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(54) HIGH-CONCENTRATION SOLID/WATER SLURRY AND PROCESS FOR PRODUCING THE SAME

(57) This invention provides a highly concentrated solid-water slurry possessing high flowability and excelling in stability during storage and transportation and a method for the production thereof.

The highly concentrated solid-water slurry is such that in the stress sweep test performed by the method for determining dynamic viscoelasticity of slurry, the largest stress of the region of linear elasticity determined at an oscillation frequency of 1 Hz is in the range of 0.3 - 10 Pa and the strain of the slurry giving the largest stress of the region of linear elasticity is not less than 2%.

Further, the highly concentrated solid-water slurry is such that in the creep • recovery test values determined in the region of linear elasticity in the method for determining static viscoelasticity of slurry, the modulus of elasticity of the Maxwell element analyzed by assuming the four-constant dynamic model using Hookean elasticity and Newtonian viscosity is in the range of 8 - 70 Pa and the modulus of elasticity of the Vogt's element is in the range of 3 - 70 Pa.

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Description

Technical Field:

[0001] This invention relates to a highly concentrated solid-water slurry and a method for the production thereof. The invention relates more particularly so a highly concentrated solid-water slurry having a solid powder dispersed in water and, in spite of high concentration of solid, exhibiting high flowability and excelling in stability of storage and stability of transportation and a method for the production thereof.

Background Art:

[0002] The oil which has been finding extensive utility heretofore as an energy source is rising markedly in price and threatening exhaustion of supply in recent years. In the circumstances, the development of other energy source which is available both inexpensively and stably now constitutes itself a task. The feasibility of utilizing such carbonaceous solids as coal and petroleum coke has come to attract renewed attention. Since the coal and the petroleum coke are solid at room temperature, however, they defy effective transfer by means of a pipeline and allow no easy handling and, moreover, entail such drawbacks as emitting dust and consequently causing an environmental pollution and hazarding dust explosion. Thus, technical difficulties still confront their utilization. The desirability of developing a technique capable of imparting flowability to such carbonaceous solids, consequently enabling then to be transferred by means of a pipeline and to be handled with ease, and preventing them from causing environmental pollution and hazarding dust explosion, therefore, has been finding widespread recognition. As one of the techniques for the impartation of flowability, the technique for transforming such a carbonaceous solid into a liquefied fuel by finely dividing the solid and dispersing the resultant powder in water thereby giving birth to a highly concentrated carbonaceous solid-water slurry is now being studied with a view to feasibilization. Generally, when the concentration of the carbonaceous solid is increased in the carbonaceous solid-water slurry to be produced, the slurry markedly gains in viscosity even to the extent of totally sacrificing flowability, disrupting ease of handling, and rendering transfer by means of a pipeline difficult. When the concentration of the carbonaceous solid is conversely lowered for the purpose of decreasing the viscosity of the slurry, the produced liquefied fuel suffers not only degradation of the efficiency of transfer and the efficiency of combustion but also loss of economy. The technical problem of increasing the concentration and decreasing the viscosity has been substantially nearing solution in consequence of the advance of the technique of dispersant in recent years. When the highly concentrated carbonaceous solid-water slurry is exposed to such unduly harsh conditions as existing in the transportation thereof in a ship or a tank lorry or when the slurry is stored in a tank for a long time, the slurry shows the phenomenon of sedimentation of carbonaceous solid particles therein. Particularly, the stabilizing technique which is capable of precluding such sedimentation of carbonaceous solid particles is yearned for because this sedimentation throws various problems on the way of realizing practical use of the highly concentrated carbonaceous solid-water slurry.

[0003] The highly concentrated carbonaceous solid-water slurry is not the sole entity that needs to adopt the slurry stabilizing technique. In the industrial field, various slurries such as cement, coating materials, and varying polymers are extensively utilized besides coal. Generally, they are required to have high concentration, low viscosity enough to fit effective transfer by means of a pipeline, high flowability, and stability sufficient for preventing the slurry while in transportation or storage from inducing separation and sedimentation of dispersible particles.

[0004] Generally, the addition of a stabilizer is usually resorted to for the purpose of stabilizing a dispersion system of solid particles. Various stabilizers, therefore, are being studied with a view to determining their feasibility for this addition. As prospective stabilizers, cellulose type semisynthetic sizing agents, inorganic mineral substances, clayish substances, natural polysaccharides, varying species of ions etc. have been reported. When these stabilizers are used in an actual production line, however, they at times fail to secure ample stability or at other times raise such problems as impairing the flowability of a highly concentrated solid-water slurry.

[0005] This invention, therefore, resides in providing a highly concentrated solid-water slurry exhibiting high flowability and offering excellent stability for storage and transportation and a method for the production thereof.

[0006] This invention meanwhile provides a highly concentrated solid-water slurry possessing such a specific viscoelastic property as described herein below. The highly concentrated solid-water slurry possessing such a property has never been known to the art. JP-A-63-113,098 and JP-A-08-73,872 mention use of a (meth)acrylic acid type polymer as the additive to the highly concentrated carbonaceous solid-water slurry. Neither of them, however, discloses anything about a highly concentrated carbonaceous solid-water slurry possessing the viscoelastic property contemplated by this invention or a method for the production thereof.

Disclosure of the Invention:

[0007] The present inventors have made a diligent study on the highly concentrated carbonaceous solid-water slurry with a view to solving the problems of the prior art mentioned above and, as a result, have found that the highly concentrated carbonaceous solid-water slurry possessing viscoelastic property of a specific magnitude exhibits fine flowability even in a highly concentrated state and offers excellent stability during storage and during transportation. They have continued a diligent study in search of a method for producing the highly concentrated solid-water slurry possessing the characteristic mentioned above and have consequently found that the highly concentrated solid-water slurry possessing the aforementioned characteristic can be produced easily and efficiently by using as the additive a (meth)acrylic acid type polymer or a salt thereof obtained by means of a reaction vessel provided with a specific stirring vane effective in generating a stirring motion in a wide range of viscosity from low viscosity through medium viscosity. This invention has been perfected as a result.

[0008] Specifically, this invention concerns a highly concentrated solid-water slurry containing solid particles and water, which in a stress sweep test by the method for determining dynamic viscoelasticity exhibits the largest stress of the region of linear elasticity measured at an oscillation frequency of 1 Hz in the range of 0.3 - 10 Pa and the strain giving the largest stress of the region of linear elasticity at a level of not less than 2%.

[0009] The present invention further concerns a highly concentrated solid-water slurry containing solid particles and water, which in a creep recovery test determined in the region of linear elasticity by the method for determining static viscoelasticity exhibits the modulus of elasticity of the Maxwell element analyzed by assuming the four constant dynamic model based on Hookean elasticity and Newtonian viscosity in the range of 8 - 70 Pa and the modulus of elasticity of the Vogt's element in the range of 3 - 70 Pa.

[0010] The present invention further concerns a method for the production of a highly concentrated solid-water slurry, characterized by using as the additive a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel provided with a stirring vane possessing characteristic values such that the $n \cdot \theta m$-Re curve represented by both logarithmic axes passes a region in which the Reynolds' number, Re, is not more than 50 and the magnitude of $n \cdot \theta m$ is not more than 400 and the average rate of change of the curve within the region is not less than -1.2.

[0011] The present invention further concerns a method for the production of a highly concentrated solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotation axis suspended in the central part of the reaction column, and a substantially planar stirring vane pivotally mounted laterally symmetrically on the rotation axis, the stirring vane provided with at least two perforated parts.

[0012] The present invention further concerns a method for the production of a highly concentrated solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotary shaft suspended in the central part of the reaction column, and stirring vanes disposed in at least upper and lower vertical stages and pivotally mounted in a staggering pattern in the axial direction on the rotary shaft, the stirring vane on the upper stage assuming a substantially planar shape and pivotally mounted laterally symmetrically on the rotary shaft and the stirring vane on the lower stage comprising a main body part assuming a substantially planar shape and pivotally mounted laterally symmetrically on the rotary shaft and a leading terminal part bent parallelly to the rotary shaft in the direction opposite the direction of rotation.

[0013] The present invention further concerns a method for the production of a highly concentrated solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotary shaft suspended in the central part of the reaction column, a supporting member pivotally mounted on the rotary shaft and formed in the shape of a frame along the longitudinal inner wall of the reaction column, and at least a pair of stirring vanes supported by the supporting member and formed each in the shape of a helical ribbon along the inner wall of the reaction column.

Brief Description of the Drawings:

[0014]

Fig. 1 is a characteristic curve obtained by the stress sweep test of the method for determination of dynamic viscoelasticity which is used in this invention.

Fig. 2 is a diagram of the procedure of analysis of the characteristic values obtained by the stress sweep test of the method for determination of dynamic viscoelasticity which is used in this invention.

Fig. 3 is a characteristic curve obtained by the creep-recovery test of the method for determining static viscoelasticity which is used in this invention.

Fig. 4 is a diagram of the procedure of analysis of each constant value of the four constant dynamic model assumed in this invention.

Fig. 5 is a four constant dynamic model of a viscoelastic material assumed in this invention.

Fig. 6 is a longitudinal section illustrating one embodiment of the laboratory grade small reaction vessel provided with a specific stirring vane to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 7 is a longitudinal section illustrating another embodiment of the laboratory grade small reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 8 is a longitudinal section illustrating still another embodiment of the laboratory grade small reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 9 is a longitudinal section illustrating one embodiment of the column type reaction vessel provided with a specific stirring vane to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 10 is a longitudinal section illustrating another embodiment of the column type reaction vessel provided with a specific stirring vane to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 11 is a longitudinal section illustrating a further embodiment of the column type reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 12 is a longitudinal section illustrating still another embodiment of the column type reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 13 is a longitudinal section illustrating yet another embodiment of the column type reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Fig. 14 is a longitudinal section illustrating still another embodiment of the column type reaction vessel provided with specific stirring vanes to be used for the production of an additive fit for permitting easy manufacture of the slurry of this invention.

Best Mode for Embodying the Invention:

[0015] This invention prefers the largest stress of the region of linear elasticity observed at an oscillation frequency of 1 Hz in the stress sweep test by the method for testing a highly concentrated solid-water slurry for dynamic viscoelasticity to be in the range of 0.3 - 10 Pa. The largest stress of the region of linear elasticity is limited for reason of the disadvantage that the stability during storage and during transportation will be markedly lowered if the largest stress is smaller than 0.3 Pa and the flowability of the slurry will be degraded with time if the largest stress exceeds 10 Pa. Further, this invention prefers the strain of the slurry that gives the largest stress of the region of linear elasticity to be not lower than 2%. The strain giving the largest stress of the region of linear elasticity is limited for reason of the disadvantage that the stability during storage and during transportation will be degraded if the strain is less than 2%.

