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(54) Title: CELLULOSE ETHER ADDITIVES FOR THE EXTRUSION OF CERAMIC MASSES

(57) Abstract: The present invention relates to extrudable ceramic masses and other masses which set as a result of baking or sintering, which masses comprise specific additives based on water-soluble cellulose ethers, an extrusion process, the extrudates and their use.

CELLULOSE ETHER ADDITIVES FOR THE EXTRUSION OF CERAMIC MASSES

The present invention relates to extrudable ceramic masses and other masses which set as a result of baking or sintering, which masses comprise specific additives based on water-soluble cellulose ethers, an extrusion process, the extrudates and their use.

Water-soluble cellulose ethers have been used for many years as water retention agents, plasticizers and lubricants in the extrusion of ceramic masses and other masses which set as a result of baking or sintering to produce honeycomb bodies or other complicated profiles having similarly fine structures (see, for example: James S. Reed, Principles of Ceramics Processing, John Wiley & Sons, 1995, Chapter 23: Extrusion and Plastic Deformation Forming, p. 450 ff.)

The extrusion of ceramic masses and other masses which set as a result of baking or sintering is carried out by pressing a plastic mass through a die orifice to produce any desired profiles, preferably honeycomb profiles as are used in catalysts or diesel soot particle filters. These masses can have various makeups and basically comprise a material, in particular a ceramic material, which is sinterable or hardens as a result of a ceramic baking process. It can further comprise catalytically active materials, fibers, aggregates and lightweight aggregates.

Technical and economic disadvantages of the usually extruded ceramic masses and other masses which set as a result of baking or sintering are high extrusion pressures which make operation of the extruders prematurely uneconomical due to high wear or high power costs. Another disadvantage is an unsatisfactorily low extrusion rate which reduces the capacity of the entire plant. The mass should undergo very little heating as a result of internal friction, since the consumption of cooling water or electric cooling likewise impairs the economics. The mass should be able to be extruded without cracks and form no cracks after drying of the extruded profile in air and subsequent baking or sintering. The cohesion of the particles in the extruded mass should be so high that even thin webs should be able

to be extruded without problems. The shrinkage on drying and the shrinkage after baking should be minimal and virtually no crack formation should take place.

Rheological measurement methods are employed, inter alia, to characterize water-soluble cellulose ethers:

EP 1 025 130 B1 claims largely fiber-free cellulose ethers which in purely aqueous solution in concentrations of 0.5% by weight display values of the loss factor (tan δ) of less than 1 at an angular frequency of 1 Hz. These are claimed as auxiliaries for applications in the cosmetics, pharmaceutical and food sectors and for the production of paints (emulsion paints and silicate paints) and also in civil engineering. Use in the extrusion of ceramic or other sinterable masses is not described.

EP 1506979 describes a cellulose ether composition as additive for the extrusion of mineral masses. The extent to which cellulose ethers prove to be advantageous in the extrusion of ceramics or other sinterable materials is not disclosed.

It has now surprisingly been found that particular water-soluble cellulose ethers are suitable for overcoming the abovementioned disadvantages in the extrusion of ceramic masses and other masses which set as a result of baking or sintering.

The invention therefore provides ceramic masses and other masses which set as a result of baking or sintering which comprise water-soluble cellulose ethers, wherein these water-soluble cellulose ethers are characterized in that an alkaline solution of 1.0 part by weight of these cellulose ethers per 100 parts by weight of solution displays elastic properties in which the ratio of loss modulus G" to storage modulus G' (tan δ = G"/G') of the solution at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent in a rheological oscillation experiment as a function of the angular frequency ω in the linear viscoelastic region at angular frequencies of less than or equal to 100 rad/s has a value of less than 1.3.

Preference is given to cellulose ethers of the abovementioned type whose solutions as described above have a tan δ = G"/G' of less than or equal to 1.2, particularly preferably less than or equal to 1.1 and very particularly preferably < 1.0, at angular frequencies of less than or equal to 100 rad/s.

The masses of the invention preferably comprise cellulose ethers of the abovementioned type which are simultaneously characterized in that an alkaline solution of 1.5 parts by weight of the cellulose ethers per 100 parts by weight of solution has a capillary breakup time in an extensional flow experiment at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent of 2.0 or more seconds.

