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(54) Titre : FLOCCULANT OU LIANT DESTINES A L'INDUSTRIE CERAMIQUE
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(57) Abrégé/Abstract:

The invention relates to a flocculant or binding agent composition for producing ceramic products, said composition containing amylopectin-potato starch (AP-KS), to a slurry for producing ceramic products and to a method for producing ceramic products.



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(54) Title: FLOCCULANT OR BINDING AGENT FOR THE CERAMICS INDUSTRY

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(57) Abstract: The invention relates to a flocculant or binding agent composition for producing ceramic products, said composition containing amylopectin-potato starch (AP-KS), to a slurry for producing ceramic products and to a method for producing ceramic products.

(57) Zusammenfassung: Beschrieben wird eine Flockungs- oder Bindemittelzusammensetzung für die Herstellung keramischer Erzeugnisse, welche Amylopektin-Kartoffelstärke (AP-KS) umfasst, ein Slurry zur Herstellung keramischer Erzeugnisse, sowie Verfahren zur Herstellung von keramischen Erzeugnissen.



WO 02/016285 A1

- 1 -

Flocculant or Binder for the Ceramics Sector

The invention relates to a flocculant or binder for the ceramics sector.

When producing ceramics products, inorganic basic materials, mostly inorganic fiber materials, are introduced into an aqueous sludge referred to as slurry. The addition of flocculants and/or binders and optionally other components will cause the formation of flocks. After the separation of the formed flocks, the moist cake is at first dried and then baked to ceramics using different thermal processes.

In order to prepare suitable slurries, a great number of additives are required, including flocculants and/or binders, by which the inorganic materials contained in the slurry are brought into a form/distribution that is suitable for the final heat treatment.

Due to the increasing concern for environmental protection of the last decade, there has been great interest in using, for the manufacture of ceramics, flocculants and/or binders that do not produce environmentally relevant noxious matter during the final heat treatment, which is also called carbonization if inorganic substances are used. While aromatic compounds such as, for instance, phenolic resins were frequently used in former times, as in DE 32 31 100-A1 for the production of shaped articles of silicon carbide, starch-containing products have recently been successfully employed for quite some time.

Flocculants and binders based on starch have, therefore, been widely applied on the ceramics sector. This is of special importance, because flocculants and binders based on starch are of natural origin and hence more environment-friendly. Thus, no hazardous substances that might have impacts on the environment are released during carbonization.

Thus, the use of potato, corn and wheat starch derivatives is described in US-5 618 767, which points at the merits of starch during carbonization. The use of the above-mentioned starches in

the manufacture of ceramics products based on silicon carbide is described, in particular.

US-3 224 927 extensively deals with the potentialities of cationic starches in the manufacture of heat-resistant products. There, the advantages of those starch products are emphasized, which can be optimally integrated in a system of fibers and the binder silica sol. The starches described comprise commercially available cationic starches from National Starch, which have to be initially gelatinized during flocculation.

WO 99/15322 describes the vacuum-forming process technique for the production of ceramic shaped bodies. In that process, flocculants are preferably added, with cold water soluble cationic starches being above all applied. Commercially available products based on corn starch or conventional potato starch are especially mentioned.

EP-094 731 A informs about the production of shaped ceramics. Also there, starch and, in particular, corn starch but also rice starch, tapioca starch or conventional potato starch are used as binders.

In the prior art described, starch products are, thus, used as flocculants or binders in native or degraded and/or modified and/or derivatized forms.

Starch is a natural plant product. It consists essentially of a glucose polymer which, as a rule, is a composition of two components, namely amylopectin and amylose. These are, in turn, no uniform substances, but mixtures of polymers having different molecular weights. Amylose essentially consists of unbranched polysaccharides in which glucose is present in an alpha-1,4-bond. Amylopectin, on the other hand, is a strongly branched glucose polymer in which the glucose moieties on the branching points are contained in 1,6-bonds besides alpha-1,4-bonds.

Natural starches, as a rule, have amylose contents ranging from 15 to 30%; only corn varieties of the waxy type yield starches that consist almost exclusively of amylopectin. The field of ap-

plication of this starch, which is called waxy corn starch, primarily pertains to the food industry. There, it is particularly appreciated that amylose-free starch tends to threading during gelatinization to a largely less extent, thus giving a more pleasant mouthfeel. It has also been shown that amylopectin starch exhibits fewer retrogradation phenomena, i.e. tends less strongly to reunifying already separated chains, than starch rich in amylose.

The cultivation of waxy corn is hardly practical, or impossible from an economical point of view in cold or tempered climates as are found in Austria, Germany, Belgium, the Netherlands, Great Britain, Poland, etc.. Waxy corn, therefore, could not find acceptance in those areas for cost reasons. By contrast, potatoes are common starch sources in those countries. Compared to cereal starch, potato starch has a lower content of lipids and proteins and contains considerable amounts of phosphate ester groups. A comparative representation in this respect, which takes into account the amylopectin potato starch presently claimed, is set out in the experimental part of the description of the present invention.

Methods for reducing the amylose content of starch by physical or chemical means are known. Yet, these involve considerable expenditures and are feasible only if justified from an economical point of view.

These methods for reducing amylose contents, however, require treatments at elevated temperatures (usually above approximately 140° C), which will inevitably result in the formation of degradation products. Yet, such degradation products may have adverse effects with many applications. Moreover, the fractionation process is very complex and cost-intensive, what has so far prevented such products from being successful in large-scale applications. In the context of the present invention, amylopectin potato starches prepared by fractionation are referred to as fractionated amylopectin potato starches (FAP-PSs).

Due to the successful genetic modification of potatoes achieved

during the last decade, which was aimed at providing a starch free of amylose, completely new types of starch could be made accessible (WO 92/11376 A). As a result, it became, for instance, feasible for the first time to obtain an amylose-poor or amylose-free potato starch in which the three-dimensional amylopectin structure typical of potato starch is completely retained without involving the formation of degradation products or deviations of the three-dimensional network from the native structure (cf. WO 92/11376). In this manner, an amylopectin potato starch is provided, which is not only substantially more defined, but also particularly well apt for derivatization processes (cf. again WO 92/11376 A).

Although a plurality of applications have been proposed for these novel starch products, only little is known about the actual technical exploitability of these starch products on account of the small amounts available so far. Thus, waxy corn starch is still the only starch product rich in amylopectin which has so far been used on an industrial scale in the prior art, having already gained ground on the market because of its ready availability as compared to FAP-PS or other waxy cereal starches that can be obtained from mutants of common cultigens.

The above-mentioned amylopectin-rich starches with native amylopectin patterns (cf. WO 92/11376), which are produced by selectively manipulating the amylose-forming enzymes contained in the potato and are referred to as amylopectin potato starches (AP-PS) for the purposes of the present invention, have already been proposed for some applications as pointed out above, yet not for the manufacture of ceramics products.

It is the object of the present invention to provide an improved flocculant or binder especially for the ceramics sector. Furthermore, an improved method for producing ceramics products is to be provided, by which ceramics having improved properties can be produced.

In accordance with the invention, this object is achieved by a flocculant or binder composition for the production of ceramics products, which is characterized in that it comprises amylo-

pectin potato starch (AP-PS).

In the production of ceramics products, amylopectin potato starch surprisingly exhibited properties substantially superior to those of products proposed so far for this purpose and, in particular, in comparison with other starch products. In the context of the present invention, it was, in fact, possible to achieve a decisive improvement particularly over fractionated amylopectin potato starch (FAP-PS) as well as over waxy corn starch and, of course, also over conventional potato starch as well as over products derived from these starch derivatives.

