

DESCRIPTION

TITLE OF INVENTION: COMPOSITE MODIFIED PILLARED MATERIAL AND PREPARATION METHOD THEREOF, FLUORINE-FREE AND ALKALI-FREE ACCELERATOR BASED THEREON AND PREPARATION METHOD THEREOF

TECHNICAL FIELD

[0001] The present disclosure belongs to the technical field of concrete admixtures. Specifically, the present disclosure relates to a composite modified pillared material modified with a hyperbranched quaternary ammonium salt and a preparation method thereof, as well as to a fluorine-free and alkali-free accelerator using the composite modified pillared material as a stabilizer and a preparation method thereof.

BACKGROUND

[0002] An accelerator is a concrete admixture that causes rapid setting and hardening of cement and concrete. The development strategy for accelerators is to utilize aluminum salts as the core component and to enhance the concentration of aluminum salts through various approaches. Fluorine-free and alkali-free accelerators can avoid the harm of alkali-aggregate reaction to concrete while also preventing hazards to production and life safety posed by fluorine-containing materials during preparation. Consequently, the development of fluorine-free and alkali-free accelerators is currently a research priority. To enhance the performance of fluorine-free and alkali-free accelerators, increasing the aluminum phase content is a mainstream strategy. However, excessively high aluminum salt content in turn leads to high supersaturation of the solution system and poor stability, resulting in issues such as product stratification. Therefore, a suitable stabilizer possesses significant practical importance.

[0003] Unlike traditional stabilizer materials, pillared materials have been extensively studied due to their inherent porous/intercalated inorganic structure which allows for wide-ranging modification, thereby imparting different structural characteristics. Currently, the more common modification targets are generally layered silicate materials, which often exhibit an orthorhombic crystal structure, such as kaolin, montmorillonite, sepiolite, and talc. Modification techniques include ion exchange modification with metal ions and intercalation modification with organic cations or anions. Among these, anionic surfactant modifications such as with sodium lauryl sulfate or cationic modifications such as with cetyltrimethylammonium bromide have been widely reported.

[0004] For instance, a technology relating to a supersaturated aluminum sulfate suspension-type alkali-free liquid accelerator and a preparation method thereof is provided. In this technology, the aluminum sulfate content ranges between 60% and 70%, and the stability of the supersaturated system is enhanced using ultrafine sepiolite powder and polyacrylamide. However, the supersaturated system employs 1% to 4% fluoride salts. The presence of fluoride ions is relatively unfavorable for the early strength of the product, often making it difficult to achieve 10 MPa. Improper dosage of polyacrylamide can readily lead to a crosslinking and flocculation effect, which is conversely detrimental to system stability. The preferred ultrafine sepiolite powder has an average particle size of less than 10 μm . Although this powder yields a significant improvement effect on system stability performance, because the ultrafine sepiolite powder is not subjected to modification treatment, the overall viscosity of the system is as high as 2000 $\text{mPa}\cdot\text{s}$ to 4000 $\text{mPa}\cdot\text{s}$, which is relatively unfavorable for practical application.

[0005] As another example, a technology exists for a modified sepiolite stabilizer for liquid accelerators and a preparation method thereof. This technology involves a method for modifying sepiolite, specifically performing the modification operation using cetyltrimethylammonium bromide and sodium silicate. However, the problem with the sepiolite stabilizer prepared by this method is that the surfactant cetyltrimethylammonium bromide, which modifies the sepiolite, gradually releases during accelerator preparation. Such release of the surfactant causes the system to generate a large quantity of bubbles. Furthermore, the saturated salt system of the accelerator is easily disturbed, subsequently leading to a phenomenon of deteriorating system stability.

[0006] As a further example, a technology exists for a special anti-settling agent for alkali-free accelerators, a preparation method thereof and an application thereof. This technology describes a method for modifying sepiolite using γ -methacryloxypropyltrimethoxysilane. In this method, sepiolite is modified with the silane and then mixed with a polymer obtained via free radical polymerization to serve as the special anti-settling agent. The mechanism relies on the synergistic co-action between the entanglement of polymer chains and the inherent three-dimensional network structure of sepiolite itself. However, the problems existing in this technology are: because the silane forms a hydrophobic layer on the surface of the sepiolite after affinity interaction, the sepiolite tends to agglomerate and is difficult to disperse in water, resulting in a deterioration of the dispersion effect. Additionally, because the polymer in this scheme is copolymerized under conditions where sepiolite is present, the presence of the sepiolite may affect the molecular weight of the final product, causing the polymer molecular

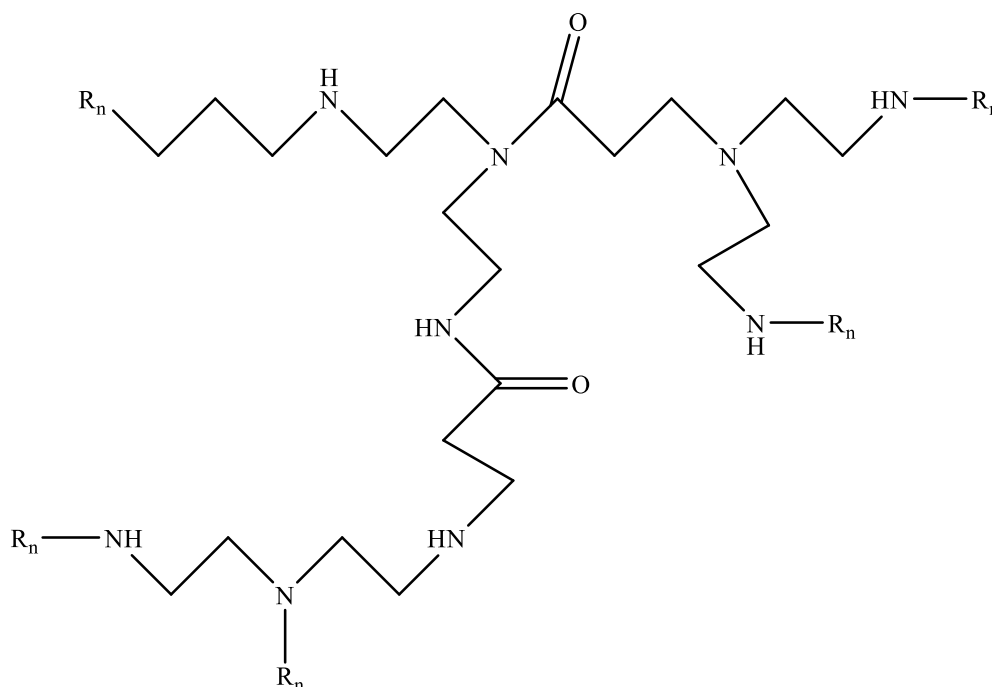
weight to be relatively low, the entanglement effect to be weakened, and the anti-settling effect to deteriorate. Apart from the aforementioned defects in preparation and use, because the polymer obtained via in-situ polymerization enhances stability through a three-dimensional cross-linked system, the overall viscosity of the system will be relatively high, leading to a weakening of the system's thixotropy, which is unfavorable for pumping during application and construction.

