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(54) Benævnelse: **PHENOLHARPIKS, FREMSTILLINGSMETODE, EFTERBEHANDLINGSSAMMENSÆTNING TIL MINERALFIBRE OG RESULTERENDE PRODUKTER**

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PHENOLIC RESIN, PREPARATION METHOD, SIZING COMPOSITION FOR MINERAL FIBERS AND RESULTING PRODUCTS

The invention relates to a phenolic resin intended to be used in the formulation of a sizing composition for mineral fibers. This resin is obtained by the condensation of phenol, formaldehyde and an amine in the presence of a basic catalyst, and it is characterized by a low content of free formaldehyde and free phenol.

The invention relates to a method of preparing this resin, to the sizing composition for mineral fibers that contains said resin, and to the insulating products that result therefrom.

Insulation products based on mineral fibers may be formed from fibers obtained by various processes, for example using the known technique of internal or external centrifugal fiberizing. The centrifugation consists in introducing molten material (in general glass or rock) into a spinner that has a multitude of small holes, the material being projected against the peripheral wall of the device under the action of the centrifugal force and escaping therefrom in the form of filaments. On leaving the spinner, the filaments are attenuated and entrained by a high-velocity high-temperature gas stream to a receiving member in order to form a web of fibers.

To assemble the fibers together and provide the web with cohesion, the fibers, on leaving the spinner, are sprayed with a sizing composition containing a thermosetting resin. The web of fibers coated with the size undergoes a heat treatment (at a temperature above 100°C) so as to polycondense the resin and thus obtain a thermal and/or acoustic insulation product having specific properties, especially dimensional stability, tensile strength, thickness recovery after compression, and uniform color.

The sizing composition is made up of the resin, which in general takes the form of an aqueous solution, of additives, such as urea, silanes, mineral oils,

aqueous ammonia and ammonium sulphate, and of water. The sizing composition is usually sprayed onto the fibers.

The properties of the sizing composition depend largely on the characteristics of the resin. From the standpoint of the application, it is necessary for the sizing composition to have good sprayability and be able to be deposited on the surface of the fibers so as to bond them effectively. The sprayability is directly related to the capability that the resin possesses of being able to be diluted in a large amount of water and to remain stable over time.

The dilution capability is characterized by the “dilutability”, which is defined as the volume of deionized water that it is possible, at a given temperature, to add to a unit volume of the aqueous resin solution before the appearance of permanent cloudiness. In general, a resin is considered to be able to be used as a size when its dilutability at 20°C is 1000% or higher.

The resin must still be stable over a given lapse of time before being used to form the sizing composition, which composition is generally prepared at the moment of use by mixing the resin and the abovementioned additives. In particular, the resin must be stable for at least 8 days at a temperature of around 12 to 18°C.

The resin that can be used in a sprayable sizing composition must have dilutability at 20°C of 1000% or higher, preferably 2000% or higher (infinite dilutability), for at least 8 days.

From the regulatory standpoint, it is necessary for the resin to be considered as non-polluting, that is to say for it to contain – and generate during the binding operation or subsequently – as few as possible compounds considered to be harmful to human health or to the environment.

The thermosetting resins most commonly used are phenolic resins belonging to the family of resoles. Apart from their good crosslinkability under the aforementioned thermal conditions, these resins are very soluble in water, possess good affinity for mineral fibers, especially glass fibers, and are relatively inexpensive.

These resins are obtained by the condensation of phenol and formaldehyde, in the presence of a basic catalyst, in a formaldehyde/phenol molar ratio generally greater than 1 so as to promote the reaction between the phenol and the formaldehyde and to reduce the residual phenol content in the resin. The residual amount of formaldehyde and phenol in the resin remains high.