[0016] This invention prefers the largest stress of the region of linear elasticity and the strain giving the largest stress to be determined with a rheology measuring device adopting the method of stress control. As a concrete example of this device, the product of HAAKE Corp sold under the trademark designation of "Rheostress RS100."

[0017] When the rheology measuring device of the method of stress control is used, the largest stress of the region of linear elasticity and the strain giving the largest stress of the region of linear elasticity can be determined by the following methods, for example. The solid concentration or the viscosity of a given solid-water slurry is adjusted in conformity with the property value intended to be normally used. The slurry is tested based on the following principles to determine the largest stress of the region of linear elasticity and the strain giving the largest stress. Here, the sine stress (τ) is exerted on the slurry to determine the strain (γ) and the phase difference (δ) which are consequently generated. When the sine stress represented by the formula (1) is exerted on the slurry, the phase of the responding sine strain is deviated in the amount of δ as represented by the formula (1), depending on the magnitude of the inherent viscosity quality.

$$\tau = \tau_0 \sin(\omega t) \ (\tau_0\text{: Largest value of stress}) \qquad (1)$$

$$\gamma = \gamma_0 \sin(\omega t + \sigma) \ (\gamma_0\text{: Largest value of strain}) \qquad (2)$$

[0018] The ratio of the stress and the strain is defined as the modulus of elasticity and the modulus of elasticity assumes a complex number because the stress and the strain both assume complex numbers. Further, the complex elastic modulus (G*) can be divided into an elasticity component (G') and a viscosity component (G") as represented by the relation of the formula (3) using the strain and the phase difference of stress.

$$G^* = G' + iG'' \text{ (i: Imaginary unit)} \tag{3}$$

[0019] Then, the complex elastic modulus is calculated as the quotient of the largest value of stress divided by the largest value of strain as represented by the relation of the formula (4) and the storage elastic modulus (G') and the loss elastic modulus (G") are calculated by using the trigonometric functions which are represented by the relations of the formula (5) and the formula (6).

$$|G^*| = |\tau_0|/|\gamma_0| \tag{4}$$

$$G'' = G^* \sin\sigma \text{ (Loss elastic modulus)} \tag{5}$$

$$G' = G^* \cos\sigma \text{ (Storage elastic modulus)} \tag{6}$$

[0020] A viscoelastic substance manifests a linear behavior dependent on stress until critical strain. When the critical strain is surpassed, the substance suffers destruction of the inner structure and consequently manifests a nonlinear behavior and shows a decrease in the storage elastic modulus. By gradually exerting on the slurry the sign stress of such a magnitude as allowing transition from the region of linear elasticity to the region of nonlinear elasticity, the region for decreasing the storage elastic modulus is made to appear and the largest stress of the region of linear elasticity and the strain giving the largest stress are decided. Generally, such a relation of the stress (τ) and the storage elastic modulus (G') as illustrated in Fig. 1 is obtained and, in accordance with the method of analysis illustrated in Fig. 2, the point, a, of stress corresponding to the point of intersection of the tangent line of the region of linear elasticity parallel to the transverse axis and the tangent line of the region of nonlinear elasticity is reported as the largest stress of the region of linear elasticity and the point, b, of strain corresponding to the stress is reported as the strain giving the largest stress.

[0021] Further, this invention, in the creep • recovery test values determined within the region of linear elasticity in the method of determining static viscoelasticity, prefers the constant values analyzed in accordance with the following equations of rheology assuming the four-constant dynamic model having further arranged serially the maxwell element having Hookean elasticity (spring) and Newtonian viscosity (dash pot) bound serially and Vogt's element bound parallelly to be in the range of 8 - 70 Pa and the modulus of elasticity of Vogt's element to be in the range of 3 - 70 Pa. The ranges of the moduluses of elasticity of the elements are limited for reason of the disadvantage that the stability during storage and during transportation is markedly degraded if the moduluses are smaller than the lower limits and the flowability of the slurry will decrease with time if the moduluses exceed the upper limits.

[0022] When the rheology measuring device of the method of stress control is used, the creep recovery test within the region of linear elasticity can be carried out by the following method, for example. The solid concentration or the viscosity of a given solid-water slurry is adjusted in conformity with the property value intended to be normally used. The stress to be exerted on a given slurry in the creep test has a magnitude which is not more than the yield stress of the slurry and does not exceed the strain giving the yield stress during the creep test and the deformation obtained in response to the spontaneous exertion of a stated stress on the slurry is determined as the function of time. The recovery test is performed continuously from the creep test, interrupted by instantaneous nullification of the stress existing since the creep test, and continued until substantial recovery of the amount of the deformation which is recoverable. In the creep • recovery test, such relation of the time, t, and the strain, γ, as shown in Fig. 3 is generally obtained. The component constant values of the four-constant dynamic model illustrated in Fig. 5 are analyzed by the following procedures using the diagram of the procedure of analysis shown in Fig. 4 and the equation of rheology.

[0023] Since the creep stress, τ, and the creep time, t, have been given in advance as the test conditions, the modulus of elasticity, E_3, of the Maxwell element is found from the relation shown in the formula (7) using the initial value, γ_3, of the strain generated when the stress is exerted.

$$E_3 = \tau/\gamma_3 \tag{7}$$

[0024] Then, the strain, γ_1, after the recovery is found and the modulus of viscosity, η_1, of the Maxwell element is found with the formula (8).

$$\eta_1 = (\tau/\gamma_1) \cdot t \tag{8}$$

[0025] Then, the value, γ_2, parallel to the change of the value, γ_1, and the delay time, λ, corresponding to the value, γ_2, are found and the modulus of elasticity, E_2, of the Vogt's element is found from the relation shown in the formula (9).

$$E_2 = (\tau/\gamma_2) \cdot (1 - e^{-t/\lambda}) \tag{9}$$

[0026] Then, the modulus of viscosity, η_2, of the Vogt's element is found from the relation shown in the formula (10).

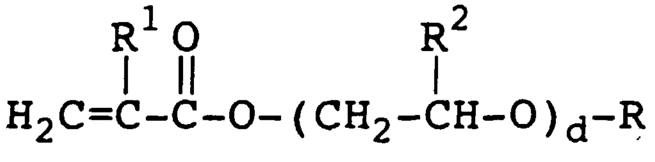
$$\eta_2 = \lambda \cdot E_2 \qquad (10)$$

[0027] The highly concentrated solid-water slurry contemplated by this invention is the product obtained by dispersing an inorganic and/or organic dispersoid in water.

[0028] As concrete examples of the dispersoid to be used in this invention, inorganic solids including inorganic pigments such as calcium carbonate, clay, alumina, zirconia, and titanium dioxide and cement and gypsum and organic solids including coal, coke, pitch, charcoal, dyes, carbon black, coating materials, microcapsules, and various polymers and organic pigments such as anthraquinone may be cited. The coal, for example, does not need to be discriminated on account of kind, producing center, water content, and chemical composition. The coal of any sort can be utilized. It may be any member selected from the group consisting of anthracite coal, bituminous coal, sub-bituminous coal, and lignite. Optionally, the coal may be used in a cleaned state or a modified state.

[0029] This invention allows use of an additive in the production of the highly concentrated solid-water slurry. The additive does not need to be particularly discriminated. As concrete examples of the additive, (meth)acrylic acid type polymers or salts thereof; polycarboxylic acid salt type polymers such as copolymers of olefins such as ethylene, isobutylene, amylene, hexene, and diisobutylene with α, β -unsaturated dicarboxylic anhydrides represented by maleic anhydride and, salts and polymaleic acid and salts thereof; polysulfonic acid salt type polymers such as naphthalene sulfonic acid and salts thereof, lignin sulfonic acid and salts thereof and formalin condensates thereof, polystyrene sulfonic acid and salts thereof, poly-aliphatic diene sulfonic acid and salts thereof, styrene sulfonic acid-maleic anhydride copolymer and salts thereof, and styrene-styrene sulfonic acid copolymer and salts thereof; natural macromolecular polysaccharides such as xanthane gum and guayule gum; cellulose derivatives such as carboxymethyl cellulose and hydroxyethyl cellulose; and clayish minerals such as montmoril-lonite, attapulgite, bentonite, kaolinite, and sepiolite may be cited. Among other additives mentioned above, poly(meth)acrylic acid type polymers and salts thereof are particularly preferable.

[0030] As concrete examples of the (meth)acrylic acid type monomer which forms the (meth)acrylic acid type polymer contemplated by this invention, acrylic acid or methacrylic acid and salts thereof such as, for example, acrylic acid, sodium acrylate, potassium acrylate, calcium acrylate, ammonium acrylate, methacrylic acid, sodium methacrylate, potassium methacrylate, calcium methacrylate, and ammonium methacrylate; alkyl esters of acrylic acid or methacrylic acid such as methyl acrylate, ethyl acrylate, 2-hydroxyethyl acrylate, methyl methacrylate, ethyl methacrylate, and 2-hydroxyethyl methacrylate; alkyl polyoxyalkylene (meth)-acrylates represented by the following general formula (I)



$$H_2C=\overset{\overset{\large R^1}{|}}{C}-\overset{\overset{\large O}{\|}}{C}-O-(CH_2-\overset{\overset{\large R^2}{|}}{C}H-O)_d-R \qquad (I)$$

(wherein R represents a hydrophobic group of 1 - 30 carbon atoms, R^1 and R^2 invariably or variably represent a hydrogen atom or a methyl group, and d represents an integer of 1 - 100); and sulfo-alkyl (meth)acrylates such as 2-sulfoethyl (meth)acrylate and 3-sulfopropyl (meth)acrylate may be cited.

[0031] When the name "(meth)acrylic type polymer" is used in this invention, it is intended to embrace (meth)acrylic acid type copolymers. That is, the (meth)acrylic acid type monomer, when necessary, may incorporate therein other copolymerizable monomer in an amount incapable of impairing the effect of this invention. As concrete examples of the other monomer so incorporated, various sulfonic acids such as vinyl sulfonic acid, styrene sulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, and 2-acrylamide-2-methyl propane sulfonic acid and monovalent metal salts, divalent metal salts, ammonium salts, and organic amine salts thereof; aromatic vinyl compounds such as styrene and p-methyl styrene; and vinyl acetate, propenyl acetate, and vinyl chloride may be cited. These monomers may be used either singly or in the form of a mixture of two or more members.