SUMMARY

[0007] In view of the technical problems associated with modifiers for pillared materials in the prior art, the present disclosure employs two types of hyperbranched quaternary ammonium salts to modify a pillared material, thereby obtaining a composite modified pillared material. This composite modified pillared material possesses a higher Cation Exchange Capacity (CEC), and delivers a superior improvement effect on long-term stability when applied as a stabilizer in an accelerator system.

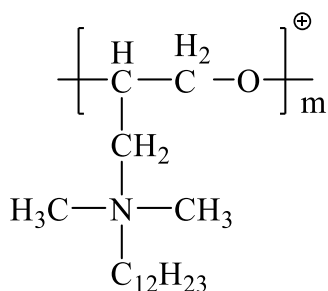
[0008] The present disclosure specifically adopts the following technical solutions:

[0009] A composite modified pillared material, wherein the composite modified pillared material includes a pillared material modified with a hyperbranched polyamine-based quaternary ammonium salt represented by the following Formula I or a hyperbranched quaternary ammonium salt represented by Formula II,



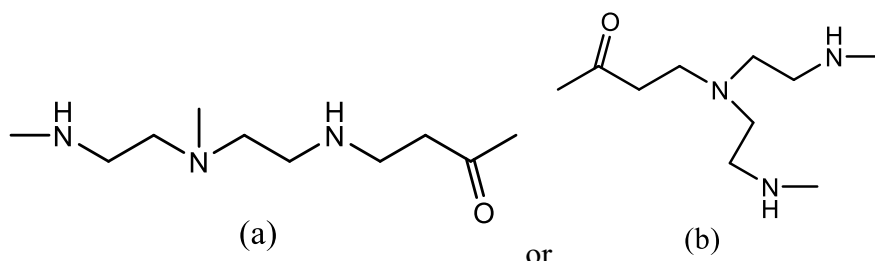
[0010]

[0011] Formula I



[0012]

[0013] Formula II



[0014]

[0015] Formula III

[0016] in Formula I, R is selected from the structures represented by (a) or (b) in Formula III, and n has a value ranging from 3 to 10; and in Formula II, m has a value ranging from 3 to 9.

[0017] It should be noted that regarding the selection of the substituent R in the aforementioned Formula I, it is not a singular choice of either the (a) structure or the (b) structure. Rather, during preparation and synthesis, both the (a) structure and the (b) structure are freely attached.

[0018] The hyperbranched polyamine-based quaternary ammonium salt represented by the aforementioned Formula I and the hyperbranched quaternary ammonium salt represented by Formula II, can all be prepared according to methods reported in the literature. Their preparation methods are not exhaustively detailed here. For example, the hyperbranched structure represented by Formula I can be prepared using the method recorded in the literature “Preparation and Properties of Amino-Terminated Hyperbranched Polymers and Its Quaternary Ammonium Salt”, and the hyperbranched polyamine-based quaternary ammonium salt can be further prepared from the hyperbranched polyamine represented by Formula I according to the method therein. The hyperbranched quaternary ammonium salt represented by Formula II can be prepared using the method recorded in the literature “Synthesis, Properties and Application of Hyperbranched Gemini Quaternary Ammonium Salt”.

[0019] The aforementioned pillared material can be sepiolite or hydrotalcite.

[0020] A method of preparing the aforementioned composite modified pillared material includes the step of:

[0021] mixing the aforementioned hyperbranched quaternary ammonium salt with the pillared material at a mass ratio of 5-10:100 to modify the resultant mixture, thereby obtaining the

composite modified pillared material.

[0022] Specifically, the modification method can be any one of conventional modification methods for pillared materials, including a direct intercalation method, a solution intercalation method, and a melt intercalation method.

[0023] The composite modified pillared material provided by the present disclosure uses the hyperbranched quaternary ammonium salt having the specific structure as the modifying material. Since the modifying material itself contains a branched structure, the modifying material differs from conventional modifying materials having a long-chain structure. This difference ensures a larger interlayer spacing and a higher CEC after the pillared material is intercalated.

[0024] A comparison with the modification effects of other conventional modifying materials in the prior art (determined via the Na^+ exchange measurement method) is shown in Table 1 below.

[0025] Table 1 CEC Values of Different Pillared Materials Before and After Modification with Different Modifying Materials

	CEC/(mol/1 kg) (based on Na^+)		
	Montmorillonite	Sepiolite	Hydrotalcite
Before Modification	0.8	0.2	0.1
Modified by Hyperbranched Quaternary Ammonium Salt Represented by Formula I	1.0	0.36	0.16
Modified by Hyperbranched Quaternary Ammonium Salt Represented by Formula II	0.9	0.40	0.18
Modified by Dodecyl Quaternary Ammonium Salt	1.1	0.28	0.11

[0026] In the aforementioned composite modified pillared material, the hyperbranched quaternary ammonium salt structure possesses strong resistance to acid, alkali, and salt. Furthermore, the CEC of the modified pillared material is significantly enhanced. This material is suitable for high-concentration fluorine-free and alkali-free accelerators, serving as the stabilizer therein. The increase in CEC for sepiolite and hydrotalcite after intercalation modification with the aforementioned hyperbranched quaternary ammonium salts is significantly greater than that for montmorillonite. This indicates that the hyperbranched quaternary ammonium salt is not suitable for every conventional pillared material. For this purpose, the present disclosure further provides a fluorine-free and alkali-free accelerator and

a preparation method thereof. Compared to traditional alkali-free accelerators, this fluorine-free and alkali-free accelerator increases the amount of aluminum sulfate therein by more than 10%, significantly raising the supersaturation of the accelerator solution system.

[0027] A fluorine-free and alkali-free accelerator includes the following uniformly mixed components (by weight percent):

[0028] aluminum sulfate: 60% to 66%;

[0029] complexing agent A: 4.5% to 9%;

[0030] complexing agent B: 0.3% to 3%;

[0031] ion stabilizer: 0.2% to 0.6%;

[0032] stabilizer: 0.6% to 1%;

[0033] the balance being water;

[0034] wherein the stabilizer is the aforementioned composite modified pillared material.

