduction rate of the composite phase-change nanomaterial, temperature self-adaptive adjustment of the polymerization rate is achieved, the reaction temperature of polyurethane is reduced, and the original foaming performance of polyurethane is ensured.

CLAIMS

1. A phase-change hydrous salt polymeric filling material, which is prepared from the following components in parts by weight: 25–35 parts of component A, 50–60 parts of component B and 20–30 parts of component C, wherein component A is mainly prepared from the following components in parts by weight: 50–60 parts of a polyether polyol, 3–8 parts of a foaming agent, 8–10 parts of a fire retardant and 1–8 parts of a thermally conductive material; component B is mainly prepared from the following components in parts by weight: 72–80 parts of a polymeric MDI and 3–4 parts of an adhesive; component C is a phase-change nanofluid, which is mainly prepared from the following components in parts by weight: 15–20 parts of a polyether polyol, 6–8 parts of a silicone oil and 10–25 parts of a composite phase-change nanomaterial, wherein the composite phase-change nanomaterial is mainly prepared from the following components in parts by weight: 10–20 parts of a porous material, 60–70 parts of a hydrous salt, 1–4 parts of a surfactant, 2–4 parts of a thickening agent, 2–3 parts of a dispersant and 4–6 parts of a fire retardant.

2. The phase-change hydrous salt polymeric filling material according to claim 1, wherein when the heat release rate of the polymer obtained by mixing component A and component B is detected to be up to or higher than 1.2 °C/s, a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) is selected; when the heat release rate of the polymer obtained by mixing component A and component B is detected to be less than 1.2 °C/s, a thermal conduction parameter-weakened porous material with a thermal conductivity of 0.02–0.2 W/(m·K) is selected.

3. The phase-change hydrous salt polymeric filling material according to claim 2, wherein the thermal conduction parameter-enhanced porous material is prepared from the following components in parts by weight: 5–10 parts of expanded graphite, 1–5 parts of graphene, 1–5 parts of carbon fiber and 1–5 parts of expanded vermiculite; and thermal conduction parameter-weakened porous material is prepared from the

following components in parts by weight: 5–10 parts of aerogel, 3–10 parts of fly ash cenosphere and 1–5 parts of expanded perlite.

4. The phase-change hydrous salt polymeric filling material according to claim 1, wherein a method for preparing the porous material comprises: grinding the starting materials for preparing the porous material, pouring and immersing the ground starting materials into hot ethanol, adding successively a certain amount of a surfactant, a dispersant and a fire retardant, stirring the mixture for 30–45 min so that the additions are uniformly dispersed, filtering the resulting mixture in vacuo, and performing drying in vacuo for 12–16 h to give the porous material.

5. The phase-change hydrous salt polymeric filling material according to claim 4, the starting materials for preparing the porous material are one or more of expanded graphite, graphene, carbon fiber, expanded vermiculite, expanded perlite, aerogel and fly ash cenosphere; the hydrous salt is one or more of disodium hydrogen phosphate dodecahydrate, sodium sulfate decahydrate, sodium acetate trihydrate, sodium carbonate decahydrate and sodium thiosulfate pentahydrate; the thickening agent is one or more of sodium carboxymethylcellulose, xanthan gum, starch and pectin; the surfactant is one or more of nonylphenolpolyoxyethylene ether, fatty alcohol polyoxyethylene ether, sodium dodecyl sulfate and benzyldodecyldimethylammonium bromide; the dispersant is one or more of aqueous sodium silicate, sodium tripolyphosphate, sodium hexametaphosphate and tetrasodium pyrophosphate; and the fire retardant is one or more of melamine pyrophosphate, zinc borate, triphenyl phosphate, zirconium phosphate, ammonium polyphosphate and tricresyl phosphate.

6. The phase-change hydrous salt polymeric filling material according to claim 1 or 2, wherein in component A, the polyether polyol has a functionality of 3, a relative molecular weight of 3000 and a hydroxyl value of 56; the foaming agent is a mixture of water and a physical foaming agent in a weight ratio of 2:5; the physical foaming agent is trichlorofluoromethane and/or HCFC-141b; the thermally conductive material is one or more of carbon fiber, thermally conductive silicone grease and expanded graphite.

7. The phase-change hydrous salt polymeric filling material according to claim 1 or 2,

wherein in component B, the polymeric MDI is polyarylpolymethyleneisocyanate with an average molecular weight of 350–400, and the mass fraction of isocyanate group is 31–32%; the adhesive is a dry-powder interface agent.

