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(54) **Method for the manufacture of mineral wool insulation products having low formaldehyde emissions**

(57) A method for producing mineral wool products with low formaldehyde emissions, comprises:
(a) preparing an aqueous solution comprising resorcinol or a derivative thereof;
(b) transporting a phenol-formaldehyde resin or a phenol-formaldehyde-urea resin to a binder application station;

(c) metering the aqueous solution continuously to said resin while it is transported to the binder application station, thereby forming a binder solution;
(d) applying the binder solution to mineral fibers; and
(e) curing the binder solution by applying heat, thereby forming the mineral wool product.

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Description

Summary and field of the invention

[0001] The present invention relates to a method for manufacturing mineral wool insulation products, from which the emissions of formaldehyde are low. The method comprises continuously adding a resorcinol derivative as an additive in the on-site preparation of a binder comprising a phenol-formaldehyde resin, immediately before the binder is applied to the mineral fibers.

Background

[0002] Mineral wool products are widely used for the thermal and acoustic insulation of different parts of buildings, transportations, or other appliances, as well as for fire protection. Mineral wool materials are mainly randomly interlaced masses of mineral fibers with varying lengths and usually bound by a resin-based binder. Three types of mineral materials are most commonly employed, glass, stone or slag. Processes for the production of mineral wool products are well known in the art, and usually comprise the steps of melting the mineral material to an adequate temperature, fiberizing the molten mixture into fine fibers, application (e.g. spraying) of a binder composition to the individual fibers while they still have some residual heat, collection of the fibers and formation of a primary fleece on a foraminous conveyor, densifying the fleece, and curing the binder at elevated temperatures. The cured mat is then cut to the desired size with transverse and edge trimmers, before it is packaged for transport.

[0003] The mineral wool products have traditionally, and still currently are, widely being manufactured by bonding the glass fibers at their cross-over points with cured binders based on phenol-formaldehyde thermosetting resins. Most common phenol-formaldehyde resins used for this purpose are resols manufactured by condensation of formaldehyde and phenol in aqueous solution, catalyzed by strong alkalis, and using a large molar excess of the formaldehyde in relation to phenol. This excess of formaldehyde avoids the possibility of phenol emissions during manufacture. In some cases, urea is included in the resin formulation to scavenge some of the not reacted excess formaldehyde, and to extend the resin.

[0004] Phenol-formaldehyde (and phenol-formaldehyde-urea) resin based aqueous binders have been preferred for very long time, due to their good performance and attractive low cost. These phenol-formaldehyde and phenol-formaldehyde-urea resins are nowadays commercially available from specialized resin producers and usually contain from about 40 to about 60 % weight solid content, and from about 0.5 to 8.0 weight % of free formaldehyde (the lower values are obtained when urea is present).

[0005] For good processability, these resins should

have a good stability during storage, good dilutability with water, suitable curing rate, and particularly a low viscosity to facilitate the application and the subsequent distribution of the binder in the cross-over points on the glass fibers. The low viscosity is also necessary to obtain satisfactory recovery of the thickness of the primary uncured mat after it is formed. The resins shall have an alkaline pH to assure stability and to avoid or minimize potential corrosion issues on carbon steel equipment. This combination of requirements is specific for the glass wool industry. In order to fulfill these requirements, the resols must be prepared in a definite manner, for example by using low amounts of alkali catalysts, low temperatures, and short reactions times. These specific reaction conditions have the objective that the level of condensation of the phenol-formaldehyde resin obtained is low.

[0006] Both the viscosity and the dilutability with water of the resin are related properties, and are an indication of its level of condensation. In fact, in the preparation of the resin, these parameters are frequently monitored online by the manufacturers to determine when the reaction needs to be stopped, depending on the intended application for the resin. The higher the viscosity and the lower the dilutability with water, the higher the condensation degree of the phenol-formaldehyde resin.