To reduce the amount of residual formaldehyde, it is known to add a sufficient amount of urea to the resin, the urea reacting with the free formaldehyde, forming urea-formaldehyde condensates (see EP 0 148 050 A1). The resin obtained contains phenol-formaldehyde and urea-formaldehyde condensates, has a free formaldehyde and free phenol content, expressed with respect to the total weight of liquid, of 3% and 0.5%, respectively, or less, and a water dilutability of at least 1000%.

Although the amount of residual phenol is acceptable, the amount of residual formaldehyde is however too high to meet the current regulatory constraints.

Moreover, it has been found that the resin is not stable under the conditions that are applied during the treatment of the sized fibers for the purpose of crosslinking the resin in order to form the final insulating products. At the temperature of the treatment, generally above 100°C in an oven, the urea-formaldehyde condensates are degraded and they release formaldehyde, which increases the undesirable gas emissions into the atmosphere. Formaldehyde may also be released from the end product during its use as thermal and/or acoustic insulation.

EP 0 480 778 A1 has proposed to substitute part of the urea with an amine, which reacts with the free phenol and the free formaldehyde via the Mannich reaction to form a condensation product having improved thermal stability. The free phenol and free formaldehyde contents of this resin are 0.20% or less and 3% or less, respectively.

One subject of the present invention is a phenolic resin which has characteristics sufficient for it to be used in a sprayable sizing composition, which has a low capacity for producing undesirable emissions, especially by having a

low free formaldehyde content and a low free phenol content, and which generates little formaldehyde during its use.

Another subject of the invention is a method of producing the resin, which does not involve urea in order to reduce the free formaldehyde content.

Another subject of the invention is a sizing composition comprising said resin, its use for binding mineral fibers, with the view to forming thermal and/or acoustic insulation products, and the products thus obtained.

The liquid phenolic resin according to the invention, intended to be used in a sizing composition for mineral fibers, essentially contains phenol-formaldehyde (P-F) condensates belonging to the family of resoles and phenol-formaldehyde-amine (P-F-A) condensates. The resin has a free formaldehyde content of 0.3% or less and a free phenol content of 0.5% or less, these contents being expressed with respect to the total weight of liquid.

Preferably, the resin has a free formaldehyde content of 0.2% or less with respect to the total weight of liquid, and advantageously of 0.1% or less.

Preferably, the free phenol content of the resin is 0.4% or less.

The resin has a dilutability, measured at 20°C, of at least 1000%.

The resin is also thermally stable, as it is free of urea-formaldehyde (U-F) condensates known for their degradability under the effect of temperature. As for the P-F-A condensates, these are stable under the aforementioned conditions – they generate little formaldehyde for example – in particular during ageing of the final insulating product.

The primary amine chosen according to the invention to react with an aldehyde, for example formaldehyde, and an organic compound comprising active hydrogen atoms, for example phenol, to form a Mannich base, satisfies to the following general formula:

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$$R—NH_2$$

in which R represents a saturated or unsaturated, linear, branched or cyclic hydrocarbon group containing 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms.

Particularly preferably, the hydrocarbon group R carries at least one hydroxyl radical.

The preferred primary amine is monoethanolamine.

According to the invention, the phenol/formaldehyde condensation reaction is followed by a reaction that consists in condensing the free phenol and the free formaldehyde with a primary amine.

To obtain the liquid phenolic resin as defined above, the invention provides a method that consists in reacting the phenol with the formaldehyde in the presence of a basic catalyst, in a formaldehyde/phenol molar ratio of greater than 1, in cooling the reaction mixture and in introducing into said reaction mixture, during the cooling, a primary amine that reacts with the free formaldehyde and the free phenol via the Mannich reaction, said primary amine being of formula:

$$R—NH_2$$

in which R represents a saturated or unsaturated, linear, branched or cyclic hydrocarbon group containing 1 to 10 carbon atoms. The invention is characterized in that the primary amine is introduced right from the start of the cooling and the reaction mixture is maintained at the introduction temperature for a time that varies from 10 to 120 minutes.