8. The phase-change hydrous salt polymeric filling material according to claim 1 or 2, wherein component A, component B and component C are all in a fluid state; component A and component B have viscosities of 170–250 cps, and component C has a viscosity of 150–200 cps.

9. The method for preparing the phase-change hydrous salt polymeric filling material as claimed in any one of claims 1-8, is achieved by using an apparatus for preparing low-exothermicity phase-change hydrous salt polymeric filling materials for use in mining, and comprises the following steps:

a. Preparation of composite phase-change nanomaterial

S1. Stirring the polyether polyol, the foaming agent, the fire retardant and the thermally conductive material according to a formulation ratio to prepare component A; stirring the polymeric MDI and the adhesive according to a formulation ratio to prepare component B;

S2. As measured according to the national standards for polymeric materials for reinforcing coal and rock mass in coal mines, measuring out component A and component B in a volume ratio of 1:1 and mixing them to form a total of 200 mL of a test sample, stirring the test sample in a mixer for 15–30 s and then measuring changes in the reaction heat release temperature before and after the prepared polyurethane is foamed so as to obtain the heat release rate of the polyurethane;

S3. Selecting a starting material for preparing the porous material according to the heat release rate of the polyurethane: selecting a thermal conduction parameter-enhanced porous material with a thermal conductivity of 1–1.5 W/(m·K) when the heat release rate of the polymer is up to or higher than 1.2 °C/s; selecting a thermal conduction parameter-weakened porous material with a thermal conductivity of 0.02–0.2 W/(m·K) when the heat release rate of the polymer is less than 1.2 °C/s;

S4. Stirring the hydrous salt at 55–65 °C so that it is melted at constant temperature into a clear liquid, adding a certain amount of the thickening agent, the dispersant, the fire retardant and the surfactant, stirring the mixture for 30–45 min, adding the porous material selected in S3 to adjust the thermal conductivity of the hydrous salt, after stirring for 1–1.5 h and the mixture was slowly cooled to room temperature in a shaker, immediately putting the mixture in a freezer and storing for 12–16 h, and finally drying the mixture using a lyophilizer for 24–30 h to give the composite phase-change nanomaterial;

b. Preparation of low-exothermicity phase-change hydrous salt polymeric filling material for use in mining

S1. Putting the polyether polyol, the foaming agent, the fire retardant and the thermally conductive material into a material tank A according to a formulation ratio and stirring them to prepare component A; putting the polymeric MDI and the adhesive into a material tank B according to a formulation ratio and stirring them to prepare component B; putting the polyether polyol, the silicone oil and the composite phase-change nanomaterial into a material tank C according to a formulation ratio and stirring them to prepare component C, a phase-change nanofluid;

S2. Mixing component A and component C in a mixing vessel I according to a formulation ratio, then premixing the mixture using a static mixer I for 1–5 min, then fully mixing the mixture in a mixing vessel II by stirring to give an A-C mixture component, and mixing the A-C mixture component with component B using a static mixer II to give the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining;

The apparatus for preparing the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining comprises a material tank A, a material tank B and a material tank C, wherein the material tank A and the material tank C communicate with a mixing vessel I through output pipelines, and the output pipelines of the material tank A and the material tank C are provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I and an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II, respectively;

The mixing vessel I communicate with a mixing vessel II through a static mixer I, and the mixing vessel II communicate with a static mixer II through an output pipeline; the output pipeline of the mixing vessel II is provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV; the static mixer I has a diameter of 140–180 mm and a length of 600–1000 mm;

The material tank B communicate with the static mixer II through an output pipeline, and the output pipeline of the material tank B is provided with an automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III; the static mixer II has a diameter of 200–250 mm and a length of 100–200 mm.

10. The method for preparing the phase-change hydrous salt polymeric filling material as claimed in any one of claims 1-8, the method for using the phase-change hydrous salt polymeric filling material comprises: allowing a spray gun to communicate with the static mixer II so that the low-exothermicity phase-change hydrous salt polymeric filling material for use in mining output from the static mixer II is sprayed from the spray gun, wherein the spray gun is provided with an infrared temperature sensing system, which is in electric signal connection with the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump I, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump II, the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump III and the automatic flow-adjusting multifunctional intelligent variable-frequency flow pump IV; allowing the infrared temperature sensing system to measure the foaming temperature of the polymeric filling material in real time, converting the foaming temperature into electronic signals, feeding the electronic signals back to the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps, allowing the automatic flow-adjusting multifunctional intelligent variable-frequency flow pumps to make decisions and process electronic data after the electronic signals are received by the flow pumps and thus to adjust the flow rate of each of the components, wherein component A and component B are both at a flow rate of 4–10 kg/min; when the foaming temperature of the polymeric filling material is lower than 70 °C, the flow rate of component C is adjusted to 0.3–0.5 kg/min; when the foaming temperature of the polymeric filling material is at 70–95 °C, the flow rate of