[0007] Phenol-formaldehyde and phenol-formaldehyde-urea resins as manufactured by the resin producer (and as commercially available) are not directly applied to the mineral fibers in the production of mineral wool. Instead, an aqueous binder solution (also known as binder, binder composition or binder formulation) is prepared by the mineral wool manufacturer. In the preparation of the binder, the resin is largely diluted with water and mixed with additives. By additives it is meant the substances which are usually needed either to assist in the manufacture of mineral wool products, or to improve the properties of the manufactured products. This dilution and mixture with additives is commonly done continuously in the same mineral wool production line, as the resin is transported to the binder application station. Frequently used additives include urea (e.g. if not already contained in the resin), de-dusting oil, emulsifiers, dyes, silanes, latent catalysts (ammonium sulfate), ammonia (ammonium hydroxide), as well as additional extenders.

[0008] Environmental and toxicological concerns related to the formaldehyde released from the products manufactured with binders comprising phenol-formaldehyde and phenol-formaldehyde-urea resins have however led in the recent years to a movement in the mineral wool industry to reduce, or even completely eliminate, the use of formaldehyde-containing resins, or to reduce the amount of excess formaldehyde they contain, with the ultimate objective of reducing the level of formaldehyde emissions from the manufactured products. Thus, different methods to reduce free formaldehyde in phenol-formaldehyde resins have been described in the art.

[0009] One group of such methods refers to the use of formaldehyde scavengers, substances capable of react-

ing with the free (excess) formaldehyde contained in the resin. Those formaldehyde scavengers are generally known in the art and some illustrative examples are given here. US 2011/111226 A1 describes the use of substances with active methylene groups as formaldehyde scavengers. A second set of solutions consists of the use of a compound able to form condensates with both phenol and formaldehyde. For example, WO 2008/043961 A1 describes the use of monoethanolamine that reacts with free formaldehyde and phenol via Mannich reaction. The method described in WO 2012/25699 A1 relates to a method for reducing free formaldehyde in resins using glycine as formaldehyde scavenger. A third group of solutions consist of the treatment of the mineral wool product with formaldehyde scavengers which reacts with the free formaldehyde being released from the fleece. For instance, the method described in WO 2008/005635 A2 consists of the use of sodium bisulfite, sodium metabisulfite and tetraethylenepentamine as formaldehyde scavengers. Another method disclosed in WO 2011/148076 A1 consists of the use of dihydrazides as formaldehyde scavengers.

[0010] The amount of free formaldehyde in a phenol-formaldehyde resin can also be reduced to less than 0.5 weight % by treating the resin with a phenol or aniline derivative as formaldehyde scavenger. In this method, the phenol-formaldehyde resin is treated with a certain amount of phenol or aniline derivative, preferably at room temperature, to produce the condensation reaction between the phenol or aniline derivative and the free formaldehyde. This modification of the resin presents however some limitations, e.g. it requires mixing the phenol or aniline derivative with the resin for long enough (preferably between 30-100 minutes) to produce the reduction of the free formaldehyde concentration to the desired level. This "premix" needs to be done as a prior step to the preparation of the binder and the application to the mineral fibers.

[0011] It is an object of the present invention to provide an alternative method for the manufacture of mineral wool insulation products with low level of formaldehyde emissions, and which does not suffer from the limitations and drawbacks of the methods of the prior art.

Description of the invention

[0012] In view of the above, a method for producing mineral wool products with low formaldehyde emissions, according to an embodiment, comprises adding at least one resorcinol derivative as an additive in an on-site preparation of a binder comprising a phenol-formaldehyde resin, immediately before it is applied to the mineral fibers.

[0013] "On-site" means in the context of this specification that the binder is prepared in the mineral wool production plant a few minutes, for example less than 5 minutes and particularly 1-5 minutes, before it is applied to the mineral fibers. The treatment is particularly suitable

if resorcinol or alkyl-resorcinol is selected as phenol derivative.

[0014] According to an embodiment, a method for producing mineral wool products with low formaldehyde emissions, comprises (a) preparing an aqueous solution comprising resorcinol or a derivative thereof; (b) transporting a phenol-formaldehyde resin or a phenol-formaldehyde-urea resin to a binder application station; (c) metering the aqueous solution continuously to said resin while it is transported to the binder application station, thereby forming a binder solution; (d) applying the binder solution to mineral fibers; and (e) curing the binder solution by applying heat, thereby forming the mineral wool product.

