

PROCESS FOR MAKING HIGH STRENGTHCURED CEMENT ARTICLE

5 This invention relates to a high strength cured cement article, and further relates to a process for manufacturing the same.

U.S. Patent No. 4,353,748 describes a high strength
10 hydraulic cured cement product showing an extremely high flexural strength, which is manufactured by kneading an aqueous mixture of a hydraulic cement, water and a water-soluble polymer such as hydroxypropyl methyl cellulose using a kneader such as a mixing roll under high shear
15 force to give a homogeneous mixed product having a reduced amount of water, and then curing the mixed product.

U.S. Patent No. 4,410,366 describes a high strength hydraulic cured cement product showing an extremely high flexural strength, which is manufactured by kneading an
20 aqueous mixture of a hydraulic cement, water and a water-soluble polymer such as a partially hydrolyzed polyvinyl acetate using a kneader such as a mixing roll under high shear force to give a homogeneous mixed product having a reduced amount of water, and then curing the mixed prod-
25 uct.

U.S. Patents No. 4,070,199 and No. 4,240,840 describe a high strength hydraulic cured cement product showing an extremely high flexural strength, which is manufactured by kneading an aqueous mixture of a hydraulic cement, water and a water-dispersible polymer using a
30 mixing roll under high shear force to give a homogeneous

mixed product having a reduced amount of water, and then curing the mixed product.

The cured cement product generally has a flexural strength of not less than 350 kgf/cm² and has a smooth surface. Therefore, the cured cement product is employable as a building material and a mechanical element.

However, there is a drawback in the cured cement product from the viewpoint of water resistance (i.e., resistance to water). In more detail, the cured cement product having the polymer is apt to show swelling and reduction of its mechanical strength, because the cured product contains a water-soluble or water-dispersible polymer which absorbs water even after being cured.

An object of the present invention is to provide a process for making a high strength cured cement article.

In one aspect the invention provides a process for preparing a article which comprises the steps of mixing starting materials including Portland cement, Portland blast furnace cement or alumina cement, water and an organic polymer which is capable of reacting with an isocyanate compound, forming the mixture into a shaped article, and subsequently impregnating the shaped article with an isocyanate compound to cause a reaction between at least a portion of the organic polymer and the isocyanate compound, the shaped article being cured either before or after the impregnation with the isocyanate compound.

In another aspect the invention provides a shaped, and cured article which has been prepared by the above process.

In the above-mentioned cured cement article the organic polymer typically has one or more urethane bonds, urea bonds, amide bonds, biuret bonds, allophanate bonds and/or acylurea bonds.

The organic polymer may be, for example, a water-soluble organic polymer or a water-dispersible polymer in the form of a polymer emulsion or a polymer latex, for example.

The cured cement article of the present invention is of high strength and can be utilized for manufacturing an exterior structure member or an interior member, particularly a member which requires high water resistance (e.g., floor, members around waterworks). The high strength cured cement article of the invention can be also utilized for manufacturing structural members which require high precision, because the cured cement article of the invention hardly changes its size on exposure to water, that is, the cement article has a high resistance to water.

The high strength cured cement article may be formed into an optional shape such as a plate, or may be formed to have an embossed surface, for example. Further, the high strength cured cement article of the invention can be improved in hardness, stability or decorativeness by coating or printing various material on its surface.

Examples of the cements suitable for use in the present invention include Portland cements such as ordinary Portland cements, rapid hardening Portland cements, extra-rapid hardening Portland cements, moderate heat Portland cements, sulfate-resisting

Portland cements and alumina cements. Commercially available cements can be used with no processing, or can be employed after adjusting their grain sizes.