[0032] In this invention, the production of the (meth)acrylic acid type polymer or a salt thereof may be accomplished by subjecting the aforementioned monomer to copolymerization through the agency of a polymerization initiator. The copolymerization can be effected by polymerization in a solvent or by any of such known methods as bulk polymerization, suspension polymerization, and emulsion polymerization. The polymerization in the solvent may be implemented batchwise or continuously. As concrete examples of the solvent to be used in this case, water; lower alcohols such as methyl alcohol, ethyl alcohol, and isopropyl alcohol; aromatic, aliphatic, and heterocyclic aliphatic hydrocarbons such as benzene, toluene, cyclohexane, n-hexane, and dioxane; ester compounds such as ethyl acetate; and ketone compounds such as acetone and methylethyl ketone may be cited. Among other solvents mentioned above, at least one member selected from the group consisting of water and lower alcohols of 1 - 4 carbon atoms is particularly favorably used from the viewpoints of the solubility of the monomer to be used as the starting material and the water-soluble copolymer to be consequently obtained and the convenience of the use of the copolymer as well.

[0033] When the method of polymerization uses water as the solvent, the polymerization initiator to be used is a water-soluble azo type initiator. As concrete examples of this polymerization initiator, 2,2 azobis(2-methylpropion amidine) dihydrochloride and 2,2' azobis(2-methyl-N-(phenylmethyl)-propion amidine) dihydrochloride may be cited. In this case, an accelerator such as, for example, sodium hydrogen sulfite may be additionally used. When the polymerization uses a lower alcohol, an aromatic hydrocarbon, an aliphatic hydrocarbon, an ester compound, or a ketone compound, the polymerization initiator to be used is an aliphatic azo compound. As concrete examples of this polymerization initiator, peroxides such as benzoyl peroxide and lauroyl peroxide, hydroperoxides such as cumene hydroperoxide, and aliphatic azo compounds such as azobis isobutyronitrile may be cited. In this case, an accelerator such as, for example, an amine compound may be additionally used. When the polymerization uses a water-lower alcohol mixed solvent, the polymerization initiator to be used and the accelerator to be optionally used may be suitably selected from among various polymerization initiators and accelerators mentioned above. The amount of the polymerization initiator is in the range of 0.001 - 10 wt. %, preferably 0.1 - 5 wt. %, based on the amount of the monomer mixture. When the accelerator is additionally used, the amount thereof is in the range of 0.01 - 10 wt. %, preferably 0.1 - 5 wt. %, based on the amount of the monomer mixture.

[0034] The polymerization temperature, which is suitably fixed depending on the solvent and the polymerization initiator to be used, is generally in the range of 0 - 150°C, preferably 30 - 120°C.

[0035] When this invention uses a (meth)acrylic acid type polymer or a salt thereof as the additive for a carbonaceous solid-water slurry, the weight average molecular weight of the (meth)acrylic acid type polymer or salt thereof is in the range of 1000 - 3000000, preferably 5000 - 2000000. Such additives may be used either alone or in the form of a mixture of two or more members. The molecular weight mentioned above can be adjusted by any of the known methods.

[0036] The methods which are available for the adjustment of the molecular weight include a method which effects the adjustment by the amount of a polymerization initiator, a method which effects the adjustment by the use of a chain transfer agent, and a method which effects the adjustment by the selection of polymerization concentration or polymerization temperature, for example. Alternatively, the molecular weight may be adjusted by selecting the method for charging a monomer component, a polymerization initiator, and/or a chain transfer agent or the method for introducing them into the reaction system.

[0037] When the (meth)acrylic acid type polymer or the salt thereof is synthesized in this invention, the polymerization solution has the viscosity thereof change from several centipoises to some thousands of centipoises with the elapse of the reaction time, though variable with the concentration of the polymerization solution, the temperature, and the kind of solvent. Any increase in the viscosity of the polymerization solution in consequence of the advance of the reaction markedly degrades the efficiency of stirring and prevents the polymerization from proceeding smoothly. The conventional low viscosity grade ordinary vanes represented by paddles, turbines, and three-leaf sweepback vanes are not easily applied to the range of medium to high viscosity and the high viscosity grade stirring vanes represented by double helical ribbon vanes are unfit for stirring in the range of low viscosity. Generally, the mixing property of any stirring vane is represented by the $n \cdot \theta m$-Re curve and the relation represented by the equation (11) exists between the revolution number (n) of the vanes and the time (θm) required for completing the mixture.

$$N_{\theta m} \equiv n \cdot \theta m = \mathrm{const} \qquad (11)$$

$$Re \equiv \rho n d2/\mu \qquad (12)$$

[0038] The stirring vane which can be used in this invention possess characteristic values such that, in the mixing property curve, namely the $n \cdot \theta m$-Re curve, represented by both logarithmic axes, the value, $n \cdot \theta m$, passes a region of not more than 400 in the region of flow in which the stirring Reynolds' number (Re) represented by the relation of the formula (12) is not more than 50 and the average rate of change of the value, $n \cdot \theta m$ within this region is not less than -1.2. The reaction vessel has only to be provided with such a stirring vane as just described and does not need to be discriminated on account of construction. When a reaction vessel provided with a stirring vane possessing the characteristic values mentioned above is used for the reaction to produce a (meth)acrylic acid type polymer or a salt thereof by polymerization, the (meth)acrylic acid type polymer or salt thereof which is used as the additive for the preparation of the slurry of this invention possessing the characteristics mentioned above can be easily and inexpensively produced with high industrial efficiency because the stirring efficient cannot be markedly degraded in a wide range of low viscosity to medium viscosity.

[0039] Concrete examples of the column type reaction vessel provided with a specific stirring vane capable of producing an additive fit for the preparation of the slurry of this invention are illustrated in Fig. 6 - Fig. 14. The column type reaction vessels which can be used in this invention do not need to be limited to the class of reaction vessels so illustrated.

[0040] The column type reaction vessels illustrated in Fig. 6 - Fig. 8 are laboratory grade small reaction vessels, provided generally with a reaction column 1, a rotary shaft 2, a baffle 13, a thermometer 15, a gas inlet tube 16, a monomer inlet tube 17, an initiator inlet tube 18, an initiator inlet tube 18, a chain transfer agent inlet tube 19, a reflux condenser 20, a rotating means 21, and a heating bath 22.

[0041] In the column type reaction vessel illustrated in Fig. 6, a stirring vane 3 is pivotally amounted laterally symmetrically on the rotary shaft 2 suspended in the central part of the substantially cylindrical reaction column 1 and is provided with substantially planar perforated parts shaped like a lattice and adapted to pass the reactants.

[0042] The column type reaction vessel illustrated in Fig. 7 is provided with vertically stepped stirring vanes, i.e. an upper stirring vane 4 and a lower stirring vane 6. The upper stirring vane 4 is pivotally mounted on the upper part of the rotary shaft 2 suspended in the central part of the reaction column 1 laterally symmetrically relative to the rotary shaft, formed in a substantially planar shape, and provided with fins 5 protruding downwardly from the leading terminal part. The lower stirring vane 6 is pivotally mounted on the lower part of the rotary shaft 2 as staggered from the upper stirring vane 4. The lower stirring vane 5 is so constructed that the main part thereof is formed in a substantially planar shape and pivotally mounted laterally symmetrically relative to the rotary shaft 2 and the leading terminal part thereof is bent parallelly to the rotary shaft 2 in the direction opposite the direction of rotation.

[0043] The column type reaction vessel illustrated in Fig. 8 is provided with a pair of helical ribbonlike stirring vanes 8 supported by a supporting member 10. The supporting member 10 is pivotally mounted laterally symmetrically on the leading terminal part of the rotary shaft 2 suspended in the central part of reaction column 1 formed in a substantially cylindrical shape and is shaped like a frame along the longitudinal inner wall of the reaction column 1. The helical ribbonlike stirring vanes 8 are shaped like a ribbon, supported by the supporting member 10, and adapted to form a pair of double helixes along the inner wall of the reaction column 1.

[0044] Fig. 9 - Fig. 14 illustrate other embodiments of the column type reaction vessel to be used in this invention. In the diagrams, 1 stands for a reaction column, 2 for a rotary shaft, and 14 for a jacket.

[0045] In the column type reaction vessels illustrated in Fig. 9 and Fig. 10, the stirring vanes 3 are invariably formed in a substantially planar shape and pivotally mounted on the rotary shaft 2 suspended in the central part of the reaction column 1, the upper part of each stirring vane 3 forming a grid part containing perforated parts 9 for passing the reactants and the lower part thereof forming a substantially planar paddle part containing no perforated part. In the column type reaction vessel illustrated in Fig. 9, the perforated parts 9 in the upper grid part forming the stirring vane 3 are shaped like a lattice and the lower paddle part has a slightly larger width than the upper grid part. In the column type reaction vessel of Fig. 10, the perforated parts 9 in the upper grid part are elliptically shaped and the upper grid part and the lower paddle part are identical in width. The stirring vanes may be in an odd number except 1 so long as they enable the axis to be smoothly rotated. In terms of ease of manufacture, about two stirring vanes are preferred to be disposed symmetrically. The length of the lower paddle part forming the stirring vane 3 is in the range of 1/10 -2/3, preferably 1/5 - 1/2, of the height of the stirring vane from the lower terminal thereof and the width thereof is generally 0.4 - 0.95 times, preferably 0.5 - 0.9 times, the inside diameter of the column. The distance between the lower terminal of the stirring vane and the bottom surface of the reaction column is preferred to be as small as permissible. The perforated parts 9 in the upper grid part forming the stirring vane 3 may be in any shape so long as they are capable of shearing and finely dividing the discharge flow from the bottom part of the column and retaining due mechanical strength. As concrete examples of such shape, circle, ellipse, square, rectangle, triangle, pentacle, and crescent may be cited. Among other shapes mentioned above, the rectangle proves particularly favorable. The height of the stirring vane does not need to be particularly limited but may be decided in consideration of the height of the column.