[0015] According to an embodiment, a method for producing mineral wool products with low formaldehyde emissions comprises preparing an aqueous binder solution, applying the binder solution to mineral fibers being produced by a fiberizer, forming an uncured mineral wool fleece over a receiving foraminous conveyor, and curing the binder in a heating oven, wherein the binder is prepared on-site by continuously diluting a phenol-formaldehyde resin, optionally also comprising urea, with an aqueous mixture of additives, while it is transported to the binder application station, and the aqueous mixture of additives is selected such that it includes at least one resorcinol derivative.

[0016] In embodiments, the at least one resorcinol derivative is selected from the group of resorcinol, alkyl-resorcinols, and mixtures thereof. Alkyl-resorcinols include methyl-resorcinols, ethyl-resorcinols, dimethyl-resorcinols and diethyl-resorcinols.

[0017] In embodiments, the phenol-formaldehyde resin, optionally also comprising urea, is selected such that it has a pH of 7 or above, a water dilutability of more than 20 times at 20°C, a viscosity lower than 100 mPa.s (at 20 °C and 40% solid content) and a curing B-time between 2-15 minutes (at 130°C).

[0018] Preferably, the suitable phenol-formaldehyde resin is selected such that it comprises from 2 wt.-% to 8 wt.-% of free formaldehyde relative to dry resin measured according to ISO 11402:2004. In the case of selecting phenol-formaldehyde-urea resins, the preferred content of free formaldehyde is from 0.5 wt.-% to 1.5 wt.-%.

[0019] Through this description, it is considered that the formaldehyde emissions are low if the mineral wool products produce formaldehyde emissions lower than 20 µg/m³, more preferably lower than 10 µg/m³, and even more preferably lower than 7 µg/m³, when stored in a test chamber with air exchange and under controlled conditions for 28 days and then, the formaldehyde concentration in the air in the chamber measured according to the standard method ISO 16000-3:2011.

[0020] Another aspect of the present invention is a method for producing mineral wool, for example of the previous embodiments, wherein the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol deriv-

ative is from 4.0 to 0.8, and preferably from 3.0 to 0.9, and more preferably from 2.5 to 1.0.

[0021] The method according to embodiments described herein presents benefits in relation to other methods, particularly if compared with the previously described "premix" method, where the phenol-formaldehyde resins are treated with phenol or aniline derivative as a previous step to the preparation of the binder. As in the "premix" method, the inventive method here also produces the aimed reduction of formaldehyde emissions. Certain practical advantages are however obtained by the inventive method compared to the referred "premix" method:

a) The inventive method does not need the "premix" step to take place, avoiding the need of extra installations and saving working time. The resorcinol solution can be prepared simultaneously and together with the solution of the binder additives. Therefore, the inventive method does not need for extra reactor or additional steps. Complementarily, the concentration of resorcinol derivative relative to the resin solid content can be adjusted in-line, meaning that the concentration can be changed while the mineral wool is being manufactured. This might be advantageous for example when products with different level of formaldehyde emissions have to be produced without stopping the manufacturing line, or when a resin batch having a certain free formaldehyde content is replaced by a resin batch with a different free formaldehyde content. In this case, the resorcinol derivative amount added can easily be adjusted in-line e.g. by adjusting the metering of its solution.

b) The stability of the resin is not compromised by the preparation of the "premix", reducing the risk of premature resin condensation and assuring that the required high water dilutability and low viscosity are not lost. The amount of resorcinol can also be higher than in the "premix" process, since there is no risk of resin pre-condensation. This can be useful if e.g. resins are selected having initially high amounts of free formaldehyde. So, it is observed that a phenol-formaldehyde resin with 7% free formaldehyde treated with 2 mols of resorcinol per mol of free formaldehyde condenses prematurely and after 45 minutes forms a gel with a viscosity that is not workable anymore (over 20,000 mPa.s). This limitation is avoided with the method of the invention, since the binder is applied immediately after the resin is contacted with the resorcinol derivative (typically between 1-5 minutes) to the mineral fibers, before the premature condensation reaction has developed extensively.