[0035] Generally, the maximum solubility of aluminum sulfate, the core component of alkali-free accelerators, under normal temperature conditions is 36 g/L (20°C), which falls far short of the performance requirements for practical application. Commonly available alkali-free accelerators on the market can typically achieve an aluminum sulfate content between 40% and 50%, with further increases being difficult. The final product solid content is around 50%. Further increasing the solid content leads to a substantial decline in system stability, including issues such as easy stratification, excessive viscosity, and prone to crystallization. The pillared material modified by the specific hyperbranched quaternary ammonium salt in the present disclosure is particularly suitable for fluorine-free and alkali-free accelerators with an aluminum sulfate concentration reaching above 60%. The advantages include: the modified poly-quaternary ammonium salt can provide more complexation sites, allowing the high CEC of this composite modified pillared material to provide interlayer exchange space for a large amount of supersaturated-state (exceeding conventional solubility) aluminum sulfate, reducing the probability of crystallization. Furthermore, the inherent characteristic of pillared materials, namely forming a three-dimensional network structure, is utilized to improve the overall system stability. Consequently, the effect of producing a high-concentration fluorine-free and alkali-free accelerator product is achieved, with the final product exhibiting good long-term stability and viscosity meeting construction requirements.

[0036] Further, the complexing agent A is selected from diethanolamine and/or triethanolamine. The complexing agent B is selected from at least one of ethylenediaminetetraacetic acid (EDTA), phosphoric acid, oxalic acid, and urea.

[0037] Further, the ion stabilizer is selected from at least one of glycerol, sodium

hexametaphosphate, sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfonate, sodium lauryl sulfate, and cetyltrimethylammonium bromide.

[0038] A method of preparing the aforementioned fluorine-free and alkali-free accelerator specifically includes the step of:

[0039] mixing the aforementioned components according to the predetermined weight percentages and dissolving the mixture uniformly, thereby obtaining the fluorine-free and alkali-free accelerator.

[0040] The fluorine-free and alkali-free accelerator provided by the present disclosure uses the aluminum sulfate component as the main aluminum phase component, leveraging the synergistic effects of components for complexation, stabilization, and viscosity reduction. Simultaneously, by using the composite modified pillared material of the present disclosure as the stabilizer, it is ensured that compared to traditional alkali-free accelerators, this fluorine-free and alkali-free accelerator increases the solid content by more than 10%, and the supersaturation of the accelerator solution system is significantly increased, thereby leading to performance enhancement. Moreover, this fluorine-free and alkali-free accelerator does not use alkali metal ions or fluoride salts, avoiding the impact of fluoride ions on early strength and the impact of alkali-aggregate reaction on later strength in the applied concrete. This is particularly valuable for early-strength shotcrete. The self-synthesized orthorhombic pillared stabilizer of the present disclosure utilizes charge and thixotropy. On the basis of ensuring product stability, the supersaturation of the fluorine-free and alkali-free accelerator system is increased, ensuring its excellent performance in concrete materials.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0041] Hereinafter, embodiments of the present disclosure will be described in detail. However, the present disclosure may be embodied in many different forms and should not be construed as limited to the specific embodiments set forth herein. Rather, these embodiments are provided to explain the principles of the present disclosure and their practical applications, thereby enabling others skilled in the art to understand the various embodiments of the present disclosure and various modifications suitable for particular intended applications.

[0042] Embodiment 1

[0043] This embodiment provides a composite modified pillared material and a preparation method thereof.

[0044] Specifically, 5 parts of the hyperbranched polyamine-based quaternary ammonium salt represented by Formula I ($n=3$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the composite modified pillared material.

[0045] Embodiment 2

[0046] This embodiment provides a composite modified pillared material and a preparation method thereof.

[0047] Specifically, 10 parts of the hyperbranched quaternary ammonium salt represented by Formula II ($m=3$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the composite modified pillared material.

[0048] Embodiment 3

[0049] This embodiment provides a composite modified pillared material and a preparation method thereof.

[0050] Specifically, 8 parts of the hyperbranched quaternary ammonium salt represented by Formula II ($m=9$) and 100 parts of hydrotalcite powder were mixed and intercalated via a melt intercalation method, thereby obtaining the composite modified pillared material.

[0051] Embodiment 4

[0052] This embodiment provides a composite modified pillared material and a preparation method thereof.

[0053] Specifically, 9 parts of the hyperbranched polyamine-based quaternary ammonium salt represented by Formula I ($n=10$) and 100 parts of sepiolite powder were mixed and intercalated via a melt intercalation method, thereby obtaining the composite modified pillared material.

[0054] Embodiment 5

[0055] Based on the composite modified pillared material provided in Embodiment 1, this embodiment uses the composite modified pillared material as a stabilizer to provide a fluorine-free and alkali-free accelerator and a preparation method thereof.

[0056] Specifically, the fluorine-free and alkali-free accelerator was obtained by heating, dissolving, and cooling according to the following mass ratios: aluminum sulfate octadecahydrate 62%, diethanolamine 7%, phosphoric acid 0.5%, stabilizer 0.8%, and the balance being water.

[0057] That is, the fluorine-free and alkali-free accelerator provided in this embodiment includes the following uniformly mixed components:

[0058] aluminum sulfate octadecahydrate: 62%;

[0059] diethanolamine: 7%;

[0060] phosphoric acid: 0.5%;

[0061] glycerol: 0.3%;

[0062] stabilizer: 0.8%;

[0063] the balance being water.

[0064] Embodiment 6

[0065] Based on the composite modified pillared material provided in Embodiment 2, this embodiment uses the composite modified pillared material as a stabilizer to provide a fluorine-free and alkali-free accelerator and a preparation method thereof.

[0066] Specifically, the fluorine-free and alkali-free accelerator was obtained by heating, dissolving, and cooling according to the following mass ratios: aluminum sulfate octadecahydrate 66%, diethanolamine 9%, phosphoric acid 0.5%, EDTA 1%, oxalic acid 0.5%, urea 0.5%, glycerol 0.3%, stabilizer 0.6%, and the balance being water.

[0067] That is, the fluorine-free and alkali-free accelerator provided in this embodiment includes the following uniformly mixed components:

[0068] aluminum sulfate octadecahydrate: 66%;

[0069] diethanolamine: 9%;

[0070] phosphoric acid: 0.5%;

[0071] EDTA: 1%;

[0072] oxalic acid: 0.5%;

[0073] urea: 0.5%;

[0074] glycerol: 0.3%;

[0075] stabilizer: 0.6%;

[0076] the balance being water.

[0077] Embodiment 7

[0078] Based on the composite modified pillared material provided in Embodiment 3, this embodiment uses the composite modified pillared material as a stabilizer to provide a fluorine-free and alkali-free accelerator and a preparation method thereof.