Amylopectin-rich starch has so far been proposed only for applications in fields where its properties have come to light at room temperature or at slightly elevated temperatures such as, for instance, in the textile and paper industries (cf., e.g., US-5 582 670). On the ceramics sector, however, the use of AP-PS in the course of production processes has neither been proposed nor encouraged. Accordingly, the completely surprising positive properties of AP-PS as against related products and, in particular, other starches rich in amylopectin such as FAP-PS or waxy corn starch, have not yet been revealed, either.

By the term "ceramics", products made of clay minerals are understood both in everyday usage and according to the invention. The diversity of ceramic materials as well as their applications have largely increased during the past decades such that, in addition to clay minerals, also carbides, nitrides, oxides or silicides are used today amongst others. Concurrently with this development, refractory ceramics became established on the market. According to DIN 51060, the term refractory materials serves to denote nonmetallic materials like high-melting oxides, refractory silicates, etc.. (yet including also those containing defined metal portions like, for instance, cermets), which have Seger cone falling points of at least 1500° C. These products stand out for being usable at temperatures of >800° C over extended periods of time.

According to the ISO recommendation R 1109, they are classified as follows:

1. Products rich in alumina group 1: $> 56\% \text{Al}_2\text{O}_3$
2. Products rich in alumina group 2: $45-56\% \text{Al}_2\text{O}_3$
3. Fireclay refractories: $30-45\% \text{Al}_2\text{O}_3$
4. Acidic fireclay refractories: $10-30\% \text{Al}_2\text{O}_3$, $< 85\% \text{SiO}_2$
5. Siliceous refractories: $85-93\% \text{SiO}_2$
6. Silica products: $> 93\% \text{SiO}_2$
7. Basic refractories: with variable amounts of magnesite- chromite,...
8. Special products based on carbon, graphite, Zr-silicate, nitrides, borides, cermets ...

Ceramics products offer a large and wide field of application. Typical examples include their use in the car industry, in industrial blast furnaces for refractory materials or high-temperature filters.

Ceramics products are above all characterized by their porosity, which is achieved especially by using starch-containing flocculants or binders.

Although, in principle, starch has been used as a flocculant in other fields (for instance in paper production), the ceramics industry makes very special demands on a flocculant, which, on the one hand, are attributed to the preparation of slurries of inorganic materials and, on the other hand, are explained by the drying/forming and firing processes following subsequently.

By flocculant, those substances are understood which influence the zeta potential (electrokinetic potential) of colloidal particles in a manner so as to cause the formation of aggregates such as, for instance, flocks. The zeta potential of dispersed particles is reduced or neutralized by flocculants. In order to enable flocculation at all, the flocculant must overcome the electrostatic repulsion of the particles which are mostly negatively charged in the solvent, primarily water.

Starches or starch derivatives cause solids particles to agglomerate to large units (flocks), said agglomeration to suspended particles being effected by bridging. According to accepted

teachings, the effectiveness of a flocculant is a function of the ionic character, on the one hand, and of the molecular chain length, on the other hand. It has not yet been recognized that the nativity of the amylopectin structure might play an important role in this respect. Moreover, starch may also have a binding function in the field of ceramics products. It may, for instance, constitute an important binding link between fibers and other auxiliary substances or binders like silica sol. On account of its organic nature, starch is a temporary binder which is converted into carbon by heat treatment, thus forming a stable three-dimensional network structure (porous matrix) with the silicon present.

It has been shown by the invention that it is exactly AP-PS which imparts special properties on the produced ceramics product by that conversion. Then there are the properties that are enhanced during the preparation process of the slurry.

AP-PS is preferably obtained from potatoes in which the starch granule-bound starch synthase I (GBSS I), which is responsible for the α -1,4-glycosidic bond to the linear amylose molecule, is limited in its activity or totally inactivated, for instance by a suitable antisense technology as described in WO 92/11376. The inhibition of GBSS I, for instance, allows for the production from potatoes, of native AP-PS with an amylopectin content that is largely increased as compared to that of natural potato starch, without having to put up with the disadvantage of fractionated amylopectin potato starch (degradation products; thermal treatment).

Therefore, AP-PS having a content of at least 95%, preferably at least 98%, of amylopectin, based on the overall starch quantity, is used in a preferred manner.

Preferably, AP-PS is obtained from a potato modified by breeding or by molecular-biological or genetic-engineering techniques for the purpose of amylose inhibition. Above all, the AP-PS to be used according to the invention is obtained from a potato inhibited by the antisense inhibition of a GBSS gene or by co-suppression in respect to amylose formation. In doing so, the

synthesis of amylose is preferably impeded or inhibited, with the amylopectin branching being preferably left unchanged. After all, this is readily feasible from a technical point of view, since the synthesis of amylose and the formation of amylopectin branching patterns are two completely independent processes occurring in the plant. The participating enzymes are specific for both processes and can each be influenced in their activities in a mutually independent and specific manner, for instance by genetic-engineering interventions. Thus, AP-PS can be obtained as a known starch (potato starch) with a modified amylose/amylopectin ratio at an otherwise completely unchanged quality (regarding its branching degree). As opposed to the preparation of FAP-PS, the starch quality in recombinantly produced AP-PS is unambiguously definable and hence accessible to a precise success control, whereby the industrial availability of AP-PS is safeguarded.

Starches obtained from genetically manipulated potatoes in which the branching degree of amylopectin has been modified (optionally at an equally high portion of amylose; WO 96/19581) turned out to be disadvantageous in the context of the present invention and, therefore, are not to be considered as AP-PSs in the sense of the present invention - because of their high amylose contents alone.

Another important characteristic of amylopectin potato starch is its molar mass distribution and its mean molecular weight. The differences from waxy starches such as, for instance, waxy corn starch, or a potato starch amylopectin prepared by physical or chemical methods, become particularly apparent by size exclusion chromatography (SEC) measurements. The respective data are set out in the experimental part.

AP-PS in the flocculant or binder composition according to the invention is preferably modified and, in particular, cationically modified. In this context, amylopectin potato starches including nitrogen-containing groups and, in particular, electropositively charged quaternary ammonium groups have proved particularly beneficial.

According to a particularly preferred embodiment, the amylopectin potato starch according to the invention is an amylopectin potato starch sulfamate.

Depending on the nature of the organic fibers used, both an anionically charged amylopectin potato starch and a cationically charged amylopectin potato starch may, however, be required. In special cases, also an amphoteric amylopectin potato starch may constitute a preferred variant.

From the literature, a plurality of derivates is known, the preparation of which is readily apparent, *inter alia*, from "Starch: Chemistry and Technology", R.L. Whistler, Chapters X and XVII, 1984, and from "Modified Starches: Properties and Uses", edited by O.B. Wurzburg, Chapters 2-6 and 9-11, CRC Press, 1986. In general, distinction is made among anionic, cationic and amphoteric starch derivates, the following derivatization options for other starch types belonging to the prior art.

Under anionic modification of amylopectin potato starch, those derivatives are summarized where the free hydroxyl groups of the starch are substituted by anionic groups. Unlike waxy corn starch, amylopectin potato starch comprises naturally bound anionic groups such that, in the true sense, one has to speak of an additional anionic modification. These are naturally chemically bound phosphate groups which impart an additional specific polyelectrolytic property on the amylopectin potato starch.