Extensional flow experiments to determine the capillary breakup time are known per se to those skilled in the art. For the purposes of the present invention, the figures for the capillary breakup time are based on measurements using a Haake Capillary Breakup Extensional Rheometer (CaBER 1) from Thermo Fischer, Karlsruhe, Germany. In the measurement, a liquid sample is introduced between two smooth concentric plates between which the liquid forms a "liquid bridge". During the measurement, the upper plate moves upward from the starting position (plate spacing 3 mm) to a plate spacing of 9 mm in 25 milliseconds and is then fixed in this position.

The sudden extension forms an unstable liquid capillary between the two plates. After extension is complete (plate spacing: 9 mm), the middle of the liquid capillary is subject to an extension which is determined by the extension properties of the sample. The decrease in the diameter in the middle of the liquid capillary is monitored as a function of time by means of a laser micrometer. To obtain reproducible measured values, the capillary breakup time is defined as the time interval from the end of the moving apart of the plates to the point in time at which the liquid capillary has a diameter of only 0.1 mm. The capillary breakup times reported were obtained by forming the mean of five individual measurements.

Preference is given to cellulose ethers of the abovementioned type whose solutions as described above have a capillary breakup time of greater than 2.5 seconds, particularly preferably greater than 3.0 seconds.

For the purposes of the present invention, ceramic masses and other masses which set as a result of baking or sintering are all masses which comprise at least one of the components listed below which can be baked or sintered by baking or sintering alone or with addition of other sintering aids:

alumina, aluminum nitride and aluminum carbide, kaolin, cordierite, mullite, silicon carbide, silicon boride, silicon nitride, titanium dioxide, titanium carbide, boron carbide, boron oxide, silicates and sheet silicates such as clay, bentonites, talc, silicon metal, carbon as carbon black or graphite, ground glass, rare earth oxides and other metal oxides, zeolites and related substances.

The term "ceramic masses and other masses which set as a result of baking or sintering" does not include hydraulic binders such as cement or gypsum and masses based on cement or gypsum. These hydraulic binders set as a result of incorporation of water into the crystal lattice.

According to the invention, cellulose ethers having the abovementioned properties are to be used. These can be water-soluble cellulose ethers such as ionic cellulose ethers such as sulfoethylcellulose or carboxymethylcellulose and salts thereof, or nonionic cellulose ethers such as alkylcelluloses, hydroxyalkylalkylcelluloses or hydroxyalkylcelluloses, in particular methylcellulose, methylhydroxyethylcellulose, methylhydroxypropylcellulose, hydroxyethylcellulose, ethylhydroxyethylcellulose, methylethylhydroxyethylcellulose, methylhydroxyethylhydroxypropylcellulose, methylhydroxyethylhydroxybutylcellulose or cellulose ethers which at the same time comprise methyl groups and longer-chain hydrophobic side chains and also mixtures of the abovementioned products.

Such cellulose ethers can easily be prepared by etherification of commercially available celluloses. An overview of the chemical fundamentals and principles in the

preparation (preparative processes and process steps) and a materials composition and description of the properties and uses of the various derivatives is given in, for example, Houben-Weyl, Methoden der Organischen Chemie, Makromolekulare Stoffe, 4th edition, Volume E 20, p. 2042, Thieme Verlag, Stuttgart (1987) and Ullmann's encyclopedia of industrial chemistry, Verlag Chemie, Weinheim/New York, (5.) A 5, p. 468.

The cellulose ethers to be used for the purposes of the invention can be selected from among the cellulose ethers mentioned without problems and without the need to be inventive with the aid of the parameters such as tan δ and capillary breakup time which are relevant to the invention and can easily be determined by a person skilled in the art by means of routine experiments. The corresponding parameters for the synthesis of the cellulose ethers used are described in the examples.

Further additives such as hydrophobicizing agents, redispersion powders, superabsorbents based on crosslinked acrylates and polysaccharides, plasticizers, gelatins, lubricants (for example polyethylene oxide homopolymers, copolymers and terpolymers), surfactants, defoamer, waxes, oils, fatty acids and esters thereof, polymers based on acids, salts, amides and esters of acrylic acids and methacrylic acids, polysaccharides such as natural or modified starches, xanthans, glucans, welans, guar, dextran, chitin, chitosan, xylan, gellan, mannan, galactan, arabinoxylan, alginates and related polysaccharides, polyvinyl alcohols including derivatives thereof and polymers based on urethanes can be added to the cellulose ethers.