Detailed description of the embodiments of the invention

[0022] The phenol-formaldehyde resin suitable for the

method of the present invention is a phenol-formaldehyde resol produced by condensation of formaldehyde and phenol in a formaldehyde:phenol molar ratio greater than 1.1, and preferably greater than 2. Usually, the formaldehyde:phenol molar ratio in the phenol-formaldehyde used as starting material in the process of the present invention is not greater than 6. The condensation process for preparing the phenol-formaldehyde resin is usually catalyzed by NaOH, KOH, Ca(OH)_2 or Ba(OH)_2 , most preferably NaOH, and it is stopped while the level of condensation is still partial and relatively low.

[0023] Optionally, the phenol-formaldehyde resin also comprises urea. In this case, urea serves both as scavenger of a part of the excess formaldehyde and as resin extender. Urea is usually added after the phenol-formaldehyde resol is prepared, and the mixture is heated to produce phenol-formaldehyde-urea resins after cooling, also called PFU-premix. Although urea might partially reduce the free formaldehyde content of the resin, formaldehyde is still released from the manufactured product. As explanation it has been reported that the adduct formed between formaldehyde and urea is not stable.

[0024] The method of the invention might be applied with both phenol-formaldehyde and phenol-formaldehyde-urea resins. In both cases, the mineral wool products manufactured have low level of formaldehyde emissions.

[0025] Ammonia (or ammonium hydroxide) might also be comprised in the phenol-formaldehyde or phenol-formaldehyde-urea resin of the invention, to adjust the pH and to improve the dilutability and storage stability of the resin.

[0026] The phenol-formaldehyde resin applicable is an aqueous solution comprising from 5 to 70 weight %, more preferable from 40 to 65 weight %, and most preferably from 45 to 55 % weight of said phenol-formaldehyde resol condensates.

[0027] According to an even more preferred embodiment, the phenol-formaldehyde resin in the present invention contains from about 2 wt.-% to 8 wt.-% of free formaldehyde, determined by the method ISO 11402:2004. When phenol-formaldehyde-urea resins are used, the content of free formaldehyde is from 0.5 wt.-% to 1.5 wt.-%. The concentration of free formaldehyde is frequently provided by the resin manufacturer as part of the specification.

[0028] The suitable resins are characterized by having a pH > 7, particularly between 7-10, and by the fact that they can be diluted with more than 20 parts by weight of demineralized water at 20°C per 1 part of resin, determined by the method ISO 8989:1995. This is normally referred to as 'infinite' dilutability in water. The viscosity of the resins is low, in particular lower than 100 mPa.s (at 20°C and at a resin concentration 40 wt.-% solid content). Another feature of the resin is that its curing B-time is in the range of 2 to 15 minutes at a temperature of 130°C, as determined using the ISO 8987:2005 method.

[0029] Particular examples of preferred phenol-formal-

dehyde resins for the present invention commercially available are Bakelite® PF 1230V from Momenive or Borofen® B-1606A supplied by Fenolit.

[0030] Urea might be added as a resin extender to the suitable resins of the invention in an amount up to 40 wt.-% based on the phenol-formaldehyde resin solid content, preferably in an amount from 10-35 wt.-% and more preferably from 20-30 wt.-%. A too high amount of urea could detrimentally affect the mechanical properties of the bonded mineral wool products.

[0031] The resorcinol derivative useful in the method according to the present invention is any resorcinol derivative capable of reacting with the free formaldehyde of the resin by condensation reaction. Particular examples of resorcinol derivatives include resorcinol and alkyl-resorcinols, as well as mixtures thereof. Examples of useful alkyl-resorcinols are methyl-resorcinols, ethyl-resorcinols, dimethyl-resorcinols, diethyl-resorcinols and their mixtures, such as shale oil phenols. Resorcinol is particularly preferred since it presents suitable condensation rate with formaldehyde, relative ease dosing and handling, non-toxicity and affordable cost.