[0046] The column type reaction vessels illustrated in Fig. 11 and Fig. 12 are invariably provided with the rotary shaft 2 suspended in the central part of the reaction column 1 and stirring vanes disposed in two vertical steps, namely the upper stirring vane 4 and the lower stirring vane 6. The upper stirring vane 4 is formed of substantially flat plates pivotally mounted laterally symmetrically on the rotary shaft 2. The width of the upper stirring vane 4 is generally in the range of 0.3 - 0.6 times, preferably 0.4 - 0.5 times, the inside diameter of the reaction column. The upper stirring vane 4, as illustrated in Fig. 12, is provided in the leading terminal part thereof with the fins 5 protruding upwardly and/or downwardly. The fins are laterally symmetrical in shape relative to the rotary shaft 2 and have a width generally in the range of 1/4 - 1/2 of one of the opposite sections of the upper stirring vane. The upper stirring vane may be provided with the perforated parts 9 shaped like a lattice. The lower stirring vane 6 is possessed of a substantially planar main body part which is laterally symmetrical relative to the rotary shaft 2. The leading terminal part 7 of this vane may be bent parallelly to the rotary shaft 2 in the direction opposite the direction of rotation. The bends are laterally symmetrical and have a width in the range of 1/3 - 1/2 of the width of one of the opposite sections of the lower stirring vane. The angle of the bend is generally in the range of 30 - 60°, preferably about 45°. The shortest width of the lower stirring vane is generally in the range of 0.3 - 0.7 times, preferably 0.5 - 0.6 times, the inside diameter of the reaction column. It may be equal to or greater than the width of the upper stirring vane. The lower stirring vane, as illustrated in Fig. 11, may be provided in the leading terminal part thereof with the fins 5 protruding upwardly. The fins are laterally symmetrical in shape and have a width generally in the range of 1/4 - 1/2 of the width of one of the opposite sections of the upper stirring vane. The distance between the lower terminal of the lower stirring vane and the bottom part of the reaction column is generally in the range of 0.01 - 0.06 times the inside diameter of the reaction column. The heights of the upper stirring vane and the lower stirring vane do not need to be particularly limited but may be decided in consideration of the height of the reaction column. The upper stirring vane 4 and the lower stirring vane 6 are pivotally amounted on the rotary shaft 2 as staggered from each other with an angle which falls generally in the range of 30 - 90°C, preferably at 45°. When the upper stirring vane is provided at the lower terminal thereof with the fins, the lower terminals of the fins of the upper stirring vane are preferred to be positioned below the upper terminal of the lower stirring vane. When the lower stirring vane is provided in the upper terminal thereof with the fins, the upper terminals of the fins of the lower stirring vane are preferred to be positioned above the upper terminal of the upper stirring vane.

[0047] The column type reaction vessels illustrated in Fig. 13 and Fig. 14 are generally provided with a supporting member 10 pivotally mounted on the lower terminal part of the rotary shaft 2 suspended in the central part of the reaction column 1 and a pair of helical ribbonlike stirring vanes 8. The supporting member 10 is formed in the shape of a frame along the longitudinal inner wall of the reaction column 1. The supporting member 10 may be in any shape so long as the shape is capable of supporting the helical ribbonlike stirring vane 8 and retaining mechanical strength for stirring the polymerization solution. As concrete examples of this shape, flat plate, rectangular pillar, and triangular pillar may be cited. Further, the supporting member 10 for the purpose of retaining mechanical strength may be provided, as illustrated in Fig. 13, with projecting objects such as a plurality of arms 11 directed toward the inner wall and/or toward the central part of the reaction column or, as illustrated in Fig. 14, with one or more beams 12 adapted to connect frames. The members forming the frame in the direction of height of the supporting member 10 have a width in the range of 0.04 - 0.16 times, preferably 0.06 -0.1 times, the inside diameter of the reaction column. They may be in an odd number except 1 so long as they enable the axis to be smoothly rotated. In terms of ease of manufacture, about two members are preferred to be disposed symmetrically. The distance from the central part of the reaction column to the central part of the member forming the frame in the direction of height is in the range of 0.6 - 0.9 times, preferably 0.7 - 0.8 times, the distance from the central part of the reaction column to the inner wall of the reaction column. The helical ribbonlike stirring vane 8 is supported by the supporting member 10 and formed in the shape of a twin helix along the inner wall of the vertical barrel part of the reaction column 1. The shape of the helical ribbonlike stirring vane 8 is substantially equal to that of the conventional helical ribbonlike stirring vane. The width of the ribbon of the vane 8 is in the range of 0.07 - 0.2 times, preferably 0.08 - 0.15 times, the inside diameter of the reaction column. The pitch with which the helix is formed is in the range of 0.7 - 1.5, preferably 0.9 - 1.3. The helical ribbonlike stirring vane which is disposed in the bottom part of the reaction column 1 is so shaped as to rise helically from the center of the bottom part of the reaction column with a stated angle relative to the circumferential direction, extend along the spiegel, and continue smoothly into the helical ribbonlike stirring vane in the vertical barrel part. The width of the ribbon is equal to that of the helical ribbonlike stirring vane disposed in the vertical barrel part.

[0048] In this invention, for the production of the highly concentrated carbonaceous solid-water slurry, a carbonaceous solid pulverized by the known wet or dry pulverizing technique generally to a particle size having a 200 mesh pass content of not less than 50 wt. %, preferably 70 - 90 wt. % is used. The slurry concentration is generally not less than 40 wt. %, preferably 50 - 90 wt. %, based on the weight of the dry powder obtained by the pulverization. The slurry concentration, of less than 40 wt. % is impracticable in this invention in terms of economy, efficiency of transportation, and efficiency of combustion.

[0049] The amount of the additive to be used for the carbonaceous solid-water slurry in this invention does not need to be limited particularly. For the purpose of imparting the aforementioned viscoelastic property of this invention to the carbonaceous solid-water slurry, it is proper to use the additive in an amount in the range of 0.005 - 2 wt. %, preferably 0.01 - 1 wt. %, based on the weight (dry basis) of the carbonaceous solid. When the additive for the carbonaceous solid-water slurry is to be used, it may be mixed in advance with the carbonaceous solid and the resultant mixture may be transformed into the slurry or the additive may be dissolved in advance in water and the resultant aqueous solution may be used for the purpose of addition. The additive may be used for the mixture all at once in its entire volume or may be used as divided. Owing to the quality of the additive, the device for forming the slurry does not need to be particularly discriminated but is only required to be capable of converting a carbonaceous solid into a slurry in water. The method of addition and the method for forming the slurry mentioned above do not impose any limit on the scope of this invention.

[0050] The additive to be used for the carbonaceous solid-water slurry in this invention, when necessary, may be used in combination with a chelating agent. As concrete examples of the chelating agent, oxalic acid, malonic acid, succinic acid, lactic acid, malic acid, tartaric acid, citric acid, glucuronic acid, glycolic acid, diglycolic acid, imino diacetic acid, nitro triacetic acid, ethylene diamine tetraacetic acid, pyrophosphoric acid, tripolyphosphoric acid, hexametaphosphoric acid, glycine, alanine, and alkali metal salts, alkaline earth metal salts, ammonium salts, and amine salts thereof may be cited. At least one member selected from the group consisting of pyrophosphoric acid, tripolyphosphoric acid, hexamethaphosphoric acid, glycine, analine, and alkali metal salts, alkaline earth metal salts, ammonium salts, and amine salts thereof proves particularly preferable. The amount of the chelating agent to be added is in the range of 0.05 - 3 wt. %, preferably 0.1 - 2 wt. %, based on the amount of the carbonaceous solid.

[0051] The additive to be used for the carbonaceous solid-water slurry in this invention, when necessary, may incorporate therein a pH adjusting agent, a rust preventive, an anticorrosive, an antioxidant, a defoaming agent, an antistatic agent, and a plasticizer. When the additive for the carbonaceous solid-water slurry of this invention is used in combination with the pH adjusting agent, the carbonaceous solid-water slurry generally has a pH value of not less than 4, preferably in the range of 7 -10.

[0052] Now, the highly concentrated solid-water slurry of this invention will be described more specifically below with reference to working examples and controls. This invention is not limited to these working examples. Wherever "parts" and "%" are mentioned in the following examples, they shall mean "parts by weight" and "% by weight" unless otherwise specified.

(Example of Synthesis 1)

[0053] The synthesis was carried out with a reaction vessel (the n • θ value at Re number 50: 150) illustrated in Fig. 6. This was a cylindrical vertical type glass reaction vessel provided with a reaction column measuring 100 mm in inside diameter, 170 mm in height, and 1 liter in volume, a thermometer, a stirring device, a gas inlet tube, and a reflux condenser. The stirring vane used in the stirring device measured 75 mm in width and 140 mm in height. The reaction column was charged with 225 parts of water, the stirring vane was set rotating at 250 rpm, the interior of the reaction column was displaced with nitrogen as kept stirred, and the reaction column was heated to 95°C in the atmosphere of nitrogen. Then, a mixture consisting of 71.6 parts of phenoxy polyethylene glycol monoacrylate (average addition mol number of ethylene oxide 20), 251.6 parts of acrylic acid, and 103 parts of water, a mixture consisting of 7.6 parts of mercapto propionic acid as a chain transfer agent and 53 parts of water, and a mixture consisting of 8 parts of ammonium persulfate and 25 parts of water were independently added into the reaction column with a pump over a period of three hours. After completion of their addition, a solution of 4 parts of ammonium persulfate in 12.5 parts of water was further added over a period of 1.5 hours. After completion of the addition, the ensuant polymerization reaction was completed by retaining the temperature at 95°C for 0.5 hour. Thereafter, the reaction product was completely neutralized with an aqueous sodium hydroxide solution to obtain a copolymer (a) having a weight average molecular weight of 5000.