Basically, there are two ways of carrying out anionic derivatization:

a) Modification is effected in a manner so as to induce the esterification of amylopectin potato starch. Modification agents include inorganic or organic heterovalent, mostly bivalent, acids or salts thereof or esters or anhydrides thereof. Thus, the following acids are suitable amongst others, their enumeration being only exemplary:

o-phosphoric acid, m-phosphoric acid, poly-phosphoric acid, various sulfuric acids, various silicic acids, various boric

- 10 -

acids, oxalic acid, succinic acid, glutaric acid, adipic acid, phthalic acid, citric acid, etc.. Mixed esters or anhydrides may be used as well. When esterifying amylopectin potato starch, this may also be effected several times so as to produce, for instance, distarch phosphoric esters.

b) Modification is effected in a manner so as to induce the etherification of amylopectin potato starch. Modification agents include inorganic or organic α -substituted acids or salts thereof or esters thereof. This type of reaction results in the cleavage of the α -substituent while forming an ether group.

Consequently, the amylopectin potato starch is additionally substituted, for instance, by phosphate, sulfate, sulfonate or carboxyl groups. This is accomplished, for instance, by the reaction of amylopectin potato starch with α -halocarbonic acid, chlorohydroxy alkyl sulfonates or chlorohydroxy alkyl phosphonates.

Under cationic modification of amylopectin potato starch, those derivatives are summarized where a positive charge is introduced into the starch by substitution. Cationization methods are carried out by the aid of amino, imino, ammonium, sulfonium or phosphonium groups. Methods for preparing cationized starches are, for instance, described in D.B. Solareck: Cationic Starches, in the book by O.B. Wurzburg (Ed.): Modified Starches: Properties and Uses, CRC Press Inc., Boca Raton, Florida (1986), pp. 113-130. Such cationic derivatives preferably contain nitrogen-containing groups, in particular primary, secondary, tertiary and quaternary amines, or sulfonium and phosphonium compounds, respectively, which are bound via ether or ester bonds. The use of cationized amylopectin potato starches containing electropositively charged quaternary ammonium groups is preferred.

In detail, also the sulfamates of amylopectin potato starch are to be mentioned herein, their production likewise falling within the scope of the present invention. This new amylopectin potato starch derivative is obtained by reaction of the presently claimed amylopectin potato starch with ammonium, earth alkali or

alkali sulfamates. An exemplary description of the preparation of this derivative will also be found in the experimental part.

Another group is represented by amphoteric starches. They contain both anionic and cationic groups, their applications thus being highly specific. These are usually cationic starches which are additionally modified either by phosphate groups or by xanthates. The preparation of such products is also described by D.B. Solareck: Cationic Starches, in the book by O.B. Wurzburg (Ed.): Modified Starches: Properties and Uses, CRC Press Inc., Boca Raton, Florida (1986), pp. 113-130.

Esters and ethers of amylopectin potato starch are of great importance. Distinction is made between simple starch esters and mixed starch esters, with different ester substituent(s) being conceivable: in the ester residue RCOO- , the residue R may be an alkyl, aryl, alkenyl, alkaryl or aralkyl residue having 1 to 17 carbon atoms, preferably 1 to 6 carbon atoms and, in particular, 1 or 2 carbon atoms. These products include the following derivatives: acetates (prepared from vinyl acetate or acetic anhydride), propionates, butyrates, stearates, phthalates, succinates, oleates, maleinates, fumarates and benzoates.

Etherifications are mainly realized by reactions with alkylene oxides containing 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms and, in particular, by using ethylene and propylene oxides. Yet, also methyl, carboxymethyl, cyanoethyl and carbamoyl ethers may be prepared and used. Further products comprise alkyl hydroxyalkyl, alkyl carboxyalkyl, hydroxyalkyl carboxymethyl and alkyl hydroxy alkyl carboxymethyl derivatives.

Besides said esters and ethers, amylopectin potato starch can also be crosslinked to different extents. Crosslinking is preferably effected by reaction with epichlorohydrin or 1,3-dichloro-2-propanol, optionally mixed with (poly)amines, furthermore with phosphoroxchloride, sodium trimetaphosphate, di- or polyepoxides, mixed anhydrides of carbonic acids with di- or tribasic acids such as, for instance, a mixed anhydride of acetanhydride with adipic acid, aldehydes or aldehyde-releasing reagents such as, for instance, N,N' -dimethylol- N,N' -ethylen-

eurea.

Pastes of these crosslinked starches at lower degrees of crosslinking exhibit rapidly increasing viscosities which, however, decrease again with crosslinking increasing. Yet, retrogradation is very low in both cases, for which reason crosslinked amylopectin potato starch is also highly advantageous with a view to obtaining a long flocculation stability. Moreover, crosslinked amylopectin potato starches additionally modified by the compounds described above also constitute advantageous starch materials.

Finally, amylopectin potato starch may also be present as a graft polymer or a graft copolymer, for instance with products from the group of polyvinyl alcohols, acrylamides, or monomers or polymers derived from petroleum hydrocarbons. In this case, the amylopectin potato starch graft (co)polymer may preferably be present as an emulsion polymer.

All the above-mentioned modifications of amylopectin potato starch are obtainable not only by reacting native starches, but also by employing degraded forms. The degradation procedures can be realized in a mechanical, thermal, thermochemical or enzymatic manner. Thus, it is not only feasible to structurally modify amylopectin potato starch, but the starch products can also be made soluble or swellable in cold water.

Cold water soluble degraded amylopectin potato starch, in particular, can be prepared with or without pre-gelatinization by drum drying, spray drying, etc.. The degree of dissociation is of great relevance to the optimum development of the properties of starch or starch derivatives soluble in cold water. Amylopectin potato starch or its derivatives do not show any lump formation, dust development and tendency to demixing during their dissociation and subsequent use and are, therefore, perfectly processable in the practical application of a suitable paste-based dry product upon stirring into water. A very special method in this context is extrusion. It offers the possibility to degrade modified amylopectin potato starch to different extents by physical action and, at the same time, convert it into

- 13 -

a product soluble or swellable in cold water. Moreover, this technology also renders feasible the direct derivatization of amylopectin potato starch in a cost-saving manner.

When producing starch derivatives, the elevated grain stability of amylopectin potato starch allows for a simpler production technology than does conventional potato starch. The realization of reactions, for instance, in slurries is more efficient, yielding higher reaction rates. Besides, amylopectin potato starch is less sensible to alkalis and temperatures than conventional starches. Derivatization reactions like, for instance, etherification or esterification reactions, as well as many other reactions preferably used for the derivatization of starches, can thus be intensified at shorter reaction times while the use of gelatinization protection salts can be markedly reduced. The saving of reaction time and the marked reduction of chemicals employed is reflected not only economically by reduced production costs, but also in terms of ecology. Thus, for instance, the salt and CSB loads of reaction waste waters are considerably reduced.

The flocculant or binder composition according to the invention may further comprise sedimentation accelerators, stabilizers, dispersants, antifoaming agents, softeners, non-starch-based adhesives or adhesive precursors, buffers, salts, preserving agents or other common additives, optionally in combination. The selection and quantity of the aforementioned additives are, above all, functions of the intended use of the flocculant or binder composition, primarily in view of the inorganic fibers employed.