[0079] Specifically, the fluorine-free and alkali-free accelerator was obtained by heating, dissolving, and cooling according to the following mass ratios: aluminum sulfate octadecahydrate 60%, diethanolamine 4%, triethanolamine 1.5%, phosphoric acid 0.5%, glycerol 0.2%, sodium hexametaphosphate 0.1%, stabilizer 0.7%, and the balance being water.

[0080] That is, the fluorine-free and alkali-free accelerator provided in this embodiment includes the following uniformly mixed components:

[0081] aluminum sulfate octadecahydrate: 60%;

[0082] diethanolamine: 7%;

[0083] triethanolamine: 1.5%;

[0084] phosphoric acid: 0.3%;

[0085] glycerol: 0.2%;

[0086] sodium hexametaphosphate: 0.1%;

[0087] stabilizer: 0.7%;

[0088] the balance being water.

[0089] Embodiment 8

[0090] Based on the composite modified pillared material provided in Embodiment 3, this embodiment uses the composite modified pillared material as a stabilizer to provide a fluorine-free and alkali-free accelerator and a preparation method thereof.

[0091] Specifically, the fluorine-free and alkali-free accelerator was obtained by heating, dissolving, and cooling according to the following mass ratios: aluminum sulfate octadecahydrate 62%, diethanolamine 4.5%, phosphoric acid 0.5%, EDTA 0.5%, glycerol 0.2%, cetyltrimethylammonium bromide 0.2%, sodium lauryl sulfate 0.2%, stabilizer 0.7%, and the balance being water.

[0092] That is, the fluorine-free and alkali-free accelerator provided in this embodiment includes the following uniformly mixed components:

[0093] aluminum sulfate octadecahydrate: 62%;

[0094] diethanolamine: 4.5%;

[0095] phosphoric acid: 0.5%;

[0096] EDTA: 0.5%;

[0097] glycerol: 0.2%;

[0098] cetyltrimethylammonium bromide: 0.2%;

[0099] sodium lauryl sulfate: 0.2%;

[0100] stabilizer: 0.7%;

[0101] the balance being water.

[0102] Embodiment 9

[0103] Based on the composite modified pillared material provided in Embodiment 1, this embodiment uses the composite modified pillared material as a stabilizer to provide a fluorine-free and alkali-free accelerator and a preparation method thereof.

[0104] Specifically, the fluorine-free and alkali-free accelerator was obtained by heating, dissolving, and cooling according to the following mass ratios: aluminum sulfate octadecahydrate 61%, diethanolamine 6%, phosphoric acid 0.3%, glycerol 0.3%, SDBS 0.3%, stabilizer 1%, and the balance being water.

[0105] That is, the fluorine-free and alkali-free accelerator provided in this embodiment includes the following uniformly mixed components:

[0106] aluminum sulfate octadecahydrate: 61%;

[0107] diethanolamine: 6%;

[0108] phosphoric acid: 0.3%;

[0109] glycerol: 0.3%;

[0110] SDBS: 0.3%;

[0111] stabilizer: 1%;

[0112] the balance being water.

[0113] To verify the effects of the fluorine-free and alkali-free accelerators provided in the above embodiments, especially the stabilizing effect of the stabilizer therein, the following comparative experiments were performed.

[0114] Comparative Embodiment 1

[0115] The setting of this comparative embodiment aims to form a comparison with Embodiment 5 that lacks a stabilizer, to illustrate the impact of the stabilizer on the performance of the fluorine-free and alkali-free accelerator.

[0116] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0117] aluminum sulfate octadecahydrate: 62%;

[0118] diethanolamine: 7%;

[0119] phosphoric acid: 0.5%;

[0120] glycerol: 0.3%;

[0121] the balance being water.

[0122] Due to the absence of the modified pillared material to provide stability for the supersaturated-state accelerator, this comparative fluorine-free and alkali-free accelerator quickly coagulated and precipitated after cooling and standing, completely lost fluidity, and became unusable.

[0123] Comparative Embodiment 2

[0124] The setting of this comparative embodiment aims to form a comparison with Embodiment 5 having an excessive amount of aluminum sulfate, to illustrate the impact of the aluminum sulfate amount on the performance of the fluorine-free and alkali-free accelerator.

[0125] This comparative embodiment provides a comparative fluorine-free and alkali-free accelerator. The only difference from Embodiment 5 is that the amount of aluminum sulfate octadecahydrate was adjusted to 67%, and the amount of water was reduced correspondingly; and the rest referred to Embodiment 5.

[0126] Although the supersaturation was increased to form a high-concentration system under the synergistic action of the complexing agent, ion stabilizer, and stabilizer, when the aluminum

sulfate amount exceeded a critical point, the excess aluminum sulfate acted as crystal nuclei, thereby reducing the system stability. Consequently, in this comparative embodiment, this comparative fluorine-free and alkali-free accelerator quickly coagulated and precipitated after cooling and standing, completely lost fluidity, and became unusable.

[0127] Comparative Embodiment 3

[0128] The setting of this comparative embodiment aims to form a comparison lacking complexing agent A, to illustrate the impact of complexing agent A on the performance of the fluorine-free and alkali-free accelerator.

[0129] This comparative embodiment provides a comparative fluorine-free and alkali-free accelerator, wherein the composite modified pillared material provided in the aforementioned Embodiment 2 is used as the stabilizer.

[0130] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0131] aluminum sulfate octadecahydrate: 61%;

[0132] phosphoric acid: 0.5%;

[0133] EDTA: 1%;

[0134] oxalic acid: 0.5%;

[0135] urea: 0.5%;

[0136] cetyltrimethylammonium bromide: 0.2%;

[0137] stabilizer: 0.8%;

[0138] the balance being water.

[0139] Due to the lack of complexing agent A, the aluminum sulfate exceeding its solubility in water could not be fully dissolved during accelerator synthesis. An effectively constructed stable system product in a supersaturated state could not be achieved, resulting in a failed product preparation.

[0140] Comparative Embodiment 4

[0141] The setting of this comparative embodiment aims to form a comparison lacking complexing agent B, to illustrate the impact of complexing agent B on the performance of the fluorine-free and alkali-free accelerator.

[0142] This comparative embodiment provides a comparative fluorine-free and alkali-free accelerator, wherein the composite modified pillared material provided in the aforementioned Embodiment 2 is used as the stabilizer.

[0143] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0144] aluminum sulfate octadecahydrate: 66%;

[0145] diethanolamine: 9%;

[0146] glycerol: 0.2%;

[0147] stabilizer: 0.6%;

[0148] the balance being water.