(Example of Synthesis 2)

[0054] The synthesis was carried out with a reaction vessel (the n • θ value at Re number 50: 35) illustrated in Fig. 7. This was a cylindrical vertical type glass reaction vessel provided with a reaction column measuring 100 mm in inside diameter, 170 mm in height, and 1 liter in volume, a thermometer, a stirring device, a gas inlet tube, and a reflux condenser and had two baffles attached therein. The stirring vanes of the stirring device were such that the upper stirring vane had a width of 54 mm and a height of 60 mm, the fins had a width of 8 mm, a protruding length of 15 mm, and an overlapping length of 5 mm with the lower stirring vane and formed an intersecting angle of 45° with the lower stirring vane and the lower stirring vane had a bend of an angle of 45° at a point separated by a distance of 20 mm from the center of the axis and had a radius of rotation of 30 mm and a height of 44 mm. The distance from the lower terminal of the lower stirring vane and the bottom of the column was 4 mm. The reaction column was charged with 205 parts of water, the stirring vane was set rotating at 200 rpm, the interior of the reaction column was displaced with nitrogen as kept stirred, and the reaction column was heated to 95°C in the atmosphere of nitrogen. Then, a mixture consisting of 13.2 parts of phenoxy polyethylene glycol monoacrylate (the average addition mol number of ethylene oxide 30), 141.2 parts of acrylic acid, and 364 parts of water and a mixture consisting of 0.1 part of 2,2'-azobis(2-methyl propion amidine)dihydrochloride and 50 parts of water were independently added into the interior of the reaction column with a pump over a period of three hours. After completion of their addition, a solution of 0.05 part of 2,2'-azobis(2-methyl propion amidine)dihydrochloride in 25 parts of water was further added over a period of 1.5 hours. After completion of this addition, the ensuing polymerization reaction was completed by maintaining the temperature at 95°C for 0.5 hour. Thereafter, the reaction product was completely neutralized with an aqueous potassium hydroxide solution to obtain a copolymer (b) having a weight average molecular weight of 1000000.

(Example of Synthesis 3)

[0055] The synthesis was carried out with a reaction vessel (the n • θ value at Re number 50: 45) illustrated in Fig. 8. This was a cylindrical vertical type glass reaction vessel provided with a reaction column measuring 100 mm in inside diameter, 170 mm in height, and 1 liter in volume, a thermometer, a stirring device, a gas inlet tube, and a reflux condenser. The helical ribbonlike stirring vane had a width of 10 mm and a pitch of 95 mm and the frames had a width of 8 mm and were separated by a distance of 65 mm. The reaction column was charged with 200 parts of water, the stirring vane was set rotating at 170 rpm, the interior of the reaction column was displaced with nitrogen as kept stirred, and the reaction column was heated to 95°C in the atmosphere of nitrogen. Then, a mixture consisting of 71.6 parts of stearyloxy polyethylene glycol monomethacrylate (average addition mol number of ethylene oxide 25), 139.3 parts of methacrylic acid, 116.6 parts of acrylic acid, and 103 parts of water and a mixture consisting of 5 parts of ammonium persulfate and 25 parts of water were independently added into the interior of the reaction column with a pump over a period of three hours. After completion of their addition, a solution of 2 parts of ammonium persulfate in 12.5 parts of water was further added over a period of 1.5 hours. After completion of this addition, the ensuing polymerization reaction was completed by maintaining the temperature at 95°C for 0.5 hour. Thereafter, the reaction product was completely neutralized with an aqueous ammonia solution to obtain a copolymer (c) having a weight average molecular weight of 100000.

(Example of Synthesis 4)

[0056] The synthesis was carried out with a glass reaction vessel which was provided with a reaction column measuring 100 mm in inside diameter, 170 mm in height, and 1 liter in volume, a thermometer, a stirring device, a gas inlet tube, and a reflux condenser. The stirring device used a three-blade sweepback vane having a width of 50 mm and a height of 10 mm (the n • θ value at Re number 50: 530). The reaction column was charged with 300 parts of water, the stirring vane was set rotating at 300 rpm, the interior of the reaction column was displaced with nitrogen as kept stirred, and the reaction column was heated to 95°C in the atmosphere of nitrogen. Then, a mixture consisting of 13.2 parts of lauroyloxy polyethylene glycol monomethacrylate (average addition mol number of ethylene oxide 15), 139.3 parts of methacrylic acid, 116.6 parts of acrylic acid, and 103 parts of water, a mixture consisting of 3.6 parts of mercapto propionic acid as a chain transfer agent and 57 parts of water, and a mixture consisting of 2 parts of ammonium persulfate and 25 parts of water were independently added into the reaction column with a pump over a period of three hours. After completion of their addition, a solution of 1 part of ammonium persulfate in 12.5 parts of water was further added over a period of 1.5 hours. After completion of the addition, the ensuant polymerization reaction was completed by retaining the temperature at 95°C for 0.5 hour. Thereafter, the reaction product was completely neutralized with an aqueous sodium hydroxide solution to obtain a copolymer (d) having a weight average molecular weight of 30000.

(Examples 1 - 4 and control 1)

[0057] For the production of a highly concentrated coal-water slurry, coal A exhibiting the property shown in Table 1, water, and a varying copolymer, (a) - (d), were placed in respectively prescribed amounts in a ball mill made of stainless steel and then pulverized until the amount of particles of a size of not more than 200 meshes measured with a laser refractory type particle-size distribution meter (made by Nikkiso K.K. and sold under the product code of "FRA") reached about 80%. After the pulverization, the formed slurry was removed from the ball mill and stirred in a homogenizing mixer (made by Tokushu Kika Kogyo K.K.) at 5000 rpm for 10 minutes to obtain a highly concentrated coal-water slurry. The produced highly concentrated coal-water slurry was tested for performance by the following testing method proposed by Usui et al. [H. Usui, T. Saeki, and T. Mori, Proc, 5th Int. Conf. on Bulk Materials Strage, Handling and Transportation, Newcastle, 39 (1995) etc.]. The test results are shown in Tables 2 - 4.

Table 1

	Item	Coal A
Technical analysis	Inherent moisture (%)	3.3
	Ash content (%)	9.1
	Volatile content (%)	32.9
	Fixed carbon (%)	58.0

Table 1 (continued)

	Item	Coal A
Elementary analyses	Carbon (%)	75.1
	Hydrogen (%)	5.4
	Oxygen (%)	8.4
	Nitrogen (%)	1.6
	Sulfur (%)	0.5
* Invariably on dry basis, except inherent moisture.		

Table 2. Highly concentrated coal-water slurry additive and property

Example/ Control No.	Species of additive	Amount added (wt. % based on coal)	Coal concentration (wt. %)	Viscosity (mPa·s)	Slurry adjusting temperature (°C)	Slurry pH
Example 1	A/STPP	0.35/0.2	71.5	950	80	8.3
Example 2	C	0.35	70.0	980	80	8.1
Example 3	A/b/STPP	0.35/0.04/0.2	69.0	970	80	8.4
Example 4	C/b	0.35/0.03	68.2	1010	80	8.3
Control 1	D/STPP	0.35/0.2	70.5	1070	80	8.3

* STPP: Sodium tripolyphosphate

Table 3

Stability of highly concentrated coal-water slurry				
Example/Control No.	Stability after one month's standing at rest		Shear stability five days' standing	
	Concentration difference in bottom part (wt. %)	Stability	Height of sediment in bottom part (mm)	Stability
Example 1	+ 1.7	○	0	○
Example 2	+ 1.5	○	0	○
Example 3	+ 1.3	◎	0	○
Example 4	+ 1.2	◎	0	○
Control 1	+ 3.6	X	1.4	X

Table 4

Viscoelastic properties of highly concentrated coal-water slurry				
Example/Control No.	Stress sweep test		Creep • recovery test	
	Largest stress in region of linear elasticity (Pa)	Strain giving largest stress (%)	Modulus of elasticity E3 of Maxwell element (Pa)	Modulus of elasticity E2 of Vogt's element (Pa)
Example 1	0.3	3	10	4
Example 2	0.5	5	15	7
Example 3	2.5	10	51	58
Example 4	1.4	7	27	20
Control 1	0.25	2	7	2

[Testing method for slurry performance]

[0058]

(1) Slurry viscosity: A given slurry was tested for apparent viscosity at a shear rate of 100 $\sec^{-1}$ at 25°C by the use of a coaxial double wall cylindrical rotary viscosimeter (made by Haake Corp. and sold under the product code of "RE2").

(2) Method for measurement and analysis of dynamic viscoelasticity by stress sweep test: A given slurry was set in a measuring vessel adjusted to 25°C, left standing at rest therein for 80 minutes, and then exposed to gradual exertion of stress at an oscillation frequency of 1 Hz by the use of a stress control type viscoelasticity measuring device (made by Haake Corp. and sold under the product code of "RS100"). The stress, r, and the modulus of elasticity, G', during storage were measured to determine such relation as shown in Fig. 1. By the scheme illustrated in Fig. 2, the point, a, of stress corresponding to the point of intersection between the tangent line of the region of linear elasticity parallel to the transverse axis and the tangent line of the region of nonlinear elasticity was reported as the largest stress of the region of linear elasticity and the point, b, of the strain corresponding to the stress was reported as the strain giving the largest stress.

(3) Method for measurement and analysis of static viscoelasticity by creep • recovery test: This experiment was performed with a stress control type viscoelasticity measuring device (made by Haake Corp. and sold under the product code of "RS100"). A given slurry was set in a measuring vessel adjusted to 25°C and left standing at rest therein for 80 minutes. In the creep test, the slurry was exposed to instantaneous exertion of stress of a prescribed magnitude not exceeding the yield stress and not exceeding the strain giving the yield stress during the course of test and the deformation produced in response to the exertion of stress was measured as the function of time. The

recovery test which followed the creep test was carried out by instantaneously nulling the stress existing since the creep test and clocking the existence of the consequent deformation until substantial extinction. The relation between the time, t, and the strain, γ, shown in Fig. 3 was obtained. The relevant constant values of the four-constant dynamic model illustrated in Fig. 5 were analyzed by the following procedure using the diagram of analytical method shown in Fig. 4 and the equation of rheology. Since the creep stress, τ, and the creep time, t, were given in advance as the testing conditions, the modulus of elasticity, E_3, of the Maxwell element was determined from the relation of the equation (7) using the initial value, γ_3, of the strain generated in consequence of the exertion of the stress.

$$E_3 = \tau/\gamma_3 \tag{7}$$

[0059] Then, the strain, γ_1, after the recovery was found and the modulus of viscosity, η_1 of the Maxwell element was determined by the formula (8).

$$\eta_1 = (\tau/\gamma_1) \cdot t \tag{8}$$

[0060] Then, the value, γ_2, parallelled to the change in the strain, γ_1, and the delay time, λ, corresponding to the value, γ_2, were found and the modulus of elasticity, E_2, of the Vogt's element was found from the relation shown in the formula (9).

$$E_2 = (\tau/\gamma_2) \cdot (1 - e^{-t/\lambda}) \tag{9}$$

[0061] Then, the modulus of viscosity, η_2, of the Vogt's element was found from the relation shown in Formula (10).

$$\eta_2 = \lambda \cdot E_2 \tag{10}$$

[Method for testing slurry stability]

[0062]

(1) Evaluation of static stability: A given slurry was placed hermetically in a cylindrical container of plastic, 23 mm in inside diameter and 150 mm in height, left standing at rest therein at room temperature for one month, and then frozen together with the container. The part of the frozen slurry equaling 10 vol. % of the total slurry was cut from the bottom part of the container and tested for slurry concentration. The stability was determined by rating the difference of the slurry concentration found at this point from that found at the time of slurry preparation on the following four-point scale.