Fibers which leave behind pores after baking or remain in the extrudate and increase the flexural strength can also be added to the masses of the invention.

For the present purposes, fibers are all types of natural or synthetic fibers such as fibers based on cellulose, bamboo, coconut, polyethylene, polypropylene, polyamide, polyacrylonitrile, carbon, glass, ceramic and other mineral fibers. Their fiber lengths and thicknesses can be varied within wide ranges.

The invention further provides a process for the extrusion of ceramic masses or other masses which set as a result of baking or sintering, which comprises mixing a ceramic mass or other mass which sets as a result of baking or sintering with at least one cellulose ether to be used according to the invention and subsequently extruding it.

The invention likewise provides the extrudates which can be obtained by the process of the invention, shaped bodies which can be obtained therefrom by thermal treatment and their use as honeycomb bodies for exhaust gas purification or as catalyst.

Examples:

Preparation of the cellulose ethers:

The cellulose ethers used were prepared as described in Houben-Weyl, Methoden der Organischen Chemie, Makromolekulare Stoffe, 4th edition, Volume E 20, p. 2042 Thieme Verlag, Stuttgart (1987).

245 g on a dry basis of cotton linters cellulose or wood pulp having a limiting viscosity indicated in the table below were placed in a 5 liter autoclave and made inert by evacuation and introduction of nitrogen. The precise reaction conditions were matched to the substitution pattern desired in each case. 257 g of dimethyl ether, 3.5-5 eq. of methyl chloride and 3-4 eq. of 50% strength by weight aqueous sodium hydroxide solution were added via an injection line while stirring. The mixture was made alkaline at 25°C over a period of 60 minutes while stirring. 0.45 eq. of ethylene oxide or 0.55 eq. of propylene oxide were subsequently added, the reactor was heated to 85°C over a period of 30 minutes and etherification was carried out at 85°C for from 120 to 240 minutes, the reactor was subsequently cooled and the volatile constituents were taken off by evacuation. The crude product was washed twice with hot water, subsequently dried and milled.

Celluloses used were wood pulp and/or linters characterized by the following limiting viscosities. The limiting viscosity was determined in accordance with ISO 5351-1 (1981).

Sample	Cellulose ether	Limiting viscosity [ml/g]
1	Methylhydroxyethylcellulose	800-1000
2	Methylhydroxypropylcellulose	1100-1300
3	Methylhydroxyethylcellulose	1200-1500
4	Methylhydroxyethylcellulose	1500-1700
5	Methylhydroxyethylcellulose	1600-1900
6	Methylhydroxyethylcellulose	1800-2200

Procedure for rheological experiments:

The rheological characterization of the cellulose ethers described was carried out on the basis of the respective cellulose ether as solid taking account of residual salt contents and residual moisture contents.

To describe the viscoelastic behavior, the storage modulus G' and the loss modulus G" or the loss factor tan δ, respectively, as the ratio G"/G' were in each case determined as a function of the angular frequency ω in a rheological oscillation experiment. The storage modulus G' corresponds to the deformation energy which is completely available after the stress is removed. The storage modulus G' indicates the elastic behavior of the sample. The loss modulus G", on the other hand, is a measure of the deformation energy consumed during the shearing process in the sample and thus represents the viscous behavior.

G' and G" were determined by means of measurements in oscillating shear flow at low amplitude (deformation $\gamma < 5\%$) and variable angular frequency. At small deformations (amplitudes), the material functions measured are independent of the magnitude of the deformation and thus dependent only on the angular frequency employed.

As measurement solutions for the determination of tan δ, the cellulose ethers were measured in a concentration of 1.0 part by weight per 100 parts by weight of a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent and at a temperature of 20°C in a rheological oscillation experiment in the linear viscoelastic range.

The measurements were carried out at 20°C using a Haake rotational rheometer RS 600 from Thermo Fischer, Karlsruhe, Germany, having a cone-plate geometry (C60/2°) and a Physica MCR 501 (Anton Paar, Ostfildern, Germany) having a cone-plate geometry (CP50/1°). Here, the sample was conditioned in the measurement gap employed for 180 seconds before the actual measurement.