[0149] This comparative fluorine-free and alkali-free accelerator, due to the absence of complexing agent B, exhibited excessively high viscosity in the product solution system in the supersaturated state, and was greatly affected by temperature. The cooled solution easily precipitated and solidified, losing fluidity, thereby rendering the product unusable.

[0150] Comparative Embodiment 5

[0151] This comparative embodiment provides a comparative fluorine-free and alkali-free accelerator, wherein the composite modified pillared material provided in the aforementioned Embodiment 1 is used as the stabilizer.

[0152] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0153] aluminum sulfate octadecahydrate: 62%;

[0154] diethanolamine: 7%;

[0155] phosphoric acid: 0.5%;

[0156] stabilizer: 0.8%;

[0157] the balance being water.

[0158] Due to the absence of an ion stabilizer, the stability of the solution system of this comparative fluorine-free and alkali-free accelerator was reduced, readily leading to partial component precipitation, thereby resulting in excessively high system viscosity.

[0159] Comparative Embodiment 6

[0160] The setting of this comparative embodiment aims to form a comparison with an excessive amount of complexing agent B, to illustrate the impact of the amount of complexing agent B on the performance of the fluorine-free and alkali-free accelerator.

[0161] This comparative embodiment provides a comparative fluorine-free and alkali-free accelerator, wherein the composite modified pillared material provided in the aforementioned Embodiment 1 is used as the stabilizer.

[0162] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0163] aluminum sulfate octadecahydrate: 60%;

[0164] diethanolamine: 6%;

[0165] triethanolamine: 1%;

[0166] phosphoric acid: 1%;

[0167] EDTA: 2.5%;

[0168] stabilizer: 0.8%;

[0169] sodium hexametaphosphate: 0.4%;

[0170] the balance being water.

[0171] The complexing agent B in this comparative fluorine-free and alkali-free accelerator exceeded the recommended dosage range. Although stability showed improvement, the viscosity was excessively high, thereby rendering the accelerator unusable. Furthermore, negative side effects manifested, affecting concrete strength.

[0172] Comparative Embodiment 7

[0173] The setting of this comparative embodiment aims to form a comparison with a hyperbranched quaternary ammonium salt represented by Formula II having a higher degree of branching, to illustrate the impact of the degree of branching of the hyperbranched quaternary ammonium salt on the performance of the fluorine-free and alkali-free accelerator.

[0174] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0175] Specifically, 10 parts of the hyperbranched quaternary ammonium salt represented by Formula II ($m=10$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0176] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative stabilizer therein.

[0177] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0178] aluminum sulfate octadecahydrate: 63%;

[0179] diethanolamine: 8%;

[0180] phosphoric acid: 0.4%;

[0181] EDTA: 1%;

[0182] oxalic acid: 0.5%;

[0183] urea: 0.5%;

[0184] glycerol: 0.3%;

[0185] comparative stabilizer: 0.7%;

[0186] the balance being water.

[0187] This comparative fluorine-free and alkali-free accelerator, due to the excessively high degree of branching of the hyperbranched quaternary ammonium salt therein, exhibited insufficient water solubility and poor intercalation effect, leading to inadequate stabilizing performance. Consequently, this comparative fluorine-free and alkali-free accelerator showed obvious stratification after standing for 1 day, had excessively high viscosity, and became unusable.

[0188] Comparative Embodiment 8

[0189] The setting of this comparative embodiment aims to form a comparison with a hyperbranched quaternary ammonium salt represented by Formula II having a lower degree of branching, to illustrate the impact of the degree of branching of the hyperbranched quaternary ammonium salt on the performance of the fluorine-free and alkali-free accelerator.

[0190] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0191] Specifically, 10 parts of the hyperbranched quaternary ammonium salt represented by Formula II ($m=2$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0192] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative stabilizer therein.

[0193] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0194] aluminum sulfate octadecahydrate: 61%;

[0195] diethanolamine: 6%;

[0196] phosphoric acid: 0.3%;

[0197] glycerol: 0.3%;

[0198] SDBS: 0.3%;

[0199] comparative stabilizer: 1%;

[0200] the balance being water.

[0201] This comparative fluorine-free and alkali-free accelerator, due to the relatively low degree of branching of the hyperbranched quaternary ammonium salt therein, exhibited overall slightly inferior stabilizing performance. Consequently, this comparative fluorine-free and alkali-free accelerator showed obvious stratification after standing for 1 day, had excessively high viscosity, and became unusable.

[0202] Comparative Embodiment 9

[0203] The setting of this comparative embodiment aims to form a comparison with a hyperbranched quaternary ammonium salt represented by Formula I having a higher degree of branching, to illustrate the impact of the degree of branching of the hyperbranched quaternary ammonium salt on the performance of the fluorine-free and alkali-free accelerator.

[0204] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0205] Specifically, 8 parts of the hyperbranched quaternary ammonium salt represented by Formula I ($n=11$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0206] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative stabilizer therein.

[0207] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0208] aluminum sulfate octadecahydrate: 61%;

[0209] diethanolamine: 6%;

[0210] phosphoric acid: 0.3%;

[0211] glycerol: 0.3%;

[0212] SDBS: 0.3%;

[0213] comparative stabilizer: 1%;

[0214] the balance being water.

[0215] This comparative fluorine-free and alkali-free accelerator, due to the excessively high degree of branching of the hyperbranched quaternary ammonium salt therein, produced molecules of excessive size, which hindered effective intercalation, resulting in overall slightly inferior stabilizing performance. Consequently, this comparative fluorine-free and alkali-free accelerator showed obvious stratification after standing for 1 day, had excessively high viscosity, and became unusable.

[0216] Comparative Embodiment 10

[0217] The setting of this comparative embodiment aims to form a comparison with a hyperbranched quaternary ammonium salt represented by Formula I having a lower degree of branching, to illustrate the impact of the degree of branching of the hyperbranched quaternary ammonium salt on the performance of the fluorine-free and alkali-free accelerator.

[0218] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0219] Specifically, 8 parts of the quaternary ammonium salt prepared from the hyperbranched polyamine represented by Formula I ($n=2$) and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0220] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative stabilizer therein.

[0221] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0222] aluminum sulfate octadecahydrate: 61%;

[0223] diethanolamine: 6%;

[0224] phosphoric acid: 0.3%;

[0225] glycerol: 0.3%;

[0226] SDBS: 0.3%;

[0227] comparative stabilizer: 1%;

[0228] the balance being water.

[0229] This comparative fluorine-free and alkali-free accelerator, due to the relatively low degree of branching of the hyperbranched quaternary ammonium salt therein, exhibited an intercalation effect close to that of conventional surfactant-type intercalation, showing no significant advantage, and thus exhibited overall slightly inferior stabilizing performance. Consequently, this comparative fluorine-free and alkali-free accelerator showed obvious stratification after standing for 1 day, had excessively high viscosity, and became unusable.