Preferably, the phenol and the formaldehyde are made to react in a formaldehyde/phenol molar ratio of between 2 and 4, and advantageously less than or equal to 3, to a degree of phenol conversion of greater than or equal to

93%, and cooling of the reaction mixture is started. The cooling takes place at a stage in the condensation that corresponds to a resin that can still be diluted with water (dilutability greater than 1000%).

The expression “degree of phenol conversion” is understood to mean the percentage amount of phenol that has participated in reaction condensing with the formaldehyde relative to the starting phenol content.

According to the invention, the primary amine is added progressively during the cooling, since the reaction between phenol and formaldehyde is exothermic, and the temperature at the moment of addition of the amine is maintained over the time mentioned above, while taking measures to ensure that the dilutability of the resin remains at least equal to 1000%.

The primary amine is introduced right from the start of the cooling, at a temperature that may vary from 50 to 65°C, preferably of the order of 60°C.

The phase during which the temperature is maintained allows the primary amine to react with almost all of the formaldehyde present in the reaction mixture, and consequently allows the free formaldehyde content in the final resin to be lowered down to a value of 0.3% or lower, advantageously of 0.1% or lower. By maintaining the mixture at this temperature, it is also possible to lower the free phenol content in the resin to a value of 0.5% or below, this being particularly advantageous when the formaldehyde/phenol molar ratio is less than 3.

The preparation of the resin takes place under a temperature cycle, which comprises three phases: a heating phase; a first temperature hold; and a cooling phase.

In the first phase, formaldehyde and phenol are made to react in the presence of a basic catalyst, while progressively heating to a temperature between 60 and 75°C, preferably about 70°C. The formaldehyde/phenol molar ratio is greater than 1, preferably varies from 2 to 4, and is advantageously equal to 3 or less.

The catalyst may be chosen from catalysts known to those skilled in the art, for example triethylamine, lime (CaO) and alkali or alkaline-earth metal hydroxides, for example sodium hydroxide, potassium hydroxide, calcium hydroxide or barium hydroxide. Sodium hydroxide is preferred.

The amount of catalyst varies from 2 to 15%, preferably 5 to 9% and advantageously 6 to 8% by weight relative to the initial weight of phenol.

In the second phase, the temperature of the reaction mixture, which is reached after heating the reaction mixture (end of the first phase), is maintained until the degree of phenol conversion is at least 93%.

The third phase is a cooling phase during which the primary amine is introduced into the reaction mixture so as to start the reaction with the residual formaldehyde and the residual phenol, and thus to form the P-F-A condensates.

The addition of the primary amine takes place progressively owing to the exothermic character of the reaction, as indicated above, and may for example be carried out at a rate of from 1 to 5%, preferably 2 to 4%, by weight of the total amount of amine per minute.

The amount of primary amine, in particular monoethanolamine, is added in an amount of 0.2 to 0.7 mol, preferably 0.25 to 0.5 mol, of amine per mole of starting phenol.

The duration of the primary amine addition may vary from 10 to 120 minutes, preferably 20 to 100 minutes and advantageously 25 to 50 minutes.

Preferably, the addition of the primary amine is carried out at a temperature between 50 and 65°C and advantageously of the order of 60°C.

After the primary amine has been added, there is a temperature hold by keeping the temperature at the end of introduction for 10 to 120 minutes, preferably at least 15 minutes, so as to continue the condensation reaction between the

formaldehyde and the phenol with the primary amine until a more advanced stage and thus reduce the amount of free formaldehyde and free phenol, the dilutability of the resin, measured at 20°C, having to be maintained at least at 1000%.

After the P-F-A condensates have been formed, the reaction mixture is cooled so that its temperature reaches about 20 to 25°C and it is neutralized so as to stop the condensation reactions.

In general, the reaction mixture is neutralized by adding an acid in sufficient amount for the pH of the mixture to be less than 8.5, preferably less than 7.0 and advantageously between 4.0 and 6.0. The acid may be chosen from sulphuric, sulphamic, phosphoric and boric acids. Sulphuric acid and sulphamic acid are preferred.