component C is adjusted to 0.5–1 kg/min, and the flow rates of component A and component B are reduced in time to be lower than 4 kg/min; when the foaming temperature of the polymeric filling material is higher than 95 °C, the flow rates of the A-C mixture component and component B are reduced until the foaming stops.

Revendications

1. Matériau de remplissage à changement de phase de polymère de sel hydraté, caractérisé en se composant de parts en poids suivantes : 25 à 35 unités de la composition A, 50 à 60 unités de la composition B, 20 à 30 unités de la composition C. Et la composition A se compose principalement de 50 à 60 unités de polyéther, 3 à 8 unités de gonflant, 8 à 10 unités de retardateur de flamme et 1 à 8 unités de conducteur de chaleur ; La composition B se compose principalement de parts en poids suivantes : 72 à 80 unités de diisocyanate de méthylène diphényle polymère (MDI), 3 à 4 unités de colleuse ; la composition C est nanofluide à changement de phase qui se compose principalement de parts en poids suivantes : 15 à 20 unités de polyéther, 6 à 8 unités d'huile de silicone, 10 à 25 unités de nanomatière composite à changement de phase ; ladite nanomatière composite à changement de phase se composent principalement de parts en poids suivantes : 10 à 20 unités de matériaux poreux, 60 à 70 unités de sel hydraté, 1 à 4 unités de tensioactif, 2 à 4 unités d'épaississant, 2 à 3 unités de dispersant, 4 à 6 unités de retardateur de flamme.

2. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 1, caractérisée en ce que quand le taux de dégagement de chaleur de la polymère obtenue par le mélange de la composition A et la composition B est égal ou supérieur à 1,2 °C/s, utiliser de préférence les matériaux poreux avec conductivité thermique renforcée à 1-1,5 W/(m·K) ; Quand le taux de dégagement de chaleur de la polymère obtenue par le mélange de la composition A et la composition B est inférieur à 1,2 °C/s, utiliser de préférence les matériaux poreux avec conductivité thermique réduite à 0,02-0,2 W/(m·K).

3. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 2, caractérisé en ce que les matériaux poreux avec conductivité thermique renforcée se composent de parts en poids suivantes : 5 à 10 unités de graphite expansé, 1 à 5 unités de graphène, 1 à 5 unités de fibre carbonique et 1 à 5 unités de voséite expansée ; les matériaux poreux avec conductivité thermique réduite se composent de

parts en poids suivantes : 5 à 10 unités d'aérogel, 3 à 10 unités de cénosphères des cendres volantes et 1 à 5 unités de perlite élargie.

4. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 1, caractérisés en méthode de préparation des matériaux poreux : Abraser les matières primaires destinés à la préparation des matériaux poreux, les immerger dans l'éthanol chaud, y ajouter l'un après l'autre le tensioactif, le dispersant et le retardateur de flamme, agiter pour 30 à 45 minutes pour obtenir un mélange uniforme. Sécher à vide pour 12 à 16 h après le filtrage à vide puis sortir les matériaux poreux.

5. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 4, caractérisé en ce que lesdits matériaux poreux se composent de l'une ou plusieurs matières premières de graphite expansé, de graphène, de fibre carbonique, de voséite expansée, de perlite élargie, d'aérogel et de cénosphères des cendres volantes ; le sel hydraté provient de l'une ou plusieurs matières telles que le phosphate de sodium dodécahydrate dibasique, le sulfate de sodium décahydraté, l'acétate de sodium trihydraté, le carbonate de sodium décahydraté et le thiosulfate de sodium pentahydraté ; l'épaississant provient de l'une ou plusieurs matières telles que le carboxyméthylcellulose de sodium, le gomme xanthane, l'amidon et la pectine ; le tensioactif provient de l'une ou plusieurs matières telles que l'éther de polyoxyéthylène de nonylphénol, l'éther monooctadécylique de polyoxyéthylène, le laurylsulfate de sodium, le bromure de dodécyltriméthylammonium ; le dispersant provient de l'une ou plusieurs matières telles que le silicate de sodium, le tripolyphosphate de sodium, l'hexamétaphosphate de sodium et le phosphate tétra-sodique ; le retardateur de flamme provient l'une ou plusieurs matières telles que le polyphosphate de mélamine, le borate de zinc, le phosphate de triphényle, le phosphate de zirconium, le polyphosphate d'ammonium et le phosphate de tripyléphényle.

6. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 1 ou 2, caractérisé en ce que dans la composition A, la fonctionnalité dudit polyéther est de 3, la masse moléculaire relative de 3000, l'indice d'oxhydryle de

56 ; Ledit agent moussant est une mixture d'eau et d'agent moussant physique mélangée à la proportion de masse de 2:5 ; Ledit agent moussant physique provient de trichlorodifluorométhane et/ou HCFC-141b ; ledit conducteur de chaleur provient de l'une ou plusieurs matières telles que le fibre carbonique, la graisse de silicone conductrice thermique et le graphite expansé.

7. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 1 ou 2, caractérisé en ce que dans la composition B, ledit MDI polymère provient d'isocyanate de polyphényle polyméthylène, avec masse moléculaire en moyenne allant de 350 à 400, la fraction de masse de NCO est entre 31% à 32% ; ladite colleuse provient de l'agent interfacial en poudre.

8. Matériau de remplissage à changement de phase de polymère de sel hydraté selon la revendication 1 ou 2, caractérisé en ce que les compositions A, B et C sont tous en état de liquide, la viscosité des parts A et B est entre 170 et 250 cps ; la viscosité de la composition C est entre 150 et 200 cps.

9. Méthode de préparation d'un matériau de remplissage à changement de phase de polymère de sel hydraté selon les revendication 1 à 8, caractérisée en ce que ladite méthode se réalise grâce au dispositif de préparation de matériau de remplissage à changement de phase de polymère de sel hydraté avec bas dégagement de chaleur destiné à l'industrie de minéral, qui suit les étapes suivantes :

a. Préparation des nanomatières composites à changement de phase

S1. Agiter selon la proportion le polyéther, le gonflant, le retardateur de flamme et le conducteur de chaleur pour préparer la composition A ; agiter selon la proportion le diisocyanate de méthylène diphényle polymère (MDI) et la colleuse pour préparer la composition B ;

S2. Mesurer selon les critères d'État sur les matériaux macromoléculaires pour renforcer le corps rocheux charbonnier de mine de houille, et mêler les compositions A et B au volume spécifique de 1:1 pour obtenir un échantillon d'essai 200 ml. Agiter pendant 15 à 30 s avec agitateur, ensuite observer le changement de température dégagée avant et après le moussage de polyuréthane pour obtenir le taux de dégagement de température du polyuréthane ;

S3. Le choix des matières premières se dépend du taux de dégagement de chaleur du polyuréthane, si son taux de dégagement de chaleur de la polymère est égal ou supérieur à 1,2 °C/s, utiliser de préférence les matériaux poreux avec conductivité thermique de référence renforcée à 1-1.5 W/(m·K) ; Si le taux de dégagement de chaleur de la polymère est inférieur à 1,2 °C/s, utiliser de préférence les matériaux poreux avec conductivité thermique de référence réduite à 0,02-0,2 W/(m·K) ;

S4. Agiter et fondre le sel hydraté à 55-65 °C jusqu'à ce qu'il deviennent en liquide clarifié, puis y ajouter l'épaississeur, le dispersant, le retardateur de flamme et le tensioactif, agiter pendant 30 à 45 minutes et y ajouter les matériaux poreux obtenus dans l'étape S3 pour ajuster la conductivité thermique du sel hydraté. Continuer à agiter pendant 1 à 1,5 h, abaisser la température jusqu'à la température ambiante dans l'oscillateur à température constante avant le mettre dans le réfrigérateur pour geler pendant 12 à 16 h. Finalement, sécher avec séchoir réfrigérant pendant 24 à 30 h pour obtenir les nanomatières composites à changement de phase ;

b. Préparation des matériaux de remplissage à changement de phase de polymère de sel hydraté à bas dégagement de chaleur, destiné à l'industrie de minéral