[0032] In the method of the invention, the phenol-formaldehyde resin is continuously diluted on-site, for example in the mineral wool manufacturing line, with an aqueous mixture of additives in order to prepare the binder, immediately before the binder is applied to the mineral fibers. The time from the moment the binder additives are contacted with the phenol-formaldehyde resin until the binder is applied to the mineral fibers usually ranges from 1 to 5 minutes. It needs to be understood that the aqueous mixture of additives may be formed by one or several fractions, and that each of the additives may be contained in one or several of the fractions. Thus, e.g. one of the fractions may be formed by fresh water or process water, without other additives. This part of the method of the invention can be done e.g. by continuously introducing the aqueous mixture of additives as one or several fractions to the canalization where the aqueous resin is being transported to the binder application station. The ratios of resin solution and of the aqueous additive mixture fraction or fractions can be controlled by adjusting the flow rate of the respective pumps. Means are adopted, which are well known in the art, to assure that the binder components are thoroughly mixed before they are applied to the fibers. This dilution is done to reach a final binder non-aqueous content preferably in the range 4-10 wt.-%.

[0033] To avoid detrimental premature condensation, the temperature of the binder solution mixture is preferably not raised over 50°C, more preferably not raised over 40°C and even more preferably the temperature ranges from 10-35°C before the binder solution is applied to the fibers.

[0034] The mixture of additives includes at least one resorcinol derivative to produce the desired reduction of formaldehyde emissions from the manufactured products.

[0035] The mixture of additives preferably also contains other binder additives as those known in the art, and in proportions described previously. Non-limiting examples of additives useful are urea (i.e. if not already contained in the resin or in addition to the urea already present in the resin), de-dusting oil (e.g. paraffin oil), emulsifiers, dyes, adhesion promoters (e.g. silanes), latent catalyst (e.g. ammonium sulfate), ammonia (ammonium hydroxide), fiber softeners, hydrophobizing agents (e.g. silicones), as well as additional extenders such as carbohydrates (e.g. sugar, starch, modified starch, dextrans) and/or lignosulfonates.

[0036] The non-aqueous content of the final binder preferably comprises 5-15 wt.-% of binder additives, 70-90 wt.-% of phenol-formaldehyde resin containing from 0 to 40 wt.-% of urea, and 5-15 wt.-% of resorcinol derivative. According to an embodiment, the non-aqueous content of the final binder consists of 5-15 wt.-% of binder additives, 70-90 wt.-% of resin containing from 0 to 40 wt.-% of urea, and 5-15 wt.-% of resorcinol derivative.

[0037] In a preferred embodiment, the binder is applied in atomized form to the attenuated individual fine fibers being produced by a fiberizer from a hot molten mineral mixture. The atomization can be produced by spraying nozzles or similar devices oriented in a direction so that the sprayed binder meets the attenuated fibers. The binder contacts the fibers when they are still warm, producing the evaporation of a large amount of water and other volatile substances present in the binder.

[0038] The binder is preferably applied in an amount to produce a content of solid binder in the final product after drying and curing between 3-12 wt.-%, relative to the weight of the mineral fibers. This amount of cured binder is measured as LOI (loss on ignition) according to ISO 29771:2008.

[0039] In preferred embodiments, the fibers impregnated with partially dried binder are then continuously collected on a foraminous conveyor located in the lower part of a forming chamber, forming a low density fleece of mineral fibers. Air is suctioned from underneath the conveyor so that the formation of the fleece is further assisted by the effect of vacuum. At this stage, the fleece is said to be in an uncured state, meaning that the partially dried binder (or the resin comprised in the binder) has not started to set (cure) as a consequence of the heat.

[0040] The uncured fleece is then transported to a heating (curing) oven, where the binder is cured to set at temperatures > 100°C, preferably between 140-200°C, and more preferably between 160-180°C. The curing time preferably ranges from 2 to 5 minutes. After curing is complete, the fibers in the mineral wool product are bonded in their cross-over points by the cured binder.

[0041] Without wanted to be bound by theory, the inventors believe that a reaction between the resorcinol derivative and the free formaldehyde mainly occurs when the warm fibers are impregnated with the binder, and

during curing. The resorcinol derivative is thought to form condensed products with both the free formaldehyde and with the resin, thus irreversibly trapping the formaldehyde in the cured products.