The invention also relates to a sizing composition that can be applied to mineral fibers, especially glass or rock fibers, as well as to the insulating products obtained from these sized fibers.

The sizing composition according to the invention is obtained by mixing the liquid phenolic resin according to the present invention with water and sizing additives selected from urea, ammonium sulfate, silanes, mineral oils and ammonia.

Given that, as indicated above, the resin according to the invention has a very low free formaldehyde content of less than 0.3%, it is unnecessary to add urea to the sizing composition, except if it is desired to control the gel time of the size in order to prevent any pregelling problems.

In general, the sizing composition according to the invention comprises the following additives, per 100 parts of solid resin and urea material, where appropriate:

- 0 to 5 parts, generally less than 3 parts, of ammonium sulphate;
- 0 to 2 parts of a silane, in particular an aminosilane;
- 0 to 20 parts, generally 6 to 15 parts, of oil; and

- 0 to 20 parts, generally less than 12 parts, of aqueous ammonia (20 wt% solution).

The role of the additives is known and will be briefly recalled: the ammonium sulphate serves as a polycondensation catalyst (in the hot oven) after the sizing composition has been sprayed onto the fibers; the silane is a coupling agent for coupling between the fibers and the resin and also acts as an anti-ageing agent; the oils are hydrophobic anti-dust agents; aqueous ammonia acts, when cold, as a polycondensation retarder; and urea, as already mentioned, acts on the pregelling of the size.

The examples that follow allow the invention to be illustrated without however limiting it.

In the examples, the following analytical methods are used:

- the amount of free phenol is measured by gas chromatography using a filled column (stationary phase: Carbowax 20 M) and a flame ionization detector (FID); and

- the amount of free formaldehyde is measured by high-performance liquid chromatography (HPLC) and post-column reaction under the conditions of the ASTM D 5910-96 standard modified so that the mobile phase is water buffered to pH 6.8, the oven temperature is equal to 90°C and the detection is carried out at 420 nm.

<u>Example 1</u>

Introduced into a two-liter reactor with a condenser on top and with a stirring system fitted, are 378 g of phenol (4 mol) and 809 g of formaldehyde (10 mol) as a 37% aqueous solution (formaldehyde/phenol molar ratio of 2.5) and the mixture is heated at 45°C with stirring.

Next, 52.7 g of sodium hydroxide as a 50% aqueous solution (i.e. 7% by weight relative to the phenol) are regularly added over 30 minutes, the temperature is then progressively raised to 70°C over 30 minutes, and this temperature is maintained for 80 minutes so as to reach a degree of phenol conversion of 93%.

Next, the temperature is reduced to 60°C over 30 minutes and at the same time 75.3 g of monoethanolamine (1.2 mol) are introduced in a regular manner into the reaction mixture. The temperature is maintained at 60°C for 15 minutes, the mixture is cooled down to about 25°C over 30 minutes, and sulphamic acid as a 15% solution is added over 60 minutes until the pH is equal to 5.0.

The resin has the appearance of a clear aqueous composition having a water dilutability at 20°C of greater than 1000% after 8 days of storage at 14°C and after 21 days at 8°C.

The resin has a free formaldehyde content of 0.06% and a free phenol content of 0.2%, the content being expressed with respect to the total weight of liquid.

Example 2 (Comparative)

Preparation of a phenolic resin according to Example 4 of EP 0 480 778 A2 involving a secondary amine.

Introduced into the reactor of Example 1 are 564.66 g of phenol (6 mol) and 1217.43 g of formaldehyde (15 mol) as a 37% aqueous solution (formaldehyde/phenol molar ratio of 2.3) and the mixture is heated at 45°C with stirring.