An organic polymer such as water-soluble polymer or a water-dispersible polymer in the form of a polymer emulsion or a polymer latex is desirably employed to obtain a high flexural strength cured cement article in accordance with the invention. The preferred water-soluble polymer or water-dispersible polymer is employed to increase the kneading efficiency of the hydraulic cement, or to increase the molding efficiency of the hydraulic cement composition. Further, the water-soluble polymer or the water-dispersible polymer improves the mechanical characteristics of the resulting cured hydraulic cement article. There is no specific limitation with respect to the water-soluble polymer and the water-dispersible polymer. Examples of water-soluble polymers include water-soluble proteins, water soluble starchs, water-soluble cellulose derivatives, partially hydrolyzed polyvinyl acetate,, polyvinyl alcohol, polyacrylic soda, polyethylene oxide, polyacrylamide, cross-linked acrylic acid polymer, water-soluble urea resin, water-soluble melamine resin, water-soluble epoxy resin, water-soluble polyester, water-soluble phenolformaldehyde resin, water-soluble amine neutralization alkyd resin, polyvinyl methylether, polyvinylpyrrolidone, polystyrene sulfonic acid, and quaternary polyvinyl pyridine. Examples of water-dispersible polymers include those in the form of rubber latex, acrylic emulsion, vinyl acetate emulsion, vinyl chloride emulsion, ethylene-vinyl acetate emulsion, polypropylene emulsion, epoxy resin emulsion, polyurethane emulsion, polyamide emulsion, and bituminous emulsion. These polymers can be used singly or in combination.

In view of the degree of improvement of water resistance of the resulting cured cement article, water-soluble polymer is preferred, and partially hydrolyzed polyvinyl acetate is most preferred.

The compounding ratio of the water-soluble polymer or water-dispersible polymer preferably is in the range of 0.1 to 20 wt.% based on the amount of the hydraulic cement (or the total amount of the hydraulic cement and filler in the case that a portion of the cement is replaced with the filler) more preferably 0.3 to 10 wt.%. In the case that the compounding ratio is less than 0.1 wt.%, or more than 20 wt.%, the flexural strength may be not satisfactorily high.

The amount of water, although it differs depending on the amount of the water-soluble or water-dispersible polymer and other additives, is preferably not more than 30 wt.% based on the amount of the hydraulic cement. In the case that the amount of water is more than 30 wt.%, the flexural strength may be not satisfactorily high.

In the present invention, the isocyanate compound is used to obtain the high flexural strength and water resistance of the cured cement article. The isocyanate compound may react with the organic polymer to produce a urethan bonding, a urea bonding, an amide bonding, a biuret bonding, an allophanate bonding or an acylurea bonding for example. The isocyanate compound may also react with the other components or otherwise undergo a polymerization reaction. By using the isocyanate compound, the hydraulic cured cement article is provided with improved water resistance. A portion of unreacted isocyanate compound may optionally remain in the hydraulic cured cement article. The isocyanate compound reacts with the water-soluble or water-dispersible polymer, whereby the water absorptiveness of the water-soluble or water-dispersible polymer

is reduced, and may optionally react with the hydraulic cement or the hydraulic cementitious hydrate, whereby the absorptiveness of the hydraulic cement or the hydraulic cementitious hydrate is reduced. The products produced by the above reactions and/or by the polymerization reaction may plug voids of the cured cement article. Accordingly, the water-resistance of the cured hydraulic cement article can be improved. There is no specific limitation with respect to the isocyanate compounds.

10 Examples of the isocyanate compounds include monoisocyanate compounds such as phenylisocyanate, p-chlorophenylisocyanate, o-chlorophenylisocyanate, m-chlorophenylisocyanate, 3,4-dichlorophenylisocyanate, 2,5-dichlorophenylisocyanate, methylisocyanate, ethylisocyanate, n-butylisocyanate, n-propylisocyanate, octadecylisocyanate; diisocyanate compounds such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, dianisidine diisocyanate, o-toluidene diisocyanate, hexamethylene diisocyanate, xylene diisocyanate, 20 1,5-naphthalene diisocyanate, transvinylene diisocyanate, lysine diisocyanate, isophorone diisocyanate, dimethyl diisocyanate, trimethylhexamethylene diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, isopropylidene bis(4-cyclohexylisocyanate), hydrogenated 4,4'-diphenylmethane diisocyanate, hydrogenated tolylenediisocyanate; 25 triisocyanate compounds such as triphenylmethane triisocyanate, tris(4-phenylisocyanate thiophosphate); polyisocyanate compounds having four or more isocyanates groups such as polymethylene polyphenylisocyanate; their dimers 30 such as N,N'-(4,4'-dimethyl-3,3'diphenyldiisocyanate)-uredione; their trimers such as 4,4',4"-trimethyl-3,3'3"-triisocyanate-2,4,6-triphenylcyanurate; their derivatives such as carbodiimide modified isocyanate; compounds obtained by reacting the isocyanate compound with polyol 35 such as polyurethane prepolymer; blocked isocyanates