S1. Mettre dans le réservoir A (1) selon la proportion le polyéther, le gonflant, le retardateur de flamme et le conducteur de chaleur, agiter pour préparer la composition A ; mettre dans le réservoir B (3) selon la proportion le diisocyanate de méthylène diphényle polymère (MDI) et la colleuse, agiter pour préparer la composition B ; Mettre dans le réservoir C (2) selon la proportion le polyéther, le silicone et les nanomatières composites à changement de phase, agiter pour préparer le nanofluide à changement de phase de la composition C ;

S2. Mélanger la composition A et la composition C dans le réservoir de mélange I (4) selon la proportion, procéder au pré-mélange dans le mélangeur statique I (5) pendant

1 à 5 min, ensuite agiter bien dans le réservoir de mélange II (6) pour obtenir le mélange multicomposant A-C, le mélange A-C sera mélangé avec la composition B dans le mélangeur statique II (7) pour obtenir le matériau de remplissage à changement de phase de polymère de sel hydraté à bas dégagement de chaleur, destiné à l'industrie de minéral ;

Les dispositifs nécessaires à la préparation du matériau de remplissage à changement de phase de polymère de sel hydraté à bas dégagement de chaleur, destiné à l'industrie de minéral comprennent le réservoir A (1), le réservoir B (3) et le réservoir C (2). Le réservoir A (1) et le réservoir C (2) sont connectés avec le réservoir de mélange I (4) à travers les tuyaux de sortie où les tuyaux de sortie du réservoir A (1) et du réservoir C (2) s'installent respectivement les pompes à flux de fréquences variables intelligentes multi-fonctionnelles I (11) et II (12) qui permettent d'ajuster automatiquement le débit ;

Le réservoir de mélange I (4) est connecté via le mélangeur statique I (5) avec le réservoir de mélange II (6), le réservoir de mélange II (6) est connecté avec le mélangeur statique II (7) à travers le tuyau de sortie où le tuyau de sortie du réservoir de mélange II (6) s'installe la pompe à flux de fréquences variables intelligentes multi-fonctionnelles IV (13) ; Le diamètre dudit mélangeur statique I (5) est allant de 140 à 180 mm et sa longueur allant de 600 à 1000 mm ;

Le réservoir B (3) est connecté avec le mélangeur statique II (7) à travers le tuyau de sortie où le tuyau de sortie du réservoir B (3) s'installe la pompe à flux de fréquences variables intelligentes multi-fonctionnelles III (10) ; Le diamètre dudit mélangeur statique II (7) est allant de 200 à 250 mm et sa longueur allant de 100 à 200 mm.

10. Méthode d'utilisation d'un matériau de remplissage à changement de phase de polymère de sel hydraté selon l'une des revendications 1 à 8, caractérisée en ce que, le pistolet (8) est connecté avec le mélangeur statique II (7), le matériau de remplissage à changement de phase de polymère de sel hydraté sorti du mélangeur statique II (7) est pulvérisé à travers le pistolet (8), le pistolet (8) est équipé d'un système de détection de température infrarouge (9). Le système de détection de température infrarouge (9) est

connecté respectivement via signal de télécommunications avec pompe à flux de fréquences variables intelligentes multi-fonctionnelles I (11), pompe à flux de fréquences variables intelligentes multi-fonctionnelles II (12) , pompe à flux de fréquences variables intelligentes multi-fonctionnelles III (10), pompe à flux de fréquences variables intelligentes multi-fonctionnelles IV (13) ; le système de détection de température infrarouge (9) mesure à temps réel la température de moussage du matériau de remplissage de polymère. Cette température sera émise en forme de signal électronique vers les pompes à flux de fréquences variables intelligentes multi-fonctionnelles qui constatent et traitent les données électroniques pour régler le débit de chaque part. En détail, le débit des parts A et B est allant de 4 à 10 kg/min. Quand la température de moussage du matériau de remplissage de polymère est inférieure à 70 °C, le débit de la composition C est réglé entre 0,3 à 0,5 kg/min ; si la température de moussage du matériau de remplissage de polymère est allant de 70 à 95 °C, le débit de la composition C est ajusté entre 0,5 à 1 kg par minute, le débit des parts A et C est réglé à moins de 4 kg/min ; si la température de moussage du matériau de remplissage de polymère est supérieure à 95 °C, réduire le débit du mélange A-C et de la part B jusqu'à ce que le moussage soit arrêté.