56.47 g of sodium hydroxide as a 50% aqueous solution (i.e. 5% by weight relative to the phenol) are regularly added over 30 minutes, then the temperature is progressively raised to 70°C over 30 minutes, and the temperature is maintained for 90 minutes so as to reach a degree of phenol conversion of 93%. Next, the temperature is reduced to 60°C over 30 minutes and at the same time 124.22 g of diethanolamine (1.2 mol) are added regularly to the reaction mixture. The temperature is maintained at 60°C for 15 minutes, the mixture is then cooled down to about 25°C over 30 minutes, and sulphuric acid as a 25% solution is added over 60 minutes until the pH is equal to 8.0-8.1.

The resin has a free formaldehyde content of 1.0% and a free phenol content of 1.3%, the contents being expressed with respect to the total weight of liquid.

Example 3 (Comparative)

Preparation of a conventional urea-free phenolic resin.

Introduced into the reactor of Example 1 are 378 g of phenol (4 mol) and 857.7 g of formaldehyde (12.8 mol) as a 45% aqueous solution (formaldehyde/phenol molar ratio of 3.2) and the mixture is heated at 45°C with stirring.

45.36 g of sodium hydroxide as a 50% aqueous solution (i.e. 6% by weight relative to the phenol) are regularly added over 30 minutes, then the temperature is progressively raised to 70°C over 30 minutes, and the temperature is maintained for 90 minutes so as to reach a degree of phenol conversion of 98%.

The mixture is cooled down to about 25°C over 45 minutes and solid sulphamic acid is added over 60 minutes until the pH is equal to 7.3.

The resin has a water dilutability at 20°C of greater than 1000% after 21 days of storage at 14°C.

The resin has a free formaldehyde content of 5.3% and a free phenol content of 0.41%, the content being expressed with respect to the total weight of liquid.

PATENTKRAV

1. Væskeformig phenolharpiks, der er beregnet til anvendelse til udvikling af en efterbehandlingssammensætning til mineralfibre, der i det væsentlige består af phenol-formaldehydkondensater tilhørende familien resoler og phenol-formaldehydamin og har en vandfortyndingsevne ved 20 °C på mindst 1.000 %, hvilken væskeformig harpiks er fri for urea-formaldehydkondensater, **kendetegnet ved, at** den har et indhold af fri formaldehyd på mindre end eller lig med 0,3 % og et indhold af fri phenol på mindre end eller lig med 0,5 %, idet indholdene udtrykkes i forhold til væskens samlede vægt, og ved, at aminen er en primær amin med formlen

$$R—NH_2$$

hvor R repræsenterer en mættet eller umættet, lineær, forgrenet eller cyklisk carbonhydridgruppe indeholdende 1 til 10 carbonatomer.

2. Harpiks ifølge krav 1, der er **kendetegnet ved, at** den har et indhold af fri formaldehyd på 0,2 % eller mindre i forhold til væskens samlede vægt.

3. Harpiks ifølge krav 2, der er **kendetegnet ved, at** indholdet af fri formaldehyd er 0,1 % eller mindre.

4. Harpiks ifølge krav 1 til 3, der er **kendetegnet ved, at** R indeholder 1 til 6 carbonatomer.

5. Harpiks ifølge et af kravene 1 til 4, der er **kendetegnet ved, at** carbonhydridgruppen R bærer mindst én hydroxylradikal.

6. Harpiks ifølge krav 5, der er **kendetegnet ved, at** aminen er monoethanolamin.

7. Harpiks ifølge et af kravene 1 til 6, der er **kendetegnet ved, at** den har et indhold af fri formaldehyd på mindre end 0,2 %, et phenolindhold på mindre end 0,4 % og en vandfortyndingsevne på 2.000 % eller mere.