The extensional flow experiments necessary to determine the capillary breakup time are based on measurements using a Haake Capillary Breakup Extensional Rheometer (CaBER 1) from Thermo Fischer, Karlsruhe, Germany. In the measurement, a liquid sample was introduced between two smooth, concentric plates between which the liquid formed a "liquid bridge". During the measurement, the upper plate moved upward from the starting position (plate spacing: 3 mm) over a period of 25 milliseconds to a plate spacing of 9 mm and was then fixed at this position. The capillary breakup time is the time until the liquid capillary formed on extension breaks again.

Solutions of 1.5 parts by weight of the cellulose ether per 100 parts by weight of a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent were used for these studies. A cushioned strike profile was used for this extension profile. The measurement of the decrease in the diameter of the liquid capillary was carried out in the real time mode at a sampling frequency of 1000 Hz. All measurements were carried out at a temperature of 20°C.

Procedure for the extrusion experiments

The dry components were firstly premixed dry, then admixed with water and mixed again. They were subsequently kneaded, compacted in a single-screw extruder and extruded through a die orifice:

35 parts by weight of silicon carbide SiC Dunkel Mikro F 280 (manufactured by ESK-SiC GmbH, Frechen, Germany), 35 parts by weight of silicon carbide Sic Dunkel Mikro F 360 (manufactured by ESK-SiC GmbH, Frechen, Germany), 30 parts by weight of silicon carbide SiC SM 10 (manufactured by ESK-SiC GmbH, Frechen, Germany) and 4 parts by weight of cellulose ether were firstly mixed dry in a fluidized-bed mixer (manufactured by Lödige, Germany) until homogeneous, water at 20°C was subsequently added, the mass was mixed further and kneaded in a kneader (manufactured by AMK, Aachen, Germany) for a few minutes. The mass was then immediately introduced into the feed trough of a single-screw extruder maintained at 20°C (Händle 8D, screw diameter 8 cm, from Händle, Mühlacker, Germany). In this, the mass was extruded through a perforated plate and passed through the vacuum chamber for degassing. It was then firstly strained (i.e. pressed through a screen having a mesh opening of 0.4 or 0.2 mm in order to separate off aggregates) and subsequently extruded through a honeycomb die orifice (for details see below) and discharged onto a conveyor belt. To be able to see differences between cellulose ethers which lubricate well and lubricate poorly, the cooling was switched off on the extruder after commencement of the experiment and the heating of the mass during the experiment was measured.

All masses extruded in this way were set to a customary consistency (Shore hardness = 10.0-11.5) by means of a water to solids ratio (W/S ratio) based on their water requirement. The consistency is a measure of the stiffness of the mass.

Cellulose ethers used:

Sample	Cellulose ether	tan δ at 100 rad/s	Capillary breakup time
1	Methylhydroxyethylcellulose	3.6	0.7 s
2	Methylhydroxypropylcellulose	1.2	2.0 s
3	Methylhydroxyethylcellulose	1.2	2.1 s
4	Methylhydroxyethylcellulose	0.8	3.6 s
5	Methylhydroxyethylcellulose	0.9	4.3 s
6	Methylhydroxyethylcellulose	0.7	4.4 s

Ex.	Cellulose ether	W/S	Current drawn	Pressure at 200 cpsi (bar)	Pressure at 300 cpsi (bar)	Heating of the compo-sition
A	6	0.165	1.88	42	50	<10°C
B	5	0.165	1.89	47	55	<10°C
C	4	0.165	1.91	51	58	<10°C
D	3	0.165	1.96	53	61	>10°C
E	2	0.165	1.96	58	>62	>10°C
F	1	0.165	Not strainable	n.e.	n.e.	>10°C
G	1	0.21	3.52	n.e.	n.e.	>10°C

Abbreviations: n.e.: not extrudable

The parts by weight of the cellulose ethers are based on 100 parts of silicon carbide (dry).

W/S is the water/solids factor. The amount of water used is calculated only on the basis of silicon carbide.

The current drawn during straining (= pressing of the mass through a metal screen having a mesh opening of 0.4 mm to remove any agglomerates) is an indicator of

the flowability of the mass and at the same time also of the economics. Currents drawn of 2 bar and above are a serious danger to bearings, motor and shaft of the extruder (extruder 8D from Händle, Mühlacker, Germany).