According to another aspect, the present invention relates to the use of AP-PS as a flocculant or binder in the production of ceramics products and the use of a flocculant or binder composition according to the invention for the production of ceramics products.

The production of ceramics products is generally performed in that an aqueous suspension of inorganic fibers is prepared, to which are subsequently added an inorganic binder, usually in the

- 14 -

form of colloidal silica sol, as well as the starch (according to the invention, that is the amylopectin potato starch), mostly in the positively charged state. Depending on the property of the product, additives and fillers may also be added. In general, the flock-containing mixture has a pH of 4 to 8. The separation of the formed flocks can be effected by decanting the liquid phase through a screened shaped body. The moist cake obtained by this procedure, which is generally referred to as green body, is initially dried and then baked to ceramics after various thermal procedures such as, for instance, sintering. The aim in any event is to carbonize the starch in order to thereby impart the desired porosity on the ceramic material. A general description for the manufacture of ceramics is to be found in "Coagulation and Flocculation", edited by Bohuslav Dobias, Chapter 11 (1993).

The slurry necessary for the production of ceramics products in most cases has a solids content of about 0.3-6% usually composed as follows (the data indicated below referring to the overall weight of the slurry):

The portion of inorganic fibers is around 0.5-4%, preferably at a concentration of 0.5-2%. In addition, organic or inorganic fillers are also added, which are usually employed at concentrations of 0-3%, preferably 0.1-2%. The binder is added in an amount of <2%, mostly <0.5%. The amylopectin potato starch is present at a concentration of from 0.001 to 0.5%, preferably 0.01 to 0.3%. Besides, up to 1% of additives such as, for instance, sedimentation accelerators, dispersants, antifoaming agents, softeners and many others may also be added, provided these additives have no adverse effects on the flocculation procedure. The large remainder in the slurry is water.

The inorganic fiber employed is of great relevance to the quality and demand of the ceramics product. The used fibers in most cases consist of aluminum silicates and are available on the market under various trade names. Examples of known product groups include the following fibers: Fiberfrax (available from Unifrax), Kaowool (Thermal Ceramics) or Maxsil (McAllister). Fibers made of zirconium, magnesium, calcium, yttrium, titanium

and other metals or oxides are primarily used for high-temperature applications. Yet, also whiskers or tabular oxides are used amongst others.

In the production of ceramics products, also fillers may be added. These substances preferably comprise oxides of aluminum or aluminum silicates, but also chalk. Moreover, organic fibers such as, for instance, celluloses or polyethylene are applied.

The flocculation process proper is then realized according to the invention by the addition of amylopectin potato starch or a derivative thereof.

Accordingly, the present invention also relates to a slurry for the production of ceramics products, which is characterized in that it comprises a flocculant or binder according to the invention.

The invention preferably provides a slurry comprising AP-PS at a concentration of 0.001 to 0.5 weight percent.

The slurry according to the invention preferably also comprises

- inorganic fibers, in particular fibers based on aluminum silicates,
 - fillers, in particular oxides of aluminum or aluminum silicates or chalk,
 - organic materials, in particular organic fibers made of celluloses or polyethylene,
 - inorganic binders, in particular colloidal silica,
- or mixtures of these ingredients as well as other common additives.

According to another aspect, the present invention also relates to a method for producing ceramics products, comprising the following steps:

- preparation of a slurry according to the invention, and
- thermal treatment at a temperature of above 300° C, in particular above 500° C.

A good distribution of the fibers and fillers is required for

- 16 -

the flocculation process to proceed in the optimum manner. The addition of amylopectin potato starch, as a rule, can be accomplished in three different ways. If cooking starch is added, the slurry must be heated until boiling in order to initiate the flocculation process. It is only by heat that the starch will be gelatinized and hence brought into a water-soluble state. Alternatively, a derivative that is soluble in cold water can be introduced into the system in powdery form under moderate stirring so as to cause the amylopectin potato starch to enter into solution without lumps. A third option is to prepare a concentrated starch paste first and add it to the slurry.

It has been shown that amylopectin potato starch and, in particular, cationic amylopectin potato starch soluble in cold water can be stirred in in powdery form very quickly and, above all, free of lumps and in a completely dissolved state, what has proved to be particularly beneficial especially in the context of the present invention. The solution dynamics of amylopectin potato starch as well as the flocculation rate, in particular, could be markedly improved upon those of conventional starch derivatives. Yet, also the capacity could be substantially raised. Agglomeration or lump formation as they repeatedly occur with conventional cationic starches have not been observed at the application of amylopectin potato starch. Consequently, also possible predissolving of modified starch may be obviated, thus saving both time and equipment. It was, moreover, shown that upon introduction of the amylopectin potato starch into the system the formed flocks were extremely uniform and exhibited a markedly improved stability, particularly during extended processing times. The formed flocks surprisingly exhibit an excellent shearing stability even by the continuous agitation at an elevated speed in the reaction vessel. By using amylopectin potato starch, also inorganic fibers are wetted more effectively, thus becoming more fluid. On account of naturally chemically bound phosphate groups, amylopectin potato starch additionally offers specific polyelectrolytic properties clearly enhancing the fixation of the subsequently introduced binder on the fiber. Also can the quantitative ratio between binder and amylopectin potato starch be better regulated.

- 17 -

A further important factor resides in the clarity of the amylopectin potato starch paste, which is markedly higher. Comparative measurements with conventional cationic starch products by measuring light transmission on a conventional spectrophotometer revealed considerable advantages. Moreover, amylopectin potato starch derivative pastes show less tendency to retrogradation and are also viscostable over extended periods of time. Comparative measurements in this respect are set out in the experimental part.

In order to optimize the production of ceramics products, the addition of an inorganic binder is also favorable. In most cases, colloidal silica, which is generally referred to as silica sol, is used as an inorganic binder. As a rule, silica sols are 30-60% aqueous solutions whose turbidity is a function of the size of the SiO_2 particles contained therein. Silica sol is usually applied within a wide particle size distribution, the particle size strongly depending on the ceramics product to be produced. Silica sols are commercially available under various trade names. The known product groups include Megasol (from Wesbond Corporation) or Ludox (DuPont Corporation). Silica sol is usually employed at a ratio of 3:1 to 2:1 relative to the starch. When using amylopectin potato starch, its quantity can be reduced as compared to conventional starches, thus enabling the ceramics end product to be produced at an elevated strength and lower shrinkage. Besides, any possible coagulation of the silica sol is prevented by the use of amylopectin potato starch. Alternatively, the silica sol may be replaced with a binder such as polyvinyl alcohol, polyvinyl acetate or natural or synthetic waxes, or used in combination therewith.

Various operating techniques are available for removing the flocks from the system, such as, for instance, "tape casting", "slip casting" or "colloidal filtration" to name but a few examples. In most cases, the formed flocks are discharged into a mold by filtration or suction through pressure application. When using amylopectin potato starch, the optimum orientation of the fibers will be obtained, which is again extremely beneficial for the quality of the ceramics product. The filtrate itself is clear and free of turbid matter. It does not contain any starch

residues such that this water can be repeatedly used within the production cycle without any risk. The thus produced moist cake (green body) is initially dried at about 120° C. After this, the green body is converted into a ceramics product by firing. This procedure basically occurs under slow and progressive heating so as to avoid destruction of the ceramics.