◎: Not more than 1.5%
○: 1.5 - 2.5%
△: 2.5 - 3.5%
X: Not less than 3.5%

(2) Evaluation of shear stability: A given slurry was placed hermetically in a coaxial double-wall cylindrical rotary container, 55 mm in radius and 180 mm in height of outer cylinder and 20 mm in radius and 163 mm in height of inner cylinder and exposed to exertion of shear at a shear rate of 1 sec^{-1} at room temperature for five days. Then, the height of the sediment in the bottom of the container was measured by the bar-penetrating method using a test bar, 30 g in weight, having a brass disk, 10 mm in diameter and 1 mm in thickness, attached to the leading terminal of a stainless bar, 3 mm in diameter. The stability was determined by evaluating the height of the sediment layer on the following three-point scale.

○: No sediment
△: Not more than 1 cm of sediment
X: Not less than 1 cm of sediment

Industrial Applicability:

[0063] Various species of highly concentrated solid-water slurry showing the magnitude of viscoelasticity property contemplated by this invention possess high flowability and excel in stability during storage and transportation. This invention, therefore, can be effectively applied to various uses such as coal-water slurry, cement slurry, slurry of inorganic particles, dye slurry, a coating material slurry, and slurry of polymer particles.

Claims

1. A highly concentrated solid-water slurry containing solid particles and water, which in a stress sweep test by the method for determining dynamic viscoelasticity exhibits the largest stress of the region of linear elasticity measured at an oscillation frequency of 1 Hz in the range of 0.3 - 10 Pa and the strain giving the largest stress of the region of linear elasticity at a level of not less than 2%.

2. A highly concentrated solid-water slurry containing solid particles and water, which in a creep recovery test determined in the region of linear elasticity by the method for determining static viscoelasticity exhibits the modulus of elasticity of the Maxwell element, analyzed by assuming the four constant dynamic model based on Hookean elasticity and Newtonian viscosity in the range of 8 - 70 Pa and the modulus of elasticity of the Vogt's element in the range of 3 - 70 Pa.

3. A highly concentrated solid-water slurry according to claim 1 or claim 2, wherein the solid particles are carbonaceous solid particles.

4. A method for the production of a highly concentrated solid-water slurry, characterized by using as the additive a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel provided with a stirring vane possessing characteristic values such that the $n \cdot \theta m$-Re curve represented by both logarithmic axes passes a region in which the Reynolds' number, Re, is not more than 50 and the magnitude of $n \cdot \theta m$ is not more than 400 and the average rate of change of the curve within the region is not less than -1.2.

5. A method for the production of a highly concentrated solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotary shaft suspended in the central part of the reaction column, and a substantially planar stirring vane pivotally mounted laterally symmetrically on the rotary shaft, the stirring vane provided with at least two perforated parts.

6. A method for the production of a highly concentrated solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotary shaft suspended in the central part of the reaction column, and stirring vanes disposed in at least upper and lower vertical stages and pivotally mounted in a staggering pattern in the axial direction on said rotary shaft, said stirring vane on the upper stage assuming a substantially planar shape and pivotally mounted laterally symmetrically on said rotary shaft and said stirring vane on the lower stage comprising a main body part assuming a substantially planar shape and pivotally mounted laterally symmetrically on said rotary shaft and a leading terminal part bent parallelly to said rotary shaft in the direction opposite the direction of rotation.

7. A method for the production of a highly concentrated, solid-water slurry, characterized by using a (meth)acrylic acid type polymer or a salt thereof obtained by the use of a reaction vessel comprising a substantially cylindrical reaction column, a rotary shaft suspended in the central part of said reaction column, a supporting member pivotally mounted on said rotary shaft and formed in the shape of a frame along the longitudinal inner wall of said reaction column, and at least a pair of stirring vanes supported by said supporting member and formed each in the shape of a helical ribbon along the inner wall of said reaction column.

Fig. 1

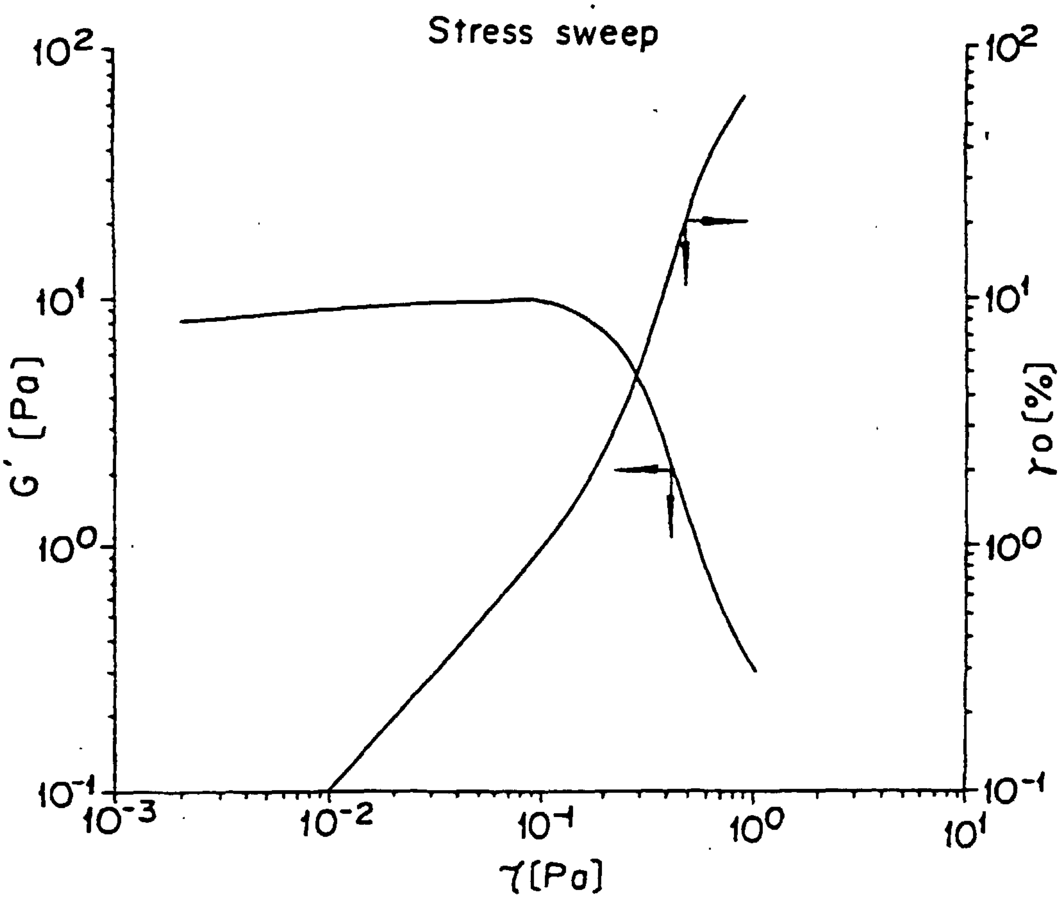

Stress sweep
10²
10¹
10⁰
10⁻¹
G' [Pa]
10²
10¹
10⁰
10⁻¹
γo [%]
10⁻³
10⁻²
10⁻¹
10⁰
10¹
τ [Pa]