Pressure is the pressure measured just before the mass passes through the honeycomb die orifice. A 200 cpsi die (web thickness = 0.30 mm) and a 300 cpsi die (web thickness = 0.26 mm) (cpsi is the number of cells per square inch) were used.

The temperature of the strained and extruded masses was measured by means of a noncontact infrared thermometer after leaving the die orifice; these temperatures coincided with those measured via the temperature sensor built into the die head.

Experimental results:

Examples A to C using cellulose ethers 6, 5 and 4 according to the invention having tan $\delta < 1$ and a capillary breakup time > 3 seconds in each case could be extruded without difficulty. Currents drawn by the extruder, extrusion pressure and heating of the mass were in a tolerable range. As examples D and E using cellulose ethers 3 and 2 show, the use of cellulose ethers having a tan δ and capillary breakup time outside the range according to the invention does not lead to a process which functions well in technical terms, since the heating of the mass in an uncooled extruder exceeds the critical figure of 10°C. In addition, the current drawn gets too close to the critical value of 2 A. At the same time, a pressure of 60 bar is exceeded during extrusion through a 300 cpsi die.

The mass in example F could not be strained at a W/S of 0.165; the addition of further water (to a W/S of 0.21, cf. example G) also did not lead to the necessary plasticization, so that the experiment had to be stopped after a current increase to 3.52 A for the main screw.

Claims

1. A ceramic mass or other mass which sets as a result of baking or sintering which comprises water-soluble cellulose ethers, wherein these water-soluble cellulose ethers are characterized in that an alkaline solution of 1.0 part by weight of these cellulose ethers per 100 parts by weight of solution displays elastic properties in which the ratio of loss modulus G" to storage modulus G' (tan δ = G"/G') of the solution at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent in a rheological oscillation experiment as a function of the angular frequency ω in the linear viscoelastic region at angular frequencies of less than or equal to 100 rad/s has a value of less than 1.3.

2. The ceramic mass or other mass which sets as a result of baking or sintering as claimed in claim 1, characterized in that a solution of 1.5 parts by weight of the cellulose ethers per 100 parts by weight of solution has a capillary breakup time in an extensional flow experiment at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent of 2.0 or more seconds.

3. The ceramic mass or other mass which sets as a result of baking or sintering as claimed in claim 1 or 2, characterized in that it comprises at least one compound from the group consisting of alumina, aluminum nitride and aluminum carbide, kaolin, cordierite, mullite, silicon carbide, silicon boride, silicon nitride, titanium dioxide, titanium carbide, boron carbide, boron oxide, silicates and sheet silicates such as clay, bentonites, talc, silicon metal, carbon black, graphite, ground glass, rare earth oxides and zeolites.

4. The ceramic mass or other mass which sets as a result of baking or sintering as claimed in any of claims 1 to 3, characterized in that it comprises fibers.

5. A process for the extrusion of ceramic masses or other masses which set as a result of baking or sintering, which comprises mixing a ceramic mass or other mass which sets as a result of baking or sintering with at least one water-soluble cellulose ether whose alkaline solution of 1.0 part by weight of cellulose ethers per 100 parts by weight of solution displays elastic properties in which the ratio of loss modulus G" to storage modulus G' (tan δ = G"/G') of the solution at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent in a rheological oscillation experiment as a function of the angular frequency ω in the linear viscoelastic region at angular frequencies of less than or equal to 100 rad/s has a value of less than 1.3 and subsequently extruding it.

6. The process as claimed in claim 5, characterized in that a solution of 1.5 parts by weight of the cellulose ethers per 100 parts by weight of solution has a capillary breakup time in an extensional flow experiment at a temperature of 20°C +/- 1°C when using a solvent comprising 98 parts by weight of water and 2 parts by weight of sodium hydroxide per 100 parts by weight of solvent of more than 2.5 seconds.

7. The process as claimed in claim 5 or 6, characterized in that a thermal treatment of the extrudate is carried out after the actual extrusion.

8. An extrudate which can be obtained by a process as claimed in any of claims 5 to 7.

9. The use of an extrudate as claimed in claim 8 as honeycomb body for exhaust gas purification or as catalyst.