[0230] Comparative Embodiment 11

[0231] The setting of this comparative embodiment aims to change the type of pillared material in the composite modified pillared material, to illustrate the impact of the type of pillared material on the performance of the fluorine-free and alkali-free accelerator.

[0232] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0233] Specifically, 8 parts of the hyperbranched polyamine-based quaternary ammonium salt represented by Formula I ($n=3$) and 100 parts of kaolin powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0234] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative

stabilizer therein.

[0235] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0236] aluminum sulfate octadecahydrate: 61%;

[0237] diethanolamine: 6%;

[0238] phosphoric acid: 0.3%;

[0239] glycerol: 0.3%;

[0240] SDBS: 0.3%;

[0241] comparative stabilizer: 1%;

[0242] the balance being water.

[0243] Since kaolin itself is a triclinic material, interlayer modification via intercalation cannot be performed due to strong hydrogen bonding. Therefore, kaolin performs poorly as a pillared material. When the comparative composite modified pillared material prepared as described above was applied to the comparative fluorine-free and alkali-free accelerator, significant stratification and high viscosity were observed after 1 day, rendering the comparative fluorine-free and alkali-free accelerator unsuitable for engineering application.

[0244] Comparative Embodiment 12

[0245] The setting of this comparative embodiment aims to employ a different intercalating material for the pillared material within the composite modified pillared material, to illustrate the impact of the type of intercalating material on the performance of the fluorine-free and alkali-free accelerator.

[0246] This comparative embodiment provides a comparative composite modified pillared material and a preparation method thereof.

[0247] Specifically, 5 parts of SDBS and 100 parts of sepiolite powder were mixed and intercalated via a solution intercalation method, thereby obtaining the comparative composite modified pillared material.

[0248] The comparative composite modified pillared material prepared above was used to prepare a comparative fluorine-free and alkali-free accelerator, serving as the comparative stabilizer therein.

[0249] The comparative fluorine-free and alkali-free accelerator provided in this comparative embodiment includes the following uniformly mixed components:

[0250] aluminum sulfate octadecahydrate: 61%;

[0251] diethanolamine: 6%;

[0252] phosphoric acid: 0.3%;

[0253] glycerol: 0.3%;

[0254] sodium hexametaphosphate: 0.3%;

[0255] comparative stabilizer: 1%;

[0256] the balance being water.

[0257] This comparative fluorine-free and alkali-free accelerator exhibited overall slightly inferior stabilizing performance, showed obvious stratification after standing for 1 day, had excessively high viscosity, and became unusable.

[0258] Comparative Embodiment 13

[0259] This comparative embodiment provides a commercially available mature fluorine-containing alkali-free accelerator for comparison, the specific model of which is Sobute SBT-N (II).

[0260] To verify the application effects of the aforementioned accelerators, application tests were conducted on the fluorine-free and alkali-free accelerators provided in Embodiments 5-9, the comparative fluorine-free and alkali-free accelerators provided in Comparative Embodiments 2-11, the fluorine-free and alkali-free accelerator prepared with conventional modified material from Comparative Embodiment 12, and the fluorine-containing alkali-free accelerator from the market in Comparative Embodiment 13.

[0261] The mix proportions of shotcrete for the application tests are shown in Table 2 below. The corresponding dosage (dosage converted based on the amount of cementitious material), rebound rate in field shotcrete tests, and 8-hour core strength are shown in Table 3 below.

[0262] Table 2 Mix Proportions of Shotcrete for Application Tests of Various Accelerators

Cement	Sand	Coarse Aggregate	Water-Reducing Admixture	Water-Cement Ratio
480 kg	800 kg	800 kg	4.5 kg	0.38

[0263] Table 3 Corresponding Dosage, Rebound Rate, and 8-Hour Core Strength During Application Tests of Various Accelerators

	Average Dosage	Rebound Rate	8-Hour Core Strength / MPa
Embodiment 5	8%	6%-8%	10.5
Embodiment 6	7%	5%-7%	12.1
Embodiment 7	9%	9%-13%	11.3
Embodiment 8	8%	6%-8%	10.0

Embodiment 9	8%	6%-8%	10.8
Comparative Embodiment 2	4%-6%	15%-25%	5.7
Comparative Embodiment 3	4%-5%	20%-25%	4.0
Comparative Embodiment 4	4%-5%	20%-25%	5.3
Comparative Embodiment 13	8%	10%-15%	5.2

[0264] As can be seen from Table 3, in Comparative Embodiment 2, because the aluminum sulfate content was higher, stability could not be guaranteed. An actual dosage of 4%-6% under actual working pump pressure resulted in a rebound rate as high as 15%-25%. In Comparative Embodiment 3, because the stabilizer dosage was relatively high, the viscosity was excessively high. Consequently, the shotcrete machine, operating at full capacity with an actual dosage of only 4%-5%, resulted in a rebound rate as high as 20%-25%, and the actual dosage could not be guaranteed. In Comparative Embodiment 4, on one hand, the viscosity of this stabilizer was relatively high, causing the shotcrete machine operating at full capacity with an actual dosage of only 4%-5% to result in a rebound rate as high as 20%-25%. On the other hand, the relatively low dosage of this stabilizer would lead to decreased long-term stability. Furthermore, the 8-hour core strengths in all Embodiments were significantly higher than those in the Comparative Embodiments, indicating that the fluorine-free and alkali-free accelerator based on the aforementioned composite modified pillared material has a positive effect on the strength development of early-age shotcrete.

[0265] Generally, the rebound rate of shotcrete should be controlled within 15%. A rate below 10% is considered excellent, while a rate close to 5% is considered extremely excellent. It can thus be seen that the aforementioned fluorine-free and alkali-free accelerators of the present disclosure have extremely excellent application effects.

[0266] Simultaneously, the performance and stability of the accelerators provided in the aforementioned Embodiments and Comparative Embodiments were tested. The specific test method was as follows: reference cement was used to test the setting time and mortar strength, with an accelerator dosage of 8%.

[0267] The test results are shown in Table 4 below.