(block agent: phenol, etc.); and their mixtures such as crude tolylenediisocyanate.

The isocyanate compound may be selected from the viewpoints of the requirement of the resulting flexural strength or the water resistance of the cured cement articles, the requirements involved in the manufacturing stage and/or the other requirements.

In the case that the weather resistance is required, aliphatic isocyanates such as hexamethylene diisocyanate, and hydrogenated aromatic isocyanates such as hydrogenated tolylenediisocyanate are preferably used, because such isocyanates are resistant to yellowing by light. In the case that heat resistance is required, an aromatic isocyanate such as tolylene diisocyanate and trimers of isocyanate compounds showing a high decomposition temperature is preferably used. In the case that the irritation of the isocyanate compound should be avoided, 4,4'-diphenylmethane diisocyanate, polyisocyanate, isocyanate compound derivatives, polyurethane prepolymer and blocked isocyanates having a relatively low vapor pressure are preferably used.

The compounding ratio of the isocyanate compound can for example be in the range of 0.1 to 32 wt.% based on the amount of the hydraulic cement, preferably 0.4 to 21 wt.%. If the compounding ratio is less than 0.1 wt.%, or more than 32 wt.%, the water resistance may be not satisfactory.

From another viewpoint, the isocyanate compound is preferably used in an amount of 10 to 300 weight % per the amount of the polymer, more preferably in an amount of 20 to 300 weight %..

The reaction products of the isocyanate compound such as an isocyanate-reacted organic polymer, a polymerization product of the isocyanate compound and any other product produced by reactions in which the isocyanate compound participate may be distributed uniformly or locally in the cured cement article. Even if the reac-

tion product is locally distributed particularly in the vicinity of the surface of the cured cement article, the water resistance of the cured cement article is very high. The water resistance is affected by the surface properties of the cured article. The reaction product is preferably distributed in an area which is deeper than 0.1 mm from the surface.

In order to improve the physical properties of the high strength cured cement article, or to improve the physical properties of the water-soluble or water-dispersible polymer, or to improve the workability for manufacturing the high strength cured cement article, various additives can be employed. In order to improve the physical properties of the high strength cured cement article such as uncombustibility, a flame retarder which is generally used for plastics and rubbers can be used. A smoke-reducing additives can be used to reduce smoking which takes place in the case of burning the cement article. An ultraviolet ray absorbent can be used to improve the weather resistance. In order to improve the physical properties of the water-soluble or water-dispersible polymer, a plasticizer can be used. There is no specific limitation with respect to the plasticizer. Examples of the plasticizers include glycerol, ethyleneglycol and diethyleneglycol. These compounds can be employed singly or in combination. The plasticizer can also be employed to improve the workability for manufacturing the high strength cured cement article. There is no specific limitation with respect to the compounding ratio for these additives. The compounding ratio can be determined by the conventional manner.

An admixture or a filler can for example be added to the hydraulic cement in addition to the above additives. Examples of the admixtures include water reducing agents such as lignin sulfonate, polyol complex, oxycarboxylic acid, alkylarylsulfate polycondensate, polycondensed triazine

compounds, polycondensed aromatic sulfonates, or melamine resin sulfonate; hydration retarders; and hydration accelerators.