By using amylopectin potato starch, carbonization without residues can be guaranteed, which means that no toxic or environmentally damaging substances will be released. Moreover, the use of amylopectin potato starch gives rise to a particularly stable three-dimensional structure, which is also reflected in the strength values measured. Due to the fact that amylopectin potato starch exhibits an excellent solubility, which prevents the formation of agglomerated particles during the flocculation process, it is also impossible for undesired hollow spaces to form in the ceramic material during firing. Such hollow spaces would otherwise be occupied by silica, which would in turn markedly reduce the strength of the ceramics. Amylopectin potato starch, in particular, also functions as a porosity control. Due to its large hydrodynamic volume, the starch is able to develop and interact more properly. Its porosity can be readily controlled by varying inputs, thus enabling the manufacture of ceramics products having graduated product properties.

In the context of the method according to the invention, the slurry is preferably prepared by

- providing an aqueous suspension of inorganic fibers and
- adding an inorganic binder, in particular silica sol, and a flocculant and binder according to the invention as well as optionally further additives and fillers.

Advantageously, a drying step is also provided prior to the thermal treatment step, which drying step is preferably carried out at 100 to 200° C and, in particular, about 120 to 140° C.

The thermal treatment step preferably comprises a sintering step. Preferred temperatures to be applied during the thermal treatment step as maximum temperatures range from 800 to 2500° C, preferably 1500 to 2000° C and, in particular, are about

- 19 -

1800° C, which is primarily due to the nature of the inorganic fibers and the demands made on the ceramics product to be produced.

If desired, the thermal treatment step and optionally also the drying step are preceded by mechanical water removal. Likewise preferred is the provision of a forming step prior to the thermal treatment step, wherein the slurry or the green body is introduced into a suitable mold in a manner known per se.

An alternative to the direct carbonization of amylopectin potato starch resides in the manufacture of ceramically reinforced products. In this case, the green bodies produced from fibers, binder and flocculant are penetrated with molten metal and/or metal alloys during forming without destroying the three-dimensional structure (matrix). During this procedure, the starch is baked out and a fiber-reinforced product is finally obtained. By using amylopectin potato starch, it is feasible to substantially raise the amount of porosity and to even better control the distribution. Moreover, the starch also functions perfectly as a binder between the mixed fibers and metals, which helps to further increase the stability.

In a preferred manner according to the invention, the thermal treatment step is therefore realized by the penetration of liquid metals or liquid metal alloys.

Ceramics products produced by the use of AP-PS according to the invention stand out particularly for their high strength, strong chemical and thermal resistance, excellent corrosion-resistant properties, special heat conductivity and altogether excellent overall porosity.

Accordingly, the present invention in a further aspect also relates to ceramics products that are obtainable by the production method according to the invention, i.e., by using AP-PS.

The invention will be explained in more detail by way of the following examples and drawing figures, to which it is, however, not limited.

Fig. 1 illustrates the viscosity development of different starches, and

Fig. 2 is a comparison of amylopectin potato starch with amylopectin-rich potato starch prepared by fractionation.

Examples :

Example 1: Preparation of cationic amylopectin potato starch

Native amylopectin potato starch is mixed into a 40% slurry.

After the addition of sodium sulfate, a pH of about 11.5 is adjusted by adding 3% soda lye. Cationization is started by admixing 2,3-epoxypropyltrimethyl ammonium chloride. After 18 hours at 34° C, the reaction is stopped by neutralizing the slurry. The cationic starch was washed with water and carefully dried.

The wash-out degree of the cationic amylopectin potato starch must be very high in order to ensure that the product contains only small quantities of alkali and earth alkali traces. It is known that the elements sodium, potassium, calcium and magnesium, but also iron and manganese induce higher shrinkage during the carbonization of a ceramics workpiece. This effect constitutes a problem particularly with high-temperature-resistant ceramics. Consequently, the following quality demands should apply to the washing out of cationic amylopectin potato starch:

Sodium:	< 0.1%	Calcium:	< 0.01%
Potassium:	< 0.01%	Magnesium:	< 0.01%

When using amylopectin potato starch, the removal of salt loads was rapidly feasible using smaller amounts of water than with derivative of conventional starches.

Example 2: Preparation of an amylopectin potato starch sulfamate
A 40% slurry of amylopectin potato starch is supplemented with 10% ammonium sulfamate (based on the starch). The reaction mixture is reacted by the gelatinization of the starch. The paste product is subsequently drum-dried.

Example 3: Variants for the preparation of amylopectin potato

starch soluble in cold water

The preparation of a derivatized amylopectin potato starch soluble in cold water may be accomplished in various ways. Two typical process variants are given as examples.

A) Drum-drying

Depending on the quality and viscosity desired of the cold water soluble end product, two method variants suggest themselves. Either the slurry of the cationic starch is dried directly on the drum, or the starch is initially gelatinized and drum-dried only subsequently. Both products are scaly.

B) Extrusion

By this method, the derivatized starch is converted into a cold water soluble product under the influence of mechanical forces and temperature in the presence of a small amount of water, the dry substance of the reaction mixture in the extruder usually being 70 to 90%. The starch obtained is present in granular form.

Example 4: Viscosity development

The viscosity development is an experimental setup to describe the dissolution rate of a cold water soluble cationic starch.

To this end, 4.5% cationic starches were stirred in at 1000 rpm for 3 minutes. The results are illustrated in Fig. 1

The curves clearly indicate that amylopectin potato starch derivatives have completed their viscosity development much earlier than conventional potato starch products. The tests, in particular, also revealed that amylopectin potato starch was clearly superior to conventional potato starch already at a low degree of substitution of 0.03, which advantage could be compensated for by conventional potato starch only through a higher nitrogen substitution.

Example 5: Structural analytics of amylopectin potato starch

In order to characterize the amylopectin potato starch, both the mean molecular weight and the molar mass distribution were determined. Both analytical methods are extensively described in the literature such as, for instance, by Chi-san Wu in Handbook of Size Exclusion Chromatography; Chromatographic Science Series, Vol. 69 (1995), Marcel Dekker Inc., New York.

In order to more clearly characterize the amylopectin potato starch, the amylopectin of a conventional potato starch was obtained by enrichment for comparative purposes. A number of methods are available for this method step, the present assay having been based on the fractionation according to the method described by J. Potze in "Starch Production Technology", Chapter 14, pp. 257-271. This method entails the heating of the starch to 155° C and the selective precipitation of amylopectin by the aid of magnesium sulfate.

For the comparative representation of the mean molecular weight, also the measuring values of two conventional starches, namely waxy corn starch and conventional potato starch, were determined.

Table 1: Comparative representation of different cooking starches.

	AP-PS	PS	WCS	FAP-PS
Mean molecular weight	190.10 ⁶	48.10 ⁶	64.10 ⁶	43.10 ⁶

PS = potato starch

AP-PS = amylopectin potato starch

WCS = waxy corn starch

FAP-PS = amylopectin-rich potato starch obtained by fractionation

From the above comparison, it is readily apparent that amylopectin potato starch (AP-PS) clearly distinguishes itself from

other starches. There is a pronounced difference between amylopectin potato starch and fractionated amylopectin potato starch (FAP-PS) prepared by chemical/physical methods.

In order to more clearly depict the differences between amylopectin potato starch (AP-PS) and fractionated amylopectin potato starch (FAP-PS), also the molar mass distribution was determined by means of size exclusion chromatography. In addition, the surface ratio of the measured distribution was characterized (cf. Fig. 2).