Fig. 2

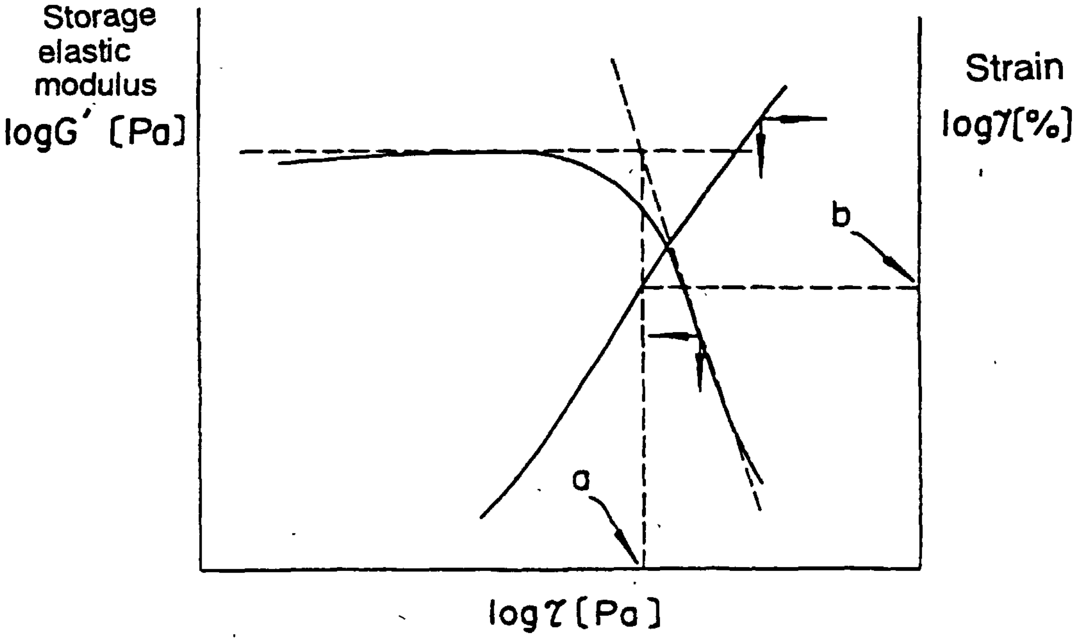


Fig. 3

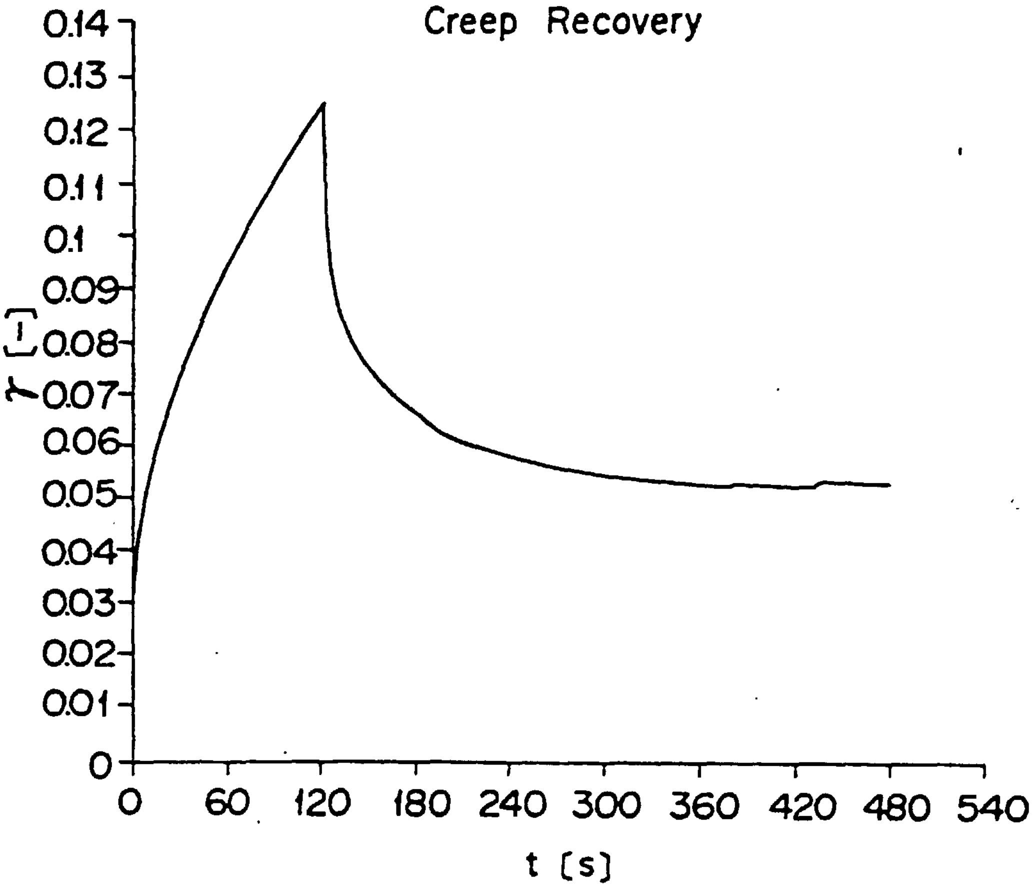

Creep Recovery
γ [ ]
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
60
120
180
240
300
360
420
480
540
t [s]

Fig. 4

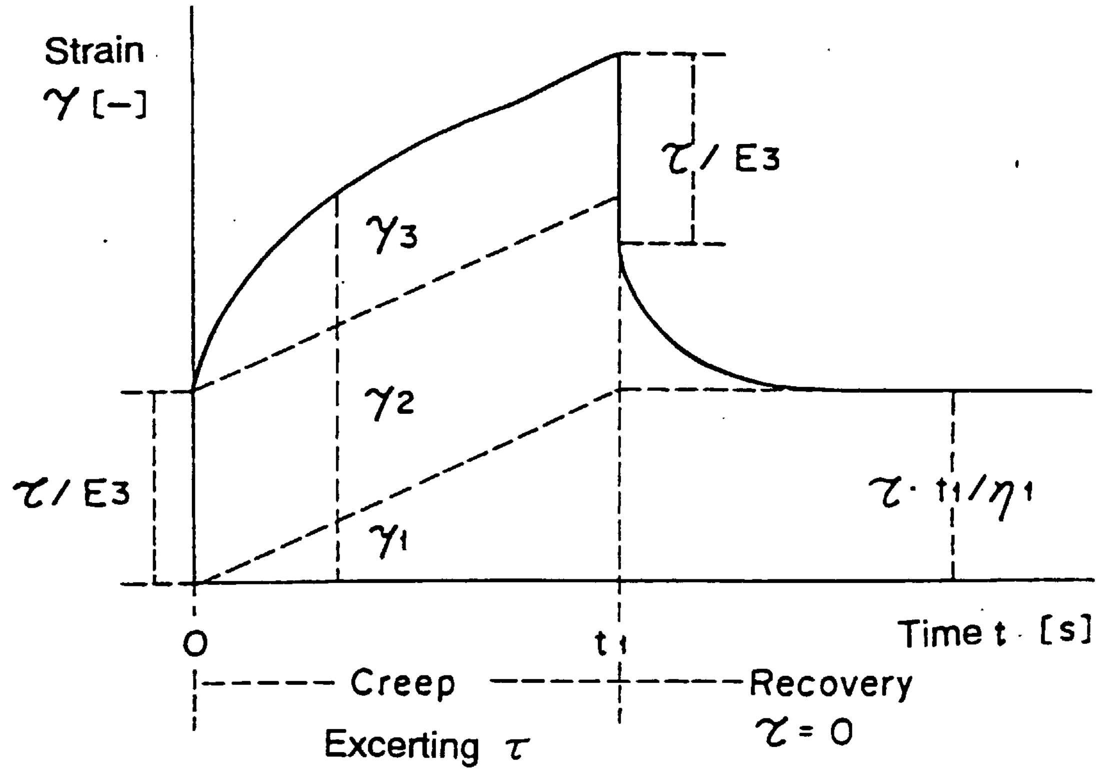

Strain
γ [−]
τ / E3
γ3
γ2
γ1
τ / E3
τ · t1/η1
0
t1
Time t [s]
Creep
Recovery
Excerting τ
τ = 0