Examples of fillers include fine grain type inorganic fillers (including hollow grains) such as fine grain type silicious materials (e.g., silica rock powder, and clay); carbon black, alkali earth metal carbonates (e.g., calcium carbonate, and magnesium carbonate), inorganic oxides (e.g., silicon dioxide, aluminum oxide, titanium dioxide, and zirconium dioxide), or inorganic hydroxides (e.g., calcium hydroxide, magnesium hydroxide, and aluminum hydroxide); fine grain type organic fillers (e.g., spherical silicon); and fibrous fillers such as inorganic fibrous fillers (e.g., aluminum oxide fiber, alkali resistance glass fiber, carbon fiber, silicon carbide fiber, asbestos, rock wool, and slag wool), organic fibrous fillers (e.g., nylon fiber, vinylon fiber and polypropylene fiber), or metal fibrous fillers (e.g., steel fiber, and stainless steel fiber). These fillers can be used singly or in combination. The fibrous filler may take a net structure. The mechanical properties such as abrasion resistance or toughness, and the physical properties such as heat conductivity or electric conductivity or vibration damping can be improved by incorporating appropriate fillers into the cement article.

A catalyst can be added to increase the reactivity of the isocyanate compound. The catalyst for polyurethane is preferred. Examples of the catalysts include amines such as 1,4-diazobicyclo(2,2,2)octane, PMDETA, N,N-dimethylcyclohexylamine, N-methyldicyclohexylamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethylpropylenediamine, N,N,N',N'-tetramethylhexamethylenediamine, N-ethylmorpholine, N-methylmorpholine, N,N-dimethylethanolamine, N,N-diethylethanolamine, or triethylamine, DBU such as 1,8-diaza-bicyclo[5,4,0]undecene-7 and its salt: metals such as stannous octoate.

dibutyltin dilaurate, trimethyltin hydroxyde, dimethyltin dichloride or tin octylate; and other compounds such as butadiene sulfone, inorganic acid, oxy acid, ester of phosphoric acid or boric acid, monobutylphthalate, p-5 toluenesulfonic acid.

An example of a known process for manufacturing a high 10 strength cured cement article is described hereinbelow.

The hydraulic cement, the water-soluble or water-dispersible polymer, the isocyanate compound and other additives are mixed with water to prepare a hydraulic cement composition. There is no specific limitation with 15 respect to the mixing procedure, so long as the procedure is performed sufficiently. Powdery solid starting materials except the liquid starting materials such as water are introduced in a mixer (e.g., planetary motion mixer), and then mixed after addition of the liquid starting 20 materials. The resulting mixture is further mixed using a high power mixer. Examples of the high power mixers include a kneader, Banbury mixer, a wet-type pan mixer, a mixing roll, a knett machine, a pugmill, and a screw extruder. Using these mixers, the amount of the bubbles 25 contained in the hydraulic cement composition is reduced. Even if a reduced amount of water is used, the kneading is sufficiently performed in the mixer. Therefore, the hydraulic cement which has a high flexural strength can be easily obtained. The kneading procedure using the 30 mixer may be performed under reducing pressure.

In the case that the isocyanate compound is a liquid material, the isocyanate compound is introduced by mixing with water or by spraying when the mixing is performed. In the case that the isocyanate compound is a solid mate- 35 rial, the isocyanate compound is introduced after mixing with the hydraulic cement, or when the mixing procedure

is done. Since the isocyanate compound is apt to react with water, the isocyanate compound having a relatively low reactivity is preferred. In the case that a blocked isocyanate is used, the isocyanate is preferably heated
5 to a temperature of not lower than the dissociation temperature of the blocking group at any following stage. The isocyanate compound can be used after dissolving in a hydrophobic solvent having a high boiling point for preventing from reacting with water when it is mixed.

10 The mixed hydraulic cement composition is shaped into a form of a sheet. The shaping procedure can be performed under reducing pressure. The hydraulic cement composition shaped into the sheet-type is then rolled to have a predetermined thickness by calendering.