Retention time	AP-PS	FAP-PS
> 41 min	69.0%	34%
< 41 min	31.0%	66%

While amylopectin potato starch (AP-PS) exhibits a significantly uniform molar distribution, fractionated amylopectin potato starch shows a much obscurer picture. What is, above all, typical is the portion of molar masses at a retention time of >41 minutes. With amylopectin potato starch, this is twice as large as with fractionated amylopectin potato starch. Due to the separation process involved in fractionation, the starch was degraded whereby also the properties of the products were changed.

Example 6: Comparative analytical characterization of amylopectin potato starch (AP-PS) in view of waxy corn starch (WCS), corn starch (CS) and conventional potato starch (PS)

The values indicated in the Table below were taken from "Starch - Chemistry and Technology" by Roy L. Whistler et al., (1965), Academic Press, and supplemented with in-house experimental values.

	MS	PS	WCS	AP-PS
% Amylose	26 - 31	23 - 27	< 2	< 2
% Lipid	0.5 - 0.9	0 - 0.1	0,5 - 0.9	0 - 0.1
% Protein	0.2 - 0.4	0.05 - 0.2	0.1 - 0.35	0.05 - 0.2

- 24 -

% Phosphorus	0.01 - 0.02	0.04 - 0.13*	0 - 0.02	0.04 - 0.15*
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* ... defined as phosphate monoester

From the comparative representation of some specific analytical data, the differences between amylopectin potato starch (AP-PS) and the three conventional starches are clearly apparent. Compared to waxy corn starch and corn starch, amylopectin potato starch contains slighter amounts of lipids and proteins, whereas the high portion of naturally bound phosphate is very typical. The difference from conventional potato starch is reflected by the content of amylose. Due to the fact that amylopectin potato starch contains up to 100% amylopectin, its viscosity, for instance, or also the turbidity behavior of pastes, differ strongly. Thus, it was found that amylopectin potato starch exhibits a constant paste clarity even over an extended period of time, while conventional starches show noticeable turbidities. It is exactly on an industrial scale that the stability of starch or starch derivatives is of relevance to the quality of flocculation and the production of green bodies.

Example 7: Dissolution behavior of starch sulfamates and cationic starches

An important characteristic of cold water soluble starches is their dissolution behavior. The manufacture of ceramics products calls for an unrestrictedly complete solubility without involving the formation of, for instance, agglomerations or lumps. In order to be able to examine the solubility of cold water soluble derivatized starches at all, the following experimental array was chosen, which is very similar to real life.

A container was filled with 15 L water under stirring at 700 rpm, and 15 g starch are rapidly admixed within a few seconds. The paste is stirred at room temperature for 3 minutes under the conditions indicated and subsequently filtered over an 800 µm sieve. Paste residues on the stirrer as well as sieve residues were subjectively assessed to evaluate solubility. The following results were obtained:

Table 2:

Cationic starches				
	Production process *	DS**	Sieve residues	Paste on stirrer
commercial PS	WATRO	0.03	+/-	+/-
commercial PS	WATRO	0.1	+/-	-
AP-PS	WATRO	0.03	+	+
AP-PS	WATRO	0.1	+	+
WCS	WATRO	0.03	-	+/-
WCS	WATRO	0.1	-	+/-
FAP-PS	WATRO	0.03	+/-	+/-
FAP-PS	WATRO	0.1	+/-	-
PS	extruded	0.03	+/-	+/-
PS	extruded	0.1	+/-	-
AP-PS	extruded	0.03	+	+
AP-PS	extruded	0.1	+	+
Starch sulfamates				
	Production process*		Sieve residues	Paste on stirrer
Commercial PS	WATRO		+/-	+/-
AP-PS	WATRO		+	+
WCS	WATRO		-	+/-
FAP-PS	WATRO		+/-	-

* ... process used for the production of the cold water soluble starch derivative, cf. Example 3

** ... degree of substitution (DS)

PS = potato starch

AP-PS = amylopectin potato starch

WCS = waxy corn starch

FAP-PS = amylopectin-rich potato starch obtained by fractionation

- 26 -

Explanations in respect to the Table:

- + no paste residues on stirrer shaft, no sieve residues
- +/- stirrer shaft slightly pasted up, sieve shows paste film and/or a few agglomerates
- stirrer shaft strongly pasted up, sieve shows many agglomerates and clots.

The dissolution tests clearly demonstrated that the amylopectin potato starch derivatives exhibited a solubility far better than that of conventional derivatives of potato starch, waxy corn starch or fractionated amylopectin potato starch obtained by enrichment. Comparative studies, furthermore, revealed that cationic products of amylopectin potato starch were clearly superior to conventional commercial products, which is again of great advantage in the manufacture of ceramics products.

Example 8: Ceramics production

To a slurry of 210 g aluminum silicate fibers of the Kaowool brand and 25 L water are added 90 g of a filler like, for instance, mullite. Then, 13 g of a cold water soluble cationic amylopectin potato starch (DS = 0.03) are introduced. Within a short period of time, the starch is dissolved and distributed in the system to the optimum degree. The optimum flock size and flock distribution could, in fact, be obtained by the addition of this starch. After this, 96 g of a commercially available 40% silica sol are added, briefly stirred, and subsequently the flock mass is sucked off via a screened mold upon application of vacuum. The shaped body is dried at about 120° C and baked at about 1800° C.

In order to elucidate the advantages of the use of amylopectin potato starch, comparative tests were carried out with conventional cold water soluble cationic starches. In the course of these tests, the flocculation time, the turbidity of the circulating water after 20 passes as well as the physical parameters of the ceramics end product were determined.

Table 3:

	PS **	WCS	AP-PS	FAP-PS
Measurements during production				
Flocculation time	3 min	3.5 min	2 min	3 min
Turbidity *	19 FTU	12 FTU	4 FTU	11 FTU
Analytics of ceramics end products				
Density	350 m ³ /kg	372 m ³ /kg	410 m ³ /kg	347 m ³ /kg
Shrinkage	2.0%	2.4%	0.9%	1.9%

* ... The turbidity, which had been caused by the presence of undissolved substances, was determined according to DIN EN 27027. Measurements were carried out by means of Lange LTP 5 turbidimeters, calibration was effected by the aid of formazin standard suspensions, results are indicated in FTU (formazine turbidity units).

** ... The cationic potato starch used here corresponds to commercially available products as described, for instance, in patent application PCT WO 99/15322.

The measurements carried out with amylopectin potato starch revealed significantly reduced flocculation times as against conventional starches; moreover, the flocculation stability was considerably higher. The latter is reflected, in particular, by the clear reaction water, which is still clear and free of turbid matter even after 20 production passes. The enhanced processability of the ceramics products obtained by the use of amylopectin potato starch is apparent from the analytical data of the end products. The density of the products was significantly higher when using amylopectin potato starch, the shrinkage of the three-dimensional body was clearly reduced.