[0042] The amount of resorcinol derivative is not particularly limited. It is however required that this amount is sufficient to produce the desired low emissions of formaldehyde from the manufactured mineral wool products. The maximum amount of resorcinol derivative is in principle mostly limited by the economic viability of the production. The amount of resorcinol also depends on the concentration of free formaldehyde of the phenol-formaldehyde resin or the phenol-formaldehyde-urea resin comprised in the binder. It has been observed that low level of formaldehyde emissions are obtained when the amount of resorcinol derivative is calculated to result in a molar ratio of free formaldehyde in the resin to resorcinol derivative from 4.0 to 0.8, and preferably from 3.0 to 0.9, and more preferably from 2.5 to 1.0. In the case of phenol-formaldehyde-urea resins, these ratios are calculated considering the free formaldehyde in the resin before urea is added.

[0043] After curing, the cured mat is subsequently cut to the desired size with trimmers and optionally rolled, before it is and packaged for transport.

[0044] The mineral wool products manufactured with the method of the invention produce formaldehyde emissions lower than 20 $\mu\text{g}/\text{m}^3$, more preferable lower than 10 $\mu\text{g}/\text{m}^3$ and most preferable lower than 7 $\mu\text{g}/\text{m}^3$, when stored in a test chamber with air exchange and under controlled conditions for 28 days and then, the formaldehyde concentration in the air in the chamber is measured according to standard method ISO 16000-3:2011.

[0045] The mineral wool products manufactured with the method of the invention can be used for instance in the insulation of buildings, transportations, air-conditioning ducts, or other appliances, or for fire protection. The mineral wool product may further comprise additional facings made of paper, aluminum, glass veil or mixtures thereof. Other non-insulation uses for the mineral wool are also feasible.

Testing methods

1) Method for measuring free formaldehyde of resin

[0046] The free formaldehyde content of the resin is measured according to the international standard ISO 11402:2004, using the hydroxylamine hydrochloride procedure.

[0047] This method involves the following general principle: The formaldehyde present in the resin is converted to the oxime with hydroxylamine hydrochloride. Then the hydrochloric acid formed during this reaction is determined by potentiometric back-titration, using a sodium hydroxide solution.

2) Method for measuring the dilutability

[0048] Resin dilutability in demineralized water is measured at 20°C according to the international standard ISO 8989:1995 method. Resin dilutability is a measure of the mass of water needed to obtain turbidity in the liquid resin.

[0049] This method involves adding water to the resin until turbidity persists for a minimum of 30 s after agitation.

3) Method for measuring the viscosity

[0050] The viscosity of the resin is measured at 20 °C using a Brookfield viscosimeter, spindle 1, 60 rpm. The viscosity as referred to in the present invention is based on a resin concentration having a solid content of 40 wt.-% in water.

4) Method for measuring the curing B-time

[0051] Curing B-Time of the resin is measured at 130°C according to the international standard ISO 8987:2005. In this method, the condensation of the phenol-formaldehyde resin is carried out to the B-stage in one heated test plate. The B-transformation time point is reached when a stirring rod is briefly raised from the resin and resin threads from the rod break.

5) Method for measuring formaldehyde emissions from mineral wool products

[0052] The amount formaldehyde emissions from cured mineral wool products is measured from freshly manufactured samples according to ISO 16000-3:2011. The method involves placing the fresh samples into a 212 L acclimatized glass chamber equipped with a ventilator and set at a temperature 23 ± 1 °C, a relative humidity of 50 ± 5 %, air flow 0.2 ± 0.1 m/s and an air exchange rate $0.5 \text{ h}^{-1} \pm 5\%$ for 28 days. Other settings are the loading factor of 1 m² of sample surface per m³ of test chamber volume, and an specific area air exchange rate of 0.5 m³/m² h. Emitted formaldehyde is determined in $\mu\text{g}/\text{m}^3$ from air samples of the air in the chamber taken on to adsorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) at the time of the measurement (after 28 days in this case) and the hydrazones formed are subsequently analyzed by high performance liquid chromatography (HPLC) with detection by ultraviolet absorption.