8. Fremgangsmåde til fremstilling af en væskeformig phenolharpiks ifølge et hvilket som helst af de foregående krav, der i det væsentlige består af phenol-formaldehydkondensater tilhørende familien resoler og phenol-formaldehydamin

med en vandfortyndingsevne ved 20 °C på 1.000 % eller højere, et indhold af fri formaldehyd på mindre end eller lig med 0,3 % og et indhold af fri phenol på mindre end eller lig med 0,5 %, idet indholdene udtrykkes i forhold til væskens samlede vægt, bestående i omsætning af phenol og formaldehyde i et formaldehyd/phenol-molforhold større end 1 i nærvær af en basisk katalysator, afkøling af reaktionsblandingen og indføring i reaktionsblandingen under afkøling af en amin, som reagerer med den fri formaldehyd og phenolen via Mannich-reaktionen, **kendetegnet ved, at** der anvendes en primær amin, som indføres ved afkølingens begyndelse, hvilken primær amin har den generelle formel

$$R—NH_2$$

hvor R repræsenterer en mættet eller umættet, lineær, forgrenet eller cyklisk carbonhydridgruppe indeholdende 1 til 10 carbonatomer, og at reaktionsblandingen holdes ved indføringstemperaturen i en periode på 10 til 120 minutter.

9. Fremgangsmåde ifølge krav 8, der er **kendetegnet ved, at** aminens indføringstid varierer fra 20 til 100 minutter, fortrinsvis fra 25 til 50 minutter.

10. Fremgangsmåde ifølge krav 8 eller 9, der er **kendetegnet ved, at** formaldehyd og phenol omsættes i et formaldehyd/phenol-molforhold mellem 2 og 4, fortrinsvis mindre end 3, og op til en phenolomdannelsesrate, der er større end eller lig med 93 %.

11. Fremgangsmåde ifølge et af kravene 8 til 10, der er **kendetegnet ved, at** den primære amin indføres ved en temperatur mellem 50 og 65 °C, fortrinsvis i størrelsesordenen 60 °C.

12. Fremgangsmåde ifølge et af kravene 8 til 11, der er **kendetegnet ved, at** R indeholder 1 til 6 carbonatomer.

13. Fremgangsmåde ifølge et af kravene 8 til 12, der er **kendetegnet ved, at** carbonhydridgruppen R bærer mindst én hydroxylradikal.

14. Fremgangsmåde ifølge krav 13, der er **kendetegnet ved, at** aminen er monoethanolamin.

15. Fremgangsmåde ifølge et af kravene 8 til 14, der er **kendetegnet ved, at** den primære amin tilsættes i en mængde på 0,2 til 0,7 mol pr. mol udgangsphenol, fortrinsvis på 0,25 til 0,50 mol.

16. Fremgangsmåde ifølge et af kravene 8 til 15, der er **kendetegnet ved, at** reaktionsblandingen efter afkøling neutraliseres med en syre i en mængde, der er tilstrækkelig til, at pH bliver mindre end 8,5, fortrinsvis mindre end 7,0 og mere fortrinsvis mellem 4,0 og 6,0.

17. Fremgangsmåde ifølge et af kravene 8 til 16, der er **kendetegnet ved, at** syren er udvalgt fra svovl-, sulfamin-, phosphor- og borsyre.

18. Efterbehandlingssammensætning til mineralfibre, der er opnået ved blanding af en væskeformig phenolharpiks ifølge et af kravene 1 til 7 med vand og efterbehandlingstilsætningsstoffer udvalgt fra urea, ammoniumsulfat, silaner, mineralolier og ammoniak.

19. Isoleringsprodukt, særlig varme- og/eller lyd-, der omfatter mineralfibre, der er efterbehandlet ved anvendelse af efterbehandlingssammensætningen ifølge krav 18.

20. Anvendelse af en efterbehandlingssammensætning ifølge krav 18 til fremstilling af mineralfiberbaserede isoleringsprodukter, særlig glas- eller stenfiberbaserede produkter.

21. Anvendelse af en harpiks ifølge et af kravene 1 til 7 til fremstilling af en efterbehandlingssammensætning ved blanding af harpiksen med vand og tilsætningsstoffer udvalgt fra urea, ammoniumsulfat, silaner, mineralolier og ammoniak.