15 The rolled hydraulic cement article is then cured by the conventional manner. Examples of the curing methods include atmospheric curing, moisture curing, curing in water, steam curing and autoclave curing.

Alternatively, the uncured, rolled hydraulic cement
20 article can be heated under pressure applied to the surface of the sheet before curing in order to accelerate the curing procedure.

The cured hydraulic cement article is then dried at a drying stage. Strength of the cured hydraulic cement
25 article can be increased by drying. There is no specific limitation with respect to the drying procedure. The drying procedure is generally performed under atmospheric condition, or under conditions heated to a temperature of not higher than 100°C.

30 The time required for heating under pressure, curing and drying is determined in consideration of the natures of the starting materials and the amount thereof. The hydraulic cement article is preferably cured and dried by interposing between porous plates for preventing the
35 cured article from warping.

The obtained cured hydraulic cement article shows a high flexural strength of more than 100 kgf/cm^2 (approx. 10 MPa).

5 The high strength cured cement article can be manufactured by the following process.

 The starting materials and the amount thereof used in this process is similar to those of the above described process for manufacturing of the high strength
10 cured cement article

 The process of the invention differs from the conventional process with respect to the manner of addition of the isocyanate compound. In the present process, the isocyanate com-
15 pound is impregnated in the cured hydraulic cement article or the intermediate product thereof (i.e., uncured shaped hydraulic cement article) which can for example be manufactured by the conventional manner using the starting materials except for using the isocyanate compound.
20

 In the present process, since the isocyanate compound is not contained in the starting materials to be mixed, the mixing efficiency increases. Further, the
25 amount of bubbles introduced into the mixture is reduced. Therefore, it enable to give a cured hydraulic cement article having high flexural strength. Furthermore, the reaction products and the inner structure thereof are not broken at the stage of mixing. Since the reaction pro-
30 ducts contribute to the improvenent of the water resistance efficiently, the water resistance of the cured hydraulic cement article increases.

 The isocyanate compound can be impregnated in the same manner as that employed for the preparation of the
35 resin impregnated cement, or in the same manner as that employed for coating or painting. For example, the iso-

cyanate compound can be impregnated into the intermediate product or the cured article by immersing, roll coating, flow coating, spraying or brushing. The intermediate product or the cured article can be placed under pressure 5 or under vibration using ultrasonic waves accelerate impregnation of the isocyanate compound into the intermediate product or the cured article when the impregnating procedure or the coating procedure is applied, or after impregnating or coating.

10 In order to impregnate the isocyanate compound into the intermediate product or the cured article, an isocyanate compound having a low viscosity is preferably employed. Even if the isocyanate compound has a high viscosity, the isocyanate compound can be used after 15 diluting with a solvent capable of lowering the viscosity. A solvent generally employed for the isocyanate compound can be used. Examples of the solvents include acetone, benzene, toluene, nitrobenzene, dibutyl ether, methylethylketone, dioxane, acetonitrile, benzylcyanide, 20 anisole, monochlorobenzene, xylene, butyl acetate, ethyl acetate and tetrahydrofuran. The solvent is preferably selected to match with nature of the isocyanate compound employed.

The catalyst of the isocyanate compound can be pre- 25 viously added to the starting materials containing no isocyanate compound. The catalyst can be impregnated into the isocyanate compound.

The shaped hydraulic cement produce or the cured article containing the isocyanate compound is preferably heated 30 to accelerate the reaction of the isocyanate compound.

The shaped hydraulic cement product or the cured article may for example be heated under a closed condition to prevent the isocyanate compound from evaporation before the reaction. Although the temperature and time of the heating differs depending 35 on nature of the isocyanate compound and catalyst, the

reaction proceeds satisfactorily within 20 hours at a temperature of 100°C.

The resulting cured hydraulic cement article typically shows a high flexural strength more than 100 kgf/cm² (approx. 10 MPa), appropriately more than 350 kgf/cm². The cured hydraulic cement article is improved in water resistance. The surface hardness also increases.