[0268] Table 4 Performance and Stability of Various Accelerators

	Initial/Final Setting Time (min:s)	6-Hour Strength / MPa	1-Day Strength / MPa	28-Day Compressive Strength Ratio	Solid Content	Accelerator Viscosity / cP	28-Day Bleeding Rate
Blank	/	0.2	15	/	/	/	/
Embodiment 5	2:00/4:40	1.1	12	102	60.4%	400	<2%
Embodiment 6	1:30/3:20	1.6	15	105	63.8%	520	<1%
Embodiment 7	3:50/9:40	1.0	9	97	59%	250	<4%
Embodiment 8	2:00/4:30	1.1	12	102	60.2%	400	<2%
Embodiment 9	2:40/6:30	1.0	11	99	59.6%	320	<2%
Embodiment 6	2:00/4:40	1.2	12	102	/	380	≈10%
Comparative Embodiment 1	2:00/4:40	/	/	/	58.9%	/	≈40%
Comparative Embodiment 2	2:00/4:40	/	/	/	64.6%	850	≈20%
Comparative Embodiment 3	2:00/4:40	1.5	15	105	59.7%	950	≈10%
Comparative Embodiment 4	1:30/3:20	1.6	15	105	63.5%	670	≈20%

Comparative Embodiment 5	2:00/4:40	/	/	/	58.7%	/	≈50%
Comparative Embodiment 6	4:00/10:00	0.78	9.2	95	58%	800	<4%
Comparative Embodiment 7	2:30/6:00	1.0	11	100	59.5%	980	≈20%
Comparative Embodiment 8	2:30/6:00	1.0	11	100	59.5%	780	≈10%
Comparative Embodiment 9	2:30/6:00	1.0	11	100	59.5%	650	≈20%
Comparative Embodiment 10	2:30/6:00	1.0	11	100	59.5%	720	≈10%
Comparative Embodiment 11	2:30/6:00	1.0	11	100	59.5%	900	≈8%
Comparative Embodiment 12	2:50/6:40	0.9	10.2	98	59.5%	800	≈9%
Comparative Embodiment 13	1:30/3:40	0.3	8	96	49.5%	180	≈5%

ve

Embodime

nt 13

[0269] Note: Mortar tests were conducted according to QCR-807-2020 specifications.

[0270] The data in Table 4 demonstrate that the products of the Embodiments achieve early high strength through synergy among the high aluminum phase, complexing agents, and auxiliary additives. Furthermore, under high solid content conditions, the products of these embodiments exhibited relatively reasonable viscosity (generally close to or below 500 cP) and very good stability (28-day bleeding rate < 5%). A viscosity above 600 cP may adversely affect actual shotcreting, causing insufficient dosage, uneven dispersion, or even pipe blockage. Additionally, in mortar experiments using reference cement, the products of the Embodiments all achieved mortar strengths greater than 1 MPa at 6 hours and greater than 8 MPa at 1 day, achieving the effect of early high strength.

[0271] Comparative Embodiments 1-6 involve the comparative fluorine-free and alkali-free accelerators prepared using the composite modified pillared materials from Embodiments 1-4. In the aforementioned mix proportions, the necessity of each component is crucial: the effect of complexing agent A and the dosage of aluminum sulfate are equally critical for system stability. Other components, such as complexing agent B and ion stabilizer materials, also significantly affect system properties such as viscosity and stability.

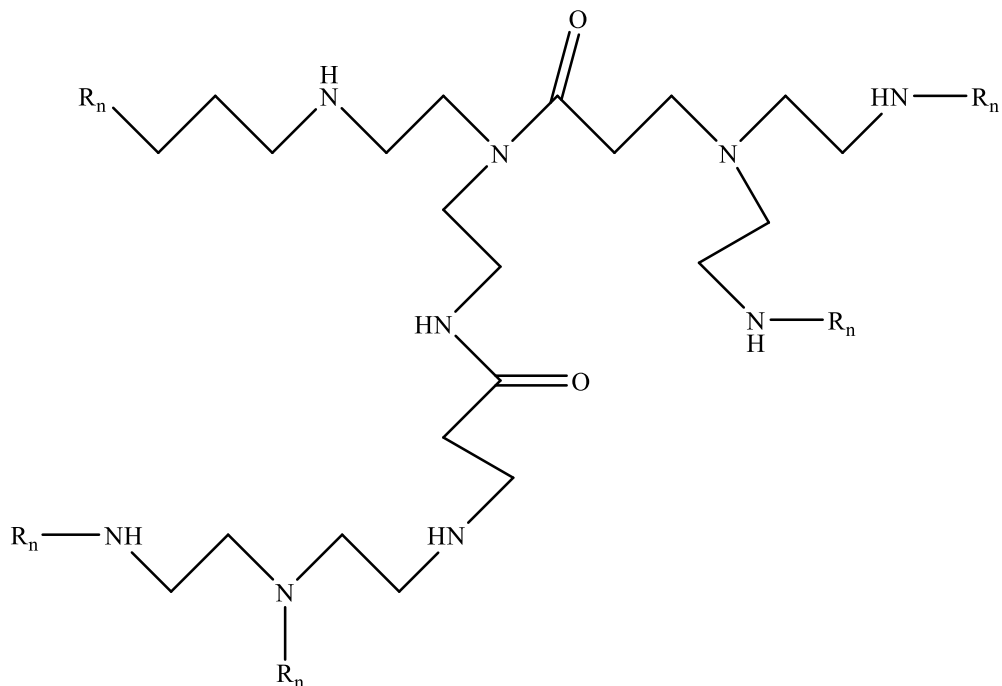
[0272] Comparative Embodiments 7-12 evaluate the impact of different modifying and pillared materials on system performance under identical mix proportion conditions. Although the mix proportions are identical, the resulting viscosity and bleeding rates differ. Kaolin induces the highest viscosity, which in turn results in a relatively lower bleeding rate. The SDBS-modified pillared material provides some stabilizing effect, but yields both higher viscosity and lower stability compared to those of the products of the Embodiments. Furthermore, modification with unsuitable structures as shown in Formulas I and II also produced inferior performance relative to the baseline product.

[0273] Comparative Embodiment 13 is a comparison with a commercially available fluorine-containing product. This product has lower solid content, low viscosity, good stability, and fast setting, but its early strength is significantly inferior to that of the fluorine-free and alkali-free products.