Claims:

1. A flocculant or binder composition for the production of ceramics products, characterized in that it comprises amylopectin potato starch (AP-PS).
2. A flocculant or binder composition according to claim 1, characterized in that said AP-PS is modified and, in particular, cationically modified AP-PS.
3. A flocculant or binder composition according to claim 1 or 2, characterized in that said AP-PS is modified with nitrogen-containing groups and, in particular, electropositively charged quaternary ammonium groups.
4. A flocculant or binder composition according to any one of claims 1 to 3, characterized in that said AP-PS is AP-PS sulfamate.
5. A flocculant or binder composition according to any one of claims 1 to 4, characterized in that said AP-PS was obtained from a potato modified by breeding or by molecular-biological or genetic-engineering techniques for the purpose of amylose inhibition.
6. A flocculant or binder composition according to any one of claims 1 to 5, characterized in that said AP-PS was obtained from a potato inhibited by antisense inhibition of a GBSS gene in respect to amylose formation.
7. A flocculant or binder composition according to any one of claims 1 to 6, characterized in that said AP-PS was obtained from a potato inhibited by cosuppression in respect to amylose formation.
8. A flocculant or binder composition according to any one of claims 1 to 7, characterized in that said AP-PS has an amylopectin content of at least 95%, preferably at least 98%.
9. A flocculant or binder composition according to any one of

claims 1 to 8, characterized in that said AP-PS is contained as a swelling starch.

10. A flocculant or binder composition according to any one of claims 1 to 9, characterized in that said AP-PS is soluble in water at 25° C at least 90%, preferably 95% and, in particular, more than 99%.

11. A flocculant or binder composition according to any one of claims 1 to 10, characterized in that said AP-PS is degraded by physical and, in particular, thermal and/or mechanical methods.

12. A flocculant or binder composition according to any one of claims 1 to 11, characterized in that said AP-PS is chemically degraded, particularly by thermochemical, oxidative or acidic methods.

13. A flocculant or binder composition according to any one of claims 1 to 12, characterized in that said AP-PS is contained in the etherified form.

14. A flocculant or binder composition according to any one of claims 1 to 13, characterized in that said AP-PS is contained as a methyl, ethyl, hydroxyl, hydroxypropyl, hydroxybutyl, carboxymethyl, cyanoethyl or carbamoyl ether.

15. A flocculant or binder composition according to any one of claims 1 to 14, characterized in that said AP-PS is contained in the esterified form.

16. A flocculant or binder composition according to any one of claims 1 to 15, characterized in that it comprises an esterified AP-PS in whose ester residue RCOO-, the residue R is an alkyl, aryl, alkenyl, alkaryl or aralkyl residue having 1 to 17 carbon atoms, preferably 1 to 6 carbon atoms and, in particular, 1 or 2 carbon atoms.

17. A flocculant or binder composition according to any one of claims 1 to 16, characterized in that said AP-PS is contained as an acetic, propionic, butyric, stearic, phthalic, succinic,

oleic, maleic, fumaric or benzoic acid ester.

18. A flocculant or binder composition according to any one of claims 1 to 17, characterized in that said AP-PS is contained in the crosslinked form.

19. A flocculant or binder composition according to any one of claims 1 to 18, characterized in that said AP-PS is crosslinked with epichlorohydrin or 1,3-dichloro-2-propanol, optionally mixed with (poly)amines.

20. A flocculant or binder composition according to any one of claims 1 to 19, characterized in that said AP-PS is crosslinked by reaction with aldehyde-releasing reagents like N,N'-dimethylol-N,N'-ethyleneurea, with phosphoroxchloride, sodium trimetaphosphate, di- or polyepoxides, mixed anhydrides of carbonic acids with di- or tribasic acids like adipic acid/ Ac_2O , glyoxal or aldehydes like formic, acetic or propionic aldehyde.

21. A flocculant or binder composition according to any one of claims 1 to 20, characterized in that said AP-PS is modified by cationic and/or anionic groups.

22. A flocculant or binder composition according to any one of claims 1 to 21, characterized in that said AP-PS is present as a starch graft polymer or a starch graft copolymer.

23. A flocculant or binder composition according to any one of claims 1 to 22, characterized in that said AP-PS graft (co)polymer is present as an emulsion polymer.

24. A flocculant or binder composition according to any one of claims 1 to 23, characterized in that said AP-PS has a degree of substitution of 0.00001 to 3, preferably 0.001 to 2 and, in particular, 0.005 to 1.

25. A flocculant or binder composition according to any one of claims 1 to 24, characterized in that said AP-PS is esterified by inorganic and/or organic, preferably heterovalent and, in particular, bivalent acids and/or salts, esters and/or anhyd-

rides of these acids and, in particular, o-phosphoric acid, m-phosphoric acid, poly-phosphoric acid, various sulfuric acids, various silicic acids, various boric acids, oxalic acid, succinic acid, glutaric acid, adipic acid, phthalic acid, citric acid or mixtures thereof.

26. A flocculant or binder composition according to any one of claims 1 to 25, characterized in that said AP-PS is etherified by inorganic and/or organic α -substituted acids and/or salts, esters and/or anhydrides of these acids and, in particular α -halocarbonic acid, chlorohydroxy alkyl sulfonates, chlorohydroxy alkyl phosphonates.

27. A flocculant or binder composition according to any one of claims 1 to 26, characterized in that said AP-PS is cationically modified by amino, imino, ammonium, sulfonium, phosphonium groups or mixtures thereof, preferably by nitrogen-containing groups and, in particular, primary, secondary, tertiary and quaternary amines.

28. A flocculant or binder composition according to any one of claims 1 to 27, characterized in that said AP-PS contains electropositively charged quaternary ammonium groups.

29. A flocculant or binder composition according to any one of claims 1 to 28, characterized in that said AP-PS is contained in the form of a mixture of several different derivatives.

30. A flocculant or binder composition according to any one of claims 1 to 29, characterized in that it further comprises sedimentation accelerators, stabilizers, dispersants, antifoaming agents, softeners, non-starch-based adhesives or adhesive precursors, buffer salts, preserving agents or mixtures thereof.

31. The use of AP-PS as a flocculant or binder in the production of ceramics products.

32. The use of a flocculant or binder composition according to any one of claims 1 to 30 for the production of ceramics products.

33. A slurry for the production of ceramics products, characterized in that it comprises a flocculant or binder according to any one of claims 1 to 30.

34. A slurry according to claim 33, characterized in that it comprises AP-PS at a concentration of from 0.001 to 0.5 weight percent.

35. A slurry according to claim 33 or 34, characterized in that it further comprises inorganic fibers, in particular fibers based on aluminum silicates, fillers, in particular oxides of aluminum or aluminum silicates or chalk, organic materials, in particular organic fibers made of celluloses or polyethylene, inorganic binders, in particular colloidal silica, or mixtures thereof.

36. A method for producing ceramics products, comprising the following steps:

- preparation of a slurry according to any one of claims 33 to 35, and
- thermal treatment at a temperature of above 300° C, in particular above 500° C.

37. A method according to claim 36, characterized in that the preparation of said slurry comprises

- providing an aqueous suspension of inorganic fibers and
- adding an inorganic binder, in particular silica sol, and a flocculant and binder according to any one of claims 1 to 30, as well as optionally further additives and fillers.

38. A method according to claim 36 or 37, characterized in that a drying step is effected prior to said thermal treatment step, said drying step being preferably carried out at 100 to 200° C and, in particular, about 120 to 140° C.

39. A method according to any one of claims 36 to 38, characterized in that said thermal treatment step comprises sintering.

40. A method according to any one of claims 36 to 39, character-

ized in that said thermal treatment step is carried out at a maximum temperature of from 800 to 2500° C, preferably 1500 to 2000° C and, in particular, at about 1800° C.

41. A method according to any one of claims 36 to 40, characterized in that said thermal treatment step and optionally said drying step are preceded by mechanical water removal.

42. A method according to any one of claims 36 to 41, characterized in that said thermal treatment step is preceded by a forming step.