Fig. 5

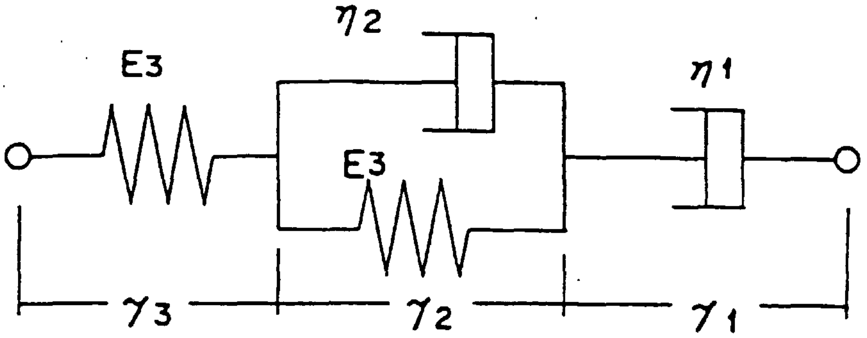


Fig. 6

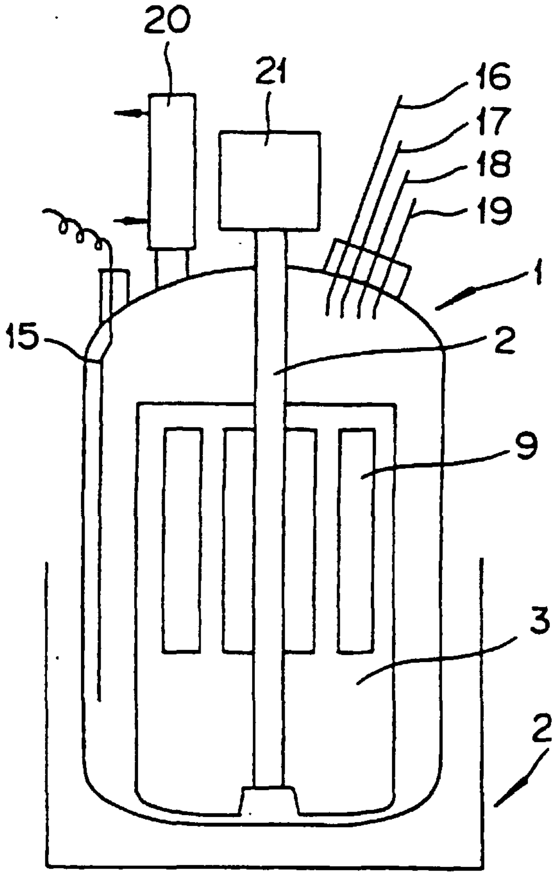


Fig. 7

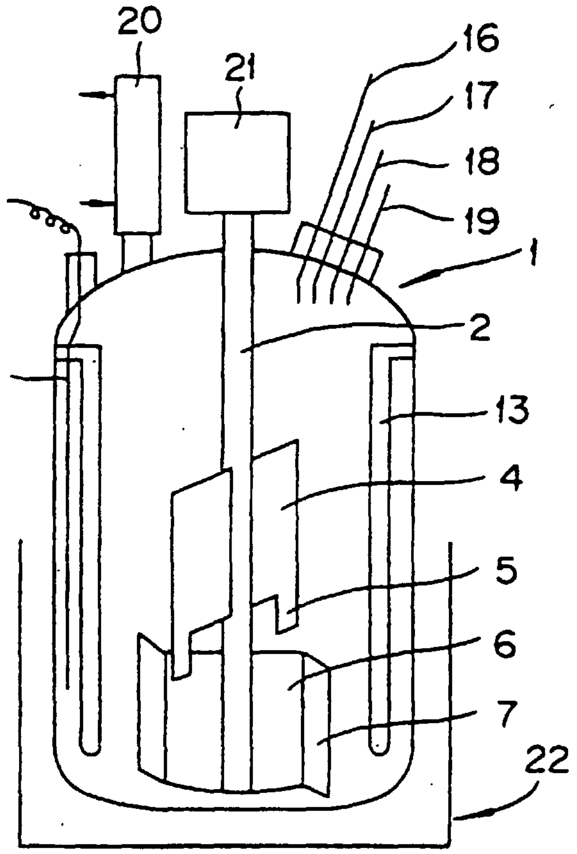


Fig. 8

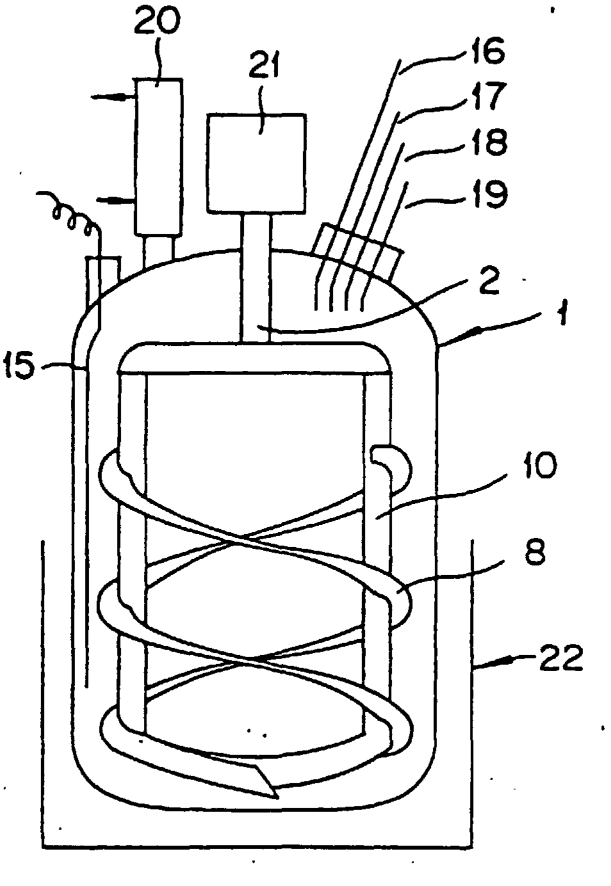


Fig. 9

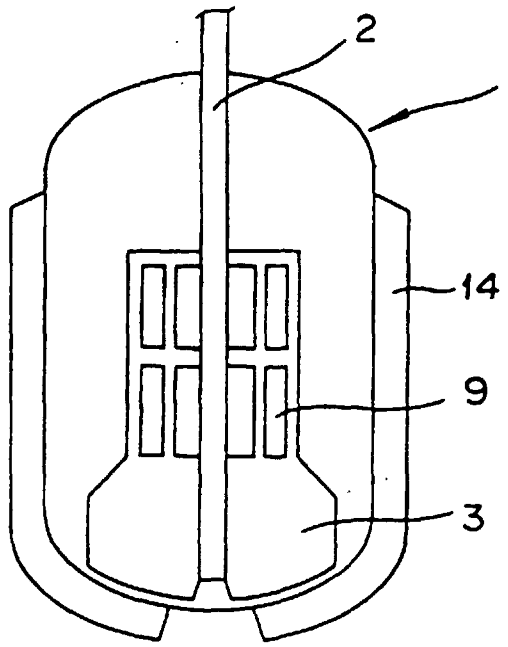


Fig. 10

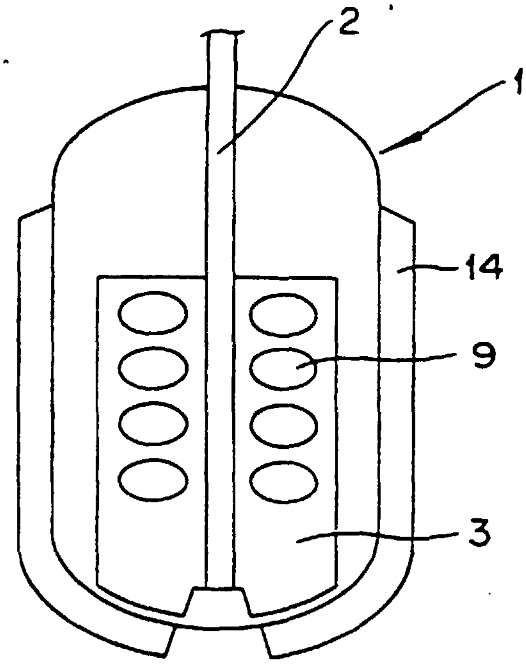


Fig. 11

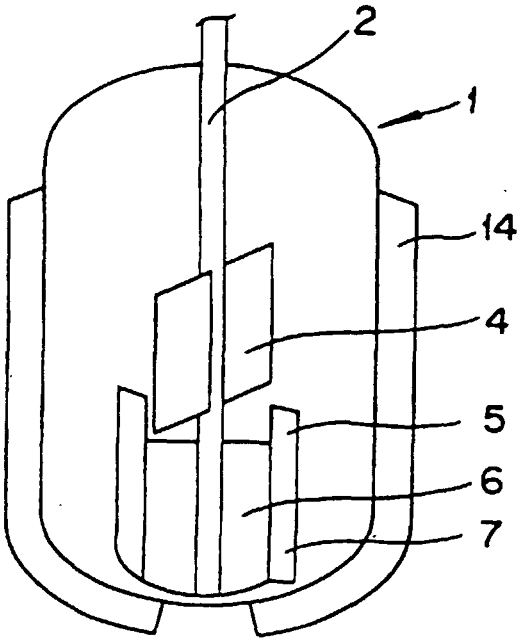


Fig. 12

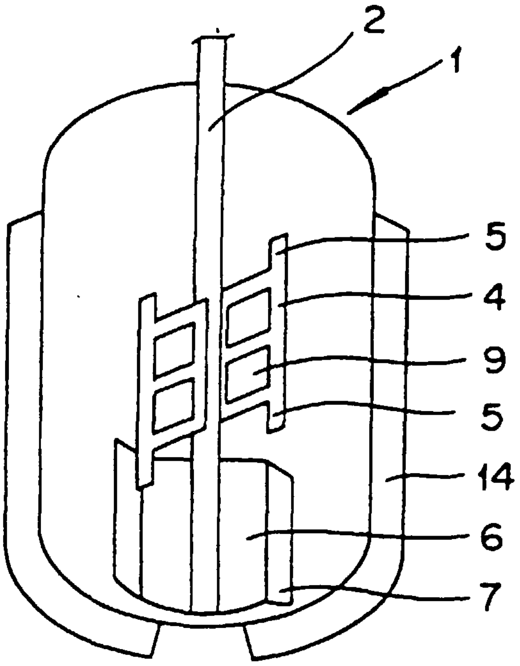


Fig. 13

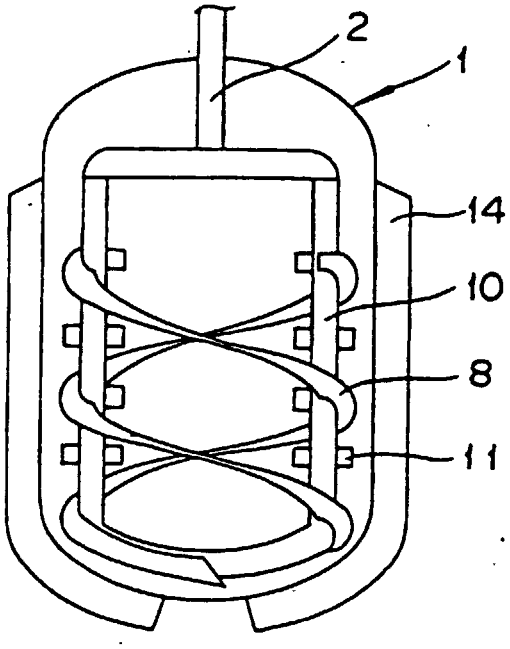
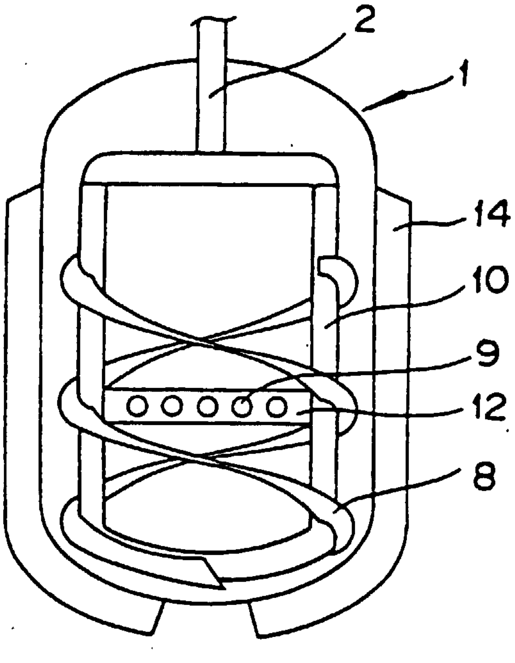


Fig. 14



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/01158

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^6 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^6 C10L1/32

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	Hiroki Usui, "Lecture on Rheology of Coal Slurry (1) (in Japanese)", The Journal of Japan Institute of Energy, Japan Institute of Energy, September 20, 1995 (20. 09. 95), Page 814, right column, line 2 to page 815, right column, line 10 ; Fig. 3	1 2-7
A	Kazuhiro Shibata, "Process for Preparing Highly Concentrated CWM (in Japanese)", The Journal of Japan Institute of Energy, Japan Institute of Energy, June 20, 1994 (20. 06. 94), Page 372, right column, line 1 to page 373, right column, line 4 ; Table 1	1-7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
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Date of the actual completion of the international search May 21, 1998 (21. 05. 98)	Date of mailing of the international search report June 2, 1998 (02. 06. 98)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/01158

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 1-165694, A (Enichem S.p.A.), June 29, 1989 (29. 06. 89), Claims ; page 4, upper right column, line 4 to page 8, lower left column, line 6 & IT, 8722626, A & FR, 2623197, A1 & GB, 2212162, A1 & CA, 1327449, A1 & AU, 2414118, A1 & DE, 3838369, A1 & US, 4915708, A & ZA, 8807949, A & PL, 275733, A & DD, 288758, A5 & SU, 1838385, A3 & IN, 172775, A	1-7
Y	JP, 8-218085, A (Nippon Shokubai Co., Ltd.), August 27, 1996 (27. 08. 96), Claims ; page 2, column 1, lines 38 to 45 (Family: none)	1-7
Y	JP, 6-264076, A (Kawasaki Heavy Industries, Ltd.), October 24, 1996 (24. 10. 96), Claims (Family: none)	1-7
Y	JP, 8-73872, A (Nippon Shokubai Co., Ltd.), March 19, 1996 (19. 03. 96), Claims & EP, 691392, A1 & CA, 2153277, A1 & AU, 9524844, A1 & CN, 1121525, A & US, 5690704, A	1-7
Y	"Technological Trend Series : Technology Concerning Processes for Polymerizing High-Molecular Organic Compounds as Viewed from the Aspect of Patent (in Japanese), edited by Patent Office, first edition, Japan Institute of Invention and Innovation, pages 7 to 37, particularly Figs. 2.2 to 2.78	1-7

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