Example 1:

[0053] A 1000-L intermediate bulk container (IBC), equipped with a mechanical stirrer, was charged with 349 kg of aqueous phenol-formaldehyde resin characterized by pH 9.4, viscosity 20 mPa.s, dilutability > 20, and B-time 2.2 min, and with 45 wt.-% solid content. The content

of free formaldehyde of this resin was 4 wt.-%. Then, 69 kg of urea were added to the resin solution as a solid and the mixture was stirred at 25 °C for 60 minutes. Separately, 39 kg of solid resorcinol and 220 L of water were mixed and stirred at 25 °C for 60 minutes to obtain a pale-yellow solution. Small amounts of mineral oil, silanes and catalyst were added to this solution. The phenol-formaldehyde-urea resin was then pumped through canalization at a flow rate of 151 kg/h to a binder application station. The resorcinol solution was simultaneously introduced to the resin canalization at a flow rate of 93 kg/h in order to prepare the binder. This flow rate ratio corresponds to a formaldehyde/resorcinol molar ratio of 1.25. Further dilution is obtained by introduction of process water at 1530 kg/h. This binder was applied on the surface of glass wool fibers, in form of small drops, by spraying rings, as the fibers attenuated by hot air blowers from a disc fiberizer fall to a foraminous conveyor belt. The fibers were collected in form of an uncured fleece onto a foraminous conveyor belt on the bottom of a forming chamber. The fleece was afterwards densified and transported to a curing oven. After curing, the produced material had a density of 12 kg/m³ and a thickness of 200 mm. The cured binder content measured as LOI was 4.9 wt.-%. The formaldehyde emissions from a sample of the cured glass wool mat at the 28th day were 6 µg/m³.

Example 2:

[0054] The same procedure of example 1 was repeated, with the following exceptions: the resorcinol solution was prepared by mixing 20 kg of solid resorcinol and 110 L of water; the phenol-formaldehyde-urea resin was pumped at a flow rate of 163 kg/h; the resorcinol solution flow rate was adjusted to 50 kg/h. The flow rate ratio in this case corresponds to a formaldehyde/resorcinol molar ratio of 2.5. The glass wool mat produced in this example had a density of 12 kg/m³ and a thickness of 200 mm. The cured binder content measured as LOI was 4.6 wt.-%. The formaldehyde emissions measured from a sample of the cured glass wool mat at the 28th day were 7 µg/m³.

Example 3:

[0055] The same procedure of example 1 was repeated, with the following exceptions: the resorcinol solution was prepared by mixing 36 kg of solid resorcinol and 200 L of water; the phenol-formaldehyde resin used was Borofen B-1606 supplied by Fenolit, having pH 8.6, viscosity 15 mPa.s, dilutability > 20, B-time 2.0 min, 46 wt.% solid content, and a content of free formaldehyde of 7 wt.-%; the phenol-formaldehyde-urea resin was pumped at a flow rate of 225 kg/h; the resorcinol solution flow rate was adjusted to 130 kg/h. The flow rate ratio in this case corresponds to a formaldehyde/resorcinol molar ratio of 2.5. The glass wool mat produced in this example had a density of 12 kg/m³ and a thickness of 200 mm. The

cured binder content measured as LOI was 4.8 wt.-%. The formaldehyde emissions measured from a sample of the cured glass wool mat at the 28th day were 9 µg/m³.
[0056] Hence, in view of the above a method for producing mineral wool products with low formaldehyde emissions according to an embodiment includes:

preparing an aqueous binder solution, applying the binder solution to mineral fibers being produced by a fiberizer, forming an uncured mineral wool fleece over a receiving foraminous conveyor, and curing the binder in a heating oven, wherein

a) the binder is prepared on-site by continuously diluting a phenol-formaldehyde resin, optionally also comprising urea, with an aqueous mixture of additives, while it is transported to the binder application station, and

b) the aqueous mixture of additives is selected such that it includes at least one resorcinol derivative.