The present invention is further described referring to the following examples without limiting the invention.

10

EXAMPLES 1 to 6

100 Weight parts (250 g) of alumina cement (Alumina Cement No. 1 produced by Asahi Glass Co., Ltd.) and 3 weight parts (7.5 g) of a partially hydrolyzed polyvinyl acetate (Gosenole (Registered Trade Mark) produced by Nippon Gohsei Chemical Industry Co., Ltd.) were mixed in a planetary motion mixer for 4 minutes, and to the mixture was added a solution containing 11 weight parts (27.5 g) of water and 0.3 weight part (0.75 g) of glycerol. The mixture was well mixed for 4 minutes.

20 The resulting mixture was kneaded for 5 minutes using a mixing roll having a rotary ratio of a pair of rolls of 1:1.12 to obtain a sheet-type shaped article having a thickness of approx. 3.4 mm, a width of approx. 160 mm and a length of approx. 180 mm.

25 The shaped article was then rolled using a calender having a rotary ratio of a pair of rolls of 1:1 to give a rolled article having a thickness of approx. 3.2 mm, a width of approx. 165 mm and a length of approx. 185 mm.

The rolled article was heated under pressure of 30 kgf/cm² at 80°C for 10 minutes, and then was left under atmospheric condition having a relative humidity of 50 % at 20°C for 24 hours for curing. The cured article was dried while keeping the temperature of 80°C to obtain a cured hydraulic cement article having a thickness of

approx. 3.0 mm, a width of approx. 170 mm and a length of approx. 180 mm.

The cured hydraulic cement article was immersed in a vat filled with the isocyanate compound indicated in

5 Table 1 for 30 minutes for impregnating the cement article with the isocyanate compound. After the immersing was complete, the cured hydraulic cement article was wrapped with an aluminum foil and was heated in a dryer kept at a temperature of 100°C for 20 hours.

10 The cured article changed to show a slightly deeper color than that before the impregnation. From observation of a section face of the article, it was confirmed that the colored portion was deeper than 0.1 mm on the opposite surface sides. Thus, it was recognized that the
15 isocyanate compound was deeply incorporated into the cured article. The content of the isocyanate compound or the reaction product which was determined according to the change of the weight was 2 to 4 wt.% in terms of the amount of the hexamethylene diisocyanate.

20 Six test pieces having a width of 20 mm and a length of 180 mm were taken out of the cured article, and the flexural strength was immediately measured for three pieces. Other three pieces were immersed in water placed in a thermostat kept at temperature of 20°C, and the
25 change of weight and length was measured. Three of these pieces were immersed in water for 28 days under the same conditions, and then the flexural strength was measured under wet condition.

The results are set forth in Table 1.

30 The flexural strength was measured by a three-point bending test. The span was set to 150 mm. The change of the length was measured using a contact gauge (defined in JIS(Japanese Industrial Standard) A-1129). The basic length was determined as 100 ± 1 mm.

35 In Table 1, "before" means "before immersion in water", and "after" means "after immersion for 28 days"

"Change of length" and "Change of weight" indicate average proportions of the change of length and weight after the immersion for 28 days.

Table 1

5 Example	Isocyanate compound	Flexural strength (kgf/cm ²)		Change of length (%)	Change of weight (%)
		before	after		
10	1 hexamethylene diisocyanate* ¹	1,020	830	0.01	0.7
	2 tolylene diisocyanate* ²	680	480	0.02	1.0
	3 polymethylene polyphenyl isocyanate* ³	750	530	0.02	3.2
15	4 isocyanate mixture* ⁴	930	710	0.01	0.3
20	5 carbodiimide modified isocyanate* ⁵	740	510	0.02	1.5
	6 hydrogenated 4,4'-diphenyl methane diisocyanate* ⁶	670	450	0.01	0.3

- Remarks
- *1 HDI produced by Nippon Polyurethane Industries Co., Ltd.
 - *2 Colionate T-100 produced by Nippon Polyurethane Industries Co., Ltd.
 - 5 *3 Milionate MR-200 produced by Nippon Polyurethane Industries Co., Ltd.
 - *4 Colionate 1021 produced by Nippon Polyurethane Industries Co., Ltd.
 - *5 Milionate MTL-C produced by Nippon Polyurethane Industries Co., Ltd.
 - 10 *6 Desmodur W (Registered Trade Mark) produced by Sumitomo Bayer Urethane Co., Ltd.