DRAWINGS OF THE SPECIFICATION

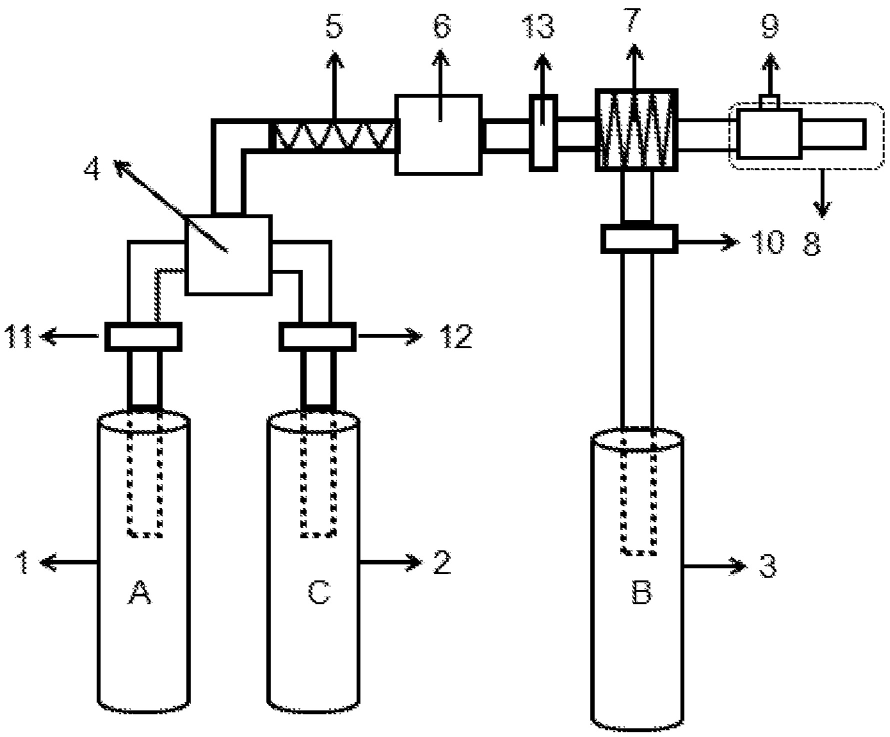

FIG. 1

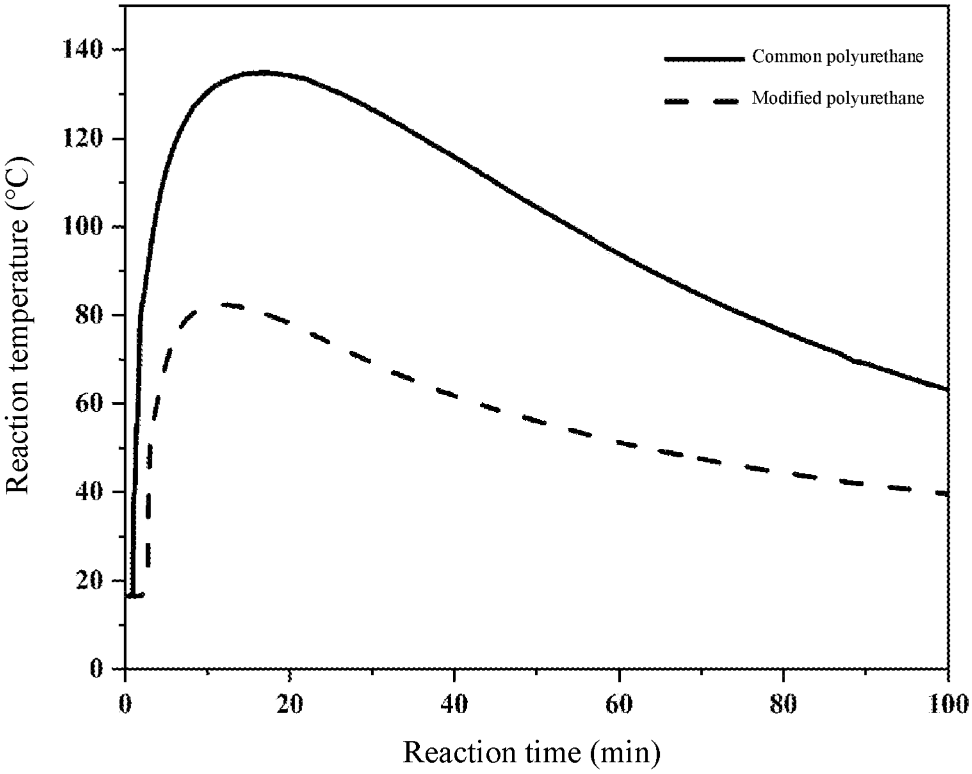

FIG. 2