[0057] The at least one resorcinol derivative can be selected from the group of resorcinol, alkyl-resorcinols, and mixtures thereof.

[0058] The phenol-formaldehyde resin, which can optionally also comprise urea, is selected according to an embodiment such that it has a pH of 7 or above, a water dilutability of more than 20 times at 20°C, a viscosity lower than 100 mPa.s (at 20 °C and 40% solid content) and a curing B-time between 2-15 minutes (at 130°C).

[0059] According to an embodiment, the phenol-formaldehyde resin can be selected such that it comprises from 2 wt.-% to 8 wt.-% of free formaldehyde relative to dry resin measured according to ISO 11402:2004, and from 0.5 wt.-% to 1.5 wt.-% in the case of selecting phenol-formaldehyde-urea resins.

[0060] According to an embodiment, the mineral wool products produce formaldehyde emissions after 28 days lower than 20 µg/m³, more preferably lower than 10 µg/m³, and even more 3 preferably lower than 7 µg/m³, when measured according to the standard method ISO 16000-3:2011.

[0061] According to an embodiment, the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol derivative is from 4.0 to 0.8.

[0062] According to an embodiment, the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol derivative is from 3.0 to 0.9.

[0063] According to an embodiment, the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol derivative is from 2.5 to 1.0.

[0064] According to an embodiment, a mineral wool product is produced with a method of any of the above

embodiments.

Claims

1. A method for producing mineral wool products with low formaldehyde emissions, comprising:
 - (a) preparing an aqueous solution comprising resorcinol or a derivative thereof;
 - (b) transporting a phenol-formaldehyde resin or a phenol-formaldehyde-urea resin to a binder application station;
 - (c) metering the aqueous solution continuously to said resin while it is transported to the binder application station, thereby forming a binder solution;
 - (d) applying the binder solution to mineral fibers; and
 - (e) curing the binder solution by applying heat, thereby forming the mineral wool product.
2. The method of claim 1, wherein step (d) comprises applying the binder solution to mineral fibers being produced by a fiberizer, and forming an uncured mineral wool fleece over a support.
3. The method of claim 1 or 2, wherein the at least one resorcinol derivative is selected from the group of resorcinol, alkyl-resorcinols, and mixtures thereof.
4. The method of any of the previous claims, wherein the phenol-formaldehyde resin or the phenol-formaldehyde-urea resin is selected such that it has a pH of 7 or above, a water dilutability of more than 20 times at 20°C, a viscosity lower than 100 mPa.s (at 20 °C and 40% solid content) and a curing B-time between 2-15 minutes (at 130°C).
5. The method of any of the previous claims, wherein the phenol-formaldehyde resin is selected such that it comprises from 2 wt.-% to 8 wt.-% of free formaldehyde relative to dry resin measured according to ISO 11402:2004, and from 0.5 wt.-% to 1.5 wt.-% in the case of selecting phenol-formaldehyde-urea resins.
6. The method of any of the previous claims, wherein the mineral wool products produce formaldehyde emissions after 28 days lower than 20 µg/m³, more preferably lower than 10 µg/m³, 3 and even more preferably lower than 7 µg/m³, when measured according to the standard method ISO 16000-3:2011.
7. The method of any of the previous claims, wherein the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol derivative is from 4.0 to 0.8.
8. The method of the claim 6, wherein the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to an optional addition of urea, to resorcinol derivative is from 3.0 to 0.9.
9. The method of the claim 8, wherein the resin is selected such that the molar ratio of free formaldehyde in the resin, prior to the optional addition of urea, to resorcinol derivative is from 2.5 to 1.0.
10. The method of any of the previous claims, wherein the time between metering the aqueous solution to the resin to form the binder solution and applying the binder solution to mineral fibers is less than 5 minutes, particularly from 1 to 5 minutes.
11. A mineral wool product produced with the method of any of the previous claims.
12. The use of the mineral wool product of claim 11 in the insulation of buildings, transportations, air-conditioning ducts, or other appliances, or for fire protection.



EUROPEAN SEARCH REPORT

Application Number
EP 13 19 0279

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 4 December 2013	Examiner Van Beurden-Hopkins
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