EXAMPLES 7 to 10

A high strength cured cement article was manufactured in the same manner as in Example 1, except that the amount of water and the partially hydrolyzed polyvinyl acetate were respectively changed. The amount of the glycerol was tenth (1/10) part of the partially hydrolyzed polyvinyl acetate.

20 Test pieces were cut from the cured article in the same manner as in Examples 1 to 6, and were examined.

The results are set forth in Table 2. In Table 2, "Polyvinyl acetate" means the amount of the partially hydrolyzed polyvinyl acetate (weight part), and "Water" 25 means the amount of water (weight part). "before", "after", "Change of length" and "Change of weight" have same meanings as in Table 1.

Table 2

Example	Poly-vinyl acetate	Water	Flexural strength (kgf/cm ²)		Change of length (%)	Change of weight (%)
			before	after		
5						
7	0.5	11	410	330	0.02	1.5
8	3	25	620	430	0.01	1.2
9	7	12	1,560	1,100	0.01	0.3
10	10	13	1,530	1,050	0.01	0.4

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EXAMPLE 11

A high strength cured cement article was manufactured in the same manner as in Example 1, except that the impregnation with hexamethylene diisocyanate employed in Example 1 (HDI produced by Nippon Polyurethane Industries Co., Ltd., referred to as "HDI" hereinafter) was done after heating under pressure by means of a rolled article, and heated in a dryer kept at a temperature of 100°C.

Test pieces were cut from the cured article in the same manner as in Examples 1 to 6, and were examined. The results were shown below.

Before immersion in water

an average flexural strength: 760 kgf/cm²

After immersion for 28 days

an average flexural strength: 420 kgf/cm²

an average proportion of change of length:

0.20 %

25

an average proportion of change of weight:

2.1 %

EXAMPLES 12 to 15

A high strength cured cement article was manufactured in the same manner as in Example 1, except that the test pieces were impregnated with a solution which was prepared by diluting the HDI or the isocyanate compound used in Example 2 (Colonate 1021 produced by Nippon Polyurethane Industries Co., Ltd., referred to as "Colonate 1021" hereinafter) with methyl acetate.

The results are set forth in Table 3. In Table 3, "Isocyanate compound" means the kind of isocyanate compound and the amount (weight part) thereof, and "Ethyl acetate" means the amount the ethyl acetate (weight part).

Table 3

Example	Isocyanate compound	Ethyl acetate	Flexural strength (kgf/cm ²)		Change of length (%)	Change of weight (%)
			before	after		
12	(HDI) 75	25	1,060	850	0.03	1.1
13	(HDI) 50	50	920	720	0.11	2.1
14	(Colonate 1021) 75	25	980	830	0.01	0.1
15	(Colonate 1021) 50	50	810	630	0.11	0.9

EXAMPLE 16

A high strength cured cement article was manufactured in the same manner as in Example 9, except that the ordinary Portland cement (produced by Ube Industries, Ltd.) was used instead of the alumina cement, and 15 weight parts of water and 3 weight parts of the partially hydrolyzed polyvinyl acetate was used per the weight of the ordinary Portland cement.

Test pieces were cut from the cured article, and 10 were examined.

The results are shown below.

Before immersion in water

an average flexural strength: 710 kgf/cm²

After immersion for 28 days

15 an average flexural strength: 400 kgf/cm²

an average proportion of change of length:
0.26 %

an average proportion of change of weight:
5.1 %

20

COMPARISON EXAMPLES 1 & 2

A cured cement article was manufactured in the same manner as in Examples 1 & 16, except that the cured article was not impregnated with the isocyanate compound and the cured article was not heated in the dryer.