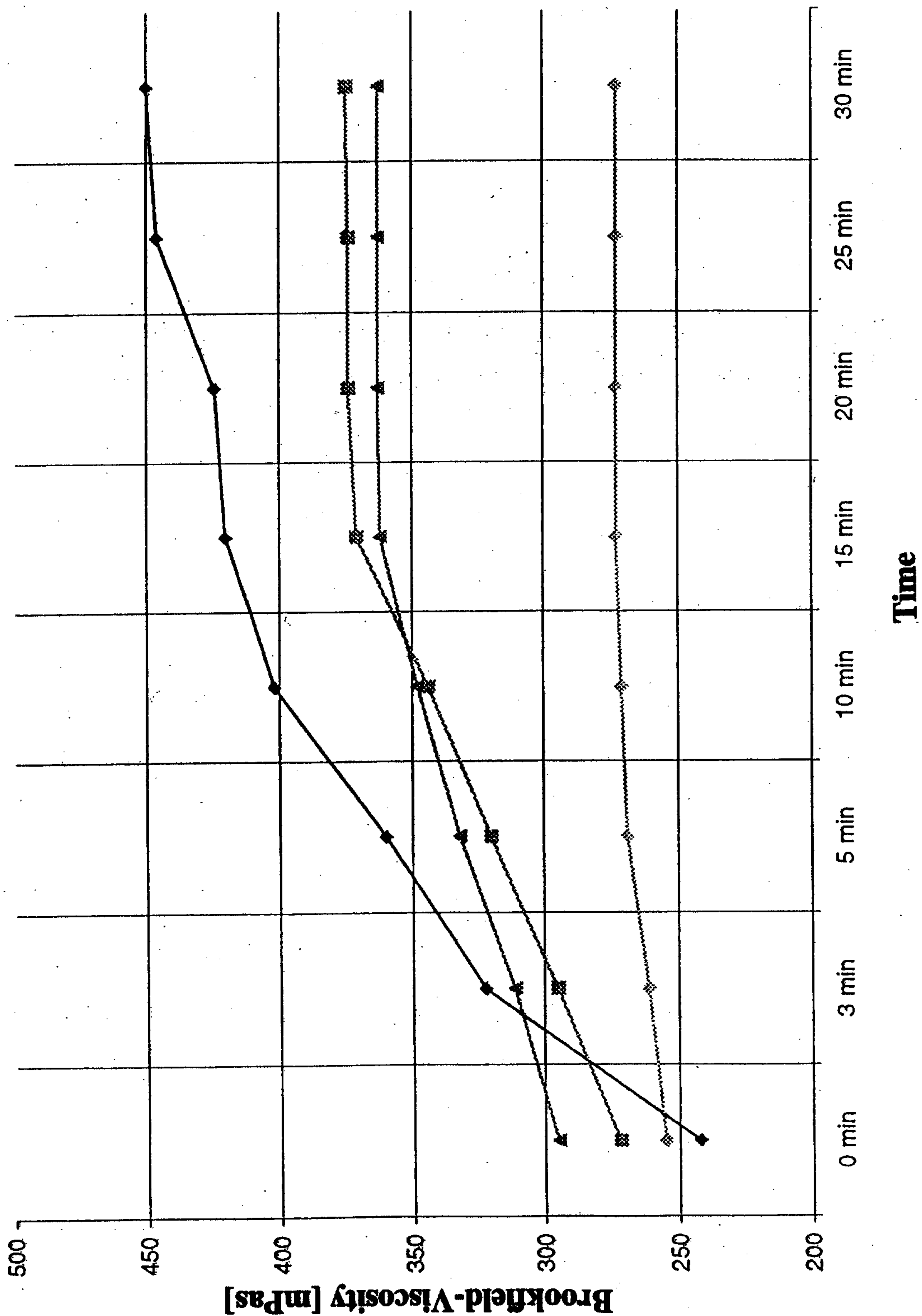
43. A method according to any one of claims 36 to 42, characterized in that said thermal treatment step is feasible by the penetration of liquid metals or liquid metal alloys.

44. A ceramics product obtainable by the method according to any one of claims 36 to 43.

1/2

FIG. 1

Viscosity Development



Comparison of Amylopectin Potato Starch with an Amylopectin-Rich Potato Starch Prepared by Enrichment

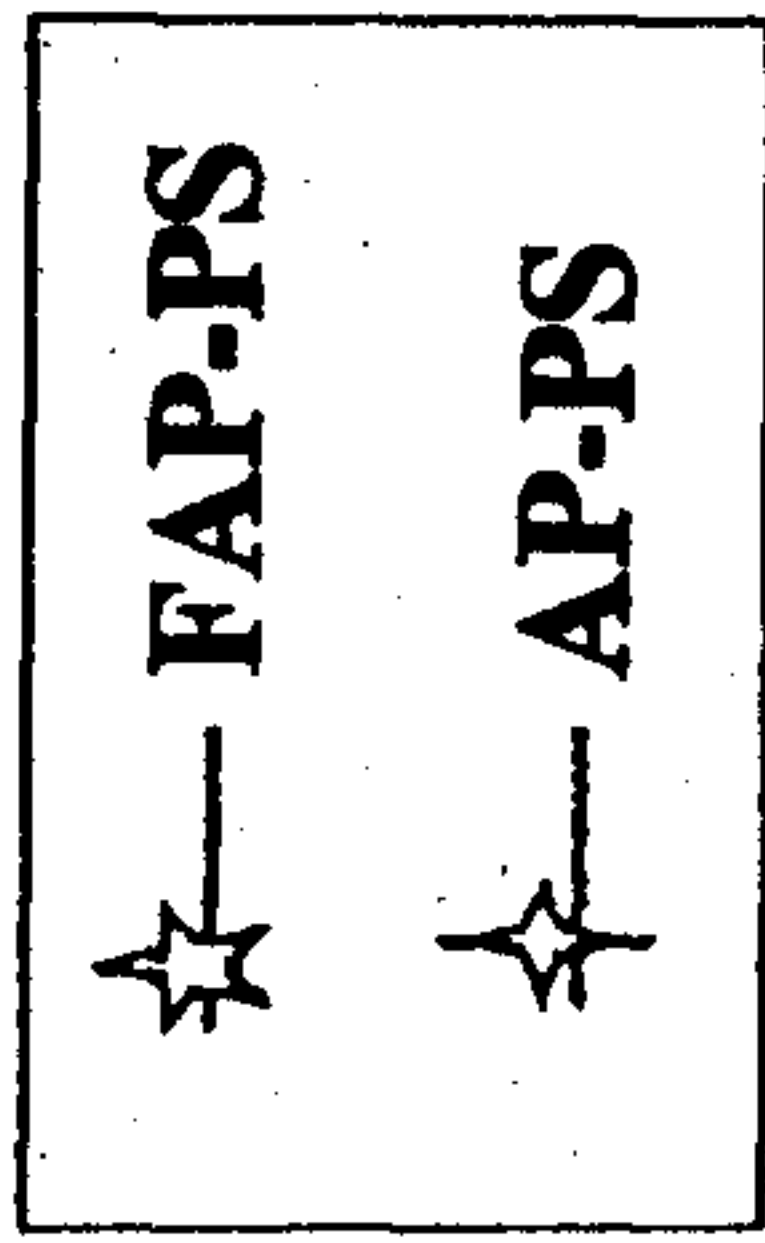


FIG. 2