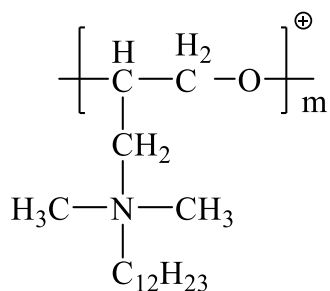
CLAIMS

What is claimed is:

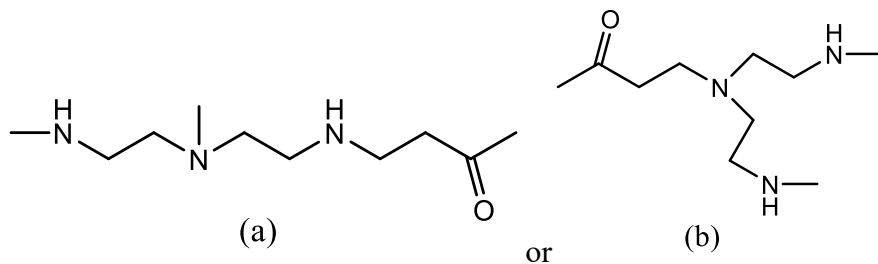
1. A composite modified pillared material, comprising a pillared material modified with a hyperbranched polyamine-based quaternary ammonium salt represented by the following Formula I or a hyperbranched quaternary ammonium salt represented by Formula II,



Formula I



Formula II



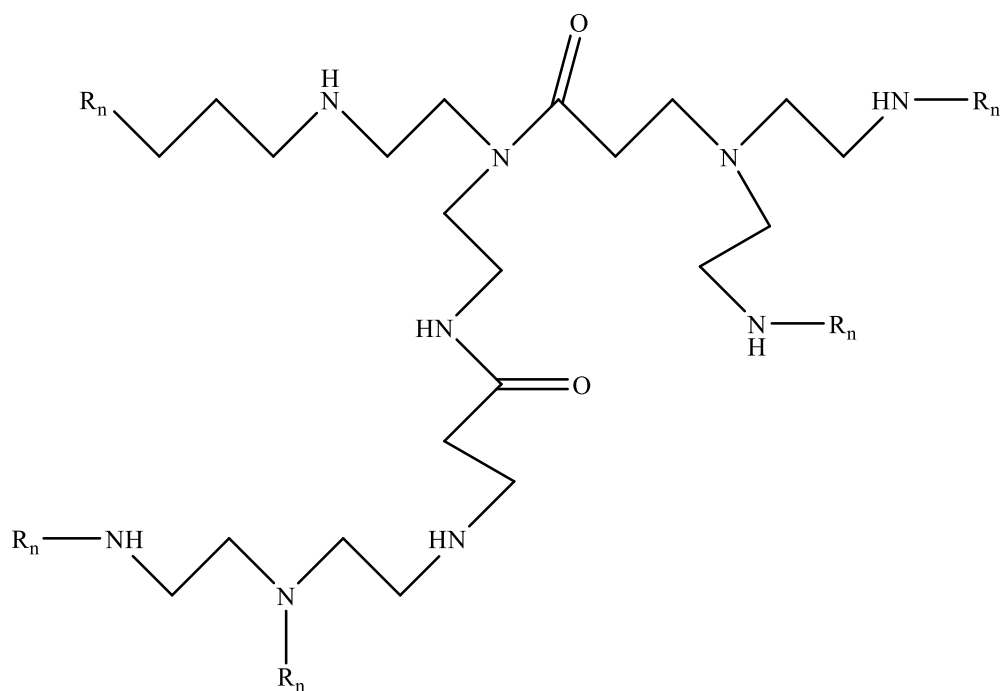
Formula III

in Formula I, R is selected from the structures represented by (a) or (b) in Formula III, and

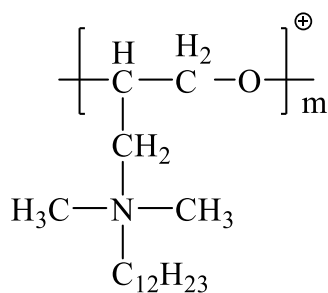
n has a value ranging from 3 to 10; and in Formula II, m has a value ranging from 3 to 9; and wherein the pillared material is sepiolite or hydrotalcite.

2. A method of preparing the composite modified pillared material according to claim 1, comprising the step of:

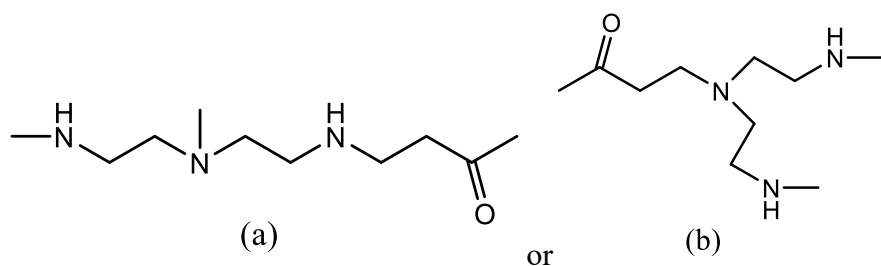
mixing the hyperbranched polyamine-based quaternary ammonium salt represented by the following Formula I or the hyperbranched quaternary ammonium salt represented by Formula II with the pillared material at a mass ratio of 5-10:100 to modify the resultant mixture, thereby obtaining the composite modified pillared material;



Formula I



Formula II



Formula III

in Formula I, R is selected from the structures represented by (a) or (b) in Formula III, and n has a value ranging from 3 to 10; and in Formula II, m has a value ranging from 3 to 9; and wherein the pillared material is sepiolite or hydrotalcite.

3. The preparation method according to claim 2, wherein the modification method is selected from the group consisting of a direct intercalation method, a solution intercalation method, and a melt intercalation method.

4. A fluorine-free and alkali-free accelerator, comprising the following uniformly mixed components:

aluminum sulfate: 60% to 66%;
complexing agent A: 4.5% to 9%;
complexing agent B: 0.3% to 3%;
ion stabilizer: 0.2% to 0.6%;
stabilizer: 0.6% to 1%;
the balance being water; and

wherein the stabilizer is the composite modified pillared material according to claim 1.

5. The fluorine-free and alkali-free accelerator according to claim 4, wherein the complexing agent A is selected from diethanolamine and/or triethanolamine.

6. The fluorine-free and alkali-free accelerator according to claim 4, wherein the complexing agent B is selected from at least one of ethylenediaminetetraacetic acid (EDTA), phosphoric acid, oxalic acid, and urea.

7. The fluorine-free and alkali-free accelerator according to claim 4, wherein the ion stabilizer is selected from at least one of glycerol, sodium hexametaphosphate, sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfonate, sodium lauryl sulfate, and cetyltrimethylammonium bromide.

8. A method of preparing the fluorine-free and alkali-free accelerator according to any one of claims 4 to 7, comprising the step of:

uniformly dissolving and dispersing 60% to 66% aluminum sulfate, 4.5% to 9% complexing agent A, 0.3% to 3% complexing agent B, 0.2% to 0.6% ion stabilizer, and 0.6% to 1% stabilizer in the balance of water, thereby obtaining the fluorine-free and alkali-free accelerator; wherein the components are present in percentages by weight, and the total weight of the fluorine-free and alkali-free accelerator is 100%; and

wherein the stabilizer is the composite modified pillared material according to claim 1.