25 Test pieces were cut from the cured article, and were examined in the same manner as in Examples 1 to 6.

The results are set forth in Table 4. In Table 4, "Hydraulic cement" means the kind of hydraulic cement which was used.

Table 4

Comparison Example	Hydraulic cement	Flexural strength (kgf/cm ²)		Change of length (%)	Change of weight (%)
		before	after		
5					
1	alumina	800	400	0.32	8.3
2	ordinary Portland	310	250	0.7	9.4

COMPARISON EXAMPLE 3

10 100 weight parts (250 g) of alumina cement (Alumina
Cement No. 1 produced by Asahi Glass Co., Ltd.) and 3
weight parts (7.5 g) of a partially hydrolyzed polyvinyl
acetate (Gosenole (Registered Trade Mark) produced by Nippon Gohsei Chemical
Industry Co., Ltd.) were mixed in a planetary motion
15 mixer for 4 minutes, and to the mixture were added 60
weight parts (150 g) of water, 0.3 weight part (0.75 g)
of glycerol and 35 weight parts (87.5 g) of HDI, and the
mixture was well mixed for 4 minutes.

The resulting mixture was introduced in a molding
20 frame, and was left in a wet box kept at a temperature of
20°C. After 3 days, six test pieces having a thickness
of 3 mm, a width of 20 mm and a length of 180 mm were
obtained.

The obtained test pieces were examined in the same
25 manner as in Examples 1 to 6.

The results are shown below.

Before immersion in water

an average flexural strength: 80 kgf/cm^2

After immersion for 28 days

an average flexural strength: 90 kgf/cm^2

5 an average proportion of change of length:
0.07 %

an average proportion of change of weight:
25 %



CLAIMS

1. A process for preparing a shaped cured cement article which comprises the steps of mixing starting materials including Portland cement, Portland blast furnace cement or alumina cement, water and an organic polymer which is capable of reacting with an isocyanate compound, forming the mixture into a shaped article, and subsequently impregnating the shaped article with an isocyanate compound to cause a reaction between at least a portion of the organic polymer and the isocyanate compound, the shaped article being cured either before or after the impregnation with the isocyanate compound.
2. A process according to claim 1 wherein said shaped article is impregnated by immersion in said isocyanate compound.
3. A process according to claim 2 wherein said shaped article is subjected to pressure or vibration to accelerate impregnation of the isocyanate compound.
4. A process according to any preceding claim wherein said isocyanate compound is a low viscosity isocyanate or is diluted with a solvent capable of lowering the viscosity.
5. A process according to any preceding claim wherein said isocyanate compound is selected from the group consisting of diisocyanates, triisocyanates, and polyisocyanates having four or more isocyanate groups per molecule, including dimers and trimers of said isocyanates and polyurethane prepolymers.
6. A process according to claim 5 wherein said isocyanate compound is a modified or a blocked isocyanate.
7. A process according to any preceding claim wherein said organic polymer is partially hydrolysed polyvinyl acetate.



8. A process as claimed in any preceding claim, wherein said mixture contains 0.1 to 20% by weight relative to the cement of said organic polymer.
 9. A process according to any of claims 1 to 6 wherein said organic polymer is water-soluble.
 10. A process according to any preceding claim wherein the amount of said isocyanate compound which is impregnated into the cured shaped cement article is 10 to 300% by weight relative to the organic polymer.
 11. A process according to any preceding claim wherein the cured shaped cement article is heated after being impregnated with the isocyanate compound.
 12. A process according to any of claims 1 to 4, wherein said organic polymer is partially hydrolysed polyvinyl acetate and said isocyanate compound is hexamethylene diisocyanate.
 13. A process for preparing a cured cement article substantially as described hereinabove with reference to any ^{of} Examples 1 to 16.
 14. A shaped, cured cement article which has been prepared by a process as claimed in any preceding claim.
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